Massive, low-temperature hydrothermal flow from a basaltic outcrop on 23 Ma seafloor of the Cocos Plate: Chemical constraints and implications

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[1] Systematic variations in pore water chemical and thermal profiles from sediment gravity cores indicate the presence of a “cool” (10–20°C) ridge-flank hydrothermal system within basement surrounding Dorado outcrop, a small basaltic edifice on 23 Ma seafloor of the Cocos Plate. Dorado outcrop is located within a 14,500-km² region of cool seafloor, where 60–90% of the lithospheric heat is removed advectively. Pore water chemical profiles from sediments on and near Dorado outcrop indicate a range of diffusive, advective, and diagenetic influences, including evidence for upward fluid seepage at up to several meters per year. The chemical composition of fluid that discharges from Dorado outcrop is only slightly different from that of bottom seawater. Pore water nitrate and geological constraints suggest a minimum volumetric flux per unit width of basement of 1800 m³ a⁻¹ cm⁻¹ and a total seawater flow through Dorado outcrop of ~3000 kg a⁻¹. This flow rate is orders of magnitude greater than that estimated from Baby Bare outcrop, a similarly sized basement edifice on younger seafloor on the eastern flank of the Juan de Fuca Ridge. The nearest likely basement recharge site is Tengosed Seamount located ~20 km away. Calculated rates for the specific discharge at Dorado outcrop are consistent with young ¹⁴C ages, suggesting a residence time in basement no greater than a few hundred years. If the fluid exiting from Dorado outcrop is characteristic of ridge-flank hydrothermal circulation in general (cool, relatively unaltered), these systems can have an important influence on global geochemical budgets for many solutes (e.g., chloride, magnesium, sulfate, potassium, lithium, boron, silica, phosphate, manganese, and iron) because the rate of fluid discharge is so large. Ridge flank fluids having the same composition of fluid exiting Dorado outcrop also may contribute to subseafloor microbial processes within basaltic basement and the overlying sediment, and suggest that oxidation reactions within basaltic crust can continue well beyond 10 Ma in some settings.

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1. Introduction

[3] The hydrothermal heat flux from seafloor ridge flanks, areas far from the magmatic and thermal influence of seafloor spreading, is ~8 TW, comprising ~30% of the total heat flux from the oceanic lithosphere [e.g., Parsons and Sclater, 1977; Stein and Stein, 1994]. Global estimates of advective seafloor cooling are based on the difference between heat flow observations and conductive predictions from lithospheric cooling models, the latter being well constrained by global bathymetric and heat flow data sets. The comparison of heat flow observations and conductive cooling models suggests that the largest fraction of ridge-flank heat loss occurs within young plates, through seafloor <10 Ma in age, but measurable advective heat loss continues on average until seafloor reaches 65 Ma. Some older seafloor sites continue to lose heat advectively beyond this age, and hydrothermal circulation redistributes heat regionally and locally at numerous sites beyond 100 Ma [e.g., Von Herzen, 2004].

[4] Although ridge-flank hydrothermal circulation has been studied for several decades, it has proven difficult to resolve several important characteristics of fluid, heat, and solute transport within these systems. It has been particularly challenging to identify and sample sites of low-temperature, ridge-flank hydrothermal egress and to quantify the global geochemical impacts of these circulation systems. There are subtle differences in the composition of most ridge-flank hydrothermal fluids, relative to bottom seawater, because typical fluid reaction temperatures are low (≤10–20°C), leading to slow inorganic reaction kinetics, and residence times are short. But because fluid flows are so large (approaching or exceeding riverine flows on a global basis), even small differences in fluid composition can have a major influence on the budgets and cycling of biochemically important solutes in seawater [e.g., Wheat et al., 2003; Wheat and Mottl, 2004].

[5] The small number of ridge-flank hydrothermal sites that has been studied fall into two general categories. Most of these sites are located on young seafloor where sediment cover is patchy and basement rocks are exposed across wide areas, leading to a large fraction of advective heat loss, and low basement fluid temperatures [e.g., Williams et al., 1974; Langseth et al., 1984; Johnson et al., 1993; Villinger et al., 2002]. In cool and open circulation systems such as these, it is difficult to trace fluid pathways, locate or link hydrothermal recharge and discharge sites, determine rates of transport or residence times, or collect samples of pristine hydrothermal fluids.

[6] At the other extreme are warmer and more restricted ridge-flank systems where basement temperatures are higher and fluids are more altered [e.g., Mottl and Wheat, 1994; Wheat and Mottl, 1994]. Fluid pathways and flow rates are more readily quantified in such settings, but the associated advective heat fluxes are relatively small and have little influence on regional heat loss. Although chemical fluxes from warm ridge flank hydrothermal systems such as these may influence some geochemical budgets, these systems are not characteristic of processes that remove large quantities of lithospheric heat on a global basis [e.g., Wheat and Mottl, 2000].

[7] Both kinds of ridge-flank hydrothermal systems are found in the FlankFlux region on the eastern flank of the Juan de Fuca Ridge, cool/open and warm/restricted [e.g., Davis et al., 1992; Wheat and Mottl, 1994; Elderfield et al., 1999; Wheat et al., 2000, 2004; Hutnak et al., 2006]. At the western end of this region close to the ridge (≤1.5 Ma seafloor), seafloor heat flow is suppressed by 60–90% relative to lithospheric predictions, and temperatures in the uppermost basaltic basement aquifer are low [Davis et al., 1992; 1999; Hutnak et al., 2006]. Here, the composition of the basaltic formation fluid is slightly different from that of overlying seawater, as inferred from pore water samples squeezed from sediment cores recovered...
from just above basaltic basement [e.g., Elderfield et al., 1999]. Because there is extensive basaltic exposure in this area, it is difficult to resolve patterns and pathways of fluid circulation.

