**Subsurface conditions in hydrothermal vents inferred from diffuse flow composition, and
models of reaction and transport**

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ABSTRACT

Chemical gradients in the subsurface of mid-ocean ridge hydrothermal systems create an environment where minerals precipitate and dissolve and where chemosynthetic organisms thrive. However, owing to the lack of easy access to the subsurface, robust knowledge of the nature and extent of chemical transformations remains elusive. Here, we combine measurements of vent fluid chemistry with geochemical and transport modeling to give new insights into the under-sampled subsurface. Temperature-composition relationships from a geochemical mixing model are superimposed on the subsurface temperature distribution determined using a heat flow model to estimate the spatial distribution of fluid composition. We then estimate the distribution of Gibb's free energies of reaction beneath mid oceanic ridges and by combining flow simulations with speciation calculations estimate anhydrite deposition rates. Applied to vent endmembers observed at the fast spreading ridge at the East Pacific Rise, our results suggest that sealing times due to anhydrite formation are longer than the typical time between tectonic and magmatic events. The chemical composition of the neighboring low temperature flow indicates relatively uniform energetically favorable conditions for commonly inferred microbial processes such as methanogenesis, sulfate reduction and numerous oxidation reactions, suggesting that factors other than energy availability may control subsurface microbial biomass distribution. Thus, these model simulations complement fluid-sample datasets from surface venting and help infer the chemical distribution and transformations in subsurface flow.

1. INTRODUCTION

Deep sea hydrothermal activity is manifest by the iconic black smoker, but measurements at a number of vent fields suggest that discharge of warm fluid ("diffuse flow") is at least as significant, if not more so, than focused high temperature venting in terms of heat flux to the ocean (Bemis et al., 1993; Veirs, 2003; Ramondenc et al., 2006) and microbial activity in the subsurface (Sogin et al., 2006; Von Damm and Lilley, 2004). The mixing between the hot, reducing venting fluid with cold, oxidizing seawater creates temperature and chemical gradients that can enhance rates of chemical transformations and support rich microbial life adapted to catalyzing thermodynamically favorable reduction-oxidation reactions (Butterfield et al., 2004). These processes are reflected in the composition of diffuse fluids (<120°C, but typically less than about 40°C) seeping from the seafloor, with microbial activity clearly evidenced by the expulsion of large amounts of biomass in the wake of magmatic or tectonic events (Embley & Chadwick, 1994; Haymon et al., 1993).

High temperature and associated diffuse hydrothermal activity have been observed in a range of mid-ocean ridge environments from Lucky Strike on the slow spreading Mid-Atlantic Ridge (Mittelstaedt et al., 2012) to Axial Volcano (Rona and Trivett, 1992), the Endeavour segment (Schultz et al., 1992) on the intermediate spreading Juan du Fuca ridge and 9N on the fast spreading East Pacific Rise (Ramondenc et al., 2006). Lacking direct samples of subsurface pore fluids, the assessment of subsurface processes largely relies on the interpretation of the observed composition of the venting fluid, which reflects the entire history of a water parcel, including mixing and abiotic and microbial transformations. These multiple processes can be quantified

and integrated using mathematical models. Comparison of predicted diffuse fluid compositions arising from, e.g., conductive heating or cooling of seawater, or mixing between vent fluid and seawater, with field observations allows identification of the dominant mechanisms (Butterfield et al., 2004).

Here we quantify inferred subsurface processes and their role in shaping the subsurface environment at the Biogeotransect on the fast-spreading East Pacific Rise (EPR) where magmatism is robust and two separate eruptions have been observed separated by roughly 14 years (Haymon et al., 1993; Tolstoy et al., 2006). We use geochemical models to estimate diffuse fluid compositions by calculating and speciating mixtures of measured vent fluid and seawater compositions. We also consider variable temperature in the seawater end member and variable composition in the high temperature end member, as manifested in data from the study site (Von Damm and Lilley, 2004). A thermal model is used to predict the subsurface temperature field, and the temperature-composition (T-C) relationships from the geochemical mixing model are then superimposed on the modeled temperature distribution to estimate the spatial distribution of fluid composition in the subsurface. From that, free energies of reactions are computed, which for temperatures below the thermal limit for life (on the order of 120°C; Kashefi and Lovley, 2003) show regions of potential microbial metabolism. Where temperatures exceed the limit for life and where relatively rapid equilibration dominates chemical dynamics, we focus our discussion on prediction of anhydrite deposition rates.

2. STUDY SITE: BIOGEOTRANSECT (9°N), EAST PACIFIC RISE

The EPR is a fast spreading mid-ocean ridge (Sinton and Detrick, 1992) with a relatively high inferred rate of magmatic resupply (Fornari et al., 2012; Liu and Lowell, 2009; Lowell et al., 2012), giving rise to vigorous hydrothermal venting at several spots along the ridge (Von Damm et al., 2003; Von Damm 2000; Von Damm et al. 1997). It is one of the best-studied mid-ocean ridge systems and copious time series datasets of chemistry, biology, and seismology exist (Tolstoy et al., 2006; Von Damm and Lilley, 2004; Shank et al., 1998). The Biogeotransect segment of the EPR (9°N) extends from 9°49.5'N to 9°50.5'N (Fig. 1) along a widened section of the axial summit collapse trough and is characterized by vigorous and long-lived high temperature (>290°C) venting and associated low temperature (<40°C) diffuse flow (Von Damm, 2000). Heat flux for a 2 km ridge segment along the Biogeotransect is estimated to be 325 ± 160 MW, with a little over 10% directly attributed to focused flow based on feature tracking in video footage of focused and diffuse flow combined with estimates of the aerial extent of each type of flow (Ramondenc et al., 2006).

