

The Sulfur Isotope Composition of Basaltic Rocks

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Abstract. The sulfur isotope composition of tholeiitic basalts, olivine alkali basalts and alkali-rich undersaturated basalts were investigated. A method of preparation was devised

(a) for the extraction of the small amounts of sulfur contained in the rock samples (about 100 ppm S),

(b) for the separation of sulfide- and sulfate-sulfur.

Tholeiitic and olivine alkali basalts show a predominance of sulfide-sulfur. Alkali-rich undersaturated basalts show sulfide- and sulfate-sulfur.

The oxidation potential of the magma is reflected in the proportions of sulfide- and sulfate-sulfur. Differences in the conditions of oxidation are also the cause of the sulfur isotope fractionation observed. The mean in the isotope composition of the sulfur in the olivine alkali basalts (with the exception of two samples which show extreme deviation) is $\delta^{34}\text{S} = +1.3$ per mil. The values for the olivine alkali basalts are concentrated around this mean in a remarkable way, showing only small deviation for the individual samples. When the tholeiitic basalts deviate from this mean, it is only with a relative enrichment in the ^{32}S isotope. With a pronounced variation of the individual values, the mean for the sulfide-sulfur is $\delta^{34}\text{S} = -0.3$ per mil. The few sulfate values of both types of basalt are without significance for the discussion of their origin. However, this does not apply to the alkali-rich undersaturated basalts. Due to the higher water content, this basaltic magma had a higher oxygen partial pressure which favoured the formation of SO_2 and SO_4^{2-} besides H_2S while pressure was released during the ascent of the magma. The sulfur isotope fractionation connected with this oxidation led to a total enrichment of ^{34}S in the rock, ($\delta^{34}\text{S}$ for total sulfur: $+3.1$ per mil) with particular favouring the sulfate ($\delta^{34}\text{S} = +4.2$ per mil).

It is accepted that the sulfur of all three types of basalts derives directly from the mantle. The olivine alkali basalts show the least deviation from the mantle value, which, in the place of origin of the basalts from the region investigated, would probably have been $\delta^{34}\text{S} = +1.3 (\pm 0.5)$ per mil. From this it may be concluded that the olivine alkali basalts — the most frequent type of basalt in this region — had their origin in the partial melting of the mantle without further differentiation. From the sulfur isotope data we concluded that the primary isotope composition of the continental tholeiitic basalts probably corresponds to that of the olivine-alkali basalts, and to that of the mantle. However, due to degassing in the layers near to the surface, some samples lost ^{34}S , which may be related to the formation of SO_2 during the release of pressure. There is no positive indication of a differentiation in shallow depths (< 15 km — in the sense of Green and Ringwood, 1967).

The reason for the obvious isotopic fractionation of the alkali-rich undersaturated basalts may be seen in their higher primary water content. This is a pronounced indication of the origin of this type of magma. Bultitude and Green (1968) proved by experiment, that the formation of alkali-rich undersaturated basaltic magma is possible in the mantle in the presence of water. Only a small amount of water is available for the formation of magma in the mantle. With a water content higher than normal for basalts, only small amounts of magma can be formed, but at lower temperatures this would allow the melting of a larger fraction of mantle material. By reaction with the wall rock, these magmas could be enriched in those components of mantle minerals which have the lowest melting point. This may help to explain their geochemical characteristics.

Contents

1.	Introduction	96
1.1.	Sample Selection	96
2.	Preparation of Sulfur for Isotope Analysis	99
2.1.	Extraction of Total Sulfur	101
2.2.	Extraction of Sulfide-Sulfur	101
2.3.	Extraction of Sulfate-Sulfur	102
2.4.	Preparation of SO ₂ from Cadmium Sulfide	102
2.5.	Mass-Spectrometric Measurements	102
2.6.	Discussion of Errors	102
3.	Results	103
3.1.	Sulfur Concentration	103
3.2.	Results of Isotope Analysis	104
3.2.1.	Tholeiitic Basalts	105
3.2.2.	Olivine Alkali Basalts	106
3.2.3.	Alkali-Rich Undersaturated Basalts	106
4.	Discussion of Results	107
4.1.	Basis of Sulfur Isotope Geochemistry of Igneous Rocks	107
4.2.	Oxidation Conditions in Gases and Magmas of Basaltic Rocks	108
4.3.	Origin of Measured Sulfur Isotope Composition of Basalts	113
4.3.1.	Tholeiitic Basalts	113
4.3.2.	Olivine Alkali Basalts	114
4.3.3.	Alkali-rich Undersaturated Basalts	117
5.	Discussion of the Results in Relation to Experimental Investigations on the Genesis of Basalts	118

1. Introduction

Basalts of the Tertiary volcanism in North Hessa and Southern Lower Saxony have been investigated from various aspects in the Geochemical Institute of the University of Göttingen (petrography and geochemistry: Wedepohl, 1950, 1954, 1961, 1963, 1968a, 1968b and in preparation; geochemistry of rare earths: Herrmann, 1968; composition of strontium isotopes: Hoefs and Wedepohl, 1968; geochemistry of magnetites: Gramse, in preparation; geochemistry of pyroxenes: Gramse, in preparation.) The analysis of the sulfur isotopes of the same rocks will be presented here. Sulfur was obtained from total rock samples without special separation or enrichment of mineral phases. Sulfide- and sulfate-sulfur were analysed separately. The results will be compared with the composition of sulfur isotopes in meteorites. The differences between basaltic rocks of varying composition will be discussed and conclusions drawn from the data about the nature of the genesis of basalts.

1.1. Sample Selection

The basaltic rocks of North Hessa and Southern Lower Saxony are outstanding because of the broad scale of their composition. Tholeiitic basalts, olivine alkali basalts, nepheline basanites, and olivine nephelinites occur in this region which measures 150 km north-south and 30 km east-west. Based on their mass and abundance and frequency, olivine alkali basalts (up to 5% nepheline in the norm) are predominant in comparison to alkali-rich undersaturated basalts and tholeiitic basalts. The tholeiitic basalts are oversaturated in SiO₂ according to Yoder and Tilley (1962). They contain quartz in the norm. More

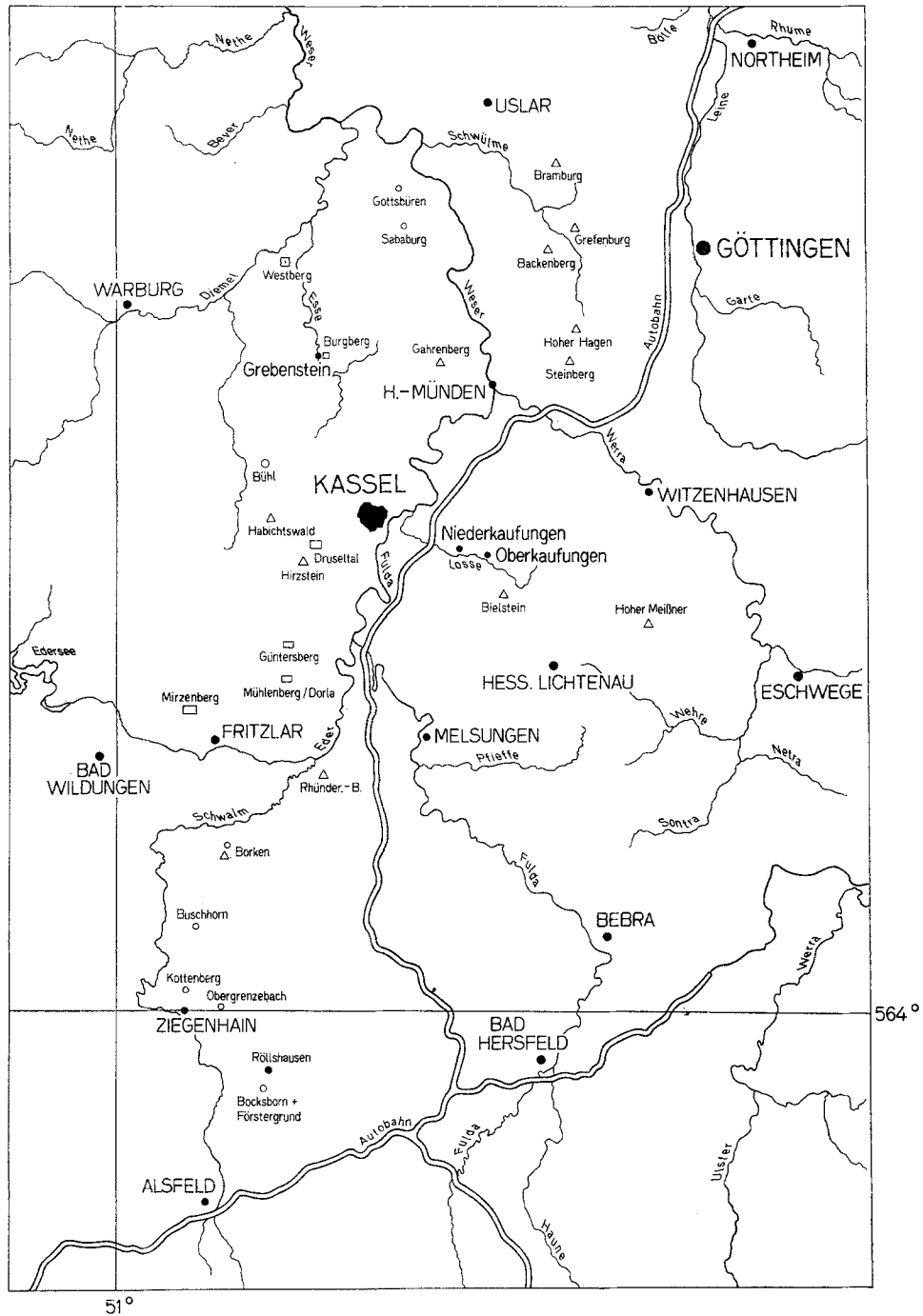


Fig. 1. Map of North Hessian and Southern Lower Saxon with the occurrences of the various basalts. ○ tholeiitic basalts, Δ olivine alkali basalts, □ alkali-rich undersaturated basalts

