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CO₂-depleted fluids from mid-ocean ridge-flank hydrothermal springs

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Abstract—Hydrothermal spring fluids were collected from Baby Bare, a basement outcrop on the sediment-covered eastern flank of the Juan de Fuca Ridge overlying 3.5 Ma-old crust. These waters are venting at 25°C but have cooled from 64°C within the upper 200–300 m of the upflow zone during their ascent. Unlike ridge-axis hydrothermal vent fluids previously sampled, the total CO₂ content of the endmember spring fluids (0.85 μmol kg⁻¹) is depleted with respect to bottom seawater. The very low alkalinities (0.43 meq L⁻¹) and high Ca²⁺ concentrations (55 mmol kg⁻¹) of endmember spring fluids suggest that the removal of C in the spring fluids is associated with carbonate precipitation in the igneous basement. Assuming that 8–20% of the total ridge-flank heat loss rate of 50 × 10¹⁸ cal yr⁻¹ (6.6 TW) is removed by porewater advecting from the sediment at ≥25°C (an upper limit dictated by the global input rate of Mg⁺² to the oceans; Mottl and Wheat, 1994), a maximum global carbon sink of 1.0–2.6 × 10¹¹ mol yr⁻¹ (1.2–3.1 Mton-C yr⁻¹) and a maximum global alkalinity sink of 140–340 × 10⁹ eq yr⁻¹ are calculated for warm (≥25°C) ridge-flank hydrothermal circulation. This carbon flux is only 2–5% of current estimates of subaerial and submarine volcanic CO₂ emissions (~50 × 10¹¹ mol yr⁻¹), indicating that hydrothermal alteration of oceanic crust on young mid-ocean ridge flanks at temperatures of a few tens of degrees Celsius is only a relatively minor sink for carbon on a global basis. It is still possible, however, that ridge-flank alteration at lower temperatures (<25°C) is an important component of the global carbon budget. Copyright © 1998 Elsevier Science Ltd

1. INTRODUCTION

1.1. Ridge-Flank Hydrothermal Circulation

Hydrothermal circulation of seawater through the oceanic crust plays an important role in many geologic and oceanographic processes, including heat loss from the earth, aging of the oceanic crust, and geochemical cycles of the elements. While the most spectacular result of this process is found along the mid-ocean ridge axis in the form of high-temperature (~350°C) springs that deposit sulfide minerals, most of the flux of both heat and seawater in fact occurs through the mid-ocean ridge flanks. It has long been known that conductive heat flow measured on young oceanic crust is much lower than the total heat flow predicted by various models for a cooling lithospheric plate. This discrepancy is attributed to advective heat loss from the crust, mainly in the form of heated seawater that exits the crust as warm or hot springs along the ridge flanks.

Estimates of the amount of heat loss from advection of seawater through the crust range from 53 to 76 × 10¹⁸ cal yr⁻¹ (7.0–10.1 TW), with a best estimate of 65 × 10¹⁸ cal yr⁻¹ (8.7 TW) (Wolery and Sleep, 1976; Anderson et al., 1977; Sleep and Wolery, 1978; Langseth and Anderson, 1979; Sclater et al., 1980). This represents about 20% of the total heat loss rate from the earth, or about 30% of the rate from the seafloor; this is also more than three times the rate along the mid-ocean ridge axis. Because this heat is lost at lower temperatures, the seawater flux through the flanks is more than ten times that at the axis. Seawater advection cools the crust out to a mean age of 65 Ma (Sclater et al., 1980), over more than a third of the ocean floor (Anderson et al., 1979). This process is also important due to its alteration of the oceanic crust, and the accompanying changes in the crust's chemistry, mineralogy, and physical

properties (e.g., Staudigel and Hart, 1983; Mottl and Wheat, 1994; Alt, 1995).

