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INTERACTION BETWEEN SEA WATER AND OCEANIC LAYER TWO AS A FUNCTION OF TIME AND DEPTH — I. FIELD EVIDENCE

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ABSTRACT

Sea water circulating through oceanic basalts may be an important mechanism in the extraction and concentration of certain elements in the oceanic crust. In this work chemical data compiled from three oceanic environments, the Mid-Atlantic Ridge at 45°N, the Bermuda seamount and the Mid-Atlantic Ridge at 36°N, are presented in an attempt to elucidate the chemical changes caused by halmyrolysis and low- medium-temperature sea water circulation.

Basalts from the Mid-Atlantic Ridge at 45°N are represented only by pillow basalts dredged from the surface of the ocean floor. In these the major chemical trends caused by halmyrolysis are a gain of K_2O, P_2O_5, MnO_2, H_2O and CO_2 with lesser gains of TiO_2 and Fe^{TOT}. SiO_2 is depleted in altered basalts and with severe alteration Al_2O_3 is also lost. Na_2O shows a small but definite decrease with alteration whereas CaO and MgO remain unchanged although they are redistributed into different crystalline phases.

Basalts of the Bermuda seamount, sampled by drilling to a depth of 800m, provided the first opportunity to study the effect of halmyrolysis with depth and with elevated temperatures. The Bermuda tholeiites, like the pillow basalts on the ocean floor, have been depleted in Al_2O_3 and SiO_2 while being enriched in K_2O, CO_2, H_2O and to a lesser extent P_2O_5. There appears to be no significant change in CaO, MnO and TiO_2 in the Bermuda lavas but in contrast to surface pillows there is enrichment in Na_2O and depletion of MgO. Chemical variations through a single volcanic unit indicate that the alteration history of the Bermuda lavas was quite complex and that considerable redistribution of elements such as Na took place. Chemical reorganization within the Bermuda basalt pile may be the result of reheating the basalt during later episodes of igneous activity.

Basalts of the Mid-Atlantic Ridge at 36°N were sampled to a maximum depth of 582.5m during leg 37 of the Deep Sea Drilling Project. It is difficult to detect chemical variation with depth attributable to halmyrolysis because its effect is commonly less than the original chemical and mineralogical variations of the basalts.

Chemical analyses of unaltered sideromelane fragments recovered at different depths in the leg 37 drill holes are thought to approximate original unaltered basalt compositions. Thus, after the chemical effects of phenocrysts within the basalts are taken into account, differences in chemistry between sideromelane and equivalent basaltic rocks may be representative of halmyrolysis effects. It is significant that glasses are enriched in SiO_2, TiO_2, Fe^{TOT} and Al_2O_3 relative to the composition of equivalent basalts. The glasses are depleted in K_2O whereas CaO, Na_2O and MgO are present in equal concentrations in both sideromelane and basalt.

SOMMAIRE

La circulation de l'eau de mer à travers des basaltes océaniques parait un mécanisme important de lessivage et concentration de certains éléments dans la croûte océanique. Dans ce travail qui porte sur trois environnements océaniques, la dorsale médio-atlantique à 45°N, à 36°N, et des Bermudes, des données chimiques permettent d'évaluer les changements occasionnés par l'halmyrolyse et par la circulation de l'eau à basses et moyennes températures. Les basaltes de la dorsale medio-atlantique à 45°N proviennent uniquement de laves en coussin draguées des fonds océaniques. L'halmyrolyse a causé un accroissement en K_2O, P_2O_5, MnO_2, H_2O, et CO_2, et des gains plus légers en TiO_2 et Fe^{TOT}. La silice diminue dans les basaltes altérés, ainsi que Al_2O_3 dans les basaltes très altérés. Le Na_2O décroît très légèrement, tandis que CaO et MgO sont demeurés stationnaires quoique redistribués parmi de nouvelles phases cristallines. Les basaltes du haut-fond des Bermudes, échantillonnés par sondage jusqu'à 800m, nous donnent l'occasion d'étudier les effets de l'halmyrolyse à profondeur et à température élevées. Les tholéiites des Bermudes, tout comme les basaltes à coussin des fonds océaniques, ont été lessivés de SiO_2 et Al_2O_3, et enrichis en K_2O, CO_2, H_2O, et à un degré moindre, P_2O_5. Il ne semble pas y avoir de changements importants en CaO, MnO, et TiO_2 dans les laves des Bermudes; contrairement aux coussins de surface, il y a eu enrichissement en Na_2O et lessivage en MgO. Les variations chimiques à l'intérieur d'unité volcanique démontrent que les phénomènes d'altération dans les laves des Bermudes ont été très complètement redistribués. La reconstitution chimique de ces coulées pourrait être un effet du réchauffage lors de venues ignées tardives. Les basaltes de la dorsale médio-atlantique à 36°N furent échantillonnés jusqu'à 582.5 m de profondeur durant le leg 37, DSDP. Il est difficile d'attribuer des changements chimiques à l'halmyrolyse, vue que ses effets sont souvent moins importants que les variations internes de la minéralogie et la composition des basaltes. Des analyses de sidéromélane nonaltérée provenant de différentes profondeurs dans ces sondages du leg 37 DSDP ressemblent aux compositions du basalte originel. En tenant compte de l'effet des phénocristaux dans les basaltes, les différences en composition entre la sidéromélane et le basalte équivalent représenteraient les effets de l'halmyrolyse. Les verres sont enrichis en SiO_2, TiO_2, Fe^{TOT}, et Al_2O_3 et lessivés en K_2O, tandis que CaO, Na_2O, et MgO ont des concentrations égales dans la sidéromélane et le basalte.

(Traduit par le journal)

INTRODUCTION

Until recently most geoscientists studying oceanic rocks regarded the effects of sea water on these rocks as an undesirable side-effect which was best overcome by either sampling the ocean floor where rocks were known to be youngest, and hence freshest, as within median valleys of ridges, or by discarding all but the least altered of the rocks collected. As a result, large areas of the ocean floor went unsampled, and many specimens received little or no attention. Geochemists who sometimes had no choice but to analyze "weathered" samples, for lack of fresher ones, attempted to understand the effects of halmyrolysis primarily so that they could calculate the original compositions of these rocks.

It was the paleomagnetists who first became aware of the importance of altered oceanic rocks. In the late 1960's Irving and his co-workers (Irving *et al.* 1970) were attempting to explain why the central axial anomaly over a median valley is generally characterized by an amplitude two or three times greater than for those immediately adjacent. Irving was working with an extensive collection of rocks dredged from across the Crest Mountains of the Mid-Atlantic Ridge at 45°N (Aumento *et al.* 1971), which contained both the freshest rocks from the median valley, and some extensively altered ones from the older High Fracture Plateaus to the east and west. Although Irving used Aumento's geochemical data, which was strongly biased towards the freshest rocks available in every case (Aumento 1971) for his correlation with the magnetic properties of these rocks (Irving *et al.* 1969), he was able to detect a marked correlation between halmyrolysis, the oxidation of titanomagnetite, and the decrease in amplitude of the magnetic anomalies away from the ridge axis (Irving *et al.* 1970). Irving did not have field data with which to estimate the vertical extent of halmyrolysis through layer 2, but was able to produce a model from paleomagnetic data which suggested that most of the alteration took place on surface flows, with the effect decreasing with depth. Irving also noted that the abundant disseminated sulfides observed in the basalts might later be concentrated into economic deposits, as are found on continents today in the greenstone belts of possible submarine origin.

Hart (1970) used 112 published analyses of basalts from the world's mid-ocean ridge system to evaluate the effects of halmyrolysis with distance from spreading centers, and hence with age. Of his samples 108 represented an estimated time span of 0 to 7 m.y., and the remaining four from 18 m.y. ago. Given that the analyses were of samples from unrelated localities, and that they probably represent the freshest samples available for each site, Hart obtained a remarkable picture of the chemical exchange taking place. He noted that, whereas the aluminum content shows no apparent change with time, silica, calcium and magnesium are lost from the basalts, with the simultaneous gain of potassium, iron, titanium, manganese, sodium and phosphorus. Similar trends had been reported by Myashiro *et al.* (1969) and Hart (1969) in studies of the concentric weathering zones of single pillows. Hart (1970) noted that a weathered ridge basalt could be confused with an alkali basalt with the exception of the low water content and iron oxidation ratio found in fresh alkali basalts.

Melson (1973) in an electron microprobe study of the compositions of palagonitized glass relative to fresh parental basaltic glass cored by D.S.D.P., found that palagonitization of basaltic glass involves loss of CaO, P_2O_5, Na_2O and possibly an increase in K_2O, Fe and TiO_2. Thompson (1973) presents chemical data on dredged pillow basalts of which the outer altered glass, an inner unaltered portion just below the glass, and an inner altered core had been analyzed. He noted that H_2O, Fe_2O_3, K and Mg increase in both altered glass and core. There is a slight decrease in Si at both margin and core whereas Ca, and to a lesser extent Fe, are depleted in the altered glass but not always in the altered core. Na and Al tend to be enriched in the altered glass but not in the core. He concluded that during halmyrolytic alteration of basalts, there is overall loss of Si, Mg and Ca with simultaneous gain of K and H_2O, and that Al, Total Fe and Mg may also be leached from, and P added to the basalts.

Christensen & Salisbury (1972) suggested that the observed decrease in sonic velocity of D.S. D.P. basalts away from the Mid-Atlantic Ridge may be the result of progressive alteration. In support of this suggestion, Hart (1973) constructed a model for chemical exchange between sea water and basalt of the upper part of layer 2, involving halmyrolysis, low-temperature retrograde greenschist metamorphism and a higher temperature (albite and actinolite) greenschist metamorphism. On the basis of this study Hart (1973) concluded that during halmyrolysis SiO_2, Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn are lost from the basalts while K^+ and H_2O are gained. Na_2O, Al_2O_3 and TiO_2 do not change but trace elements Ba, Rb, Sr, V, Zr, Cs and U are gained by the basalt whereas Co, Cr, and Ni are lost to sea water.

Previously Hart (1969) had demonstrated the extreme dependence on the state of alteration of the concentration of Cs, B, Rb, K, Ba and Sr. He suggested that the unique characteristics of fresh mid-ocean ridge basalts might be extremely low Cs, B, Rb and possibly U. Aumento (1971) measured the U content of 32 of the freshest basalts available from a traverse across the MAR at 45°N, and found that whereas the basalts extruded with an U content between 0.19 to 0.30 ppm, the concentrations increased systematically through halmyrolysis to a maximum of more than 2 ppm in 16 m.y. The increase in U could be correlated with increasing iron oxidation ratio, total water, and potash content.

Given that more than 100 basalt analyses were available on file from the MAR at 45°, Aumento (1973) plotted the variations in major, minor, some trace-element and isotope concentrations against distance from the axis of the ridge. The 168km-wide area sampled represents some 16 m.y. of exposure of the uppermost basalt pillows to sea water. As for the data used by Hart (1969), the analyses represented data from the freshest material available in every case. The geochemical trends which emerged from one restricted sampling locality were very similar to those reported by Hart on major-element variations for his ocean-wide study. Additional data in Aumento's (1973) compilation included the enrichment of Sr (97 to 280 ppm, the concentrations given being mean values for 0 m.y. and 16 m.y.), Ba (61 to 140 ppm), B (5 to 70 ppm), Rb (5 to 25 ppm), U (0.2 to 1.0 ppm), Cs (0.02 to 0.5 ppm), Sr^{87}/Sr^{86} (0.703 to 0.706 ppm), $\delta\ O^{18}/O^{16}$ (+5 to +12), and depletion of S (800 to 100 ppm). However, uncertainties were raised as to the behavior of some of the elements, such as the behavior of aluminum and phosphorus, and the enrichment of sodium and titanium.