Despite the disruptive effects of volcanism along the Biogeotransect, venting style has maintained a characteristic pattern through time in which low temperature diffuse fluids emanate as unfocused flow directly from basalt through cracks and broken lava pillars in close proximity to long-lived high temperature vents (Scheirer et al., 2006). Furthermore, previous observations of evolving phase separation within a single high temperature vent at EPR suggest that source fluids at depth flow along the same conduits over time (Von Damm et al., 1997; Von Damm and Lilley, 2004). Seismically-driven perturbations and co-registered variability in diffuse flow suggest a connection between diffuse and focused flow (Sohn et al., 1998), possibly via a warm

subsurface reservoir created by mixing of endmember fluid with seawater, and tapped by sites of diffuse venting (e.g., near the Rusty and Bio9 sites) but with varying degrees of additional seawater entrainment during ascent from the reservoir (Scheirer et al., 2006; Germanovich et al., 2011; Lowell et al., 2013).

In a comprehensive review of EPR diffuse fluids by Von Damm and Lilley (2004), differences between the diffuse fluid and adjacent high temperature endmember fluid were best explained by nearly conservative mixing with a minor component of conductive heating of seawater. Thus, we build on this work and model diffuse fluid as a result of mixing heated seawater with vent fluid, undergoing reactions in the subsurface.

3. METHODS

3.1. Diffuse fluid composition

For a comparison between locations sampled at various times, it is important that samples are collected using the same technique (Luther et al., 2001b; LeBris et al., 2006a, b). Diffuse flow fluid chemistry was thus compiled only from Von Damm and Lilley (2004) and related unpublished data (M. Lilley and J. Bryce, pers. comm., 2014; Table S1); gas-tight samplers were used to collect fluid for analysis of volatile components and titanium syringe major samplers were used to collect fluid for analysis of major and trace elements. Analytical methods for each type of analysis are detailed in the source publication. Both surface biota and subsurface microbial activity can cause deviation of fluid composition from a conservative mixing line between vent endmember and seawater by either consuming or producing a chemical species of interest. This study is concerned primarily with non-conservative behavior arising from

subsurface activity and we assume here that samples reported in Von Damm and Lilley (2004) have been minimally altered by surface macrofauna.

3.2. Heat transport model

Lowell and coworkers have developed a number of approaches to modeling diffuse flow near mid-ocean ridges (Lowell et al., 2003; Crowell et al., 2008; Craft and Lowell, 2009; Lowell et al., 2014). For this study, a steady-state temperature field for an axial basalt-hosted hydrothermal system is simulated by solving the coupled equations of conservation of mass, momentum and energy, assuming Darcy flow using the numerical simulator FISHES (Lewis and Lowell, 2009) in a two-dimensional model domain 2 km wide x 1.5 km deep divided into 25 m x 25 m nodes (Fig. 2). In brief, the sides of the domain are insulated and impermeable, the top is open and maintained at a constant pressure of 25MPa. 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. The heat transport model assumes uniform seawater salinity and uses a layered permeability structure representative of a fast to intermediate spreading mid-ocean ridge consisting of a 400 m thick region with a permeability of 10^{-12} m^2 (corresponding to crustal layer 2A) overlying the remaining region with permeability 10^{-13} m^2 . This permeability model is based on single pass modeling (Lowell and Germanovich, 2004; Lowell et al. 2013), which suggests that deep permeability in ridge crest hydrothermal systems is typically $\sim 10^{-13} \text{ m}^2$, and on

borehole measurement of permeability that typically ascribes a higher value in layer 2A (e.g., Fisher, 1998; Carlson, 2011). Although this model is in the single-phase flow regime, it yields discharge temperatures (approaching 300°C) and heat outputs (~100 MW) that are roughly consistent with field observations (Fig. 2) (e.g., Ramondenc et al., 2006).

3.3. Reaction path model

We used Geochemist's Workbench (GWB; Bethke, 2008) to create a reaction path model based on mixing between seawater and a vent fluid. In addition, a model of heated seawater was constructed (Wheat and Mottl, 1994). In reaction path models of conductive heating or cooling, temperature is changed incrementally with each reaction step and the fluid is speciated under the new condition. In contrast, in reaction path models of mixing between seawater and hydrothermal vent fluids, a starting fluid (e.g., seawater) is equilibrated and with each successive reaction step some mixing fluid (e.g., vent fluid) is added to the solution and the mixture instantly re-equilibrated. The temperature is determined by the mixing between modified seawater percolating through the subsurface and the end-member hydrothermal fluid, taking into account the difference in respective heat content. A 1000-fold dilution of hydrothermal fluid (350°C) into 5°C seawater results in a mixed fluid of 349.6°C. Two high temperature (350°C) end members were considered to bracket the range of observed vent compositions at 9°N EPR: a near-seawater chlorinity fluid with low gas content from Ty and Io measured in 1997 and a gas-rich fluid depleted in chloride with respect to seawater from Bio9/9' measured in 1992 (Table 1; Von Damm and Lilley, 2004). In addition, we tested mixing models with bottom seawater and heated seawater (39.5°C and 74°C) (Table 1). To explore the impact of end member variability on putative mixing processes and evaluate the results with diffuse fluid data, we first consider

data from 1997 for both end-member and diffuse fluids from the Ty-Io vents on the middle transect (shown as large filled squares in Fig. 3). We then also consider fluid data from all other years in the 1991-1997 time frame (shown as small open markers in Fig. 3) to bracket the likely range of conditions over the course of this time period. Data plotted in Fig. 3 are summarized in Von Damm and Lilley (2004) and tabulated in full in the present study (Table S1).

