The isotopic composition of carbonate carbon from deep-sea basalts

HANS-W. HUBBERTEN*

Institut für Petrographie und Geochemie der Universität (TH)
Karlsruhe, Kaiserstrasse 12, D-7500 Karlsruhe, FRG.

(Received October 2, 1981; Accepted December 28, 1981)

Oceanic basalts are often altered by circulating seawater. During this process carbonates are formed frequently as veinlets and crystal aggregates. Additionally hydrothermal carbonate is found occasionally.

The isotopic composition of secondary and possibly primary carbonates has been investigated for 75 samples from Hole 418 A, a 550m long basalt sequence drilled during DSDP Legs 52 and 53 to the south of the Bermuda Rise, in the Atlantic Ocean. Isotope ratios of secondary carbonates, carbonate rich basalts and some of the so called "fresh" basalts have values typical for marine carbonates, i.e., $\delta^{13}\text{C} + 2.8$ to -2.3‰ vs. PDB. Isotope ratios of samples with small carbonate content fall in the range of primary magmatic carbon, i.e., $\delta^{13}\text{C} - 4$ to -8‰ .

The carbon isotope composition of carbonates in oceanic basalts is therefore constituted by an overprinting of seawater-derived secondary carbonates on traces of primary carbonate carbon.

INTRODUCTION

Carbon occurs in basaltic rocks in different forms: as reduced carbon, CO_2 in inclusions and as carbonate which can be present in basaltic rocks in amounts of up to thousands of ppm (HOEFS, 1965).

Isotopic investigations of carbonate carbon in basaltic rocks are rare, compared with carbon isotope investigations for other igneous rocks such as carbonatites. The isotope ratios of carbonate carbon in basaltic rocks which have been published vary in a broad range from $+3.7$ to -25‰ vs. PDB (O'NEIL *et al.*, 1970; HOEFS, 1973; RÖSLER *et al.*, 1977; JAVOY and FOUILLAC, 1980). These results are much scattered from the isotope composition of magmatic carbon in carbonatites, volcanic CO_2 gases and CO_2 in inclusions which ranges from -4 to -8‰ (TAYLOR *et al.*, 1967; DEINES, 1970; PINEAU *et al.*, 1976; PUCHELT and HUBBERTEN, 1980). Because of geological and petrological arguments that favor deep-seated origin and because of balance calculations it is assumed that primary carbon will isotopically fall in this range (PINEAU *et al.*, 1976).

If an isotopic composition of -4 to -8‰ is assumed for primary carbonate carbon, the above mentioned widespread values must be due to an alteration of the isotope composition. This alteration can be produced mainly by three different processes:

- Isotopic fractionation due to a partial degassing during the ascent and cooling of magma (PINEAU *et al.*, 1976).
- Alteration of the primary isotopic composition due to an isotopic exchange with carbonate species of different isotopic composition.
- Overprinting of the primary carbon isotope ratio by the formation of secondary carbonates from low temperature solutions in fractures and vesicles.

Investigations on oceanic basalts which have been cored during various cruises of the D/V Glomar Challenger (Deep Sea Drilling Project) revealed that circulating seawater plays an important role in the alteration processes of the crustal rocks. Besides smectites, zeolites, Fe-Mn-hydroxides and sulfides, various carbonates occur as secondary minerals in the altered parts as vesicle fillings and veins with up to centimeter size.

* Present adress: Inst. de Geol., Univ. Autonoma de Nuevo Leon, Apdo. Postal 104, 67700 Linares, Mexico.

The working hypotheses were tested by analyzing possibly different carbonate carbon species in carbonate aggregates, carbonate rich basalts and "fresh" basalts with a carbonate content of less than 0.3%, from a 550m long basaltic sequence cored during Legs 52 and 53 in the Bermuda Rise region of the Atlantic Ocean.