Apart from chemical changes produced in basalts by halmyrolysis, there must also be a compensating change in the chemistry of sea water which has circulated through and interacted with basalts. It is of course virtually impossible to measure chemical changes in sea water circulating through basalts on the ocean floor but Björnsson *et al.* (1972), in an economic evaluation of the Reykjanes thermal brine area in Iceland, reported on the chemistry of the brines which are of sea-water origin. This area closely duplicates an ocean floor geologic environment as the Reykjanes peninsula is underlain by a basalt, glassy basalt breccia and tufaceous sediment sequence quite similar to the geologic sequence of oceanic layer 2A penetrated on Leg 37 of the Deep Sea Drilling Project. Furthermore, a series of fractures transecting the Reykjanes peninsula are the extension of the median rift zone of the Mid-Atlantic Ridge.

Björnsson *et al.* (1972) found that, relative to ordinary sea-water, concentrations of K^+ and Ca^{2+} in the brines have increased 5 to 6 times. Na^+ and Cl^- show slight increases in the brines but Mg^{2+} and SO_4^{2-} have been drastically reduced relative to sea water. These results are surprising especially in that concentrations of K^+ and even Na^+ seem to have increased and Mg^{2+} has decreased in the brines relative to sea water. This is quite a different picture of exchange than that noted by Hart (1970) for the same elements, and may be the result of different thermal regimes.

A more detailed investigation of the oceanic environment was obviously needed, using samples specially selected for the problems at hand rather than using data previously screened for other purposes. Three vast suites of ocean-floor specimens were readily available to us at Dalhousie: the tons of rocks from the Mid-Atlantic Ridge at 45°N, the 800 m core of altered oceanic rocks from the deep hole drilled into Bermuda in 1972 (Aumento & Gunn 1976), and the five holes drilled deep into the oceanic crust by the GLOMAR CHALLENGER on Leg 37 (Deep Sea Drilling Project, 1974). Samples were specially selected from these three suites to investigate the effects of halmyrolysis.

MID-ATLANTIC RIDGE SAMPLES

Twelve large pillows were selected from sites at 0, 6, 20, 25, 47, 60, 70, 82, 96, 120, 124 and 136 km from the axis of the Mid-Atlantic Ridge at 45°N. The freshest portions of some of these pillows had already been analyzed routinely in the past, and those data used in Aumento's (1973) investigation of halmyrolysis discussed above. For this investigation, samples were taken from opposite margins of these pillows, and from at least two intermediate positions distributed on a line between the margins sampled. In some cases whole pillows were not available, so that only an incomplete section could be sampled

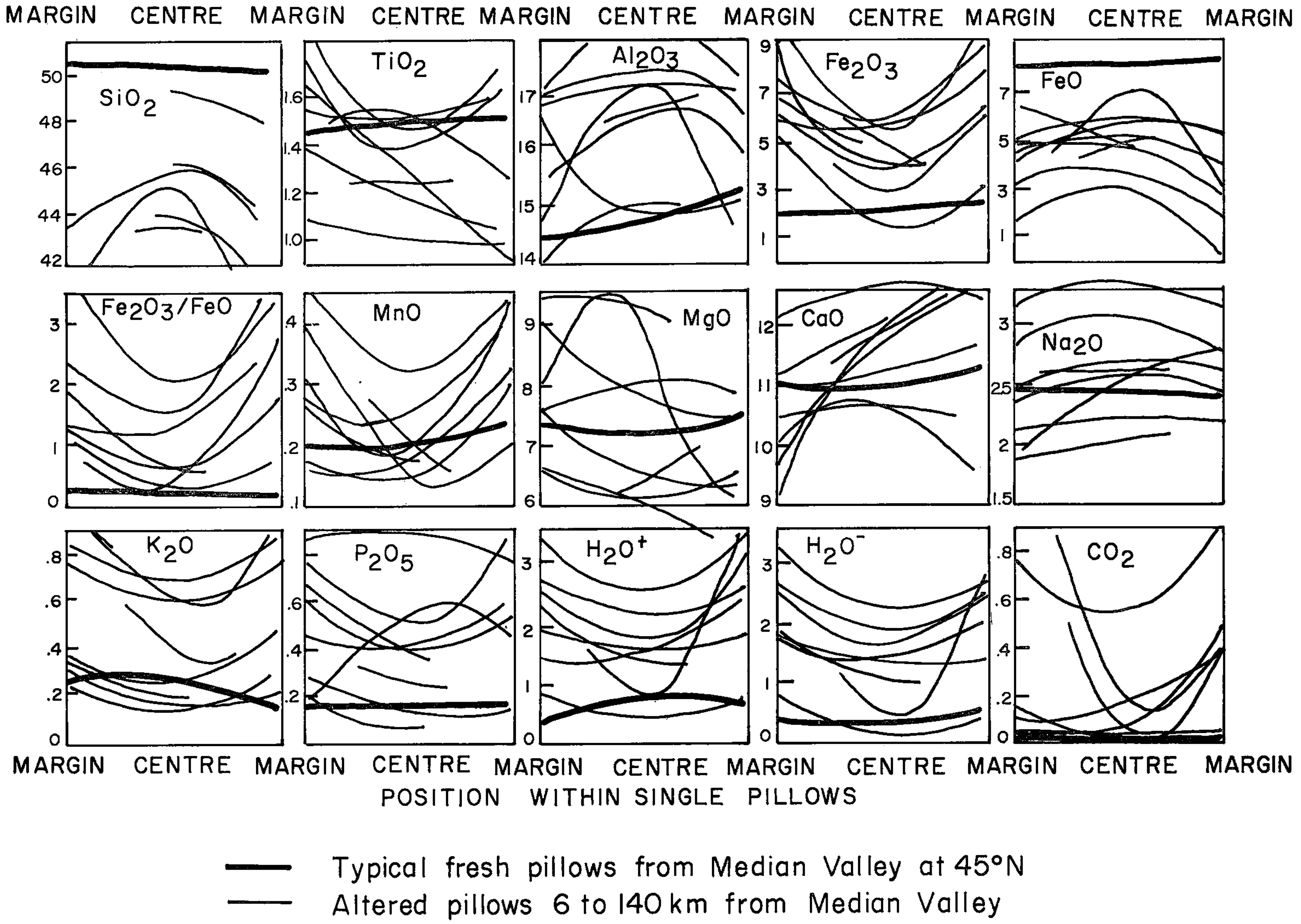

FIG. 1. Geochemical variations through 12 pillows taken on a traverse from 0 to 136 km from the axis of the Mid-Atlantic Ridge at 45°N, and one pillow 40 km from the axis at 36°N. Each of the full curves is drawn through four data points.

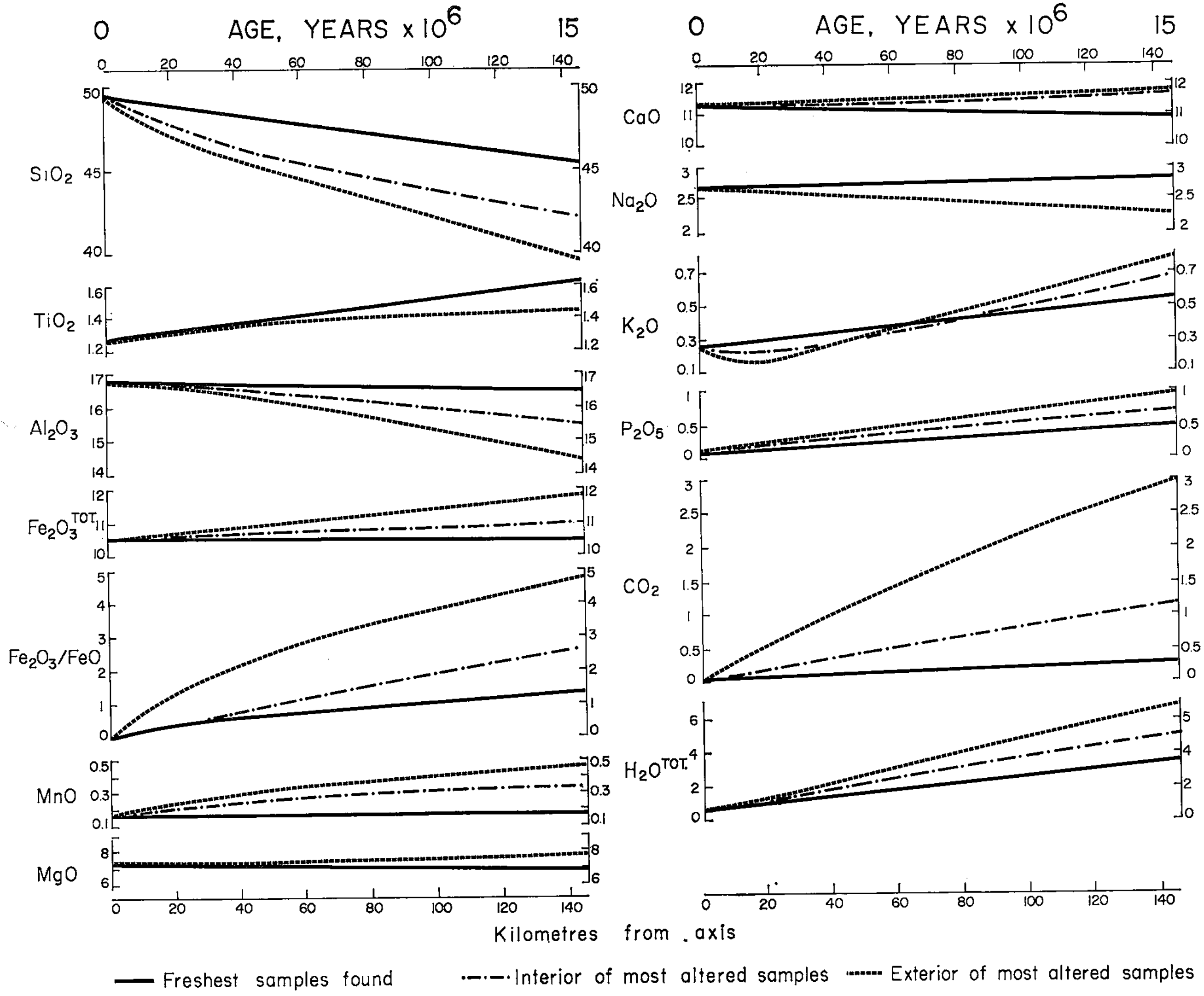

FIG. 2. Least-squares regression lines through the two extreme cases of the data from Figure 1 (dashed lines) and the original data of Aumento (1973) (solid line) plotted as a function of distance (time) from the axis of the Mid-Atlantic Ridge.