All models used thermodynamic data generated with SUPCRT92 (Johnson et al., 1992) using the 2007 database (Plyasunov and Shock, 2001; Shock et al., 1997) at 250 bars, or seafloor pressure. Although our model results are applied to subsurface depths of 500 mbsf, the effect of higher pressures on fluid speciation models is minimal (Helgeson, 1969). All minerals except anhydrite were prevented from precipitating. In addition, one scenario was modeled in which anhydrite and pyrite were allowed to precipitate if oversaturated, following the findings of Von Damm and Lilley (2004) (see below). Anhydrite (and pyrite where applicable) were not allowed to back-react in the system so that mixing-driven changes in fluid composition more accurately represent the composition along the flow pathway (Fig. 3). Aqueous redox pairs ($\text{H}_2\text{S}/\text{SO}_4$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, H_2/O_2 , CH_4/CO_2) were also prevented from equilibrating to enable calculation of maximum energy available for catabolic reactions below 120°C, which occur on shorter timescales than abiotic equilibration (Janzen et al., 2000; Rickard, 1997; Ohmoto and Lasaga, 1982; Foustoukos et al., 2011; Horita and Berndt, 1999). The predicted fluid composition as a function of temperature was used to calculate the free energy for a number of reactions (Table 2). Free energy of reactions at hydrothermal conditions was calculated as:

$$\Delta G = RT \cdot \ln(Q/K) \quad (1)$$

where ΔG is the free energy of reaction (J/mol), Q is the reaction quotient, K is the equilibrium constant at *in situ* temperature, T (K), and R is the ideal gas constant (8.314 J/mol/K). Our thermodynamic modeling does not account for cumulative biological processes along the flow-path, which catalyze exergonic transformations not at equilibrium at temperatures amenable for life. Thus deviations between model predictions for ‘biologically active’ chemical species at the surface and measurements in diffuse fluid samples taken from bare rock environments may reflect a subsurface biological imprint.

3.4. Subsurface fluid composition and anhydrite deposition rates

We estimate the concentration of the full suite of chemical species throughout the model domain using the heat transport model and modeled composition (C) – temperature (T) trends. However, this mapping between T and C depends on whether a fluid parcel obtained its temperature through conductive heating and cooling, mixing, or direct hydrothermal input. We delineate the zone dominated by conductive heating versus mixing by calculating the difference in temperature fields between the full heat transport model (which includes both advective and diffusive terms) and a purely conductive heating model with equivalent boundary conditions. The division, indicated by the bold red line in Figs. 2, 4 and 5, is set at the point where the difference exceeds an offset of 1°C; locations closer to the vent axis are considered dominated by mixing. However, in the downward path of the recirculating seawater, the temperature field is consistent with conductive heating. We therefore mix vent fluid with fluid of seawater composition which had been first heated. We used GWB to incrementally heat the ‘cold’ seawater (at 5°C) to higher temperatures (‘warm’ seawater at 39.8°C and ‘hot’ seawater at 74.3°C) under the same assumptions used in the mixing model (i.e., only anhydrite precipitation

allowed). While the difference in chemical composition is small (Table 1), a seawater parcel entering the mixing zone at the surface at 5°C nevertheless will exhibit a different T-C relationship than a parcel that has been heated to a higher temperature before entering the region where seawater and venting fluid mix.

Rates of anhydrite deposition during the in-mixing of vent fluid into the percolating seawater are estimated by keeping track of the amount of anhydrite formed in progressively hotter equilibration steps, then dividing by the time between each step ($\Delta t = \text{distance/velocity}$ as obtained from the flow simulations). To estimate sealing times, volumetric rates are translated into volume changes using the molar volume of anhydrite.

4. RESULTS

4.1. Subsurface temperature and flow field

The flow model describes a fast or intermediate-spreading ridge segment dominated by cross-axis flow, and leads to discharge temperatures approaching 300°C and a heat output of ~100 MW. The heat transport model predicts the 120°C isotherm to parallel the rising hot vent fluid from the surface to a depth of approximately 300 mbsf at which point the isotherm bends and the temperature field resembles a typical geothermal heat gradient (Fig. 2). Thus, the subsurface zone of life (temperatures < 120°C) is extensive, and 0.5 km away from the vent axis is estimated to reach on the order of 500 m beneath the seafloor (Fig. 2). The zone where mixing rather than conductive heating dominates the thermal regime extends ~600 meters away from the focused flow discharge zone, then begins tapering at ~1000 meters below the seafloor to a vanishingly small width at the base of the model domain (Fig. 2).

4.2. Comparison of modeled and observed fluid composition

Diffuse fluids emanating from non-colonized surfaces at the East Pacific Rise illustrate the wide range of temperatures and salt concentrations in different vents (Fig. 3). Data in Fig. 3 are plotted against Mg, considered a conservative tracer, rather than temperature; fluid temperature is generally higher at low Mg concentrations, but this relationship is typically weak during individual sampling campaigns (Fig. 3b). Modeled temperatures tend to be lower than the measured values, consistent with conductive heating inferred by Von Damm and Lilley (2004), a process that renders temperature less suitable for identifying conservative and non-conservative species. Based on comparison between data and modeled mixing trends, some species follow conservative mixing trends (e.g., Cl), and others show significant deviation from these trends (e.g., Fe and CH₄).

Filled squares in Fig. 3 show diffuse fluid composition for Ty-Io in 1997, the vent/year combination used as the basis for the gas-poor hydrothermal end member in the mixing models. Dissolved H₂S increases with decreasing Mg, generally exceeding mixing predictions both with and without Fe-S precipitates (solid lines in Fig. 3a). Dissolved CO₂ reported at 9N increase linearly with Mg with some scatter around the model estimates using a Ty-Io vent fluid endmember (Fig. 3c). Total Fe concentrations in diffuse samples from Ty-Io fall below predictions (Fig. 3d, solid line). Mixing in which Fe-S precipitation or FeS complexation occurs (Luther et al., 2001a) produces a fluid depleted in all dissolved iron (model results not shown). Diffuse fluids tend to show excess methane relative to conservative mixing and do not correlate with temperature or Mg (Fig. 3e).

