

Dissolved inorganic carbon isotopic composition of low-temperature axial and ridge-flank hydrothermal fluids of the Juan de Fuca Ridge

Brett D. Walker^{a,*}, Matthew D. McCarthy^a, Andrew T. Fisher^b, Thomas P. Guilderson^{a,c}

^a University of California, Santa Cruz, Department of Ocean Sciences, 1156 High Street, Santa Cruz, CA 95064, United States

^b University of California, Santa Cruz, Department of Earth and Planetary Sciences, 1156 High Street, Santa Cruz, CA 95064, United States

^c Lawrence Livermore National Labs, Center for Accelerator Mass Spectrometry, P.O. Box 808, L-397, Livermore, CA 94550, United States

Received 13 November 2006; received in revised form 25 October 2007; accepted 13 November 2007

Available online 22 November 2007

Abstract

We analyzed stable carbon ($\delta^{13}\text{C}$) and radiocarbon ($\Delta^{14}\text{C}$) isotopes of ocean crustal fluid samples from two low-temperature environments on and near the Juan de Fuca Ridge (JDFR), a seafloor spreading center in the northeastern Pacific Ocean. The major goals of this work were to resolve relative dissolved inorganic carbon (DIC) sources and removal processes, and characterize the isotopic signatures of DIC vented to the overlying ocean. DIC was isolated from diffuse vents on the Main Endeavour Field (MEF), on zero age seafloor, and from two ridge-flank sites located 100 km to the east, on 3.5 Ma seafloor; the Baby Bare outcrop and Ocean Drilling Program (ODP) Hole 1026B. Low-temperature MEF fluids were enriched in DIC (3.13 to 5.51 mmol kg^{-1}) relative to background seawater (2.6 mmol kg^{-1}), and their $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values are consistent with simple two-endmember mixing of pure high-temperature (≥ 300 °C) hydrothermal fluid and bottom seawater (secondary recharge). These data suggest that no major sedimentary or biological DIC sources are present, however our results do not preclude a minor sedimentary influence on low-temperature MEF vent fluids. DIC $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of ridge-flank fluids from this area are consistent with an off-axis recharge source, followed by water–rock interaction at moderate temperatures (60 – 70 °C) during flow through basement. An observed offset in radiocarbon ages between fluids from Baby Bare outcrop and Hole 1026B (~ 1100 yr) is consistent with crustal flow from south to north, at rates similar to those inferred from other geochemical and thermal tracers. The ridge-flank hydrothermal fluids are strongly depleted in DIC and $\delta^{13}\text{C}$ relative to bottom seawater, suggesting more extensive carbon removal in this setting ($\sim 5.7 \times 10^{12}$ mol C yr^{-1}) than has been previously suggested. DIC isotopic depletion is consistent with carbonate vein precipitation in conjunction with a minor addition of CO_2 from basalt vesicles, and suggests that ridge-flank systems may be an important sink for seawater inorganic carbon, and comprise an important global reservoir of isotopically depleted and “pre-aged” DIC.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Dissolved inorganic carbon; Hydrothermal; Isotope fractionation; Bicarbonate removal; Endeavour; Juan de Fuca Ridge; Baby Bare; Cascadia Basin

1. Introduction

The chemical, geological, biological, and physical processes occurring within young oceanic crust are important to many fundamental ocean processes. Hydrothermal

* Corresponding author. University of California, Santa Cruz, Department of Ocean Science, 1156 High Street, Santa Cruz, CA 95064, United States. Tel.: +1 831 459 1533; fax: +1 831 459 4882.

E-mail address: bwalker@ucsc.edu (B.D. Walker).

fluid circulation at mid-ocean ridges helps support chemosynthetic microbial communities, and may represent significant sources/sinks of carbon and nitrogen to the overlying ocean (Huber et al., 2002, 2003; Lang et al., 2006). To date, most seafloor hydrothermal research has focused on high-temperature (HT) ridge and near-ridge on-axis systems, but these are responsible for only a small fraction of global seafloor hydrothermal circulation (e.g., Parsons and Sclater, 1977; Stein and Stein, 1992; Elderfield and Schultz, 1996; Mottl, 2003; Veirs et al., 2006). The majority of oceanic hydrothermal circulation occurs at much lower temperatures, primarily on ridge-flanks (areas distant from active mid-ocean ridges), but considerable low-temperature (LT) circulation also occurs at on-ridge and near-ridge environments. The global hydrothermal flux through ridge-flanks is estimated to be at least 10–100 times greater than that on and near ridges (e.g., Mottl, 2003), and the majority of the ridge flux is thought to occur through LT “diffuse” vent sites (e.g., Schultz et al., 1992; Baker et al., 1993). Despite their likely biogeochemical and microbial habitat significance, little is known about the influence of LT hydrothermal circulation on global carbon budgets.

Ridge-flank hydrothermal circulation is relatively common out to crustal ages of 100 Ma and beyond (e.g., Von Herzen, 2004), but measurable advective heat loss from oceanic crustal fluids tends to diminish by 65 Ma on average (Parsons and Sclater, 1977; Stein and Stein, 1992), suggesting that circulation at older sites is more isolated. Within younger ridge-flanks, the exchange of seawater and hydrothermal fluid between the crust and overlying ocean is facilitated by the exposure of permeable basaltic seamounts and other basement outcrops (e.g., Davis et al., 1992; Villinger et al., 2002; Fisher et al., 2003a,b). Recharging fluids are drawn into the crust in many settings by a “hydrothermal siphon”, maintained by modest differences in fluid pressure at the base of recharging (cool) and discharging (warm or hot) fluid columns (e.g., Strens and Cann, 1986; Stein and Fisher, 2003). The area of actively circulating ridge-flanks is likely to be vast. It may comprise over 50% of global ocean basins and could hold up to 2% of the world’s seawater within the porous upper crust (Johnson and Pruis, 2003). This global hydrothermal flux is sufficient to recycle a volume of fluid equal to that of the ocean every 100 to 500 kyr, and has a profound influence on the chemical properties of the ocean and the ocean lithosphere (e.g., Mottl and Wheat, 1994; Elderfield and Schultz, 1996; Alt, 2004).

Located ~300 km from the western US/Canada border, the Juan de Fuca Ridge (JDFR) represents one of the best-studied global ridge systems. The proximity of this system to major ports has made it a convenient laboratory to

examine a range of ridge processes. In addition, a series of ODP holes and basement outcrops on the eastern flank of the JDFR have provided an excellent opportunity to examine ridge-flank fluid chemistry in the context of a well-studied hydrothermal system. Fluids circulating through the eastern flank of the JDFR have substantially different chemistries from those typically found circulating within HT ridge systems (e.g., Butterfield et al., 1994). Although the LT ridge-flank fluids are chemically less evolved than on-axis HT fluids, the ridge-flank fluids are strongly depleted in DIC, alkalinity, Mg, sulfate, nitrate and phosphate, relative to bottom seawater, and are enriched in Ca, Cl, NH₄, Fe, Mn, H₂S, H₂, CH₄ (Mottl et al., 1998; Sansone et al., 1998). Thermal considerations and DIC concentrations suggest that ridge-flanks may sequester a large mass of inorganic carbon from the overlying ocean (Mottl and Wheat, 1994; Sansone et al., 1998). In addition, the chemical nature of inorganic carbon species within ridge-flank hydrothermal fluids may have significant implication for a vast sub-surface microbial biosphere.

Stable (¹³C) and radiocarbon (¹⁴C) isotopes are powerful tools for tracing carbon origin and biogeochemical cycling. DIC isotopic values comprise tracers for the fluids that carry it, and have been used to model fluid circulation pathways within oceanic crust (e.g., Elderfield et al., 1999; Proskurowski et al., 2004). Because seawater and magmatic δ¹³C values are widely separated, DIC δ¹³C can be used as an indicator of carbon sources in hydrothermal systems (Kroopnick, 1985; Blank et al., 1993; Sansone et al., 1998). In addition, δ¹³C values can indicate sedimentary sources, magmatic inputs and biological processes (e.g. chemoautotrophic carbon fixation and heterotrophic respiration; Fisher et al., 1990; Rau and Hedges, 1979). Changes in DIC δ¹³C composition will also reflect subsequent fractionation processes. These can include inorganic reactions occurring in the crust such as Fischer–Tropsch reactions (e.g. Horita and Berndt, 1999), carbonate precipitation (e.g. Alt, 1996; Brady and Gislason, 1997) and the reduction of DIC via hydrogen gas produced during serpentinization (e.g. McCollom and Seewald, 2001 and references therein). Δ¹⁴C of DIC has primarily been used as a “clock” in off-axis systems to constrain apparent fluid age, flow rate and direction (Elderfield et al., 1999). It has also been suggested that DIC Δ¹⁴C can indicate diffusive interaction between flowing and stagnant fluids within young oceanic crustal aquifers (e.g., Sudicky and Frind, 1981; Sanford, 1997; Bethke and Johnson, 2002; Stein and Fisher, 2003). In the case of on-axis hydrothermal systems (where magmatic CO₂ contains no radiocarbon) Δ¹⁴C can also be used as a highly sensitive source indicator.

Together, Δ¹⁴C and δ¹³C provide a unique tracer suite for DIC sources, removal processes, and timescale of fluid

cycling. While previous work has commonly incorporated CO_2 concentration and $\delta^{13}\text{C}$ measurements to investigate ridge processes (e.g. Sansone et al., 1998), few studies have linked DIC concentration with both stable and radiocarbon DIC signatures (e.g. Proskurowski et al., 2004). We present here coupled stable and radiocarbon DIC fluid data from fluid samples in two distinct hydrothermal environments. Ridge-flank fluid samples were collected from Ocean Drilling Program (ODP) Hole 1026B and nearby Baby Bare outcrop, and on-axis fluids were collected from several LT diffuse vents on the Main Endeavour Field (MEF) of the JDFR (Fig. 1). The sample set was obtained using methods specifically designed to limit contamination and, in the case of ridge-flank fluids from Hole 1026B, benefited from the over-pressured formation having vented undisturbed for over 3 yr before sampling. This sample set represents one of the first opportunities to directly compare temporally coherent on-axis vs. off-axis DIC isotopic compositions from the same ridge system.