LOCALITY AND SAMPLING

Figure 1 shows a map of the Bermuda Rise with the various holes which have been drilled during Legs 51 - 53 of the DSDP (November, 1976 to April, 1977).

The Bermuda Rise is a broad topographic feature about 2,000km long and 1,000km wide with a relief of about 1.3km. The material for this investigation came from Hole 418 A which is located at the southern end of the Bermuda

Rise at 25° 02,10' N, 68° 03,44' W in a water depth of 5,511m. The sediment cover in this area is about 320m thick overlying a basaltic basement of Cretaceous age. The oceanic crust consists mainly of pillow basalts and pillow breccia, minor massive basalts and microdolerites which are cut by dykes in deeper levels of the hole. The basalts are almost exclusively plagioclase phyric with subordinate and variable amounts of clinopyroxene and olivine phenocrysts, and rare microphenocrysts of spinel (cf. FLOWER *et al.*, 1980; ROBINSON *et al.*, 1980). Chemically they are classified as K-poor olivine tholeiite and show only little variation throughout the whole cored sequence (EMMERMANN and PUCHELT, 1980).

Most of the basalts appear to be quite fresh. Alteration marked by presence of smectites is locally intense in glassy margins. Secondary carbonates as infillings of veins and vesicles, and

Fig. 1. Map of the Bermuda Rise showing positions of the various Holes drilled during DSDP Legs 51-53.

as groundmass replacement are common (HUMPHRIS *et al.*, 1980). The secondary carbonates mainly consists of calcite and sometimes build up crystals 5 to 10mm in length.

30cc mini-core rock samples were collected on board ship. On one hand, "fresh" samples were collected covering the whole cored sequence; on the other hand particularly carbonate rich samples, as shown by veins or crystal aggregates have been chosen.

ANALYTICAL TECHNIQUES

Wherever possible pure carbonates from veins or crystal aggregates were hand picked before grinding. The samples were then ground in an agate mill to finer than 200 mesh.

The carbonate content was determined for all samples by thermal volatilization and electrochemical determination using an automatic carbon analyzer (Ströhlein Coulomat 701). The precision of the measurements is better than $\pm 5\%$. The preparation for the carbon and oxygen isotope determinations was done according to the method described by McCREA (1950) by disintegrating the carbonates with 100% phosphoric acid. The measurements were carried out on a VG-Micromass 602 C gas-mass spectrometer, the total error of the measurements is less than $\pm 0.2\text{‰}$. The results were corrected after CRAIG (1953) and are given in the usual δ - form relative to the PDB standard.

RESULTS

The carbon and oxygen isotope ratios as well as the CO_2 content of the samples are given in Table 1 and are shown as a function of depth in Fig. 2.

The carbon isotope data for all separated carbonates, for all carbonate rich basalts, and for part of the "fresh" basalts range between $+2.8$ and -2.3‰ and lie therefore within the field of normal marine carbonates. Two samples of the overlying sedimentary sequence show typical values for marine carbonates (-0.2 and $+1.6\text{‰}$). Some "fresh" basalt samples show

lighter carbon isotope values (-3.3 to -8.0‰) and reach the range of primary magmatic carbon. The oxygen isotope ratios lie also mostly in the range which is typical for marine carbonates of Cretaceous age (-2 to -7‰ ; KEITH and WEBER, 1964).

In some of the samples which are depleted in ^{13}C , the oxygen isotope ratios are also shifted to lighter values but they never reach the range which is typical for carbonates formed at high temperatures (-20 to -25‰ (PDB); TAYLOR *et al.*, 1967).

No systematic variation is observed in either $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ - values in relation to the depth.

DISCUSSION

At first sight, it seems as if practically all

Fig. 2. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope ratios of the investigated materials from Hole 418 A as a function of depth.

