

"2nd Maurice Ewing Symposium (Deep Drilling Research in the Atlantic Ocean : Ocean crust) - Talwani, Harrison and Hayes Editors."

p. 352-368 - 1979 - Copyrighted by the American Geophysical Union.

ALTERATION, FRACTIONAL CRYSTALLIZATION, PARTIAL MELTING, MANTLE PROPERTIES
FROM TRACE ELEMENTS IN BASALTS RECOVERED IN THE NORTH ATLANTIC

Henri Bougault

Centre Oceanologique de Bretagne, B.P. 337, 29273 Brest Cedex, France

Jean-Louis Joron and Michel Treuil

Institut de Physique du Globe, 4, place Jussieu, 75230 Paris cedex 05,
et Laboratoire Pierre Sue, Centre d'Etudes Nucleaires, B.P. n 2,
91190 Gif-sur-Yvette, France

Abstract.—Alkali metals prove to be very sensitive to alteration process even if this process is moderate. It is very difficult to use these elements to trace magmatic processes since their concentration may vary within an homogeneous "unaltered" unit.

From all the basaltic units investigated, a classification of "low partition coefficient" elements is presented (Sc, Ti, V, Y, Zr, Nb, La-Tb, Hf, Ta, Th).

The incompatible elements ratios (Y/Tb, Zr/Hf, Nb/Ta) are constant in the samples studied and are nearly equal to the same ratios in chondrites. This is consistent with the existence of an homogeneous primordial mantle at the scale of the North Atlantic, compatible with a chondritic composition of the earth. —

More than two distinct mantle sources derived from the primordial mantle (invoking the possibility of mixing of sources), are needed to explain the data. Moderate "incompatible" or "hypermagnaphile" element/highly "hypermagnaphile" element ratios are function of a partial melting.

Partial melting (variable), magma chamber dynamics (possibility of mixing) and only one or two eruptions is a cycle frequently repeated : variability of partial melting and limited sampling of liquids derived from the same initial liquid explain the variable rare-earth patterns encountered in one single hole and makes it difficult to determine the proportion of minerals crystallizing.

Introduction

Several sites have been drilled into the oceanic crust in the North Atlantic up to and including Leg 53 of the Glomar Challenger (DSDP-IPOD program) : Leg 37, sites 332 to 335 at 36° N along a track perpendicular to the ridge ; Leg 45 sites 395 and 396 at 22° N almost symmetric with respect to the ridge in crust about 7 and 10 m.y. old ; Leg 46, site 396 again ; Leg 49, three sites 407, 408, 409 at 63° N, along a track perpendicular to Reykjanes Ridge, one site 410 at 45° N and three sites 411, 412 and 413 at about 36° N near the FAMOUS area ; the megalec (Legs 51, 52, 53) at 25° N, at 110 m.y. old sites 417 and 418. In addition the FAMOUS operation at 36° N provided an intensive sampling both by dredging and by submersible in the Rift valley and adjacent fracture zones.

During the drilling program, we have operated the CNEXO X-ray fluorescence van on board the Glomar Challenger to obtain on board major elements analysis (and some trace elements during Legs 45 and 46). These shipboard chemical data have been useful in defining the different basalt units and for selection of samples for shore-based studies (Bougault, 1977). Our contribution to the shore based studies has been the systematic study of trace elements both through X ray fluorescence spectrometry and neutron activation analysis in samples which have been selected on board for shipboard analysis (XRF : V, Cr, Ni, Co, Rb, Sr, Y, Zr, Nb ; NAA : Sc, Ni, Co, Zr, La, Eu, Tb, Hf, Ta, Th).

Leg 53 marks the end of first phase of the IPOD program as far as drilling the crust in the Atlantic Ocean is concerned and we feel it is important to draw out major conclusions which now

† Contribution n° 595 du Département Scientifique, Centre Océanologique de Bretagne.

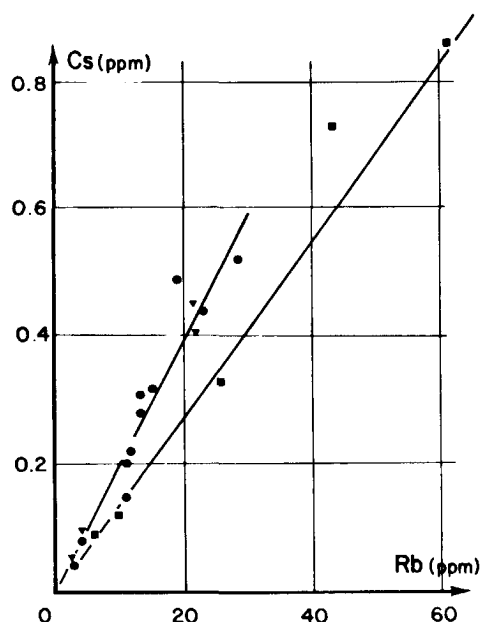


Fig. 1 : Cs versus Rb in Hole 417 A. The black dots represent the data below core 30 and the squares represent the data above core 30. The triangles represent altered samples in Hole 417 D.

can be made. Discussions related to alteration, magmatic units, fractional crystallization, magmatic cycles, partial melting, heterogeneity or homogeneity of the mantle or upper mantle can be now made as a consequence of the data which have been made available through the DSDP program and FAMOUS operation. We have analysed more than 400 samples ; results (sample by sample) are given (or will be) in DSDP Initial Reports, in Arcyana (1977) and in Bougault *et al.* (in press) and are not duplicated in this paper ; only tables for specific samples or group of samples necessary for the discussion are reported.

Alteration process. Alkali metals and strontium

Basalt alteration is discussed with respect to the behavior of alkali metals (K_2O , Rb, Cs) and Sr. Two examples are considered, sites 417 and 418 (Leg 51) on one hand, and site 395 (Leg 45) on the other. Basalts of sites 417 and 418 have experienced a high degree of alteration which resulted in extensive change of major element composition. Site 395 basalts experienced only slight alteration and can be considered to be fresh samples on the basis of their low water contents.

At site 417, the variation of alteration effects are observed at two scales, which may be related to water circulation.

- Within a single core (e.g. core 35 of hole 417 A), Rb varies from 12 to 29 ppm, Cs from 0.22 to

0.56 ppm and K_2O from 0.98 to 2.04 %. This is probably due to local cracks or fissures through which water circulates resulting in the formation of alteration minerals (Joron *et al.*, in preparation).

- Major interstice differences are observed between hole 417 A and hole 417 D (and 418 A) which are about 400 meters apart (Joron *et al.*, in preparation). Hole 417 A is highly altered ; the volcanic pile has been divided into several zones according to the occurrence of different minerals : montmorillonite and celadonite occur in all zones ; chlorite, scolecite and analcite occur in different zones (Legs 51, 52 ; scientific party ; in preparation). Potassium varies from $\sim 6\%$ K_2O in very highly altered zones (top) to classical values in oceanic tholeiites ($< 0.2\%$) at the bottom. Thus a general decrease of alteration is observed from the top to the bottom. At the opposite, in hole 417 D, some 400 meters from hole 417 A, strikingly fresh basalts were recovered including fresh glass.

This difference in alteration between 417 A and 417 D (110 m.y. old) only 400 meters apart is explained by a difference in topography between both holes. The 417 A altered site is a topographic high which remained unburied approximately 20 m.y. after eruption (lack of cretaceous sediments) (Leg 51, 52 ; scientific party, in preparation). According to Donnelly (1978) "we might regard the hill as a sort of upside down drain, which, lacking an impermeable sedimentary cap, becomes the principal conduit for convective effluent water".

If this interpretation is correct, it means that much of the alteration process (at least the type of alteration observed) takes place shortly after eruption. When the basalts are covered by a sufficient sedimentary thickness they are protected from further sea water circulation.

A good correlation is found between Cs and Rb (fig. 1) (K versus Rb is also similar). But the dispersion of points is far greater than the analytical precision ($K_2O \pm 0.02\%$, Rb ± 2 ppm, Cs ± 0.02 ppm). The abundances of these elements

TABLE 1. Comparison of uptake of alkali metals from sea-water and residence times of alkali metals in the ocean. Sea-water concentrations and residence times are from Goldberg (1965).

	K	Rb	Cs
Uptake Altered sample/ sea water proportional to	44.7	242	1 120
Residence time	$1.1 \cdot 10^7$	$2.7 \cdot 10^5$	$4 \cdot 10^4$

BOUGAULT

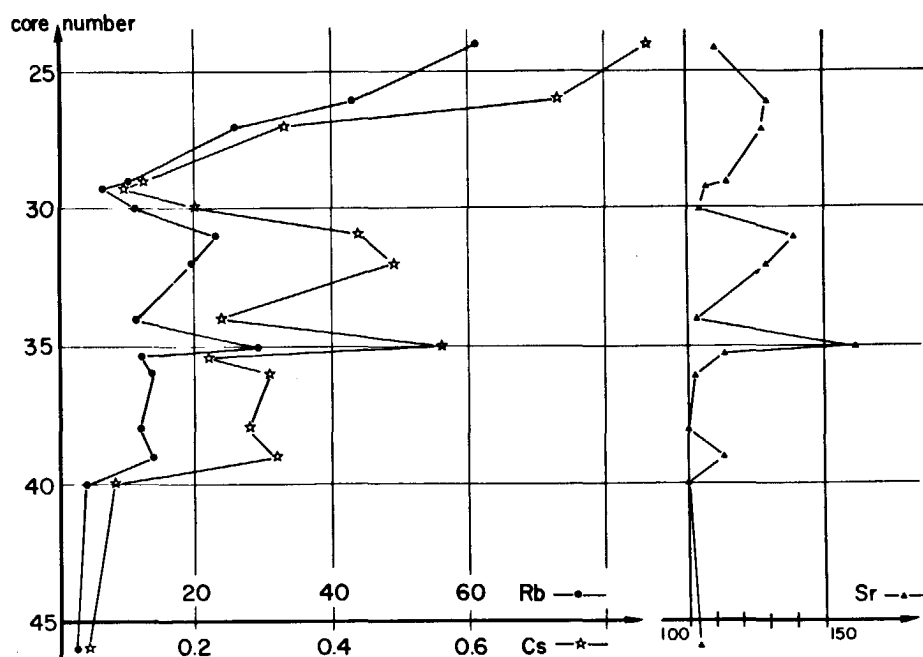


Fig. 2 : Hole 417 A : Rb (ppm), Cs (ppm), Sr (ppm) variation down the hole. Core 25 is about 270 m, core 45 is about 405 m.

correlates positively with the abundances of alteration minerals (unaltered to highly altered samples) but the elemental ratios, at least in first approximation, may be a function of the proportion of the different kinds of minerals present in the different zones. This could account for the dispersion of points observed in Figure 1. If sea water circulation is responsible for alteration, the uptake by rocks of alkali metals from sea water can be defined by the ratio of the concentration of these metals in altered rocks (in hole 417 A, initial concentration in fresh

rocks can be neglected compared to concentration due to alteration) to sea water concentration. Thus, the figures mentioned Table 1, which represent the ratio of concentrations of one representative sample to sea water concentrations (for K, Rb and Cs), are proportional to the uptake of these metals. Cs uptake is higher than Rb uptake which in turn is higher than K uptake. We observe that the uptake of investigated elements varies in the opposite way compared to residence times (table 1). These observations are in agreement with a sea water origin of alkali metals

TABLE 2. Hole 395 A, aphyric unit A 3, 200 m thick. Note the possible variation in alkali metal concentrations compared to other elements.