2. Sample collection and methods

2.1. Geologic setting

The Main Endeavour Field (MEF) is located at a depth of 2200 m on <0.1 Ma crust of the Endeavour segment, northern JDFR (Delaney et al., 1992). This part of the JDFR has a

spreading half-rate of ~ 30 mm/yr (Karsten et al., 1986). Large sulfide deposits of the MEF are aligned sub-parallel to the axial valley, comprising a diverse array of HT vent chimneys (>300 °C) and LT diffuse vents (<100 °C), with the latter found under chimney flanges and within a few meters of HT chimneys. MEF vents host a rich diversity of macrofaunal and microbial assemblages (Sarrazin et al., 1999; Huber et al., 2002). LT samples were collected in the MEF within 5 m of large sulfide structures where warm fluids seep from exposed basaltic crust (Fig. 1). MEF sites are identified using names that correspond to individual sulfide structures and clusters of structures (e.g. Hulk, South Milli-Q, and West Grotto vents).

The ridge-flank sites sampled as part of this study are located 100 km to the east of the ridge axis, on 3.5 Ma seafloor of the Juan de Fuca Plate. This ridge-flank is draped with a thick accumulation of turbidites and hemipelagic mud, much of which was deposited during Pleistocene sea level low-stands, when most of the nearby North American continental shelf was exposed (Davis et al., 1992; Underwood et al., 2005). The seafloor in this area is relatively flat, except where isolated basement outcrops penetrate the otherwise-continuous sediments. ODP Site 1026 is located over a buried basement high, above the same abyssal hill upon which basement outcrops are located to the north and south of the drill site (Fig. 1). ODP Hole 1026B penetrated 247 m of sediments and 48 m of the uppermost basement, and was cased and sealed with a long-term borehole observatory to facilitate monitoring pressure, temperature and collecting fluid samples (Davis et al., 1997). Basement fluids at Site 1026 are over-pressured with respect to ambient

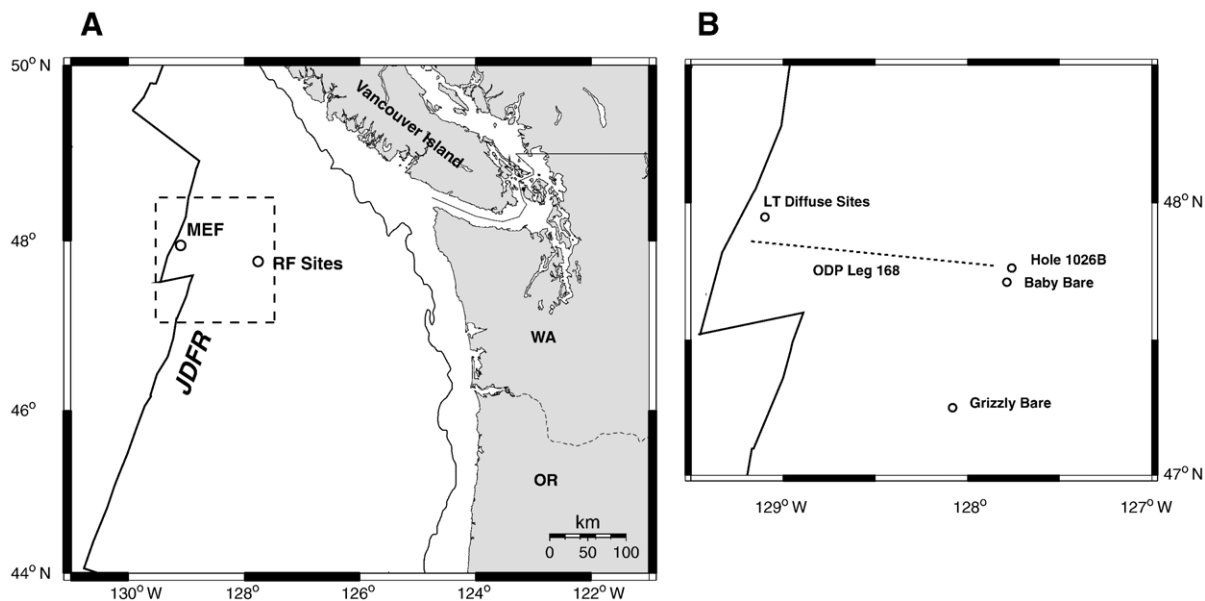


Fig. 1. *Regional site map.* Geographical locations of indicated study areas. A) The Juan de Fuca Ridge (JDFR) is indicated on the western edge of the map by the solid black line. Small circles indicate general locations of MEF and ridge-flank (RF) sampling environments. B) Detailed map of sampling locations as indicated by dashed rectangular box in part A. Sampling locations of LT diffuse vents (Hulk, South Milli-Q, West Grotto) are represented by a single circle due to their close proximity. Hole 1026B, Baby Bare outcrop and Grizzly Bare seamount are depicted by individual circles. ODP Leg 168 transect is marked by the dashed line.

hydrostatic conditions, and incomplete seals in the Hole 1026B borehole observatory allowed formation fluid to vent for several years prior to collection of samples analyzed in this study.

Baby Bare outcrop is located 6.3 km to the south of Hole 1026B, and is a volcanic edifice that rises 400–500 m above regional (sediment-buried) basement and extends another 70 m above the seafloor (Mottl et al., 1998; Wheat and Mottl, 2000). Much of Baby Bare outcrop is covered with a thin (<20 m) coating of pelagic sediment, but basement is exposed near the outcrop margin and along several ridge-parallel normal faults (Wheat et al., 2004). Fluid samples were collected from Baby Bare outcrop using metal probes 3 and 4 (“break-away” core barrels) that were installed during an earlier project for the study of sub-surface chemical and microbiological conditions (Johnson and LEXEN, 2003). Basement fluids flow freely from the probes in Baby Bare outcrop, much as they do from the borehole observatory at nearby Site 1026, greatly simplifying sample collection.

2.2. Sample collection

Fluids were recovered via a novel large-volume elevator barrel sampler (constructed for the LEXEN program), capable of recovering over 150 l of pure hydrothermal fluid per deployment. Construction and operation of this sampler has been described previously (Bjorklund and McCarthy, 2004). Briefly, the sampler was designed to collect large volumes of non-contaminated vent fluid, using a reverse pressure gradient to passively draw fluids into gas-tight, *Tedlar* sampling bags housed within two padded 120 l external barrels (Bjorklund and McCarthy, 2004; Johnson et al., 2006). Prior to deployment, all components of the sampler that come into contact with fluids (*Tedlar* sample bags and Teflon® tubing) are acid-cleaned and rinsed with 18.2 MΩ Milli-Q water. Only samples from fully intact (undamaged) gas-tight *Tedlar* bags are reported. The shipboard crew of the ROV Jason II operated the “manual” pump controls on the sampler, and monitored fluid temperatures.

Fluid temperatures were measured via a customized temperature probe fitted to the ROV Jason II submersible, capable of measuring temperatures ranging from –5 to 50 °C. The temperature probe used in this study was calibrated in water of different temperatures against an Ultra High Accuracy Omega HH-41 calibration thermometer to an accuracy of ±1 °C to assure that the probe worked across the range of temperatures expected at LT diffuse sites.

Because common methods used for sampling hydrothermal fluids (e.g., placing a needle or inverted funnel into a stream of venting fluid) may entrain background seawater, ancillary inorganic measurements (typically Mg concentration) are often made to constrain the “purity” of sampled fluids (e.g., Massoth et al., 1989; Sansone et al., 1998). For on-axis sites, LT fluids are often interpreted to comprise a mixture of a higher-temperature endmember that represents the true crustal fluid, and low-temperature bottom water that comprises a component of secondary recharge (e.g., Edmond et al., 1979; Butterfield et al., 2004). Thus it can be challenging to resolve

the amount of bottom water that was present originally in LT on-axis fluids from that entrained during sampling. In contrast, there has never been an evidence for natural entrainment of a bottom-water endmember at Baby Bare outcrop or near Site 1026, where ridge-flank fluids are relatively isolated in basement and there is little opportunity for secondary recharge (e.g., Mottl et al., 1998; Elderfield et al., 1999; Wheat et al., 2004). Thus the appearance of a bottom-water endmember in ridge-flank fluids sampled from these sites would likely indicate mixing during sampling.

All fluids analyzed in the present study were collected with a customized sampler system designed specifically to minimize seawater contamination, even when sampling from diffuse flow environments, using very slow intake rates that were carefully adjusted so that the sample temperature matched that of the source fluid (e.g. Bjorklund and McCarthy, 2004; Johnson et al., 2006). At Baby Bare, custom Teflon® female attachments were machined to fit tightly to the metal sample probe and connected directly to a Teflon® sampling tube. At Hole 1026B, because warm fluids were vigorously venting from the re-entry cone, samples were taken by inserting a weighted Teflon® tube several meters into the re-entry cone.

We assess the possible extent of bottom-water contamination in these samples using coupled carbon isotope ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) and DIC data, as well as by comparison to previously published inorganic composition data for other samples taken on our cruises from the same fluids. Unfortunately, Mg concentrations were not directly measured in the samples on which we made our C isotopic measurements. While ancillary inorganic data can be helpful in resolving the extent of fluid mixing, the carbon isotopic values we report can also supply similar information. $\Delta^{14}\text{C}$ data in particular provides ≥ 100 -fold greater sensitivity to seawater admixture relative to Mg concentration, the most common tracer used to assess potential bottom-water contamination, based on endmember fluid compositions (0 to $-1000\text{‰} \pm 5\text{‰}$ vs. 0 to 50 ± 1 mmol kg^{-1} , respectively). Mg data was generated for a subset of ridge-flank fluid samples collected from these sources during the same dive program as those reported herein (Lang et al., 2006 and references therein); these data show that the fluids we sampled from these sites are essentially unmodified by bottom-water contamination.

Once on deck, fluid sub-samples were immediately taken from the barrel sampler via a peristaltic pump and acid-cleaned Teflon® tubing and collected into 500 ml Biological Oxygen Demand (BOD) bottles using common DIC (^{14}C -free) collection protocols (Kroopnick, 1985; McNichol and Druffel, 1992). CO_2 loss due to outgassing was minimized as a result of: 1) the very large sample volume collected, 2) the immediate sampling of the fluid once on deck, and 3) the low volatility of CO_2 within these LT fluids. Bottles were poisoned with 200 μl concentrated HgCl_2 as a preservative. *Apezion M* grease was applied to glass BOD bottle stoppers to create an airtight seal, in order to assure minimal atmospheric CO_2 interaction with the sample during storage. Samples were sealed and stored for several months at room temperature prior to carbon isotopic analysis.

