28. THE SULFUR CONTENT AND ISOTOPIC COMPOSITION IN BASALTS FROM HOLES 558, 559, 562, AND 564[1]

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ABSTRACT

The sulfur contents of 21 basalt samples from four DSDP Leg 82 holes were determined and the isotopic compositions of sulfur were measured on 15 of them. Most of the basalts are altered and have sulfur contents of about 100 ppm. Isotopic ratios for sulfate and total sulfur range from +0.7 to +10.5‰, indicating almost complete leaching of the igneous sulfide in low-sulfur samples by alteration.

Total sulfur content of some samples ranges between 960 and 1170 ppm, somewhat higher than expected for tholeiitic basalts. The isotope ratios of total sulfur in these samples are slightly shifted to values heavier than the generally assumed mantle ratio of zero, and this shift is thought to result from a secondary source of sulfur.

INTRODUCTION

Numerous investigations of the sulfur contents and sulfur isotopic compositions of ocean basalts have enlarged our understanding of the behavior of this element and its isotopes during the formation and alteration of ocean crust (Moore and Fabbi, 1971; Kanehira et al., 1973; Grinenko et al., 1975; Sakai et al., 1978; Puchelt and Hubberten, 1980; Hubberten and Puchelt, 1980; Sakai et al., 1982; Hubberten, 1983a; Hubberten, 1983b).

Basalt melts commonly erupt in a sulfur-saturated or nearly saturated stage (Mathez, 1976); the degassing of sulfur is inhibited by water pressure at depths exceeding 500 m (Moore and Fabbi, 1971; Sakai et al., 1982). The concentration of primary sulfur in rocks formed from such a melt varies between 800 and 1700 ppm, depending mainly on the iron content of the melt (Mathez, 1976; Czamanske and Moore, 1977; Erzinger, 1981; Hubberten, 1983b). This sulfur should reflect the isotopic composition of the mantle; that is, it should display $\delta^{34}S$ values around zero (Kanehira et al., 1973; Puchelt and Hubberten, 1980). Deviations from the zero value in the isotopic composition of the primary sulfur have been observed by Schneider (1970) for terrestrial basalts with different degrees of fractionation. Similar observations have not so far been made for ocean tholeiites. Several investigators have described a rather strong variation in the isotopic composition of sulfur in altered basalts, caused by interaction with cold seawater or hydrothermal solutions (Field et al., 1976; Krouse et al., 1977; Hubberten, 1983a; Alt et al., 1983).

The rocks retrieved during DSDP Leg 82 southwest of the Azores Platform in the central Atlantic are mostly aphyric to plagioclase-phyric pillow basalts showing a wide compositional variability (Sachtleben and Schmincke, 1982; Puchelt, this volume). Our study is based on 21 samples from four of the holes (558, 559, 562, 564) cored during Leg 82. With respect to chemical and petrographic parameters, almost all samples were altered in greater or lesser degree, and did not allow determination of the isotopic composition of primary sulfur (cf. Puchelt, this volume). The amount of sample in most cases was too small to determine the three possible sulfur phases (total S, sulfide-S, sulfate-S). The samples used for these investigations are all dense plagioclase-phyric or aphyric fine-grained basalts. Neither basalt glass nor serpentinite (Hole 558) was available for these analyses.

ANALYTICAL PROCEDURE

The samples were cleaned with distilled water, crushed, and pulverized (<200 mesh) for analysis. The total sulfur content was determined by combustion in oxygen, using the Leybold Heraeus Carbon Sulphur Analyzer 302. The total error of the determinations is less than ±15%. Sulfur-isotope determinations were made according to the method described by Puchelt and Hubberten (1980). In this procedure the igneous sulfides are first decomposed by treatment with hydrochloric acid, yielding the sulfide-S fraction. In a second step, the remaining S in the sample (sulfate-S fraction) is extracted with a reducing-acid mixture (Thode et al., 1961). Another split of the sample is directly decomposed with the reducing-acid mixture to obtain the total sulfur concentration. In each step, the sulfur is expelled as H_2S, which is then precipitated as CdS. This compound is oxidized to form the measuring gas SO_2 for mass spectrometry (cf. Ricke, 1964). Isotope ratios were measured on a VG-Micromass 1202 S mass spectrometer. The total error (preparation and measurement) of these determinations is less than ±0.2‰ for samples of normal size, but it can reach ±1‰ for undersized samples. The results are given in the usual δ-notation with respect to the Cañon Diablo standard.

RESULTS AND DISCUSSION

Sulfur Content

As can be seen from Table 1 and Figure 1, most of the samples have total sulfur contents close to 100 ppm; seven others range between 960 and 1170 ppm. The lower sulfur concentrations may result from two main processes: (1) relative to the rim, the interior of the pillow is depleted in sulfur, which may have escaped along cool-

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Table 1. Sulfur content and sulfur-isotope ratios for Leg 82 basalts.