Table 1. CO_2 content and the isotopic composition of oxygen and carbon for all investigated samples

DSDP Sample Designation (Core-Section, Interval)		Material	Depth (m)	CO_2 (%)	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$
15-1	17-19	Sediment	320.2	n.d.	+1.6	-1.3
15-1	21-22	Carbonate + Sediment	320.2	n.d.	-0.2	-2.8
17-1	101-103	Basalt	333.5	0.33	-2.3	-9.6
18-1	38-40	Basalt	339.4	0.34	-0.6	-5.2
20-2	20-22	Basalt	358.7	0.77	-0.7	-2.0
24-1	95-97	Basalt	377.0	0.45	-5.2	-8.2
26-1	91-93	Basalt	385.4	0.93	-1.1	-4.0
26-4	59-61	Basalt + Carbonate	301.1	6.76	+2.8	-1.7
27-1	36-38	Basalt	393.9	2.47	+2.6	-2.6
30-1	63-65	Basalt	415.1	0.86	+1.1	-5.2
30-1	118-120	Basalt + Carbonate	415.6	24.51	+1.9	-4.7
36-4	10-12	Basalt	471.6	0.32	-3.3	-10.5
37-1	66-68	Carbonate	476.7		+2.1	-5.3
37-1	66-68	Carbonate	476.7		+2.1	-5.5
37-1	66-68	Carbonate	476.7		+1.4	-6.1
38-5	119-121	Basalt	486.7	0.60	-2.7	-10.3
40-2	102-104	Basalt + Carbonate	499.2	6.07	+0.5	-1.1
41-4	32-34	Basalt	503.3	0.45	-1.8	-7.0
43-3	66-68	Basalt	520.2	0.94	-1.5	-3.2
44-3	54-56	Basalt	529.1	0.69	-2.1	-7.5
45-3	118-120	Basalt	538.7	0.26	-6.3	-9.7
45-4	22-30	Basalt	539.2	n.d.	+0.5	-1.1
45-4	36-40	Basalt + Carbonate	539.4	1.33	+0.7	-2.7
46-5	62-64	Basalt	550.1	2.70	+1.2	-1.4
48-2	132-134	Basalt	564.3	2.67	-0.2	-2.5
48-5	21-23	Basalt	567.7	1.35	-0.4	-3.5
49-3	cc	Basalt	573.6	0.30	-1.1	-6.3
50-2	29-32	Basalt	575.3	0.23	n.d.	n.d.
50-3	32-34	Basalt	576.8	0.99	-2.1	-6.3
51-4	69-71	Basalt	588.1	0.30	-1.9	-8.0
52-1	98-100	Basalt	593.0	0.58	0.0	-1.8
52-4	20-25	Basalt + Carbonate	596.9	17.65	+0.8	-6.2
54-2	31-33	Basalt	612.8	0.20	-6.6	-10.4
54-2	45-48	Basalt	613.0	0.70	-0.6	-4.8
55-3	12-14	Basalt	623.5	0.47	+0.1	-1.7
56-6	135-137	Basalt	638.7	0.71	+0.7	-2.8
57-2	80-82	Basalt	641.3	n.d.	-2.8	-5.9
59-2	132-134	Basalt	660.2	0.63	-0.1	-4.3
60-1	18-20	Basalt	667.2	0.28	-2.7	-9.3
62-3	87-90	Basalt + Carbonate	689.9	1.80	-0.3	-8.0
63-2	43-45	Basalt + Carbonate	691.9	8.23	+0.5	-6.7
63-3	109-111	Basalt	694.1	0.16	-5.7	-12.0
64-4	21-23	Basalt + Carbonate	700.2	1.20	-0.4	-5.8
65-4	79-82	Basalt + Carbonate	705.9	12.97	+0.2	-9.7
66-5	244-248	Basalt	712.6	0.86	-0.1	-4.3
66-cc	25-29	Basalt	722.1	0.86	+0.1	-3.7
68-3	19-21	Basalt	732.3	1.09	-2.9	-4.6
69-1	118-122	Basalt	734.8	0.72	-4.9	-10.1
69-1	118-122	Basalt + Carbonate	734.8	4.38	-1.4	-11.7
69-4	100-105	Sediment	740.6	23.50	+0.6	-4.5
69-5	90-95	Basalt + Pyrite	741.8	n.d.	-1.6	-5.4
69-6	64-66	Basalt + Pyrite	742.7	0.34	-2.3	-6.0
70-1	83-87	Basalt + Pyrite	744.0	1.43	+0.2	-1.4
70-4	108-111	Basalt	748.8	0.87	+0.2	-4.3
70-5	9-13	Basalt	749.2	0.64	+0.1	-2.9
70-5	93-95	Basalt	750.0	0.75	-0.6	-3.5
71-3	120-124	Basalt	756.9	1.47	+0.7	-1.8
73-2	137-140	Basalt + Carbonate	767.7	1.33	+0.8	-1.3
74-1	12-14	Basalt + Carbonate	774.4	15.77	+0.8	-8.9
74-6	85-86	Basalt	782.7	0.18	-6.7	-14.6
76-2	33-36	Basalt	788.9	0.75	n.d.	n.d.
77-2	42-44	Basalt + Carbonate	795.0	3.87	+1.2	-1.9
77-2	42-44	Carbonate	795.0		+0.9	-3.9
77-3	88-90	Basalt	796.9	0.76	-0.8	-2.9
78-5	117-120	Basalt	809.6	1.10	+0.3	-4.0
79-5	65-67	Basalt	819.1	0.41	-0.3	-2.0
80-4	22-26	Basalt	826.7	1.05	+0.2	-3.4
81-4	136-140	Basalt	836.9	0.10	-5.4	-10.9
83-1	144-147	Basalt	842.0	0.73	0.0	-3.7
83-4	60-63	Basalt	845.6	0.81	+0.1	-3.7
85-1	146-148	Basalt	851.5	0.21	-2.4	-3.2
85-5	120-122	Basalt	857.2	5.12	-0.5	-10.9
85-6	127-131	Basalt	859.3	n.d.	-8.0	-10.1
85-7	86-88	Basalt	859.9	0.81	-1.3	-3.6
86-3	144-147	Basalt + Carbonate	864.0	6.90	+0.9	-9.0
?	?		?	0.70	-1.2	-5.4

