21. INTERSTITIAL WATER CHEMISTRY OF DEEP SEA DRILLING PROJECT SITE 503 AND ITS IMPLICATIONS FOR SUBMARINE HYDROTHERMAL CIRCULATION¹

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INTRODUCTION

Recent discoveries relating to the circulation of fluids within the oceanic crust include the finding of both important fluxes of elements and isotopes into the oceans by ridge-crest hydrothermal convection and important fluxes of heat out of the oceanic crust by convection at ridge crests and at some distance from ridge crests. In the present chapter, I present isotopic, chemical, and physical data from sediments and pore waters of Deep Sea Drilling Project (DSDP) Holes 503A and 503B. These results are modeled in terms of pore-water diffusion, advection, and production to ascertain the relative contribution of these processes at this location, 7.5 m.y. removed from ridge-crest hydrothermal activity. The observations made here contribute to the understanding of chemical and heat transport in oceanic crust of moderate age.

METHODS

Pore waters were extracted and analyzed by the methods of Gieskes (1974). Samples from Hole 503B were squeezed on board ship, but, because of time constraints, samples from Hole 503A were not squeezed until the cores were returned to the repository. Evaporation of these samples, determined by Cl-titration, was less than 1%. Analyses of oxygen isotopes from the pore waters followed the methods of Epstein and Mayeda (1953); duplicate samples were determined within $\pm 0.03\%$. The solid chemical analyses are adaptations of those of Donnelly and Wallace (1976a, 1976b): the sediments were dried at 110°C, weighed, fluxed with lithium metaborate-tetraborate, and dissolved in dilute sulfuric acid. These solutions were analyzed by colorimetric methods for Si, Al, Ti, Fe, P, and Mn and by atomic absorption for Na, K, and Mg. The chemical compositions were corrected for the presence of pore water salts by the titration of chloride on a separate weighed and dried sample dissolved in 50 ml of warm water. The pore water correction is only significant for Mg, Sr, and Na. Carbonate content was determined indirectly by leaching a separate portion of the sample in an acetitc acid-sodium acetate solution of pH = 5.5, titrating the dissolved Ca^{2+} , and calculating it as $CaCO_3$. This solution was also analyzed for Sr^{2+} by atomic absorption. Ca, Ba, S, and H₂O were not determined on the total sediment and represent the chief components not measured.

Formation factors were determined by measuring resistivity with a probe on the same core sections which were squeezed (but not on the same samples). The method of measurement is described by Manheim and Waterman (1974). Porosities were measured on those samples for which resistivities were measured; they were determined from water content and grain densities, the latter calculated on the basis of the mineralogical analyses. These values were corrected for salt content.

RESULTS

The chemical and isotopic data are presented in Tables 1 and 2 for solids and pore waters, respectively. Table 3 presents data on the formation factor and porosity.

The solid chemistry will not be discussed in detail. The trends are for carbonate content to increase with depth, and silica content to decrease. Likewise, magnesium, titanium, aluminum, iron, sodium, potassium, and phosphorous contents also decrease with depth. The ratio of Sr/Ca in the acetic acid leach (Table 1) remains fairly constant throughout the section at about 2×10^{-3} moles/mole. This value demonstrates that there has been very little carbonate recrystallization, a process which would lower the Sr/Ca ratio toward its equilibrium value (under these conditions) of about 0.5 $\times 10^{-3}$ moles/mole (Baker et al., in preparation).

The oxygen isotope values and Sr²⁺/Cl- ratios of pore waters are shown in Figure 1. There is a 1‰ decrease in δ^{18} O and a 25% increase in Sr²⁺ with depth. It can also be seen that Sr^{2+} values differ in the two holes. despite their being geographically separated by only about 100 meters. Figure 2 shows that Mg²⁺/Cl⁻ decreases by 10% with depth over the same interval in which Ca²⁺/Cl⁻ increases by 30%. These values contrast with those from nearby Site 83 (Sayles et al., 1972), which showed no significant change in pore water Ca2+, Mg2+, or Sr2+, from near-surface sediments to nearbasement. Other significant observations from Table 2 include a limited amount of SO42- reduction (also seen by Sayles et al., 1972); high values of dissolved silica as expected for diatom-rich sediments with only slight opal-A to opal-CT recrystallization present; and a decrease in PO_4^{2-} with depth (especially in carbonates) in the four samples analyzed for this constituent.

