Sea-Floor Evolution: Rare-Earth Evidence

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A systematic survey of rare-earth (r.e.) abundances in submarine tholeiitic basalts along mid-oceanic ridges has been made by neutron activation analysis. The r.e. fractionation patterns are remarkably uniform along each mid-oceanic ridge and from one ridge to another (Juan de Fuca Ridge, East Pacific and Chile Rise, Pacific–Antarctic, Mid-Indian and Carlsberg Ridge, Gulf of Aden, Red Sea Trough and Reykjanes Ridge). The patterns are all depleted in light r.e. except for three samples (Gulf of Aden and Mid-Indian Ridge) which are unfractionated relative to chondrites. They contrast markedly with tholeiitic plateau basalt which are shown to be related to the early volcanic phases associated with continental drift. Tholeiitic plateau basalts are light r.e. enriched as are most continental rocks. Mid-ocean ridge basalts are also distinguishable from spatially related oceanic shield volcanoes of tholeiitic composition (Red Sea Trough–Jebel Teir Is., East Pacific Rise–Culpepper Island). Thus on a r.e. basis there are tholeiites within tholeiites. The r.e. difference between mid-ocean ridge tholeiites and tholeiitic plateau basalts can be related to distinct thermal and tectonic régimes and consequently magmatic modes and rates of intrusions from the low velocity layer in the upper mantle. The difference between continental and oceanic volcanism appears to be triggered by: (1) presence or absence of a moving continental lithosphere over the low velocity layer, and (2) whether or not major rifts tap the low velocity layer through the lithosphere. Fractional crystallization during ascent of melts before eruption at the ridge crest does not affect appreciably the relative r.e. patterns. R.e. in mid-ocean ridge basalts appear to intrinsically reflect their distribution in the upper mantle source, i.e. the low velocity layer. Based on secondary order r.e. variation of mid-ocean ridge basalts: (1) If fractional crystallization is invoked for the small r.e. variations, up to approximately 50 % extraction of olivine and Ca-poor orthopyroxene in various combinations can be tolerated. However, only limited amount of plagioclase or Ca-rich clinopyroxene can be extracted, the former because of its effect on the abundance of Eu abundance and the latter because of its effect on the $[La/Sm]_{e.f.}$ ratio, alternatively. (2) If partial melting during ascent is invoked, and a minimum of 10 % melting is assumed, the permissible degree of melting of originally a lherzolite upper mantle may vary between 10 and 30 %. It is not possible to establish readily to what extent these two processes have been operative as they cannot be distinguished on the basis of r.e. data only. However, there is evidence indicating that both have been operative and are responsible for the small r.e. variations observed in mid-ocean ridge basalts. An attempt to correlate second order r.e. variations along or across mid-oceanic ridges with spreading rate, age, or distance from ridge crests has been made but the results are inconclusive. No r.e. secular variation of the oceanic crust is apparent. R.e. average ridge to ridge variations are attributed to small lateral inhomogeneities of the source of basalts in the low velocity layer, and to a certain extent, to its past history. The remarkable r.e. uniformity of mid-oceanic ridge tholeiites requires a unique and simple volcanic process to be operative. It calls for upward migration of melt or slush from a relatively homogeneous source in the mantle—the low velocity layer, followed by further partial melting during ascent. The model, although consistent with geophysics, may have to be reconciled with some evidence from experimental petrology. Models for r.e. composition of the upper mantle source of ridge basalt, formation of layers 2 and 3, and the moho-discontinuity, are also presented.

1. Introduction

Rare earth (r.e.) abundances and patterns of fractionation of lavas within a subaerial volcanic region are now known to vary systematically with the mineralogy and bulk chemistry of the lavas (Schilling & Winchester 1969). Major lava types within a volcanic area can thus be distinguished on the basis of their r.e. abundances. Consistently, there is a regular concentration increase of the light r.e. elements with increasing degree of alkalinity of the lavas regardless of the degree of silica saturation or undersaturation (the larger the lanthanide ion, the larger the increase). Illustration of such variations is reviewed in figure 1 for (1) the Hawaiian Islands—

located in a deep oceanic area; (2) Ascension and Gough Islands—perched on the crest of the Mid-Atlantic Ridge; (3) the Japanese islands—an island arc system; (4) central Germany—a continental area.
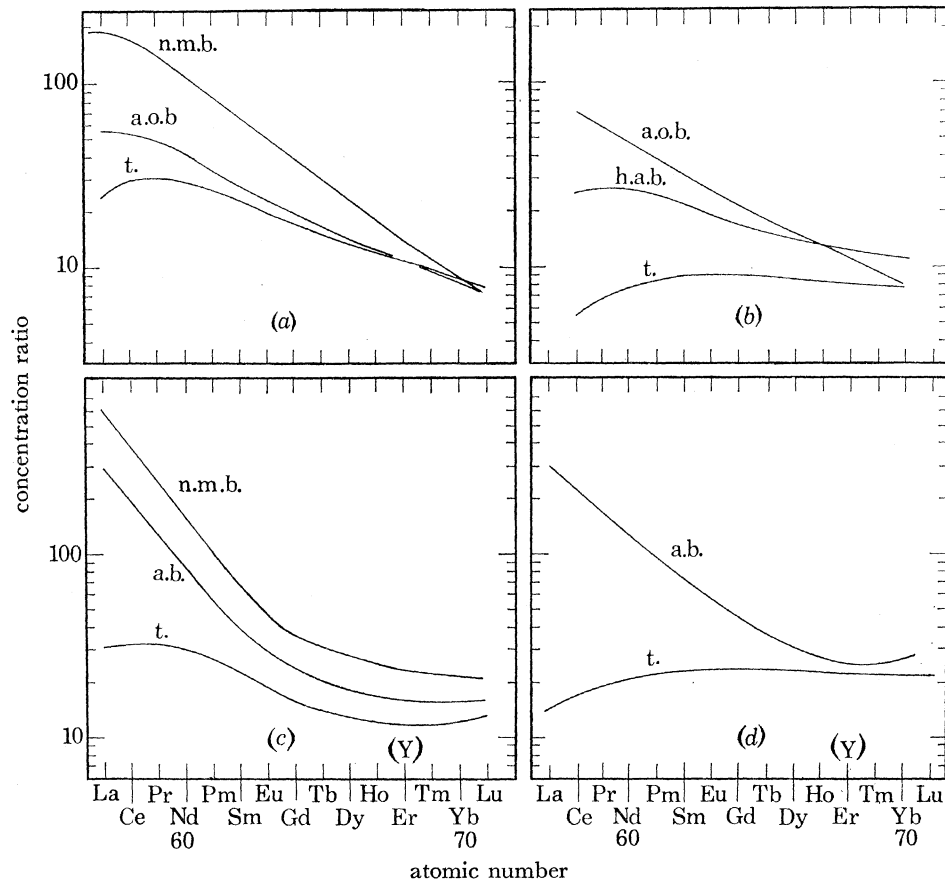

FIGURE 1. Average rare-earth fractionation patterns for the major basalt types i.e., tholeiite (t.), alkali olivine basalt (a.o.b.), nepheline-melilite basalts (n.m.b.) for: (a) Hawaiian Islands: (b) Japan (h.a.b. stands for high aluminium basalt); (c) Central Germany and (d) Mid-Atlantic Ocean (t. stands for submarine tholeiites from the M.A.R. and a.b. for lavas of the alkali series from Gough and Ascension Islands). Data are respectively from Schilling & Winchester (1969), Masuda (1966), Herrmann (1968) and Frey et al. (1968).

Perhaps of greatest importance in figure 1 is the apparent r.e. pattern variations of a single lava type, such as tholeiitic basalts, from one volcanic province to another. Tholeiites from Hawaii and central Germany (typical shield volcanoes) are somewhat light r.e. enriched (larger ions), while the Mid-Atlantic submarine basalts are depleted in the lighter r.e. (Frey & Haskin 1964). The tholeiite from Izu Peninsula (Masuda 1966) has a nearly identical r.e. pattern to the Mid-Atlantic basalts although the overall level of enrichment is lower by more than a factor of two. With the sea-floor spreading model in mind, genetic relations might be expected between mid-ocean ridge basalts and island arc tholeiitic volcanism, the latter presumably being related to the consumption (subduction) of older crust underthrust at the island arc system. Complete melting of a tholeiitic oceanic crust would produce a tholeiite and a similar relative r.e. pattern would be expected. Alternatively, if not fortuitous, the r.e. similarities could simply reflect a similar or related upper mantle source for both types of tholeiitic basalts.

It is thus important to ascertain whether such r.e. variations in a single basalt type (namely, tholeiitic basalt) from separate volcanic provinces reflect different mechanisms of volcanism, or inhomogeneities between the parts of the mantle from which these lavas are derived, or other possibilities. Consequently a global survey of *tholeiitic basalts only* was undertaken some three years ago at the Graduate School of Oceanography of the University of Rhode Island.

2. Method

To fully appreciate the r.e. results and the discussion presented below, a brief review of earlier pertinent work is required.

Some ability to distinguish between different operative magmatic processes by r.e. scrutiny have been theoretically demonstrated; e.g. partial melting, fractional crystallization, and zone melting mechanisms (Schilling & Winchester 1967); as well as mixing and wall rock reactions (Schilling 1966). Further insights have been gained on the extent of pre-eruptional fractionation processes from recent r.e. abundance determinations of common rock-forming minerals and partition coefficient measurements between phenocrysts and basalt matrix or glass (Schnetzler & Philpotts 1968, 1970). More recently, Schilling & Winchester (1969) suggested that four important factors are likely to influence '*whole rock*' r.e. *patterns* of lavas appreciably. These are: (1) rare earth composition of source rocks in the mantle (i.e. *source effect*); (2) minerals involved during processes of partial melting and lava ascent to the surface (i.e. *mineral effect*); (3) mechanism of magma formation and fractionation including mixing processes and magma evolution (i.e. *dynamic* or *kinetic effects*); and possibly but to a lesser extent (4) selective formation and transport of volatile r.e. complexes (i.e. *complexing effect*).

Some simplifications can be made to limit the number of variables. One can eliminate with confidence the complexing effect by considering basalts only. Furthermore, the mineral effect can be minimized by sampling only a limited range of basalt compositions (namely, tholeiitic basalts). Tholeiitic basalt was chosen as it represents the most important lava type erupted on the surface of the Earth in terms of volume, space and time. In this way, two main influential factors remain to be separated, namely the source effect and dynamic or kinetic effect. These two factors pertain importantly to basalt genesis. Insights may thus be gained on these two aspects of vulcanism if other discriminants can be found. *Type of volcanicity* and related operative *tectonics* are the next most important and obvious discriminants to consider. Accordingly, the global survey of r.e. in *tholeiitic basalts only* was undertaken as follows:

(1) Along *mid-ocean ridges*: the loci of ocean floor spreading. This will be the main theme in this paper.

(2) *Across and away* from mid-ocean ridges, as along *fracture zones* or *escarpments*, where older oceanic crust is exposed. This is to seek any possible secular variations associated with sea-floor spreading.

(3) Near and at *trenches and island arc systems*: where oceanic crust is disposed of by under-thrusting and possibly consumed (subduced) in whole or in part.

(4) *Subaerial shield volcanoes* of tholeiitic composition wherever spatially related to mid-ocean ridges: studied in order to contrast two modes of volcanicity, that is, spreading type and central eruption type, and to gain insights into the volcanic dynamics.

(5) *Plateau basalts*: fissure type of eruptions, probably similar to that mode of eruption occurring at mid-oceanic ridge crests, but continental or intramarginally so. These basalts are
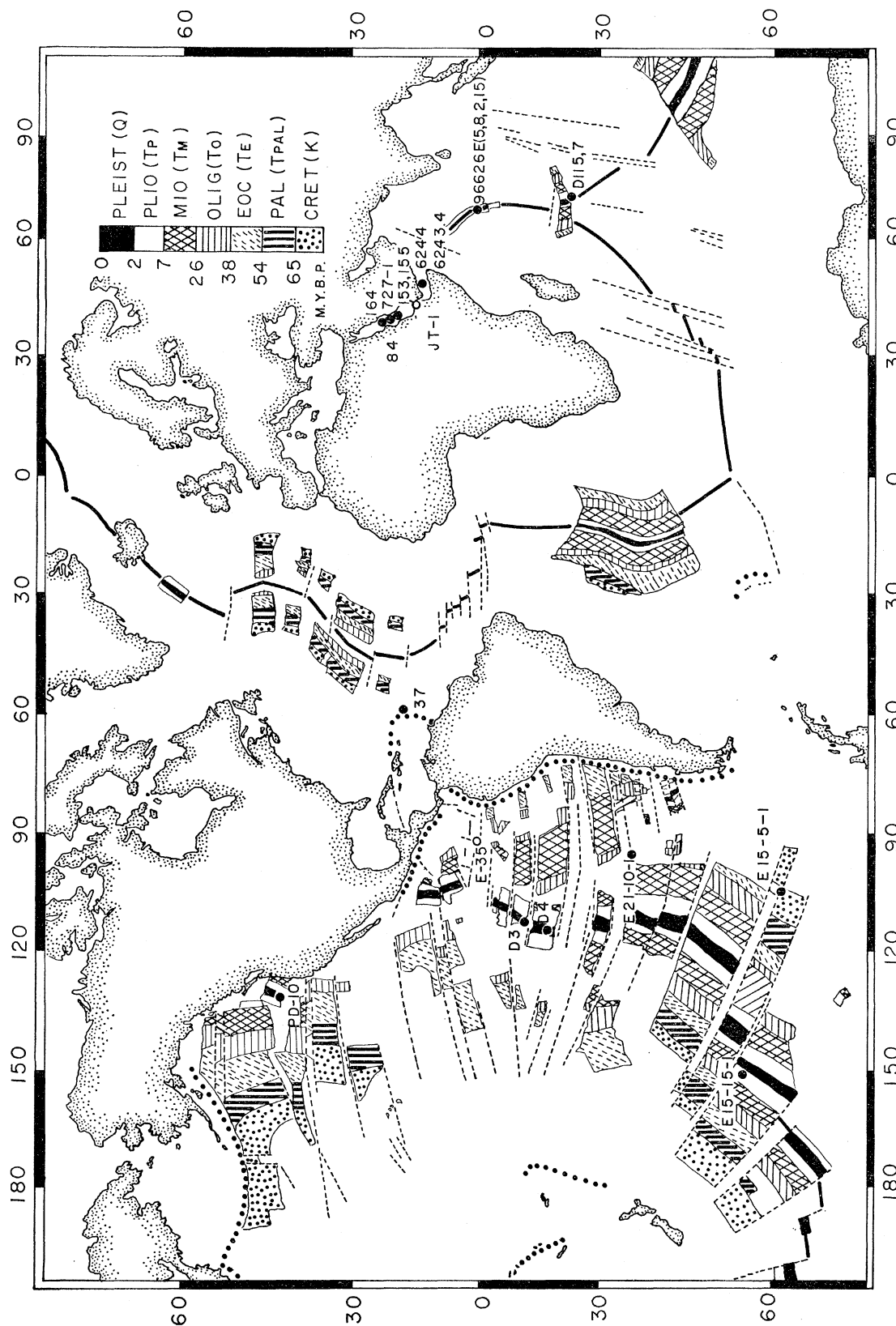
FIGURE 2. Location of tholeiitic basalts surveyed with respect to age of the sea floor as determined from magnetic lineaments (J. R. Hertzler & W. C. Pittman III 1969, personal communication). Black dots represent submarine basalt and open circles subaerial basalts. See table 1 for exact location.

studied in order to gain insights into early volcanic phases of continental drift and sea-floor spreading, since such volcanism occurred at the onset of continental break-up and drift at several places on the globe.

Only the results accumulated until now on mid-oceanic ridges are presented. Their possible implications on the evolutionary mechanism of mid-oceanic ridges and spreading of the sea floor are discussed in some detail. Comparison of mid-ocean ridge tholeiitic volcanism to continental tholeiitic volcanism and oceanic subaerial tholeiitic volcanism is made on the basis of r.e. evidence.

3. Sampling

The sampling of mid-oceanic ridges was limited mainly by scarcity of dredged samples available. Restriction to tholeiitic composition did not limit seriously the sampling, as until now, more than 90 % of basalts dredged from mid-oceanic ridges are of tholeiitic composition. Petrochemical criteria based on normative composition (Yoder & Tilley 1962) were used to decide on *tholeiitic basalt composition*. The few submarine basalts definitely containing normative nepheline were not considered. It might be argued that alteration and degree of oxidation (iron mainly) may alter significantly the normative composition of a lava. Thus normative criteria in some cases may be misleading. Such objections however can hardly affect the arguments presented here inasmuch as submarine ridge basalts show remarkably uniform r.e. patterns despite the small petrochemical variations present in the samples considered. Samples with unusually high water and/or ferric oxide contents were avoided. Both quartz and olivine normative tholeiites were analysed for r.e. regardless of their degree of silica saturation. The petrochemical and other characteristics of the tholeiitic basalts used in this study have been previously reported by various groups and need not be duplicated here. References to these studies are given in table 1.

An attempt to cover most important oceanic ridges is made except for the Mid-Atlantic Ridge which has already been well documented by Frey and co-workers (Frey & Haskin 1964; Frey, Haskin, Poetz & Haskin 1968).

The survey covers samples from the Juan de Fuca Ridge, East Pacific Rise, Chile Rise, Pacific–Antarctic Ridge, Mid-Indian and Carlsberg Ridge, Gulf of Aden, Red Sea Trough and Reykjanes Ridge. The location of the samples with respect to the axes of mid-ocean ridges is shown in figure 2 and their exact positions are given in table 1 with other data.

4. Results

The r.e. abundances (La_{57} to Lu_{71}, including Y_{39}) in nineteen tholeiitic basalts from mid-ocean ridges, were determined by a neutron activation method (Schilling 1966): accuracy and precision of the method have been checked. Reproducibility ranges from 4 to 10 % depending on the element. The concentration in parts/10^6 are given in table 1 with other pertinent data on the samples.

