37. OXYGEN- AND HYDROGEN-ISOTOPE COMPOSITION OF SOME BASALTS FROM DEEP SEA DRILLING PROJECT HOLE 504B, COSTA RICA RIFT, LEGS 69 AND 70[1]

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ABSTRACT

Whole-rock basalt samples from the upper half of Deep Sea Drilling Project Hole 504B have oxygen-isotope compositions typical of mid-ocean-ridge basalts which have experienced a moderate degree of low-temperature alteration by sea water. By contrast, $\delta^{18}O$ values in the lower half of the hole correspond to basalts which have experienced almost no detectable oxygen-isotope alteration. These observations suggest that the overall water/rock ratio was lower in the lower half of the drilled crust. A correlation between $\delta^{18}O$ values and $^{87}Sr/^{86}Sr$ ratios suggests that the water/rock ratio, rather than temperature variation, was the main factor determining basalt $\delta^{18}O$ values. Hydrogen-isotope data appear to be consistent with a low water/rock ratio in the lower part of the crust.

INTRODUCTION

In order to provide further data on the extent of alteration of the 5.9-m.y.-old basalt crust drilled at Hole 504B (1°14′N, 83°44′W, near the Costa Rica Rift), the oxygen-isotope composition of whole-rock samples has been determined. Sr-isotope data (Barrett, this volume) indicate that the basalts in the upper part of the hole have been isotopically altered by basalt–sea-water interaction, whereas basalts in the lower part of the hole have maintained essentially primary Sr-isotope ratios. It is therefore of interest to establish whether $\delta^{18}O$ values reveal the same pattern of isotopic alteration. δD values were also measured to determine if variations with depth exist.

Mid-ocean-ridge basalts which have not experienced sea-water alteration have a very restricted range in $\delta^{18}O$ values: $5.8 \pm 0.3‰$ (Taylor, 1968; Muehlenbachs and Clayton, 1972; Muehlenbachs, 1980). However, basalts affected by low-temperature sea-water alteration display increased $\delta^{18}O$ values. This results mainly from the formation of secondary smectitic clays, which have $\delta^{18}O$ values notably higher than that of fresh basalt. Javoy and Fouillac (1980) reported $\delta^{18}O$ values of about 27‰ for vein smectites from Legs 51 to 53. A basalt containing 10% smectite of this isotopic composition would have an initial whole-rock value of 5.8‰ increased to 7.6‰.

The extent of oxygen-isotope alteration depends in part on the amount of oxygen made available to the basalts by circulating sea water, i.e., the water/rock ratio. A second factor is the temperature at which alteration takes place. With increasing temperatures, O-isotopic fractionations between silicates and water decrease, so that—all other factors being equal—whole-rock ^{18}O enrichments are lessened. Eventually, at temperatures of about a few hundred degrees, rock–water fractionations decrease to the point where the $\delta^{18}O$ value of an altered basalt is essentially the same as that of fresh basalt. Basalts from ophiolite complexes metamorphosed in the zeolite to lower greenschist facies commonly have $\delta^{18}O$ values of 7 to 13‰ (Spooner et al., 1974; Heaton and Sheppard, 1977; McCulloch et al., 1980). However, for upper greenschist to amphibolite facies metabasic rocks, these authors report $\delta^{18}O$ values ranging from about 6‰ down to as low as 3‰. Such low values are due primarily to the much-reduced whole-rock–water fractionation factors at high temperatures.

In the case of Hole 504B basalts, the presence of smectitic but absence of chloritic secondary minerals suggests that the temperature range over which alteration by sea water occurred probably was limited, and temperatures relatively low. At present, the temperature at the base of the hole (563 m sub-basement) is about 120°C. Over most of the crustal history, temperatures were likely lower, not higher, because of entrainment of cold sea water through basement outcrops now covered by sediment (R. Von Herzen, pers. comm., 1981). Therefore, temperature may not have been an important parameter in determining whole-rock $\delta^{18}O$ variations. Instead, as discussed below, the water/rock ratio appears to have been the controlling factor.

