

35. SULFUR-ISOTOPE COMPOSITION OF HYDROTHERMAL SULFIDES FROM HOLE 504B, DEEP SEA DRILLING PROJECT LEG 70, COSTA RICA RIFT¹

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INTRODUCTION

In recent years much effort has been made to throw light on the dynamics and chemistry of interaction between sea water and basalts during formation of oceanic lithosphere. For the upper 300 to 600 meters of basalts aged 2.5 to 3.0 m.y. and more, the typical result of such an interaction is oxidation, hydration, and disintegration of primary magmatogenic phases, and precipitation of authigenic minerals, commonly phyllosilicates (saponite and celadonite), goethite, hematite, calcite, phillipsite, palagonite, and pyrite (Bass, 1976; Andrews, 1977, 1979, 1980; Honnorez et al., 1979; Seyfried et al., 1978; Böhlke et al., 1980). The distribution of sulfides and their morphology and interrelations with the general pattern of alteration indicate that infiltration of sea water into massive crystalline rocks leads to progressive removal of sulfur from them, and on the average to significant reduction of the original sulfur content. Simultaneously, part of the sulfides are redeposited as secondary pyrite, which is the main sulfur-containing phase in altered basalts (Andrews, 1979). Data on the isotopic composition of sulfide sulfur in oceanic basalts affected to varying degrees by secondary alterations point to the possibility of significant variations of $\delta^{34}\text{S}$ values for the rocks of Layer 2 as a whole, exceeding 60‰ (Fild et al., 1976; Seyfried et al., 1976; Krouse et al., 1977; Grinenko et al., 1978).

As part of the geochemical-petrological study of basalts recovered from DSDP Hole 504B (Leg 70) on the southern flank of the Costa Rica Rift, we investigated specially the relationships between the distribution and isotopic composition of sulfur of scattered and vein sulfides on the one hand, and the observed pattern and processes of secondary alterations on the other. The following groups of observations are essential: (1) variations in the contents and isotopic composition of sulfur of different forms of sulfides are clearly interrelated and are observed solely in porous horizons established on the basis of detailed geophysical experiments; (2) the enrichment of sulfides in the light sulfur isotope decreases from the upper to the lower horizons, and within horizons in the direction of the less-altered rock; (3) the increase of $\delta^{34}\text{S}$ values of scattered sulfides in individual permeable zones parallels a decrease in the degree of

iron oxidation in the contents of crystallization water, and in the concentrations of Mg, K, and Li in the rock.

Description and interpretation of these results are the main purposes of the present paper.

SAMPLES AND EXPERIMENTAL PROCEDURE

Samples were taken from the lower portion of Hole 504B, drilled during Leg 70, beginning with Core 34, where the first secondary sulfides were noticed. In addition, one sample apiece from Galapagos Rift Holes 507B and 510, also drilled during Leg 70, were studied. Site locations are shown on Figure 1.

Sulfur was isolated from interstitial water as BaSO_4 , and in its pyrite and monosulfide forms from rocks by the method suggested by Volkov and Zhabina (1977). Isotopic analysis of SO_2 was performed by means of the MI-1305 mass spectrometer, following the procedure suggested by Ustinov and Grinenko (1965). The experimental error was 0.3‰; $\delta^{34}\text{S}$ data are expressed as per mil relative to the meteorite standard.

RESULTS

Isotopic and chemical analyses of basalts from Holes 504B, 507B, and 510 are summarized in Tables 1 and 2. Some correlative relationships are shown in Figures 2 through 5.

Pyrite of hydrothermal veins is common in Hole 504B, beginning at about 250 meters from the sediment/basalt boundary. The $\delta^{34}\text{S}$ values of 26 studied samples were found to vary from -18.3 to 1.6‰ (Table 1). More than 80% of the samples are enriched in the ^{32}S isotope relative to the meteorite standard. Figure 2 shows the relationship between the isotopic composition of sulfur of vein pyrites and the position of individual porous, water-bearing horizons identified on the basis of log data (porosity, sonic velocity, and data on the content of interstitial water [H_2O^-]).

Comparison of lithologic and geophysical data (see Site 504 report, and Cann and Von Herzen, this volume) shows that the most porous horizons are those of pillow basalts, breccia zones, boundaries between pillow basalts and flows, and boundaries between flows. It is for such portions of the profile that we recorded the enrichment of vein pyrites in the light sulfur isotope (Fig. 2). Maximum variations of $\delta^{34}\text{S}$ values for pyrites, on the order of 10 to 20‰, were observed in hydrothermal veins of the upper permeable zones, between 550 and 630 meters sub-bottom. For lower horizons the range of variability decreases to 5 to 7‰ (680–770 m); values attain minima of less than 3 to 4‰ in the deepest horizon of pillow basalts cored (800–830 m).

Scattered forms of sulfur were studied primarily in Hole 504B, where we determined the isotopic composi-

¹ Cann, J. R., Langseth, M. G., Honnorez, J., Von Herzen, R. P., White, S. M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office).