The results are best studied and discussed by using Masuda–Coryell practice (Masuda 1962; Coryell, Chase & Winchester 1963). The r.e. abundance pattern of each rock, element by element, is compared with a common reference, for example, the average of ordinary chondritic meteorites (Schmitt, Smith & Olehy 1964). The relative abundance of each r.e. (that is, enrichment factor relative to the reference) is plotted logarithmically against a linear scale of the atomic numbers of r.e. These elements decrease in size with increasing atomic number, and an

TABLE 1. RARE-EARTH CONCENTRATION (PARTS/10^6) OF NINETEEN SUBMARINE BASALTS
AND TWO SUBAERIAL OCEANIC THOLEIITES

References to major element chemistry is given below. Spreading rates were estimated from
Le Pichon (1968), Morgan et al. (1969) and Menard (1967).

ridge or rise ...	Juan de Fuca	East-Pacific	East-Pacific	Chile	Pacific–Antarctic	Pacific–Antarctic
sample number ...	PD–10	D–3	D–4	E–21–10–1	E–15–5–1	E–15–15–1
La	4.50	2.55	1.72	1.84	2.51	2.34
Ce	—	16.5	9.67	—	—	8.24
Pr	2.47	1.49	1.15	1.29	1.71	1.49
Nd	13.7	8.23	7.77	7.44	9.56	8.32
Sm	4.35	2.94	2.28	2.55	3.09	2.94
Eu	1.54	1.09	1.01	0.966	1.16	1.13
Tb	1.04	0.695	0.623	0.595	—	0.713
Ho	1.45	0.913	0.819	0.799	0.938	0.938
Tm	0.555	0.412	0.352	0.312	—	0.352
Yb	3.79	2.37	2.32	2.14	2.65	2.59
Lu	0.650	0.411	0.403	0.444	0.517	0.487
Y	39.3	25.5	25.4	23.6	27.6	27.2
$[La/Sm]_{e.f.}$	0.723	0.61	0.52	0.50	0.57	0.56
$[Yb]_{e.f.}$	22.3	13.9	13.6	12.6	15.4	15.2
rock type	—	oliv. thol.	oliv. thol.	oliv. thol.	oliv. thol.	oliv. thol.
FeO/MgO	—	1.72	1.08	1.26	1.23	1.31
K_2O/Na_2O	—	0.082	0.040	0.041	0.083	0.046
Al_2O_3 (% by mass)	—	14.88	16.19	15.0	14.8	14.8
latitude	44° 40′ N	12° 52′ S	18° 25′ S	37° 19′ S	61° 06′ S	56° 02′ S
longitude	130° 20′ W	110° 57′ W	113° 20′ W	94° 39′ W	104° 58′ W	149° 40.9′ W
water depth/m	2212	2300	3200	3292	4828	3256
dist. to ridge axis/km	0	0	0	15	840	100
spreading rate/cm a^{-1}	2.9	6	6	2.7	—	3.9–3.7
age	Pleist.	Pleist.	Pleist.	Plio-Mioc.	Palaeo.	Plioc.
reference†	11	1	1	2	2	2

ridge or rise ...	Mid-Indian	Carlsberg	Carlsberg	Carlsberg	Carlsberg	Gulf of Aden
sample number ...	D–115–7	96626E(15)	96626E(12)	96626E(8)	96626E(5)	6243.4
La	3.96	2.00	2.73	3.48	3.57	3.85
Ce	—	6.13	5.75	12.15	28.5	—
Pr	1.65	1.32	2.25	2.15	2.19	1.68
Nd	—	8.44	12.00	12.4	12.2	8.08
Sm	2.68	2.53	3.74	4.46	4.96	2.33
Eu	0.998	1.00	1.43	1.53	1.62	0.809
Tb	0.658	0.730	1.09	1.09	1.21	0.520
Ho	0.876	0.862	1.42	1.29	1.50	0.656
Tm	0.351	0.377	0.587	0.582	0.572	0.262
Yb	2.44	2.88	5.21	4.07	3.37	1.80
Lu	0.415	0.507	0.871	0.731	0.573	0.294
Y	24.7	25.8	38.7	40.0	41.1	20.3
$[La/Sm]_{e.f.}$	1.03	0.56	0.47	0.55	0.50	1.16
$[Yb]_{e.f.}$	14.3	16.9	30.6	23.9	19.8	10.6
rock type	thol.	diabase	oliv. thol.	qtz. thol.	qtz. thol.	oliv. thol.
FeO/MgO	1.13	1.01	1.11	1.48	1.82	1.07
K_2O/Na_2O	0.079	0.027	0.024	0.052	0.012	0.083
Al_2O_3 (% by mass)	16.48	14.36	15.04	15.02	15.05	15.5
latitude	24° 02′ S	1° 26′ S	1° 26′ S	1° 26′ S	1° 26′ S	12° 34′ N
longitude	70° 14.1′ E	66° 34′ E	66° 34′ E	66° 34′ E	66° 34′ E	47° 39.5′ E
water depth/m	3700	3385	3385	3385	3385	2400
dist. to ridge axis /km	85	40	40	40	40	—
spreading rate/cm a^{-1}	2.2	1.6	1.6	1.6	1.6	1
age	Plio-Pleist.	Pleist.	Pleist.	Pleist.	Pleist.	—
reference†	6	3	3	3	3	5

TABLE 1 (*cont.*)

ridge or rise ...	Gulf of Aden	Red Sea Trough	Red Sea Trough	Red Sea Trough	Red Sea Trough	Red Sea Trough
sample number ...	6244	84	153	155	164	H-727-1
La	2.72	1.89	1.15	2.61	2.96	1.90
Ce	8.85	7.54	3.82	4.58	11.0	5.50
Pr	1.26	1.11	0.669	1.21	1.96	1.13
Nd	5.66	7.01	3.77	8.05	10.8	5.74
Sm	1.95	2.61	1.68	2.90	4.25	2.71
Eu	0.794	1.04	0.699	1.14	1.49	0.949
Tb	0.498	0.727	0.524	0.871	0.974	0.753
Ho	0.677	0.946	0.732	1.22	1.25	0.930
Tm	0.278	0.388	0.338	0.536	0.501	0.391
Yb	1.77	2.71	2.44	3.82	3.74	2.44
Lu	3.65	0.495	0.433	0.598	0.656	0.414
Y	19.1	27.4	22.0	32.0	34.4	25.9
$[La/Sm]_{e.f.}$	0.98	0.51	0.48	0.63	0.49	0.49
$[Yb]_{e.f.}$	10.4	15.9	14.3	22.5	22.0	14.4
rock type	oliv. thol.	—	—	qtz. thol.	oliv. thol.	—
FeO/MgO	1.07	—	—	1.97	1.62	—
K_2O/Na_2O	0.090	—	—	0.086	0.069	—
Al_2O_3 (% by mass)	16.4	—	—	12.80	13.10	—
latitude	12° 34' N	21° 21' N	19° 43' N	19° 23.5' N	21° 59' N	21° 24.4' N
longitude	47° 28' E	28° 03.8' E	38° 41' E	38° 54' E	37° 58.5' E	38° 03.6' E
water depth/m	2600	1984	2703	2030	2282	1895
dist. to ridge axis/km	—	—	—	—	—	—
spreading rate/cm a^{-1}	1	1	1	1	1	1
age	—	—	—	—	—	—
reference†	5	4	4	4	4	4

ridge or rise ...	Barracuda scarp	Culpepper Island	Jebel Teir Island	Mid-Ocean Ridge average	average of 20 chondrites
sample number ...	36-5-37	E-35	JT-1		
La	2.53	7.29	11.26	2.67 ± 0.85	0.30
Ce	11.6	20.9	31.5	9.99 ± 6.12	0.84
Pr	1.76	2.86	3.86	1.58 ± 0.46	0.12
Nd	9.06	16.7	17.3	8.79 ± 2.54	0.58
Sm	3.67	3.70	5.19	3.09 ± 0.86	0.21
Eu	1.50	1.48	1.47	1.15 ± 0.27	0.074
Tb	0.960	0.773	1.02	0.793 ± 0.214	0.049
Ho	1.34	1.02	1.26	1.03 ± 0.27	0.064‡
Tm	0.501	0.419	0.521	0.425 ± 0.106	0.025‡
Yb	3.30	3.02	3.42	2.94 ± 0.86	0.17
Lu	0.552	0.643	0.562	0.517 ± 0.136	0.031
Y	34.6	31.0	35.5	29.2 ± 6.7	1.8
$[La/Sm]_{e.f.}$	0.48	1.38	1.52	0.622 ± 0.200	1
$[Yb]_{e.f.}$	19.4	17.8	20.0	16.22 ± 5.14	1
rock type	thol.	thol.	thol.	—	—
FeO/MgO	1.23	1.53	2.06	—	—
K_2O/Na_2O	0.057	0.133	0.128	—	—
Al_2O_3 (% by mass)	14.95	15.22	14.64	—	—
latitude	16° 43' N	—	—	—	—
longitude	58° 05' W	—	—	—	—
water depth/m	3270-5840	—	—	—	—
dist. to ridge axis/km	1500	—	—	—	—
spreading rate/cm a^{-1}	1.5	—	—	—	—
age	Cret.	—	—	—	—
reference†	7	8	9	—	10

† Engel, Engel & Havens (1965); 2, Paster (1968); 3, Wiseman (1937); 4, Chase (1969); 5, Cann (1970a); 6, Engel, Fisher & Engel (1965); 7, Chase (1968); 8, McBirney & Williams (1969); 9, Gass (1968); 10, Schmitt, Smith & Olehy (1964); 11, Gottfried (1970).
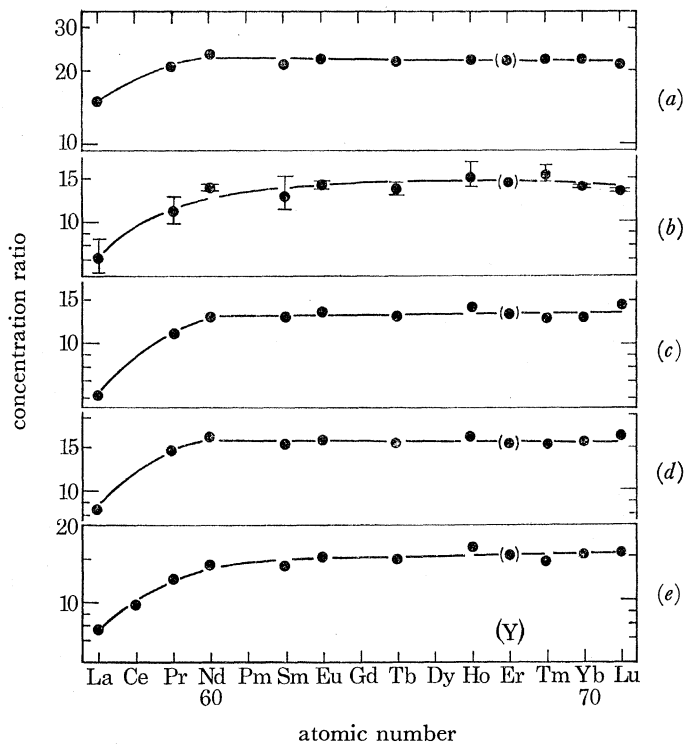
‡ Preferred value.

FIGURE 3. Abundance of rare earths relative to chondrites of submarine tholeiitic basalts of the Pacific Ocean. Error bars represent maximum deviation from the mean. (a) Juan de Fuca Ridge; (b) East Pacific Rise (2); (c) Chile Rise; (d) S.E. Pacific; (e) Pacific–Antarctic Ridge.
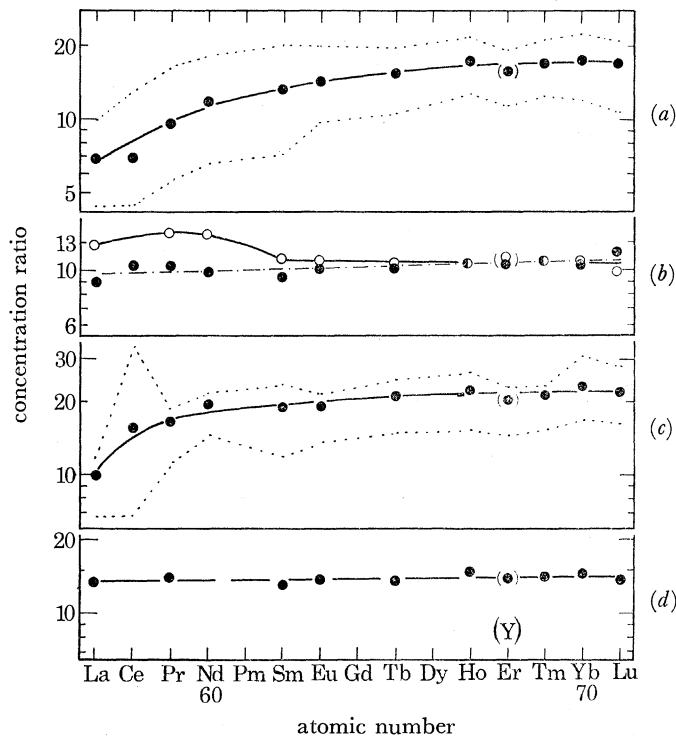

FIGURE 4. Abundance of rare earths relative to chondrites of submarine tholeiitic basalts of (a) Red Sea axial trough (5), (b) Gulf of Aden, (c) Carlsberg Ridge (4) and (d) Mid-Indian Ridge. Dotted lines represent maximum deviation from the mean.

approximately linear relation exists between atomic number and reciprocal ionic radius (Templeton & Dauben 1954).

Figures 3 and 4 are such plots for the nineteen tholeiitic basalts from seven different ridges and the Red Sea axial trough. Presented in these two figures are patterns of: (1) individual rocks (Juan de Fuca Ridge, Chile Rise, SE Pacific, Pacific–Antarctic Ridge, Gulf of Aden, Mid-Indian Ridge), (2) averages of nearby localities of the same ridge or trough (East Pacific Rise, Red Sea Trough), and (3) the average of rocks from the same dredge haul (Carlsberg Ridge). *Maximum variation* for average of two rocks are shown by a vertical bar, and for more than two rocks by dotted lines. A detailed scrutiny of the data for each individual rock analysed indicates that tholeiitic basalts along mid-ocean ridges, or from one ridge to another, have *very uniform* r.e. patterns; this is, despite small variations in chemical composition, mineralogy and degree of alteration of the tholeiitic basalts investigated. Except for two localities (Gulf of Aden and a Mid-Indian Ridge basalt) the abundance trend shows a progressive increase of the enrichment factor from the light r.e. (larger ions) toward the heavy r.e. (progressively smaller ions), while the latter stay relatively more constant.

The absolute level of r.e. pattern enrichment of these basalts varies only by a maximum factor of two to three (less than three for the light r.e. and approximately two for the heavy r.e.). The variation is smaller for basalts from the same ridge than from one ridge to another; it is minimum for samples from the same dredge haul (see table 1).

The relative fractionation pattern of these basalts thus indicate that the larger the trivalent r.e. ion, the more pronounced is the depletion relative to the smaller r.e. ions. This is particularly so for the lighter r.e. end of the series (La_{57} to approximately Sm_{62}) but in some cases also over the entire r.e. series (Red Sea Trough, Carlsberg Ridge and especially the Reykjanes Ridge).

The distinct r.e. pattern of mid-ocean ridge basalts was first noted by Frey & Haskin (1964). Although they insisted particularly on the similarity of the *relative* heavy r.e. abundances to chondritic and achondritic values, they did not emphasize the light r.e. depletion probably because of the limited number of analysed samples available at the time. Later analyses of basalts from the Mid-Atlantic Ridges by Frey *et al.* (1968), Kay, Hubbard & Gast (1970) and this work indicate that the lighter r.e. depletion is indeed real for more than 90 % of the basalts analysed and must be taken into consideration for the genesis of these basalts. Whether the heavy r.e. abundance similarities of submarine tholeiitic basalts to those found in chondritic or achondritic meteorites have some genetic implications, such as to indicate that mid-ocean ridge basalts are of so-called '*primitive nature*' (Frey & Haskin 1964; Engel, Engel & Havens 1965 a), or are simply fortuitous, need to be and will be discussed further later.

Having established the remarkable uniformity of r.e. patterns of tholeiitic basalts collected along mid-ocean ridges, it is now important to determine: (1) How characteristic of mid-ocean ridges are such typical light r.e. depleted patterns? (2) How and to what extent such data, including second-order variations, can reveal some of the details of the ocean ridge volcanic mechanism? This is the subject of the following sections.

5. Relation to continental plateau basalts

The uniformly light r.e. depleted patterns of mid-ocean ridge tholeiitic basalts contrast markedly with tholeiites from Tertiary plateau basalts (figure 5). The r.e. patterns of pleateau basalts are light r.e. enriched and resemble other continental rocks. Such distinct types of r.e.

patterns contrast two principal tholeiitic volcanic provinces, i.e. *oceanic* against *continental* areas. Tholeiitic plateau basalts from various provinces have very uniform major element composition. The uniformity also includes the r.e. abundances; as, for instance, r.e. abundances of the Deccan and Columbia tholeiitic plateau basalts (Balashov & Nesterenko 1966; Schmitt *et al.* 1964; Haskin, Frey, Schmitt & Smith 1966) are very similar despite the fact that they are geographically widely separated.
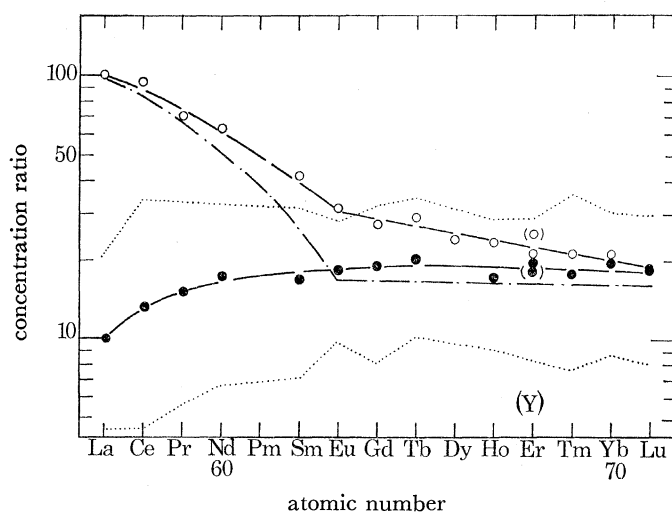
FIGURE 5. Average abundance of rare earths of tholeiitic basalts relative to chondrites; ●, mid-oceanic ridges (East Pacific Rise, M.A.R., Carlsberg Ridge, and Red Sea Axial Trough) the two dotted lines delineate the maximum deviation from the mean; ○, plateau basalts. Data for Columbia Plateau is from Schmitt *et al.* (1964) and Deccan plateau-basalts from Haskin *et al.* (1966), and Balashov & Nesterenko (1966); —·—·—, estimated r.e. abundance average for the upper part of the continental crust.

The r.e. difference between mid-ocean ridge and continental plateau basalts cannot simply be attributed to petrochemical variations between the two types (e.g. degree of silica saturation). The tholeiitic plateau basalts are usually quartz normative. Mid-ocean ridge tholeiites are also uniform in major element composition (Engel *et al.* 1965 *a*); they are in great part olivine normative, although quartz normative tholeiitic basalts do also occur (see table 1). No systematic variation of the r.e. could be observed between the quartz and olivine normative mid-ocean ridge basalts. Thus, such r.e. pattern difference must be attributed to some other controlling factors.

Plateau basalts erupt along tensional fractures at the onset of continental break-up and drift. Such volcanism may well represent an early magmatic phase of continental drift and spreading of the sea floor; whereas submarine ridge tholeiites are produced by eruption along the crest of mid-ocean ridges, partly healing the gap produced by the divergence of rigid plates of lithosphere, i.e. at the loci of the most recent oceanic crust formation produced by spreading of the sea floor. It is thus tempting to relate the r.e. pattern variations of these different tholeiitic types to such tectonic episodes.