In contrast, at the eastern end of the FlankFlux region (3.5–3.6 Ma seafloor), fluid flow in basaltic basement below thick sediment redistributes heat locally [Davis et al., 1992; Spinelli and Fisher, 2004], and a few basaltic outcrops (e.g., Baby Bare outcrop) focus discharge of warm, highly altered basaltic formation fluids [Wheat and Mottl, 2000; Wheat et al., 2004]. Sampling warm formation fluids in this area is easier because discharge is so restricted; however, the small flows have virtually no influence on regional heat loss from the plate [Davis et al., 1999; Fisher et al., 2003a; Hutnak et al., 2006]. Hydrothermal circulation in this area is currently a weak vestige of what was once a much more open and efficient system, like the western FlankFlux region, before Pleistocene sedimentation buried large areas of basaltic basement [Underwood et al., 2005; Hutnak and Fisher, 2007].

In the current study we present pore water geochemical data from a ridge-flank hydrothermal system on 23 Ma seafloor of the Cocos Plate, eastern Pacific Ocean (Figure 1). This hydrothermal system has characteristics that make it ideal for quantifying the global impacts of low-temperature fluid circulation. Similar to the eastern FlankFlux area, fluid recharge and discharge are focused through a small number of basement outcrops that penetrate thick, low-permeability sediments [Fisher et al., 2003b; Hutnak et al., 2007]. But like the western FlankFlux area, fluid circulation extracts 60–90% of lithospheric heat across a large region, and fluid temperatures are generally low [Hutnak et al., 2008]. We present data from sites and samples on and adjacent to Dorado outcrop (Figure 1), a small basement edifice that discharges cool hydrothermal fluid from the underlying crust. Fourteen gravity cores were collected on and near Dorado outcrop; twelve of these cores were instrumented with thermal probes that allowed determination of the local thermal gradient [Hutnak et al., 2008]. We present pore water chemical data from these cores to constrain the rate of seawater flow through the outcrop and surrounding crust, and provide insights as to the influence of low-temperature ridge-flank hydrothermal fluids on oceanic geochemical budgets.

2. Geologic and Geophysical Setting

The seafloor of the Cocos Plate offshore the Nicoya Peninsula, Costa Rica, is underlain by 18–24 Ma lithosphere generated at the fast spreading East Pacific Rise (EPR) to the west, and the medium spreading Cocos Nazca Spreading Center (CNS) to the south [e.g., Meschede et al., 1998; Ranero and von Huene, 2000; Bäckman et al., 2001] (Figure 1). The boundary between EPR- and CNS-generated seafloor, known as the “plate suture,” separates areas having isochrons that are subparallel or perpendicular to the nearby Middle America Trench. Here the TicoFlux surveys examined regional patterns and processes and assessed the influence of seamounts, faults, and other local features in guiding fluid flow [Fisher et al., 2003b; Hutnak et al., 2007, 2008] (Figure 1a). Swath-map data overlain on satellite gravimetric data [Smith and Sandwell, 1997] helped to locate basaltic basement outcrops (Figure 1b). The largest outcrops (seamounts) were apparent in satellite-based bathymetric maps, and swath data revealed additional smaller outcrops. Basaltic outcrops are most common on the EPR-generated seafloor northwest of the plate suture and on CNS-generated seafloor located to the south of a ridge-jump trace. Multichannel seismic reflection data were used to locate regional tectonic features and to map sediment thickness and basement relief. Multipenetrator heat flow stations, and additional measurements made with outrigger probes attached to sediment core barrels, were generally located along seismic reflection profiles to assess the temperatures in upper basaltic basement and constrain patterns of hydrothermal circulation. Coring operations targeted buried basement highs and areas of thin sediment adjacent to basaltic outcrops, with the intent of characterizing the composition of formation fluids in areas with upward fluid seepage.

TicoFlux surveys define an abrupt thermal transition between warmer and cooler parts of the Cocos Plate. This transition is more closely associated with the distribution of basement outcrops than with major tectonic boundaries [Fisher et al., 2003b; Hutnak et al., 2007] (Figure 1b). The Tico-Flux and earlier surveys delineated a 14,500 km² region within which seafloor heat flow was typically 10–40 mW/m², just 10–40% of lithospheric values [Hutnak et al., 2008]. Ten seamounts and other basaltic outcrops mapped within this cool region of the survey area. Collectively, these seamounts and outcrops comprise ~260 km² of exposed basaltic basement, <2% of the seafloor area. Heat flow and seismic surveys oriented radially away from individual outcrops indicate that some basaltic outcrops/seamounts allow hydrother-
nal recharge whereas others allow hydrothermal discharge [Hutnak et al., 2007, 2008], a pattern observed on younger seafloor east of the Juan de Fuca Ridge [Davis et al., 1992; Wheat et al., 2000; Fisher et al., 2003a; Wheat et al., 2004; Hutnak et al., 2006]. Cold fluid recharge is indicated by a decrease in seafloor heat flow and a downward sweeping of isotherms where sediment thins in proximity to a basaltic outcrop. In contrast, warm fluid discharge results in extremely high seafloor heat flow and an upward sweeping of isotherms adjacent to an area of exposed basaltic basement. In the latter case, the temperature of the sediment-basement contact often remains nearly isothermal as the contact shallows toward the seafloor.