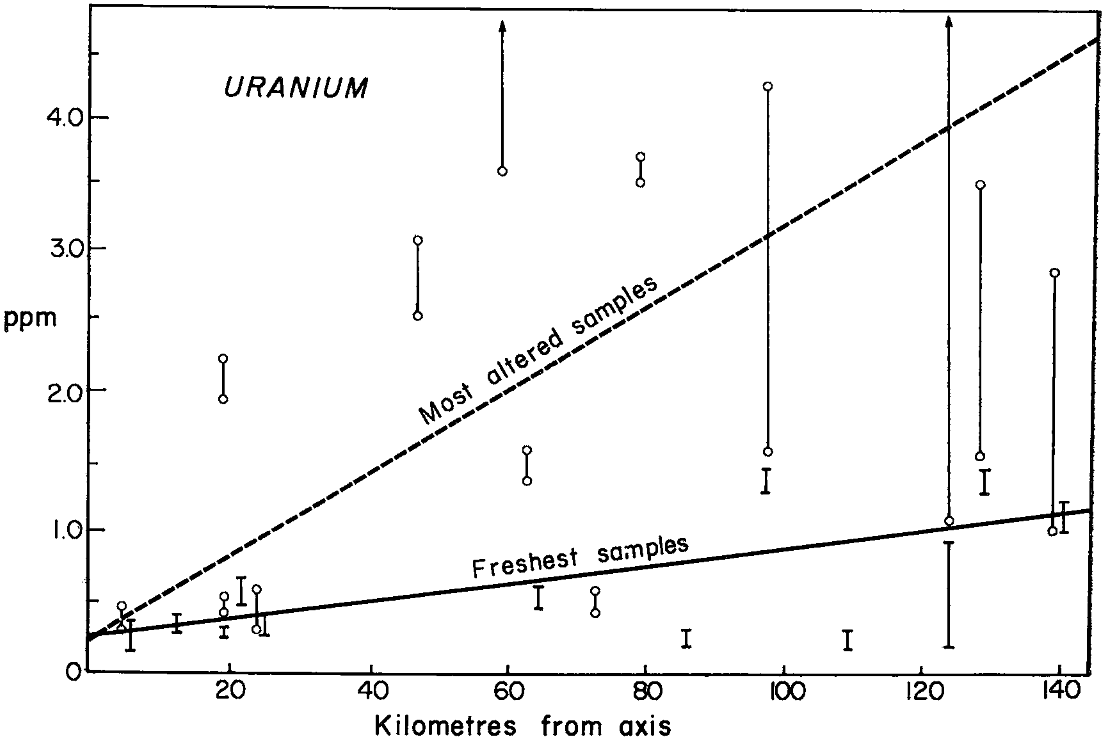

FIG. 3. Least-squares regression lines through the variation in uranium contents for the freshest and the most altered samples as a function of distance (time) from the axis of the Mid-Atlantic Ridge.

(i.e. one sample at the margin, one at the estimated centre, one intermediate between the two). In addition, one large pillow dredged some 40 km from the axis in the FAMOUS area at 36°N was sampled in nine radially located points. All the major and minor elements, and the trace element U, were determined for these samples by a combination of neutron activation analysis, gravimetric, atomic absorption, titration, and fission track techniques. Standard samples (Wl, PB, BR) were analyzed simultaneously. Results are presented graphically in Figure 1, where, for simplicity, the dimensions of the pillows have been discarded, and the data have been plotted on an arbitrary scale: margin—centre—margin. Since the dimensions of the pillows dredged do not vary drastically, such a simplified plotting technique will not give an erroneous picture. What is more difficult to represent, however, is the situation where only a segment of pillow is available: the positions of the samples taken relative to the whole then have to be estimated, and are represented on Figure 1 by incomplete lines. Also plotted on Figure 1 is the chemistry of very fresh pillows from the medial valley at 45°N.

In Figure 2 the data are plotted as a function of distance (and hence time) from the spreading centre. Least-squares regression lines of the data are given for three cases: for the freshest samples available (the older, "ideal" analyses from Aumento 1973), for the interiors (i.e. least altered parts) of the most altered pillows shown in Figure 1, and for the exteriors of the same pillows (i.e. the worst possible cases of halmyrolysis given the distance/time factor). Figure 3 gives the same data for U, a trace element which is particularly susceptible to halmyrolysis. The behavior of the different elements is best discussed individually.

Silicon. The SiO_2 content of fresh pillows from the median valley of the Mid-Atlantic Ridge can vary between 47 and 52% (Leg 37, The Volcanic Layer, 1974). In altered basalts the variation in SiO_2 is considerably more accentuated than this and there is a marked depletion of SiO_2 at the margins of the pillows relative to the centres (Fig. 1). The variation in SiO_2 with distance from the spreading centre (Fig. 2) is even more pronounced with extreme values of less than 40% SiO_2 being present in the oldest, most altered samples analyzed. This, together with the marked depletion of SiO_2 at pillow margins, indicates quite clearly that Si^{4+} is being lost to sea water with time.

Titanium. Ti is not quite so clear to interpret. Pillows can show both marginal enrichment and depletion, but relative to fresh pillow basalts overall TiO_2 levels seem to fall in altered pillows. Plotting the data against distance reveals an interesting characteristic: TiO_2 for the freshest samples seems to increase with distance; one might have wondered whether this is a primary feature of magma variation with time or whether it is a secondary effect. Looking at the worst cases of halmyrolysis, the increase with time is reduced rather than accentuated. It seems, therefore, that if anything, exchange with sea water is masking what might be a primary magmatic variation trend which produces progressively younger basalts with ever decreasing TiO_2 content. Such magma variations with time appear for some of the other elements also, although none is quite as marked as for titanium.

Aluminum. The original Al_2O_3 content of pillow lava is so variable (14-23%), due to the plagioclase phenocryst content, that trends resulting from other factors are difficult to evaluate on a regional scale. However single pillow data show a marked depletion of alumina in the margins in all but one case; surprisingly the plots vs. distance retain this trend over and above the "original" compositional scatter. These results are in marked contrast to those reported by Hart (1970, 1973) and Aumento (1973), but mobility of Al is suggested by the observations of Melson & Thompson (1973) on the alteration products of basalts. Data presented by Thompson (1973) also indicate that Al can be leached from basalts. Obviously severe halmyrolysis does strip Al from the rocks; neither Hart nor Aumento had noticed it previously because of their exclusive use of data from least altered specimens.

Iron. Total iron shows a small but definite increase with alteration; this increase appears to be connected with the manganese precipitation as a thin ferromanganese film lining minute fractures and cavities. Independent of the total iron gain, the Fe_2O_3/FeO ratio is more responsive to alteration. While FeO shows extensive overall depletion, most marked at the margins of the pillow, Fe_2O_3 is enriched with alteration in the same localities. Consequently, the value of Fe_2O_3/FeO ratios rise from a low of 0.2 to about 2.0 in the centre of pillows and to 5.0 at their margins in the time span of 15 m.y. or less.

Manganese. Mn shows a systematic enrichment both with time and from centres of pillows to their margins. Clearly, manganese is being added to the pillows from sea water; thus it is unlikely that the latter can provide manganese for subsequent re-precipitation as manganese crusts or nodules.

Magnesium. Mg is very problematic. Studies of original MgO concentrations in fresh pillows show that values can range from 6 to 20%, a range much greater than the total variation (5 to 10%) found for all the fresh and altered specimens at 45°N. Individual fresh pillows also show MgO zonation due to the olivine phenocryst control, so that one can neither define a "baseline" composition, nor evaluate the radial redistribution of the element through halmyrolysis. In Figure 1 the distribution of MgO through pillows appears to be almost random: there are both marginal enrichments and depletions, as well as asymmetrical distributions. The original MgO variation is obviously far more important than the secondary effects. Plotting the data against distance gives an unconvincing picture, showing only the slightest MgO enrichment through halmyrolysis: the data scatter is greater than the calculated variation. Magnesia, therefore, is an unreliable indicator of halmyrolysis of natural samples, for although there may be considerable redistribution of MgO into secondary alteration minerals (e.g. chlorite and smectites), there does not seem to be any great actual gain or loss of the element from the rock.

Calcium. Like magnesium, calcium gives confusing results. Concentrations of CaO in young, fresh lavas can range from 7.5 to 16%. Single pillow alteration trends show either marginal depletions or highly asymmetrical variations. There are also sporadic high values of CaO in altered basalts, commonly connected with unusually high calcite contents. On the whole, however, the calcium content in any suite of rocks is randomly scattered around mean values not too different from those of fresh basalt suites (see Fig. 2).

Sodium. Here the more systematic marginal depletion evident for the single pillow studies (Fig. 1) is reflected also in the distance/age plots of Figure 2. The latter shows a very slight Na_2O increase with age for the freshest samples, a trend which might be real since halmyrolysis tends to depress it rather than accentuate it. Hart (1970) had shown inconsistent Na_2O patterns, although he favored a case of slight increases with alteration. The current data seem to swing conclusions the opposite way: loss of sodium to sea water, which at first sight might appear rather surprising. However, it is worth noting that Melson (1973) also reported loss of Na on palagonitization of basaltic glass and that Thompson (1973) reported the anomalous behavior of Na, which seems to be enriched in altered glassy margins but not in the cores of pillows.

Potassium. Over the 15 m.y. period investigated, potassium shows a marked marginal enrichment which, given time, increases the K_2O content of the pillow centres as well. This trend is very systematic and no exceptions have been noted. However, the behavior of potassium over the period 0 to 3 m.y. is more interesting. It seems that soon after extrusion, pillows start losing K_2O from their margins, hence the margin-depleted curve for the "typical fresh pillow" curve plotted on Figure 1. This loss is evident primarily in the glassy selvages, but also extends some way in; it probably occurs very rapidly, since it is difficult to find a fresh pillow without this characteristic marginal depletion. This distribution is not thought to represent a cooling phenomenon. Soon thereafter this trend is opposed by the overwhelming one of marginal enrichment, resulting at first in a reduction in rate of marginal loss, then a period of balance, and eventual replacement by marked enrichment right through to the cores.

Phosphorus. Fresh pillows contain from 0.02 to 0.25% P_2O_5. In most of the cases studied, phosphorus is enriched, both marginally and throughout the pillows, to values of 1% or more. Two of the pillows investigated show a marked overall enrichment coupled with unexplainable low concentrations at the margins. The overall trend with distance/age (Fig. 2), however, is a clear one of enrichment through halmyrolysis, even with the inclusion of the two anomalous pillows.

Water. Both H_2O^+ and H_2O^- show systematic increases, commencing with the margins and eventually overwhelming the whole pillows. Indeed it is hard to find a pillow with less than 3% total water when sampling the surface of the ocean floor some 150 km from a spreading centre. The few rare cases have occurred when pillow rinds were protected from alteration by thick ferromanganese crusts (Aumento 1969).

Carbon dioxide. CO_2 is a very sensitive indicator of halmyrolysis. From less than 0.1% CO_2 in fresh pillows, one can find as much as 3% in highly altered crusts. The relative ease of making numerous rapid analyses for CO_2 makes it a most convenient oxide with which to screen rocks for "freshness".

Much of the CO_2 in basalts is normally combined in calcium carbonate. Thus, with considerable increase in the amount of CO_2 present, one would expect a concomitant increase in calcium. However, as previously noted, there is no equivalent calcium enrichment in altered rocks and it appears that silicate calcium is being redistributed by halmyrolytic fluids into carbonates with little overall gain or loss of calcium in the rocks. Solutions producing the alteration could at any instant of time be considerably enriched in calcium relative to sea water, as are the thermal brines of Iceland.

Uranium. U follows water, CO_2 and the iron oxidation ratio very closely, with marginal increases early on in time, followed by complete infiltration of up to 4.5 ppm in the most altered samples (Fig. 3). There are indications that, like K_2O, uranium may be depleted in the first few instants of geological time from the glassy selvages and outermost margins. Hence the importance of mapping the U distribution in these volcanic glasses by fission track techniques (Aumento & Hyndman 1971) prior to dating them using spontaneous fission tracks.

