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Chemical composition of basement fluids within an oceanic ridge flank: Implications for along-strike and across-strike hydrothermal circulation

C. Geoffrey Wheat,^{1,2} Henry Elderfield,³ Michael J. Mottl,⁴ and Christophe Monnin⁵

Abstract. Compositions of basement fluids are presented for four sites along a 3.5-m.y.-old, partly buried basement ridge on the eastern flank of the Juan de Fuca Ridge. This ridge is roughly parallel to the active ridge axis of the Endeavor Segment ~100 km to the west. From south to north these sites are Baby Bare Outcrop, Ocean Drilling Program (ODP) Site 1026, and the southern and northern sides of Mama Bare Outcrop. The composition of basement fluids is determined or estimated from analyses of pore water samples that were extracted from sediments at each of these sites, spring waters from Baby Bare, and basement fluids that vented from the open ODP Hole 1026B. Chemical trends in basement fluids along this transect show increasing alteration from south to north. A similar trend was observed along an ODP transect perpendicular to the ridge axis with increasing fluid alteration from west to east. Much of the increase in fluid alteration along the ODP transect is explained by greater water-rock exchange with increasing basement temperature to the east. In contrast, the trend along the 3.5-m.y.-old ridge is best explained by diffusive exchange with the overlying sediment. The rate of this exchange is used to constrain hydrologic properties within basaltic basement. Flow within the 3.5-m.y.-old ridge is inferred to occur from south to north and lacks significant exchange with basement fluids from the active ridge crest to the west. Thus the two flow systems are hydrologically distinct, and flow paths are likely influenced by the complex distribution of permeability in basement, the pattern of seafloor morphology, and the type and rate of sedimentation.

1. Introduction

Researchers have examined oceanic basement alteration and evolution resulting from hydrothermal circulation for the past 30 years, but central questions remain unanswered [Baker and McNutt, 1998]. Chemical and physical processes associated with this flow alter basement porosity and bulk chemical composition [e.g., Wilkens *et al.*, 1991; Jacobson, 1992]. Much of this alteration occurs at low-temperatures in ridge flanks [Hart and Staudigel, 1982; Thompson, 1983; Alt, 1995; Alt *et al.*, 1996], where convection of seawater from the crust is possible even in crust as old as 80 m.y. [Embley *et al.*, 1983; Noel and Hounslow, 1988]. This low-temperature alteration impacts global chemical budgets [Bloch and Bischoff, 1979; Mortlock *et al.*, 1993; Mottl and Wheat, 1994; Wheat *et al.*, 1996a; Elderfield and Schultz, 1996; Alt, 1995; Sansone *et al.*,

1998; Wheat and Mottl, 2000], but the principal uncertainty in each of these budgets is the magnitude of the seawater flux for different thermal and chemical domains.

Seawater circulation through oceanic crust has been simulated using numerical models [e.g., Fehn *et al.*, 1983; Fisher *et al.*, 1990, 1994; Davis *et al.*, 1996] and constrained by geochemical measurements [Mottl, 1989; Wheat and Mottl, 1994; Wheat and McDuff, 1995]. Recent simulations suggest that basement permeability and geometry greatly influence fluid flow through the oceanic crust [Fisher and Becker, 1995; Wang *et al.*, 1997; Fisher, 1998]. For example, basement topographic highs tend to be sites of seawater egress [Wheat and Mottl, 1994, 2000; Wheat and McDuff, 1995; Mottl *et al.*, 1998], while topographic lows can provide a pathway for the introduction of seawater into basement [Mottl, 1989; Fisher *et al.*, 1990]. Most models have represented flow in a two-dimensional plane perpendicular to a ridge axis, in part, because quantitative evidence for three-dimensional circulation is limited and also because there is little information on the three-dimensional permeability structure in basement.

In this paper we present the chemical compositions of basement fluids at four locations along a 3.5-m.y.-old basaltic ridge on the eastern flank of the Endeavor Segment of the Juan de Fuca Ridge. Fluid samples were obtained from sediment cores from which pore waters were extracted, hydrothermal springs, and a cased borehole from which basement fluids vented. These data are unique in that they were collected along a basement ridge that is roughly parallel to the present ridge axis, thus providing an opportunity to investigate flow

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along structural strike. *Delaney et al.* [1992] suggested that along-strike faults guide seawater circulation along the active ridge axis on the Endeavor Segment, and as we will show below, our data are consistent with flow along strike in a ridge flank setting. These along-strike geochemical data are similar to cross-strike data collected along a transect that was drilled during Leg 168 of the Ocean Drilling Program (ODP). This transect, which is perpendicular to the ridge axis, shows increasing alteration from west to east. These two geochemical transects highlight the occurrence of multiple, hydrologically distinct flow systems within young basement on a ridge flank.

2. Geologic Setting

The 3.5-m.y.-old basement ridge is ~100 km east of the active Juan de Fuca Ridge (Figure 1). Most of this ridge is covered with Pleistocene turbidites, but there are three basaltic outcrops near 48°N where basement is exposed. The southern outcrop, Baby Bare, probably formed by a combination of tectonic activity and off-axis volcanism [*Karsten et al.*, 1997; *Becker*, 1997]. The origin of the northern outcrop, Mama Bare, is unknown but may be similar. Sediment thickness along buried parts of the ridge generally increases to the north with accumulations of hundreds of meters. In adjacent topographic lows, 400 to 600 m of sediment has accumulated. Surprisingly, the upper basement temperature along this ridge and in the area defined by the bares is estimated to be nearly uniform [*Davis et al.*, 1997b], based on hundreds of measurements of heat flow with co-located seismic reflection profiles from which the temperature in upper basement is estimated by extrapolating measurements of surficial heat flow and sediment thermal conductivity throughout the thickness of the sediment column. Such a relatively uniform temperature in basement despite greatly differing sediment thicknesses requires vigorous seawater circulation in the upper basement [*Davis et al.*, 1997b].

Four locations along this 3.5-m.y.-old ridge were sampled: Baby Bare, ODP Site 1026, and both south and north of Mama Bare (Figure 1). Baby Bare, which extends ~70 m above the surrounding seafloor, covers an area of 0.5 km², but ~99% of the edifice is covered with 0.1 to 1 m of sediment [*Becker*, 1997]. Fifteen dives with the submersible DSV *Alvin* were used to map the area, conduct 16 transects radially inward toward the summit to collect sediment cores and measure heat flow and to locate and sample 25.0°C springs that support communities of Thysirid clams [*Mottl et al.*, 1998]. Three distinct springs, elevated heat flow, and focused upwelling of sediment pore waters were found along a fault ~10 m below the summit and roughly parallel to the buried ridge [*Becker*, 1997]. The integrated seawater and energy fluxes from Baby Bare are ~4-13 dm³/s and 2-3 MW, respectively [*Wheat et al.*, 1996b; *Mottl et al.*, 1998]. This venting generates a detectable thermal and chemical plume in the overlying water column [*Thomson et al.*, 1995; *Wheat et al.*, 1997].

