RARE EARTH FRACTIONATION

IN HAWAIIAN VOLCANIC ROCKS

by

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SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF
PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF
TECHNOLOGY

August, 1966

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ABSTRACT

The procedure for determination of the rare earth elements and yttrium utilizing tracer-monitored group separation, neutron activation and carrier-free partition chromatography developed by Volfovsky et al. (1963) has been revised and improved.

A fully automatic device, electronically controlled and all transistorized, was designed and built for the chromatographic step. This allows five simultaneous elutions and considerably accelerates the procedure.

Using this improved procedure, rare earth and yttrium abundances were measured in twenty Hawaiian lavas of known chemical and mineralogical composition, one peridotite inclusion from Salt Lake Crater, Oahu, and one olivine-rich nodule and its host 1801 basalt flow from Hualalai, Hawaii, and a diabase from Oahu

When comparing the rare earths, element by element, in the twenty lavas, to a low potassium olivine tholeiite, four distinct groupings were observed: 1. Tholeiite basalts, including the olivine tholeiite and a diabase; 2. Alkali series, including one ankaramite, alkali olivine basalts, basanite-basanitoids, hawaiites and mugearite; 3. Trachyte, a variation of the alkali series; 4. Nepheline-melilite basalts. Variation diagrams of individual rare earths against major element oxides confirm these groupings. These groupings also coincide remarkably well with other recognized petrochemical classifications.

The origin and genetic relationships of these different groups are discussed in the light of their rare earth patterns, mineral patterns from other localities, experimental petrology, theoretical and geochemical reasoning. Possible processes operative in the formation of these lavas, such as fractional crystallization,

partial melting, fractional melting, limestone syntexis and fractional resorption are explored. The origin of the ultramafic inclusions is also briefly discussed.

A theoretical analysis of the smooth rare earth fraction patterns and their significance was undertaken prior to the analytical part of this work. The partition ratio of concentration, solid/liquid, for rare earths between crystallized silicate and its melt may increase linearly with Z from La to Lu, as assumed by Masuda and Matsui, if rare earths are incorporated into lattice sites smaller than Lu. In the absence of direct experimental measurements but using this assumption, and well established co-precipitation laws, rare earth abundances relative to chondritic are predicted for solids and liquids in the following processes: Fractional crystallization, partial melting, fractional melting, zone melting, and mixing. On this theoretical basis and analytical results Hawaiian tholeiite is found to resemble the last solid to have crystallized in the mantle (i.e. the low-melting portion of the upper mantle) from an initially chondritic earth, leaving the crust as the residual liquid. Hawaiian nepheline-melilite basalt resembles the residual liquid or a partial melt of the solid which is indistinguishable. Some high temperature peridotites, which are depleted in the light rare earths, resemble a deep seated solid after repeated zone refining, and Mid-Atlantic Ridge basalts resemble a similar solid at shallower depth. Although the earth's crust and mantle must have a complex history, and the details of rare earth partition are certainly dependent on mineralogy, the correlation between observed rare earth abundance patterns and those predicted according to simple models is striking.

As an additional study, the rare earth contents (exclusive of Er) of the standard granite G-1 and standard diabase W-1 have been determined in duplicate and triplicate analysis respectively. The results are for the most part in rather good agreement with data of Haskin and Gehl (1963) and Towell et al. (1965). Some discrepancies are discussed.

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PART ONE

RARE EARTH FRACTIONATION IN

HAWAIIAN VOLCANIC ROCKS

J-G. Schilling

ABSTRACT

Rare earth abundances were measured by neutron activation in twenty Hawaiian lavas of known chemical and mineralogical composition, one peridotite inclusion from Salt Lake Crater, Oahu, and one olivine-rich nodule and its host of 1801 basalt flow from Hualalai, Hawaii.

When comparing the rare earths, element by element, in the twenty lavas, to a low potassium olivine tholeiite, four distinct groupings were observed: 1. Tholeiite basalts including the olivine tholeiite and a diabase; 2. Alkali series, including one ankaramite, alkali olivine basalt, basanite-basanitoids, hawaiites and a mugearite; 3. Trachyte, a variation of the alkali series; 4. Nepheline-melilite basalts. Variation diagrams of individual rare earths against major element oxides confirm these groupings. These groupings also coincide remarkably well with other recognized petrochemical classifications.

The origin and genetic relationships of these different groups are discussed in the light of their rare earth patterns, mineral patterns from other localities, experimental petrology, theoretical and geochemical reasoning. Possible processes operative in the formation of these lavas, such as fractional crystallization, partial melting, fractional melting, limestone syntexis and fractional resorption are explored. The origin of the ultramafic inclusions is also briefly discussed.

INTRODUCTION

The rare earth group of elements $_{57}La$ to $_{71}Lu$, including $_{39}Y$, has fascinated analytical chemists and geochemists for many years because of the close similarity in chemical properties within the group and the resulting challenge of chemical separation in the laboratory and great coherence of the group in nature. It has not been until quite recently, however, that analytical data on the natural occurrence of the rare earths has become precise enough to allow quantitative interpretation of geochemical abundance patterns. The high precision analyses for rare earths in silicate rocks and minerals now in the literature (Balashov, 1962; Balashov and Turanskaya, 1962; Haskin and Gehl, 1962; Balashov, 1963; Schmitt et al., 1963; Schmitt et al., 1964; Balashov, 1964; Frey and Haskin, 1964; Haskin et al., 1965; Towell et al., 1965; Wildeman and Haskin, 1965) have revealed that the group is fractionated smoothly and gradually as a function of atomic number, Z. The absolute abundances of even Z elements are greater than those of adjacent odd Z owing to the greater number of stable isotopes of the former, but any natural sample may be compared element by element with a standard rock and the relative abundances computed. When this is done, the zig-zag variation of the absolute abundances with Z disappears and invariably a strikingly smooth curve pattern is found.

In general crustal whole rocks show a marked enrich-
ment of the lighter rare earths relative to the heavy
end of the series. Common silicate rock forming minerals,
on the other hand, show much more diversified rare earths
fractionation patterns, demonstrating the greater select-
ivity for small rare earth ions (Towell et al., 1965;
Gavrilova & Tyranskaya, 1958). These differential rare
earth affinities of rock forming minerals, presumably
controlled by their crystal-chemical properties, and
the effect of paragenetic sequences, should influence
strongly the "whole rock" rare earth fractionation
patterns of derivative igneous rocks. Moreover, be-
cause of this great mineral selectivity, the rare
earth fractionation patterns in primary melts formed
by selective fusion of the upper mantle, and directly
erupted to the surface as lavas, should reflect the
mineral composition of the upper mantle in a simple
or complex manner, depending on the equilibrium condi-
tions prevailing during this process.

To our knowledge at this time, only two rare
earth studies of genetically and geographically re-
lated suites of differentiated igneous rocks have been
accomplished (Towell, et al., 1965; Balashov, 1962).
Both are from continental areas. Ambiguities arise
when interpreting the results, because of the complica-
tions introduced by various secondary processes such as
assimilation, metamorphism, hydrothermal alternations,
etc.

Powell et al. (1965) have shown that Hawaiian ba-
salts of differing mineral and chemical composition
have small but systematically different Sr^{87}/Sr^{86}
ratios. They concluded that these differences
could be explained by either a heterogenous mantle zoned
in Rb/Sr ratio, this ratio decreasing with depth, or
possibly by some differentiation mechanisms in the upper-
mantle as proposed by Yoder and Tilley (1963).

Gast, Tilton and Hedge (1964) reported systematic
differences of radiogenic strontium and lead between
Ascension and Gough Islands lavas. An inverse relation-
ship between radiogenic lead and strontium was observed.
These data imply that the postulated enrichment of
uranium with respect to lead would have taken place with-
out enrichment of rubidium with respect to strontium.
This is contrary to common geochemical knowledge of the
relative behavior of these elements during crustal mag-
matic differentiation. Gast et al. concluded that this
is more an indication of our ignorance of chemical frac-
tionation processes in subcrustal regions than an argu-
ment against the existence of chemically differentiated
regions in the mantle. One could add that this reflects
also our ignorance of the exact nature of the physico-
chemical factors influencing the relative behavior of
trace elements. It also points out the difficulty of
using single trace elements or trace element pairs as
sensitive indicators of the history of chemical differ-
entiation. It is by no means our intention to diminish

the merit of such approaches, but merely to emphasize the urgent need of using jointly several geochemical tracing techniques on the same samples,when studying the differentiation of the earth and seeking for the evolutionary mechanisms by which this differentiation took place.

When seeking for intrinsic properties of ions which influence their behaviour as trace elements, groups of closely related elements with very similar physico-chemical properties should be considered. The rare earth series seems to be one of the best groups available in the Periodic Table of elements. Invariably, the rare earths show smooth relative abundance variations in rocks and minerals with increasing atomic number, or what amounts to the same thing, with increasing reciprocal ionic radius (Templeton and Dauben, 1954), or ionic potential (Goldschmidt, 1954). The gradual lanthanide contraction of trivalent ionic radius with increasing Z underlies this systematic behavior. There are apparently only two singular elements in crustal materials and only under special conditions. Ce, which may be selectively oxidized to Ce^{4+}, is enriched in manganese nodules from the sea floor (Goldberg et al., 1963; and Volfovsky Spirn, 1965). Eu, which may be reduced to Eu^{2+}, is either enriched or depleted in minerals of granitic rocks and sometimes depleted in granites relative to chondrites (Towell et al., 1965). However, neither of these elements appear to have singular behavior in basic igneous rocks studied to date and we presume the trivalent oxidation state is

the predominant state for Ce and Eu as well as for the rest of the rare earth group.

Recent theoretical considerations of the rare earth fractionation by Masuda & Matsui (1963, 1966); Part III of this work; and Schilling & Winchester (1966) suggest that the lanthanide may possibly help to discriminate between different physico-chemical processes of differentiation. Thus, by combining a scrutiny of rare earth patterns with isotopic methods, the latter being a good indicator of sources and time of differentiation, geochemists should have a powerful approach for studying the chemical history of the earth and meteorites.

Nevertheless, before interpretation of the data and theoretical considerations are carried too far, it is obviously necessary to demonstrate that the absolute rare earth abundances and types of relative patterns closely and systematically follow major mineralogical and chemical variations. For these reasons and to try to shed some light on the problems mentioned above, a suite of closely related samples was collected for which we have maximum available information such as mineral, major element chemical, isotopic and trace element compositions as well as geophysical data. Lavas from the Hawaiian Islands were the obvious choice, for this area has been under intensive investigation from petrological, chemical and geophysical standpoints by a great number of researchers. Moreover, the thin crust underlying these

Figure 1-1. K_2O content (weight percent) of 20 Hawaiian
lavas and one diabase plotted on a logarithmic scale as
a function of SiO_2 content (weight percent). Field above
the dashed line represent the alkali series and field
below represent the tholeiitic series. The small field
delimited by the dashed curve represent the Engel's
oceanic basalt (low K_2O) field. Data from Winchell,
1947; Wentworth and Winchell, 1947; Macdonald and Katsura,
1954; Tilley, 1960; Macdonald & Powers, 1946; Muir &
Tilley, 1961; Cross, 1915; Washington, 1923; Daly, 1944.
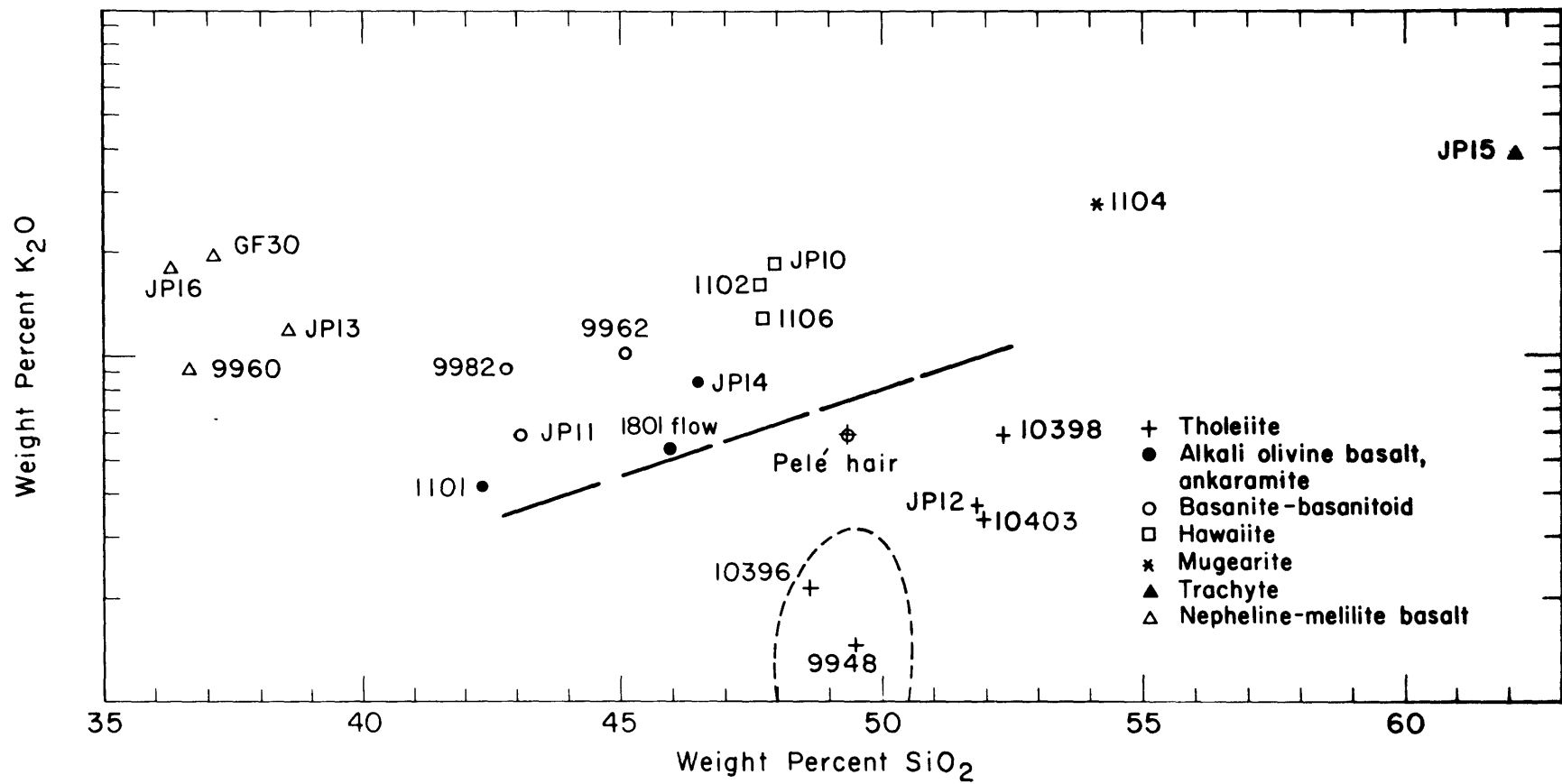
islands and their remote location from continental areas,
minimize crustal contamination of these lavas, most pro-
bably derived from the upper-mantle. Twenty lavas, one
diabase, and two olivine nodules, all from Hawaiian
Islands, were analyzed for the rare earths by means of
neutron activation.

SAMPLES

The samples numbered JP in Table 1 were supplied by
J. L. Powell, Oberlin College. The sample GF-30 was given
by G. Faure, Ohio State University. The samples 1101-1106
and 9948-10403 and the Pele's hair were supplied by J. B.
Thompson, Harvard University. The Hualalai olivine nodule
and sample of the host 1801 alkali basalt flow were fur-
nished by G. R. Tilton, and the Salt Lake Crater olivine
nodule by J. H. Crocket, McMaster University.

The chemical composition calculated norms and loca-
tion of these samples are given in Appendices A and B,
except for the Pele's hair, the Hualalai olivine nodule
and the 1801 alkali basalt and Salt Lake Crater samples
which have no analyses available. The petrology, petro-
graphy and genesis of these very same samples have been
discussed in great detail by Winchell (1947), Wentworth
& Winchell (1947), Macdonald & Powers (1946), Macdonald
& Katsura (1964), Muir & Tilley (1961), Washington (1923)
and Cross (1915). The Strontium isotopic composition of
the 8 samples numbered JP and GF have been determined by

Powell, Faure and Hurley (1965). Uranium and Thorium analyses of the Hualalai olivine nodule and its host alkali basalt of the 1801 flow is given by Tilton and Reed (1963). Finally, all these samples have been analyzed for Rubidium and Strontium as well as the Strontium isotopic composition by Bence (1966), except samples GF-30, the Pele's hairs, Hualalai and its host alkali basalt and the Salt Lake Crater olivine nodule.

The potassium and silica content of these samples is shown in a variation diagram à la Engel (Engel et al., 1965) in Figure 1-1.

EXPERIMENTAL PROCEDURE

Except for the two olivine nodules, the analytical procedure used for this study consisted of group isolation of the rare earths (including Yttrium) followed by neutron activation and partition chromatography. Erbium was not determined and Gadolinium only in three samples. Accuracy and precision varied with the element but in general were in the range of $\pm$ 4 - 10%. Reagent blank corrections had to be applied since they were much smaller than the experimental errors. The details of this procedure will appear in Part II, and (Ehrlich, Schilling and Winchester, 1966). The accuracy of the procedure as applied to the analyses of rock standards G-1 and W-1 will be discussed in Appendix C.

Samples weighing up to 0.5 g were dissolved using a mixture of perchloric and hydrofluoric acids, and carrier-free Ce^{139} and Y^{88} were added. The rare earth group separation was done by coprecipitation on calcium oxalate followed by coprecipitation on ferric hydroxide and then separation from the iron by anion exchange (Dowex 1x8, 50-100 mesh resin). Specially purified reagents were prepared for the pre irradiation chemistry (Appendix C). Chemical yields were determined at this stage by measuring the tracer radioactivities. Aliquots of the sample solutions and of a reference solution of known rare earth content (approximating ten times chondrites) were sealed in polyethylene tubes and irradiated for three hours in the MIT reactor pneumatic tube facility at a flux of 2×10^{13} neutrons/cm^2-sec. The reference solution used had a rare earth pattern similar to that of chondrite but at an approximately ten-fold higher concentration level. The irradiated samples and reference solutions were chromatographed by gradient elution with hydrochloric acid on columns consisting of a mixed bed of 75% by volume of refined diatomaceous silica made hydrophobic by dimethyldichlorosilane and coated with bis(2-ethylhexyl) orthophosphoric acid (Winchester, 1963, and Towell, 1963) and 25% untreated diatomaceous silica. The eluates were collected on polypropylene planchets, dried in an oven at about $100^{\circ}C$ and then sprayed with clear Krylon.

Radioactivity measurements were made by gross beta counting with a standard end-window, gas flow proportional counter.

A fully automated step-wise concentration gradient elution device, electronically controlled, was developed for the chromatographic step (Appendix D). Due to this improvement, four samples and one reference solution, or three samples and two reference solutions could be processed at the same time.

For the two olivine nodules the preparation of samples for analyses was as follows: for the Salt Lake Crater nodule small fragments with freshly broken surfaces were prepared by crushing with a hammer. The Hualalai nodule, which was received already crushed into individual grains, was inspected under a binocular microscope and small bits of basalts were removed from the olivine nodule. This was easily done; the basalt being grey and the olivine nodule green. Both fragmented samples were washed for 15 minutes in hot 6N hydrochloric acid. The pieces were washed several times in hot specially distilled-demineralized water. Finally, they were crushed to a fine powder in a new steel mortar used solely for ultrabasic rocks. Sizing was done by sliding the powders down inclined sheets of paper, no metal sieves were used.

Approximately 1 g. powder samples sealed in small polyethylene vials and aliquots of reference solutions of known rare earth contents sealed in polyethylene

tubes were irradiated for 8 hours. After the samples had cooled for several hours, carrier-free Ce^{139} and Y^{88} were added to samples weighing approximately 0.5 g., and were fused with Na_2O in zirconium crucibles. The rare earth group separation was done in much the same way as described above, except that special care was taken to remove silica gels, as well as to remove zirconium lost from the crucible during the fusion by three successive extractions with a TTA-xylene solution. The rare earths were then chromatographed and finally, chemical yields were determined after gross beta counting was done.

RESULTS

The analytical results are presented in Tables 1-1, for $_{57}La$ to $_{71}Lu$ including $_{39}Y$. $_{68}Er$ was not determined and $_{64}Gd$ only in three samples. The estimated precision for individual rare earths is given in Table 1-1, column 26. These estimations were made on the basis of 9 samples run with two reference solutions, combinations of 5 sets of duplicates, 3 sets of triplicates and 1 quadruplicate of the same or different sample solutions. For inter-laboratory control and estimation of accuracy, the standard granite G-1 and diabase W-1 were analyzed. The results are presented in Table 1-1, columns 24 and 25, respectively. Results for the two nodules are in Table 1-1, column 22 and 23, both are average of duplicate analysis. The range of concentrations of each individual rare earth

TABLE 1-1.

Table 1-1 Rare earth concentrations given in ppm. The
estimated standard deviations from the mean*are given
in column 26 unless specified as for G-1 and W-1.

Column #	1	2	3	4	5
Sample #	9948	10398	JP.12	10396	10403
La	5.30	6.24	7.22	8.41	8.78
Ce	-	-	25.83	-	-
Pr	2.56	2.86	3.48	3.86	4.32
Nd	12.78	14.59	20.11	19.31	20.9
Sm	3.74	4.09	4.94	5.26	5.06
Eu	1.28	1.31	1.77	2.03	1.77
Gd	-	-	-	-	-
Tb	.663	.728	.847	1.00	.868
Dy	3.72	4.20	3.14	4.80	4.99
Ho	.574	.666	.852	.746	.787
Er	-	-	-	-	-
Tm	.198	.218	.320	.265	.267
Yb	1.26	1.45	1.85	1.81	2.06
Lu	.191	.199	.299	.246	.288
Y	16.42	18.75	15.16	22.38	22.11

$$* \quad \sigma = \sqrt{\frac{\sum_{n=1}^{n}(X_i-\bar{X})^2}{n-1}}$$

TABLE 1-1 (Reference notes)

9948	Olivine Tholeiite, Koolau series, Oahu.
10398	Diabase, Koolau series, Oahu.
JP.12	Tholeiite, Mauna Loa, Hawaii.
10396	Tholeiite, Koolau series, Oahu.
10403	Tholeiite, Koolau series, Oahu.

TABLE 1-1 (Continued)

Column #	6	7	8	9	10
Sample #	Pele Hair	1801 Flow	1101	JP.14	JP.11
La	11.42	13.33	13.91	17.76	14.49
Ce	33.68	–	–	–	36.63
Pr	4.89	4.88	5.73	4.61	4.93
Nd	20.12	21.52	25.78	20.74	22.14
Sm	5.41	4.78	5.32	4.36	4.94
Eu	1.81	1.55	1.80	1.48	1.73
Gd	–	–	–	–	–
Tb	1.20	.689	.788	.662	.737
Dy	5.17	3.80	4.56	3.99	4.26
Ho	.825	.685	.639	.683	.655
Er	–	–	–	–	–
Tm	–	–	.197	.274	.193
Yb	1.67	1.70	1.40	1.63	1.14
Lu	.238	.278	.199	.242	.181
Y	28.56	19.31	18.54	18.84	17.70

Pele hair   Kilauea, Hawaii
1801 flow   Alkali olivine basalt, Hualalai, Hawaii
1101   Ankaramite, Haleakala, Maui.
JP.14   Alkali olivine basalt, Hualalai, Hawaii
JP.11   Basanitoid, Honolulu series, Oahu.

TABLE 1-1 (Continued)

Column #	11	12	13	14	15
Sample #	9982	9962	1106	JP.10	1102
La	18.08	21.29	24.59	31.65	36.09
Ce	50.84	62.06	-	100.1	-
Pr	6.30	7.89	9.94	13.04	13.11
Nd	27.00	34.70	43.98	60.95	61.94
Sm	5.98	7.74	9.05	13.17	11.27
Eu	2.07	2.60	2.83	4.32	3.38
Gd	-	-	-	-	-
Tb	.892	1.07	1.36	1.63	1.42
Dy	4.84	5.79	7.54	10.82	8.84
Ho	.757	.959	1.23	1.52	1.26
Er	-	-	-	-	-
Tm	.207	.287	.352	.424	.384
Yb	1.23	1.82	2.40	2.74	2.44
Lu	.250	.263	.393	.427	.347
Y	19.50	24.51	31.79	40.39	33.46

9982   Nepheline basanite, Honolulu series, Oahu.
9962   Linosaite, Honolulu series, Oahu.
1106   Hawaiite, Haleakala, Maui.
JP.10   Hawaiite, Mauna Kea, Hawaii.
1102   Hawaiite, Haleakala, Maui.

