13. BOREHOLE FLUID CHEMISTRY IN HOLE 504B, LEG 137: FORMATION WATER OR IN-SITU REACTION?¹

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ABSTRACT

Circulation of seawater through basaltic basement for several million years after crustal emplacement has been inferred from studies of surface heat flow, and may play a significant role in the exchange of elements between the oceanic crust and seawater. Without direct observation of the fluid chemistry, interpretations regarding the extent and timing of this exchange must be based on the integrated signal of alteration found in sampled basalts. Much interest has thus been expressed in obtaining and analyzing fluids directly from basaltic formations.

It has been proposed that open oceanic boreholes can be used as oceanic groundwater wells to obtain fluids that are circulating within the formation. Water samples were collected from the open borehole in Hole 504B prior to drilling operations on Leg 137, with the original intention of collecting formation fluids from the surrounding basaltic rocks. Past results have yielded ambiguous conclusions as to the origin of the fluids recovered—specifically, whether or not the fluids were true formation fluids or merely the result of reaction of seawater in the borehole environment.

The chemistry of eight borehole fluid samples collected during Leg 137 is discussed in this paper. Large changes in major, minor, and isotopic compositions relative to unaltered seawater were observed in the borehole fluids. Compositional changes increased with depth in the borehole. The samples exhibit the effect of simple mixing of seawater, throughout the borehole, with a single reacted fluid component. Analysis and interpretation of the results from Leg 137 in light of past results suggest that the chemical signals observed may originate predominantly from reaction with basaltic rubble residing at the bottom of the hole during the interim between drilling legs. Although this endeavor apparently did not recover formation waters, information on the nature of reaction between seawater and basalt at the prevalent temperatures in Hole 504B (\geq 160°C) has been gained that can be related to reconstruction of the alteration history of the oceanic crust. Isotopic analyses allow calculation of element-specific water/rock mass ratios (Li and Sr) and are related to the extent of chemical exchange between the borehole fluids and basalt.

INTRODUCTION

One of the most elusive questions regarding the alteration history of the oceanic crust is the degree and timing of alteration that occurs on the ridge flank due to reaction with circulating fluids. Direct observations of high temperature (250°C–400°C) axial hydrothermal activity are documented at many ridge crests around the globe (e.g., Von Damm, 1990). The effects of low temperature weathering of the basaltic crust by seawater over tens of millions of years have been documented by observation of dredged and drilled basalts from the shallower sections of the ocean crust (e.g., Staudigel and Hart, 1983; Alt and Honnorez, 1984; Böhlke et al., 1980). However, relatively little is known about the extent of alteration in the moderate temperature regimes (75°C–250°C) of ridge flank environments and hydrothermal recharge zones, where circulation of fluids is inferred from heat flow anomalies (e.g., Anderson et al., 1977).

Circulation of seawater in the ridge flank area near Hole 504B has been documented by Langseth et al. (1988), and modeled by Fisher et al. (1990). Drill core samples from Hole 504B provide direct evidence for seawater alteration at temperatures below about 350°C (cf., Alt et al., 1986). The presence of anhydrite, zeolites, and some clays reflects alteration temperatures in the moderate 150°C–250°C temperature range, similar to the current crustal temperatures at the bottom of Hole 504B. At present it is unclear whether significant elemental fluxes between seawater and the ocean can occur in these off-axial hydrothermal environments. Attempts to locate sites of off-axis hydrothermal discharge to elucidate elemental fluxes have been disappointing (Baker et al., 1991; Hess et al., 1991).

In principle, fluids circulating within Layer 2 can be sampled from open-oceanic boreholes, in a manner analogous to that of groundwater wells on land. However, this task has proven to be quite difficult as water depth, sampler deployment, temperature gradients, and drilling strategies all inhibit success of these endeavors. Mottl and Gieskes (1990) provide a review of the various attempts and strategies to sample fluids from open boreholes. Sampling strategies can be divided into two categories: active and passive. Active mode sampling requires that a sampler is sealed in the borehole annulus or wall, and fluid is actively extracted from the formation using a pressure gradient (Mottl and Gieskes, 1990). Whereas some degree of success has been achieved in sedimentary formations using the Barnes-Uyeda Tool and prototypes, attempts to actively withdraw fluids from basaltic formations have not succeeded. In the passive sampling mode, the borehole is left open and undisturbed by drilling operations for an extended period of time (several years), allowing formation fluids to exchange with the borehole fluids. Exchange could result from either direct flow into the borehole by advection through a fracture or fractures, or slower diffusive exchange (Mottl and Gieskes, 1990). Advective introduction of the formation fluids into the open borehole in Hole 534A along a sedimentary fracture has been demonstrated by Gieskes and Magenheim (1992). The passive mode has been the only successful sampling strategy to date in basaltic basement, but the origin of the reacted fluids is still in question.

Hole 504B has received the greatest effort toward obtaining formation fluids by sampling the open borehole. Samples have been obtained during six Deep Sea Drilling Project/Ocean Drilling Program (DSDP/ ODP) expeditions as outlined in Table 1. The times between drilling

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Table 1. Summary of borehole fluid sampling attempts at Hole 504B.

Drilling leg	Maximum depth (mbsf)	Maximum temperature (°C)	Time. (days)	
70	489	80	39	
83	836	112	711	
92	1350	145	470	
111	1350	145	1233	
137	1562	162	1633	

Notes: Time is the time interval between the end of drilling operations on the previous leg and borehole fluid sampling on the leg of interest. The maximum borehole depth and maximum temperatures are before drilling operations on the leg of interest.

legs, borehole depths, and maximum borehole temperatures were variable for each of these visits as the hole was deepened (Table 1). Attempts to deploy active samplers were not successful and resulted in collection of fluid from the borehole itself, and thus collected "passive" type samples. Changes in fluid chemistry relative to normal seawater composition have been observed during each attempt to collect borehole fluids, suggesting interaction with the basaltic basement (Mottl and Gieskes, 1990). The fluids reveal a two-component mixture between seawater and a reacted fluid component. In principle, this could be due to either a component of true formation fluid or reaction within the borehole itself. In addition, downhole mixing of bottom seawater into the open borehole has been inferred (Mottl and Gieskes, 1990).

Mottl et al. (1985) and Mottl and Gieskes (1990) provide support for the concept of molecular diffusion of formation water into the borehole through the wall rocks. This argument is based on the use of tritium concentrations to trace the original surface seawater placed in the borehole at the end of drilling operations on previous legs. In the Pacific Ocean, tritium is only present in surface waters, and therefore, it provides a definitive tracer for the original fluid left in the hole. Displacement with either deep water or formation fluids would result in a decreased concentration of tritium in the borehole. Mottl and Gieskes (1990) calculated that molecular diffusion can supply a component (as much as 30%) of formation fluid to the borehole. One of the major objectives of the borehole water sampling program for Leg 137 was to attempt to answer the question of whether formation fluid was actually recovered from the borehole, or whether reaction in the borehole environment is responsible for the observed chemical changes.

Elemental abundances and isotopic compositions were determined for fluids obtained during Leg 137 from the open borehole at Hole 504B. This information is used to elucidate the origin of the reacted fluid component present in the borehole. In addition, analyses of anhydrite crusts, and basaltic rubble, collected from the bottom of Hole 504B prior to drilling on Leg 137, are presented. Information regarding the nature of elemental exchange between seawater and the basaltic crust in the temperature range of the borehole is discussed in light of the observed chemistry of the borehole samples from this and prior expeditions.