PORE WATER MODEL CALCULATIONS

As a result of the observed magnitudes and curvatures of the pore water chemical and isotope profiles, the following questions were raised: (1) What would be the shape of the concentration profile if the solutes were conservative and affected only by the processes of reaction with basaltic basement "diffusion" and advection resulting from sediment compaction? (2) What would be the predicted shape of the concentration profile if we imposed an external advective movement of pore waters such as the input of hydrothermal fluids originating in the underlying basement? (3) Can the profiles be explained by production in the sediment column and diffusion, without advection?

To solve the first problem, the algorithm of McDuff and Gieskes (1976) was used. We assume for the procedure a stable and conservative tracer, steady-state diffusion, and a nonconstant diffusion coefficient. The vari-

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Sample (interval in cm)	Depth (m)	SiO ₂	CaCO3	Al2O3	TiO ₂	Fe2O3	MnO ₂	Na ₂ O	K20	MgO	P205	Molar × 10 ³ Sr/Ca Acid Soluble
Hole 503B		-			-		-	-				
1-2.0-10	2	30.3	30.7	4.68	0.106	5 34	1.16	3.83	0.90	1.82	0.39	1.93
3-2, 140-150	10	21.5	54.9	3.27	0.088	3.20	0.50	2.61	0.72	1.51	0.21	1.91
5-2, 140-150	19	36.2	24.5	4.74	0.085	4.53	1.00	11.44	1.12	2.62	0.37	1.60
7-2, 140-150	28	38.1	17.5	5.16	0.094	5.21	0.73	4.18	0.83	2.88	0.33	2.02
10-2, 140-150	41	27.9	29.5	3.75	0.051	3.58	0.79	5.86	0.96	2.13	0.27	1.82
11-2, 140-150	45	29.7	39.4	3.27	0.062	3.10	0.72	4.02	0.78	2.15	0.20	1.71
13-2, 140-150	54	26.7	37.0	2.92	0.048	2.00	6.98	4.81	0.84	1.92	0.26	1.76
15-2, 140-150	63	31.9	29.5	4.23	0.066	3.29	0.77	3.64	1.07	2.57	0.27	1.78
17-2, 140-150	72	34.4	33.4	3.89	0.055	2.50	1.67	3.58	0.91	2.32	0.24	2.01
19-2, 140-150	81	29.5	36.0	3.25	0.048	2.41	2.20	3.65	0.85	2.08	0.24	1.73
21-2, 140-150	89	13.2	41.7	3.67	0.060	2.50	0.56	3.56	0.87	1.95	0.24	1.85
24-2, 140-150	102	12.6	61.0	2.06	0.038	1.42	0.52	2.17	0.46	1.18	0.18	2.13
Hole 503A												
24-2, 80-85	101	17.1	71.2	1.47	0.024	0.71	1.06	2.01	0.27	2.99	0.15	2.07
Hole 503B												
26-2, 180-150	111	21.6	75.8	1.12	0.005	0.65	0.68	1.53	0.24	0.42	0.10	2.04
Hole 503A												
29-2, 85-90	123	23.4	62.9	1.53	0.021	0.85	0.70	1.49	0.24	0.59	0.10	2.09
31-2, 125-130	131	20.7	62.0	1.92	0.037	1.32	0.95	1.87	0.32	0.87	0.13	2.07
34-2, 40-45	145	17.7	70.9	1.20	0.024	0.74	1.13	2.22	0.18	0.53	0.12	2.03
39-2, 85-90	167	24.9	-	1.33	0.070	1.44	0.59	1.59	0.26	0.86	0.11	
44-2, 115-120	189	37.1	51.0	1.06	0.005	0.77	0.45	1.49	0.15	0.48	0.11	1.74
48-2, 115-120	206	19.9	70.4	0.77	0.005	0.75	0.55	1.22	0.16	0.75	0.09	2.00
50-2, 115-120	215	22.6	65.6	1.14	0.009	0.86	0.73	1.92	0.27	0.72	0.06	1.84
54-2, 127-132	233	29.9	61.0	0.72	0.009	0.50	0.63	1.41	0.12	0.52	0.06	1.88

Table 1. Chemistry of Site 503 solids.

