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14. MINERALOGY AND STABLE ISOTOPIC COMPOSITIONS OF THE HYDROTHERMALLY ALTERED LOWER SHEETED DIKE COMPLEX, HOLE 504B, LEG 140[1]

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ABSTRACT

Drilling during Legs 137 and 140 of the Ocean Drilling Program deepened Hole 504B, the only hole to penetrate through the volcanic section and into the underlying hydrothermally altered sheeted dike complex, by 438.1 m to a total depth of 2000.4 meters below seafloor. This paper presents the secondary mineralogy, bulk-rock sulfur contents, and stable isotopic (O, S) compositions, plus oxygen isotopic compositions of secondary minerals from the lower sheeted dike complex drilled during Legs 137 and 140. Various evidence indicates higher temperatures of hydrothermal alteration in the lower dikes than in the upper dikes, including: the local presence of secondary clinopyroxene in the lower dikes; secondary anorthite and hornblende in the lower dikes vs. mainly actinolite and albite-oligoclase in the upper dikes; generally increasing Al and Ti contents of amphibole downward in the dike section; and greater ^{18}O depletions of the lower dikes ($\delta^{18}O = 3.6–5.0‰$) compared with the upper dikes. Early high-temperature alteration stages (T = 350°–500°C) resulted in ^{18}O depletions and losses of metals (Cu, Zn) and sulfur from the rocks. Local incorporation of reduced seawater sulfate led to elevated $\delta^{34}S$ values of sulfide in the rocks (up to 2.5‰). Quartz + epidote formed in crosscutting veins at temperatures of 310°–320°C from more evolved fluids ($\delta^{18}O = 1‰$). Late-stage lower-temperature (~250°C) reactions producing albite, prehnite, and zeolites in the rocks caused slight ^{18}O enrichments, but these were insufficient to offset the ^{18}O depletions caused by earlier higher-temperature reactions. Addition of anhydrite to the rocks during seawater recharge led to increased S contents of rocks that had previously lost S during axial hydrothermal alteration, and to further increases in $\delta^{34}S$ values of total S in the rocks (up to 12‰). Despite the evidence for seawater recharge to near the base of the sheeted dike complex, the paucity of late zeolites in the lower dikes suggests that late-stage, off-axis circulation was mainly restricted to the volcanics and shallowest dikes, or to localized high-permeability zones (faults) at depth.

INTRODUCTION

Hole 504B is the deepest borehole in the ocean crust, and is the only hole to penetrate through the volcanic section altered at low temperatures and into the underlying hydrothermally altered sheeted dike complex. The hole has become a reference section for the structure, chemistry, physical properties, and hydrothermal alteration of the upper oceanic crust (Anderson et al., 1982; Becker et al., 1989). To date, seven legs of the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP) have been devoted to coring and logging operations in Hole 504B, and total penetration reaches to 2000.4 meters below seafloor (mbsf). ODP Leg 137 returned to Hole 504B in the spring of 1991 to clean the hole of a drill bit left from a previous leg. This operation was successful and the hole was cored ahead 59.2 m to 1621.5 mbsf. Subsequently, in the fall of 1991 Leg 140 returned to Site 504 with the goal of deepening the hole through the dikes of Layer 2C and into seismic Layer 3, which is thought by many to comprise gabbroic rocks (Dick, Erzinger, Stokking, et al., 1992). Drilling during Leg 140 penetrated 378.9 m farther into the sheeted dike complex, to 2000.4 mbsf, but did not recover any gabbros. Petrographic and seismic evidence, however, suggest that following Leg 140 the bottom of the hole lay near the base of the sheeted dikes (Dick, Erzinger, Stokking, et al., 1992). This portion of the crust is particularly interesting from the perspective of hydrothermal processes, because in this zone, just above the top of the axial magma chamber, reactions controlling the compositions of hydrothermal fluids venting on the seafloor are thought to occur (Seyfried et al., 1988; Seyfried and Ding, 1993). In ophiolites, the rocks in this zone are commonly depleted in metals and exhibit increasing metamorphic grade, from greenschist to amphibolite grade mineralogies (Schiffman et al., 1987; Harper et al., 1988; Baragar et al., 1989).

This paper presents data on the secondary mineralogy, bulk-rock sulfur contents, and bulk-rock stable isotopic (O, S) compositions, plus oxygen isotopic compositions of secondary minerals from the lower sheeted dike complex drilled during Legs 137 and 140. Our goals are to constrain the conditions of hydrothermal alteration and determine the effects of alteration on the stable isotopic composition of this critical portion of the oceanic crust. This work is a continuation of previous studies on the volcanics and upper dikes of Hole 504B (Alt et al., 1985, Alt, Honnorez, Laverne, and Emmermann, 1986; Alt, Muehlenbachs, and Honnorez, 1986; Alt, Anderson, Bonnell, and Muehlenbachs, 1989; Alt, Anderson, and Bonnell, 1989). More detailed and extensive analyses of secondary mineral chemistry are given by Laverne et al. (this volume), and other bulk chemical variations are discussed by Zuleger et al. (this volume). The results of our study indicate significant changes in the oxygen and sulfur isotopic compositions, mineralogy, and bulk-rock chemistry of the lower sheeted dike complex compared with the upper dikes.

SITE 504

Hole 504B is located in 5.9-Ma. crust, 200 km south of the intermediate-spreading-rate Costa Rica Rift in the eastern Pacific (Fig. 1). Drilling during several previous legs plus Leg 140 penetrated 274.5 m of sediments, a 571.5-m volcanic section, a 209-m transition zone, and 945 m into the sheeted dike complex (Fig. 2). Recovery from the 379 m cored during Leg 140 averaged 13%. The recovered cores consist of fine-grained massive basalts having microcrystalline to diabasic textures. Four chilled intrusive margins were recovered, and the rocks cored are interpreted to be a continuation of the sheeted dike complex drilled during previous legs. The rocks contain variable amounts of plagioclase, olivine, and clinopyroxene phenocrysts, as well as common accessory chrome spinel. The compositions of dikes recovered during Leg 140 are similar to those from the overlying dikes. They are quartz-normative tholeiites and generally fall in the

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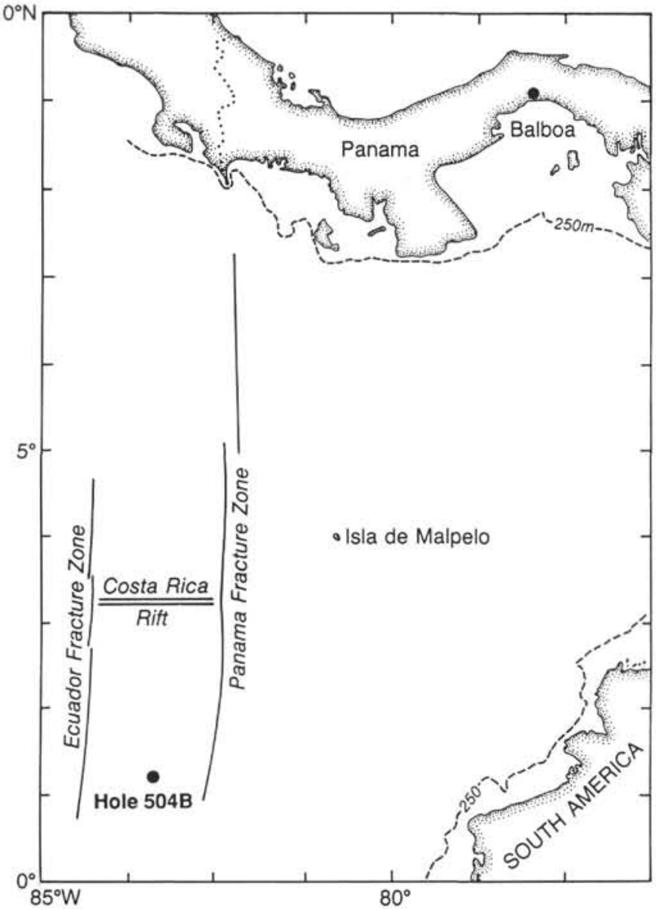

Figure 1. Location of Hole 504B in the eastern Pacific.

range of moderately evolved mid-ocean-ridge basalt (MORB), having incompatible element ratios comparable to normal type-I MORB (Dick, Erzinger, Stokking et al., 1992). The rocks are unusually depleted in incompatible elements (Ti, Y, and Zr), however, and have been interpreted as being primitive (Emmermann, 1985; Natland et al., 1983), or the result of multistage melting of a normal MORB mantle source followed by a moderate extent of crystal fractionation (Autio and Rhodes, 1983). The overall uniformity in composition of the basalts from Hole 504B has been interpreted to indicate the presence of a nearly steady-state magma chamber beneath the rift axis (Natland et al., 1983). Despite the general uniformity in composition, local small variations in the extent of differentiation and plagioclase and olivine accumulation occur in the rocks, which may be related to the injection of dikes in packets (Zuleger et al., this volume), and two units of transitional or enriched basalts occur in the core above the Leg 140 section (Emmermann, 1985).

