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SULFUR ISOTOPE AND TOTAL SULFUR STUDIES OF BASALTS AND GREENSTONES FROM DSDP HOLE 504B, COSTA RICA RIFT: IMPLICATIONS FOR HYDROTHERMAL ALTERATION

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ABSTRACT

Hole 504B, located on the flank of the Costa Rica Rift, Galapagos Spreading Center, is the first DSDP site where both hydrothermally altered rocks and stockwork-type sulfide precipitation have been discovered. Relative to fresh basalts, basement rocks from 275 m to 550 m sub-bottom depth (0 m to 275 m sub-basement) are depleted in sulfur (av. 420 ppm) owing to oxic weathering. Sulfur contents of basalts from 550 m to 890 m sub-bottom depth, where suboxic and anoxic alteration occurred, lie within the range of fresh basalts (av. 1040 ppm). Underlying greenstones average 5690 ppm S from 890 m to 1050 m, and 740 ppm S from 1050 m to 1350 m sub-bottom depth. The high S values from 890 to 1050 m suggest that the greenstones in this part of Hole 504B initially were located at a near-surface discharge zone. Total $\delta^{34}S$ values of pyrite from the greenstones range from 1.5 to 5.8‰. The estimated $\delta^{34}S$ values of H_2S in hydrothermal solutions, assuming equilibrium with precipitated sulfides, vary between about +0.5 and +4.6 ‰. Water/rock ratios of 2–7 by weight are calculated on the basis of sulfur contents and sulfur isotopic compositions of sulfides in greenstones. These values are consistent with the water/rock ratio (~1.6) estimated from previous Sr isotope studies. If subseafloor chemical environments of axial hydrothermal systems are similar to those of Hole 504B, alteration of about 1.2 km^3 of oceanic crust would be required to produce a large size (~3 million tonnes) sulfide deposit.

Keywords: sulfur isotopes, sulfur content, weathering, hydrothermal alteration, greenstones, sulfides, sulfates, pyrite, anhydrite, Costa Rica Rift, Galapagos.

SOMMAIRE

Le forage DSDP 504B, situé en bordure du rift de Costa Rica, une composante de la ride de Galapagos, constitue le premier exemple d'une association étroite entre des roches modifiées par altération hydrothermale et la précipitation de sulfures massifs de type stockwork. Comparées aux basaltes frais, les roches du socle prélevées entre 275 et 550 m sous le fond océanique (les premiers 275 m dans le socle) sont appauvries en soufre (420 ppm en moyenne) à cause d'une halmyrolyse oxygénée. Entre 550 et 890 m de profondeur, milieu d'altération suboxyque à anoxyque, la teneur en soufre concorde avec celle des basaltes frais (1040 ppm en moyenne). Les roches vertes sous-jacentes contiennent 5690 ppm S entre 890 et 1050 m, et 740 ppm entre 1050 et 1350 m de profondeur. Les teneurs élevées entre 890 et 1050 m laissent penser que ces roches vertes étaient jadis situées près d'une zone de décharge sous-marine. Les valeurs $\delta^{34}S$ pour la pyrite des roches vertes varient de 1.5 à 5.8‰. Les valeurs estimées $\delta^{34}S$ du H_2S dans les solutions hydrothermales en supposant l'équilibre avec les sulfures précipités, varient entre environ +0.5 et +4.6‰. Des rapports de masse d'eau à masse de roche affectée entre 2 et 7 calculées à partir des teneurs en soufre et de la composition isotopique des sulfures dans les roches vertes, concordent un rapport d'environ 1.6, calculé d'après une étude antérieure des isotopes de Sr. Si les milieux chimiques en profondeur dans tout système hydrothermal axial resssemblent à ceux que nous avons rencontrés dans le forage 504B, une enveloppe d'altération d'environ 1.3 km^3 de croûte océanique serait requise pour rendre compte d'un gros gisement de sulfures (~3 millions de tonnes).

(Traduit par la Rédaction)

Mots-clés: isotopes de soufre, teneur en soufre, lessivage, altération hydrothermale, roches vertes, sulfures, sulfates, pyrite, anhydrite, rift, Costa Rica, Galapagos.

INTRODUCTION

Numerous sulfide deposits have been discovered in the last decade on the seafloor along the East Pacific Rise (EPR), Juan de Fuca Ridge, Explorer Ridge, and the Mid-Atlantic Ridge (*e.g.*, Hékinian *et al.* 1980, East Pacific Rise Study Group 1981, Koski *et al.* 1984, 1985, CASM 1985, McConachy *et al.* 1986). These deposits are formed from hydrothermal solutions which are considered to result from the reaction between circulating seawater and the underlying rocks (*e.g.*, Upadhyay & Strong 1973, Spooner & Bray 1977, Bischoff & Dickson 1975, Hajash 1975, Wolery & Sleep 1976, Seyfried & Bischoff 1977, 1979, Mottl & Holland 1978, RISE Project Group 1980, Rona 1984). Before Leg 83 of the Deep Sea Drilling Project extended Hole 504B to a sub-basement depth of 1075 m, no greenshist-facies rocks with appreciable sulfides precipitated below the seafloor had been discovered in spite of several legs which drilled the basement to depths in the order of 500 m.

Hole 504B provided the first opportunity to observe directly the subseafloor environment to a depth of more than 1 km, and to examine the relations between the formation of oceanic crust and axial hydrothermal activity. The hole also provided the opportunity to study the distribution of sulfides in greenshist-facies metabasalts at a typical mid-ocean ridge.

The purposes of this paper are: (1) to describe the distribution of total sulfur contents and opaque minerals through an upper oceanic crustal section; (2) to estimate the $\delta^{34}S$ value of the hydrothermal solutions; and (3) to relate both sulfur content and sulfur isotopic composition to water/rock ratio. To attain these objectives, both the sulfur content of the greenstones and sulfur isotopes of associated sulfides were analyzed.