Table 1a. *Basalts from North Hessa and Southern Lower Saxony*

Sample number	Locality	$\delta^{34}\text{S}$ (per mil)		
		total-S	sulfide-S	sulfate-S
<i>(a) Peridotite nodule</i>				
3907	Hirzstein near Elgershausen	+ 3.4 ^c		
<i>(b) Tholeiitic basalts</i>				
1416	road from Gottsbüren to Gieselwerder	- 0.3 ^a		
1485	road from Sababurg to Gottsbüren	+ 1.0	+ 1.0	+ 1.1
3931	Kottenberg near Ziegenhain	- 0.7	- 0.6	- 0.6
3994	1.5 km W. of Obergrenzebach, near the road to Niedergrenzebach	- 3.0	- 3.0	
3992	quarry at the end of the Förstergrund near Röllshausen	- 0.6	- 0.5	- 0.4
3993	quarry at the Bocksborn, W. of Röllshausen	- 2.1	- 2.1	
3903	Borken, Southern Blumenhain, 80 m S. of the Söhreweg	+ 1.4 ^d		
3934	Southern part of the Buschhorn near Ziegenhain	+ 0.8	+ 0.5	
3916	Bühl near Weimar, area of Kassel	+ 1.1	+ 0.7	
<i>(c) Olivine alkali basalts</i>				
3653	Lower Bramburg, sample I, near Hardeggen	+ 0.5	0.0	+ 0.2 ^b
3653	Lower Bramburg, sample II (1969), near Hardeggen	+ 3.5	+ 3.1	
3651	Grefenburg near Barterode, sample I	+ 8.6 ^b		
3651	Grefenburg near Barterode, sample II (1969)	+ 7.7 ^b		
3655	Backenberg near Güntersen	+ 1.5	+ 1.1	+ 2.6
3661	Hoher Hagen near Dransfeld	+ 1.4		
3666	Steinberg near Meensen	—	—	—
3911	quarry "Menke", Ahnatal, Habichtswald near Kassel	+ 1.5	+ 1.7	
3906	Hirzstein near Elgershausen, W. of Kassel	+ 5.8 ^b	+ 4.1 ^b	+ 8.4 ^b
3921	Bilstein near Helsa, upper lava flow	+ 0.9	+ 1.7	
3922	Bilstein near Helsa, lower lava flow	+ 0.9	+ 1.3	
3847	Hoher Meißner, "Kalbe"	+ 1.7	+ 1.2	
3981	Rhünder Berg, quarry S. of the Rhünder Bach near Rhünda	+ 1.8	+ 1.3	
3904	Borken, Northern part of the Blumenhain	+ 1.4	+ 1.0	
1486	Gahrenberg in the Reinhardswald	+ 5.2 ^b	+ 4.5 ^b	
<i>(d) Nepheline basanite</i>				
3901	Druseltal near Kassel, quarry "Kuhberg"	+ 3.2	+ 1.8	+ 4.4

Table 1 a. (continued)

Sample number	Locality	$\delta^{34}\text{S}$ (per mil)		
		total-S	sulfide-S	sulfate-S
<i>(e) Melilite-bearing olivine nephelinites</i>				
3952	Westberg near Hofgeismar (southern quarry)	+2.4	-0.5	+3.1
3961	Burgberg near Grebenstein	+3.3	+1.8	+5.0
<i>(f) Olivine nephelinites (melilite-free)</i>				
3996	Güntersberg near Gudensberg quarry of the Melato Co.	+2.6	+1.1	+5.3
3986	Mirzenberg near Fritzlar,	+2.0	+1.4	+2.5
3991	Mühlenberg near Dorla	+4.5	+2.4	+6.2
Rocks of the Vesuvius (Italy)				
<i>(g) Tephritic leucitite</i>				
13353	Vesuvius, lava flow from 1944	+2.2	+1.8	+3.1
<i>(h) Phonolitic tephrite</i>				
13354	Vesuvius, Somma (original material, sample no. SV 13, C. Savelli, 1967)	+4.2		+4.2

^a See text.

^b These samples were not taken into account for the calculation of the mean (see text).

^c The sample contained a minimal amount of sulfur. It can be supposed that this sulfur is present in the form of sulfides.

^d Although the sample contains very little sulfur, its value was taken into account for the calculation of the mean.

specific data on the extrusive rocks of this region may be found in the papers already mentioned. The investigated occurrences are presented in Fig. 1, and the investigated samples in Table 1 a. With this selection of samples the Tertiary volcanism of this area and the types of rocks which occur are adequately represented.

In addition to these samples hauyne-bearing rocks and nosean-bearing rocks from the volcanism of the Eifel region (Western Federal Republic of Germany), and samples from the Kaiserstuhl near Freiburg and from Vesuvius (Italy), (Table 1 b) were investigated.

2. Preparation of Sulfur for Isotope Analysis

Sulfur is present in basaltic rocks as S^{2-} (in sulfides) and S^{6+} (in sulfate). A method of preparation was worked out, enabling the two to be separated. In individual steps of preparation, use could be made of the experience of the „Zentrallaboratorium für die Geochemie der stabilen Isotope“, (Ricke, 1964). The sulfides to be expected in basalts are, according to Newhouse (1936) and Ramdohr (1940), pyrrhotite and chalcopyrite. The occurrence of pyrite is extremely rare. It is not to be expected because pyrite melts incongruently at 742°C , forming pyrrhotite and sulfur vapor. Desborough, Anderson and Wright (1968) investigated sulfides in various basaltic lavas from Hawaii. They defined two main phases, which were analysed by means of a microprobe:

pyrrhotite with small amounts of nickel and

a copper-iron sulfide which in its chemical composition resembles cubanite (CuFe_2S_3).

Table 1 b. *Alkali-rich undersaturated rocks from the Eifel, Western Germany*

Type of rock	Sample no.	Locality	$\delta^{34}\text{S}$ (per mil)	
			total-S	sulf- ide-S
Sanidinite ejecta (with nosean)	2331/1	Laacher-See, Eifel	+ 5.6	+ 6.2
Sanidinite ejecta (with nosean)	2331/2	Laacher-See, Eifel	+ 6.1	+ 5.8
Nosean (picked out of sanidinite ejecta)	2331/3	Laacher-See, Eifel		+ 5.7
“Leucitophyre”	2393	Rieden, Eifel	+ 4.1	+ 4.3
Nosean phonolite	2351	Kempenich, Eifel	+ 3.8	+ 3.4
Nosean phonolite	2382	ruin of Castle Olbrück, near Oberzissen, Eifel	+ 3.6	+ 3.8
Nosean phonolite	2372	Schellkopf near Brenz, Eifel (1958)	+ 3.0	+ 3.6
Nosean phonolite	2371	Schellkopf near Brenz, Eifel (1955)	+ 4.0	+ 3.5
Sanidinite ejecta (with haüyne)	2333/1	between Laach and Kruft, Eifel	+ 4.1	+ 4.7
Haüyne (picked out of sanidinite ejecta)	2332/1	Laacher-See, Eifel	+ 4.9	+ 5.9
Haüyne (picked out of sanidinite ejecta)	2332/2	Laacher-See, Eifel	+ 4.7	+ 4.6
Haüyne (picked out of leucite nepheline tephrite)	2342	Niedermendig, Eifel	+ 4.8	+ 4.9
Leucite nepheline tephrite (with haüyne)	2341	Niedermendig, Eifel	+ 3.3	+ 3.7
		Average	+ 4.4	+ 4.7
(Samples from the Kaiserstuhl, Breisgau, Western Germany)				
Phonolite (with haüyne)	4521/1	Kirchberg near Nieder- rottweil, Kaiserstuhl	+ 5.9	+ 5.6
Tinguaite (from a dike in eruptive breccia)	4506/1	“Meisensalz”, Kaiserstuhl	- 1.6	- 1.4

The samples listed in Table 1 b contain, without exception, several times more sulfur than the basalts in Table 1 a. The greatest proportion is present in sulfate bearing phenocrysts. Some of the samples of Table 1 b were investigated for sulfide-sulfur, but none was found.

Pyrite and bornite were not detected. The investigated sulfides are associated with titanium-free magnetite. The authors concluded, therefore, that they must have crystallized from sulfide melt droplets because of the immiscibility between sulfide and silicate melt. The composition of these sulfides agrees with the data derived from experiments in the system Cu—Fe—S—O when the oxygen fugacity and the cooling history of basaltic magmas are taken into account. In the investigated samples the sulfide droplets were formed during the incipient crystallization of the magma. They were partially included in the silicate phases which were the first to crystallize.

The presence of sulfate ions may be expected in different phases of basalts provided that the oxygen fugacity of the magma makes possible their existence:

(a) Sulfate minerals such as baryte and anhydrite from basalts have never yet been described, although sulfate-containing silicates such as nosean and haüyne appear in several rocks. However, it cannot be excluded that these minerals occur in exceedingly small quantities and submicroscopic size near grain boundaries and cracks in rocks, where they cannot be detected by means of a microscope.

(b) SiO_4^{2-} and PO_4^{3-} may be substituted by SO_4^{2-} . Accordingly, sulfate-sulfur is to be expected within the crystal lattice of silicates and apatite (Schneider, 1968).

(c) It is very difficult, however, to calculate the quantity of the sulfate groups mentioned above since sulfate ions may also be found in fluid inclusions (Ricke, 1960).

The manner in which sulfide- and sulfate-sulfur occur is very important for the separation and preparation of samples.

2.1. Extraction of Total Sulfur

For the extraction of the total sulfur from the basalts the "Thode-solution" (816 ml HCl, conc. + 245 ml H_3PO_2 + 500 ml HJ, $d = 1.7$) is a suitable solvent and reduction reagent, attacking sulfate as well as sulfides. Since part of the sulfate-sulfur probably occurs in small fluid inclusions and since grain size of the sulfides may be very small, it is necessary to thoroughly disintegrate the rock samples. After mechanical grinding, the "Thode-solution" proved sufficiently effective to ensure the quantitative extraction of rock sulfur, within a period of approximately 15 hours. It was observed that after three hours of extraction the yield of total sulfur was 70% of the amount present. After a further six hours the yield of sulfur was still exceedingly small, although the process continued for a further nine hours. This may be easily explained. In the first stage, only those sulfur compounds react which are released by mechanical grinding — sulfates from large fluid inclusions and sulfides. In the second stage, sulfur is released during the chemical disintegration of the silicates. This sulfur is derived from two sources, the first being sulfate groups in the lattice of the silicates and the second being very small fluid inclusions and sulfide inclusions, the size of which is usually much smaller than the normal grain size of the ground material. The breaking down of silicates determines the speed of sulfur extraction. As far as we can judge this step is in no way connected with fractionation of the sulfur isotopes. In this way, it is possible to shorten the disintegration time to six hours although this means losing a small amount of the sulfur. After a positive preliminary experiment for the preparation of total sulfur, 25 g of each basalt sample were disintegrated with 100 ml "Thode-solution" for at least six hours at approximately 80° C. The H_2S which formed was precipitated as CdS. For most samples it was necessary to repeat this procedure several times with fresh material before a sufficient amount of sulfur was obtained.

2.2. Extraction of Sulfide-Sulfur

Until now, sulfides have been disintegrated with hydrochloric acid in the presence of tin in granule form according to the method described by Ricke (1964). It is impossible to use tin with basalts because the dissolving sulfates are reduced with considerable fractionation. This alters the true proportion of both sulfide- and sulfate-sulfur isotopes. Tin was, therefore, replaced by aluminium which does not have this effect. However, the solution disintegrates the silicates only very slowly which means that a long reaction period is necessary for the extraction of the sulfide-sulfur. A quantitative extraction is not absolutely necessary

in this case either. The larger amount of sulfide present reacts in the first three hours of disintegration, although the rest, approximately 30%, demands a further 10 to 15 hours. Isotope fractionation was not observed in the individual stages of disintegration. This is not to be expected, since the sulfides only begin to react as disintegration of the sulfides bearing silicates progresses, and there is no appreciable difference in the isotope composition between individual sulfide grains occurring in the basalt. Therefore, for the preparation of sulfide-sulfur, aliquotes (25 g) of finely ground basalt were disintegrated for 6–8 hours with 100 ml hydrochloric acid in the presence of 5 g of metallic aluminium at a temperature of 80° C. The resulting H₂S was precipitated as CdS. For mass-spectrometric analysis, at least 2 mg of sulfur are required. In order to obtain this amount up to 200 g of basalt must be disintegrated.