A chemical balance seems to be maintained throughout the 15 m.y. alteration process illustrated in Figure 2. This can be demonstrated by summing up roughly the oxide weights at time 0 (at the ridge axis) and comparing with the sum at time 15 m.y. (145 km from the axis) for the most altered cases. The compositions produced are given in Table 1, analyses 1 and 2. Ultimately, the loss or gain of any element depends on the low-temperature mineral changes that take place on the ocean floor. In this environment both the minerals and the volcanic glass of the basalts are metastable, and their tendency to convert to more stable phases is aided by the hydrolysis process of sea water. The end products are determined by the composition of the original rocks and that of the sea water, and by their interaction.

An example of this is the behavior of calcium. Despite some scattered low and high values found in our analyses, it is interesting to note that on the whole the concentration of this element remains constant, with a slight tendency towards higher values in more altered suites, as shown by the extrapolated analyses #1 and #2 of Table 1.

Due to the presence, in analyses #2 of Table 1, of 3% CO_2, one can calculate that approximately 3.8% of the total CaO is bound as $CaCO_3$. This leaves some 8.0% of what can be called silicate CaO in contrast to the former carbonate CaO.

Silicate CaO has thus been drastically reduced by halmyrolysis, in parallel with SiO_2, quite clearly as a result of the breakdown of some plagioclase and clinopyroxene. While Si^{4+} was leached out of the altered rock, Ca^{2+} (and probably some Mg^{2+}) was readily captured by HCO_3^{2-} from the sea water and redeposited as calcite in the fractures and spongy network of the altering rock. This would then indicate that the amount of total CaO in an altered basalt can and should be taken as a fair approximation of the original silicate CaO.

Some Na from the albitic component of plagioclase is also released, but finds few stable secondary minerals into which to enter, resulting in a slight overall decrease of Na_2O in the most altered basalt members.

The loss and gains of certain elements, and their change in oxidation state, play an important role on the outcome of the norm calculations and the rock classification based on them. Note, for example, that both the composition and norms of analysis #2 in Table 1, taken as is, do not correspond to those of an alkali basalt (see Manson 1967, for example). Only some individual elemental concentrations might confuse one into believing that an altered oceanic tholeiite has alkali tendencies.

Slightly altered samples, where the major change was an increase of the Fe_2O_3/FeO ratio, tend to move toward the "quartz" normative field, whereas strongly altered samples with loss of SiO_2 tend to move toward the "nepheline" normative field (Kempe 1975).

The accepted practice of reducing Fe_2O_3 to 1.5% or to some other small arbitrary value, in order to take care of the secondary oxidation of iron, can be quite misleading, if applied across the board, without due consideration of the degree of alteration and possible loss of SiO_2. This is exemplified in the norm of analysis #3 of Table 1; this analysis is the same as #2 except for the iron content, which was recalculated so as to give 1.5% Fe_2O_3. The norm changes drastically, with the appearance of some nepheline, the disappearance of hypersthene, a great reduction in magnetite, and an increase in olivine.

The investigations discussed above report extensively on but one aspect of halmyrolysis: that of pillows totally submerged in cold sea water at the surface of the ocean floor. Given that the data suggest strong gradients across concentric zones in pillows, one wonders, as did Irving *et al.* (1970), how far down into the solid oceanic crust one can detect the effects of halmyrolysis. Our first opportunity to investigate this problem came with the drilling of a deep hole into the islands of Bermuda.

TABLE 1

	1	2	3	4
SiO_2	49.00	39.00	39.00	48.16
TiO_2	1.30	1.70	1.70	1.31
Al_2O_3	16.80	14.50	14.50	14.16
Fe_2O_3	1.50	6.80	1.50	1.50
FeO	9.00	5.00	9.76	7.92
MnO	.20	.50	.50	0.16
MgO	7.20	7.50	7.50	5.53
CaO	11.30	11.80	11.80	11.45
Na_2O	2.70	2.30	2.30	3.81
K_2O	.20	.80	.80	.66
P_2O_5	.10	.90	.90	.16
$CO_{2\,TOT.}$	0.00	3.00	3.00	3.21
H_2O	.50	5.50	5.50	2.72
TOTAL	99.80	99.30	99.30	99.94
Fe as Fe_2O_3	11.52	12.37	12.37	8.61
Q	0.00	0.00	0.00	0.00
OR	1.19	5.04	5.07	3.98
AB	23.00	20.75	20.36	32.88
AN	33.37	28.65	28.82	19.98
NE	0.00	0.00	.28	0.00
DI	18.39	5.70	5.99	13.32
HY	9.60	10.07	0.00	12.01
OL	9.54	6.34	24.14	5.24
MT	2.19	10.51	2.33	2.22
IL	2.49	3.44	3.46	2.54
AP	.23	2.23	2.24	.38
CC	0.00	7.27	7.32	7.45
	100.00	100.00	100.00	100.00

Column 1. Average chemical composition of freshest pillow lava from the Median Valley of the M.A.R. at 45°N.
Column 2. Projected chemical composition of the most altered pillow lava 145 km from the spreading centre of the MAR at 45°N.
Column 3. As for Column 2, with Fe_2O_3 normalized to 1.5%.
Column 4. Average for 59 analyses of altered tholeiites from Bermuda, with Fe_2O_3 normalized to 1.5% (after Aumento & Gunn 1976).

Bermuda

During Deep Drill-1972 an 800 m deep diamond-drill hole was sunk into the Island of Bermuda through thin capping limestones into the basement igneous rocks. The latter consist of more than 1000 thin interlayered flows and sheets. The flows, many of them pillow lavas, are typical low-potassium oceanic tholeiites which extruded near the axis of the Mid-Atlantic Ridge some 90-100 m.y. ago (Reynolds & Aumento 1973). Sea-water alteration has resulted in chemical reconstitution of most of tholeiites, the mean composition of which is given in Table 1, analysis 4.

The data for analysis 4 are taken from Aumen-

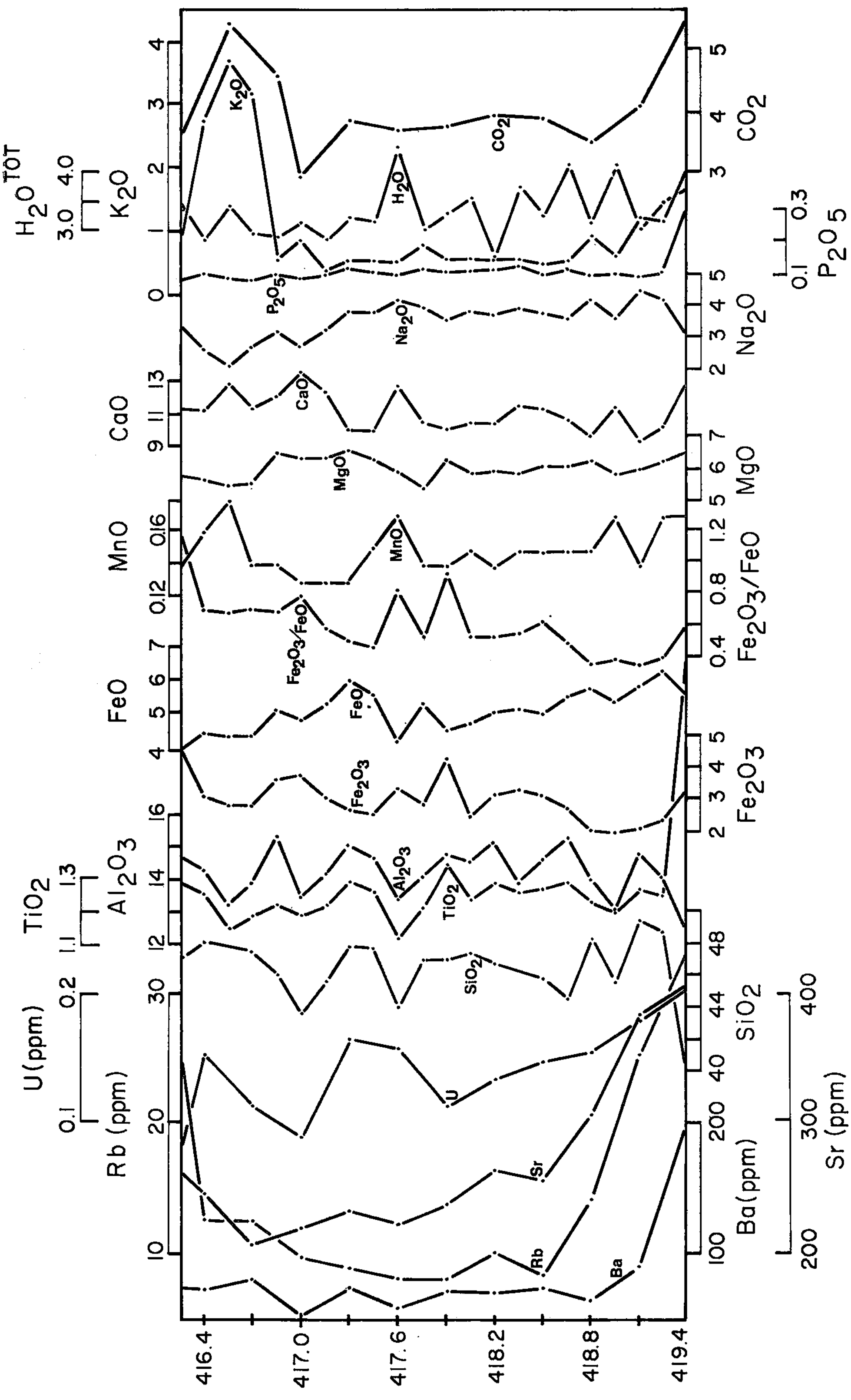

FIG. 4. Major, minor and trace-element variation through a thick tholeiitic basalt flow 416 m below sea level in the Bermuda drill hole.

to & Gunn (1976) and represent the mean of 59 pillow analyses which have been recalculated on the basis of 1.5% Fe_2O_3. Each analysis represents data from a composite sample made up of a minimum of three horizons (often five or more) through pillows and flows. Hence all concentration variations within individual pillows were eliminated by homogenization.

Analysis #4 is of interest because it represents oceanic tholeiites which have not only undergone halmyrolysis on the surface of the ocean floor, but also subsequent sea-water interaction, possibly at higher temperatures, with burial. Indeed, these presented to us the first examples of that elusive material lying beneath the surface of the ocean floor which could not be sampled by dredging.

Changes in their major-element chemistry indicate, that as for the younger surface pillows, they may have been depleted in Al_2O_3 and SiO_2, and have been enriched in K_2O, CO_2 and H_2O^{TOT}, and possibly P_2O_5 to a lesser extent. However, unlike the surface pillows, they show no significant change in TiO_2, MnO and CaO but in complete contrast show a marked enrichment in Na_2O and depletion in MgO.

