5. MINERALOGY AND ISOTOPIC COMPOSITION OF SULFUR IN LAYER 3 GABBROS FROM THE INDIAN OCEAN, HOLE 735B

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ABSTRACT

Sulfide mineralogy, sulfur contents, and sulfur isotopic compositions were determined for samples from the 500-m gabbroic section of Ocean Drilling Program Hole 735B in the southwest Indian Ocean. Igneous sulfides (pyrrhotite, chalcopyrite, pentlandite, and troilite) formed by accumulation of immiscible sulfide droplets and crystallization from intercumulus liquids. Primary sulfur contents average around 600 ppm, with a mean sulfide δ34S value near 0‰, similar to the isotopic composition of sulfur in mid-ocean ridge basalt glass. Rocks from a 48-m interval of oxide gabbros have much higher sulfur contents (1090–2530 ppm S) due to the increased solubility of sulfur in Fe-rich melts. Rocks that were locally affected by early dynamothermal metamorphism (e.g., the upper 40 m of the core) have lost sulfur, averaging only 90 ppm S. Samples from the upper 200 m of the core, which underwent subsequent hydrothermal alteration, also lost sulfur and contain an average of 300 ppm S. Monosulfide minerals in some of the latter have elevated δ34S values (up to +6.9‰), suggesting local incorporation of seawater-derived sulfur. Secondary sulfides (pyrrhotite, chalcopyrite, pentlandite, troilite, and pyrite) are ubiquitous in trace amounts throughout the core, particularly in altered olivine and in green amphibole. Pyrite also locally replaces igneous pyrrhotite. Rocks containing secondary pyrite associated with late low-temperature smectitic alteration have low δ34S values (up to +6.6‰). These low values are attributed to isotopic fractionation produced during partial oxidation of igneous sulfides by cold seawater. The rocks contain small amounts of soluble sulfate (5% of total S), which is composed of variable proportions of seawater sulfate and oxidized igneous sulfur. The ultimate effect of secondary processes on layer 3 gabbros is a loss of sulfur to hydrothermal fluids, with little or no net change in δ34S.

INTRODUCTION

Reaction of seawater with the oceanic crust influences the concentrations of many elements in the oceans and has been suggested to affect the mass and isotopic composition of sulfur in seawater (Edmond et al., 1979). Subduction of altered crust may contribute to the 34S-enrichment of igneous rocks in island arcs (Sasaki and Ishihara, 1979; Ueda and Sakai, 1984; Woodhead et al., 1987) and to sulfur isotopic heterogeneities in the mantle (Chaussidon et al., 1987; Harmon et al., 1987). Studies documenting the distribution and isotopic composition of sulfur in the upper oceanic crust (volcanics and dikes of oceanic layer 2) have been published (Andrews, 1979; Hubberten, 1983; Field et al., 1984; Alt et al., 1989), but little is known about the geochemistry of sulfur in gabbros of oceanic layer 3. The 500 m of gabbros penetrated by Hole 735B during Leg 118 provide an excellent continuous section through a portion of layer 3. This study presents the mineralogy of sulfides, whole-rock sulfur contents and sulfur isotopic compositions of gabbros from Hole 735B, with the goals of (1) understanding the geochemistry of sulfur in the lower oceanic crust and (2) providing some preliminary constraints on the role that layer 3 plays in cycling of sulfur in the oceans and in subduction zones.

SITE 735

Site 735 is located on the eastern rim of the Atlantis II Fracture Zone in the Indian Ocean (Fig. 1). The site is on an uplifted block, 5 × 2 km in size, in about 700 m of water.


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Drilling at Hole 735B penetrated 500.7 m of gabbroic rocks, with a total recovery of 87%. Six major lithologic units were defined by shipboard scientists, primarily on the basis of igneous mineralogy, mineral compositions, and deformation features (Shipboard Scientific Party, 1989; Dick et al., this volume; Fig. 2). Lithologic Unit I is a 37.4-m-thick sequence of foliated metagabbro (gabbronorite and olivine gabbro). Igneous textures have been completely destroyed, and the rocks consist mostly of neoblasts of plagioclase, clinopyroxene, and brown amphibole. Unit II comprises 132.75 m of olivine gabbro and olivine-bearing gabbro. Most of the rocks are mesocumulates and chemically are fairly primitive. Thin layers rich in Fe-Ti oxides are common, however, often associated with zones of deformation. Unit III is a 53.35-m-thick section of oxide-bearing olivine gabbro with intervals of oxide gabbro. The section is similar to Unit II, but the rocks are chemically more evolved. Unit IV consists of 50.49 m of oxide gabbros. These contain abundant opaque Fe-Ti oxide minerals (5–25 vol%) and have FeO3 contents ranging up to about 25 wt%. Small amounts of olivine are also present in the rocks. Unit V is a 108.34-m section of relatively uniform olivine gabbro. Most rocks are mesocumulates that are mineralogically and chemically similar to Unit II. Unit VI is a 118.30-m interval of olivine-rich gabbro with abundant layers of troctolite. These gabbros are similar to Unit V, but are more olivine rich. The interlayered troctolites and troctolitic gabbros are the most mafic rocks encountered in the hole.

The gabbros are variably altered, with alteration related to local deformation and permeability. Several different stages and types of alteration have been recognized, including (1) early dynamothermal metamorphism, (2) brittle deformation and static metamorphism, and (3) low temperature alteration (Vanko and Stakes, this volume; Shipboard Scientific Party, 1989). An early stage of dynamothermal metamorphism pro-
Isotopic data indicate temperatures of 500° to 600°C for deformation and penetration of seawater into the gabbros. This resulted in static alteration of undeformed gabbros and the formation of near-vertical veins filled mainly with hornblende and sodic plagioclase. Mineral compositions and oxygen isotopic compositions ranged from about 700° to 600°C (Vanko and Stakes, this volume).