Notes: Concentrations are in weight percent (except Sr/Ca). Important phases not determined include H2O, Ba (present as barite), and CaO (present as plagioclase feldspar). Concentrations of Na2O, K2O, MgO, and Sr/Ca are all salt-corrected. The last column contains the molar ratio of Sr/Ca in the acid-soluble fraction of the total sediment.

Table 2. Chemistry of Site 503 pore waters.

Sample (core/section)	Depth (m)	CI- (mM)	Ca ²⁺ (mM)	Mg ²⁺ (mM)	Sr ²⁺ (mM)	SO4 ^{2 -} (mM)	РО4 ³⁻ (µМ)	H4SiO4 (mM)	δ ¹⁸ O‰ (SMOW)
Hole 503B									
1-2	2	561	11.05	52.47	0.102	23.4		0.902	0.23
3-2	10	561	11.61	50.89	0.110	23.6	1.8	0.909	0.19
5-2	19	563	12.58	50.35	0.116	25.0		0.924	0.08
7-2	28	563	12.98	49.52	0.120	24.0		0.993	0.22
10-2	41	562	13.22	49.41	0.121	22.4		0.932	-0.04
11-2	45	560	13.44	49.06	0.124	20.6		1.065	0.03
13-2	54	-	-	-	-	21.4		1.000	-
15-2	63	566	13.86	49.15	0.126	21.4		1.048	-0.23
17-2	72	560	13.44	48.81	0.126	21.4	0.8	0.968	-0.31
19-2	81	557	13.92	49.43	0.126	21.4		1.028	-0.28
21-2	89	559	14.15	49.12	0.128	20.6	-	1.035	-0.47
24-2	102	566	13.56	48.35	0.128	20.6	-	1.073	
Hole 503A									
24-2	101	567	13.71	49.81	0.120	19.8	-	0.934	-0.46
Hole 503B									
26-2	111	555	13.97	48.45	0.126	21.4	-	1.084	-0.51
Hole 503A									
29-2	123	573	14.01	50.87	0.124	26.0		0.998	-0.32
31-2	131	565	15.90	50.59	0.120	29.0	-	0.976	-0.35
34-2	145	567	14.93	50.20	0.122	26.8		1.115	-0.58
39-2	167	565	14.78	50.44	0.122	25.8	0.6	1.126	-0.61
44-2	189	567	15.78	49.86	0.116	25.8	-	1.010	-0.69
48-2	206	563	14.99	49.21	0.119	29.6		0.845	-0.57
50-2	215	566	15.67	50.23	0.116	24.0		0.872	-0.69
54-2	233	571	15.31	49.31	0.116		0.0	1.179	-0.69

Note: The last column contains the oxygen isotope values of these waters.

ation of the diffusion coefficient is determined from the measurement of electrical resistivity and porosity as shown by the following relationship:

$$D_b = D_x/(pF),$$

where D_b and D_x are, respectively, the bulk and pore water diffusion coefficients (units of cm²/s); p is the fractional porosity (dimensionless); and F is the formation factor (dimensionless). The validity of this procedure has recently been demonstrated by McDuff and Ellis (1979). The log F versus log p relationship mea-

Table 3.	The	formation	factors	and	salt-corrected	po-
rositie	es of	Site 503 sa	amples.			

Sample (core/section)	Depth (m)	Formation Factor	Porosity (salt-corrected)
Hole 503B			
1-2	2	1.24	87.1
3-2	10	1.44	86.3
5-2	19	1.20	92.8
7-2	28	1.24	93.0
10-2	41		87.9
11-2	45	1.17	90.6
13-2	54	1.56	86.7
15-2	63	1.29	89.9
17-2	72	1.26	89.4
19-2	81	1.22	88.7
21-2	89	1.40	86.6
24-2	102	1.44	89.9
Hole 503A			
24-2	101	1.53	85.8
Hole 503B			
26-2	111	1.62	78.9
Hole 503A			
29-2	123	1.62	80.3
31-2	131	1.42	82.9
34-2	145	1.48	81.6
39-2	167	1.50	85.7
44-2	189	1.77	78.8
48-2	206	1.74	76.3
50-2	215	1.84	78.4
54-2	233	1.75	80.3

sured for these sediments is shown in Figure 3. The best fit to these data produced the equation:

$$F = 1.03 p^{-2.11}$$
.



Figure 1. Pore water oxygen isotope composition and molar concentration of Sr²⁺/Cl⁻.