[11] The focus of the present study is Dorado outcrop, a 0.25-km² area of basement exposure on 23-Ma seafloor of the cool side of the Cocos Plate (Figure 1c). Dorado outcrop is the seafloor expression of a much larger basaltic edifice that is mostly buried by sediments. This feature is similar in some ways to Baby Bare outcrop in the eastern FlankFlux area. Dorado and Baby Bare outcrops have similar shapes and areas of basement exposure. Both extend 50 to 80 m above the seafloor, have a seafloor expression that is elongated in the north-south direction, parallel to an active spreading center to the west, are surrounded by 400–500 m of widely continuous sediments, are separated from potential recharge sources by tens of kilometers (Baby Bare outcrop and Grizzly Bare outcrop are separated by 52 km; Dorado outcrop and Tengosed Seamount are separated by 20 km) (Figure 1b), and were likely formed during off-axis volcanism [Karsten et al., 1998; Becker et al., 2000; Barckhausen et al., 2001; Silver et al., 2004].

[12] However, the two outcrops are different in several critical respects. Baby Bare outcrop lies on 3.5 Ma crust that was generated at an intermediate spreading rate. The temperature in uppermost basaltic basement around Baby Bare outcrop is 60–65°C and measured heat flow values within a few kilometers from the outcrop are near those predicted by lithospheric cooling models. Here warm hydrothermal formation fluids that seep from the crust are highly altered and discharge at 4–13 kg/s [Mottl et al., 1998]. In contrast, Dorado outcrop overlies 23 Ma crust that was formed at a fast spreading rate. Hydrothermal fluids in basaltic basement within and surrounding this feature are generally 10–20°C. The mass flux of hydrothermal fluid from Dorado outcrop appears to be about three orders of magnitude greater than that from Baby Bare outcrop, as discussed below.

3. Sampling and Analytical Methods

[13] Fourteen gravity cores, many equipped with self-contained temperature recorders, were attempted on and near Dorado outcrop (Figure 1c). Most of these cores recovered 0.4–3.8 m of sediment, one core recovered basalt chips, and one core failed to penetrate the seafloor and returned empty and with a damaged core cutter, indicating that Dorado outcrop has a thin and patchy sediment cover with likely areas of exposed basalt. Two piston cores (PC-44 and −48) were collected far from Dorado outcrop (locations shown in Figure 1b) and provide useful regional data for comparison to those derived from Dorado gravity cores.

[14] Sediment pore water was extracted by splitting the gravity cores and placing sediment not affected by smearing along the edge of the core liner into centrifuge tubes. These tubes were cooled to 1–4°C and spun for 5 min at ~11,000 rpm using a rotor head that was precooled to −20°C so that samples did not warm during centrifugation. Pore waters recovered after centrifugation were filtered through 0.45 μm filters and stored in a variety of acid-washed plastic and glass containers for ship and shore-based analyses. Some aliquots were acidified with subboiled 6N HCl. Sediment samples intended for pore water C isotopic analyses were intended for pore water C isotopic analyses were...
processed within a nitrogen-filled glove bag. After centrifugation, aliquots for C isotopic analysis were transferred within a nitrogen-filled glove bag into evacuated containers containing a few milligrams of HgCl2.

[15] Ship-based analyses included ion selective electrodes (pH), potentiometric titration (alkalinity and chlorinity), and colorimetric (phosphate) techniques. Shore-based analysis included inductively coupled plasma (ICP) emission spectrometry, ion chromatography, colorimetric, and mass spectroscopic techniques (Tables 1 and 2; auxiliary material includes all of the data). Stable isotopic analyses were conducted by D. McCorkle at Woods Hole Oceanographic Institute and radiocarbon measurements were made at the National Ocean Sciences Accelerator Mass Spectrometry Facility in Woods Hole.

4. Geochemical Results

4.1. Evidence for Pore Water Flow Through Sediments

[16] Pore water chemical profiles for alkalinity, phosphate, nitrate, and manganese are presented in Figure 2. Data are shown for all cores collected near Dorado, and results are highlighted for four cores that illustrate the influence of particular conditions (Cores GC-36, —40, —43, and —50). Systematic variations in pore water chemical profiles indicate a range of diagenetic effects caused or limited by the degree to which basaltic formation fluids seep upward through thin sediment (Figure 2). In general, if the flow of basaltic formation fluids through sediment is rapid, diagenetic reactions and the associated diagenetic flux from the sediment to/
from the pore water are small relative to the advective flux. In this case, diagenetic reactions have a minimal effect on solute concentrations during ascent, and the pore water composition remains close to that in basaltic formation fluids. For example, Cores GC-40 and GC-50 were taken where sediment thins along the southwestern side of Dorado and have systematic pore water chemical profiles consistent with rapid upward seepage. These profiles are similar to those observed at the Mariana Mounds in the western Pacific Ocean, where there are seafloor springs [Wheat and McDuff, 1994]. However, if the speed of pore water seepage is slower, such that the advective flux is of the same magnitude as the diagenetic flux, then diagenetic reactions affect pore water profiles (e.g., GC-43); it may still be possible to estimate the composition of the basaltic formation fluid even if a complete sediment section is recovered. Core GC-36 was taken 2 km northeast of Dorado, where sediment cover is thick and chemical profiles are consistent with diffusion and reaction being the dominant diagenetic processes. These sediments are sufficiently thick to prevent upward fluid seepage, even if basement is slightly over-pressured [e.g., Wheat and McManus, 2005].