Temperatures of metamorphism derived from mineral chemical and oxygen isotopic compositions ranged from 250 to 275 m and from 430 to 498 m. Major fracture zones indicated by heavy lines.

Figure 1. Map showing the location of Site 735 in the Indian Ocean. Major fracture zones indicated by heavy lines.

Dynamothermal metamorphism was followed by brittle deformation and penetration of seawater into the gabbros. This resulted in static alteration of undeformed gabbros and the formation of near-vertical veins filled mainly with hornblende and sodic plagioclase. Mineral compositions and oxygen isotopic data indicate temperatures of 500° to 600°C for most of the hornblende-plagioclase vein (Vanko and Stakes, this volume). Pyroxene and plagioclase in the wall rock around veins and microcracks were also replaced by green amphibole and sodic plagioclase, respectively. Veins and fractures are most abundant in the upper 200 m of the core and are less common at greater depths. In addition to veins, three zones of brecciation occur around 180, 275, and 330 m, where clinopyroxene, clinozoisite, sphene, actinolite, chlorite, and zeolites fill former open spaces. The mineral paragenesis, fluid inclusions and oxygen isotope ratios indicate decreasing temperatures of alteration in these zones, from amphibolite grade (550°-400°C) to greenschist (<400°C) and lower temperatures (Vanko and Stakes, this volume). In undeformed rocks, static metamorphism is characterized by the formation of reaction "coronas" around igneous minerals and replacement by secondary Mg-Fe amphibole, talc, phlogopite, pargasite, actinolite, and chlorite.

Evidence for low-temperature alteration is scattered throughout the core, and is most intense at 33 to 39 m and in the three brecciated zones (at around 180, 275, and 330 m). Low-temperature alteration is characterized by smectite ± Fe-oxyhydroxide ± carbonate in veins, as pseudomorphs of olivine and orthopyroxene, and disseminated in the rocks. This alteration is thought to be related to late circulation of cold seawater along permeable zones.

METHODS

Opaque minerals were studied, and whole-rock sulfur contents and sulfur isotopic compositions measured for 22 samples representative of the six different lithologic units. Minerals were identified and phase relationships determined by optical examination of polished thin sections in transmitted and reflected light. Chemical compositions of sulfide minerals were analyzed using a JEOL 733 electron microprobe. Operating conditions were the following: 15-kV accelerating voltage; 30-nA sample current; 1-µm spot size; and 30- to 40-s counting times. Sulfur and carbon contents of whole-rock powders were measured using a LECO CS-244 carbon-sulfur analyzer. Replicate analyses of samples were generally reproducible to within 10% of reported values for sulfur and to within 5% for carbon.

Various forms of sulfur were extracted from whole-rock powders for isotopic analysis using a stepwise technique modified from Puchelt and Hubberten (1979). In the first step, monosulfides (such as pyrrhotite, chalcopyrite, pentlandite, etc.) were decomposed by reaction with 6N HCl at 80°C for at least 1 hr in a closed vessel, through which nitrogen continuously flowed. Zinc metal was added to reduce cuprous sulfides (Ueda and Sakai, 1984). Evolved H₂S was precipitated as Ag₂S by bubbling the N₂ carrier gas through AgNO₃ solution. Soluble sulfate extracted from the rock during this first stage was precipitated as BaSO₄. Pyrite sulfur was extracted from the residue of the previous step by reaction with a CrCl₃-HCl solution at 80°C in a stream of nitrogen (Canfield et al., 1986), and evolved H₂S was precipitated as Ag₂S. Sulfur isotope ratios were measured on SO₂ gas, which was produced from Ag₂S by combustion with Cu₂O, or from BaSO₄ by combustion with sodium metaphosphate, at 950°C under vacuum. Data are reported as delta notation relative to Canyon Diablo troilite (CDT). Instrument uncertainty for individual measurements is ± 0.2‰, but reproducibility of replicate extractions and analyses is approximately ± 0.5‰.

RESULTS

Opaque Mineral Petrology

Igneous Sulfides

The predominant sulfide minerals in samples from Hole 735B are igneous sulfides. These occur in most samples, but are particularly abundant in the oxide gabbros of Unit IV. However, the foliated megagabbros of Unit I contain only traces of igneous sulfides enclosed in relics of primary silicates. Igneous sulfides are also relatively rare in Unit II, which contains more abundant veins and where the rocks are more extensively recrystallized than deeper in the core. The absence of igneous sulfides in these units is most likely due to the breakdown of these minerals along with igneous silicates during early dynamothermal metamorphism and later vein-related hydrothermal metamorphism.

Igneous sulfides occur as irregular to round or oblong globular shapes, from tens to several hundreds of micrometers in size. They are typically enclosed in brown igneous amphibole surrounding pyroxenes or in interstitial areas between igneous minerals (Fig. 3). They are also present as inclusions within plagioclase and pyroxene (Fig. 3A). In the oxide gabbros of Unit IV, igneous sulfides occur as intergrowths with and inclusions in magnetite and ilmenite. In one sample (118-735B-68R-2, 20-24 cm), igneous sulfide is partially enclosed in olivine and appears to be an intergrowth of sulfide and olivine.
Figure 2. Sulfur data for Hole 735B. Lithostratigraphic column at left is explained in text. A. Whole-rock sulfur contents. Vertical lines are average values for individual lithostratigraphic units. B. Sulfur isotopic composition in per mil, CDT. Open circles = monosulfide sulfur; solid circles = pyrite sulfur; open squares = sulfate sulfur. Vertical lines indicate isotopic composition of sulfur in MORB glass and seawater (Sukai et al., 1984; Rees et al., 1978).