The data presented above are based on homogenized powders, and as such do not indicate any discernible trends in halmyrolysis or other secondary alteration at more elevated temperatures. Indeed most units, be they flows or pillows, being small, were completely altered. However, a 3.4 m thick flow, found between 416 and 419.4 m depth, showed signs of incomplete alteration. The flow, like the rest of the Bermuda sequence, was full of small cracks and veinlets, each crack surrounded with its own localized alteration products. The flow is overlain by a chloritic breccia zone with another chemically similar basalt above, while a sheet, unusually rich in K_2O, TiO_2, Ba, Rb and Sr (Aumento & Gunn 1976) was subsequently intruded along the base of the flow during the later intrusive episode detected by Reynolds & Aumento (1973). The flow was sampled at 0.15 m intervals, care being taken to avoid as many of the small cracks and veins as possible. Nevertheless, some of the samples were contaminated, as at 417.6 m, and these gave spurious values for some of the elemental concentrations. All the major and minor elements, as well as the trace elements Ba, Rb, Sr, and U were determined from top to bottom of the flow at 0.15 to 0.3 m intervals. The trace-element concentrations proved to be enriched, with 0.2 ppm U, 32 ppm Rb, 200 ppm Ba, and 400 ppm Sr at the upper and lower contacts (see Fig. 4), the concentrations decreasing systematically inwards to 0.1 ppm U, 10 ppm Rb, 70 ppm Ba and 200 ppm Sr at the centre. Some of the major and minor elements, namely K_2O, MnO and CO_2, follow the trace-element pattern; K_2O, for example, varies from 3.5% to 0.6% between margin and centre. K_2O, MnO, CaO and U reach high, often peak values 0.3 m below the upper contact, the concentrations decreasing sharply upward from this 416.5 m level. Concentrations of TiO_2 and P_2O_5 are considerably enriched at the lower margin of the flow but there is no equivalent increase in these elements towards the upper contact.

Other major elements do not exhibit so clear a pattern; concentrations through the unit are more scattered, making marginal enhancements more difficult to see. Al_2O_3, for example, shows a cyclic variation of ±2%, which tends to obscure a possible depletion down to 12.4% at the lower margin. Overall Fe_2O_3 values decrease slightly downward, with marginal enrichment; these, combined with a sharp downward increase in FeO, give a marked upward increase in the iron oxidation ratio from 0.4 to 0.8, with an additional enhancement at both upper and lower contacts (0.6 and 1.2 respectively). MnO, though scattered, follows K_2O and Fe_2O_3/FeO, with enrichment 0.3 m below the upper contact, at the lower contact, and at 417.6 m. MgO and CaO have an almost antipathetic relationship, but there is a slight trend of enrichment for both oxides at the lower contact. Na_2O concentrations are quite constant at around 3.7% for the inner part of the unit, with a gradual depletion to 2.1% at 0.3 m below the upper contact level, and to 3% at the lower contact.

X-ray diffraction was used to determine mineralogical variations, particularly of secondary alteration minerals, across the flow. Montmorillonite was found to be present at the top of the flow but not at the base. This undoubtedly explains why the concentration of Al_2O_3 is greater at the top of the unit than at the base. Montmorillonite was also detected at around 418.2 m at which level Al_2O_3 is quite high; it seems quite possible that the cyclic variation in Al_2O_3 reflects the irregular development of aluminous clay minerals through the flow. Chlorite and biotite are unevenly distributed through the flow, and there is no obvious increase in any of the secondary minerals at the 417.6 m level with the possible exception of carbonates.

The horizon at 417.6 m shows anomalous high values for Fe_2O_3/FeO, MnO, CaO, Na_2O, K_2O and U, and possibly low values for Al_2O_3, TiO_2, FeO, and MgO; this may represent a zone of fractures and veinlets which could not be avoided in sampling, along which alteration fronts were able to attack the unit in addition to those along the upper and lower contact. There are countless other such alteration fronts dispersed throughout all the Bermuda units; many occur in the 3.6 m unit under investigation, but most were eliminated by sampling.

The alteration history of the thick unit described appears to be complex. Some elements, like sodium, were able to migrate throughout the unit, and to enrich (or deplete) it accordingly. Others migrated more slowly, so that zones nearest the contacts and fractures still show evidence of differential enhancement. Subsequent to the main halmyrolitic alteration episode, temperatures may have increased, possibly due to the later intrusive stage, resulting in remobilization of some of the elements. This may explain the depletion of some elements, notably U, Mn, K and CO_2 at the upper contact, with a possible further enhancement of some of the others. Considerable enrichment of K, Ti, P, Ba, Rb and Sr at the base of the flow could also have taken place by ion exchange with the intrusive sheet, which, as previously noted, is considerably enriched in these elements.

The different behavior of the element migration, both between the two suites of samples de-

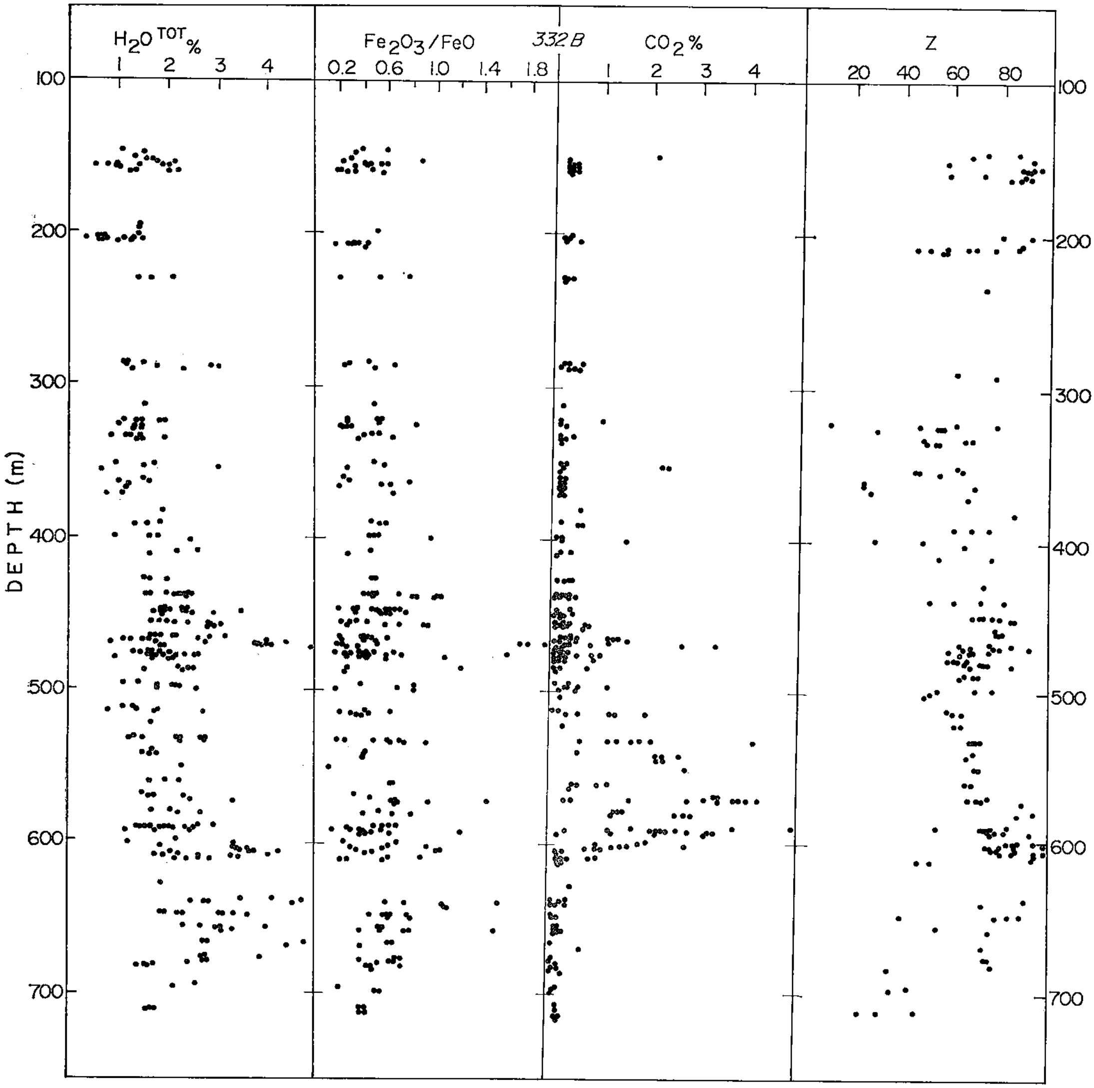

FIG. 5. Down-hole variation in total water, carbon dioxide, iron oxidation ratio and titanomagnetite cation deficiency factor (Z) for hole 332B.

scribed (MAR and Bermuda), and within Bermuda itself, may well reflect the varying conditions of halmyrolysis. The MAR samples were subjected only to sea water at 3.5°C (Garner & Ford 1969) whereas the Bermuda samples must have been heated up through first their burial and then by the later intrusive episodes detected by Reynolds & Aumento (1973).

Deep Drilling of Layer Two

During Leg 37 of the Deep Sea Drilling Project two holes, separated by less than 100 m (332A and 332B), were drilled to depths of 333 m and 582.5 m beneath acoustic basement into the young oceanic crust of the Mid-Atlantic Ridge near the FAMOUS area (36°N). Rocks from the sites were dated by fission track techniques (Mitchell and Aumento 1976) and found to be 3.67 m.y. old. Three other holes were also drilled: #333A, some 1.5 km to the SW of 332, penetrated 312 m; #334, in 8.9 m.y. old crust, penetrated 117.5 m, and #335 in 16.5 m.y. old crust penetrated about 108 m.

On visual inspection the bulk of the rocks collected appeared fresh from top to bottom of each core. Visible alteration, with typical iron oxide coloration, is limited to zones a few cm wide surrounding interfaces (cracks, joints, pillow and flow margins), in the same way as young surface pillows show incipient alteration along their cracks. The extent of this localized alteration did not appear to increase with depth, although joint surfaces in the lower part of hole 332B, for example, seemed more prone to secondary sulfide mineralization.

These localized alteration zones have already been investigated in detail, and numerous reports will appear in the Initial Reports of the Deep Sea Drilling Project, Leg 37. Investigators reported increases of H_2O, Fe_2O_3/FeO, K_2O, CaO, and in Rb, Sr, B, Li and U, with losses of SiO_2 and possibly MnO and MgO. However, discre-