Evidence exists that plateau basalts do represent an early phase of continental drift and spreading of sea floor (e.g. see Dutoit 1937; Bodvarsson & Walker 1964). Furthermore, for the South Atlantic region, palaeomagnetic data indicate that the igneous activity that produced the Karroo and Parana plateau basalts and dolerites was still in progress when Africa and South

America began to separate (Holmes 1965, p. 1221). The age range for the Karroo dolerites is 190 to 154 Ma, i.e. at the beginning of Jurassic time (McDougall 1963). The older dates should probably be applied to the Karoo and Parana plateau basalts associated with these dolerites if Tyrell's (1937) Tertiary plateau basalt sequence of the Thulean Province can be applied (i.e. plateau basalt, followed by centre eruptions, then doleritic dykes). Mean values for initial $^{87}Sr/^{86}Sr$ isotopic ratio for Karroo and Serra Geral tholeiites are identical (Compston, McDougall & Heier 1968). Palaeomagnetic reconstruction of Australia and Antarctica matches remarkably well spatially and in time eruption of the Ferrar dolerites of Victoria Land in Antarctica (147 to 163 Ma) and the Red Hill dolerite in Tasmania (159 to 168 Ma) (Irving 1964). This also corresponds approximately to the time that the Australia–Antarctica block began to separate from Gondwanaland. Ferrar and Tasmania dolerites have similar initial $^{87}Sr/^{86}Sr$ isotope ratios but higher than for the Karroo system (Compston et al. 1968). For the Indian Ocean, palaeomagnetic evidence also shows that India drifted northward during the period of lava extrusion (Holmes 1965, p. 1224). Also, Davies (1968) gave some evidence for Palaeocene volcanic activity on the Seychelles and the Deccan region being related to the early development of the Carlsberg Ridge.

Similar evidence on the Thulean Tertiary plateau basalt activity (East Greenland, Antrim, British Isles, etc.) indicates that it is related to the early stages in the formation of the North Atlantic (Brooks 1970).

As for the Columbia Plateau, Bodvarsson & Walker (1964) suggested that tectonic spreading may be a feature of this plateau basalt. The hypothesis has found some support from palaeomagnetism in these Miocene lavas (Watkins 1965). However, the relation of the Miocene Columbia plateau volcanism to the East Pacific Rise and Basin and Range is complex and remains to be deciphered (Holmes 1965, p. 1095; Cook 1965).

Thus, a volcanic sequence for continental drift and sea-floor spreading appears to be repeated systematically regardless of time and space. This is: (1) continental eruptions of tholeiitic plateau basalts enriched in larger electro-positive trace element ions at the onset of drifting of continental blocks of lithosphere, followed later by (2) eruption along oceanic rifts of tholeiites depleted in these larger ions.

Present data show that this is the case for the Deccan–Carlsberg Ridge system in early Tertiary time and possibly for the Columbia–East Pacific Rise system. The sequence is further corroborated by the Karroo dolerites in the South Atlantic. These can be considered for lack of better data on the Karroo–Parana plateau basalts which have been partly eroded away. Extremely uniform light r.e. enriched patterns have been observed in undifferentiated chilled margins of dolerite dykes from the Palisades (New Jersey), Karroo (South Africa), Ferrar (Antarctica), and Red Hill (Tasmania), by Philpotts & Schnetzler (1969). This data is further testimony to the general uniformity of these dolerites regardless of age or geographic situation (Turner & Verhoogen 1960, p. 210). Their relative r.e. patterns are very similar to plateau basalts but somewhat lower in absolute abundance. The variation may be simply related to the difference between extrusive and intrusive magmatic modes. This appears also to be the case for oceanic diabases and basalts from the same dredged haul as for the Carlsberg Ridge (table 1), or between spatially related plateau basalts and dolerites of the Siberian Platform (Balashov & Nesterenko 1966). These data suggest a similar volcanic sequence between Karroo and Parana basalts and the light r.e. depleted patterns of mid-ocean ridge basalts in the South Atlantic (Frey et al. 1968). The two types represent, respectively, the volcanic activity associated with

the early and recent development of the South Atlantic since Mesozoic time. The suggested r.e.-volcanic sequence is presently being tested in the Thulean Province (J.-G. Schilling, in preparation).

It is important to determine whether the change of tholeiitic volcanism from light r.e. enriched to light r.e. depleted patterns represents: (1) a progressive variation during the opening and spreading of an ocean which could be traced continuously in the oceanic crust from the plateau basalts on the margin of continents toward the crest of a mid-ocean ridge, or alternatively (2) a more abrupt change in time and space which would reflect fundamental differences between continental and oceanic volcanic conditions. Such information is highly desirable to comprehend the volcanic mechanism of sea-floor spreading and related subcrustal processes in the upper mantle. A progressive change should reflect secular variations of the upper mantle source region of these basalts. As shown in § 9, no secular variation in the oceanic crust is evident from the available data. The sequence from light r.e. enriched to light r.e. depleted patterns seems to occur abruptly and rapidly in space and time. The difference appears to be intrinsic to oceanic and continental areas. Such variations of tholeiitic volcanism are thought to reflect different thermal regimes prevailing underneath oceanic and continental areas. This subject will be discussed further in § 11.

6. RELATION TO PETROCHEMISTRY

In reconstructing volcanic processes operating underneath mid-ocean ridges and in the upper mantle, it is necessary to estimate the extent of fractionation that tholeiitic basalts may have suffered during their ascent, before erupting along the oceanic rift. This is a difficult task which required certain assumptions. Several approaches are at hand.

(a) Covariance

One way is to search for possible covariance between trace element abundance variations (namely, r.e.) and variable petrochemical parameters in order to trace back the primary magma composition. The nature of the samples considered in this survey precludes definite conclusions based on an investigation of this sort inasmuch as the samples studied are not directly related in the field. The only known relation is that they occur either along similar tectonic features (i.e. the ridges) or in the same dredge haul. In addition, identical rock suites from subaerial volcanic provinces are known to be characterized by different absolute levels of trace element content, although the variation trend may be similar for identical suites. Superimposition of such regional variations for basalts of the sea floor should mask, in part, possible covariance. This is particularly critical as small variations within an already relatively uniform group are sought, namely, tholeiitic group. Average ridge-to-ridge variations are indeed suggested as shown in figure 20. These variations will be further discussed in § 10. Furthermore, additional dispersions are certainly introduced by comparing silicate analyses from different laboratories which used different methods of analyses with variable precisions and accuracies. Nevertheless, attempts to seek covariances have been made in order not to bypass some obvious and possible suggestive correlations.

At least three functions reflecting the fractionation of (1) the light r.e. end, (2) the heavy r.e. end, and (3) the overall enrichment of the lanthanide series need to be used to describe the r.e. pattern characteristics. These are respectively:

(1) The ratio of the enrichment factors (e.f.) of lanthanum over samarium $[La/Sm]_{e.f.}$. The light r.e. have the largest r.e. ionic radius and are the most sensitive to crystal and melt processes of fractionation (Schilling & Winchester 1966, 1969). A ratio: (*a*) less than unity—reflects a progressive depletion (positive slope) of the light r.e. relative to chondritic r.e. distribution; (*b*) greater than unity—a progressive enrichment (negative slope); and (*c*) equal to unity—no fractionation (horizontal slope).

(2) A similar ratio of terbium over ytterbium $[Tb/Yb]_{e.f.}$ reflects the heavy r.e. fractionation. The heavy r.e. are the smallest r.e. of the series and are the least sensitive to fractionation processes. Usually a nearly horizontal heavy r.e. trend is preserved in submarine basalts so that $[Sm/Yb]_{e.f.}$ approaches unity.

(3) Because of the horizontal trend of the heavy r.e., the overall enrichment of the r.e. pattern can then be represented by the enrichment factor of one of the heavy r.e. Ytterbium enrichment $[Yb]_{e.f.}$ has been chosen.

As for petrochemical variables, the ratio of total iron to magnesium FeO/MgO and potassium to sodium K_2O/Na_2O have been considered. They respectively reflect the extent of ferromagnesian mineral and feldspar crystallization and fractionation trends. The alumina content has also been considered. High Al_2O_3 contents have been proposed as characteristic of basalts from oceanic ridges (Engel *et al.* 1965*a*; Nicholls 1965; Green & Ringwood 1967). However, this criterium needs to be re-evaluated and will be criticized later. Finally, the quartz normative content is also discussed. Other petrochemical variables were investigated as a function of r.e. abundance, but the results were inconclusive. The results of these latter scrutinies are not inconsistent with the conclusions presented.

Figures 6 to 11 show the $[La/Sm]_{e.f.}$, $Yb_{e.f.}$ as a function of K_2O/Na_2O, FeO/MgO and Al_2O_3 of the ocean ridge tholeiitic basalts surveyed. While the K_2O/Na_2O and FeO/MgO ratios vary by as much as a factor of 10 and 2, respectively, the $[La/Sm]_{e.f.}$ stays remarkably uniform and vary only between 0.46 and 0.6 (figures 6, 7). This is only true if the three anomalous samples from the Gulf of Aden (6244 and 6243.4) and the Mid-Indian Ridge (D 115.7) are excluded ($[La/Sm]_{e.f.} \simeq 1$). These three samples appear to have a rather unique chemistry and will be further discussed below. The dispersion of $[La/Sm]_{e.f.}$ for the light r.e. depleted patterns is considerably increased if the data of Frey *et al.* (1968) and Kay *et al.* (1970) are included. No obvious systematic correlation could be observed for the variation of $[La/Sm]_{e.f.}$ with indices of increasing fractionation, i.e. increasing FeO/MgO or K_2O/Na_2O ratios (figures 6, 7). If one considers in figure 8 the $[Yb]_{e.f.}$ against FeO/MgO variation trend obtained on spatially closely related samples from the Gorda Rise and Juan de Fuca Ridge (Kay *et al.* 1970), a similar positive correlation may be surmised for the samples being studied. The correlation is admittedly poor, if at all existent. No correlation can be ascertained for $[Yb]_{e.f.}$ against K_2O/Na_2O ratio (figure 9), contrary to the results from the Hawaiian Islands, where the degree of alkalinity of the lavas of the alkali series increase sympathetically with the heavy r.e.

The Al_2O_3 content of the suite of basalts varies significantly and, contrary to what has been previously suggested (Engel *et al.* 1965; Nicholls 1965; Green & Ringwood 1967), a high Al_2O_3 content does not seem to be necessarily characteristic of submarine tholeiites. The low Al_2O_3 content of tholeiitic basalts from the Red Sea axial trough illustrates this point clearly. These basalts have an Al_2O_3 content of about 13 %, yet their r.e. fingerprints unambiguously characterize them as belonging to tholeiitic basalt of the worldwide oceanic rift system. Miyashiro, Shido & Ewing's (1969) further distinction between high and low Al_2O_3 ridge tholeiites cannot

be observed in the suite of samples surveyed. This can be attributed to the greater dispersion produced by comparing analyses from various laboratories, or that Miyashiro's distinction holds only locally. No distinct correlation could be detected between $[La/Sm]_{e.f.}$ or $[Yb]_{e.f.}$ and Al_2O_3 (figures 10, 11).

The nearly chondritic r.e. patterns of tholeiitic basalts of the Gulf of Aden (6244, 6243.4) and the Mid-Indian Ridge (D 115.7) are quite distinct not only on r.e. basis (figure 4) but also on
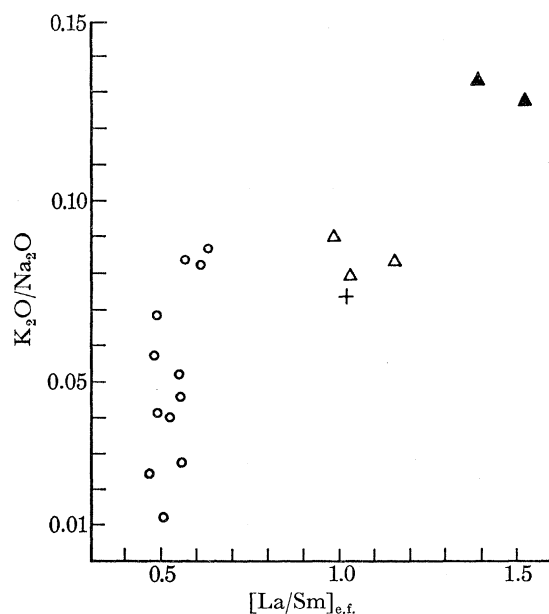
FIGURE 6. The K_2O/Na_2O ratio is plotted against $[La/Sm]_{e.f.}$ ratio for the tholeiitic basalts surveyed. Note how the subaerial tholeiites (▲) plot distinctly from the submarine ones (○). The constancy of the $[La/Sm]_{e.f.}$ ratio for most submarine ridge tholeiites (△) should be noted, also note the distinct submarine basalt subgroup (△) for $[La/Sm]_{e.f.}$ (~1) which includes sample KD11 (+)(Kay *et al.* 1970).
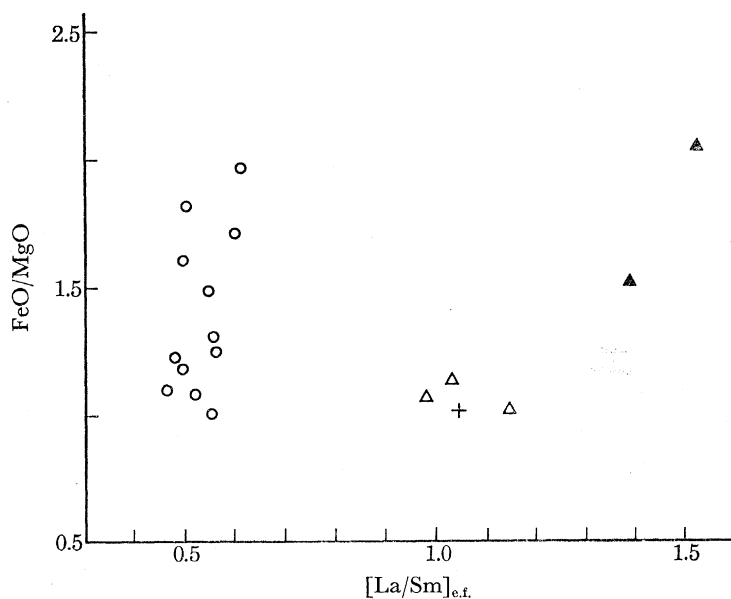

FIGURE 7. FeO/MgO ratio is plotted against $[La/Sm]_{e.f.}$ ratio for the tholeiitic basalts surveyed. The same symbols and comments as given in figure 6 apply.

petrochemical r.e. basis as shown in figures 6 to 11. This minor group merits discussion. Invariably included in this particular group is also a similar tholeiite (KD 11) from the Gorda Rise analysed by Kay *et al.* (1970). Because of the unfractionated r.e. nature of this sample relative to chondrites, these workers used this rock as reference standard for Masuda–Coryell
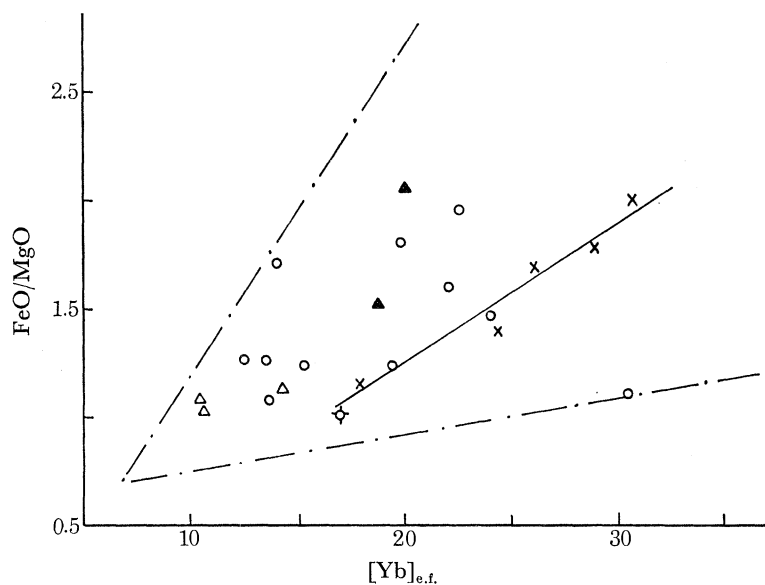

FIGURE 8. FeO/MgO ratio is plotted against Yb enrichment relative to chondrites for the tholeiitic basalts surveyed. The regular trend obtained by Kay *et al.* (1970) for basalts of the Gorda Rise is drawn (line passing through crosses). Other symbols used are given in figure 6.
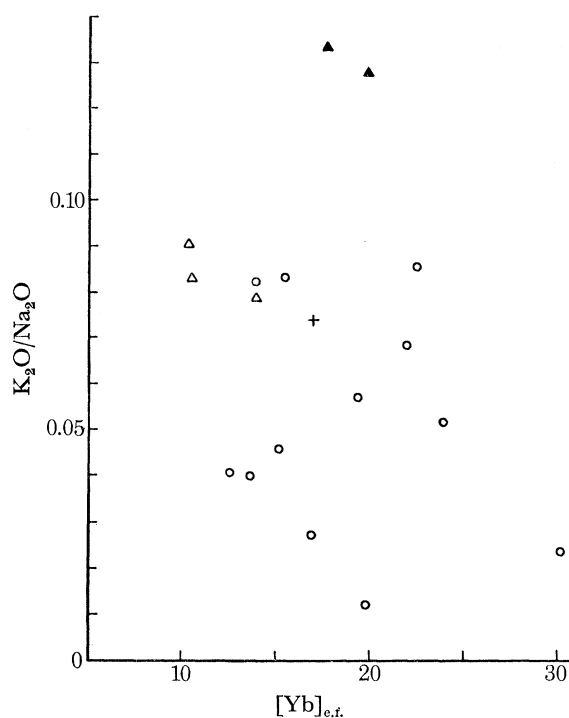

FIGURE 9. K_2O/Na_2O ratio is plotted against Yb enrichment relative to chondrites for the tholeiitic basalts surveyed. Note that the submarine tholeiitic subgroup with $[La/Sm]_{e.f.}$ near one tend also to have low Yb concentration. Symbols used are given in figure 6.