2.3. Extraction of Sulfate-Sulfur

A part of the sulfate-sulfur of basaltic rocks is soluble in water. If a basalt is ground for approximately 2 hours in water, then the sulfate which has dissolved may be precipitated with barium ions. However, tests showed that even after 12 hours of grinding, sulfate was still being leached. Results are unsatisfactory, because of the insufficient yield.

It is less difficult to obtain sulfate-sulfur by the method for the preparation of total sulfur from those samples already freed of sulfide-sulfur. The disintegration of the sulfides was interrupted before completion of the reaction and the residue was dried at a temperature of about 150° C. In this way the disintegration process of the silicates and sulfides is completed. A further process of disintegration with hydrochloric acid and aluminium showed no reaction for sulfide. Sulfates are still present in this residue. They are extracted with "Thode-solution" in the way described for the extraction of total sulfur and are now also present as CdS for the next stage of the experiment.

2.4. Preparation of SO₂ from Cadmium Sulfide

Total sulfur, sulfide-sulfur and sulfate-sulfur are obtained as cadmium sulfide in the course of preparation; further processes are the same in the case of all samples. CdS, purified by heating in vacuum, is mixed with V₂O₅ and poured into a silica test tube. Test tubes containing samples are then evacuated for 12 hours at approximately 150° C, in order to remove air and water vapour. After being sealed, the test tubes are heated to 1,000° C. At this temperature, vanadium pentoxide releases sufficient oxygen to oxidize the sulfide. SO₂ is formed — the gas necessary for the mass-spectrometric determinations of the isotope composition of the sulfur. This stage of preparation has been described by Rieke (1964), it has been slightly modified.

2.5. Mass-Spectrometric Measurements

The mass-spectrometric measurements were carried out using an ATLAS CH 4 mass spectrometer with a viscose inlet system. Samples were measured against a galena reference sample whose $\delta^{34}\text{S}$ value is -0.23 ± 0.05 per mil when compared with the isotope composition of sulfur from the Canon Diablo troilite as a standard. Each measurement was repeated ten times and the necessary corrections were calculated with a FORTRAN IV program. The methods of measuring and correction are described in more detail by Nielsen (1968).

2.6. Discussion of Errors

With a pressure of 100 torr SO₂ in the inlet system of 100 ml capacity, the statistical error is ± 0.02 per mil (in $\delta^{34}\text{S}$) (Nielsen, personal communication). The sulfur concentration of basalts was frequently so low, that we were obliged to work with correspondingly smaller storage volumes. For the same reason, the conditions under which the measurements were made also varied for individual samples. Both processes increase the possible error. Since the errors resulting from the preparation process were also significant, all samples were prepared in duplicate. Comparison of the results of measurements of sulfide-sulfur, sulfate-sulfur and total sulfur and the extent to which the duplicate measurements agreed, showed

that the total error in preparation and measurement rarely exceeded ± 0.5 per mil (in $\delta^{34}\text{S}$). The errors become smaller with an increasing sulfur content of the samples. Causes of error are:

- (a) contamination due to sulfur from the reagents,
- (b) possible neglect of one phase when the disintegration was incomplete,
- (c) contamination of the sulfate-sulfur by sulfide-sulfur,
- (d) fractionations when the preparations are incomplete.

The errors due to causes (b) to (d) may be reduced by lengthening the time of reaction. This has a pronounced effect on the amount of contaminating gases in the sample. If the cadmium sulfide precipitate remains in contact for too long a time with the cadmium formate solution, it will then be contaminated by carbon in the form of an unknown compound which cannot be removed by washing, heating or evacuation during the further course of preparation. One has to avoid reprecipitation in order to exclude a further source of error. In these cases, the prepared SO_2 contained disturbing quantities of CO_2 . Causes of error (b) to (d) only effect the results if the individual phases of sulfur have different isotopic composition, or if fractionation during preparation occurs in the case of homogeneous isotope distribution. The size of the error depends on the quantitative relations between sulfide- and sulfate-sulfur. The more similar the isotope composition of the two sulfur compounds and the more sulfate-sulfur present, the less the sulfate-sulfur isotope composition is influenced by the small quantities of sulfide still present during the disintegration of the sulfates. When both sulfide-sulfur and sulfate-sulfur are present in the same sample, the isotope composition of the total sulfur must fall between the values of sulfide- and sulfate-sulfur. The difference in the isotopic composition between total sulfur and either sulfate-sulfur or sulfide-sulfur depends on the quantitative proportions of sulfate and sulfide in the sample. This relationship was observed in all samples. Samples originating in the weathering zone may be contaminated by sulfur-bearing weathering products. This is the case, for instance, in the sample 1416 (tholeiitic basalt from an outcrop near the road from Gottsbüren to Gieselwerder). This sample had already been influenced by weathering. According to Gramse (personal communication) the magnetites of this sample show distinct disintegration. With a $\delta^{34}\text{S} = -5.3$ per mil for total sulfur and -12.8 per mil for sulfate-sulfur, this sample has the lightest sulfur of all the basalts investigated. These values are to be evaluated in connection with the soil formation above the basalt. However, if the sample is ground for two hours in water, the sulfates present at the surface dissolve. Possibly they are of secondary origin. The remaining total sulfur of the basalt, purified in this manner, has a $\delta^{34}\text{S} = -0.3$ per mil, and therefore coincides with the mean of the tholeiitic basalts. Obviously only a few sulfides of this basalt remain uninfluenced by weathering, particularly those which are present in unweathered silicates. These are only attacked by chemical decomposition. They are the most significant representatives of the primary sulfur compounds of the rock.

Table 2. *The preparation of total sulfur from basalts by decomposition with "Thode-solution"*

The influence of decomposition period on the isotope composition

Sample: Tholeiitic basalt from Kottenberg near Ziegenhain.

Time of reaction	$\delta^{34}\text{S}$ (per mil)
6 hours	-0.7
6 hours	-0.5
6 hours	-0.7
8 hours	-0.9
12 hours	-0.5

The deviations from the mean lie within the error of preparation and measurement.

3. Results

3.1. Sulfur Concentration

An exact quantitative analysis of the sulfide- and sulfate-sulfur content of the samples was not carried out. The relationship between the amount of the decomposed sample substance

and the CdS obtained makes a semi-quantitative estimation possible. Accordingly, the total sulfur concentration varies considerably in all types of basalt. While the tholeiitic basalts of Sababurg, Bocksborn and Kottenberg contain relatively large amounts of total sulfur, those of Buschhorn and of the Blumenhain near Borken contain very little (< 100 ppm). Five samples of the Recent tholeiitic volcanism from Hawaii could not be measured because their sulfur concentration of < 50 ppm was too low.

Even in the case of olivine alkali basalts the sulfur concentration is not uniform. The basalt from Steinberg near Meensen has far less than 50 ppm of total sulfur, while the basalt of Hirzstein contains at least 200 ppm S. The same observations are obtained in the case of the alkali-rich undersaturated basalts. The phonolitic tephrite of the Somma (Italy) has the lowest sulfur content in this type of basalt. This sample only allows the preparation of total sulfur. In the olivine nephelinite of the Mirzenberg, the sulfur concentration is about six times as high. It may be seen from these pronounced differences that the various types of basalt have no characteristic sulfur concentration. Since H_2S and SO_2 are important components of the gaseous phase of volcanic activity, the sulfur content of these rocks is strongly connected with the history of their extrusion. However, it depends on the type as to whether the rocks contain predominantly sulfide- or sulfate-sulfur. In the tholeiitic basalts and in the olivine alkali basalts, sulfide-sulfur is always predominant; in the alkali-rich undersaturated basalts sulfate-sulfur predominates. This is an indication of the oxidation conditions during the eruption.

3.2. Results of Isotope Analysis

Published data on sulfur isotopes of basalt rocks have been restricted to single phases. Smitheringale and Jensen (1963) investigated sulfides from Triassic sills in the Eastern United States and from mineral deposits and extrusions immediately connected with these rocks. Table 2 of the quoted paper contains all previously published data on sulfides of rocks and mineral deposits of magmatic origin. The $\delta^{34}S$ values of these sulfides vary between -5.7 and 13.6 per mil. The mean is $+3.3$ per mil.

Puchelt, Nielsen and Hoefs (in preparation) carried out sulfur isotope investigations on solfataras of the mediterranean region. In addition to elementary sulfur, they also analysed sulfates from incrustations and H_2S dissolved in water. The investigated sulfur compounds originated at low temperatures; partly at the surface and influenced by the atmosphere. Therefore it is impossible to draw unrestricted conclusions about the conditions in a magma from these results.

The fractionation of sulfur isotopes in volcanic gases has been investigated by Sakai and Nagasawa (1958). The temperature of the gases was between 100 and $661^\circ C$. The fractionation of the sulfur isotopes corresponded well with the theoretical fractionation factor for the respective temperatures considering that the temperature in the fumaroles is generally lower than the equilibrium temperature of the escaping mixture of gases. During the rise of gases in a fissure, their temperature falls, but the rise is so fast that no new equilibrium is achieved.

The analysis of the sulfur isotopes of sulfides and sulfate, as far as they occur together in basaltic rocks, and the comparison with the value for the total sulfur of the same rocks, make it possible to discuss the sulfur isotope composition in a broader context, since the quantitative proportions between sulfides and sulfates may also be taken into account.

It is from these aspect that the results presented in Table 1 and Fig. 2 will now be discussed.