Pyrrhotite is the most common igneous sulfide mineral, followed by chalcopyrite, troilite, and pentlandite. The globular igneous sulfides are most commonly multiphase aggregates composed of pyrrhotite plus one or more of the other phases (Fig. 3B), but monomineralic grains of pyrrhotite and, less commonly, chalcopyrite occur. Small amounts of magnetite also are sometimes present. Troilite occurs in lenslike intergrowths with pyrrhotite in Units V and VI, and in one sample each from Units III and IV (Fig. 3B). The mineralogy and occurrence of igneous sulfides in Hole 735B are typical of igneous sulfides that separated and crystallized from basaltic liquids (Craig and Kullerud, 1969).

No consistent difference in mineralogy was observed between igneous sulfides included in silicate or Fe-Ti oxide minerals and those in interstitial areas. Likewise, the mineralogy of igneous sulfides in Units II, III, V, and VI is essentially identical. The oxide gabbros of Unit IV, however, do not contain any pentlandite in igneous sulfide globules, nor was any secondary pentlandite observed in these samples.

Representative microprobe analyses of sulfides are given in Table 1. Igneous pyrrhotites contain 93.3 to 95.5 mol% FeS, with nickel contents ranging up to 0.82 wt% and Co contents of up to 0.3%. The highest Co contents and lowest Ni contents for pyrrhotite occur in the oxide gabbros of Unit IV. Where pyrrhotite coexists with troilite, the pyrrhotite has consistently higher Ni contents (0.09–0.74%) than troilite (<0.04% Ni). Co contents of coexisting troilite and pyrrhotite are variable, but both are low (<0.12%). Cooling of Fe-rich pyrrhotite (>48 atomic % Fe) to temperatures less than 140°C results in exsolution of troilite and hexagonal pyrrhotite (Kissin and Scott, 1982), giving rise to the textures observed in Figure 3B. The composition of pyrrhotite coexisting with troilite in Hole 735B samples (95.5 ± 0.7 mol% FeS) is identical to the experimentally determined composition of hexagonal pyrrhotite of structural type 6C, which is stable at temperatures less than about 80°C (95.6% FeS, Kissin and Scott, 1982).

Igneous pentlandites have compositions close to the intermediate Fe₄₅Ni₄₅S₈ formula, and contain minor amounts of Co (1.09%–4.45%). All analyzed Cu-Fe sulfides have stoichiometric chalcopyrite compositions (not shown in Table 1).

Secondary Sulfides

Secondary sulfides occur in trace amounts throughout the core: in olivine pseudomorphs, in recrystallized and interstitial areas, as pseudomorphs of igneous sulfides, and in small veinlets. Secondary sulfides are extremely rare, however, in the deformed metagabbros of Unit I. The most common occurrence of secondary sulfides is in the alteration coronas replacing olivine (Fig. 4A). Secondary sulfides also are sometimes present in similar alteration coronas around the margins of orthopyroxene. These alteration rims or coronas occur in all samples except the foliated metagabbros of Unit I and several samples of Unit IV oxide gabbros. There is a general zonation in the coronas from relict olivine outward to talc plus magnetite and then colorless amphibole plus magnetite. These zones are followed outward by green amphibole, chlorite, or phlogopite. This is a generalized zonation: one or several minerals of the sequence are often missing, and in many cases, the olivine has been totally replaced. Sulfides are common in small amounts with magnetite in the talc and/or colorless amphibole zones. Pyrrhotite is the most common sulfide, occurring as laths up to several tens of micrometers long, intergrown with magnetite and silicates (Fig. 4A). Chalcopyrite and pentlandite also occur, generally as individual grains or intergrown with magnetite, but multiphase grains of pyr-
rhodite ± chalcopyrite ± pentlandite are also observed. In some samples (from Units III, V, and VI), exsolutions of troilite are present in the secondary pyrrhotite. Pyrite occurs in a few samples throughout the core as a later pseudomorph of secondary pyrrhotite. Small fractures in the central olivine relics contain talc, magnetite and sometimes pyrrhotite (Fig. 4A). These microcracks can sometimes be traced into adjacent plagioclase crystals, where they are delineated by trains of fluid inclusions along healed fractures in the plagioclase. In many samples the central olivine relic surrounded by an alteration corona is veined or partly replaced by a magnesian smectite ± magnetite ± pyrrhotite or pyrite. Carbonate and/or Fe-oxhydroxide is present and replaces the central olivine in some samples.
Secondary sulfides occur in trace amounts in recrystallized areas of green amphibole, which also contains disseminated secondary magnetite. Pyrrhotite is most common, chalcopyrite and pyrite are less abundant, and pentlandite is rare. These occur as small (up to about 40 µm in width, cut igneous morphs and the association with Fe-oxyhydroxides suggest with orange smectite. The porous nature of the pyrite pseudomorphs laths of secondary pyrrhotite intergrown with marcasite in finely crystalline aggregates. Pyrite also generally are associated with Fe-oxyhydroxides and orange pseudomorphs of igneous pyrrhotite, and with smectite in small veinlets and interstitial areas. Pyrite veinlets, of these Unit IV samples. The pyrite ± marcasite pseudomorphs generally are associated with pentlandite in a 20 µm grain in green amphibole. These occur as small (up to a few tens of micrometers) individual grains or intergrowths. Millerite (NiS) was identified in one sample (118-735B-34R-2, 96–100 cm), where it occurs with pentlandite in a 20 µm grain in green amphibole. Chalcopyrite, pyrite, and pyrrhotite are present as similar small grains in interstitial areas with chlorite, and in aggregates of granular secondary plagioclase.