	Ni	Ti	Tb	La	Ta	K ₂ O	Rb	Cs
33-2 127-129	114	10 200	0.85	4.3	0.22	0.24	2.9	0.02
35-1 53-54	113	10 260	0.91	4.0	0.23	0.18		0.05
37-1 136-141	121	10 200	0.85	4.4	0.22	0.29	4.7	0.28
39-1 102-107	128	10 320	0.85	4.0	0.22	0.29	3.1	0.17
41-1 142-144	121	10 440	0.93	4.0	0.24	0.27	4.4	0.21
42-1 86-89	115	10 600	0.92	4.0	0.23	0.16	< 1.5	< 0.02
45-1 124-127	111	10 660	0.90	4.2	0.24	0.18	2.8	< 0.02
47-1 63-67	119	10 020	0.87	4.0	0.22	0.21	< 1.5	< 0.02
48-1 135-140	120	10 260	0.87	4.1	0.23	0.25	3.6	0.081
49-2 13-17	118	10 520	0.90	4.1	0.23	0.17	2.3	< 0.02
51-2 41-44	119	10 520	0.89	3.9	0.225	0.23	1.5	0.02
52-1 48-53	118	10 440	0.90	4.0	0.22	0.18	2.2	0.03
53-1 7-11	119	10 320	0.88	3.9	0.23	0.18	2.5	0.02
54-1 48-51	111	10 320	0.90	4.0	0.23		< 1.5	0.015
55-1 49-54	115	10 380	0.91	4.1	0.24	0.17	5.4	0.20

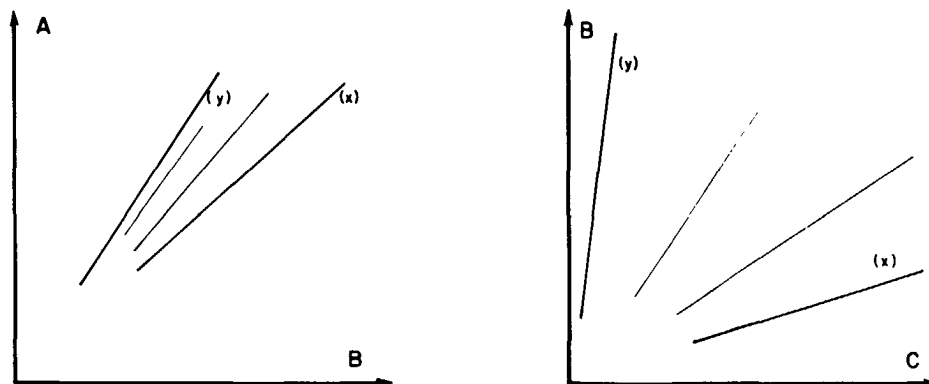


Fig. 3 : Hole 395 A ; variation of Cs and K₂O within three different basaltic units.

in altered basalts and if so, alteration of the oceanic crust could play a role in the budget of these elements in sea water.

The variation of Rb, Cs and Sr with depth in hole 417 A is given in figure 2. As previously mentioned a general decrease in concentration of Rb and Cs is observed. This agrees with the general decrease of alteration with depth (core numbers). The variation of Sr in alteration is very slight compared to the variation of alkali metals. In core 35 for instance the Rb concentration is 25 times higher than in unaltered samples while for Sr the enrichment ratio is 1.5. If we take into account that Sr occurs largely in carbonate phases, leaching moderately altered samples with acid solutions may enable us to measure reasonable values for ⁸⁷Sr/⁸⁶Sr (if no isotopical equilibration).

In hole 395 A (leg 45, 22° N, 7 m.y. old) most samples selected for shipboard analysis can be considered to be fresh (H₂O⁻, loss on ignition). In this hole, within a single homogeneous unit 200 meters thick we observe the variation of alkali metals due to moderate alteration of samples which otherwise are considered fresh. Table 2 shows the values obtained for a high partition coefficient element (bulk partition coefficient) Ni, and four low partition coefficient elements Ti, Tb, La, Ta together with K₂O, Rb and Cs. The Ni, Ti, Tb, La and Ta concentrations do not vary throughout this unit. The major elements and some other trace elements investigated confirm this homogeneity. Only the alkali metals (and Sb) show variation in the unit (Bougault et al., in press) with the greatest variation exhibited by Cs. In addition, with the exception of K₂O in 55 # 1 49-54, K₂O, Rb and Cs covary. Figure 3 shows the variation of Cs versus K₂O for three different units of hole 395 A of Leg 45.

These observations indicate that the use of alkali metal concentrations in oceanic basalts as petrogenetic indicators should be made with extreme caution. Alteration processes can produce extensive variation in the concentration of these elements, even when the samples appear from other criteria to be fresh.

Partition coefficients and physico-chemical properties of trace elements

Through the behavior of trace elements, it has been attempted for several years to model the different parameters or processes involved in magma genesis. This modelling requires the knowledge of the mineral/melt partition coefficients for the trace elements and phases involved in the process to be modelled. Rare earths, K, Rb, Sr, Ba and the first transition series elements have been the object of numerous investigations of this type. This section is concerned with elements which behave incompatible or low bulk partition coefficient (< 1) or are "hygromagmaphile" (Treuil, 1973). These elements are presented in Table 3.

BOUGAULT

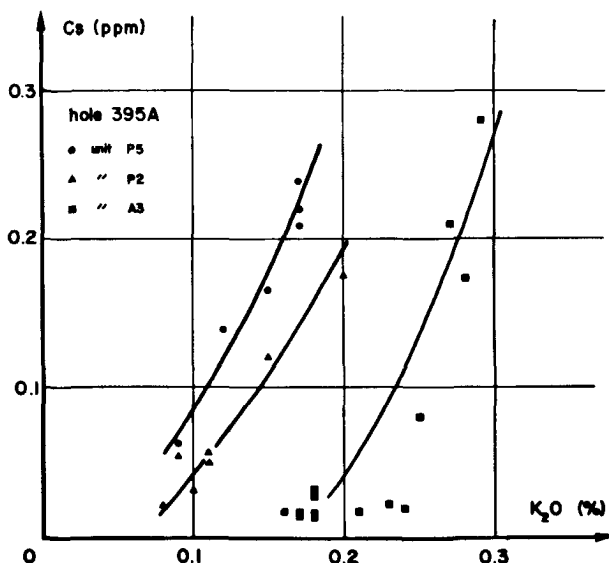


Fig. 4 : Way used to classify the elements according to their partition coefficients (see text). A versus C would show a similar figure.

From the data obtained in the North Atlantic we will classify these elements according to their bulk partition coefficients and then discuss this classification with respect to their physico-chemical properties.

This classification utilizes the relative behaviors of the trace elements in fractionation processes. Considering three elements, A, B, C : A is plotted versus B and B versus C for different series of samples from series x to y (Fig. 4). If we know from previous investigation that the bulk partition coefficient for C (D^C) is lower than the bulk partition coefficient for A (D^A), the partition coefficient of B (D^B) can be classified with respect to A and C by comparing the position of the different series of samples (from x to y) and the observed range of slopes. In the given example, D^B lies between D^A and D^C .

Figures 5 and 6 show such a comparison for elements belonging to the third transition series : Tb, Hf, and Ta. Hf and Ta are fractionated to a large degree, whereas the fractionation of Tb and Hf is less. We know from other investigations (comparing Ta to La) that D^{Ta} is lower than D^{Tb} .

From the position of each series of samples in each diagram, it is deduced that D^{Hf} lies between D^{Tb} and D^{Ta} . Following the same method of comparison, it can also be deduced that D^{Hf} is lower than D^{Ta} (Fig. 7). In this way, a classification based on rock/melt partition coefficients is obtained. This classification is as follows :

$$D^{Sc} > D^V > D^Y \approx D^{Tb} > D^{Ti} > D^{Zr} \approx D^{Hf} > D^{Nb} \approx D^{Ta} \\ \approx D^{La} > D^{Th}$$

Is this classification compatible with the properties of elements ? To account for the "incompatible" or "hygromagmaphile" character of these elements, two processes at least have to be considered :

i) Cation substitutions in the structure of a mineral. No stabilization through crystal field (Burns, 1970 ; Curtis, 1964) needs to be considered since all cations investigated have a rare gas configuration. The ease with which such cations enter a crystal structure depends mainly upon their