TABLE 1-1 (Continued)

Column #	16	17	18	19	20
Sample #	1104	JP.15	GF.30	JP.13	JP.16
La	47.98	44.13	41.06	51.96	62.61
Ce	112.49	117.26	-	129.0	146.6
Pr	14.23	13.74	14.54	15.18	17.46
Nd	54.58	45.37	57.64	53.02	74.29
Sm	11.24	8.68	13.49	11.13	16.04
Eu	3.59	2.37	4.05	3.70	4.98
Gd	-	-	-	12.05	14.83
Tb	1.25	1.37	1.10	1.53	1.67
Dy	7.55	7.95	6.35	7.86	5.92
Ho	1.33	1.43	.931	1.03	.866
Er	-	-	-	-	-
Tm	.425	.681	.140	.410	.212
Yb	3.08	4.56	1.88	2.01	.899
Lu	.412	.676	.248	.265	.134
Y	35.7	42.51	26.14	28.05	19.75

1104	Mugearite, Haleakala, Maui.
JP.15	Trachyte, Puu Anahulu, Hawaii.
GF.30	Melilite-nepheline basalt, Honolulu series, Oahu.
JP.13	Nepheline basalt, Honolulu series, Oahu.
JP.16	Melilite-nepheline basalt, Honolulu series, Oahu.

TABLE 1-1 (Continued)

Column #	21	22	23	24	25
Sample #	9960	Salt Lake Crater Nodule	Huala- lai Nodule	G-1	W-1
La	78.07	.995	.115	88.95	8.54
Ce	188.02	-	-	207.6	26.84
Pr	21.48	.277	-	20.0	2.90
Nd	86.32	1.36	.294	57.6	12.14
Sm	15.56	.336	.051	6.85	3.15
Eu	4.91	.103	.0138	1.20	1.03
Gd	1.88	-	-	3.57	-
Tb	2.02	.060	-	.573	.595
Dy	9.27	.318	-	2.88	3.76
Ho	1.20	.048	.0077	.487	.687
Er	-	-	-	-	-
Tm	.305	.0215	-	.153	.257
Yb	1.96	.112	.0254	1.04	2.18
Lu	.262	.0198	.0038	.165	.320
Y	-	1.87	.319	13.14	22.36

9960   Nepheline-melilite basalt, Honolulu series, Oahu.

Salt Lake Crater Nodule   Peridotite nodule, Oahu

Hualalai nodule   Olivine-rich nodule in 1801 flow
          Hualalai, Hawaii

G-1   Standard granite, Westerly, Rhode Island

W-1   Standard diabase, Centerville, Virginia

TABLE 1-1 (Continued)

Column #	26 Estimated Errors in %		27 Range of Concentration Minimum	Maximum	28 Variation Factor Max./Min.	29 20 Chondrites Average
La	±	4	5.30	78.07	14.7	.30
Ce	±	10	25.83	188.02	7.3	.84
Pr	±	4	2.56	21.48	8.4	.12
Nd	±	6	12.78	86.32	6.8	.58
Sm	±	5	3.74	16.04	4.3	.21
Eu	±	6	1.28	4.98	3.9	.074
Gd	±	15	-	14.83	-	.32
Tb	±	9	.662	2.02	3.1	.049
Dy	±	6	3.14	10.82	3.4	.31
Ho	±	7	.574	1.52	2.6	.073
Er	-		-	-	-	.21
Tm	±	8	.140	.681	4.86	.031
Yb	±	9	.899	4.56	5.07	.17
Lu	±	9	.134	.676	5.04	.031
Y	±	6	15.16	42.51	2.8	1.8

for the 20 basalts and the diabase are given in Table 1-1,
column 27, and the corresponding variation factor in
column 28. Also given in Table 1-1, column 29, is the
average rare earth abundance in a series of 20 chon-
dritic meteorites analyzed by Schmitt et al. (1963);
Schmitt, Smith and Olehy (1964). This includes one
analysis by Haskin and Gehl (1962).

DISCUSSION

The practice of this laboratory (Coryell, Chase
and Winchester, 1962) is to compare the rare earth
abundance pattern of each rock element by element with
a common reference, e.g. the average of ordinary chon-
dritic meteorites (Table 1-1, column 29). The relative
abundance of each rare earth (i.e. enrichment factor
relative to the reference) is plotted logarithmically
versus a linear scale of rare earth atomic number. The
rare earths decrease in size with increasing atomic
number, and an approximately linear relationship exists
between atomic number and reciprocal ionic radius
(Templeton and Dauben, 1954).

Figure 1-2 is such a plot for three lavas:
an olivine tholeiite, an ankaramite and a nepheline-
melilite basalt. The olivine tholeiite was found to have
the lowest abundances for most of the rare earths and
the least fractionation. It is characterized by a broad
maximum enrichment in the lighter rare earths near Nd

Figure 1-2. Abundances of the rare-earth elements relative to 20 chondrites (Schmitt et al., 1963, 1964) in three basalts from the Hawaiian Islands, plotted on logarithmic scale as a function of the atomic number. The olivine tholeiite has the lowest rare earth concentrations and is the least internally fractionated of the samples analyzed. The nepheline-melilite basalt is the most enriched in the light rare earth region and is characteristic of the most fractionated lavas analyzed.

o Nepheline-melilite basalt 9960
  Oahu, Honolulu Series

● Olivine Tholeiite 9948
  Oahu, Koolau Series

x Ankaramite 1101
  Maui, Haleaka Volcano

ppm Rock / ppm Chondrites

1000

100

10

1

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
57   (Y)   71
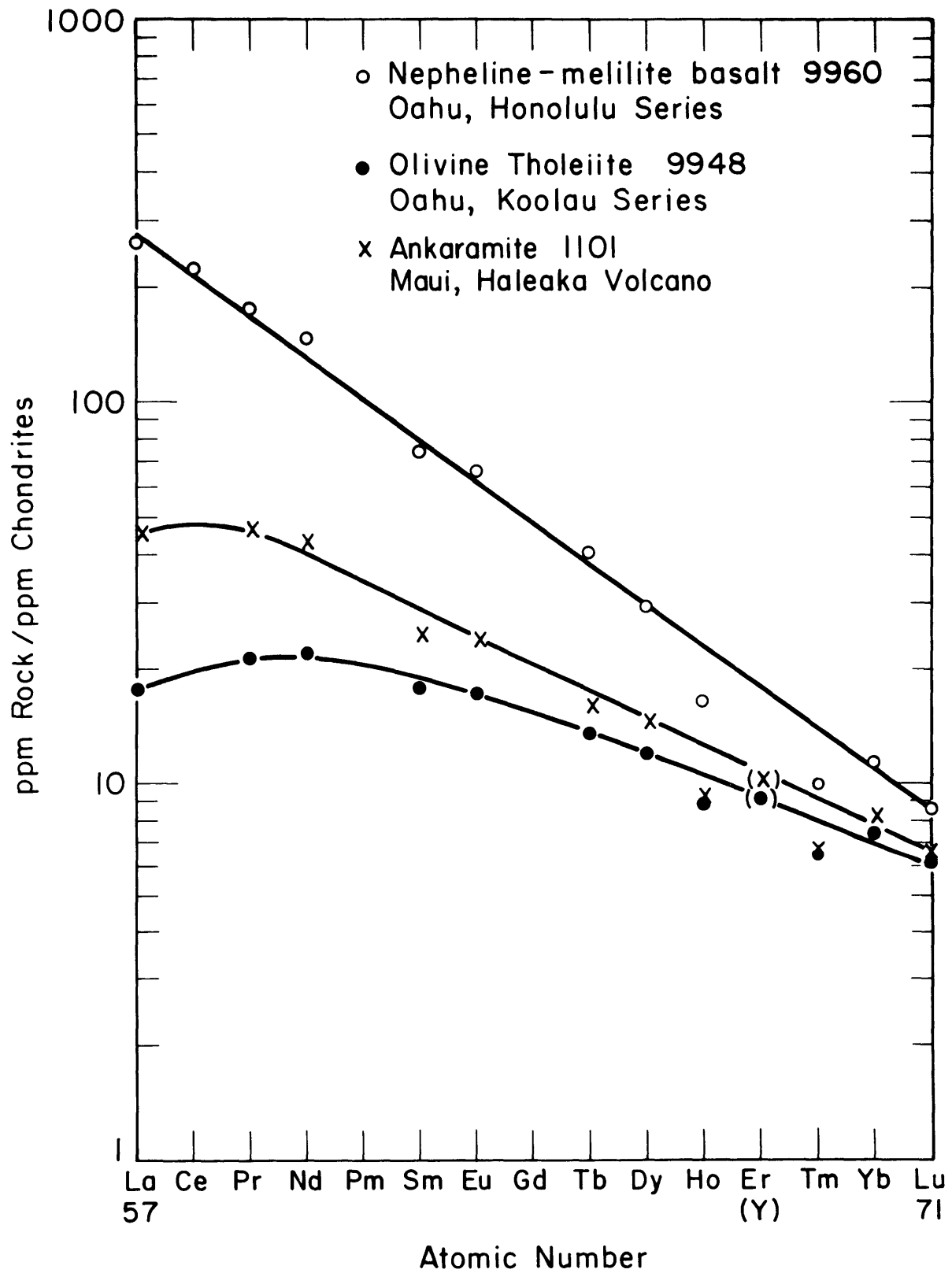
Atomic Number

relative to chondrites and on exponential decrease (linear, on a semi logarithmic paper) with increasing atomic number for the heavy rare earths, from Sm to Lu. The maximum enrichment of the lighter rare earths and the greatest relative fractionation was found in the nepheline-melilite basalt shown on Figure 1-2. This type of lava is characterized by a remarkable exponential decrease of the rare earth enrichment relative to chondrites with increasing atomic number from La to Lu. All lavas analyzed in the suites tholeiite alkali olivine basalt, basanite-basanitoid, and nepheline basalt were found to lie in the envelope formed by the two rocks described above. The ankaramite (picrite basalt) is shown on Figure 1-2 as an example of the intermediate members of this suite.

One example of the silica and alkali enriched lavas of the series Hawaiites-mugearite and trachyte is shown in Figure 1-17 . Its relation with respect to the olivine tholeiite-nepheline-melilite envelope basalts is also shown. The lighter rare earth end of this suite forms patterns identical to the previous one. They lie within the characteristic envelope. On the other hand, the heavy rare earth end tends to level out and depart from the envelope. All other lavas of this latter suite show this same noticeable tendency.

Although it is risky to categorize basic igneous rocks too sharply because intermediate types will certainly be found, all lavas were tentatively grouped according to the similarity of rare earth abundance patterns

given above.

Figure 1-3 is such a plot for the average of four
of the tholeiitic basalts analyzed relative to the
chondrite reference. The extreme deviations of each
element for any of the tholeiites in the group, as
shown by the vertical bars, indicate that the rare
earth abundances are very similar in the four rocks.
Individual rocks in any one of the other groups shown
in Figures 1-3 to 1-9, are likewise closely similar
in rare earth concentration, although the groups are
distinct to within $\pm$ 25% from each other. The basanite-
basanitoids are identical to the alkali olivine ba-
salt group but on the average the lighter rare earths
are about 20% higher. These groups coincide closely
with groupings based on mineralogy and major element com-
position. The patterns in all groups are fractionated
relative to the chondrites in the heavy as well as in
the light element regions, but to different degrees in
the different groups of lavas. Thus the maximum abundance
variation occurs in the light element region. The vari-
ation factor (Table 1-1, column 28) decreases regularly
from La to Ho with increasing atomic number or the re-
ciprocal ionic radius, reaches a minimum near Ho and then
increases slightly with increasing Z to Lu. If the late
differentiates, silica-rich trachyte and mugearite, which
show a noticeable tendency for the heavy rare earths to
increase slightly with Z, are excluded, the variation
factor for the heavy rare earths stays practically

Figure 1-3. Rare earth abundance averages of four tholei-
ites (including a diabase) relative to 20 chondrites
(Schmitt et al., 1963, 1964) plotted on logarithmic
scale as a function of the atomic number. Vertical
bars represent extreme deviations of each element from
the mean.
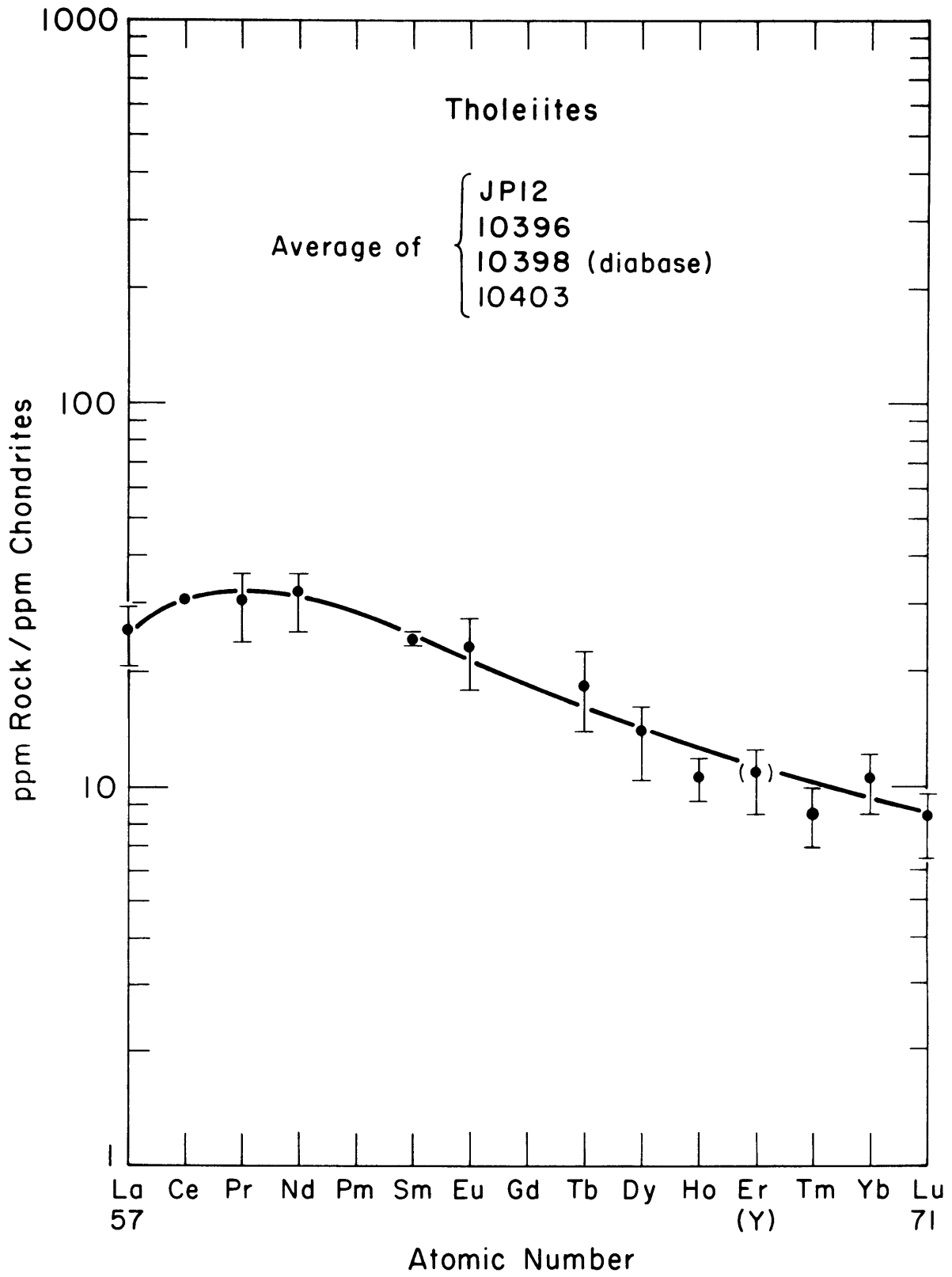
Figure 1-4. Rare earth abundance averages of two alkali
olivine basalts and an ankaramite relative to 20 chondrites
(Schmitt et al., 1963, 1964) plotted on logarithmic scale
as a function of the atomic number. Vertical bars represent
extreme deviations of each element from the mean.

Alkali olivine basalts

Average of { JP14
            1101
            Hualalai 1801 flow
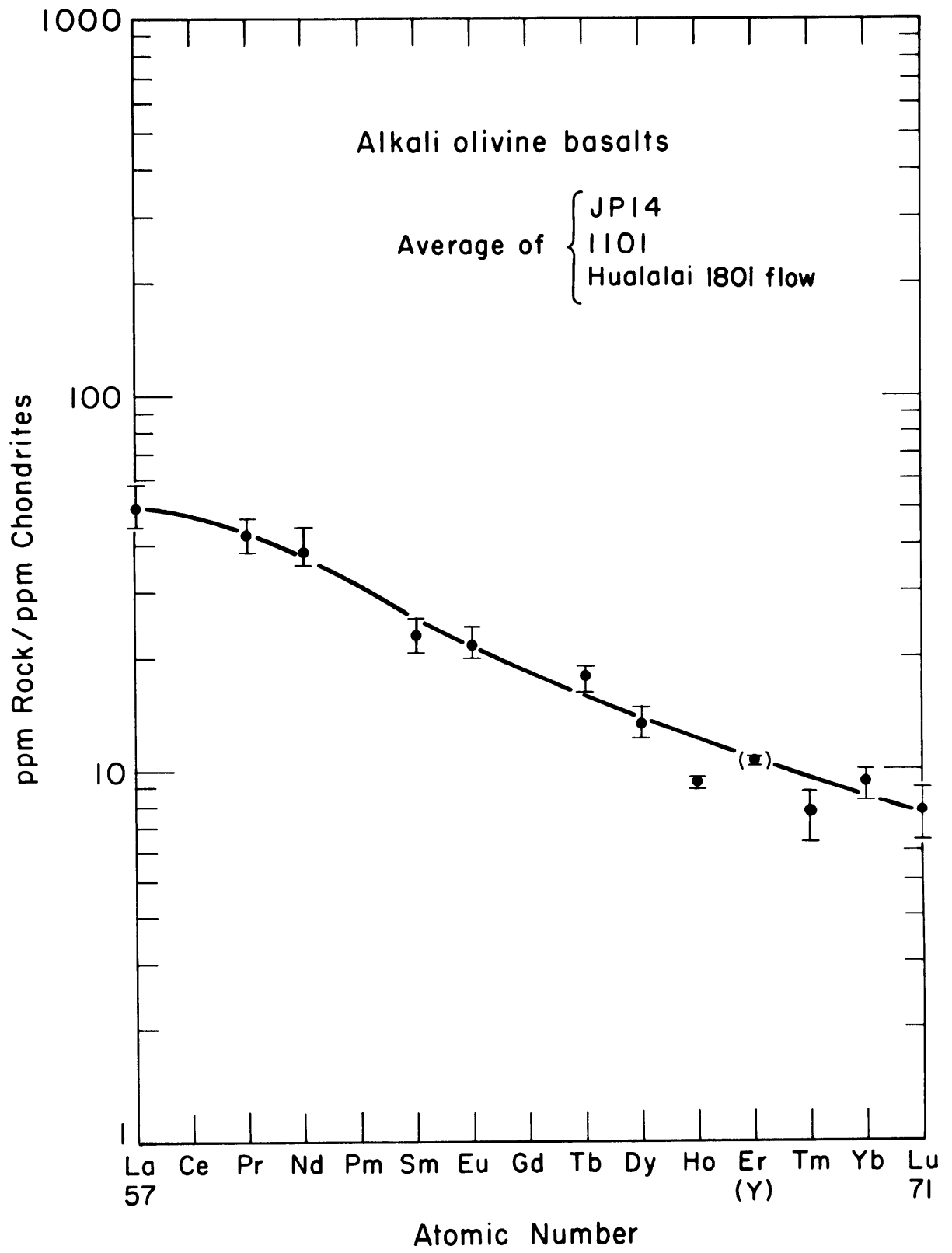
Figure 1-5. Rare earth abundance averages of three basanites-
(oids) relative to 20 chondrites (Schmitt et al., 1963,
1964) plotted on logarithmic scale as a function of the
atomic number. Vertical bars represent extreme deviations
of each element from the mean.
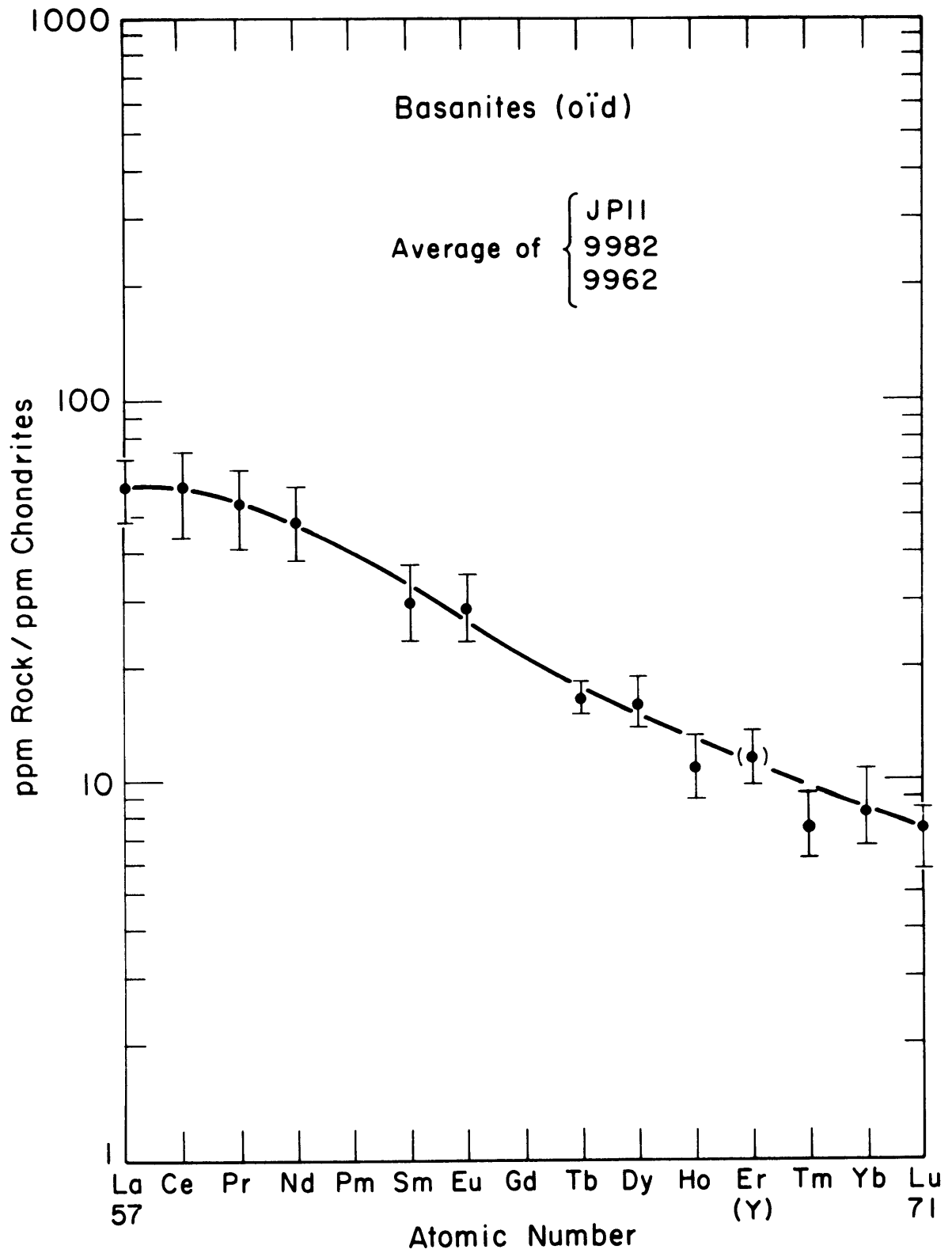
Figure 1-6. Rare earth abundance averages of three
Hawaiites relative to 20 chondrites (Schmitt et al., 1963,
1964) plotted on logarithmic scale as a function of the
atomic number. Vertical bars represent extreme deviations
of each element from the mean.
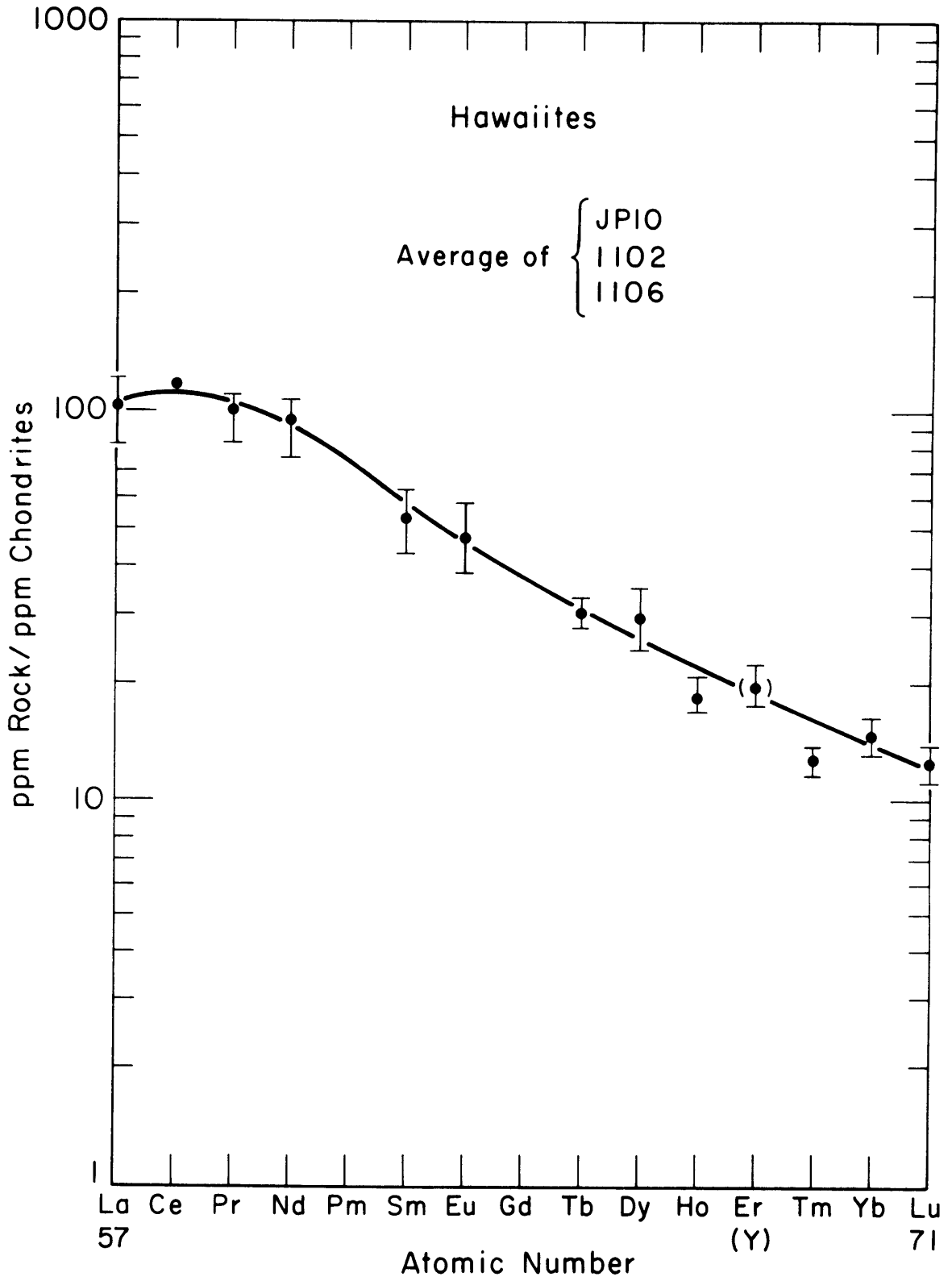
Figure 1-7. Rare earth abundances of a mugearite relative to 20 chondrites (Schmitt et al., 1963, 1964) plotted on logarithmic scale as a function of the atomic number.