Figure 2. Pore water molar concentrations of Mg^{2+}/Cl^{-} and Ca^{2+}/Cl^{-} .

Because the porosities are so high (see also Mayer, this volume), it is immediately evident that D_b will not vary greatly from its value in seawater at the relevant temperature. The parameters employed in the calculation are described by McDuff and Gieskes (1976). The particular



Figure 3. Log-log plot of the measured formation factors, F, against the measured porosities, p.

Table 4. Parameters used in the calculations following the algorithm of McDuff and Gieskes (1976). Also shown are the outputs in reduced concentration units for two different initial sedimentation rates.

	Output						
	Depth	$S_0 = 3.2 \text{ cm}/10^3 \text{ yr}.$	$S_0 = 1.5 \text{ cm}/10^3 \text{ yr}$				
Input Parameters	(m)	$(C - C_0)/(C_b - C_0)$	$(C - C_0)/(C_b - C_0)$				
Input parameters	0	0.000	0.000				
Depths, x, in meters	22	0.086	0.091				
Basement depth, $x_h = 240 \text{ m}$	44	0.172	0.182				
Potosity, $p = 0.9081 - 0.0005X$	65	0.259	0.272				
Formation factor, $f = 1.03p^{-2.11}$	87	0.347	0.362				
Initial sedimentation rate, So	109	0.436	0.452				
Pore water diffusion coefficient at $X = 0$.	131	0.526	0.542				
$D_{\rm x0} = 4 \times 10^{-6} {\rm cm}^2 {\rm s}^{-1}$	153	0.617	0.633				
Pore water diffusion coefficient.	175	0.710	0.723				
$D_{\mathbf{x}} = (1 + f \tau f \mathbf{p} \mathbf{x}) D_{\mathbf{x}} \mathbf{p}$	196	0.805	0.815				
Geothermal gradient, $f_T = 0.05 ^{\circ}\text{C m}^{-1}$	218	0.902	0.907				
Thermal coefficient of diffusivity $f_D = 0.04 ^\circ \text{C}^{-1}$	240	1.000	1.000				

values chosen for Site 503 are listed in Table 4. Initial sedimentation rates of both 1.5 and 3.2 cm/1000 yr. (the range of sedimentation rates at the site) were tried, but the choice of sedimentation rate has no significant effect upon the model profiles.

Before calculating the concentration profile, it is wise to verify that the model of steady state holds (given our assumptions). This calculation again follows the derivation of McDuff and Gleskes (1976). Assuming an initial sedimentation rate of 3.2 cm/1000 yr., a bulk diffusion coefficient of 4×10^{-6} cm²/s, appropriate for the diffusion of Mg²⁺, Ca²⁺, and Sr²⁺ at *in situ* temperatures (Li and Gregory, 1974), one can calculate the time to reach steady state. For an initial perturbation of concentration, in a 240-meter-long section, this time is about 2.2×10^{6} yr., clearly less than the age of the basement sediment. A higher diffusion coefficient, as would be more appropriate for the diffusion of ¹⁸O in H₂O (Wang et al., 1953), results in a shorter time. Thus, the steady-state assumption seems to be valid for the major cations and ¹⁸O.

The results of the calculation are shown in Figure 4. Neither the effect of a nonconstant diffusion coefficient nor variation of the sedimentation rate are important considerations at this site. The generated concentration profiles do not explain the curvature observed for all major constituents.

Next, the equation for diffusion (with a constant coefficient and constant porosity) plus advection (w), but without production, was solved:

$$D \frac{d^2c}{dx^2} - w \frac{dc}{dx} = 0,$$

where c refers to concentration and x is depth below the seawater/sediment interface.

The boundary conditions were:

at
$$x = 0$$
, $c = 0$,



Figure 4. Calculated normalized Ca^{2+} concentration profiles for the model without advection or production, along with a line representing the trend of the observed concentration profile (labeled Ca^{2+}/Cl^{-}). (The profiles were calculated for two different sedimentation rates, S_o , of 1.5 and 3.2 cm/1000 yr.)

at
$$x = x_b$$
, $c = c_b = 1$,

where subscript b refers to the sediment/basement interface (or any other chosen depth in the sediment column). The solution to the equation is:

$$c = \frac{c}{c_b} = \frac{(\exp(wx/D) - 1)}{(\exp(wx_b/D) - 1)}$$

Several examples of the solution of this equation for Ca^{2+} , Mg^{2+} , or Sr^{2+} (all ions with $D = 4 \times 10^{-6} \text{ cm}^2/\text{s}$) are shown in Figure 5. The equation was fit to data from Hole 503B alone, because this provided a more coherent data set, and the two holes have different concentrations for most elements. The best fit is achieved for an advection of -15 (\pm about 2) $\times 10^{-10}$ cm/s, that is, an upward advection of about 47 (\pm 6) cm/1000 yr.