2.3. Sample analyses

The isolation of DIC from crustal fluid samples was performed by vacuum line extraction, following methods established for the extraction of ΣCO_2 from seawater (McNichol et al., 1994). Fluid samples were first transferred into 250 ml amber septa bottles in a glove box under N_2 . Stripping, purification and graphitization of DIC from sample fluids was performed on a dedicated CO_2 stripping line at the Center for Accelerator Mass Spectrometry (CAMS) in Lawrence Livermore National Labs (LLNL). Briefly, samples were acidified to pH ~ 1 , using 3 ml 85% H_3PO_4 , and stripped using high-purity N_2 at 6 l min^{-1} for 20–30 min. DIC was then condensed and purified into calibrated quartz traps, and total CO_2 recovery (μmol) was measured manometrically. The sample was subsequently split for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ analyses. $\delta^{13}\text{C}$ ($\pm 0.05\text{‰}$) was determined with an overall analytical error of $\pm 0.2\text{‰}$ via standard gas ion source stable isotope ratio mass spectrometer at the University of California-Davis, Department of Geological Sciences. CO_2 splits for radiocarbon were graphitized using standard procedures at LLNL (Vogel et al., 1987). $\Delta^{14}\text{C}$ was measured via accelerator mass spectrometry at CAMS and is reported in accordance with conventions set forth by Stuiver and Polach (1977) using the Libby half-life of 5568 yr. Results are presented with reference to the absolute international standard activity (AISA). Reported values are given after subtracting sample preparation backgrounds based

on a ^{14}C -free calcite standard and have been corrected for isotopic fractionation of $\delta^{13}\text{C}$. Isotopic results are reported as Fraction Modern (FM), $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and conventional radiocarbon age (ybp). Results are reported in standard per mil (‰) notation and for $\delta^{13}\text{C}$, relative to V-PDB.

3. Results and discussion

3.1. On-axis low-temperature diffuse vents

Fluid temperatures from on-axis diffuse vents West Grotto, South Milli-Q, and Hulk were measured at 28.0 °C, 29.0 °C, and 21.7 °C, respectively. Corresponding DIC concentrations were 5.51, 5.42 and 3.13 mmol kg^{-1} for the same sites. Fluid temperatures are much lower than those measured in adjacent HT vent fluids ($>300\text{ °C}$), but are typical of many diffuse vents on the MEF (Massoth et al., 1989; Seewald et al., 2003; Huber et al., 2003; Lang et al., 2006). Low temperatures in diffuse vents could result from either extensive dilution of HT fluids with recently entrained bottom seawater (1.8 °C), extensive cooling of formerly HT fluid during circulation, or advective mixing of different fluid sources. Previous geochemical measurements on HT on-axis vent fluids from the JDFR suggest that LT vent fluids are mainly mixtures of HT fluids with entrained bottom seawater (Edmond et al., 1979; Butterfield et al., 2004). Our measured background seawater DIC concentration ($\sim 2.6\text{ mmol kg}^{-1}$) aligns closely with previously-reported values for the NE

Table 1
Summary of geochemical data from hydrothermal fluids

Sample ID	Site name	Latitude	Longitude	Fluid Temp °C	DIC (mmol/kg)	CAMS#	$\delta^{13}\text{C}$	\pm	$\Delta^{14}\text{C}$	\pm	Fraction Modern	\pm	^{14}C Age	\pm
<i>Ridge-flank fluid data</i>														
1026B-1	ODP Hole 1026B	47.7627N	127.7592W	62.5	0.57	105092	-7.27	0.05	-805.1	0.7	0.1949	0.0007	13135	35
1026B-2	ODP Hole 1026B	47.7627N	127.7592W	62.5	0.53	105093	-5.84	0.05	-798.8	0.9	0.2012	0.0009	12880	35
BBP3	Baby Bare probe 3	47.7113N	127.7864W	18.0	0.20	105137	-9.73	0.05	-766.7	1.0	0.2333	0.0010	11690	35
BBP4	Baby Bare probe 4	47.7100N	127.7860W	19.6	0.21	105091	-9.30	0.05	-778.1	0.9	0.2219	0.0009	12095	35
ATL SW-1	2540 m CTD cast	47.7000N	127.6300W	1.8	2.60	107200	-1.30	0.05	-250.7	2.8	0.7542	0.0028	2265	30
ATL SW-2	2540 m CTD cast	47.7000N	127.6300W	1.8	2.63	107204	-1.50	0.05	-254.6	2.7	0.7503	0.0027	2305	30
<i>On-axis low-temperature fluid data</i>														
W. Grotto	West Grotto diffuse	47.9494N	129.0986W	28.0	5.51	107203	-5.38	0.05	-790.8	0.9	0.2106	0.0009	12515	35
S. Milli-Q	South Milli-Q diffuse	47.9471N	129.0988W	29.0	5.42	107201	-4.93	0.05	-696.3	1.2	0.3056	0.0012	9520	35
Hulk	Hulk diffuse	47.9479N	129.1020W	21.7	3.13	107202	-2.55	0.05	-431.4	2.1	0.5723	0.0021	4485	30

Site names for on-axis diffuse vents refer to established study locations on the MEF of the JDFR. Latitude and Longitude reflect ship location at time of sampling, and thus are approximations of diffuse vent locations. Radiocarbon and manometric data are reported using conventions of the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Lab (LLNL). Stable carbon ($\delta^{13}\text{C}$) values determined at UC Davis (see Methods) are reported with an overall analytical precision of $\pm 0.2\text{‰}$ relative to V-PDB.

Cascadia Basin (WOCE transect PR06, station #4: DIC = 2.58 mmol kg⁻¹, depth = 1290 m). LT vent DIC concentrations are thus consistent with a major component of CO₂-enriched HT fluid (reported on the Endeavour segment to contain 11.6 to 110.6 mmol kg⁻¹, Lilley et al., 1993; Proskurowski et al., 2004) mixed with background seawater. For DIC concentrations we observe at West Grotto and South Milli-Q sites (~5.5 mmol kg⁻¹), two-endmember mixing with seawater would indicate that these diffuse vents contain 3 to 30% HT fluid, depending on concentration of the HT source.

Carbon isotopic measurements represent more detailed indicators for DIC source and removal processes. A wide range of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ isotopic values were observed in the on-axis LT fluids (Table 1), but all were significantly depleted relative to bottom seawater in the region ($\Delta^{14}\text{C} \sim -250\text{‰}$, $\delta^{13}\text{C} \sim -1.4\text{‰}$). We note that our observed bottom seawater isotopic values are also very consistent with those previously reported for the deep North East Pacific Ocean (WOCE P17N transect, station 68: $\Delta^{14}\text{C} = -246.5\text{‰}$, $\delta^{13}\text{C} = -0.54\text{‰}$, depth = 2020 m). West Grotto, South Milli-Q, and Hulk fluids had $\Delta^{14}\text{C}$ values of -790.6‰ , -696.3‰ and -431.4‰ respectively, corresponding to apparent radiocarbon “ages” of 12.5, 9.5, and 4.5 kyr. These apparent ages are much older than would be expected on the basis of residence time estimates from radiochemical tracers and analyses of heat budgets from hydrothermal plumes and associated hydrothermal reservoir geometries (Kadko and Moore, 1988; Kadko et al., 1990; Fisher, 2003), on the order of 1–10 yr, but are readily explained by fluid mixing within a large crustal aquifer containing older magmatic and younger seawater fluid endmembers.

While the $\delta^{13}\text{C}$ of Hulk (-2.55‰) is close to average bottom seawater (-1.40‰), the $\delta^{13}\text{C}$ of West Grotto and South Milli-Q (-5.38‰ and -4.93‰ , respectively) are closer to estimates of magmatic CO₂ on the Endeavour ridge (-4.8‰ to -9.3‰ , Blank et al., 1993; Proskurowski et al., 2004). If these LT fluids are conservative mixtures of seawater and HT fluids, then the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of all sites would be expected to fall close to a linear mixing line, with exact positions indicating the relative contributions of magmatic and oceanic DIC sources. However, if other significant sources or sinks were present at any site, those values would be expected to plot away from the seawater-HT fluid continuum.

We plotted an ideal mixing line between the seawater FM, $\delta^{13}\text{C}$ and the corresponding literature values for JDFR magmatic CO₂ (Fig. 2A). For HT fluid CO₂ $\delta^{13}\text{C}$ endmember, we chose the mid-point (-7.05‰) of the reported range in values (-4.8‰ to -9.3‰) from CO₂ vesicles within MEF basalts (Blank et al., 1993). The observed $\delta^{13}\text{C}$ vs. FM values for West Grotto, South Milli-Q, and Hulk all plot on this line within experimental error ($R^2 = 0.994$; Fig. 2A). Any residual seawater bicarbonate in our samples would slightly alter our modeled results toward the seawater endmember. While the sample group is small, the consistency of the relationship is strong, suggesting that inorganic carbon in West Grotto, South Milli-Q, and Hulk fluids is composed of 28%, 40% and 76% seawater DIC, respectively. We note that data from HT sites on the JDFR indicates a small and variable amount of seawater bicarbonate that may remain in some HT fluids (Proskurowski et al., 2004). The effects of residual seawater bicarbonate would be expected to vary strongly based on fluid composition

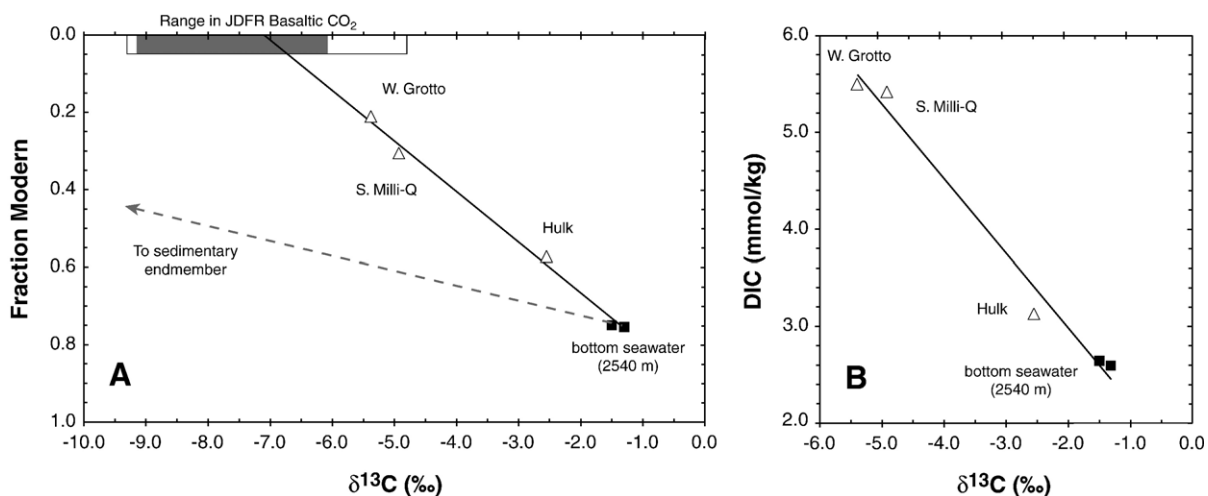


Fig. 2. On-axis low-temperature vent mixing plots. A) Solid line indicates the ideal mixing line between projected DIC isotopic endmembers. Open triangles are on-axis diffuse vent values; dark squares are measured background seawater values. For the magmatic CO₂ source, the open rectangle represents total range in $\delta^{13}\text{C}$ of CO₂ within basalt vesicles of the only the Endeavour ridge (Blank et al., 1993). Interior shaded box represents reported range in $\delta^{13}\text{C}$ of CO₂ within basalt vesicles of the only the Endeavour ridge (Blank et al., 1993). The plotted mixing line originates at the mid-point of reported total range and indicates a regression analysis ($R^2 = 0.994$). Grey dashed line represents an alternate mixing line toward a sedimentary endmember (FM = 0.102, $\delta^{13}\text{C} = -17.8\text{‰}$) using reported mean values from Proskurowski et al. (2004). B) DIC concentration vs. $\delta^{13}\text{C}$ for on-axis LT fluids. Symbols are as in part A. The solid line indicates a regression analysis ($R^2 = 0.984$).