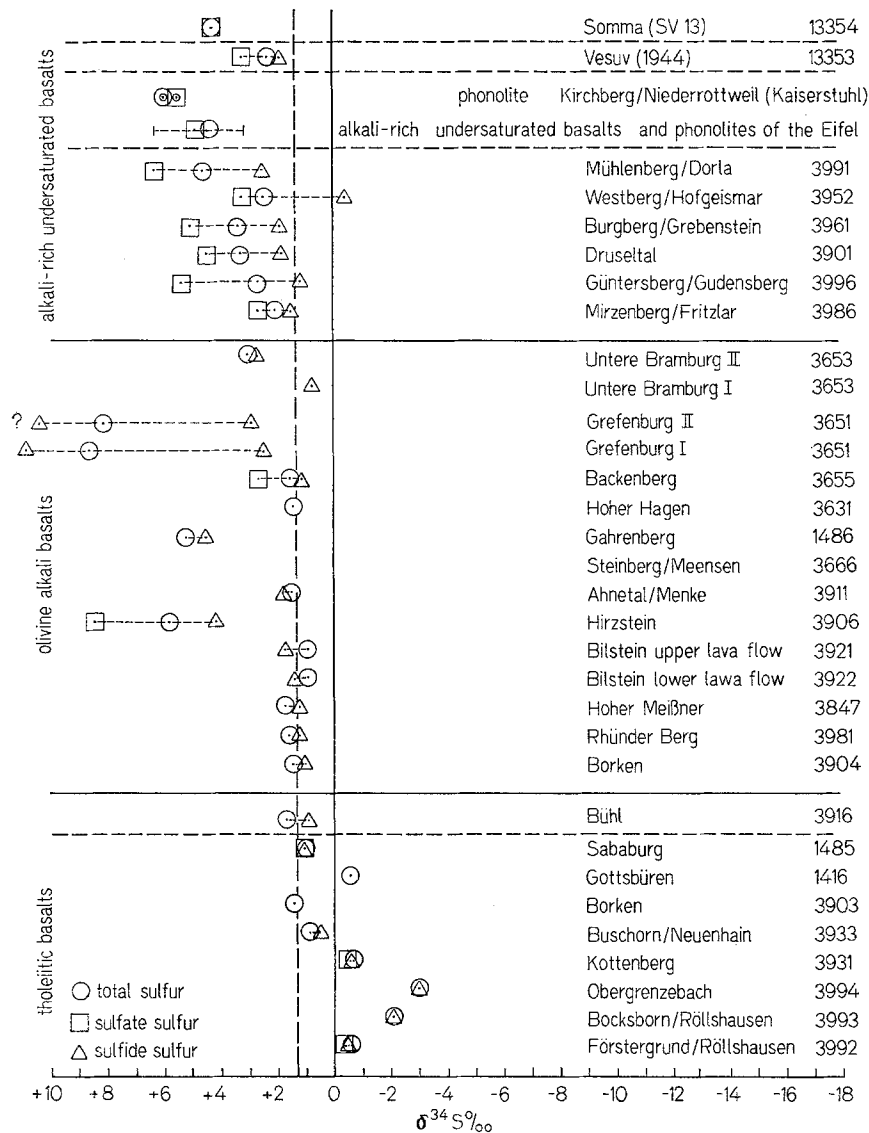


Fig. 2. Sulfur isotope composition of the investigated samples

3.2.1. Tholeiitic Basalts

Of the three groups of basalts investigated, the tholeiitic have on an average the lightest total sulfur ($\delta^{34}\text{S} = -0.3$ per mil), the lightest sulfide-sulfur ($\delta^{34}\text{S} = -0.3$ per mil) and the lightest sulfate-sulfur. The means of these three sulfur groups are equal within the limit of error. It must be taken into account that sulfate-sulfur could only be prepared from three out of nine samples. The sulfate-sulfur of these three samples does not have to be primary. It can originate either from sulfides oxidized during the process of weathering or from sulfides un-

affected by the preceding separation of sulfide sulfur. All three samples show incipient weathering. It is certain that tholeiitic basalts have by far the lowest proportion of sulfate-sulfur. The distribution of the values is greater than for those of the olivine alkali basalts. The samples from Bocksborn near Röllshausen, and from Obergrenzebach have the lightest sulfur of all the basalts investigated in this paper (respectively $\delta^{34}\text{S} = -2.0$ per mil and -3.0 per mil).

3.2.2. Olivine Alkali Basalts

The results obtained from the olivine alkali basalts are heterogeneous only at the first glance. This group of rocks includes some occurrences containing either heavy sulfate-sulfur (Hirzstein) and/or heavy sulfide-sulfur (Grefenburg, Gahrenberg and Hirzstein), which seriously affect the mean. The average values, excluding these three samples, are:

	$\delta^{34}\text{S}$ (per mil)
Total sulfur	+1.3
Sulfide-sulfur	+1.2
Sulfate-sulfur	+1.4

In comparison with the tholeiitic basalt a slight enrichment in ^{34}S was observed in these samples. The scattering of the $\delta^{34}\text{S}$ values was negligible. Of the 12 rocks of this group, four samples contain in addition sulfate-sulfur. However, the $\delta^{34}\text{S}$ value was in two cases considerably higher than the mean for all the samples. Both of the other samples show $\delta^{34}\text{S}$ values for sulfate, which are near to those of sulfide-sulfur. The concentration of sulfide-sulfur is predominant in these samples. The tholeiitic basalts and the olivine alkali basalts resemble one another in that often they contain either no sulfate sulfur, or only very minute amounts. Several samples deviating from this rule have sulfur isotope compositions which vary greatly from the mean.

3.2.3. Alkali-Rich Undersaturated Basalts

The term "alkali-rich undersaturated basalts" is ment to include nepheline basanites, olivine nephelinites and melilite-bearing olivine nephelinites occurring in the region being investigated. In their sulfur isotope composition, these rocks vary considerably from the group of rocks previously described. The mean of the results of this group of rocks is, with only negligible scattering of the individual values, as follows:

	$\delta^{34}\text{S}$ (per mil)
For total sulfur	+3.1
For sulfide-sulfur	+1.4
For sulfate-sulfur	+4.2

The proportion of sulfide-sulfur and sulfate-sulfur to total sulfur shows that in these samples, sulfate-sulfur is of special significance. All eight samples in-

investigated bear sulfate-sulfur, however, in varying proportions. All the sulfates are heavier than their coexisting sulfides. On an average, these sulfides are only negligibly heavier than the sulfides of the olivine alkali basalts and those of the tholeiitic basalts.

In the samples from the Eifel only the presence of sulfate-sulfur was proved. The sulfur isotope composition of the isolated sulfate-bearing minerals hauyne and noseane do not differ from that of the total sample, so that these results do not indicate the presence of sulfide-sulfur. With an average value of $\delta^{34}\text{S} = +4.7$ per mil for the sulfate-sulfur, these samples do not vary considerably from the alkali-rich undersaturated basalts of the North Hessian and Southern Lower Saxony region.

The most important results so far are:

The sulfide-sulfur becomes heavier from the tholeiitic basalts to the olivine alkali basalts and this trend continues into the alkali-rich undersaturated basalts.

Sulfate-sulfur rarely occurs in the tholeiitic basalts and olivine alkali basalts; sulfate-sulfur is present predominantly in alkali-rich undersaturated basalts. In these rocks there is a pronounced enrichment of ^{34}S in the sulfate-sulfur in comparison to the sulfide-sulfur. The individual values of total sulfur result from the proportion of sulfide-sulfur and sulfate-sulfur and from their isotope composition.

In the case of olivine alkali basalts there are several obvious exceptions. These samples have heavy sulfate in addition to heavy sulfide.

4. Discussion of Results

4.1. The Basis of Sulfur Isotope Geochemistry of Igneous Rocks

The terrestrial distribution of the sulfur isotopes ^{32}S and ^{34}S is only known approximately. Fractionation processes in the geological and biological cycles have led to $^{32}\text{S}/^{34}\text{S}$ ratios between 20.4 and 23.6 depending on their occurrence. This is a deviation of more than 15% (Jensen, 1967). There are three hypothetical ways of estimating the initial value of all fractionation processes on the earth.

(a) Meteoritic material is similar in many aspects to the undifferentiated material of the earth's mantle. Sulfur from troilite of various meteorites has, within the precision of measurements, the $^{32}\text{S}/^{34}\text{S}$ ratio 22,220. This value is defined as an international standard. For all data in general, the deviation from this value will be given in reference to the isotope ^{34}S in δ in per mil. Accordingly, meteoritic sulfur has the value $\delta^{34}\text{S} = 0.00 \pm 0.01$ per mil. This definition would be particularly useful if the $^{32}\text{S}/^{34}\text{S}$ ratio coincides with the undifferentiated sulfur isotope ratio of the earth, since then, on the basis of the δ values, the enrichment of the isotope ^{34}S (positive values) or the impoverishment (negative values) compared with the initial value could be expressed.

(b) The earth's crust is the differentiation product of the earth's mantle and the composition of the sulfur isotopes of the earth's mantle is the initial value for the fractionation processes taking place, both in the crust and at the surface. Representative for the sulfur of the mantle are sulfides from magmatic intrusions and related sulfide deposits, provided these sulfides have an uniform isotope composition. Smitheringale and Jensen (1963) investigated Triassic tholeiitic basalts from dikes and sills of the Newark group in the Eastern United States and determined $\delta^{34}\text{S} = +0.1$ per mil for the sulfides of the normal undifferentiated basalts of tholeiitic composition. The standard deviation of all of their analytical results was ± 0.4 per mil. The uniformity of these results is all the more surprising since all samples are from a region of approximately 2,000 km in North-South direction, and since the individual

intrusives are surrounded by totally different types of rocks and have passed through totally different rocks on their way up. This would indicate that the mantle in this region is homogeneous as far as the sulfur isotope composition is concerned and that the sulfur of the mantle in this region has a $\delta^{34}\text{S}$ which lies near zero. These results are not supported by the analysis of the sulfides of other mafic intrusions (Table 2 in Smitheringale and Jensen, 1963).

(c) Since today sulfur isotope measurements exist from many different rocks, an attempt was made to draw up geochemical balance calculations. In this way, Ault and Kulp (1959) determined a $^{32}\text{S}/^{34}\text{S}$ ratio of 22.14 ($\approx \delta^{34}\text{S} = +3.6$ per mil) as an average for the earth's crust. The calculation is based on average values for sea water sulfate, evaporite sulfate and sedimentary sulfides. Sulfides of the magmatic rocks were not included in the calculation. A later calculation by Field (1960), carried on new data, resulted in 22.19 ($\approx \delta^{34}\text{S} = +1.4$ per mil) as an average for the earth's crust.

Apart from the fact that many cosmochemical and geochemical investigations and theories suggest the comparability of mantle and meteoritic material, the agreement of the $^{32}\text{S}/^{34}\text{S}$ ratio between the tholeiitic intrusive rocks of a geographically widespread series, and the same ratio for meteoritic sulfur, may be viewed as additional confirmation of this comparability. It is postulated on the basis of these observations that the sulfides of rocks of tholeiitic composition, occurring in the crust or at the surface, are taken over from the mantle in an undifferentiated form and that the total sulfur of the mantle is adequately represented by these sulfides.

This is only the case, if a series of conditions are fulfilled. Either the sulfur in the mantle may exist only in a single oxidation state, or all oxidation states occurring have the same $^{32}\text{S}/^{34}\text{S}$ ratio. A second possibility is that the sulfur in the state of oxidation producing the sulfur for the tholeiitic magma is predominant in comparison to all the sulfur present in the other oxidation stages. In all cases, the passage of the sulfur from the mantle rock into the magma must not be combined with fractionation of the sulfur isotopes. It is, therefore, necessary to test basic rocks for the possible presence of sulfate-sulfur. According to the results of this work, sulfate-sulfur, if it is present at all, comprises only a very small proportion of the total sulfur of the tholeiitic and olivine alkali basalts.