METHODS

Shipboard Operations

Shipboard operations are described in detail in the Leg 137 Initial Reports (Shipboard Scientific Party, 1992a). At the end of Leg 111 in 1985 several volumes of surface seawater were flushed through the borehole to remove drilling mud and debris (Shipboard Scientific Party, 1988). The borehole remained undisturbed for 1633 days until reoccupation of the site during Leg 137 in 1991. Fluid sampling was conducted before any drilling operations, and the drill string was lowered only 50 m into the casing to avoid any disturbance to the borehole fluids. Samples were collected using two flow-through type samplers: a modified Leutert sampling tool (from the Los Alamos National Laboratories) activated by a mechanical clock, and a tool from the Lawrence Berkeley Laboratories (LBL) triggered through the logging cable. The samplers were lowered into the hole and

slowed to a stop 100 m above the desired sampling location. Every effort was made to provide undisturbed samples, but as indicated by the Leg 137 Shipboard Scientific Party (1992a) some dilution was evident. Sampling artifacts can come from two potential sources: disturbance of the borehole fluid column resulting in downhole mixing, or leakage of the samplers, often as a result of shrinkage upon recovery of the sample. The latter problem was checked by recording the mass of fluid recovered and comparing it to the expected mass based on the temperature and pressure of the samples at the intended sampling depth. Detailed analysis of the mass of sample recovered indicated that all the samples were subject to some leakage as the recovered mass was greater than the mass expected for the volume of the sampler (Shipboard Scientific Party, 1992a). This internal overpressure created some problems during removal of samples as it prevented normal operation of the sample extraction device on the Los Alamos tool. In particular, the first sample, from 350 mbsf, was exposed to the atmosphere because of the need to completely dismantle the sampler to remove the sample. Exposure to atmospheric oxygen was unavoidable, resulting in a large amount of orange iron oxyhydroxide precipitation prior to filtration. This problem was avoided in subsequent samples (details are given in Shipboard Scientific Party, 1992a). Despite these sampling difficulties, much useful information can be extracted from the sample data as the dilutant, seawater, is the same for all samples (see following discussion). Extraction and preservation of the samples is described in detail in Shipboard Scientific Party (1992a).

Because the primary goals of Leg 137 were to remove a diamond core bit left behind from Leg 111 and to clean the borehole for future drilling, we were able to collect material that resided at the bottom of the borehole during the 1633-day interim between the end of Leg 111 and Leg 137. This material included cm-sized pieces of anhydrite crust, which apparently precipitated directly from the borehole fluids (Shipboard Scientific Party, 1992a, fig. 21). Also, pieces of basaltic rubble from the hole bottom were examined for evidence of reaction with the borehole fluids. All pieces examined were taken from the first junk basket deployment and were recovered before any drilling or milling operations. Many of the pieces of basaltic rubble were worn with rounded edges, suggesting some degree of mechanical disturbance in the past, probably caused by bit recovery attempts at the end of Leg 111.

Analytical Methods

Many of the fluid analyses were performed within hours to days by standard methodology aboard the *JOIDES Resolution*. A brief summary of the methods, including analytical errors (2σ) , is given in Table 2.

Sulfur isotopic measurements of dissolved sulfate were performed by first precipitating the seawater sulfate as BaSO₄, which was then combusted with sodium metaphosphate at 1000°C. Evolved SO₂ gas was analyzed on a VG 602 Mass Spectrometer. Isotopic results are presented in per mil deviation, as δ^{34} S (‰), relative to Canyon Diablo Triolite (CDT). Since H₂S was below detectable limits, the values for δ^{34} S are considered to be unaffected by sulfide oxidation.

Boron concentrations were determined by isotope dilution (ID) mass spectroscopy. Boron isotopic compositions (for selected samples) were determined using the positive ion thermal ionization mass spectrometry (TIMS) technique of Spivack and Edmond (1986), after purifying the boron following the procedures of Nakamura et al. (1992). Isotopic ratios are determined by TIMS of the $Cs_2BO_2^+$ molecular ion on a VG 336 mass spectrometer. Boron isotopic compositions are reported as per mil deviations, $\delta^{11}B$ (‰), relative to measured values of the NBS 951 standard. The measured ratio for NBS 951 is 4.0552

Sr isotope ratios were determined by dynamic multicollection TIMS on a VG 336 mass spectrometer. The Sr was first separated on ion exchange resin columns using standard techniques and then loaded onto a W filament. Measured ratios of ⁸⁷Sr/⁸⁶Sr were normalized to ${}^{86}Sr/{}^{88}Sr = 0.1194$ using an exponential law correction. Using this procedure, the standard NBS 987 yielded an isotopic composition of 0.710283 ± 0.000012 (2σ , n = 9). The measured data have been normalized to the accepted value of NBS 987 (${}^{87}Sr/{}^{86}Sr = 0.710250$). This procedure produces a very small correction, but is performed for comparative purposes. Measured values for IAPSO Standard Seawater (0.709232, n = 5) result in the accepted value for contemporaneous seawater of 0.709199 after this correction is applied.

Li isotope ratios were determined using dynamic multicollection TIMS. The Li was first separated using cation exchange chromatography as in Chan and Edmond (1988). The isotopic ratios were determined on the LiNaBO $\frac{1}{2}$ molecular ion (Chan et al., 1992). Li isotope ratios are reported as per mil deviations (‰) from the NBS isotope standard (L-SVEC), in which the Li isotope ratio was determined to be ⁶Li/⁷Li = 0.083062 ± 0.00054 (Chan et al., 1992).

The rare earth element (REE) concentrations were determined by inductively coupled plasma-mass spectrometry (ICP-MS) after preconcentration using the chromatographic techniques of Zuleger and Erzinger (1988).

Analyses were also made of the anhydrite crusts. The anhydrite was first washed and then leached with water, to avoid dissolving any contaminants in the anhydrite. Sr and Ca were measured on the leach solutions by flame atomic absorption as were the borehole fluids. Sr isotopic compositions were measured by the same technique employed for the borehole fluids (Table 2).

RESULTS AND DISCUSSION

General Observations

The results of chemical analyses performed on the borehole fluids are presented in Table 3, and downhole profiles for the various chemical species are given in Figure 1. The data from Sample 137 504B BB-004 are not included in the profiles as this sample contained fluid with a composition close to that of seawater, and is thought to have leaked or pre-tripped (Shipboard Scientific Party, 1992a). A number of downhole trends are clear: pH, alkalinity, Mg, SO₄, Na, K, Sr, and Rb decrease with depth in the borehole; while Cl, Ca, H₄SiO₄, Li, Mn, and Ba increase with depth. Some scatter from the drawn profile lines is apparent, particularly for the samples from 1400 and 1550 mbsf. This scatter is presumed to be due to sampling artifacts resulting from either downhole mixing from repeated running of the samplers, or leaking of the sampler during recovery. The sources of potential sampling artifacts are discussed in detail by the Shipboard Scientific Party (1992a).

These trends are in general agreement with results of experimental simulations of seawater/basalt interactions at the in-situ temperatures (80°–150°C). One significant exception is the decrease in Na concentration in the borehole fluids, as Na is usually constant or rises during the experimental simulations in this temperature range (Seyfried and Bischoff, 1979). Charge balance calculations indicate that the increase in Ca is nearly balanced by decreases in Na and Mg. This situation suggests exchange of Na and Mg from seawater for Ca during reaction of seawater and basalt. Increases in Cl concentration with depth are consistent with the precipitation of hydrous clay minerals.