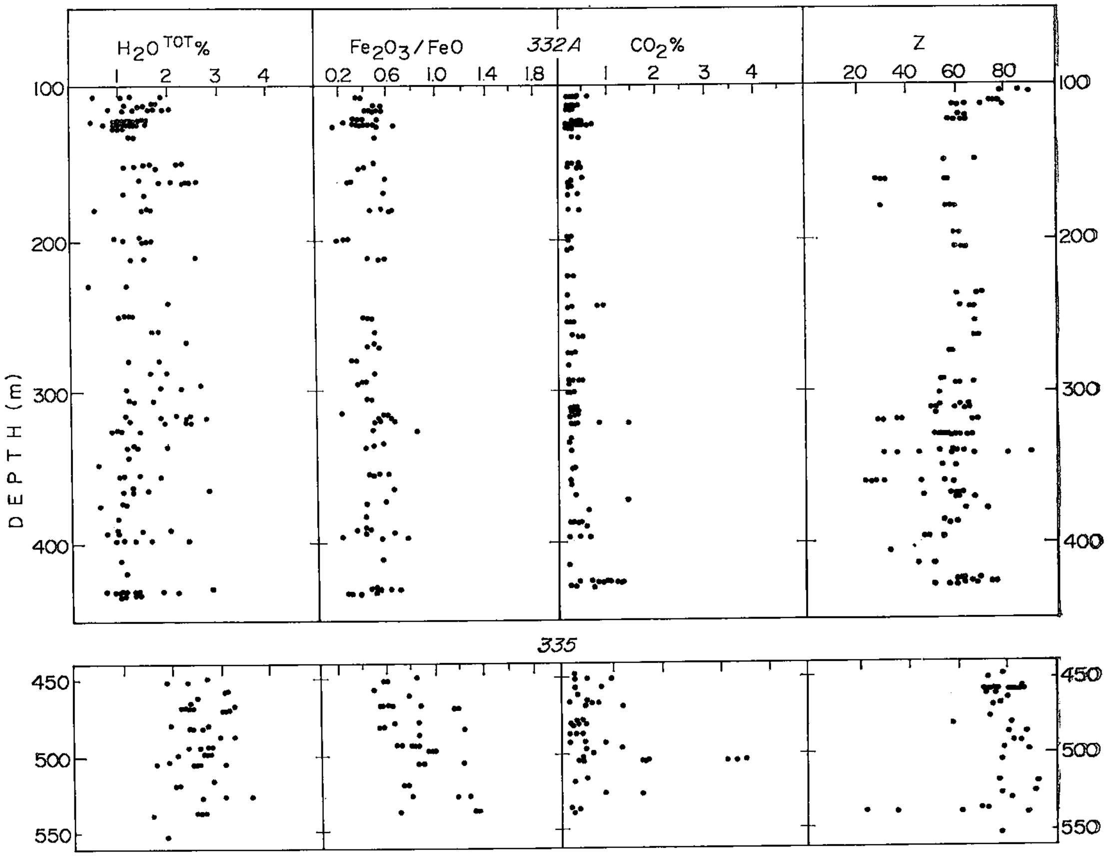

Fig. 6. Down-hole variation in total water, carbon dioxide, iron oxidation ratio and titanomagnetite cation deficiency factor (Z) for holes 332A and 335. Values of these parameters are on average higher in the older (16.5 m.y.) basalts of hole 335.

pancies occurred in many cases, and it was generally agreed that these did not appear to be positive evidence for a systematic exchange of elements between rocks and sea water. Indeed, alteration seemed to be more a function of the rock structure than of age and depth.

In order to overcome the problem of the localized alteration just discussed, samples for geochemical investigations were selected away from interfaces: these tend to represent the bulk of the volcanic sequence. Previous shipboard investigations (Leg 37 — the Volcanic Layer, 1974) had already shown that the major-element variations of these rocks were so extensive, and so dependent on the primary mineralogy, that it might not be possible, using these elements, to detect the minor, superimposed effects of halmyrolysis over long sequences of cores. However, some key elements and oxides found to be so sensitive in the previous MAR investigations were thought to be potentially informative. Figures 5 and 6 show the down-hole variations detected in the holes 332A, 332B and 335 for the iron oxidation ratio, the total water and carbon dioxide content. Also plotted is the down-hole variation of *Z*, the cation deficiency factor of titanomagnetite crystals within the lavas. *Z* was determined by paleomagnetic techniques (Hall & Ryall 1976) and since it is thought to be dependent on the state of secondary oxidation of the magnetites, it may well be a very sensitive indicator of alteration. Additional work on these samples, including other trace element and isotope investigations, was carried out by our colleagues (see the Initial Reports of the Deep Sea Drilling Project, Volume 37) and, because of their relevance, will be summarized here briefly.

TABLE 2

PEARSON'S PRODUCT-MOMENT CORRELATION COEFFICIENTS FOR THE DIFFERENT PARAMETERS GENERALLY INDICATIVE OF ALTERATION FOR LEG 37 D.S.D.P. HOLES 332A, 332B, 333A, 334 AND 335

	Depth	$H_2O_{(TOT)}$	Fe_2O_3/FeO	CO_2	U	Z	
Depth	1	- .06	+ .07	+ .33	+ .37	- .28	HOLE 332A
$H_2O_{(TOT)}$	- .06	1	- .20	- .34	- .11	- .17	
Fe_2O_3/FeO	+ .07	- .20	1	+ .29	+ .23	+ .04	
CO_2	+ .33	- .34	+ .29	1	+ .32	- .08	
U	+ .37	- .11	+ .23	+ .32	1	- .22	
Z	- .28	- .17	+ .04	- .08	- .22	1	
Depth	1	.57	.05	.20	.11	- .00	HOLE 332B
$H_2O_{(TOT)}$	.57	1	.24	.16	.17	.33	
Fe_2O_3/FeO	.05	.24	1	.22	.05	.25	
CO_2	.20	.16	.22	1	.02	.26	
U	.11	.17	.05	.02	1	.09	
Z	- .00	.33	.25	.26	- .09	1	
Depth	1	.33	.00	.12	.26	- .29	HOLE 333A
$H_2O_{(TOT)}$	.33	1	.32	.17	- .21	- .18	
Fe_2O_3/FeO	.00	.32	1	.44	- .14	.27	
CO_2	.12	.17	.44	1	.08	.39	
U	.26	- .21	- .14	.08	1	- .02	
Z	.29	- .18	.27	.39	- .02	1	
Depth	1	- .29	.06	- .16	.25	- .03	HOLE 335
$H_2O_{(TOT)}$	- .29	1	.33	.86	.01	.18	
Fe_2O_3/FeO	.06	.33	1	.13	.45	.30	
CO_2	- .16	.86	.13	1	.01	.10	
U	.25	- .01	.45	.01	1	.00	
Z	- .03	.18	.30	.10	.00	1	

A statistical approach (Pearson's product-moment correlation coefficient) was also used to see whether there was any meaningful correlation between the different potential indicators of alteration and depth. Table 2 presents these data: a correlation coefficient of unity indicates perfect dependence of one variable to the other; the smaller the coefficient the less the dependence.

The isotopes. S, Sr, Pb and O isotopes show little downhole variation, although slightly higher Sr^{87}/Sr^{86} ratios, δO^{18} and δS^{34} values in the upper levels suggest more pronounced sea-water contribution. Similarly, averages for the same isotopes and ratios increase systematically from hole 332A to 335, indicating that the passage of time, as well as proximity to the oceanic waters, has contributed to isotopic exchange with sea water. The oxygen isotopes suggest that basalts have been altered from 1 to 15% by volume, through the production of clay minerals, which themselves pick up ions from cold sea water; indeed, one O^{18}-rich calcite analyzed gave a paleo-temperature of only 2°C (Muehlenbachs 1976).

Trace elements. Table 3 gives the mean values for all the major, minor and trace elements determined for the five deep holes by all the investigators. There appears to be little systematic variation with distance from the spreading centre, even for such sensitive indicators as Sr and Cs. Andrews *et al.* (1976), and Shaw (1976), reporting on the distribution of the trace elements Ti, Ni, Co, Cu, Zr, Sr, Tl, Li, Rb and Ba, concluded that there was no correlation with depth.

TABLE 3. AVERAGE VALUES FOR ALL THE MAJOR, MINOR AND TRACE ELEMENTS DETERMINED FOR THE LEG 37 D.S.D.P. HOLES 332A, 332B, 333A, 334 and 335.

HOLE	% Si	% Ti	% Al	% Cr	% Fe_3	% Fe_2	% Mn	% Ni	% Mg	% Ca	% Na	% K	% P	% CO_2	% S	% H_2O^-	% H_2O^+	ppm B
332A	49.7	1.02	15.3	.03	6.3	6.4	.16	.015	7.4	12.8	2.1	.27	.12	.22	.04	.83	.57	14
B	48.3	.80	16.1	.10	5.3	5.8	.15	.055	8.8	12.6	2.0	.20	.09	.87	.05	1.13	1.09	21
333A	49.2	1.02	15.2		5.2	6.1	.16		8.0	12.5	2.1	.24	.11	.35	.06	1.11	1.00	18
334	50.5	.80	15.1		5.0	6.6	.16		8.2	12.7	1.9	.20	.08	.08	.04	.63	.74	41
335	48.8	1.10	15.5		6.1	5.8	.16		8.0	12.4	2.4	.30	.11	.79	.08	1.34	1.22	25

HOLE	ppm Li	ppm Rb	ppm Sr	ppm Cs	ppm Ba	ppm Tl	ppm Th	ppm U	ppm Y	ppm Zr	ppm Hf	ppm Nb	ppm Ta	ppm Co	ppm Ir	ppm Pb	ppm Au	ppm Sb
332A	6.9	4.2	82.9	2.7	59.9		.77	.50	13.2	36.6	1.7	5.2	.92	43		.59		.73
B	8.4	3.4	94.1	2.3	51.7	.03	.75	.28	13.2	32.5	4.3	3.5	.80	48	.07	.94	7.9	.66
333A	11.3	4.2	107.7	3.1	82.9		.88	.47	21.6	58.1	1.5	9.1	1.20	44				.88
334	7.2	3.7	69.6	2.5	71.8	.02	.45	.24	15.8	32.3	1.2	5.1	.64	47	.02		1.6	.64
335	17.4	5.2	104.8	2.5	64.1		1.00	.10	27.2	50.3	1.5	2.8	.81	50				.62

They concluded there had been little interaction with low-temperature sea water, and Shaw suggested that if any major alteration had taken place then it must have occurred below the levels penetrated by Leg 37 drilling.

Mitchell & Aumento (1976) reported on the distribution of uranium down all the holes (see Fig. 7). This study involved a total of 328 whole-rock analyses, and hence was capable of providing a much more detailed picture than that based on the limited number of samples used for isotopic and other trace-element studies. The basic U pattern shows repetitive cycles of decreasing concentration with depth, varying from 0.4 to 0.05 ppm U, corresponding to major-element cycles involving decreasing SiO_2, Al_2O_3, K_2O, TiO_2 and P_2O_5 and increasing MgO with depth.

Superimposed on this repetitive pattern are anomalously high U values at different horizons. Hole 332B, for example, has whole series of U-enriched samples at around 475 m, where concentrations exceed 1 ppm; minor enrichments are also evident at 590 m and 720 m. In hole 332A enriched horizons occur at 200 m and 320 m. The whole top of 333A, down to 325 m seems to have excess U, whereas the lower half has a very constant concentration around 0.2 ppm. The same upper-section enrichment is true for 334, whereas 335 has the lowest and most consistent U values for any of the holes, at around 0.09 ppm U.

Uranium, therefore, does not seem to show any systematic effects due to halmyrolysis either with depth or with time: the oldest hole 335, appears to have the least U, for example. In contrast, seemingly unrelated specific horizons have considerable U enrichment. Some of the horizons, however, can be related to both lithological changes and other elemental concentrations, but certainly not to the overall isotopic variations found by our coworkers. The statistical correlation coefficients of Table 2 show only a poor correlation of increasing U with depth (the coefficients ranging between +0.11 and +0.37). No meaningful correlation was found with the other alteration parameters.

Water. Total water concentrations for #332B show a systematic increase with depth (the correlation coefficient is a meaningful +0.57); there are notable exceptions. In the upper levels of the hole (100-400 m) concentrations range from 0.5 to 2%, whereas at depths of 400-600 m values increase to 1.5 to 3% and below that from 2-5% total water. Superimposed on this trend is a group of values up to 4.75% at 470 m, corresponding to the high-U horizon mentioned, and the odd, sporadic high, as at 285 m and 640 to 665 m for example, which have no expression in the U plot. It is worth noting that Thompson (1973) found no correlation between U and H_2O in basalts from D.S.D.P. Legs 2, 3 and 22. Exceptionally low water concentrations occur only at the top of the hole, where values ranging from 0.3 to 0.5% total water can be found. Correlation with other parameters (Table 2) is poor to non-existent, with the possible exception of water to *Z*: even so a coefficient of +0.32 is not very meaningful.