Mama Bare is located 14.7 km to the northeast of Baby Bare, encompasses an area of 1.4 km², and extends 140 m above the turbidite plain. Only one *Alvin* dive was conducted on Mama Bare. No springs were discovered on two crossings of the summit, but a temperature of 18.0°C (bottom seawater is 1.8°C) was measured at a depth of 0.51 m below the seafloor, resulting in a heat flow that is 2 orders of magnitude greater than that in the surrounding area. This high heat flow coupled with systematic variations in pore water chemistry

with depth indicates diffuse pore water flow through the sediment section.

ODP Site 1026 is located between Baby and Mama Bares. Here the sediment is ~229 m thick, and the temperature at the sediment-basement interface is ~64°C [*Davis et al.*, 1997a]. ODP Hole 1026B was drilled and cased into the upper basaltic basement. Because the basement fluid pressure in this hole is greater than ambient hydrostatic, basement fluids flowed from the open borehole at a rate of 1.4 to 2 dm³/s before the borehole was instrumented [*Fisher et al.*, 1997].

One additional basement outcrop has been located within a few kilometers of Baby and Mama Bares. This outcrop, Papa Bare, resides on a buried ridge which is parallel to the 3.5-m.y.-old ridge and ~7 km to the east. Papa Bare is the largest of the three outcrops, covers an area of 4.2 km², and extends ~210 m above the sediment plain. ODP Site 1027 was drilled between these two basaltic ridges in a basement trough where the sediment thickness is ~614 m. Extensive seismic surveys suggest that no other basaltic outcrops exist within ~40 km of the three bares [*Davis et al.*, 1989, 1992, 1997b].

ODP Sites 1026 and 1027 and the associated ridges mark the eastern end of the ODP Leg 168 drilling transect (Figure 1) [*Davis et al.*, 1997a]. This transect is perpendicular to the active ridge axis of the Endeavour Segment of the Juan de Fuca Ridge and comprises 10 sites (ODP Sites 1023-1032). These sites are spaced 22 to 103 km from the ridge axis in crust 0.86 to 3.6 m.y. old. Rational for drilling this transect was centered around elucidating the geochemical and physical processes that alter and evolve a young oceanic ridge flank and, in particular, the influence of hydrothermal circulation on these processes. The ODP transect is divided among three classifications based on basement roughness and heat flow. From west to east these classifications are hydrothermal transition (ODP Sites 1023-1025), buried basement (ODP Sites 1028-1032), and rough basement (ODP Sites 1026 and 1027). Each site was drilled into basement to estimate thermal and chemical conditions in upper basement and the extent of basement alteration [*Davis et al.*, 1997a; *Elderfield et al.*, 1999; *Davis et al.*, 1999].

3. Sample Collection and Analytical Methods

Fluid samples were collected directly from springs on Baby Bare and in the open borehole at ODP Hole 1026B and by extraction from sediment cores at each location to provide an estimate of the composition of the fluid in basement. Thirty-nine samples from three springs provide a comprehensive data set that constrain the composition of basement fluids at Baby Bare [*Wheat and Mottl*, 2000]. Spring fluids were collected using the titanium Walden-Weiss samplers with the National Oceanic and Atmospheric Administration (NOAA) manifold sampler mounted on the DSV *Alvin* [*Massoth et al.*, 1989]. Two samples of basement fluids were collected directly using the water-sampler-temperature probe (WSTP) in ODP Hole 1026B [*Davis et al.*, 1997a]. These samples originated from the upper 10 m of basaltic basement, based on the thermal structure of hole shortly after drilling [*Fisher et al.*, 1997]. However, because of fluid reactions with drilling muds (e.g., Si), casing (e.g., Fe), and/or greases (e.g., Li) some measured concentrations do not reflect in situ concentrations. Samples of spring and basement fluids were filtered through a 0.45- μ m membrane and aliquots were stored in acid-washed high-density polyethylene bottles and glass ampules.