To evaluate the relative changes in the borehole fluid chemistry without the potential sampling artifacts, particularly dilution with seawater upon ascent, the data are presented in element vs. element diagrams in Figure 2. The data are presented relative to Mg for consistency and similarity to studies of ridge crest hydrothermal fluids. Mg is chosen as it is known to be removed from seawater at all temperatures during reaction with basalt. This format for data presentation provides a basis to establish mixing trends and the degree of enrichment or depletion of elements with respect to each other. For most elements, the data fall on remarkably linear trends, including samples from 1440 and 1500 mbsf (Fig. 2A–L). The lines intersect near the composition of seawater, indicating that it is one endmember of the two-component mixture. The other endmember lies along the Table 2. Summary of analytical methods for the borehole fluids.

Analyte	Method	Error	Reference
Alkalinity, pH	pH electrode, alkalinity titration	5%	1
Salinity	Goldberg Refractometer		1
CI ⁻	Potentiometric titration	0.5%	2
SO4-	Dionex ion chromotography	2.0%	1
Ca ²⁺	EGTA titration	1.0%	1
Mg ²⁺	EDTA titration	2.0%	1
NH [‡] , NO ³ , H ₄ SiO ₄ , PO ³⁻ ₄	Standard colorimetric techs.	Varies	3
Br ⁻ ,I ⁻ , H ₂ S			
K ⁺ , Na ⁺	Flame AES	2.0%	1
Li*	Flame AES	3.0%	1
Sr ²⁺ , Fe	Flame AAS	3.0%	1
Mn	Flameless AAS	2.0%	4
Ba, Rb	ICP M.S., standard additions	≤2.0%	
REE	ICP MS	<10%	5,6
В	Isotope dilution	<1.0%	
δ ¹¹ B (NBS 951)	TIMS	0.5%	7
⁸⁷ Sr/ ⁸⁶ Sr	TIMS	20×10^{-6}	
$\delta^{34}S$ (CDT)	SO ₂ gas MS	0.4%	
δ ⁶ Li (L-SVEC)	TIMS	0.8%	8
δ18O (SMOW)	M.S.		
δD (SMOW)	M.S.		
δ ¹³ C (PDB)	M.S.		

Notes: Errors reported as 2 times the standard deviation. References: 1 = Gieskes et al. (1991); 2 = Gieskes and Peretsman (1986); 3 = Shipboard Scientific Party (1992a); 4 = Magenheim (1989); 5 = Zuleger and Erzinger (1988); 6 = Totland et al. (1992); 7 = Ishikawa and Nakamura (1992); 8 = Chan (1987).

line somewhere beyond the lowest Mg concentration, and will be referred to as the reacted fluid endmember. Two conclusions are clear from the linear elemental mixing trends: (1) samples that fall off the general downhole trends (Fig. 1) are most likely the result of sampling artifacts, and (2) mixing of seawater with a reacted fluid component occurs in the borehole.

Figure 2M-O shows elements that do not display simple mixing trends in the borehole. High concentrations of Fe are present both in the shallow and deep parts of the borehole (Fig. 1Q). We suspected that this shallow enrichment is due to a contamination of the borehole fluids by the steel casing, and any flakes of rust knocked off during the sampling process. Goethite and X-ray amorphous iron hydroxides were observed by X-ray diffraction spectrometry (XRD) on the suspended solids recovered from the samples. Precipitation of orange Fe oxides in the untreated sample aliquots was observed for approximately one week following sampling. Iron precipitation was clearly caused by atmospheric exposure in Sample 137 504B BL-001M, as a result of difficulties during sample extraction (see above). Other samples were filtered and acidified with minimal exposure to the air. Precipitation of iron oxyhydroxides in the borehole itself is likely, particularly at shallow depths where relatively oxic bottom water is in contact with the steel casing, potentially causing oxidation and mobilization of iron. Red filaments (<10 mm diameter, and <200 mm long) were present on the filters from the borehole fluid samples. Scanning electron microscope (SEM) investigation of similar filaments from Leg 111 (Shipboard Scientific Party, 1988) revealed that these were probably bacterial in origin, and resembled iron oxidizing bacteria. The presence of iron oxidizing bacteria may indicate that oxidation of the casing or of dissolved Fe produces Fe-oxyhydroxides in the borehole environment. The source for high Fe at depth is equivocal: it may originate from a basaltic source, or merely from the dissolution of rust fallen from the casing. For iron and elements with similar element vs. element trends, distribution in the borehole fluids may be controlled by dissolution (oxidation) of the casing, precipitation as iron oxyhydroxides, and/or redissolution upon sinking to the more reducing borehole fluids deeper in the hole. For example B vs. Mg (Fig. 2N) shows a mirror image of the Fe vs. Mg trend, and may be produced by co-precipitation of B with Fe-oxyhydroxide phases in high Fe environments, or during sampling.

Sample: Depth (mbsf):	137 504B BL-001M 350	137 504B BL-002M 520	137 504B BB-003M 800	137 504B BL-004M 950	137 504B BB-005M 1100	137 504B BB-007M 1400	137 504B BL-008M 1500	137 504B BB-009M 1550	Surface water	Deep water*
pH	6.87	7.2	7.13	7.27	6.82	7.08	5.66	5.84	8.03	7.62
Alk (mM)	2.32	2.50	2.10	2.03	1.90	1.90	1.74		2.36	2.50
Salinity(g/kg)	34.2	34.8	34.8	35.2	34.1	34	33.4	33.5	33.5	34.8
Cl ⁻ (mM)	554	552.9	553.2	555	556.9	557.8	564.3	559.9	554	554
$Mg^{2+}(mM)$	54.02	50.74	45.29	53 67	42.32	43.92	26.88	35.91	53.75	5341
$Ca^{2+}(mM)$	10.7	13.5	19.8	10.3	22.8	21.9	43.0	31.2	10.3	10.5
$SO^{2-}(mM)$	29.6	27.0	23.1	28.0	19.9	20.2	61	14.4	27.7	28.6
H.SiO. (mM)	0.019	0 305	0.051	0.027	1 213	1.066	1 802	1 728	0.002	0.165
Na ⁺ (mM)	481	173	462	173	1.215	455	400	123	173	475
$K^{+}(mM)$	10.5	10.1	402	4/5	0.4	455	84	400	10.3	10.4
$Sr^{2+}(nM)$	10.5	10.1	9.0	96.0	75.0	9.5	66.2	72.0	26.0	10.4
J_{i+1}^{i+1} (uNI)	27.6	07.0	01.9	30.0	75.0	79.1	52.2	12.0	20.0	
LI (µM)	57.0	33.5	34.4	32.0	39.0	37.1	33.3	40.9	29.0	
NH 3 (µM)	24	4	16	6	16	17	35	24	0	20.1
$NO_3(\mu M)$	23.5	22.5	6.25	38.8	8.59	8.07	1.06	2.75	8.02	39.1
$NO_{2-}(\mu M)$	1.38	2.49	3.45	0.23	2.82	1.44	0.33	0.25	0.38	
$PO_{A}^{3-}(\mu M)$.00	.29	.50	.00	.70	.29	.70	.70	.70	
$Br'(\mu M)$	821	816	799	829	819	813	812	821	820	
1 (µM)	19.8	18	50.6	9.2	21.9	21.8	37	27.3		
Fe (µM)	338	437	191		202	180	686	237	0	
Mn (uM)	50	35	59		75	75	116	97	0	
B (µM)	386	416	422	407	423	423	381	412	407	
δ11B (%c)		37.9		37.9		38.3	37.4		38.8	
δ34S (%c)	20.1			20	197	19.7	19.5		20	
³ He/ ⁴ He (R.)	4.84		1 103	1 039	4 001	1 301				
8180 (%)	0.44	0.11	1.58	0.38	0.02	0.02	-0.13	-0.05		
8D (%)	-3.3	-8.9	4.9	5.4	-6.5	7.6	-5.2	-57		
813C (%)	-1.1	-0.9	-4.9	-3.4	1.2	-1.0	2.1	-2.2		
875-/865-	0.700212	0.700210	0 709954	-2.1	0.708627	0.709750	0 707575	0.708240	0 700104	
S61 ; (01.)	0.709212	0.709210	0.7000.04		0.706027	0.708750	18.0	22.0	0.709194	
0 L1 (700)	0 6 47	0.907	0.470		-24.0	0.512	-10.0	-22.0		
La (µg/kg)	0.047	0.007	0.479		0.004	0.515	1.005	0.472		
Ce (µg/kg)	0.890	3.275	0.609		0.007	0.593	0.088	0.652		
Pr (µg/kg)	0.07	0.183	0.05		0.077	0.052	0.068	0.00		
Nd (µg/kg)	0.214	0.542	0.155		0.240	0.17	0.215	0.189		
$Sm (\mu g/kg)$	0.028	0.071	0.022		0.023	0.025	0.052	0.03		
Eu (µg/kg)	0.043	0.017	0.011		0.021	0.019	0.104	0.029		
Gd (µg/kg)	0.041	0.081	0.029		0.035	0.033	0.07	0.041		
Tb (µg/kg)	0.007	0.010	0.005		0.005	0.005	0.007	0.006		
Dy (µg/kg)	0.022	0.025	0.014		0.015	0.014	0.022	0.02		
Ho (µg/kg)	0.003	0.004	0.002		0.002	0.002	0.004	0.003		
Er (µg/kg)	0.015	0.018	0.011		0.010	0.01	0.014	0.014		
Tm (µg/kg)	0.004	0.004	0.002		0.002	0.002	0.004	0.003		
Yb (ug/kg)	0.014	0.015	0.009		0.008	0.007	0.016	0.012		
In (nalka)	0.005	0.005	0.000		0.000	0.000	0.000	0.004		