The rate of diffusion of ¹⁸O in sedimentary pore waters is not known, but by assuming that the advective term (-15×10^{-10}) is correct, the diffusion coefficient can be determined. Ignoring temperature dependence of the diffusion coefficient, the best fit to the observed data, Figure 6, was obtained with a constant diffusion coefficient of roughly 15×10^{-6} cm²/s. Unfortunately, the scatter is fairly large due to combining errors in the measurements of C_0 , C_b , and C_x . There is also significant variability outside this scatter. The self-diffusion of pure water using H₂¹⁸O as a tracer (Wang et al., 1953) corrected by the formation factor and the average tem-



Figure 5. Calculated normalized Ca²⁺ concentration profile for the model, assuming a constant diffusion coefficient with advection. (The observed normalized Ca²⁺ data from Hole 503B are plotted as well. The three lines represent three different advective velocities.)



Figure 6. Calculated profile of pore water δ^{18} O for the model of advection with diffusion. (The advective velocity is assumed to be -15×10^{-10} cm/s, and the lines shown are profiles calculated for three different diffusion coefficients. Observed data from Hole 503B are shown for comparison.)

perature (8°C) yields a value of about 15×10^{-6} cm²/s. In this work, the value of 15×10^{-6} cm²/s has been used.

Finally, the equation for diffusion (with a constant coefficient and constant porosity) and constant production (J), but without advection

$$D\frac{d^2c}{dx^2} + J = 0$$

can be solved for the boundary conditions:

at
$$x = 0$$
, $c = c_0$
at $x = x_b$, $c = c_b$

where subscript 0 refers to the bottom water value. The solution is:

$$c = \frac{J(x_b - x)x}{2D} + \frac{(c_b - c_0)x}{x_b} + c_0.$$

For Ca²⁺, a production of 4×10^{-19} mole/cm³s produces the concentration profile shown in Figure 7. This curve does not reproduce the observed curvature.

The same production equation can be solved for δ^{18} O by first separating the isotopes ¹⁶O and ¹⁸O into their absolute concentrations. The best fit to the observed data (from Holes 503A and 503B combined—a minimum



Figure 7. Calculated profile of Ca^{2+} concentrations for the model assuming a constant diffusion coefficient with production. (The observed data from Hole 503B are shown for comparison. The three lines represent three different production rates.)

value) is with a production of ¹⁸O of -8×10^{-21} moles/ cm³s. At Site 503, for every cm³ of water there is about 0.2 cm³ of sediment. After 7.5×10^6 years, the total production of ¹⁸O would be -19×10^{-7} moles. The most efficient reaction utilizing ¹⁸O during sediment diagenesis in the deep sea is probably the alteration of volcanic ash to smectite (Lawrence et al., 1979). If the sediment were initially 100% volcanic ash, and the ash is assumed to have an initial δ^{18} O of $+6\%_{\text{SMOW}}$, then the concentration of ¹⁸O in the ash is:

 c_{18O} ash = (0.075 mole oxygen/cm³ of ash) (0.2 cm³)

$$c_{18O} \text{ ash } = \left(\frac{\delta^{18O}}{1000} + 1\right) (2 \times 10^{-3} \text{ mole } {}^{18O}\text{/} \text{mole SMOW})$$

= 3.018 × 10⁻⁵ mole ${}^{18}\text{O}\text{/cm}^3$ pore water
(the ${}^{18}\text{O}$ abundance in SMOW is after
Craig. 1961).