Table 2. Concentration, Isotopic Compositions, and Calculated Ages for Seawater and Pore Water Samples From Near the Base of the Sampled Section in Cores From Areas With Upwelling Formation Fluids

<table>
<thead>
<tr>
<th>Sample</th>
<th>TCO₂ (mmol/kg)</th>
<th>δ¹³C (‰ PDB)</th>
<th>¹⁴C (y)</th>
<th>¹⁴C Error (y)</th>
<th>Heat Flow (W/m²)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater</td>
<td>2.336</td>
<td>−0.19</td>
<td>2165</td>
<td>25</td>
<td>N.A.</td>
<td>2</td>
</tr>
<tr>
<td>GC-50</td>
<td>2.734</td>
<td>−0.37</td>
<td>2495</td>
<td>25</td>
<td>1.0</td>
<td>10</td>
</tr>
<tr>
<td>PC-44d</td>
<td>0.862</td>
<td>−5.13</td>
<td>35600</td>
<td>280</td>
<td>0.63</td>
<td>75</td>
</tr>
<tr>
<td>PC-48e</td>
<td>2.181</td>
<td>−4.73</td>
<td>14650</td>
<td>63</td>
<td>0.13</td>
<td>40–45</td>
</tr>
</tbody>
</table>

Locations are shown in Figure 1. Analyses were conducted by D. McCorkle at WHOI and at the National Ocean Sciences Accelerator Mass Spectrometry Facility in Woods Hole.

Heat flow data tabulated and reported by Hutnak et al. [2008].

Upper basement temperature below sediment cores estimated by downward continuation of measured thermal gradient [Hutnak et al., 2007]. Temperature values are higher in areas of higher heat flow and/or thinner sediment.

Core was collected 88 km NE of GC-50 [e.g., Friedmann, 2003; Wheat and McManus, 2005].

Core was collected 142 km SSE of GC-50 [e.g., Wheat and McManus, 2005].

Adaptive flux is much smaller than the diagenetic flux, then diagenetic reactions dominate pore water profiles, making it difficult to estimate the composition of the basaltic formation fluid even if a complete sediment section is recovered. Core GC-36 was taken 2 km northeast of Dorado, where sediment cover is ~100 m thick and chemical profiles are consistent with diffusion and reaction being the dominant diagenetic processes. These sediments are sufficiently thick to prevent upward fluid seepage, even if basement is slightly over-pressured [e.g., Wheat and Mottl, 1994; Spinelli et al., 2004].

[17] Measured heat flow values are consistent with fluid flow in basement around Dorado outcrop. Away from Dorado outcrop heat flow values are low, generally 20–30 mW/m², whereas on or near Dorado outcrop (e.g., GC-40 and GC-50) values exceed 600 mW/m² [Hutnak et al., 2008].

Figure 2. Pore water profiles for selected chemical species (alkalinity, phosphate, nitrate, and manganese) with results highlighted from four of the fourteen cores collected on and near Dorado outcrop. Cores GC-40 and – 50 were taken on/near Dorado outcrop and are affected by the upward seepage of a basaltic formation fluid that is slightly altered relative to bottom seawater. Core GC-36 was collected ~2 km northeast of Dorado outcrop. Pore water chemical profiles from this core are characteristic of diagenetic profiles in the absence of fluid seepage. Data from core GC-43 illustrate an intermediate case of fluid seepage.
though some of the elevated heat flow near the outcrop may result from rapid upward fluid seepage, high heat flow results mainly from relatively isothermal conditions in uppermost basement (typical basement temperatures of 10–20°C), as the sediment cover thins adjacent to a local area of basement exposure. Isothermal basement conditions are caused by vigorous local convection, which can also be associated with overpressured fluids and lead to seepage at chemically significant rates where sediments are thin. None of the seepage rates estimated from chemical data in the present study are sufficiently rapid so as to result in curved thermal gradients within the upper few meters of sediment.

[18] Chemical profiles from GC-40, −43, and −50 are consistent with the upward seepage of a basaltic formation fluid having a nitrate concentration close to that of bottom seawater [e.g., Gieskes and Boulegue, 1983; Bender et al., 1985; Wheat and McDuff, 1994]. In the present case, as this fluid seeps upward through the sediment near the edge of the outcrop, microbial activity within the sediment reduces the concentration of nitrate. Slower flow results in lower pore water nitrate concentrations. Nitrate is fully depleted in GC-36, in which there is no evidence for advective transport. Pore water data are also consistent with a basaltic formation fluid that has phosphate and alkalinity concentrations lower than those of seawater, whereas manganese concentrations are elevated above seawater concentrations (Table 1, Figure 2). Similar arguments can be used to describe pore water phosphate, alkalinity, and manganese profiles in response to microbial degradation of organic matter in the context of upward pore water seepage.

[19] The rate that formation fluids seep upwards though the sediment is quantified using an advection-diffusion-reaction model. An example, based on nitrate profiles, constrains order-of-magnitude fluid seepage rates and provides a visualization of expected nitrate profiles at a variety of flow conditions and sediment thicknesses. A more precise estimate of flow rates is not warranted at present because of uncertainties in the sediment thickness and rate of denitrification near the sediment-basalt contact.