Table 3. Raw data for Leg 137 borehole fluids.

Note: *Mottl and Gieskes, 1990.

Scavenging of boron onto iron oxyhydroxides is likely as high boron concentrations have been observed in metalliferous sediment on the East Pacific Rise (Marchig et al., 1986).

Figure 3 shows the REE patterns for the borehole fluid samples normalized to normal mid-ocean-ridge basalt (N-MORB). All fluid samples are enriched in REEs relative to seawater. The patterns are similar to those observed in hydrothermal vent fluids (Michard, 1989) with an enrichment in light REE (LREE) relative to heavy REE (HREE) and a positive Eu anomaly. In general, Eu increases with decreasing Mg (Table 3). A very large Eu anomaly is observed in the shallowest sample (137 504B BL-001M, 350 mbsf), whereas the major element chemistry is very close to seawater composition. Sample 137 504B BL-002M (520 mbsf), is the only sample in which a slightly negative Eu anomaly is observed, and the LREE are enriched relative to all other samples. Perhaps the elevated REE and lack of a positive Eu anomaly originates from redissolution of Fe-oxyhydroxides as they fall deeper into hotter, more reducing conditions (Sholkovitz et al., 1989). Figure 3 (inset) shows the Eu anomaly, defined as Eu/Eu^{*}, where Eu^{*} = (Sm + Gd)/2, plotted vs. Mg. A reasonable mixing line is observed, with the exception of Sample 137 504B BB-002M (520 mbsf). The fact that the Eu anomaly for 137 504B BB-002M falls off the mixing trend observed for all other samples suggests a different source for the Eu anomaly than for the other samples. This, combined with the observation that the REE are enriched in all samples (even those with little or no change from seawater chemistry), suggests that there is a source of REE in addition to seawater/basalt reaction. This contamination may arise from interaction of the fluids with: (1) drill string greases, (2) drilling mud, and/or (3) steel components of the casing. Enrichment of Fe in the shallowest samples argues in favor of contamination by dissolution and oxidation of the steel casing.

 $NO_3 + NO_2$ and NH_4 show behavior similar to B and Fe when plotted vs. Mg (Fig. 20). The presence of these species is likely due to contamination of the borehole fluids with greases from the drill string, as only a small amount of pipe grease could account for the observed changes in $NO_3 + NO_2$ in the samples (Shipboard Scientific Party, 1992a). Perhaps the inverse relationship between NH_4 and NO_3 + NO_2 is due to higher temperatures and more reducing conditions at depth in the borehole (Table 3). In any case it is important to note that whereas in the past $NO_3 + NO_2$ measurements have been used to correct for any entrainment of bottom water into the samples (Mottl and Gieskes, 1990), in this study no such corrections have been made. Br displays no noticeable change relative to Mg (Fig. 2P) in the borehole within analytical resolution.

Anhydrite Precipitation

The recovery of anhydrite crusts (Shipboard Scientific Party, 1992a, fig. 21) during the initial equipment recovery operations of Leg 137 suggests that this mineral precipitated within the borehole. Sulfur isotopic studies of the anhydrite and of dissolved sulfate in the borehole fluids provide further support for this conclusion (Table 3 and Fig. 1G). The fluid sample from 350 mbsf has a δ^{34} S equal to that of modern seawater (δ^{34} S = +20‰). With depth the δ^{34} S decreases to a value of +19.5‰ at 1500 mbsf. The sulfur isotopic composition of the anhydrite crust was +21.4‰. The results are consistent with a slight positive fractionation of sulfur isotopes expected during precipitation of anhydrite (Holser and Kaplan, 1966). XRD analysis of



Figure 1. Component vs. depth profiles for Hole 504B borehole fluids collected during Leg 137. Values in parentheses are isotopic composition for the elements at the depth specified. Dashed line in Figure 1N is the ⁸⁷Sr/⁸⁶Sr for the anhydrite crusts recovered from the hole before drilling.

the suspended solids also revealed the major peaks of anhydrite in samples from below 1100 mbsf (Shipboard Scientific Party, 1992a). Gypsum was observed in the "fluid" samples recovered during Leg 92 from Hole 504B (Gieskes et al., 1986). However, the extent to which this observation was caused by the large quantity of drilling mud left in the borehole, as a result of inefficient flushing at the end of Leg 83, left this conclusion somewhat ambiguous.

Further indication that anhydrite precipitation is expected from the moderate temperature borehole fluids comes from experimental investigations. Anhydrite has been observed to precipitate during heating of seawater to temperatures as low as 200°C (Bischoff and Seyfried, 1978) and 150°C during experimental reaction of seawater and basalt (Seyfried and Bischoff, 1979). The thermodynamic saturation index of anhydrite (Ω = ion activity product divided by the solubility product) has been calculated for the borehole fluids at their in situ conditions and compositions. This has been done using the database of D. Janecky (pers. comm., 1992) and the results are presented in Figure 4. The logarithm of the saturation index for anhydrite reaches a value of $\Omega = 0$ (saturation) near 1100 mbsf (T = 140°C), revealing that the borehole is at or above saturation below this depth. This is coincidentally the same depth at which anhydrite was first observed in the suspended solids from the borehole fluid samples. The slight degree of supersaturation in the deepest sample may be the result of dilution of fluids during ascent of the sample (entrainment evident in downhole profiles; see Fig. 1), resulting in an apparent supersaturation (Mazor, 1992).

Six replicate analyses of Sr isotopes on different pieces of the anhydrite crusts, including analysis across a single crust, yielded a surprisingly uniform result with a mean isotope ratio of ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.708600$ (std. dev. = 0.000021). This value is considerably more radiogenic than the water sample from 1500 mbsf, which had ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.707575$, and matches closely with the ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ of the sample from



Figure 2. Component vs. Mg for Hole 504B borehole fluid collected during Leg 137. Values for Ca and Sr are also presented as corrected for anhydrite precipitation (Ca* and Sr*), based on the deficit of SO_4 from the seawater value of 28 mM (see text).

