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# Dissolved organic carbon in ridge-axis and ridge-flank hydrothermal systems

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**Abstract**

The circulation of hydrothermal fluid through the upper oceanic crustal reservoir has a large impact on the chemistry of seawater, yet the impact on dissolved organic carbon (DOC) in the ocean has received almost no attention. To determine whether hydrothermal circulation is a source or a sink for DOC in the oceans, we measured DOC concentrations in hydrothermal fluids from several environments. Hydrothermal fluids were collected from high-temperature vents and diffuse, low-temperature vents on the basalt-hosted Juan de Fuca Ridge axis and also from low-temperature vents on the sedimented eastern flanks. High-temperature fluids from Main Endeavour Field (MEF) and Axial Volcano (AV) contain very low DOC concentrations (average = 15 and 17 μM, respectively) compared to background seawater (36 μM). At MEF and AV, average DOC concentrations in diffuse fluids (47 and 48 μM, respectively) were elevated over background seawater, and high DOC is correlated with high microbial cell counts in diffuse fluids. Fluids from off-axis hydrothermal systems located on 3.5-Ma-old crust at Baby Bare Seamount and Ocean Drilling Program (ODP) Hole 1026B had average DOC concentrations of 11 and 13 μM, respectively, and lowered DOC was correlated with low cell counts. The relative importance of heterotrophic uptake, abiotic sorption to mineral surfaces, thermal decomposition, and microbial production in fixing the DOC concentration in vent fluids remains uncertain. We calculated the potential effect of hydrothermal circulation on the deep-sea DOC cycle using our concentration data and published water flux estimates. Maximum calculated fluxes of DOC are minor compared to most oceanic DOC source and sink terms.


## 1. Introduction

Circulation of seawater through hydrothermal systems in the oceanic lithosphere plays a major role in maintaining the balance of seawater chemistry. Hydrothermal circulation on the crest and flanks of mid-ocean ridges is a major source or sink for many elements in the ocean (Edmond et al., 1979; Wheat and Mottl, 2000). The pool of deep-water dissolved organic carbon (DOC) constitutes one of the largest reservoirs of organic matter on the earth's surface (∼680 Gt), and is of the same magnitude as atmospheric carbon dioxide (Hansell and Carlson, 1998). DOC concentrations vary across the ocean basins, but the sources and sinks of DOC along the deep-water circulation pathway from the Northern Atlantic Ocean to the Northern Pacific remain poorly constrained (Hansell and Carlson, 1998). Although hydrothermal processes are capable of modifying deep ocean DOC during passage through the crustal reservoir, the extent to which they do so is largely unexamined.

Fundamental measurements such as dissolved organic carbon (DOC) concentrations have been made for only a limited number of deep-sea vents (Comita et al., 1984; Sarradin et al., 1999), and the results of previous studies are inadequate to address the question of what happens to DOC during circulation through mid-ocean ridge hydrothermal systems. The present work contributes new data

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on DOC concentration in representative hydrothermal environments and makes a preliminary estimate on the magnitude of the hydrothermal DOC flux to the oceans.

In addition to understanding the role of hydrothermal circulation in the global carbon cycle, the study of DOC in hydrothermal systems can elucidate biogeochemical processes. With the new data on DOC concentrations, one can speculate about the relative importance of different processes in controlling DOC in a range of environments and the impact of hydrothermal processes on the properties of marine DOC. More definitive resolution of alternative processes affecting DOC requires identification of compounds undergoing alteration.

## 2. Study sites

The Juan de Fuca Ridge contains some of the best-studied hydrothermal systems, with well-characterized high-temperature vents as well as low-temperature diffuse axial vents (e.g., Delaney et al., 1992; Lilley et al., 1993; Butterfield et al., 2004). Active venting is also present on the eastern flank of the Juan de Fuca Ridge, at bare rock outcrops located on 3.5-Ma-old crust (Mottl et al., 1998). In 2002, we sampled two young (<0.1 Ma old) axial sites, Main Endeavour Field (MEF) and Axial Volcano (AV), and two off-axis flank sites, Baby Bare Seamount and nearby Ocean Drilling Program (ODP) Hole 1026B (Fig. 1a). In 2003, we returned to sample fluids from AV.

MEF is an unsedimented hydrothermal field with numerous large sulfide structures and both high temperature (>300 °C) and diffuse (<100 °C) venting (Delaney et al., 1992). AV is located ~190 km south of the MEF along the Juan de Fuca Ridge axis, and also contains both high temperature and diffuse venting (Embley et al., 1990; Butterfield et al., 1990, 2004). The temperature of venting at AV fields has fluctuated over several years and the apparent overall heat flux has declined slowly since the most recent volcanic eruption in January, 1998 (Baker et al., 2004; Butterfield et al., 2004).

The source water for high-temperature vents at MEF and AV is North Pacific Deep Water (NPDW; DOC concentration 36 μM, this study), which penetrates the crust, becomes heated by magma or hot rock, and buoyantly rises to the seafloor. The hot fluid becomes highly reducing and metal-rich through interactions with the host rock (Edmond et al., 1979; Seyfried, 1987). Low-temperature diffuse vents are primarily subsurface mixtures of this hot, reducing fluid with cold, oxygenated local seawater (Edmond et al., 1979; Butterfield et al., 2004). There is evidence for biologically mediated chemical reactions in the subseafloor mixing zone beneath diffuse vents (Butterfield et al., 1997, 2004; Von Damm and Lilley, 2004). Alteration to entrained deep seawater DOC during local re-charge could occur anywhere along this circulation pathway.

Both MEF and AV have dense macrofaunal communities near areas of active venting which include abundant populations of tube worms, palm worms, and gastropods (Sarrazin et al., 1999). Microbiological and geochemical studies from both sites show evidence for subsurface