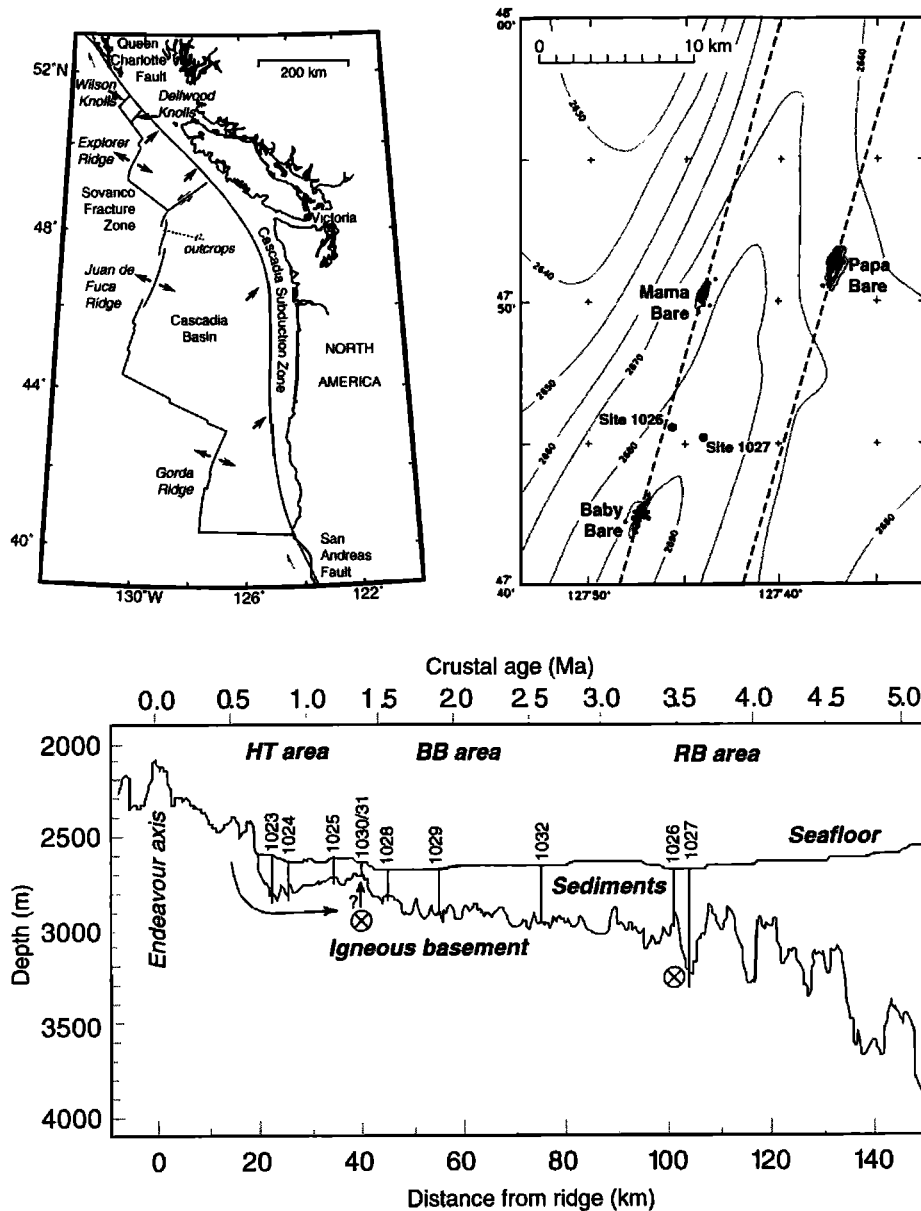


Figure 1. Juan de Fuca Ridge flank east of the spreading axis at about 48°N. Data were collected from one along-strike and one across-strike transect. The along-strike transect is located on a basaltic ridge that overlies 3.5-m.y.-old crust, ~100 km from the active ridge axis to the west (labeled outcrops). This transect includes Baby and Mama Bares, which lie along a partially buried ridge that is represented by a dashed line. Another ridge is to the east and is exposed at Papa Bare. Data from the across-strike transect are from a series of drilled boreholes (ODP sites 1023 to 1032). These holes were drilled during ODP Leg 168, span a length of 81 km (dashed line in regional map) ending at ODP Site 1027, and are categorized according to basement roughness and thermal structure (HT, hydrothermal transition ODP Sites 1023-1025; BB, buried basement ODP Sites 1028-1032; RB, rough basement ODP Sites 1026 and 1027). The cross section of the ODP transect shows borehole location relative to basement roughness, sediment thickness, crustal age, and distance from the mid-ocean ridge. Ridges near ODP Sites 1026 and 1027 are those on which the bares reside. Arrows are shown to indicate directions of flow most consistent with chemical data. The symbol ⊗ is used to indicate along-axis flow into the page (toward the north).

Pore waters were extracted from sediment cores at each site. Cores were retrieved using a variety of surface (piston and gravity), submersible (push), and drilling (ODP Sites) techniques. Pore waters from Baby Bare were extracted from 48 piston and gravity cores and 93 push cores [Wheat and Mottl, 2000]. Similarly, pore waters were extracted from five push

cores from the southern side of Mama Bare and two gravity cores from the northern side. One gravity core was collected near Papa Bare, but the slow rate of pore water flow through the sediment at this location precluded definitive interpretations regarding the composition of basement fluids [Wheat and Mottl, 2000]. Pore waters from the ODP sites were

Table 1. Fluid Compositions and Analytical Methodologies

Ion	Bottom	Baby	1026B	Mama Bare	
	Seawater	Bare		South	North
Calcium ^a , mmol/kg	10.3	55.2 ± 0.3	56.15	56.1 ± 0.6	57.6 ± 0.9
Strontium ^b , μmol/kg	86	110 ± 3	111	113 ± 3	122 ± 2
Sr ⁸⁷ / Sr ⁸⁶ ^c	0.7092	0.70745	0.70728		0.70715
Sulfate ^d , mmol/kg	28.1	17.8 ± 0.4	17.01	16.9 ± 0.5	16.3 ± 0.2
Alkalinity ^a , meq/kg	2.5	0.43 ± 0.06	0.40 ± 0.09	0.7 ± 0.2	
Chlorinity ^a , mmol/kg	542.2	554.4 ± 0.8	552.5	557 ± 2	556 ± 2
Sodium/Chlorinity ^e	0.861	0.853 ± 0.002	0.8385	0.846 ± 0.002	0.838 ± 0.002
Potassium ^f , mmol/kg	10.1	6.88 ± 0.08	6.57	6.6 ± 0.6	6.4 ± 0.7
Lithium ^f , μmol/kg	26.6	9.0 ± 0.9	13.7 ± 1.4	14.6 ± 0.8	
Rubidium ^f , μmol/kg	1.38	1.12 ± 0.06	0.94	1.2 ± 0.2	1.2 ± 0.2
Ammonium ^g μmol/kg	0.3	76 ± 4	121	~100	110 ± 30
Boron ^b , μmol/kg	410	560 ± 30	541	540 ± 20	580 ± 20
Magnesium ^h , mmol/kg	52	0.98	2.20	0.5	2.4
Temperature, °C	1.8	25.0	64	18.0	4

Data for bottom seawater and ODP Site 1026 are based on measured values [Wheat and Mottl, 2000; Davis et al., 1997a; Mottl et al., 2000]. Data for the Bares are based on extrapolations of the data to a 0 mmol Mg/kg hydrothermal end-member [Wheat and Mottl, 2000]. The Sr isotopic data are from Elderfield et al. [1999] and D. A. Butterfield et al. (submitted manuscript, 2000). Concentrations of Mg represent the lowest measured value and temperatures are the highest measured value.

^a Potentiometric titration.

^b Inductively coupled plasma emission.

^c Mass spectrometry.

^d Ion chromatography.

^e Difference.

^f Atomic adsorption spectrometry.

^g Colorimetric.

^h Colorimetric titration.

extracted from sediment collected through out the entire sediment column (with the exception of ODP Site 1032) with the greatest sampling density near the sediment-water and sediment-basement interfaces [Davis et al., 1997a; Mottl et al., 2000]

Pore waters from piston, gravity, and push cores were extracted from the sediment by centrifugation at 1°-5°C, about the bottom temperature of 1.8°C [Wheat and Mottl, 1994, 2000]. Pore waters from the ODP transect were squeezed at room temperature. Similar to the procedure for the spring samples, each pore water sample was filtered through a 0.45-μm membrane and stored in a variety of acid-washed high-density polyethylene bottles and glass ampules. Only alkalinity and pH were measured at sea for all samples. Some additional analyses were performed at sea, but most were conducted ashore using routine techniques (Table 1).

4. Results

Chemical and thermal compositions of pore and spring waters can be used to determine the location of basement fluid egress, estimate the rate of this egress, define the composition of the fluid in basement, and constrain exchange processes within the crust as well as the path of fluid circulation within the crust [i.e., Wheat and Mottl, 1994, 2000]. Support for fluid egress near Baby and Mama Bares is based on systematic variations in chemical and thermal profiles of pore water and from visual observations at springs [Mottl et al., 1998; Wheat

and Mottl, 2000] (Figure 2). Most of the pore water chemical data are consistent with the flow of seawater from basement at speeds of centimeters per year to meters per year, which is the limit for detecting flow by this method [Wheat and McDuff, 1995; Wheat et al., 1998]. The only other evidence of fluid egress along this 3.5-m.y.-old ridge is from ODP Hole 1026B where basement fluids vented from the open borehole [Fisher et al., 1997].

The chemical composition of basement fluids were determined from these pore and spring waters. We used the linear relationship between dissolved ions and Mg in hydrothermal spring fluids from Baby Bare and extrapolated this relationship to a zero Mg basement fluid; the lowest measured value was 0.98 mmol Mg/kg (Figure 2). Wheat and Mottl [2000] concluded that bottom seawater loses Na, K, Li, Rb, Mg, alkalinity, phosphate, and TCO₂ to the crust but gains Ca, Sr, Mn, and B. Reactions within basaltic basement beneath Baby Bare involving sulfate, nitrate, and ammonium are equivocal, but the overall effect is that the oceanic crust consumes sulfate and nitrate but releases ammonium to the vented waters. This method works for both spring and pore waters provided the pore waters are upwelling at speeds in excess of several centimeters per year [Wheat and Mottl, 2000]. Several centimeters per year is required in the Bares region for the advective flux from basement to dominate reactive fluxes from diagenesis in the sediment section; required minimum upwelling speeds may be faster or slower in other areas depending on the sediment composition and thermal gradient.