graphical r.e. representation. Despite the widely separated occurrence of these four tholeiites, they apparently have a rather unique major and trace element chemistry. Although some overlaps occur petrochemically, they are distinctly on the lowest values of FeO/MgO, and on the highest values of K_2O/Na_2O and Al_2O_3 content of ocean ridge tholeiitic basalts studied by Kay *et al.* (1970), Frey *et al.* (1968), and this study. Furthermore, Cann (1970*a*) notes that the Gulf of Aden
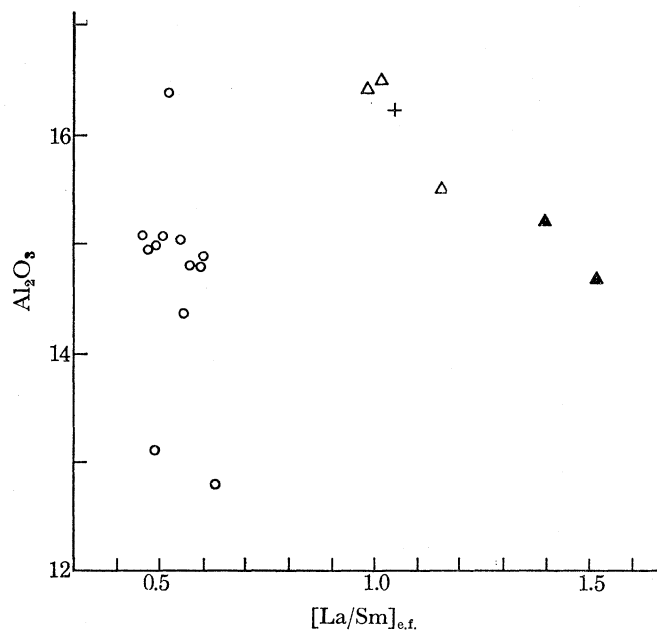
FIGURE 10. Al_2O_3 content is plotted against $[La/Sm]_{e.f.}$ ratio for the tholeiitic basalts surveyed. Note that the submarine tholeiitic subgroup with $[La/Sm]_{e.f.}$ near one also tend to have high Al_2O_3 content and low Yb enrichment factor. Symbols used are the same as given in figure 6.
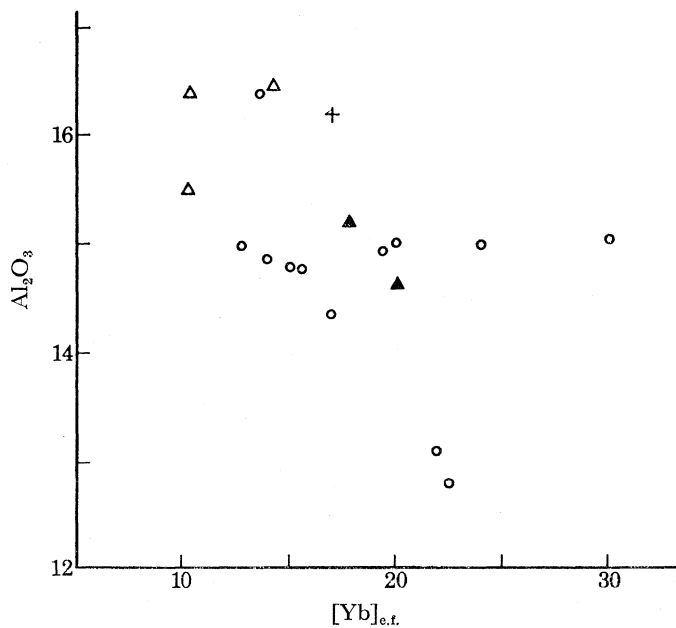
FIGURE 11. Al_2O_3 content is plotted against Yb enrichment relative to chondrites for the tholeiitic basalts surveyed. Note that the submarine tholeiitic subroup with $[La/Sm]_{e.f.}$ ∼ 1 also tend to have high Al_2O_3 content. Symbols used are the same as given in figure 6.

tholeiites differ in several respects from other mid-ocean ridge tholeiites in showing lower than usual Na_2O and higher than usual CaO contents. Cann attributed this unusual composition to reflect possibly abnormal mantle composition or melting conditions different from those normal under mid-ocean ridges. Kay *et al.* (1970) suggested that the KD–11 tholeiite of the Gorda Rise is almost indistinguishable from chondritic meteorites not only in terms of relative r.e. abundances, but also in terms of Sr and Ba relative to r.e. abundances. It appears to be the only fresh oceanic basalt analysed to date with a chondritic K/Rb ratio (361 relative to 330 for the usually quoted average for chondritic meteorites). However, the majority of the r.e. patterns of the other analysed tholeiites from the Gorda Rise (4) did not differ from the usual light r.e. depleted patterns. Another sample (7F) showed light r.e. enriched patterns similar to those found in tholeiitic basalt with alkali affinities at 45° N on the Mid-Atlantic Ridge (Frey *et al.* 1968; Muir & Tilley 1964). Additional scrutiny shows that although the pattern of constant r.e. concentration ratios obtained from these four anomalous tholeiites are nearly identical to those of Ca-rich achondrites, the K_2O/Na_2O are somewhat lower than achondrites and definitely lower than chondritic meteorites. Furthermore, one of the Gulf of Aden tholeiites (6243.4) shows a small but noticeable light r.e. enrichment relative to tholeiite (6244) from the same area. Such minor light r.e. enrichment ($[La/Sm]_{e.f.} \simeq 1.2$) is similar but slightly less pronounced than that found in tholeiites forming some oceanic shield volcanoes. As discussed in §8, these small light r.e. enrichments can possibly be attributed to fractional crystallization (in great part of clinopyroxene) at shallow depth in magma chambers underlying volcanoes. The variability of light r.e. enrichment of the Gorda Rise and the Gulf of Aden requires fractionation to a variable extent and unusual conditions. The nearly achondritic r.e. distribution of such unusual ridge tholeiites could be attributed to intermediate stages of fractionation between tholeiites rapidly erupted along oceanic rifts (characteristically and overwhelmingly light r.e. depleted) and the slightly light r.e. enriched tholeiites intermittently erupting from magma chambers underlying shield volcanoes (§8). Thus, the relatively achondritic or chondritic r.e. pattern for mid-ocean ridge tholeiites would be purely fortuitous, would have no genetic implication, and would not be primary, contrary to what has often been suggested (Frey & Haskin 1964; Engel *et al.* 1965; Kay *et al.* 1970). However, the lower overall r.e. enrichment of these constant ratio patterns, relative to common ocean ridge tholeiite patterns, the low FeO/MgO, and the high K_2O/Na_2O, are not consistent with this crystallization scheme. R.e. partition factors between basaltic melts and phenocrysts of olivine, orthopyroxene, clinopyroxene and plagioclase feldspar are generally less than unity for the entire r.e. series (see §6c). Upon crystallization of such crystals, residual melts should then be r.e. enriched over the entire series from La_{57} to Lu_{71}, although to different degrees depending on the values of the r.e. partition factors of the minerals (Schilling & Winchester 1966, 1967). Derivation of basalts with constant ratio r.e. patterns from the more commonly erupted basalts characterized by light r.e. depleted pattern is not possible by fractional crystallization of such minerals. Extraction of a combination of minerals including garnet and a minor phase concentrating the light r.e. preferentially from a tholeiitic melt, under eclogitic facies conditions, could possibly be responsible for such unusual r.e.-petrochemical characteristics. This scheme would explain the heavy r.e. decrease, inasmuch as garnet concentrates these r.e. preferentially relative to the co-existing melt. The high K_2O/Na_2O and low FeO/MgO ratios of these basalts are also consistent with such a scheme. However, no unique solution appears to be available at present. The origin of such patterns should be further investigated and tested.

Finally, no systematic r.e. variation is detected relative to variations in degree of silica saturation or oversaturation of tholeiites from the same station (Carlsberg Ridge) or from nearby localities (Red Sea axial trough).

To summarize, the overwhelmingly light r.e. depleted patterns ($[La/Sm]_{e.f.} < 1$) of ocean-ridge tholeiites studied show no distinct correlation with various petrochemical indices of differentiation. The $[La/Sm]_{e.f.}$ ratio is surprisingly constant and further corroborates the extreme uniformity of ocean-ridge basalts. The overall enrichment of these patterns varies mostly by less than a factor of 2.5, and only occasionally up to 3. Larger variations occur only in rare instances (Kay *et al.* 1970; Frey *et al.* 1968); but the relative r.e. fractionation patterns remain nearly identical, i.e. light r.e. depleted.

(b) *Europium anomaly*

Another approach intended to estimate the extent of pre-eruptional plagioclase crystallization is to use the europium anomaly (Chase, Winchester & Coryell 1963; Towell, Winchester & Spirn 1965; Philpotts & Schnetzler 1968b, 1969; Towell, Spirn & Winchester 1969).

For yet unclear reasons, plagioclase feldspar, in its uptake of trace elements has a marked affinity for Eu relative to other neighbouring r.e. This produces an Eu anomaly in the middle of the r.e. series. Thus, extraction of plagioclase from a magma with normal r.e. distribution (i.e. without any Eu enrichment or depletion) would leave a residual melt depleted in Eu to an extent depending on the amount of plagioclase extracted. Conversely, flotation of feldspar in a magma chamber, or preferential rise of feldspar during ascent of lavas, should produce an Eu enrichment in the upper part of the chamber or early erupting lavas, respectively.

During this survey no europium anomaly was observed which is not within experimental uncertainties of the method or of the interlaboratory normalization procedure used. However, some depletions have been reported for apparently more fractionated mid-ocean ridge lavas (Frey *et al.* 1968; Kay *et al.* 1970). Satisfying both the europium anomaly and petrochemical requirements Kay *et al.* (1970) were able to estimate the relative proportions of feldspar and olivine to be extracted from a presumed original magma in order to produce the sequence high alumina basalt, olivine tholeiite, iron-rich quartz tholeiite. The method represents a good example of a combined petrochemical–geochemical attempt toward more definite solutions in petrogenesis; unfortunately, this solution is not the only one possible.

(c) *Theoretical*

Because of lattice energy restrictions on ion substitution, common rock-forming silicate minerals can be very selective in uptaking trace amounts of r.e. (Towell *et al.* 1965). The selection appears to be strongly dependent on ionic size for electro-positive elements such as the r.e. (Schilling & Winchester 1966).

Thus a more fruitful approach to interpret r.e. patterns is to estimate directly the effect on residual melts of the removal of silicate phenocrysts commonly present in lavas. For this, one needs to know: (1) the r.e. partition coefficients between crystal and melt as a function of temperature, pressure, and composition, (2) the r.e. composition of the original melt, and (3) a mathematical–thermodynamical model to describe the process to any stage. Obviously, certain assumptions are necessary for lack of both proper data and exact theories on trace element distribution. Only a semi-quantitative estimate can be presented.

Figure 12 illustrates the r.e. partition coefficient trends of common volcanic phenocrysts

determined by Schnetzler & Philpotts (1968, 1970). Only averages of many determinations are shown. Each individual determination has a similar trend to the average, but the r.e. partition coefficient trends distinctly differ depending on the mineral type. This indicates that the r.e. partition coefficient *trend* is an intrinsic property of the phenocryst and is controlled by lattice energy restrictions of the mineral. To a first approximation, pressure and composition of the melt do not seem to affect these intrinsic trends appreciably (Cooke & Schilling 1969). Variations of the absolute values for a particular mineral probably reflects prevailing kinetic and
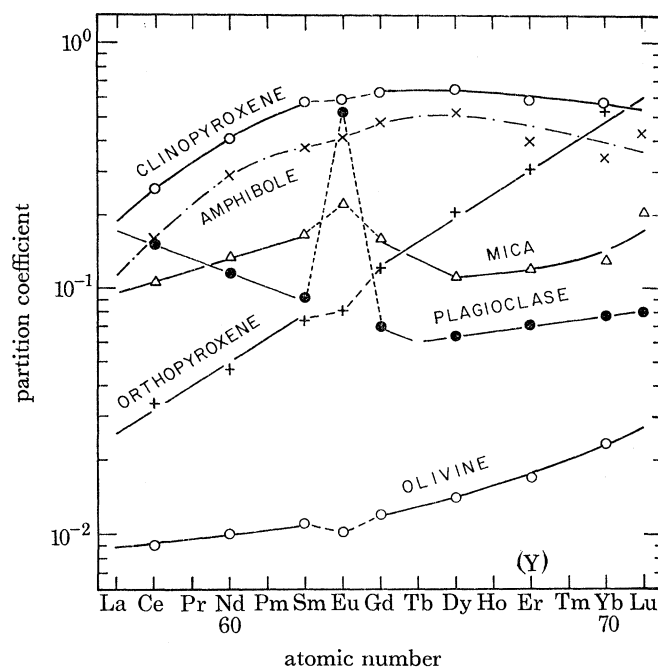

FIGURE 12. Phenocryst/matrix r.e. partition coefficients top ○, Ca-rich clinopyroxenes (average of 10); ×, amphibole (average of 3); △, Fe,Mg-rich mica (average of 3); ●, plagioclase feldspar (average of 9); +, Ca-poor orthopyroxene (average of 2); bottom ○, olivine. Data are from Schnetzler & Philpotts (1968, 1970).

kinematic conditions of intrusions and extrusions. On the absolute scale, the partition trend can vary by slightly more than an order of magnitude for augite and feldspar. Only limited data is yet available for olivine, orthopyroxene, and garnet (not shown). These variations limit purely quantitative solutions. Only two r.e. partition coefficient trend determinations on orthopyroxene are yet available, and their slopes differ (Schnetzler & Philpotts 1970; Cooke & Schilling 1969). Tentatively, figures 13 and 14 show the effect of extracting variable amounts of olivine, Ca-poor orthopyroxene, Ca-rich clinopyroxene, and plagioclase feldspar, from an original melt of r.e. composition represented by the average of mid-ocean ridge tholeiitic basalts as well as from a chondritic melt. R.e. partition coefficient trends shown in figure 12 were used and the Doerner–Hoskins trace element distribution law (logarithmic law) was assumed as a reasonable assumption for fractional crystallization processes (Doerner & Hoskins 1925; McIntire 1963; Schilling 1966). The use of mathematical models describing intermediate cases between the homogeneous Berthelot–Nernst law and the Doerner–Hoskins law, possibly more realistic, would not change appreciably the results obtained. The lack of appreciable r.e. fractionation in most of the Skaergaard layered intrusive except in its uppermost top (Haskin

& Haskin 1968) is not surprising at the light of such calculations. These results indicate: (1) The r.e. pattern of the primary melt is preserved up to a large extent of olivine extraction. (2) Ortho-pyroxene extraction does not change appreciably the light r.e. of the primary melt up to 50 to 60 % extraction, but tends to fractionate slightly the heavy r.e. (3) Clinopyroxene may enrich and fractionate appreciably the light r.e. depending on the extent of extraction. The heavy r.e. are also fractionated and enriched but to a much smaller degree. A large extent of
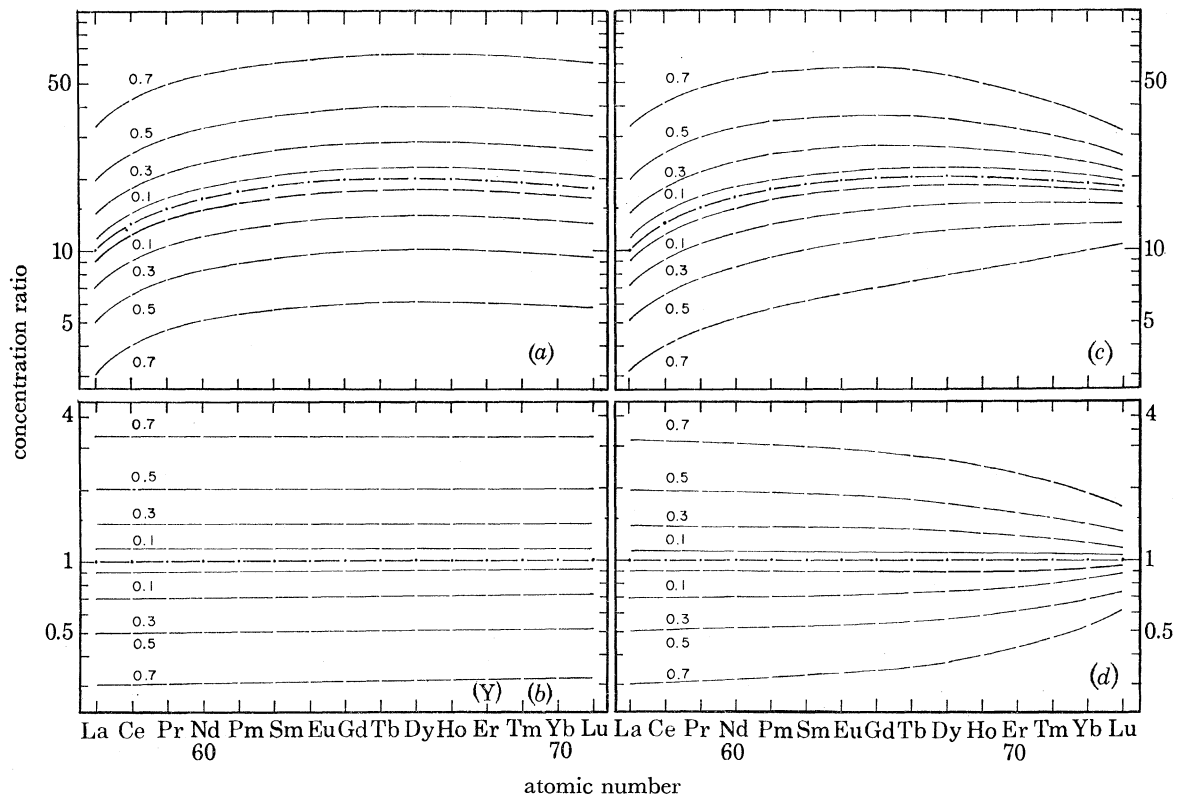

FIGURE 13. Olivine and Ca-poor orthopyroxene fractional crystallization effect on r.e. pattern of residual melts. The dotted–dashed line (average of mid-ocean ridges basalts) represents either: (1) The original liquid from which 0.1, 0.3, 0.5, 0.7, and 0.9 of the melt has crystallized as olivine (a) or Ca-poor orthopyroxene (c). The r.e. patterns of residual melts after fractional crystallization of both minerals are shown by the curves above the dotted–dashed line. (2) The residual melt. The curves below the dotted–dashed line represent then the original melt which upon 0.1, 0.3, 0.5, 0.7, and 0.9 of fractional crystallization of olivine (a) or Ca-poor orthopyroxene (c) would produce a residual melt with a pattern represented by the dotted–dashed line. Figure (b) and (d) represent the same cases as above but with a horizontal r.e. pattern (dotted–dashed line) as an original melt for case (1), or residual melt for case (2).

extraction of clinopyroxene could produce a minimum in residual liquids near the middle of the r.e. series depending on the original r.e. pattern of the primary melt. (4) Plagioclase extraction does not change appreciably the relative r.e. pattern of the original melt up to 50 % removal— above, a slight enrichment of the heavy r.e. occur. The europium anomaly put some stringent limits on the extent of extraction of this mineral. Basalts with no europium anomaly should not have suffered appreciable feldspar extraction unless primary melts had an excess of europium. There is no evidence to believe that this can be the case. Less than 10 to 20 % extraction cannot be detected with assurance. The magnitude of the europium anomaly would be similar to uncertainties due to: (1) the analytical method used, (2) the interlaboratory chondrite

normalization procedure, and (3) the specific values chosen for the r.e. partition coefficients for plagioclase which can vary largely (Schnetzler & Philpotts 1968, 1970).