Karlsruhe lab. number	Sample (interval in cm)	S-content (ppm)	$\delta^{34}S$ (‰)		
			Total sulfur	Sulfide-S	Sulfate-S
086 01	558-27-3, 46–48	100	+ 3.1		
086 02	558-28-2, 6–8	100			
086 03	558-29-2, 6–8	1020	+ 2.6		+ 6.3
086 04	558-34-1, 113–115	100			
086 05	558-36-3, 44–46	160	+ 7.6		
086 06	559-1-1, 134–136	100			
086 07	559-1-4, 40–42	1000	+ 0.7		
086 08	559-6-2, 17–20	100			
086 09	559-7-1, 143–146	100	+ 8.7		
086 10	559-7-3, 15–17	100	+ 7.4		
086 11	562-2-5, 65–67	1090	+ 3.0		+ 7.8
086 12	562-4-2, 4–7	1160	+ 2.4	+ 1.6	
086 13	562-7-2, 7–10	120	+ 9.1		
086 14	562-8-1, 127–129	140	+ 9.5		
086 15	564-H1,CC (11)	120	+ 8.6		
086 16	564-1-1, 122–124	100	+ 7.4		
086 17	564-2-3, 110–114	150	+ 9.5		
086 18	564-5-2, 111–114	960			
086 19	564-7-2, 136–138	1170	+ 3.2		+ 7.1
086 20	564-9-1, 72–74	100	+ 10.5		
086 21	564-9-3, 76–79	1010			

Note: Blanks indicate that samples were too altered for determination of $\delta^{34}S$ and/or that the samples were too small for determining the three sulfur phases.

Figure 1. Total sulfur contents and isotope ratios of total sulfur, sulfide-sulfur, and sulfate-sulfur for DSDP Leg 82 basalt samples.

Figure 2. Total sulfur content versus K_2O content for Leg 82 basalts.
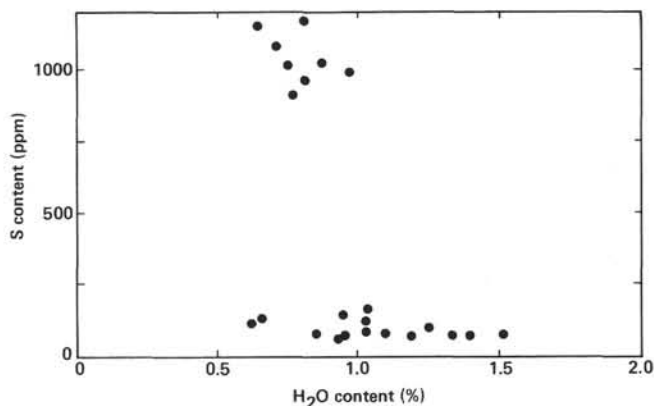
Figure 3. Total sulfur content versus H_2O content for Leg 82 basalts.

ing fractures (Moore and Fabbi, 1971; Hubberten, 1983b); or (2) during the low-temperature oxidative alteration of basalts, the igneous sulfides may have been completely oxidized to SO_4^{2-}, which would probably have been removed from the rock (cf. Andrews, 1979). Because the depletion of sulfur in most samples is too high, the first process seems to be less important. In addition, chemical evidence favors the second process. Alteration-sensitive components such as K, Tl, and the water content show a clear relation to the sulfur content (cf. Hubberten, 1983a). Higher concentrations of these components are mostly correlated with low sulfur contents (Figs. 2 and 3).
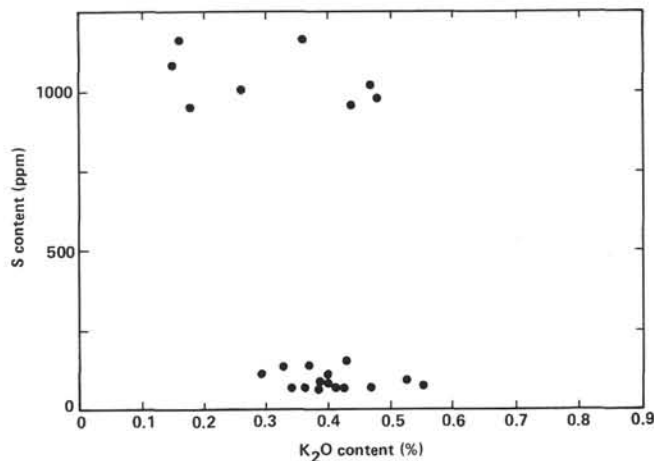
From these arguments it seems evident that the strong decrease in the sulfur content resulted from oxidative alteration of the igneous sulfides. Variations occurring because of sample locations at different distances from the pillow rim are overprinted by the larger effect of alteration. The relatively low iron contents of the investigated samples suggest, however, that sulfur was added during alteration or from a hydrothermal source. The rather high K_2O and H_2O contents of these samples classify them as altered and support this suggestion (Figs. 2 and 3).