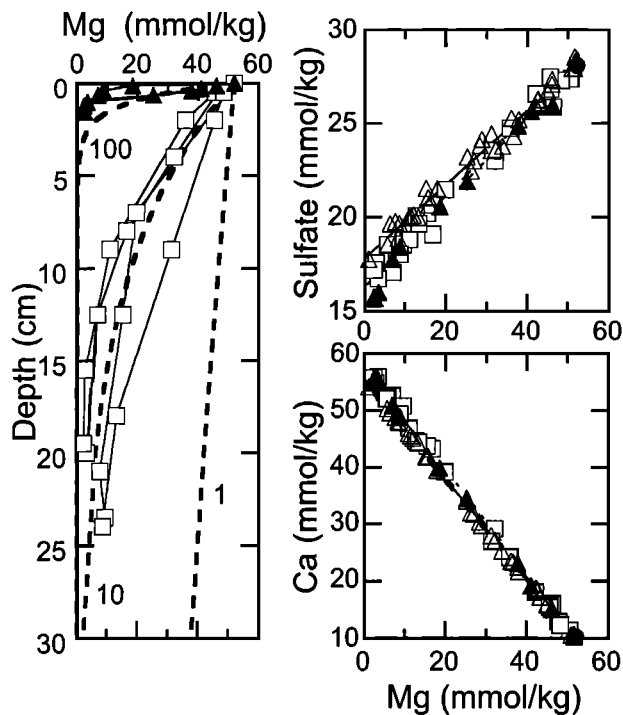


Figure 2. Estimates of pore water velocities and the composition of basement fluids. Systematic variations in pore water profiles of Mg are used to determine pore water velocities from calculated profiles (dashed lines). Numbers next to the dashed lines are upwelling speeds in centimeters per year. Cores from the southern side of Mama Bare (open squares) have upwelling speeds of several to tens of centimeters per year. Pore waters that upwelled at speeds of hundreds of centimeters per year were collected on the northern side of Mama Bare (triangles). The composition of the fluid in basement can be estimated from the asymptotic concentration at depth; however, this method is subject to error from subsurface mixture with bottom seawater or pore fluids. Instead, we determined the composition of the fluid in basement by extrapolating the linear mixing line defined by the data to the y intercept (depleted Mg for the examples shown). Lines shown in plots of Ca versus Mg and sulfate versus Mg represent the best fit to the data; Baby Bare springs (open triangles), southern side of Mama Bare (open squares), northern side of Mama Bare (solid triangles), and bottom seawater (solid circle).

Therefore we can estimate reliably the composition of basement fluids where springs are absent or have yet to be located and where pore water chemical profiles can be collected from zones of fluid upflow.

The second method that we employed to calculate the composition of basement fluids is based on extrapolating the systematic variations in chemical profiles from sediment pore waters to a concentration at the sediment-basaltic basement interface (Figure 2). Although this method provides a good estimate, the error in this estimate is larger than the error based on the first method above. The larger error results from basement fluids mixing with bottom and/or "normal" pore waters that have been altered by diagenetic processes as the fluid ascends. Thus the asymptotic concentration will reflect

the mixture of basement fluid with bottom seawater or normal pore waters.

Chemical data from pore and spring waters from the four locations along the 3.5-m.y.-old ridge were used to calculate the composition of basement fluids using the first method described above (Table 1). These results indicate a trend with more altered fluids to the north (Figure 3). For example, within the range of error, concentrations of Ca and Sr increase monotonically from south to north, while concentrations of sulfate decrease along this transect. Similar trends are apparent in chlorinity, K, and ammonium concentration and in the Na/chlorinity ratio. Concentrations of Li and Rb generally increase to the north but are still at concentrations below that of bottom seawater.

The trend of greater alteration of basement fluids from south to north along the 3.5-m.y.-old ridge with the more altered basement fluid to the north of Baby Bare is similar to that observed along the ODP transect to the west [Davis *et al.*, 1997a; Elderfield *et al.*, 1999]. Basement fluids along the ODP transect are cooler and generally less altered to the west, based on extrapolation of pore water thermal and chemical compositions near the sediment-basement interface. The increase in temperature to the east results from greater sediment thickness which acts to insulate and isolate the basaltic crust. The trend of increasing chemical alteration to the east results from reactions in basement at higher temperatures and, for some elements, from continued diffusive exchange between basement fluids and the overlying pore waters. The combination of these two transport processes (advection and diffusion) and the variety of ions and isotopes that are readily measurable in seawater provide constraints on hydrologic processes associated with hydrothermal transport through this ridge flank. In the discussion below, we use the composition of basement fluids to decipher the importance of these two transport mechanisms along the 3.5-m.y.-old ridge and to constrain the source of the basement fluids and the volumetric seawater flux along this ridge.

5. Discussion

5.1. Reaction in Basement

Wheat and Mottl [1994] suggested that one of the fundamental properties controlling the composition of basement fluids in ridge-flank hydrothermal settings is temperature. This hypothesis is based on (1) composition-temperature

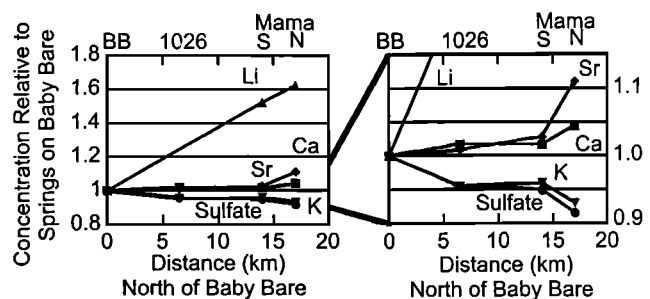


Figure 3. Concentration of basement fluids relative to those at Baby Bare are presented along a south-north transect that includes data from ODP 1026 and the southern (S) and northern (N) sides of Mama Bare. Chemical differences are greater than the errors or uncertainties in the measurements.

continuum for magnesium [Mottl and Wheat, 1994], phosphate [Wheat *et al.*, 1996a], and several major ions in seawater [Elderfield *et al.*, 1999], and (2) similarity in basement fluid composition at ODP Site 504 on the southern flank of the Costa Rica Rift and that along the 3.5-m.y.-old ridge. Both of these sites have about the same temperature in basement and composition of basement fluids, yet they have different crustal ages, sediment thicknesses and compositions, and geologic settings [Wheat and Mottl, 2000]. Another property that may control the composition of fluids in basement is the amount of time that seawater spends in basement. While this may be true in some cases, residence time does not appear to be a factor that controls the composition of basement fluids via water-rock reactions along the eastern flank of the Juan de Fuca Ridge. This conclusion is based on ^{14}C dating and observations of younger basement fluids being more altered than older fluids [Elderfield *et al.*, 1999]. Therefore one may infer that the more altered basement fluids to the north of Baby Bare result from a trend of increasing temperature to the north.