METHODS

About 250 polished thin sections were examined by reflected-light microscopy and electron-microprobe analysis at the University of Tokyo to identify sulfide minerals and their chemistry. Forty-five samples were selected to determine the total sulfur content of basalts and dolerites, and to evaluate the effects of oxic and anoxic weathering, and hydrothermal alteration on sulfur contents.

The total sulfur content of the samples was determined with a Kokusai Electric I.R.-Matic "C-S" VK-111 AS analyzer by fusion of the sample in an oxygen flow, followed by Luft-type non-dispersive infrared absorption. The reproducibility of these measurements is better than 6% (Terashima 1978, 1979).

The water content of samples was determined by the Carl–Fisher method in which the samples are combusted in a nitrogen flow at 900°C, followed by electric titration of the Carl–Fisher reagent. The reproducibility of these determinations is better than 15%.

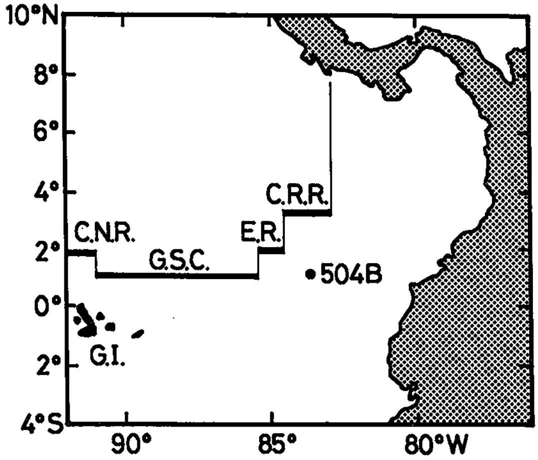

FIG. 1. Location map of Hole 504B. C.N.R. Costa Rica Rift; G.S.C. Galapagos Spreading Center; E.R. Ecuador Rift; C.R.R. Costa Rica Rift; G.I. Galapagos Islands.

Samples for sulfur isotope study were selected based upon textures of hydrothermally altered rocks and whole-rock sulfur content. Pyrite and chalcopyrite were separated by hand-picking. Mineral separates were fine-milled to <200 mesh for analysis. Sulfides were leached by boiling in a solution of aqua regia; the residue consisted of pure barite. Barite was heated with V_2O_5 and SiO_2 up to 900–950°C, and converted to SO_2 using the procedure described by Yanagisawa & Sakai (1983). Mass-spectrometric analyses of SO_2 gas were done at the University of Tokyo. The isotopic-ratio measurements were done using a McKinney-type mass spectrometer. The total error (preparation and measurement) of these determinations is less than $\pm 0.2‰$. Sulfur isotope ratios are conventionally expressed as $\delta^{34}S$ (per mil) relative to troilite sulfur from the Cañon Diablo meteorite.

GENERAL SETTING

Hole 504B is located in 6-Ma-old basement about 200 km south of the Costa Rica Rift, which is the easternmost segment of the Galapagos Spreading Center (Fig. 1). The combined penetration of Legs 69, 70, and 83 exceeds 1 km, making it the deepest drillhole in mid-ocean ridge-generated crust (CRRUST 1982, Anderson *et al.* 1982). A sequence of pelagic sediment, 275 m thick, resulting from the high sedimentation rate within the equatorial high-productivity belt, seals convective circulation within the basements (Anderson *et al.* 1982). As a result, the observed heat flow (200 mW/cm^2) is almost the same as that deduced from a simple conductive-cooling plate model (Anderson *et al.* 1982). Present downhole temperature increases as a function of depth to a maximum of 160°C at 1350 m sub-bottom depth.

ALTERATION ZONES IN HOLE 504B

Summary of alteration

Basalts and dolerites were recovered from 274.5 m to the bottom of the hole at 1350 m below sub-seafloor. Their alteration characteristics can be divided into four zones (Zones I to IV) based on the secondary mineral assemblages, bulk-chemical and strontium, oxygen, and hydrogen isotopic compositions, and distribution of veinlets (Table 1) (Barrett & Friedrichsen 1982, Hubberton *et al.* 1983, Alt *et al.* 1985a, Honnorez *et al.* 1983, 1985, Kawahata & Furuta 1985, Kawahata *et al.* 1987). These studies indicate that Zone I (275–550 m sub-bottom depth) has experienced oxic submarine weathering at low temperatures (0–30°C), whereas Zone II (550–890 m) is characterized by low-temperature (60–110°C) suboxic to anoxic alteration. Strontium isotopic and bulk geochemical data indicate circulation of seawater was much more restricted in Zone II than in Zone I (Barrett & Friedrichsen 1982, Hubberten *et al.* 1983, Kawahata *et al.* 1987).

Greenschist-facies minerals represented by chlorite, epidote, actinolite and albite appear in Zone III (890–1050 m) and Zone IV (1050–1350 m) (Alt *et al.* 1985a,b, Kawahata & Furuta 1985). Intense veining of pillow basalts occurs in Zone III. Strontium isotopic data on greenstones indicate that water/rock ratios (by weight) were generally low (about 1.6, Kawahata *et al.* 1987, Friedrichsen 1985) and similar to those at 86°W, Galapagos Spreading Center (1.0, Edmond *et al.* 1979) and 21°N, EPR (1.5, Albarede *et al.* 1981, Von Damm *et al.* 1985). Although Alt *et al.* (1983, 1985b) reported several minor occurrences of anhydrite in veins of Zones II and III, these authors suggested that the anhydrite was formed at an off-axis discharge site at relatively low temperatures.