Study of the secondary mineralogy, stable isotopic compositions, and fluid inclusions led to a model for the hydrothermal history of the upper crust at Site 504 (Fig. 3; Alt, Honnorez, Laverne, and Emmermann, 1986; Alt, Muehlenbachs, and Honnorez, 1986; Alt, Anderson, Bonnell, and Muehlenbachs, 1989; Alt, Anderson, and Bonnell, 1989). The volcanic section was affected by low-temperature (<100°C) oxidizing alteration at high seawater/rock ratios (~100), whereas the lower volcanics underwent low-temperature alteration under more restricted circulation and more reducing conditions, at lower seawater/rock ratios (~10). There is an abrupt change to the underlying transition zone and sheeted dikes, which were altered to greenschist facies minerals (Fig. 2) at higher temperatures (250°–380°C). At the spreading axis, hydrothermal fluids upwelling along fractures in the relatively "tight" dikes mixed with larger volumes of cooler seawater circulating in the more porous and permeable volcanic section, causing the formation of a stockwork-like sulfide mineralization in the transition zone and the development of a sharp alteration boundary in the crust. Evolution of the compositions of hydrothermal fluids resulted in deposition of a sequence of secondary minerals filling fractures in the sheeted dikes: first chlorite and actinolite formed from more seawater-like fluids, followed by epidote and quartz ± sulfides from more evolved fluids. Later recharge of seawater into hot rocks led to the deposition of anhydrite in veins, and finally, off-axis circulation of highly evolved fluids at lower temperatures (<250°C) resulted in the formation of zeolites in veins and rocks of the upper dike section. Trends toward increasing amounts of actinolite, increasing alteration of pyroxene, and decreasing alteration of plagioclase were recognized in samples from Leg 111 (1075.5–1287.8 mbsf; Fig. 2), and suggested generally increasing temperatures of alteration downward in the dikes (Alt, Anderson, Bonnell, and Muehlenbachs, 1989).

METHODS

Secondary minerals were studied in transmitted and reflected light, and identifications were aided by energy-dispersive X-ray analyses. Chemical compositions of secondary minerals were determined by electron microprobe (Cameca CAMEBAX instrument with three wavelength-dispersive spectrometers). Some secondary mineral chemistry is presented in this paper, but more detailed and comprehensive analyses are given elsewhere (Laverne et al., this volume). Oxygen was extracted from whole-rock powders and from minerals separated from veins by reaction with ClF_3 and converted to CO_2 gas using the techniques of Clayton and Mayeda (1963). Oxygen isotope ratios were then analyzed on a Finnegan Delta-S mass spectrometer. Results are reported as δ notation relative to standard mean ocean water (SMOW; Craig, 1961), where $\delta^{18}O = [(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{SMOWD}] \times 10^3‰/(^{18}O/^{16}O)_{SMOW}$. Repeated extractions and measurements of samples and standards were reproducible within ±0.2‰. Sulfur was extracted from whole-rock powders in a step-wise process. First, sulfur from acid-soluble sulfides (pyrrhotite, pentlandite) was liberated as H_2S by reaction of whole-rock powders with 6N HCl at 80°C under nitrogen atmosphere, and H_2S was precipitated as Ag_2S by reaction with $AgNO_3$ solution. Second, the residue from the previous stage was reacted with $CrCl_2$ solution at 80°C for at least 2 hr to break down pyrite plus chalcopyrite, and the sulfur liberated as H_2S was precipitated as Ag_2S. Finally, the reaction solution was filtered, warmed to near boiling, and $BaCl_2$ solution added to precipitate any soluble sulfate as $BaSO_4$. Ag_2S was reacted with CuO, and $BaSO_4$ was reacted with Na_2PO_4 under vacuum at 1000°C to produce SO_2 gas, which was analyzed on a VG Micromass 602E mass spectrometer. Results are reported as δ notation relative to Canyon Diablo Troilite (CDT), and are based on $\delta^{34}S$ values of 17.09‰ for NBS 123 sphalerite and 20.32‰ for NBS 127 $BaSO_4$ (Hut, 1987). Instrumental uncertainty for reported $\delta^{34}S$ values is better than ±0.2‰ (standard deviation), and repeated analyses of standards give standard deviations of +0.2‰. Multiple extractions and analyses give uncertainties of ±0.5‰, however.

The degree of alteration, defined as the modal abundance of secondary minerals, was visually estimated in thin section. Alteration also was estimated in shipboard thin sections that were point counted for alteration phases to ascertain the reliability of the visual estimates. The visual estimates agree within 5%–10% of the estimates from shipboard modal analyses by point counting.

RESULTS

Petrography of the Lower Sheeted Dikes of Hole 504B

The rocks recovered during Legs 137 and 140 are affected by a pervasive background alteration and are generally 10%–20% recrystallized, but locally are more intensively recrystallized (50%–100%) in centimeter- to decimeter-size alteration patches and centimeter-

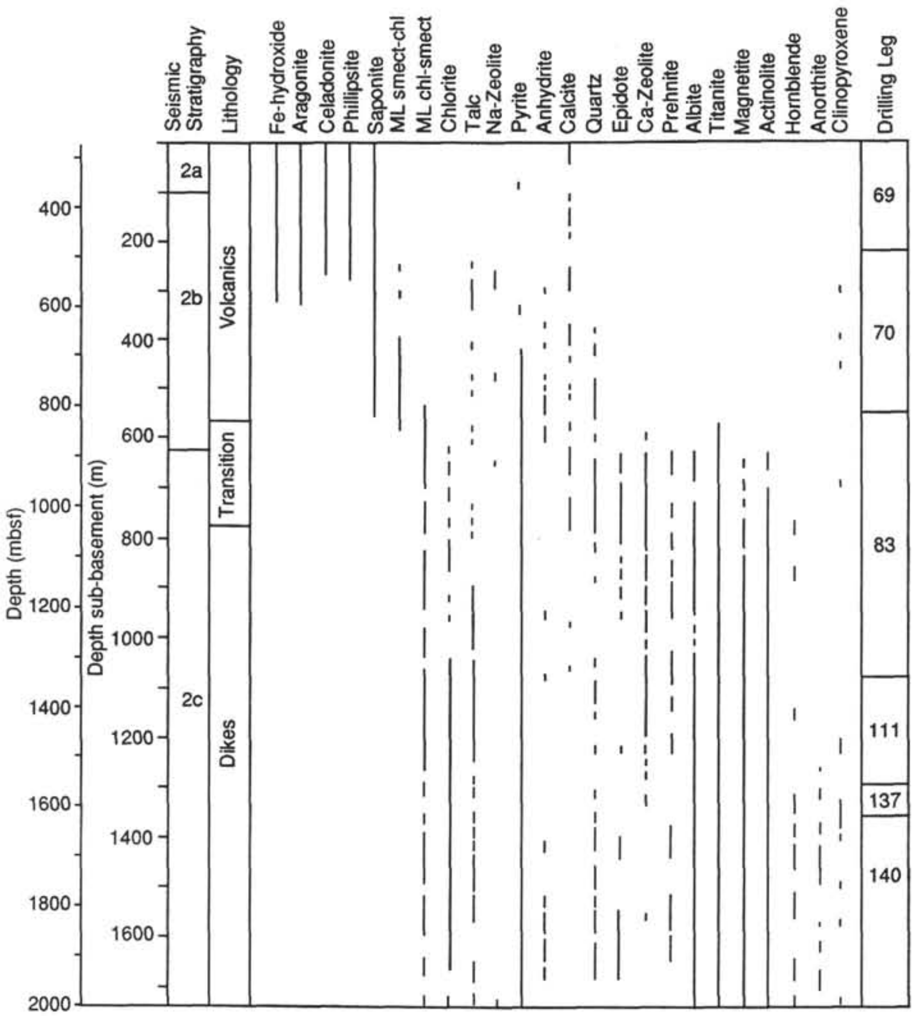

Figure 2. Lithostratigraphy of Hole 504B, showing distribution of secondary minerals with depth in the core. The lower dike section is characterized by secondary clinopyroxene, anorthite, hornblende, epidote, and anhydrite. Also shown are depths penetrated by different drilling legs, and seismic stratigraphy of the crust at Site 504. ML = mixed-layer.

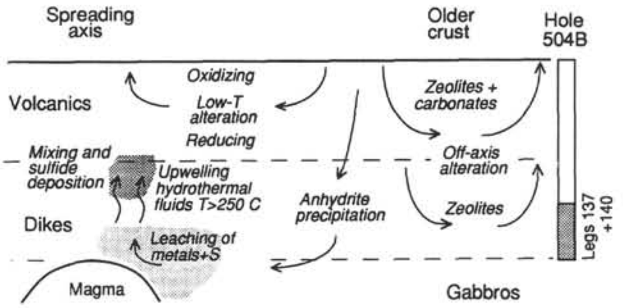

Figure 3. Cartoon illustrating various stages of alteration undergone by the different portions of Site 504 crust as it moved away from the spreading axis. Also shown is the depth interval of the Leg 137/140 sheeted dike section discussed in this paper. See text for details of alteration stages.

wide alteration halos around veins (Fig. 4). In this sense they are quite similar to rocks recovered from the upper dike section in Hole 504B (Alt et al., 1985; Alt, Honnorez, Laverne, and Emmermann, 1986; Alt, Anderson, Bonnell, and Muehlenbachs, 1989), but significant differences in mineralogy and compositions of secondary minerals occur in the Leg 137/140 section.