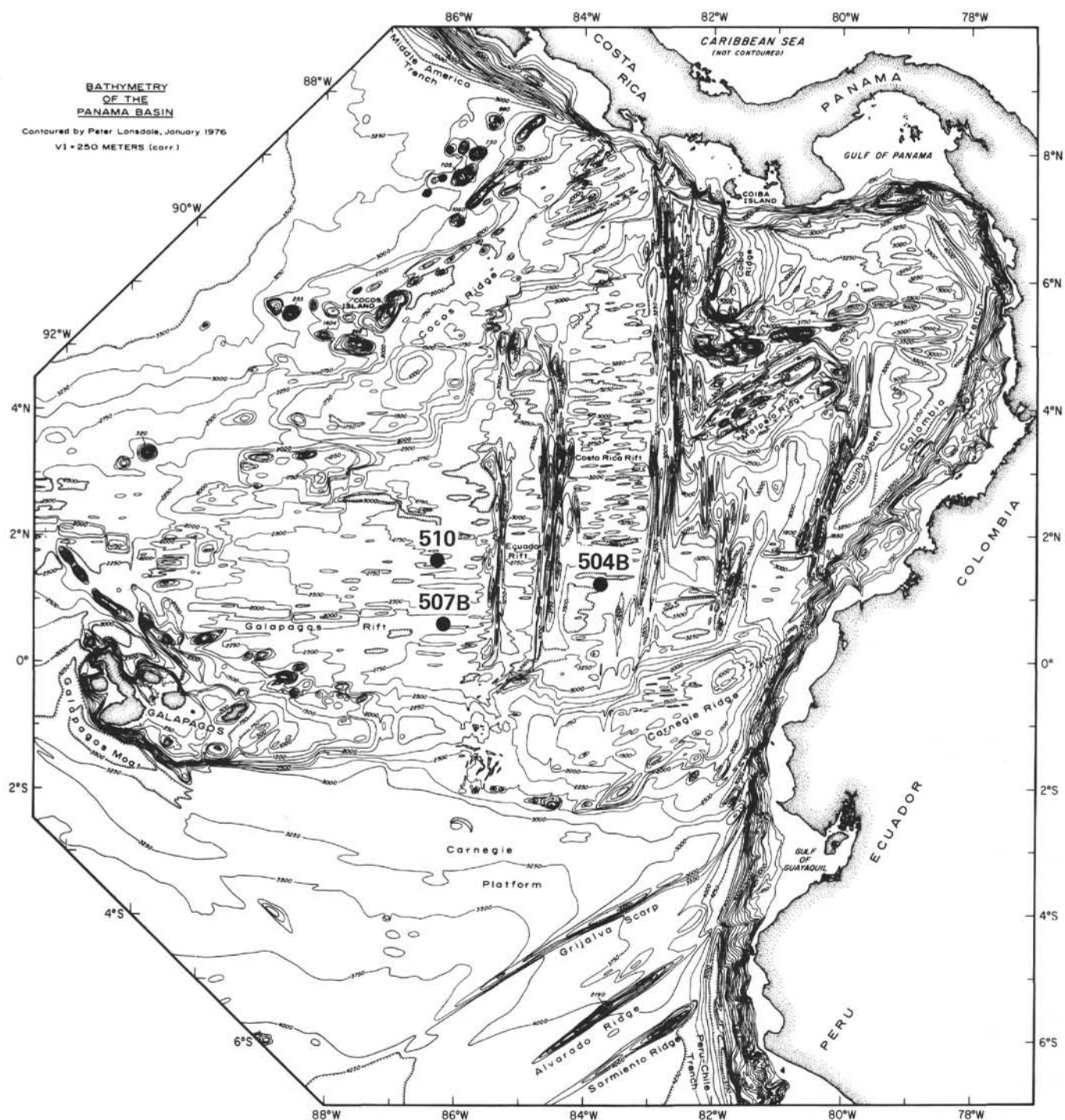


Figure 1. Location of Hole 504B, on the Costa Rica Rift, and Holes 507B and 510, on the Galapagos Rift.

tion of pyrite sulfur of hydrothermal veins, as well as in two basalt samples from Hole 507B and Hole 510. As demonstrated by data in Table 1, in 90% of the cases the main form of sulfur in basalts is pyrite sulfur. Monosulfides were recorded in 40% of the samples. In only one of the samples did we observe a sharp increase in the monosulfide form over the pyrite form (504B-36-1, 91–

110 cm; Table 1). In a few other cases, an insignificant quantity of sulfate sulfur occurs (504B-49-2, 7–10 cm; 504B-52-2, 90–100 cm; and 504B-510, 10-1, 69–83 cm; Table 1).

The total sulfur content (pyrite + monosulfide + sulfate) in the studied basalts was found to vary within three orders of magnitude, from 0.249 to 0.002 wt. %

Table 1. Sulfur concentrations and sulfur-isotope ratios of basalts from Holes 504B, 507B, and 510.

Sample (interval in cm)	Sub-bottom Depth (m)	Vein Pyrite $\delta^{34}\text{S}$ (‰)	Sulfur Dispersed in Rock				Sulfate S (wt. %)
			Pyrite S (wt. %)	$\delta^{34}\text{S}$ (‰)	Monosulfide S (wt. %)	$\delta^{34}\text{S}$ (‰)	
507B-1-1, 32-36	—	—	0.091	—	0.026	-1.7	n.d.*
510-10-1, 69-83	—	—	0.143	0.0	0.029	5.1	0.019
504B-34-1, 19-24	525.5	—	0.032	-1.5	n.d.	—	n.d.
35-1, 14-18	536.0	—	0.004	n.d.	n.d.	—	n.d.
36-1, 91-110	545.5	—	<0.001	—	0.055	-0.4	n.d.
36-3, 70-75	550.0	-6.9	—	—	—	—	—
40-1, 55-60	580.0	-10.4	0.106	-6.8	n.d.	—	n.d.
40-2, 72-88	582.0	—	0.029	—	0.035	-3.6	n.d.
41-3, 146-148	591.5	-0.2	0.042	-8.5	n.d.	—	n.d.
41-4, 50-60	592.0	-8.6	0.069	-11.0	<0.001	—	n.d.
43-1, 80-82	602.5	—	0.092	-0.1	n.d.	—	n.d.
45-2, 70-72	623.5	-18.3	0.075	-0.2	<0.001	—	n.d.
46-1, 100-105	630.0	-2.2	—	—	—	—	—
46-3, 10-15	635.0	-3.0	—	—	—	—	—
47-1, 27-34	638.0	-1.9	—	—	—	—	—
47-1, 46-48	638.5	-0.3	0.044	0.0	0.026	-0.6	n.d.
47-4, 28-30	646.0	0.0	—	—	—	—	—
48-2, 35-37	650.0	-2.3	—	—	—	—	—
49-1, 140-147	657.5	-2.5	0.070	-0.4	n.d.	—	n.d.
49-2, 7-10	659.0	—	0.091	-4.1	n.d.	—	0.023
52-1, 140-150	680.0	-4.5, -7.1	—	—	—	—	—
52-2, 78-80	682.0	—	0.062	-1.0	0.036	0.8	0.029
56-2, 90-100	709.5	0.4	—	—	—	—	—
56-2, 98-101	709.5	0.0	—	—	—	—	—
57-3, 31-43	721.0	0.5	—	—	—	—	—
58-3, 10-15	729.5	-0.2	—	—	—	—	—
61-2, 67-70	753.0	-3.7	—	—	—	—	—
63-2, 140-143	768.0	1.6	—	—	—	—	—
64-2, 32-35	775.5	-2.6	0.053	-1.4	0.051	0.0	n.d.
64-4, 10-12	780.0	-0.2	—	—	—	—	—
68-1, 107-111	810.0	-1.8	0.021	—	n.d.	—	n.d.
69-1, 14-17	818.0	-3.7	0.043	-5.0	n.d.	—	n.d.
69-1, 74-77	818.5	-2.2	0.238	-3.5	n.d.	—	n.d.
70-1, 79-82	827.5	—	0.002	—	n.d.	—	n.d.
70-1, 127-130	828.0	0.0	0.074	-0.9	n.d.	—	n.d.
70-2, 20-23	831.5	—	0.249	-1.0	n.d.	—	n.d.