Hole 332A has insufficient depth to exhibit a clear pattern. Overall, however, it resembles the top of 332B, with the lowest concentrations at the top (0.5 to 2%), and the highest at the bottom (0.6 to 3%), but the trend is not convincing. Some of the localized enrichments can be associated with high U, such as at 210 m, 320 m and 400 m, whereas in other horizons, as at 430 m, there is excess water, up to 3%, with exceptionally low U values. Total water for this hole, as for #333A and 335 has practically non-existent correlation coefficients of varying signs.

Iron. The iron oxidation ratio, which is more sensitive to halmyrolysis than either increasing Fe_2O_3 or decreasing FeO taken individually, follows total water for part of hole 332B. High H_2O^{TOT} values are associated with high Fe_2O_3/FeO ratios, especially at horizons where U concentrations are also high, as at 470 m. However, below 600 m, where H_2O^{TOT} is high, both the iron oxidation ratio and U are normal: only the odd sample appears to be exceptionally oxidized. The overall down-hole variation shows only the slightest increase with depth (correlation coefficient +0.23), detectable only by a slight increase in the lowest ratios below 600 m and an especially poor correlation (+0.23) with total water, CO_2 and *Z*. Hole 332A shows no depth trend whatsoever, and no visible relationship to the total water content. However, it is significant that in 332A the Fe_2O_3/FeO ratio never

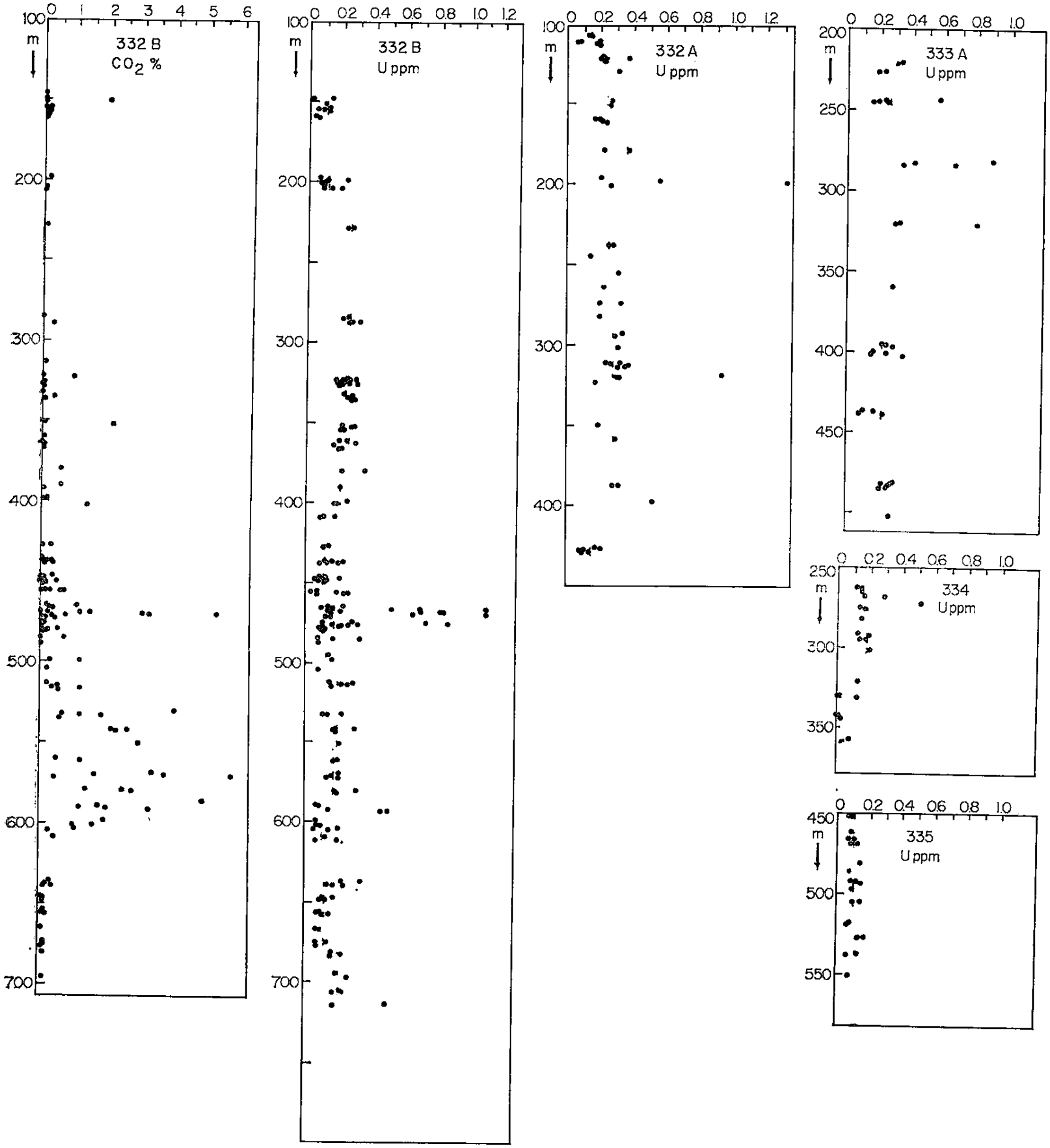

FIG. 7. Down-hole variation in the U content for the Leg 37 D.S.D.P. holes. The U content is compared with that of CO_2 for the deepest hole, 332B.

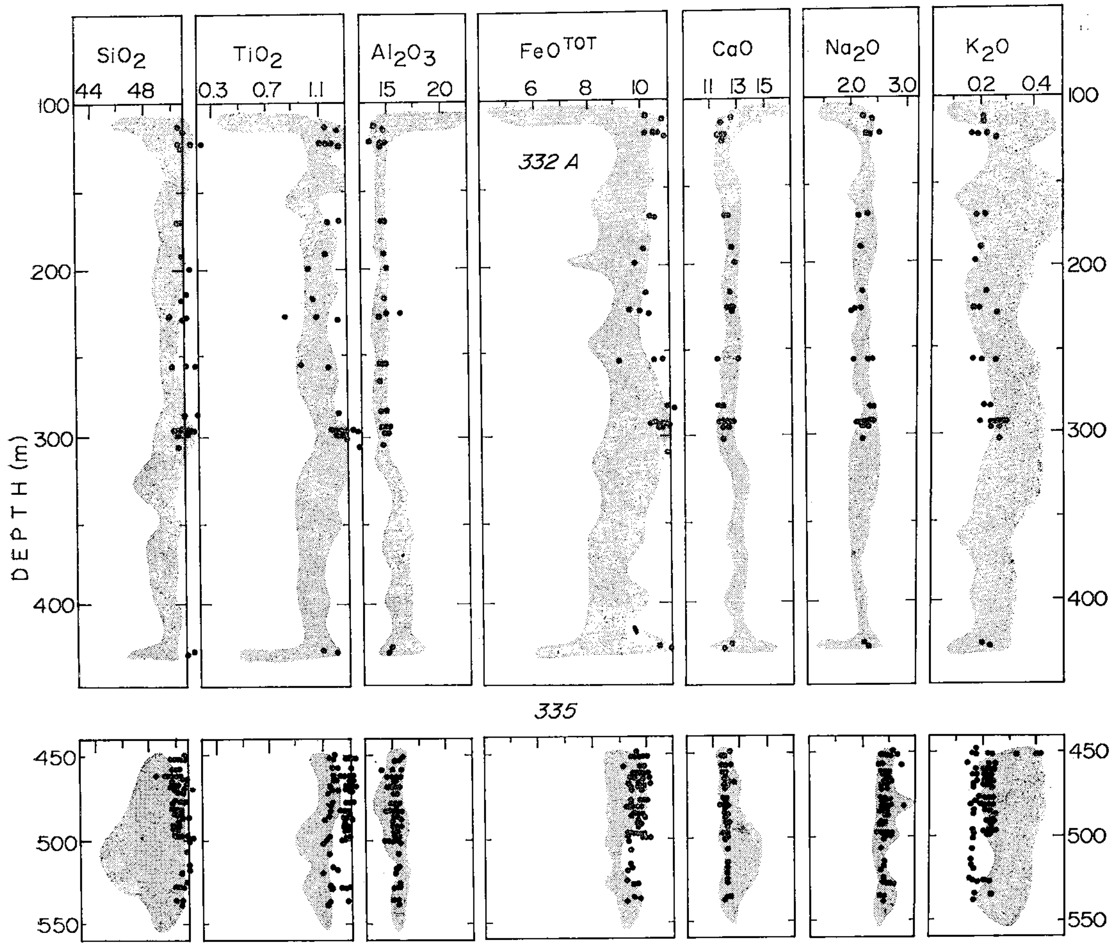

FIG. 8. Major-element concentrations for the fresh basaltic glasses from Leg 37 D.S.D.P. holes 332A and 335 superimposed on the whole-rock composition fields formed by the associated crystalline rocks.

exceeds unity, indicating that these rocks as a whole have suffered less oxidation. Hole 333A shows a slight positive correlation (+0.44) with CO_2, and hole 335 with U (+0.45). The oxidation ratio shows a slight increase with distance from the spreading centre; holes 332A, 332B, 333A, presumably of the same age, have values of 0.50, 0.63 and 0.53 respectively whereas 334 and 335 have values of 0.70 and 0.76.

Carbon dioxide. Low CO_2 values can be found at any depth in any of the holes. Sporadic highs become more common with depth in both 332A and 332B, and these can sometimes be correlated with high total water, and iron oxidation values. Statistically hole 332A shows a very slight correlation with depth (+0.32), and 332B would show a slightly stronger one down to 600 m (+0.36) but beneath that level CO_2 concentrations drop off unexplainably to some of the lowest values for any of the holes, reducing the overall correlation with depth to an insignificant +0.20. The other holes are too shallow to show any meaningful variation. Correlation with the other alteration parameters is generally poor when holes are taken as whole units, but individual horizons show good, but never systematic, correlation. In hole 332B, for example, the high-CO_2 horizon at 470 m is reflected in high U, Fe_2O_3/FeO and H_2O^{TOT}, but the high CO_2 values between 500 and 600 m are not generally matched by the other parameters. Table 3 shows that there is no systematic increase of CO_2 with distance from the spreading centres, due primarily to the high overall values in 332B and the very low ones in 334.

Basalt glasses. One of the basic problems of the foregoing investigation is that one is attempting to detect the effects of halmyrolysis superimposed on original rock variations which are commonly greater than the effects being investigated. At best, the observations are relative, and little can be said of the original composition of the rocks prior to any alteration effects.

The basaltic glasses associated with these rocks occur in varying stages of devitrification, from fresh to totally palagonitized. Their different alteration states are recognized quite readily, so that from the drill core one can select a number of very fresh examples which one can be sure will represent original glass compositions. Aumento *et al.* (1976) reported more than 190 analyses for the basalt glasses from the Leg 37 holes. When the glass analyses are plotted against depth on a diagram on which the compositional fields formed by the associated crystalline whole-rock analyses are also plotted, one finds a systematic compositional shift between the glasses and the crystalline whole rocks. Figure 8, given as an example, shows this shift for holes 332A and 335.

The glasses are always enriched in SiO_2, TiO_2, FeO^{TOT}, and in some instances in Al_2O_3 as well, and depleted in K_2O relative to the crystalline basalts. CaO and Na_2O (and MgO, which is not plotted) do not show systematic differences, although for hole 335 CaO in glasses is lower than in their crystalline counterparts. Lower concentrations of potassium, a lithophile element, in the glass phase, is one of the more surprising finds revealed by these plots.