In the rocks affected by background alteration, clinopyroxene is partly to totally replaced by actinolitic hornblende plus fine (<1–5 μm) magnetite. In the least altered rocks, clinopyroxene is only slightly corroded and altered to fibrous amphibole and magnetite around the rims and in irregular patches. Plagioclase is generally only slightly altered to albite-oligoclase and chlorite along fractures and grain boundaries, but is locally more extensively altered to albite-oligoclase and secondary anorthite. Epidote, prehnite, laumontite, and anhydrite also replace plagioclase locally in small amounts. Titanomagnetite generally exhibits ilmenite exsolution lamellae, and is partly to extensively altered to titanite. Olivine is generally totally altered to chlorite, mixed-layer chlorite-smectite, actinolite, talc + magnetite, quartz, and sulfide minerals. Rocks from 1710–1740 mbsf are characterized by generally slight alteration (<20%), with lower abundances of actinolite and chlorite than other cores, by the presence of talc replacing olivine and in interstitial areas, and by the presence of relict igneous olivine in the rocks. This same type of slightly altered rock also occurs sporadically at greater depths in the lower dikes, and similar rocks (but lacking fresh olivine) were observed locally in the upper dikes (1189–1319 mbsf and locally from 1350 mbsf to 1480 mbsf; Alt et al., 1985; Alt, Honnorez, Laverne, and Emmermann, 1986; Alt, Anderson, Bonnell, and Muehlenbachs, 1989).

Sulfide minerals are commonly present in interstitial areas and as inclusions in plagioclase and rarely in clinopyroxene, Cr spinel, and olivine. The sulfide minerals occur as 2- to 40-mm equant to globular grains of pyrrhotite or pyrite, ± chalcopyrite ± magnetite, or chalcopyrite alone. The sulfide inclusions in primary silicates are clearly

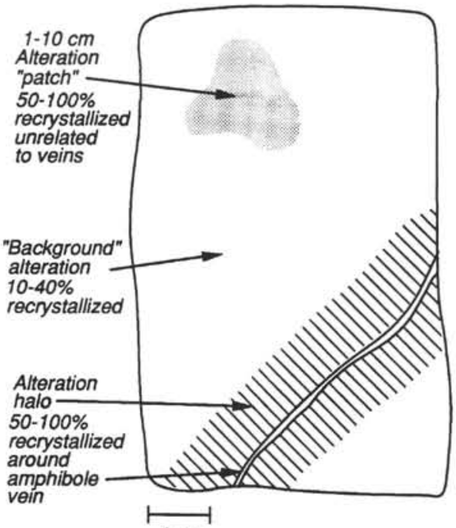

Figure 4. Sketch of hand specimen, illustrating various alteration features observed in core from Legs 137 and 140. See text for description.

recrystallized igneous grains, and the small size and globular textures of interstitial sulfides in the slightly recrystallized rocks affected by background alteration suggest that these are also recrystallized igneous sulfides. Secondary pyrite is present in trace amounts as pseudomorphs of igneous sulfides, as 10- to 800-µm equant to irregular, porous grains in interstitial areas, and replacing silicates. Pyrite is present in some cases as overgrowths on and replacing igneous titanomagnetite or as small (<20 µm) veinlets in the groundmass. Secondary chalcopyrite is commonly present intergrown with or as inclusions in the pyrite. Secondary chalcopyrite is also present in trace amounts as 2- to 100-µm anhedral grains in interstitial areas and replacing silicates. Secondary sulfide minerals are particularly common in phyllosilicate pseudomorphs after olivine. Magnetite is also commonly present with sulfides in phyllosilicate pseudomorphs after olivine. Trace amounts of hematite occur in olivine pseudomorphs in several samples, but it is never associated with sulfides, and it only occurs in what is interpreted to be the last or most recent replacement products of olivine in zoned pseudomorphs (mainly smectite and mixed-layer smectite-chlorite).

The rocks are much more intensively recrystallized (50%–100%, but generally 70%–90%) in irregularly shaped 1- to 10-cm-sized alteration patches, which occur in the coarser-grained interior portions of dikes. The secondary mineralogy of these patches is generally the same as in the background alteration, but secondary anorthite, anhydrite, epidote, and prehnite replacing plagioclase are more abundant, and sulfide minerals are rare in the patches. The patches commonly surround 0.1- to 10-mm irregularly shaped to slightly round amygdules, which are filled with actinolite, chlorite, quartz, epidote, anhydrite, prehnite, and laumontite. The amygdules are filled primary pore spaces, which allowed greater amounts of water into the rock and facilitated the more intensive alteration of the surrounding rock, producing the alteration patch.

More intensively recrystallized rock (50%–100%) also occurs in ~1-cm-wide alteration halos around amphibole ± chlorite veins. The mineralogy of these halos is generally similar to the host rocks, but the rocks are more intensively altered, clinopyroxene is up to 100% altered to amphibole, and secondary anorthite is more common replacing plagioclase. Fine-grained rocks are commonly more intensively recrystallized and are light gray in color. These rocks contain abundant thin (<1 mm) amphibole ± chlorite veins and the more intensive alteration of these samples may be the result of coalescing of alteration halos around the veins.

Veins mostly consist of multiple generations of amphibole, chlorite, or amphibole + chlorite, and commonly contain trace amounts of titanite and apatite (Laverne et al., this volume). Secondary clinopyroxene also occurs in veins with amphibole in a few samples (e.g., Sample 140-504B-177R-1, 11–14 cm; Laverne et al., this volume). Rare quartz, epidote, and quartz + epidote veins cut across the amphibole and chlorite veins, consistent with vein sequences from the upper dike section and transition zone (Alt, Honnorez, Laverne, and Emmermann, 1986; Alt, Anderson, Bonnell, and Muehlenbachs, 1989). Late anhydrite is present in a vein cutting quartz and epidote in one sample (140-504B-192R-1, 13–15), and rare late prehnite and laumontite veins also were observed (Dick, Erzinger, Stokking, et al., 1992).

Secondary Mineralogy

Phyllosilicates

Talc in Leg 137/140 rocks is characteristically colorless and exhibits high birefringence. Analyses of talc indicate the presence of trace amounts of Al and interlayer cations plus minor Fe (Table 1). These data suggest that minor amounts of chlorite (or smectite or mixed-layer chlorite-smectite) are present and that the talc is Fe-bearing, as was observed in talc from the upper dikes (Alt et al., 1985; Alt, Anderson, Bonnell, and Muehlenbachs, 1989; Shau and Peacor, 1992).

What was identified optically as smectite in Leg 137/140 rocks on the basis of comparison with results from the upper dikes (Alt et al., 1985; Alt, Anderson, Bonnell, and Muehlenbachs, 1989) is actually smectite-rich mixed-layer smectite-chlorite. This phase is yellow to brownish in thin section and exhibits second-order interference colors. Microprobe analyses indicate Mg-rich compositions, and calculated formulae indicate a trioctahedral structure (Table 1). Octahedral occupancies are slightly greater than six (formula based on layer charge of 44), indicating the presence of minor chlorite layers (e.g., Sample 140-504B-197R-1, 123–126 cm, in Table 1). Leg 137/140 smectite-chlorite analyses fall along trends of decreasing Fe/Fe+Mg and increasing Si contents on a chlorite classification diagram (Fig. 5), and fall within the field of smectite-rich mixed-layer smectite-chlorite from Hole 504B rocks determined by X-ray diffraction and microprobe (Alt et al., 1985; Alt, Anderson, Bonnell, and Muehlenbachs, 1989).

Chlorite in Leg 137/140 rocks is generally greenish in thin section and exhibits anomalous blue to purple and brown interference colors. Mixed-layer chlorite-smectite, identified optically on the basis of comparison with the upper dikes (Alt et al., 1985), is more strongly colored than chlorite and exhibits first- to second-order birefringence. Chlorites and mixed-layer chlorite-smectites from Leg 137/140 samples fall mainly within the fields of chlorite and chlorite-rich mixed-layer chlorite-smectite from the upper dikes (Fig. 5). "Chlorite" in Sample 140-504B-192R-1, 13–15 cm, has a relatively high formula Ca content (0.112) and a low octahedral cation total (11.78, Table 1) indicating the presence of smectite layers. No consistent differences between the compositions of phyllosilicates from the upper and lower dikes were detected. Leg 137/140 chlorites are generally not more Mg-rich than those shallower in the dikes as predicted aboard ship from optical properties. In one Leg 137/140 sample (140-504B-215R-1, 59–63 cm), however, chlorite replacing olivine and plagioclase is Mg-rich (Fe/Fe+Mg = 0.19 compared with 0.30–0.45 for most other chlorites at similar Si contents).

Chlorite compositions vary systematically with occurrence. Veins plot within the most Al- and Fe-rich compositions, and are more Al+Fe rich than in adjacent alteration halos and host rocks. Chlorite in alteration halos around veins and in alteration patches is more Al-rich than that in adjacent dark gray host rocks, but there is no consistent variation in Fe-Mg contents in these zones. Chlorite in fine-grained dike margins is also among the most Al- and Fe-rich: these rocks are extensively altered and light greenish-gray in color, similar to alteration halos around veins.

Serpentine was described aboard ship on the basis of its occurrence and optical properties (replacing olivine, colorless, first-order

Table 1. Representative electron microprobe analyses and calculated structural formulas for phyllosilicates and amphiboles.