carbonates occurring in the studied deep sea basalts would have resulted from cold seawater interaction. When studying in detail the data, a systematic distinction between two groups can be shown. The carbonates and the carbonate rich basalts display a trend which is different from that of the "fresh" basalts when all samples are plotted as a function of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ (see Fig. 3).

The "fresh" basalts (filled symbols) show a decrease in $\delta^{13}\text{C}$ with decreasing $\delta^{18}\text{O}$. The carbonates and the carbonate rich basalts show only a decrease in $\delta^{18}\text{O}$ without a simultaneous decrease in $\delta^{13}\text{C}$ which only varies about the mean value of normal marine carbonate. The effect observed in the "fresh" basalts can either be due to an equilibrium fractionation of both isotopic species at lower temperatures or to varying admixtures of secondary marine carbonates to a primary magmatic carbonate.

To produce isotope ratios as those observed in the carbonate rich basalts and the separated carbonates a larger carbon reservoir has to be assumed which could correspond to seawater. It seems that an alteration process accompanied by the formation of secondary marine carbonates affected most of the samples, even those

Fig. 3. $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ of the investigated samples (the shaded area indicates the range of the assumed primary carbon).

Fig. 4. Carbonate content (% CO_2) in relation to the carbon isotope composition.

which were considered to be "fresh".