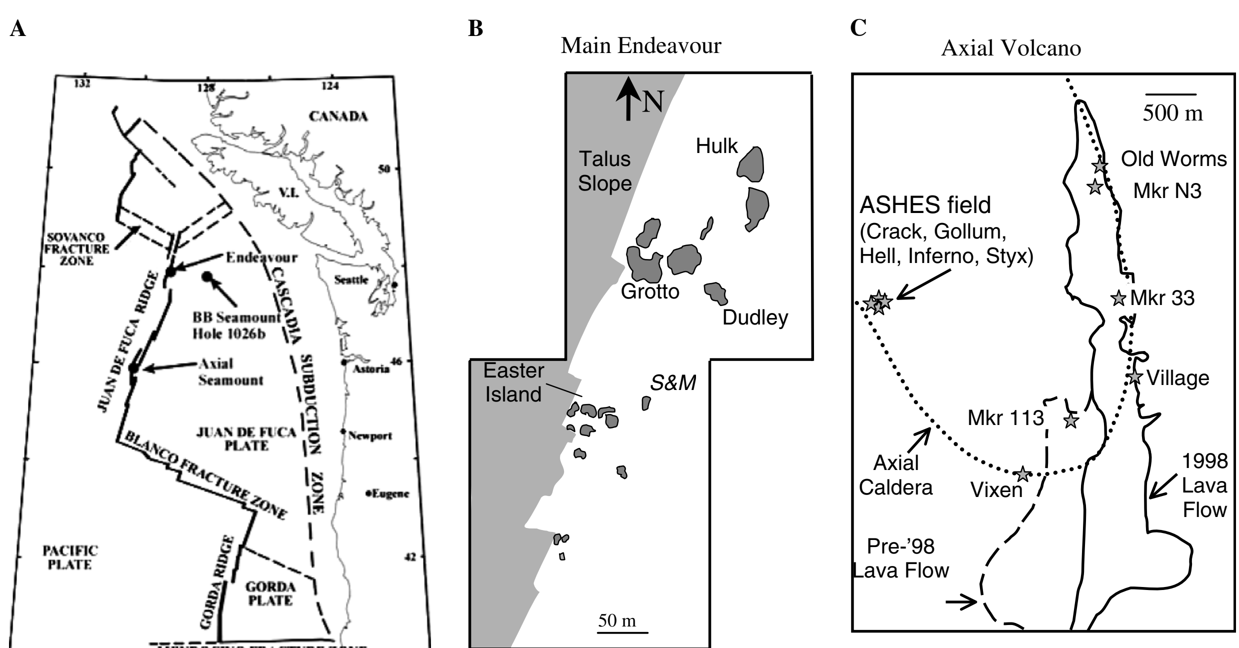


Fig. 1. Map of study sites on and near Juan de Fuca Ridge. (A) Map of northeast Pacific, showing the locations of MEF, AV, Baby Bare Seamount, and ODP Hole 1026B. Baby Bare and ODP Hole 1026B are too close together on the map to be distinguished. (B) Map of specific vent locations at MEF, modified from Delaney et al. (1992). Raven Field is 200 m north of MEF and not shown. (C) Map of specific vent locations at AV modified from Butterfield et al. (2004).

microbial populations living within the voids of the porous basaltic crust where high-temperature hydrothermal fluid mixes with entrained deep seawater (Holden et al., 1998; Summit and Baross, 2001; Huber et al., 2002, 2003; Mehta et al., 2003; Butterfield et al., 2004).

While ridge-axis systems are the best-studied hydrothermal sites, off-axis hot springs account for more than 60% of the total advective heat loss (Stein and Stein, 1994; Johnson and Pruis, 2003). Heat loss occurs at lower temperatures than in axial systems, and the seawater flux through off-axis systems is approximately 10 times larger than along the mid-ocean ridge axis (Mottl, 2003). Even minor changes in the concentrations of chemical species that occur from passage through ridge-flank systems can create significantly larger fluxes than those from ridge-axis circulation (Mottl and Wheat, 1994). In older ridge-flank crust, impermeable sedimentary caps generally prevent advection of seawater. However, heat flux measurements demonstrate advective heat loss continues to occur in crust approximately 65 Ma old (Stein and Stein, 1994; Johnson and Pruis, 2003).

Baby Bare Seamount is a small basement outcrop with thin to non-existent sediment cover located 100 km east of the ridge axis on 3.5-Ma-old crust and is a site that has actively vented ~20 °C water in the past (Mottl et al., 1998; Wheat and Mottl, 2000; Fig. 1). Geochemical and heat flow measurements suggest that the fluids from Baby Bare Seamount have an off-axis recharge zone from an exposed basement outcrop located 50 km to the south (Elderfield et al., 1999; Fisher et al., 2003). The inorganic chemical alterations to the basement fluids are dominated by the low-temperature reaction with the basement basalt, but some diffusive exchange between basement fluids and pore waters in the overlying sediment also appears to be occurring (Elderfield et al., 1999; Wheat and Mottl, 2002). Thermal gradients near the sediment–basement interface and measured temperatures within the basement at near-by ODP Hole 1026B indicate that the Baby Bare warm spring fluids have cooled from 64 °C basement formation fluids (Davis et al., 1997; Fisher et al., 1997, 2003; Davis and Becker, 2002; Becker and Davis, 2003). ODP Hole 1026B, sampled for this study, actively vented ~63 °C water when it was drilled in 1996 (Davis et al., 1997) and has continued to vent fluid at that temperature (Butterfield et al., 2001; Cowen and German, 2003; Johnson and Party, 2003).

We sampled a variety of diffuse flow sites at MEF and AV fields during the summer of 2002 and 2003 (Fig. 1b and c). Several warm water vent sites were located within cracks in the basaltic seafloor and microbial mats colonized the walls of the cracks (Marker 33 and Marker 113 at Axial, near S&M at Endeavour). The sample near Marker N3 was taken from beneath an overhanging rock with adjacent tube worms and white microbial mats. The Easter Island samples were taken beneath flat, layered mineral structures with diffuse water wafting out from below. Samples were also taken adjacent (<5 m) to high-temperature vents, where diffuse flow leaks out from cracks in the base of the sulfide structure or from nearby basalt (e.g., near Dudley, Hulk, Vixen, Village, Raven vent structures), sites that are colonized by a variety of vent fauna. The samples taken represent a range of high-temperature and low-temperature diffuse sites on the ridge axis.

## 3. Sampling and methods

### 3.1. Sampling equipment

Hydrothermal fluids for this study were sampled by ROV Jason II using previously described 'major' samplers (Von Damm et al., 1985) and the Hydrothermal Fluid and Particulate Sampler (HFPS; Huber et al., 2002; Butterfield et al., 2004). Major fluid samplers are fully titanium and Milli-Q blanks of the sampler were below the DOC detection limit of our system. Temperatures of the fluids sampled with the major samplers were determined by inserting a high-temperature probe into the fluid stream and then removing it prior to sampling.

The HFPS flushes fluids through a main conduit for ~3–5 min before being redirected into Tedlar bags. The bags were washed with 5% HCl then rinsed with Milli-Q water three times. The samples collected only came into contact with titanium, Teflon® tubing, and the Tedlar bags. Milli-Q water was allowed to sit in a Tedlar bag for 8 h, the approximate length of time before samples would be returned to the surface ship after sampling, and the measured blank level was below DOC detection limits. Local North Pacific deep seawater collected with the HFPS had identical DOC concentrations to water collected with Niskin rosette bottles deployed over the side of the ship (36 and 36 μM, respectively). These values also agreed well with deep Eastern North Pacific concentrations measured by other investigators (33.8 μM, Hansell and Carlson, 1998; 33–39 μM, Bauer et al., 1998). Fluid temperature at the intake of the sampler was monitored, which allowed temperatures to be recorded during the entire sampling period. To sample Baby Bare fluids that were free of sedimentary influences and to reduce mixing with seawater, two stainless steel probes 1.5 and 3 m in length were driven into the highly altered crust of the seamount using a 2000 kg coring weight (Johnson and Party, 2003).