Note: n.d. = not detected.

(Tables 1 and 2). The $\delta^{34}\text{S}$ values of pyrite and monosulfide sulfur are 0.0 to -11.0‰ and 5.1 to -3.6‰, respectively (Table 1).

Figure 2 shows the variation of isotopic relations of scattered pyrite sulfur with depth in Hole 504B. Isotopic trends in vein pyrites are the same as in dispersed sul-

fides, except that in most cases dispersed pyrites are consistently less enriched in the ^{32}S isotope.

The relationship between secondary alteration of basalts and redistribution of sulfur and its isotopes was studied in some of the most porous portions of Hole 504B. In two cases, these were breccia zones in permeable, water-bearing horizons of pillow basalts: 818.5 to 827.5 meters and 827.5 to 828.0 meters sub-bottom depth (504B-69-1, 74-77 cm, 504B-70-1, 79-82 cm; and 504B-70-1, 127-130 cm); and 657.5 to 659.0 meters (504B-49-1, 140-147 cm; and 504B-49-2, 7-10 cm). The boundary between highly porous pillow basalts and less porous flows is represented by the interval 591.5 to 592.0 meters (504B-41-3, 146-148 cm; and 504B-41-4, 50-60 cm) and 536.0 to 544.5 meters (504B-35-1, 14-18 cm; and 504B-36-1, 91-110 cm). The latter example is at the boundary of two flows that are also from 580.0 to 582.0 meters sub-bottom (504B-40-1, 55-60 cm; and also 504B-40-2, 72-88 cm).

The degree of alteration in the samples was assessed from the abundance of combined water (H_2O^+) in them and the $\text{Fe}_2\text{O}_3/\text{FeO}_{\text{tot}}$ ratio (Table 2), compared with values usually adopted for fresh oceanic tholeiites ($\text{Fe}_2\text{O}_3/\text{FeO}_{\text{tot}} \sim 0.18-0.25$; $\text{H}_2\text{O}_{\text{tot}}$ is <0.5 wt. %). Another feature is the isotopic composition of total sulfur, which for deep-lying rocks must be little different from the meteorite standard. Although the latter criterion is not very explicit, the simultaneous use of all three quantities permits us with sufficient confidence to identify little-altered basalts. Table 2 presents some mean values characterizing little-altered basalts in Hole 504B, which were calculated on the basis of isotopic and chemical analyses. As revealed by calculation, the original content of total magmatic sulfur in the rocks of Hole 504B was close to 0.065 wt. %.

Table 2. Chemical composition (wt. %) and concentration of sulfur in basalts of Hole 504B.

Sample	Sub-bottom Depth (m)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O^+	$\frac{\text{Fe}_2\text{O}_3}{\text{FeO}_{\text{tot}}}$	S_{tot} (wt. %)	Li (ppm)
Zones of maximum oxidation of rock and extraction of sulfur																
504B-35-1, 14-18	536.0	46.8	0.83	17.20	3.84	4.91	0.19	7.99	12.55	2.33	0.126	0.034	2.41	0.46	0.004	8.9
70-1, 79-82	827.5	49.6	0.91	14.65	4.87	4.62	0.13	9.52	11.11	2.33	0.096	0.054	1.71	0.54	0.002	3.4
Average:								8.75			0.111		2.06	0.50	0.003	6.1
Zones of secondary enrichment of pyrite																
40-1, 55-60	580.0	47.6	0.82	15.80	2.74	5.95	0.16	11.23	12.16	1.86	0.073	0.050	2.03	0.33	0.106	17.5
43-1, 80-82	602.5	49.3	0.92	15.65	3.90	5.94	0.16	8.41	12.78	2.24	0.077	0.050	0.47	0.41	0.092	5.0
49-2, 7-10	659.0	49.0	0.88	15.45	4.21	6.16	0.14	9.54	10.68	1.94	0.201	0.046	1.98	0.42	0.114	7.5
52-2, 78-80	682.0	49.5	0.88	16.05	3.47	5.88	0.15	8.84	13.03	1.98	0.081	0.054	0.66	0.38	0.127	17.5
64-2, 32-35	775.5	50.0	1.23	14.05	4.18	7.22	0.20	8.63	12.04	2.25	0.078	0.080	0.42	0.38	0.104	0.75
69-1, 74-77	818.5	49.6	1.03	14.03	4.51	6.20	0.19	8.99	11.92	1.98	0.050	0.070	1.09	0.44	0.238	2.5
70-2, 20-33	831.5	49.8	0.99	15.04	3.57	5.34	0.18	8.87	12.97	2.14	0.070	0.050	0.72	0.38	0.249	3.9
Average:								9.21			0.090		1.05	0.39	0.147	7.8
Zones of unaltered or slightly altered rocks																
36-1, 91-110	544.5	50.4	1.00	15.55	2.62	7.34	0.14	8.26	12.99	2.01	0.040	0.078	0.76	0.27	0.055	7.0
40-2, 72-88	582.0	49.6	0.86	17.11	2.16	6.79	0.13	8.51	12.33	1.89	0.030	0.068	0.71	0.25	0.064	7.0
47-1, 46-48	638.5	50.2	1.04	14.80	3.02	7.32	0.17	8.86	12.35	2.16	0.065	0.064	0.25	0.30	0.070	5.0
49-1, 140-147	657.5	50.0	0.88	16.30	2.16	7.19	0.17	8.14	13.03	2.16	0.096	0.054	0.55	0.24	0.070	5.3
Average:								8.44			0.058		0.56	0.26	0.065	6.1

Note: S_{tot} = pyrite S + monosulfide S + sulfate S.