Some of the chemical data (e.g., Ca, Sr, Sr isotopes, Na/Cl, K; Table 1) are consistent with more alteration and warmer reaction temperatures to the north, yet there is no evidence for a warmer basement fluid to the north based on extrapolations of measured surficial heat flow [Davis *et al.*, 1997b]. This, however, does not preclude the possibility of fluids reacting deeper within the crust and thus at a warmer temperature. For example, pore waters from ODP Sites 1030/31 are much more altered than expected, based on measured surficial heat flow, temperature measurements made throughout the sediment section during drilling operations, and the composition-temperature continuum (Figure 4) [Davis *et al.*, 1997b]. Even

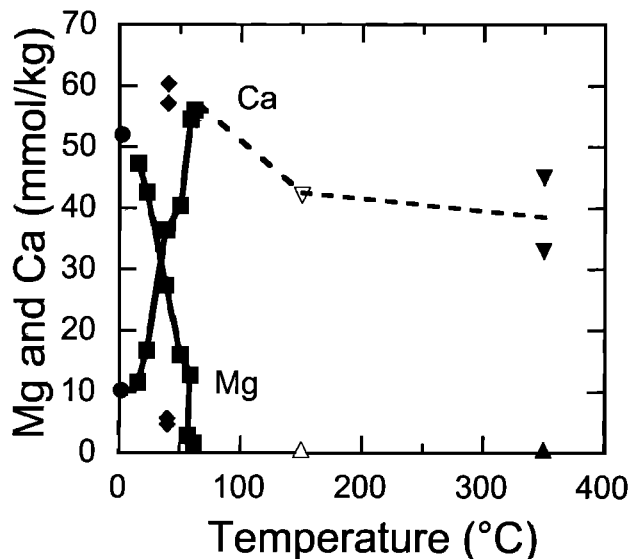


Figure 4. Mg and Ca in bottom seawater (circles), basement fluids (squares and diamonds), laboratory experiments (open triangles) [Seyfried and Bischoff, 1979], and high-temperature hydrothermal vents (solid triangles) [Von Damm, 1995] versus temperature. The two diamonds are from ODP Sites 1030/31. These data are not joined with the other basement fluid data because we believe that they were altered deeper within the crust at temperatures significantly above that estimated from pore waters near the sediment-basement interface. The high-temperature data reflect the range of values for a fluid with a chlorinity about that of bottom seawater.

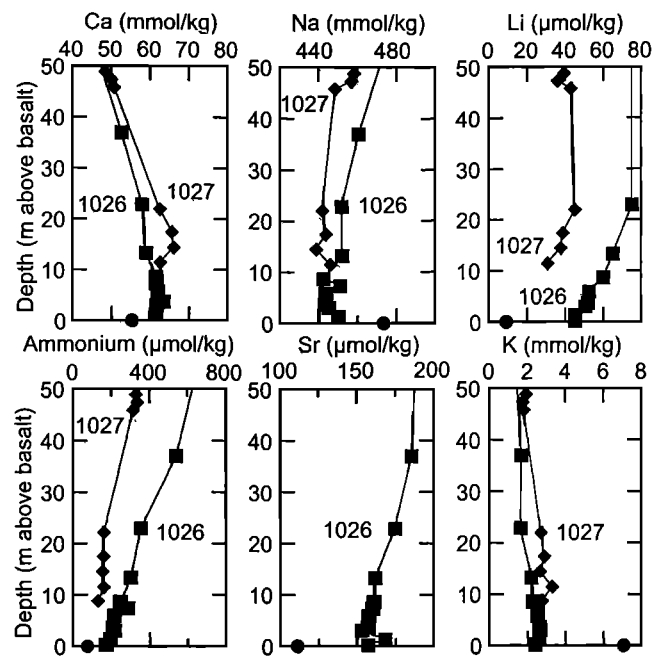


Figure 5. Pore water concentration-depth profiles for Ca, Na, Li, ammonium, Sr, and K in the bottom most 50 m of the sediment column for ODP Sites 1026 and 1027 [Davis *et al.*, 1997a; Mottl *et al.*, 2000]. Circles represent the value from the in situ samples from ODP Site 1026 or from springs on Baby Bare. Gradients presented in the text were determined from the bottom-most samples for Ca and Na and the general trend for Li, ammonium, and Sr. Note that the gradients from ODP Site 1027 accurately project to the expected composition in basement at the sediment-basalt interface, in contrast to the data from ODP Site 1026. Here, either the formation factor at the sediment-basement interface must be much larger than measured values, thus maintaining a uniform flux through out the bottommost sediment, or the well-mixed hydrological chemical basement is at least 10 m deep within the crust, consistent with the source depth of fluids that vented through the open borehole [Fisher *et al.*, 1997].

if fluids to the north reacted at higher temperatures, it is not clear if there would be a measurable impact on the composition given the composition-temperature continuum and an upper basement temperature of $\sim 64^\circ\text{C}$ (Figure 4).

Alternatively, the observed trend of the more altered fluids to the north could result from diffusive exchange between basement fluids and pore waters in the overlying sediment. For example, there is no evidence for the removal of sulfate in basement from reaction, only for the diffusive transport of sulfate from basement fluids to pore waters in the overlying sediment [Elderfield *et al.*, 1999]. A close inspection of the pore water data from ODP Sites 1026 and 1027 also supports a diffusive transport of Ca, Li, Sr, and ammonium into basement and Na and K out of basement (Figure 5), consistent with measured trends if basement fluids flow north along the ridge and diffusive fluxes are significant relative to advective fluxes. Thus reaction temperatures in basement cannot be the sole cause for the observed trends on the 3.5-m.y.-old ridge. Diffusive communication between the sediment and basement is required to account for some of these trends.

Table 2. Sulfate Systematics in the Basal Portion of the ODP Drill Sites

Site	Depth to Basalt, m	Dist, km	SO ₄ ²⁻ Base, mmol/kg	Npts	SO ₄ ²⁻ Grad, mmol/kg/m	Temp, °C	φ	FF	Flux
1023	192.8	22.4	24.9	6	0.70	15.5	0.55	4.0	8.7
1024	167.8	25.6	24.7	6	0.48	22.6 ^a	0.55	3.8	7.6
1025	97.5	33.6	26.6	5	0.30	39.6 ^a	0.65	3.2	6.4
1028	132.5	44.8	15.1	6	0.17	50.5	0.65	3.3	4.2
1029	220.1	54.8	18.3	7	0.20	58.7	0.55	6.5	3.3
1032	290.3	74.6	17.5	7	0.36	57.1	0.53	10	3.9
1026	228.9	101.1	14.7	6	0.19	64.6 ^a	0.55	6	3.6
1027	613.8	103.3	17.5	7	0.29	61.4 ^a	0.40	10	4.3

Bottom seawater has a SO₄²⁻ concentration of 28.0 mmol/kg. Dist is the distance of the site to the active ridge axis to the west. The concentration of sulfate in the basement fluid (base.; mmol/kg) is extrapolated in part from the sulfate gradient (Grad.; mmol/kg/m), which is determined from 5 to 7 samples (Npts) collected within 20 m of the sediment-basalt interface. Temperature (Temp), porosity (φ) and the formation factor (FF) are estimated from the deepest most samples [Davis *et al.*, 1997a]. Flux has units of 10⁻⁴ mmol sulfate cm⁻² yr⁻¹.