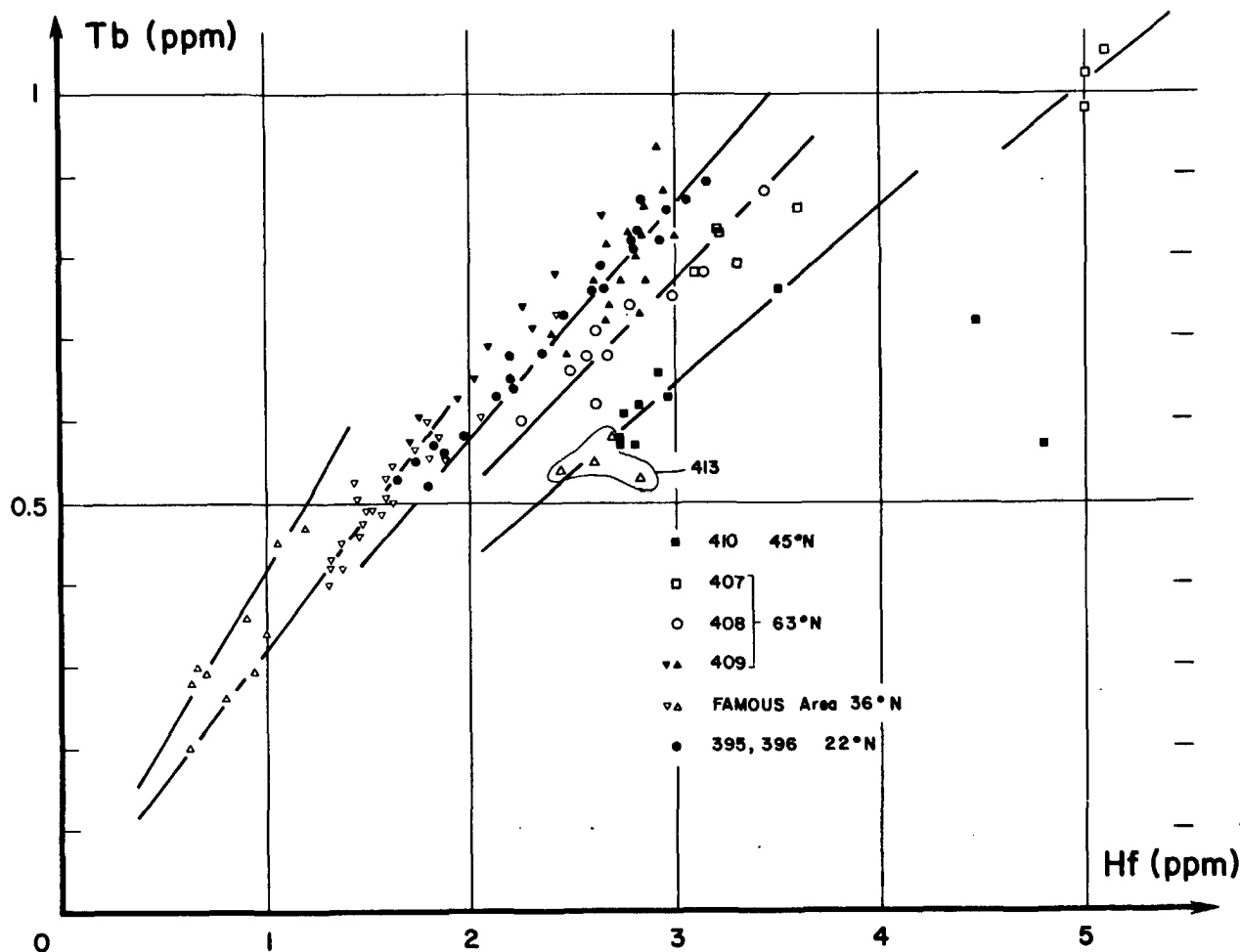


Fig. 5 : North Atlantic : Tb versus Hf.

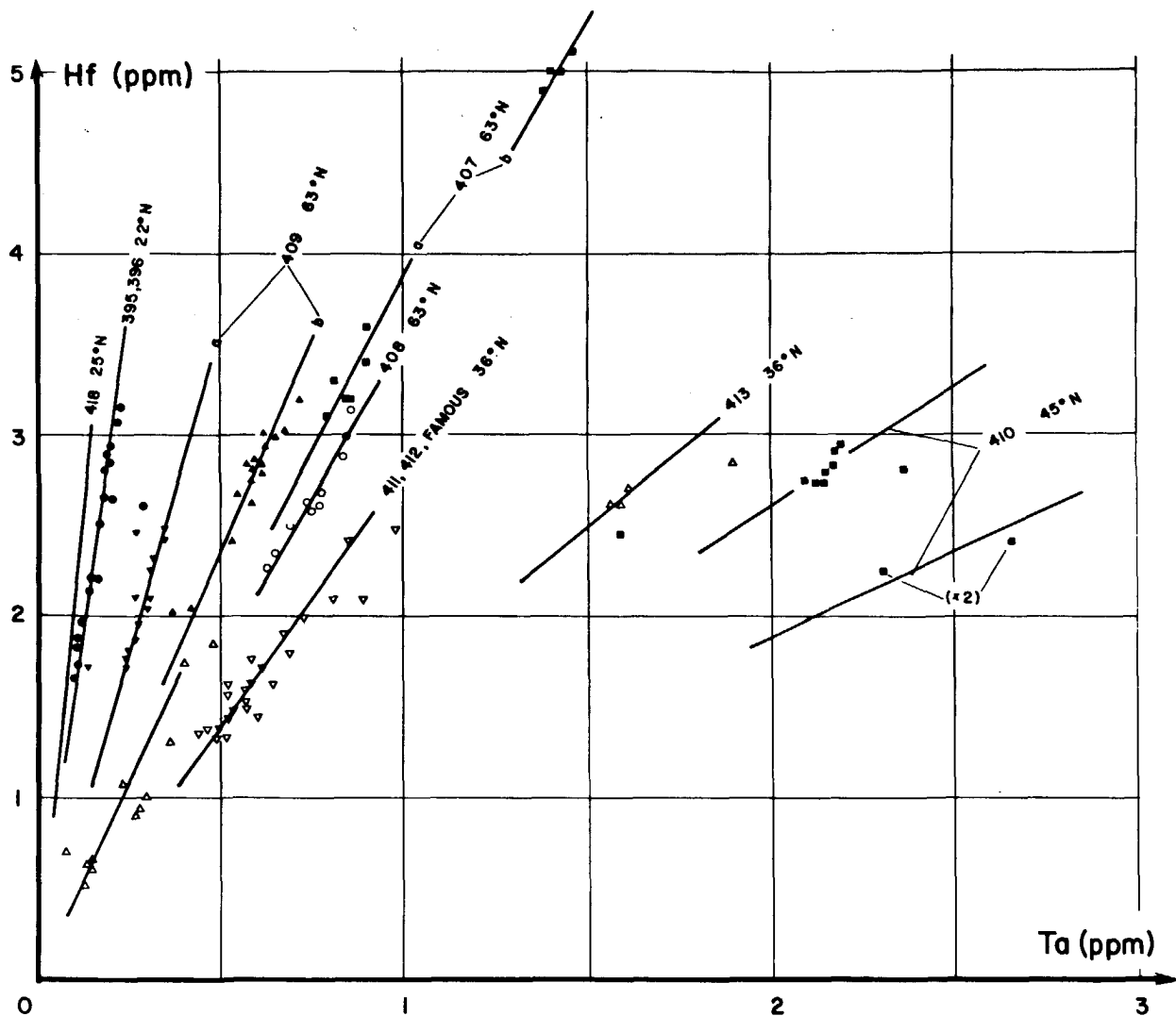


Fig. 6 : North Atlantic : Hf versus Ta.

ionic radii and their charges ; this corresponds to the "incompatible" character of the elements with respect to the host structure.

ii) Complex formation in the liquid (Treuil, 1973). This also depends upon charges and sizes of cations, but in a different way, for instance through the ratio n/r (charge/ionic radius) ; the higher is this ratio, the greater is the stability of a complex. The possibility of complex formation accounts for the "hygromagnaphile" character of these elements.

Table 3 shows for the elements of concern, the charge most common in nature, the ionic radius and charge/ionic radius ratio.

If we consider only the size of the ions, we note that the ionic radius decreases from Y to Zr to Nb (0.92, 0.79, 0.69 Å) and thus it is not possible to explain why the partition coefficients decrease from Y to Zr to Nb. But if we

consider charges (3, 4 and 5 respectively, incompatibility increasing with respect to crystal structure) and even more n/r (3.26, 5.06, 7.25 ; possibility to form complexes in the liquid increasing) it is possible to explain why the partition coefficients decrease from Y to Zr to Nb.

Considering elements belonging to groupe IIIA, IV A, V A, of the second and third transition series, we observe that for each of the element pairs, Y-Tb, Zr-Hf and Nb-Ta, the two ions have the same charge and the same ionic radius (as a consequence the same n/r ratio). Consequently it can be concluded that each element in the pair processes the same incompatibility with respect to a crystal structure and the same possibility of forming complexes in the melt. The elements in each pair do not fractionate with respect to the other since they have equal or nearly equal partition coefficients.

BOUGAULT

D^{La} is close to D^{Ta} or D^{Nb} in spite of their differing charges, ionic radii and n/r ratios. La is more incompatible based on ionic radius, less incompatible based on charge and less hygromagnaphile based on n/r than Ta (see Table 3). These different effects compensate to produce similar partition coefficients for both elements. Despite the similarity in D^{La} and D^{Ta} (or D^{Nb}) it is important to keep in mind the differences (radius, charge, n/r) which exist between La and Ta when compared to Nb-Ta similarity. This point will be discussed later.

In the group IV A elements (Ti^{4+} , Zr^{4+} , Hf^{4+} , Th^{4+}) (table 3) the low value of D^{Th} is a consequence of its large ionic radius (1.02 Å) as compared to Zr^{4+} or Hf^{4+} radii (0.79 and 0.78 Å). A similar observation can be made comparing Zr^{4+} - Hf^{4+} (0.79 and 0.78 Å) to Ti^{4+} (0.68 Å). Within a column the classification of the elements according to their partition coefficients is dominated by the incompatible character rather than by the hygromagnaphile character of each element. Similar deductions can be made considering Sc^{3+} , Y^{3+} and the heavy rare earths (Tb^{3+} for instance).

From the results for the group III A (Sc, Y, heavy rare earths) and group IV A (Ti, Zr, Hf and Th) elements the following rule can be formulated :

(a) within a group (column) the higher is the ionic radius, the lower is the partition coefficient. Considering the second and third transition series (Y, Tb, Nb) and (heavy rare earths, Hf, Ta), it can be deduced :

(b) the higher is the possibility to form complexes in the liquid (n/r), the lower is the partition coefficient.

D^V is an exception to the rules : it satisfies rule (a) but does not satisfy rule (b), since its partition coefficient is classified between Sc and Ti. A possible explanation of this anomaly is that V may have a lower state of oxidation. If so, n/r would be lower and V would not be anymore in a rare gas configuration. Consequently it would be subject to some crystal field stabilization in octaedral structures.

The present study confirms known properties of these elements. It confirms the geochemical similarity of Y and heavy rare earths, and the incompatible behavior of Ti, see for example Cann (1970), Bougault (1977) and Bougault *et al.* (b) (in press).