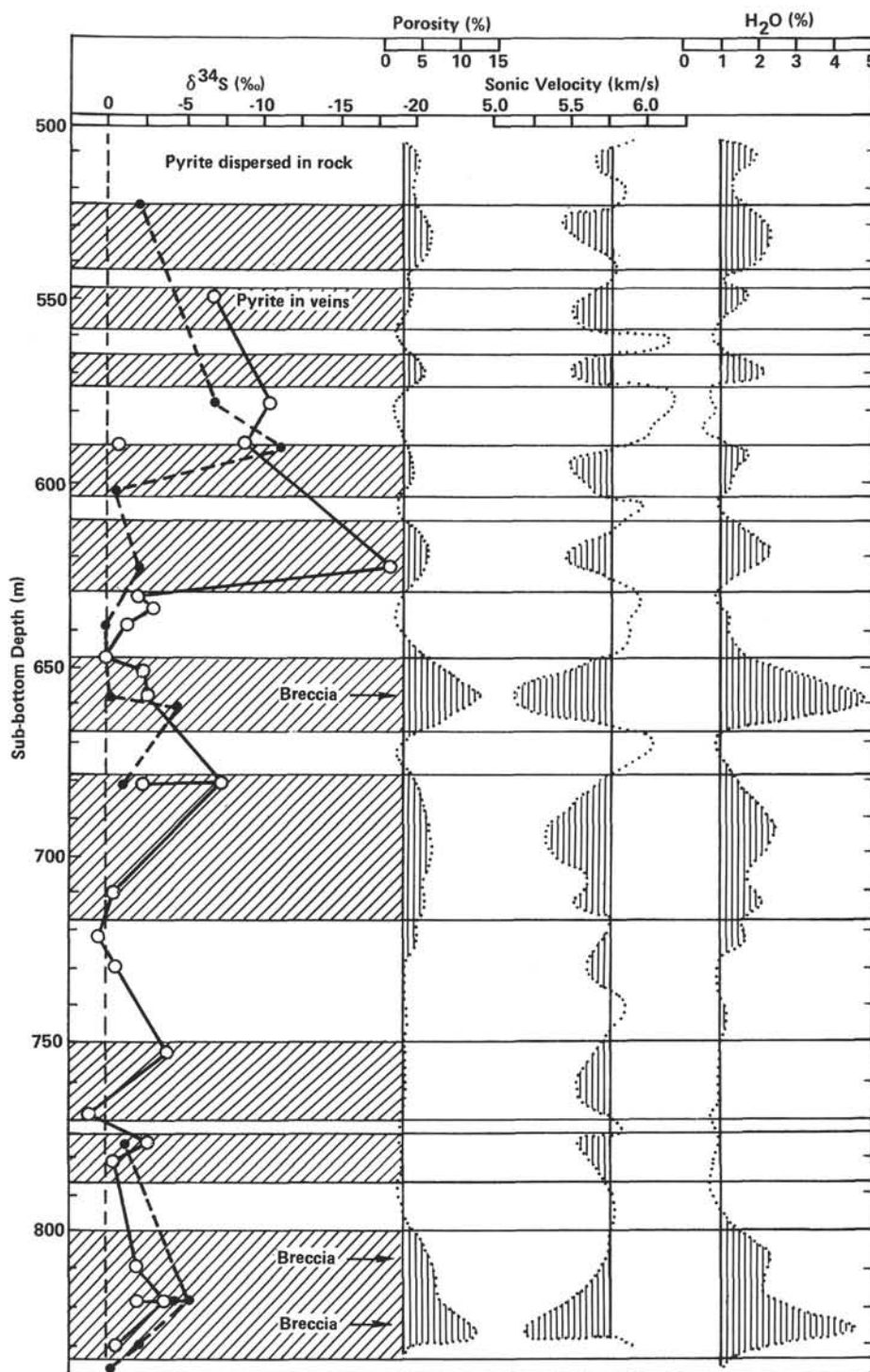


Figure 2. Variation of the isotopic composition of dispersed-pyrite (solid circles) and vein-pyrite (open circles) sulfur relative to occurrences of permeable horizons (ruled pattern) of basalts in Hole 504B. The porosity, sonic velocity, and water content trends are hand smoothed from downhole logs (Cann and Von Herzen, this volume).

The overall patterns of variation in the content and isotopic composition of total sulfur² and the extent of alteration of rocks with depth are shown in Figure 3.

² We took the $\delta^{34}\text{S}$ values of the predominant sulfide form for the isotopic composition of total sulfur.

The vertical dotted line indicates concentration limits and the isotopic composition of sulfur in unaltered basalts. The data in Figure 3 indicate that the redistribution of sulfur and its isotopes, as well as the increasing hydration and oxidation of rocks, are distinctly interrelated and are greatest in one and the same porous part