[20] We use first order reaction terms for nitrification:

\[ D_s(NO_3) \frac{\partial^2 NO_3}{\partial z^2} - \nu \frac{\partial NO_3}{\partial z} + \gamma_n k_n O_2 = 0 \]  

and denitrification

\[ D_s(NO_3) \frac{\partial^2 NO_3}{\partial z^2} - \nu \frac{\partial NO_3}{\partial z} - k_d NO_3 = 0, \]

where \( D_s(NO_3) \) is the sediment diffusion coefficient for nitrate, \( NO_3 \) is the nitrate concentration, \( z \) is depth, \( \nu \) is the pore water velocity, \( \gamma_n \) is the Redfield ratio of nitrate produced to oxygen consumed during nitrification, \( k_n \) is the rate of nitrification, and \( k_d \) is the rate of denitrification [Wheat and McDuff, 1994]. The equations are solved subject to the boundary conditions:

\[ NO_3(z=0) = NO_3(0) \]  

and

\[ NO_3(z=bot) = NO_3(bot), \]

where \( NO_3(0) \) is the nitrate concentration in bottom seawater and \( NO_3(bot) \) is the nitrate concentration in the basaltic formation fluid [e.g., Wheat and McDuff, 1994, Appendix A].

[21] Simulated and measured nitrate profiles are shown in Figure 3. A 100-m-thick sediment section
is used for the case of no flow, as in the location of core GC-36. Here the rate of denitrification must be sufficiently rapid to remove the nitrate from the pore water in the upper 25 cm of the sediment (assuming that the upper tens of centimeters of sediment was not lost during gravity coring operations, consistent with observations). A slower rate of denitrification is suggested at core locations where there is evidence for seepage, perhaps because of differences in sedimentation or compaction histories associated with basement relief. These calculations suggest that seepage rates may be as high as several meters per year through the thin sediment immediately adjacent to and on Dorado outcrop (Figure 3). These calculations also suggest that there is a net flux of nitrate into the crust during seawater circulation in basement, prior to upward seepage through sediments, which could result from processes within basaltic basement or the overlying sediments. Nitrate could be removed from basaltic formation fluids by diffusion to the overlying sediment pore waters [e.g., Wheat and McDuff, 1995; Bender et al., 1985] or by microbial reactions within basaltic basement [Huber et al., 2006; Santelli et al., 2008]. At much higher temperatures than those observed at Dorado outcrop, nitrate concentrations in seawater can be reduced within basaltic basement in the presence of reduced iron [e.g., Gieskes et al., 1983].

4.2. Chemical Constraints for Seawater Circulation Through the Basaltic Crust

[22] Pore water data are consistent with a basaltic formation fluid that has a nitrate concentration of 41 μmo/kg (40.9 ± 0.6 μmo/kg). This value is based on pore water samples from GC-40 and −50 (excluding the deepest sample) that were extracted from sediment at least 50 cm below the seafloor, thus minimizing artifacts caused by nitrification. This average is slightly less than the seawater concentration of 42.3 μmo/kg (Table 1). This interpretation constrains a conceptual hydrologic model (Figure 4). High concentrations of nitrate in basaltic formation fluids require that seawater enters basaltic basement though outcrops or other areas of basement exposure with minimal sediment contact or interaction because diagenetic reactions involving sediment and pore water would rapidly deplete the fluid of nitrate (e.g., GC-36). The closest area of basement exposure to Dorado outcrop, based on nearly complete swathmap coverage around Dorado outcrop, is Tengosed Seamount, a much larger outcrop located 20 km to the east (Figure 1b). In contrast to patterns of seafloor heat flow observed near Dorado outcrop, heat flow profiles oriented radially adjacent to Tengosed Seamount show abrupt decreases in heat flow immediately adjacent to areas of exposed basement, resulting from downward sweeping of iso-

Figure 4. Conceptual model of the crustal hydrogeologic system that results in fluid discharge at Dorado outcrop. Cold oxygenated seawater enters basaltic basement at Tengosed Seamount, consistent with a depressed heat flow surrounding the seamount [Hutnak et al., 2007, 2008]. This basaltic formation fluid flows toward Dorado outcrop, located ~20 km away. Here the heat flow is elevated relative to local values, even through the circulating fluid is relatively cool, because mixed convection and the rapid flow rate in basement helps to keep the sediment-basement interface relatively isothermal. As seawater transits within basaltic basement between Tengosed Seamount and Dorado outcrop, the fluid warms by ~8–18°C, reacts with basaltic crust, undergoes diffusive exchange with overlying sediment pore water, and may be altered by microbial processes. Gravity cores targeted the thinnest sediment on the Dorado outcrop with the intent of sampling fluids from a region with upward fluid seepage.
therms, consistent with the seamount being a site of seawater recharge [Hutnak et al., 2008]. There may be other (more distant) recharge sites that supply formation fluids that discharge at Dorado outcrop, but we focus discussion on Tengosed Seamount because it is the nearest edifice through which there is thermal evidence of recharge and associated basement cooling. There may be additional smaller outcrops near Dorado outcrop that remain unmapped, but observational and modeling studies suggest that smaller outcrops are favored sites for hydrothermal discharge, whereas larger outcrops are favored sites of hydrothermal recharge [e.g., Fisher et al., 2003a; Hutnak et al., 2006, 2008].

Seawater that recharges through Tengosed Seamount flows within upper basaltic basement where it warms and reacts via biotic or abiotic processes (Figure 4). There is a diffusive flux of nitrate from the basaltic formation fluid to overlying sediment pore water, with nitrate being consumed by microbial processes in the sediment. The (slightly) warmed and altered formation fluid then seeps through thin sediment or discharges from areas of basement exposure on Dorado outcrop. If the discharge rate is sufficiently rapid, the formation fluid composition is maintained until the fluid exits the seafloor and is diluted by bottom seawater. The observation that formation fluids seeping from Dorado outcrop have nitrate concentrations only slightly different from that of seawater, despite steep nitrate gradients within the sediment, requires that the advective flux of nitrate through the upper basaltic crust be much greater than the sum of removal fluxes from diffusion exchange with the overlying sediment pore water and any reactions occurring within basaltic basement.