Core-section:	197R-1	208R-1	236R-1	238R-1	192R-1	197R-1	197R-1	177R-1	177R-1	214R-1	214R-1	215R-1
Interval (cm):	123–126	88–91	26–28	8–9	13–15	123–126	123–126	11–14	11–14	73–76	73–76	59–63
Rock:	dark	bkgd	patch	bkgd	halo	bkgd	bkgd	halo	bkgd	patch	patch	bkgd
Mineral:	chl	chl	chl	chl	chl	talc	sm	act	act-hblde	act-hblde	ed-hblde	Fe-act hblde
Occ.:	ol	ol	vug	vug	ol	ol	ol	vein	vug	cpx	cpx	cpx
Wt%												
SiO_2	29.89	27.02	26.40	26.51	29.12	59.79	51.20	50.32	48.20	49.84	44.05	45.76
Al_2O_3	14.96	16.32	18.40	18.00	15.75	0.40	3.84	0.99	1.97	3.22	9.02	3.71
MgO	23.91	17.19	22.32	20.12	18.21	30.63	24.90	9.77	11.20	17.43	14.53	7.99
FeO	16.94	25.32	18.14	21.66	22.37	2.50	9.34	23.81	14.79	12.09	14.61	26.34
TiO_2	0.06	0.06	0.04	0.05	0.01	0.02	0.02	0.06	0.30	0.41	0.21	0.65
MnO	0.10	0.17	0.12	0.16	0.17		0.09	0.46	0.33	0.19	0.14	0.28
ZnO		0.06	0.08	0.06	0.10		0.01	0.03	0.03			
CaO	0.22	0.19	0.08	0.09	0.50	0.07	1.21	11.41	19.95	11.66	10.87	9.55
Na_2O	0.04	0.02	0.01		0.02	0.11	0.04	0.03	0.23	0.65	2.13	0.85
K_2O	0.02	0.03			0.04	0.02	0.04	0.02	0.01	0.04	0.07	0.25
Cl	0.01	0.02	0.03	0.01	0.02	0.04	0.02	0.00	0.01	0.10	0.26	0.42
Total	86.16	86.39	85.61	86.66	86.30	93.57	90.70	96.90	97.02	95.62	95.91	95.81
Atomic												
Si	6.134	5.811	5.514	5.570	6.143	9.950	9.214	7.728	7.326	7.379	6.654	7.277
Al	3.616	4.136	4.525	4.453	3.913	0.078	0.814	0.179	0.353	0.561	1.605	0.695
Mg	7.311	5.510	6.945	6.297	5.722	7.593	6.675	2.235	2.536	3.844	3.269	1.892
Fe	2.901	4.545	3.161	3.797	3.936	0.347	1.402	3.050	1.875	1.493	1.840	3.495
Ti	0.009	0.010	0.006	0.008	0.001	0.003	0.003	0.007	0.034	0.045	0.024	0.077
Mn	0.026	0.047	0.033	0.044	0.045		0.021	0.090	0.064	0.036	0.028	0.058
Zn		0.010	0.012	0.009	0.016		0.001	0.003	0.003			
Ca	0.048	0.044	0.019	0.020	0.112	0.012	0.234	1.879	3.252	1.852	1.761	1.630
Na	0.016	0.008	0.003		0.007	0.035	0.014	0.009	0.067	0.184	0.622	0.261
Cl	0.003	0.007	0.009	0.004	0.006	0.011	0.006	0.000	0.003	0.024	0.067	0.112
Fe/Fe+Mg	0.284	0.452	0.313	0.376	0.408	0.044	0.174	0.577	0.425	0.280	0.360	0.649
No. ox.	28	28	28	28	28	22	22	23	23	23	23	23

Notes: bkgd = background; act = actinolite; hblde = hornblende; Occ. = occurrence; ol = replacement of olivine; vug = filling pore space; cpx = clinopyroxene; blanks = none detected; No. ox. = number of oxygens.

gray interference color), but was not found by microprobe. An analysis of optically identified "serpentine" in one sample (140-504B-197R-1, 123–126 cm) plots in the smectite-rich mixed-layer chlorite-smectite field (Si = 6.5–7, Fe/Fe+Mg = 0.28), transitional between analyses of chlorite and smectite from Leg 137/140.

Amphiboles

Amphiboles in Leg 137/140 rocks are mainly actinolitic hornblende, but commonly range to actinolite and magnesio-hornblende (Fig. 6). The amphiboles are mostly calcic, but common subcalcic amphiboles are present. Edenite to edenitic hornblende occurs in Sample 140-504B-214R-1, 73–76 cm, which is from the extensively altered portion of the coarsest-grained rock recovered from the hole. These edenitic amphiboles also have the highest Ti contents (0.083–0.168 per formula).

The amphiboles are mostly green in color, but more brownish and bluish-green amphiboles occur locally. No consistent difference in composition was detected among amphiboles of different color. The compositions of amphiboles from veins and alteration zones (halos along veins and isolated patches) overlap those from other rocks, but the most Al- and Ti-rich amphiboles occur in veins and more altered zones. Significant variations in compositions of amphiboles also occur within individual samples. For example, amphiboles in a vein in Sample 140-504B-177R-1, 11–14 cm, range from actinolite to magnesio-hornblende in composition, with Mg/Mg+Fe ranging from 0.42 to 0.77. Actinolite to actinolitic hornblende replaces pyroxene in other samples, and actinolitic hornblende is present in the same sample in which edenite and edenitic hornblende also occurs.

In the lower dikes, two mechanisms apparently control the Cl contents of amphiboles, which range up to 0.4 weight percent (wt%). Cl contents exhibit generally positive correlations with Al^{IV} and Na+K formula contents (Fig. 7), suggesting dependence of Cl content on coupled Al^{IV} + (Na, K) substitution for Si. There is a generally negative correlation of amphibole Cl contents with Fe content, but the two samples that plot off the general trend to high Cl contents in Figure 7 have high formula Fe/Fe+Mg ratios (0.64–0.70 vs. <0.5 for most Leg 137/140 amphiboles), suggesting that Cl also may be preferentially incorporated into high-Fe amphiboles. Both these types of structural control of the Cl contents of amphiboles in altered seafloor rocks have been previously proposed, as well as a fluid salinity control on high-Cl amphiboles (>1 wt% Cl; e.g., see Vanko, 1986).

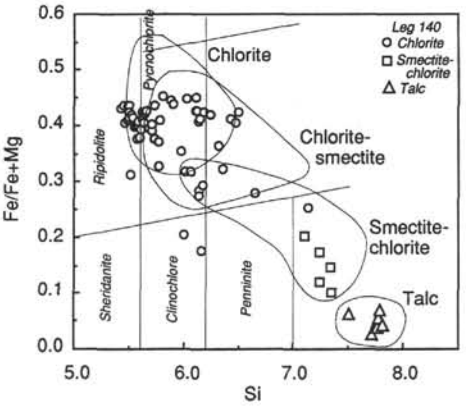

Figure 5. Compositions of phyllosilicates in the lower sheeted dikes of Hole 504B sampled during Leg 137/140 (atomic formula contents). Chlorite formulas were calculated on the basis of a layer charge of 56, whereas smectite-chlorite and talc formulas were calculated on the basis of a layer charge of 44. Fields of chlorite, mixed-layer chlorite-smectite, mixed-layer smectite-chlorite, and talc from Legs 83 and 111, which were identified by combined X-ray diffraction and microprobe analyses (Alt et al., 1985; Alt, Honnorez, Laverne, and Emmermann, 1986; Alt, Anderson, Bonnell, and Muehlenbachs, 1989), are shown for comparison.

Amphibole compositions show a general trend with depth in the dikes. Amphiboles in the upper dikes are mainly actinolite and actinolitic hornblende, whereas the lower dikes are mainly actinolitic hornblende and magnesio-hornblende (Fig. 6). Ti contents of amphiboles also exhibit a general increase from the upper to lower dikes (Fig. 6). Although the compositional variations are large, the generally higher Al and Ti contents of amphibole in the lower dikes indicate

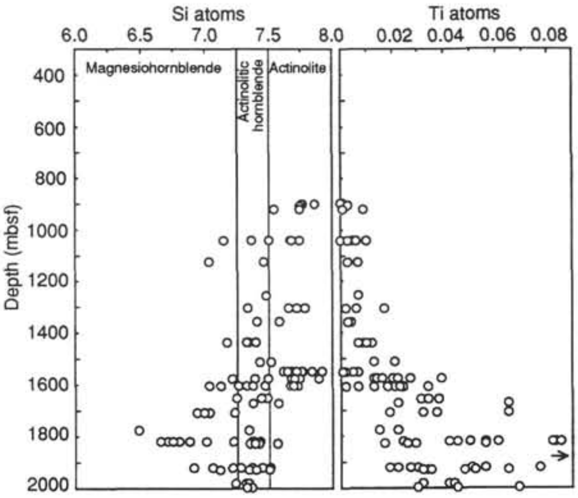

Figure 6. Amphibole compositions vs. depth in Hole 504B (atomic formula contents). Magnesio-hornblende becomes common and Ti contents are generally greater below about 1550 mbsf, consistent with generally greater temperatures of alteration in the lower dikes. Data from this work and Alt et al. (1985); Alt, Honnorez, Laverne, and Emmermann (1986); Alt, Anderson, Bonnell, and Muehlenbachs (1989).

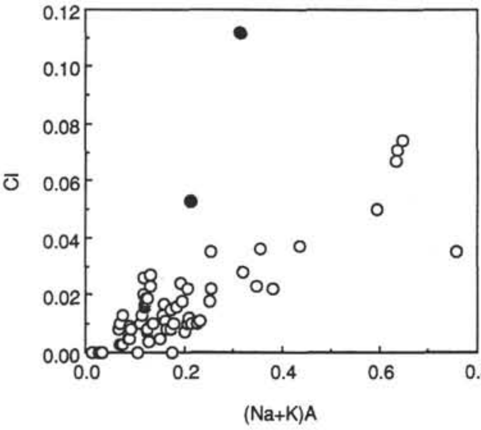

Figure 7. Cl vs. (Na+K) contents of Leg 137/140 amphiboles (atomic formula contents). Cl contents are generally structurally controlled by substitution of Al + (Na+K) for Si. Two points (solid circles) that fall off the main trend have high formula Fe/Fe+Mg ratios (0.65–0.7 vs. <0.5 for most Leg 137/140 amphiboles) indicating a second structural control of Cl by Fe content.

higher temperatures of alteration than shallower in the dikes (Raase, 1974; Robinson et al., 1982). The general positive correlation of Cl contents with Al and Ti suggests increasing incorporation of Cl into amphibole at higher temperatures.