Mugearite
Maui, Haleaka Crater

1104
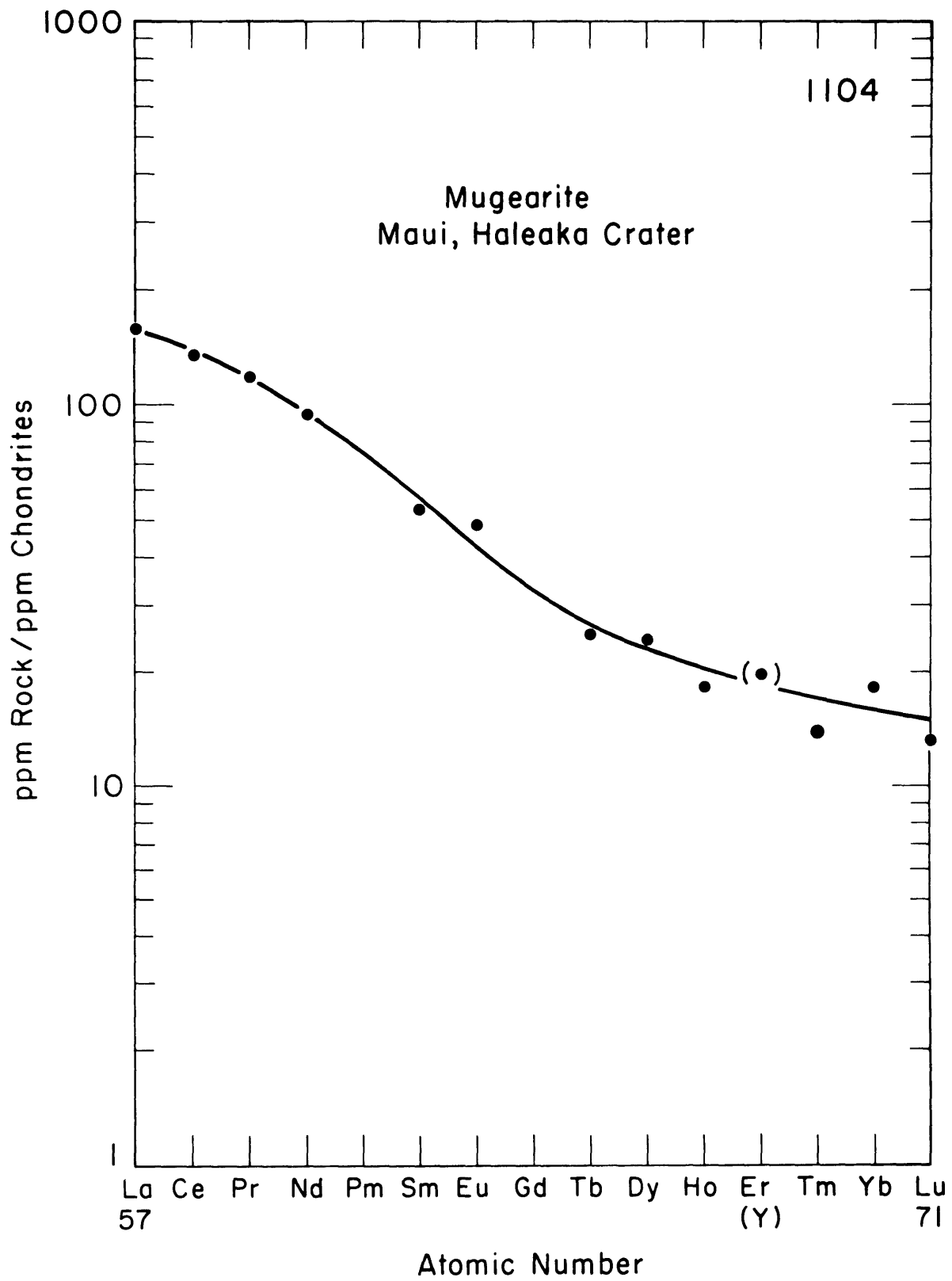
Figure 1-8. Rare earth abundances of a trachyte relative
to 20 chondrites (Schmitt et al., 1963, 1964) plotted on
logarithmic scale as a function of the atomic number.

Trachyte
Hawaii, Puu Anahulu

JP15
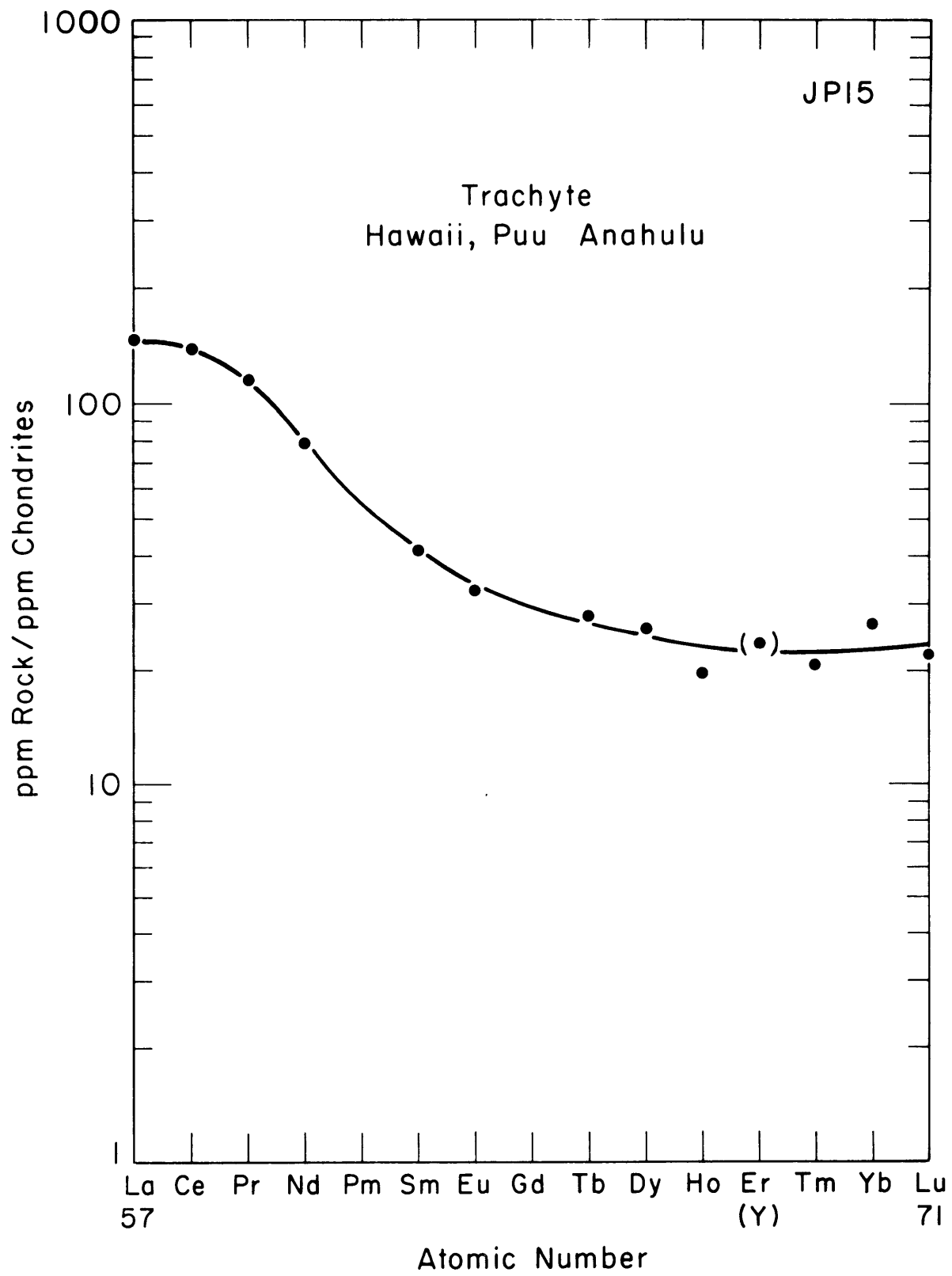
Figure 1-9. Rare earth abundance averages of four
nepheline-melilite basalts relative to 20 chondrites
(Schmitt et al., 1963, 1964) plotted on logarithmic scale
as a function of the atomic number. Vertical bars rep-
resent extreme deviations of each element from the mean.

Nepheline-melilite basalts

Average of { JP13, JP16, GF30, 9960 }
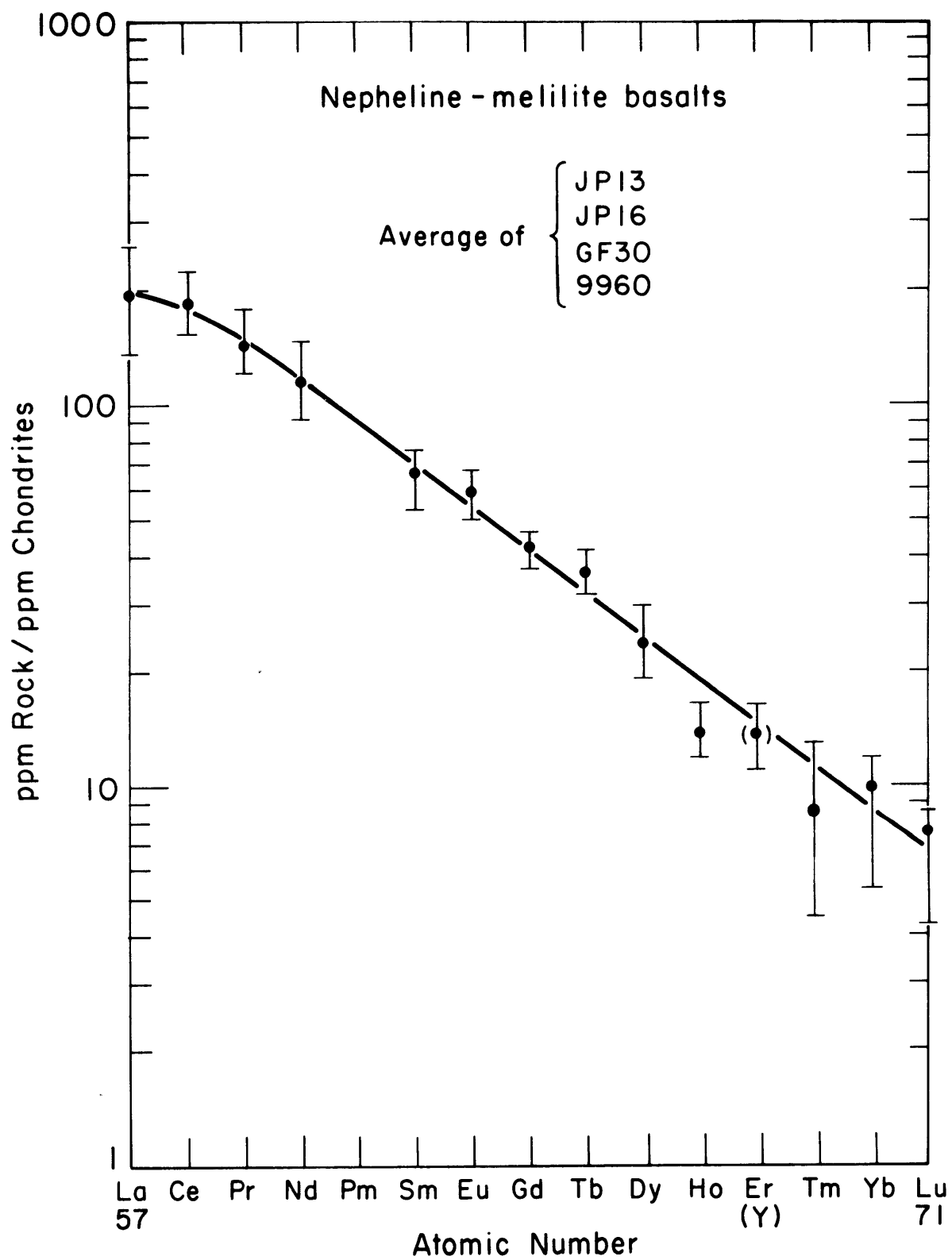
constant from Gd to Lu.

GENETIC RELATIONSHIPS

The genetic relationships between these different types of lavas based on the rare earth data are best seen by comparing them to a comagmatic reference rock of somewhat more primitive character (Schilling and Winchester, 1966a). Figure 1-10 presents element by element the rare earth concentrations of each rock group relative to the olivine tholeiite sample 9948 as a reference. Sample 9948 was chosen as reference because it is the least internally fractionated, has the lowest in K_2O and rare earths of the samples analyzed, and is the only tholeiite which contains normative olivine. Its composition has often been identified as the primary magma for the tholeiite series in Hawaii. The other tholeiites have virtually the same rare earth abundance pattern but are somewhat enriched in total rare earths compared to sample 9948. The alkali olivine basalts, the basanites, and the hawaiites all show a remarkable break near Gd. The heavy rare earths are in the same relative abundance as in tholeiite, giving nearly horizontal trends in Figure 1-10, but in the lighter element region the relative abundance of these rare earths shows progressive increase as the atomic number decreases from Gd to La. The nepheline melilite basalts do not show such a break, but the progressive enrichment with decreasing atomic number extends

over the entire range and is approximately linear on these
semi-logarithmic graphs. The mugearite shows a minimum
near Gd and a slight rise in the heavy element region.
The trachyte also shows this minimum near Gd but a de-
finite rise of the heavy rare earths with increasing
atomic number. On this normalization basis, four
distinct groups emerge: 1. the tholeiitic series which
includes the olivine tholeiite and a diabase. 2. the
alkalic series which comprises alkali olivine basalts,
ba.sanite-basanitoids, hawaiites, one mugearite. All
these later lavas are characterized by patterns with a
break in the middle of the rare earth series. 3. the
trachyte seems to be a variation of this group, because
of its marked progressive enrichment of the heavy rare
earths with increasing Z, from Gd to Lu. 4. the nephe-
line-melilite basalts, which do not show any break.

The same grouping is observed when considering
the variation of individual rare earths as function of
the concentration of various major elements of these lavas.
Figures 1-11 and 1-12 show the dependence of La (which
shows the greatest concentration variation of all rare
earths) with two indexes of differentiation, $\frac{SiO_2}{3} + K_2O -$
(CaO+MgO+FeO) and MgO X 100 / MgO+FeO+CaO (Kuno et al.,
1957), respectively. Other variation diagrams such as
La-Na_2O, La-Al_2O_3, La-SiO_2 and La-K_2O or Yb-K_2O (Appendix E)
have also been examined but are not shown here. In all
cases, invariably the same grouping as mentioned above
was observed.

Figure 1-10. Rare earth abundance average of rock groups relative to the low-potassium olivine theolelite No. 9948. Plotted on a logarithmic scale as a function of the atomic number.
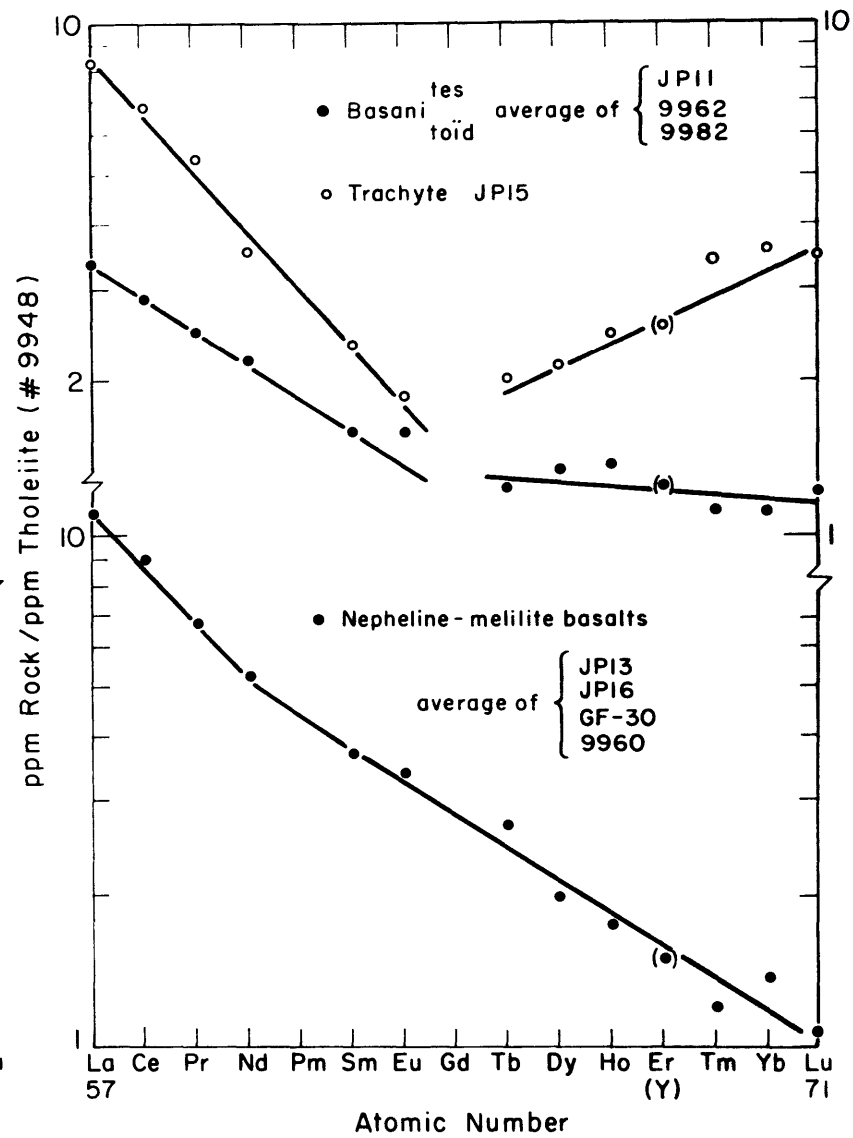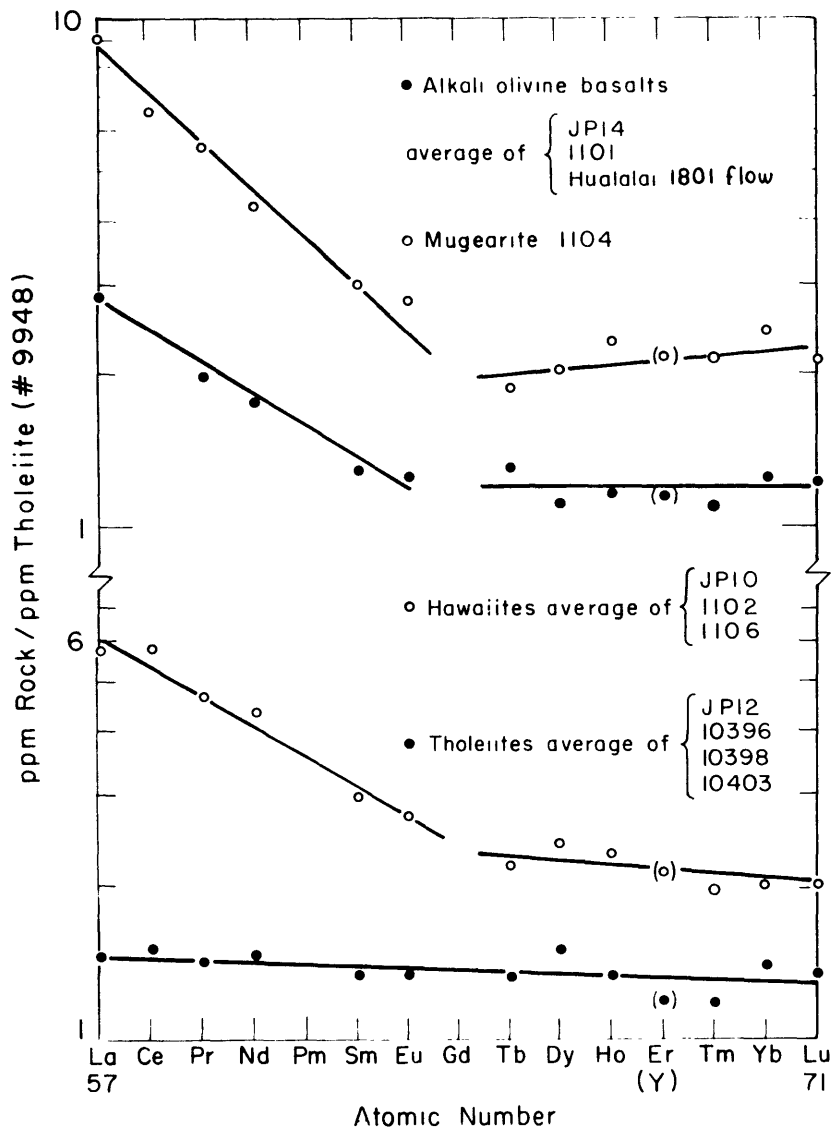
Figure 1-11. Variation diagram. La abundances (ppm) of 21Hawaiian lavas and a diabase are plotted on logarithmic scale as a function of the index of fractionation $SiO_2/3$ + K_2O - MgO - FeO - CaO. Four groupings are apparent. + = tholeiites; ● = Alkali olivine basalts + ankaramite; O = Basanite-basanitoids; Δ = Nepheline-melilite basalts; □ = Hawaiites; * = Mugearite; ▲ = Trachyte.

Figure 1-12. Variation diagram. La abundances (ppm)
of 21 Hawaiian lavas and a diabase are plotted on logarithmic
scale as a function of the Kuno's (1957) index of frac-
tionation S.I $=$l00MgO/MgO + FeO + Fe_2O_3 + K_2O + Na_2O.
Distinct groupings are apparent. $+$ $=$ Tholeiites; $\bullet$ $=$ Alkali
olivine basalts + ankaramite; O $=$ Basanite-basanitoids;
$\triangle =$ Nepheline-melilite basalts; $\square =$ Hawaiites; $*$ $=$ Mugearite;
$\blacktriangle =$ Trachyte.