We expand upon this conceptual model to construct a coupled fluid-solute transport and consumption model to estimate the advective flux through basaltic basement (Figure 5). This model is consistent with the general processes and hydrologic pattern outlined above [e.g., Wheat and Fisher, 2007] and at a variety of ridge flank sites [e.g., Baker et al., 1991, Wheat and McDuff, 1995; You et al., 2003]. The volumetric flux per unit width perpendicular to flow (m$^3$ a$^{-1}$ cm$^{-1}$) within upper basaltic basement is determined from the diffusive flux at the sediment-basalt interface ($F_d$) and the concentrations of bottom seawater ($C_{sw}$) and formation fluid. For simplicity, reactions within upper basaltic basement are ignored, although additional losses may occur through biotic and abiotic processes (requiring volumetric fluxes larger than those calculated herein). The diffusive flux perpendicular to fluid flow is modeled as [Berner, 1980],

$$F_d = -D_s \frac{\partial C}{\partial z}$$  \hspace{1cm} (5)

where $D_s$ is the porosity- and temperature-dependant sediment diffusion coefficient [Li and Gregory, 1974] and $\partial C/\partial z$ is the basal pore water chemical gradient. The nitrate gradient immediately above the sediment-basalt interface is assumed to be the same as that at the seafloor. A conservative estimate for the seafloor gradient is 4 $\mu$mol nitrate/kg/cm. This value is based on data from the shallowest pore water samples and seawater concentrations from gravity cores that are not affected by advection.
The model consists of a diffusive flux through a length ($l$), defined by the distance to the nearest possible recharge site, a unit width ($w$) of one centimeter, and an advective flux within upper basaltic basement. The advective flux along the flow path is calculated from the nitrate concentration in seawater, seawater density ($\rho$), and the volumetric flux ($Q$). Provided the volumetric fluid flux is conserved, the chemical flux out ($F_{\text{out}}$) of the box is the sum of diffusive and advective fluxes:

$$F_{\text{out}} = F_{\text{diff}} - C_{\text{in}}\rho$$

(6)

The calculated composition of the formation fluid that exits the box is compared with the estimated composition of 41 $\mu$mol nitrate/kg in the formation fluids. A volumetric flux per unit width of 1800 m$^3$ a$^{-1}$ results in a calculated fluid concentration of 41 $\mu$mol nitrate/kg, matching the observed data (Figure 5). The calculated volumetric flux per unit width scales linearly with the assumed nitrate gradient above basement. For example, even if we use a gradient that is one fourth the size, the calculated volumetric flux per unit width is $\sim$450 m$^3$ a$^{-1}$ cm$^{-1}$. In contrast, if a component of the formation fluid is derived from a seamount or outcrop more distant than 20 km (the distance from Dorado outcrop to Tengosed Seamount), then the volumetric flux must be greater to maintain the near-seawater nitrate concentration. This analysis does not account for seawater-basalt and microbial reactions within the basaltic basement. Similar to the case of a more distal recharge site, higher volumetric fluxes would be required if these reactions were to have a significant influence on the nitrate concentration in the formation fluid. Last, we highlight the case for a nitrate concentration of 35 $\mu$mol/kg, which is the concentration of the sample at the base of GC-50. Even if this concentration represents the concentration in formation fluids, thus requiring an oxygenated formation fluid that allows nitrification to generate higher nitrate concentrations than are observed in the shallower portion of the sediment core, the calculated volumetric flux per unit width remains high (300 m$^3$ a$^{-1}$ cm$^{-1}$).

Given a characteristic volumetric flux per unit width (1800 m$^3$ a$^{-1}$ cm$^{-1}$), we calculate the specific discharge (volume flux per area) through upper basaltic basement assuming an effective height for the interval through which most seawater flows ($h_{\text{effective}}$). The effective height is the thickness of the basaltic layer multiplied by the effective porosity ($\phi_{\text{effective}}$), the fraction of rock comprising a well-connected pore network (probably much less than the bulk porosity of upper basement). If the effective porosity is 1 to 5% and flow occurs within the upper 500 m of basaltic crust, then the calculated specific discharge is 35 to 7 km a$^{-1}$, respectively, and the nominal travel time from recharge to discharge (Tengosed Seamount to Dorado outcrop) is 0.6 to 3 years, respectively.

Such a short travel time is consistent with the $^{14}$C age of the sediment pore water from near the base of GC-50 (Table 2). The $^{14}$C age of this sample, thought to be representative of the $^{14}$C age of the basaltic formation fluid, is only 340 years older than a bottom seawater sample. This age must be considered the maximum travel time from recharge to discharge sites because diffusive exchange with old carbon reservoirs during transport increases the apparent age of the fluid [e.g., Sanford, 1997]. Diffusive exchange processes during flow through heterogeneous oceanic crust are likely to increase the apparent age of the fluid by at least one to two orders of magnitude [e.g., Fisher, 2004].