1100 mbsf with 87 Sr/ 86 Sr = 0.708627 (Fig. 1N). This suggests that the recovered anhydrite may have formed near 1100 mbsf, coincidentally the same depth at which anhydrite saturation is first approached in the borehole fluids (Fig. 4). Alternately, the recovered anhydrite may have formed deeper in the borehole at a time when the fluids were more radiogenic than at present, perhaps as the fluid was rapidly heated to the formation temperatures.

Evidence For Seawater/Basalt Interaction

While anhydrite precipitation appears to occur directly from the water in the borehole itself, most of the large chemical changes cannot be explained without evoking seawater-basalt exchange. In fact, the quantity of Ca released into the borehole fluids due to reaction with basalt is greater than measured because of the removal of Ca into anhydrite. Corrected Ca is presented as Ca^{*} on the mixing diagram Figure 2A, where Ca^{*} is the Ca concentration in absence of anhydrite precipitation as calculated form the decrease in SO₄ from seawater concentration. A similar correction can be made for Sr. While the data show a decrease in Sr with depth in the borehole, analysis of the anhydrite crusts revealed a Sr/Ca molar ratio of 0.0012 ($2\sigma = 0.00005$, n = 4). Accounting for this export of Sr from the fluids based on the decrease in SO₄ concentration indicates a net input of Sr to the borehole fluids through reaction with basalt (Sr^{*} in Fig. 2I).

The Sr isotopic evidence is one of the most convincing arguments for basaltic input to the borehole waters. Sr in the fluids is a mixture of seawater-derived Sr (87 Sr/ 86 Sr = 0.70918) and basaltic Sr (87 Sr/ 86 Sr = 0.70272; Shimizu et al., 1989). Similar evidence is reflected in the 3 He/ 4 He results (Table 3). While many of the samples have R_a (R_a = 3 He/ 4 He measured divided by 3 He/ 4 He in air) near 1, two samples have ratios near 4. The samples with ratios near 1 were probably contaminated by atmospheric gas during either sampling or storage. Ratios as high as 4 cannot be explained by contamination, and reflect the greater abundance of mantle-derived 3 He trapped in fresh basalts. Hence both Sr and He isotopes support seawater/basalt interaction, but the location of reaction, whether in the formation or in the borehole, is unresolved.

Scanning electron microscopic (SEM) analyses of pieces of basaltic rubble from the bottom of Hole 504B (Fig. 5A), collected prior to any drilling operations during Leg 137, revealed the ubiquitous presence of 100-200 µm coatings of Mg-rich smectite/chlorite clays. The presence of these reaction products on the exterior surfaces of many of the rubble fragments strongly suggests that the clay coatings formed after the rubble fell to the bottom of the hole. Mg-rich smectite was observed intergrown in the anhydrite crusts as well (Fig. 5B). Results of electron microprobe analyses on the clay coatings and from within the anhydrite are presented in Figure 6 in an attempt to distinguish these clays from those occurring within the cored basalts. The clays coating the rubble have compositions quite similar to mixed-layer clays collected in the cored samples, but the clays interbedded in the anhydrite matrix are quite distinct, having very low Fe and Al contents, near the talc-chlorite endmember. Although the chemistry of the clay coatings does not unequivocally support in-situ formation, the fact that the surfaces of many of the pieces were covered with these skins of reaction products supports the hypothesis that reaction occurred at the hole bottom. The Al-poor nature of the smectite within the anhydrite crusts is consistent with direct precipitation from solution.

Mg-rich clays are the likely sink for Mg from the borehole fluids. Alteration of basalt by seawater often involves the formation of Mg-rich clays in experimental simulations at temperatures as low as 70°C with the net result being an approximately 1:1 exchange of Mg for Ca (e.g., Seyfried and Bischoff, 1979). However, in the borehole fluids there is almost a 2:1 Ca:Mg exchange (Ca^{*}; see above, Fig. 2A). Na is also removed from the borehole fluids, but a sink for Na is less readily identified. Zones of albitized plagioclase were observed during elemental mapping using electron dispersive spectrometry of some of the pieces of rubble (Magenheim et al., 1991). However, albite is an observed alteration product in the cored formation itself, and thus this evidence is equivocal in respect to the sink for Na within the borehole. Other potential sinks for Na are the formation of sodic zeolites or clays.

Isotopic Investigations: Reaction Zone Constraints

One of the strongest arguments against reaction with the borehole walls as the source for the reacted fluids observed in Hole 504B was that the borehole itself is a system physically dominated by the quantity of fluid (Mottl and Gieskes, 1990). Water in a borehole of radius 15 cm reacting with 0.5 mm of basalt lining the hole yields a water/rock mass ratio (w/r) of near 60. This value is a minimum, as the borehole contains a larger volume of water relative to surface area due to the uneven diameter of the walls as a consequence of cave-ins. At w/r ratios this high, a small volume of altered rock is required to gain up to 6% MgO, 9% Na₂O, and lose 20% CaO to account for the changes observed in the fluid chemistry based on results from Leg 111 (Mottl and Gieskes, 1990). Thus, it seems unlikely that the degree of reactivity observed could be explained merely by reaction with the basalts on the borehole walls.

An alternate reaction zone is in the rubble at the bottom of the hole. This reaction zone would, of course, have a much lower physical w/r than the open borehole, thus eliminating the above inconsistency. As already discussed, analysis of the alteration rinds on these rock pieces does not conclusively eliminate the possibility that the secondary



Figure 3. N-MORB (Sun and McDonough, 1989) normalized rare-earth element (REE) distributions for Leg 137 Hole 504B borehole fluids, and seawater. Europium anomaly (Eu/Eu*) vs. Mg (inset), where Eu = (Sm + Gd)/2. Open circle = 137 504B BL-001M; solid circle = 137 504B BL-002M; open box = 137 504B BB-003M; solid box = 137 504B BB-005M; open triangle = 137 504B BB-007M; solid triangle = 137 504B BL-008M; diamond = 137 504B BB-009M; x's = seawater (Holland, 1978).



Figure 4. Anhydrite saturation state in Hole 504B. Calculation of anhydrite saturation (Ω = ion activity product/K_{sp}) is based on the in-situ temperatures and measured composition of the borehole fluids. Calculations made using database of D. Janecky (pers. comm., 1992).

minerals formed in the formation prior to falling to the hole bottom (Fig. 6). Isotopic investigations of Sr, O, H, Li, and B were undertaken to evaluate the chemically derived water/rock mass ratios (w/r) in the reaction zone and the degree of reactivity of basalts at these intermediate temperatures.

To evaluate the systematics in the reaction zone it is necessary to use an extrapolated "endmember" composition of the fluids. This is necessary as the recovered solutions are clearly mixtures of the endmember and seawater, and thus, the reacting fluid must lie beyond the lowest value of Mg measured. Extrapolations for each isotope were made to zero Mg, defining a single reacted fluid endmember for the borehole system. This extrapolation is justified because for moderate to low w/r experimental systems at temperatures greater than 150°C Mg is completely removed in periods of less than or equal to one year (Mottl, 1983; Seyfried, 1987; Seyfried and Bischoff, 1979). Such extrapolations are commonly used during the study of high temperature (\geq 300°C) hydrothermal fluids, to remove the effects of entrainment of seawater during sampling (e.g., Von Damm et al., 1985). While it is possible that there is not a fluid with Mg = 0 mM in the borehole, reaction to this extent is likely in the fine- to coarse-grained A



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Figure 5. SEM image of (A) basaltic rubble piece coated with reaction products, and (B) anhydrite crust with interbedded clay.

basaltic rubble at the bottom of the borehole. In addition, extrapolation to zero Mg provides a uniform reference to previous sample suites from Hole 504B. The subject of borehole fluid endmembers will be discussed further in a later section.