Secondary pyrite is scattered in trace amounts throughout the core. It is present in interstitial areas with chlorite, as pseudomorphs of igneous and secondary pyrrhotite, and with smectite in veins and replacing olivine. In Sample 118-735B-58R-4, 54–58 cm, pyrite is common as small (2–10 µm) grains disseminated in smectite that replaces plagioclase and in smectite veinlets. Pyrite is most common in the oxide gabbros of Unit IV (and in Sample 118-735B-43R-2, 86–90 cm), where it is the dominant sulfide phase and occurs mainly as pseudomorphs of igneous pyrrhotite (Fig. 4B). The pyrite is generally porous and often intergrown with marcasite in finely crystalline aggregates. Pyrite also pseudomorphs laths of secondary pyrrhotite intergrown with silicates replacing olivine. Little or no pyrrhotite remains in most of these Unit IV samples. The pyrite ± marcasite pseudomorphs generally are associated with Fe-oxhydroxides and orange smectite in small veinlets and interstitial areas. Pyrite veinlets, from a few micrometers up to about 40 µm in width, cut igneous minerals, talc, green amphibole, and chlorite in two samples from Unit IV (118-735B-52R-2, 22–26 cm, and -53R-2, 53–56 cm). Like the pyrite pseudomorphs, these veinlets are associated with orange smectite. The porous nature of the pyrite pseudomorphs and the association with Fe-oxhydroxides suggest origin of the pyrite by oxidation of pyrrhotite, with consequent Fe-loss and volume reduction, rather than sulfidation of pyrrhotite, which would cause a volume increase.

No consistent differences in composition were detected between igneous and secondary pyrrhotites (Table 1). Secondary pentlandites generally have Ni contents similar to those of igneous pentlandites; however, the secondary pentlandite associated with millerite is Ni-rich (Fe₂₅Ni₇₅S). Co contents of secondary pentlandites in olivine coronas range to higher values (5.4%–10.1%) than igneous pentlandites. Like the igneous sulfides, all analyzed secondary Cu-Fe sulfides have stochiometric chalcopirite compositions.

**Sulfur and Carbon Contents**

Sulfur contents of rocks from Hole 735B vary considerably, ranging from 60 to 2530 ppm (Table 2). The extensively recrystallized foliated metagabbros of Unit I have low sulfur contents, averaging only 90 ppm (Fig. 2). In contrast, Unit IV oxide gabbros have high sulfur contents, ranging from 1090 to 2530 ppm. These high sulfur contents reflect the abundant igneous sulfides (and pyrite pseudomorphs) observed in the rocks, suggesting that sulfur was concentrated through igneous processes. Units III, V, and VI, which contain the least altered rocks in the core, average 460, 510, and 730 ppm S respectively, whereas Unit II contains only 300 ppm S.

With the exception of one sample, the carbon contents of Hole 735B samples are uniform and range from 150 to 400 ppm (Table 2), and have a mean of 230 ± 60 ppm. This value is identical to that assumed by Staudigel et al. (1989) for the carbon content of the lower oceanic crust. Sample 118-735B-24R-2, 132–136 cm, contains 1400 ppm C, which is significantly greater than all other samples. The high carbon content of this sample can be attributed to the abundant secondary calcite observed that replaces olivine.
Sulfur Isotopes

Results of sulfur isotopic analyses are given in Table 2. The total sulfur extracted for isotopic analyses averages 93% of the total sulfur content of the rocks, as determined by the LECO combustion technique. The proportions of the different types of sulfur extracted from the rocks vary widely, but monosulfide, pyrite, and soluble sulfate sulfur average 53%, 41%, and 6%, respectively, of the total sulfur.

There do not appear to be any consistent trends in $\delta^{34}$S values with depth or according to lithostratigraphic unit (Fig. 2). Monosulfide sulfur has $\delta^{34}$S values that range from $-3.2$ to $+6.9\%$, with a mean of $+0.5 \pm 2.4\%$. This mean is similar to the average $\delta^{34}$S of sulfur in mid-ocean ridge basalt (MORB).
glasses (+0.1 ± 0.5‰, Sakai et al., 1984). Nonetheless, significant variations do occur in the isotopic composition of sulfide in Hole 735B (Fig. 2). Two samples (118-735B-39R-2, 30-34 cm, and -58R-4, 54-58 cm) have highly negative δ34S values for pyrite sulfur (−11.2 and −16.6‰, respectively). Pyrite sulfur in the other samples has δ34S values that range from −2.1 to +0.8‰, with a mean of −0.3 ± 0.8‰, near the MORB value. For the pairs analyzed, pyrite sulfur tends to have a lower δ34S value than co-existing monosulfide sulfur (Fig. 2), the reverse of equilibrium fractionation (Ohmoto and Rye, 1979).

The δ34S of soluble sulfate varies widely, from +3.2 to +23.5‰ (Table 2). Three samples have δ34S values near that of seawater (+21‰, Rees et al., 1978; Table 2). The lower δ34S values of sulfate from the other analyzed samples fall between the values for seawater sulfate and basaltic sulfur (Table 2).

**DISCUSSION**

**Distribution of Igneous Sulphides and Sulfur**

The assemblages of pyrrhotite ± pentlandite ± chalcopyrite ± troilite in the globular interstitial sulfides and enclosed in cumulate silicates are typical of igneous sulfides separated and crystallized from mafic magmas, and which have re-equilibrated at lower temperatures (Craig and Kullerud, 1969). Troilite is a relatively uncommon igneous sulfide phase that indicates exsolution from Fe-rich pyrrhotite (>48 atomic % Fe) at low temperatures (<140°C, Kissin and Scott, 1982). The presence of such Fe-rich pyrrhotite indicates lower sulfur fugacities in the troilite + hexagonal pyrrhotite-bearing rocks than in those containing only pyrrhotite that is poorer in Fe (Toupin and Barton, 1964). The troilite-pyrrhotite exsolution may also indicate lower oxygen fugacity in host rocks than in rocks containing pyrrhotite only (Pasteris, 1984; 1985).