1.2. Ridge-Flank Crustal Alteration and Associated Porewater Modification

The modification of porewater major-ion composition in ridge-flank settings has been shown to be dominated by (1) loss of Mg²⁺ and addition of Ca²⁺ resulting from basalt-seawater reactions, and (2) subsequent loss of alkalinity and Ca²⁺ from precipitation of CaCO₃ (e.g., Sayles and Manheim, 1975; Lawrence et al., 1975; Gieskes, 1983; Mottl et al., 1983; Mottl, 1989). Moreover, data from the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP) have provided evidence of potentially large scale low-temperature hydrothermal alteration of oceanic crust on ridge flanks (e.g., Alt and Honnorez, 1984; Alt et al., 1986, 1992; Staudigel et al., 1989; Alt, 1995; Alt et al., 1996; Teagle et al., 1996). However, there is disagreement as to the magnitude of these reactions on a global scale, a controversy that is complicated by the lack of suitable samples of ridge-flank crust from deep drilling cores or other sources. Specifically, there has been a vigorous debate as to whether late-stage hydrothermal alteration of oceanic crust is a major global sink of carbon on geological time scales (e.g., Staudigel et al., 1989; Berner, 1990; Staudigel, 1990; François and Walker, 1992; Kadko et al., 1995; Brady and Gislason, 1997).

In the absence of samples of oceanic crust from a range of locations to help resolve these issues, an examination of the venting fluids from ridge-flank hydrothermal sites may provide valuable complementary information on the dominant reactions associated with late-stage hydrothermal processes and the degree to which these reactions are globally uniform. This paper

Fig. 1. Location of the study site on the eastern flank of the Juan de Fuca Ridge overlying 3.5 Ma-old crust. Bold north-south lines mark the location of the ridge axis. Dashed lines indicate isochrons for the oceanic crust. Adapted from Davis et al. (1989).

provides initial data on the inorganic carbon chemistry of spring fluids collected from such a study.

2. STUDY SITE

The eastern flank of the Juan de Fuca Ridge has become one of the most thoroughly studied ridge flanks over the past decade. The FlankFlux 90 and 92 cruises studied the hydrology of three outcrops, located on a pair of adjacent 3.5–3.8 Ma-old, north-south, ridge-axis-parallel basement ridges that are almost entirely buried by turbidite sediments typically a few hundred meters thick (Wheat and Mottl, 1994). Except for the young crustal age, these outcrops are typical of a large number of similar outcrops that protrude through otherwise continuous sediment cover on ridge flanks throughout the oceans. It has long been suggested that such outcrops play a key role in seafloor hydrology, acting as direct conduits between igneous basement and the oceans, concentrating vertical flow and inducing lateral flow of seawater over large distances through basement (Mottl and Wheat, 1994, and references therein). These cruises demonstrated that the outcrops are sites of hydrothermal upwelling of highly altered, Mg-depleted seawater that is precipitating hydrothermal clays and ferromanganese deposits (Mottl et al., 1998).

The smallest outcrop, Baby Bare, is 0.5 km² and rises 70 m above the sediment and 300 m above the buried ridge crest (Fig. 1). Extensive heat flow and seismic reflection surveys indicate that the buried basement interface in the region is isothermal at 60–70°C (Davis et al., 1992).

In August 1995 a team led by M. J. Mottl and C. G. Wheat successfully dove on the outcrops with the manned submersible *Alvin* in order to conduct fine-scale measurements and collect samples for a definitive test of their model of ridge flank hydrology. Heat flows exceeding 70 W m⁻², indicating upward porewater advection at velocities >300 cm yr⁻¹, were measured throughout a large region near the summit of Baby Bare (Wheat et al., 1995; Mottl et al., 1998). In addition, venting of highly altered, seawater-derived fluids at a temperature of 25°C

was observed at hydrothermal springs approximately centered in the region with the highest heat flow (Mottl et al., 1995, 1998). No other vents this hot or this active have ever been found on a mid-ocean ridge flank, particularly on crust this old. Later drilling just north of Baby Bare at ODP Site 1026 found the temperature of fluids in the uppermost basement to be 63.8°C (Davis et al., 1997; Fisher et al., 1997); these waters apparently cool conductively to 25°C during their ascent beneath the Baby Bare springs.