For δD and $\delta^{13}C$ the measured values are lower than of fresh seawater (~0% for both) and show no definable trends when compared with Mg. This indicates the possibility of contamination of the samples for these isotopes. Evaporation can be ruled out as the samples were stored in sealed glass vials, and evaporation would increase the values of both δD and $\delta^{13}C$. Boron concentration shows a minimum in both the shallowest and deepest samples (Fig. 2N). As discussed earlier, B appears to be affected by the cycling of Fe in the borehole, and its concentration and isotopic composition are likely influenced by oxidation of the casing in the upper hole and subsequent removal into iron oxyhydroxide phases. The endmembers for $\delta^{13}C$, δD , and $\delta^{11}B$ cannot be defined due to the non-conservative mixing observed. Li, Sr, and oxygen isotopes, however, do reflect exchange between basalt and the borehole fluids, and these results will be used to elucidate information about the reaction zone.

Oxygen isotopes show a mixing trend with Mg (Fig. 2L), revealing an endmember of $\delta^{18}O = -0.41\%$ at zero Mg, and intersecting close to 0.1‰ for seawater at Mg = 54 mM. Equilibrium models for isotopic exchange (Cole et al., 1987) reveal that water in equilibrium with fresh basalt ($\delta^{18}O = 5.7\%$) at T = 162°C should have a $\delta^{18}O = -3.2\%$. While this value is significantly lower than the endmember value from Leg 137, it is important to note that the borehole system is probably far from equilibrium conditions with only 4.5 years of reaction. Cole et al. (1987) calculate that it would take on the order of 104 years to reach 90% of equilibrium between basalt and seawater at 200°C.

Water/Rock Mass Ratios

To calculate the w/r for the conditions of alteration based on trace element isotopic systematics (such as Sr isotopes) it is desirable first to make a decision on a reaction path (e.g., Elderfield and Greaves, 1981; Berndt et al., 1988). There are two extreme paths for reaction: precipitation followed by reaction and vice-versa. Calculation of w/r from these two paths differs in that the concentration of Sr prior to dissolution of the basalt is different from that of the initial fluid, whereas precipitation does not alter the isotopic ratio of the fluid. A more rigorous approach to these calculations would be to make the calculation of w/r by using infinitely small dissolution and precipitation steps. The incremental change in concentration of a single isotope in solution (dX) can be described as a function of its concentration in fresh rock (X_r), the alteration products (X_{alt}), and the incremental amount of altered rock (dr) for a fixed mass of solution (w):

$$dX/dr = \frac{X_r - X_{alt}}{w} \tag{1}$$

Here X_{alt} is a function of the concentration of X in solution, and w is a mass of fluid. Implied in this expression is conservation of mass between fresh rock and alteration products. A distribution coefficient K (where $X_{alt} = K \cdot X$) can then be introduced into Equation 1 yielding:

$$dX/dr = \frac{X_r - KX}{w}$$
(2)

The distribution coefficient, *K*, is specific for each path specified and does not imply equilibrium reversible conditions. Equation 2 can be applied to another isotope of the same element (*Y*), realizing that the distribution coefficient may require a fractionation correction ($K_{y} = \alpha K$):

$$\frac{dY}{dr} = \frac{Y_r - \alpha KY}{w} \tag{3}$$

Integration of Equations 2 and 3 yields two independent expressions for r/w:

$$r/w = K^{-1} \times \ln \left[\frac{X_r - KX}{X_r - KX_0} \right]$$
(4)

and

$$r/w = (\alpha K)^{-1} \times \ln \left[\frac{Y_r - \alpha K Y}{Y_r - \alpha K Y_0} \right]$$
(5)

Thus, it is possible to obtain information on the distribution of an element between fluid and alteration product (K) and on the water/



Figure 6. Chlorite/smectite compositional diagram after Hey (1954). Formulas calculated on a basis of 26 oxygens. Field from clays recovered in the cored formation are included for reference (Alt et al., 1989).

rock mass ratio (w/r) from the concentration and isotopic composition of an element in the initial and final fluids and in the fresh rock. The w/r ratio calculated in this manner is an indication of the degree of reactivity of the rock for the specific element from which it is calculated. In this respect, the calculated w/r ratio represents the quantity of rock from which the element has been completely mobilized into a constant amount of water. Hence, an element that is incompletely mobilized will result in calculation of a larger w/r than for an alternate element that is more mobile. Calculation of w/r due to elemental/isotopic exchange will always yield a higher value than the w/r calculated based on the physical mass of water and rock in the system (see above) in the absence of 100% mobilization of the element in question.

Calculations have been made for w/r and the distribution coefficient, K, for the exchange of Sr and Li based on abundance and isotopic measurements. To make these calculations it is necessary to use the extrapolated endmember compositions for the Leg 137 borehole fluids as the final fluid concentration, and seawater as the starting fluid. Data for "unaltered" Hole 504B basalts were taken from several sources (Table 4).

Strontium concentration and isotopic composition were discussed briefly in the previous section on anhydrite precipitation. Although there is net Sr removal from the borehole waters (Fig. 1M), there is clearly an input of basaltic Sr (fresh Hole 504B basalt ⁸⁷Sr/⁸⁶Sr = 0.70272; Shimizu et al., 1989), as the isotopic ratio of Sr in the borehole fluids is much less radiogenic than that of seawater (seawater 87Sr/86Sr = 0.70918). The endmember contains approximately 28% Sr derived from basalt. Most of the decrease in Sr concentration is due to incorporation into anhydrite (see Fig. 2I). Thus, extrapolation of the measured values beyond $SO_4 = 0$ (Mg = 6 mM) to Mg = 0 is invalid, as no more anhydrite (and hence Sr) can be removed beyond this point. Because we are predominantly interested in the endmember for reaction in absence of precipitation of anhydrite (seawater/basalt reaction alone), we will use the SO₄ corrected Sr^{*} endmember (97 µM, Fig. 2G). For a heavy element, like Sr, mass fractionation is relatively unimportant and α is assumed to be equal to 1. Calculation of the water/rock ratio yields w/r = 23.5 and K = 4.6 (Table 4). The w/r ratio is significantly less than that calculated for the open borehole based on the physical constraints (w/r >60; see discussion above). From this value of K we can calculate the concentration of Sr in the secondary minerals (in the absence of anhydrite) to be equal to 42 ppm. Calculation of K, based on the fluid composition at $SO_4 = 0$, using the uncorrected (measured) Sr concentrations, yields a value of K = 32.8, for all alteration products including anhydrite, and a concentration of 115 ppm Sr in the alteration products (Table 4). From this information and the knowledge that the anhydrite has a concentration of 774 ppm Sr (see above), it is possible to calculate that anhydrite can be a maximum of 8.5% of the total mass of reaction products.

Table 4. Comparison of water/rock ratio (w/r) calculated based on borehole fluid endmembers, and calculations of w/r based on Sr and Li abundance and isotopic composition.