^aTemperatures are from borehole studies and differ from that estimated from extrapolation of temperature gradients in the sediment by <3°C [Davis *et al.*, 1997b; E. E. Davis and K. Becker, unpublished data, 1999].

5.2. Transport in Basement

Elderfield *et al.* [1999] illustrate the effects of diffusive communication of sulfate between basement fluids and the deepest sediment pore waters. Here we use a similar approach to show that the basement fluids along the ridge on which Baby and Mama Bares reside do not originate from the exposed basement 80 km to the west. We then use these results to extrapolate to the estimated source area of fluids in basement along the 3.5-m.y.-old ridge.

5.2.1. Transport across strike. Measurements of heat flow at the west end of the ODP transect suggest that seawater enters basement through the exposed basalt adjacent to the active ridge axis. This seawater then flows through basement towards the first buried ridge, 39 km east of the ridge axis. This ridge was penetrated by drilling ODP Sites 1030 and 1031 and is a site where pore waters seep from the seafloor at speeds of millimeters per year [Wheat and Mottl, 1994; Davis *et al.*, 1999] (Figure 1). Interpretations of pore water compositions (sulfate, chlorinity, and ¹⁴C) near basement are consistent with this direction of transport [Elderfield *et al.*, 1999]. Here we focus on one line of evidence, the sulfate data, to illustrate (1) that fluids in basement underlying the bares are not hydrologically connected to this across-strike transport and (2) that this across-strike transport is likely confined to the uppermost permeable layers of basement.

On the basis of sulfur isotopic data the only loss of sulfate from basement fluids is from diffusive transport into the overlying sediment [Elderfield *et al.*, 1999]. We consider the simple case for the inflow of bottom seawater into basaltic crust west of the ODP transect, with fluid advection to the east. Coupled to this advective transport is diffusive exchange of sulfate with the overlying sediment. This vertical diffusion can be idealized as [Berner, 1980]

$$\text{Flux}_{\text{diffusion}} = (D_s / (\phi_E \text{ FF})) \partial C / \partial z \quad (1)$$

where D_s is the sediment diffusion coefficient and is dependent on temperature [Li and Gregory, 1974], ϕ_E is the effective porosity defined by the extent of well-connected void space through which flow occurs, FF is the formation factor, and

$\partial C / \partial z$ is the sulfate gradient based on sediment pore waters from just above basement (Table 2 and Figure 6). With this model of transport and diffusive exchange we can calculate the amount of dissolved sulfate in a volume of crust for a cross-sectional area and estimate the change in concentration with time, assuming that basement fluids are well mixed:

$$C_t = (C_o \rho z \phi_E A - \text{Flux}_{\text{diffusion}} t A) / (\rho z \phi_E A) \quad (2)$$

$$C_t = C_o - \text{Flux}_{\text{diffusion}} t / (\rho z \phi_E) \quad (3)$$

where C_t is concentration (mol/kg) at time t , C_o is the initial concentration (mol/kg), $\text{Flux}_{\text{diffusion}}$ is from equation (1), ρ is the density of seawater, z is the depth of the well-mixed basaltic layer in which seawater convects, and A is a cross-sectional area (1 cm²). Thus there are three variables: the volume of water per area perpendicular to flow (depth times effective porosity), time (distance from the point of sediment cover divided by the specific discharge or Darcy velocity), and the diffusive flux. Given the estimated concentration for basement fluids from the ODP transect, diffusive fluxes from Table 2, and the distance from the ridge, a lateral specific discharge for the fluids in basement is calculated. We present several scenarios based on different depths of circulation and distance from the source with an effective porosity of 10%, an average sulfate flux of 7.9 mmol cm⁻² yr⁻¹ from ODP Sites 1023-1025 (Table 2), and a specific discharge of 1 m/yr [Davis *et al.*, 1999; Elderfield *et al.*, 1999] (Figure 7). These calculations are not sensitive to the distribution of the volumetric flux (depth times effective porosity). For example, the trend resulting from a depth of lateral transport of 300 m with an effective porosity of 10% is identical to the trend defined by a depth of 600 m with an effective porosity of 5%. Similarly, if specific discharge is increased, depth times effective porosity decreases proportionally. Four additional points stem from Figure 7:

1. The transect from ODP Sites 1023 to 1030/31 is the only section with a clearly defined difference between the measured and theoretical heat flow and the only section where the eastward flow of seawater in basement is indicated [Davis *et*

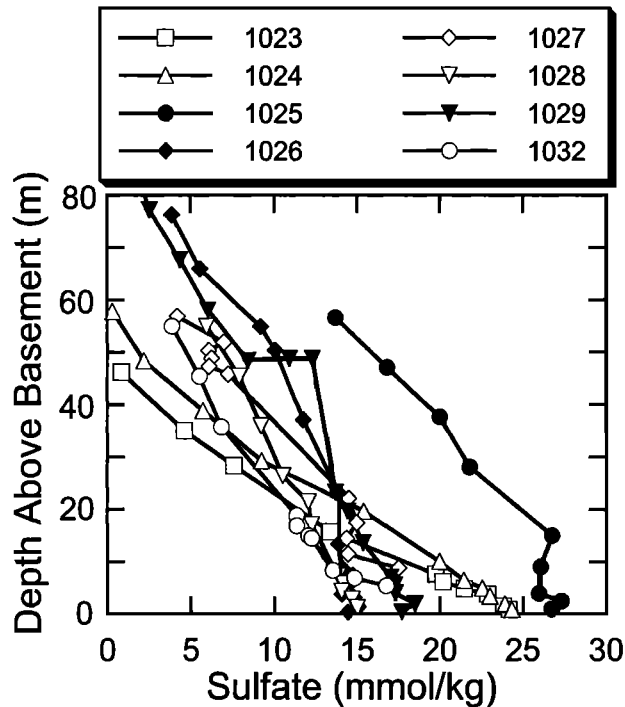


Figure 6. Concentrations of sulfate in pore fluids from the bottommost sediment sections of ODP Sites 1023-1032 excluding ODP Sites 1030/31.

et al., 1999]. If flow traverses the 20 km from the exposed outcrop at the western boundary of the ODP transect to ODP Site 1030/31 in $\sim 10,000$ years [Elderfield *et al.*, 1999], a specific discharge of 2 m/yr is required. Given this discharge, the best fit to the sulfate data in Figure 7 requires that the product of the depth of circulation multiplied by the effective porosity is 15 m. If the crustal section through which this fluid flows is 600 m thick, which is the depth of seismic layer 2A along this portion of the ODP transect [Rohr, 1994], then an effective porosity of 2.5% is required. A reasonable bulk porosity for the upper 150 m of basement is 11-14% with an average porosity of $\sim 10\%$ for a section of pillow lavas in a similar setting [Becker, 1985]. Because the effective porosity is less than the bulk porosity, a maximum effective porosity of 10% results in a minimum depth of 150 m for seawater circulation in homogeneous basement. A thicker section of crust is required if flow is predominately confined to thinner well-connected layers.