3. METHODS

Spring fluids were sampled by *DSV Alvin* both directly and through dome-shaped inverted funnels that were deployed to concentrate the flow; one spring so capped delivered 0.02 L s⁻¹ at 0.02 cm s⁻¹ (5000 m yr⁻¹) into the base of the funnel. Spring-fluid samples for dissolved gas analysis were collected with titanium gas-tight samplers in conjunction with the NOAA manifold sampler (Massoth et al., 1989). Other spring fluid samples were collected with titanium-syringe majors samplers (Von Damm et al., 1985) operated in conjunction with the manifold sampler. Bottom seawater samples were collected with a Niskin bottle attached to *Alvin's* sample basket.

Gas samples were acidified with sulfamic acid to pH <2, and the gases were then vacuum-extracted at sea with a glass/stainless-steel vacuum line. The total gas volume was determined with high precision capacitance manometers, and the extracted gas from each sample was sealed in several breakseal glass ampoules for analysis ashore. The extracted spring-fluid gases were analyzed by cryogenic gas chromatography (6-m Haysep-Q analytical column operated from -50°C to 70°C) to separate H₂, O₂, Ar, N₂, CH₄, CO, and CO₂ with a single injection. The samples were injected by means of a sample loop valve attached to a high-vacuum inlet system; the sample inlet pressure was monitored with a capacitance manometer. The precision of the total CO₂ (TCO₂) measurements was ±2%. Analyses for the stable carbon isotopic composition of dissolved total CO₂ (δ¹³C-TCO₂) used sub-samples of the extracted spring fluid gases which were processed offline using conventional techniques, sealed in glass ampoules, and analyzed using a Finnigan-MAT 252 mass spectrometer. The precision of the isotopic measurements was 0.05 per mil. Alkalinity analyses were made aboard ship by potentiometric Gran titration (±0.02 meq L⁻¹). Measurements of Ca²⁺ and Mg²⁺ were made by colorimetric titration (±0.2%; Kremling, 1983) for the titanium-syringe samples, and by inductively coupled plasma atomic emission spectroscopy (±3%) for the gas-tight samples.

4. RESULTS AND DISCUSSION

4.1. Spring Fluid Composition

The lowest Mg⁺² concentration measured in the Baby Bare spring samples was 0.98 mmol kg⁻¹ (Fig. 2a). As with other submarine hydrothermal systems, we assume that this small amount of Mg⁺² is a contaminant from seawater introduced during sampling and that the endmember (undiluted by seawater) spring fluid has a Mg²⁺ concentration of 0 mmol kg⁻¹ (e.g., Von Damm et al., 1985; Seyfried and Mottl, 1995); this assumption is supported by the Baby Bare sediment porewater Mg⁺² concentrations, which converge on 0 mmol kg⁻¹ with depth (Mottl et al., 1998). From this assumption we can extrapolate an endmember alkalinity of 0.43 meq kg⁻¹ (Fig. 2a), ~1/5 that of bottom seawater (2.44 meq kg⁻¹, Table 1). Similarly, we extrapolate an endmember Ca²⁺ concentration of 55 mmol kg⁻¹ (Fig. 2b), ~5 times that of bottom seawater (10.3 mmol kg⁻¹, Table 1).

Unlike hydrothermal vent fluids previously collected along mid-ocean ridges, the Baby Bare spring fluids, which are the first collected from a ridge flank, are depleted in TCO₂ with

Fig. 2. Composition of Baby Bare spring fluid samples collected with syringe (●) and gas-tight (■) samplers: (a) titration alkalinity vs. dissolved Mg²⁺, (b) dissolved Ca²⁺ vs. dissolved Mg²⁺, (c) TCO₂ vs. dissolved Mg²⁺, and (d) $\delta^{13}\text{C}\text{-TCO}_2$ vs. TCO₂. Lines are linear regressions of the data; only the syringe-sample data are included in the regression in (b). Data plotted in (c) and (d) are for the eight gas-tight samples which plotted on the syringe-sample Mg-Ca regression line in (b). Error bars in (d) indicate the analytical errors.

respect to seawater (Fig. 2c). Note, however, that the gas-tight samples were not filtered before processing, so it is possible that carbonate particles suspended in the samples may have led to erroneous TCO₂ values due to sample acidification before gas analysis. Thus we have only used data from gas-tight samples that fell upon the Ca-Mg regression line obtained from the filtered titanium-syringe majors samples (Fig. 2b). These selected samples yield an extrapolated endmember TCO₂ concentration of 0.85 mmol kg⁻¹ (Fig. 2c), which is only ~1/3 that of bottom seawater.