EXPERIMENTAL

The sample powders used for isotopic analysis represent splits of whole-rock samples which have also been analyzed (in a different laboratory) for strontium and lead isotopes (Barrett, this volume). Samples are vein-free, and do not include local breccia zones or the volumetrically insignificant glassy flow margins. Oxygen-isotope compositions were measured with a 60°, 15-cm single focusing mass spectrometer. Oxygen was extracted from powders by the bromine pentafluoride procedure (Clayton and Mayeda, 1963). Oxygen-isotope compositions are reported in common δ-notation relative to SMOW (Standard Mean Ocean Water). Routine reproducibility of $\delta^{18}O$ values of replicate analyses is typically 0.15‰. Hydrogen was extracted from the samples, following overnight heating at 150°C, using the method described by Godfrey (1962). Typical reproducibility of δD values is 2‰.

[1] Cann, J. R., Langseth, M. G., Honnorez, J., Von Herzen, R. P., White, S. M., et al., *Init. Repts. DSDP*, 69: Washington (U.S. Govt. Printing Office).
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RESULTS AND DISCUSSION

Oxygen Isotopes

Whole-rock $\delta^{18}O$ values are given in Table 1 and plotted as a function of sub-basement depth in Figure 1. $\delta^{18}O$ values range from 6.4 to 7.8‰ in the upper 260 meters, 6.2 to 6.4‰ in the interval 270 to 320 meters, and 5.8 to 6.2‰ in the interval 320 to 560 meters. The $\delta^{18}O$ values in the upper 260 meters overlap with, but are toward the lower end of, the data range reported for basalts recovered from deep holes in the ocean crust (Fig. 2). By contrast, the $\delta^{18}O$ values in the lower interval from 320 to 560 meters are uniformly very low, and correspond to basalts which have experienced almost no detectable oxygen-isotope alteration. The deep holes drilled to date in the oceanic crust have not intersected comparable large vertical intervals with such uniformly low $\delta^{18}O$ values.

In Figure 3, the $\delta^{18}O$ data for the Hole 504B basalts are plotted against $^{87}Sr/^{86}Sr$ ratios for the same sample set (Barrett, this volume). The strontium-isotope composition of a basalt provides an indication of the water/rock ratio during sea-water–rock interaction, higher values reflecting greater water/rock ratios (see discussion in Barrett, this volume). Strontium-isotope fractionations, unlike $\delta^{18}O$ values, are not affected by temperature. The positive linear correlation seen in Figure 3 between $\delta^{18}O$ values and $^{87}Sr/^{86}Sr$ ratios therefore suggests that the range in $\delta^{18}O$ values has resulted from variation in the water/rock ratio, not temperature, during alteration. The observed downhole changes in vein mineralogy (summarized in Barrett, this volume) would also be consistent with changes in water/rock ratio.

The main alteration mineral in Hole 504B is smectite, which pseudomorphs olivine phenocrysts, replaces interstitial glass, and occasionally fills vesicles. Its modal abundance is typically 5 to 10%, and there appears to be no significant variation in its non-vein distribution throughout the hole. The fact that basalts from the lower part of the hole have oxygen-isotope compositions close to that of fresh oceanic basalt therefore may seem rather surprising. This observation requires that smectites in the lower part of the hole have lower $\delta^{18}O$ values than those in the upper part, so that whole-rock $\delta^{18}O$ values are thereby lowered. Smectite $\delta^{18}O$ values of 10‰ or less would be required to account for the whole-rock $\delta^{18}O$ values of less than 6.2‰ for the lower half of the hole.