Additional information is also available. These include the non-fractionation of Zr/Hf and Nb/Ta. Knowing D^{La} and D^{Tb} it is possible to place limits

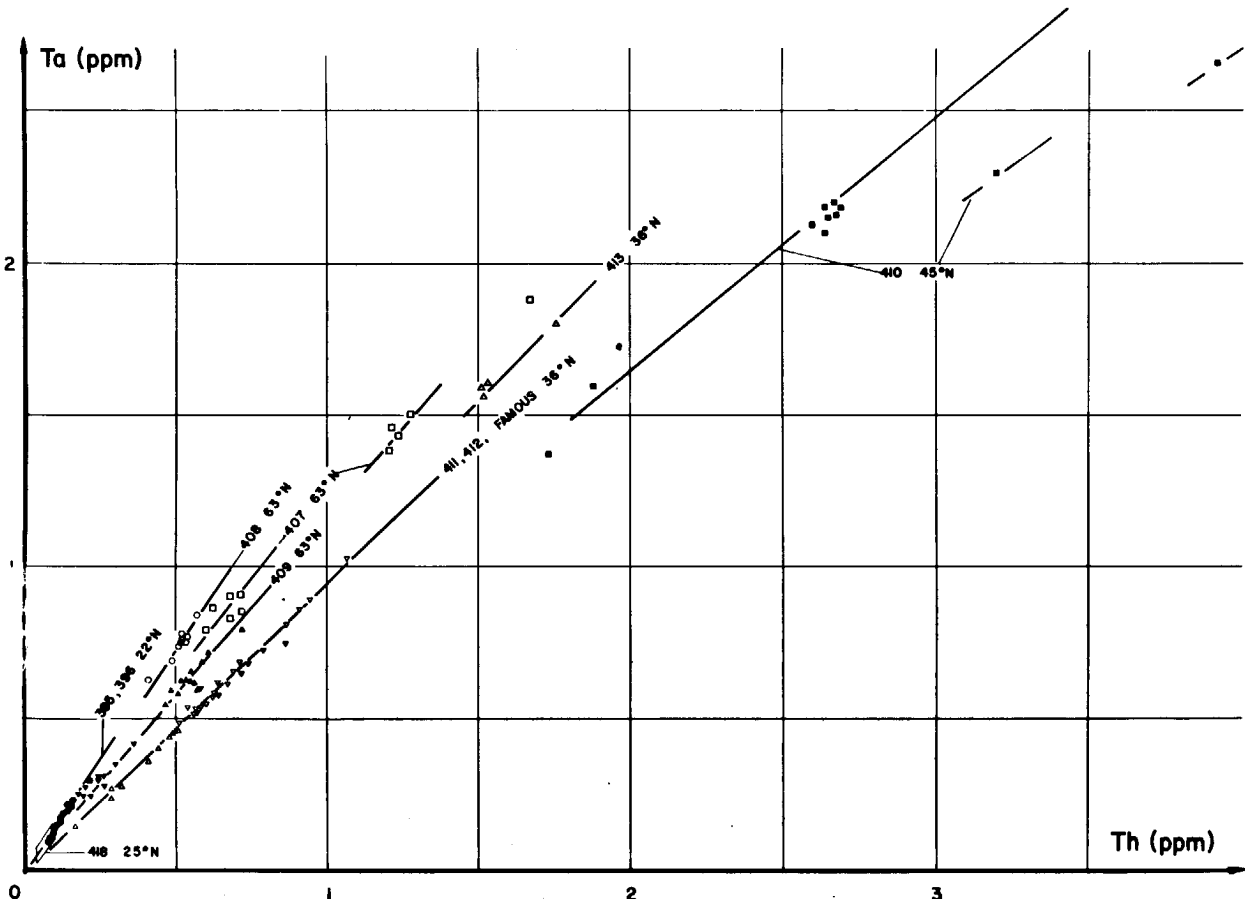


Fig. 7 : North Atlantic : Ta versus Th.

TABLE 3. "Low partition coefficient" elements investigated : ionic radii are from Goldschmidt (1926). > (or <) means that partition coefficients of the elements in left side (or up) is classified higher (or lower) than the element in right side (or down). = means equal or similar, partition coefficients.

	III A		IV A		VA	
Transition series	0.81	3+	0.68	4+	0.59	5+
1	Sc	>	Ti		V	
	3.70		5.88		8.47	
					<i>n</i> lower <i>n</i> , <i>r</i> / <i>n</i> / <i>r</i> \	
					CFSE	
2	0.92	3+	0.79	4+	0.69	5+
	Y	>	Zr	>	Nb	
	3.26		5.06		7.25	
3	1.14	3+	0.92	3+	0.78	4+
	La	<	Tb	>	Hf	>
	2.63		3.26		5.13	
4			1.02	4+		
			Th			
			3.92			

r: ionic radius n: charge

Element

n/r

on D's for other elements and classify them accordingly.

Mantle homogeneity or heterogeneity : Y/Tb, Zr/Hf, Nb/Ta, La and Th. A comparison with chondrites and lunar samples

In the previous section, it has been shown that within each element pairs Y-Tb, Zr-Hf, Nb-Ta, fractionation of one element with respect to the other is not observed. In fact, two conditions are required to maintain Y/Tb, Zr/Hf, Nb/Ta ratios constant or nearly constant (fig. 8, 9 and 10) for all studied samples, although the absolute concentrations vary over a wide range (for instance, Nb varies between 2 to 90 ppm). These conditions are : (1) little or no fractionation of the elements in the pair has occurred, and (2) the ratios in the source regions prior to magma gene-

rations were constant and equal to that in the derivative basalts.

Because the samples studied were recovered in different parts of the North Atlantic (latitudes from 22° N to 63° N ; crustal ages from 7 m.y. at 22° N to 110 m.y. at 25° N), the point (2) can be interpreted in terms of homogeneity of the mantle at the scale of the North Atlantic. These couples of elements give us the opportunity to compare the primordial mantle with chondrites. Table 4 shows the values obtained for the ratios of these elements both in the North Atlantic samples and in chondrites. The Y/Tb ratio in chondrites is from Frey *et al.* (1968) and the range of ratios for Zr/Hf is obtained from Ehman and Rebagay (1970) and Ehman and Chi (1974). Ganapathy *et al.* (1976) give lower range of values for Zr/Hf in chondrites. Ehman *et al.* (1975) mention the difficulty in obtaining precise ratios of Zr/Hf in chondrites

BOUGAULT

because of the small size of samples available and because of low abundance levels and error limits (+ 10 %).

Very little data are available for Nb and Ta. The values of 14 and 17 are from Graham and Mason (1972) and Vinogradov (1962).

The limits of the ratios reported in Table 4 for the North Atlantic samples include both analytical errors and possible fractionations within element pairs. The limits for Nb/Ta correspond very closely to analytical error limits whereas the limits for Y/Tb and Zr/Hf are approximately twice that of the analytical error limits. This suggests that despite the range of variation of concentrations (shown in Table 4 by the factor of variation), Y/Tb and Zr/Hf may fractionate a little more easily than Nb/Ta. This can be attributed to some slight differences between partition coefficients and to the orders of magnitude of the partition coefficients (Nb and Ta being the lowest).

Taking into account the chondritic data, analytical precisions, and comparisons of data

from different laboratories, the ratios of Nb/Ta, Zr/Hf and Y/Tb attributed to a primordial mantle favor a chondritic composition for the earth.

Ehman *et al.* (1975) found Zr/Hf ratio to be 39 ± 1 in the Palisades Sill (New Jersey), 39 in two chilled margins and 47.3 ± 0.8 in the Littletown metamorphic series. These figures are in good agreement with our own data for oceanic rocks but contrast with the range of values that these authors have found for lunar rocks. Wanke *et al.* (1975) similarly found variations in Zr/Hf for lunar rocks as well as for Nb/Ta using the data of Willis *et al.* (1972). These authors attempt to explain the possible fractionation of Zr-Hf (and Nb-Ta) invoking possible different oxydation states of these elements. They state that achondrites which have Zr/Hf ratio higher than chondrites may reflect an even greater fractionation. This model is supported by oxygen fugacities calculated from $\text{Eu}^{2+}/\text{Eu}^{3+}$ which decreases from achondrites to lunar ferro-basalts to terrestrial rocks. If such an interpretation is correct, *i.e.* the possibility

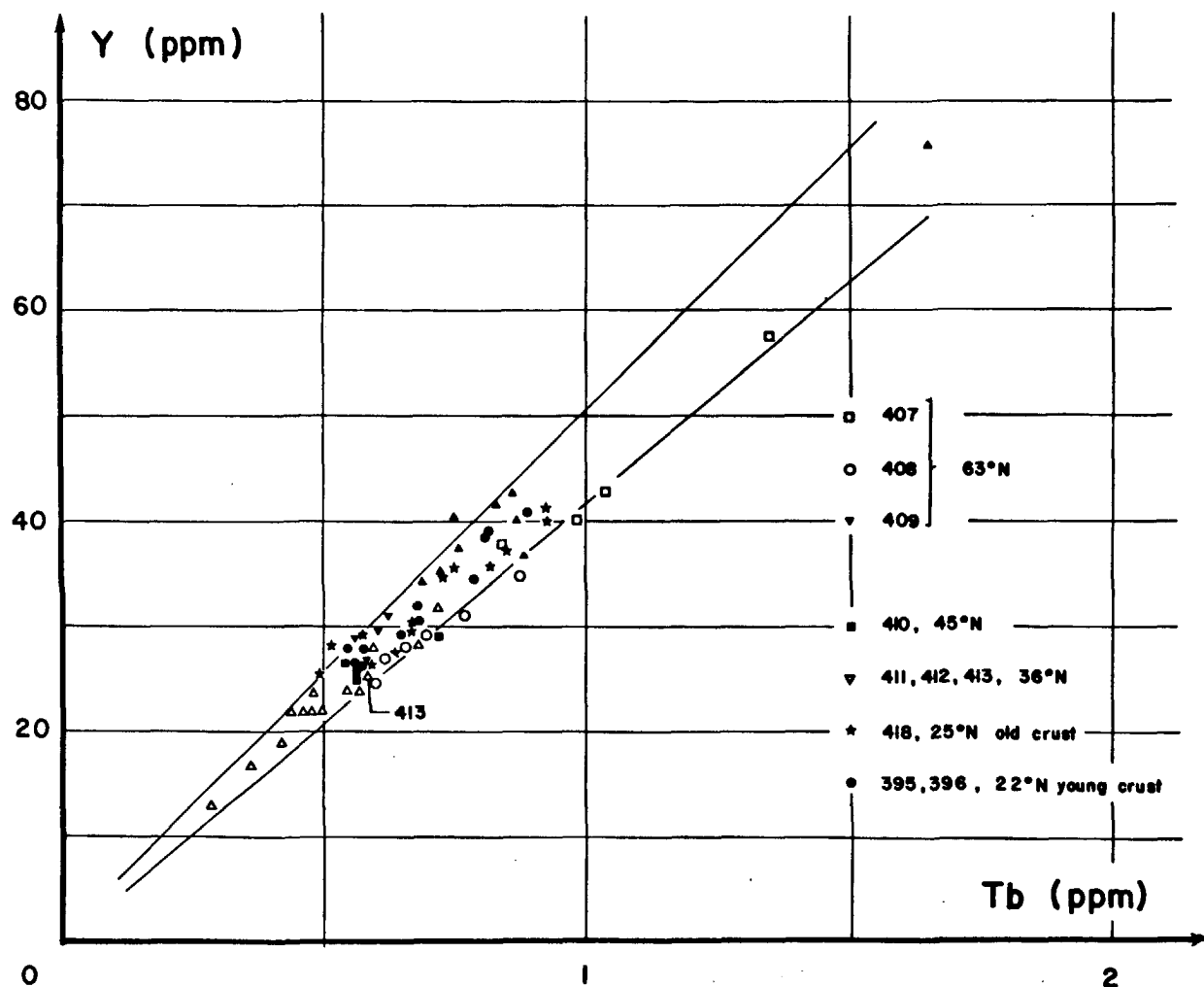


Fig. 8 : North Atlantic : Y versus Tb.