These theoretical calculations indicate that reasonable amounts of crystallization and extraction of one or more type of phenocrysts before eruption along mid-ocean ridges (e.g. up to 50 %, see O'Hara 1968 a, b) will not affect appreciably the r.e. pattern of the original basaltic melt. Thus, the characteristic light r.e. depleted pattern of mid-ocean ridge basalt appears to
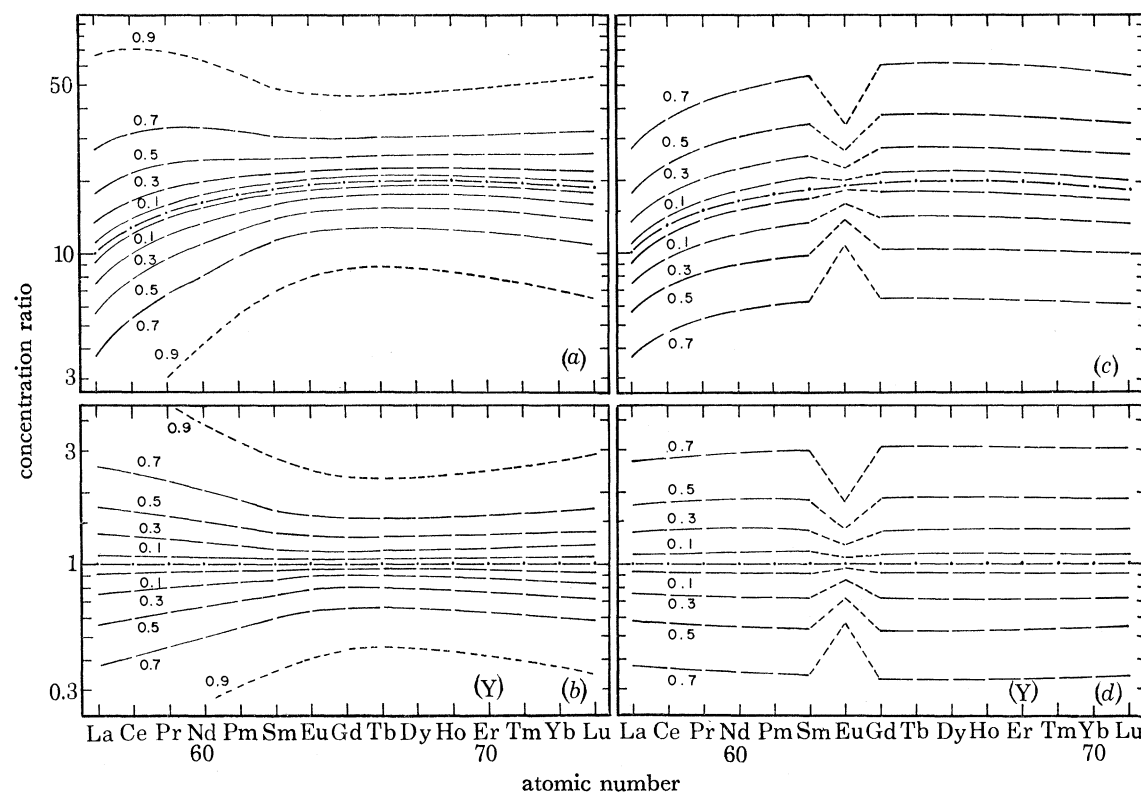

FIGURE 14. Ca-rich clinopyroxene and plagioclase feldspar fractional crystallization effect on r.e. pattern of residual melts. The same two cases as explained in figure 13 were considered. Note the europium depletion of the residual melt upon crystallization of plagioclase feldspar (curves above the dotted–dashed line) of (c) and (d). Also note the necessary europium enrichment of the original melts (curves below the dotted–dashed line) of (c) and (d) were plagioclase to fractionally crystallize and give rise to a residual liquid (dashed–dotted curve) with a normal europium value as most submarine basalts have. Rocks with an Eu enrichment are unusual and rare. These calculations preclude much *extraction* of feldspar before eruption of mid-ocean ridge basalt, although crystallization may have occurred as evidence by the presence of plagioclase phenocryst in submarine basalts. The phenocrysts, however, must not have been preferentially concentrated or extracted from the melt from which they crystallized. Thus they must be near equilibrium with the lava matrix so as to balance the abundance of Eu of the 'whole rock'.

reflect intrinsically the r.e. pattern of the primary melt. This is further corroborated by reporting the results of figures 13 and 14 on a $[La/Sm]_{e.f.}$ against $[Yb]_{e.f.}$ diagram as shown in figure 15. This theoretical diagram helps to decipher the variations obtained during this survey (figure 16). It explains the rather constant $[La/Sm]_{e.f.}$ ratio of mid-ocean ridge basalts despite that some fractional crystallization probably occurred before eruption (compare olivine, Ca-poor ortho-pyroxene and plagioclase control lines in figure 15). It also limits qualitatively the type and semiquantitatively the extent of mineral extraction. Ca-rich clinopyroxene appears to be a

critical phenocryst able to change appreciably the r.e. pattern (i.e. $[La/Sm]_{e.f.}$). The slope of the Ca-rich clinopyroxene control line is a sensitive function of both light r.e. and heavy r.e. partition coefficient trends (figure 12). The variation of measured partition coefficients can change significantly the position and slope of the clinopyroxene control line but not the plagioclase one, although both sets of partition coefficients vary by nearly one order of magnitude
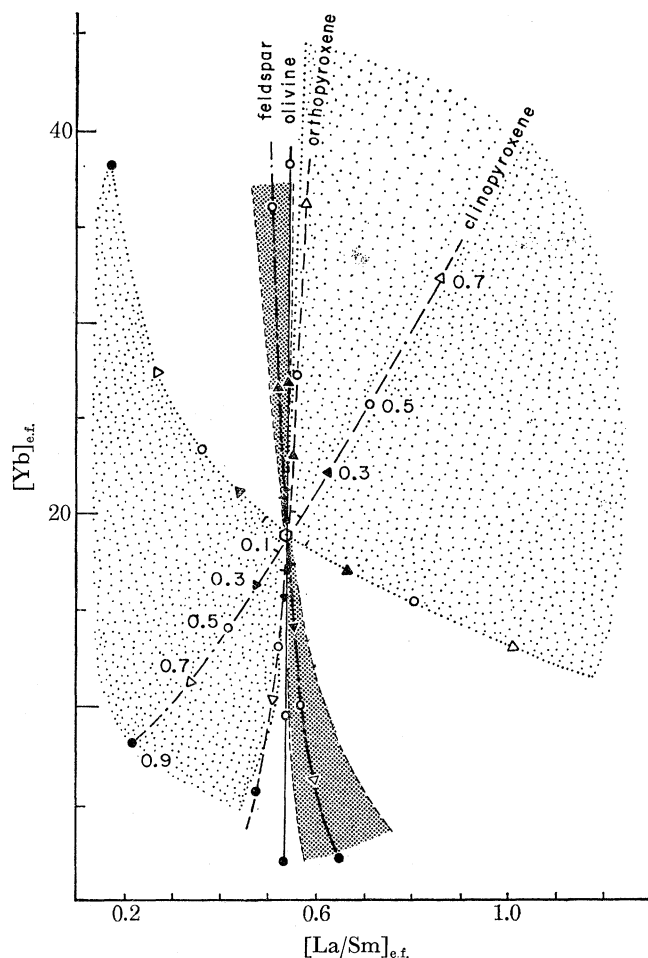

FIGURE 15. Theoretical variations of $Yb_{e.f.}$ against $[La/Sm]_{e.f.}$ for fractional crystallization cases considered in figures 13 and 14. The control lines for feldspar, Ca-rich clinopyroxene, Ca-poor orthopyroxene, and olivine extraction are drawn. $|$, $\blacktriangle$, $\bigcirc$, $\triangle$ and $\bullet$ of the upper curves respectively represent the $[La/Sm]_{e.f.}$ and $[Yb]_{e.f.}$ ratio of residual melts after 0.1, 0.3, 0.5, 0.7, and 0.9 of the original melt (submarine tholeiite average) has fractionally crystallized. The lower curves represent original melts with different $[La/Sm]_{e.f.}$ and $[Yb]_{e.f.}$ which upon 0.1, 0.3, 0.5, 0.7, and 0.9 fractional crystallization would give a residual melt represented by the average of submarine tholeiites (point of convergence of the curves). The average partition coefficients shown in figure 12 have been used. The dotted area represents the maximum range of variation that residual liquids (clinopyroxene control lines) can take using the maximum and minimum set of r.e. partition coefficients measured by Schnetzler & Philpotts (1968, 1970) for Ca-rich clinopyroxene. The shaded area is the maximum range of variation for plagioclase feldspar (plagioclase control lines). Although both feldspar and clinopyroxene set of r.e. partition coefficient vary by approximately an order of magnitude, the $[La/Sm]_{e.f.}$ of residual melts is sensitive only to clinopyroxene extraction. Extraction of Ca-poor orthopyroxene, olivine, and feldspar do not change appreciably the $[La/Sm]_{e.f.}$ ratio of residual melts. Compare this theoretical diagram with figure 16 and see how tholeiites from shield volcanoes or the submarine subgroup with $[La/Sm]_{e.f.} \approx 1$ can possibly be linked by fractional crystallization to submarine tholeiites depleted in light rare earths, i.e. $[La/Sm]_{e.f.} < 1$. Only Ca-rich clinopyroxene extraction can do it but large extents of fractional crystallization are required. Amphibole crystallization and extraction would have the same effect as clinopyroxene inasmuch as both r.e. partition coefficient trends are similar.

(figure 15). By fractional crystallization of clinopyroxene, possibilities appear of linking the two fields representing shield volcanoes and the Gulf of Aden type of submarine tholeiites (i.e. $[La/Sm]_{e.f.}$ near the value of one) from light r.e. depleted mid-ocean ridge basalt field. However limitations do occur and are discussed in §8. Limited extraction of clinopyroxene and feldspar before eruption appear to be necessary to keep *most* mid-ocean ridge basalts with a relatively constant $[La/Sm]_{e.f.}$ ratio and without a noticeable europium anomaly, respectively. Evaluation of the extents of crystallization of olivine and of Ca-poor orthopyroxene are more difficult. Separately or combined, they should not exceed 50 %, assuming the basalts have derived from a source with identical r.e. composition given by the r.e. average of mid-ocean ridge basalts.
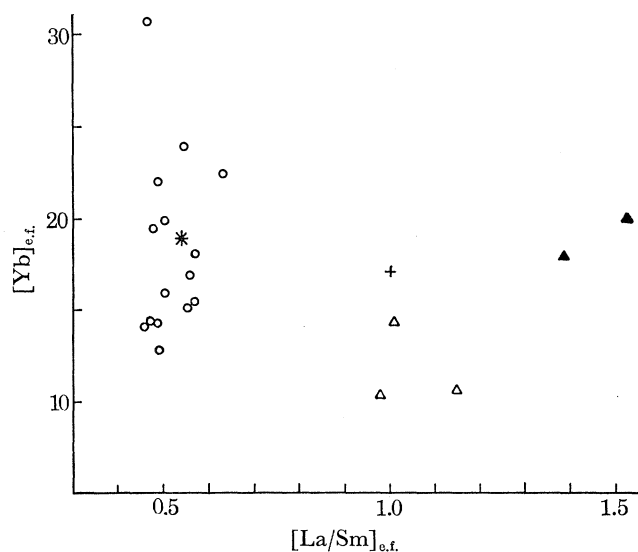

FIGURE 16. The ratio of enrichments factor $[Yb]_{e.f.}$ is plotted as a function of the $[La/Sm]_{e.f.}$ enrichment factor relative to chondrites for the tholeiitic basalts surveyed. Note that the same remarks as given in figures 6 and 9 for respectively the $[La/Sm]_{e.f.}$ and $[Yb]_{e.f.}$ variations apply. Compare this figure with theoretically derived figure 15.

However, this average does not apparently coincide with the most probable value shown by the clustering of points with low $[Yb]_{e.f.}$ values (figure 16). The latter values may indeed be a better choice for estimating the r.e. composition of a primary melt for mid-ocean ridge basalts, if the $[Yb]_{e.f.}$ variations are explained by fractional crystallization during ascent. As the partition coefficients are usually less than unity, $[Yb]_{e.f.}$ should increase in the residual melt as fractional crystallization proceeds. Consequently primary melts should have a low $[Yb]_{e.f.}$.

The possible extent of fractional crystallization at depth in the eclogitic facies can not yet be evaluated because of the lack of reliable r.e. partition coefficients for garnet and other relevant minerals. Of what is known, garnet extraction should enrich residual melts in the light r.e. and impoverish the heavy r.e. (Schilling 1966); to what extent remains to be determined.

Further limits and better estimates of crystallization extent before eruption can be put forward by satisfying simultaneously: (1) the major element chemistry and modal abundances of the lavas, (2) evidence from experimental petrology under controlled conditions, and (3) r.e. mineral data and mathematical-thermodynamical models of trace element distribution. As discussed earlier in this section, lack of adequate data and the scope of this paper preclude discussion of such an approach.

To summarize, this theoretical section shows that light r.e. depletions of mid-ocean ridge basalt reflect intrinsic properties of primary melt(s) despite the fact that some fractional crystallization may have occurred before eruption during the ascent of magmas. How representative of the mantle source of these lavas are such light r.e. depleted patterns remains to be evaluated. An attempt is made in the following section.

7. PARTIAL MELTING: RELATION OF RIDGE BASALTS TO ULTRAMAFICS

A wealth of oceanographic geophysical and geological data (see Cann 1968; Vogt, Schneider & Johnson 1969) indicates that volcanic activity and formation of new oceanic crust is limited to a very narrow zone, a few kilometres wide, over the crest of ocean ridges. This implies localized dyke, diapiric or like intrusions from the upper mantle. Unless only melts are rising from the low velocity layer (Lliboutry 1969), some partial melting will occur during the ascent of the material regardless of whether slush or solid upper-mantle rock is advecting to fill the gap. This is because of: (1) near-adiabatic decompression during ascent, (2) the closeness in the upper mantle of the geothermal gradient to the melting-point gradient relative to pressure, and (3) the greater steepness of the melting point gradient relative to the adiabatic one.

The question is, to what extent partial melting will occur and what effect it will have on major and trace element chemistry of the generated melts? This is a difficult question. Also related to this problem is the genetic relation, if any, of dredged tholeiitic basalts to the serpentinites and peridotites usually dredged at lower stratigraphic levels of the oceanic crust (Cann & Funnel 1967; Bonatti 1968; Engel & Fisher 1969). This bears importantly on the make-up of layers 2 and 3, the nature of the Mohorovičič discontinuity, and details of the spreading mechanism.

The ability to determine the effect of *degree of partial melting* on the abundance and fractionation of trace r.e. in melts and residual solids was demonstrated for simplified systems by Schilling (1966) and Schilling & Winchester (1967), and later further emphasized and discussed by Gast (1968). The model treats melting as nothing more than an extreme case of metamorphism during which a new phase (the melt) is introduced. The model assumes that the distribution of trace r.e. can be described by the Berthelot–Nernst homogeneous equilibrium distribution law (Schilling 1966). For a multiphase system at equilibrium the concentration $C_L(z)$ of a trace element z in the melt is controlled by the concentration of solid phases coexisting $C_R^\alpha(z)$, $C_R^\beta(z)$, $C_R^\gamma(z)$,..., etc. in the following manner:

$$K_L^\alpha(z) = \frac{C_R^\alpha(z)}{C_L(z)}, \ K_L^\beta(z) = \frac{C_R^\beta(z)}{C_L(z)}, \ K_L^\gamma(z) = \frac{C_R^\gamma(z)}{C_L(z)}, \ ..., \text{etc.}, \quad (1)$$

where $K_L^\gamma(z)$ is the partition coefficient of element z between phase α, β, γ,..., etc. and the coexisting melt.

The concentration in the original solid before partial melting is given as a function of the degree of melting of coexisting phases, as weight fractions of the bulk, y^α, y^β, y^γ, ..., etc., and the weight fractions of the original phases X^α, X^β, X^γ, ..., etc. These are related by mass balance as follows:

$$C_L(z)\,(y^\alpha + y^\beta + y^\gamma + ...) + C_R^\alpha(z)\,(X^\alpha - y^\alpha) + C_R^\beta(z)\,(X^\beta - y^\beta) + C_R^\gamma(z)\,(X^\gamma - y^\gamma) + ...,$$
$$\text{etc.} = C_P(z), \quad (2)$$

where the overall original concentration of z is given by

$$C_{\mathrm{P}}(z) = X^{\alpha}\,C_{\mathrm{P}}^{\alpha}(z) + X^{\beta}C_{\mathrm{P}}^{\beta}(z) + X^{\gamma}\,C_{\mathrm{P}}^{\gamma}(z) + \ldots, \text{ etc.}$$

$C_{\mathrm{P}}^{\alpha}(z)$. $C_{\mathrm{P}}^{\beta}(z)$, $C_{\mathrm{P}}^{\gamma}(z)$, ..., etc. are the original concentrations of phase α, β, γ, ..., etc. Also

$$X_{\mathrm{R}}^{\alpha} + X_{\mathrm{R}}^{\beta} + X_{\mathrm{R}}^{\gamma} + \ldots + y^{\alpha} + y^{\beta} + y^{\gamma} + \ldots = 1$$

and

$$X^{\alpha} + X^{\beta} + X^{\gamma} + \ldots = 1.$$

Combining equations 1 and 2:

$$C_{\mathrm{L}}(z) = \frac{C_{\mathrm{P}}(z)}{Y + K_{\mathrm{L}}^{\alpha}(X^{\alpha} - y^{\alpha}) + K_{\mathrm{L}}^{\beta}(X^{\beta} - y^{\beta}) + K_{\mathrm{L}}^{\gamma}(X^{\gamma} - y^{\gamma}) + \ldots}, \tag{3}$$

where $Y = y^{\alpha} + y^{\beta} + y^{\gamma} + \ldots$ is the overall degree of melting expressed as a weight fraction of the bulk.

Rigorously, equation (3) holds for a fixed T, P, and composition. A Berthelot–Nernst equilibrium is assumed and also a degree of melting which does not exhaust any of the phases α, β, γ, ..., etc. originally present (Schilling 1966). Partial melting affects trace element concentrations and fractionation between melt and crystalline phases in an inverse fashion compared to fractional crystallization. R.e. enrichment and fractionation in a residual melt becomes noticeable only after an important fraction of the original melt has been fractionally crystallized, whereas small degrees of melting affect most the fractionation of r.e. (Schilling & Winchester 1967).

Although the recently determined partition coefficients between phenocrysts and lava matrix may be applicable, no experimental data are yet available fully to justify their use for partial melting model calculations. The characteristic r.e. partition coefficient trends shown in figure 12 can possibly be altered by the presence of coexisting mineral phases which may selectively and significantly take up r.e. during partial melting. Such competitive effects should not be overlooked and remain to be evaluated.

Using r.e. data from dredged basalts and ultramafics, computation of unknowns such as y^{α}, y^{β}, y^{γ}, and $C_{\mathrm{P}}(z)$ in equation (3) is possible provided that (1) a qualitative knowledge of mineral phases present in the upper mantle is known, and their relative proportions can be estimated; (2) these mineral phases are sufficiently limited in number; (3) none of these phases are used up during partial melting (a critical assumption); and (4) the crystal and melt partition coefficients are known (or some of them depending on the degree of freedom of the model system).