A possible way of producing low smectite $\delta^{18}O$ values (other than by increase in temperature) is by forming the smectite from pore waters which have been depleted in $\delta^{18}O$ by previous sea-water–basalt interaction. Formation of alteration minerals such as smectite and Fe-hydroxides will produce modified sea-water $\delta^{18}O$ values of less than zero (cf. Lawrence et al., 1975). Pore waters could become substantially depleted if convective circulation does not occur in the basement, i.e., if water/rock ratios are low. To date, we have been able to separate only one sufficiently pure smectite for reliable analysis. This sample, from the upper part of the hole (504B-22-2, 74–78 cm), yielded a $\delta^{18}O$ value of 14.1‰. This is notably lower than values of about 27‰ recorded from Legs 51 to 53 (Javoy and Fouillac, 1980) for vein fillings apparently formed from normal, freely flowing sea water (Lawrence, 1980; Muehlenbachs, 1980). It seems possible that smectites from whole-rock samples in the lower part of the hole could have even lower $\delta^{18}O$ values, given the lower water/rock ratios for this part of the hole indicated by the strontium-isotope compositions. Work in progress should help to resolve this question. (It is worth noting that low water/rock ratios can provide enough water for smectite formation without significantly affecting whole-rock oxygen-isotope composition. For example, a water/rock ratio as low as 1 to 100 could still provide enough OH for the formation of 10% smectite if all of the water were incorporated into the basalt during alteration.)

Table 1. $\delta^{18}O$ and δD whole-rock values, lithology, and nature of alteration of basalts from Hole 504B, Costa Rica Rift.

Sample No.	DSDP Sample	Lithology	Alteration[a]	$\delta^{18}O$ (‰)	δD (‰)
1	504B-3-1 (Piece 253, 102–105 cm)	Fine-grained aphyric basalt; pillow or thin flow (80 cm thick); sample from middle	G,R	7.4	−108
2	504B-8-3 (Piece 540, 75–80 cm)	Medium-grained, subaphyric basalt; massive flow (at least 1.5 m thick); sample from middle	G	7.0	−107
3	504B-13-2 (Piece 779, 86–89 cm)	Fine-grained aphyric basalt; pillow or thin flow; sample from middle	G,R	7.7	−112
4	504B-19-2 (Piece 1145, 82–85 cm)	Fine-grained moderately Pl-Ol-Cpx-phyric basalt; pillow; sample from middle	G	6.6	−101
5	504B-25-2 (Piece 1434, 97–101 cm)	Fine-grained aphyric basalt; pillow or thin flow (55 cm thick); sample from middle	G	6.6	−101
6	504B-29-1 (Piece 1569, 50–52 cm)	Fine-grained aphyric basalt; probably pillow material	G	6.9	−108
7	504B-33-1 (Piece 184, 28–30 cm)	Medium-grained highly Ol-Pl-phyric basalt; massive unit (~3 m thick); sample from ~70 cm below top	G,R	6.8	−97
8	504B-34-2 (Piece 242, 32–37 cm)	Fine-grained moderately Pl-Ol-phyric basalt; pillow; sample from margin	G,R	7.4	−103
9	504B-36-2 (Piece 307, 44–46 cm)	Medium-grained moderately Pl-phyric basalt; massive unit ~6 m thick); sample from ~2 m below top	G,P	6.3	—
10	504B-38-1 (Piece 420, 90–92 cm)	Medium-grained moderately Ol-Pl-Cpx-phyric basalt; pillow interior	G,R,P	6.2	−111
11	504B-41-2 (Piece 599, 17–19 cm)	Medium-grained moderately Pl-Ol-phyric basalt; massive flow (~14 m thick); sample from margin	G	6.4	−87
12	504B-46-1 (Piece 778, 112–116 cm)	Fine-grained sparsely Pl-phyric basalt; pillow; sample from margin	G	6.2	—
13	504B-52-3 (Piece 1030, 62–65 cm)	Medium-grained sparsely Ol-Pl-phyric basalt; massive unit (at least 4 m thick); sample from middle	G,P	6.0	−84
14	504B-57-1 (Piece 1139, 83–88 cm)	Fine-grained moderately Pl-Ol-phyric basalt; pillow; sample from margin	G	6.1	−86
16	504B-64-2 (Piece 1436, 125–130 cm)	Medium-grained aphyric basalt; massive flow (~1.5 m thick); sample from lower portion	G,P	6.0	−116
17	504B-70-2 (Piece 1563, 3–7 cm)	Coarse-grained ophitic basalt; massive flow (or sill) of unknown thickness; sample from ~25 cm below top	G	5.8	−89
Average of samples 1 to 8 inclusive				7.1	
Average of samples 9 to 11 inclusive				6.3	
Average of samples 12 to 17 inclusive				6.0	