La (ppm)

Pele's hair

Mg x 100 / MgO + FeO + Fe$_2$O$_3$ + Na$_2$O + K$_2$O (wt.%)
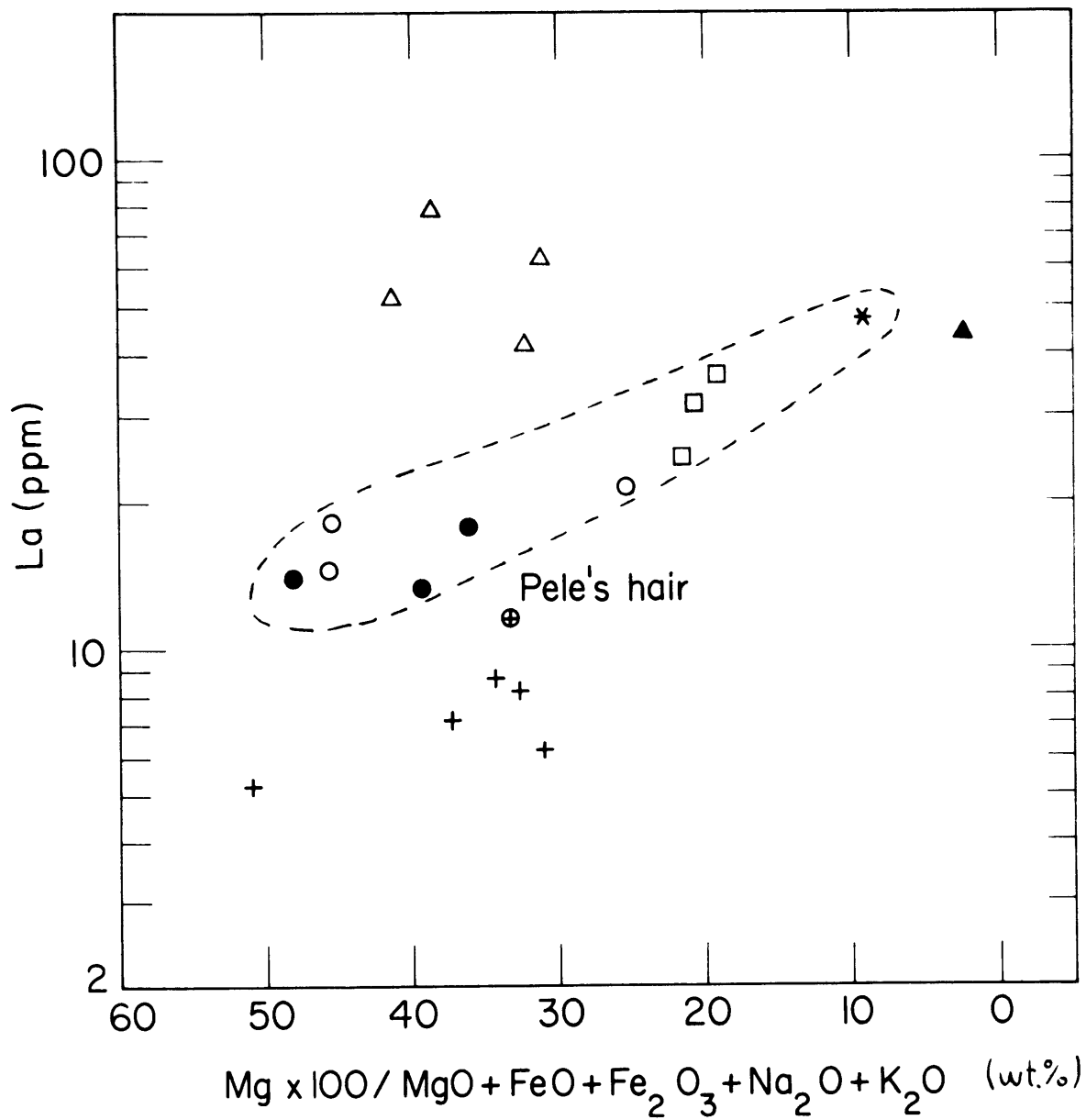
We realize that with additional rare earth analyses, it is probable that these groupings may tend to be masked, and a continuum rather than rare earth concentration spectra may be observed. This seems already to appear when the Pele's hair and the Hualalai alkali basalt of the 1801 flow (whose major element analyses were not available, but were estimated from other analyses of lavas from the same localities, given by Tilley, (1960) Daly, (1944) and Washington, (1923) are plotted. The two latter rocks seem to be intermediate between the tholeiitic and alkalic series, (alkali olivine basalt). Nevertheless, the close correspondence of these groupings based on this study and the same already well recognized groupings based on petrological, mineralogical and geological evidences, does not seem to be pure coincidence. It must be of genetic significance. We feel confident that even with many more additional analyses available from these islands, this spectra of rare earth concentrations will most probably persist if proper weighting is given to the rock analyses, in order to take into account their relative occurrences with respect to volume.

The rare earths effectively bring up the principal and well recognized petrological groups of lavas and their close relationships with respect to distinct stages of volcanic evolution of the Hawaiian Islands as described by Stearns (1940, 1946), Macdonald and Katsura, 1964). This is most encouraging and permits us to hope that the rare earths may indeed be a powerful tool in the study

of geochemical processes, when more data will be available.

In the following sections, we will discuss separate-
ly the rare earth evidence and its possible bearing on
the petrogenesis of the four groups.

The origin of these volcanic series is a matter
of debate. Several hypotheses have been presented: one
primary tholeiitic magma with a magmatically differenti-
ated alkali phase (Macdonald, 1949a, 1949b; Tilley, 1950;
Powers, 1955); one primary tholeiitic magma subsequently
contaminated to produce the alkali phase (Daly, 1944);
several primary magmas (tholeiitic, alkali, etc.) de-
rived by partial melting of the upper mantle at different
depths or partial melting under different conditions or
to different degrees (Kuno et al., 1957; Yoder and
Tilley, 1962, respectively); or combinations of these
alternatives (O'Hara and Mercy, 1963; O'Hara, 1965). For
all these cases and others the principal evolutionary
mechanisms evoked are: fractional crystallization, part-
ial melting, assimilation, hydrothermal alternations and
gaseous transfer. None of these processes were found
completely satisfactory to explain fully and uniquely the
volcanic evolution of the Hawaiian rocks. Nevertheless,
fractional crystallization and partial melting are found
to be more probable. Assimilation and hydrothermal alter-
ations have now been mostly rejected as major operative
processes of differentiation, although it cannot be denied
that they have been operative in localized areas. Gaseous
transfer was proposed mainly as a way out, after all other

possibilities were rejected. Little experimental evidence is yet available on this process. (It has of course the advantage that it can almost be anything since almost nothing is known about this process).

The fact that the Hawaiian lavas contain many phenocrysts, cummulates, gabbroic inclusions, and that some lavas such as picrite basalts have been formed by accumulation of phenocrysts, indicates that fractional crystallization must have been an operative process of differentiation.

On the other hand, the fact that these lavas were extruded as melts most probably derived from the upper-mantle, which from geophysical inferences is mostly crysalline, also indicates, from pure common sense, that these melts have been produced by melting (partial or total) of subcrustal regions, and thus melting must also have been an operative process. Yoder and Tilley (1962) have discussed the far reaching significance of the proximity of basalt composition to the four phases curve in the simplified, iron free, basalt tetrahedra Di-Fo-An-Ab. "It clearly suggests that most basalts are themselves a product of fractional melting or crystallization."

The question to be raised is: can inferences be drawn about these processes and their relative importance from the present rare earth data available?

We will examine the four different groupings assuming first that fractional crystallization has been the important evolutionary mechanism and then separately

consider evidence for partial melting and assimilation processes.

FRACTIONAL CRYSTALLIZATION

As mentioned in the introduction the few rare earth analyses available on common rock forming minerals show greatly diversified rare earth fractionation patterns (Towell et al., 1965; Gavrilova and Turanskaya, 1958). Crystallization and removal of different phenocrysts from the melt should thus noticeably influence the rare earth patterns of residual liquids. No data on mineral phenocrysts occurring in Hawaiian lavas is yet available. Thus to be fair, no really meaningul conclusions can be drawn about this process before such data are available. Nevertheless, inferences can possibly be drawn by considering some rare earth data available on other related rocks and minerals as well as other evidences.

Alkali Series

Alkali olivine basalt has often been proposed as the primary magma of this series. Figures 1-11 and 1-12, and other variation diagrams examined show that La increases regularly with increasing degrees of differentiation for this series in the order ankarimite, alkali olivine basalts and basanite-basanitoids (which are

Figure 1-13. Rare abundances in Bonsall tonalite, Woodson
Mountain granodiorite and Rubidoux Mountain Leucogranite
relative to San Marcos gabbro.plotted on logarithmic scale
as a function of the atomic number. Data from Towell
et al., 1965.
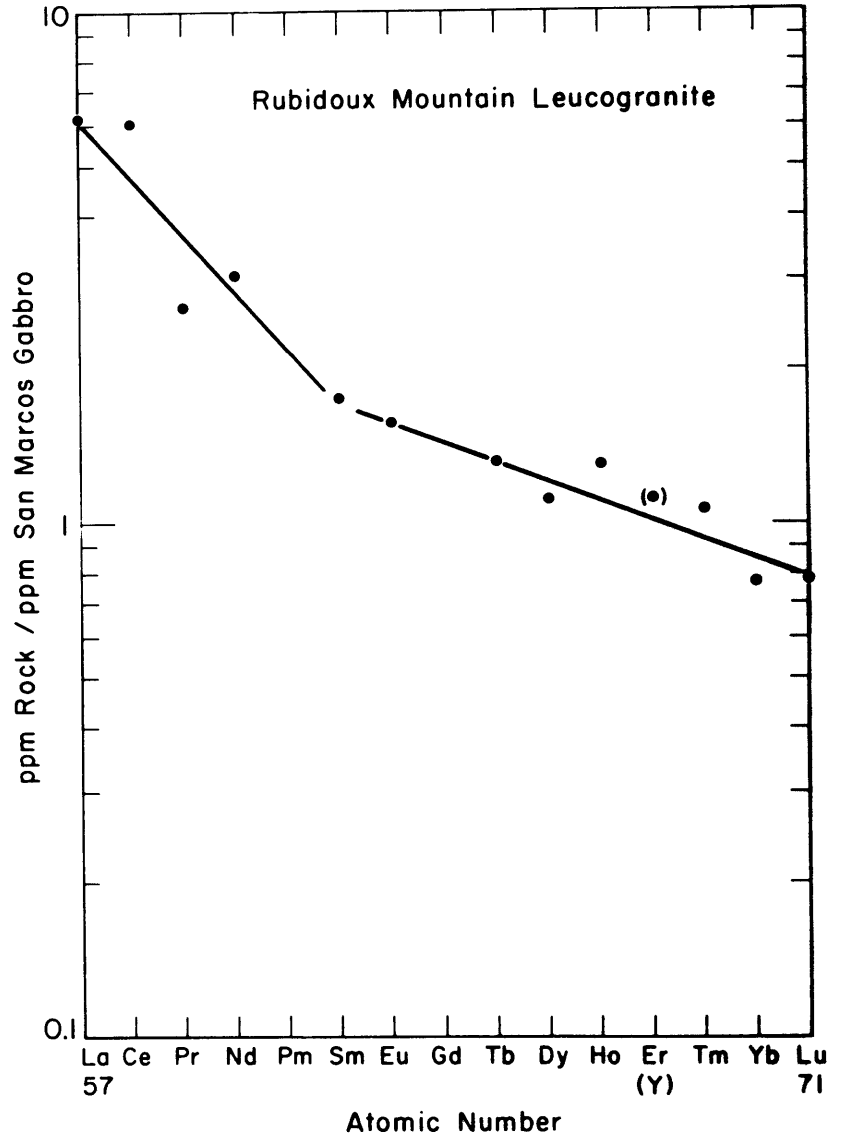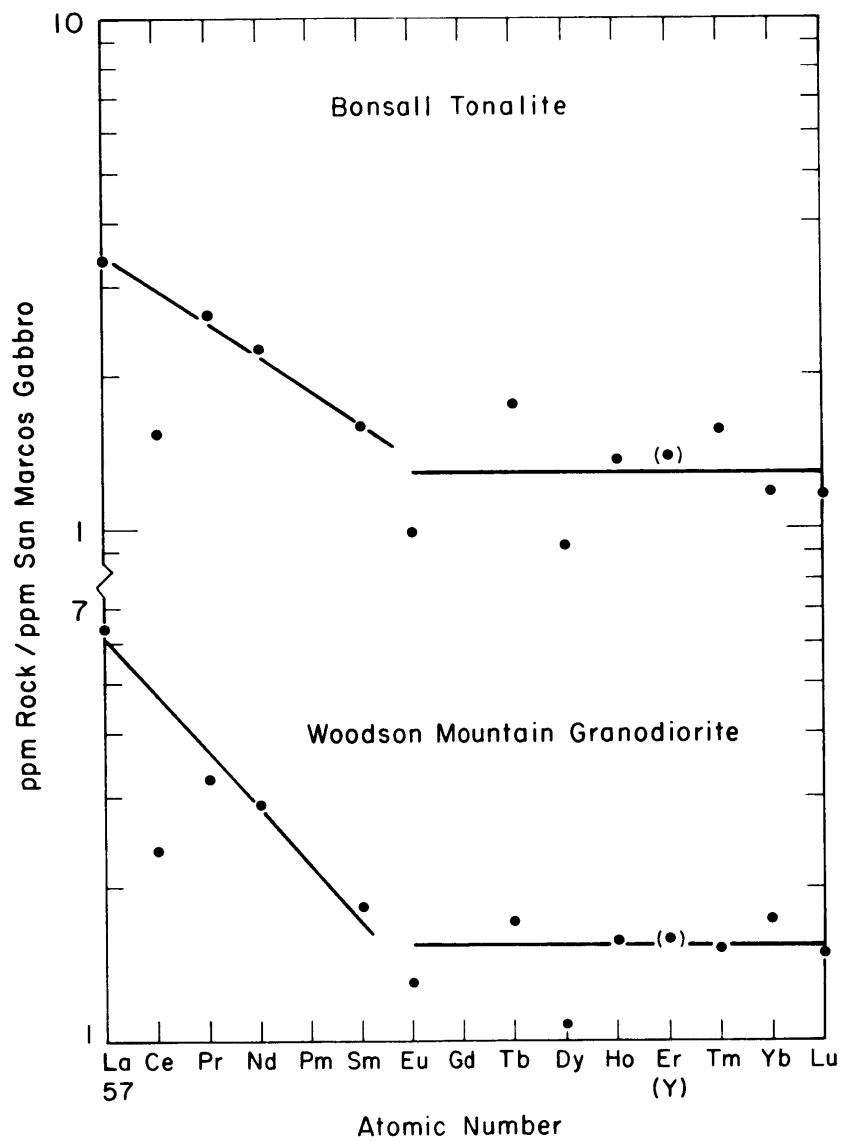
almost undistinguishable, see below), hawaiites and mugearite. Figure 1-10 shows also that both the lighter rare earth content and the negative fractionation slope increase progressively in the same order given above. Although the absolute heavy rare earth content increases in the same direction, there is no relative fractiona-tion, from Gd to Lu, with increasing degrees of differenti-ation till the mugearite is reached. Except for the pic-rite basalt which is known to have formed mainly by accumu-lation of olivine and augite phenocrysts, the alkali oli-vine basalt has the lowest rare earth abundances of the series and thus could represent the primary magma of this suite. Nevertheless, in the absence of real proof, it is debatable whether the alkali olivine basalt is primary and directly derived from the upper mantle or was differentiated from a tholeiitic magma.

Using data for the rare earths in the Southern California Batholith (Towell et al., 1965), we have com-pared, element by element, the Bonsall tonalite and the Woodson Mountain granodiorite with the San Marcos gabbro Figure 1-13. The result is a similar pattern for both cases, with a negative slope from La to the middle of the rare earth series and a horizontal trend of the rel-ative abundances in the heavy element region. (The Rubidoux Mountain leucogranite pattern also shows a break in the middle, but the heavy element trend still has a negative slope.) Furthermore, separated mineral data for the San Marcos gabbro (Towell et al., 1965),

Figure 1-14 show that augite (and hornblende which is an alteration product of augite) contains the heavy rare earths with the whole rock abundance pattern, but the light elements are sharply discriminated against.

Assuming that the gabbro represents an earlier stage of differentiation, subtraction of some early formed minerals having characteristic rare earth patterns could be informative as to what kind of patterns to expect in residual melts. Or vice-versa, what mineral ought to be removed from the primary melt to produce the characteristic late differentiate rare earth patterns.

One should be very cautious about such a procedure. Different patterns for the same mineral crystallizing in different conditions is expected. The rare earth partition coefficients of melts in different geological settings but of similar major element composition and at about the same temperature may be the same. However, it should be realized that the mineral pattern will be inherited from the rare earth composition of the melt at the time of separation of this mineral. It will also be dependent on the crysto-chemical properties of other phases separating simultaneously. Or put in an other way, the rare earth pattern of a given mineral will depend on the rare earth composition of the original melt, the paragenetic sequence previous to its crystallization (Maddonald, 1949a) and on other phases separating simultaneously from the melt. Thus, even when normalizing the rare earth

Figure 1-14. (Left hand diagram) Upper three curves show rare element abundances in the whole rock, San Marcos gabbro and in the augite and plagioclase mineral concentrates (multiplied by their estimated modal abundances) relative to 20 chondrites (Schmitt et al., 1963, 1964) plotted on a logarithmic scale as a function of the atomic number. Lower curve is the calculated abundance pattern relative to the whole rock gabbro for a residual liquid after subtracting contributions from augite and plagioclase from the whole rock (multiplied by the weight fraction of this liquid), plotted on a logarithmic scale as a function of the atomic number. (Data from Towell et al., 1965).

(Right hand diagram) Rare earth abundances in the whole rock San Marcos gabbro and in the augite mineral concentrate only (multiplied by its modal abundance) relative to 20 chondrites (Schmitt et al., 1963, 1964) plotted on a logarithmic scale as a function of the atomic number. Also is shown the calculated abundance pattern for a residual liquid after subtracting contribution from augite from the whole rock (multiplied by the weight fraction of this liquid) relative to 20 chondrites (Schmitt et al., 1963, 1964), as well as relative to the whole rock San Marcos gabbro, plotted on a logarithmic scale as a function of the atomic number. Data from Towell et al., 1965.

San Marcos Gabbro

- Whole Rock
- Augite   } weighted by modal } relative
- Plagioclase (An$_{55}$) } abundances, n_A, n_B } to chondrites
+ Residual liquid x $[1-(n_A+n_B)]$
   subtracting Augite & Plagioclase / whole rock

o Residual liquid x $(1-n_A)$ after
   subtracting augite relative to
   chondrites

+ same as o, but relative to
   whole rock.
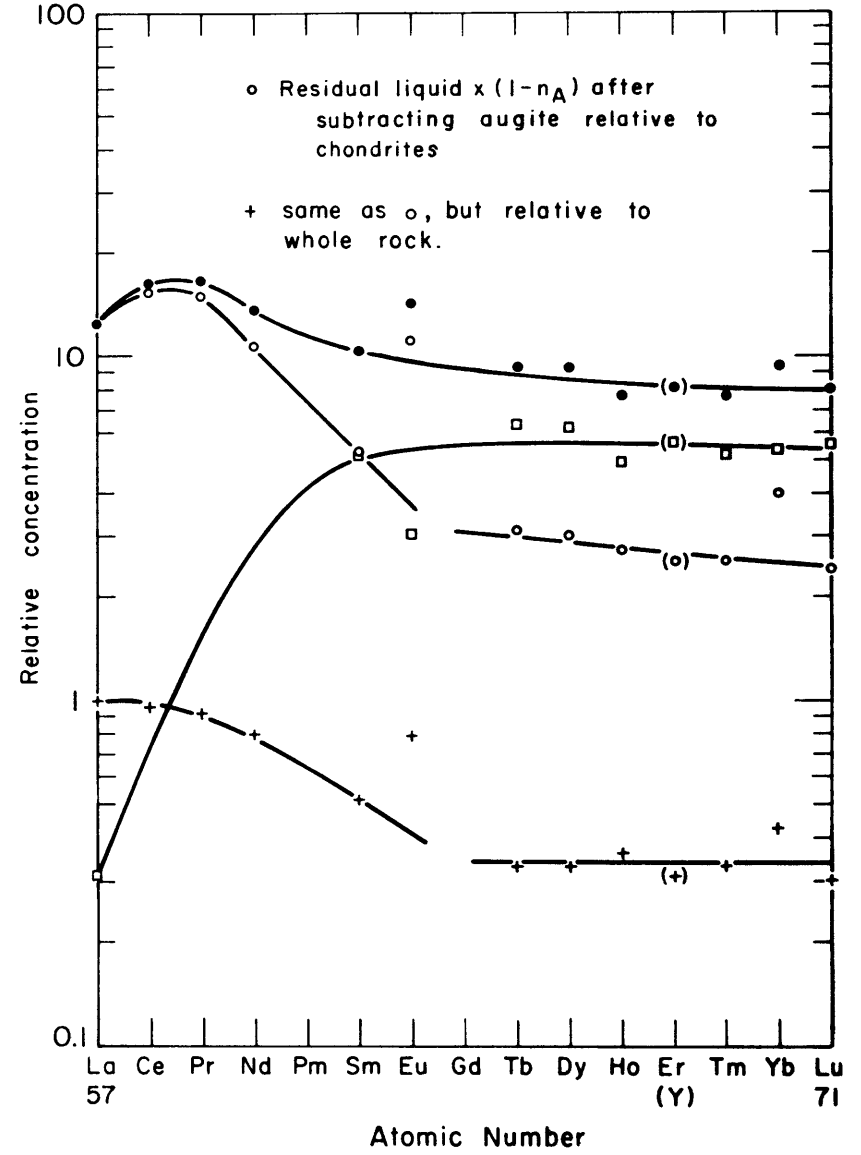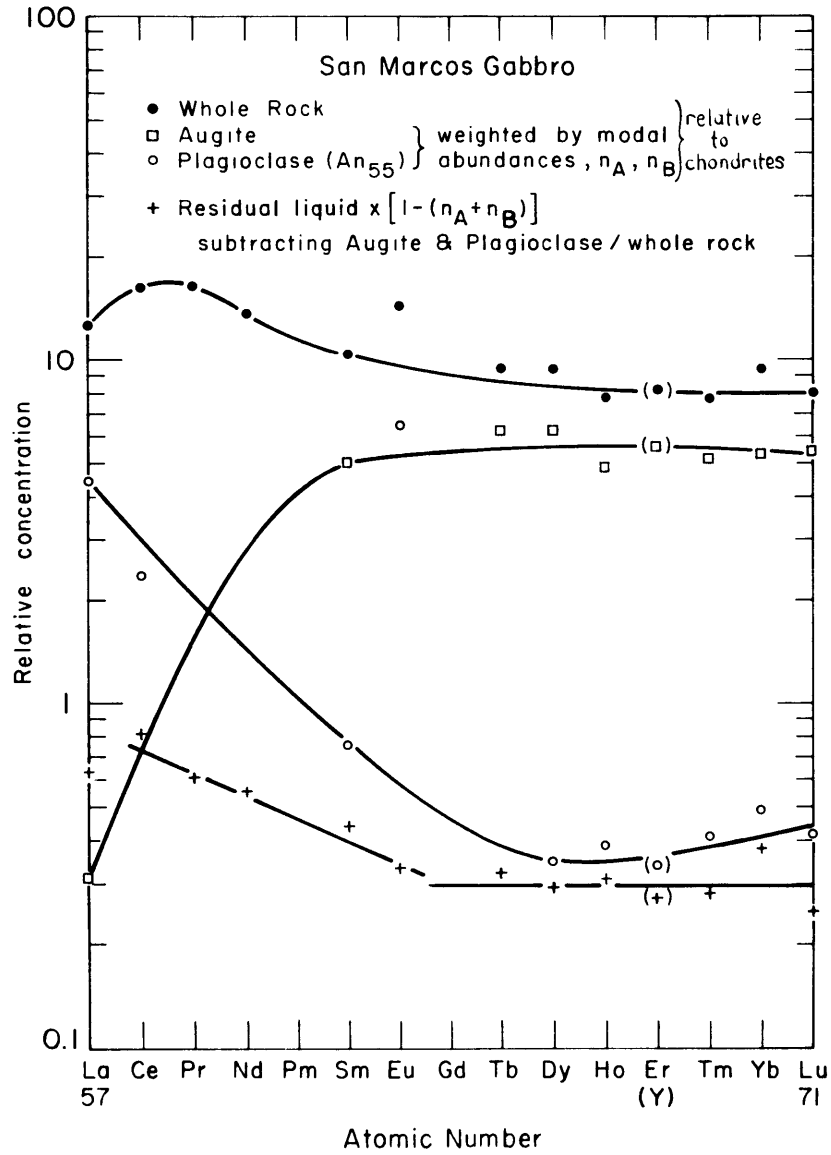
abundances of a mineral to those of the melt at the time
it separated (rarely known), different patterns for this
particular mineral could be expected in different condi-
tions depending on what other phases are separating at
the same time and in which proportions (Part III; Turner
and Verhoogen, p 166, 1960).