Sulfur Isotopes

The isotope values of the total sulfur in the investigated basalts are obviously split into two groups (see Fig. 1 and Table 1). In one group $\delta^{34}S$ (total sulfur) ranges between + 7.4 and + 10.5‰, and this corresponds to samples with low sulfur content. In the other group, $\delta^{34}S$ is closer to zero (+ 0.7 to + 3.2‰), and this group includes (with one exception: our sample no. 086 01) only samples with higher sulfur content.

According to numerous investigators, the isotopic composition of primary mantle sulfur is assumed to be close

to the meteoritic value, that is, the zero point of the δ-scale (Kanehira et al., 1973; Grinenko et al., 1975; Sakai et al., 1978; Puchelt and Hubberten, 1980; Hubberten and Puchelt, 1980; Sakai et al., 1982; Hubberten, 1983a; Hubberten, 1983b). Most published investigations of sulfur isotopes in ocean basalts have demonstrated, until now, only small variations around this zero value (-0.5 to $+1.5‰$). Neither systematic variations related to the degree of fractionation of a rock nor an isotopic inhomogeneity of sulfur in the upper mantle could be detected. It is therefore assumed that the large deviations from zero determined in the Leg 82 basalts do not reflect variations in the primary isotopic composition, but probably result from secondary processes during alteration of the rocks.

During low-temperature alteration of basalts by seawater, the igneous sulfides are dissolved (Andrews, 1979), and the resulting SO_4^{2-} will be removed from the rock. Sulfur occurs in ocean tholeiites mainly as sulfides (pyrrhotite, chalcopyrite, and other sulfides of the Fe–Cu–(Ni)–S system), but variable amounts of primary sulfate have been mentioned (Ricke, 1960; Schneider, 1970; Sakai et al., 1978; Puchelt and Hubberten, 1980; Sakai et al., 1982). The results of the last two groups of authors showed that between 5 and 35% of the total sulfur in basalts may exist in the form of sulfate. With isotopic equilibrium between sulfide and sulfate in a basalt melt, the sulfate form of sulfur is always enriched in the heavier isotope ^{34}S (Sakai, 1968). Sakai et al. (1982) demonstrated in their investigation of basalts from Kilauea Volcano, Hawaii, that the sulfate in these rocks is 7.5 ± 1.5‰ heavier than the coexisting sulfide. Assuming a δ^{34}S value of zero for the sulfide sulfur in the Leg 82 basalts, and a fractionation between sulfide and sulfate similar to that observed by Sakai et al. (1982), the sulfate values for our samples should range between $+6$ and $+9‰$, which coincides rather well with the range of δ^{34}S (total sulfur) ($+7.4$ to $10.5‰$) determined for the samples having low sulfur contents. (One of the low sulfur samples, however, plots slightly outside this range [$+3.1‰$].) If the unaltered sulfur content of the Leg 82 basalts ranges around 800 ppm as a typical value for rocks of this composition (cf. Moore and Fabbi, 1971; Hubberten, 1983b), a sulfate fraction of somewhat more or less than 10‰ could be reflected in the total sulfur content of the low-sulfur samples (from less than 100 to 160 ppm S). From this we assume that the determined δ^{34}S values of the total sulfur represent the isotopic composition of the primary sulfate not leached during alteration of the rocks. The three determined isotope ratios for sulfate-S fit perfectly in this range, and thus support our assumption. The slight shift toward heavier total-sulfur δ^{34}S values ($+9.1$ to $+10.5‰$) of four low-sulfur samples was probably caused by the addition of small amounts of seawater-derived sulfate (δ^{34}S $= +20‰$) or by a somewhat lower solidification temperature of these basalts.

Only one of the high-sulfur samples shows a total-sulfur δ^{34}S value ($+0.7‰$) similar to the assumed mantle value. This sample represents the freshest basalt of this study. The others are enriched in ^{34}S to various degrees, and attain values of up to $+3.2‰$. If we considered these values to be the typical isotopic compositions of sulfur in unaltered basalts in the area, we should attribute them either to a slightly ^{34}S-enriched mantle source in this region of the Atlantic or to minor isotopic fractionation during the evolution of these rocks. But except for the one sample with a normal sulfur-isotope ratio, all the high-sulfur samples are altered, so we have to consider the effects of a possible secondary sulfur source. During alteration under oxic conditions, the primary sulfides are normally dissolved and the sulfate-S is removed from the system (see foregoing discussion). An addition of sulfur, as observed in the high-sulfur samples, may be caused by hydrothermal solutions precipitating epigenetic pyrite or by addition of seawater-derived sulfate (δ^{34}S $= +20‰$). Because of the relatively minor enrichment of ^{34}S in the high-sulfur basalts, we assume that these samples have been altered by hydrothermal solutions, which normally are slightly enriched in ^{34}S when compared to primary magmatic sulfur ($~0‰$, Hubberten, 1983b). The addition of seawater sulfate would result in a higher enrichment of ^{34}S in the Leg 82 samples.

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