The spring-fluid ¹³C-TCO₂ values are largely invariant with respect to TCO₂ concentration (Fig. 2d), indicating that the process(es) responsible for the TCO₂ removal do not strongly isotopically fractionate the spring-fluid TCO₂. In contrast, significant amounts of isotopic fractionation, with preferential removal of light TCO₂, would be expected if biological TCO₂ uptake (such as in CO₂ reduction to CH₄) was a major carbon

Table 1. Chemical and physical characteristics of the Baby Bare endmember spring fluid and bottom seawater (2650 m depth).

	Computed endmember	Bottom seawater
Total CO ₂ (mmol kg ⁻¹)	0.85 ± 0.2	2.38 ^a
Alkalinity (meq kg ⁻¹)	0.43 ± 0.07 ^b	2.44 ^a
Mg ²⁺ (mmol kg ⁻¹)	0	52 ^b
Ca ²⁺ (mmol kg ⁻¹)	55.2 ^b	10.3 ^b
Temperature (°C)	64 ^c	2

^aGEOSECS Stn 217, Craig et al. (1981)

^bWheat et al. (1995)

^cDavis et al. (1997)

sink (e.g., Nissenbaum et al., 1972). Conversely, inorganic precipitation of CaCO_3 would be expected to exhibit at most a small degree of fractionation, with preferential removal of heavy TCO_2 (e.g., Romanek et al., 1992); this is consistent with the weak trend seen in Fig. 2d.

4.2. Ridge-Flank Seafloor Alteration

Low-temperature seafloor alteration has been suggested as a possible long-term control on such factors as the alkalinity budget of seawater and atmospheric CO_2 levels (Staudigel et al., 1989; Spivack and Staudigel, 1994). In contrast, recent modeling by Caldeira (1995) indicates that terrestrial silicate-rock weathering is a more important control on long-term atmospheric CO_2 content than is low-temperature oceanic basalt alteration. In light of the paucity of oceanic crustal samples that could help resolve these issues, the availability of hydrothermal fluids from a ridge-flank hydrothermal system offers an attractive alternative approach for addressing this controversy.

We propose that the extensive TCO_2 and alkalinity removal in the Baby Bare spring fluids is associated with calcium carbonate precipitation in the underlying basement during off-axis hydrothermal alteration of the oceanic crust. Such carbonate precipitation would be promoted by the elevated Ca^{2+} concentrations (55 mmol kg^{-1}) in the spring fluids (Wheat et al., 1995; Mottl et al., 1998), presumably the result of basalt weathering. The strong linear relationship between TCO_2 and Mg^{2+} indicates a predominantly hydrothermal control on spring fluid TCO_2 concentrations. In addition, ridge-flank carbonate precipitation has previously been postulated on the basis of (1) analyses of DSDP/ODP cores, in which calcium carbonate appears to be a major product of late-stage hydrothermal alteration of mid-ocean ridge basalts (e.g., Alt and Honnorez, 1984; Alt et al., 1986, 1992; Alt, 1995; Teagle et al., 1996), (2) the apparent increase in carbonate content of oceanic crust with increasing age (Staudigel et al., 1981; Alt, 1993), and (3) thermodynamic calculations and experimental results (Brady and Gislason, 1997). Calcium carbonates and zeolites have been identified as the last secondary phases to form at temperatures $<250^\circ\text{C}$ under such conditions; these seawater-basement reactions can be approximated as:

where CaSiO_3 in this case represents the calcium silicate component of primary igneous minerals in basalt. Such a reaction scheme was originally proposed by Urey (1952, 1956) to predict limits on atmospheric CO_2 levels over geological time. Finally, the carbonates recovered at DSDP Sites 417 and 896 were low-Mg (0–5 mol% MgCO_3), implying that they were formed from seawater solutions with lowered Mg/Ca ratios (Alt and Honnorez, 1984; Teagle et al., 1996); again, this is consistent with the chemistry of Baby Bare spring fluids, which had endmember Mg/Ca ratios of <0.02 , compared to the seawater ratio of 5.1 (Table 1).