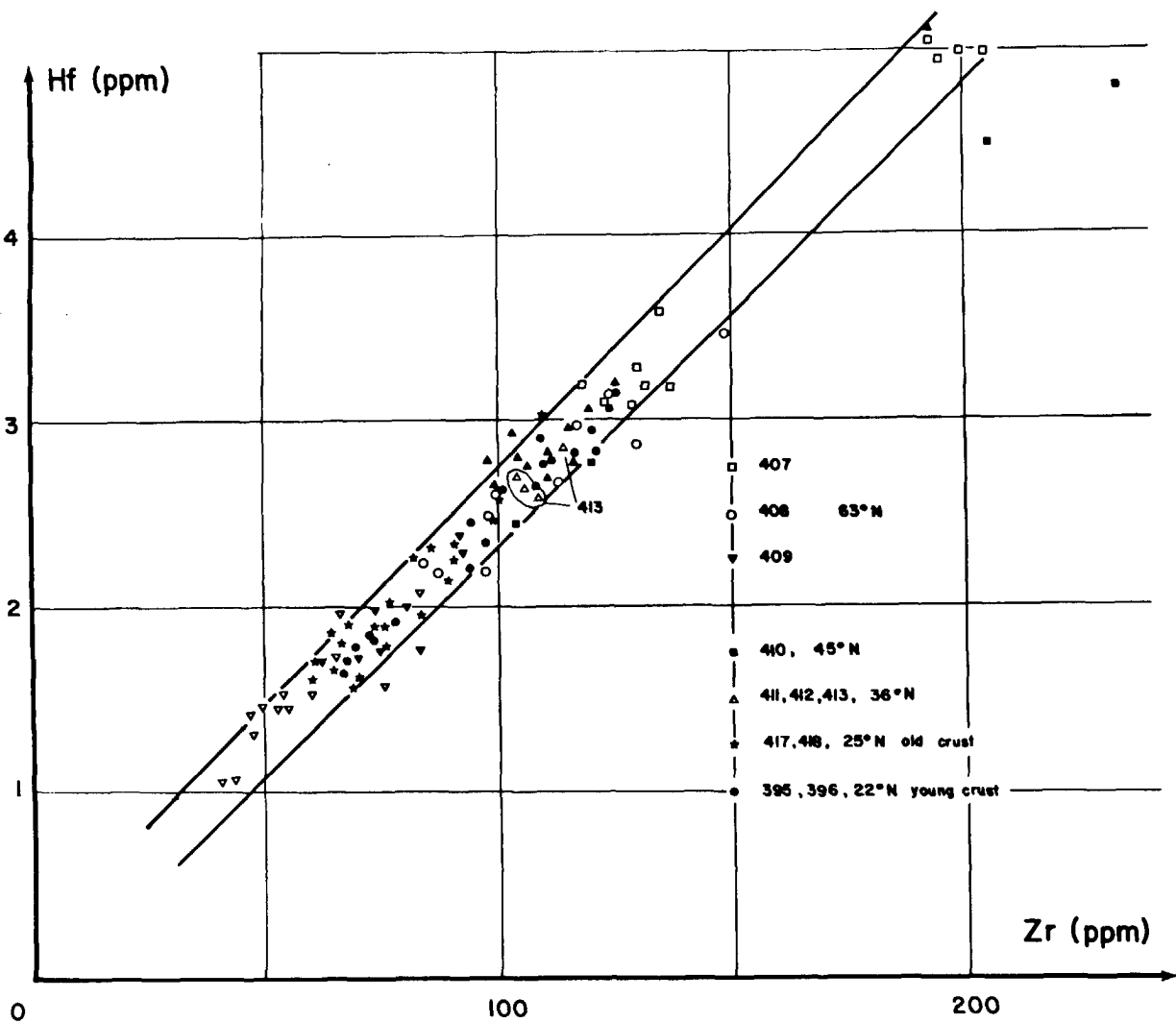


Fig. 9 : North Atlantic : Hf versus Zr.

of Zr-Hf or Nb-Ta fractionating by changing oxygen fugacity, we would conclude that relatively stable conditions exist in the terrestrial mantle.

A plot of La versus Ta for the North Atlantic samples defines two different lines. One of them includes samples recovered at 36° N, 45° N and 63° N which have large variations in absolute concentration. The second line includes samples recovered at 22° N (young crust) and 25° N (old crust). The similarity of D^{La} and D^{Ta} was deduced from the first line on the basis of a constant ratio for a large variation of absolute concentrations. We also mentioned previously that this similarity can be explained by a compensation of the incompatible and hygromagnaphile characters of La and Ta. However, because of differences between ionic radii and charges it is more likely that a fractionation may occur between La and Ta rather than between Nb and Ta. Large variations in the percentage of

partial melting (see below) do not affect the La/Ta ratio. For this reason we interpret the two different La/Ta ratios as characteristic features of the mantle sources related to the two groups of samples. The highest La/Ta ratio corresponds to a characteristic "depleted" oceanic mantle (22° N and 25° N) and the lowest ratio corresponds to a less depleted mantle (36° N, 45° N, 63° N).

If a "primordial mantle" is confirmed through the constant values of Y/Tb, Zr/Hf and Nb/Ta ratios, then it may be deduced that one mantle type may derive from the other type through a mantle differentiation process. The variation of Ta/Th ratio (fig. 7), two elements which have very low but slightly different partition coefficients would reflect different degrees of this differentiation. The jump of La/Ta ratio would correspond to a major change of the solid (mineralogical for instance) through mantle differentiation.

BOUGAULT

Multiple source model, mixing of sources, mixing of magmas, partial melting

Langmuir *et al.* (1978) propose a method for testing different kinds of mixing in which an hyperbolic function represents the behavior of two elements or of ratios of two couples of elements.. We postulate that the ratio of two hygromagnaphile elements is not (or little) modified through fractional crystallization process. Then, the ratios of two elements have to be interpreted in terms of partial melting, mantle sources, mixing of magmas and (or) mixing of sources. Figure 13 represents the plot of Hf/Ta (deduced from fig. 6) versus Ta/Th (deduced from Fig. 7). If the studied samples were derived from two end members, the points defined by the various basaltic units should lie on an hyperbolic line. This is obviously not the case.

Partial melting and magma mixing. The variation of the ratios of two elements with percentage of partial melting is a question of the magnitude of the difference between their bulk D's which in turn are dependent upon the residual mineralogy. If both partition coefficients are low (~ 0.01 or lower ; ex.: Ta, Th) the ratio varies little, when the partial melting degree is sufficiently high. If the D's have different orders of magnitude (0.1 and 0.01 ; Tb/La, Ti/Th, Hf/Ta ...) the elements

fractionate. We can test such possibilities of variations in the data of Leg 49 site 409 and from the FAMOUS area.

Site 409 (Leg 49): Unit b cannot be derived from unit a through fractional crystallization process. The similar Ta/Th and La/Ta ratios (fig. 7 and 11, and Table 5) and the increase of hygromagnaphile element concentrations from unit a to b (table 5) are consistent with fractional crystallization. However, at the same time Ni (and Cr) should decrease while the opposite is observed (Table 5). Partial melting can generate the observed elemental relationships. For similar Ta/Th or La/Ta ratios we observe different Ti/Th, Tb/La ratios (Table 5) and a different Hf/Ta ratio (fig. 6). In addition, one unit in hole 407 also has the same Ta/Th ratio and a different Hf/Ta ratio (Fig. 13). Rare earth patterns for these three basaltic units (Wood *et al.*, in press) are presented figure 14. These patterns, for a single Ta/Th ratio, vary in the same way as the Hf/Ta ratio.

FAMOUS area : The three samples reported in Table 5 may be considered as unfractionated on the basis of their MgO ($Mg^{2+}/Mg^{2+} + Fe^{2+}$) and Ni values. Each of them belongs to one of the three basaltic units of the FAMOUS area (Fig. 13). For similar Ta/Th ratios different concentrations in Ta, Th and other hygromagnaphile elements are

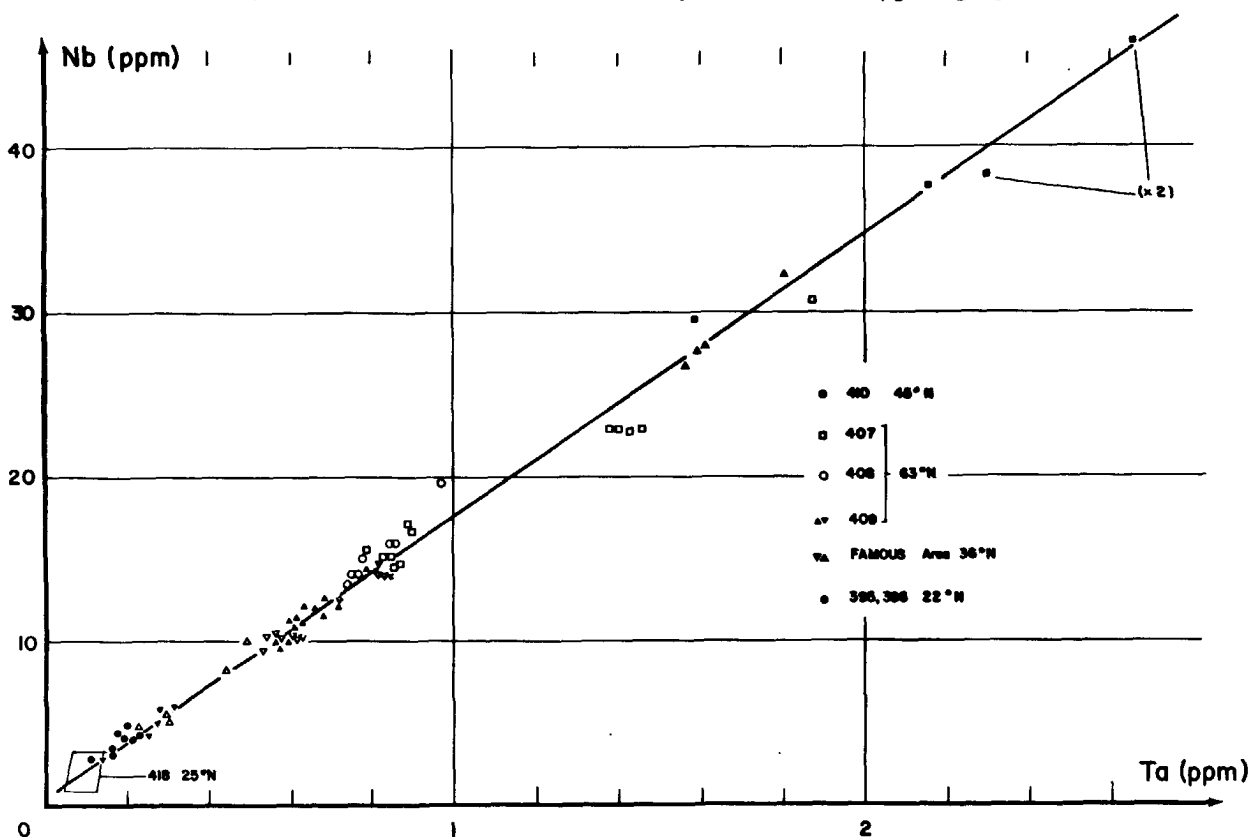


Fig.10 : North Atlantic : Nb versus Ta : (x 2) for the two right samples means that both Nb and Ta concentrations are twice higher.