and are difficult to precisely estimate (Proskurowski et al., 2004), and we have not included such a correction in our data. In addition, despite the careful sampling procedures to exclude ambient seawater (see Methods) it is possible that small amounts were entrained. Together these considerations suggest that these are maximum estimates of percent seawater in pure fluids. However, small amounts of additional seawater would not obscure the influence of other major DIC sources, if present. Extrapolating to the “purely magmatic” endmember (FM=0) would predict the magmatic DIC source for all sample sites to be $\delta^{13}\text{C} = -7.0\%$. This is in excellent agreement with reported JDFR basalt CO_2 vesicle $\delta^{13}\text{C}$ values (Blank et al., 1993).

A similar relationship between seawater DIC concentration and $\delta^{13}\text{C}$ also yields a strong relationship ($R^2 = 0.984$; Fig. 2B), suggesting that related processes govern DIC isotopic composition and concentration. Collectively, these data are consistent with binary mixing, where increasing DIC concentration from HT fluids varies directly with progressive $\delta^{13}\text{C}$ depletion. Using our estimate of magmatic DIC $\delta^{13}\text{C}$ (-7.0%), this relationship would predict a pure HT fluid DIC concentration of $\sim 6.8 \text{ mmol kg}^{-1}$ and yields similar results for West Grotto, South Milli-Q, and Hulk fluids, with estimated seawater contributions of 30%, 32%, and 87% respectively. Given the small range for seawater and “pure” hydrothermal DIC endmember values (range $\sim 4 \pm 0.03 \text{ mmol kg}^{-1}$), mixing estimates based on DIC concentration alone are less sensitive than those based on radiocarbon determinations, which have a much greater sensitivity (range $\sim 750\% \pm 1.5\%$). An independent mixing estimate (Lang et al., 2006), that used temperature constraints of bacteria sampled from fluids in this region (Holden et al., 1998), suggested a 20:80 mix of HT fluid and bottom seawater for JDFR LT fluids. These proportions of HT fluid and seawater result in $\Delta^{14}\text{C}$ “ages” ($\sim 10,000 \text{ ybp}$) and DIC concentrations ($\sim 6.4 \text{ mmol kg}^{-1}$) very close to those reported here.

Previous inorganic measurements have indicated some sedimentary influence on the composition of HT fluids at MEF (Lilley et al., 1993; You et al., 1994; Seewald et al., 2003; Proskurowski et al., 2004). Although our data do not indicate the presence of a substantial sedimentary source (assumed sedimentary $\delta^{13}\text{C} \sim -17.8\%$, FM ~ 0.10 ; Proskurowski et al., 2004 and references therein), neither do they preclude a minor contribution of sedimentary DIC (Fig. 2A). The range in the magmatic CO_2 $\delta^{13}\text{C}$ estimates and associated analysis error could easily obscure a minor sedimentary DIC contribution. Analysis of a previous sample set suggested that MEF HT vents contained $<10\%$ sedimentary DIC (e.g. Proskurowski et al., 2004). A contribution of this magnitude would shift our estimated FM endmember by less than 0.03, very close to our overall analytical error of $\pm 1.5\%$, or FM ± 0.0015 . The reaction zone below the diffuse vents sampled for this study is thought to be distinct from that for which sediment sources were inferred during earlier studies. However, the consistent relationship between DIC concentrations and $\delta^{13}\text{C}$ isotopic composition suggests that HT fluids feeding these diffuse sites are in fact similar to those sampled in previous studies.

3.2. Low-temperature ridge-flank fluids

Temperatures previously measured in fluids flowing from ODP Hole 1026B are $62\text{--}65 \text{ }^\circ\text{C}$, consistent with values inferred within surrounding shallow basement (Davis et al., 1992; 1997; Fisher et al., 1997; Hutnak et al., 2006). Measured temperatures of the geochemically similar fluids exiting Baby Bare probes 3 and 4 were $18.0 \text{ }^\circ\text{C}$ and $19.6 \text{ }^\circ\text{C}$, respectively (Lang et al., 2006). Baby Bare fluids are most likely cooler than fluids in basement rocks because they cool as they rise towards the edifice summit (e.g., Wheat et al., 2004). In contrast to the on-axis LT vents discussed in previous sections, chemical properties of ridge-flank fluids are most consistent with water–rock reaction at low to moderate temperatures ($5\text{--}70 \text{ }^\circ\text{C}$), rather than mixing of bottom seawater and HT hydrothermal fluid (e.g., Mottl et al., 1998; Elderfield et al., 1999; Wheat et al., 2004).

Two separate samples taken from different sites at Baby Bare outcrop (LEXEN project, probes 3 and 4), had $\Delta^{14}\text{C}$ values of -766.7% and -778.1% , and $\delta^{13}\text{C}$ values of -9.73% and -9.30% , respectively. Two sample duplicates from Hole 1026B had $\Delta^{14}\text{C}$ values of -805.1% and -798.8% , with corresponding $\delta^{13}\text{C}$ values of -7.27% and -5.84% . These measurements represent the first $\delta^{13}\text{C}$ DIC data reported for Hole 1026B and the first $\Delta^{14}\text{C}$ data reported for Baby Bare seamount. Due to the strong agreement in Hole 1026B $\Delta^{14}\text{C}$ values and the overall analytical precision of $\delta^{13}\text{C}$ (2540 m CTD cast duplicates; $\pm 0.2\%$), we believe that the observed range in Hole 1026B $\delta^{13}\text{C}$ values is due to an analytical error. Nevertheless, because we have no firm basis to exclude either value, we use the average of the Hole 1026B $\delta^{13}\text{C}$ values (-6.56%) in interpreting the new data.

The general agreement in both radiocarbon and stable carbon DIC between Baby Bare outcrop and Hole 1026B fluids suggests that basement fluid carbon chemistry in this region of the JDFR flank is determined by similar DIC sources, cycling, and removal processes. It is not surprising that the isotopic values of crustal fluids from these two locations are similar; the sites are only 6.3 km apart, and fluids are thought to have originated in the same crustal reservoir. However, radiocarbon values from Site 1026B (-805.1% and -798.8%) are substantially depleted relative to those reported previously from this site (-413.8% to -419.6% , yielding ^{14}C ages of 4.3 and 4.4 kyr; Elderfield et al., 1999). These previously-reported 1026B $\Delta^{14}\text{C}$ values also departed significantly from nearby measurements (Elderfield et al., 1999).

One possible explanation for the offset between the newer and older measurements may relate to the relatively short period of time that passed between the drilling of Hole 1026B and earlier sampling. Hole 1026B required several days to drill, during which time a large volume of surface seawater was pumped into the underlying basement in order to lubricate seafloor drill bits and to flush fragments of upper oceanic crust from the hole. Additional basement operations, including hole cleaning, stabilization, and hydrogeologic experiments, resulted in additional pumping of cold seawater into the open hole. After drilling, the resulting thermal imbalance caused the hole to

actively entrain deep seawater for an additional 10–14 days, until the formation could reestablish positive pressure. Any of this surface or deep seawater DIC remaining in the formation would act to increase fluid ^{14}C content (and thus decrease apparent ^{14}C ages) relative to pure crustal fluids. Fluids then vented freely for 10–14 days before samples were collected using an open hole fluid sampler (Davis et al., 1997; Fisher et al., 1997; Elderfield et al., 1999). However, due to the highly porous and heterogeneous nature of young oceanic crust, a longer period of time may have been required to fully purge seawater introduced during drilling and entrained during the subsequent several weeks. Hydrological models based on push–pull tests have suggested that a venting time of months to years may be needed to fully expel fluids introduced during drilling and other basement operations (e.g., Lessoff and Konikow, 1997). A comparison of stable DIC isotopic signatures could help elucidate this disparity in DIC ages, but no prior $\delta^{13}\text{C}$ values for Hole 1026B fluids have been published.

Data produced with DI^{14}C samples collected as part of the present study were taken with customized tools designed for this purpose, after Hole 1026B had been venting freely for over 3 years; these are almost certainly more pristine than samples collected just a few weeks after drilling. At the same time, independent sampling in the years since drilling suggests that the major ion chemistry (Mg, Li, Si, etc.) of Hole 1026B has not changed appreciably (Wheat et al., 2004). This decade-long stability of major ion chemistry would seemingly preclude two- or three-endmember mixing (pure basement fluid plus surface and/or deep seawater injected/entrained during drilling) suggested by new DI^{14}C isotopic data. Such an offset in DIC isotopic character and major ion chemistry could result if major ions from introduced drilling sources reacted quickly with warm basement rock, whereas ^{14}C -depleted pure basement fluid was diluted by DI^{14}C -enriched seawater. However, given the high fluid temperatures and long times required for such reactions to occur (e.g. Bischoff and Dickson, 1975), this mechanism seems unlikely. Additional time-series sampling of Hole 1026B, and other basement holes drilled into over-pressured oceanic crust, may help to resolve this conundrum.

3.2.1. JDFR flank circulation

Fluid cycling within upper oceanic crust has an important impact on crustal hydrothermal alteration, carbonate vein precipitation, and conditions in which a sub-surface microbial biosphere may reside. Our average $\Delta^{14}\text{C}$ values (-787‰) are $\sim 150\text{‰}$ depleted relative to on-axis values (average $\sim -639\text{‰}$). This is consistent with a growing body of work indicating that fluids found in many ridge-flank settings are both chemically distinct and hydrologically isolated from on-axis sources (Lilley et al., 1993; Fisher et al., 2003a). Recent work has refined this conclusion, suggesting that ridge-flank circulation occurs as a continuum of isolated circulation cells, with flow paths influenced strongly by the structural fabric of the crust, which includes a ridge-parallel bias (e.g., Macdonald et al., 1996; Wheat and Mottl, 2000; Fisher et al., 2003a; Hutnak et al., 2006).