Epidote

Leg 137/140 epidotes average 19 mol% pistacite component (range = 5%–29%), similar to epidotes from the upper dikes (16%–28% pistacite; Alt et al., 1985; Ishizuka, 1989). Significant variations in composition occur within individual crystal aggregates, but no consistent zonation was detected. Epidote is associated with variable combinations of oligoclase, laumontite, prehnite, and anhydrite replacing plagioclase in many samples, but there is no clear genetic association of epidote with these minerals.

Feldspars

Secondary feldspars range in composition from albite to oligoclase and anorthite. The occurrence of albite and oligoclase is similar to that in the shallower dikes, where it variably replaces the cores of phenocrysts in patches and along fractures, and partly to totally replaces groundmass plagioclase in more intensively altered rocks (Alt et al., 1985; Alt, Anderson, Bonnell, and Muehlenbachs, 1989; Ishizuka, 1989). The composition of secondary calcic plagioclase (An70–An87) falls within the range of igneous plagioclase phenocrysts in the dikes: An65-An90 (Alt, unpubl. data; Ishizuka, 1989; Kusakabe et al., 1989), but the porous, inclusion-riddled appearance of secondary anorthite and its occurrence as replacement rims on plagioclase crystals clearly indicate its secondary origin (Laverne et al., this volume).

Prehnite

The single prehnite occurrence analyzed contains 1.74 wt% Fe_2O_3T, and falls within the range of prehnite from the upper dike section, but at the low-Fe end of the latter (Alt et al., 1985; Ishizuka, 1989).

Clinopyroxene

Hydrothermal clinopyroxene occurs in a 0.6-mm-wide vein in Sample 140-504B-177R-1, 11–14 cm. A 30-µm subhedral crystal of augite occurs near the center of a vein rimmed by prismatic hornblende at the edge and filled by fibrous actinolite and chlorite. The augite crystal exhibits patchy compositional zoning in back-scattered electron images, and is similar in composition to Fe-poor hydrothermal clinopyroxenes from active geothermal areas (Bird et al., 1984). Estimated temperatures of formation on the basis of the composition of the hydrothermal clinopyroxene in Sample 140-504B-177R-1, 11–14 cm, are about 500°C (Kretz, 1982; Perchuk, 1969). Other secondary clinopyroxenes occur in the Legs 111, 137, and 140 sections; some are similar in composition to that reported here, whereas others have variably higher Ca, Na, Fe, and Ti contents (Ishizuka, 1989; Laverne et al., this volume).

Oxygen Isotopes

Quartz separated from two quartz + epidote veins has $\delta^{18}O$ values of 9.0‰ and 10.8‰ (Table 2). Epidotes separated from the same veins have $\delta^{18}O = 3.4‰$ and 5.1‰, yielding relatively constant fractionations between coexisting quartz and epidote (5.6‰–5.7‰). Assuming equilibrium and using the experimentally determined quartz-zoisite fractionation of oxygen isotopes, modified for the iron content of epidote (Matthews and Schliestedt, 1984), yields temperatures of 310°–320°C. Using these temperatures and applying the quartz-water isotopic fractionation then gives fluid $\delta^{18}O$ values of 0.9‰–1.2‰ (Clayton et al., 1972).

The Leg 137/140 whole rocks have $\delta^{18}O$ values ranging from 3.6‰ to 5.2‰ (Table 2), and are depleted in ^{18}O relative to unaltered MORB ($\delta^{18}O = 5.8 + 0.2‰$; Taylor, 1968; Muehlenbachs and Clayton, 1972). The less altered, dark gray "background" rocks have $\delta^{18}O$ values of 4.0‰–5.2‰ (mean = 4.6‰), generally higher than the more intensively altered patches and halos, which have $\delta^{18}O = 3.5‰–5.0‰$ (mean = 4.2‰).

Sulfur Contents and Sulfur Isotopes

Sulfur contents of Leg 137/140 dikes generally range from ~10 ppm to 1200 ppm, with locally higher values (Fig. 8). The proportion of sulfide to total sulfur (sulfide + sulfate) ranges from 1% to 99% (Table 2). The sulfide is predominantly "pyrite" sulfur (pyrite and chalcopyrite), with only traces of monosulfide sulfur present. This is consistent with petrographic observations of pyrite and chalcopyrite as the main sulfide phases in the rocks, and pyrrhotite commonly present in trace amounts.

Table 2. Stable isotope data for Leg 137 and 140 samples, Hole 504B.

Core, section,	Depth			Alt	$d^{18}O$		S (ppm)				$\delta^{34}S$		
interval (cm)	(mbsf)	Unit	Type	(%)	Rock	Mineral	HCl-S	Py-S	SO_4-S	Total	Py-S	SO_4	Bulk
173R-1, 134–137	1575.12		D	15	4.9		–	190	240	430	2.0	4.0	3.1
174R-1, 62–64	1578.76		L	70			–	25	160	185		8.0	7.0
174R-2, 82–84	1586.35		L	15	4.8		–	90	30	120			
177R-1, 11–14A	1605.81		D	20	4.3								
177R-1, 11–14B	1605.81		L	50	4.8								
178R-1, 21–23A	1615.90		D	10			tr	660	60	720	1.0	7.0	1.5
181R-2, 88–91A	1621.56		H	50	5.0		–	70	60	130	0.7		3.5
181R-2, 88–91B	1621.56		D	10			–	160	60	220	2.0		3.3
189R-1, 85–88	1652.33	218	D	12			–	730	40	770	1.0		1.3
189R-2, 15–17	1653.51	218	P	85	4.4		–	140	110	250	0.5	8.6	4.1
192R-1, 13–15	1672.10	218	Qz			10.8							
	1672.10	218	Ep			5.1							
193R-1, 22–24	1676.73	220	P	60	4.2		–	520	160	680	–0.5	11.2	2.3
194R-1, 36–40	1680.85	220	D	20	5.2		–	790	0	790	0.9		0.9
197R-1, 29–31	1704.24	222	H	70			–	100	70	170	2.5		4.3
197R-1, 123–126	1708.91	223	D	15	4.8		–	210	60	270	1.6		2.8
200R-2, 53–57	1732.32	227	D	10	4.9		–	720	120	840	0.9	3.8	1.3
204R-1, 0–4	1756.50	232	L	50	3.7								
208R-1, 88–91	1780.73	239	H	35	5.0		–	1530	40	1570	0.7		0.9
208R-1, 110–116	1781.41	239	D	18	5.0		–	980	10	990	0.7		0.8
209R-1, 35–41A	1788.39	240	P	50			–	60	30	90	–0.5		1.9
209R-1, 35–41B	1788.39	240	D	15			–	780	120	900	0.4		1.3
214R-1, 73–76	1819.75	244	P	90	3.5		–	20	4860	4880		11.9	11.9
215R-1, 59–63	1827.12	244	D	15	4.8		–	580	90	670	0.0	4.2	0.6
218R-1, 7–9	1850.23	247	L	55	3.7								
222R-1, 115–120A	1895.53	256	D	45	4.0		–	25	80	105		6.7	5.3
222R-1, 115–120B	1895.53	256	P	70			–	10	130	140		5.5	5.2
	1895.53	256	Qz			9.0							
	1895.53	256	Ep			3.4							
225R-2, 68–72A	1919.52	260	D	20	4.5		–	240	20	260	1.0		1.4
225R-2, 68–72B	1919.52	260	H	60	3.9		–	30	40	70			
227R-1, 67–70	1928.71	260	P	60			–	20	50	70			
230R-1, 11–14	1953.28	265	L	40	3.7		–	90	90	180	1.6	3.4	2.5
231R-1, 0–3A	1953.50	265	L	55			–	10	10	20			
231R-1, 0–3B	1953.50	265	H	50			–	110	40	150	1.4		2.8
236R-1, 26–28	1981.78	269	P	60	3.7		–	–	–	240			
238R-1, 8–9	1994.87	269	D	25	4.0								

Notes: $\delta^{18}O$ in per mil SMOW; δ34S in per mil CDT; dashes = none detected; blanks = not analyzed; D = dark, background alteration; L = light, more intense alteration; H = alteration halo; P = alteration patch; Qz = quartz; Ep = epidote; Alt = alteration; HCl-S = acid-extractable monosulfide sulfur; Py-S = "pyrite sulfur," actually pyrite + chalcopyrite sulfur; SO_4-S = sulfate sulfur. Where only pyrite-S or sulfate-S $\delta^{34}S$ values were available, bulk sulfur $\delta^{34}S$ were calculated assuming average $\delta^{34}S$ values for the missing pyrite-S and sulfate-S analyses (mean pyrite-S = 0.9‰, SO_4-S = 6.8‰).

Sulfide has $\delta^{34}S$ = –0.5‰–2.5‰ (Table 2), ranging from unaltered MORB glass compositions (0.1‰ ± 0.5‰; Sakai et al., 1984) to slightly enriched in ^{34}S. Sulfate extracted from whole rocks has $\delta^{34}S$ values of 3.4‰–11.9‰.