Mottl and Wheat (1994) estimated that a global heat loss of $50 \times 10^{18} \text{ cal yr}^{-1}$ ($6.6 \times 10 \text{ TW}$) resulted from convection of

seawater through mid-ocean ridge flanks. They showed that if only 8–20% of this heat was lost by advection at temperatures $\geq 25^\circ\text{C}$, as measured at the sediment/basement interface, then this type of ridge-flank hydrothermal circulation could remove into the crust the entire river input of Mg. Disposal of this much Mg sets an approximate upper limit to the rate of advection at these relatively warm basement temperatures, as typified by the Baby Bare springs, and allows us to estimate an upper limit on carbon fluxes into oceanic crust by this process. Assuming that the TCO_2 concentrations of other endmember ridge-flank spring fluids at $\geq 25^\circ\text{C}$ are similar to those of the computed Baby Bare endmember, an upper limit on the global carbon sink associated with warm ridge-flank hydrothermal circulation can be calculated:

$$S_c = \frac{H_g f r_c}{cT} \quad (4)$$

where S_c is the global carbon sink, H_g is the global ridge-flank heat flux [$64 \pm 11 \times 10^{18} \text{ cal yr}^{-1}$ ($8.6 \pm 1.6 \text{ TW}$; Mottl and Wheat, 1994)], f is the fraction of H_g that is due to warm ridge-flank venting (i.e., that with temperatures in the uppermost basement of $\geq 25^\circ\text{C}$), r_c is the TCO_2 removed (mol kg^{-1}) from bottom seawater during the formation of endmember spring fluid, c is the specific heat of water ($955 \text{ cal } ^\circ\text{C}^{-1} \text{ kg}^{-1}$), and T is elevation of the temperature of the basement hydrothermal fluids with respect to the 2°C bottom seawater. Using the endmember and seawater temperatures and TCO_2 concentrations given in Table 1, and the Mottl and Wheat (1994) maximum estimate for f of 0.08–0.20, a flux of $1.0\text{--}2.6 \times 10^{11} \text{ mol yr}^{-1}$ ($1.2\text{--}3.1 \text{ Mton-C yr}^{-1}$) is calculated as an upper limit for the global carbon sink in warm ridge flanks. Note that the choice of temperature is not especially critical: the composition of basement water on the eastern flank of the Juan de Fuca Ridge, as inferred from the sediment porewater data from ODP Leg 168 (Davis et al., 1997), indicates that r_c is approximately proportional to T over the relevant temperature range of $25\text{--}65^\circ\text{C}$ for warm ridge-flank circulation (i.e., changes in r_c and T in Eqn. 4 will cancel out).

This net flux is an order of magnitude lower than the $22\text{--}29 \times 10^{11} \text{ mol yr}^{-1}$ value of Staudigel et al. (1989) for global carbon uptake by ridge axis and flank seafloor alteration, derived from estimates of carbon accumulation in 120 Ma-old hydrothermally altered oceanic crust from DSDP Sites 417 and 418. Conversely, our estimate is similar to the $1.5\text{--}3.5 \times 10^{11} \text{ mol yr}^{-1}$ value calculated by Alt et al. (1996) for ridge flank seafloor alteration using carbon accumulation data from ODP Sites 504 and 896 on 6 Ma-old crust. It is possible that this difference reflects the very different crustal ages at these two localities: perhaps the younger crust reflects uptake of carbon from warmer waters, whereas the older crust has taken up carbon from cooler waters as well. If the other 80–92% of the heat lost by advection on ridge flanks occurs at basement temperatures of $5\text{--}25^\circ\text{C}$ and is accompanied by a loss in TCO_2 that is only 10% of that in the Baby Bare spring water, the calculated carbon flux is $2.8\text{--}25 \times 10^{11} \text{ mol yr}^{-1}$, much larger than estimated above for warmer flow even though the Mg flux would still be less than the annual river flux; a larger TCO_2 loss results in an even higher carbon flux into the crust. However, as noted by both Staudigel et al. (1989) and Alt et al. (1996), there