Since smectite precipitated from cold seawater has a value of about $\delta O^{18} = +27\%_{0\text{SMOW}}$, ash totally altered to smectite would contain 3.081×10^{-5} moles O^{18}/cm^3 of pore water. These calculations assume an oxygen concentration of 0.075 moles/cm³ for both ash and smectite. We can compute the production assuming total alteration of 100% ash to smectite as:

$$3.018 \times 10^{-5} - 3.081 \times 10^{-5} = -6.3 \times 10^{-7} \text{ moles/cm}^3$$
,

less than the necessary consumption of ¹⁸O derived above. To make matters much worse, the actual amount

of ash observed in these sediments is a few percent at most, and it is not totally altered. Ash alteration or any other reaction in the sediment column can therefore be eliminated as the major cause of the observed ¹⁸O pro-file. This, of course, does not rule out a small amount of reaction in the sediment column.

A final simple but revealing calculation can be performed. From Fick's first law (e.g., Berner, 1980), the total flux of solute, *i*, across the sediment/basalt interface, $f_{b,i}$, is given by the diffusive plus the advective flux:

$$f_{b,i} = D \frac{dc_i}{dx} + c_b w$$

Approximating this equation:

$$f_{b,i} = D \frac{c_b - c_0}{x_b} + (c_b - c_0) w,$$

and assuming that $D = 15 \times 10^{-6}$ cm²/s, yields a total flux of ¹⁸O across the sediment/basalt interface of -22.0 $\times 10^{-17}$ moles/cm²s, more than three times the diffusive flux alone. After 7.5×10^6 years, this would result in a flux of -5.2×10^{-2} moles ¹⁸O/cm². Assuming a basalt porosity of 15% (after Lawrence et al., 1979), an original δ^{18} O of 6%_{SMOW}, and an oxygen concentration of 0.075 mole/cm³ of basalt, gives 1.283×10^{-4} moles ¹⁸O/cm³ of total volume of basalt. Low-temperature smectite of the same porosity would contain $1.309 \times$ 10⁻⁴ mole/cm³ of ¹⁸O. Complete alteration of basalt would yield -2.678×10^{-6} moles ¹⁸O for each cm³ of original porous basalt. Most deep-sea basalts are altered about 10% average (Muehlenbachs, 1977). This implies that about 1.9 km of basalt must be altered to be consistent with the observed flux of ¹⁸O through the sediment/basalt contact. The assumption of open-system reaction with respect to basalt and pore water ¹⁸O is justified on the basis of the heavy oxygen and strontium isotope compositions of the separated basalt alteration products and of diagenetic calcite veins (Muehlenbachs, 1977 and 1979; Kastner et al., 1980; Richardson et al., 1980). Closed-system reaction should lead to the precipitation of alteration products with substantially lighter isotopic ratios.

HYDROTHERMAL CIRCULATION

The data and calculations from Site 503 reveal that chemical convection is occuring at present. As determined above, for ¹⁸O the convective flux is about three times the diffusive flux. For Ca²⁺, Mg²⁺, and Sr²⁺, it is slightly more important. The advection of fluid is thermally driven and may exhibit the geometry of a cell. The data of Anderson et al. (1979) suggest that the lateral dimensions of such cells are on the order of 1–10 km. The present data indicate that Holes 503A and 503B, only 100 meters apart, may be located on different parts of such a cell: extrapolation of near-surface trends from Site 503B to greater depths indicates that Hole 503A is relatively depleted in Sr²⁺ and Ca²⁺ and enriched in Mg^{2+} and $\delta^{18}O$. Hole 503B, therefore, has a larger basement influence and probably more rapid upward fluid flow. Site 83 (located about 10-km southwestward), which showed constant concentrations throughout the section, may have been located in an area of recharge. In all these sites, it is conceivable that some lateral fluid movement may take place.

If chemical convective flux is greater than diffusive flux in sediments 7.5 m.y. old, it must be of increasing importance in younger crust. Only lack of representative sampling of sediments on young crust and lack of detailed sampling in such sections have thus far prevented similar identification of off-ridge convection at other sites. Mottl et al. (1980) have recently observed hydrothermal activity at Site 504 on the flank of the Costa Rica Rift (6.2 m.y. old).

Many recent studies of the chemical and isotopic composition of pore waters have identified the importance of alteration of basalt and of volcanic ash in controlling the major element fluxes in deep-sea sediments (e.g., Lawrence et al., 1975; Lawrence et al., 1979; Gieskes, in press; Lawrence and Gieskes, in press). McDuff and Gieskes (1976) modeled the Ca^{2+} and Mg^{2+} pore water concentrations of four DSDP sites and concluded that the location of the reactions which supported the gradients of these elements is close to (or below) the basalt/sediment interface.