The few exceptions to this rule show extreme isotope composition. Apart from these exceptions, the isotope composition of sulfate-sulfur does not vary greatly from that of sulfide-sulfur with $\delta^{34}\text{S} = -0.3$ per mil for the tholeiitic basalts, and $+1.3$ per mil for the olivine alkali basalts. If the $^{32}\text{S}/^{34}\text{S}$ ratios of the meteoritic sulfur are identical with those of the mantle sulfur, then these two rock types may be representative for the isotope composition of the sulfur in the mantle. The sulfur isotope composition of rocks which developed from the mantle by differentiation only vary radically if the oxidations conditions in the magma change. The oxidation conditions may be concluded, with certain limitations, from the mineral association of the rocks.

4.2. Oxidation Conditions in Gases and Magmas of Basaltic Rocks

The chemical potential of oxygen in a magma is expressed by the oxygen fugacity. In ideal gases this is equal to the partial pressure of oxygen. Oxygen fugacity regulates the ratio of sulfide-sulfur and sulfate-sulfur in the magma and the ratio $\text{H}_2\text{S}/\text{SO}_2/\text{S}_3$ in the gaseous phase. The gas forming phases are generally in equilibrium with each other and with the magma (Ellis, 1957; Heald, Naughton and Barnes, 1963; and Heald, 1968). The equilibrium of volcanic gases is seriously affected if surface waters join them during the ascent of the gas or if other substances are taken up from adjacent rocks during evaporation under

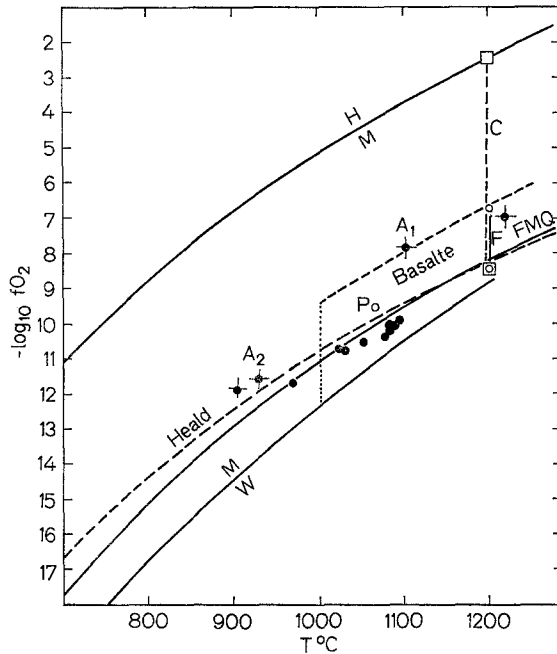


Fig. 3. The crystallisation of basalts, depending on oxygen fugacity and on temperature, at a pressure of 1 atm, according to Eugster and Wones (1962) and Carmichael and Nicholls (1967). *HM*, *FMQ* and *MW* indicate the equilibrium conditions of the systems hematite-magnetite, fayalite-magnetite-quartz and magnetite-wüstite (Eugster and Wones, 1962). The heavy dots represent oxygen fugacity and temperature, as determined by Carmichael and Smith by micro probe analysis of iron-titanium oxides of basaltic rocks. *P*: measured oxygen fugacity of a lava from Kilauea, Hawaii (Peck and Wright, 1966). *F*: oxygen fugacities determined experimentally by Fudaly (1965). *C*: oxygen fugacities determined by Conquére and Girod (1968). (All determined in basalts.) *A*₁ and *A*₂: oxygen fugacities determined by Anderson (1968) in trachyandesite (*A*₁) and trachyte (*A*₂)

the given circumstances. For this reason, the isotope analysis of sulfur in different compounds from volcanic exhalations show stronger and more irregular scattering of values than would be expected if the basalts were the only source of the sulfur (Nielsen, Puchelt, Hoefs, in preparation).

With regard to oxygen, basaltic magmas have a high buffering capacity. Iron acts as a buffer since the rate of increase of the oxygen partial pressure is reduced by oxidation of Fe^{2+} to Fe^{3+} . The mineralogically recognisable consequence is a change in the mineral composition and that of the iron-titanium oxides in particular. The stability of the paragenesis hematite-magnetite, magnetite-fayalite-quartz, and magnetite-wüstite as a function of the temperature and the oxygen fugacity at 1 atm were determined by Eugster and Wones (1962), (Fig. 3). These parageneses mark the upper and lower limits of the fugacity of oxygen in basaltic rocks. At 900°C they lie between $f_{(\text{O}_2)} = 10^{-15}$ and 10^{-7} bars, at $1,100^\circ\text{C}$ between $f_{(\text{O}_2)} = 10^{-10}$ and 10^{-4} bars and at $1,300^\circ\text{C}$ at 10^{-7} for the buffer system fayalite-magnetite-quartz and 10^{-2} for the buffer system hematite-magnetite (Fig. 3) (Carmichael and Nicholls, 1967; Anderson, 1968). In addition to the determination

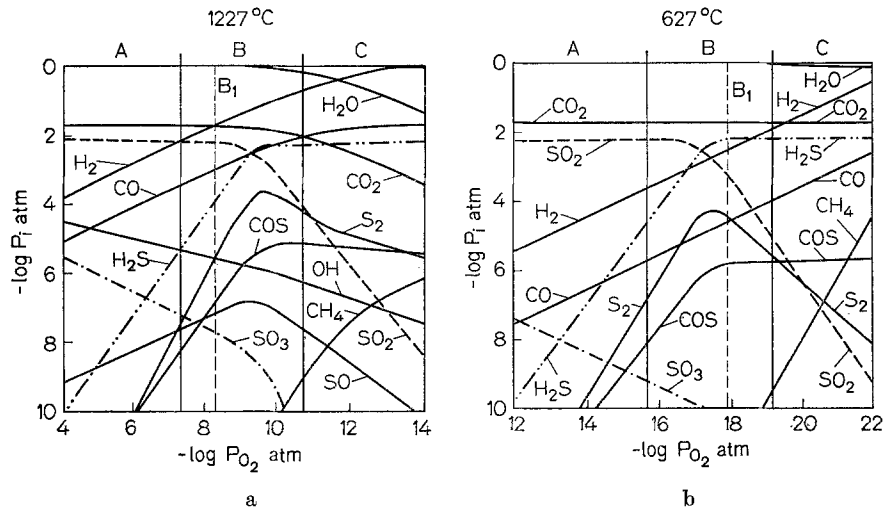


Fig. 4a and b. Original Fig. 4 and 3, from Heald, Naughton, and Barnes (1963). Variation of the equilibrium composition of an actual volcanic gas with degree of oxidation at 1 atm. In a gas with the equilibrium composition „B₁“, at a temperature of 1,227° C, SO₂ predominates over H₂S. At 627° C, the oxygen partial pressure of the same gas is considerably less, and the H₂S/SO₂ relation is now reversed

of the equilibrium fugacity for the given mineral paragenesis, attempts were made to determine directly the oxygen fugacities of various basaltic rocks. This is possible by experimental determination on natural samples with the known ratio FeO/Fe₂O₃ (Fudali, 1965); by the analysis of volcanic gases, assuming that the gases are in equilibrium with the magmas from which they derive; or by exact analysis of the equilibrium assemblages of the iron-titanium oxides, provided no subsequent oxidation has occurred (Buddington and Lindsley, 1964; Anderson, 1968). The results of these determinations are represented in Fig. 3. For the evaluation of the results of the sulfur isotope analysis, it is important to take into account those parameters which influence the proportions of the sulfur-containing components in the region of the defined oxygen fugacity. It is easier to understand these processes if they are first studied in natural gases which would suggest equilibrium with a basaltic magma. Criteria for this are described by Ellis (1957); Matsuo (1962); Heald, Naughton and Barnes (1963); Heald (1968), and others. Various gaseous compounds of the elements hydrogen, carbon, oxygen and sulfur account in general for more than 99% of volcanic gases. Water is the most frequent component providing more than 90% of the gaseous phase in volcanic exhalations. This is followed by CO₂, H₂S, SO₂ and other gaseous phases of the elements quoted in various proportions as approximated in Fig. 4. This figure is based upon the composition of a natural gas which was collected during and after an eruption of the Kilauea Iki volcano, Hawaii (Heald, Naughton and Barnes, 1963).

The fugacity of oxygen is very often replaced by oxygen partial pressure which in the case of gases at low pressures and high temperatures is in first approximation equal to the fugacity. In other words, the behaviour of gases at low pressures

and high temperatures is almost ideal. This restriction is to be observed, however. The oxidation agent of volcanic gases is water provided the system is open for hydrogen. Parallel to the dissociation of water, the partial pressure of oxygen increases with increasing temperature. This has a remarkable effect on the equilibrium composition of the volcanic gases. It must be taken into consideration that, while the gas is in equilibrium with the magma, the oxygen partial pressure is not free to take on any arbitrary value, because the system is internally buffered. It may be seen from Fig. 3 that, in the range of temperature between 1,000 and 1,300° C, the oxygen fugacity for basaltic magmas is between 10^{-12} and 10^{-6} atm. Conquére and Girod (1968) described basalts from the Algerian Sahara whose oxygen fugacity was between $10^{-8.5}$ and $10^{-2.5}$ atm during crystallization (formation of hematite beside ulvöspinel-magnetite solid solutions has been observed). Under the conditions of oxydation thereby determined, the behavior of the sulfur-bearing components of volcanic gases at various pressures and temperatures may be estimated. This is also true for a magma as long as the gases are in a concentration below their saturation point; i.e. under increased pressure. The process of the eruption is an exception characterized by a steep pressure gradient. The most important sulfur containing compounds in the gaseous phase are H_2S and SO_2 ; S_2 and SO_3 are present in comparatively minor amounts while COS , SO and CS_2 are present in such small amounts that they are quite without importance in this discussion. The partial pressure influences the quantity and the chemical efficiency of all compounds and these react according to their respective concentrations, with greater or lesser sensitivity with change of pressure, temperature and oxygen fugacity. These changes are significant for the discussion of the sulfur isotope composition because the oxidation of the H_2S to SO_2 and other more oxidized sulfur compounds are linked with isotope fractionation. Since the dissociation of water at low temperatures of approximately 200° C is only slight, the most important sulfur-bearing gas compound is H_2S ; the partial pressure of the remaining gaseous sulfur compounds are 5 to 10 orders of magnitude lower at this temperature. With increasing temperature, the proportions of S_2 , SO_2 and SO_3 increase. At 900° C, the partial pressure of SO_2 exceeds that of H_2S and at 1,100° C it is already 50 times as great. From 300 to 1,100° C the partial pressure of SO_3 and O_2 rises by ten to twelve orders of magnitude. On the one hand, this value is still some orders of magnitude lower than that of the partial pressure of SO_2 ; however, on the other hand, this shows the increase of the oxidation potential. The influence of pressure on the components H_2S and SO_2 is opposite to that of temperature. For all the most important gas phases consisting of the components H, C, O and S, the partial pressure increases with increasing pressure at a given temperature. This is also true for H_2S and SO_3 , but the partial pressure of SO_2 decreases, and in fact so strongly, that even at a temperature of 1,200° C, and at 100 atm (corresponding to 350 m depth), the partial pressure of H_2S is a hundred times greater than that of SO_2 ; at 2,000 atm (7 km depth) it becomes 1000 times greater. The behavior of the gaseous components at 1 atm pressure may be most easily explained by referring to Fig. 4a. Here is shown the equilibrium composition of the gases already mentioned from the Kilauea Iki volcano in relationship to the oxygen partial pressure. Since the negative logarithms of the partial pressure

are plotted on both axes, the increasing values are relative to decreasing partial pressure. The diagram may be divided into three areas.