The apparent $^{14}$C age of the basaltic formation fluid from Dorado outcrop is considerably younger than the ages of basaltic formation fluids from the FlankFlux area, ($\geq$4000 years) [e.g., Elderfield et al., 1999; Walker et al., 2008], and the ages of two additional TicoFlux pore water samples (PC-44 and PC-48, Table 2, Figure 1b). These TicoFlux pore water samples were collected by piston coring in areas of upward fluid seepage on warmer parts of the Cocos Plate. Fluids collected from these cores are more chemically altered than the basaltic formation fluids from near Dorado outcrop, much like pore waters recovered in the eastern FlankFlux area. The sample from PC-44 (which is about as warm and altered as formation fluid from Baby Bare outcrop) has a $^{14}$C age $\sim$33,000 years older than bottom seawater, whereas the sample from PC-48 (which is not as warm or altered as that from PC-44, but is both warmer and more altered than the GC-50 sample from near Dorado outcrop) has a $^{14}$C age $\sim$12,000 years older than bottom seawater (Table 2).

These warmer, older, more altered TicoFlux pore waters were collected in areas where there is no seafloor heat flow deficit [Fisher et al., 2003b; Hutnak et al., 2007, 2008] (Figure 1b) and in areas where hydrothermal circulation is less open and not as efficient in mining lithospheric heat relative to that observed near Dorado outcrop. Interestingly, some of the western FlankFlux fluids that were collected in areas where the measured heat flow is a small fraction of the theoretical (lithospheric) value
also have \(^{14}\)C ages on the order of 10,000 years (ODP Sites 1023, 1024, and 1025) [Elderfield et al., 1999] even though potential recharge sites are tens of kilometers away, similar to the distance between Dorado outcrop and Tengosed Seamount. This suggests that formation fluids that circulate through basaltic basement and discharge from the seafloor at Dorado outcrop move very rapidly compared to those in the FlankFlux area, spending relatively little time within the basaltic aquifer between recharge and discharge sites. This observation illustrates that the heat flow deficit alone is an incomplete measure of fluid flow rates within basaltic crust. The apparent age of the formation fluid is likely a function of the heat flow deficit and crustal permeability.

[31] If fluids flow through the entire 500-m-long-axis width of Dorado outcrop, the volumetric fluxes calculated from chemical data suggest a total flow on the order of 3000 kg/s, two to three orders of magnitude more fluid than is flowing from Baby Bare outcrop (4–13 kg/s) [Mottl et al., 1998]. This chemical-based estimate of the volumetric fluid flux is at the lower end of the range calculated for discharging outcrops in this area based on the regional thermal deficit, 1000–20,000 kg/s [Hutnak et al., 2008]. The advective heat flux associated with a flow of 3000 kg/s is 100–210 MW, assuming that formation fluids are warmed by 8–18°C relative to bottom water. This flux is equivalent to the heat output from a medium-sized black smoker vent field [Baker, 2007]. The fluid flux from a single hydrothermal black smoker vent is on the order of 5 kg/s (assuming flow rate of 1 m/s through an 8-cm diameter orifice). Thus the fluid flux from the 0.25 km\(^2\) area of Dorado outcrop may be as great as that from \(~600\) black smokers.

4.3. Implications for Global Chemical Fluxes From Ridge Flanks

[32] If the entire convective heat loss from ridge flanks (\(~8\) TW) [Parsons and Sclater, 1977; Stein and Stein, 1994] were to result from warming seawater by 8–18°C (resulting in fluid that reacts with basement at 10–20°C), then the flux of seawater through the oceanic crust would be 3 to \(8 \times 10^{15}\) kg a\(^{-1}\), somewhat less than the flux of \(21 \times 10^{15}\) kg a\(^{-1}\) calculated from the global heat flow, sediment thickness, and crustal age data sets [Wheat et al., 2003]. Given a seawater flux of \(5 \times 10^{15}\) kg a\(^{-1}\) (based on warming the hydrothermal fluid by 13°C), we estimate the chemical flux from low-temperature, ridge-flank hydrothermal processes from the measured difference in seawater and the basaltic formation fluid (average pore water compositions from GC-40 and –50) at Dorado outcrop (Table 1). For many of the chemical species, calculated fluxes associated with ridge-flank hydrothermal fluids comprise a significant fraction of riverine fluxes.

[33] For some dissolved elements (e.g., calcium, sodium, strontium, and barium) the composition of basaltic formation fluid appears to be little different from that of bottom seawater, indicating that there is little influence of rapid, cool hydrothermal circulation on the concentration of these elements. In Table 1 we assume a 1% change in the concentration of these elements (differences that would be measurable in pristine samples collected from a focused discharge site on basement), to quantify the potential global impact of low-temperature reactions for these four elements. The estimated flux for two of the elements, sodium and strontium, is a substantial portion of the riverine flux, yet it remains to be determined if these assumed chemical anomalies are typical of natural systems.

[34] Clearly, there is a need to collect pristine fluids from many such hydrothermal systems, and focused discharge sites like Dorado outcrop offer...
critical opportunities to sample and understand these systems. Results from one system alone will not resolve global fluxes due to the complexity of these systems. For example, pore water data from near Dorado outcrop are consistent with a net removal of nitrate during hydrothermal circulation, as observed at other ridge-flank sites [e.g., Wheat and Mottl, 2004], and as indicated by the high nitrogen content of alteration products in oceanic basalts [Busigny et al., 2005]. In contrast, there may be ridge flank hydrothermal systems in which the crust is a net source of nitrate to the oceans [Gieskes and Boulegue, 1983; Erzinger and Bach, 1996]. It remains to be determined which condition is more widespread on a global scale.