Figure 3 demonstrates that the bulk of all data (e.g., H_2S , Cl_T , CO_2) over the time period of interest fall between trends defined by mixing between seawater and either hydrothermal fluid with very low chloride (Bio 9 from 1992) or hydrothermal fluid with chloride comparable to seawater and low gas content (Ty-Io from 1997). Some chloride concentrations fall outside the brackets and point to an even higher chloride concentration than the selected Ty-Io 1997 sample, which we use as vapor-poor endmember in our models because it had the lowest gas content. Total Ca is modeled to vary little with Mg, and the observed values are also largely scattered around seawater values (Fig. 3f). Thus, these two hydrothermal end member types approximately bracket mixing conditions over several years for this site. By considering how energy and anhydrite deposition rate change within this range, and assuming the models accurately represent mixing processes at depth, we can extrapolate the possible range of subsurface conditions over a seven-year period.

4.3. Subsurface reactions and energetics

The composition of the fluid in conjuncture with the flow field provides insight into anhydrite deposition rates in the hydrothermal vent subsurface (Fig. 4). Rates in each of the three swaths of particle tracks shown in Fig. 4 are calculated as described in section 3.4, combining the results of the transport model with those of a mixing model, whose hydrothermal end member composition is Ty-Io and whose seawater end-member composition is that of seawater heated to the temperature at the point of entry to the mixing zone.

The change of permeability associated with the transition from extrusives of layer 2A to the underlying sheeted dike pinches together the lateral temperature gradient near the high temperature hydrothermal upflow zone at ~400 mbsf (Fig. 2). This pinch point results in steep chemical gradients in the combined model for this portion of the system. The chemical transition between the hotter and cooler parts of the system (centered ~100 meters off axis between the 150 and 225 °C isotherms) leads to the highest calculated anhydrite deposition rates for the model domain, reaching a maximum of 4.25×10^{-7} mol/m³/s at reference point #1 (Fig. 4; Table 3). Another notable feature in the temperature field occurs at ~100 mbsf and 50 m away from the vent axis, where the thermal model predicts sub-horizontal isotherms and thus a thermal gradient across the direction of upflow. SO₄ concentrations at this point in the circulation path are sufficiently low as to prohibit any further anhydrite precipitation.

The relative importance of hydrothermal and seawater end member composition on the rate of anhydrite deposition is shown for 2 reference points (numbered circles in Fig. 4), with rate estimates tabulated in Table 3. Based on our combined model, calculated rates vary by less than a factor of 2 over all 6 mixing scenarios (Table 3), suggesting that even gas-rich and calcium-depleted fluids can support robust anhydrite deposition.

Prior to its transition to flow at temperatures inhospitable to microbes, a fluid parcel meanders through to a regime where temperature conditions are favorable for microbial reactions. Here, the free energy for a number of key metabolic processes at temperatures below the upper threshold for life is substantial (Table 2). Free energy estimates of mixed solutions depend on the fluid composition of the end members. We observe some difference in spatial distribution for

the warm and hot cases (Fig. 5c, d) compared with the cold case alone (Fig. 5a, b). In the case of methanogenesis, these differences manifest themselves as less exergonic conditions deeper in the model domain (Fig. 5c, d), but the effect is most pronounced at the edge of the mixing zone where the impact of conductive heating is most prevalent. However, overall, the energetics of most reactions show little variation with respect to changes in either hydrothermal end member composition or seawater end member temperature, especially in the most exergonic parts (Table 2). The higher variability for iron redox reactions (for which standard deviation of the 6 scenarios may be as high as 36%) reflects the influence of low concentrations of Fe^{2+} on the reaction quotient term in equation (1). In most cases, however, the redox reactions considered remain thermodynamically favorable throughout the mixing zone (Table 2). Oxidation reactions involving sulfur species, methane and iron are the most energetically favorable processes, provided that molecular O_2 is present in sufficient quantities (Table 2). For example, marine microaerophilic chemolithoautotrophs metabolize at dissolved oxygen concentrations as low as 1-10 μM (Krieg and Hoffman, 1986). Reduction of iron oxyhydroxides provides more energy than sulfate reduction and methanogenesis, but all of them are energetically favorable (Table 2).

5. DISCUSSION

5.1. Flow and temperature of the diffuse fluid

Kilometer-simulations of heat transport in mid-ocean ridges commonly show the development of convection in the vicinity of the ridge axis (Lowell et al., 2014; Fontaine et al., 2014; Coumou et al., 2009; Wilcock, 1998), with maximum upflow velocities ranging from 10^{-6} to 10^{-7} m/s. Two-dimensional models employing a bi-layer permeability configuration (e.g. Wilcock 1998, Lowell et al., 2015), as used in this study, yield temperatures of the discharging vent fluid slightly lower

than those obtained with models that include a third dimension and cross-axis permeability variation (Fontaine et al., 2014; Coumou et al. 2009), which represent the observations more closely. This is attributed to the induced circulation in layer 2A which results in enhanced mixing between the high-temperature discharge and seawater. Furthermore, the 25 m grid size does not resolve finer scale phenomenon relevant in the field. Nevertheless, entrainment of seawater into the focused flow is coarsely approximated by our temperature and flow field, which shows shallowly circulating cold and warm solutions intersecting rapidly ascending hot water. Importantly, the permeability contrast between an extrusive volcanic layer and an intrusive layer of sheeted dikes (Larson et al., 2009; Fontaine and Wilcock, 2006) drives mixing and is consistent with 9N crustal structure inferred from seismic studies (e.g., Sohn et al., 2004).