BOUGAULT

TABLE 4. Y/Tb, Zr/Hf, Nb/Ta in North Atlantic basaltic samples and in chondrites.

	Y/Tb	Zr/Hf	Nb/Ta
North Atlantic ratio	42.5±5	39±5	17.5±2
Factor of variation	4.25	5	50
Chondrites ratio	41.7	30-40	15-17

observed. These features are believed to be due to different degrees of partial melting. Different Hf/Ta ratios (fig. 13), different Ti/Th and Tb/La ratios (Table 5) are observed together with different rare earth patterns (fig. 15).

The hole 409 example, no more than the FAMOUS example, is not compatible with magma mixing. Rhodes *et al.* (in press) interpret the different Ti concentrations observed for a single Mg/Fe ratio as the result of mixing a new unfractionated magma with a magma which has already undergone some fractional crystallization. The different Ti (and

other low partition coefficient element) concentrations related to unfractionated magmas (FAMOUS example) cannot be interpreted in the same way. This observation does not mean that magma mixing does not exist but we would not consider this process as a rule as suggested by Rhodes *et al.*

Mixing of mantle sources or evolution of separate sources. The variation of Hf/Ta ratio (fig. 13) or of rare earth patterns (fig. 14, 15) with partial melting makes it difficult to recognize mixing of sources on Hf/Ta (or Sm/La) versus Ta/Th (or isotopic ratios) plots. Data for a large number of samples are required to see and recognize through the effects of partial melting variations in Hf/Ta representative of the source or as a consequence of the mixing of sources (Schilling, 1973). Langmuir *et al.* (1978) suggest that if mixing can be diagnosed from ratios of elements it should be confirmed by other elements or ratios of elements. On figure 13, an hyperbolic line could fit the points representing the different groups. If it is assumed that the scatter within groups is due to variable degrees of partial melting it could be concluded that

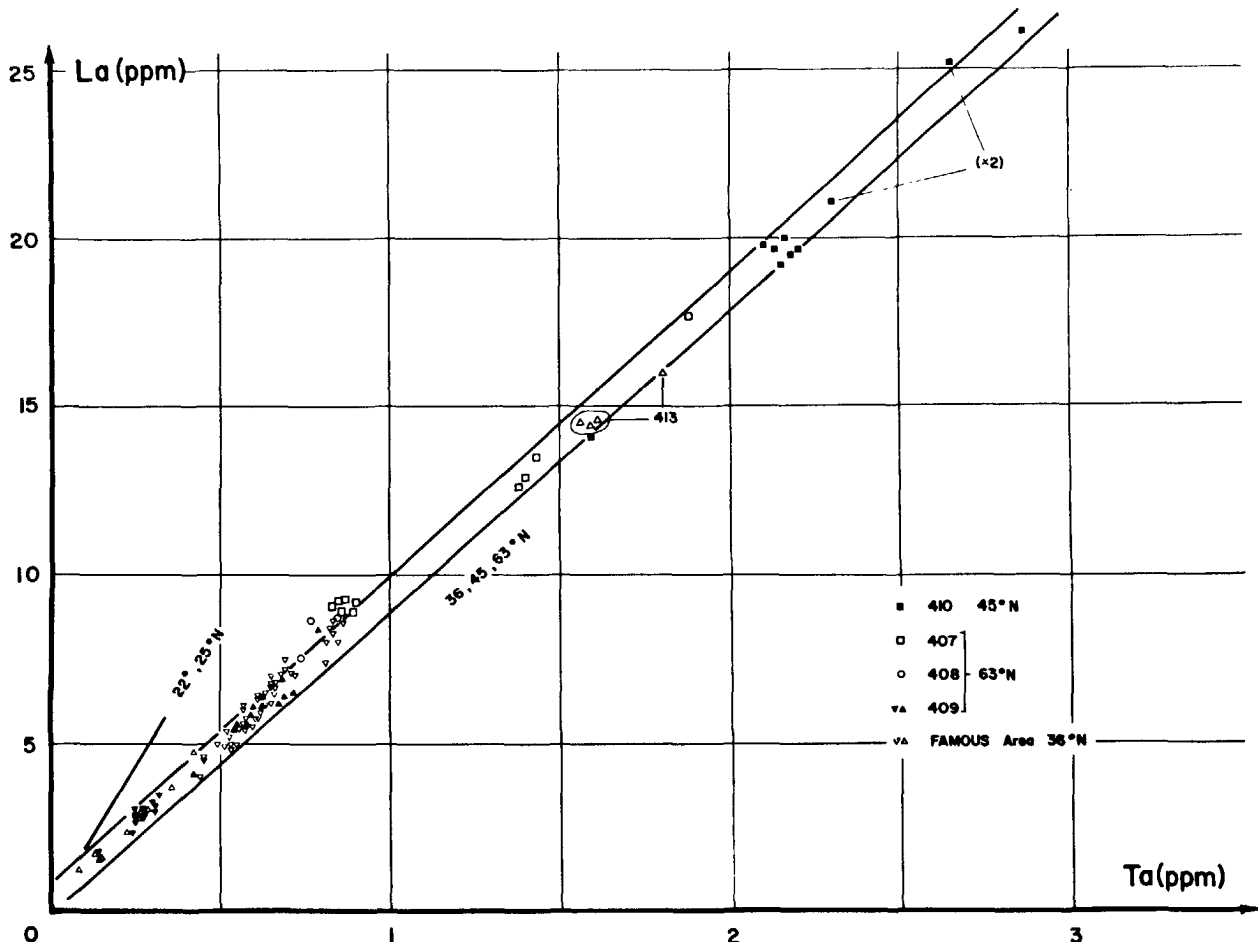


Fig.11 : North Atlantic : 36° N, 45° N, 63° N : La versus Ta (x2) for the two right samples means that both La and Ta concentrations are twice higher.

BOUGAULT

mixing of two different mantle sources is possible. But, considering another ratio, La/Ta (Fig. 11, 12), only two values have been found (Fig. 13) making impossible an hyperbolic fit of La/Ta versus Ta/Th. Consequently, it is necessary to consider more than two sources. Langmuir *et al.* (1978) using other elements and other samples conclude that several models are possible. Mixing of sources is one of them, but even then more than two mantle sources are required. If several mantle sources are required, it is necessary to account for a multiple source model (O'Nions *et al.*, 1976). Each source would be derived from a primordial mantle which is evidenced by Y/Tb, Zr/Hf, Nb/Ta.

Co, Ni, Cr : fractional crystallization process

Because of their ionic configuration (presence of d electrons), Co²⁺, Ni²⁺ and Cr³⁺ ions are subject to crystal field stabilization in octahedral structures (Burns, 1970 ; Curtis, 1964). The partition coefficients found agree with this observation (Bougault and Hékinian, 1974 ; Dale and Henderson, 1972). Crystal field stabilization has the effect of giving these elements a quite different behavior than low partition coefficient elements.

From theoretical considerations Co, Ni and Cr (to a lesser extent) should vary within a narrow range in the liquid phase as partial melting proceeds. This is independant of the chosen model and the type of initial solid material, except chromium which may depend upon spinel content (Bougault *et al.* (a), in press). Olivine being the major constituent of the solid and melting in low proportion relative to clinopyroxene for instance acts as a buffer for Co and Ni during the melting process. In addition, the results found for Ni, Co, Cr in the undifferentiated samples mentioned above fit with the theoretical calculation obtained from concentrations observed in peridotites and currently accepted bulk partition coefficients (Bougault *et al.*, in press (a)). Thus, variations in the concentrations of these

three elements in basalts are largely due to fractional crystallization.

Because these three elements are enriched in minerals like olivine, clinopyroxene and spinel, it is important to note that basalt samples used for interpretation of the Ni, Co and Cr abundances should be free of these minerals. Glasses, aphyric basalts and plagioclase phyrical basalts are appropriate. Plagioclase is a diluant of Co, Ni and Cr.

In the samples that we have analysed Co varies within a narrow range 40-50 ppm, Ni between 30 to 250 ppm and Cr between 30 to 600 ppm. This is observed for most of the oceanic tholeiites with the condition of selecting samples as mentioned above. Two ways of interpretation of these data can be given according that oxide and sulphide phases are involved or not in the process of fractionation.

i) The large variation of Ni reflects crystallization of olivine (Kd = 12) and or clinopyroxene (Kd = 4.4). However the narrow range of variation of Co (40-50 ppm) precludes that more than a few percents of olivine or (olivine + spinel) have crystallized because the Co partition coefficients in these minerals are 3 and 5 respectively. More likely the bulk partition coefficient of Co is probably close to one in order to explain its narrow range of concentration. This implies that a low Kd mineral with respect to Co has also crystallized, *i.e.* plagioclase.