(A) At high oxygen partial pressures (from $p_{(O_2)} = 10^{-4}$ to 10^{-8} atm), the most important sulfur-bearing compound is SO_2 .

(B) Between $p_{(O_2)} = 10^{-8}$ and 10^{-11} atm, the partial pressure of SO_2 decreases rapidly, while the partial pressure of H_2S correspondingly rises.

(C) From $p_{(O_2)} = 10^{-10}$ atm to lower oxygen partial pressures H_2S predominates over SO_2 .

In the regions A and C either SO_2 or H_2S , respectively, predominates so strongly that the remaining sulfur-bearing phases may be disregarded. The region B is that of the predominating oxygen fugacity during the crystallization of basaltic magmas (Fig. 3). Slight variations in temperature and in the oxygen partial pressure (Fig. 4 a and b) have, in this region, a particularly strong influence upon the $H_2S:SO_2:SO_3$ ratios of the gaseous phases and the corresponding sulfur compounds which are in equilibrium with the gaseous phase. It must be taken into account that an initial composition deviating from the composition of the gas given in Fig. 4 would only change the individual points of the curve in a direction parallel to the ordinate. This does not influence the ratio H_2S/SO_2 as related to the oxygen partial pressure, so that this figure may still be used for other compositions of volcanic gases, providing that no other components are introduced.

On the basis of these facts and with regard to the ratio of H_2S/SO_2 , the following conclusions may be drawn:

- (a) The oxygen fugacity increases with rising temperature.
- (b) The SO_2 content rises because of this while the H_2S content falls.
- (c) The SO_2 content falls with increasing pressure resulting very quickly in a predominance of H_2S .
- (d) Although the SO_3 content rises with the increasing pressure, it remains very low in the total concentration (e.g.: max $P_{(SO_3)} = 10^{-4}$ atm at a total pressure of 10,000 atm and at a temperature of 1,227° C).
- (e) The adjustment of the equilibrium of volcanic gases is achieved in a region of oxygen fugacity as was also found to apply to the basaltic magmas during crystallization.
- (f) The adjustment of equilibrium between the gaseous phases and the magma is a fast process. The adjustment of equilibrium between crystallized mineral phases during the cooling history of a rock is such a slow process that equilibrium is not always achieved (Anderson, 1968).

This means that for the discussion of the sulfur isotope composition the instance of the crystallization of sulfur-bearing minerals is of particular significance. The main question is when did the first sulfides crystallize, since sulfates as minerals have not been found in tholeiitic or in olivine alkali basalts.

To simplify the discussion, two extreme cases will be outlined in order to demonstrate any possible course of fractionation.

- (i) The magma reaches the surface at a certain temperature without sulfides having crystallized and without separation of sulfide as an immiscible liquid phase in the basaltic magma.
- (ii) The sulfides observed in the investigated rocks had already crystallized prior to the extrusion of the magma, or have been separated as an immiscible liquid phase from basaltic magma (Desborough, Anderson and Wright, 1968).

In case (i) the sulfides would have crystallized at low pressure and within a certain range of temperature (Yoder and Tilley, 1962).

In case (ii) the sulfides would have formed within an large range of pressure, the temperature being similar to case (i). Equilibrium in the magma would be more probable in case (ii). In case (i) both the amount of gas dissolved in the magma and the temperature would decrease quickly while the viscosity would increase. Whereas the gaseous phase conforms to these conditions, the time of reaction within the magma increases and the crystallizing sulfides will no longer react with the magma. It would be expected that, after crystallization the rock would contain little sulfur, since sulfur is predominantly part of the gaseous components. Examples demonstrating this are the analysed basalts from Hawaii which show no detectable amounts of sulfur. When sulfides are crystallizing, the proportion of sulfur in the form of sulfide is determined by the H_2S/SO_2 ratio in the remaining dissolved gases. Under conditions of possible temperature and oxygen fugacity, both H_2S and SO_2 may be favoured.

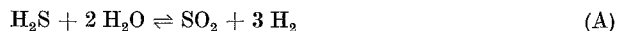
4.3. Origin of the Sulfur Isotope Composition of Basalts

4.3.1. Tholeiitic Basalts

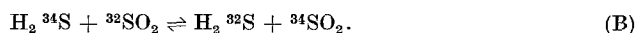
Two groups of basalts may be distinguished, based to their sulfur content: (a) The samples 1485 — Sababurg, 3931 — Kottenberg, 3992 — Förstergrund near Röllshausen, 3993 — Bocksborn near Röllshausen, 3994 — Obergenezbach, and 3916 — Bühl near Weimar contain a large amount of sulfide-sulfur while some contain a little sulfate-sulfur as well.

(b) Samples 3933 — Buschorn and 3904 — Borken contain little sulfide-sulfur and no sulfate-sulfur.

If large amounts of sulfur are found in the samples investigated it may be supposed that this had already been in crystalline phases, or had originated as immiscible droplets of sulfide in silicate liquid when the magma reached the surface. That would explain why, in all types of basalts investigated, both samples with low sulfur content and samples rich in sulfur were found; for it may not be assumed that either the degree of crystallization or the degree of segregation between basaltic magma and sulfide melt had been the same for all investigated basalts at the time of eruption. Further information may be gathered from the sulfur isotope measurements. The reaction



is representative for all reactions leading to the formation of sulfide or sulfate ions, depending on the oxidation conditions in the magma. It must be borne in mind, however, that the formation of SO_2 is only a preliminary step in the formation of the sulfate ions. The reaction for the isotope equilibrium related to (A) is:



Even at the high temperatures between 1,000 and 1,200° C this reaction is connected with an isotope fractionation of 3 to 4 per mil, favouring ^{34}S in the SO_2 (Sakai, 1957).

If the equilibrium (A) favours H_2S , only very small amounts of SO_2 , with corresponding enrichment in ^{34}S , will be formed. However, the possible loss of

heavy sulfur would on no account affect the mean of the isotope composition of sulfides seriously, as long as there is a strong predominance of H_2S . If sulfides are formed from this H_2S , their isotope composition will be the same as that of the H_2S .

The data on the sulfur isotopes of the tholeiitic rocks among the investigated samples leads to the assumption that the equilibrium of the sulfur isotopes was achieved under high pressure and at high temperatures, i.e. at low oxygen fugacity. The equilibrium reaction (A) totally favours H_2S if one considers the gaseous phase dissolved in the magma.

If, for the reasons mentioned above, one takes the sulfur isotope composition of the mantle to be $\delta^{34}\text{S} = \pm 0.0$ per mil, the sulfur contained in the tholeiitic basalts of the investigated region may be seen to be only slightly fractionated.

The sulfides of the tholeiitic rocks of the Newark group show a $\delta^{34}\text{S} = +0.1$ per mil with only slight variation. The tholeiitic rocks of the North Hessa and Southern Lower Saxony area are characterized by even more deviation, but, with $\delta^{34}\text{S} = -0.3$ per mil for the sulfides, and with the same value for the total sulfur, they have very similar mean values which differ only in the range of error from the samples investigated by Smitheringale and Jensen (1963).

It must also be observed that while the rocks of the Newark group were intrusive, those of the area investigated in this paper are extrusive. It can be supposed that in the latter, the sulfate-sulfur was formed secondarily by oxidation of the sulfides. This must not necessarily be linked with a fractionation even at low temperatures if the speed of the reaction is determined by the releasing of the sulfur atoms from the sulfide lattice and not by the oxidation process. The samples of the Newark group were not examined for sulfate sulfur.

Two tholeiitic basalts have, with $\delta^{34}\text{S} = -2.1$ per mil and -3.0 per mil, the lightest sulfur of all the investigated samples. Therefore it may be concluded that fractionation process occurred even in the tholeiitic basalts and this, in fact, near the surface; heavy SO_2 must have left the magma in order to cause the enrichment of ^{32}S in the sulfide. This is a process which can only take place under relatively low pressures.

4.3.2. Olivine Alkali Basalts

The sulfur of the olivine alkali basalts is on average heavier than the sulfur of tholeiitic basalts. It must now be discussed whether or not these deviations may be explained by the occurrence of fractionation during a differentiation process. Smitheringale and Jensen (1963) observed that in the case of the intrusions of the Newark group, the later differentiation products of the tholeiitic rocks contained heavier sulfides. Similar results were found by investigation of the intrusions Sudbury, Stillwater and Inizwa (Thode, Monster and Dunford, 1961). It may be assumed that the origin of an olivine alkali basalt magma occurs under sufficiently high pressure and it is, therefore, certain that H_2S is by far the most predominant sulfur-bearing phase. If crystallized sulfides or immiscible sulfide droplets were removed from this magma, the gaseous components H_2S , SO_2 and also SO_3 would then be enriched in the residual magma. This sulfur, prevented from further reaction with the magma, would then be slightly enriched in ^{32}S in comparison to the total sulfur before separation of the

sulfides and would cause the sulfur of the residual magma to become gradually heavier. This is true even if the sulfide-sulfur predominates. The total amount of isotopic fractionation between the sulfur of that proportion of the melt already crystallized and separated, and the sulfur of the olivine alkali basalts could not be large. This is due to the small fractionation factor, the small proportion of SO_2 (and SO_3) and to the fact that the proportion of the residual magma could not be infinitesimally small in comparison to the total magma. The course of the fractionation described above is expressed by the formula

$$R_t = R_o f^{(\alpha-1)} \quad (\text{Epstein, 1959}). \quad (\text{C})$$

R_t = $^{32}\text{S}/^{34}\text{S}$ ratio for the residual magma,

R_o = $^{32}\text{S}/^{34}\text{S}$ ratio for the original magma, before sulfur was removed by crystallization or unmixing,

f = proportion of total sulfur remaining in the residual magma,

α = the factor of fractionation between H_2S , from which the sulfides are formed, and the total sulfur which remains in the residual magma.

In order to calculate a model case the following conditions should be fulfilled. The reacting proportions of H_2S to SO_2 should remain constant, i.e. the magma should not change with regard to pressure, temperature and oxygen fugacity. Under this restriction α remains constant. R_t will show an exponential dependency on f , i.e. on the proportion of sulfur remaining in the residual magma. At the beginning of crystallization, this proportion should still be large and the change in the ratio $^{32}\text{S}/^{34}\text{S}$ should be accordingly very light in the residual magma. However, when during the differentiation f becomes smaller, R_t will change more rapidly.