Nevertheless, in a purely informative way, Figure
1-14 shows that subtraction of reasonable amounts of
augite (Figure 1-14 left), augite + plagioclase (Fig-
ure 1-14 right), from the San Marcos gabbro whole rock
leads to rare earth patterns of residual liquids show-
ing the heavy element horizontal trend, the break in the
middle, and increasing rare earth concentrations in the
region of light elements from Gd to La. It would there-
fore appear that development of a rare earth distribution
with a break in the middle and a horizontal heavy element
trend may be produced in the residual liquid by Calcium
mineral crystallization.

Substitution of trivalent rare earths for Calcium
sites with a preference for the heavier elements is plaus-
ible in the light of ionic radii. Goldschmidt (1954) gives
the radii La+++ 1.14, Gd+++ 1.11, Lu+++ 0.99, Ca++ 1.06,
Mg++ 0.78, and Fe++ 0.83 Angstrom units. Rare earths of
radius similar to and smaller than Calcium may substitute
for Ca++ site or vacancies without fractionation, but
larger ions may be discriminated against to a degree in-
creasing with increasing radius. As crystallization pro-
ceeds and clinopyroxenes and limited amounts of plagioclase

are removed from the tholeiitic liquid, the residual
liquid should develop the pattern of the basanites,
alkali olivine basalts, and hawaiites showing the
break in the middle and the horizontal trend for the
heavy elements, according to this simple model.
(Schilling and Winchester 1966a).

It is well recognized that the characteristic
phenocryst found in this series are mainly olivine, augite
and plagioclase. The rare earth abundance in olivine is
expected to be very low (see below). Addition or re-
moval of this mineral from the melt should have only a
diluting effect on this latter, and therefore should
not change appreciably the rare earth pattern of the
melt unless a relatively great proportion is involved.

The ankaramite has generally been considered to
form by some accumulation of olivine and augite pheno-
cryst in a melt probably of alkali olivine composition.
Judging from the norms (Appendix B), approximately
7% augite, 4% olivine and 12% of plagioclase would have
been added to a melt of alkali olivine composition. The
ankaramite and the two alkali olivine basalts analyzed
have identical rare earth abundances to within ± 20%.
Thus it would appear that addition or removal of small
amounts of these phenocrysts will not change appreciably
the rare earth pattern of the related melt. Rough cal-
culations based on augite and plagioclase rare earth com-
positions of the San Marco's gabbro and for the olivine
from the olivine nodules (see below), do not contradict

this statement.

The basanite-basanitoid basalt group, which were found to be identical in the rare earth content to the alkali olivine group to within $\pm$ 25%, was included in the alkali series. This is rather intriguing, since these lavas are usually closely associated in the field with the nepheline-melilite group. Nevertheless, their rare earth patterns are definitely related to the alkali trend. More detailed studies of these rocks should perhaps reveal whether or not this is of genetic significance.

It is interesting to note that the trachyte pattern seems to be a modified form of the alkali series, particularly by having a positive slope in the heavy element region (Figure 1-10). Moreover, La-Rb, La-Sr and Rb-Sr variations also show a departure from the alkali trend for the trachyte (Appendix E).

Based on field study, Daly (1925) suggested that in oceanic islands rocks of intermediate composition between basalt and trachyte are much less common than trachyte. Barth (1939) pointed out that Washington's per cent analyses of Hawaiian lavas showed an unfilled gap between 53 and 58 per cent SiO_2. This point was re-emphasized by Turner and Verhoogen (1960, p. 199). More recently, Chayes (1963) has called attention to the distinctly bi-modal distribution of major element analyses of oceanic volcanics about two maxima, one basaltic and the other trachytic. He showed a clearly defined central minimum of SiO_2 sample distribution and an even more pronounced

minimum for CaO (see also Harris, 1963, for discussion
of Chayes's paper). These authors concluded that al-
though fractional crystallization could explain the com-
plete chemical gradation from olivine basalt to mugearite,
the trachyte could not have been derived from the alkali
series by this process alone.

The variation diagrams in Figures 1-11 and 1-12
show that although there is a progressive increase of
La with increasing indexes of differentiation, La and
other light rare earths stay practically constant (or
decrease slightly) from mugearite to trachyte. On the
other hand, the heavy rare earths of the trachyte show
a noticeably marked increase with increasing atomic
number (Figure 1-10). This phenomenon is also observ-
able in some late differentiates such as syenitic and
granitic rocks, and needs explanation. The role of vola-
tiles, in particular water, may be important in determin-
ing the distribution of rare earths inasmuch as the
smaller ions form stronger complexes in solution. Peg-
matites (Sahama and Vähätalo, 1939) have been observed
to have a strong enrichment of the heavy rare earths,
in contrast to granitic and syenitic rocks which are Lae
enriched. This difference may reflect the presence of
volatiles in the late stages of differentiation.

It is interesting to note that according to Shand
(1933) and Turner and Verhoogen (1960), some mechanisms
involving boiling of an increasingly aqueous residual
liquid under reduced pressure is strongly suggested for

the formation of trachytes. As the most reasonable alternative to crystal fractionation, Chayes (1963) proposed partial melting, but also pointed out a variety of objections to such a mechanism. In the same vein, Bailey and Schairer (1966) have argued in favor of partial melting. They emphasized that the trachyte could represent the optimum fraction during progressive melting. This would represent the stage at which the available volatiles exert their maximum influence. Thus it would appear that the rare earth evidence bearing on the origin of trachyte is in agreement with other evidence as far as pointing out the influence of volatiles. Perhaps crystallization of a new phase other than augite, olivine and plagioclase could also explain the heavy rare earth rise in late residual liquids. Assimilation as another possible process will be discussed later. Only one trachyte was analyzed in this study. Obviously more data are needed for a satisfactory explanation of the heavy rare earth abundance rise in late differentiate and its possible bearing on petrogenesis.

A partial melting mechanism bearing on the trachyte problem will be discussed below.

Nepheline-melilite basalts

Rocks of this family are rare in the oceanic provinces. In terms of volume they are insignificant. They appear only in late stages of renewed volcanic activity. In

Hawaii they occur only in the island of Oahu (Hono-
lulu series) and in Kaui (Koloa series), (Winchell,
1947).

The remarkable exponential decrease of the rare
earths (linear on semi logarithmic diagram), the great-
est lighter rare earth enrichment, and the maximum
fractionation make this group quite distinct from the
others (Figures 1-2, 1-9). Moreover, Powell et al.,
(1965) reported a somewhat distinct and smaller
Strontium 87/86 isotopic composition relatively to
the other hawaiian lavas for the very same samples.
The particular character of this family is also
portrayed in Figures 1-11 and 1-12.

Based on theoretical considerations (Masuda and
Matsui, 1966; Part III; and Schilling and Winchester,
1966b) this type of pattern is characteristic of resid-
ual liquid products of extreme fractional crystalliza-
tion, or of very small degrees of partial melting, of
presumably upper mantle material (Part III and
Schilling and Winchester, 1966).

No entirely satisfactory hypothesis for the origin
of nepheline-melilite basalts has yet been put forward.
Assimilation of sedimentary material (Daly, 1944),
fractional resorption of hornblende and micas (Bowen,
1956) and fractional crystallization in particular condi-
tions are among mechanisms evoked most often. Fraction-
al resorption and assimilation will be discussed later.

Yoder and Tilley (1962) have shown that there is

apparently a thermal divide between SiO_2 undersaturated and critically undersaturated magma types. The problem lies in how a single primary liquid of, e.g. olivine tholeiitic composition, can produce both nepheline bearing products and silica bearing products. Mechanisms such as liquid crystal separation, effect of pressure on melting relations and thermal divides, certain solid solution variations and oxidation conditions were discussed in detail by these authors and O'Hara and Mercy (1963), O'Hara (1965) and Abelson (1961-1965).

One may ask: how can the rare earths shed light on such problems? Bowen (1956), Yoder and Tilley (1962), O'Hara and Mercy (1963) and O'Hara (1965) pointed out that very different schemes of crystal differentiation should be considered depending in what mineral facies or at what depth the melts evolved. Thus at low pressure, the production of residual liquids will depend upon the physico-chemical properties of the feldspar series, hypersthene-augite pyroxene series and olivine. At greater depth in the eclogitic facies, complex solid solution of garnets and enstatite-jadeite pyroxenes in addition to olivine should be considered.

Thus as previously, information may be gained on the genesis of these rocks, by examining the rare earth mineral data of interest. Unfortunately such data are very scarce. Keeping in mind the restrictions discussed in the previous section in using such an approach, it would appear that the Calcium crystallization model cannot

account for the nepheline melilite basalt pattern which shows no break in the middle. (Figure 1-10). This is consistent with the suggestion that these lavas are derived from greater depths (Yoder and Tilley, 1962), and somewhat substantiated by Powell et al. (1965) from Sr^{87}/Sr^{86} isotopic data.

Holmes and Harwood (1932), Powers (1935), Winchell (1947), Macdonald (1949a), Green and Ringwood (1964) and O"Hara (1965) suggested that crystallization and removal of excess orthopyroxene from olivine tholeiitic magmas may lead to nepheline normative residual liquids at intermediate or great pressures. This mechanism was criticized by Tilley (1950) and found improbable by Yoder (1964) on experimental evidence. No rare earth data is yet available for orthopyroxenes. Nevertheless, following this possibility, we may ask how fractional crystallization of Mg^{++} and Fe^{++} minerals will affect the rare earth pattern of the residual liquid. Because the cation sites of orthopyroxene are smaller than the smallest rare earth, progressive discrimination against rare earths with increasing radius may be expected over the entire range from Lu to La. We may expect the residual liquid to be enriched in the rare earths to a degree which increases with increasing ionic radius. The observed nepheline melilite basalt pattern would be consistent with this model.

Another mechanism at high pressure was put forward by Yoder and Tilley (1962). They show that in the eclogite facies early removal of garnet (which contains

most of the normative anorthite, hyperstene and olivine) from a melt of eclogitic composition, would lead to a residual liquid of alkali character. Recently, Haskin et al. (1965), reported rare earth analyses of a Japanese eclogite and its mineral fractions garnet and pyroxene (presumably omphacitic). Although the "whole rock" analysis is almost not fractionated but enriched by a factor of 6 relative to chondrites, the mineral fractions are strongly fractionated. The pyroxene shows a strong preference for the lighter rare earths ($La_{px} = 17XLa_{chondrites}$) which decrease gently from La to Sm ($Sm_{px} = 8XSm_{chondrites}$) and then drop rapidly to Tm ($Tm_{px} = 0.17XTm_{chondrites}$). On the other hand, the garnet fraction shows a marked enrichment of the heavy rare earths, which decrease gently from Lu ($Lu_{garnet} = 16XLu_{chondrites}$) to Sm ($Sm_{garnet} = 8XSm_{chondrites}$) and somewhat more rapidly but irregularly to La ($La_{garnet} = 2.6 La_{chondrites}$). This preference for the heavy rare earths by the garnet is somewhat expected from synthetic Mn, Mg, Fe rare earth garnets which show greater stabilities for the heavy rare earths. (Yoder and Keith, 1951; Bertaut and Forrat, 1956, a and b; Warshaw and Roy, 1959 and 1962). Other garnets (Goldschmidt & Peters, 1931; Sahama, 1936; and Gavrilova and Turanskya, 1958) also show a preference for the heavy rare earths.

Thus crystallization and progressive removal of garnet from a melt already slightly enriched in the lighter rare earths would tend to deplete the heavy rare

earth end relative to the lighter one. This would therefore lead to the characteristic nepheline-melilite rare earth pattern at lower pressure. This simple model would also support this second mechanism for the production of alkali nepheline normative liquids.

Before such arguments are carried further more rare earth data on minerals of interest are required. Moreover, we need experimental work to study rare earth partitioning between silicate minerals and melts under various conditions.

Tholeiite group

Despite small variations in major element chemistry, this set of samples have very uniform rare earth patterns. This pattern is characterized by a broad maximum enrichment of the lighter rare earths relative to chondrites near Nd, followed by an exponential decrease (linear, on semi logarithmic paper) of the enrichment factor with increasing atomic number from Sm to Lu, as shown in Figure 1-2 and Figure 1-3.

This group on the average is characterized by the lowest abundance and least fractionation of rare earths of all the lavas analyzed. It is the most abundant lava type of the Hawaiian Islands (> 90% in volume) and appears first in the volcanic sequence (shield-building stage). If the other lava types were to be derived from a single primary magma by fractional crystallization,

the tholeiite group would be the most obvious choice
(Turner and Verhoogen, 1960) and in particular the olivine-
tholeiite (Yoder and Tilley, 1962). The rare earth data
supports this hypothesis. Figure 1-10 shows that, within
the group, relative to the olivine tholeiite, the rare
earth patterns of the other tholeiites, including the dia-
base from the Palolo quarry, are practically not frac-
tionated; although absolute abundance levels are higher
up to a factor of about two.

It is generally accepted that the chemical variation
in the tholeiitic series is produced by addition or sub-
traction of olivine. (Macdonald, 1944, 1949a; Powers,
1955). However, Muir, Tilley and Scoon (1957) suggested
that it is also necessary to extract some pyroxene and
plagioclase in small amounts. If only olivine is in-
volved, the rare earth data on the tholeiite would indi-
cate that either the rare earth content in olivine is
very low or that its rare earth pattern is identical to
the tholeiite. Thus addition or removal of this mineral
would not change the relative rare earth distribution.
The two olivine nodules (although not composed of 100 per
cent olivine) set an upper limit for the rare earth con-
tent of this mineral. The rare earths in olivine is ex-
pected to be at least 100 times lower than the tholeiite
with perhaps a slight preference for the heavy rare
earths. Thus, it would appear that addition or removal
of olivine would have only a diluting effect without
changing the relative rare earth pattern.

The lack of a break in the middle of the rare earth series for the tholeiites (Figure 1-10) precludes the possibility of extraction of large amounts of plagioclase and augite in the differentiation of the tholeiites. However, extraction of only small amounts of these minerals cannot be excluded since it cannot be detected by the presently available rare earth data alone (see previous discussion regarding the ankaramite).

Powers (1955) has argued, on the basis of detailed chemical and geological data and in particular on SiO_2 variations, that the different primitive shield-building lavas came from different magma batches. Although the chemical variation between different flows of the same batch could be explained by differential movement of olivine, the variations between batches could not. The samples analyzed in this study cover three different areas: Oahu (Koolau series), Mauna Loa and possibly the Pele's hair from Kilauea volcano. Although these three sets of samples have almost undistinguishable relative patterns their absolute rare earth abundances differ slightly. Figures 1-11 and 1-12 and other variation diagrams show that La in tholeiites (and other rare earths as well) shows no systematic variation with indexes of differentiation and other major element variations, (including K_2O, except perhaps TiO_2 which increases regularly from 1.5 to 2.5% with increasing La (5 ppm to 9 ppm). This lack of systematic rare earth variation with major element chemistry, within this series

quite contrary to what is observed in the alkali series where fractional crystallization seems to be well established, would tend to support Powers's hypothesis. Nevertheless, before rare earth data on olivines and other phenocrysts, if present, and tholeiitic rocks with a better sampling coverage, are available, no sure conclusion can be drawn.

Finally, the difference between rare earth patterns of the Hawaiian tholeiites and the Mid-Atlantic tholeiites (Frey and Haskin, 1964; Haskin et al., 1965) merits comment.

(Engel et al. (1965), have pointed out clearly some of the important chemical differences between the oceanic ridge or rise tholeiites and the tholeiites forming the large shield volcanoes, the so called "intermediate types". Figure 1-1 shows the K_2O-SiO_2 relations of our analyzed Hawaiian tholeiites and Engel's arbitrary field of his so called "oceanic tholeiites", as well as the alkali field. The average rare earth abundances of the Mid-Atlantic ridge basalts (Haskin et al, 1965), the Hawaiian tholeiites and the Hawaiian alkali and SiO_2 rich differentiates (hawaiites, mugearite and trachyte) are compared in Table 1-2. Figure 1-15 shows also two typical rare earth patterns in Mid-Atlantic tholeiites relative to the chondrite averages. The reader is referred to Figure 1-2 for comparison with the Hawaiian olivine tholeiite and to Figure 1-3 for the other Hawaiian tholeiites.

The rather "flat" relative rare earth patterns in

TABLE 1-2. Rare earth concentration averages in Mid-Atlantic ridge tholeiite, and Hawaiian tholeiites are compared with alkali and SiO_2 rich Hawaiian lavas.

	Mid-Atlantic Ridge Tholeiite Average	Olivine Tholeiite Hawaii	Hawaiian Tholeiite Average	Alkali and SiO_2 rich Hawaiian lavas Average
La	4.7	5.3	7.2	36.9
Ce	15.9	-	-	109.9
Pr	2.36	2.56	3.42	12.8
Nd	14.08	12.78	17.58	53.36
Sm	4.9	3.74	4.62	10.68
Eu	1.88	1.28	1.63	3.30
Gd	6.96	-	-	-
Tb	1.38	.663	.82	1.41
Dy		3.72	4.17	8.54
Ho	1.7	.574	.725	1.35
Er	4.93			
Tm	.82			.55
Yb	3.94	1.26	1.69	3.04
Lu	.74	.191	.24	.451
Y	39.0	16.42	18.96	36.77

Figure 1-15.   Abundances of the rare-earth elements rela-
tive to 20 chondrites (Schmitt et al., 1963, 1964) in 2
Mid-Atlantic Ridge tholeiites, plotted on a logarithmic
scale as a function of the atomic number.   Data from F. A.
Frey and L. A. Haskin (1964) and Haskin et al. (1965).

Mid Atlantic Ridge Tholeiitic basalts

● GE60

○ D-2-1-b

Data from Frey + Haskin 1964
Frey + Haskin + Poetz 1965
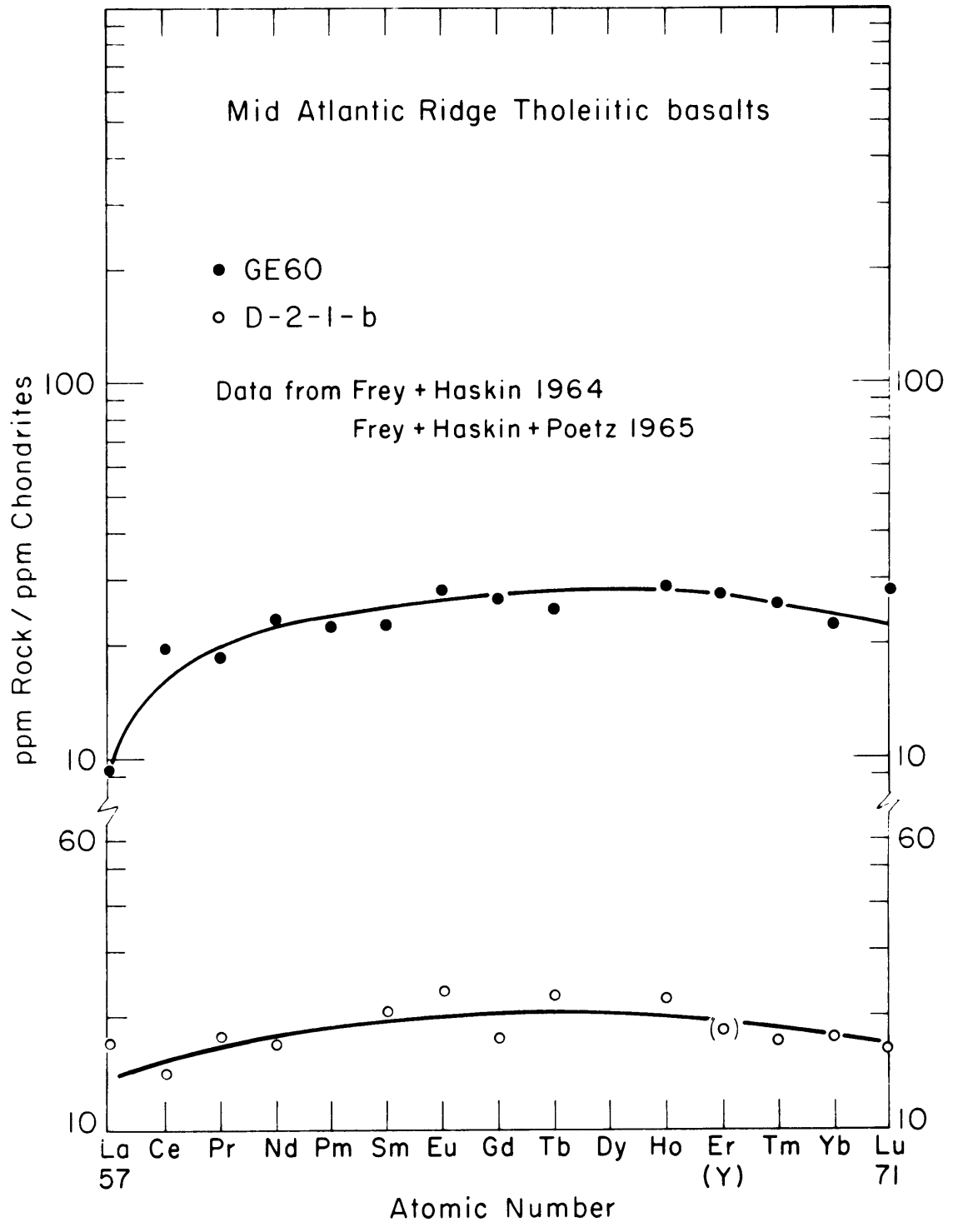
the Mid-Atlantic ridge basalts led Frey and Haskin (1964) to believe that these basalts are "nearly undisturbed chondritic rare earth distribution patterns" and that these "oceanic basalts are decidedly primitive". This statement of far reaching consequences was criticized by Morgan and Lovering (1965) and Lovering and Morgan (1966) on the basis of other trace element data (see reply, Haskin and Frey, 1966). Closer examination of these latter tholeiites, indicates the heavy rare earth concentrations to be very high, some 30 times higher than chondritic and 3 times higher than Ca-rich achondritic concentrations and as high as Hawaiian late alkali differentiates (Table 1-2) and many granites (Towell et al., 1965; Haskin et al., 1965). Rather than being primitive, it seems more likely that these tholeiites are quite differentiated but such that the relative rare earth patterns are only slightly fractionated. Table 1-2 shows that although the lighter rare earths, from La to Nd (i.e. the large ions) in the ridge basalts are slightly lower than in the Hawaiian tholeiites (10 to 50% lower), the heavy rare earths (i.e. the smaller ions) are relatively quite enriched (up to a factor of 3). Thus it would appear from the rare earth and other trace element data that the ridge basalts are somewhat depleted in large ions and enriched in small trace element ions. This anomalous behaviour of small ions may have far reaching consequences on the interpretation of the origin of these lavas (Appendix E).

Engel et al. (1965) have suggested that the oceanic ridge basalts are the principal or only primary magma generated in the upper mantle under the oceans. They argued that the shield building tholeiites, including those in Hawaii, followed by the alkali cap differ- entiates are derived from this primary magma. Al- though this mechanism seems plausible in the light of data on trace elements of large ionic size, data on the heavy rare earths or relatively small ionic size put strong restrictions on such a possibility; at least as far as Hawaiian volcanism is concerned. The fact that the ridge basalts have heavy rare earth con- centrations as high or higher than the late alkali and silica-rich differentiates, and definitely higher than the Hawaiian tholeiites, does not support Engel's views on the origin of oceanic volcanism as applied to the Hawaiian Islands. Table 1-1 clearly shows that there is a definite progressive enrichment of all the rare earths, including the heavy ones (although to different degrees), with increasing differentiation in the order tholeiite, alkali olivine basalt, hawaiite and mugearite- trachyte. This is expected from geochemical reasoning.

These fundamental chemical differences between Mid-Atlantic ridge basalts and shield building Hawaiian tholeiites seem to require very different mechanism of formation or derivation from different sources (Part III and Schilling and Winchester, 1966b).