Combined with petrochemical limitations on major element compositions, melting conditions, and isotopic information, such an approach should indeed be quite useful in tracing back the composition of the source rock of mid-ocean ridge basalts in time and space. The relation of serpentinites and other ultramafic rocks to submarine basalts can possibly be determined. This work is still in progress.

Meanwhile, some estimates of the shape of the r.e. distribution pattern of the *original mantle source* rock should be useful for comparing with known r.e. patterns of dredged ultramafic and mafic rocks of the sea floor.

Clues on the origin of these rocks may consequently be gained. Crude qualitative arguments for the lowest permissible r.e. concentrations of a hypothetical upper-mantle source can be made by scrutinizing equation (3) and using the partition factors given in figure 12. Equation (3) can be considered for each individual r.e., or one can assume that $C_{\mathrm{P}}(z)$, $C_{\mathrm{L}}(z)$, $C_{\mathrm{R}}(z)$, ...

and $K_L^\alpha(z)$, $K_L^\beta(z)$, $K_L^\gamma(z)$,... are continuous functions of the atomic number z, although in reality only discrete values exist. Maximum r.e. fractionation between the primary source rock and the melt is produced for very small degrees of partial melting, i.e. when $Y \to 0$ in equation (3). In this equation: $Y = y^\alpha + y^\beta + y^\gamma + \ldots$, these take the following values: $0 \leqslant Y \leqslant 1$, $0 \leqslant y^\alpha \leqslant Y$, $0 \leqslant y^\beta \leqslant Y$, $0 \leqslant y^\gamma \leqslant Y$,.... As $Y \to 0$ also $y^\alpha \to 0$, $y^\beta \to 0$, $y^\gamma \to 0$,..., and equation (3) reduces to

$$C_P(z) = C_L(z) \, [X^\alpha K_L^\alpha(z) + X^\beta K_L^\beta(z) + X^\gamma K_L^\gamma(z) + \ldots] \tag{4}$$

or

$$C_P(z) = [C_L(z) K_L^\alpha(z)] X^\alpha + [C_L(z) K_L^\beta(z)] X^\beta + [C_L(z) K_L^\gamma(z)] X^\gamma + \ldots. \tag{5}$$

The functions $C_L(z) K_L^\alpha(z)$, $C_L(z) K_L^\beta(z)$, $C_L(z) K_L^\gamma(z)$,..., for olivine, Ca-rich clinopyroxene, Ca-poor orthopyroxene, amphibole, plagioclase feldspar, and ferromagnesian mica are shown
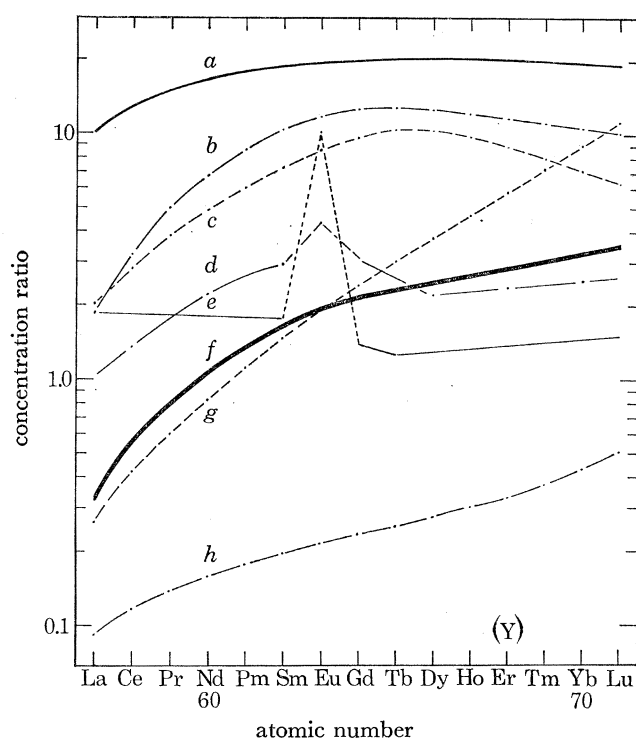

FIGURE 17. Upper mantle partial melting model. Rare-earth pattern (a) represent a typical mid-ocean ridge basalt (average of mid-ocean ridge tholeiites) assumed to be produced by partial melting of upper mantle rock. The other curves (theoretically derived, $C_L K_L^\eta(z)$) represent the *lowest permissible* r.e. pattern ($Y \to 0$) of original upper mantle rock or partial melting for (1) a *monomineralic* upper mantle made of: (b) Ca-rich clinopyroxene composition, (c) amphibole, (d) Fe, Mg-rich micas, (e) plagioclase feldspar, (g) Ca-poor ortho-pyroxene, and (h) Mg-rich olivine, and (2) a multi-phase upper mantle of *lherzolite* composition (f) (Harris 1967). The upper permissible r.e. pattern ($Y \to 1$) for the upper mantle is also represented by curve a. This is the case of total melting (eclogite upper mantle). For more reasonable degrees of partial melting (0.1 < Y < 0.3) the original lherzolite upper mantle should have a r.e. pattern intermediate between curve f and a and have the same general trend. Partition coefficients shown in figure 12 and equation five were used to derive the theoretical curves.

in figure 17, using the same sets of partition coefficients illustrated in figure 12 (Schnetzler & Philpotts 1968, 1970). Unfortunately garnet could not be considered as no reliable partition factors are yet available for this mineral. Further analyses of equation (5) will be made by considering only olivine, clinopyroxene, orthopyroxene and amphibole because: (1) Feldspar

is probably unstable in the depth range where partial melting occurs beneath mid-ocean ridges (O'Hara 1968a, b; Green & Ringwood 1967), and thus can be disregarded in the discussion. This is corroborated by the rare occurrence of feldspathic peridotites and particularly by the lack of europium anomalies in the majority of ocean ridge basalts. Some europium anomalies would be expected were feldspar to take part in the partial equilibrium (see figure 14). (2) Although ferromagnesian micas may play some roles in volcanic processes of continental areas, presumably their role is minimal and negligible under oceanic areas. Were small amounts of mica and plagioclase feldspar to take part in the partial melting equilibrium discussed below, they would not significantly alter the conclusion reached. Other minor phases, although possibly of some importance, will be neglected for lack of proper data (Gast 1968).

Figure 17 shows that the function $C_L(z) K_L^\eta(z)$ has the same general trend for each mineral likely to be important during partial melting of the upper mantle such as olivine, Ca-poor orthopyroxene, Ca-rich clinopyroxene, and amphibole, omitting minerals of the eclogite facies. The function increases progressively with increasing r.e. atomic number. These curves represent the maximum r.e. fractionation ($Y \to 0$) to be expected for monomineralic primary source materials which upon partial melting would generate light r.e. depleted ocean ridge basalts. Each of these curves represents also a lower concentration limit for monomineralic upper-mantle sources. A larger degree of melting $0 < Y < 1$ would give an r.e. pattern intermediate between $C_L(z) K_L^\eta(z)$ and the light r.e. depleted ocean ridge pattern (curve A in figure 17).

Considering the more general and important case where several minerals coexist with the melt during partial melting, the *sum* of $C_L(z) K_L^\alpha(z)$, $C_L(z) K_L^\beta(z)$, $C_L(z) K_L^\gamma(z) \ldots$, will have to be intermediate and be included in the envelope formed by the two extreme $C_L(z) K_L^\eta(z)$ curves. This is true for any values taken by $X^\alpha, X^\beta, X^\gamma, \ldots$ provided $X^\alpha + X^\beta + X^\gamma + \ldots = 1$ and values of X vary as follows: $0 \leqslant X^\alpha \leqslant 1$, $0 \leqslant X^\beta \leqslant 1$, $0 \leqslant X^\gamma \leqslant 1, \ldots$.

In the case of partial melting of a *lherzolite* (olivine, Ca-poor orthopyroxene and Ca-rich clinopyroxene) the primary source material should be intermediate between the $C_L(z) K_L^\alpha$ of clinopyroxene and $C_L(z) K_L^\beta$ of olivine. The r.e. enrichment factor should increase regularly and smoothly as a function of the r.e. atomic number since the $C_L(z) K_L^\eta(z)$ for olivine, clinopyroxene and orthopyroxene also increase regularly with increasing r.e. atomic number. Its exact shape depends on values taken by X^{olivine}, $X^{\text{orthopyroxene}}$, and $X^{\text{clinopyroxene}}$, i.e. the modal abundance of the primary lherzolite.

As an example, an upper mantle of mineralogical composition given by Harris et al. (1967) was considered. The upper-mantle model was based in five high Ca and Al_2O_3 olivine nodules. The average modal abundance is olivine 65.3 %, orthopyroxene 21.8 %, clinopyroxene 11.3 % and spinel 1.5 %. This composition has been recalculated on a spinel-free basis, as no r.e. partition coefficient for this mineral is available. However, such omission should not affect significantly the qualitative arguments presented, inasmuch as the modal abundance of spinel is generally low and the r.e. abundances of two spinels vary within the range of those found in olivine, clinopyroxene, and orthopyroxene for the Lizard intrusion (Frey 1969). The modal abundances used are $X^{\text{olivine}} = 0.664$, $X^{\text{orthopyroxene}} = 0.222$, and $X^{\text{clinopyroxene}} = 0.115$. The r.e. pattern obtained for the primary source lherzolite ($Y \to 0$ case) is shown by the heavy line (F) in figure 17. It represents the lowest r.e. abundances and maximum depletion of light r.e. expectable within the limitations of the model and the mode's assumptions (i.e. average partition coefficients used for fixed T, P, and composition, the lherzolite modal abundances,

and that equation (3) adequately describes the process). For more reasonable degrees of melting (perhaps 5 to 30 % rather than $Y \to 0$) the *primary lherzolite upper mantle source* should have an r.e. pattern intermediate between curve F ($Y \to 0$ case) and the light r.e. depleted pattern of ocean ridge basalt (the melt, i.e. curve A). Consequently one might expect for the upper mantle source a pattern with a slightly less pronounced light r.e. depletion and more constant heavy r.e. than curve F shown in figure 17. The overall r.e. concentration of this lherzolite would also be intermediate between curve A and F. The residual rock left after partial melting of this primary lherzolite should have lower overall r.e. abundances and a more pronounced depletion of the lighter r.e. than predicted for the primary source material (as most r.e. partition coefficients appear in general to be less than unity, excluding garnet and perhaps other minor phases). The estimated r.e. abundances of the residual rock compare remarkably well with r.e. abundances for high temperature peridotites of the Mt Albert, Tinaquillo, and Lizard intrusions (Frey 1969, 1970a; Haskin *et al.* 1966). In fact, they have been used for more refined estimates of primary source mantle rocks which are beyond the scope of this paper (J.-G. Schilling, in preparation).

Figure 17 also shows that $C_{\mathrm{L}}(z) K_{\mathrm{L}}^{\eta}(z)$ for olivine represents the lowest permissible r.e. abundances for primary source material of ocean ridge basalts in the range of depths where olivine co-exists with the melt, provided that: (1) the partition factors used for olivine are essentially correct, and (2) no other phases with $K_{\mathrm{L}}^{\eta}(z)$ trends lower than for olivine are co-existing with the melt; which appears unlikely. However, if $K_{\mathrm{L}}^{\eta}(z)$ for olivine is lower as suggested by Frey (1969), the estimated lower limit would have to be moved further down, accordingly.

Similar estimates in the eclogite facies could be made were r.e. partition coefficients for garnet known reliably.

Furthermore, if the partial pressure of water were sufficiently high and amphibole were one of the liquidus phases present during partial melting, the estimated r.e. pattern of the primary *hornblende peridotite* would be very similar to the one obtained for a *dry lherzolite*. This is because the curve $C_{\mathrm{L}}(z) K_{\mathrm{L}}^{\eta}(z)$ for amphibole is very similar to the Ca-rich clinopyroxene one, and that the other co-existing phases are identical. However, presence of feldspar in the partial melting equilibrium could change significantly the estimated r.e. pattern for the primary source rock (including the europium anomaly).

Based on meagre data, Schilling & Winchester (1967) have surmised that melting of amphibolite at shallow depth may explain the light r.e. depletion and relatively high heavy r.e. contents of mid-ocean ridge basalts. More recent estimates of r.e. partition coefficients for amphiboles (Schnetzler & Philpotts 1968, 1970) give further support to the suggestion. Using the same treatment as before, the r.e. pattern of the primary source *amphibolite* would again have to lie between curve $C_{\mathrm{L}}(z) K_{\mathrm{L}}^{\eta}(z)$ for amphibole (curve C in figure 17) and the light r.e. depleted pattern of ocean ridge basalts (curve A), were this latter derived by partial melting of amphibolite. In fact it should be very close but lower than the r.e. pattern of the basalts, as nearly total or total melting of hornblendite would be required to satisfy the petrochemistry of both the ocean ridge basalts and hornblendites (Lacroix 1917, p. 974; Yoder & Tilley 1962, p. 455). This model is attractive as it would easily explain the extreme r.e. uniformity of ocean ridge basalt. However objections can be raised. This possibility will be evaluated further in §11*d*.

How do such r.e. pattern estimation for the upper mantle source of ridge basalts compare with amphibolites or ultramafic rocks dredged from the ocean floor? Although such data are

still very scarce, one amphibolite from the Mid-Atlantic Ridge at 31° N (Kay *et al.* 1970, sample A 1508C) conforms well with the predicted values for the amphibolite model discussed above. The model was derived completely independently (model calculations and independent partition coefficients). Kay's amphibolite falls within the range predicted for amphibolite source rock (i.e. between curves *A* and *C* in figure 17).

To the author's knowledge, no data has yet been published on serpentinites or other ultra-mafic rocks of the sea floor. Compared with similar theoretical predictions, such data should be enlightening as to the nature of such rocks and of layers 2 and 3 of the oceanic crust.

Of further interest are St Paul and St Peter ultramafic rocks in the Equatorial Atlantic. These rocks have often been suspected to represent undifferentiated mantle (Wiseman 1966; Melson, Jarosewich, Bowen & Thompson 1967). Their r.e. patterns are quite variable depending on their mineralogy (Frey 1970). These r.e. patterns bear no resemblance to the calculations made here for residual or primary upper mantle source material. This conforms with Frey's conclusion that none of these rocks appear to be examples of undifferentiated upper mantle or simple residues left after partial melting. Models for the origin of these rocks are discussed further by Frey (1970*b*).

To summarize this section, various crude but useful attempts have been made to derive the r.e. pattern of upper-mantle source material for mid-ocean ridge basalts. These patterns show lower absolute abundances and more pronouncedly depleted light r.e. than the typical and uniform r.e. pattern of ocean ridge basalts; a point of considerable importance which conforms with continental drift and spreading models to be discussed in §11.

8. Oceanic shield volcanoes—mid-ocean ridge volcanism relations

The relation between centre-type volcanism over the crest or flanks of a mid-ocean ridge and fissure type volcanism associated with spreading of the sea floor is of great interest but remains yet much unexplored. Most volcanic islands presently perched on mid-ocean ridges appear to be located at, or near by, the juncture of mid-ocean ridge crests and transecting tectonic elements (J.-G. Schilling, in preparation). Location of oceanic islands at the branching of aseismic ridges from active mid-ocean ridges have been noted by Wilson (1963*a*). The growth of chains of volcanoes from ocean-ridge spreading centres has been discussed in some detail by Wilson (1963*b*, 1965), Vogt & Ostenso (1967) and more recently by Menard (1969). Other types of structural controls for the development of centre-type volcanism over an otherwise steadily spreading ridge can be recognized (J.-G. Schilling, in preparation).

Whether the growth of a volcano drifting over a spreading lithospheric plate is done by inter-mittently tapping magma chambers trapped within the moving plate, or beneath it in the low velocity layer, is an important problem (Menard 1969). The difference may be reflected in the chemistry of the volcanoes. Some attempts have been made to determine such effects and models have been surmised (McBirney & Gass 1967; Aumento 1967). These models need to be tested. Toward such ends, an r.e. survey of shield volcanoes and seamounts has been undertaken but is yet incomplete. Only preliminary, but suggestive, results can be presented.

To gain insights into the two modes of volcanicity, the trace element comparison should again be limited to tholeiitic basalts if at all possible. Tholeiitic shield volcanoes which are presently, or were once, located over the crest of mid-ocean ridges are not common. Most oceanic volcanic islands are characterized by lavas of the alkali series, at least subaerially. Such observations

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probably have genetic implications (Engel *et al*. 1965; Vogt *et al*. 1969). Dredge hauls from flanks of volcanic islands and seamounts are too scarce to determine critically whether a gradation exists between seafloor tholeiitic basalts over the ridge and alkalic basalts towards the top of such volcanic edifices.
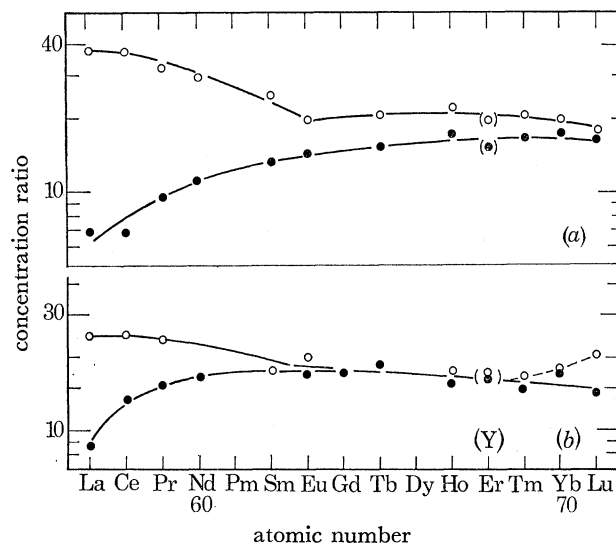

FIGURE 18. Rare-earth pattern relation between (o) tholeiitic basalts of shield volcanoes and (●) spatially related mid-ocean ridge tholeiites. Note the light r.e. enrichment for shield volcanoes in contrast to the heavy rare earths which are similar for both the shield volcano and the mid-ocean ridge. (*a*) Jebel Teir tholeiite and average of five Red Sea axial trough basalts; (*b*) Culpepper tholeiite and average of six East Pacific rise tholeiites.