The offset in $\Delta^{14}\text{C}$ DIC values observed on this ridge-flank can be used to estimate fluid flow rates and direction. When converted to ^{14}C “ages”, Hole 1026B fluids (13,010 ybp) are ~ 1110 yr older than those from Baby Bare outcrop (11,890 ybp). Using this difference and the distance by which these outcrops are separated (6.3 km), a simple “plug flow” model suggests a lateral fluid flow rate in upper basement of 5.7 m yr^{-1} , in general agreement with plug-flow estimates from this and similar settings (e.g., Stein and Fisher, 2003). The age offset in our data is also consistent with a hypothesized south to north trend from Baby Bare to Hole 1026B, with the original recharge source being Grizzly Bare outcrop, 52 km to the south (Wheat and Mottl, 2000; Fisher et al., 2003a). However, the plug-flow estimate is considerably slower than estimates based on diffusive-loss flow models, which suggest that due to the heterogeneous nature of upper basement, actual flow rates could be 10 to 1000 times greater (Sudicky and Frind, 1981; Sanford, 1997; Bethke and Johnson, 2002; Stein and Fisher, 2003). If diffusive-loss models prove more representative of ridge-flank hydrothermal circulation, this could have vast implications for how we perceive vent processes, which influence fluid chemistry and the ecology of a sub-surface microbial biosphere.

3.2.2. Ridge-flank DIC removal

DIC concentrations in samples collected from Baby Bare outcrop probes 3 and 4 and ODP Hole 1026B had concentrations of 0.20, 0.21 and $0.55 \text{ mmol kg}^{-1}$, respectively, significantly depleted relative to bottom seawater (2.60 to $2.63 \text{ mmol kg}^{-1}$). Since these fluids originate from seawater in off-axis recharge zones, these concentrations indicate that $\sim 80\%$ inorganic carbon is removed during circulation. Losses of CO_2 in hydrothermal fluids have been widely observed, and are commonly attributed to several mechanisms. Within high-temperature systems ($>300 \text{ °C}$) for example, Fischer–Tropsch hydrocarbon synthesis has been proposed as a mechanism to remove DIC (Horita and Berndt, 1999; McCollum et al., 1999). However, in low-temperature ridge-flank systems ($<100 \text{ °C}$), chemical data, the presence of carbonate veins in ODP cores, and thermodynamic calculations have all indicated that the precipitation of calcite and aragonite directly within fluid flow paths is likely the primary pathway for CO_2 removal (Mottl and Wheat, 1994; Brady and Gislason, 1997; Sansone et al., 1998; Alt and Teagle, 1999). Analysis of basement samples recovered from the ODP Leg 168 transect of sites, including Site 1026, illustrates the importance of carbonate deposition in basement of this ridge-flank (Hunter et al., 1999; Yatabe et al., 2000; Coggon et al., 2004). Recent evidence for diverse microbial communities in off-axis crust also suggests that CO_2 uptake via chemosynthesis could be an additional sink of unknown magnitude (Cowen, 2004 and references therein; Huber et al., 2006).

While consistent with previous evidence for major CO_2 depletion in ridge-flank fluids, our DIC concentrations for Baby Bare outcrop are lower than previously calculated for this same site ($0.85 \text{ mmol kg}^{-1}$, Sansone et al., 1998). In addition, earlier samples exhibited $\delta^{13}\text{C}$ values close to

seawater (−0.4 to −0.7‰), invariant with DIC concentration (i.e. seawater entrainment), whereas our samples exhibit strongly depleted $\delta^{13}\text{C}$ signatures (−9‰). One possible explanation for this difference is that fluid sources have changed between 1995 and 2003. Hydrothermal systems are dynamic and since the exact locations of sampling were different and substantial time had elapsed, it is possible that different source fluids were sampled.

An alternative explanation is that these chemical differences result from different methods of fluid collection and DIC estimation. In the 1995 data set of Sansone et al., fluids were collected with inverted funnels and gas-tight samplers (e.g. Von Domm et al., 1985; Massoth et al., 1989) from diffuse “seeps” or springs located on top of the outcrop, and DIC was measured in mixed seawater/fluid samples. The Baby Bare endmember concentration was estimated mathematically, based on compositional differences across the sample set. In contrast, our measurements were made directly in samples obtained using specialized watertight, Teflon® attachments on titanium probes (see Methods) emplaced 1.5 and 3 m directly into the rock outcrop (Johnson and LEXEN, 2003; Johnson et al., 2006). Other samples taken from these probes exhibited very low Mg concentrations, indicative of pure hydrothermal fluid with little or no seawater entrainment during sampling (Lang et al., 2006).

Our lower DIC observations would have an important impact on existing model predictions of ridge-flank carbon sequestration. Estimates for global ridge-flank CO_2 sequestration can be calculated using the relationship previously described by Sansone et al. (1998):

$$S_c = (H_g f r_c) / (cT) \quad (1)$$

where S_c = global carbon sequestration projected for ridge-flank environments, H_g = global heat flux (estimated by Mottl and Wheat, 1994 for global ridge-flanks at 8.6 ± 1.6 TW), f = the percent of global ridge-flank heat flux associated with given fluid temperatures, r_c = the difference between DIC concentrations of crustal fluids vs. bottom seawater (mol kg^{-1}), c = the specific heat of seawater ($955 \text{ cal } ^\circ\text{C}^{-1} \text{ kg}^{-1}$), and T = the difference in temperature between observed fluids and bottom seawater.

Using fluid temperature and DIC values reported in Table 1, this model for carbon sequestration yields two potential carbon removal fluxes. Using Hole 1026B fluid conditions (DIC = $0.55 \text{ mmol kg}^{-1}$, $62.5 \text{ }^\circ\text{C}$) and assuming $f = 0.1$ of H_g (Mottl and Wheat, 1994; fraction of global $\geq 25 \text{ }^\circ\text{C}$ venting), ridge-flank environments sequester a minimum of $1.6 \times 10^{11} \text{ mol C yr}^{-1}$. This result is consistent with estimates made by Sansone et al. (1998). In contrast, using Baby Bare outcrop fluid conditions (DIC = $0.20 \text{ mmol kg}^{-1}$, $18.8 \text{ }^\circ\text{C}$) and assuming $f = 0.8$ of H_g (Mottl and Wheat, 1994; fraction of global $\leq 25 \text{ }^\circ\text{C}$ venting), the sequestration rate is $57 \times 10^{11} \text{ mol C yr}^{-1}$. This result is roughly double the maximum hypothesized CO_2 sequestration rate estimated by Sansone et al., 1998 ($25 \times 10^{11} \text{ mol C yr}^{-1}$), but is in agreement with other sequestration rates for ridge-flank environments derived from observed carbonate abundance within

crustal cores by Staudigel et al. (1989) of $3.7 \times 10^{12} \text{ mol C yr}^{-1}$, and Alt and Teagle (1999) of $1.5\text{--}2.4 \times 10^{12} \text{ mol C yr}^{-1}$.

3.2.3. Ridge-flank DIC isotopic fractionation

DIC $\delta^{13}\text{C}$ signatures obtained from Baby Bare outcrop and Hole 1026B indicate that ridge-flank DIC removal processes strongly fractionate carbon isotopes. DIC remaining in both fluid sources is significantly depleted in $\delta^{13}\text{C}$ (−6.5‰ to −9‰) with respect to the original source seawater (−1.5‰). This offset indicates that the dominant processes removing DIC from these fluids preferentially enriches the heavier isotope (^{13}C), leaving the residual fluid DIC progressively depleted in $\delta^{13}\text{C}$. This is consistent with CO_2 sequestration within ridge-flanks via carbonate vein precipitation, which has been experimentally determined to preferentially remove ^{13}C from solution (e.g., Turner, 1982; Romanek et al., 1992). However, in order to reach our observed $\delta^{13}\text{C}$ ridge-flank fluid values, Rayleigh fractionation of seawater DIC during calcium carbonate precipitation alone would require >99.9% removal of all seawater DIC (Fig. 3). While several sources of depleted $\delta^{13}\text{C}$ exist within ridge-flank environments (including CO_2 from basaltic vesicles, magmatic CO_2 , sedimentary carbon, and biological respiration of organic matter), we believe the most likely secondary source of depleted $\delta^{13}\text{C}$ is CO_2 leached from basalt via water–rock interaction at elevated temperatures. This is consistent with previous observations of low Baby Bare alkalinity, which indicate that calcium carbonate precipitation is likely accompanied by basalt–seawater interactions that remove Mg^{2+} (Bischoff and Dickson, 1975; Sansone et al., 1998).

A combination of quantitative DIC removal with small inputs of ^{13}C -depleted CO_2 from basalt vesicles could explain our DIC isotopic values. By comparing $\delta^{13}\text{C}$ vs. DIC concentration values directly between bottom seawater and those of Baby Bare and Hole 1026B, our results yield a strong relationship ($R^2 = 0.998$, Fig. 3). This model combines the effects of open Rayleigh fractionation due to calcium carbonate precipitation with the continuous addition of CO_2 leached from basaltic vesicles. We use the average MEF CO_2 vesicle concentration (4.2 mmol/kg) and maximum depleted $\delta^{13}\text{C}$ value (−9.3‰) observed previously (Blank et al., 1993). Using this combined approach we determine that in order to attain our fluid DIC and isotopic values, Baby Bare and Hole 1026B fluids would require a 99.8% and 92% removal of seawater DIC via calcium carbonate precipitation with a 5% and 8% addition of basalt CO_2 , respectively (Fig. 3). These data are consistent with observed isotopic fractionation associated with the precipitation of calcium carbonate at low temperatures combined with minimal inputs of CO_2 from basaltic vesicles (Turner, 1982; Romanek et al., 1992; Blank et al., 1993). Although this process mainly involves the preferential removal of both ^{14}C and ^{13}C relative to ^{12}C , our $\Delta^{14}\text{C}$ measurements include a $\delta^{13}\text{C}$ fractionation correction to account for mass dependent fractionation relative to a common measured reservoir (bottom seawater) in addition to the V-PDB standard (Stuiver and Polach, 1977).