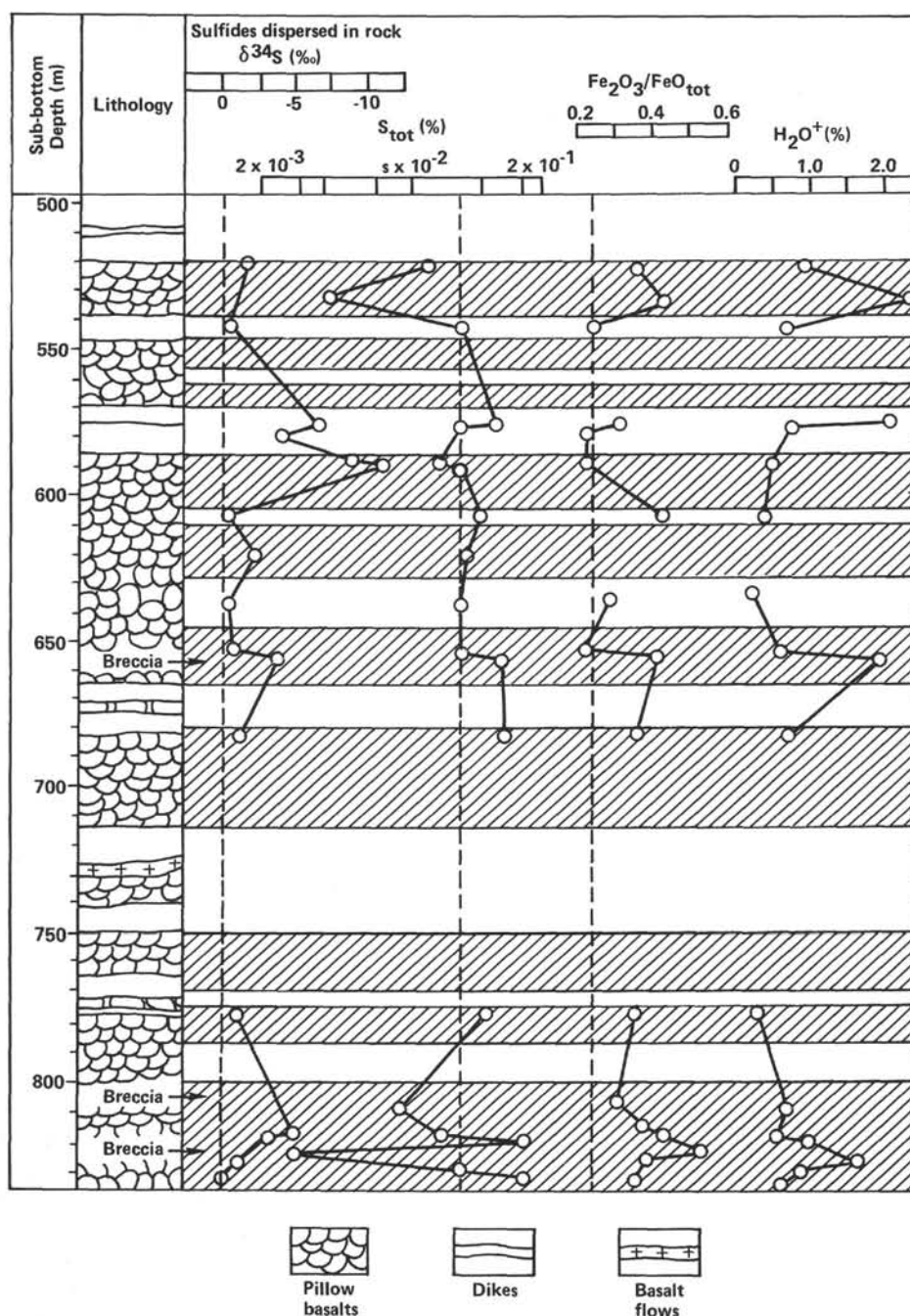


Figure 3. $\delta^{34}\text{S}$ of dispersed pyrite, total sulfur, and $\text{Fe}_2\text{O}_3/\text{FeO}_{\text{tot}}$ variations through Hole 504B basalt section. Isotopic composition and total sulfur pertain to unaltered basalts. Permeable horizons indicated by ruled pattern.

of the section. Grouping of samples according to their position in a given porous zone or a given permeable water-bearing horizon enables us to throw light on some essential details of such relationships.

Within each such horizon or zone in the direction of decreasing permeability of rocks we observe progressive declines in their hydration and oxidation. Simultaneously, there is a very regular approach of the content and isotopic composition of total sulfur to those of unaltered basalts (Fig. 3). The most-permeable and, cor-

respondingly, most-altered zones are characterized by maximum leaching of sulfur (94–97%). Total sulfur contents here are not above 0.002 to 0.002 wt. % (504B-35-1, 14–18 cm; and 504B-70-1, 79–82 cm; Tables 1 and 2). Further, we clearly identify the zones directly adjoining the most-oxidized parts of individual permeable horizons. Here, against the background of continuing decline of hydration, and with $\text{Fe}_2\text{O}_3/\text{FeO}_{\text{tot}}$ ratios amounting to 0.44 to 0.33, there are many sites of secondary, epigenetic accumulations of pyrite sulfur. A distinguish-

ing feature of such zones is the lightest isotopic composition of scattered pyrite sulfur (504B-40-1, 55-59 cm; 504B-49-2, 7-10 cm; and 504B-69-17, 74-77 cm; Table 1). Even less-altered basalts have lower concentrations of sulfide sulfur and are also enriched in the ^{34}S isotope (Fig. 4).

The occurrence of these effects in or near zones of maximum porosity implies that the zones are primary routes for the passage of solutions within the rocks. Furthermore, we note that the mineralogical-geochemical zonation of secondary alteration and the data on isotopic composition of scattered and vein sulfides are symmetrical about individual porous zones in the rock (Figs. 2-4). This suggests the existence of lateral migra-

tion of solutions chiefly in thick accumulations of pillow basalts. Also, oxygen was an important component finding its way into basalts along with circulating solutions. It would be logical to assume that compounds of other elements, also were present in the solution, which could likewise accumulate in the rocks during secondary alteration. In altered zones, the contents of such elements must decline progressively along with decreasing porosity of the rocks, the degree of their hydration, and their oxidation. Analysis of the chemical analyses of basalts from Hole 504B (cf. Sharaskin et al., this volume) shows that MgO , K_2O , and Li contents are higher in the permeable horizons and zones (Table 2; Fig. 5).

The content and isotopic composition of sulfate sulfide formation waters was studied in five samples (Table 3). Four of the samples were taken within the basement by means of the Barnes sampler (17-20 overflow) and one by means of the Gearhardt-Owen Sampler (GO-1) (cf. Mottl et al., this volume). In accordance with sampling conditions the samples 17-20, apart from an insignificant proportion of formation water proper, contain a mixture of sea water (main part) and distilled water. The GO-1 sample was a mixture of sea water (main part) and an insignificant addition of formation water.