The fact that primary carbonate carbon unaffected by secondary processes is present in some of the basalts is indicated in Fig. 4 which shows the relationship between the $\delta^{13}\text{C}$ values and the CO_2 content. In a large range of carbonate content the carbon isotope values are scattered about the value of marine carbonate carbon. With decreasing carbonate content, the almost vertical trend turns toward isotopically lighter carbon at a carbonate content of about 1% CO_2 . The lower the carbonate content, the lighter are the carbon isotope ratios until they reach values of -4 to -8‰ .

These values are in the same range as in carbonatites, volcanic gases and CO_2 inclusions in oceanic basalts (TAYLOR *et al.*, 1967; DEINES,

1970; PINEAU *et al.*, 1976; PUCHELT and HUBBERTEN, 1980), all of which are assumed to represent primary carbon. The preservation of such primary carbonate was assumed by JAVOY and FOUILLAC (1980) in some of the samples they analyzed from Holes 417A and 417D of Leg 51, DSDP.

Due to a low temperature alteration resulting, among other authigenic products, in the formation of seawater-derived carbonates a progressive increase in carbonate content up to about 1% CO₂ will produce a gradual enrichment in ¹³C. Assuming $\delta^{13}\text{C}$ values of -6 and 0‰ for primary and secondary carbonates, respectively, $\delta^{13}\text{C}$ of -0.6‰ is expected when 0.2% CO₂ increases to 1% by addition of secondary carbonate.

Compared with the alteration of terrestrial basalts, seawater alteration of oceanic basalts produces a different shift of the primary carbon isotope composition. Terrestrial basalts are affected by solutions containing carbon species which can be derived from various sources: air CO₂, dissolved HCO₃, organogenically derived CO₂, etc. The result of this alteration will be a shift to lighter or to heavier values. The widely scattered values which have been reported by O'NEIL *et al.* (1970) and HOEFS (1973) can partly be explained by such mechanisms.

When alteration by cold seawater takes place, the carbonate carbon isotope composition can only be shifted toward heavier values. No lighter carbonate can therefore be formed through submarine alteration processes but can only be of primary origin. Light carbon isotope values (to the -25‰ range) as observed by O'NEIL *et al.* (1970) and HOEFS (1973) in carbonate bearing terrestrial basalts were not measured in the investigated oceanic basalts.

The alteration mechanisms of oceanic basalts and the fact that light isotope values are found in carbonate poor basalts lead to the conclusion that traces of primary carbonate carbon with an isotopic ratio from -4 to -8‰ are present in these carbonate-poor basalts.

Acknowledgements—This study was suggested by Prof.

Dr. H. PUCHELT, Karlsruhe who made valuable suggestions during the investigations and writing up of the manuscript. Drs. J. HOEFS, Göttingen and J. HONNOREZ, Miami critically reviewed the manuscript. The investigations were supported by a grant of the Deutsche Forschungsgemeinschaft, Bonn.

I want to thank all individuals and institutions which thus contributed to the investigations.