[a] G = colorless to green smectites occurring as alteration products of olivine and glass, and as vesicle fillings. R = reddish-brown alteration minerals indicative of relatively oxidizing conditions (hematite, Fe-hydroxide, iddingsite), occurring as alteration products of olivine and glass, and as vesicle fillings. P = pyrite, suggestive of relatively reducing conditions; where pyrite is indicated, it is not present in the sample, but in veins within 30 cm above or below it.

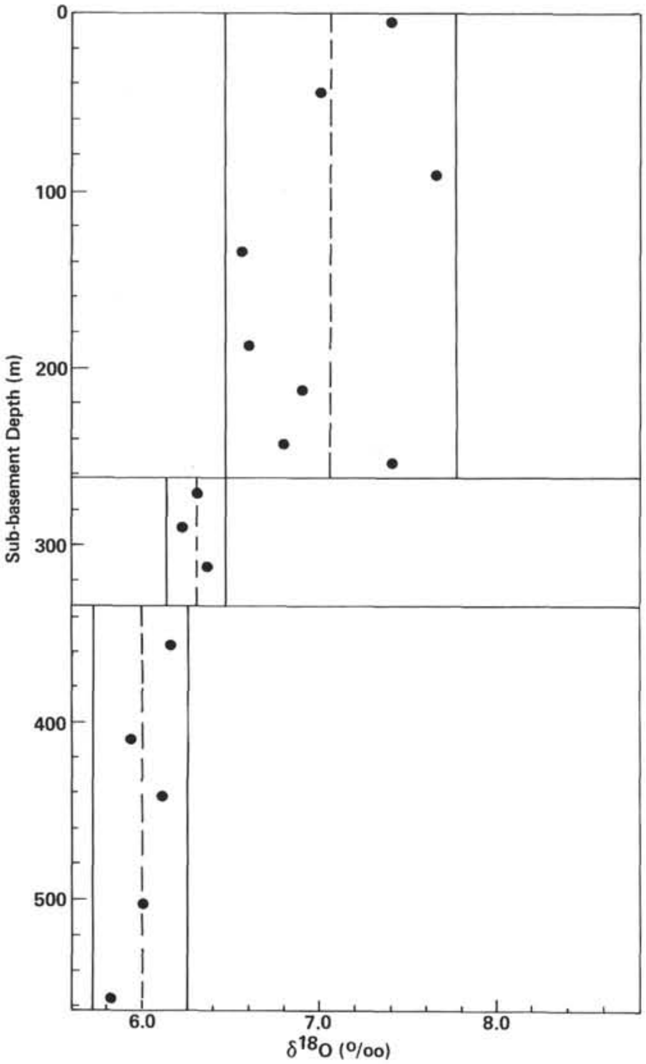

Figure 1. $\delta^{18}O$ values versus sub-basement depth for basalts from Hole 504B, Costa Rica Rift. The solid vertical lines give the range in $\delta^{18}O$ values for a given section of the hole; the dashed lines represent the mean. The horizontal divisions between sections are arbitrarily drawn halfway between flanking data points.