DISCUSSION

Sequence and Conditions of Alteration of the Lower Sheeted Dike Complex in Hole 504B

The sequence and conditions of alteration in the lower dikes of Hole 504B have been divided into five stages on the basis of secondary mineral relationships in veins and host rocks, and from detailed mineral chemistry (Laverne et al., this volume).

1. The first stage occurred at high temperatures, up to about 500°C. Access of fluids to the rocks exerted a strong control on restricting the effects of this stage to veins, associated alteration halos, and alteration patches. Secondary clinopyroxene formed locally, mainly by replacement of primary pyroxene, but also as precipitates from solutions in veins. Edentitic hornblende and magnesio-hornblende replaced pyroxene, and secondary anorthite replaced primary plagioclase in alteration halos and patches. Estimates assuming calcic plagioclase-magnesio-hornblende equilibria suggest temperatures of at least 400°C for this alteration stage (Laverne et al., this volume).
2. Pervasive alteration occurred throughout the rocks at temperatures of up to ~350–400°C, but the most intense recrystallization occurred where fluids had more efficient access to the rocks (i.e., in alteration halos and patches). Actinolitic hornblende, titanite, and oligoclase formed at the higher temperatures (~350°–400°C), while actinolite, chlorite, and albite formed at decreasing temperatures (probably less than 350°C). The formation of mixed-layer clays and smectite may be related to further decreases in temperature, but are more likely influenced by decreasing water/rock ratios and lower intensity of reaction. Where fluid access to the rocks was minimal, talc + magnetite partly to totally replaced olivine in the rocks. This latter alteration could have taken place over a wide range of temperatures, up to as high as 500°–600°C.
3. Quartz and epidote formed in crosscutting veins and pore space in the rocks, and epidote locally partly replaced plagioclase in the host rocks. Oxygen isotopic data indicate temperatures of 310°–320°C for the formation of epidote and quartz in the lower dikes (Table 2), similar to the range of temperatures estimated for quartz + epidote veins in the upper dikes and transition zone (300°–350°C; Alt, Muehlenbachs, and Honnorez, 1986). Quartz veins in the transition zone formed at temperatures as low as 200°C, however, which is attributed to mixing of hydrothermal fluids with cold seawater in this zone (Alt, Muehlenbachs, and Honnorez, 1986). The fluids in equilibrium with quartz-epidote veins in Leg 137/140 rocks were enriched in ^{18}O (~1‰), consistent with their interpretation as being evolved fluids that had previously reacted with basalt at high temperatures (>300°C; Alt, Muehlenbachs, and Honnorez, 1986).
4. Anhydrite formed locally in veins, in microcracks in the rocks, and replacing plagioclase during seawater recharge into the rocks.
5. Laumontite and prehnite formed locally in veins, filling pore space, and replacing plagioclase. Temperatures inferred for this stage are less than 250°C, and reactions are interpreted to have occurred during continued circulation of more evolved (Mg-depleted, Ca-enriched) off-axis hydrothermal fluids (Alt, Honnorez, Laverne, and Emmermann, 1986).

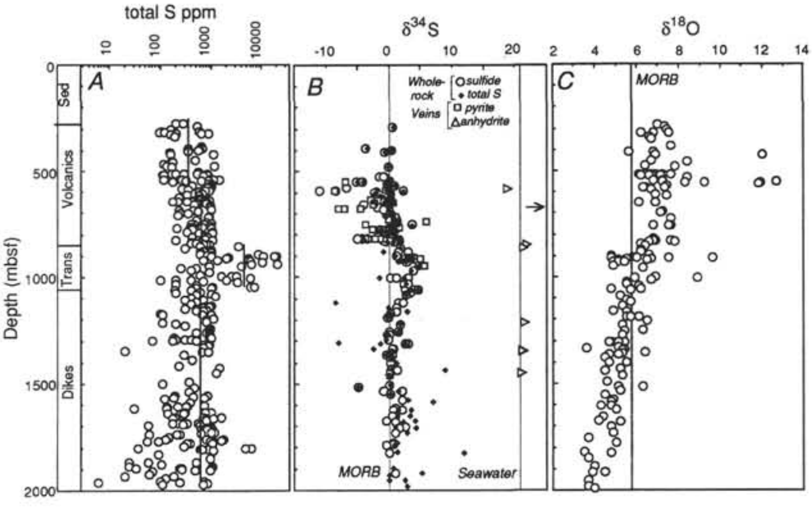

Figure 8. Total sulfur contents (**A**), sulfur isotopic compositions in per mil CDT (**B**), and whole-rock oxygen isotopic ratios in per mil SMOW (**C**) of samples from Hole 504B. Sulfur contents and $\delta^{18}O$ values decrease and total S $\delta^{34}S$ values increase in the lower dikes, below about 1500 mbsf. Data from Table 2; Alt et al. (1985); Alt, Honnorez, Laverne, and Emmermann (1986); Alt, Muehlenbachs, and Honnorez (1986); Alt, Anderson, Bonnell, and Muehlenbachs, (1989); Alt, Anderson, and Bonnell (1989); and Nesbitt et al. (1987). Vertical lines in (A) indicate average S contents for different zones in the core. Vertical lines in (B) indicate compositions of unaltered mid-ocean-ridge basalt (MORB) and seawater, and in (C), the composition of unaltered MORB.

The alteration stages are generally similar in the upper and lower dikes, and the temperatures of alteration in these two zones overlapped significantly. However, the peak alteration temperatures were greater in the lower dikes, and more of the alteration in the lower dikes took place at higher temperatures than in the upper dikes, as indicated by secondary mineralogy, mineral chemistry, and intensity of recrystallization of the rocks.

Oxygen Isotopes

The volcanic section of Hole 504B exhibits ^{18}O enrichments relative to unaltered basalt (Fig. 8) as the result of alteration by seawater at low temperatures (<100°–150°C; Alt, Muehlenbachs, and Honnorez, 1986). The abrupt appearance of ^{18}O-depleted rocks at 898 mbsf coincides with the presence of greenschist minerals in the rocks, and reflects the higher temperatures of hydrothermal alteration of the transition zone and upper dikes (~250°–380°C; Alt et al., 1985; Alt, Muehlenbachs, and Honnorez, 1986; Alt, Anderson, Bonnell, and Muehlenbachs, 1989).

The lower dikes from Leg 137/140 exhibit significant differences in oxygen isotopic composition from the hydrothermally altered upper dikes and transition zone (above 1562 mbsf). First, the lower dikes are more depleted in ^{18}O relative to unaltered MORB than the upper dikes and transition zone (Fig. 8). Second, the more intensively altered patches and halos in the lower dikes are depleted in ^{18}O relative to adjacent dark gray host rocks, whereas the opposite pattern is observed in the upper dikes and transition zone (Fig. 9). These differences can be explained by a combination of higher temperatures and greater intensity of reaction in the lower sheeted dikes.

In the transition zone and upper dikes, progressive reaction and decreasing temperatures led to increased $\delta^{18}O$ in the more intensively altered portions of the rocks (Alt, Muehlenbachs, and Honnorez, 1986). During initial alteration at temperatures of about 250°–350°C, fixation of Mg and formation of low-$\delta^{18}O$ phases such as chlorite and actinolite led to pervasive ^{18}O depletions in the rocks. As reactions proceeded at progressively lower water/rock ratios, secondary albite formed in the more intensively altered rocks. Because of the greater fractionation of oxygen isotopes between albite and fluid, this led to increased ^{18}O enrichments of the patches and halos. Both ^{18}O enrichments of hydrothermal fluids and decreasing temperatures of alteration also could have contributed to the higher $\delta^{18}O$ of the more intensively altered rocks as reactions progressed in these zones. Late zeolites are more abundant in the more altered rocks, and the greater isotopic fractionation and lower temperatures of formation of these phases also contributed to the ^{18}O increases in these rocks.

In contrast, progressive water-rock reactions in the lower dikes generally did not cause ^{18}O enrichments of the rocks (Fig. 9). Initial high-temperature reactions (T = 400°–500°C), which produced secondary clinopyroxene, hornblende, and calcic plagioclase in alteration halos and patches, led to ^{18}O depletions in these zones. Reactions were mainly restricted to these more intensively altered zones, where fluids had easy access, but minor reaction may have occurred in the adjacent host rocks. The superimposed pervasive background alteration at somewhat lower temperatures (~350°–400°C) led to further reaction and ^{18}O depletion of halos and patches, plus the host rocks reacted at this time causing decreases in $\delta^{18}O$ of the host rocks (Fig. 9). Continued reactions at lower temperatures (250°–300°C) led to variable ^{18}O depletions or possibly to slight ^{18}O enrichments, depending upon the phases that formed and the temperatures of reaction. Thus, although the lines connecting adjacent intensively altered patches and halos and less-altered host rocks suggest continuous ^{18}O depletion of the lower dikes (Fig. 9), the more intensively altered rocks actually may have been enriched slightly in ^{18}O. Small amounts of late zeolites and prehnite occur in the Leg 137/140 rocks, and are interpreted to have formed at lower temperatures (<250°C), from more evolved, off-axis fluids (Alt et al., 1985; Laverne et al., this volume). Formation of these minerals resulted in ^{18}O enrichments of rocks from the upper dikes (Fig. 9; Alt et al., 1985; Alt, Muehlenbachs, and Honnorez, 1986), whereas in the lower dikes, early higher temperature alteration produced sufficiently great ^{18}O depletions and the later minerals are present in sufficiently small amounts that they did not generally raise the $\delta^{18}O$ of the more intensively altered patches and halos above those of the host rocks.