The depth, degree, and conditions of basalt alteration are problems of interest because of their influence on the chemical and isotopic composition of seawater. It is now known that hydrothermal solutions escaping directly from ridge crests are relatively common phenomena (Galapagos, East Pacific Rise 21°N, TAG hydrothermal field on the Mid-Atlantic Ridge) and that the high-temperature interaction of circulating seawater with basalt may contribute important fluxes of many elements to the oceans (Edmond et al., 1979).

Global fluxes of elements resulting from hydrothermal activity were calculated by Edmond et al. (1979) on the following basis. An oceanic flux of ³He of 4 ± 1 atom/cm²s (Craig et al., 1975) was combined with the ³He-tranported heat correlation found for Galapagos hot water samples (Jenkins et al., 1978) to yield a convective hydrothermal heat flux (cal/yr.). The measured temperature dependence of the elements' concentrations in the Galapagos samples (moles/cal.) was multiplied by this heat flux to yield an element flux (moles/yr.). Using the measured value of $\delta^{18}O = +1.6\%_{SMOW}$ of Craig et al. (1980) for the high-temperature end-member of hydrothermal fluids from the East Pacific Rise 21°N, and assuming that the ambient seawater is about $\delta^{18}O =$ 0% SMOW, the hydrothermal convective flux of 18O can be calculated in a similar manner:

 $\Delta \text{ moles/l } ^{18}\text{O} = (\text{moles/l } ^{18}\text{O} \text{ in high T fluid}) \\ - (\text{moles/l } ^{18}\text{O} \text{ in low} \\ \text{T fluid}) \\ = 1.778 \times 10^{-4}$

 Δ moles/l Mg = -5.304 × 10⁻² (Edmond et al., 1979)

$$\frac{\Delta \text{ moles/l}^{18}\text{O}}{\Delta \text{ moles/l}^{18}\text{O}} = -3.351 \times 10^{-3}.$$

Using values from Edmond et al. (1979), the ¹⁸O-heat relationship becomes:

$$(-3.351 \times 10^{-3})(-154 \,\mu\text{mole/kcal.})$$

= 0.5161 μ mole/kcal.

This can be combined with their value for total convective heat to give:

$$(5.161 \times 10^{-10} \text{ mole/cal.}) (4.9 \times 10^{19} \text{ cal./yr.}) = 2.5 \times 10^{10} \text{ mole/yr.}$$

Thus, a production by hydrothermal convection of 2.5 $\times 10^{16}$ moles of ¹⁸O per million years is obtained by the methods of Edmond et al. (1979).

The present oceans are probably in a steady state with regard to δ^{18} O (Muehlenbachs and Clayton, 1976); hence input of ¹⁸O by hydrothermal sources must be matched by a similar output-the only comparable size sink being the low-temperature hydrothermal alteration of basalt. Muehlenbachs and Clayton (1976) assumed that 2.94 km²/yr. (Chase, 1972) of basalt is produced at ridge crests and subsequently altered by 10% to 600 meters depth at low temperature by reaction with seawater before being finally subducted. From the work of Gregory and Taylor (1981) on the Samail Ophiolite, it appears that low-temperature alteration of oceanic crust actually extends to depths of about 2 km sub-bottom. Thus, $(2.94 \text{ km}^2/\text{yr.}) (10^6 \text{ yr.}) (2 \text{ km}) (10^{15} \text{ cm}^3/\text{km}^3) =$ 5.88×10^{21} cm³ of rock is altered every million years. A 10% low-temperature open-system alteration of basalt to smectite would change the oxygen isotope composition of the bulk rock from about +5.7% smow to +8[%]_{SMOW} (Yeh and Savin, 1977), the average number found by Gregory and Taylor for upper crustal rocks of the ophiolite. Using an oxygen concentration in gabbros, basalts, and smectites of 0.08 moles/cm3 (Lawrence et al., 1979), the concentration of ¹⁸O in the fresh crustal rock and in the altered rock is:

$$c_{18_{O}}, \text{ fresh} = (0.08 \text{ mole/cm}^3) \\ (2 \times 10^{-3} \text{ mole} {}^{18}\text{O/mole} \\ \text{SMOW}) \\ \left(\frac{5.70}{1000} + 1\right) \\ = 1.6091 \times 10^{-4} \text{ moles} {}^{18}\text{O/cm}^3 \\ c_{18_{O}}, \text{ altered} = (0.08)(2 \times 10^{-3}) \left(\frac{8.00}{1000} + 1\right) \\ = 1.6128 \times 10^{-4} \text{ moles} {}^{18}\text{O/cm}^3$$

The difference between the two is the production of ¹⁸O due to low-temperature alteration of oceanic crust:

$$-3.7 \times 10^{-7}$$
 mole ¹⁸O/cm³ of altered rock,

and after 10^6 years, the total production of 18 O by alteration is:

$$-2.2 \times 10^{15}$$
 mole ¹⁸O.