### 3.2. Sample analysis and seawater entrainment correction

Upon arrival on deck, samples were stored under refrigeration until processed. To put DOC measurements into the appropriate chemical and microbial context, each sample was also analyzed for alkalinity, pH, hydrogen sulfide, ammonia, magnesium, iron, and microbial cell counts. Alkalinity, hydrogen sulfide, and ammonia were analyzed on-board ship while sub-samples for magnesium and iron concentrations were stored in acid-cleaned polyethylene bottles until shore-based analysis.

Techniques can be found in Butterfield et al. (1997). Subsamples of fluids were preserved for microbial cell counts by DAPI staining and epi-fluorescence counting (Porter and Feig, 1980).

DOC concentrations were measured at sea less than 12 h after sampling with a modified MQ-1001 DOC Analyzer (Peterson et al., 2003). Five milliliter samples were acidified to pH 2 with 5 µL of 12 M HCl and purged with $O_2$ to remove inorganic carbon. Each sample was injected three to four times and the reproducibility between replicate injections was typically <5%. Very low concentration samples (<20 µM) had reproducibility <10%. Deep Sargasso Sea reference water (Hansell, 2001) was analyzed every 10 samples. Over the course of the 2002 and 2003 cruises, the average value for the reference water was 46 ± 2 and 49 ± 4 µM, respectively, in good agreement with Sargasso Sea water measured by a variety of laboratories (Sharp et al., 2002).

On the HFPS, samples could either be filtered in situ or taken unfiltered. Filters used in situ were either combusted GF/F (5 h, 500 °C) or 0.2 µm nitrocellulose filters. Samples taken of identical water using the two different types of filters showed no measurable difference in DOC concentration. Samples that were not filtered in situ were run unfiltered for TOC concentrations and stored at 2 °C. If the TOC concentration was elevated over 60 µM, the samples were filtered on deck using acid-washed Teflon syringes and filter holders with combusted GF/F filters and re-analyzed within 4 h. With the exception of two samples, the difference in DOC concentration before and after deck filtering was <5 µM. For the two samples where a significant concentration difference was observed, the lower concentration is reported.

Inevitably, some seawater is entrained into the sample during collection (Edmond et al., 1979), and DOC concentrations must be corrected to represent pure vent fluid. Undiluted high-temperature vent fluids from the high-temperature axial sites, the Baby Bare Seamount fluids, and ODP 1026B fluids have Mg concentrations less than 1 mmol/kg, much lower than deep seawater concentrations of 53 mmol/kg (Von Damm et al., 1985; Mottl et al., 1998; Butterfield et al., 2001). We therefore assume that Mg present in the fluids occurs from the entrainment of background seawater (BSW) during sampling. Variable entrainment of BSW during sampling at ODP Hole 1026B allowed a test of this assumption (Fig. 2). A plot of DOC vs. Mg for 1026B fluids has a zero Mg intercept of 13 µM with a $r^2 = 0.90$ ($n = 8$, $p < 0.001$), demonstrating that the mixing of low DOC fluids with deep seawater is indeed conservative. We could thus calculate the DOC concentration in pure hydrothermal fluids by assuming measured values were a mixture of the hydrothermal endmember (Mg = 0 mmol/kg) and BSW (Mg = 53 mmol/kg, DOC = 36 µM). This correction was only made for fluids with a Mg endmember close to zero, i.e., high-temperature fluids and off-axis fluids. Corrections typically changed the measured DOC concentration by less than 4 µM (Table 1). Diffuse fluids from on-axis vents have a significant component of entrained crustal seawater and should not be extrapolated to zero Mg content.

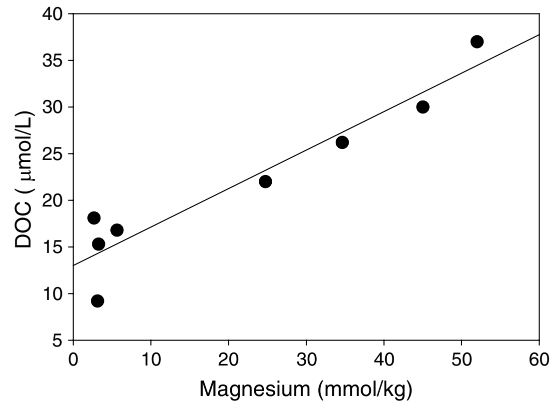


Fig. 2. Composition of 1026B fluids. The linear trend demonstrates conservative mixing between spring water fluids (low Mg and DOC concentrations) and background seawater (high Mg and DOC concentrations).

## 4. Results

High-temperature vent fluids sampled at the MEF and AV have temperatures ranging from 212 to 374 °C (Table 1; Fig. 3a). Table 1 lists the endmember DOC concentrations for high-temperature fluids along with the uncorrected, measured values. Endmember DOC concentrations from MEF and AV high-temperature vents were all significantly depleted compared to North Pacific Deep Water (NPDW; 36 µM). Four of the samples from MEF fell into a tight range of DOC concentrations from 11 to 13 µM (Table 1) while a sample from Hulk had a higher DOC concentration of 26 µM. The average endmember DOC concentration for high-temperature vent fluids from MEF was 15 ± 5 µM. Fluids from high-temperature fluids at AV had a DOC concentration range from 8 to 24 µM and average of 17 ± 8 µM.

We also measured DOC concentrations from diffuse, low-temperature (9–85 °C) vents issuing from the base of sulfide structures and adjacent cracks in the basaltic seafloor at MEF. These vent fluids ranged in DOC concentrations from 39 to 69 µM, with an average concentration of 49 ± 9 µM (Table 1; Fig. 3a). DOC concentrations of five samples from basalt-hosted diffuse (20–40 °C) vents at AV in 2002 had concentrations very similar to background seawater (35–38 µM) and two diffuse vent fluids were significantly elevated over background seawater (53 and 60 µM). In 2003, concentrations from AV ranged from 34 to 71 µM and averaged 50 ± 10 µM (Table 1).