In addition a process akin to zone melting (Part III;

Schilling and Winchester, 1966b), another possible process,
in analogy to pegmatites, would involve volatiles or
water which may complex the heavy rare earths preferential-
ly in solution. Partial melting of serpentinites or
amphibolites at shallow depth with evolution of volatiles
may have been important in the Mid-Atlantic Ridge, where-
as in Hawaii, where earthquake foci are at greater depth
(Eaton & Murata, 1960; Heezen, 1960; and Heezen & Ewing,
1960) silicate melts may have been relatively dry. In ad-
dition, eruption of lavas under a high column of water
should prevent, to a certain extent, exsolution of vola-
tiles, relative to lavas erupted under 1 bar atmospheric
pressure. The presence of hornblende in the source rocks
may well turn out to be of fundamental importance in the
genesis of these lavas. Only one rare earth analysis of
hornblende is yet available (Towell et al., 1965). It
is quite enriched in the heavy rare earths relative to
the lighter end of the series. However, this particular
hornblende is in obvious reaction with augite which is
also relatively high in heavy rare earths. The crystal-
chemical properties of hornblende are complex and great
compositional variations are usually found for different
geological and experimental conditions (Colville and Ernst,
1966; and Hart et al., 1965). Thus, present data can
hardly be applicable to this discussion and must await
additional data before continuing such scrutiny. Data
on hornblende minerals as found in the ultramafic rocks
of the St. Paul Island on the Mid-Atlantic Ridge (Tilley,

1947, 1966; Hart 1964) and others may well shed some light on the origin of the oceanic ridge tholeiites.

Finally, it is interesting to note that the olivine tholeiite rare earth composition is identical to the Delegate eclogite (Schmitt et al., 1964), Figure 1-3, Part III, to within $\pm$ 20%. With the present experimental data available, there is no way of proving that this eclogite represents the composition of an undifferentiated liquid by partial melting of the upper mantle; but yet, there is good evidence that it is approaching it (Yoder and Tilley, 1962; O"Hara, 1963a; and Davis, 1964). These authors have also shown that very different residual melts are produced depending on the pressure at which the melt is crystallizing. Thus, the similarity of the rare earths in these two rocks suggests that melts similar to the tholeiitic composition can exist at depth and perhaps that the tholeiitic melt was not fractionated appreciably at shallower depth during its journey to the surface.

PARTIAL MELTING

The three groups of lavas discussed previously can be either the product of partial melting or fractional crystallization (Yoder and Tilley, 1962; O'Hara and Mercy, 1963; O'Hara, 1965). Freezing and melting under the same conditions is, in principle, a reversible process. Therefore, complete melting of

a rock followed by crystallization in a closed system,
leads to a residual melt indistinguishable from the one
formed by a small degree of melting of this same primary
rock. Theoretical considerations (Part III; and Schilling
and Winchester, 1966b) show that the rare earth patterns
formed by different degrees of melting or fractional
crystallization are practically indistinguishable. Never-
theless, some clues on the possible origin of the different
groups of Hawaiian lavas can be gained by considering the
relation between the absolute rare earth abundance of the
melt, the degree of melting and the volume and sequence
of lavas erupted.

The concentration C_L of a given trace element in the
liquid in terms of the primary material composition, C_p,
and the fraction melted, $0 \leq y \leq 1$, at fixed T and P, and
assuming complete equilibration (Berthelot, 1872; Nernst,
1891) is given by $C_L = \dfrac{C_p}{y + D\ (1-y)}$ (1-1)

where $D(T,P,y) = C_R/C_L$ is the joint effective partition
factor between the entire residual solid and the liquid,
Or, $D = \sum\limits_{n=i+1}^{n} p_i D_i$, where p_i is the modal fraction of mineral
or phase i in the residual solid, and D_i is the partition
factor between phase i and the melt. A further discussion
of the variation of the parameter D with temperature, pres-
sure, degree of melting, composition of the melt and appear-
ance or disappearance of individual phases, is given in
Part III. Equation 1-1 shows that for a given D value,
the concentration of a trace element in the melt formed
by partial melting, will decrease with increasing degree

of melting. The smooth rare earth fractionation patterns imply regular variations of individual rare earth partition factors with the atomic number Z, where D_{La} < D_{Ce} < D_{Pr} ...... < D_{Lu}, and a value of D_{Lu} not too far from one, since not much abundance variation is observed for Lutecium (Masuda & Matsui, 1966; Part III; and Schilling and Winchester, 1966b).

Therefore the olivine tholeiitic group may be interpreted as the product of a large degree of melting of presumably the low melting portion of the upper mantle. The other tholeiites, from the same magma batch, would be the product of fractional crystallization of mainly olivine. The alkali olivine basalt would represent a smaller degree of melting than the tholeiitic group, from source material of identical composition but at different pressure or depth. Finally, the nepheline-melilite basalts would represent only a very small degree of melting of this low melting portion of the upper mantle, presumably at still greater depths. Thus the primary material need not be of very different composition. The different series may be explained by different degrees of melting to satisfy the trace rare earth concentrations, and different depths or pressures to satisfy major element oxide compositions and thermal divides requirements (Yoder and Tilley, 1962). Within a certain facies, slightly different degrees of melting would produce melts with slight chemical variations but

belonging to the same series. The olivine tholeiite with lower rare earth concentrations would represent a slightly greater degree of melting than the other tholeiites. This is in good agreement with Reay and Harris's (1964) experiment of partial fusion to different degrees of material of peridotite composition at low pressure, and Power's (1955) arguments for different tholeiitic magma batches of slightly different composition.

The rather remarkable compositional constancy of tholeiites in the earth may imply that the liquidus surfaces of source materials increase rapidly after a certain point, and that there is rarely enough energy available to overcome this increase of temperature with change of composition; rather than having always the same amount of energy available to produce similar compositional melts. The alternative would be, of course, to have complete melting of the source region of similar composition, or that these melts are residual liquid products of fractional crystallization (O'Hara, 1965).

A strong degree of melting implies large volume of melt. Chayes (1963) has emphasized this point in discussing the trachyte problem. A statistical approach is of fundamental importance in order to determine the relative volume of the different types of lavas. It is interesting to note that the sequence of volcanic activity, and corresponding relative volumes and types of lavas generally recognized in Hawaii (Stearns, 1940, 1946; Macdonald 1964) is consistant with degrees of melting inferred from the

rare earth data.

The source of energy or mechanisms required to induce melting are poorly understood (Yoder, 1952; Powers, 1955; Uffen, 1959) and need not be discussed here. Nevertheless, the change of intensity of melting, as inferred from the rare earth relative to the sequences of Hawaiian volcanic activities, would require rapid increase of melting energy to produce the tholeiitic stage followed by recurrent increases of much smaller intensities at different source regions to produce the alkali stage and negligible amount of nepheline bearing lavas by partial melting. If stress release or drop of pressure is considered to bring about melting (Yoder, 1952; Uffen, 1959) this sequence would require a pronounced decrease of pressure followed by mechanical readjustment and small sporadic decreases of pressure with time.

Stearns (1940, 1946); Macdonald (1964) have pointed out that the first primitive shield-building stage of Hawaiian volcanoes is always tholeiitic in composition and that intermediate stages or late stages are not necessarily present in all volcanoes. The chance for a large volume of melt to reach the surface is great relative to a small volume of liquid produced by a small degree of melting. The latter has greater probability of being trapped at depths unless channels have been opened by the rise of large volumes of tholeiitic melt. This may perhaps also explain the

sequence of eruption of different lava types. This reasoning may perhaps lead to the belief that production of melts by small degrees of melting is greater than one might infer from surface occurrence alone!

Finally, the similarity of the rare earth patterns in the olivine tholeiite and the Delegate eclogite (Schmitt, 1964) might suggest that the tholeiite lavas are not far from being unfractionated melts produced in the upper mantle by partial or complete melting although this may be pure coincidence.

Besides the possibility of different degrees of melting the change of composition of this group of lavas could also be produced by melting in different pressure or depth facies (Yoder and Tilley, 1962; O'Hara and Mercy, 1963; O'Hara, 1965; MacGregor, 1965; Abelson, 1960, 1965). Melting at different depth where the composition of the primary source rock is changing is another possibility (Kuno et al., 1957).

Because of the great rare earth selectivity of common rock forming minerals and the difference of mineralogy with changing facies (inferred from experimental petrology) the rare earth patterns of lavas directly derived from the upper mantle should reflect the rare earth composition of the upper mantle and perhaps its mineralogy. Nevertheless, the lack of such rare earth mineral data and lack of complete theoretical understanding of partition of trace elements precludes further discussion. Only with the aid of experimental petrology, additional rare earth

and other trace element mineral and rock data, and
experimentally determined trace element partition
data under controlled conditions for systems of
interest one could perhaps distinguish between pro-
cesses by which lavas are formed and differentiated.

OLIVINE-RICH NODULES

Two olivine-rich nodules were analyzed. The rare
earth abundances are given in Table 1-1, column 22
and 23 and their patterns relative to chondrites in
Figure 1-16.

Hualalai Nodule:

The 1801 host basalt has also been analyzed and
its pattern is typical of the alkali olivine basalts.
Although several rare earths were not determined, the
relative pattern of this nodule is roughly identical
to the host basalt, but the absolute rare earth
abundances are 100 times lower. This light green in-
clusion has sugar granular texture and is very friable.
It is composed mostly of olivine grains (98%, averaging
1.5mm in diameter.) It can be called a dunite. Very
conspicuous dark green grains were present but could
not be identified, beside about 1% of opaque minerals.
Other nodules from this locality are described by
Macdonald (1949a, 1553); Macdonald (1949b, p 76);
Cross (1919, p 35) and Ross et al. (1954, p 697).

Figure 1-16. Rare earth abundances in 2 olivine rich nodules relative to 20 chondrites (Schmitt et al., 1963, 1964) plotted on logarithmic scale as a function of the atomic number. Both curves are averages of duplicate analysis . Vertical bars represent extreme deviations of each element from the mean.

Figure showing ppm Rock / ppm Chondrites versus Atomic Number.

Y-axis: ppm Rock / ppm Chondrites, ranging from 0.01 to 10.

X-axis: Atomic Number — La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu, 57 (Y) 71

- Olivine Nodule, Salt Lake Crater, Oahu
  (Average of 2 analyses)

○ Olivine Nodule, Hualalai, Hawaii
  (Average of 2 analyses)
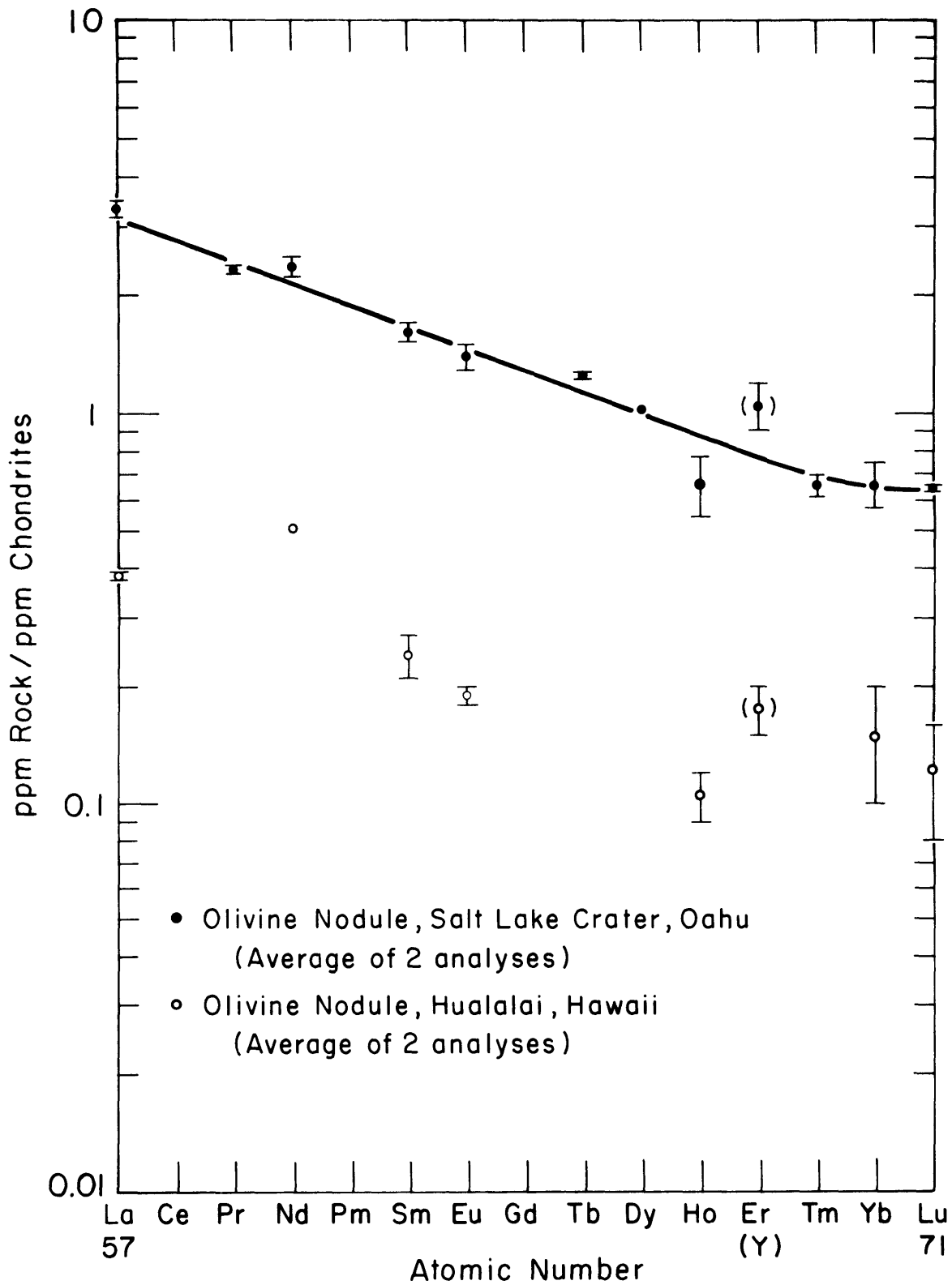
Great variations in proportions of olivine and pyroxene
are reported. This rare earth analysis gives an upper
limit for the rare earth content of olivine and is pro-
bably not too far off being representative of this mineral.
U, Th and Pb concentrations for this particular inclusion
and the 1801 host lava flow are reported by Tilton and
Reed (1963).

Salt Lake Crater Nodule

Nodules from this locality, which occur in tuffaceous
beds, are described by Winchell (1947, p 13); Macdonald
(1949a, p 1553); Macdonald and Katsura (1964, p 102) and
Ross et al. (1954, p 697). They are very variable in
mineralogy and modal abundances. This particular sample
was composed of 70-75% of light green olivine grains and
irregularly distributed dark bottle green mineral grains.
This mineral was hand picked and identified as enstatite
by the X-ray powder method. No further effort was made
to determine whether dioside-augite mineral was present
or not. Both grain types averaged 3mm in diameter.
Small calcite veinlets were observed in altered regions,
but were avoided for analysis. It can be classified as
peridotite. The relative rare earth pattern is roughly
identical to the Hualalai nodules, but the absolute con-
centrations are ten times higher, or ten times lower
than alkali olivine basalts. These absolute abundances
and relative rare earth distributions of this nodule are

similar to one of the three samples from St. Paul Rocks (Brazil) reported by Haskin et al. (1965, sample PI1), although the other two are quite different. Palladium content of this inclusion is available (Crocket, personal communication).

Three possible origins are generally considered for ultramafic inclusions (Forbes and Kuno, 1965, namely: they are primary mantle material, residual material after extraction of the basaltic component portion (low melting portion) by partial melting, and finally, accumulates of early crystallized minerals from the lavas. It is difficult to decide on the basis of the presently available rare earth data which possibility is most likely. Theoretical considerations on partial melting (Part III; Schilling and Winchester, 1966b) indicate that residual materials should have a maximum enrichment in the intermediate to lighter region of the rare earth series, a marked depletion of La and somewhat less pronounced depletion for the heavy rare earth end of the series. On this basis alone, the fact that these two inclusions are progressively enriched with decreasing atomic number, would exclude the possibility of being residual in nature. The Hualalai sample, which is almost pure olivine, could well be the product of accumulation. Rare earth data on other olivine phenocrysts of the same host basalt would certainly be very informative. Whether the Salt Lake Crater peridotite is primary material of the upper mantle

or the product of accumulation, is hard to decide. If
a chondritic rare earth abundance is assumed for the
earth, the lighter rare earths are enriched by a factor
of three, the intermediate ones roughly equal and the
heavy end of the series depleted by approximately 60%
relative to chondrites. Up to a depth of 400 km it is
expected that the rare earths should be enriched by a
factor of 1.3 to 2 relative to chondrites, without much
internal fractionation except for a slight preference for
the intermediate rare earths. Below this depth, a pro-
gressive depletion of the lighter rare earths is expected
with increasing depth (Part III, Figure 3-11; and
Schilling and Winchester, 1966b). Thus the pattern of
the Salt Lake peridotite seems to preclude the possibil-
ity that this peridotite represents primary material from
the upper mantle. Therefore it would be of accumulative
nature. This is not incompatible with the fact that many
Hawaiian inclusions were found to be stratified with al-
ternating monomineralic layers of olivine and pyroxene
indicating a similar origin to dunite-peridotite layers
of large stratiform lopoliths found in the crust. Never-
theless individual phases of these inclusions should
be analyzed. Much more work needs to be undertaken be-
fore any serious conclusions can be drawn on the nature
of these inclusions.

✓

FRACTIONAL MELTING

Fractional melting, that is to say, successive partial melting of the same source material and removal of the melt each time (Part III; Schilling and Winchester, 1966b), cannot account reasonably for the rare earth variation of the Hawaiian volcanic rocks. It is expected that the rare earth concentrations should decrease with successive stages of volcanic activities; the contrary is observed in Hawaiian lavas which show an increase of the lanthanides in the succession: tholeiites-alkali series and nepheline-melilite basalts, respectively.

MIXING

All of the foregoing discussion has been directed toward processes which could fractionate the rare earths by extraction processes involving solid-liquid equilibria. Mixing of different rare earth abundance patterns, such as by complete assimilation of foreign material by a melt must certainly have taken place. Perhaps the highly differentiated lavas will never be satisfactorily explained unless such processes are considered.

Daly (1944) suggested that nepheline bearing melts (nepheline-melilite basalts) could be produced by assimilation of calcareous sediments. The rare earths in carbonate bearing sediments and limestones are shown in Figure 1-17. These patterns are representative of many

Figure 1-17. Abundances of the rare-earth elements rela-
tive to 20 chondrites (Schmitt et al., 1963, 1964) in
three sedimentary materials and one trachyte from Hawaii
plotted on logarithmic scale as a function of the atomic
number. The two dashed curves represent two basalts from
the Hawaiian Islands shown on Figure 1-2. Data for the
red clay and globigerina tests are from R. Volfovsky
Spirn for the Florida Bay from L. Haskin and M. A. Gehl
(1962).
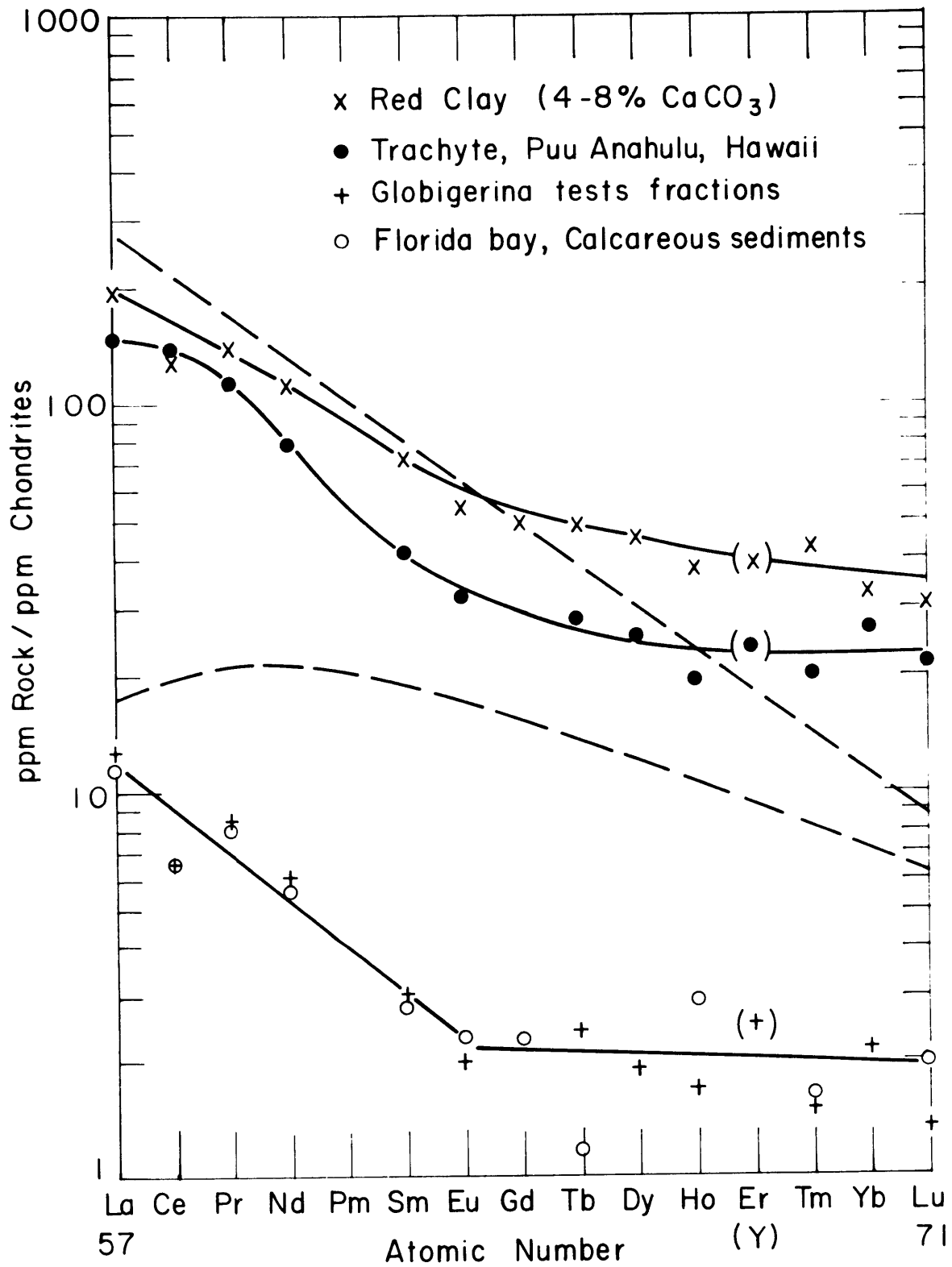
other similar materials (Volfovsky-Spirn, 1965; Haskin
& Gehl, 1962). The pattern of the olivine tholeiite,
trachyte and one nepheline-melilite basalt is presented.
The limestones are very low in rare earth abundances.
Assimilation of such sediments in any proportions can
hardly produce the high light rare earth enrichment and
extreme fractionation observed in the nepheline-melilite
basalts. The low Sr^{87}/Sr^{86} ratios found in the same
nepheline-melilite basalts (Powell et al., 1965) also in-
dicate that assimilation of limestone in proportions neces-
sary to produce the state of SiO_2 undersaturation is un-
likely. This hypothesis has also been rejected on other
evidence (Macdonald, 1949a; Winchell, 1947; Watkinson
and Wyllie, 1964).

No satisfactory explanation for the origin of
trachyte has yet been put forward. It is interesting
to notice in Figure 1-17 that the trachyte pattern lies
in the envelope formed by the red clay sediments and by
the tholeiite (for that matter, the alkali olivine basalt
as well). Thus, assimilation of red clay material by a
basaltic magma could produce the trachyte, as far as the
rare earths are concerned and would be particularly suit-
able in explaining the heavy rare earth rise. The major
element chemistry of the two components is not incompat-
ible with this hypothesis. It could also explain the
somewhat unexpected large volume of trachytes relative
to the other late differentiates (Chayes, 1963). How-
ever, strong objections can also be put forward, e.g.,

it would be difficult to explain the lack of intermediate lavas betweentrachytes and mugearite indicated by Chayes's study. Also the Sr^{87}/Sr^{86} ratio of the same powder sample (Bence, 1966) would not seem to support this hypothesis, although Sr^{87}/Sr^{86} data on red clay sediments on Hawaiian regions is not available yet.

FRACTIONAL RESORPTION

Bowen (1956) suggested that crystals of horn-blende brought into contact with hot magma by convection, could by differential resorption (fusion) give rise to basic liquid notably enriched in nepheline and pyroxene molecule. This is not a likely mode of origin for nepheline basalt containing no trace of hornblende phenocrysts (Turner and Verhoogen, 1960).

No rare earth data on hornblende is available except for Towell's analysis from the San Marcos gabbro (Towell et al., 1965). Although conclusions based on only one hornblende analysis may be premature, judging on this mineral alone seems hardly recommended. It would seem, on this basis alone, that assimilation of such a mineral by a basaltic magma would tend to increase the heavy rare earths of the melt relative to the lighter end of the series. This unlikely process would make it even more difficult to explain the high enrichment of the lighter rare earths characteristic of the nepheline-melilite basalts.