Overall, the temperatures of hydrothermal alteration and intensity of reaction of the lower dikes were greater than in the upper dikes, which can account for the general decrease in whole rock $\delta^{18}O$ values downward in the dikes (Fig. 8). The much lower abundances of zeolites in general, and specifically the near-absence of zeolite veins in the lower dikes, suggest that significant amounts of cooler, off-axis fluids did not circulate through the lower dikes. Off-axis circulation may have been restricted mainly to shallower depths in the crust, where zeolites in veins are more common, but also could have been channelled along more permeable horizons (faults) deeper in the crust or at similar depths adjacent to Hole 504B.

Sulfur Contents and Sulfur Isotopes

Rocks of the volcanic section exhibit losses of sulfur and decreases in $\delta^{34}S$ values (Fig. 8), which result from the oxidation of igneous sulfides and the local precipitation of secondary sulfides during seawater alteration (Alt, Anderson, and Bonnell, 1989). The S- and ^{34}S-enrichments of the transition zone (Fig. 8) are the results of transport and deposition of crustal sulfide from deeper in the dikes and upper gabbros by hydrothermal solutions, as well as incorporation of ^{34}S-rich sulfide derived from the reduction of seawater sulfate

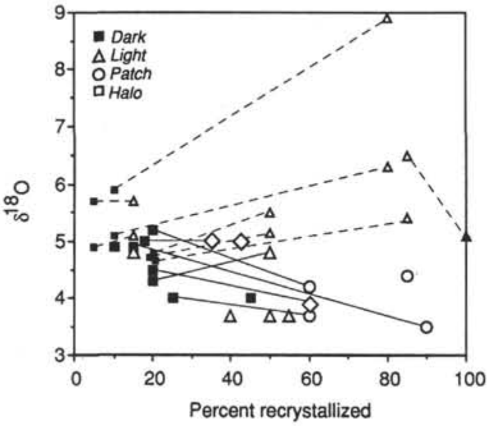

Figure 9. Oxygen isotopic compositions of bulk rocks vs. percent recrystallization (as indicated by modal percent secondary minerals) for samples from the lower sheeted dikes (>1562 mbsf) sampled on Legs 137 and 140 (large symbols and solid lines) and pairs of samples from the shallower dikes (<1562 mbsf) sampled on Legs 83 and 111 (smaller symbols and dashed lines). Lines connect adjacent samples affected by background and more intensive alteration. The shallower dikes exhibit ^{18}O enrichments as the result of progressive reaction at lower temperatures from more evolved fluids, whereas such effects were less extensive in the lower dikes (see text for discussion).

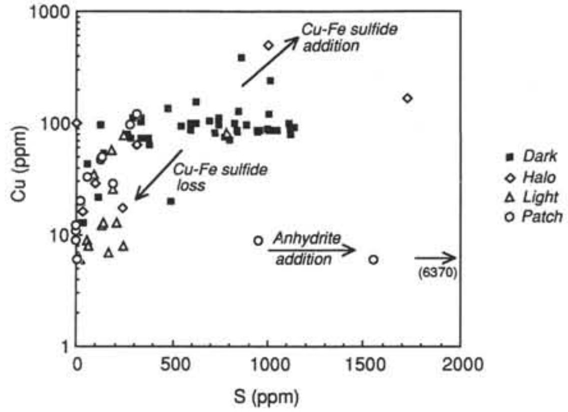

Figure 10. Cu contents vs. S contents for lower dikes from Legs 137 and 140, Hole 504B. Trends toward losses of Cu and S are the result of leaching of metal sulfides from the rocks, and high S contents at low Cu contents were caused by later addition of anhydrite to the rocks. Data from Zuleger et al. (this volume). See text for discussion.

during mixing of hydrothermal fluids with seawater and the consequent formation of the stockwork-like sulfide mineralization (Alt, Anderson, and Bonnell, 1989). The S contents and $\delta^{34}S$ values of the upper dikes reflect the local incorporation of small amounts of reduced seawater sulfur and losses of some basaltic sulfide to hydrothermal fluids.

The wide range in sulfur contents of the lower dikes from Hole 504B cored during Legs 137/140 (<10–6370 ppm) results from several processes. A general decrease in sulfur contents occurs with increasing percentage of alteration of the rocks, and the more intensively altered patches and halos contain significantly less sulfur (<250 ppm) than adjacent host rocks (~250–1200 ppm; Fig. 10; Zuleger et al., this volume). Cu exhibits similar trends of decreasing Cu contents at increasing intensities of alteration, and the halos and patches are depleted in Cu compared with the host rocks (Fig. 10; Zuleger et al., this volume). These trends are the result of leaching of Fe- and CuFe-sulfides during alteration of the rocks. Variation in the amount of Fe-sulfide in the rock leads to variable S contents at relatively constant Cu, and local addition of CuFe-sulfides resulted in increased Cu and S in a few samples. Zn contents progressively decrease with depth in the lower dikes (Fig. 11), although this trend may be attributed to alteration of pyroxene in the rocks to amphibole (Zuleger et al., this volume). The concentrations of metals and S in solution during alteration of basaltic rocks by seawater increase significantly at temperatures above 350°C (Seyfried et al., 1988; Seewald and Seyfried, 1990). Thus, the decreased Cu, Zn, and S contents of the lower dikes in Hole 504B are consistent with the higher temperatures of alteration of these rocks than shallower in the dikes. Similar losses of metals and S occur in the lower portions of sheeted dike complexes in ophiolites (Harper et al., 1988; Baragar et al., 1989; Alt, unpubl. data). The metals and sulfur were lost from the lower Hole 504B dikes to hydrothermal fluids, and were probably transported and redeposited as metal sulfide deposits at the seafloor or in the subsurface, such as the stockwork-like sulfide mineralization in the transition zone in Hole 504B (Fig. 11). Indeed, mass balance calculations indicate that the Cu and Zn enrichments of the transition zone in Hole 504B can be accounted for by the amounts of these metals lost from the lower dikes (Zuleger et al., this volume).

The $\delta^{34}S$ values of sulfide in the rocks (–0.5‰–2.5‰) overlap the range for sulfide in unaltered MORB glass (0.1‰ ± 0.5‰; Sakai et al., 1984), but extend to significant ^{34}S enrichments. The latter are attributed to reduction of seawater sulfate ($\delta^{34}S = 20‰$) and incorporation of resultant ^{34}S-enriched sulfide into the rocks. At the relatively high temperatures (350°–400°C) and conditions indicated by the sulfide mineral assemblage in the rocks (pyrite + chalcopyrite ± pyrrhotite), sulfate reduction should be rapid, and essentially all sulfur in solution should be present as sulfide (Ohmoto and Rye, 1979; Ohmoto and Lasaga, 1985). There is no correlation of sulfide contents of the rocks with $\delta^{34}S$ values of sulfide, so various combinations of reduction of seawater sulfate, leaching of basaltic sulfide, and incorporation of resultant hydrothermal sulfide into the rocks must have occurred. Seawater sulfate was likely reduced through conversion of igneous pyrrhotite to secondary pyrite and through oxidation of ferrous iron in the rocks (Fig. 11; Shanks and Seyfried, 1987: Alt, Anderson, and Bonnell, 1989).

Other processes also have affected the sulfur contents of some of the lower dikes in Hole 504B. Several samples plotted in Figure 10 contain large amounts of S (up to 6370 ppm) but have very low Cu contents (<10 ppm). These same samples also have high SO_4/Total S contents, consistent with petrographic observation of anhydrite filling pore space and replacing plagioclase in the rocks. It has been suggested recently that anhydrite may be present in subsurface high-temperature reaction zones, where it maintains mildly oxidizing conditions that control the Fe/Cu ratios of seafloor vent fluids (Seyfried and Ding, 1993). However, there is no evidence that anhydrite in the lower dikes of Hole 504B formed at high temperatures (>300°C). In contrast, anhydrite is present in at least one vein and fills pore space (as well as replacing plagioclase) and is commonly associated with microfractures, and hence is interpreted as a relatively late mineral that formed during recharge of seawater into the rocks (Alt, Anderson, and Bonnell, 1989; Dick, Erzinger, Stokking et al., 1992; Laverne et al., this volume). Consequently, anhydrite formation resulted in addition of sulfur to rocks that had previously lost sulfur and metals during axial hydrothermal metamorphism.