5.2. Surface manifestation of subsurface activity

Geochemical model predictions match observed concentrations of chlorinity (a conservative tracer assuming no further phase separation) in fluids emanating from non-colonized surfaces, in particular those that mix cold seawater with the 1997 Ty-Io end member (Fig. 3b). Deviations from model predictions we interpret to be indicative of reactions in the subsurface. Our model indicates depleted Fe_T for the 1997 Ty-Io diffuse fluids (compare filled squares and solid line in Fig. 3d), suggesting the occurrence of pyrite precipitation that is not matched in H_2S (Fig. 3a). The excess H_2S in the 1997 Ty-Io fluids suggests a significant population of sulfate reducers active in the subsurface. Likewise, dissolved CH_4 in the 1997 Ty-Io fluids is elevated relative to model predictions, suggesting subsurface methanogenesis (see below).

The bracketing of all diffuse fluid measurements between endmember model estimates for the conservative constituents subject to mixing of seawater and vent fluid (Fig. 3b) allows us to employ the C-T relationship determined from geochemical equilibrium modeling to estimate the spatial distribution of fluid composition in the subsurface given the modeled temperature distribution (Fig. 2). This provides the foundation for two novel assessments: 1) when combined with the flow field, deposition rates for anhydrite, for which the assumption of instantaneous precipitation is kinetically justified (Goldfarb et al., 1983), can be estimated; 2) it allows the quantification of available chemical energy across space, which may indicate preferred zones of active microbial metabolism. However, it is noteworthy that the modeled subsurface temperature field does not show tightly coupled diffuse and focused flow at the surface, even though observations of this venting style are widespread.

As the modeled concentration fields are based on thermodynamic equilibria and do not account for microbial process thriving on redox disequilibria, we estimate the potential for their occurrence from available energies of reaction. Sulfate reduction and methanogenesis, two metabolic processes with clear signatures in diffuse fluids (Figure 3a,e), show favorable reaction energetics (up to ~ -18 and ~ -13 kJ/mol electron, respectively). The observed excess $\text{CH}_4(\text{aq})$ (Fig. 3e) has been attributed to microbial methanogenesis in the subsurface (Proskurowski et al., 2008; Von Damm and Lilley, 2004; Lilley et al., 1993), an interpretation consistent with our model predictions, which also reveal that abiotic methane production at higher temperatures is energetically unfavorable (not shown). A number of diffuse fluids (predominantly Bio 9' samples) have iron that exceeds all modeled trends. The source mechanism for this excess remains elusive. There is clear evidence in the fluid signature of methanogenesis (Fig. 3e),

consistent with favorable reaction energetics (Table 2). H₂S concentrations exceed modeled estimates for 1997 at Ty-Io, but generally stay within the range encompassed by the modeled endmember conditions. This comparison implies that both sulfate reduction and sulfide removal are viable. While O₂ levels are poorly constrained and represent an upper limit, the highly favorable energetics for sulfide oxidation (Table 2) coinciding with strong indication of dominant sulfate reduction suggest that factors other than maximum available energy govern the establishment of metabolic pathways, or close oxidation-reduction coupling that precludes a permanent imprint in reactant pools. Pyrite oxidation and (to a much smaller extent) elemental sulfur disproportionation are also predicted to provide free energy, in keeping with recent studies suggesting the importance of sulfur-based metabolism in hydrothermal environments (Anantharaman et al., 2013; Rogers and Schulte, 2012; Slobodkin et al., 2012). Because the Gibbs free energies do not vary strongly with temperature, uncertainties with regard to subsurface flow are not expected to have a major impact on the distribution of free energy available for microbial metabolism.

5.3. Anhydrite formation

Model simulations show a distinct spatial pattern in the distribution of anhydrite formation, with peak anhydrite deposition occurring ~100 meters away from the zone of focused up flow (Fig. 4). Wilcock (1998) suggests an anhydrite shell could explain the discrepancy between measured and modeled temperature, a conclusion qualitatively supported by our combined model. Our results also show that anhydrite deposition is relatively independent of vent fluid composition, indicating it has the potential to ubiquitously affect flow channels under a variety of conditions, though we do see lower overall rates of deposition with Bio9' compared with Ty-Io.

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398 To assess the likely impact of anhydrite formation on permeability changes, we used the modeled
 399 anhydrite deposition rates. The particle tracks in Fig. 4 depict a curved region between the 150°C
 400 and 200°C isotherms extending from ~200 down to ~300 mbsf where the rate of anhydrite
 401 deposition is at its maximum (approximately 4.25×10^{-7} mol/m³/s; Fig. 4). The rate, $R_{\Delta V}$, at
 402 which the volume of open space is reduced by anhydrite precipitation is then:

$$403 \quad R_{\Delta V} = \frac{\phi \cdot MW_{CaSO_4}}{\rho_{CaSO_4}} \cdot R_{rxn} \quad (2)$$

404 where ρ_{CaSO_4} is the density of anhydrite (2.935 kg/L, Hurlbut and Klein, 1977), MW_{CaSO_4} is its
 405 molecular weight (0.13614 kg/mol), ϕ is porosity (0.1) and R_{rxn} is the rate at which anhydrite
 406 precipitates ($\sim 4 \times 10^{-7}$ mol/m³/s). Using the parameter values outlined here, we calculate a value
 407 for $R_{\Delta V}$ of 6.2×10^{-5} yr⁻¹. The sealing time can then be computed as

$$408 \quad t_s = \frac{\Delta\phi}{R_{\Delta V}} \quad (3)$$

409 where $\Delta\phi$ is the difference between the porosity and the percolation limit. For massive anhydrite
 410 samples, Gribblin et al. (2008) report a permeability of approx. 10^{-13} m², and Zhu et al. (2013)
 411 report a very strong dependency on porosity, Thus, $\Delta\phi$ of 0.02-0.04 represents a reasonable
 412 choice and translates to a sealing time of ~320-640 years.