DISCUSSION

The wide occurrence of secondary sulfides and the anomalously low sulfur content in altered oceanic basalts have been noted by numerous authors (Scott, 1974; Seyfried et al., 1976; Honnorez et al., 1979; Naldrett et al., 1978). Redeposition of magmatic sulfur associated with the oxidation of massive crystalline rocks by sea water circulating in the crust was studied in particularly great detail from the materials of DSDP Leg 37 (Andrews, 1979). Interrelationships between alteration in basalt and the quantity and isotopic composition of sulfur, as observed in Hole 504B, likewise point out that secondary alteration was taking place under the effect of oxygenated sea water moving along fissure zones in the basement. This is evidenced by the oxidation and hydration of those rocks having greater abundances of Mg- and K-rich mineral phases (particularly veins of Mg-rich saponite), as well as by the enrichment of altered basalts in Li (Fig. 5). The effect of oxygenated sea water on unaltered basalts is that magmatic sulfides are oxidized and sulfur is removed from zones of oxidation (Tables 1 and 2; Fig. 3). Depletion of the fluids in oxygen by reaction with the rocks causes sulfide deposition, forming zones of secondary sulfide accumulation. In this process sulfide sulfur becomes isotopically lighter (Fig. 4), and vein sulphides form in association with hydrosilicates (presumably of the saponite type). Variations in the content and isotopic composition of various forms of sulfide sulfur, as observed in permeable water-bearing horizons (Figs. 2 and 3), point out the large-scale migration of solutions at the stage of secondary mineral formation.

FORMATION OF ISOTOPIC ZONATION

Penetration of oxygenated sulfate containing water into porous reduced rocks leads on numerous occasions

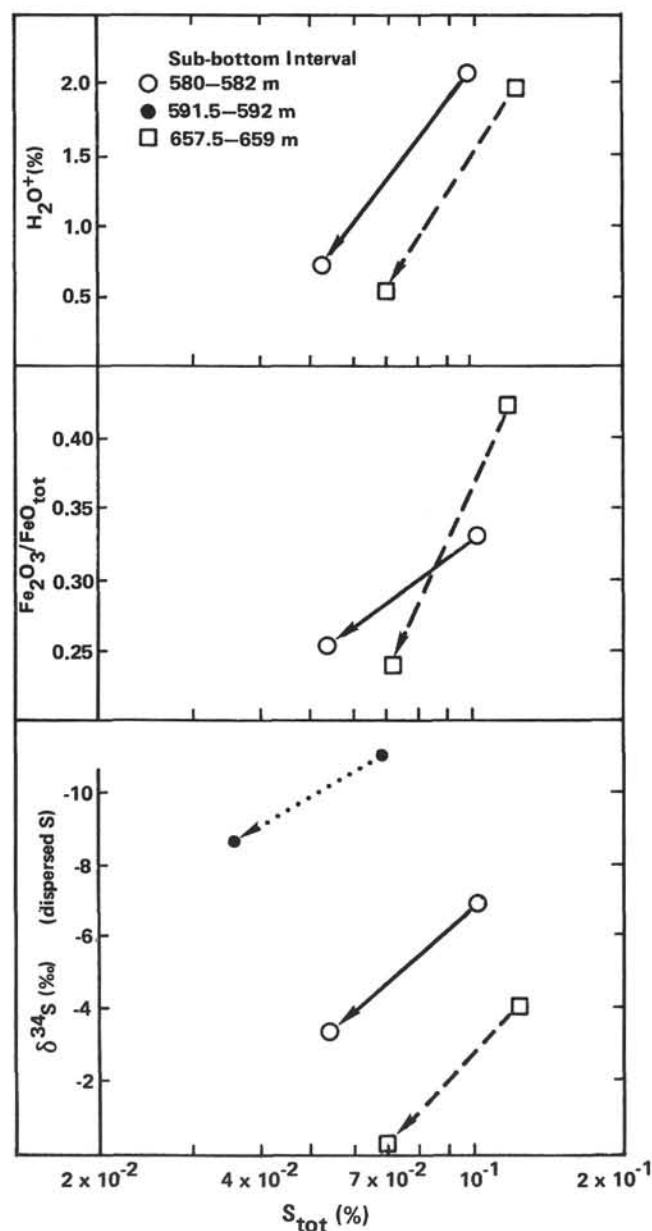


Figure 4. Variations of H_2O^+ content, $\text{Fe}_2\text{O}_3/\text{FeO}_{\text{tot}}$, and $\delta^{34}\text{S}$ of sulfur dispersed in rock, versus total sulfur in basalts, Hole 504B. Arrows indicate direction of decreasing permeability.

Table 3. Variation in $\delta^{34}\text{S}$ values and concentrations of sulfate sulfur in down-hole water samples from basalts of Hole 504B.

Sample Origin	Sample No.	Sulfate Sulfur (wt.%)		Sulfate $\delta^{34}\text{S}$ (‰) (CDT)
		Measured	Corrected ^a	
17 overflow	173	0.072	0.098	15.8
18 overflow	174	0.063	0.086	19.1
19 overflow	175	0.060	0.082	18.0
20 overflow	194	0.102	0.138	18.6
GO-1	202	0.098	—	18.8
Costa Rica Rift		0.102		20.2
Bottom Water		0.093		19.2
Average:		0.097		19.7

^a Corrected by taking into account dilution of samples by de-ionized water.