Estimated conditions for the calculation of R_t in this special case of fractionation are:

- (a) Let the fractionation factor α between H_2S and SO_2 at the temperature of the magma (at least 1,000° C) be 1,003 ($\cong \delta \text{SO}_2 - \delta \text{H}_2\text{S} = 3.0$ per mil; Sakai, 1957 and 1968).
- (b) Let in the original magma the ratio of $\text{H}_2\text{S}/\text{SO}_2$ equal 1000:1. This ratio should not change in the residual magma, while sulfide is removed from the magma by differentiation.
- (c) In the case being discussed, let the residual magma still be 80% of the original magma, and correspondingly contain 80% of the total sulfur.
- (d) Let the sulfur of the original magma have a $\delta \text{ }^{34}\text{S} = \pm 0.0$ per mil.

As a result of these calculations, it can be shown for the olivine alkali basalts that the enrichment of ^{34}S is much less than the measured values for the investigated samples.

According to the progress of this fractionation, the possibility for measuring a change in the isotope composition of the components of the residual magma depends on the value of the factor of fractionation. Since the fractionation factor used in this example is dependent on the ratio of H_2S and SO_2 in the residual magma, it decreases as the ratio $\text{H}_2\text{S}/\text{SO}_2$ increases. However, the proportion of H_2S to SO_2 is determined by the pressure and the oxygen fugacity of the magma. The measured sulfur isotope composition of most olivine alkali basalts could be explained by the described fractionation process if only 1 part olivine alkali basalt magma resulted from 100 parts parental magma, and provided that the sulfur concentration is the same in both magmas. However, if the sulfur in the residual magma is enriched, smaller ratios between parental and residual magmas lead to the measured isotope fractionation. Three samples do not fit into this scheme.

- (a) The sulfur content of the sample from the Hirzstein is not unusual when compared with the other samples analysed, Sulfide-sulfur predominates. Peridotite nodules are common in this basalt. The total sulfur of this basalt has a $\delta \text{ }^{34}\text{S} = +5.8$ per mil, the sulfide-sulfur +4.1 per mil and the sulfate-sulfur +8.4 per mil. The value for the total sulfur of the peridotite nodules is +3.4 per mil. The sulfur content of the nodules is very small.

(b) The sulfur content in the basalt from Gahrenberg is extremely small. The results of repeated measurements of the isotope composition of sulfide-sulfur as for the total sulfur deviate more strongly than for the other samples. The mean for sulfide-sulfur and total sulfur is $\delta^{34}\text{S} = +4.5$ per mil and $+5.0$ per mil respectively.

(c) The two samples from Grefenburg also deviate from the mean of the olivine alkali basalts. Both samples contain heavy total sulfur ($\delta^{34}\text{S} = +8.6$ and $+7.7$ respectively).

A change in the isotope composition would then also occur if the fractionation processes, coupled with a differentiation before the extrusion, were superimposed still further by reactions taking place near the surface. In this situation, the magma is characterised by high temperatures and low pressures. The equilibrium reaction (A) favours SO_2 formation but the total gaseous content becomes smaller. It is possible that the magma already contains sulfides, which contribute to the isotope composition of the sulfide sulfur. In this stage, the magma loses both SO_2 and H_2S due to processes of degassing, and their proportion is determined by the prevailing conditions. It may be concluded that, in the possible region of oxygen fugacity in basalts at 1 atm, both H_2S and SO_2 may be favoured. In this special case two stages are important for the isotopic composition of sulfur:

(a) The formation of more SO_2 in comparison with the region of high pressure seriously changes the isotope composition of H_2S because the strong dilution due to the high ratio of $\text{H}_2\text{S}/\text{SO}_2$ is no longer valid.

(b) The process of degassing favours the lighter molecules, so that on the one hand, comparatively more H_2S than SO_2 is leaving the magma and within each of these compounds those molecules with the lighter isotopes are favoured.

As a result, ^{34}S is enriched in the total sulfur and sulfide-sulfur, while the difference in isotope composition between sulfide-sulfur and sulfate-sulfur becomes greater. The extent of this change is determined by:

(a) the position of the equilibrium between H_2S and SO_2 ;

(b) the intensity and the mechanism of the process of degassing, and;

(c) the quantity and the isotope composition of the sulfides already present in the magma at the time of extrusion.

However, the direction of the isotope fractionation remains unchanged: due to degassing the sulfur of the crystallized phases on an average becomes enriched in ^{34}S .

Since the scattering of the measured isotope composition of the olivine alkali basalts is very small, it must be concluded from the conditions discussed above that, apart from a few exceptions, these basalts have had a relatively uniform extrusion and degassing history. On the other hand, an isotope fractionation resulting from crystal fractionation is very improbable because of the unfavourable proportions between the parental and the residual magma. Therefore it still remains possible that the parental isotope composition of the mantle region, where the olivine alkali basalts originated, is characterised by a $\delta^{34}\text{S}$ value, which shows an enrichment of ^{34}S compared with meteoritic sulfur, i.e. $\delta^{34}\text{S} = +1.0$ to $+1.5$ per mil, as opposed to ± 0.0 per mil. As is shown in Fig. 2, 18 out of 31 samples investigated have $\delta^{34}\text{S}$ values of the sulfide-sulfur which fall into this region, taking into account the range of error. Of the remaining 13 samples, 9 are seriously affected by fractionation which must necessarily have led to a different isotope composition of the sulfide-sulfur. One is justified in using the results of the sulfide-sulfur for this comparison, because, throughout the greater part of their history preceding crystallization, the magmas exist under conditions which lead to the formation of sulfide with negligible oxidation of sulfur. As a result of this, even when SO_2 or sulfates are formed, sulfides very frequently predominate so that their isotope composition changes only slightly or not at all and the initial value of sulfur isotope composition is, therefore, remains.

4.3.3. Alkali-Rich Undersaturated Basalts

Not all the details previously discussed may be applied without restriction to the alkali-rich undersaturated basalts, since this group of rocks is characterized by several petrological peculiarities. The eruption of these basalts is in general particularly explosive and it is connected with considerable amounts of pyroclastics which would indicate a high gas content. Since the content of the gaseous phases of these magmas consists almost totally of water, the degree of oxidation of these magmas, which may be read from the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio, must be higher than the degree of oxidation of the tholeiitic and olivine alkali basalt magmas. This is clearly indicated by the following comparison of results of analysis of various basalts from the area of investigation (Hoefs and Wedepohl, 1968).

	Tholeiitic basalts (3)	Olivine alkali basalts (25)	Alkali-rich undersaturated basalts (18)
$\frac{\text{Fe}_2\text{O}_3}{\text{FeO}}$	$\frac{2.75}{7.89} = 0.35$	$\frac{3.56}{7.07} = 0.50$	$\frac{4.75}{6.27} = 0.76$

The results of various hydrogen isotope analyses show that a considerable proportion of the water emanated by volcanic activity is contributed by the water circulating near the surface. If the sulfur isotope composition measured in the alkali-rich undersaturated basalts should permit a genetic conclusion, then the first question to be discussed is the role of this water during the oxidation of the rocks. If it is only the absorption of water during the eruption that causes the various oxidation states of the tholeiitic basalts, olivine alkali basalts and alkali-rich undersaturated basalts, the question will remain unanswered as to why these in particular should absorb water near the surface. This never happens in the case of olivine alkali basalts, which occur more frequently, nor in the case of tholeiitic basalts. Therefore, it is more probable that the higher oxidation state of alkali-rich undersaturated magmas is already connected with their formation in the mantle.

Conquére and Girod (1968), using the method devised by Buddington and Lindsley (1964), determined the oxygen fugacity prevailing during the eruption of lava in samples of alkali-rich undersaturated basalts from Algeria. The $f_{(\text{O}_2)}$ values from $10^{-8.5}$ to $10^{-2.5}$ at $1,200^\circ\text{C}$ are higher than the values determined by Carmichael and Nicholls (1967), Fudali (1965) and others for basaltic rocks of different composition.

The same tendency may be demonstrated by the fact that only alkali-rich undersaturated basalts contain sulfate-sulfur in addition to sulfide-sulfur without exception. The ratio of $\text{H}_2\text{S}/\text{SO}_2$ is changed in favour to SO_2 by the higher oxygen fugacity. The results of the isotope measurements indicate that the average isotope composition, measured as total sulfur, shows a pronounced enrichment in ^{34}S , as opposed to both the other types of basalts ($\delta^{34}\text{S} = +3.0$ per mil). In comparison to the average, the sulfide-sulfur is depleted in ^{34}S (+1.6 per mil) to the same extent as the sulfate-sulfur is enriched (+4.2 per mil). Supposing this to

be an equilibrium composition, it would have been formed with a fractionation of about 3 per mil. According to Sakai (1957), this value is not improbable, even at a temperature of 1,000° C. This is especially true as one may conclude, that in these samples equilibrium between H_2S and SO_4^{2-} , and not between H_2S and SO_2 has been achieved. This is connected with a larger fractionation factor.

Apart from this, processes must have taken place which in comparison to the other basalts investigated led to an enrichment of ^{34}S before the magma crystallized. This can be seen in combination with the obvious enrichment of the gaseous components connected with the formation of alkali-rich undersaturated magmas (Bultitude and Green, 1968). A magma originating in the upper mantle by partial melting should, in the place of its generation, have the same isotope composition as the parental material. However, due to a higher water content of the magma, the oxygen fugacity rises, as may be seen by the listed ratios of $\text{Fe}_2\text{O}_3/\text{FeO}$. Under these conditions, the further development of the sulfur isotope composition during the rise of the magma will be discussed. While at first H_2S is present in excess and sulfides crystallize, the ratio $\text{H}_2\text{S}/\text{SO}_2$ changes in favour of SO_2 . As a result, the sulfur of H_2S is depleted in ^{34}S , while the residual magma is enriched in it if more sulfides crystallize. In the last stage of extrusion, both sulfate and sulfide are stable, while the more oxidized sulfur compounds predominate. Because of these dynamic processes, the measured isotope compositions only prove that, in general, the investigated alkali-rich undersaturated basalts have about the same amount of sulfide-sulfur as sulfate-sulfur. They do not, however, prove that the measured fractionation is the result of equilibration. The change in the oxidation conditions and the necessary segregation of sulfides enriched in ^{32}S are both dynamic processes. Since the ratio of the sulfur compounds involved changes during these processes, they may lead to different isotope composition of the total sulfur in the samples investigated. Consequently the δ values of sulfide-sulfur and sulfate-sulfur measured provide averages for the existing sulfide and sulfate phases, which may have differing isotope composition, according to the time of their formation during the process of eruption and subsequent cooling of the magma.

According to the above discussion of the sulfur isotope composition of the alkali-rich undersaturated basalts, the assimilation of sulfate (from Zechstein evaporites) is improbable. An investigation of sulfate inclusions in a melilite-bearing olivine nephelinite from Westberg near Hofgeismar has been started. Preliminary results show that the sulfates are not related to Zechstein evaporites.