413

414 For comparison, Lowell et al. (2003) use scale analysis to show that the sealing time can be
 415 given approximately by the expression

$$416 \quad \tau_s = \frac{\Delta\phi \rho_{CaSO_4} (v/\alpha) \ell}{\rho_f T_m^2 (dC/dT) k} \left(\frac{x}{w} \right) \quad (4)$$

417 where α and v are the thermal expansion coefficient and kinematic viscosity of the fluid,
 418 respectively; ℓ is the thickness and k is the permeability of layer 2A, respectively; ρ_f is fluid

density, g is the acceleration due to gravity; T_m is the temperature of anhydrite precipitation; dC/dT is the derivative of the solubility of anhydrite as a function of temperature, x is the width of the mixing zone, and w is the width of the zone of the induced downward circulation in layer 2A. Equation (4) is modified slightly from equation (18) in Lowell et al. (2003) to take into account that the width of the mixing zone may differ from that of the downgoing limb of the induced convection cell in layer 2A. Using $v/\alpha = 10^{-2} \text{ }^\circ\text{C}\cdot\text{m}^2/\text{s}$ in the downgoing fluid, $\ell = 400 \text{ m}$, $g = 9.8 \text{ m/s}^2$, $T_m = 150^\circ\text{C}$, $\rho_f = 0.948 \text{ kg/L}$ – calculated according to Driesner (2007 and Heinrich) at 250 bars and T_m , a temperature at which the chloride concentration is 434 mmol/kg – $dC/dT = 3 \times 10^{-5} \text{ kg}/(\text{kg}\cdot^\circ\text{C})$, $k = 10^{-12} \text{ m}^2$, and $x/w = 0.25$, we obtain $\tau_s \sim 300 - 600$ years for the same porosity reduction used in equation (3) above ($\Delta\phi = 0.02\text{-}0.04$), which is surprisingly similar to our estimate.

While we do not know the required porosity reduction for anhydrite formation to shut off circulation, the above estimates suggest that it is unlikely that these calculated deposition rates are sufficiently fast to seal off flow channels (even with our relatively small required porosity reduction). Tectonic and magmatic events at both intermediate (Dziak et al., 2011) and fast-spreading (Fornari et al., 2012) mid-ocean ridges occur on timescales shorter than our calculated sealing times, and these events have the potential to control the extent of permeability change and its impact on subsurface flow either by mechanically breaking anhydrite barriers (Crone et al., 2010; Germanovich et al., 2011) or by producing high temperature vapor-rich fluid that can dissolve these barriers (Blounot and Dickson, 1969; Von Damm et al., 1997).

If the above estimate of the ratio of the mixing width to the recharge width, x/w in equation (4), is reduced by an order of magnitude, the sealing time drops to 30 years, which is much closer to the time observed between eruptions at this site (~17 years). A similar result from our model would require steeper temperature gradients or faster flow velocities. The latter seems unlikely because of general agreement between our study and other studies that look at convection of this scale (Coumou et al., 2009; Fontaine et al. 2014). Steeper temperature gradients, however, might be achieved with higher spatial model resolution, an advance that may also better show adjacent diffuse and focused flow as has been observed in the field.

A different approach for estimating anhydrite deposition rate was taken by Pontbriand and Sohn (2014) who estimate a 'seismogenic' deposition rate of 27-51 m³/yr by using the number of microearthquakes detected per day and assuming anhydrite precipitation is the underlying cause of microseismicity. This leads to formation times for the TAG mound between 391-727 years. The difference in assumptions between Pontbriand and Sohn (2014) and the current study regarding the effect of anhydrite deposition (i.e., cracking in the former, flow constriction in the latter) prevents a direct comparison of formation time with sealing time. In both cases, however, the effects of anhydrite deposition on hydrothermal circulation are expected to unfold over long time scales.

5.4. Limitations

The combined thermal and chemical model presented here relies on simplifying assumptions, such as the fast kinetics implied by the equilibrium speciation calculation (Goldfarb et al., 1983) and steady state flow fields (Scheirer et al., 2006). These assumptions are considered appropriate

for the study site and allow us to hone in on the effects of mixing seawater and vent fluids, and the possible extent, dimensions and energetics of a hydrothermally supported Zone of Life.

Our approach shows chemical changes in regions where flow paths cross isotherms (Fig. 4), reflecting the use of temperature as the master variable in applying C-T trends to the steady state temperature field. It cannot account for dynamic feedbacks between flow and reaction, as may emerge over longer timescales through the precipitation of anhydrite.

Our model is limited in its spatial accuracy by the resolution of the transport model predictions, which may need to be increased to quantify steeper temperature gradients; this could lead to shorter estimates of sealing times. In fact, the observations of diffuse fluids reported here are taken in close proximity of focused flow, while the model predicts such discharge about 100 m away from the vent axis. Thus, resolving small-scale diffuse flow embedded in large-scale ridge circulation models may be required to better capture adjacent diffuse and focused flow observed in the field. The need for high spatial resolution in parts of a large domain poses significant challenges to the modeling of hydrothermal vents. Furthermore, only a limited number of existing codes, e.g., TOUGHREACT (Xu et al., 2011) and PFLOTRAN (Hammond et al., 2012) are capable of simulating multiphase reactive transport across a range of pressure and temperature conditions relevant to parts of hydrothermal vent environments. However, Larson et al. (2012) demonstrated that TOUGHREACT source code can be modified to accommodate an EOS suitable for most MOR hydrothermal conditions ($p > 500$ bars °C, $T > 600^{\circ}\text{C}$), though gaps in the thermodynamic database required for chemical modeling persist.