Fluid samples from older, ridge-flank crust were obtained from Baby Bare Seamount and ODP Hole 1026B. At the Baby Bare site, DOC concentrations in the fluids were relatively elevated during ROV dives immediately following the insertion of the probes, while the effluent fluid was still cloudy with sediment, but after 48 h dropped to significantly lower levels (Fig. 4). Microbial cell counts

Table 1
Sampling locations and dissolved organic carbon measurements

| Location | Temp. (°C) | Mg (mmol/kg) | $DOC_{(meas)}$[a] (μM) | $DOC_{(corr)}$[b] (μM) |
|---|---|---|---|---|
| *High-temperature samples: Main Endeavour Field (2002)*[c] | | | | |
| Raven | 347 | 8.5 | 15 | 12 |
| Hulk | 212 | 2.2 | 27 | 26 |
| Puffer | ND | 4.5 | 15 | 14 |
| South Grotto | 374 | 0.9 | 11 | 11 |
| Dudley | 323 | 17.1 | 21 | 14 |
| S&M | ND | 1.4 | 16 | 16 |
| | | | Average | 15 ± 5 |
| *High-temperature samples: Axial Volcano (2003)* | | | | |
| Hell | 283 | 1.5 | 18 | 17 |
| Hell | 284 | 1.9 | 25 | 24 |
| Inferno | 274 | 5.7 | 8 | 8 |
| | | | Average | 17 ± 8 |
| *Off-axis samples: Baby Bare Samples (2002)* | | | | |
| BB, Probe 3 | 20.4 | 6 | 14 | 11 |
| BB, Probe 3 | 19.9 | 3.9 | 15 | 14 |
| BB, Probe 3 | 20 | 4.2 | 11 | 9 |
| BB, Probe 3 | 20 | 2.4 | 28 | 27 |
| BB, Probe 4 | 20 | 7.8 | 13 | 10 |
| BB, Probe 4 | 20.1 | 10.7 | 13 | 7 |
| BB, Probe 4 | 19.1 | 7.6 | 19 | 16 |
| BB, Probe 4 | 18.9 | 3.5 | 13 | 11 |
| BB, Probe 4 | 19 | ND | 11 | 11 |
| | | | Average | 11 ± 3 |
| *Off-axis samples: ODP Hole 1026B (2002)* | | | | |
| 1026b | 62.4 | 2.7 | 18 | 17 |
| 1026b | 62.5 | 3.1 | 9 | 8 |
| 1026b | 62.2 | 3.3 | 15 | 14 |
| 1026b | 62.2 | 5.6 | 17 | 15 |
| | | | Average[d] | 13 ± 4 |
| *Local North Pacific Deep Water* | | | | |
| NPDW | 2 | 53 | 36 | |
| *Diffuse samples: Axial Volcano (2002)* | | | | |
| Marker 33 | 21.2 | 45.4 | 35 | |
| Marker 113 | 17.9 | 51.3 | 38 | |
| Village | 31.1 | 46.4 | 36 | |
| Village | 31.1 | 47.5 | 36 | |
| Vixen | 40.2 | 46.1 | 53 | |
| Vixen | 39.9 | 47.3 | 37 | |
| Near Marker N3 | 30.8 | 51.7 | 60 | |
| | | Average | 42 ± 10 | |
| *Diffuse samples: Axial Volcano (2003)* | | | | |
| Crack | 35.3 | 49.3 | 34 | |
| Collum | 16 | 51.7 | 48 | |
| Marker 33 | 12.4 | 52.1 | 41 | |
| Marker 113 | ND | 49.6 | 71 | |
| Marker 113 | ND | 51.1 | 52 | |
| Marker N3 | 7.8 | 53.3 | 40 | |
| Marker N41 | 11.2 | 50.7 | 54 | |
| Old Worms | 12 | 53 | 53 | |
| Old Worms | 12 | 53.5 | 54 | |
| Styx | 13 | 49.9 | 51 | |
| | | Average | 50 ± 10 | |
| *Diffuse samples: Main Endeavour Field (2002)* | | | | |
| Raven field | 37.8 | 49.1 | 42 | |
| S&M, MT2 | 8.7 | 51.9 | 46 | |
| Raven | 38.4 | 49.5 | 56 | |
| Hulk | 17.5 | 48.8 | 45 | |
| Hulk | 17.5 | 52 | 40 | |
| Easter Island | 23.9 | 48.8 | 39 | |
| Easter Island | 23.3 | 48.7 | 48 | |

Table 1 (*continued*)

| Location | Temp. (°C) | Mg (mmol/kg) | $DOC_{(meas)}$[a] (μM) | $DOC_{(corr)}$[b] (μM) |
|---|---|---|---|---|
| Near Dudley | 54.5 | 45.7 | 69 | |
| Near Dudley | 82.1 | 40.7 | 47 | |
| Near Dudley | 85.9 | 39 | 57 | |
| South Grotto | 21 | 49 | 39 | |
| | | Average | 49 ± 9 | |

[a] The reproducibility between 3 and 4 replicate injections was <5% except for high temperature and off-axis samples, when reproducibility was <10%.

[b] DOC values of high temperature and off-axis samples corrected due to entertainment of seawater during the sampling process. We assume that high temperature and off-axis vent fluids have a [Mg] = 0 mmol/kg, and seawater a [Mg] = 53 mmol/kg, and [DOC] = 36 μmol/L. Entrainment corrections were not made for diffuse samples because in that case endmember fluids do not have a Mg concentration of 0 mmol/kg.

[c] ND, no data. Temperature probe broken on dive; temperatures given as lower bound estimates.

[d] *Q*-tests at a 95% confidence limit show that the Baby Bare Probe 3 sample (27.2 μM) is an outlier. The average concentration of Baby Bare fluids are calculated excluding this sample.

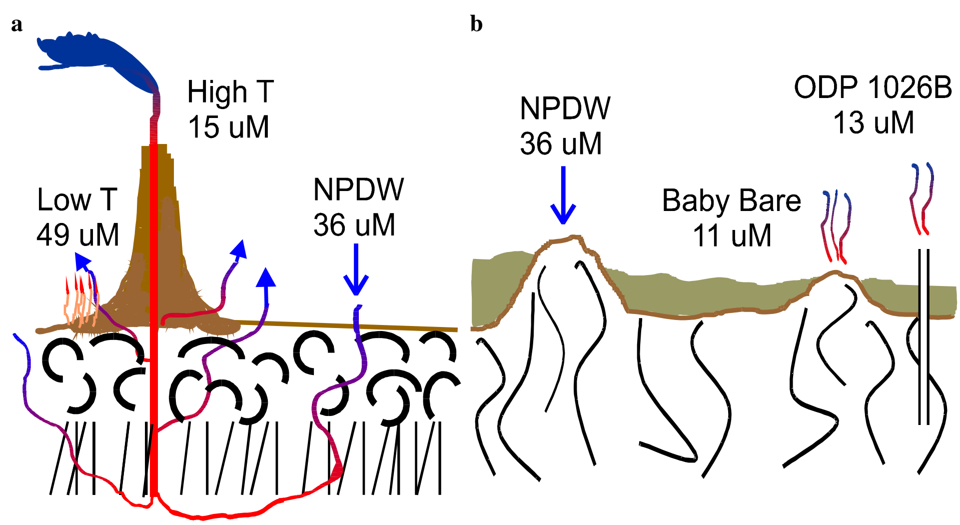


Fig. 3. (a) Two on axis (<1 Ma old) sites on the Juan de Fuca Ridge, MEF and AV, were sampled. Average DOC concentrations (μM) are given for MEF. High temperature ($T = 200$–$350$ °C) sites are characterized by high fluid velocities, low pH's, and high metal concentrations. Diffuse ($T = 20$–$85$ °C) sites are a subsurface mixture of high-temperature fluids and deep local seawater. (b) Baby Bare Seamount and ODP Hole 1026B are located on 3.5-Ma-old crust approximately 100 km east of the Juan de Fuca Ridge. These sites have a local re-charge zone, possibly a near-by exposed basement outcrop (Elderfield et al., 1999; Fisher et al., 2003). Temperatures for Baby Bare and ODP 1026B were ~20 and 63 °C, respectively.