is considerable uncertainty in their estimates due to the natural inhomogeneity of the ridge-flank volcanics and the limited number of samples thus far examined. For comparison, these calculated fluxes are considerably smaller than current estimates of combined subaerial and submarine volcanic CO₂ emissions (e.g., 60–70 × 10¹¹ mol y⁻¹ (Holland, 1978), 110 × 10¹¹ mol yr⁻¹ (Berner, 1990), 30–40 × 10¹¹ mol yr⁻¹ (Gerlach, 1991), 50 × 10¹¹ mol yr⁻¹; Mackenzie, 1995).

In a similar fashion, it is possible to use the Baby Bare spring fluid data to estimate the global alkalinity sink associated with warm ridge-flank hydrothermal reactions:

$$S_A = \frac{H_R f r_A}{cT} \quad (5)$$

where S_A is the global alkalinity sink, r_A is the alkalinity removed (eq kg⁻¹) from bottom seawater during the formation of endmember hydrothermal fluid, and the other variables are the same as for Eqn. 4. Again using the data in Table 1, the calculated global alkalinity sink is 140–340 × 10⁹ eq yr⁻¹ for ridge flank hydrothermal systems with temperatures ≥25°C.

This net flux is comparable to the global acidity flux of 350 ± 300 × 10⁹ eq yr⁻¹ estimated by Spivack and Staudigel (1994) for low-temperature alteration of the upper oceanic crust. As noted by these authors, fluxes of such magnitude are only a few percent of the global primary alkalinity flux, indicating that low-temperature weathering of the upper crust at temperatures ≥25°C is not a significant factor in the global alkalinity budget. However, weathering at temperatures <25°C may be a more significant global flux.

Finally, the Baby Bare spring fluid data indicate that the observed loss of alkalinity is not solely due to CaCO₃ precipitation. If CaCO₃ precipitation were solely responsible, the $r_A:r_C$ ratio would be ~2 eq mol⁻¹, rather than the observed value of 2.01:1.53 = 1.31 eq mol⁻¹. It is likely that the additional alkalinity loss is associated with hydrothermal basalt-seawater reactions that remove Mg⁺² (e.g., Bischoff and Dickson, 1975).

5. CONCLUSIONS

The data presented here indicate that ridge-flank hydrothermal fluids can be highly depleted in TCO₂ with respect to the original seawater. However, hydrothermal alteration of oceanic crust on young mid-ocean ridge flanks at temperatures of a few tens of degrees Celsius is only a relatively minor sink for carbon on a global basis. It is still possible, however, that ridge-flank alteration at lower temperatures (<25°C) is an important component of the global carbon budget. Although these data are not sufficient to determine unequivocally the roles of oceanic crust alteration on global carbon cycling, they do indicate that these processes merit consideration in global carbon models. In particular, as pointed out by Caldeira (1995), ocean basement carbon accumulation may be particularly important in assessing the impact of subduction zone metamorphism on atmospheric CO₂ content.

There is clearly a strong need for similar studies at other ridge-flank sites to determine the consistency of spring fluid composition and the rate of venting (both as discrete springs and as more diffuse upward porewater advection) at such sites. This is particularly important in light of the observed hetero-

geneity in off-axis alteration due to such factors as basement temperature and the degree of restriction of circulation of hydrothermal fluids (e.g., Alt, 1995; Alt et al., 1996; Teagle et al., 1996). However, despite the uncertainties in our knowledge of ridge-flank crustal alteration, the carbon and alkalinity removal estimates presented here should be a useful first step in quantitatively evaluating the role of off-axis venting in global hydrothermal chemical fluxes.

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