Sulfate extracted from the lower dikes has low $\delta^{34}S$ values compared to seawater (3.4‰–11.9‰ vs. 20‰, respectively), suggesting that perhaps seawater had reacted with the rocks during recharge and anhydrite formation. One possibility is that the low values resulted from oxidation of basaltic sulfides and the release of basaltic S (~0‰) to solution during recharge, which would have decreased the $\delta^{34}S$ of sulfate in the recharge solutions. Oxidation of igneous sulfides and loss of sulfur are characteristic of rocks in the volcanic section (Alt, Anderson, and Bonnell, 1989), suggesting that these rocks could have been a source of basaltic S to recharge solutions. Anhydrite in veins of the transition zone and upper dikes, as well as sulfate extracted from a dike rock at 1437 mbsf that contains visible anhydrite, has $\delta^{34}S$

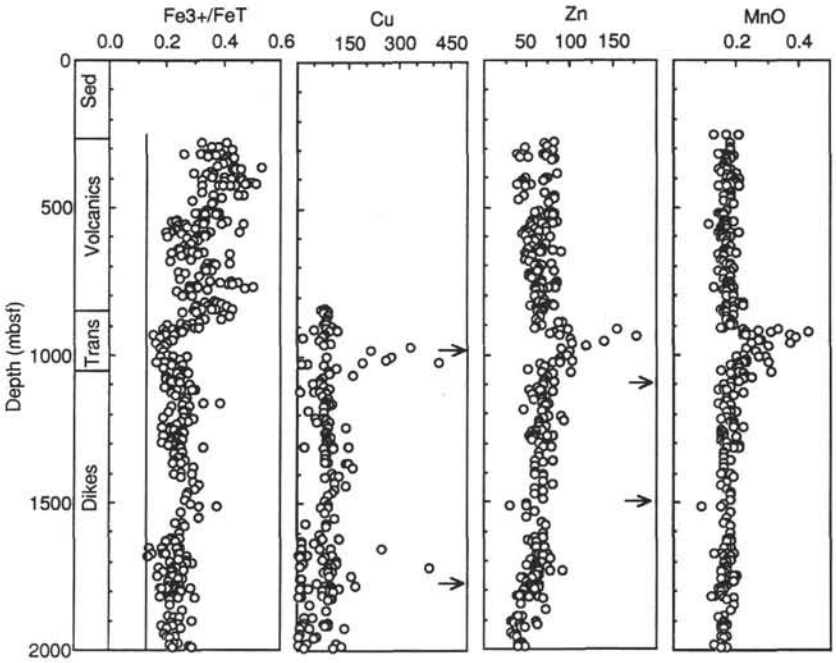

Figure 11. Plot of metal concentrations and oxidation ratio of iron vs. depth in Hole 504B. Vertical line indicates Fe^{3+}/Fe^{T} for unaltered glass. Arrows indicate samples that plot off-scale. Data from Alt et al. (1985); Alt, Honnorez, Laverne, and Emmermann (1986); Alt, Anderson, Bonnell, and Muehlenbachs (1989); and Zuleger et al. (this volume).

values near seawater, however (Fig. 8; Alt, Anderson, Bonnell, and Muehlenbachs, 1989; Alt, Anderson, and Bonnell, 1989). These data indicate that incorporation of oxidized basaltic sulfur from the volcanics was not an important control on the sulfur isotopic compositions of recharge fluids. There is no evidence to indicate oxidation of sulfide minerals to Fe- or Cu-oxides or oxyhydroxides in the lower dikes, either. Thus, the low values for the Leg 137/140 sulfates are attributed to oxidation of low-$\delta^{34}S$ sulfide to sulfate during the extractions, and combination of this sulfur with seawater sulfate derived from dissolution of anhydrite in the rocks.

The presence of anhydrite in the lower dike section exerts an important influence on the isotopic composition of total sulfur in the rocks. Figure 12 shows that as the proportion of sulfate sulfur to total sulfur increases, the $\delta^{34}S$ of total sulfur in the rocks increases. Thus, addition of anhydrite to the rocks led to increased $\delta^{34}S$ of the rocks. Although the $\delta^{34}S$ values of sulfide are similar throughout the dikes (Fig. 8), the $\delta^{34}S$ of total sulfur in the lower dikes is higher than in the upper dikes because of the presence of anhydrite in whole-rock samples from the lower dikes. The ^{34}S-enrichment of the lower dikes thus differs from that in the transition zone, which results from the addition of hydrothermal sulfide ($\delta^{34}S$ = 3‰–5‰) to the rocks (Alt, Anderson, and Bonnell, 1989).

Recent modeling of anhydrite formation in the oceanic crust on the basis of thermal constraints (Sleep, 1991) suggested two main modes of formation of anhydrite in the crust: (1) precipitation of anhydrite at shallow depths during recharge in the axial region, which allows later dissolution of anhydrite by circulating cold seawater and return of sulfate to seawater; and (2) deposition of anhydrite at the base of vigorous hydrothermal circulation, where it is not easily leached by lower-temperature off-axis circulation. Both situations exist in Hole 504B: anhydrite occurs in veins in the transition zone and upper dikes, but is also present within the rocks in the lower dikes.

Storage of seawater sulfate as anhydrite in the lower dikes is important because it may influence the sulfur isotopic composition of seawater (Bischoff and Dickson, 1975) and, because of the high Sr contents of anhydrite, it could also affect Sr in submarine hydrothermal systems and in the axial vent fluids (Berndt et al., 1988). Moreover, if sufficient anhydrite is present to increase the $\delta^{34}S$ of the crust, subduction of altered crust could contribute to the ^{34}S-enrichment of arc volcanics (Alt et al., 1993) and to heterogeneities in sulfur isotopic composition of the mantle (Chaussidon et al., 1987). Alt, Anderson, and Bonnell (1989) calculated a mass balance for sulfur in the upper 2 km of oceanic crust on the basis of data for Hole 504B, and extrapolated data for the upper 500 m of dikes to a 1-km-thick dike section. The calculated $\delta^{34}S$ of altered upper crust was about 1‰, compared with near 0‰ for unaltered crust. Making the same calculation, but including the lower dikes from Leg 137/140, yields a $\delta^{34}S$ of 1.6‰ for the altered upper 2 km of the crust. However, new data for oceanic gabbros indicate little net change in the sulfur isotopic composition of the lower ocean crust (Alt and Anderson, 1991), and if these data are included in the calculation, the net $\delta^{34}S$ of the entire altered ocean crust is about 1‰. It would be desirable to determine if the observed sulfate-enrichment of the lower dikes continues with depth into underlying gabbros. This would allow testing of these results and a better evaluation of the role that alteration of the ocean crust plays in cycling of sulfur in the oceans and in subduction zones.

SUMMARY AND CONCLUSIONS

Legs 137 and 140 deepened Hole 504B by 438.1 m to a total depth of 2000.4 mbsf. The hole extends 945 m into the sheeted dikes, and the bottom of the hole is interpreted to lie near the base of the sheeted dike complex.

Significant differences in secondary mineralogy occur with depth in the dikes and indicate higher temperatures of alteration in the lower dikes than in the upper dikes. These changes include the local presence of secondary clinopyroxene in the lower dikes; secondary anorthite and hornblende in the lower dikes vs. mainly actinolite and albite-oligoclase in the upper dikes; generally increasing Al and Ti contents of amphibole downward in the dike section.

Rocks from the entire dike section are generally depleted in ^{18}O compared to unaltered MORB, but $\delta^{18}O$ values of the lower dikes (3.6‰–5.0‰) are lower than in the upper dikes, reflecting higher alteration temperatures in the lower dikes. An early high-temperature (up to ~500°C) alteration stage produced secondary clinopyroxene, magnesiohornblende, and anorthite in more intensively altered halos along veins and patches around vugs, where fluids had easy access. Progressive reactions at somewhat lower temperatures (~350°–400°C) resulted in pervasive formation of actinolitic hornblende, albite-oligoclase, chlorite, and titanite. Both these stages caused ^{18}O depletions and losses of metals (Cu, Zn) and sulfur from the rocks, but metal sulfides were more efficiently leached from the more intensively altered halos and

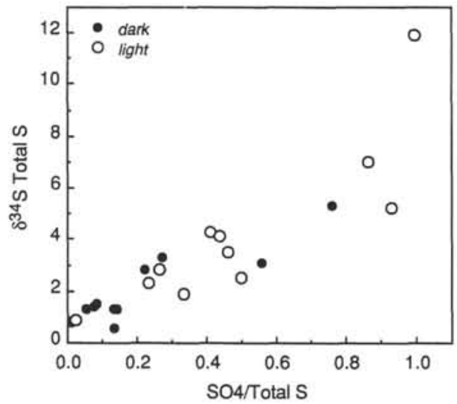

Figure 12. Sulfur isotopic composition (per mil CDT) vs. proportion of sulfate sulfur present in lower dike zone rocks from Hole 504B. Dark = background alteration; light = more intensively altered patches and halos.

patches. Local incorporation of reduced seawater sulfate led to elevated $\delta^{34}S$ values of sulfide in the rocks (up to 2.5‰). Quartz + epidote formed in crosscutting veins at temperatures of 310°–320°C from more evolved fluids ($\delta^{18}O_{fluid} = 1$‰). Late-stage, lower temperature (~250°C) reactions producing albite, prehnite, and zeolites in the rocks caused slight ^{18}O enrichments, but the amounts of these reactions in the lower dikes were insufficient to offset the ^{18}O depletions caused by earlier higher-temperature reactions. In contrast, such reactions were more extensive in the upper dikes and transition zone, leading to significant local ^{18}O enrichments of the rocks. The formation of anhydrite replacing plagioclase and filling pore space in the lower dikes during seawater recharge led to increased S contents of rocks that had previously lost S during axial hydrothermal alteration, and to further increases in $\delta^{34}S$ values of total S in the rocks (up to 12‰). Despite this evidence for penetration of seawater recharge near the base of the sheeted dike complex, the general scarcity of late zeolites in the lower dikes suggests that late-stage, off-axis circulation was mainly restricted to the volcanics and shallowest dikes, or to localized high-permeability zones (faults) at depth.

The lower sheeted dikes cored during Legs 137 and 140 are similar in many ways to the lower portions of sheeted dikes in ophiolites, where metamorphic grade increases significantly and the rocks have lost metals and S. The lower dikes in Hole 504B are a source of metals and S to hydrothermal fluids that form massive sulfide deposits where they vent onto the seafloor.

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