6. CONCLUSION

This study presents a novel combination of heat and geochemical models, adding a previously lacking spatial context to free energy calculations, and providing estimates for rates of abiotic deposition of anhydrite. Comparison of model results with published diffuse fluid compositions from the East Pacific Rise (Von Damm and Lilley, 2004) reproduces the previously observed prominent signature indicative of sulfate reducers and methanogens in the subsurface. Our model calculations allow predictions of free energy, and indicate significant available energy for several reactions involving sulfur compounds and methane, and to a first order, supports considering diffuse flow fluids as a mixture between cold seawater (e.g., Table 1) and a generic hydrothermal (e.g., reducing and calcium-rich) end member. The absence of strong spatial variability in Gibbs free energy suggests energetics may not be the factor controlling the extent and distribution of microbial growth. Predicted rates of anhydrite deposition are also relatively independent of variability in hydrothermal end member composition and the temperature of seawater entering the mixing zone, and appear to be too slow to seal off large-scale circulation. However, assuming steeper temperature gradients can be achieved on a more local level without changes to fluid velocity or the range of temperatures, (a change that would enhance deposition rates without impacting the predicted range of energy), the interplay of end member composition and anhydrite solubility could influence the delivery of hydrothermal energy sources to microbial communities in nearby diffuse environments. The configuration of energy conduits could thus play a larger role than the energetic hierarchy in shaping microbial habitats.

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FIGURE CAPTIONS

Table 1: Compositions of end member vent and seawater solutions. Endmember vent fluid compositions were reported by Von Damm and Lilley (2004) for the northern transect of the EPR in 1992 (Bio9') and the middle transect in 1997 (Ty and Io vents), with data for Na, Ca and pH provided by M. Lilley and J. Bryce. Prior to mixing, endmembers were speciated at 350°C, the maximum temperature of the thermodynamic database, which is 5 and 38°C lower than measured temperatures for Ty-Io and Bio 9' respectively. The 1992 sample of Bio9' is significantly depleted in chloride and enriched in CO₂ and other volatiles, so we use this composition to bound end member variability at the vapor-rich end. The Ty-Io solution from 1997 has higher chloride and lower gas content than Bio 9', so we use this to bound end member variability at the vapor-poor end. Other high temperature sites have higher chloride concentration than Ty-Io, but we selected the 1997 sample from this site for the current study because it has the lowest vapor content of all high temperature samples reported in Von Damm and Lilley (2004). Cold seawater composition is given to the right of the high temperature end member fluids, followed immediately by the composition for seawater that has been heated to progressively higher temperatures. We arrive at the heated seawater compositions by using Geochemist's Work Bench to speciate the fluid incrementally during heating.

Table 2: Catabolic (energy-gaining) reactions considered. The number of electrons transferred are shown for each reaction and available energies are given in kJ/mol of electron transferred. Shown are maximum and minimum energy values, computed as the average ($\pm$ standard deviation) of the extrema in each of the six mixing scenarios (Ty-Io and Bio 9' end members

each mixed with seawater of 5, 40 and 74°C). Reactions are sorted according to energetic favorability, with the most exergonic (pyrite oxidation) at the top, and the least exergonic (sulfur disproportionation) at the bottom.

Table 3. Comparison of anhydrite deposition rates (in mol/m³/s) for each of the six mixing models at reference points in anhydrite transition zones as shown in Fig. 4. Reference points 1 and 2 reflect mixing between the Ty-Io end member and either cold or 74°C seawater, respectively. The other five rates at each of these reference points were calculated by applying each of the 5 remaining mixing trends to the given point in space. Asterisks indicate the rate shown graphically in Fig. 4. The rate varies by less than a factor of 2 across all 6 mixing scenarios. Rates for cases involving the vapor-rich end member are lower than for the cases that use the vapor-poor end member.

Figure 1: Location of 9N EPR with inset of expanded view of vent field. Dots indicate individual vent sites. The map was created with the GeoMapApp website application (<http://www.geomapapp.org>; Ryan et al., 2009).

Figure 2: Isotherms over the full 2000 m x 1500 m heat transport model domain used for applying temperature-concentration trends in the combined model. Both contours and colors reflect temperature in °C. Arrow size is proportional to flow velocity, with vertical speeds ranging from 10⁻¹⁰ to 10⁻⁵ m/s for downgoing fluid and from 10⁻⁹ to 10⁻⁶ m/s for rising fluids. Horizontal speeds range from 10⁻¹² to 10⁻⁶ m/s. The black box shows the 500 m x 700 m subregion of the model domain used for showing combined model results in Figs. 4 and 5. This

subregion includes the permeability transition at ~400 m where isotherms are pinched together.
The red line outlines a mixing zone where temperature-concentration trends are most applicable.

Figure 3:

Comparison of available diffuse fluid chemistry over non-colonized surfaces from Biogeotransect (9N EPR) provided to the authors by M. Lilley and J. Bryce. Diffuse fluids from Y and TWP are displayed as open triangles; Bio9 are open circles; Ty-Io are crosses, except for Ty-Io in 1997, which are solid squares. Predicted fluid composition of mixing between cold seawater and the 1997 Ty-Io endmember vent fluid or the 1992 Bio9 vent fluid are indicated with solid lines and dashed lines, respectively. Models allowing anhydrite precipitation are shown with thick lines and models with additional pyrite precipitation are shown with thin lines. Seawater is shown as a dotted line for reference.