TABLE 1. SUMMARY OF HYDROTHERMAL ALTERATION IN HOLE 504B

Alteration Zone	I	II	III	IV
Subbottom depth (m)	274-550	550-890	890-1050	1050-1350
Rock type	basalt	basalt	basalt + dolerite	
Alteration type	oxic weathering	suboxic-anoxic weathering	hydrothermal alteration (greenschist facies)	
Alteration temp.	0-30°C	60-110°C	>200-350°C	
Secondary minerals	iron oxide "iddingsite"	saponite calcite	chlorite, laumontite, epidote quartz, actinolite, calcite pyrite, chalcopyrite	

Mode of occurrence of major opaque minerals

Pyrite. Pyrite is the dominant sulfide throughout the hole. Pyrite is absent or negligible in Zone I, but is present in Zone II (Hubberten *et al.* 1983). Pyrite is abundant, especially along veins, in Zone III, and

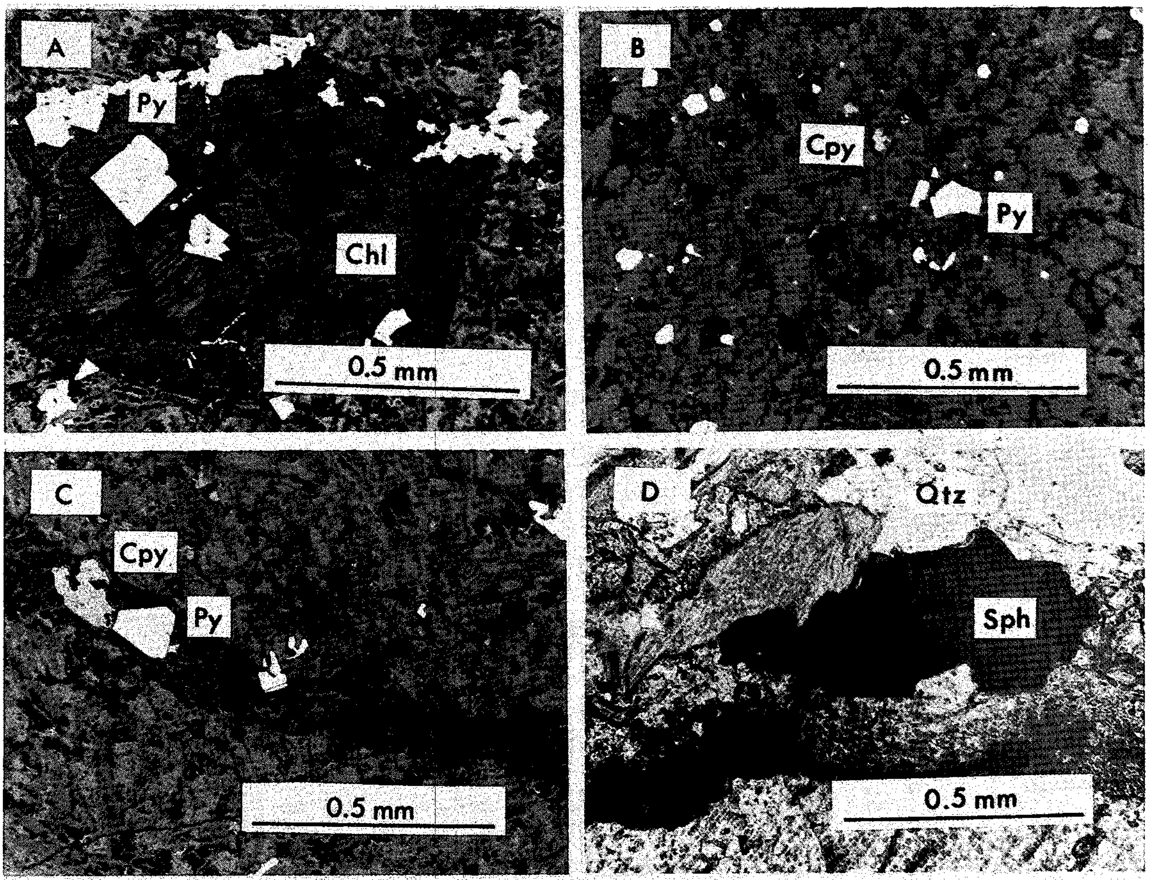

FIG. 2. A) Olivine phenocryst replaced by chlorite (Chl) and pyrite (Py) (sample 86-1: 28–30 cm); B) pyrite and chalcopyrite (Cpy) scattered in a fine-grained groundmass of greenshist-facies basalt (sample 90-1: 47–49 cm); C) pyrite and chalcopyrite in chlorite and quartz veins (sample 94-2: 8–10 cm); D) sphalerite (Sph) in vein with quartz (Qtz) and epidote (sample 84-2: 86–88 cm).

is present in Zone IV. In general, pyrite content correlates with the total sulfur content.

Pyrite of two different origins is recognized: (1) hydrothermal pyrite found in the most altered rocks and (2) comparatively rare, small globules of iron-rich magmatic sulfides within fresh plagioclase phenocrysts. Hydrothermal pyrite occurs in three habits: (1) as replacements of olivine and clinopyroxene (Fig. 2A); (2) as disseminated grains in altered groundmass and interstitial to phenocrysts (Fig. 2B); and (3) as veinlets (Fig. 2C).

Large pyrite grains (up to 5 mm) are present in the intensely altered basalts of Zone III. Small grains of pyrite are especially associated with chlorite, and some are with quartz and chalcopyrite. Honnorez *et al.* (1985) analyzed vein pyrite from the stockwork zone (910–927 sub-bottom depth) and obtained Ni contents from 0.0 to 0.17 wt.%. We analyzed about 100 grains of secondary pyrite disseminated in hydrothermally altered basalts and dolerites; their Ni and Co contents, although scattered, are generally higher than those of vein pyrite and range, respectively, from 0.0 to 1.1 wt.%, and 0.0 to 0.8 wt.%.