REFERENCES

- CRAIG, H. (1953) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochim. Cosmochim. Acta* 12, 133–149.
- DEINES, P. (1970) The carbon and oxygen isotopic composition of carbonates from the Oka carbonatite complex, Quebec, Canada. *Geochim. Cosmochim. Acta* 34, 1199–1225.
- EMMERMANN, R. and PUCHELT, H. (1980) Major and trace element chemistry of basalts from Holes 417D and 418A, Deep Sea Drilling Project Legs 51–53. In DONNELLY, T., FRANCHETEAU, J., BRYAN, W., ROBINSON, P., FLOWER, M., SALISBURY, M., *et al.*, Initial Repts. Deep Sea Drilling Project, 51, 52, 53, Part 2; Washington (U.S. Government Printing Office), 987–1000.
- FLOWER, M. F. J., OHNMACHT, W., ROBINSON, P. T., MARINER, G. F. and SCHMINCKE, H.-U. (1980) Lithologic and chemical stratigraphy at Deep Sea Drilling Project Sites 417 and 418. In DONNELLY, T., FRANCHETEAU, J., BRYAN, W., ROBINSON, P., FLOWER, M., SALISBURY, M., *et al.*, Initial Repts. Deep Sea Drilling Project, 51, 52, 53, Part 2; Washington (U.S. Government Printing Office), 939–956.
- HOEFS, J. (1965) Ein Beitrag zur Geochemie des Kohlenstoffs in magmatischen und metamorphen Gesteinen. *Geochim. Cosmochim. Acta* 29, 399–428.
- HOEFS, J. (1973) Ein Beitrag zur Isotopengeochemie des Kohlenstoffs in magmatischen Gesteinen. *Contrib. Mineral. Petrol.* 41, 277–300.
- HUMPHRIS, S. E., THOMPSON, R. N. and MARINER, G. F. (1980) The mineralogy and geochemistry of basalt weathering, Holes 417 A and 418 A. In DONNELLY, T., FRANCHETEAU, J., BRYAN, W., ROBINSON, P., FLOWER, M., SALISBURY, M., *et al.*, Initial Repts. Deep Sea Drilling Project, 51, 52, 53 Part 2: Washington (U.S. Government Printing Office), 1201–1217.
- JAVOY, M. and FOUILLAC, A. M. (1980) Stable isotope ratios in Deep Sea Drilling Project Leg 51 basalts. In DONNELLY, T., FRANCHETEAU, J., BRYAN, W., ROBINSON, P., FLOWER, M., SALISBURY,

- M., *et al.*, Initial Repts. Deep Sea Drilling Project, 51, 52, 53 Part 2: Washington (U.S. Government Printing Office), 1153–1157.
- KEITH, M. L. and WEBER, J. N. (1964) Isotopic composition and environmental classification of selected limestones and fossils. *Geochim. Cosmochim. Acta* 28, 1787–1816.
- MCCREA, J. M. (1950) The isotopic chemistry of carbonates and a palaeotemperature scale. *J. Chem. Phys.* 18, 849–864.
- O'NEIL, J. R., HEDGE, C. E. and JACKSON, E. D. (1970) Isotopic investigations of xenoliths and host basalts from the Honolulu volcanic series. *Earth Planet. Sci. Lett.* 8, 253–257.
- PINEAU, F., JAVOY, M. and BOTTINGA, Y. (1976) $^{13}\text{C}/^{12}\text{C}$ ratios of rocks and inclusions in popping rocks of the Mid-Atlantic Ridge and their bearing on the problem of isotopic composition of deep-seated carbon. *Earth Planet. Sci. Lett.* 29, 413–421.
- PUCHELT, H. and HUBBERTEN, H.-W. (1980) Vulkanogenes Kohlendioxid: Aussagen zur Herkunft aufgrund von Isotopenuntersuchungen. *ZfI Mitt.* 30, Leipzig, 198–210.
- RÖSLER, H.-J., NESTLER, P., MUCKE, D. and DIETZE, W. (1977) Zur Herkunft der Karbonate in basischen Gesteinen aufgrund von ^{18}O und ^{13}C - Isotopenuntersuchungen. *Z. angew. Geol.* 23, 390–393.
- ROBINSON, P. T., FLOWER, M. F. J., SWANSON, D. A. and STAUDIGEL, H. (1980) Lithology and eruptive stratigraphy of Cretaceous oceanic crust, Western Atlantic Ocean. In DONNELLY, T., FRANCHETEAU, J., BRYAN, W., ROBINSON, P., FLOWER, M., SALISBURY, M., *et al.*, Initial Repts. Deep Sea Drilling Project, 51, 52, 53 Part 2: Washington (U.S. Government Printing Office), 1535–1555.
- TAYLOR, H. P., FRECHEN, J. and DEGENS, E. T. (1967) Oxygen and carbon isotope studies of carbonatites from the Laacher See district, West Germany and the Alno district, Sweden. *Geochim. Cosmochim. Acta* 31, 407–430.