It is also interesting to note that despite the overall northward flow indicated by $\Delta^{14}\text{C}$ data discussed above, the DIC and $\delta^{13}\text{C}$ values at the more “downstream” location (Hole 1026B) have slightly greater DIC, and less depleted

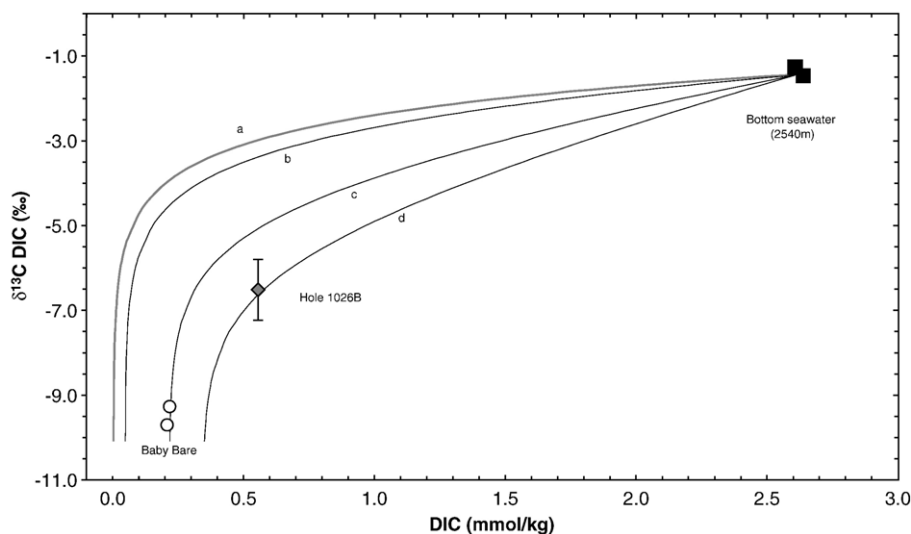


Fig. 3. DIC vs. $\delta^{13}\text{C}$ for off-axis fluids. White circles represent fluids from Baby Bare seamount, grey diamond represents Hole 1026B average value ($\delta^{13}\text{C} = -6.56 \pm 0.7\text{‰}$). Dark squares indicate background seawater values taken from a 2540 m CTD cast (see Table 1). Solid grey line (a) represents the effect of only Rayleigh fractionation of seawater DIC concentration and $\delta^{13}\text{C}$ due to calcium carbonate precipitation. Thin black lines represent the combined effect of both quantitative bicarbonate removal (Rayleigh) and the addition of b) 1%, c) 5%, and d) 8% of total measured CO_2 from basaltic vesicles (MEF Basalt $\text{CO}_{2(\text{g})} = 4.2 \text{ mmol/kg}$, $\delta^{13}\text{C} = -9.3\text{‰}$; Blank et al., 1993). Applied exponential regression analysis (not shown) to Baby Bare, Hole 1026B and seawater endmembers yielded $R^2 = 0.998$.

corresponding $\delta^{13}\text{C}$ signature vs. seawater. Recalling that $\Delta^{14}\text{C}$ values are already corrected for isotopic fractionation (see Methods), this suggests that DIC removal (and associated isotopic fractionation) is not solely controlled by the residence time of fluids within the crust, but is also influenced by details of reaction pathways and water–rock interactions, including differences in fluid temperatures. In addition, our model indicates that more CO_2 from basalt must be added to Hole 1026B fluids in order to achieve the observed isotopic and DIC signature. This would also be consistent with continual leaching of basaltic CO_2 during northward fluid flow from Baby Bare seamount to Site 1026.

4. Overview and conclusions

Fig. 4 summarizes the DIC concentrations and isotopic compositions discussed above within a schematic of fluid circulation in ridge-axis and ridge-flank regions of the JDJR. Our isotopic data supports accumulating evidence that ridge-flank fluid circulation is decoupled from on-axis fluid circulation. There has been a tendency to view crustal hydrothermal circulation patterns in cross-section, oriented perpendicular to spreading, and to assume a continuum of fluid circulation paths from the ridge-axis to ridge-flank areas, rather than to consider ridge-flank circulation to occur largely independently from the ridge and along the direction of structural strike (e.g., Elderfield et al., 1999; Fisher, 2004; Hutnak et al., 2006). Our data

support the idea that recharge and fluid cycling on ridge-flanks occurs independently of recharge and venting on ridges, and thus it may be most appropriate to consider the inorganic carbon sources, sinks, and isotopic composition of each region independently.

For LT ridge fluids, our results indicate DIC composition is governed mainly by a conservative mixing between HT fluid and seawater (Fig. 4). These appear to be the first reported DIC $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ data for LT on-axis diffuse vents. LT on-axis “seeps” host vibrant biological assemblages as well as connections to sedimentary sources, which could have important impacts on the DIC of fluids discharged to the ocean. While certainly not ruling out such processes (e.g., chemosynthetic DIC fixation is well documented in ridge organisms, Rau and Hedges, 1979; Fisher et al., 1989; Childress et al., 1993; Scott et al., 1999), our results suggest that other potential DIC sources or sinks are not large enough to greatly influence observed isotopic compositions. Because of the very large $\Delta^{14}\text{C}$ offsets between seawater, sedimentary, and magmatic DIC ($\sim 700\text{‰}$ range), $\Delta^{14}\text{C}$ in particular represents an extremely sensitive indicator for on-axis fluid carbon sources and should prove a useful companion to common chemical indices used to constrain bulk fluid mixing.

Ridge-flank environments of the JDJR are likely comprised of independent systems of LT hydrothermal

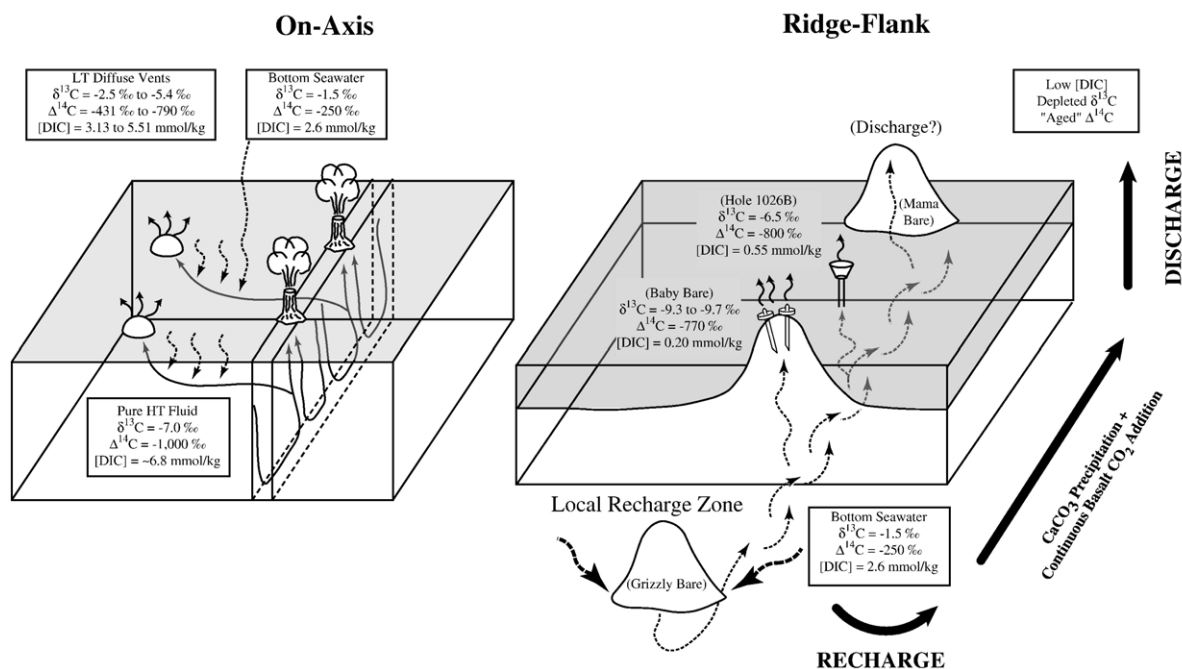


Fig. 4. JDFR circulation with DIC sources, sinks and isotope values. Cartoon depicting overall on-axis and ridge-flank area fluid circulation, major DIC endmembers, removal processes and isotopic compositions. For on-axis region, solid arrows represent venting hydrothermal fluids. Dashed arrows indicate bottom seawater entrainment. For ridge-flank, dashed arrows represent the net direction of complex fluid flow paths through the upper basement (white regions) capped by sediments (shaded regions). Thick black arrows indicate overall patterns of ocean water cycling through off-axis crust.

circulation (Fig. 4). The radiocarbon content of DIC from Hole 1026B and Baby Bare outcrop fall in a similar range, but with an apparent-age offset of 1110 ybp. This indicates that fluids at Hole 1026B have a longer residence time in the crust than those at Baby Bare outcrop, consistent with previous data suggesting South to North fluid flow, parallel to the ridge axis on this section of the JDFR (Wheat and Mottl, 2000; Fisher et al., 2003a). This represents the first direct DIC radiocarbon confirmation of ridge-parallel flow on a ridge-flank, consistent with previous thermal and chemical data suggesting that Grizzly Bare outcrop, 52 km to the south of Baby Bare outcrop, as a major recharge location (Wheat and Mottl, 2000; Fisher et al., 2003a). The observed age offset also agrees well with previous estimates of lateral fluid flow rates in basement ($1\text{--}5$ m yr^{-1} , Elderfield et al., 1999). While no DIC isotopic data has been published for other ridge-flank outcrops in this region, the trends observed suggest that fluids from these sites should have similar, but somewhat further "aged" $\Delta^{14}\text{C}$ signatures from those reported here. This hypothesis is readily testable.

Our data strongly support previous indications that ridge-flanks are major regions of inorganic carbon

sequestration, and also represent sources of DIC to the ocean having substantially altered stable and radiocarbon isotopic composition. DIC $\delta^{13}\text{C}$ signatures support abiotic carbonate precipitation as the major processes sequestering DIC on ridge-flanks. We propose this processes is accompanied by minimal additions of ^{13}C -depleted CO_2 from basalt, resulting in strongly $\delta^{13}\text{C}$ -depleted DIC vented to hydrothermally active regions. Our data suggests global CO_2 removal rates of 1.6×10^{11} mol C yr^{-1} to 5.7×10^{12} mol C yr^{-1} from ridge-flanks. While consistent with observations of carbonate abundance in crustal cores, the latter removal rate is roughly double that estimated previously (Sansone et al., 1998) and exemplifies the need to better characterize ridge-flank fluids and their role in global carbon sequestration. The overall trends we observe between DIC concentration, $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$, further suggest that specific concentration and isotopic values of vented ridge-flank DIC may be strongly dependent not only on residence time in the crust, but also on mineralogy, temperature, and other aspects of specific flow paths. More detailed measurements from both the JDFR and other ridge-flank environments are needed to constrain the effects of ridge-flank circulation on the oceanic carbon cycle over long timescales.