[35] Around Dorado outcrop, the concentration of nitrate decreases from a bottom seawater value of 42.3 μmol/kg to 41 μmol/kg prior to discharge. A portion of this flux stimulates microbial processes in the overlying sediment and other nitrate-removing processes also could occur within basaltic basement. Because we assumed the same rate of nitrate removal for both the seawater-sediment and sediment-basalt interfaces, using the same nitrate gradient at the top and base of the sediment section, the calculated flux of nitrate into the sediment is about twice the early diagenetic flux calculated from the uppermost sediment. The same argument should apply to other microbially mediated ions such as phosphate [e.g., Wheat et al., 2000] and in some cases ammonium, sulfate, manganese, and iron. Likewise, highly sediment-reactive elements such as silica and germanium are expected to behave similarly at both interfaces [e.g., Wheat and McManus, 2005, 2008].

[36] Diffusive exchange with overlying sediment can account for all of the documented nitrate loss in basement around Dorado outcrop, indicating that there might be little reaction within basaltic basement in this area. Bach and Edwards [2003] document the extent of basaltic Fe and S oxidation based on drilling studies at numerous sites, and provide constraints for the oxidation of these elements using dissolved oxygen and nitrate. However, they restrict their calculations to a convective heat loss of 3 TW, which is the amount of heat advected from crust aged 1 to 10 Ma. With this restriction, their calculations lead to a prediction for the complete removal of dissolved oxygen and nitrate from circulating seawater during the first 10 Ma of crustal aging. In contrast, formation fluid from Dorado loses only ~3% of its initial seawater nitrate concentration during ridge-flank circulation, suggesting that crustal oxidation can extend well beyond 10 Ma.

[37] There is a need to collect pristine hydrothermal fluid from features like Dorado outcrop, ideally by sampling focused seepage sites or springs on bare basalt, so that uncertainties in estimates of formation fluid compositions and processes can be reduced. Areas of focused, low-temperature, ridge-flank discharge offer critical opportunities to avoid the confounding influence of diageneric reactions in sediments during pore water seepage. There is also a need to locate and collect fluid samples from similar discharge sites on seafloor across a range of crustal ages, to assess whether or not the fluid and chemical fluxes documented at Dorado outcrop are typical of global processes, and to quantify properties and processes that influence the chemical composition of basaltic formation fluids in these systems. Only through systematic surveys, sampling, and analyses of this kind can we quantify with certainty the integrated impacts of ridge-flank hydrothermal circulation on global geochemical budgets.

5. Conclusions

[38] Pore water chemical data were collected by gravity coring and near Dorado outcrop, a small basement edifice that discharges cool hydrothermal fluid from the underlying crust on 23 Ma seafloor of the Cocos Plate. Pore water samples collected just above basaltic basement were used to infer the composition of the basaltic formation fluid, which is only slightly different from that of bottom seawater in this area, and flow rates through the thin sediment cover adjacent to areas of outcrop exposure. Pore water profiles indicate a range of diffusive, advective, and diageneric influences that are the basis for one-dimensional reactive transport modeling. A comparison of model calculations and pore water data suggest that seepage rates through sediments on and adjacent to Dorado outcrop are as great as several meters per year.

[39] Chemical and geologic constraints are used to estimate flow rates through basaltic basement that allow Dorado outcrop fluids to remain relatively unaltered compared to seawater. Given the nearest likely basement recharge site is Tengosed Seamount, ~20 km away, we estimate a minimum volumetric flux per unit width of basement of 1800 m³ a⁻¹ cm⁻¹, and a total fluid flow through Dorado outcrop of at least 3000 kg a⁻¹. This flow is orders of magnitude greater than that estimated.
to discharge from Baby Bare outcrop, on younger seafloor on the eastern flank of the Juan de Fuca Ridge. The $^{14}$C age of pore water thought to be characteristic of basement formation fluids near Dorado outcrop suggests an extremely short residence time in the crust, no more than a few hundred years. This short residence time contrasts with much longer residence times estimated using $^{14}$C measurements on the eastern flank of the Juan de Fuca Ridge, and on other parts of the Cocos Plate where basement fluids are warmer and more altered. These differences in fluid residence times and chemical compositions suggest significant differences in flow rates, and perhaps differences in the geometry and nature of flow paths within the crust.

If the hydrothermal fluid exiting from Dorado outcrop is characteristic of ridge-flank hydrothermal circulation in general (10–20°C, relatively unaltered), these systems can still have an important influence on the geochemical fluxes and budgets for many solutes on a global basis, particularly for chloride, magnesium, sulfate, potassium, lithium, boron, silica, phosphate, manganese and iron. The implications of these analyses for subseafloor microbial processes and communities remain to be determined. Thermal and chemical conditions within basaltic basement near Dorado outcrop appear to be similar to those in many young ridge flanks. This suggests that microbial conditions may be similar as well.

Unfortunately, there are few samples of fluids from these kinds of ridge-flank hydrothermal systems, and most samples (including those analyzed in the present study) are from sediment pore water. We need to locate and sample focused discharge sites for cool, ridge-flank hydrothermal systems in order to develop and test hypotheses like those presented. A challenge in the past has been to identify focused discharge sites in areas where the fluid temperatures and fluid compositions are typical of global systems, but this study shows that such sites do exist. The key is to find places where there are thick sediments and relatively few areas of basement exposure, then use thermal data to distinguish between recharge and discharge locations to map fluid pathways. Not all such sites will have fluid circulation that is vigorous enough to remove a significant fraction of lithospheric heat, but these sites must be sampled in order to understand how heat advection from ridge flanks influences global geochemical budgets and subseafloor microbiology.

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