Accepting the Rayleigh distribution during crystallization, the relationship between Cr and Ni in the liquid is :

$$\log [\text{Cr}] = \frac{D^{\text{Cr}} - 1}{D^{\text{Ni}} - 1} \log [\text{Ni}] + K$$

D^{Cr} and D^{Ni} being respectively the bulk partition coefficients of Cr and Ni ; K is a constant depending upon partition coefficients and initial concentrations of Cr and Ni. Data for glasses, aphyric samples or plagioclase phyrical samples are

TABLE 5. Concentrations of some elements in the two units of Hole 409 and three samples in the Famous area

	MgO	Mg/(Mg ⁺ Fe ²⁺)	Ni	Ti	Tb	Th	La	Ta	Ti/Th	Tb/La	La/Ta	Ta/Th
<u>409</u>												
Unit a	~ 8	-	80	7500	0.6	0.25	3.1	0.27	3 10 ⁴	.19	11.5	1.08
Unit b	~ 7.5	-	110	10200	0.8	0.53	6.0	0.63	1.9 10 ⁴	.13	9.5	1.19
<u>Famous area</u>												
411-1-1 78-82	11.5	0.70	265	4184	.44	.28	2.4	.23	1.49 10 ⁴	.18	10.4	0.82
Cyp 31-35	10.6	0.72	253	5100	.42	.58	5.4	.52	.88 10 ⁴	.08	10.4	0.90
413 3-1 44-48	10.6	0.68	240	8573	.58	1.53	14.6	1.61	.56 10 ⁴	.04	9.1	1.05

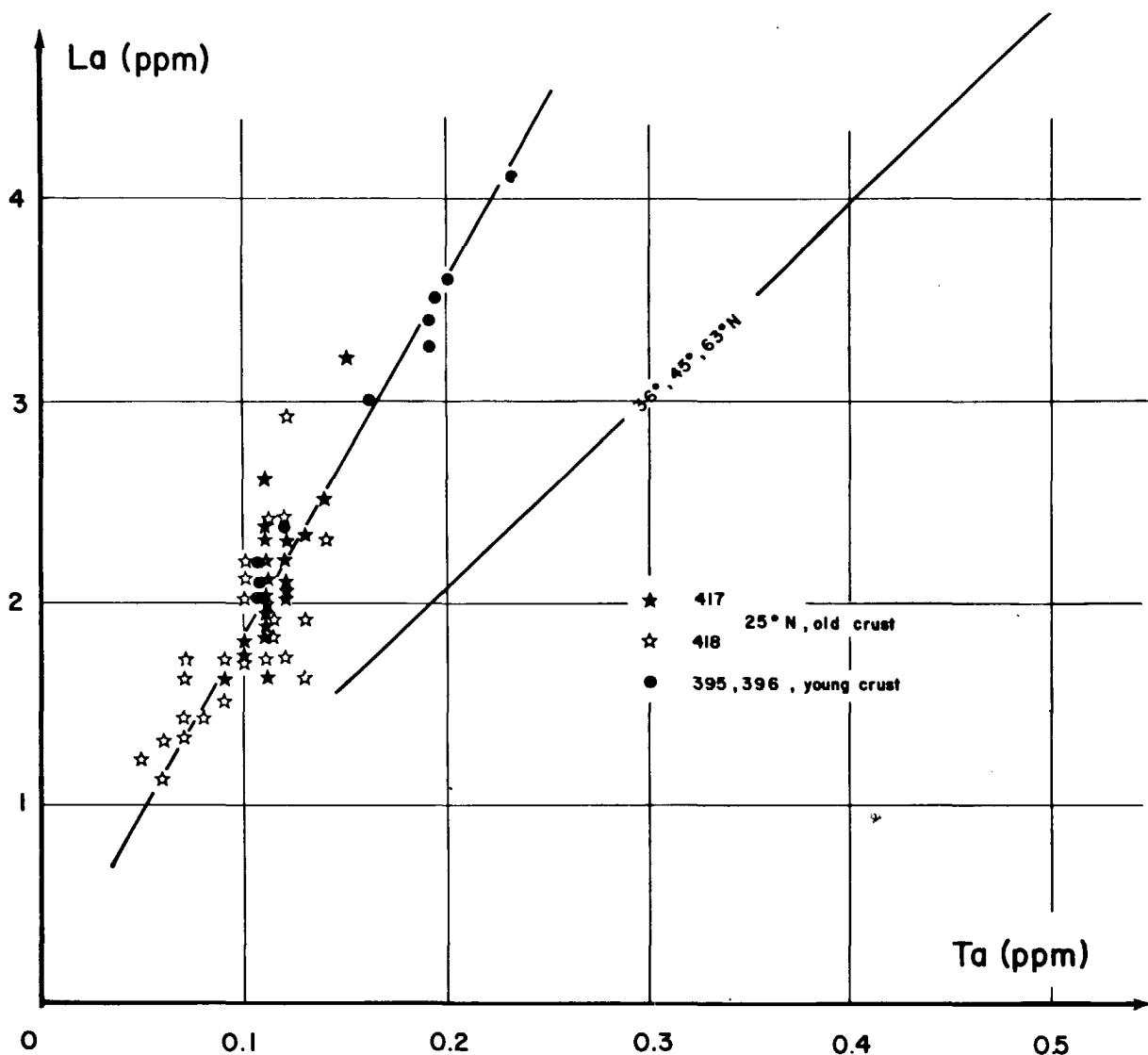


Fig.12 : North Atlantic : 22° N (young crust) and 25° N (old crust) La versus Ta.

plotted in figure 16. The scatter may be partly due to the presence of olivine, spinel or clinopyroxene phenocrysts in some of these samples. The upper part of the field (Ni : 250 ppm, Cr : 600 ppm) correspond to the most primitive liquids. The field cannot be a consequence of the fractionation of olivine alone ; Ni would be depleted extensively whereas Cr would be unchanged in the liquid (K_{ol}^{Cr} is around 1). Olivine + spinel is possible in the early stages but we have seen above that this possibility is also limited by the Co range of variation. The scattering in the upper part of the field (early stages of crystallization) is probably due to different proportions of olivine (+ small amount of spinel) and plagioclase removal. The lower part of the field tends to be narrower and the slope

$$\frac{D^{Cr} - 1}{D^{Ni} - 1}$$

is compatible with plagioclase-clinopyroxene fractionation with very little or no olivine. The FAMOUS data, which fall along the average line which could be defined for the overall field is not a straight line (as suggested by the relationship from the Rayleigh law) ; the variation of slope needs a variation in bulk partition coefficients attributed to variation of partition coefficients themselves and the proportions of minerals as crystallization proceeds. Precise calculations of the amount of minerals crystallizing at different steps is difficult for several reasons. The basalts investigated to not derive from the same initial liquid produced by the same partial melting, even in a single hole. Ti, and other hygromagnaphile

BOUGAULT

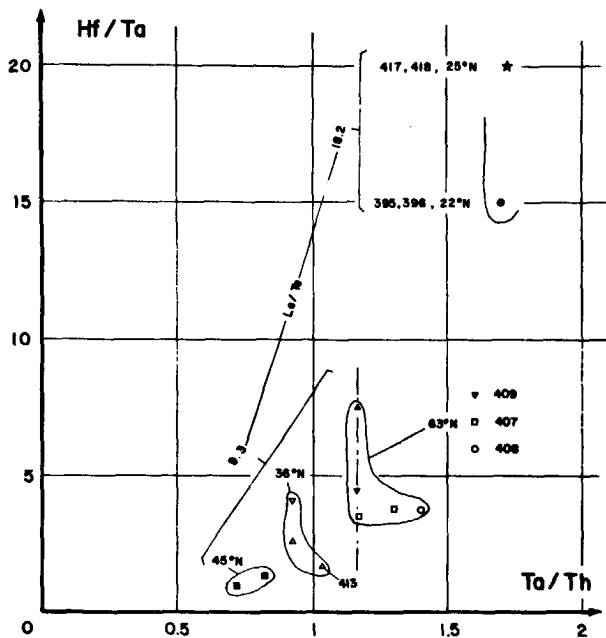


Fig. 13 : North Atlantic : Hf/Ta versus Ta/Th.

elements do not increase regularly as Cr and Ni decrease (Bougault, 1977). Major element relationships show the same results : Ti does not fit (Bryan and Thompson, in press). Magma mixing (Rhodes *et al.*, in press) is an additional possibility.

ii) Oxides and sulphides even if in low proportions are an additional difficulty in estimating, through trace elements, the nature and the proportions of crystallizing minerals. If opaque minerals occur as crystallizing phases, they would probably deplete the liquid in Co and Ni and in addition in Cu and Zn as well. Such a fractionation does not fit the observed behavior of Co, Cu and Zn since these elements are not depleted. However, if sulphides are considered as an immiscible liquid, sulphides could be a buffer in respect of these

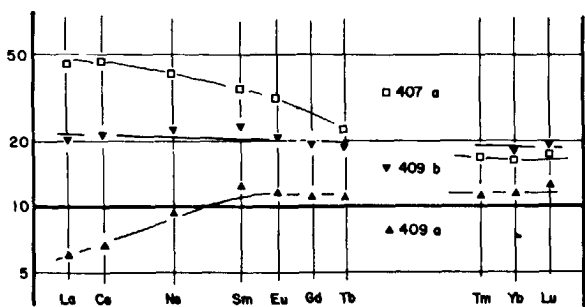


Fig. 14 : Variation of rare earth patterns in Hole 409 (from Wood *et al.*, in press). 407 a pattern is also shown : both units of 409 and 407 a have similar Ta/Th and La/Ta ratios.

BOUGAULT

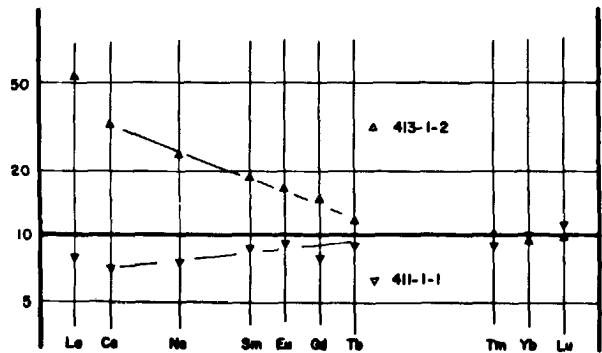


Fig. 15 : Variation of rare earth pattern in the FAMOUS area (from Wood *et al.*, in press). Both samples have similar Ta/Th and La/Ta ratios.

elements except for elements whose bulk D relative to crystallizing phases is higher than D relative to the immiscible liquid (Cr and Ni possibly). This late interpretation is only tentative as liquid (sulphides) - liquid (silicate) partition coefficients are not known for the investigated elements in these types of rocks.