The r.e. relation between tholeiitic shield volcanoes and spatially related mid-ocean ridge basalts is shown in figure 18. Only two areas have yet been investigated, namely: (1) Jebel Teir Island—a shield volcano located at the southern end of the Red Sea trough (I. Gass 1968, personal communication); (2) Culpepper Island (Galapagos Archipelago) east of the East Pacific Rise. In both instances, one observes a noticeable enrichment of the light r.e. content for the subaerial shield volcano relative to spatially related mid-ocean ridge basalts, while the heavy r.e. contents stay more constant. The two distinct modes of volcanicity are further corroborated on the $[Yb]_{e.f.}$ against $[La/Sm]_{e.f.}$ diagram in figure 16. Despite being spatially widely separated, both shield volcanoes plot in the same field and are distinct from the mid-ocean ridge basalts. Do these two tholeiitic basalt types reflect two modes of volcanicity completely unrelated or are the two linked by some kind of a process? For instance, such volcanoes could result from an unusual melt accumulation due to additional structural or tectonic controls—presumably superimposed on the rather steady-state volcanic process associated with the crest of mid-ocean ridges and spreading of the sea floor. Imagine melts in a magma reservoir at depth intermittently feeding the overlying volcanic edifice and slowly cooling during the dormant periods. This mechanism would produce some fractional crystallization which might explain the increase of the light r.e. Such a model can be tested with the aid of partition data and mineral extraction control lines theoretically derived and shown in figure 15. By comparing figures 15 and 16 it becomes clear that extraction of olivine, orthopyroxene, and feldspar in any proportions from typical mid-ocean ridge basalts cannot produce the desirable $[La/Sm]_{e.f.}$ ratio. The lack of europium anomaly further limits the amount of feldspar which can be extracted in this instance

($< 10 \%$). Further comparison of figures 15 and 16 indicates clearly that only extraction of clinopyroxene could increase sufficiently the $[La/Sm]_{e.f.}$ ratio without changing appreciably the $[Yb]_{e.f.}$, therefore linking the two basalt types by fractional crystallization. Clinopyroxene composition is sufficiently close to that of a basalt so that the original composition of the melt is not appreciably changed for a small extent of fractional crystallization of this mineral. However, based on figure 15, more than 70 % of the clinopyroxene needs to be extracted with olivine and/or orthopyroxene. The exact proportions depend on the $[La/Sm]_{e.f.}$ ratio assumed for the original melt (average or most probable value in figure 16); 70 % clinopyroxene crystallization seems excessive although not impossible. If this were the case, a residue of pyroxenetic or peridotitic composition would be expected to underlie such volcanoes.

Other models can be put forward which relate rate of spreading and magma feeding, volume of the volcanic edifice, previous degree of melting in the mantle before accumulation of melts in the magma chamber, extent of fractional crystallization and light r.e. enrichment, and which satisfy the final tholeiitic composition of the residual melt. They cannot be tested with the presently available data.

To summarize, the limited r.e. data show that a clear distinction can be made between typical mid-ocean tholeiitic basalts erupting along oceanic rifts and tholeiitic basalts of shield volcanoes, despite the fact that they are spatially closely related. The difference must reflect the two modes of volcanicity and their dynamics. A third similar situation appears to emerge between the Reykjanes Ridge and Iceland (J.-G. Schilling, in preparation).

9. Secular variations

It is important to determine any spatial variations of the absolute and relative r.e. abundances of the volcanic layer across ocean floors. Such variations, in time and space, should provide information on possible secular changes of the upper mantle source of these lavas once erupted at the trailing edge of oceanic crustal plates. As a result, inferences on spreading mechanism can be made and a model formulated by selectively eliminating or answering questions of the following nature: Are ocean ridge basalts derived from an upper mantle source uniform in time and space? Or, to what extent are ocean ridge basalts derived from an overturning upper mantle replenishing the shallow mid-ocean ridge zone with material brought from greater depths (e.g. the low velocity layer)? Were such overturns operative, what is their cycle period and to what depth to they operate?

While awaiting the return of basalts cored across the Atlantic and Pacific Oceans by J.O.I.D.E.S., spot tests across oceans can be made on samples collected along fracture zones or escarpments exposing the volcanic layer 2 of various ages. Again the r.e. comparison during this preliminary survey has been limited to tholeiitic basalts only.

The extent of r.e. fractionation produced during transformation of a basalt by posteruptional metamorphic or weathering processes needs to be evaluated before any true secular variation can be found. Such variation can be evaluated by studying rocks exposed to various degrees of such posteruptional processes.

Different eocene pillow lavas from Oregon, altered to various extents, show nearly identical relative r.e. patterns and only small overall absolute concentration variations (J.-G. Schilling unpublished analyses). Also, greenstones (apparently metabasalts) collected across the M.A.R. show only small r.e. variations relative to unmetamorphased fresh ocean ridge basalts (Frey

et al. 1969; Graham & Nicholls 1969). Furthermore, if the Juan de Fuca amphibolite (Kay *et al.* 1970) is considered to be a metamorphosed basalt (Yoder & Tilley 1962), then again no change of the relative r.e. abundances can be detected with respect to fresh mid-ocean ridge basalts; only a small decrease of the absolute r.e. values is noted. Hart and others (this volume, p. 573; Philpotts, Schnetzler & Hart 1969) have investigated in detail the effect of weathering on trace element distribution of submarine basalts. Trace element ratios for the alkali metals are the most affected, followed by the bivalent alkaline earths. The r.e. are the least affected of the trace elements studied. The relative r.e. fractionation pattern appears to change only for extreme cases of alteration of these basalts.
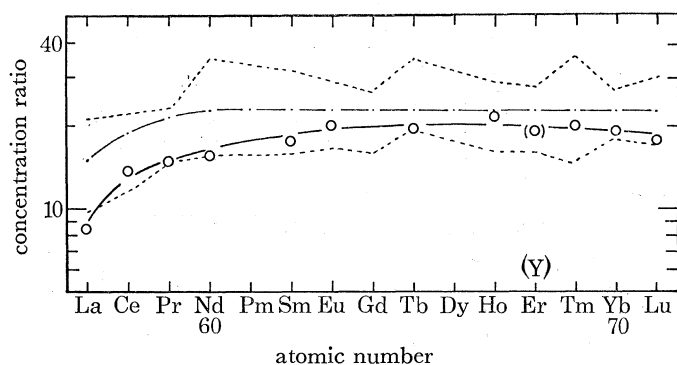

FIGURE 19. Rare-earth fractionation pattern of a tholeiite from the Barracuda Scarp (O) located approximately 1500 km west of the M.A.R. The dotted–dashed line represents an average of 6 M.A.R. tholeiites (Frey *et al.* 1968) for comparison. The upper and lower dotted lines indicate the maximum deviation from the mean for the M.A.R., excluding the Reykjanes Ridges which show more pronounced light r.e. depletions.

Consequently, weathering or metamorphism apparently will not seriously affect the relative r.e. pattern of submarine basalts—an intrinsic property of primary magmas and related upper-mantle sources. However, absolute changes of the overall pattern can be expected and do occur to a degree depending on addition or removal of major components of the basalts during such posteruptional processes. The r.e. inertness toward metamorphism and weathering probably reflects the marked and homologuous affinity of these elements for oxygen, their refractory nature, high valence charge, and relatively large ionic sizes.

Table 1 gives the age of the basalt samples analysed. These ages were determined from the relative position of the samples with respect to the new oceanic geological time scale determined by Hertzler on the basis of magnetic lineaments and reversals (J. R. Hertzler & W. C. Pittman III 1969, personal communication). Plots of $[La/Sm]_{e.f.}$, $[Tb/Yb]_{e.f.}$, $Yb_{e.f.}$ as a function of magnetic ages or distance perpendicular to ridges show no systematic correlations. Samples most distant from ridges, consequently the oldest, show r.e. patterns in no way different from the more recent basalts over the crests of ridges. For instance, as shown in figure 19, the r.e. pattern of a tholeiitic basalt form the Barracuda escarpment (R. L. Chase 1968, personal communication), some 1500 km west of the M.A.R. and of approximately upper Cretaceous age, falls within the range found in fresh basalts on the crest of the M.A.R. (Frey *et al.* 1968). In the Pacific–Antarctic basin, abyssal basalt E–15–5–1, located 850 km southeast of the Pacific–Antarctic Ridge and of Palaeocene to Cretaceous age, has also an r.e. pattern identical to tholeiitic basalt from the Pacific–Antarctic Ridge (E–15–15 in figures 2 and 3). Furthermore, the Experimental Moho basalt cored at the Guadelupe Site and dated by K/Ar as Miocene in age (Krueger 1964),

shows similar r.e. abundances relative to other East Pacific Rise basalts (Frey *et al.* 1968; Masuda 1968*a*).

If the survey of tholeiites is extended across oceans and into island arcs, noticeable r.e. differences become apparent. Although similar relative r.e. patterns with respect to mid-ocean ridge basalts are often noticed in island arc tholeiites, they have definitely lower absolute abundances (e.g. see: for Japan, Masuda (1966, 1968*b*); for the Mariana Arc, Taylor, Capp, Graham & Blake (1969); and for the Scotia Arc, unpublished analyses by this laboratory). Recent tholeiitic basalts from the convex side of island arcs are, however, not continuous in time with basalts of the sea floor in this region. These latter were formed at the crest of mid-ocean ridges and then carried across ocean basins. The origin of island arc tholeiites is related in time and space to destruction of the oceanic crust—a different volcanic mechanism than the one operating at the trailing edge of the crustal plates.

To summarize, these few results suggest that ocean-ridge volcanism has been remarkably uniform from Cretaceous to Recent time. No secular variations are apparent.

Furthermore, judging from r.e. data on plateau basalts and doleritic swarms of dykes (§5), an abrupt discontinuity in the type of tholeiitic volcanism appear to occur during the earliest developmental phase of a new ocean basin expanding between two continents. Narrow oceans such as the Red Sea already show unambiguously ocean-ridge type of volcanism on the basis of r.e. data (Schilling 1969), despite that the mid-ocean ridge is not yet fully developed. However, the rift must already extend to the low velocity layer, judging from the thermal régime which is typical of oceanic ridges (Sclater 1966). Consequently, the change of tholeiitic volcanism must be rather abrupt. The difference is attributed to fundamentally different thermal regimes in the upper mantle during these two distinct stages of volcanism and spreading. The presence or absence over the low velocity layer of a floating continental crustal block may play the major role in controlling the two distinct phases of tholeiitic volcanism—*continental* against *oceanic*. Contrary to oceanic plates, continents contain an important fraction of the heat producing elements of the earth. This difference can significantly influence the chemistry of rocks derived from the low velocity layer under oceanic or continental areas. This subject will be discussed further in §11.

10. Relations to spreading rates and oceanic crustal structures

Bott (1965) has discussed how rising mantle undergoes partial melting under a mid-oceanic ridge and produces basaltic volcanism. Cann (1968) has developed a crude relation between degree of melting with the speed and width of the ascending mantle column, the rate of crustal spreading, and the thickness of the basaltic and residual layers. Independently, this present author has arrived at a similar formulation taking, however, into account density differences between melt, residue, and primary material caused by partial melting. None of these models appear to be satisfactory nor do they explain uniquely and unambiguously all known structural features of the oceanic crust and underlying upper mantle.

Formulation of such models is hampered by some major problems. Some of these are: (1) Lack of knowledge of the relation of layer 3 to layer 2 and the make-up of layer 3. Although a general consensus exists that layer 2 is mostly made of basalt, no agreement has been reached for layer 3; serpentinite, amphibolite and basalt have been suggested respectively by Hess (1962), Poldervaart (1957), Cann (1968) and Oxburgh & Turcotte (1968). (2) Some relations

need to be assumed between horizontal spreading velocity and rates of ascent of magma, residual crystals and/or primary advecting material. Also, the rate of discharge of lava is related to (1) the rate of magma generation by partial melting during ascent of upper mantle rock (2) rate of magma segregation from refractory material as well as (3) the rates of crystallization at shallower depth (Shimazu 1961). No good theories exist describing the relation between these variables. Bott's (1965) estimate of extent of partial melting is based purely on thermodynamical arguments. It represents the maximum permissible melting allowed from excess temperature over the melting curve during adiabatic decompression. Other considerations of hydro-dynamical nature need to be taken into account, but are beyond the scope of this paper.

However, as the degree of melting is related by equations (1) to (5), to the concentration of a trace element in the melt, primary source material, or residue, one might expect some indirect relations between the variables mentioned above and the r.e. abundances. For instance, assuming magma generation needs to be increased due to a greater degree of melting caused by increasing spreading velocities, one would expect the r.e. concentrations to decrease according to equation (3). On the contrary, a larger volume of melt could also be obtained by keeping the extent of partial melting constant, but by melting over a wider or thicker region under the ridge followed by rapid upward transfer of the melts by buoyancy. In this latter case, the r.e. concentrations should stay constant, as the degree of melting is kept constant regardless of rates of spreading. Whether the entire magma produced segregates completely and reaches the surface is another question. Models of such nature can be developed but remain speculative unless tested.

Spreading rates for each ridge investigated have been plotted as a function of r.e. abundances and parameters described earlier. No systematic or noticeable correlation have emerged between the r.e. abundance patterns of mid-ocean ridge basalts and spreading rates.

The small r.e. abundance variations of mid-ocean ridge basalts or older basalts of the second layer seem to be independent of: (1) presence or absence of layer 3 at the crest (Le Pichon, Houtz, Drake & Nafe 1965; Talwani, Le Pichon & Ewing 1965; Vogt *et al.* 1969), of a median valley and of anomalous mantle of $V_P = 7.2$ km s^{-1} (Anderson & Sammis 1970); (2) variation in thickness of layer 2 and/or 3; (3) heat flow anomaly variations and spreading rates.

The r.e. abundance averages for each ridge are shown in figure 20. Again these variations cannot be correlated with the above-mentioned structural or geophysical variables. The small r.e. variations from one ridge to another seem to be provincial and intrinsic of the upper-mantle source in these regions. The differences probably reflect the past chemical history of these mantle sources.

Finally, if the r.e. variations of mid-ocean ridge basalts (factor of 3 and 2 for the light and heavy r.e., respectively) are assumed to reflect different extent of partial melting of a homo-geneous upper mantle source, a permissible range of degree of partial melting can be computed on a *relative* basis—and on an *absolute* basis provided a minimum or maximum value is assumed. A minimum melting of 10 % has been assumed. It falls within the generally accepted extent of partial melting necessary to generate a melt of basalt composition from an ultramafic source (Kushiro & Kuno 1963; Reay & Harris 1964; Green & Ringwood 1967). With this assumption, with the r.e. partition factors of common upper mantle rock-forming minerals shown in figure 12, and with the aid of equation (3), the permissible range of partial melting is found to vary between 10 and 30 % maximum. Bott (1965) showed that dry upper mantle rock had to be on the liquidus for 33 km of rise in order to produce a total of 10 % melting. Consequently 30 % partial melting would require a 100 km path. This is the depth of incipient melting and

coincides favourably with the top of the low velocity layer as a source of advecting mixture of rock and melt. This independent estimate is in good agreement with Anderson & Sammis (1970) recent convincing thermodynamic arguments indicating that the low velocity layer corresponds to a zone of incipient melting of the upper mantle. Such a zone is mechanically very unstable. It can fruitfully be considered as the upper mantle region from whence most volcanic and tectonic processes observable on the surface of the Earth probably originate.
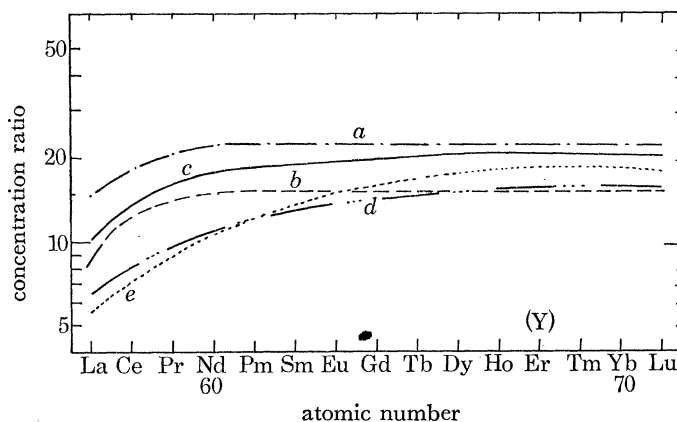

FIGURE 20. Average r.e. pattern of tholeiitic basalts for (a) the M.A.R. (Frey et al. 1968), (b) East-Pacific Rise, (c) Carlsberg Ridge, (d) Red Sea Trough, and (e) the Reykjanes Ridge (unpublished).

Regarding layer 3, whether it is the partial melting product of a dry or wet upper-mantle, or it is produced by metamorphism, cannot be tested by r.e. scrutiny inasmuch as the partition trends of amphibole and clinopyroxene are nearly identical. Consequently, very similar r.e. patterns are expected.

However, one can test whether layer 3 can reasonably represent the serpentinized dunitic residue of partial melting of upper mantle rock which generated the basaltic layer 2. Taking typical average values of 1.71 and 4.86 km for the thickness of layers 2 and 3, respectively (Vogt et al. 1969) the degree of partial melting is estimated as 23 %—a value within the permissible range estimated earlier. Consequently, Hess's (1961) hypothesis for the make-up of layer 3 cannot be ruled out on r.e. basis alone (see Cann 1968 for further arguments). R.e. data on serpentinites are needed.

11. DISCUSSION

(a) Model requirements

Formulation of any satisfactory volcanic models for the evolution of the oceanic lithosphere and the related continental drifts must take into account the major r.e. findings discussed here. These findings are:

(1) The *remarkable uniformity* of r.e. patterns of submarine tholeiitic basalts erupted along mid-ocean ridges from Cretaceous until Recent time, and the lack of secular variation across oceans.

(2) The *characteristics* of such patterns, i.e. the light r.e. depletion and slight enrichment of the heavy r.e. relative to estimated average r.e. abundances for continental blocks.

(3) The *abrupt* change from continental tholeiitic plateau basalts (light r.e. enriched) to purely oceanic ridge tholeiitic basalts (light r.e. depleted).

(4) The *established time sequence* of tholeiitic volcanism from r.e. enriched (plateau type) to light r.e. depleted (mid-ocean ridge type) respectively representing the early phase of continental break-up followed by more typical sea-floor spreading. Such change appears to be a true sequence of events independent of geological time. It has happened in Jurassic time for the development of the South Atlantic Ocean, in Palaeocene to Eocene time for the development of the Carlsberg Ridge and Arabian Basin, and possibly in Miocene time for the more complex development of the Columbia Plateau–East Pacific Rise–Basin and Range system.

(5) The *lack of correlation* between spreading rates and degree of melting.

(6) The contrast of r.e. patterns between centre-type volcanism (shield volcanoes) and spatially related mid-ocean ridge crestal volcanism (rift type).

No matter what explanation is given to account for the uniformity of r.e. in basalts, the geophysical model which explains best all data requires that the low velocity layer (low viscosity, low rigidity) is the region where most tectonic and volcanic processes observed on the surface of earth originate (Anderson & Sammis 1970).

Anderson & Sammis (1970) have demonstrated convincingly that incipient melting is the cause of the low velocity channel. Such a partially molten layer in the upper mantle is mechanically unstable and is important in the release of tectonic energy. 'The top of the low-velocity zone can be considered a self-lubricated surface upon which the top of the mantle and the crust can slide with very little friction' (Anderson & Sammis 1970). Lateral displacement of the lithosphere away from oceanic rises and sinking of the lithosphere at trenches are counterbalanced by flow of partially molten material in the low-velocity layer towards the rise where the material eventually emerges as new crust (Isacks, Oliver & Sykes 1968).

The exact cause of movement of lithospheric plates is not yet entirely resolved as *cause and effect* are always difficult to separate. Other than convection, several mechanisms have been considered (e.g. Dutoit 1937; Pollack 1969; Lliboutry 1969; Hales 1969; Matthews 1969; Dehlinger 1970). These are all compatible with the sliding of lithospheric plates over the low velocity layer and appear to produce forces in directions satisfying plate tectonic requirements. These mechanisms are not necessarily mutually exclusive, and may all or in part have been operating simultaneously, at one time or another.