2. Davis *et al.* [1999] suggest that the heat flux from this portion of the ridge flank is ~ 3 MW for each kilometer along axis. If this heat is lost via advection along the buried ridge on which ODP Sites 1030/31 were drilled and where there is seepage through the sediment section [Wheat and Mottl, 1994; Giambalvo *et al.*, 2000], then the volumetric flux of seawater per centimeter of ridge axis is ~ 5.5 m³/yr for a seawater that is warmed by $\sim 40^\circ\text{C}$. This volumetric flux is an order of magnitude greater than the flux used to generate the best fit line in Figure 7; a volumetric flux this large with a specific discharge of 1 m/yr results in a calculated sulfate concentration that is only 2 mmol/kg less than the initial concentration even after the fluids have traversed the entire 83-km-long transect, in contrast to any of the chemical data. Given the order of magnitude difference in the chemical and thermal

parameters required to satisfy the data, either there is along-strike transport of seawater in basement in addition to the across-strike transport, or much of the heat and mass transport (and thus an associated chemical transport) occur through deeper sections in basaltic crust and are not connected to transport in the upper layer of the crust similar to the perceived transport at ODP Sites 1030/31 [Davis *et al.*, 1997].

3. Given a specific discharge of 2 m/yr, an effective porosity of 10%, a depth of circulation of 150 m, and the sulfate flux listed above, most of the sulfate in the basement fluid would be gone in 50,000 years, about 100 km from the input and about the location of the bares (same as the line listed as 300 m in Figure 7). Even if a lower sulfate flux were used that is more consistent with the data from drill holes east of ODP Sites 1030 and 1031 (3.5 mmol cm⁻² yr⁻¹), the calculated amount of sulfate in the basement fluids is 14.8 mmol/kg at the bares (dashed line in Figure 7), lower than the measured concentration of 17.8 mmol/kg. This calculation results in a basement fluid age of 42,000 years, much older than the estimated age of 4300 years from ¹⁴C data [Elderfield *et al.*, 1999]. To be consistent with the measured age, a specific discharge of at least 8 m/yr is required. A greater volumetric flux (i.e., a deeper depth of circulation or larger effective porosity) results in less of a chemical anomaly, in contrast to the sulfate data. Even if the basement fluids that vent at the bares were a mixture of this low sulfate fluid from the west and bottom seawater from an additional source, no more than three quarters of the basement fluid at the bares would come from the basaltic outcrop 83 km to the west. This ratio is an upper bound because it precludes the loss of sulfate from diffusion into the overlying sediment. Thus a source in addition to or other than exposed basement to the west is required to resupply basement fluids to the bares.

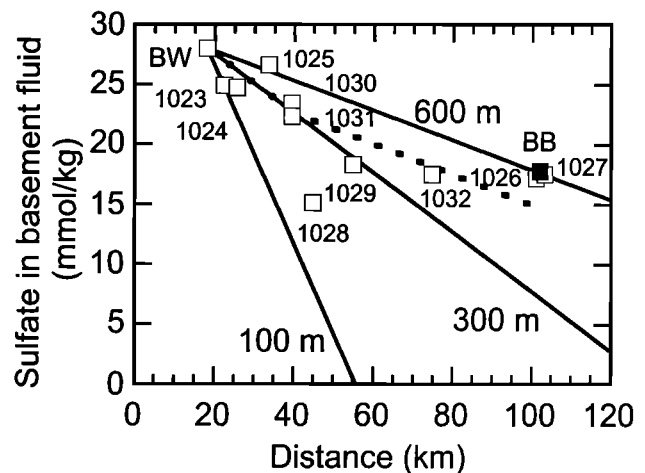


Figure 7. Concentration of sulfate in basement fluids (ODP Sites 1023 through 1032, Baby Bare (BB), and bottom seawater (BW)) based on gradients in sulfate near the sediment-basement interface are plotted versus distance from the active portion of the Juan de Fuca Ridge. Solid lines are determined using an effective porosity of 10%, a specific discharge of 1 m/yr, a sulfate flux of 7.9 mmol cm⁻² yr⁻¹, and the depth of circulation listed next to each line. The dashed line is based on the parameters above with a 300 m depth of circulation for the first 20 km of the transect and using a of 3.9 mmol cm⁻² yr⁻¹ for the remaining eastward portion of the transect.

4. The nonuniform nature of the sulfate concentration in basement fluids along the ODP transect, in contrast to many of the other major ions in seawater (e.g., Figure 3), suggests a complex pattern of seawater convection or compartmentalization of flow within the crust. For example, the anomalous low concentration of sulfate in basement at ODP Site 1028 suggests that continued flow to the east is minimal or negligible, since there is no evidence for sources of sulfate to basement fluids other than from recharge of bottom seawater [Elderfield *et al.*, 1999]. Thus seawater is transported across strike in the western portion of the transect and likely vents along the first buried ridge into which ODP Sites 1030/31 were drilled. An additional sulfate anomaly at ODP Site 1025 may reflect local recharge of bottom seawater, perhaps south of ODP Site 1030/31 where the ridge shoals and penetrates the sediment cover.

5.2.2. Transport along strike. If the basement fluids sampled along the 3.5-m.y.-old ridge did not originate from the exposed western boundary of the ODP transect, from where did the fluid originate? One possible source for seawater in basement is downwelling through the sediment in basement topographic troughs [e.g., Mottl, 1989]. Near the bares the sediment section is much thicker than 160 m, which is the thickness at which hydrothermally driven advection of pore water through the sediment section ceases in this area [Wheat and Mottl, 1994]. In addition, if downwelling through the sediment did occur, then sulfate reduction in the sediment section would greatly lower the sulfate concentration in the basement fluid, in contrast to the data (Table 1).

Basement fluids at the bares require an input that avoids reaction with sediment, most likely faults and/or outcrops. Neither of these features have been or are likely to be found to the east or north of the bares given the thick sediment cover. We have shown that small basaltic outcrops, such as Baby Bare, serve as crustal hydrothermal ventilators. It is possible that basaltic outcrops could also be sites of seawater recharge, but there are no thermal or chemical data to confirm significant recharge at Baby Bare. Similarly, basement fluids vent from Mama Bare. The recharge of seawater into Mama Bare cannot be ruled out because few measurements have been made on and around the outcrop, but significant recharge of seawater appears unlikely since there is no heat flow depression.

One possible source for recharge of basement fluids are two large (up to 4 km in diameter) basaltic outcrops about 40 km to the south, one of which apparently lies on the same ridge as the bares. Given an age of 5000 years for the basement fluid at ODP Site 1026, consistent with a ^{14}C age of 4300 [Elderfield *et al.*, 1999], a specific discharge of 8 m/yr is required if basement fluids enter one of the basaltic outcrops to the south. If we allow this flow to occur in the upper 300 m of basement with an effective porosity of 2.5%, a sulfate flux of $15 \text{ mmol cm}^{-2} \text{ yr}^{-1}$ is required to match the data. This flux is greater than the measured values along the ODP transect but is not unreasonable. If we use these same physical parameters and a flux of $4 \text{ mmol sulfate cm}^{-2} \text{ yr}^{-1}$, consistent with the results from ODP Sites 1026 and 1027, then a change of $1 \text{ mmol sulfate/kg}$ is calculated for the time required for basement fluids to flow from Baby Bare to the northern side of Mama Bare. This concentration is similar to the observed difference in sulfate ($1.5 \pm 0.4 \text{ mmol sulfate/kg}$). A better fit to the data requires a lower volumetric flux; however, as we will show below, the trend for other chemical species is consistent with this volumetric flux.