Acknowledgements

We acknowledge the following institutions and individuals who contributed greatly to the success of this study: Constanze Weyhenmeyer, CAMS/LLNL for their help in fluid DIC stripping and radiocarbon analysis, Paul Quay (University of Washington) and Sheila Griffin (UC Irvine) for their help in sampling protocols and donation of field sampling supplies, Tor Bjorkland for development of vent temperature measurement and *barrel sampler* elevator, Paul Johnson (Chief Scientist) and the crews of the R/V Thompson and the ROV Jason II. This manuscript greatly benefited from careful comments by Ed Peltzer, Giora Proskurowski and one anonymous reviewer. This study was funded through the support of NSF: OCE/LEXEN 0004211 (MDM), UC Office of the President (UCOP) Campus-Laboratory Collaborative research grant: “Radiocarbon and Geochemistry” (MDM, TPG), the Packard Foundation (MDM), USSSP Awards T301A7 and T301B7 (ATF), NSF OCE 0326699 and OCE 0550713 (ATF), and through the gracious support of the Friends of Long Marine Lab. Radiocarbon analyses were performed under the auspices of the U.S. Department of Energy (contract W-7405-Eng-48).

References

- Alt, J.C., 1996. Ridge flank alteration of upper ocean crust in the eastern Pacific: a synthesis of results for volcanic rocks in holes 504B and 896. *Proceedures of the Ocean Drilling Program. Scientific Results* 148, 435–452.
- Alt, J.C., 2004. Alteration of the upper oceanic crust: mineralogy, chemistry, and processes. In: Davis, E.E., Elderfield, H. (Eds.), *Hydrogeology of the Oceanic Lithosphere*. Cambridge University Press, Cambridge, UK, pp. 495–533.
- Alt, J.C., Teagle, D.A.H., 1999. The uptake of carbon during alteration of ocean crust. *Geochimica et Cosmochimica Acta* 63 (10), 1527–1535.
- Baker, E.T., Massoth, G.J., Walker, S.L., Embly, R.W., 1993. A method for quantitatively estimating diffuse and discrete hydrothermal discharge. *Earth and Planetary Science Letters* 118, 235–249.
- Bethke, C.M., Johnson, T.M., 2002. Paradox of groundwater age. *Geology* 30 (2), 107–110.
- Bischoff, J.L., Dickson, F.W., 1975. Seawater–basalt interaction at 200 degrees C and 500 bars — implications for origin of sea-floor heavy-metal deposits and regulation of seawater chemistry. *Earth and Planetary Science Letters* 25 (3), 385–397.
- Bjorklund, T.A., McCarthy, M.D., 2004. A large volume deep-ocean sampler for hydrothermal fluids. *Sea Technology* 44 (11), 49–51.
- Blank, J.G., Delaney, J.R., Desmarais, D.J., 1993. The concentration and isotopic composition of carbon in basaltic glasses from the Juan-De-Fuca Ridge, Pacific-Ocean. *Geochimica et Cosmochimica Acta* 57 (4), 875–887.
- Brady, P.V., Gislason, S.R., 1997. Seafloor weathering controls on atmospheric CO₂ and global climate. *Geochimica et Cosmochimica Acta* 57 (4), 875–887.
- Butterfield, D.A., McDuff, R.E., Mottl, M.J., Lilley, M.D., Lupton, J.E., Massoth, G.J., 1994. Gradients in the composition of hydrothermal fluids from the Endeavour segment vent field — phase separation and brine loss. *Journal of Geophysical Research* 99 (B5), 9561–9583.
- Butterfield, D.A., Lilley, M.D., Huber, J.A., Roe, K.K., Embley, R.W., Massoth, G.J., 2004. Mixing, reaction and microbial activity in the sub-seafloor revealed by temporal and spatial variation in diffuse flow vents at axial volcano. In: Wilcock, W.S.D., Kelley, D.S., Baross, J.A., DeLong, E., Cary, C. (Eds.), *The Sub-seafloor Biosphere at Mid-ocean Ridges*. Geophys. Monogr. AGU, pp. 269–289.
- Childress, J.J., Lee, R.W., Sanders, N.K., Felbeck, H., Oros, D.R., Toulmond, A., Desbruyeres, D., Kennicutt, M.C., Brooks, J., 1993. Inorganic carbon uptake in hydrothermal vent tubeworms facilitated by high environmental CO₂. *Nature* 362, 147–149.
- Coggon, R.M., Teagle, D.A.H., Cooper, M.J., Vanko, D.A., 2004. Linking basement carbonate vein compositions to porewater geochemistry across the eastern flank of the Juan de Fuca Ridge, ODP Leg 168. *Earth and Planetary Science Letters* 219 (1–2), 111–128.
- Cowen, J.P., 2004. The microbial biosphere of sediment-buried oceanic basement. *Research in Microbiology* 155, 497–506.
- Davis, E.E., Chapman, D.S., Mottl, M.J., Bentkowski, W.J., Dadey, K., Forster, C., Harris, R., Nagihara, S., Rohr, K., Wheat, G., Whiticar, M., 1992. FlankFlux: an experiment to study the nature of hydrothermal circulation in young oceanic crust. *Canadian Journal of Earth Sciences* 29 (5), 925–952.
- Davis, E.E., Fisher, A.T., Firth, J.V., et al., 1997. *Proc. ODP, Init. Repts*, 168. Ocean Drilling Program, College Station, TX.
- Delaney, J.R., Robigou, V., McDuff, R.E., Tivey, M.K., 1992. Geology of a vigorous hydrothermal system on the Endeavour Segment, Juan de Fuca Ridge. *Journal of Geophysical Research* 97, 19663–19682.
- Edmond, J.M., Measures, C., McDuff, R.E., Chan, L.H., Collier, R., Grant, B., Gordon, L.I., Corliss, J.B., 1979. Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean — Galapagos data. *Earth and Planetary Science Letters* 46 (1), 1–18.
- Elderfield, H., Schultz, A., 1996. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annual Review of Earth and Planetary Sciences* 24, 191–224.
- Elderfield, H., Wheat, C.G., Mottl, M.J., Monnin, C., Spiro, B., 1999. Fluid and geochemical transport through oceanic crust: a transect across the eastern flank of the Juan de Fuca Ridge. *Earth and Planetary Science Letters* 172 (1–2), 151–165.
- Fisher, A.T., 2003. Geophysical constraints on hydrothermal circulation: observations and models. In: Halbach, P., Tunnicliffe, V., Hein, J. (Eds.), *Energy and Mass Transfer in Submarine Hydrothermal Systems*. Dahlem University Press, Berlin, Germany.
- Fisher, A.T., 2004. Rates and patterns of fluid circulation. In: Davis, E.E., Elderfield, H. (Eds.), *Hydrogeology of the Oceanic Lithosphere*. Cambridge University Press, Cambridge, UK, pp. 339–377.
- Fisher, C.R., Childress, J.J., Minnich, E., 1989. Autotrophic carbon fixation by the chemoautotrophic symbionts of riftia-pachyptila. *Biological Bulletin* 177 (3), 372–385.
- Fisher, C.R., Kennicutt, M.C., Brooks, J.M., 1990. Stable carbon isotopic evidence for carbon limitation in hydrothermal vent vestimentiferans. *Science* 247, 1094–1096.
- Fisher, A.T., Becker, K., Davis, E.E., 1997. The permeability of young oceanic crust east of Juan de Fuca Ridge determined using borehole thermal measurements. *Geophysical Research Letters* 24 (11), 1311–1314.
- Fisher, A.T., Davis, E.E., Hutnak, M., Spiess, V., Zuhlsdorff, L., Cherkaoui, A., Christiansen, L., Edwards, K., Macdonald, R., Villinger, H., Mottl, M.J., Wheat, C.G., Becker, K., 2003a.