CONCLUSIONS

    1. Independent of other petrochemical evidence, the rare earth patterns relative to olivine tholeiite of Hawaiian lavas points out clearly three distinct groups, and a possible fourth one. These are: the tholeiite series; the nepheline-melilite basalts; the alkali series, which include anakaramites, alkali olivine basalts, hawaiites, and mugearite. The trachyte, a variation of the alkali series, forms the possible fourth group. These groupings coincide remarkably closely with other petro-chemical and mineralogical evidence.

    2. The lighter rare earth abundances were found to increase markedly in the following order: tholeiites, ankaramite, alkali olivine basalts, basanite-basanitoids, hawaiites and mugearite-trachyte. The relative enrich-ment increases with decreasing atomic number or increas-ing ionic radius. Therefore a progressive increase in the degree of fractionation was observed for these rocks, in the same order. Lanthanium was found to increase most rapidly. Except for the nepheline-melilite basalts and the trachyte, the heavy rare earths are not internally fractionated. The variation of their absolute abundances are small and their concentrations increase in the fol-lowing order: tholeiites, ankaramite-alkali olivine ba-salts-basanite-basanitoids, hawaiites mugearite and trachyte. The relative heavy rare earth abundances of the nepheline-melilite basalts decrease with increasing atomic number or the inverse of the ionic radius. The

reverse is found for the trachyte.

3. Based on these patterns alone it cannot be decided for sure whether the alkali series and the nepheline-melilite group are derived from a tholeiitic magma by fractional crystallization under different conditions, or whether these three major groups formed independently by partial melting under different conditions. Additional rare earth data on phenocryst minerals from Hawaiian lavas may resolve this duality. The rare earth similarity of the Delegate eclogite (Schmitt, 1964) and the olivine tholeiite, strongly suggests that melts of tholeiitic composition can exist at depth, and that the tholeiites have reached the surface without further and appreciable fractionation at intermediate depth. Before it can be proved that the Delegate eclogite represents an undifferentiated melt it cannot be assumed that the olivine tholeiite is representative of a primary melt formed in the upper mantle.

4. Within the limits of experimental errors, no Cerium or Europium anomalies were observed for these "whole rock" analyses.

5. Assuming that fractional crystallization was the major process of differentiation, and using rare earth mineral data from other localities, the rare earths indicate: Alkali basalt group may have been derived from tholeiites by crystallization and removal of augite, some plagioclase and olivine, presumably at low pressure, the latter mineral having little effect

on the residual liquid patterns. The formation of trachyte requires crystallization of some other as yet unsuspected new phases or some special conditions possibly produced by increase of volatiles. The nepheline-melilite basalts could be derived from a tholeiitic melt presumably by crystallization of either orthopyroxenes at intermediate or high pressure or garnet at greater pressure. Both possibilities are plausible from rare earth reasoning but cannot be distinguished with the present available rare earth data.

6. Assuming that these three groups were derived independently by partial melting of the upper mantle, theoretical considerations (Part III; Schilling and Winchester, 1966b) would indicate that olivine tholeiite was formed by a large degree or total melting of the low melting portion of the upper mantle; the alkali olivine basalt by relatively a smaller degree of melting of this material but in a different facies and the other members of this group being derived from the alkali olivine basalt by fractional crystallization. Nepheline-melilite basalts would be derived by an even smaller degree of melting of the low melting portion of the upper mantle. The degree of melting of these lavas would be consistent with the relative volumes of lavas erupted and the sequence of volcanic activities recognized in Hawaiian volcanism.

7. Daly's limestone assimilation hypothesis to explain the origin of nepheline-melilite basalts is unlikely on the basis of rare earth patterns of the components

involved.

Bowen's hypothesis of fractional resorption of horn-
blende to produce nepheline-melilite basalts also seems
to be an unlikely process, although rare earth data on
hornblende minerals is needed to substantiate this
point.

Assimilation of red clay sediments by basaltic
magma to produce trachyte is not incompatible with
rare earth patterns of the components involved.

8. Engel's suggestion that the Hawaiian shield-
building tholeiites are derived from oceanic ridge ba-
salts and are intermediate between alkali cap differ-
entiates and these ridge basalts is incompatible with
the heavy rare earth data. The oceanic tholeiites have
rare earth abundances as high or higher than hawaiite-
mugearite-trachyte late differentiates, and much higher
than the Hawaiian tholeites.

The further suggestion that oceanic ridge basalts
are the principal or only primary magma generated in
the upper mantle under the oceans should be abandoned
as far as the Hawaiian Islands are concerned.

Frey and Haskin's (1964) suggestion that the Mid-
Atlantic ridge basalts have "nearly undisturbed chondri-
tic rare earth distribution patterns" and that these
"oceanic basalts are decidedly primitive" should also
be abandoned. Rather than being primitive and unaltered,
it seems more likely that oceanic ridge basalts are
quite differentiated but such that the relative rare

earth patterns are only slightly fractionated.

The presence of hornblende in source rocks or the effect of volatiles and melting of hornblendite or serpentinite is suggested to explain the high heavy rare earth enrichment of Mid-Atlantic ridge basalts.

9. Based on theoretical considerations (Masuda & Matsui, 1963, 1966; Part III of this work; Schilling and Winchester, 1966b), the major Hawaiian lava types conform surprisingly well to a two-stage process for the differentiation of the earth, namely: 1. early crystallization of the mantle and formation of small continental nucleii enriched in the large rare earth ions (Masuda & Matsui, 1963, 1966); 2. Partial melting of the upper mantle to produce basaltic melts through-out geological time (Part III, of this work; Schilling and Winchester, 1966b). On this basis the maximum enrichment near Nd is predicted for the low melting portion of the upper mantle. The slight depletion of the largest rare earth ions relative to the intermediate ones is thus well explained.

The Mid-Atlantic ridge basalts cannot be explained by this model, but a process akin to zone melting (Harris, 1957; Part III of this work; Schilling and Winchester, 1966b) for the differentiation of the mantle in this area is found to fit the rare earth data surprisingly well. The oceanic tholeiite would represent total melting at shallow depth of the upper mantle previously modified by zone melting.

The differences between the Hawaiian shield-building tholeiites and the Mid-Atlantic ridge tholeiites suggest very different volcanic mechanism of formation or source regions of different compositions, or both. It may also suggest that different processes have been operative in different areas for the differentiation of the mantle.

10. Finally, it is remarkable that the four groupings based on rare earth alone coincide so closely with well recognized petrochemical and mineralogical classifications. This raises much hope that the rare earths may be used successfully in conjunction with other techniques such as isotopic work and experimental petrology, in solving some of the problems regarding the evolution of the earth and meteorites. Nevertheless, much more rare earth data on minerals and rocks are needed, as well as experimentally determined partition factors between solid phases and melts, under controlled P, P_{H_2O} and T conditions in systems of interests.

ACKNOWLEDGEMENTS

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PART TWO

A REVISED NEUTRON ACTIVATION PROCEDURE
FOR DETERMINATION OF THE RARE EARTH
ELEMENTS IN ROCKS AND MINERALS

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and J. W. Winchester

ABSTRACT

A revised procedure for determination of the rare earth elements in rocks and minerals is reported.

INTRODUCTION

Work in this laboratory has resulted in changes in the procedure for determination of the rare earth elements from that reported by Volfovsky, et al., 1963.

In the pre-irradiation chemistry, the cation exchange with hydrochloric acid has been replaced by a co-precipitation with calcium oxalate (Gordon et al., 1959) followed by ignition to remove the oxalate and co-precipitation with ferric hydroxide to remove the alkaline earths. As has been described previously, the samples were then passed through an anion exchange column (Dowex 1X-8) 50-100mesh) to remove iron and were then converted to nitrates. (Volfovsky et al., 1963) Chemical yields are generally better than 75% and, with care, can be kept above 90%.

The samples were packaged in nitric acid washed sealed polyethylene tubes (Winchester and Hashimoto, 1965) and irradiated in the pneumatic tube of the MIT Reactor at a flux of $2x10^{13}n/cm^2/sec.$ for three hours.

The post-irradiation separation by reversed phase chromatography was carried out on mixed bed columns containing 25% (by volume) untreated Johns Manville celite (diatomaceous silica) and 75% (by volume) celite which had been made hydrophobic by exposure to vapours of dimethyldichlorosilane and then coated with 15% (by weight) bis-(2-ethylhexyl)orthophosphoric acid

(Winchester, 1963; Towell, et al., 1965). The mixed bed columns packed much more tightly and could be maintained longer. Longer columns were used to provide a greater number of theoretical plates and the drop rate was slowed to provide more time for exchange and thus better separations.

The acid concentrations determined by Winchester (1963) Towell (1963) and Spirn (1965) were changed to promote better separation. In several trial elutions, the position of a particular rare earth (in terms of vial number or ml. of eluant) was plotted against concentration of that rare earth's elution acid. Concentrations were changed to smooth out the curve and space the elution positions more evenly. It was determined eventually that the use of 6 ml. for each of thirteen acids of the particular concentrations listed below gave better separations than the use of fifteen acids, some 4ml., some 6ml.. The acids used are listed in Table 2-1.

An electronic device was designed and constructed to automatically drop in the proper acid at the proper time (Schilling, Jaillet, and Cichocki, 1966; and Appendix D. The samples were collected on a fraction collector having a capacity of 160 planchets on a wheel 2.5 ft. in diameter. The collector, which works on a spiral principle, was designed and built by Salco Electronics, Salisbury, Massachusetts.

The eluant was collected on polypropylene ringed planchets, dried, and counted for beta activity using

TABLE 2-1.

Concentrations of Elution Acids (HCl).

Acid number	Concentration moles/liter
1	0.18
2	0.22
3	0.26
4	0.31
5	0.43
6	0.51
7	0.72
8	1.02
9	1.32
10	1.68
11	2.07
12	3.30
13	3.71

TABLE 2-2.

Rare earths standard solutions.

Rare Earth	Stock solution conc. (mg/ml)[*]	Volume used (micro-liters)	Conc. after 10 fold dilution (g/ml)	Chondrites (Average of 20 - ppm)[**]
La	5.42	500	2.22	.30
Ce	62.6	100	6.26	.84
Pr	.731	1500	1.09	.12
Nd	13.5	400	5.38	.58
Sm	1.41	1300	1.84	.21
Eu	2.45	300	.74	.074
Gd	2.88	1000	2.88	.32
Tb	2.84	200	.564	.049
Dy	15.2	200	3.04	.31
Ho	1.38	500	.69	.073
Er	.626	3000	1.88	.21
Tm	1.27	200	.255	.033
Yb	.700	2000	1.40	.17
Lu	1.45	200	.29	.031
Y	7.34	2600	19.1	1.8

[*] Ehrlich, 1966
[**] Schmitt, et al., 1965.

standard gas flow proportional beta counting techniques. These planchets have the combined advantages of low cost, chemical resistance, heat resistance to 135°C., and translucence allowing labellings on the back to be seen through the material. The planchets were designed in this laboratory and fabricated by Sloane Plastics, Inc., West Concord, Massachusetts.

PROCEDURE

Pre-Irradiation Group Separation. Sample Cleaning and Preparation. The bulk samples were brushed and washed free of surface debris and were ground in an agate or mullite mortar to a mesh size finer than 140. A stainless steel mortar may be used if contamination of low abundance samples is feared.

Sample Dissolution. Up to 500 mg. of sample was weighed into a platinum dish and known amounts of 108 d. ^{88}Y and 140 d. ^{139}Ce tracers, about 250,000 cpm each, were added. Exactly the same amounts of each tracer were diluted, in separate volumetric tubes, to 1.0 ml. with 3N HNO_3 and aliquots were taken for chemical yield determination. About 25 ml. of 48% HF (Transist AR) and 5 ml. of 70% $HClO_4$ (AR) were added, the dishes were heated strongly to 100°C. until dissolution of silicates was obtained, using more HF if necessary. The samples were then taken to dryness, taking care

to prevent conversion of the perchlorates to oxides.
Then 5-10 ml. of 2N HCl was added with heating, followed
by 5-10 ml. portions of water or additional acid was
necessary to dissolve the salts. The samples were trans-
ferred to a 50 ml. polypropylene centrifuge tube.
This entire process takes about four hours.

Separation. 10 mg. of Ca^{++} were added to the samples.
The samples were adjusted to a pH of 1-1.5 with 6N NH_4OH,
and were heated on a water bath. 25 ml. of a previously
prepared solution 2% each of oxalic acid and ammonium
oxalate was added, hot, to the sample solution, and the
precipitate was digested until the solution was clear
(around 10 minutes). A drop of ammonia was added to
check for completeness of precipitation, and the sample
was cooled and centrifuged. The precipitate was washed
twice with 2% oxalic acid, and the combined supernatants
were checked to be sure no significant activity was left
in the solution. Three ml. of 6N HCl were added, and the
sample was heated to dissolve the precipitate, more
acid being added if needed. 6N ammonia was added drop-
wise to the hot sample until a precipitate again formed.
This was digested, cooled, centrifuged and washed as
before.

Now, the precipitate was decanted into a platinum
crucible, dried in an oven at $110°C$. and then ignited
with a Meker burner. After the crucible cooled, a few
drops of water and then 2 ml. of 6N HCl were added slowly.
If all residue did not dissolve, the crucible was heated

very slightly. The contents of the crucible were then transferred to a centrifuge tube. 3 drops of 2N $NaHSO_3$ were added to reduce any tetravalent oxidized cerium, and the tube was heated in a water bath for a few moments to drive off any excess bisulfite.

5 mg. of Fe^{+++} and then 6N NH_3 were added until ferric hydroxide was precipitated. The precipitate was digested for 10 minutes (or until the precipitate settled), a drop of ammonia was added to check for completeness of precipitation, and the tube was cooled and centrifuged. The precipitate was washed once with 6N NH_3 and the two supernatants were checked to see that no significant activity remained in the supernatant. The precipitate was dissolved, with heating, in a minimum of 6N HCl and the precipitation was done again.

When the precipitate was redissolved in 6N HCl, the solution was put on a Dowex 1 X 8, 50-100 mesh column 6mm. x 12 cm. which had been conditioned with 6N HCl. The rare earths were eluted with about 4 - 5 column volumes of 6N HCl. The last 1 ml. was checked to be sure rare earth activity was not still eluting. The column was washed with 0.01N HCl and reconditioned with 6N HCl . If breakthrough of iron is feared, the sample is dried on a steam bath with a filtered air stream directed at it. 6N HCl is then added to dissolve the salt and the solution is again passed through the column.

Preparation for Irradiation. The sample was evaporat-
ed with a filtered air stream on a water bath to incipient
dryness. 5 ml. of concentrated nitric acid were added
and evaporated to dryness. Here the air stream also
helped reduce bumping. A second portion of concentrated
nitric acid was added, and it too was evaporated to in-
cipient dryness. If at this point the residue is still
yellow, 6N HCl should be added to dissolve the salt and
it shoudl again be passed through anion exchange: 5 ml.
of $1\underline{N}$ HNO_3 were added and the activity was transferred
to a 15 ml. tapered bottom polypropylene centrifuge tube.
This was evaporated to dryness. 4 to 5 drops of1N HNO_3
were added, the tube was heated, cooled, and centrifuged,
and the liquid transferred to a 1 ml. volumetric tube.
This process was repeated until all activity had been
transferred, and the volumetric tube was then filled to
the mark with $1\underline{N}$ HNO_3. The solid residue, apparently
derived from the resin, did not carry any rare earth
activity. The mixture was stirred with a small teflon
stirring rod. A 100 microliter aliquot was put into a
1 dram vial and kept for chemical yield determinations.
Additional 100 microliter aliquots were placed into 2 in.
x 1/4 in. I.D. Intramedic polyethylene tubing which had
been washed with dilute nitric acid for one hour and had
then been sealed at one end. The other end was then sealed
and the sample was ready for irradiation.

Standard Solution. The standard solution was made from solution of rare earths in 3$\underline{N}$ HNO$_3$ prepared by Towell (1963). The actual values were redetermined by titration with EDTA using Alizarin Red S as indicator (Ehrlich, 1966). These standard solutions were tailored to approximate the concentrations of rare earths expected in the samples. The aliquots of each rare earth stock solution were all placed into one 100 ml. volumetric flask which was then filled to the mark with 3.0 N HNO$_3$. Immediately prior to the irradiation, a 100 microliter aliquot of the mixture was diluted to 1.0 ml. with 1N HNO$_3$ and a 100 microliter aliquot of this dilute solution was packaged in a sealed polyethylene tube for irradiation. Table 2-2 lists values for the various dilutions.

Post Irradiation Chromatography. Prior to irradiation, columns were prepared from material containing 25% by volume Johns Manville celite filter aid and 75% by volume of celite made hydrophobic by exposure to vapours of dimethyldichlorosilane (Winchester, 1963) followed by coating with 15% by weight bis-(2-ethylhexyl)-orthophosphosric acid. The coating was accomplished by dissolving the DEP in acetone and heating a mixture of hydrophobic celite, acetone, and water to which a small amount of acid had been added to dryness. Successive additions of slightly acid water and heatings to dryness ensured uniform coating of the DEP and removal of acetone.

The columns were packed in jacketed tubing 6 mm. in diameter to a height of 9 cm. with a cap of 1 cm. of untreated celite. The packing was done at $70^{\circ}C$. under 8-10 psig and was aided by tamping the column bed at intervals with a flat-ended rod. An ideal column was one which had a free column volume of about 2.0 cm^3 and a drop-rate at 8-10 psig. of about 15 sec./drop. The column was washed with 15 ml. of 6N HCl and conditioned with 15 ml. of 0.01N HCl. The free column volume could be easily measured by following the band which develops at the interface of 6N HCl over 0.01N HCl or the turbulence which is set up in a graduated cylinder when 0.01N HCl follows 6N HCl.

Before the sample was returned from the reactor, the column and the elution acids were heated up to $70^{\circ}C$. to drive off dissolved gases. The sample was opened, and the aliquot withdrawn and placed into a teflon beaker. Successive small aliquots of 1N HCl were bubbled through the polyethylene tubes to remove activity, and fresh 2M NaHSO$_3$ was added (1-2 times the moles of acid) to reduce tetravalent cerium and partially neutralize the sample to a pH of 2. The solution was heated on a hot plate until gas bubbles disappeared, taking care that no NaHSO$_3$ began to crystalize out. Then the aliquot, at a pH about 2, was placed on the column with a syringe and allowed to soak in under the very slightest possible pressure from a nitrogen tank (about one drop every 3 min.). The spike was washed twice with 0.01 N HCl which

was pushed through the column very slowly as before.
Then 6 ml. of 0.01N HCl were placed on the column,
and the column was hooked up to a device which auto-
matically adds the hot acids in proper sequence
(The machine was designed and built by Schilling,
Jaillet, and Cihocki, 1966). Pressure was increased
to about 8-10 psig which, for a properly packed
column of 9 cm. length, caused a drop rate of 0.5 ml.
each 150 seconds (1-13 drops per 0.5 ml.). An addition-
al 6 ml. of 6.01 NHCl was passed and collection of frac-
tions was begun when the .18N HCl dropped onto the
column. The acids used are listed on Table 2-1.
The samples were collected on polypropylene ringed
planchets 1 in. in diameter and 1/4 in. deep. A few
drops of wetting agents solution were added (e.g.
0.1% by volume of Union Carbide non-ionic sulfactant
TP-9 in water) to spread the eluant portion over the
entire planchet. The samples were dried at 110°C in
an oven, sprayed with clear Krylon, and mounted on
folders by use of double-sided tape (Scotch or
Permacel).

Five set ups were maintained so that any combina-
tion of blanks, standards, and samples were eluted
simultaneously.

Counting was done on standard gas flow-propor-
tional beta counting equipment (Baird-Atomic). In
some cases, the samples were counted in an interleaved
manner, i.e., planchet number one from each elution

followed by planchet two, etc. Later on, when five coun-
ters became available each elution was counted in its en-
tirety on one counter simultaneously with the other four
(two people could maintain five counters simultaneously)
and the counters were cross-calibrated.

Chemical Yield Determination. It will be recalled
that Ce-139 and Y-88 tracers counting about 200,000 to
250,000 counts per minute were added to the sample.
Eventually the sample was brought to 1.0 ml. and a
100 microliter aliquot was taken for chemical yield. The
same series of dilutions were carried out on the chemical
yield standards. The identical amounts of Ce-139 and Y-88
that had been used for the sample were pipetted into
volumetric tubes. These tubes were filled to 1.0 ml.,
and 100 microliter aliquots were taken for chemical
yield standards.

Multi-channel analyzer data were used for calculating
chemical yields. As an example, the chemical yields cal-
culation for a particular sample illustrated. The multi-
channel analyzer was calibrated as follows:

TMC Pulse Height Analyzer Model 402

Input No. 1

High Voltage = 1100 volts

Amplifier gain = 2.40

Base Line = 0.10

Upper Level = 10

Accumulation: channels 1-199

On August 24, 1966 these settings placed the
Y-88 gammas of .90 and 1.83 MeV in channels 85 and
180, respectively. Channels 7-24 then contain essential-
ly all the Ce-139 activity (.166 MeV) and channels
67-199 encompassed the two Yttrium peaks (.90 and 1.83
MeV). The activities were counted for 4 minutes
(live time) and the analyzer memory was then in-
tegrated over channels 67-199 and 7-24. Following
are the results (less background):

Channels	Samples	Y-88	Ce-139
7-24	30,334	3,141	34,871
67-199	7,429	9,220	3

Two equations in two unknowns can now be set up
(J. W. Winchester, private communication):

Let L = the sample count rate in the low channels

   H   "   "   "   high   "

   Yh   yttrium "   "   high   "

   Yl   "   "   "   low   "

   Cl   cerium   "   "   low   "

   Ch   "   "   "   high   "

   Ac   cerium chemical yield

   Ay   yttrium chemical yield

Then, L = YlAy + ClAc

   H = YhAy + ChAc

This leads to

$$Ay = \frac{ClH - LCh}{ClYh - ChYl}$$ (2-1)

If Ch is small then

$$Ay = ClH/ClYh = H/Yh$$ (2-2)

Also, $Ac = \dfrac{LYh-Y1H}{C1Yh-ChY1}$, (2-3)

If Ch is small

$Ac = \dfrac{LYh-Y1H}{C1Yh} = L/C1 - \dfrac{Y1H}{C1Yh}$ (2-4)

The solution of the determinants, Equations 2-1 and 2-3 above,are the rigorous solutions. Since Ch is indeed negligible, Equations 2-2 and 2-4 are useable. The description of chemical yield determination by Towell (1963) essentially uses Equations 2-2 and 2-4.

Using Equations 2-1 and 2-3 with the data on the previous page:

$$Ay = \dfrac{(34871)(7429) - (30,334)(3)}{(34871)(9220) - (3)(3141)} = .8055$$

$$Ac = \dfrac{(30,334)(9220) - (3141)(7429)}{(34871)(9220) - (3)(3141)} = .7973$$

Yields generally run above 70% and, if care is taken in the chemical procedure, yields above 90% are obtainable. The two numbers usually agree to within a few percent and are averaged. When the cerium yield is substantially lower, that number is used for Cerium alone and the Yttrium number is used for all other rare earths.

DISCUSSION:

In the work done in various laboratories on rare earth determinations in geologic materials, several different procedures have been developed (Schmitt et al, 1963; Haskin & Gehl, 1962; Høgdal, 1966). The basic differences center around three areas: 1. the use of pre-irradiation

or post irradiation chemistry, 2. the mode of separation of one rare earth from another, and 3. techniques for collection and counting of samples.

Post irradiation group separation of the rare earths has the obvious advantage of eliminating any problems from rare earth contaminants introduced in the chemical steps. However, the blank determinations made in this laboratory (Towell, 1963; Spirn, 1965; Ehrlich, 1965; Schilling, 1966; and Ehrlich, 1966) have shown this to be of the order or less than one per cent, a negligible error in terms of other uncertainties. In this case, the need for minimal radiation protection and the lack of necessity for speed in the face of decaying species make the pre-irradiation group separation more acceptable. Specifically, by using pre-irradiation group separation, Dy with a half-life of 2.5 hr. can be collected and counted 10-12 hours after the irradiation whereas post-irradiation group separation prior to chromatography leads to a delay of over 24 hours. Of course, for samples containing a very low rare earth content, post irradiation group separation becomes desireable (Schilling, 1966).