Although the Hole 504B basalts do display a range of $\delta^{18}O$ values, it is clear from Figure 2 that the *overall* degree of oxygen-isotope alteration is limited relative to that of other deep holes. This limited alteration is not simply a function of the youth of the 504B crust. In the Atlantic, rocks of Hole 395A, of similar age, and rocks of Holes 332A and 332B, which are younger, display higher degrees (and deeper extents) of oxygen-isotope alteration. It appears that the crust at these latter sites has experienced higher overall water/rock ratios than at 504B. One reason for this may be the greater number of deep faults which dissect slow-spreading ridges; this could allow more thorough penetration of sea water into the crust. The lower water/rock ratio of the lower part of Hole 504B crust (relative to the upper part) additionally may have been affected by factors such as decrease in void space through mineral precipitation and overburden pressure, and increase in the proportion of massive lava flows below about 230 meters sub-basement depth.

Hydrogen Isotopes

Whole-rock δD values are given in Table 1 and plotted as a function of sub-basement depth in Figure 4. The dashed lines in the figure represent the range of most analyses (90% of 111) previously reported for basalts from deep DSDP holes (Hoernes et al., 1978; Hoernes and Friedrichsen, 1978; Friedrichsen and Hoernes, 1980).

The upper 300 meters of basalts from Hole 504B have δD values ranging from −97 to −112‰, and lie within the range of typical oceanic basalts which have undergone low-temperature alteration. These values mainly reflect the δD composition of smectite, which, as the main hydrated mineral in the basalts, is the dominant source of hydrogen. The δD values of basalts below 300 meters are, with one exception, isotopically somewhat heavier than basalts from the upper part of the hole. These heavier values are consistent with a lower water/rock ratio in the lower part of the hole. In such a case, initial smectite-forming reactions could raise the δD value of the "stagnant" sea water (to values greater than zero), so that later smectites, and therefore whole rocks, would have heavier δD compositions.

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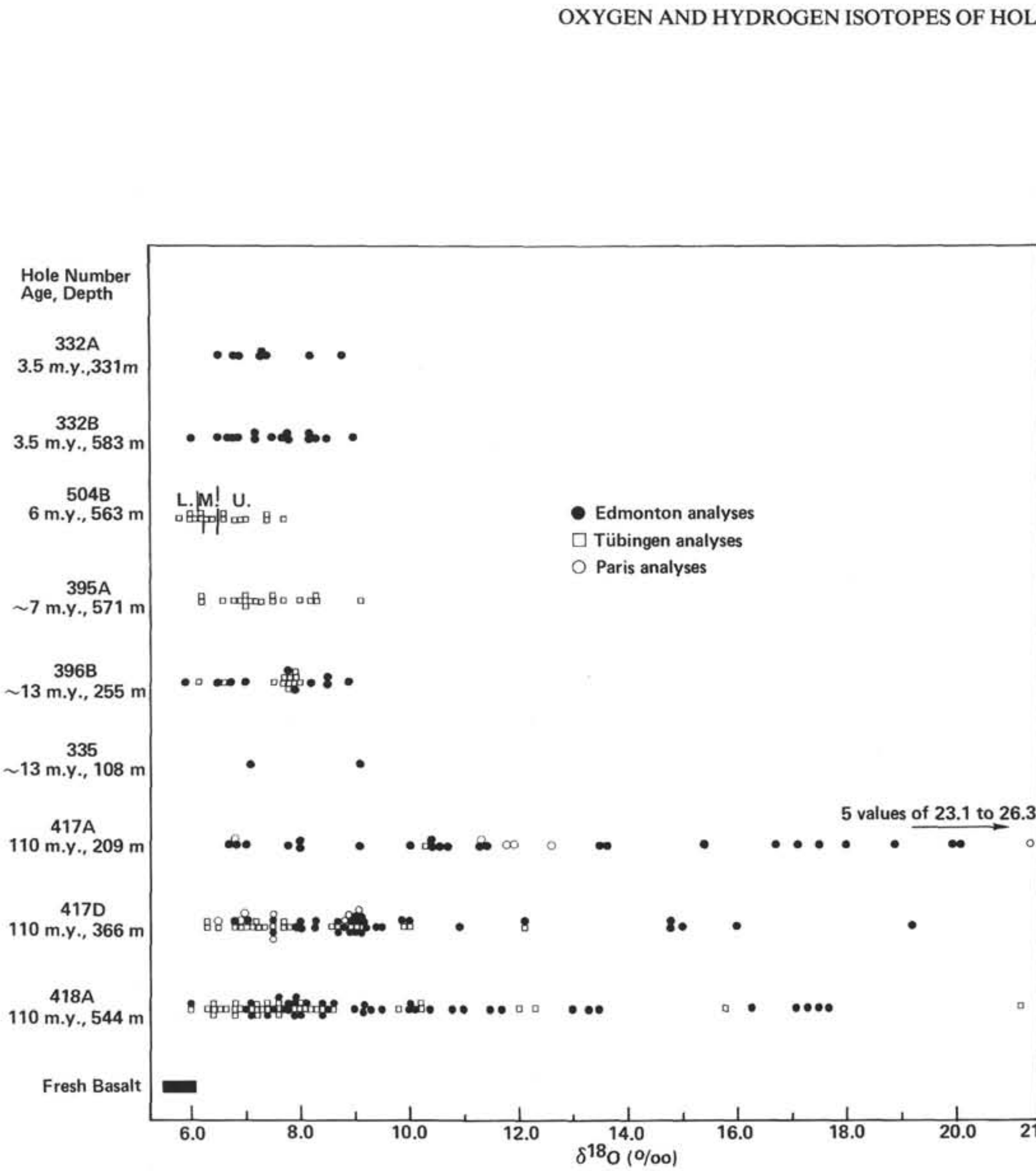