Various processes can account for the distribution of igneous sulfides in Hole 735B, including accumulation of droplets of immiscible sulfide liquid along with cumulate silicates, as well as separation and crystallization of sulfides from late-stage silicate melt. The common occurrence of sulfides as inclusions in silicates indicates that the melts were saturated with sulfur, causing separation of an immiscible sulfide liquid during at least one period early in the crystallization history. Sulfide might have increased in the gabbroic cumulates of Hole 735B through accumulation of sulfides containing these inclusions. Accumulation of immiscible sulfide droplets along with the silicate cumulate phases may also have taken place and is consistent with the occurrence of globular igneous sulfides in interstitial areas. Separation and crystallization of sulfide from crystallizing intercumulus silicate melt can also account for globular interstitial sulfides. In particular, the sulfide and magnetite-sulfide globules, which are enclosed in brown igneous amphibole rims on pyroxenites, probably formed by this process.

Transition metal contents of whole-rock samples from Hole 735B provide additional constraints on what processes may account for the distribution of igneous sulfides in the rocks. Two trends can be observed on plots of Ni and Cu vs. Fe3O4 (Fig. 5). First, Ni and Cu both increase independently of Fe at low values of Fe3O4 in Units V and VI. Ni and Cu are strongly fractionated into sulfide melt relative to coexisting mafic silicate melt (Naldrett, 1981), suggesting that accumulation of immiscible sulfide melt may account for the increases in Ni and Cu at low iron contents. There is a slight correlation of Ni with Cu in Unit V (Fig. 6), which may reflect accumulation of sulfides. Samples from Unit VI, as well as from all other units, do not exhibit this correlation, however, suggesting that simple accumulation of sulfide minerals cannot account for the trends of increasing Cu and Ni at constant Fe in Figure 5. These trends are better explained by accumulation.

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Table 2. Sulfur data for Hole 735B.

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</tbody>
</table>

*Where δ34S sulfate not analyzed, δ34S total S calculated assuming δ34S sulfate = +21‰.
Blanks = not analyzed; δ34S in per mil CDT; dashes = none detected.*
of both olivine and sulfide. Between olivine and coexisting sulfide melt, Ni is preferentially partitioned into olivine, whereas Cu is partitioned into sulfide (Naldrett, 1981; Fleet and MacRae, 1987). Thus, accumulation of olivine can account for the trend of increasing Ni at constant low Fe, while accumulation of Cu-bearing sulfides can account for the increase of Cu at constant low Fe in Units V and VI.

The second trend of increasing Cu and decreasing Ni with rising Fe contents (Fig. 5) occurs mainly in the oxide gabbros of Unit IV. The high Fe and Ti contents of these rocks, the uniform high Fe contents of olivine and pyroxene, and the presence of sodic plagioclase all indicate formation from a highly differentiated, Fe-rich liquid (Dick et al., this volume). The oxide gabbros are interpreted to have formed through expulsion of highly differentiated Fe-rich intercumulate liquids from crystallizing olivine gabbros into zones of brittle-ductile deformation, where the liquids penetrated and perhaps reacted with the host olivine gabbros (Dick et al., this volume). The high sulfur contents of the oxide gabbros (Fig. 2) and the abundance of sulfides, as well as Fe-Ti oxides, are consistent with formation from an evolved silicate melt. Factors affecting the sulfur content of basaltic melts include temperature, pressure, $f_{O_2}$, and melt composition, with the solubility of sulfur increasing significantly as iron content increases (Haughton et al., 1974; Katsura and Nagashima, 1974; Carroll and Rutherford, 1985). The oxide gabbros of Unit IV have high Fe$_2$O$_3$ contents, ranging up to about 25 wt% (Shipboard Scientific Party, 1989). The high sulfur contents of these rocks are consistent with differentiation and iron enrichment, with a corresponding increase in the solubility of sulfur in the melts.

The trend of increasing Cu and Fe contents of the oxide gabbros in Figure 5 correlates with extremely high sulfur contents (Fig. 2, Table 2). The increase in Cu in these rocks is attributed to the increase in solubility of Cu-Fe sulfide in basaltic melt as Fe content increases (Haughton et al., 1974). Fractional crystallization of olivine and extraction of Ni from the melt can account for the low Ni contents of these Fe-rich rocks. Separation of immiscible sulfide liquid also occurred, however, which probably contributed to the Ni depletion of these rocks and to the relative Cu-enrichment of the sulfide present.

Segregation of sulfide liquid from a basaltic melt generally begins with separation of a Ni-Fe-Cu sulfide liquid, with the Ni/(Ni$^+$Cu) ratio of subsequent sulfide decreasing as separation of sulfide proceeds (Duke, 1979; Naldrett, 1981). Mafic intrusions typically exhibit this effect in the sequence from early pyrrhotite + pentlandite + chalcopyrite assemblages to later pyrrhotite + chalcopyrite assemblages (Chamberlain, 1967; Naldrett, 1981). The distribution of igneous sulfides in rocks from Hole 735B is consistent with these trends. Igneous sulfides in Units II, III, V, and VI from Hole 735B are characterized by pyrrhotite + pentlandite + chalcopyrite (± tavorite) assemblages, whereas igneous sulfides in Unit IV oxide gabbros lack pentlandite and are composed of chalcopyrite + pyrrhotite (the pyrrhotite is now mostly pseudomorphed by secondary pyrite and marcasite). The lowest Ni contents of pyrrhotite also occur in Unit IV, consistent with prior extraction of Ni in olivine and sulfide. Fractionation of olivine plus sulfide from mafic magmas results in a progressive decrease in the Ni/Co ratio of sulfide separating from the melt (Duke, 1979; Naldrett, 1981). This process thus might also account for the relatively high Co contents of pyrrhotite in the oxide gabbros of Unit IV.