Before drilling into the oceanic crust started, the hypothesis to find in a single hole different units deriving one from each other from the same initial liquid through fractional crystallization process seemed reasonable. This hypothesis now appears to be wrong. No more than one or two

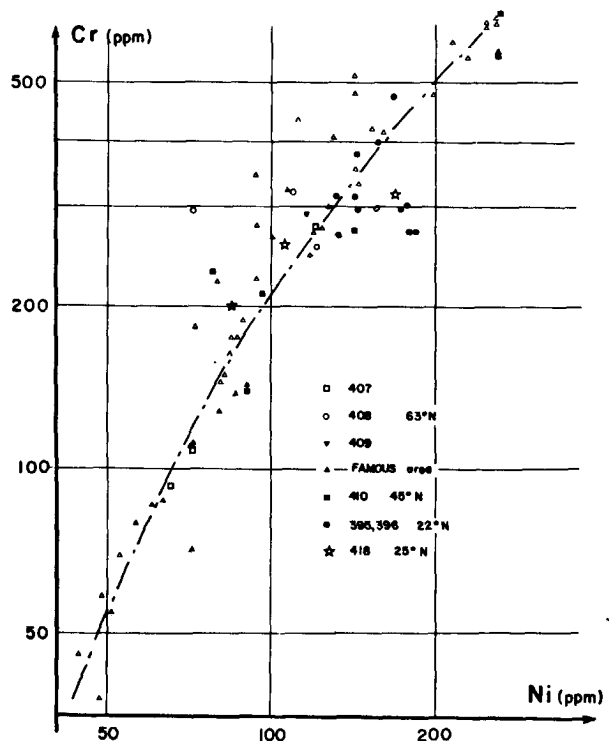
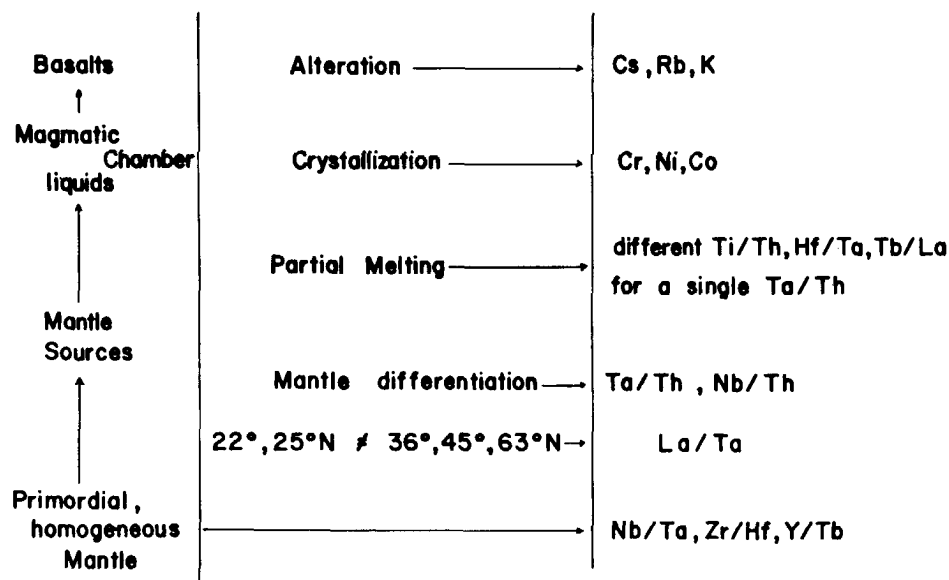


Fig. 16 : North Atlantic : log Cr versus log Ni.

TABLE 6. Oceanic basalt genesis : summary of the behavior of trace elements.



eruptions occur involving the same initial liquid. Partial melting, formation of a magma chamber (possibility of mixing), crystallization and one or two eruptions seem to be a cycle that is frequently repeated. This corresponds to the notion of magma cycles proposed by Flower *et al.* (1977). This is why, accepting the hypothesis of dynamic melting (Langmuir *et al.*, 1977) or melting a solid which is already a residue (Bougault *et al.*, in press), different percentages and mechanisms of melting can explain the different rare earth patterns found within a single hole.

Conclusion

The major features resulting from this study are summarized in table 6. These include :

Y/Tb, Zr/Hf and Nb/Ta ratios are constant in basalts from the North Atlantic (22° N to 63° N) and do not vary with age. The values of these ratios, which are close to chondrite values, are in agreement with an homogeneous primordial mantle and with a chondritic composition of the earth.

Highly "incompatible" or "hygromagnaphile" element ratios (La/Ta, Ta/Th) require several mantle sources derived from the initial primordial mantle.

The variability of partial melting is responsible for the variation of moderately "incompatible" to highly "incompatible" element ratios.

High partition coefficient elements bring some constraints about the proportions of minerals which crystallize; it is not possible to deduce quantitatively these proportions of minerals since very few basaltic units, even in a single hole, derive from the same initial liquid (variability of partial melting).

The variation of alkali metals cannot be used to trace magmatic processes because of their extreme sensitivity to alteration.

References

- Arcyana, Rocks collected by bathyscaph and diving saucer in the Famous area of the mid-Atlantic Rift Valley : petrological diversity and structural setting, *Deep-Sea Research*, 24, 565-589, 1977.
- Bougault, H., and R. Hékinian, Rift valley in the Atlantic ocean near 36° 50' N : petrology and geochemistry of basaltic rocks, *Earth Planet. Sci. Lett.*, 24, 249-261, 1974.
- Bougault, H., Major elements : analytical chemistry on board and preliminary results, in *Initial Reports of the Deep-Sea Drilling Project*, vol. 37, 1977, Washington (U.S. Govt. Printing Office).
- Bougault, H., First transition series elements : fractional crystallization and partial melting, Leg 37 DSDP, in *Initial Reports of the Deep-Sea Drilling Project*, vol. 37, 1977, Washington (U.S. Government Printing Office).
- Bougault, H., Cambon, P., Corre, O., Joron, J.L., Treuil, M. (a), Evidence for variability of magmatic processes and upper mantle heterogeneity in the axial region of the Mid-Atlantic Ridge near 22° N and 36° N, *Tectonophysics*, in press.
- Bougault, H., Treuil, M., and Joron, J.L. (b), Trace elements from 22° N and 36° N in the Atlantic ocean : fractional crystallization, partial melting and heterogeneity of the upper mantle, Leg 45, DSDP, in *Initial Reports of the Deep-Sea Drilling Project*, vol. 45, in press, Washington (U.S. Government Printing Office).
- Bryan, W.B., Thompson, G., Compositional variation in a steady-state zoned magma chamber : Mid-Atlantic ridge at 36° 50' N, *Tectonophysics*, in press.

BOUGAULT

- Burns, G., Mineralogical application of the crystal field theory, Cambridge Earth Sci. Series, 1970, Cambridge Univ. Press, 224 p.
- Carn, J.R., Rb, Sr, Zr and Nb in some ocean floor basaltic rocks. Earth and Planet. Sci. Lett., 19, 10, 7-11.
- Curtis, G.D., Application of the crystal field theory: the inclusion of trace transition elements in mineral during magmatic differentiation. Geochim. Cosmochim. Acta, 1964, v. 28, p. 389-403.
- Dale, S.M., and P. Henderson, The partition of transition elements in phenocrysts bearing basalts and the implications about melt structure, 24th IGC Section 10, 1974.
- Dornelly, T.W., Low temperature alteration of the oceanic crust: an exceptionally well developed case from DSDP Megaleg. 2nd Ewing symposium, Lamont-Doherty Geological Laboratory, 1978. See also this volume.
- Ehman, W.D. and Rebagay, Zr and Hf in meteorites by activation analysis, Geochim. Cosmochim. Acta, vol. 34, pp. 649-658, 1970.
- Ehman, W.D. and L.L. Chyi, Zr and Hf in meteorites, Earth and Planet. Sci. Lett., 21, 230-234, 1974.
- Ehman, W.D., L.L. Chyi, A.N. Garg, B.R. Hawke, M. S. Ma, M.D. Miller, W.D. James and R.A. Pacer, Chemical studies of the lunar regolith with emphasis on Zirconium and Hafnium, Proc. Lunar Sci. Conf. 6th, p. 1351-1361, 1975.
- Flower, M.J.F., P.T. Robinson, H.U. Schminke and W. Ohnmacht, Deep-sea drilling project, Leg 37: geochemical evidence for processes of crustal construction, Bull. Soc. Géol. France, 7, XVIII, n° 4, p. 819-823, 1976.
- Flower, M.F.J., P.T. Robinson, H.U. Schminke and W. Ohnmacht, Petrology and geochemistry of igneous rocks: DSDP Leg 37, in Initial Reports of the Deep-Sea Drilling Project, vol. 37, Washington (U.S. Government Printing Office), 1977.
- Frey, F.A., M.A. Haskin, J. Ann Poetz, and L.A. Haskin, Rare earth abundances in some basic rocks, Journal of Geophysical Research, vol. 73, 18, 6085-6098, 1968.
- Ganapathy, R., G.M. Papia and L. Grossman, The abundance of Zr and Hf in solar system, Earth and Planet. Sci. Lett., 29, 302-308, 1976.
- Goldberg, E.D., Minor elements in sea water, in Chemical Oceanography, Ed. by J.P. Riley and G. Skirrow, vol. 1, 163-196, Academic Press, 1965.
- Goldschmidt, V.M., Probleme und Methoden der Geochemie, Gerlands Beitr. Geophys., 15, 38-50, 1926.
- Graham, A.L. and B. Mason, Nb in meteorites, Geochim. Cosmochim. Acta, 36, 917-922, 1972.
- Joron, J.L., C. Bollinger, J.P. Quisefit, H. Bougault and M. Treuil, Trace elements in basalts at 25° N, old crust, in the Atlantic ocean: alteration, mantle and magmatic processes, in Initial Reports of the Deep-Sea Drilling Project, Washington (U.S. Government Printing Office) (in preparation).
- Langmuir, C.H., R.D. Vocke, G.N. Hanson and S.R. Hart, A general mixing equation with application to Icelandic basalts, Earth and Planet. Sci. Lett. 37, 380-392, 1978.
- O'Nions, R.K., R.J. Pankhurst and K. Gronvold, Nature and development of basalt magma sources beneath Iceland and the Reykjanes Ridge, J. Petrol., 17, 315-338, 1976.
- Rhodes, J.M., M.A. Dungan, D.P. Balnchard and P.E. Long, Magma mixing at mid-ocean ridges: evidence from basalts drilled near 22° N on the Atlantic ridge, Tectonophysics, in press.
- Schilling, J.G., Iceland mantle plume: geochemical study of Reykjanes Ridge, Nature, 242, 565-571, 1973.
- Treuil, M., Critères pétrologiques géochimiques et structuraux de la genèse et de la différenciation des magmas basaltiques: exemple de 1' Afar, Thèse, Université d'Orléans, 1973.
- Vinogradov, A.P., Atomic abundance of the chemical elements in the Sun and in stony meteorites, Geokhimiya, 4, 291-295, 1962.
- Wanke, H., H. Palme, H. Baddenhausen, G. Drelbus, E. Jagoutz, H. Kruse, C. Palme, B. Spettel, F. Teschke, R. Thacker, New data on the chemistry of lunar samples: primary matter in the lunar highlands and the bulk composition of the moon, Proc. Lunar Sci. Conf. 6th, 1313-1340, 1975.
- Willis, J.P., A.J. Erlank, J.J. Gurney, R.A. Theil, and L.H. Ahkens, Major, minor and trace element data for some Apollo 11, 12, 14 and 15 samples, Proc. Lunar Sci. Conf. 3rd, 1269-1273, 1972.
- Wood, D.A., J. Varet, H. Bougault, O. Corre, J.L. Joron, M. Treuil, H. Bizouard, M.J. Norry, C.J. Hawkesworth, and J.C. Roddick, The petrology, geochemistry and mineralogy of North Atlantic basalts: a discussion based on IPOD Leg 49, in Initial Reports of the Deep-Sea Drilling Project, vol. 49, Washington (U.S. Government Printing Office), in press.