Figure 2. Plot of $\delta^{18}O$ values of Hole 504B basalts, and $\delta^{18}O$ data obtained from the deep holes drilled by DSDP in the Atlantic Ocean. The Hole 504B basalts are divided into upper (U.), middle (M.), and lower (L.), as in Figure 1. Sources of data are as follows: Holes 332A, 332B, and 335: Gray et al. (1977) (filled circles), Muehlenbachs (1977) (calcite-bearing samples omitted) (filled circles); Hole 395A: Hoernes et al. (1978) (squares); Hole 396B: Hoernes and Friedrichsen (1978) (squares), Muehlenbachs and Hodges (1978) (filled circles); and Holes 417A, 417D, and 418A: Muehlenbachs (1980) (filled circles), Friedrichsen and Hoernes (1979) (squares), Javoy and Fouillac (1980) (open circles). The data indicate that $\delta^{18}O$ values of Atlantic oceanic crust less than about 10 to 15 m.y. old range from 6 to 9‰, with a mean of 7.5‰ (69 analyses). In Holes 417D and 418A, situated in 110-m.y.-old Atlantic crust, there is a clustering of data over the range of 6 to 10‰; however, much higher values also occur. The average $\delta^{18}O$ value for these two holes is 9.2‰ (131 analyses). Hole 417A is considered separately, because it contained common breccias and hyaloclastites, and because it probably was subjected to cold-water alteration longer than the other sites, as a result of being on a topographic high (Muehlenbachs, 1980). The average $\delta^{18}O$ value for Hole 417A is 15.5‰ (30 analyses). Most of the high values in 110-m.y.-old crust come from the upper 100 to 300 meters of the basalt section. It appears that oceanic crust in the Atlantic achieves a significant degree of oxygen-isotope alteration before ~10 to 15 m.y., and possibly as early as 3.5 m.y. After this, oxygen-isotope alteration by cold sea water probably proceeds slowly, sea-water circulation generally being restricted to the upper few hundred meters of crust (Muehlenbachs, 1980). However, given sufficient time and access to sea water, the degree of oxygen-isotope alteration can become extensive. Data from Hoernes and Friedrichsen (1977) for Hole 332A basalts (28 values with a mean of 5.9‰) have not been included in the diagram, because their samples were not selected randomly, but specifically for freshness.