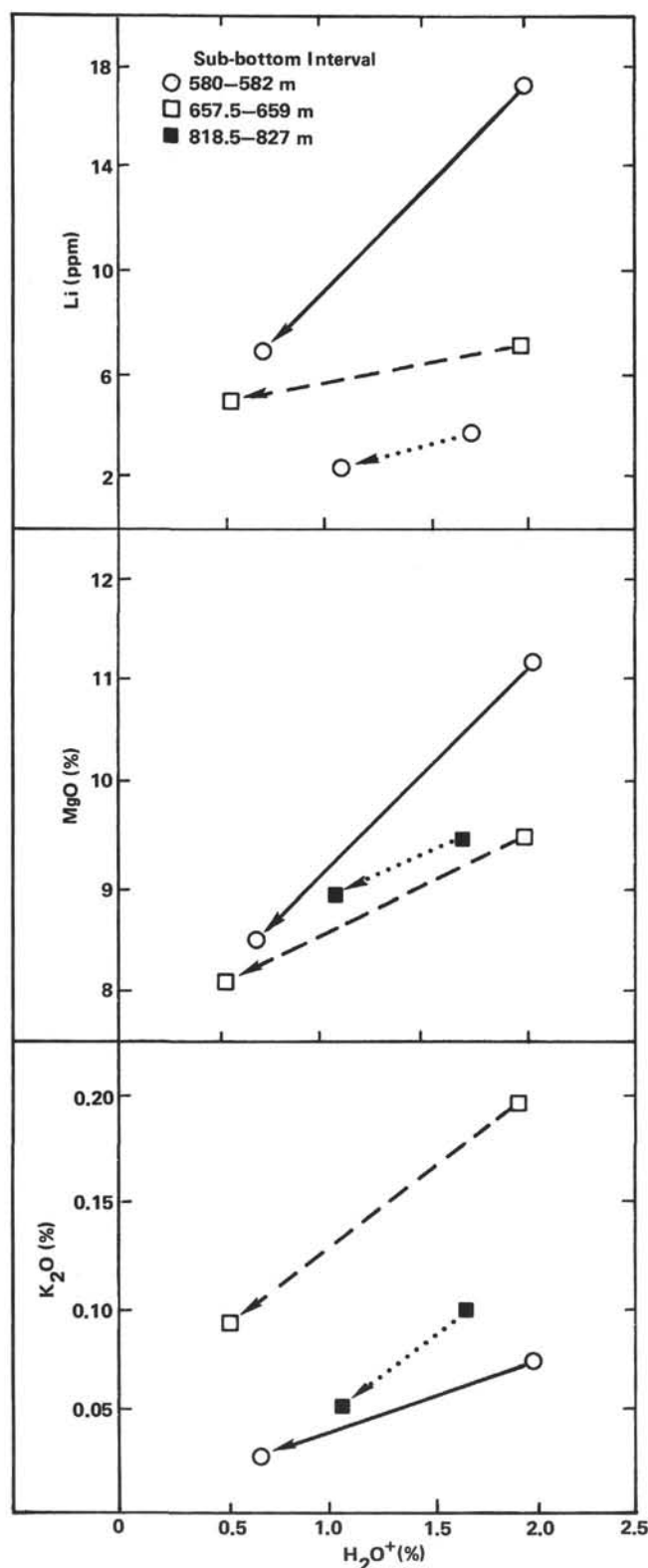


Figure 5. Variation of Li, MgO, and K_2O versus amount of H_2O^+ in basalts from some permeable zones. Arrows indicate direction of decreasing permeability.

to a characteristic mineralogical-geochemical zonation, which has been well studied in sedimentary deposits of the continents (see, for example, the survey by Perelman et al., 1968). Indispensable in such zonations are horizons of stratal oxidation (limonitization). At the pinch-outs of these horizons isotopically light sulfide and sulfate sulfur sometimes accumulates (Chenney and Jensen, 1966; Austin, 1970; Belyi et al., 1972, 1973; Warren, 1972). Given sufficiently prolonged development of the process, at the oxidation/reduction boundary the content of sulfide sulfur and its enrichment in the light isotope are found to progressively increase depending on the total amount of oxygen brought into the rock (Belyi et al., 1972, 1973). As demonstrated above, redeposition of sulfides associated with the filtering of oxygenated solutions is distinctly reflected in the redistribution of sulfur and its isotopes in pillow basalts in Hole 504B. It may be assumed consequently that in Hole 504B, the secondary isotopic and mineral zonations also were controlled by the total amount of oxygen reacted with each unit volume of rock.

On the largest scale (i.e., for the entire studied section of basalts), there is a gradual decline with depth in the variability of $\delta^{34}\text{S}$ values for vein and scattered sulfides (Figs. 2 and 3). This proves to be the result of reduction with depth in the total amount of oxygen reaching basement rocks during the period of fluid circulation. This conclusion agrees well with vertical changes in secondary minerals in Hole 504B: the ubiquitous presence of iron hydroxides in the upper 250 meters of the basement combined with the complete absence of pyrite, and the fairly intensive pyritization of rocks below 250 meters combined with the insignificant occurrences of hydroxides (see Site 504 report, this volume). On a smaller scale (i.e., within separate porous horizons and zones), the quantity of incoming oxygen, as well as some other elements (K, Mg, Li), declined with diminishing permeability of basalts (Figs. 4 and 5). It may consequently be expected that as permeability decreases, the proportion of secondary sulfides likewise must diminish, whereas the isotopic composition of scattered sulfide sulfur must approach that of unaltered basalts. As seen from

Figure 4, in all intervals within the zone of secondary sulfide accumulation this regularity exists, so that the concept of sulfide-sulfur redeposition under the effect of oxygen-containing waters can be deemed valid.

Another criterion appears to be the isotopic composition of sulfate sulfur of formation waters. In the general case of sulfate formation this should, be displaced toward low $\delta^{34}\text{S}$ values compared to initial oceanic sulfate because of oxidation of scattered sulfide sulfur. Judging from the analyzed samples (Table 3), this inference is also correct; because the formation water in the down-hole samples is diluted by sea water, the real $\delta^{34}\text{S}$ values of the sulfate of formation waters must be even lower than those in Table 3.

TEMPERATURES OF SULFIDE REDEPOSITION

A crucial question arising in the interpretation of isotopic and chemical data is that of the causes (or cause) behind the formation of secondary, epigenetic hydrogen sulfide across oxidation/reduction boundaries in the basalts. An answer to this question essentially depends on the temperatures controlling redeposition of sulfides. Some information on this can be obtained by analysis of the available temperature data. Moreover, examination of the temperature regime is necessary if we are to reconstruct the dynamics of sea-water circulation in the basement of Site 504.