Secondary Sulfides and Behavior of Sulfur During Hydrothermal Alteration

The sulfide mineralogy and behavior of sulfur resulting from the alteration of Hole 735B gabbros are discussed in
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relation to the major metamorphic processes that affected silicate minerals in the rocks (dynamothermal metamorphism, brittle deformation and static metamorphism, and low temperature alteration). To understand the behavior of sulfur during hydrothermal alteration, however, some constraints must be placed on the original, igneous sulfur contents of the rocks. Various information indicates that the most altered rocks occur in the upper 200 m of the core, reaching maximum abundance in Units II and III (Vanko and Stakes, this volume); secondary amphibole in the rock matrix is most abundant in the upper 150 m of the core (Dick et al., this volume); and pyroxenes have elevated $^{87}$Sr/$^{86}$Sr ratios in the upper 200 m, indicating greater extent of interaction with seawater in the upper half of the core (Kemppton and Hawkesworth, 1988). Thus, excluding the unusual oxide gabbros of Unit IV, the least altered rocks occur in Units V and VI. Petrographically, these rocks are mostly unaltered. Sulphides contained in the rocks are predominantly igneous, with only traces of secondary sulphides present in alteration rims on olivine. Sulphur contents of samples from Units V and VI range from 430 to 790 ppm, with a mean of 610 ± 180 ppm. This value is taken as the starting igneous sulphur content of gabbroic rocks from Hole 735B. Because Hole 735B rocks are cumulates, however, this sulphur content does not represent the sulphur content of the parent magmas.

The foliated metagabbros of Unit I are depleted in sulphur relative to the rest of the core (Fig. 2). This sulphur depletion correlates with the near absence of igneous sulphides from the rocks, and with the presence of only traces of secondary sulphide minerals, implying that early dynamothermal metamorphism resulted in breakdown of igneous sulphides and nearly complete loss of sulphur from the rocks. Additional sulphur may have been lost from the rocks during subsequent veining and static metamorphism and late, low-temperature alteration (see below), but these processes also affected the upper 200 m of the core, whereas there is a distinct break in sulphur contents at the base of Unit I (Fig. 2). This suggests that the main process responsible for the sulphur depletion of Unit I was early plastic deformation and high temperature metamorphism (600°–700°C; Vanko and Stakes, this volume).

Subsequent brittle deformation and associated static hydrothermal metamorphism also resulted in loss of sulphur from the more extensively altered rocks. Igneous sulphides are scarce or absent in extensively altered portions of the rocks containing abundant green amphibole and secondary plagioclase associated with hornblende veins (e.g., in Unit II). These zones also contain only traces of secondary sulphide minerals. Unit II, which was significantly affected by alteration of this type, contains on average 300 (± 130) ppm S, significantly less than the least altered rocks from the core (600 ppm), indicating that sulphur was lost from the rocks to hydrothermal fluids during brittle deformation and static metamorphism.

Even though sulphur was locally lost from the rocks at this stage, secondary sulphides formed in trace amounts throughout the core during static metamorphism. These include the sulphides enclosed in green amphibole, but the most common secondary sulphides are associated with altered olivine. Most secondary sulphides probably formed by recrystallization of igneous sulphide, but sulphur isotopic data indicate at least local incorporation of a component of sulphide derived from reduced seawater sulphate (see section on sulphur isotopes).

Temperatures estimated for the reaction of olivine to anthophyllite + magnetite or talc + magnetite at P$_{FeO}$ = P$_{total}$ = 0.5 to 2 kbar are in the range of 500°–600°C (Ferry, 1985; Bird et al., 1988). These temperature estimates are similar to those for most of the hornblende-plagioclase veins in Hole 735B core (Vanko and Stakes, this volume). The presence of talc + magnetite and MgFe amphibole + magnetite along microcracks in olivine in relatively fresh rocks suggests that these minerals formed at very low water/rock ratios. Oxidation of Fe$^{2+}$ in olivine probably occurred through the decomposition of water during initial hydration reactions such as:

$$1.104 \text{H}_2\text{O} + 1.67(\text{Fe}_{0.2}\text{Mg}_{1.8})\text{SiO}_4 + 2.33 \text{SiO}_2(aq) = \text{olivine}$$

$$0.111 \text{Fe}_2\text{O}_3 + 2\text{Mg}_3\text{Si}_4\text{O}_6(\text{OH})_2 + 0.104 \text{H}_2\text{O} = \text{magnetite + talc}$$

The last secondary minerals to form in the rocks were low-temperature phases: smectite ± sulphides (pyrrhotite, pyrite) ± carbonate ± Fe oxyhydroxides in veinlets and replacing olivine. This low-temperature alteration probably occurred through circulation of cold seawater along permeable zones and may be related to fracturing associated with uplift of the gabbroic block. Conditions varied from more reducing (smectite ± pyrrhotite ± pyrite ± carbonate) to more oxidizing (smectite + Fe oxyhydroxides ± carbonate). This stage resulted in formation of secondary sulphides in some rocks, whereas small amounts of sulphur were probably lost from others through oxidation of sulphides. Fe-oxyhydroxides are scattered in trace amounts throughout the core; thus, there does not appear to be a distinct zone of “seafloor weathering” and consequent sulphur loss, such as occurs in the volcanic section of ocean crust (Alt et al., 1989). The replacement of igneous and secondary pyrrhotite by pyrite and marcasite most likely occurred during late, low-temperature alteration. By analogy with the formation of similar phases in submarine basalts, low-temperature alteration probably occurred at temperatures less than about 100°C, perhaps approaching 0°C (Bohle et al., 1984). Sulfide phases in rocks from Hole 735B (trollite, millerite) indicate at least partial re-equilibration at low temperatures (less than about 100°C; Craig, 1973; Kissin and Scott, 1988), whereas some rocks lost a significant amount of sulphur associated with the formation of the rocks and re-equilibration of sulphides at these temperatures relate to the timing of low-temperature alteration.