TABLE 2. TOTAL SULFUR AND WATER CONTENTS OF BASALTS AND DOLERITES FROM HOLE 504B

Sample No.	Depth (m)	Sulfur (ppm)	Water (%)
Zone I			
2-1 112-115	275.6	126	–
4-5 77-82	286.8	451	4.60
7-4 98-104	313.0	119	–
8-5 33-36	322.8	1130	0.53
16-3 51-54	380.0	78	–
21-2 12-15	422.6	123	–
34-2 59-61	527.6	104	1.58
36-2 85-87	545.9	1210	0.48
Zone II			
40-3 36-38	582.9	984	0.69
45-1 10-12	620.1	897	0.50
52-2 30-32	680.3	1140	0.58
61-2 80-83	752.8	945	0.60
70-1 20-30	827.3	684	–
70-2 21-24	828.7	1280	0.78
72-4 38-40	848.4	1330	–
Zone III			
77-2 76-78	890.8	224	1.59
78-1 42-44	897.9	263	–
79-3 145-147	909.0	34500	2.35
80-1 19-21	910.2	162	2.97
80-2 27-29	911.8	6140	2.78
81-1 114-116	920.6	4140	–
83-2 4-6	939.0	6990	1.89
84-2 86-88	948.9	12100	2.34
85-1 65-70	956.1	4140	7.34
86-1 13-15	964.6	10000	–
89-1 40-42	985.9	19200	5.86
89-2 4-7	987.1	658	–
90-3 65-67	998.3	192	5.83
91-2 68-70	1005.8	35	4.47
92-2 32-34	1014.3	1680	–
93-3 32-34	1024.8	596	2.15
94-2 109-111	1033.1	1360	–
96-1 15-17	1048.7	36	3.01
Zone IV			
97-3 9-11	1060.5	628	2.93
99-1 69-71	1072.2	137	1.54
104-3 27-29	1119.8	23	0.92
107-1 99-101	1144.5	1090	0.99
108-1 62-64	1153.1	937	–
122-1 132-134	1214.8	1110	–
122-2 17-19	1215.2	1300	1.90
123-1 11-13	1222.6	196	7.81
132-2 22-24	1295.2	1230	0.76
133-2 17-19	1305.7	68	2.67
136-1 82-84	1322.8	969	–
141-1 34-38	1345.9	1190	–

Chalcopyrite. Chalcopyrite, which is almost absent from the less altered rocks, occurs both as isolated grains and in association with pyrite. Chalcopyrite occurs as disseminated grains in altered groundmass or olivine (Fig. 2B), and in veinlets (Fig. 2C). We analyzed 40 grains of chalcopyrite and obtained Ni and Co contents of <0.03 wt.%.

Sphalerite. Sphalerite occurs in veinlets in Zone III (Fig. 2D). The FeS content ranges from 5 to 14 mole %, and averages 11 mole %. Sphalerite is associated with epidote, quartz, chlorite, and pyrite.

Millerite. One grain of millerite was found in altered groundmass in Zone III, suggesting a secondary origin through hydrothermal alteration.

Titanian magnetite. Primary titanian magnetite occurs throughout the hole. The mineral has been altered at low temperatures in Zones I and II, and at high temperatures in Zones III and IV (Furuta 1983, Kinoshita *et al.* 1985). A few grains are replaced by titanite in Zones III and IV. Small grains of secondary magnetite occur as a replacement of olivine and clinopyroxene.

TOTAL SULFUR AND WATER

Table 2 lists the sulfur and water contents of 45 samples from the four alteration zones. Sulfur in Hole 504B basalts and veins occurs entirely as sulfides; no sulfates were observed. The down-hole distribution of sulfur is highly erratic (Fig. 3). Oxic-weathered basement rocks in Zone I contain from 78 to 1210 ppm S, with 5 of the 8 samples containing <200 ppm. Both the range and the clustering of values below about 200 ppm are characteristic of basalts recovered from the Mid-Atlantic Ridge by the Deep Sea Drilling Project (Andrews 1979). By contrast, the sulfur contents of suboxic and anoxic altered basement rocks in Zone II range from 680 ppm to 1330 ppm, and lie within the range of fresh, deep ocean-floor basalt (640–1570 ppm; Moore & Fabbi 1971, Sakai *et al.* 1984, Ueda & Sakai 1984). Rocks in Zone II are not appreciably altered, as indicated by their relatively low water contents (<0.8%; Fig. 3), by whole-rock potassium results (Hubberten *et al.* 1983), and by strontium isotopic data (Barrett & Friedrichsen 1982). Our data for sulfur contents of basalts from Zones I and II are consistent with those reported by Hubberten *et al.* (1983).

The total sulfur content of greenstones in Zones III and IV ranges from 23 to 35000 ppm. More than half of the samples in zone III are very rich in sulfur (av. 10000 ppm), whereas the rest have much lower contents (av. 270 ppm). Samples with very high values (>4000 ppm) contain abundant pyrite, sphalerite, and chalcopyrite in fractures. All samples in Zone IV consist of dolerite with few sulfide veinlets; the average sulfur content of this zone is 740 ppm.

Fresh basalts have very low water contents (H_2O^+) of 0.2 to 0.5 wt.% (Kyser & O'Neil 1984). The water contents of weathered basalts from Zones I and II range from 0.48 to 1.60 % (with one high exception), whereas the water content of hydrothermally altered basalts is generally higher, ranging from 0.76 to 7.81 wt.% for Zones III and IV, respectively (Figs. 3, 4). The water content in Zone III generally is higher than in Zone IV, apparently because this section of oceanic crust is strongly veined and was more hydrothermally altered.