5. Discussion of the Results in Relation to Experimental Investigations on the Genesis of Basalts

The sulfur isotope composition of the basalts of North Hessa and Southern Lower Saxony is different for each of the three groups of rocks distinguished. It will now be discussed whether these differences and their interpretation are in agreement with contemporary knowledge on the genesis of basalts. Green and Ringwood (1967), and Bultitude and Green (1968) conclude from their experiments that partial melting of mantle material and fractional crystallization under various pressures are the causes of the genesis of various types of basalts. Indications of

the composition of the mantle are found in the spinel- and garnet-bearing peridotites. However, it must be taken into account that they have possibly already changed the composition representing the mantle, for they have been included in processes of differentiation of the mantle. According to Green and Ringwood (1967), the olivine alkali basalt, the most frequently occurring type of basalt in the area investigated in this paper, may originate

(a) if, at a depth of 35 to 70 km, approximately 20% of the mantle material is mobilised by partial melting, or

(b) by fractional crystallization of an olivine tholeiitic magma at the same depth.

The experiments show that orthopyroxene is the first liquidus phase. Clinopyroxene occurs as a second phase only if about 10% of the orthopyroxene has been crystallized. This clinopyroxene has a low calcium content. The separation of these two phases causes a differentiation of the olivine tholeiitic basalt composition of the parental magma to an olivine alkali basalt composition of the residual magma. In this change of composition, the crystallization of orthopyroxene plays the most important role. Since the Ca content is lower in the phases separated than in the parental magma, the residual magma will be enriched in Ca.

What influence would this differentiation process have on the sulfur isotope composition? In the case of the assumed proportion of the residual magma and the crystallized part of the magma, an isotope fractionation would only be measurable if the residual magma were considerably depleted in sulfur. As evidence against crystal fractionation, it must be mentioned that the olivine alkali basalts of the region under investigation contain no relicts of the primary pyroxene. Phenocrysts of pyroxene in these basalts, thoroughly analysed by Gramse (personal communication) by means of an electron microprobe, are normal Ca-rich diopsides, with only slight differences in concentration of the individual elements between the core and outer zones of the crystals. Furthermore, they are hardly different in their composition from the clinopyroxenes of the groundmass of these basalts.

It may, therefore, be concluded that the olivine alkali basalts originated by partial melting of the mantle at depths of 35 to 70 km and that they rose to the surface without a measurable change in their sulfur isotope composition. It is very probable that the parental material for this magma had a sulfur isotope composition of $\delta^{34}\text{S} = +1.0$ to $+1.5$ per mil. This value does not agree with the isotope composition of meteoritic sulfur, but shows, in comparison, an enrichment in ^{34}S of 1.0 to 1.5 per mil. It is not certain whether or not this deviation can be interpreted as a local inhomogeneity of the upper mantle resulting from differentiation processes in the course of the earth's history.

The tholeiitic basalts in the region investigated are, without exception, oversaturated in silica. On an average, the rocks contain 11% quartz in the norm. The basalt from Bühl near Weimar falls near the plane of "silica oversaturation", characterised by the minerals clinopyroxene-plagioklase-orthopyroxene in the "tetrahedran presentation" of Yoder and Tilley (1962). There is no modal hypersthene (Hentschel, 1958), but there is about 20% hypersthene and 2 to 3% quartz in the norm. On the contrary, the tholeiitic basalts of the region under investigation contain without exception orthopyroxenes *and* clinopyroxene.

According to Green and Ringwood (1967), oversaturated basalts may be formed by crystal fractionation under pressure conditions prevailing in less than 15 km depth. In their experiments, only an olivine tholeiitic composition of the parental magma led to an oversaturated tholeiitic composition of the residual magma by segregation of the liquidus phases olivine, clinopyroxene and plagioclase. The opinion of Green and Ringwood is contradicted by the fact that oversaturated tholeiitic basalts from a depth of 60 or more km are particularly frequent, without there being reasons to suppose that the magmas formed at this depth, stopped on their ascent at a more shallow level, started crystal fractionation under the changed pressure and finally continued their ascent. It is particularly disturbing to observe that the tholeiitic basalts are free from those phases whose crystallization and segregation are held responsible for the changing composition of the residual magma. Since this process could only be regarded as a dynamic development finally interrupted by the subsequent eruption, it should be possible to trace the fractionation process from the extruded magmas. Olivine should be present as phenocrysts. However, in the tholeiitic basalts in the region of investigation, this is by no means the case: tholeiitic basalts show no olivine rich inclusions which may be recognised as a residue of fractionation.

Kushiro, Syono and Akimoto (1968) and Kushiro, Yoder and Nishikawa (1968) concluded from their experiments in the system forsterite-quartz-diopside that oversaturated tholeiitic basalts could be formed by partial melting of material of peridotitic composition, provided the H_2O pressure is sufficiently high. The experiments were carried out at 20 kb water pressure. The objection to the possibility that oversaturated basaltic magmas are formed by direct partial melting of the mantle is that a great amount of water is necessary, which cannot be derived from the composition of the mantle. At 20 kb, a forsteritic melt may take up 20% of water. Evidence against high water content in these magmas is the low Fe_2O_3/FeO ratio (0.35) present in the tholeiitic basalts of the investigated area. Engel, Engel and Havens (1965) refer to the relationship between oceanic tholeiitic basalts (olivine tholeiitic basalts) and tholeiitic basalts of the continental regions (oversaturated tholeiitic basalts). They allot the role of a "primitive" parental magma, to the oceanic tholeiitic basalts, the original material of the evolution of magmas of different composition. The elements Si and K, and the trace elements Ba, Cs, Pb, Rb, Sr, Th, U and Zr, enriched in the continental basalts, are regarded as the products of contamination by crustal material. However, this assumption may lead to difficulties in the case of Sr, for indeed, the continental tholeiitic basalts contain more Sr while their $^{87}Sr/^{86}Sr$ ratio, however, is the same as that of the mantle.

The tholeiitic basalts of this kind form the greatest proportion of the continental basalts. Alkali-rich undersaturated basalts and olivine alkali basalts are, however, comparatively rare. According to the estimation of Engel, Engel and Havens (1965), their proportion falls between 1% and 1 0 / $_{00}$ of the total amount of basalts extruded in the course of the earth's history. These observations must be emphasized in any discussion of the genetic relations between the different types of basalts.

The sulfur isotope composition of the tholeiitic basalts investigated leads to the assumption, that their origin differs only slightly from that of the olivine alkali basalts.

In the discussion of the origin of olivine alkali basalt magma, it was assumed that these were derived from mantle material whose sulfur had the isotope composition of $\delta^{34}\text{S} = 1.0$ to 1.5 per mil. This δ value is the highest found in the tholeiitic basalts investigated. In comparison with this value, the greater part of these rocks is depleted in ^{34}S . This is only possible if the pressure and temperature conditions of the magma allow the formation of SO_2 , which, enriched in ^{34}S , may be able to escape from the magma while H_2S is fixed by the sulfides. This is only possible at low total pressure of the magma.

The concentration of the sulfur in the samples of tholeiitic basalts investigated is usually very high, however, in two cases (Borken and Buschhorn) it is very low. If the isotope composition of the sulfur were only determined by the degassing of SO_2 and the fixing of H_2S as sulfide, there should then exist an interdependency between the sulfur isotope composition and the amount of sulfur still present in the rocks. This is not the case, however. This simplified process may, therefore, be superimposed by other processes:

- (a) Gaseous SO_2 as well as H_2S may escape from the magma.
- (b) Different amounts of sulfide may be separated from the magma as an immiscible liquid phase.
- (c) Because of the possible, although only slight, variations in temperature during the eruption of the magma, different amounts of sulfur may be dissolved in the gaseous phase.

Because of their higher oxygen fugacity, the sulfur of the alkali-rich undersaturated basalts is oxidized to form sulfate. This process requires stronger oxidation conditions than the formation of SO_2 . Only after surpassing a particular limiting value of the oxygen fugacity, sulfur may be fixed as sulfate in the crystallizing phases of the rocks. Phenocrysts of hauyne and noseane indicate an early removal of sulfate from the equilibrium between the gaseous and the liquid phases of the magma. In the case of tholeiitic basalts and the olivine alkali basalts, the oxidation of SO_2 to SO_4 is prevented by insufficient oxygen partial pressure. In these rocks SO_2 remains a component of the gaseous phase. As a result, the sulfur isotope composition of the alkali-rich undersaturated basalts is quite different from that of the olivine alkali basalts and the tholeiitic basalts. Bultitude and Green (1968) concluded from their experiments that alkali-rich undersaturated magmas may originate by partial melting of the mantle in the presence of water. Water causes considerable reduction in the temperature of the beginning of melting. The amount and composition of a magma originated in the mantle at a given temperature strongly depends on the amount of water present, apart from other factors. As water is only a minor constituent of the mantle, the relative amount of water in a magma decreases as the amount of magma formed by partial melting increases.

The oxidation conditions prevailing both during the formation of alkali-rich undersaturated basalt magmas and during their crystallization, together with the resulting sulfur isotope compositions, support the theory that these magmas have been formed during rising temperatures in a particular region of the mantle. Their composition may be influenced by processes described as wall rock alteration.

The conclusions drawn from the sulfur isotope composition of the basalts investigated are in agreement with those from the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the same rocks (Hoefs and Wedepohl, 1968). The basalts of the investigated area have low

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7032 to 7049). The mean of 0.7040 corresponds very well with that found for oceanic tholeiitic basalts. Differences between the three types of basalts are very slight. Inhomogeneties of the mantle in the investigated area may be disregarded in the same way, as may be the assimilation of carbonates in the genesis of the alkali-rich undersaturated magmas. If one compares the genetic relationships determined from the sulfur isotope data with the rare earth composition of these samples (Herrmann, 1968), a difference will become obvious: the tholeiitic basalts have approximately the same pattern in lanthanide distribution as the chondrites, while olivine alkali basalts show considerable enrichment of the light rare earth elements. The difference in the sulfur isotope composition of both rocks is much less pronounced. This is only possible if the fractionation processes of the rare earth elements take place under conditions of pressure and temperature which keep the $\text{H}_2\text{S}/\text{SO}_2$ ratio constant.

If the distribution of trace elements and the results of isotope analysis are discussed in connection with the genesis of basalts, the result will be additional facts making it easier to evaluate the various hypotheses, provided that the data from various experiments on phase equilibria, and the behavior of the main chemical components are in agreement.

The analyses of the sulfur isotope composition were carried out because their results provide additional evidence about the oxidation conditions and depth during possible differentiation processes. The sulfur isotope data of the investigated basalts agree only partly with the conclusions on the genesis of basalts based on experiments of Yoder and Tilley (1962), Green and Ringwood (1967), and Bultitude and Green (1968). Their experimental results leave many questions unanswered and contradict several natural observations. However, the sulfur isotope data agree with conditions determined by the analysis of trace elements and isotope analysis of basalts (Gast, 1968). They are based on intensive investigation of the petrographic and chemical features and on numerous trace element and isotope analysis of samples selected for this paper (Wedepohl, 1950, 1954, 1961, 1963, 1968a and 1968b, and in preparation; Herrmann, 1968; Hoefs and Wedepohl, 1968; Gramse, 1968 and in preparation).

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