**Sulphur Isotopes**

Most of the sulphur $^{34}$S values for Hole 735B are near that for sulphur in MORB glasses (+0.1 ± 0.5‰, Sakai et al., 1984), reflecting primary magmatic sulphur from a MORB-type mantle source (Fig. 7). Sulfide from the least altered rocks in Units V and VI (excluding Sample 118-735B-58R-4, 54–58 cm, discussed below) has $^{34}$S values that average +0.8 ± 0.9‰, and $^{34}$S of most of the sulphide from Hole 735B is within ±2‰ of the MORB value (Fig. 7), which can be attributed to primary igneous processes. Mafic intrusions exhibit similar variation in the isotopic composition of sulphide, with $^{34}$S mostly ranging from −1.5 to around +5‰ (Fig. 7; Thode et al., 1962; Shima et al., 1963; Sasaki, 1969a, 1969b). In some cases, $^{34}$S of sulphide increases with differentiation in mafic intrusions, whereas in others no clear trend is evident, or $^{34}$S may decrease in more differentiated rocks (Thode et al., 1962; Shima et al., 1963; Sasaki, 1969a, 1969b). Slight variations in oxygen and sulphur fugacities implied by the presence or absence of igneous troilitre in Hole 735B rocks could affect the speciation of sulphur in the melt (Katsura and Nagashima, 1974; Ueda and Sakai, 1984), consequently resulting in slight vari-
sulfide in the rock-dominated system, and the sulfide acquires a δ34S value approaching that of the unaltered rock. The high δ34S value of sulfide in hydrothermal fluids reach maxima at depth in the magma (the proportion of sulfide vs. sulfate sulfur), separation and removal of sulfide minerals from the silicate melt could result in small increases or decreases of a few per mil in δ34S of residual sulfide in the magma (Ueda and Sakai, 1984).

Monosulfide sulfur in Sample 118-735B-24R-2, 132-136 cm, (+6.9‰, Table 2) has a significantly higher δ34S value than that in the other samples. Mafic intrusions exhibit similar spreads in δ34S values of 2 to 7‰ (Fig. 7), so that the high δ34S value from Hole 735B might conceivably be attributed to igneous variation. Sample 118-735B-24R-2, 132-136 cm, however, is extensively recrystallized, has a very low sulfur content, and the only sulfides observed in thin section are secondary (pyrrhotite and chalcopyrite in olivine coronas and in green amphibole). These observations suggest that monosulfide minerals in the rock formed from hydrothermal fluids containing a mixture of sulfide derived from basaltic (near 0‰) and seawater (+21‰, Rees et al., 1978) sources. (The relatively low δ34S value of coexisting pyrite in this sample [Table 2] is due to late, low-temperature formation of pyrite [see below].)

Extensively altered basalts from DSDP Hole 504B are similarly enriched in δ34S, although these are interpreted to have formed where upwelling hydrothermal fluids mixed with seawater in the shallow subsurface (Alt et al., 1989). Reduction of seawater sulfate and incorporation into sulfide minerals are interpreted to have occurred in proximity to the shallow mixing zone in Hole 504B, whereas sulfide in upwelling hydrothermal fluids originating at depth in the crust is believed to be rock-dominated, with δ34S values around +1‰ (Shanks and Seyfried, 1987; Alt et al., 1989; Bowers, 1989). Modeling of sulfur in submarine hydrothermal systems, however, predicts a zone where both reduction of seawater sulfate and the δ34S of sulfide in hydrothermal fluids reach maxima at depth in the crust (Bowers, 1989). These fluids then react and equilibrate in the rock-dominated system, and the sulfide acquires a δ34S value approaching that of the unaltered rock. The high δ34S value of monosulfide sulfur in Sample 118-735B-24R-2, 132-136 cm, may have derived from fluids containing a mixture of basaltic sulfide and sulfide from reduction of seawater sulfate, which penetrated relatively deep into the crust. Sample 118B-735B 30R-2, 82-87 cm, is similar to Sample 118B-735B-24R-2, 132-136 cm: it is extensively recrystallized and only secondary sulfides are observed in thin section. This sample also has a relatively high δ34S value for monosulfide sulfur (+2.6‰), which may similarly be due to incorporation of seawater-derived sulfide. In contrast, Sample 118B-735B-13R-2, 75-79 cm, which is from the same lithologic unit as the above samples, contains monosulfide sulfur with δ34S of +0.2‰. This is near the presumed igneous value (around +0.1‰), suggesting incorporation of little or no seawater-derived sulfide. Indeed, this sample is only slightly recrystallized and retains igneous sulfides, consistent with incorporation of little or no seawater-derived sulfide.

Pyrite sulfur commonly has low δ34S values that are lower than coexisting monosulfide sulfur in Hole 735B (Fig. 2). This fractionation is in the opposite sense for equilibrium, where pyrite is enriched in 34S relative to coexisting monosulfide minerals (Ohmoto and Rye, 1979). The low δ34S values of pyrite relative to monosulfide sulfur can be accounted for by the presence of a component of late, low-temperature pyrite, which has lower δ34S values. In particular, pyrite sulfur from Sample 118B-735B-58R-4, 30-34 cm, has the lowest measured δ34S value from Hole 735B (-16.6‰, Table 2). This sample is unique in that it is part of a hydrothermal breccia containing a vein of clinopyroxene, zoisite, actinolite, chlorite, sphene, and plagioclase, as well as abundant intermediate-mature pyrite. Small grains of disseminated secondary pyrite are common in the smectite in veinlets and replacing plagioclase in this sample. Pyrite associated with similar low temperature alteration of submarine basalts has comparable low δ34S values, mostly ranging from -24 to +2‰ (Krouse et al., 1977; Hubberten, 1983; Belyi et al., 1983). The most likely explanation for such low δ34S values involves partial oxidation of igneous sulfides by seawater at low temperatures (<100°C; Andrews, 1979; Belyi et al., 1983). This produces sulfur species of intermediate oxidation state, which are unstable in solution and disproportionate into oxidized sulfide and reduced sulfide components. Fractionation of sulfur isotopes between the oxidized and reduced species (Uyama et al., 1985) leads to loss of 34S-rich sulfide to seawater, whereas 34S-depleted sulfide can form secondary pyrite with low δ34S values. Significant amounts of secondary pyrite were not observed in the thin section of the other sample with a low δ34S value for pyrite sulfur (Sample 118B-735B-39R-2, 30-34 cm, -11‰, Table 2). Instead, the rock appears mostly fresh with common igneous sulfides present, along with traces of secondary pyrrhotite and chalcopyrite in green amphibole and with talc and Mg-Fe-amphibole replacing olivine. Smectite occurs in this sample replacing olivine and in small veinlets. Although no pyrite was observed, it is possible that low-temperature pyrite is present in this sample, perhaps in a veinlet, but that it was not intersected by the thin section. This would account for the presence of a small amount of pyrite sulfur with a low δ34S value.