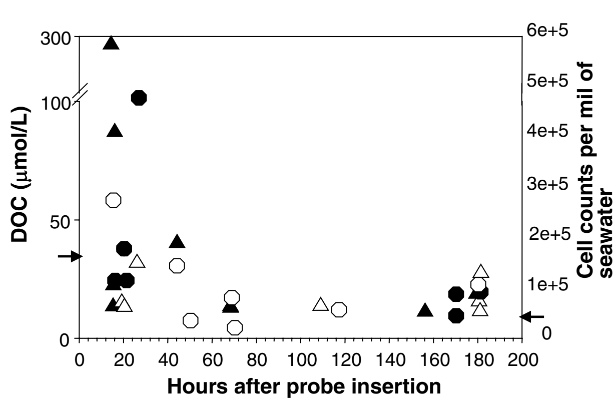


Fig. 4. DOC concentrations (triangles) and cell counts (circles) at the Baby Bare probes vs. time since the probes were inserted into the crust. Probe 3, open symbols; Probe 4, closed symbols. During early observations, the water exiting the probes was cloudy with sediment. After ~48 h, the effluent became visibly clearer and appeared free of sedimentary influence. Arrows on each axis indicate local deep seawater concentrations.

followed a similar trend (Fig. 4), showing the initial sedimentary influence on the fluid immediately after probe insertion. After 48 h, fluids sampled from Baby Bare Seamount probes contained extremely low DOC concentrations when corrected for seawater entrainment: 6–16 μM, with only one higher sample at 27 μM (Table 1; Fig. 3b). A *Q*-test at a 95% confidence limit shows this sample is an outlier, and when excluded, our average Baby Bare fluid DOC concentration is 10 ± 3 μM ($n = 9$).

Nearby ODP Hole 1026B was venting ~63 °C water from the crustal reservoir with an inorganic chemical composition very similar to the fluids from Baby Bare (Davis et al., 1992; Butterfield et al., 2001; Wheat and Mottl, 2000). Samples from this site with <10 mmol/kg Mg (e.g., <20% seawater) were corrected for seawater entrainment, and had similar DOC concentrations (8–17 μM, Table 1) to the endmember concentrations determined by a mixing line of DOC vs. Mg (Fig. 2). The DOC concentration of

Table 2
Chemical composition of diffuse and off-axis sites[a]

| | Year sampled | $T$ (°C) | pH at 22 (°C) | Alkalinity (meq/L) | $NH_4$ (μmol/kg) | $H_2S$ (mmol/kg) | Fe (μmol/kg) | $CO_2$ (mmol/kg) | $CH_4$ (μmol/L) | $H_2$ (mmol/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| *Off-axis sites*[b] | | | | | | | | | | |
| Probe 3 | 2002 | 19.3 (1.2) | 8.44 (0.08) | 0.37 (0.04) | 100 (5) | <0.001 | | | 0.10–0.74[c] | 0.03–0.67[c] |
| Probe 4 | 2002 | 19.6 (0.6) | 8.36 (0.1) | 0.35 (0.02) | 97 (4) | <0.001 | | | | |
| ODP 1026B | 2002 | 62.3 (0.13) | 7.49 (0.09) | 0.34 (0.04) | 97 (4) | <0.001 | | | | |
| Probe 3 | 2003 | 19.7 (0.08) | 8.42 (0.04) | 0.35 (0.08) | 99.8 (4) | <0.001 | 0.5 (0.1) | | | |
| Probe 4 | 2003 | 19.7 (0.14) | 8.45 (0.3) | 0.35 (0.07) | 95.3 (5) | <0.001 | | | | |
| ODP 1026B | 2003 | 61.5 (0.3) | 7.55 (0.02) | 0.39 (0.05) | 104 (4) | <0.001 | 2.7 (0.25) | | | |
| *Axial Volcano* | | | | | | | | | | |
| High Temp[d] | 1998–2000 | 190–315 | 3.6–5.0 | 0 to −0.5 | 10–18 | 5–47 | 12–400 | >150 | 25–400 | 0.27–0.65 |
| Marker 33[d,e] | 2000 | 20–32 | 5.8 | 2.2 | 2.2 | 0.2 | 2 | ND | 6 | 0.002 |
| *Main Endeavour Field* | | | | | | | | | | |
| High Temp[b] | 2000 | 344–382 | 3.0–4.2 | −1 to 0.25 | 425–550 | 4–13 | 1000–5000 | 20.0–26.2 | 130–1220 | 0.13–2.1 |
| Puffer | 2000 | 17–39 | 6.0–6.5 | 2.4 | 32.5 | 0.3–0.47 | 0.4 | ND | ND | ND |
| Deep sea | | 2 | 7.9 | 2.5 | <1 | 0 | <1 | | 0 | 0 |

[a] Uncertainties (1 sigma) given in parentheses. ND, no data.
[b] Gas data from Lilley et al. (2003).
[c] Not extrapolated to zero Mg endmember. Highest concentration measured at Baby Bare Seamount during FlankFlux 95 cruise.
[d] From Butterfield et al. (2004).
[e] From Huber et al. (2002).

ODP 1026B samples is similar to that of Baby Bare, averaging $13 \pm 4$ μM ($n = 4$).

The inorganic chemistry of Baby Bare and ODP Hole 1026B fluid appears similar to samples from past years with low alkalinities, low concentrations of iron and hydrogen sulfide, and high ammonia concentrations (Table 2; Sansone et al., 1998; Wheat and Mottl, 2000; Cowen et al., 2003). Methane and hydrogen concentrations in the ridge-flank fluids are also low compared to those found in axial systems (Table 2).

## 5. Discussion

### *5.1. Mechanisms for DOC depletion in high temperature and ridge-flank hydrothermal systems*

Approximately 70% of the DOC entering both high temperature and off-axis hydrothermal systems is removed during circulation of fluid through the crustal reservoir. The endmember DOC concentrations in high-temperature vents are significantly less than concentrations in NPDW, averaging $15 \pm 5$ μM at MEF and $17 \pm 8$ μM at AV. These results are consistent with low concentrations of amino acids measured in high-temperature vents (Haberstroh and Karl, 1989; Horiuchi et al., 2004). Low DOC concentrations (near 12 μM) in off-axis fluids are more surprising. Off-axis fluids have been shown capable of supporting microbial communities (Cowen et al., 2003; Huber et al., 2006) and thermodynamic studies suggest off-axis crustal reservoir conditions are favorable for organic synthesis (Shock, 1992).