- Hydrothermal recharge and discharge across 50 km guided by seamounts on a young ridge flank. *Nature* 421 (6923), 618–621.
- Fisher, A.T., Stien, C.A., Harris, R.N., Wang, K., Silver, E.A., Pfender, M., Hutnak, M., Cherkaoui, A., Bodzin, R., Villinger, H., 2003b. Abrupt thermal transition reveals hydrothermal boundary and role of seamounts within the Cocos Plate. *Geophysical Research Letters* 20 (11), 1550. doi:10.1029/2002GL016766.
- Holden, J.F., Summit, M., Baross, J.A., 1998. Thermophilic and hyperthermophilic microorganisms in 3–30 °C hydrothermal fluids following a deep-sea volcanic eruption. *Fems Microbiology Ecology* 25, 33–41.
- Horita, J., Berndt, M.E., 1999. Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. *Science* 285, 1055–1057.
- Huber, J.A., Butterfield, D.A., Baross, J.A., 2002. Temporal changes in archaeal diversity and chemistry in a mid-ocean ridge seafloor habitat. *Applied and Environmental Microbiology* 68 (4), 1585–1594.
- Huber, J.A., Butterfield, D.A., Baross, J.A., 2003. Bacterial diversity in a seafloor habitat following a deep-sea volcanic eruption. *Fems Microbiology Ecology* 43 (3), 393–409.
- Huber, J.A., Butterfield, D.A., Johnson, H.P., Baross, J.A., 2006. Microbial life in ridge flank crustal fluids. *Environmental Microbiology* 8 (1), 88–89.
- Hunter, A.G., Kempton, P.D., Greenwood, P., 1999. Low-temperature fluid–rock interaction — an isotopic and mineralogical perspective of upper crustal evolution, eastern flank of the Juan de Fuca Ridge (JdFR), ODP Leg 168. *Chemical Geology* 155 (1–2), 3–28.
- Hutnak, M., et al., 2006. Hydrothermal recharge and discharge guided by basement outcrops on 0.7–3.6 Ma seafloor east of the Juan de Fuca Ridge: observations and numerical models. *Geochemistry Geophysics Geosystems* 7.
- Johnson, H.P., LEXEn Scientific Party, 2003. Probing for life in the ocean crust with the LEXEN Program. *EOS* 84 (12), 109–116.
- Johnson, H.P., Pruis, M.J., 2003. Fluxes of fluid and heat from the oceanic crustal reservoir. *Earth and Planetary Science Letters* 216 (4), 565–574.
- Johnson, H.P., Baross, J.A., Bjorklund, T.A., 2006. On sampling the upper crustal reservoir of the NE Pacific ocean. *Geofluids* 6, 251–272.
- Kadko, D., Moore, W., 1988. Radiochemical constraints on the crustal residence time of submarine hydrothermal fluids — Endeavor Ridge. *Geochimica et Cosmochimica Acta* 52 (3), 659–668.
- Kadko, D.C., Rosenberg, N.D., Lupton, J.E., Collier, R.W., Lilley, M.D., 1990. Chemical reaction rates and entrainment within the Endeavour Ridge hydrothermal plume. *Earth and Planetary Science Letters* 99, 315–335.
- Karsten, J.L., Hammond, S.R., Davis, E.E., Currie, R.G., 1986. Detailed geomorphology and neotectonics of the endeavor segment, Juan-De-Fuca Ridge — new results from Seabeam Swath Mapping. *Geological Society of America Bulletin* 97 (2), 213–&.
- Kroopnick, P.M., 1985. The distribution of ¹³C of sigma-CO₂ in the world oceans. *Deep Sea Research* 32 (1), 57–84.
- Lang, S.Q., Butterfield, D.A., Lilley, M.D., Johnson, P.H., Hedges, J.I., 2006. Dissolved organic carbon in ridge-axis and ridge-flank hydrothermal systems. *Geochimica et Cosmochimica Acta* 70 (8), 3830–3842.
- Lesoff, S.C., Konikow, L.F., 1997. Ambiguity in measuring matrix diffusion with single-well injection/recovery tracer tests. *Ground Water* 35 (1), 166–176.
- Lilley, M.D., Butterfield, D.A., Olson, E.J., Lupton, J.E., Macko, S.A., McDuff, R.E., 1993. Anomalous CH₄ and NH₄⁺ concentrations at an un-sedimented mid-ocean-ridge hydrothermal system. *Nature* 364 (6432), 45–47.
- Macdonald, K.C., Fox, P.J., Alexander, R.T., Pockalny, R., 1996. Volcanic growth faults and the origin of Pacific abyssal hills. *Nature* 380, 125–129.
- Massoth, G.J., Butterfield, D.A., Lupton, J.E., McDuff, R.E., Lilley, M.D., Jonasson, I.R., 1989. Submarine venting of phase-separated hydrothermal fluids at axial volcano, Juan-De-Fuca Ridge. *Nature* 340 (6236), 702–705.
- McCullom, T.M., Seewald, J.S., 2001. A reassessment of the potential for reduction of dissolved CO₂ to hydrocarbons during serpentinization of olivine. *Geochimica et Cosmochimica Acta* 65 (21), 3769–3778.
- McCullom, T.M., Ritter, G., Simoneit, B.R.T., 1999. Lipid synthesis under hydrothermal conditions by Fischer–Tropsch-type reactions. *Origins of Life and Evolution of the Biosphere* 29 (2), 153–166.
- McNichol, A.P., Druffel, E.R.M., 1992. Variability of the del-¹³C of dissolved inorganic carbon at a site in the north Pacific Ocean. *Geochimica Cosmochimica Acta* 56 (9), 3589–3592.
- McNichol, A.P., Jones, G.A., Hutton, D.L., Gagnon, A.R., Key, R.M., 1994. The rapid preparation of seawater sigma-Co₂ for radiocarbon analysis at the National Ocean Sciences AMS Facility. *Radiocarbon* 36 (2), 237–246.
- Mottl, M.J., 2003. Partitioning of energy and mass fluxes between mid-ocean ridge axes and flanks at high and low temperature. In: Halbach, P.E., Tunnicliffe, V., Hein, J.R. (Eds.), *Energy and Mass Transfer in Marine Hydrothermal Systems*. Dalhem University Press, Berlin, pp. 271–286.
- Mottl, M.J., Wheat, C.G., 1994. Hydrothermal circulation through midocean ridge flanks — fluxes of heat and magnesium. *Geochimica Et Cosmochimica Acta* 58 (10), 2225–2237.
- Mottl, M.J., Wheat, G., Baker, E., Becker, N., Davis, E., Feely, R., Grehan, A., Kadko, D., Lilley, M., Massoth, G., Moyer, C., Sansone, F., 1998. Warm springs discovered on 3.5 Ma oceanic crust, eastern flank of the Juan de Fuca Ridge. *Geology* 26 (1), 51–54.
- Parsons, B., Sclater, J.G., 1977. An analysis of the variation of ocean floor bathymetry and heat flow with age. *Journal of Geophysical Research* 82, 803–829.
- Proskurowski, G., Lilley, M.D., Brown, T.A., 2004. Isotopic evidence of magmatism and seawater bicarbonate removal at the Endeavour hydrothermal system. *Earth and Planetary Science Letters* 225, 53–61.
- Rau, G.H., Hedges, J.I., 1979. C-13 depletion in a hydrothermal vent mussel — suggestion of a chemosynthetic food source. *Science* 203, 468–469.
- Romanek, C.S., Grossman, E.L., Morse, J.W., 1992. Carbon isotopic fractionation in synthetic aragonite and calcite — effects of temperature and precipitation rate. *Geochimica et Cosmochimica Acta* 56 (1), 419–430.
- Sanford, W.E., 1997. Correcting for diffusion in carbon-14 dating of ground water. *Ground Water* 35 (2), 357–361.
- Sansone, F.J., Mottl, M.J., Olson, E.J., Wheat, C.G., Lilley, M.D., 1998. CO₂-depleted fluids from mid-ocean-ridge-flank hydrothermal springs. *Geochimica et Cosmochimica Acta* 62 (13), 2247–2252.
- Sarrazin, J., Juniper, S.K., Massoth, G., Legendre, P., 1999. Physical and chemical factors influencing species distributions on hydrothermal sulfide edifices of the Juan de Fuca Ridge, northeast Pacific. *Marine Ecology-Progress Series* 190, 89–112.
- Schultz, A., Delaney, J.R., McDuff, R.E., 1992. On the partitioning of heat flux between diffuse and point source seafloor venting. *Journal of Geophysical Research* 97, 12299–12315.
- Scott, K.M., Bright, M., Macko, S.A., Fisher, C.R., 1999. Carbon dioxide use by chemoautotrophic endosymbionts of hydrothermal vent vestimentiferans: affinities for carbon dioxide, absence of carboxy-somes, and delta C-13 values. *Marine Biology* 135 (1), 25–34.

- Seewald, J., Cruse, A., Saccocia, P., 2003. Aqueous volatiles in hydrothermal fluids from the Main Endeavour Field, northern Juan de Fuca Ridge: temporal variability following earthquake activity. *Earth and Planetary Science Letters* 216 (4), 575–590.
- Staudigel, H.R., Hart, S.R., Schmincke, H.U., Smith, B.M., 1989. Cretaceous ocean crust at DSDP Sites 417 and 418: carbon uptake from weathering versus loss by magmatic outgassing. *Geochimica Cosmochimica Acta* 53 (11), 3091–3094.
- Stein, C.A., Stein, S., 1992. A model for the global variation in oceanic depth and heat flow with lithospheric age. *Nature* 359, 123–137.
- Stein, J.S., Fisher, A.T., 2003. Observations and models of lateral hydrothermal circulation on a young ridge flank: numerical evaluation of thermal and chemical constraints. *Geochemistry Geophysics Geosystems* 4 (3), 1–20.
- Strens, M.R., Cann, J.R., 1986. A fracture-loop thermal balance model of black smoker circulation. *Tectonophysics* 122, 307–324.
- Stuiver, M., Polach, H.A., 1977. Discussion: reporting of ¹⁴C data. *Radiocarbon* 19 (3), 355–363.
- Sudicky, E.A., Frind, E.O., 1981. C-14 dating of groundwater in confined aquifers — implications of aquitard diffusion. *Water Resources Research* 17 (4), 1060–1064.
- Turner, J.V., 1982. Kinetic fractionation of C-13 during calcium-carbonate precipitation. *Geochimica et Cosmochimica Acta* 46 (7), 1183–1191.
- Underwood, M.B., Hoke, K.D., Fisher, A.T., Davis, E.E., Giambalvo, E., Zuhlsdorff, L., Spinelli, G.A., 2005. Provenance, stratigraphic architecture, and hydrogeologic influence of turbidites on the mid-ocean ridge flank of northwestern Cascadia Basin, Pacific Ocean. *Journal Of Sedimentary Research* 75 (1), 149–164.
- Veirs, S.R., McDuff, R.E., Stahr, F.R., 2006. Magnitude and variance of near-bottom horizontal heat flux at the Main Endeavour hydrothermal vent field. *Geochemistry Geophysics Geosystems* 7.
- Villinger, H., Grevemeyer, I., Kaul, N., Hauschild, J., Pfender, M., 2002. Hydrothermal heat flux through aged oceanic crust: where does the heat escape? *Earth and Planetary Science Letters* 202 (1), 159–170.
- Vogel, J.S., Southon, J.R., Nelson, D.E., 1987. Catalyst and binder effects in the use of filamentous graphite for AMS. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms* 29 (1–2), 50–56.
- Von Domm, K.L., Edmond, J.M., Grant, B., Measures, C.I., Walden, B., Weiss, R.F., 1985. Chemistry of submarine hydrothermal solutions at 21 N, East Pacific Rise. *Geochimica Et Cosmochimica Acta* 49, 2197–2200.
- Von Herzen, R.P., 2004. Geothermal evidence for continuing hydrothermal circulation in older (>60 Ma) ocean crust. In: Davis, E.E., Elderfield, H. (Eds.), *Hydrogeology of the Oceanic Lithosphere*. Cambridge University Press, Cambridge, UK, pp. 414–450.
- Wheat, G.C., Mottl, M.J., 2000. Composition of pore and spring waters from Baby Bare: global implications of geochemical fluxes from a ridge flank hydrothermal system. *Geochimica Cosmochimica Acta* 64 (4), 629–642.
- Wheat, C.G., Mottl, M.J., Fisher, A.T., Kadko, D., Davis, E.E., Baker, E., 2004. Heat and fluid flow through a basaltic outcrop on a ridge flank. *Geochemistry Geophysics Geosystems* 5 (12). doi:10.1029/2004GC000700.
- Yatabe, A., Vanko, D.A., Ghazi, A.M., 2000. Petrography and chemical compositions of secondary calcite and aragonite in Juan de Fuca Ridge basalts altered at low temperature. In: Fisher, A.T., Davis, E.E., Escutia, C. (Eds.), *Proc. ODP, Sci. Results. Ocean Drilling Program, College Station TX*, pp. 137–148.
- You, C.F., Butterfield, D.A., Spivack, A.J., Gieskes, J.M., Gamo, T., Campbell, A.J., 1994. Boron and halide systematics in submarine hydrothermal systems — effects of phase-separation and sedimentary contributions. *Earth and Planetary Science Letters* 123 (1–4), 227–238.