SULFUR ISOTOPES

The sulfur isotopic analyses are listed in Table 3. $\delta^{34}S$ values for pyrite from veins and groundmass from Zones III and IV range from +1.8 to +5.2 ‰ and from +1.7 to +5.8 ‰, respectively. There is no systematic difference in $\delta^{34}S$ values for pyrite from vein and groundmass occurrences. One analysis of chalcopyrite gave 3.3 ‰. Honnorez *et al.* (1985) reported values for vein pyrite from Zone III (910 to 927 m) that vary from +3.0 to 5.0 ‰. The $\delta^{34}S$ values for sulfides from Zones III and IV are within the range reported in previous studies of seafloor sulfide deposits (Fig. 5; Arnold & Sheppard 1981, Styrt *et al.* 1981, Kerridge *et al.* 1983, Shanks *et al.* 1984, Zierenberg *et al.* 1984, Koski *et al.* 1985, Peter 1986). However, the values differ appreciably from those for pyrite from Zones I and II, which vary from -11.0 to +3.6 ‰ (Hubberten *et al.* 1983, Belyi *et al.* 1983).

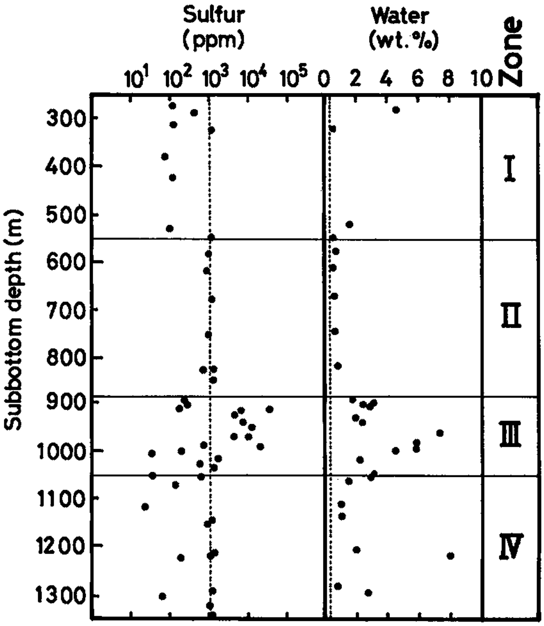

FIG. 3. Total sulfur and water content plotted as a function of sub-bottom depth. The dotted lines represent the average total sulfur and water contents of fresh mid-ocean ridge basalt.

DISCUSSION

Sulfur distribution in the upper oceanic crust

The data of Figure 3 indicate that the average values for total sulfur are 420 ppm in Zone I, 1040 ppm in Zone II, 5690 ppm in Zone III, and 740 ppm in Zone IV (Table 4). These values are a function of the original sulfur content and degree of alteration.

The original sulfur content of the basalt is controlled by pressure, rock crystallinity, and iron content. Because the basalts from Costa Rica Rift were undoubtedly erupted at depths of 2 to 4 km below sea level (pressures of 200–400 bars), large depletions of sulfur by degassing would not be expected (Moore & Schilling 1973). Sheeted dykes are, in general, feeders through which magma ascended; therefore, the sulfur content of diabase in the sheeted dykes is expected to be the same as that of the extrusive basalts.

Basement in Zone II has undergone little alteration, as is evident from major- and minor-element data, and from strontium and oxygen isotopic results (Barrett & Friedrichsen 1982, Kawahata & Furuta

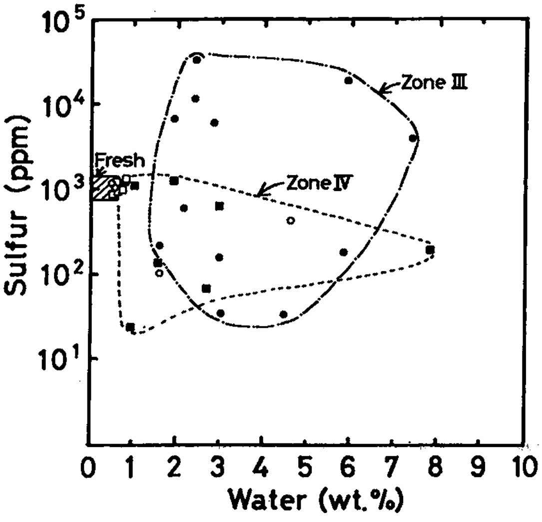

FIG. 4. Sulfur content *versus* H_2O^+ in basement rocks: open circles, Zone I; open squares, Zone II; solid circles, Zone III; solid squares, Zone IV. The shaded area indicates the approximate range of total sulfur and values in fresh mid-ocean ridge basalt.

TABLE 3. SULFUR ISOTOPE VALUES (per mil CDT) OF SULFIDES FROM DSDP HOLE 504B

Sample No.	Depth (m)	Sulfur isotopes $\delta^{34}S$ (o/oo)		
		Pyrite	Chalcopyrite	
Zone III				
80-2 27-29	911.8	3.9 (v)		
82-1 133-137	929.9	4.2 (v)	3.3 (v)	
83-1 19-22	937.7	4.8 (v)		
84-2 28-30	948.3	5.1 (v)		
84-2 86-88	948.9	3.6 (g)		
85-1 65-70	956.1	3.2 (g)		
86-1 13-15	964.6	3.0 (v)		
Zone IV				
97-3 9-11	1060.5	5.8 (g)		
101-1 33-35	1089.8	5.2 (v)		
107-1 99-101	1144.5	1.7 (g)		
122-1 132-134	1214.8	1.8 (v)		
Zone I	275-550	-3.7 ~ +0.5		(1)
Zone II	550-890	-5.2 ~ +3.6		(1)
Zone II	550-890	-11.0 ~ 0.0		(2)
Zone III	910-928	+3.0 ~ +5.0		(3)