The three samples that have pyrite sulfur with δ34S values less than -2‰ also have low δ34S values for monosulfide sulfur (<-2‰; Fig. 2, Table 2). This suggests that in these samples there may be a component of late, low-temperature monosulfide (pyrrhotite or chalcopyrite) with low δ34S values that formed through processes similar to those giving rise to the late pyrite. Indeed, secondary chalcopyrite with low δ34S values occurs in seafloor basalts altered at low temperatures (Hubberten, 1983).

The isotopic compositions of sulfates extracted from Hole 735B samples are generally consistent with introduction of seawater during late, low-temperature alteration. The δ34S of
The mean $\delta^{34}$S of total sulfide sulfur for samples with both monosulfide and pyrite sulfur analyses is $-0.1 \pm 1.6$‰ and is not significantly different from the average for total sulfur. These average values are indistinguishable from the mean value for sulfur in MORB glasses ($+0.1 \pm 0.5$‰, Sakai et al., 1984) and indicate no significant net change in the isotopic composition of sulfur in Hole 735B from the presumed MORB mantle value, either as a result of magmatic processes or seawater interaction. Thus, although our results for Hole 735B indicate that layer 3 gabbros contain seawater-derived sulfur locally as soluble sulfate or fixed as sulfide, this $\delta^{34}$S-enrichment at Hole 735B appears to be offset by the formation of late, low-$\delta^{34}$S secondary pyrite at low temperatures.

Results from Hole 735B thus indicate that the ultimate effects of seawater interaction on sulfur in oceanic layer 3 are (1) loss of crustal sulfur to hydrothermal fluids and (2) little or no net change in isotopic composition of sulfur in layer 3.

**SUMMARY AND CONCLUSIONS**

Igneous sulfides in gabbroic rocks from Hole 735B comprise pyrrhotite, chalcopyrite, pentlandite, and trolite, and are generally typical of sulfides formed from mafic magmas. The sulfides occur interstitial to cumulate silicates and as inclusions in plagioclase and pyroxene, and formed by accumulation of immiscible sulfide droplets and crystallization from intercumulus liquids. Trends toward high Cu and Ni contents at low Fe contents are consistent with accumulation of sulfide and olivine in Units V and VI. Trolite formed as exsolutions from Fe-rich pyrrhotite (>48 atomic % Fe) as the rocks cooled to temperatures less than 140°C. Fe-rich pyrrhotite (+trolite) formed in rocks at lower sulfur, and perhaps oxygen fugacities than those that contain pyrrhotite only. The least altered rocks contain an average of 610 ppm S, and the mean sulfur $\delta^{34}$S value is near 0‰, similar to the isotopic composition of sulfur in MORB glasses ($+0.1 \pm 0.5$‰, Sakai et al., 1984) and indicate no significant net change in the isotopic composition of sulfur from the presumed MORB mantle value, either as a result of magmatic processes or seawater interaction. Thus, although our results for Hole 735B indicate that layer 3 gabbros contain seawater-derived sulfur locally as soluble sulfate or fixed as sulfide, this $\delta^{34}$S-enrichment at Hole 735B appears to be offset by the formation of late, low-$\delta^{34}$S secondary pyrite at low temperatures.

The mean $\delta^{34}$S of total sulfide sulfur for samples with both monosulfide and pyrite sulfur analyses is $-0.1 \pm 1.6$‰ and is not significantly different from the average for total sulfur. These average values are indistinguishable from the mean value for sulfur in MORB glasses ($+0.1 \pm 0.5$‰, Sakai et al., 1984) and indicate no significant net change in the isotopic composition of sulfur in Hole 735B from the presumed MORB mantle value, either as a result of magmatic processes or seawater interaction. Thus, although our results for Hole 735B indicate that layer 3 gabbros contain seawater-derived sulfur locally as soluble sulfate or fixed as sulfide, this $\delta^{34}$S-enrichment at Hole 735B appears to be offset by the formation of late, low-$\delta^{34}$S secondary pyrite at low temperatures.

Results from Hole 735B thus indicate that the ultimate effects of seawater interaction on sulfur in oceanic layer 3 are (1) loss of crustal sulfur to hydrothermal fluids and (2) little or no net change in isotopic composition of sulfur in layer 3.
is composed of variable proportions of seawater sulfate and oxidized basaltic sulfur.

The ultimate effect of secondary processes on layer 3 garnet is a loss of sulfur to hydrothermal fluids. This sulfur is likely redeposited as sulfide mineralizations within the crust or at the seafloor. Local $^{34}$S-enrichments attributed to the fixation of seawater sulfur in hydrothermally altered rocks and to incorporation of seawater sulfate in pore fluids or as traces of anhydrite appear to be offset by the formation of late, low-$^{34}$S secondary pyrite during low-temperature alteration. This results in little or no net effect of secondary processes on the average isotopic composition of total sulfur in the rocks (±0.4 ± 1.8%).

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