The fluid circulation pathways of these systems differ in several important aspects and the processes controlling the DOC concentrations may not be similar. However, the proposed removal mechanisms overlap between the two locations and so they will be considered together while discussing the potential processes contributing to the observed DOC depletion. First, the organic matter may be thermally degraded to $CO_2$ or $CH_4$ with the help of mineral catalysts. Second, a subsurface heterotrophic community may be consuming the entrained seawater DOC. Finally, organic matter may become sorbed to mineral surfaces along the circulation pathway in the highly porous upper crustal rocks.

Abiotic decomposition is a plausible explanation for the DOC loss, especially in high-temperature vents. Loss of DOC concentration requires organic matter breaking down to volatile species (e.g., $CO_2$, $CH_4$) and not simply recombining. Cracking of organic matter does not occur until temperatures reach 150 °C and even then may require mineral catalysis (Hunt, 1979; Tissot and Welte, 1984; Simoneit et al., 1992; Mango and Elrod, 1999). In laboratory studies of diatomaceous ooze at high temperatures and pressures (>250 °C, >400 bar), DOC concentrations initially increased as organic matter desorbed from the sediments then decreased with a simultaneous increase in $CO_2$ and $CH_4$ (Seewald et al., 1990, 1994). Experiments with similar conditions demonstrated small organic acids, *n*-alkanes, toluene, and benzoic acid also decompose (McCollom and Seewald, 2003a,b; Seewald, 2001).

The observed DOC depletion may also be due to consumption by a heterotrophic subsurface microbial community. In high-temperature systems, these microbial communities could reside in the low-temperature environment of the downwelling limb of the fluid circulation pathway. While DOC in the North Pacific is largely recalcitrant to further biological activity (Barber, 1968), the warm crustal temperatures may alter the organic matter sufficiently to allow it again to become biologically available (Karl, 1995). Additionally, surface-attached communities living within crustal pore spaces may be better adapted to the consumption of dissolved organics than free-living water column biological communities. Ridge-flank fluids within the upper crustal reservoir have been shown capable of supporting microbial communities, including thermophilic heterotrophs (Cowen et al., 2003; Huber et al., 2006). Biotic alteration has been observed on basalt from older crust (e.g., Fisk et al., 2003) and the utilization of seawater DOC was suggested through stable carbon isotope studies (Furnes et al., 2001).

A third plausible DOC removal mechanism is that DOC is sorbed to the minerals of the basaltic crust during circulation. The efficiency by which DOC sorbs depends on temperature, pH, the water/rock ratio, and redox conditions (Montluçon and Lee, 2001; Schwarzenbach et al., 2003; Svensson et al., 2004). Elevated temperatures and reducing redox conditions disfavor sorption (Seewald et al., 1990; Arnarson and Keil, 2000; Montluçon and Lee, 2001; Schwarzenbach et al., 2003; Svensson et al., 2004). Highly acidic fluids would favor sorption; however in situ pHs in high-temperature fluids are probably no more than 1–2 pH units more acidic than neutral (Ding and Seyfried, 1996). Baby Bare and ODP Hole 1026B fluids have slightly elevated pH relative to seawater (Table 1; Wheat and Mottl, 2000; Butterfield et al., 2001; Wheat et al., 2004). The ability of specific basaltic minerals to sorb organic compounds under these conditions is largely unknown.

One way to distinguish between the potential removal mechanisms would be to measure thermal and microbial decomposition by-products such as $CO_2$ and $CH_4$, which would not be elevated if sorption were the dominant process. Unfortunately, both of these species are present in high-temperature hydrothermal fluids at Endeavour in millimolar concentrations due to magmatic degassing and other processes (Lilley et al., 1993), so an additional source of these gases from the degradation of micro-molar concentrations of DOC would be nearly impossible to detect. $CO_2$ concentrations in off-axis hydrothermal systems are 1/3 that of background seawater concentrations, and this component is likely to be precipitated within the rock matrix as calcite (Sansone et al., 1998). In this environment, a micro-molar source of $CO_2$ from DOC degradation would also be difficult to detect in the presence of millimolar decreases due to other processes.

### *5.2. Mechanisms for DOC elevation in diffuse vents*

DOC concentration in axial hydrothermal fluids varies widely and do not appear to systematically change with temperature ($r^2 = 0.02$; $p = 0.8$; $n = 28$). The differences in concentrations likely reflect heterogeneous physical conditions in the subsurface. These results are consistent with elevated POC concentrations from diffuse (15–40 °C) fluids from East Pacific Rise which are as high as those in productive surface upwelling sites (Comita et al., 1984).

Only a handful of DOC measurements have previously been made from diffuse ridge-axis hydrothermal vents and even these small data sets appear to conflict (Comita et al., 1984; Sarradin et al., 1999). DOC from diffuse vents from East Pacific Rise Axis are slightly lower (53–71 μM) than non-vent bottom seawater (84 μM; Comita et al., 1984), while diffuse vents from the Mid-Atlantic Ridge generally measure higher (247 μM, $n = 17$) than regional non-vent seawater (143 μM; Sarradin et al., 1999). In both cases, local non-vent bottom seawater DOC concentrations were higher than the generally accepted values for deep DOC concentrations, (e.g., deep Pacific water: 39 μM; deep Atlantic water: 44–45; Hansell and Carlson, 1998) rendering these measurements somewhat suspect.

Possible sources of DOC in diffuse low-temperature vent fluids include both non-biological desorption of organic matter from sediments and biological production. Sediments are unlikely to affect DOC concentrations at AV, a bare rock field with no evidence for such an influence on other chemical species (Butterfield et al., 1990, 2004). Elevated concentrations of methane and ammonia in high-temperature vents at MEF are unusual for an unsedimented system and are believed to be produced by interaction with buried turbiditic sediment along the circulation pathway (Lilley et al., 1993; Butterfield et al., 1994; You et al., 1994; Proskurowski et al., 2004). If this interaction were similarly affecting DOC concentrations, it would be apparent in the high-temperature fluids. Instead, high-temperature fluids have uniformly depleted concentrations of DOC, which requires either that the buried sediment contains no extractable organic material or that any organic material that may be extracted from buried sediment must subsequently be removed by the time the fluid has passed through the high-temperature reaction zone. The implication is that the excess DOC in MEF diffuse vents is not derived from buried sediment but is produced in the subseafloor zone where primary hot fluids mix with crustal seawater.

Mounting observational evidence confirms that the diffuse effluent from subsurface regions adjacent to high-temperature vents harbor significant microbial communities. These populations are supported by the energy produced from the disequilibria between highly reduced, metal-rich, hydrothermal fluids and oxic background seawater (Holden et al., 1998; Summit and Baross, 2001; Huber et al., 2002, 2003; Butterfield et al., 2004) where the autotrophic production of several biomolecules is thermodynamically favorable (Shock and Schulte, 1998; Amend and Shock, 2001; Schulte and Rogers, 2004). Evidence for microbial productivity within subsurface diffuse hydrothermal environments includes increased microbial cell counts, production of methane, nitrate reduction, sulfide oxidation (Butterfield et al., 2004), and highly diverse microbial populations (Huber et al., 2002, 2003). This autotrophic microbial population could be the primary source of DOC in diffuse hydrothermal fluids. Just as DOC accumulates in the open ocean due to the decoupling of biological production and consumption, similar processes could be occurring during hydrothermal circulation within the upper crustal reservoir, where continual flow through the system may remove dissolved substrates before they can be locally utilized.