We can point to two groups of facts pertaining to the issue in question.

1) Mineralogical-geochemical criteria, including data on oxygen-isotope composition associated with secondary pyrites of saponites and calcites point out that in the upper parts of typical ocean crust the redeposition of sulfide sulfur in altered basalts takes place at low temperatures (not more than 45–75°C; Muehlenbachs, 1980; Lawrence et al., 1979). Furthermore, the large-scale occurrence of secondary minerals in basalts means that the circulation of oxygen-containing pore solutions takes place under conditions of free connection with oceanic bottom water. The isotopic composition of sulfur in veins and disseminated pyrite in Hole 504B permits application of this inference to all 562 meters of the basement recovered here.

2) Temperature investigations made directly while Hole 504B was being drilled point, however, to a broadly conductive *in situ* temperature gradient (0.12°C/m at depths greater than 440 m sub-bottom), with temperatures reaching 120°C at 562 meters into the basement (Becker et al., this volume).

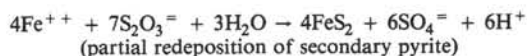
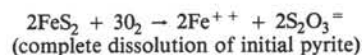
A conductive thermal regime presupposes a complete absence of free connections between oceanic bottom water and the basalt basement (Lister, 1972, 1974). Accordingly, interpretation of available data enables us to assume that at present no active circulation of pore waters in the basement at Site 504 is taking place (however, see Zoback and Anderson, this volume). Then the logged temperatures prove merely to be an estimate of the maximum possible temperatures at the final stage of filtration of oxygen-containing solutions. We measured the homogenization temperature of fluid inclusions in analcime ($42 \pm 2^\circ\text{C}$) from a hydrothermal vein crossing al-

tered basalt at about 550 meters sub-bottom depth (Sample 504B-37-1, 96–99 cm). If we assume that the present position of the sample (4020 m below sea level) closely corresponds to the depth of analcime precipitation, the total pressure during the process of mineral formation can be put at about 400 bars. Making a correction for this pressure (about 12 bars per 1°C), the temperature of analcime precipitation at 550 meters sub-bottom depth did not exceed 75°C. Calculation of the present temperature at the same horizon by using the temperature gradient 0.12°C/m and 120°C temperature measured in Hole 504B at 562 meters into the basement yields 85°C, a value in good agreement with the estimate made above.

Thus, we may assume that the formation of secondary sulfides in basalts at Site 504 took place at temperatures lower than the present measured temperatures, apparently close to the precipitation temperatures of saponite and analcime associated with pyrite. For discussion purposes, we shall assume that for the 550- to 830-meters sub-bottom depth interval temperatures of secondary mineral formation were below 75 to 110°C.

MECHANISM OF FORMATION OF SECONDARY HYDROGEN SULFIDE

Although the temperature estimates of secondary mineral formation processes are not very definite, they show that in the deepest parts of Hole 504B the temperatures of oxidative hydrothermal solutions were equal to or greater than the maximum temperature at which sulfate-reducing bacteria can survive (75–85°C). Therefore, the formation of secondary hydrogen sulfide by bacterial reduction of sulfate cannot be considered here as the sole possibility. On the other hand, we note that in the process of low-temperature sulfide oxidation, metastable sulfur compounds of the thiosulfate and sulfite type can form, which, because of spontaneous disintegration (disproportionation), give rise to secondary sulfide sulfur. For instance, we list the following equations:



Because disproportionation is accompanied by significant isotopic fractionation (>20‰), it may lead to great variations of $\delta^{34}\text{S}$ values for epigenetic sulfides (Granger and Warren, 1969; Warren, 1972). Furthermore, fractionation of sulfur isotopes in disproportionation reactions of polysulfides (including thiosulfate) is associated with intra- and intermolecular kinetic effects and is independent of temperature, at least within the range 25 to 47°C (Agawala et al., 1956). Consequently, we conclude that redistribution of sulfur and its isotopes in pillow basalts at Site 504 in the inferred temperature interval resulted from chemical (rather than biochemical) processes.

CONCLUSIONS

Data presented in this paper show that migration of oxygenated-sea water in the crust is the principal process

determining the redistribution of sulfur and its isotopes at Site 504. The process occurred mainly in extensive porous zones of pillow basalts. Sulfur was repeatedly affected by cycles of oxidation-reduction which took place at moving oxidation/reduction boundaries in the basalts. The final result was formation of a zonation, as follows: zone 1, oxidation (output) of sulfur → zone 2, epigenetic (secondary) accumulation of pyrite → zone 3, slightly altered rock. The isotopic composition of pyrite sulfur in zone 2 becomes successively lighter, depending on the integrated mass of water and the total amount of oxygen reacted with each unit volume of rock. The increase in $\delta^{34}\text{S}$ values for scattered and vein sulfides with depth in the profile of Hole 504B is a reflection of this process. Similar patterns occur in the direction of decreasing porosity of rocks within each water-bearing horizon. The conclusions are in accordance with strontium- and oxygen-isotope compositions of basalts from Hole 504B which indicate a gradual decrease with depth in the influence of sea water on the basement (Barrett and Friedrichsen, this volume).

Temperatures below 75 to 110°C for the interval 550 to 830 meters sub-bottom were obtained as preliminary estimates of the temperatures of secondary sulfide formation. Thus, temperatures of hydrothermal solutions were equal to or greater than the temperature limit of sulfate-reducing bacteria; therefore, biochemical mechanisms of the hydrogen sulfide formation are unlikely. In addition, biochemical mechanisms are problematic because it is not known whether massive basalts at depths of hundreds meters below the sea floor are a suitable environment for normal metabolic activity of bacteria. In Hole 504B, reactions involving disproportionation of metastable compounds such as sulfite and thio-sulfate, suggested primarily for geochemical systems by Granger and Warren, seem to be the most realistic mechanism of secondary sulfide generation. This mechanism would also result in isotopic fractionation of sulfur Hole 504B basalts.

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