These compositional shifts, which are not the result of analytical discrepancies between the different methods of analysis, could result from: (i) the accumulation, in the crystalline rocks, of distinct mineral phases in a groundmass of composition similar to that of the glasses, or (ii) the halmyrolytic alteration of the groundmass of the crystalline rocks, in contrast to the fresh glasses selected for analysis.

The main mineral phases found in both the glasses and the crystalline rocks include plagioclase, olivine, clinopyroxene and spinels. Addition of modal concentrations of these phases to the glasses, thereby approximating the crystalline whole-rock compositions, will cause the +Ve or −Ve shifts shown in Table 4. It will be seen that this multiple-phase addition will explain adequately the lower SiO_2 and TiO_2 content of the rocks compared to the glasses, and may explain in part the similar concentrations of Al_2O_3 and CaO found in both media, but not the tendency for Al_2O_3 to be lower, or CaO to be higher in the crystalline rocks. More important, these mineralogical additions in no way explain the lower FeO^{TOT} and much higher K_2O values for the rock; similarly, their addition would disrupt the similar MgO and Na_2O concentrations found in both the crystalline and glassy media. Obviously, therefore, adding modal amounts of the visible mineral phases to these

TABLE 4

	1	2	3	4	5	6	7	8
	Whole Rock Composition Relative to Glass	Effect of Mineral Addition to Glass				Modal Mineral Addition Effect	Postulated Halmyrolysis Effect on Glass	Inferred Halmyrolysis Effect on Glass
		Plag.	Ol.	CPX	SP.			
SiO_2	-	-	-	=	--	-	-	-
TiO_2	-	--	--	-	--	--	-	-
Al_2O_3	-or=	++	--	--	+	=	-	-or=
FeO^{TOT}	-	--	+	+	+	+or=	+	-
CaO	+or=	+	--	+	--	=	+	+or=
MgO	=	-	++	+	++	+	=	-
Na_2O	=	-	--	--	--	--	-	+
K_2O	+	-	--	--	--	--	+	+

Column 1 gives the relative compositional differences between the whole rock analyses and the associated fresh glasses for the D.S.D.P. Leg 37 holes; columns 2 to 5 give the shifts expected from original glass compositions through the addition of the minerals plagioclase, olivine, clinopyroxene and spinel; column 6 attempts to show the total overall changes expected in the glass analyses with the addition of modal concentrations of these minerals; column 7 shows the halmyrolysis effects expected on the original glass compositions; and column 8 shows the halmyrolysis effects inferred on these glasses from the data at hand.

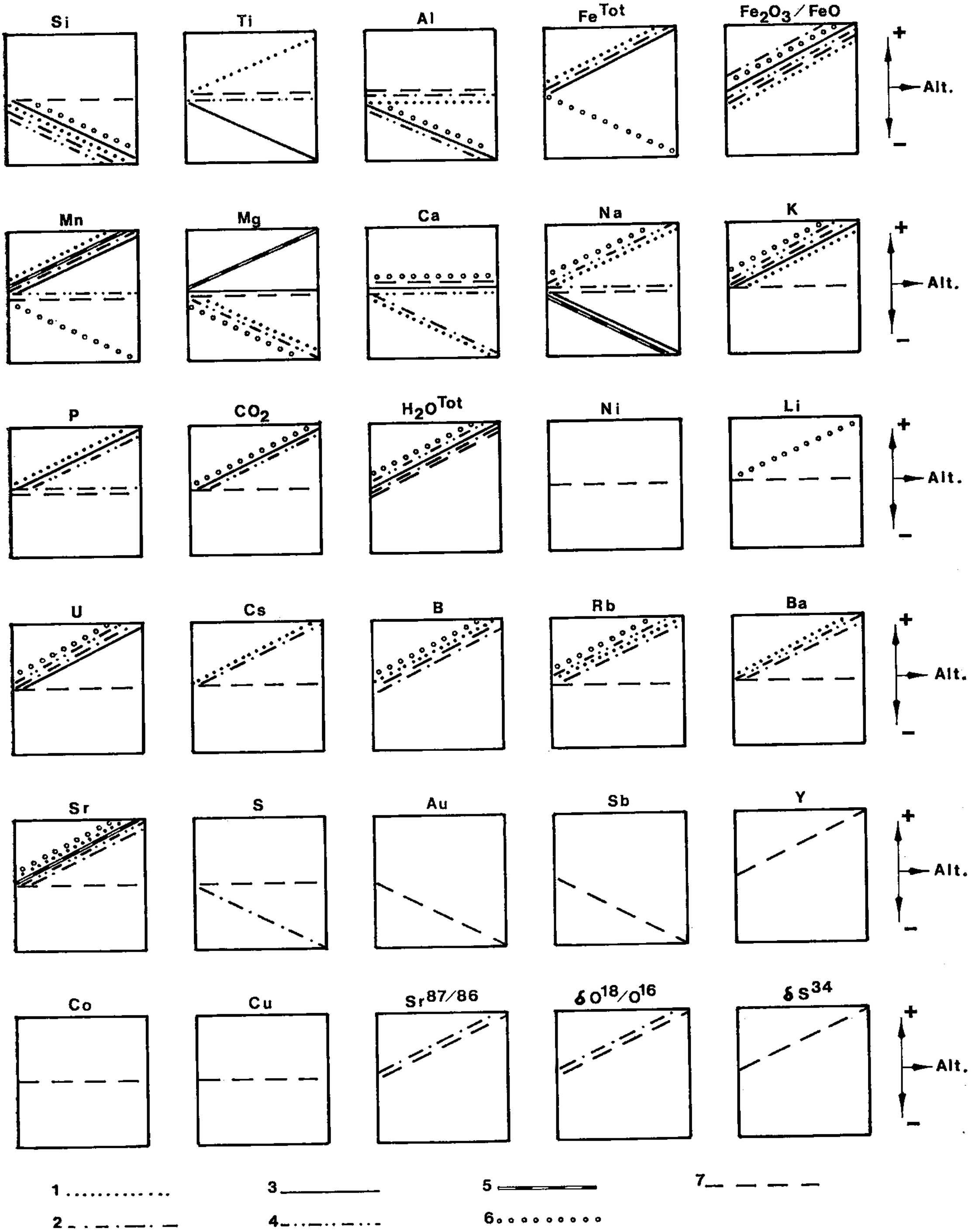

FIG. 9. Summary of all the alteration trends discussed in this study. Only the direction, and not the magnitude, of the trends is shown. The lines indicate the following: (1) MAR studies (Hart 1970) on freshest available pillows. (2) MAR studies (Aumento 1973) on freshest available pillows. (3) Most altered pillows from MAR (this study). (4) Overall alteration trends in Bermuda (this study). (5) Localized alteration trends in Bermuda (this study). (6) Localized alteration trends in Deep Drill-74 holes (this study). (7) Overall alteration trends in Deep Drill-74 holes (this study).

glasses will not help all the compositional discrepancies to converge; the opposite is true, especially in the case of K_2O and possibly of Na_2O, MgO and FeO^{TOT}.

Halmyrolysis may be the other agent affecting the compositional discrepancies. Table 4 also shows the direction of chemical variations one might expect the glass compositions to take given exposure to sea water according to the MAR studies reported here. Halmyrolysis should enhance the mineral addition effects in the cases of SiO_2 and TiO_2, and assist the otherwise nonexistent Al_2O_3 and CaO trends. At the same time it will enhance the glass/rock divergence by increasing the -Ve effect of Na_2O and the +Ve one of FeO^{TOT}. However, it will oppose the -Ve mineralogical K_2O effect, thereby providing a possible explanation for the lower K_2O concentrations found in the fresh glass relative to the crystalline whole-rock analyses.

The examination of these fresh glasses shows quite clearly that halmyrolysis has affected all the Leg 37 basalts to a considerable extent. Some of the trends detected, notably those of FeO^{TOT} and Na_2O, seem to be working in directions opposite to those detected for the surface pillows, thereby confusing the issue further. What is clear, however, is that examination of these fresh glasses offers us the only opportunity of measuring original compositions free from the effects of halmyrolysis. We should use the glass data in conjunction with detailed modal mineralogical data and apply corrections to the whole-rock oxide values measured, thereby reproducing their original, pre-halmyrolysis compositions.

CONCLUSIONS

The diversity of alteration trends for all the foregoing data is rather confusing; therefore, an attempt is made to summarize these various trends in Figure 9. In the Figure no attempt is made to demonstrate the magnitude of the trends: the diagrams are simplified to show only the direction in which specific elemental concentrations have been noted to move with increasing alteration in the different environments studied. We see diversities not only between different oceanic settings, but also within the settings themselves. We find, amongst the major elements, that only H_2O^{TOT} and the iron oxidation ratio give consistent trends no matter what the environment or type of sample. If one disregards the non-existent trends (those represented by horizontal lines in Fig. 9) then SiO_2, K_2O, Al_2O_3, CaO, P_2O_5 and CO_2 can also be thought to undergo predictable enrichment or depletion under different alteration conditions. Variations in the other major and minor elements, especially MnO, MgO, and Na_2O are so dependent on the origin of the sample, and thus presumably on the local environmental conditions, that a diversity of trends is detected.

Trace elements and isotopes, given the lesser amount of data in hand, seem to give more consistent results: they produce either no detectable trends whatsoever, or well-defined trends, always in the same sense no matter what the origin of the samples. U, Cs, B, Rb, Ba and Sr are good examples of this conformity. One wonders, however, what would happen to these systematic trends, and especially to those less well-defined of S, δS^{34}, Sr^{87}/Sr^{86} and $\delta O^{18}/O^{16}$, if the quantity of data were increased to the level of that available for the major elements.

A number of interesting observations have come out of this study of diverse oceanic settings. Firstly we have the diversity of trends for some of the key elements. We feel this reflects the environmental conditions which existed around the rocks at the time of active interaction with sea water, be it halmyrolysis or at more elevated temperatures. We shall report on this aspect in a subsequent paper when the results of experimental investigations of basalt/sea-water interaction under realistically simulated oceanic conditions will be discussed.

Secondly, we have shown that the alteration effects detected by us and others on surface pillow lava are only of local importance, and by no means representative of even the upper part of oceanic layer 2. Similar, or opposite effects can be detected in very localized horizons throughout the layer, generally associated with pillow margins, veins or fractures. Therefore, alteration through the oceanic crust is more a function of the local rock structure than of depth below the ocean floor.

Thirdly, isotopic data indicate that there is an overall decrease in sea-water interaction with depth. The increasing total water content detected with depth in the deep hole 332B cannot therefore be due to sea water circulating downward from the ocean floor, but to the increasing effect of primeval waters derived from deep in the crust of uppermost upper mantle. Given the geochemical data presented here one cannot envisage, at least not on the Mid-Atlantic Ridge 36°N, the action of convection cells of sea water postulated by Lister (1972) migrating through the oceanic crust, supposedly helping to cool the crust and causing extensive alteration of the basalts. Quite possibly, however, the postulated convection cells may still exist, but with upwelling limbs of a very restricted, localized extent, affecting only a very small percentage of the crust.

Finally, we have found little evidence, apart from very preliminary isotopic data, for a systematic change in the composition of oceanic layer two as whole with time, at least for the last 16 m.y. We cannot say whether the time interval we have observed is too short, or whether our penetration and sampling of the crust is still too shallow. Perhaps these effects would become more evident given deeper holes into older oceanic crust.

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