Note: (v) vein
(g) groundmass
References: (1) Hubberten et al. 1983
(2) Sulfides: Belyi et al. 1983
(3) Honnorez et al. 1985

1985, Alt & Emmermann 1985, Alt *et al.* 1985a,b, Kawahata *et al.* 1987). Although completely unaltered basalts are not found in Hole 504B, the average sulfur content of fresh basalt is assumed to be 1040 ppm. The reasons are that Zone II has escaped metasomatism, and that the assumed value is within the range expected from total iron content (10.4 wt.%). Only 1.4 % of the total sulfur is attributable to oxidized sulfur (sulfate), by analogy with fresh basalt glass from the Galapagos Spreading Center (Sakai *et al.* 1984).

If we assume that the density of basement rocks is 2.9 g/cm^3 (Karato 1983), and that the bulk porosity is 0.10, the supply or sink of sulfur in the rock column per square cm (S) can be estimated in each zone (i) from $S(i) = D(i) \times 10^{-6} \times L(i) \times 2.9/0.9$, where D (ppm) is the amount of sulfur added or leached from fresh rock during seawater–rock interaction, and L (cm) is the thickness of each zone. The results are shown in Table 4. Two possible sources are suggested for the enrichment of sulfur in Zone III: (1) sulfur was leached from the basement in a recharge zone and precipitated in a discharge zone, or (2) the sulfur was supplied directly from a magma chamber as volatile components (*e.g.*, H_2S, SO_4^{-2}, *etc.*). Although Zone Although Zone III is now at a sub-basement depth exceeding 700 m, it may have represented a near-surface discharge zone earlier in the history of basaltic extrusion at Hole 504B. This possibility is also supported by the strontium isotopic data of Friedrichsen (1985).

The $\delta^{34}S$ values of pyrite from zones III and IV range from about +1.7 to +5.8 ‰ (Table 3). Previously cited studies of fluid inclusions, oxygen and hydrogen isotopes, and alteration minerals suggest

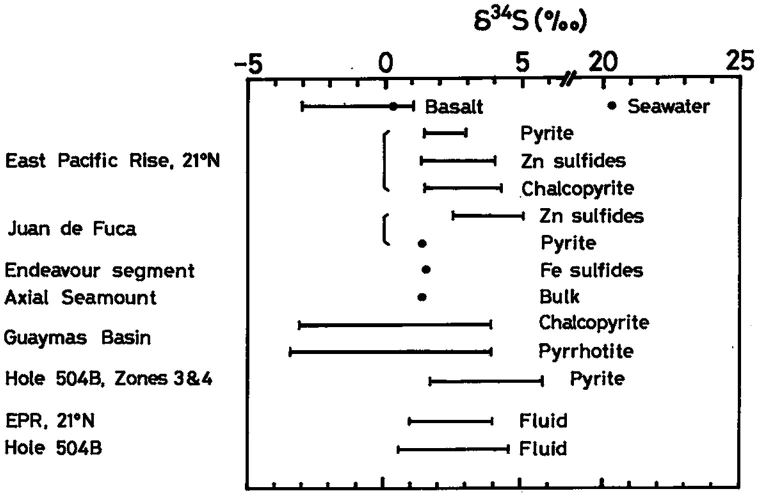

FIG. 5. Sulfur isotope values of seawater, fresh basement rocks, and sulfides from various submarine hydrothermal areas. Basalt: Schneider 1970, Kanehira *et al.* 1973, Ueda & Sakai 1984; seawater: Claypool *et al.* 1980; sulfides: 21° N, EPR: Styrt *et al.* 1981, Kerridge *et al.* 1983, Zierenberg *et al.* 1984; Juan de Fuca, Endeavor Segment, Axial Seamount: Shanks *et al.* 1984; Guaymas Basin: Koski *et al.* 1985, Peter 1986; Hole 504B: this study; measured fluid at 21°N, EPR: Kerridge *et al.* 1983; estimated fluid of Zone III and IV: this study.

precipitation of pyrite at $T = 200\text{–}350°C$. This implies that the $\delta^{34}S$ values of H_2S in the hydrothermal solutions varied between about +0.5 and +4.6 ‰ assuming equilibrium fractionation (the isotopic fractionation factor between H_2S and pyrite is about 1.2 at 300°C; Ohmoto & Rye 1979). This range of values is consistent with the $\delta^{34}S$ values (+1 to +4 ‰) of H_2S in hydrothermal solutions from 21°N, EPR (Kerridge *et al.* 1983, Styrt *et al.* 1981). However, as Kerridge *et al.* (1983) have pointed out, the aqueous sulfide is not in isotopic equilibrium with precipitated sulfides. The sulfur in hydrothermal fluids and pyrite in Hole 504B likewise may not be in equilibrium.

The high Ni and Co contents of some secondary pyrite in the groundmass of Hole 504B basalt are enigmatic. These elements are clearly depleted in seafloor sulfide deposits (Bischoff *et al.* 1983). It is possible, however, that some secondary sulfides are derived from primary sulfide globules, which have high Ni and Co contents (Kanehira *et al.* 1973, MacLean 1977).

Relation of the effect of water/rock ratio or total sulfur contents and sulfur isotopes

Water-rock interaction at elevated temperature affects the sulfur contents and sulfur isotope ratios of both rocks and hydrothermal solutions. Several authors (Hékinian *et al.* 1980, Arnold & Sheppard 1981, Shanks *et al.* 1981, Styrt *et al.* 1981, Zierenberg *et al.* 1984) have discussed the possible sources of sulfur for the seafloor sulfide deposits. All agree that both basaltic sulfide ($\delta^{34}S$ = +0.3 ‰) (Sakai *et al.* 1984) and seawater sulfate ($\delta^{34}S$ = +20.3 ‰) (Claypool *et al.* 1980) must be involved.