Figure 4: Particle tracks shown as sequence of circles, color-coded to anhydrite deposition rate in $\text{mol}/\text{cm}^3/\text{s}$ according to the color bar. The solid red line delineates the region where mixing is the dominant control on fluid temperature, a key requirement for using the steady state temperature field from the transport model to calculate chemical concentrations in the model domain based on C-T relationships given by the mixing model. From the upper left to the lower right, these three entry points occur at ~5, 40, and 74°C. The backdrop shows temperature contours, which are the same as in Fig. 2. Numbered circles denote the two reference locations discussed in Table 3. White colored dots in the tracks prior to mixing zone entry represent the

portion of the transport model domain where temperature is dominated by conductive heating and where C-T relationships calculated by mixing models are not applicable.

Figure 5. Comparison of free energy (kJ/mol of electrons) for methanogenesis based on mixing between each of the two hydrothermal end members Ty-Io (A,C) and Bio 9' (B,D) and either cold seawater only (A, B) or cold, warm and hot seawater within the appropriate fluid pathway (C, D). The use of warm and hot mixing trends yields less exergonic conditions in the two lower (and hotter) fluid pathways. However, maximum available free energy and the pattern of energy distribution (most exergonic near the seafloor, less so further down) are independent of the seawater end member temperature.

FIGURES

1
2 **Figure 1.**

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3 **Figure 2.**

Figure 3

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2 **Figure 4.**

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3 **Figure 5.**

TABLES

1 **Table 1.**

Input Parameter	Units	Ty-Io Nov. 1997	Bio-9' March 1992	Cold Seawater	Heated seawater I (warm)	Heated seawater II (hot)
T	°C	350	350	5	39.5	74
pH		3.1	3.3	7.8	7.454	7.245
Mg ⁺⁺	mmol	1.00E-10	1.00E-10	52.2	52.2	52.2
Cl ⁻	mmol	403	75.5	540	540	540
Na ⁺	mmol	359	75	464	464	464
SO ₄ ⁻⁻	mmol	1.00E-15	1.00E-15	27.9	27.9	27.9
Ca ⁺⁺	mmol	17	7.8	10.2	10.2	10.2
H ₂ S	mmol	10.3	26	1.00E-10	1.00E-10	1.00E-10
Fe ⁺⁺	μmol	3780	1670	1.00E-15	1.00E-15	1.00E-15
Fe ⁺⁺⁺	μmol	1.00E-15	1.00E-15	0.0005	0.0005	0.0005
CO ₂	mmol	67.4	130	2.3	2.3	2.3
H ₂	μmol	390	2010	1.00E-15	1.00E-15	1.00E-15
CH ₄	μmol	50	89	1.00E-15	1.00E-15	1.00E-15
O ₂	μmol	1.00E-15	1.00E-15	76	76	76

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1 **Table 2.**

Rxn Name	Catabolic Reaction	# Electrons Transferred	$\Delta G_{\min}$ (kJ/mol)	$\Delta G_{\max}$ (kJ/mol)
Pyrite Oxidation	$2\text{FeS}_2(\text{s}) + 7\text{O}_2 + 2\text{H}_2\text{O} = 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+$	28	-187.2 ± 1.1	-172.1 ± 1.1
Methanotrophy	$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$	8	-99.2 ± 0.7	-95.1 ± 0.4
Hydrogen Sulfide Oxidation	$\text{H}_2\text{S}(\text{aq}) + 2\text{O}_2(\text{aq}) = \text{SO}_4^{2-} + 2\text{H}^+$	8	-97.9 ± 0.6	-89.7 ± 0.8
Iron Oxidation	$4\text{Fe}^{2+} + \text{O}_2 + 6\text{H}_2\text{O} = 4\text{FeO}(\text{OH})(\text{s}) + 8\text{H}^+$	4	-89.9 ± 4.0	-81.5 ± 5.0
Knallgas	$2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$	4	-46.1 ± 2.5	-41.4 ± 2.1
Iron Reduction	$2\text{FeO}(\text{OH})(\text{s}) + \text{H}_2 + 4\text{H}^+ = 2\text{Fe}^{2+} + 4\text{H}_2\text{O}$	2	-29.8 ± 7.5	-18.1 ± 6.5
Sulfate Reduction	$\text{SO}_4^{2-} + 2\text{H}^+ + 4\text{H}_2 = \text{H}_2\text{S} + 4\text{H}_2\text{O}$	8	-17.7 ± 2.0	-10.1 ± 2.5
Methanogenesis	$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$	8	-13.3 ± 2.0	-8.8 ± 2.2
AOM	$\text{CH}_4 + \text{SO}_4^{2-} + 2\text{H}^+ = \text{CO}_2 + \text{H}_2\text{S} + 2\text{H}_2\text{O}$	8	-5.1 ± 0.2	-3.1 ± 0.3
Sulfur Disproportionation	$4\text{S}_{(\text{s})}^0 + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 3\text{H}_2\text{S} + 2\text{H}^+$	6	-3.3 ± 0.8	-0.8 ± 0.6

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Table 3.				
Model ID	Seawater EM (°C)	Hydrothermal End Member	Rate (mol/m ³ /s) × 10 ⁻⁷ Ref. 1: (x,y) = (64,208)	Rate (mol/m ³ /s) × 10 ⁻⁷ Ref. 2: (x,y) = (86,369)
1	5	Ty-Io	4.25*	3.26
2	40	Ty-Io	4.60	3.73
3	74	Ty-Io	5.08	4.13*
4	5	Bio 9'	3.54	2.91
5	40	Bio 9'	3.66	3.03
6	74	Bio 9'	3.84	3.17