### 5.3. Comparison of off-axis and diffuse vents

Elevated DOC concentrations are observed in the high-productivity environment of ridge-axis diffuse vents with high microbial cell counts. Much lower DOC concentrations are observed in the energy-poor environment represented by fluids which have low cell counts that vent from basaltic basement on the ridge flanks. A key difference between the two sites may be the potential for autotrophic production, derived primarily from the mixing of hot, reducing fluids with cool, oxygenated seawater. Thermodynamically, the oxidation of sulfur species and $H_2$ will yield the majority of the required energy (McCollom and Shock, 1997; Shock and Holland, 2004). These thermodynamic calculations are supported by chemical and microbial evidence of $H_2S$ and $H_2$ oxidation within low-temperature fluids at AV (Butterfield et al., 2004). The chemical energy available for autotrophic production is high in diffuse vents, where there are elevated concentrations of $H_2S$, $H_2$, $CH_4$, and Fe (Butterfield et al., 2004; Table 2). Off-axis fluids have no measurable hydrogen sulfide and very low levels of iron and dissolved reduced gases, and the chemical energy available for microbial production during mixing with seawater is extremely low compared to ridge-axis diffuse flow environments (Table 2). Furthermore, subseafloor mixing of reduced fluids with seawater is extremely limited in the off-axis vents on the Juan de Fuca Ridge flank as seen in the very low Mg content (Table 1), leading to an energy-poor microbial habitat consistent with the low observed cell counts. In this study, high DOC concentrations are linked to high microbial cell counts.

## 6. Effect of hydrothermal circulation on deep-sea DOC

### 6.1. Hydrothermal flux of DOC

Concentrations of deep water DOC decrease by ~14 μM during the transit from the northern Atlantic to the northern Pacific Ocean (Hansell and Carlson, 1998), but the mechanisms of this removal are not fully understood (Williams, 2000; Carlson, 2002; Hansell, 2002). Hydrothermal circulation through the upper oceanic crustal reservoir is a currently unconstrained process that could affect the oceanic DOC pool, particularly the deep water DOC pool.

Estimates of the flux of organic carbon through these systems were made using the concentration data presented here and published water fluxes. Water fluxes are determined through estimates of crustal heat loss occurring from seawater convection. The current estimate is that $9.9 \pm 2$ TW ($31.2 \pm 6.3 \times 10^{19}$ J/year) of heat is lost out to a crustal age of ~65 Ma (Stein and Stein, 1994; Johnson and Pruis, 2003; Mottl, 2003). Estimates of the flux of water, and thus the flux of carbon, through these systems are dependent on how this heat loss is partitioned between high temperature on-axis (<1 Ma crust; 350 °C), diffuse on-axis venting (<1 Ma crust; <100 °C) and off-axis venting along the flanks (1–65 Ma crust). At present, we assume that results from the Juan de Fuca Ridge axis and east flank are representative of global high temperature, diffuse, and off-axis hydrothermal systems, so these calculations of DOC flux must be treated with caution. For simplicity, we assume the concentration changes observed in the Pacific Ocean are the same as would be observed in the Atlantic Ocean. Since deep water in the Atlantic Ocean has higher DOC concentrations than in the Pacific (45 μM vs. 36 μM), this assumption would require concentrations in endmember fluids to be ~10 μM higher than observed here. Further measurements from other systems will enable us to better constrain the fluxes and determine if the Juan de Fuca concentration data are a valid global representation.

Mottl (2003) estimated that $3.0–5.9 \times 10^{13}$ kg of seawater/year pass through high-temperature vent systems. The average endmember high-temperature vent DOC concentration is ~20 μM less than the measured deep DOC concentration of 36 μM. With 20 μmol DOC lost for every liter passing through high-temperature vents, there would be a global loss of $0.7–1.4 \times 10^{10}$ g C/year through high-temperature axial vents (Fig. 5).

Off-axis vents can be divided into two categories: (i) warm upper crustal reservoirs with basement temperatures >45 °C, resulting from the conductive cooling of sediment-covered basement, with large chemical changes in the circulating fluid and >80% losses of Mg or (ii) cool crustal reservoirs with basement temperatures <25 °C resulting from unsedimented basement with convective cooling and relatively small chemical changes and <10% losses of Mg (Mottl and Wheat, 1994). Warm ridge-flank crustal reservoirs account for a maximum of ~12% of off-axis heat loss as constrained by the magnitude of the Mg sink (Mottl and Wheat, 1994). The remaining 88% of the chemical losses presumably occur through small concentration changes in cool off-axis ridge flanks, although to date no good examples of these systems have been observed (Mottl and Wheat, 1994).

Crustal fluids from Baby Bare and ODP Hole 1026B result from basement temperature of 60 to 70 °C (Davis et al., 1997) and these sites represent "warm" off-axis vents. If other warm off-axis vents are similar to these two sites, the maximum water flux through these systems is ~7.4–$43 \times 10^{13}$ kg of seawater/year, assuming they account for ~12% of the heat loss at temperatures between 20 and 65 °C (Mottl, 2003; Fig. 5). Both sites have fluid with DOC concentrations ~25 μM less than background seawater, which gives a total loss of $2–13 \times 10^{10}$ g DOC/year; significantly larger than calculated for high-temperature vents

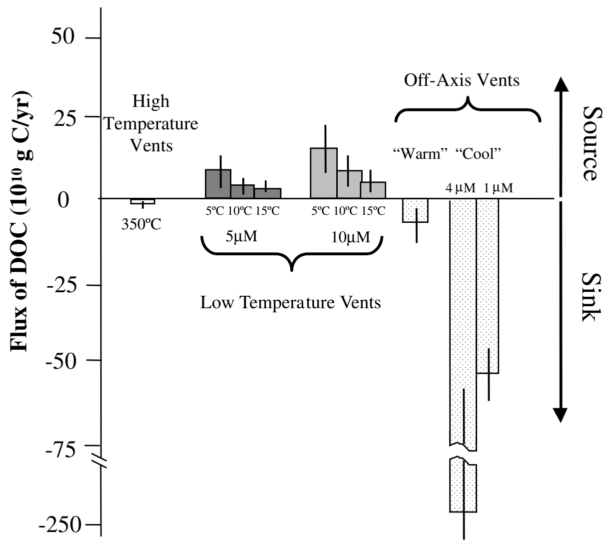


Fig. 5. Global DOC flux assuming various hydrothermal conditions. High-temperature organic carbon fluxes were calculated assuming a loss of 20 µmol C for every liter passing through the vents. Diffuse vent organic carbon fluxes were calculated assuming effluent temperatures of 5, 10, 15 °C and an addition of 5 or 10 µmol C/liter. Error bars indicate the range which occurs by varying the amount of axial heat loss through diffuse vents as opposed to high-temperature vents (varied from 25% to 50%). Carbon losses for off-axis vents were calculated assuming "warm" vents account for 12% of the off-axis heat loss and a DOC concentration loss of 25 µM. Error bars demonstrate the range of values which occurs by varying the effluent temperature from 20 to 65 °C. No good examples of "cool" off-axis vents have been found and the composition of such fluids remains speculative. DOC fluxes through these systems are included as a demonstration of the possible size of fluxes should only 10% or 2% of deep DOC concentration (4 or 1 µM) be lost during passage through these vents. See text for other assumptions inherent in these calculations.