Shanks *et al.* (1981) indicated that only a small amount of the original sulfate in convecting seawater is introduced into the high-temperature part of the hydrothermal system. Most of the sulfate is precipitated as anhydrite during initial heating of seawater (above 150°C), a process which utilizes calcium dissolved in seawater and calcium released from rocks (Bischoff & Dickson 1975, Bischoff & Seyfried 1978). By contrast, McDuff & Edmond (1978) proposed that all seawater sulfate is reduced to sulfide. The sulfur isotopic values (1.5–4.5 ‰) of sulfides from 21°N, EPR, can be explained best by Shanks's model, with total reduction of a small amount of seawater sulfate (Zierenberg *et al.* 1984).

The sulfur content and isotopic composition of hydrothermally altered rocks should be related to the degree of reduction of seawater, as well as to the original sulfur isotopic compositions both of the solutions and of the rocks in zones III and IV. Water/rock ratios can be estimated by two methods: i) the mass-balance equation (1) for sulfur contents; and ii) simultaneous mass-balance equations for sulfur content and sulfur isotopic composition (equations 1 and 2).

TABLE 4. THE AVERAGE TOTAL SULFUR CONTENTS OF EACH ALTERATION ZONE, AND ADDITION (+) AND LOSS (-) OF SULFUR OF EACH ZONE PER SQUARE CM THROUGH THE BASALT COLUMN

		Subbottom depth (m)	Average sulfur content (ppm)	Gain (+) or loss (-) of sulfur in each zone (mole/cm^2)
LOW-TEMPERATURE ALTERATION				
Zone I	Oxidative alteration	274.5-550	418	-1.4
Zone II	Non-oxidative alteration	550-890	1040	0
HYDROTHERMAL (HIGH-TEMPERATURE) ALTERATION				
Zone III	Strong veining	890-1050	5690	+6.1
Zone IV	Minor veining	1050-1350	740	-0.7

$$C_i^R \times W^R + C_i^S \times W^S = C_e^R \times W^R + C_e^S \times W^S \tag{1}$$

$$C_i^R \times \delta^{34}S_i^R \times W^R + C_i^S \times \delta^{34}S_i^S \times W^S = C_e^R \times \delta^{34}S_e^R \times W^R + C_e^S \times \delta^{34}S_e^S \times W^S \tag{2}$$

In these equations, C stands for the total sulfur concentration, W the weight, and $\delta^{34}S$ the sulfur isotopic composition (in ‰); the subscript and superscripts i, e, R, S represent initial and equilibrium stages, for rocks and solutions. Variable C_i^R and $\delta^{34}S_i$ are measurable or known, and C_e^S *can be* estimated. Thus, it is possible to calculate C_e^R and $\delta^{34}S_e$ as a function of the ratio of W^S to W^R (water/rock ratio by weight).

The $\delta^{34}S$ values of initial seawater sulfate and basaltic sulfide are taken to be +20.3 and +0.3 ‰, respectively (Claypool *et al.* 1980, Sakai *et al.* 1984). The sulfur concentration of unaltered basalt (C_i^R) from Hole 504B is taken as 1040 ppm, the Zone II average. The alteration temperature of hydrothermal alteration of zones III and IV is above 200°C based upon secondary mineral assemblages (Kawahata & Furuta 1985). The sulfate concentration of hydrothermal seawater prior to reaction with basalt is estimated to be about 1 mmole/kg H_2O at 200°C on the basis of anhydrite solubility studies (Dickson *et al.* 1963); sulfate concentrations are 3.13 mmole/L at 150°C and 0.63 mmole/L at 200°C during basalt–seawater interaction experiments (Bischoff & Seyfried 1978, Seyfried & Bischoff 1979). All soluble sulfate remaining after the precipitation of anhydrite is assumed to be subsequently reduced. In addition, we assume that at equilibrium the total sulfur concentrations of hydrothermal solution (C_e^S) and greenstones (C_e^R) are 0.005 mole/kg and 740 ppm (Zone IV average), respectively. Total sulfur concentration of basalt–seawater experiments at 300°C and at a water/rock ratio of 1 is around 0.005 mole/kg (Mottl *et al.* 1979), which is similar to that measured from hydrothermal solutions from 21°N, EPR (Von Damm *et al.* 1985). Also, greenstones in Zone IV were formed under seawater–dolerite interaction at a water/rock ratio of about 1 (Friedrichsen 1985, Kawahata *et al.* 1987) and escaped much precipitation of vein sulfides which characterize Zone III. It is also assumed that the sulfur isotopic composition

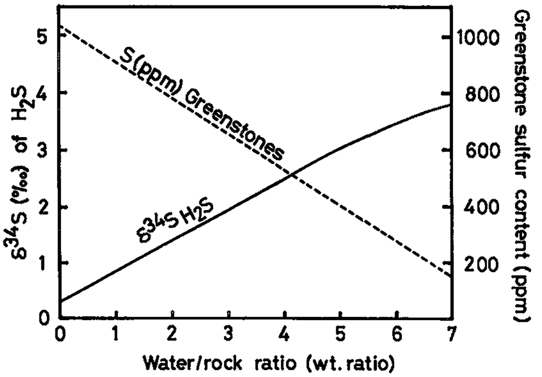

FIG. 6. Graphical illustration of sulfur isotope values of H_2S (left axis and solid line) produced during basalt – seawater interaction at various water/rock ratios. Calculations assume that seawater sulfate is mostly removed as anhydrite, that any residual sulfate is reduced by iron oxidation in reacting basalt, and that there is quantitative leaching of basaltic sulfide (+0.3‰) and homogeneous mixing of both sulfides (equations 1 and 2 in text). Dashed line represents the relation between sulfur content of greenstones (right axis) and water/rock ratio, as calculated from equation (2).

of altered rocks falls between those of pyrite and H_2S in the hydrothermal solution (calculated values of +2.6 to 3.8 ‰). The results of calculations are shown in Figure 6. A water/rock ratio of 2.3 is obtained from sulfur content (equation 1), whereas a ratio of 4.3–7.0 is calculated from sulfur isotopic composition and sulfur content (equations 1 and 2). Considering the range of sulfur concentrations and isotopic values of altered rocks, these ratios are in reasonable agreement with the ratio of 1.6 estimated from strontium isotopes (Friedrichsen 1985, Kawahata *et al.* 1987).