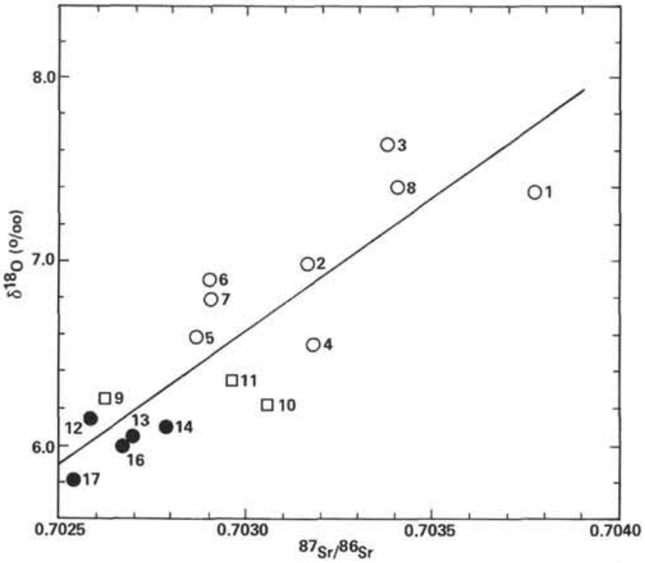

Figure 3. Plot of $\delta^{18}O$ versus $^{87}Sr/^{86}Sr$ for basalts from Hole 504B, Costa Rica Rift. Numbers correspond to samples listed in Table 1 (and also to samples in Table 1 of Barrett, this volume). Open circles: 0 to 270 meters; squares: 270 to 320 meters; closed circles: 320 to 560 meters. The least-squares fit is given by the equation $\delta^{18}O = (1.435 \times 10^3)(^{87}Sr/^{86}Sr) - (1.002 \times 10^3)$; correlation coefficient, $r = 0.72$.

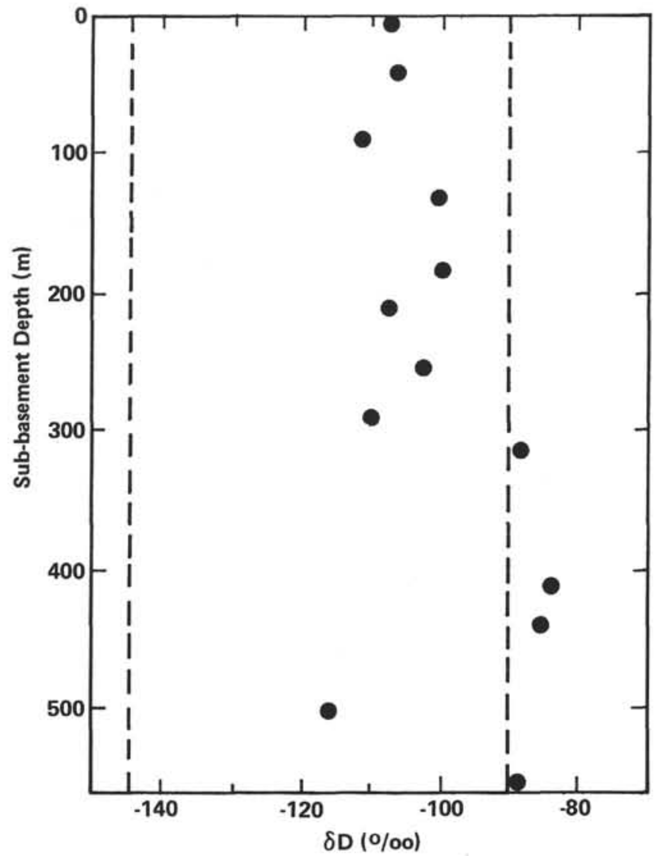

Figure 4. δD values versus sub-basement depth for basalts from Hole 504B, Costa Rica Rift. Dashed lines discussed in text.