(b) *Magma generation*

Whatever may be the cause of movement of the lithospheric plates, a low-pressure region is produced at the loci of divergence, allowing for flow and intrusion of mantle material from the low velocity layer and for formation of new crust. The important questions are: what flows and how? Does the mixture of crystals and melt move as a whole, or does some preferential movement occur between the melt and the refractory crystals, the melt moving faster due to buoyancy? Additional melting must occur during ascent of the slush. Furthermore, some segregation of the melt from the refractory material must occur during ascent, as the material erupting on the sea floor is mostly molten lava and not a slush of lava and refractory material. The depth of segregation will have an important bearing on trace element equilibrium partition relations (§7) and on the composition of the melt (Yoder & Tilley 1962; O'Hara 1968*a*, *b*; Green & Ringwood 1967). This depth may well be reflected in the oceanic crustal structure. Perhaps it may explain the *oceanic* Mohorovičič discontinuity as also implied by Cann (1970*b*). To a certain extent depth of segregation can be determined from evidence based on experimental petrology. Abrupt changes of basalt composition may occur depending on the mineral stability

field in which the segregation occurs. However, within the stability-depth range of a particular mineral assemblage, major element compositions are much less sensitive to increasing degrees of partial melting, contrary to trace element concentrations which are sensitive indicators of the extent of melting. At a certain depth under partial melting conditions, the composition of the melt at the minimum liquidus (eutectic) is nearly fixed and independent of the degree of melting until one of the solid phase originally present is used up.

However, the r.e. concentration of the melt is a function of the degree of melting, as described by equation (3), and will change with increasing melting during ascent, although the major element composition may not. For example, congruent melting of a monomineralic rock could be extended to complete melting without changing the major element composition, while the r.e. would change widely to a degree dependent on the values of operative partition coefficients. Thus, the greater the number of original mineral phases before melting, the more limited will be the melting range for which the major element composition of the magma generated remains constant and independent of the degree of melting. As the mantle mineralogy is likely to be relatively simple with only a limited number of phases being present (Ringwood 1966) it may explain in part the rather uniform composition of basalts.

The r.e. abundances, on the other hand, are sensitive indicators of the degree of melting or the extent of crystallization during ascent of lavas. In addition, r.e. patterns also reflect the past chemical history of the upper mantle source of magmas. How can the r.e. requirements presented above be more specifically satisfied and incorporated within the realm of a model for spreading of the sea-floor and continental drift?

(c) Preferred mantle model

If partial melting in the low velocity layer and during ascent is evoked, the apparent uniformity of r.e. patterns of mid-ocean ridge basalts can be satisfied by tolerating 10 to 30 % of partial melting of an *ultramafic mantle*. A mantle of *lherzolite* composition (Ca-poor orthopyroxene, Ca-rich clinopyroxene, olivine, and possibly spinel) would satisfy the r.e. requirements. Melting of a *feldspathic peridotite*, or segregation of solid and melt within this mineralogical facies, appear to be excluded because of the lack of europium-anomaly in most mid-ocean ridge basalts.

Presence of *water* in the mantle is necessary for the low velocity layer to be a region of incipient melting (Anderson & Sammis 1970). Water does not affect the arguments based on r.e., provided it is present as a phase and/or in solution with the melt, i.e. at depth where hydrous minerals are unstable. Alternatively, if partial melting occurs in the amphibolite facies, with hornblende taking part in the partial melting equilibrium, the *ultramafic-partial melting* model also is not affected significantly, inasmuch as hornblende and clinopyroxene partition coefficients are similar. Lambert & Wyllie (1968) have given evidence that the low velocity layer is caused by the presence of interstitial hydrous magma resulting from the instability of hornblende and possibly phlogopite. Partial melting of a *hornblende peridotite* is not inconsistent with r.e. evidence. However, on the basis of the r.e. distributions, it would be practically indistinguishable from partial melting of dry lherzolite. The plausibility of partial melting of a *garnet peridotite* could not be evaluated for lack of reliable and applicable r.e. partition coefficient data for garnet.

(d) Alternative mantle models

As only a range of melting can be ascertained and not absolute values, *nearly complete* melting of an *amphibolite* would also be consistent with the r.e. pattern and major element composition

of mid-ocean ridge basalt, provided no plagioclase feldspar (or a very limited amount) enters into the partial melting equilibrium as required by the lack of europium-anomaly. Such a model would easily explain the r.e. uniformity, but not the structural layering of the oceanic crust and upper-mantle as suggested by seismic refraction and gravity surveys (Talwani *et al.* 1965; Le Pichon *et al.* 1965). This is because the amount of residual material would be quite insufficient to form the denser material underlying layer 2, or 2 and 3 (if the velocity change between layers 2 and 3 is attributed to posteruptive metamorphic changes (Poldervaart 1957; Cann 1968)). With an amphibolite mantle, the diversity of the oceanic crustal and upper-mantle structures in the Atlantic and Pacific would also be difficult to explain on the basis of compositional changes. The discontinuities would have to be attributed to solid phase transitions only—a more difficult task.

Nearly complete melting of an *eclogite* would encounter difficulties similar to those for amphibolite melting. Although Philpotts *et al.* (1970) have recently indicated a marked preference for the eclogite model, objections to the validity of their approach can be raised (J.-G. Schilling, in preparation). Contrary to what these authors appear to believe, a complete evaluation of the plausibility of this model, on r.e. basis alone, must await reliable determination of: (1) partition coefficients applicable to partial melting in the eclogite facies, and (2) r.e. abundances in minerals constituting the primary upper-mantle rocks of this facies prior to partial melting.

The mid-ocean ridge partial melting model of a *peridotite* is preferred, with segregation of the melt in the depth range where *lherzolite* is stable. This model is consistent with the r.e. of mid-ocean ridge tholeiitic basalts and with experimental petrology. It also allows more freedom for the interpretation of the oceanic crustal and upper-mantle structure by both compositional and solid phase transitions of one sort or another, including hydration–dehydration.

Kay *et al.* (1970) have called for a mechanism in which water would play a major role in buffering partial melting around 30 % during ascent of advecting material. This is not necessary, as variation of degree of melting between 10 to 30 % (on a relative scale assuming 10% being the minimum) would be satisfactory and explain most observed r.e. abundance variations of mid-ocean ridge *tholeiitic* basalts. In fact, the mechanism proposed by Kay appear to cause certain problems which will be discussed elsewhere (J.-G. Schilling & J. L. Robinson, in preparation).

Rather than considering partial melting during ascent, one could as well assume a relatively large degree of melting at the depth of the low velocity layer, followed by fractional crystallization during ascent. Then the maximum permissible extent of crystallization during ascent is estimated to be 50 % at most from the r.e. variations. This compares well with other estimates based on other arguments (O'Hara 1968 *a*, *b*). The melt would be a picrite basalt. It should be noted, however, that the two processes cannot practically be distinguished on the basis of the r.e. only. Other arguments must be used to decide the relative extent of the two processes. Some crystallization caused by rapid cooling must certainly occur at shallow depths in the oceanic crust, where the magma is forced up along small narrow fissures. Phenocrysts present in submarine lavas testify to that.

(e) *Generation of oceanic crust*

There are no simple explanations for the lack of correlation between rates of spreading, type of crustal and upper-mantle structures beneath ridges, and the r.e. abundances. Menard (1967) has shown that if only layer 2 represents the low melting basaltic discharge of advecting mantle rock, its rate of generation per unit length along the ridge is approximately constant, despite

marked variations of spreading rates (2 to 12 cm a^{-1}). This is no longer true if layers 2 and 3 together are taken to represent the low melting portion of the advecting mantle. In this case the wave velocity difference between layers 2 and 3 is assumed to be produced by posteruptional metamorphic change while the crust is carried aside. The combined thickness of layers 2 and 3 together, when both are present (if layer 3 is ever really absent), is approximately constant and independent of spreading rates. Consequently, the rate of magma discharge is no longer constant but directly related to spreading rates. Because rates of crustal growth vary between 2 and 12 cm a^{-1} and because the tolerable degree of melting based on r.e. variations varies only between 0.1 and 0.3, partial melting apparently must occur over a greater depth range for fast-growing ridges than slower ones. Rapid migration of the melts should follow to feed the fast growing layers 2 and 3, as for the Equatorial East Pacific Rise. Vogt *et al.* (1969) have attempted to explain in some detail the developments of crustal and upper-mantle structures beneath various ridges. However, no simple unified model satisfying the r.e. abundance uniformity, permissible degree of melting and the various oceanic structures could be put forward.

(f) Contrast of oceanic and continental volcanism

Finally, worthy of discussion is the contrast between *ocean ridge tholeiitic volcanism* and *continental plateau tholeiitic volcanism*, the latter occurring at the onset of continental break-up. The major element chemistry of the two types is not markedly different. Both are tholeiitic. Plateau basalts are usually quartz normative (Washington 1922), but so are some ocean ridge basalts. The r.e. patterns are however well contrasted between oceanic and continental regions. The difference is interpreted as reflecting intrinsic differences between continental and oceanic volcanism. The difference does not necessarily reflect different mantle sources, as the source of both types is assumed to be derived from the low velocity layer. In fact, for the South Atlantic, what is now assumed to be the mantle source beneath the Mid-Atlantic Ridge must in Jurassic time have been near the source of the Parana and Karroo plateau volcanism; since then the continents have drifted apart, and new mantle material has replenished this region by counter-flow in the low-velocity layer. The only difference is that in Jurassic time a continental blanket was overlying the low velocity layer in this area, and as a result, the thermal régime must have differed from that occurring today.

In addition since it is mechanically unstable, the low velocity layer can be considered as a heat engine within which partial melting occurs. The engine is overlaid by different heat sinks, i.e. oceanic or continental lithospheres, and underlaid by heat sources (except for example where the cold descending lithosphere penetrates the low velocity layer at the island arcs). As Bott (1964) has clearly pointed out, continental regions provide a less efficient sink for heat rising by convection in the mantle owing to their excess radioactive heat production in the continental crust compared to oceanic crust. Although the model of lithospheric plates floating on a low viscosity layer as adopted here is different from Bott's convection model, the arguments for intrinsically different thermal régimes between a mantle overlaid by a continental or oceanic lithosphere remain qualitatively the same. 'The rate at which heat can be lost by conduction is controlled by the temperature gradient and thermal conductivity immediately above the upper surface' of the low velocity layer (Bott 1964). If the heat production by naturally radioactive elements per unit vertical column is likely to be greater for a continental lithosphere than for an oceanic one, the heat flow *beneath* the continental crust is then likely to be substantially lower than the heat flow at the continental surface. Thus, once a true oceanic thermal régime

has been set up underneath the crest of a mid-ocean ridge, i.e. the oceanic rift is tapping the low velocity layer, heat is carried upwards from the low velocity layer mainly by *mass transport*. This is a much more efficient way than by *conduction* which appears to prevail under continental lithospheric blocks. Consequently, the difference between *oceanic* and *continental* magmatic processes become mainly a matter of rates and modes of transport of magmatic products from the low velocity layer; the difference being induced by the type of thermal régime prevailing beneath and within such blocks and by the tectonics.

This is also well reflected in the type of magmatism and in the major and trace element chemistry of volcanic products of the two contrasted oceanic and continental regions. Rates of heat loss and mode of transport control the extent to which magmatic processes can be carried before intrusion and extrusion at upper levels of the earth. As heat may be lost from the low velocity layer at a slower rate under continental than oceanic areas, magmatic processes can evolve further under continental regions. In some instances, magma may even rise by a process of zone melting (Shimazu 1961). Such slow processes allow for large electro-positive trace elements, as are the light r.e. K, Rb, Cs, Ba, etc., to be enriched and relatively fractionated much more effectively (Harris 1957; Schilling & Winchester 1967). Small amounts of melts (due to small degrees of melting, or as residual liquids) can be maintained (Pfann 1955, 1966; Shimazu 1961). Continuous re-equilibration with surrounding rocks during ascent of such magmas allows both for a large enrichment of volatiles and trace elements and for fractionation. If such evolutionary magmatic processes beneath a continental lithosphere are not arrested by the breaking up of a continent (Bott 1964), they will evolve further and further to finally give rise to very explosive magmatic activity. Diatrems may pierce through the continental lithosphere because of the fluxing effect produced by the pressure increase of volatiles, mainly water and carbon dioxide. Potassium-rich alkali lavas, nephelinites, kimberlites as well as carbonatites are all intruded through the continental crust as explosive pipes or diatrems. These magmas are also highly enriched in the larger electropositive ions (Harris 1967), and the r.e. are fractionated to extremes (Volfovsky-Spirn 1965; Haskin *et al.* 1966; Schilling 1966). The association of such igneous activity near continental rifts is readily explained if such tectonic features are assumed to represent the loci of early break-up of continental blocks. Due to later global tectonic readjustments of lithospheric plates, such breaks may or may not have been allowed to form an ocean and tap the low velocity layer. These sutures remain as major lines of weakness in the continental lithosphere and should serve as major channels for later explosive magmatic emanations. High-pressure mineral phases, hydrated minerals and brecciation, all reflect the complexity of magmatic processes operating in and beneath a continental lithosphere. For example the suggestion of DeAssuncao, Machado & Serralheiro (1968) that carbonatites in the Cape Verde Islands may reflect the presence of an older continental rift before drifting is corroborated by this model.

In contrast, beneath mid-ocean ridges at the rift, fresh magmatic material is rapidly brought from the low velocity layer up to the surface by advection and buoyancy forces, and is further partly melted during the ascent. Under such a volcanic mode, melts have less time for re-equilibration with country rocks during ascent and consequently are not as much fractionated. It is a well recognized phenomena in metallurgy and transistor technology that partition coefficients between crystals and melt approach the value of one as rates of melting and cooling are increased (Pfann 1966). As a result, no concentration and fractionation of trace element impurities occur between the solid and melt. Magmatic processes under ridge crests may tend

toward such conditions due to geologically relatively rapid advection of interstitial melts with upper mantle rock (Schilling 1968). Simple model calculations based on mass balance show that because the intrusion zone under the crestal area is narrow (Cann 1968), rates of advection several times faster than crustal spreading rates are required. The uniformity of mid-ocean ridge basalts is consequently relatively easy to explain; they are likely to reflect the composition of primary melts and to some extent the composition of the low velocity layer.

Consequently, plateau tholeiitic basalts occurring at the onset of continental break-up may reflect volcanic conditions at the early phase of spreading and advection of material from the low velocity layer. The trace element chemistry of tholeiitic plateau basalt is intermediate between typically continental volcanism (strongly light r.e. enriched and fractionated) and the mid-ocean ridge volcanism (light r.e. depleted and with little fractionation of the heavy r.e.). Potassium, which is undersaturated in mafic melts, consequently behaves more like a trace element during tholeiitic volcanism. Its abundance variation is consistent with the model. It is covariant with lanthanum to a first approximation.

(g) Cause of r.e. patterns as related to mantle evolution

The cause of the depletion of light r.e. (or other large electro-positive ions) is of considerable interest. It relates to the overall composition of the earth and its history or differentiation since early geological times. In §7, an estimate of the r.e. composition of the primary source material was ventured. A lower limit is shown in figure 17 (curve F). A more plausible pattern should be intermediate between this lowest limit and the mid-ocean ridge r.e. patterns (curve A in figure 17). The pattern should have a progressive increase from La_{57}, with a concentration around that of chondrites, to Lu_{71} with a concentration probably between 4 to 10 times that of chondrites. In accordance with the model adopted, this pattern should represent the upper-mantle r.e. composition of the low velocity layer region before reaching incipient melting. General agreement apparently exists that such depletion of light r.e. and other large electro-positive trace ions reflects an early mantle differentiation from a primitive Earth with r.e. patterns similar to those in chondrites; but the average concentration for the whole Earth being some multiple of chondritic meteorite concentrations (Masuda & Matsui 1966; Schilling & Winchester 1967; Gast 1968). However, this constant multiplier is unknown for the r.e. and other trace elements with similar geochemical behaviour. Schilling & Winchester (1967) have shown that such an estimate depends significantly on the mechanism of differentiation chosen for such model calculations. Melting followed by crystallization theoretically gives significantly different results from a multipass zone melting model or any similar process (Schilling & Winchester 1967; Lubimova 1967). The shape of the r.e. pattern estimated for the upper mantle source of mid-ocean ridge basalts appears to be more similar to a family of curves obtained for multipass zone melting, the mantle being considered to have differentiated before the Cretaceous. This age corresponds to the oldest lava investigated in this study. The apparent lack of secular variation and uniformity of the r.e. patterns of the tholeiitic basalts across oceans, from Cretaceous to Present, appears to preclude major differentiation of the source upper mantle during this time. One can make a good case for the average contents of r.e. and similar trace elements for the overall Earth being enriched relative to chondritic meteorites by a factor lying between one and ten. A closer estimate would be open to considerable uncertainties and conjecture.

12. Conclusions

The r.e. data in *oceanic tholeiitic basalts* suggest noticeable differences between rift type eruptions and the more localized centre-type of volcanism occurring along mid-ocean ridges. Furthermore, the survey reveals fundamental differences between *oceanic* and *continental* volcanism. Both types of magmatism appears to originate in the low velocity layer, but their modes and rates of upward transport, and thereby the chemistry of these magmas, are strongly influenced by prevailing thermal régimes. Whether or not major rifts tap the low velocity layer is critical. It is suggested that the presence or absence of a continental crust, which contains an important fraction of the heat producing radioactive elements of the Earth (Schilling & Winchester 1967), is the important controlling factor for the major trace element differences between continental and oceanic magmatism. The general chemistry of magmas of continental and oceanic platforms is consistent with the model presented; only the details remain to be worked out!

The theory then requires tectonic movements of continental and oceanic blocks of lithosphere floating over the partially molten low viscosity layer with re-adjusting counter flows in this latter. Distinct thermal régimes are assumed to prevail within the continental and oceanic lithospheres. Acceptance of this theory demands an important change of present geochemical and petrological concepts of magma formation and differentiation. A fruitful approach is to consider the low velocity layer as a heat engine in which many magmatic processes originate. Magmas are then transferred to upper levels in a manner and to an extent which depends on the tectonic movements and prevailing thermal régimes of the overlying lithospheric plates. Furthermore, in addition to controlling the thermal régime prevailing beneath lithospheric blocks, the amount and distribution of heat producing radioactive elements in lithospheric blocks may even itself control the movements of such blocks, at least in part (Howard *et al.* 1970).

Time sequence, space, rates, kinetics, and hydrodynamics must be taken into consideration, as they may have influenced the chemical composition of the final product intruded and extruded at the surface of the Earth—the only material yet available to us for direct scrutiny of the depths of the Earth.

Detailed studies of the low velocity layer from geophysical, geochemical, rheological, and geological viewpoints are urged. The Du Toit (1937) and Daly (1933) concepts of such a layer, and its implications for continental drift and other aspects of surficial tectonism and volcanism may not have been so different from present ones, only the nomenclature appears to have changed.

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