($0.7–1.4 \times 10^{10}$ g C/year). However, heat fluxes and geochemical changes from Baby Bare and ODP Hole 1026B appear to be too large to be typical of warm off-axis vents (Butterfield et al., 2001; Wheat et al., 2003) and for that reason, these DOC fluxes are likely maximums.

Cool off-axis vents could account for up to 88% of the heat loss in ridge-flank systems, although the composition of such fluids remains speculative. Johnson and Pruis (2003) recently estimated the seawater flux through cool off-axis vents to be $4800 \times 10^{13}$ kg of seawater/year. Chemical species are predicted to have smaller (<20%) concentration changes in these low-temperature systems. We have no measurements from cool off-axis vents and any flux calculations are completely speculative. If observed concentrations from Baby Bare and ODP hole 1026b are due to a process such as sorption to crustal rocks, it is possible that similar losses will occur in these cooler vents. To illustrate a potential scenario, if 10% (4 µM) of the DOC is lost, cool ridge-flank circulation would represent a global DOC concentration loss of $230 \times 10^{10}$ g DOC/year (Fig. 5).

Greater uncertainties both in the water flux and in the changes in DOC concentration make it difficult to extrapolate the effect of low-temperature diffuse vents at the ridge axis. Estimates vary for the volume of high-temperature hydrothermal water that mixes in the subsurface and exits the seafloor in a diffuse vent. We assume 25–50% of the global axial heat flux is lost through diffuse vents at temperatures between 5 and 15 °C (Johnson et al., 2002; Veirs et al., 2006). If there is a DOC addition of 5–10 µmol/L of seawater passing through diffuse vents, $3–28 \times 10^{10}$ g DOC/year could be added to the deep ocean seawater pool (Fig. 5).

These fluxes are minor when compared to the major sources and sinks of DOC such as riverine input ($2.5 \times 10^{14}$ g C/y, Cauwet, 2002; Hedges et al., 1997). The removal rates from high temperature and off-axis vents can account for <2% of the observed 14 µM concentration loss of DOC along the oceanic deep circulation pathway (Hansell and Carlson, 1998).

### *6.2. Possible source of 'old' DOC*

Oceanic DOC is a complex mixture of organic components with varying sizes, ages, and reactivities (Amon and Benner, 1996; Aluwihare et al., 2002; Loh et al., 2004). The deep DOC pool is predominantly composed of low-molecular-weight material (<1000 Da; LMW; Amon and Benner, 1996) has a $^{14}$C age of 4000–6000 ybp (Druffel et al., 1992). This observation suggests that either deep-water DOC has persisted through several ocean circulation cycles or that it has one or more pre-aged sources (Druffel et al., 1992; Loh et al., 2004). The apparent age of the high-molecular-weight DOC pools results from a combination of large amounts of younger, rapidly cycling material and minor amounts of a highly $^{14}$C aged component (Loh et al., 2004). The age of the entire DOC pool may similarly be a result of one or more highly aged sources.

Because of the possibility of exchange with DIC sources within the crustal reservoir, DOC in hydrothermal effluent produced in the subseafloor may be depleted in $^{14}$C compared to DOC produced in non-hydrothermal oceanic locations. Hydrothermal $CO_2$ has a magmatic component that is $^{14}$C dead, and organic carbon produced from a mixture of seawater and magmatic carbon would be expected to be $^{14}$C depleted relative to organic carbon produced solely from background seawater DIC. Four high-temperature vents sampled in the year 2000 from MEF had an average $CO_2$ concentration of $23.1 \pm 4.4$ mmol/kg and a fraction modern $F_{mod}$ of $0.0225 \pm 0.007$ while NPDW has a $CO_2$ concentration of 2.3 mmol/kg and $F_{mod}$ of 0.76 (Proskurowski et al., 2004). Concentrations of $CO_2$ in high-temperature fluids from AV are a factor of 10 higher than background seawater due to the influence of magmatic degassing (Butterfield et al., 1990, 2004). Hyperthermophilic tracers indicate the presence of subseafloor habitat temperature of 50–100 °C, which requires a mixture of ~20% high-temperature hydrothermal fluids and 80% background seawater (Holden et al., 1998). Application of a simple mixing equation to these measurements argues for a DIC concentration of ~6.4 mmol/kg with a $^{14}$C age of

~10,000 ybp for inorganic carbon in the Endeavour subseafloor diffuse hydrothermal zone. If the DOC produced in diffuse vents has a $^{14}C$ age reflecting this DIC, the freshly produced material would appear a full 4000 years "older" than the average $^{14}C$ age of deep DOC in the North Pacific (Druffel et al., 1992; Loh et al., 2004). The effect of this potentially pre-aged source on the oceanic organic carbon cycle will depend largely on how long it persists in the environment. If the material survives long enough to make a significant contribution to the DOC pool, it could bias measured average $^{14}C$ ages to older values.

## 7. Summary and conclusion

We have undertaken the first systematic measurements of DOC concentrations within the upper crustal reservoir, and have made initial estimates of the organic regimes present in a range of hydrothermal systems. DOC is depleted in high-temperature ridge-axis vent fluids and also in warm off-axis crustal reservoirs. The elevated DOC concentrations observed in low-temperature diffuse hydrothermal systems from MEF and AV are likely due to subsurface biological production. In this study, high DOC concentrations are linked to the high-productivity environment of ridge-axis diffuse vents while energy-poor off-axis environments have much lower DOC concentrations.

This study does not constitute a comprehensive global survey of hydrothermal DOC, but it provides the basis for an initial estimate of the impact of hydrothermal circulation on DOC in the oceans. Calculations based on these initial data indicate that hydrothermal fluxes of DOC are small relative to other oceanic sources and sinks. More measurements from a wider range of hydrothermal systems, combined with stable and radiocarbon isotopic measurements, are necessary to better constrain hydrothermal carbon fluxes and their effect on the deep-sea carbon cycle. Measurements of biomarkers from diffuse vents will significantly improve our understanding of the processes at work in these locations.

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