Lawrence and Gieskes (in press) arrived at a production of ¹⁸O by low-temperature semiclosed-system alteration of -2.3×10^{15} mole ¹⁸O/10⁶ year on the basis of worldwide averaging of diffusive pore water fluxes alone.

The source of ¹⁸O supporting the flux into ocean water (and eventually back into altered basalt) is the high-temperature alteration of lower crustal rock, chiefly cumulate gabbro. In the Samail Ophiolite (Gregory and Taylor, 1981), high-temperature reaction with seawater extended throughout a 5.5 km vertical section from the paleo-Moho into the base of the sheeted dike complex, with the average offset in δ^{18} O from $+5.7\%_{\text{SMOW}}$ to about $+4.6\%_{\text{SMOW}}$. These values yield a total production of ¹⁸O from high-temperature alteration of oceanic crust of:

 1.74×10^{-7} mole ¹⁸O/cm³ of altered rock,

and after 10⁶ years the total production of ¹⁸O from alteration of 5.5 km of lower crust would be:

$$2.81 \times 10^{15}$$
 mole ¹⁸O/10⁶ yr.

As required by oceanic steady state, the major (hightemperature) source of ¹⁸O is approximately balanced by the major (low-temperature) sink.

The critical point of these calculations is clear: to balance the hydrothermal flux of ¹⁸O calculated above by the methods of Edmond et al. (1979) would require ten times more low-temperature alteration than is observed and would also require a source of ¹⁸O ten times greater than is observed. Restating this point, the fluxes of elements calculated by Edmond et al. (1979) are as much as ten times too high.

The agreement between ridge-crest heat flow predicted by the ³He-heat correlation (Jenkins et al., 1978) and the total global convective heat anomaly (Sleep and Wolery, 1978) was cited by the former authors as evidence in support of their methodology. Recently, however, Sleep et al. (1980) estimated that only about onesixth of the total ridge hydrothermal activity can actually occur within the axial region. Any one vent can remove a large amount of heat (MacDonald et al., 1980). If only this rapidly discharge fluid, directly overlying the magma chamber and in contact with fresh mantlederived rocks, transports significant quantities of ³He (Craig and Clark, 1970), the use of an observed ³Heheat correlation at venting sites to calculate global heat or elemental fluxes due to hydrothermal flow must lead to an overestimate.

SUMMARY

For the first time the existence of convective transport of chemicals through the sediment column at a deep-sea site, removed from the ridge crest, has been demonstrated. The flux of elements and isotopes at Site 503 can be accounted for only by a very substantial amount of low-temperature alteration of basaltic basement. Adjacent Holes 503A, 503B, and 83 display different chemical concentrations, suggesting that convection may be localized.

In summary, I suggest the following simple model: (1) Advection of fluid at ridge crests is widespread and of high velocity, such that fluxes of elements and isotopes may be of globally important magnitude (but of considerably lesser magnitude than suggested by Edmond et al., 1972). (2) At sites near ridge crests where sediment cover is less than 300 meters (Anderson et al., 1979), the advection of fluids is often great enough that heat flow and chemical transport are convective in nature. (3) At sites where sediment cover is thicker (usually farther removed from the ridge crests), heat flow is conductive but slow fluid flow may still cause chemical convection. (4) Finally, at sites sufficiently far from spreading centers and with sufficient sediment cover, convective heat flow, convective chemical transport, and fluid advection are all negligible.

ACKNOWLEDGMENTS

Four colleagues helped greatly in the preparation of this manuscript: Joris Gieskes, Miriam Kastner, Douglas Kent, and Keir Becker. Professor Gieskes especially has been a constant source of knowledge on all aspects of this problem. Professors Gieskes and Kastner have kindly reviewed and improved the manuscript. This work was supported by ONR Contract No. USN-N00014-80-C-0440.

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