Sulfur isotopic values and sulfur contents of hydrothermally altered rocks, combined with the above assumptions, suggest that marine sulfur contributes 11% of the total sulfur of secondary sulfides. Initially, 3 kg of seawater should precipitate 2.7 g of sulfur as anhydrite out of the hydrothermal system. In addition, 0.88 mg of sulfur should precipitate: 0.78 mg of the reduced sulfur is leached from the basalts by seawater, and 0.10 mg is of marine derivation. During this process, secondary sulfide with $\delta^{34}S = +2.6$ ‰ could be produced.

Volatile components (*e.g.*, rare gases and methane) originate from magma by degassing processes as well as from the decomposition of basalts and dolerites during hydrothermal alteration (Welhan *et al.* 1984). Seawater–rock reactions are very important in controlling the contents of non-volatile components (*e.g.*, Sr and Mg). The consistency of water/rock ratios based on sulfur and strontium suggests that sulfur behaves as a non-volatile component rather than as a volatile component in hydrothermal systems.

Formation of large sulfide deposits

The sulfur isotope values of sulfide deposits from axial submarine hydrothermal systems fall within a relatively small range, as shown in Figure 6. Based upon sulfur isotope modelling, the estimated water/rock ratios from 21°N on the EPR, the Juan de Fuca Ridge, and Axial Seamount are about 1 to 3. This low range is consistent with ratios determined from strontium and oxygen isotopic compositions and elemental concentrations of greenstones and hydrothermal vent-fluids (Albarede *et al.* 1981, Alt *et al.* 1985a, Von Damm *et al.* 1985, Kawahata *et al.* 1987). This similarity suggests that axial hydrothermal systems generally have experienced similar water–rock interaction below the seafloor.

Large sulfide deposits are known at 86°W, Galapagos Spreading Center (5–6 million tonnes; Malahoff 1982), Explorer Ridge (3–5 million tonnes; Scott 1986), 13°N, EPR (2–4 million tonnes; Francis 1985, Hékinian & Bideau 1988). The sulfur content of these deposits is estimated to be about 40%.

The volume (V) of rocks that must be leached to form 3 million tonnes of sulfide deposits can be calculated using equation (3) as 1.2 (km^3) if 300 ppm S is leached from greenstones, and the density of altered rocks is 2.9 g/cm^3.

$$V = (3\times10^6\times10^6\times0.89)\times0.4/(300\times10^{-6})\times2.9 = 1.2\times10^{15}\ (cm^3) \qquad (3)$$

This estimate seems reasonable if we consider a thickness of 1 km of sheeted dykes, and an area of about 1.2 km^2 as the hydrothermal alteration zone. This implies that the zone of leaching extends a considerable distance laterally from the zone of final sulfide deposition. Also, 1.2 km^2 is probably only a minimum value because some of the sulfide sulfur in hydrothermal solutions is vented into ambient seawater as hydrothermal particulates or is precipitated within the crust (or both).

SUMMARY AND CONCLUSIONS

(1) Sulfide minerals are common in hydrothermally altered basalts of Hole 504B. Pyrite is the most common secondary sulfide. Some pyrite is rich in Ni (up to 1.1 wt.%) and Co (up to 0.8 wt.%). Sphalerite occurs in veins in Zone III; its FeS mole fraction ranges from 5 to 14 %, and averages 11 %. Chalcopyrite occurs mainly in zones III and IV.

(2) Basement rocks in Zone I are depleted in sulfur owing to oxic weathering (av. 420 ppm). The sulfur contents in Zone II, which experienced suboxic and anoxic alteration, are within the range of fresh, deep ocean-floor basalt (av. 1040 ppm). The average sulfur values of underlying greenstones are high 5690 ppm) in Zone III, but are relatively low (740 ppm) in Zone IV.

(3) The addition and loss of sulfur indicates that Hole 504B was located at a discharge zone during hydrothermal activity in zones III and IV. This implies that a section of the crust now at a subbasement depth of at least 700 m was once located near the surface of the crust.

(4) The $\delta^{34}S$ values for 11 pyrite samples from zones III and IV range from + 1.7 to + 5.8 ‰; one chalcopyrite value of +3.3 ‰ was obtained. The estimated $\delta^{34}S$ value of H_2S in the hydrothermal solutions varies between +0.5 and +4.6 ‰. The pyrite values are within the range of seafloor sulfide deposits (*e.g.*, 21°N, EPR). The marine sulfur contribution is calculated to be about 11% of the total sulfur, with the other 89% derived from basaltic sulfide sulfur.

(5) We calculate water/rock ratios (by weight) of 2–7 from the total sulfur content of the greenschist rocks and the sulfur isotopic composition of the sulfides they contain. The water/rock ratios are fairly consistent with those estimated from strontium and oxygen isotopes.

(6) The sulfur in a large (3 million tonnes) sulfide deposit could be provided by alteration (leaching) of 1.2 km^3 of oceanic crust.

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