	Sr (µM)	⁸⁷ Sr/ ⁸⁶ Sr	Li (µM)	⁶ Li/ ⁷ Li (%e)
Seawater	87	0.70918	29	-32.3
504B-008	66.3	0.70756	53	-18.0
Endmember $(Mg = 0)$	97 ^a	0.70743	78	-13.7
$[SO_4 = 0]$ Fresh basalt (504B) Fractionation factor (α)	[60] 60 ppm ^b	[0.70754] 0.70272 ^c 1.0000	2 ppm ^d 1.008-1.009	-5.0 ^e
		Sr		Li
w/r		23.5 [32.8]		2.2-3.1
K		4.9 [21.8]		3.0-2.4

Notes: Calculations are described in text. Li, w/r, and K are given for a range of the isotopic fractionation of \u03c6 = 1.008-1.009, intermediate between fraction observed for axial high temperature reaction and seafloor weathering. Disagreement between different isotopic systems reflects differing mobilities. All calculations are supportive of a low w/r (<50) suggesting a rock-dominated system.</p>

^aSr* corrected for anhydrite is used in this calculation; see text. Values for Sr and Sr isotopes at SO₄ = 0 are not corrected for anhydrite precipitation; these values, and w/r and K calculated from them, are presented in brackets for comparison; see text.
^bShipboard Scientific Party (1992b).

^cShimizu et al. (1989).

^dMengel and Hoefs (1990).

^eChan et al. (1992).

The systematics of Li exchange between seawater and the ocean crust is a current topic of great interest (e.g., Chan et al., 1992; Chan and Edmond, 1988). Li is considered to be a mobile element during reaction of seawater with basalt at temperatures greater than 70°C (Seyfried et al., 1984); it is leached from basalt altered at moderate to high temperature. Evidence from dredged and drilled basalts from shallow in the crust suggests that Li is taken up from seawater into secondary alteration products under low temperature (0°-50°C) seafloor weathering conditions (Berndt and Seyfried, 1986; Ryan and Langmuir, 1987). Li concentrations in the borehole fluids show an excellent correlation with Mg (Fig 2I). Hence, Li is interpreted to be supplied by reaction with basalt, and mixed conservatively in the borehole. Information on the temperature dependence of the fractionation of Li isotopes during basalt-seawater interaction is sparse. A fractionation factor of $\alpha = 1.004$ for 350°C has been inferred from studies of hydrothermal vent fluids (Chan and Edmond, 1988). The fraction factor for basalt weathered by fresh seawater at the seafloor $(T = 2^{\circ}C)$ is estimated to be near $\alpha = 1.019$ (Chan et al., 1992). The w/r ratio was calculated from the borehole fluid endmember (T =162°C) using fractionation factors of $\alpha = 1.008$ and 1.009, intermediate between these two extremes (Table 4). The distribution coefficient is calculated to be K = 2.4 - 3.0, suggesting a Li concentration of 1.3-1.6 ppm in the alteration products formed. This value of the distribution coefficient is similar in direction and magnitude to the distribution constant between seawater and secondary smectite at 200°C (K = 2.3) derived experimentally by Berger et al. (1988). Water/rock ratios calculated based on the Li systematics yield values of 3.1 and 2.4 for $\alpha = 1.008$ and 1.009, respectively. This low value of w/r is clearly not possible in the open borehole, but could be attained in the rubble at the hole bottom or within the formation itself.

The w/r calculated using Li systematics is significantly lower than that calculated based on Sr, and the discrepancy is most likely related to the greater mobility of Li compared to Sr. Similar discrepancies arise in experimental investigations and analysis of hydrothermal fluids collected at mid-ocean ridges (e.g., Von Damm et al., 1985; Berndt et al., 1988). It is important to note that w/r calculated from chemical and isotopic compositions will depend on the mobility of the individual element(s) on which the calculations are based. Berndt et al. (1988) suggest that the degree of reactivity of Sr (and therefore Ca) bearing phases can be estimated by comparing the w/r calculated by B or Li systems to that of Sr. For the borehole environment, B appears to be influenced by processes other than simple mixing of a basalt reacted component with seawater; therefore, we use comparison between calculations based on Li and Sr. The degree of reactivity of Sr (and therefore Ca bearing phases), relative to the mobile element Li, can be expressed as the w/r (Li) divided by the w/r (Sr) (Berndt et al, 1988). For the case of the Hole 504B endmember, this value is 0.113 or 11.3%, using the mean of the two values for w/r (Li). For 1 kg of water, 42.6 g of basalt could be altered using the mean w/r = 2.65 calculated from the Li systematics. If all the altered material were plagioclase of composition An75, the concentration of Ca in the fluid would increase by 106 to 116 mM, close to the observed Ca* for the borehole fluid endmember at Mg = 0 (Table 5). Given the composition of the endmember borehole fluid and a minimum w/r of 2.65 (Li calculation), the 1 kg of fluid would lose 144 moles of Na capable of forming 37.7 g albite, and 54 mmoles of Mg capable of forming 8.0 g of saponite, for a total of 45.7 g of alteration products in agreement with the assumption of conservation of mass between alteration products and initial basalt used in the w/r calculations (Eq. 1). The above calculation ignores the precipitation of anhydrite. However, if 28 mmoles of seawater SO₄ are precipitated as 3.8 g of anhydrite, anhydrite is 8.3% by weight of the alteration products. This is very close to the calculations based on the Sr systematics (see above), which revealed that anhydrite is a maximum of 8.5% of the total mass of alteration products. The excellent agreement of the calculations originating from (1) the degree of reactivity, from Li and Sr isotope systematics, and (2) the changes in major element borehole fluid composition show that the comparison of multiple elemental isotope systematics for geothermal fluids can reveal important physical constraints on the reaction zone. Thus, for the case of Hole 504B borehole fluids, the w/r ratio in the reaction zone must be low to support the observed chemical and isotopic changes.

Formation Water Or In-situ Reaction?

A low water/rock ratio in the reacted fluid endmember seems to eliminate the possibility of reaction within the open borehole between the borehole fluids and the exposed walls of the hole. However, the low value of w/r does not distinguish between the possibility of a true formation component or reaction in the rubble pile at the borehole bottom. If the calculations of Mottl and Gieskes (1990) are correct, considerable exchange of borehole fluids with fluids from the surrounding formation should occur by molecular diffusion. These calculations are based on analysis of tritium, a definitive tracer for surface seawater, placed in the borehole during cleaning operations at the end of each drill leg. Mottl and Gieskes (1990) suggested that up to 30% of the borehole fluid should have been replaced by formation fluid in the interim between Legs 92 and 111 by molecular diffusion. However, the porosities used to calculate the diffusive exchange are based on uncorrected logging data (Mottl and Gieskes, 1990). These porosity data have since been corrected downward to values of 1%-2%, because of the effect of alteration products on the electrical resistivity measurements (Pezard, 1990). Thus, exchange between the open borehole and formation will be small. We estimate, based on the corrected porosities, that less than 1% of the borehole fluid will be replaced in the 1233 days due to molecular diffusive exchange.

Correction of the porosities used in the calculations of Mottl and Gieskes (1990) argues against the possibility of significant exchange through the borehole walls, but advective exchange of formation fluid through a fracture or crack cannot be ruled out. It would be expected that the composition of this reacted fluid would be the same for each visit to Hole 504B if the source of reacted fluid is through a fracture rather than reaction at the borehole bottom. On the other hand, the increasing temperature at the hole bottom as Hole 504B has been drilled deeper should cause regular variation in the reacted fluid endmember if the reaction zone is at the bottom of the borehole. Reaction at the hole bottom is supported by the fact that on each leg the most reacted fluid (lowest Mg) is nearest the bottom (e.g., Shipboard Scien-

tific Party, 1992a). Mottl and Gieskes (1990) plotted element vs. Mg diagrams that included data for all legs, and extrapolated the combined data to a single endmember at zero Mg. This multi-leg extrapolation was justified in that the Ca vs. Mg plot showed exceptional agreement for all legs. Substantial scatter from Leg 92, when a large amount of drilling mud was recovered in the borehole fluids, further obscured inter-leg differences for other elements. The measured Ca values are controlled by the saturation of the fluid with respect to anhydrite, and Magenheim et al. (1992) argue that significant and regular changes in the borehole fluid endmember did occur as the hole was drilled deeper.