Concentrations of Ca, Sr, Li, Rb, and ammonium increase along the ridge to the north whereas concentrations of Na (Na/chlorinity) and K and $^{87}\text{Sr}/^{86}\text{Sr}$ decrease along this trend (Table 1). Of these chemical species the observed trend in Ca, Na, and Li can be accounted for solely by diffusive exchange, based on the approach shown above in equations (1)-(3) and chemical fluxes determined from pore water gradients, which is not easily achieved here. For example, in the basal sediments of ODP Sites 1026 and 1027, reactions occur that release Ca yet consume Na and K (Figure 5). Given a Ca flux of $12 \times 10^{-4} \text{ mmol cm}^{-2} \text{ yr}^{-1}$, which is the average from Site 1026 and 1027, and the flow conditions in the previous calculation, a gain of 2.9 mmol Ca/kg is calculated for basement fluids that flow from Baby Bare to the northern side of Mama Bare, essentially that measured ($2.5 \pm 0.9 \text{ mmol Ca/kg}$). A similar result exists for Na which has a flux of $60 \times 10^{-4} \text{ mmol/cm}^2 \text{ yr}^{-1}$ from the basement. The calculated loss is 14 mmol Na/kg relative to a measured difference of $7 \pm 2 \text{ mmol Na/kg}$. Last, a Li flux of $30 \times 10^{-4} \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ results in a gain of $7 \mu\text{mol Li/kg}$ compared with a measured difference of $6 \pm 1 \mu\text{mol Li/kg}$. In Figure 8 we present a range of these types of calculations to determine the change in concentration along this transect if the specific discharge is 8 m/yr. Note that larger or smaller values for effective porosity times depth of penetration are not consistent with the measured data.

The case for the other chemical tracers (Sr, Rb, ammonium, K, and $^{87}\text{Sr}/^{86}\text{Sr}$) is less certain because of known sampling artifacts, the lack of a definitive gradient, or likely reactions in basement. These tracers do, however, provide both an example of consumption in basement and the release from basement. For example, there is a clear flux of ammonium from the sediment pore waters to basement fluids (Figure 5). Using an average flux of $250 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$, based on data from ODP Sites 1026 and 1027, the calculated gain during transport from Baby Bare to the northern side of Mama Bare is $60 \mu\text{mol/kg}$. This gain is at the high end for the range in the measured difference ($34 \pm 30 \mu\text{mol/kg}$). Ammonium is likely consumed in basaltic basement either during exchange reactions with secondary clays or possibly by microbially mediated processes. In contrast, basement fluids require a source of Sr from basaltic basement even though there is a diffusive flux of Sr into basement. Given a diffusive flux of

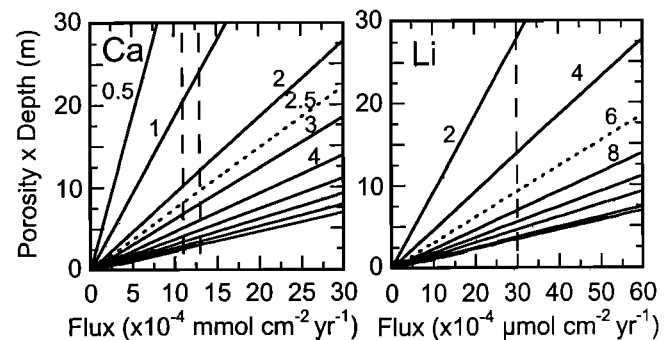


Figure 8. Calculated changes in concentration along the transect between Baby Bare and the northern side of Mama Bare for a specific discharge of 8 m/yr and a range of diffusive fluxes to basement and length scales (effective porosity multiplied by the depth of circulation). Dashed vertical lines are measured fluxes. Measured chemical changes are $2.5 \pm 0.9 \text{ mmol Ca/kg}$ and $6 \pm 1 \mu\text{mol Li/kg}$ (dotted lines).

0.9 $\mu\text{mol Sr cm}^{-2} \text{ yr}^{-1}$, a gain of only 3 $\mu\text{mol/kg}$ is calculated, compared to a measured difference of $12 \pm 4 \mu\text{mol/kg}$. The "extra" Sr likely results from reaction in basement, consistent with the decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio toward the north.

This technique of using the extent of diffusive exchange between the sediment and basaltic basement to infer hydrologic parameters works well along the 3.5-m.y.-old ridge. The same techniques were used to determine the source of basement fluid in the Mariana Mounds [Wheat and McDuff, 1995]. Common features in both settings are the lack of a significant flux from water-rock reactions in basement and a small difference in temperature along the flow path. In contrast, the ODP transect spans a relatively large range of crustal temperatures (almost 50°C). Here, the composition of basement fluids responds to temperature, resulting in vastly different compositions that for the most part are not affected by diffusive communication with the overlying sediment.

Diffusive exchange, in contrast to water-rock reactions in basement, provides a mechanism to constrain several hydrologic parameters in basement. In the exercise above, a depth of 300 m for seawater convection, a 2.5% effective porosity, and a specific discharge of 8 m/yr fit the data from the 3.5-m.y.-old ridge. These parameters produce a volumetric fluid flux of about 2 dm^3/s for each kilometer of length. This is about the volumetric flux from ODP Site 1026 (1.4 to 2 dm^3/s) [Fisher et al., 1997] when it was open to the seafloor and at the low end of the flux from Baby Bare (4 to 13 dm^3/s) [Wheat et al., 1996b; Mottl et al., 1998], suggesting that along-strike flow need not be confined to the ridge itself but could be a large-scale phenomenon.

6. Summary and Conclusions

The composition of pore, spring, and basement fluids helps to constrain hydrologic parameters within the oceanic crust, such as the source and volumetric flux of basement fluids. While across-strike flow is consistent with the chemical composition of basement fluids for the segment of crust to the first buried ridge into which ODP Sites 1030/31 were drilled, along-strike flow is required to explain the basement fluid compositions to the east of this first buried ridge. One similarity between the flow from the east to the west and flow from the south to the north is that basaltic ridges and outcrops provide a means to ventilate basement fluids. Although these two linear transects could be modeled using two independent two-dimensional models, the complex structure of permeability in basement requires a better understanding of this structure in three dimensions before the hydrology of the ridge flank can be assessed.

We conclude that a combination of reaction temperature and diffusive exchange with the overlying sediment controls the composition of basement fluids in this setting. Depending on the global significance of diffusive exchange, it may be an important process for some elemental budgets. Before quantitative budgets can be determined, however, the paths, patterns, and distribution of seawater convection in the oceanic crust must be constrained. The data presented herein provide some insights on seawater convection through the oceanic crust, but additional data are required to address the effects of basement roughness and of the permeability structure of the upper basaltic basement on paths of seawater circulation.

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