Figure 7 shows the element vs. Mg mixing diagrams for each leg as a comparison. In the Ca vs. Mg plot it appears that all legs extrapolate to a single Ca concentration at Mg = 0 (Fig. 7A). However, when accounting for the precipitation of anhydrite, Ca* increases monotonically between Leg 69 and 137 relative to Mg (Fig. 7B). This trend coincides with deepening of the hole and hence the increased bottomhole temperature. More Ca was liberated as the maximum borehole temperature increased from 80°C on Leg 70 to 162°C on Leg 137 (Table 1). This observation is of course supported by an increase in the SO₄ removed (relative to Mg) over the same interval (Fig. 7C). In fact no SO₄ removal was observed on Leg 70, in agreement with the experimental observations that anhydrite precipitation from seawater requires temperatures between 150° and 200°C (Seyfried and Bischoff, 1979; Bischoff and Seyfried, 1978). Increased temperature and Ca concentration on subsequent legs resulted in monotonic decreases in SO₄ concentration as the hole was deepened. Sodium is removed in greater amounts as the maximum borehole temperatures increase (Fig. 7D). Potassium, on the other hand, appears to be removed in lesser quantities as the borehole temperature rises (Fig. 7E).

Oxygen isotopes show a trend between Legs 111 and 137 in agreement with this argument (Fig 7F). The δ^{18} O values from Leg 92 are quite scattered and are most likely affected by the large amount of bentonite left in the borehole following Leg 83 (Gieskes et al., 1986). The oxygen isotopes from Leg 111 extrapolate to a value of between -1.3‰ and -1.8‰, lower than the -0.41‰ for Leg 137. Since fractionation of ¹⁸O between fluid and rock decreases as temperature increases, one would expect a lower value of $\delta^{\rm 18}O$ for fluids from a lower temperature environment. Assuming the same extent of reaction, calculation of the difference in equilibrium fractionation between basalt and water for Legs 111 ($T_{max} = 145^{\circ}C$) and 137 ($T_{max} =$ 162°C) (1000ln $\alpha = \delta^{18}O_{\text{basalt}} - \delta^{18}O_{\text{water}} = \Delta$) yields values of 10.42 and 8.96, respectively. Thus, if the $\delta^{18}O$ of the altered basalt is assumed constant, we can predict that the endmember from Leg 111 would be approximately 1.3‰ lighter than that from Leg 137 as observed (Fig. 7F). The oxygen isotopic evidence and comparison to theoretical fractionation support the concept that the reacted fluid originates at the hole bottom.

The regular changes in the reacted fluid "endmember" between legs (Fig. 7A-F), summarized in Table 5, can be interpreted as the result of reaction in the rubble pile at increasing temperatures as the borehole has been deepened between drilling legs. Alteration of the basalt releases Ca as Mg-rich clays and chlorite are formed. This reaction scheme would produce an increase in Ca" equivalent to the decrease in Mg. This 1:1 Ca* increase to Mg decrease is observed on Leg 70, but on subsequent legs excess Ca is released relative to Mg consumed. This charge imbalance is made up for by removal of Na from the borehole fluids. Na is presumably removed into albite or at lower temperatures analcime or other Na-zeolites, replacing the anorthic plagioclase of fresh basalt. Surprisingly few experimental investigations have shown Na removal from solution during seawater/basalt interaction. However, many experiments have shown definitive formation of albite by observation of the reacted solids (e.g., Mottl and Holland, 1978). The majority of these experiments have been performed at water/rock mass ratios near 5, and temperatures ≥300°C. Perhaps a lower w/r and temperature are necessary for albitization to occur. Based on observations of seafloor metabasalts, Mottl (1983) suggests that albitization occurs only in strongly rock-dominated sys-

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Table 5. Comparison of borehole fluid endmembers at Mg = 0 mM for Hole 504B borehole fluids.

Leg	Depth (mbsf)	Temp. (°C)	Mg (mM)	Na (mM)	Ca* (mM)	K (mM)
70	489	80	0		65.0	-
83	836	112	0	421	98.2	3.9
92/111	1350	145	0	380	104.0	5.2
137	1562	162	0	337	120.0	6.2
Seawater Mottl & Gieskes 83–111			53.4 0	475 400	10.45 70	10.4 4.5

Note: -- = not analyzed,

tems. Sodium uptake on the order of that observed in Hole 504B has been observed in one water/rock experiment at high temperature and low water/rock ratio (T = 300°C, w/r = 1; Mottl and Holland, 1978). Theoretical calculations of Seyfried (1987), suggest that Na is not removed from solution at high temperature (>300°C) due to enhanced stability of epidote solid solutions resulting in redistribution of Ca in the solid phases. At lower temperatures, however, the stability of epidote decreases, while that of albite increases. Competition between albite and epidote for the Si and Al mobilized during alteration of plagioclase would thus seem to favor formation of albite at lower tem- peratures. Mass balance calculations in the previous section also sup- port precipitation of albite or analcime as the sink for Na from the fluids. Uptake of K, while not of major importance to the charge bal- ance, decreases as the maximum borehole temperature increases. Experimental evidence suggests that K should be released at temperatures above 150°C, while taken up at low temperatures (Mottl, 1983). The direction of change in K is in agreement with this transition, but the temperature of the borehole during Leg 137 is slightly higher than would be expected for continued uptake of K. This is perhaps due to the relatively low percentage of rock altered as calculated above; hence, relatively little K is released in comparison to experiments run on very fine grain material where all the K is mobilized.

SUMMARY

Borehole fluids sampled during Leg 137 were analyzed for major, minor, and isotopic composition for various elements. Changes in fluid chemistry reflect the result of seawater/basalt interaction. Element vs. element diagrams reveal that the fluid samples can be described as mixtures between a single reacted fluid component and seawater. Clay-coated basaltic rubble and anhydrite collected from the borehole prior to drilling suggest the possibility of reaction occurring within the borehole itself. Sr and Li isotopic investigations reveal a low w/r ratio and incomplete mobilization of Sr from the basalt, suggesting incomplete reaction of fresh basalt in the reaction zone. Comparison of the borehole fluid endmembers between drilling legs reveals a regular change in chemistry as the borehole temperatures increase. Combined, this information suggests that reaction in the rubble and not true formation fluid is responsible for the observed changes in borehole fluid chemistry.

Important information of the nature of exchange at intermediate temperatures has nonetheless been gained through this study. A sink for sodium during reaction between seawater and basalt at temperatures of 80°C to at least 162°C has been observed. Chemical exchange between seawater and the crust at these temperatures may not be limited to removal of anhydrite and seawater Sr as some simple models of axial hydrothermal systems might suggest. Results from this study imply that significant reactions in the recharge zones of hydrothermal systems can occur as the fluids heat up in contact with basalt. Similarly, reaction of seawater with cooling basalts on the flanks of the mid-ocean ridges may result in significant fluxes of Na, an element elusive to flux calculations due to its high concentration in seawater. Li was found to be leached at moderate (160°C) borehole temperatures, with some redistribution into solid phases. The bore-



Figure 7. Comparison of element vs. Mg mixing lines for all legs from Hole 504B. Data from previous legs are from Mottl et al. (1985), Gieskes et al. (1986), and Shipboard Scientific Party (1988).

hole sampling program in Hole 504B has provided an in-situ basalt/ seawater experiment, which has evolved as the hole has been drilled deeper into the hotter formation.

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^{*} Abbreviations for names of organizations and publications in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

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