In the chromatographic separation, this laboratory has used reverse phase partition chromatography with bis-(2-ethylhexyl)orthophosphoric acid adsorbed on celite. The advantage of this procedure is that the separation factors average about 2.5 for

separating one rare earth from another (Winchester, 1963).
This leads to good separations with somewhat smaller
columns. The advantage to the alternate technique,
anion exchange with an organic chelating acid at slowly
increasing acidity (Schmitt et al., 1963; Haskin et al.,
1962; Høgdahl, 1966; Hayes, 1964 and Rengan & Meinke,
1964) accrues in the ease of maintaining and loading
the columns. In some cases, the columns are packed and
used for one separation only (Haskin and Frey, personal
communication), and the packing takes 15-30 minutes;
in other cases (Høgdahl, 1966 &Schmitt et al., 1963), the
columns are kept for some time with apparently easy
maintenance. Also, loading of the ion exchange columns
takes a short time, about 15 minutes, whereas the load-
ing of the DEP columns takes about two hours. The length
of elution time with the ion exchange procedure is much
longer since more capacity is needed to gain the same
quality of separation as can be obtained from the DEP
in 8 hours. However, in the ion exchange procedure,
if samples are collected in small portions and each sample
is collected (see below), no added carrier would be
needed, and in that case this procedure may turn out
to be quicker.

This laboratory has used the practice of collecting
the eluant in 1/2 ml. portions (no added carrier), evapor-
ating the liquid so that an invisible spot is left, count-
ing each fraction for beta activity and plotting activity

against planchet number. After the first few experiments, in which the half lives and gamma spectra of each peak were inspected, it is possible by looking at the elution curve to tell which rare earth is which. Figure 2-1 shows that the rare earths occur in characteristic patterns in this elution curve. The first grouping involves La, Ce, Pr, and Nd with La having a very high activity, Ce and Pr moderately high and Nd low. Pm stands alone. The second grouping contains Sm, Eu, and Gd. Sm and Eu have very high activity, whereas Gd activity is low. Tb then stands alone. The third grouping involves Dy, Ho, and Er and Y superimposed on each other. The Dy is low by the time the entire curve is counted; Ho and Y are high (Er is only about 1% of the beta activity in the Er-Y peak). Tm then stands alone and the last grouping involves Yb and Lu.

Having an entire elution curve also allows one to determine the quality of separation and the extent of contamination by previous rare earths, to correct for these problems and to assign approximate errors to each rare earth rather than a constant error for the group. This allows assigning of more confidence to higher activity peaks (e.g., La, Sm, Eu, Ho, Y) and making corrections whenever necessary for interference in poorer separations (e.g., Ce-Pr, Pr-Nd, Eu-Gd, Yb-Lu). In laboratories where carriers are used and gravimetric chemical yields are measured, it

Figure 2-1. Typical elution curve of a rock sample (Trachyte JP.15) irradiated for 3 hours in a thermal neutron flux of $2x10^{13}$ n/cm^2-sec. 6 ml. volume is used per acid.
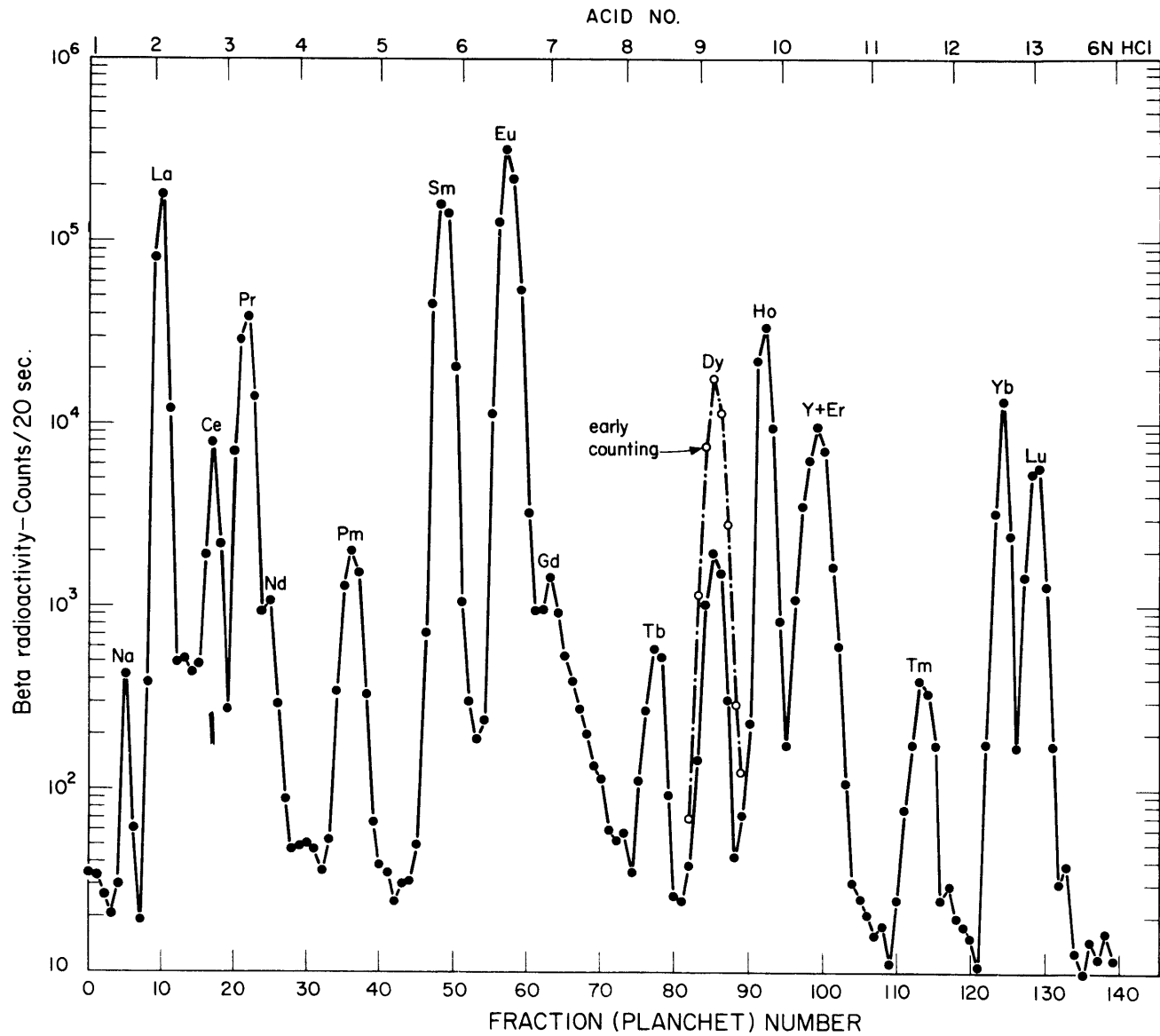
is impossible to determine how much of that weight is actually contributed by another rare earth, and one is forced (Haskin, 1966) to involve oneself with sophisticated gamma spectroscopic techniques and perhaps with tentative explanations of the reasons why some rare earths habitually seem to measure higher or lower abundances than expected. For instance, Haskin (1966) mentions that Gd always appears to be higher in abundance than should be the case and he attributes this tentatively to tailing from Eu. In a full elution curve, one can see immediately that the Gd peak is indeed perched upon the Eu tail and the effect of the tailing of the Europium can be actually calculated.

It is our conclusion, therefore, that pre-irradiation group separation is acceptable, and easier, for ordinary rocks and minerals; that the relative merits of ion exchange separation of rare earths from each other and of separation by reversed phase partition chromatography with DEP need still be investigated; and that the time and effort to collect and count a full elution curve consisting of many small fractions of eluant yields great dividends in assigning levels of confidence and approximate errors for a particular experiment and for each rare earth abundance calculated in a particular experiment (Schilling, 1966; Ehrlich, 1966).

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PART THREE

RARE EARTH FRACTIONATION AND

MAGMATIC PROCESSES

Some Theoretical Considerations

J-G. Schilling

ABSTRACT

Fractional crystallization, partial melting, fractional melting, and zone melting may cause observed differences in terrestrial rare earth abundance patterns. The partition ratio of concentration, solid/liquid, for rare earths between crystallized silicate and its melt may increase linearly with Z from La to Lu, as assumed by Masuda and Matsui, if rare earths are incorporated into lattice sites smaller than Lu. In the absence of direct experimental measurements but using this assumption, rare earth abundances relative to chondritic are predicted for solids and liquids in the four processes, and published rare earth analyses of basic igneous rocks are compared. Hawaiian tholeiite resembles the last solid to have crystallized in the mantle (i.e. the low-melting portion of the upper mantle) from an initially chondritic earth, leaving the crust as the residual liquid. Hawaiian nepheline-melilite basalt resembles the residual liquid or a partial melt of the solid which is indistinguishable. Some high temperature peridotites, which are depleted in the light rare earths, resemble a deep seated solid after repeated zone refining, and Mid-Atlantic Ridge basalts resemble a similar solid at shallower depth. Although the earth's crust and mantle must have a complex history, and the details of rare earth partition are certainly dependent on mineralogy, the correlation between observed rare earth abundance patterns and those predicted according to simple models is striking.

INTRODUCTION

The physico-chemical processes involved in the differentiation of the earth and meteorites are perhaps best studied by examining systematic fractionation patterns developed among groups of elements possessing very similar properties. This is true especially when these elements are in trace concentration, allowing the application of ideal limiting laws of thermodynamics with greater confidence.

The Lanthanide series seems to be the best group available.

This series belongs to group IIIB in the periodic table and is usually taken to include all elements from Lanthanum to Lutecium, atomic numbers 57 to 71 respectively. In contrast to the d orbitals of the first, second and third transition series, the 4f orbitals in the Lanthanide elements are rather deeply buried in the atoms. The electrons which occupied the 4f orbitals are largely screened by the overlying shell of the 4d electrons. The effect is that the reciprocal interaction between the 4f electrons and the surrounding of the atoms or the ions is of little chemical significance. Thus many of the properties of a Lanthanide ion with a partly filled shell are quite sensitive to the number and arrangement of the f electrons present. This is why the chemistry of the Lanthanides is so homologous, in marked contrast to the erratic and irregular variations in chemical properties with progressive change of the atomic

number in the so called first three transition series.

In natural environment, the trivalent state is the characteristic one for all the Lanthanides. Under special oxidation-reduction conditions, Eu^{3+} can be reduced in part to Eu^{2+}, and Ce^{3+} may be oxidized to Ce^{4+}. This can result in an anomalous behavior of these two elements relative to their neighboring Lanthanides (Towell et al., 1965; Goldberg et al., 1963).

Although the progressive filling of the 4f shell does not change significantly the relative chemical properties, there is a systematic change of the physical properties of the Lanthanides. The most striking is the decrease of the trivalent ionic and atomic radii with increasing atomic number. This is known as the Lanthanide contraction (Goldschmidt, 1954). It is interesting to note that an approximately linear relationship exists between atomic number and reciprocal trivalent ionic radius (Templeton and Dauben, 1954).

Since other chemical parameters for the lanthanides are homologous, the relative incorporation of these elements in trace amounts into the ordinary silicate structures (which are mainly ionic) will be strongly influenced by their relative size.

An interesting illustration of this point is the behavior of Yttrium (atomic number 39) another element of the group IIIB of the periodic table. Yttrium has chemical properties very similar to the Lanthanides. Its trivalent ionic radius is close to Erbium (atomic number 68) and

although its mass is lower by 29 units relative to Erbium, Yttrium behaves very similarly to Erbium during the chemical evolution of the earth and meteorites. The Lanthanide series plus Yttrium will be referred to subsequently the rare earths.

Aspects of the geochemistry of the rare earths have been discussed by a number of authors (Goldschmidt, 1954; Rankama and Sahama, 1955; Ahrens, 1964, 1965; Fleisher, 1965; Haskin et al., 1965; Jensen and Brunfelt, 1965). Recent development in chemical analytical techniques have made rare earth analysis data of terrestrial and meteoritic materials more readily available.
Following the practice of our laboratory (Coryel et al., 1963; also, see Figure 3-1), we compare the rare earth abundance pattern of each rock, element by element, with a common reference,--e.g. the average of ordinary chondrites (Schmitt et al., 1963, 1964). The relative abundance of each rare earth (i.e. enrichment factor relative to the reference) is plotted logarithmically versus a linear scale of rare earth atomic number or the inverse of ionic radii.

Contrary to earlier belief that the rare earth group was not internally fractionated relative to chondrites, and behaved as an entity, it emerged (Schmitt et al., 1963) that the rare earths were fractionated relative to each other. This point is not only true for terrestrial material but also among meteorites such as Eucrites and the silicate phase of the pallasites. Some rare earth

Figure 3-1. Abundance of the rare-earth elements in the
basalt Kilauea Iki-22 (broken line) and mean of 20 chond-
rites, (solid line) plotted on a logarithmic scale as a
function of atomic number. Data from R. A. Schmitt et al.
(1963). The lower curve gives the ratios of the rare earth
abundances in basalt and chondrites. A best straight
line has been drawn.
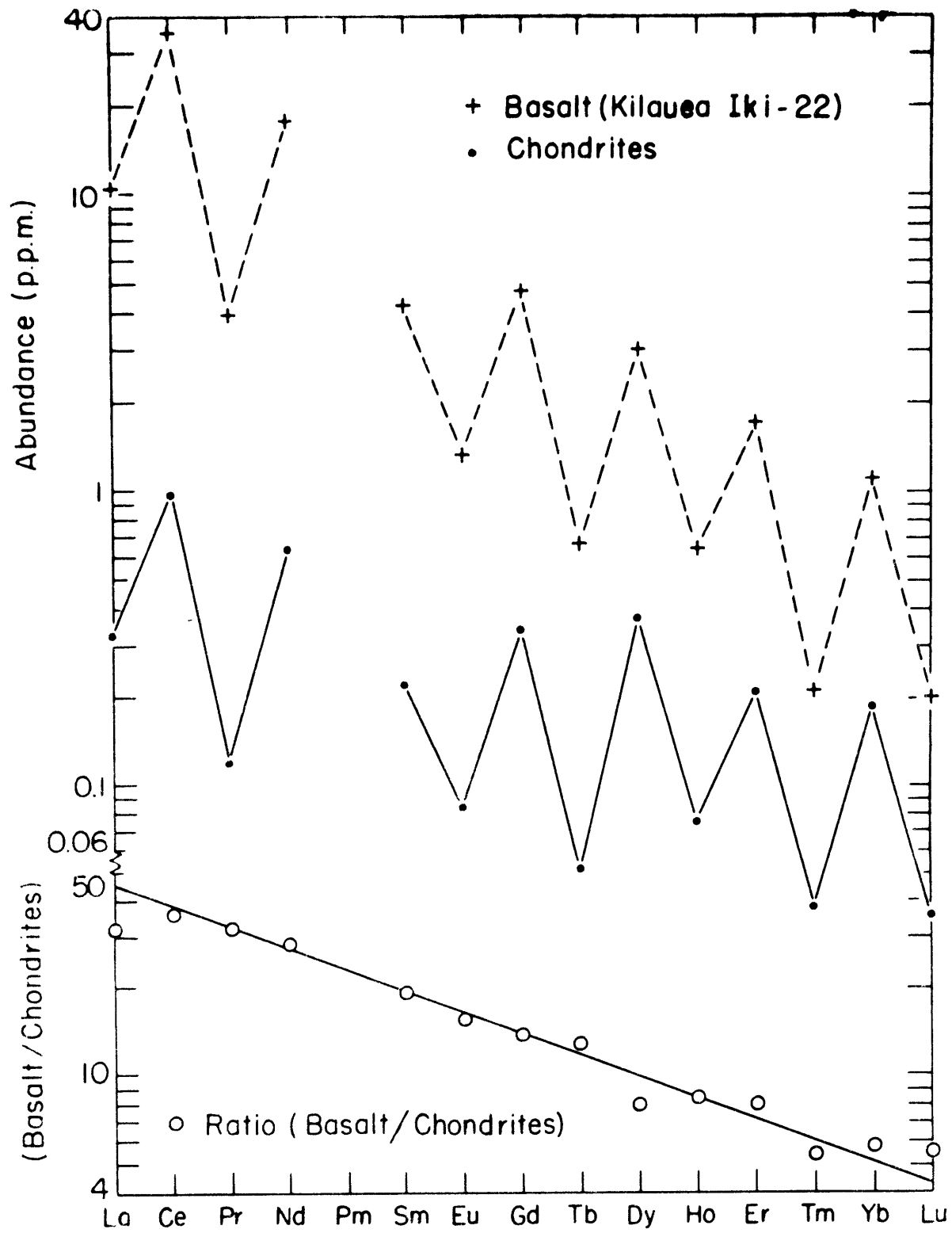
Figure 3-2. Abundances of the rare-earth elements relative to 20 chondrites (Schmitt et al., 1963, 1964) in one composite of shale and the Norton County Ca-poor achondrite plotted on logarithmic scale as a function of the atomic number. Data for the composite shale are taken from E. Minami (1935) and the meteorite from R. A. Schmitt et al. (1963, 1964).

100

ppm Rock / ppm Chondrites

10

1

● Composite Shales (E. Minami, 1935)
+ Norton County - Ca-poor Achondrite
(R. A. Schmitt, 1963)

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
57   Atomic Number   71
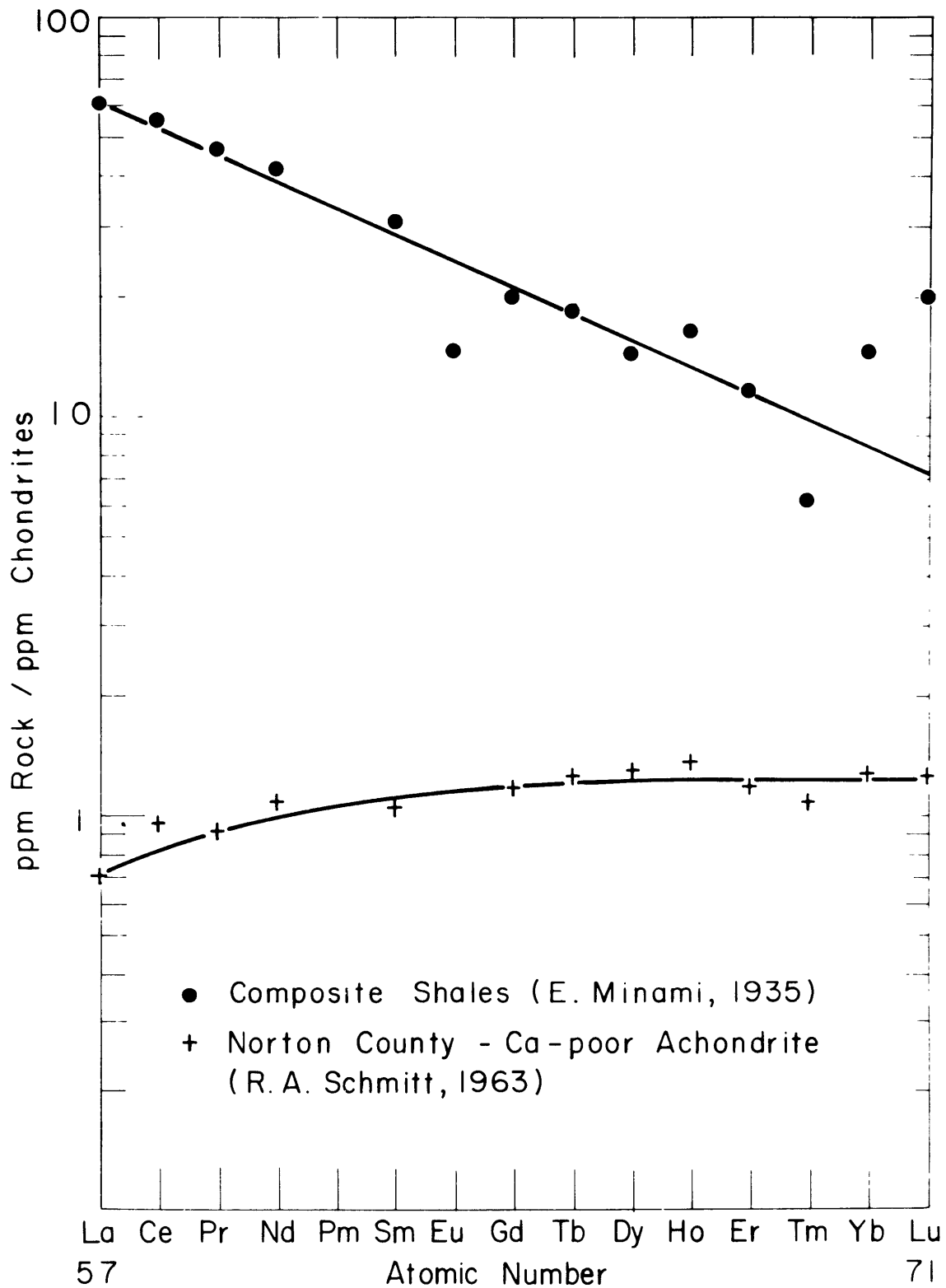
Figure 3-3. Abundances of the rare earth elements rel-
ative to 20 chondrites (Schmitt et al., 1963, 1964) in
Delagate eclogite, Australia, plotted on a logarithmic
scale as a function of the atomic number. Data from
Schmitt et al. (1964).

Delegate Eclogite
(R.A. Schmitt, 1964)
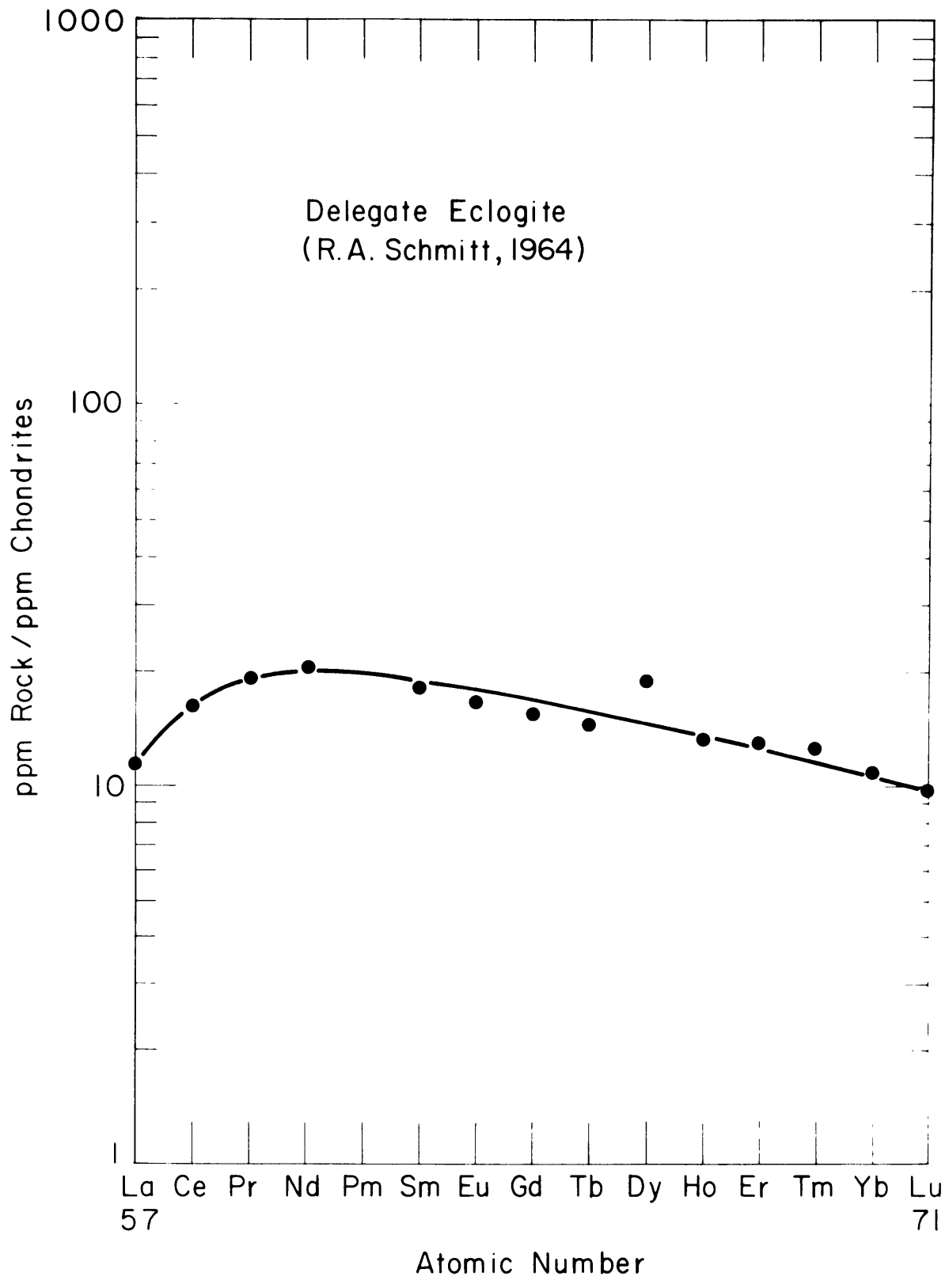
Figure 3-4. Abundances of the rare-earth elements relative to 20 chondrites (Schmitt et al., 1963, 1964) in three basalts from the Hawaiian Islands, plotted on logarithmic scale as a function of the atomic number. Data from this work.
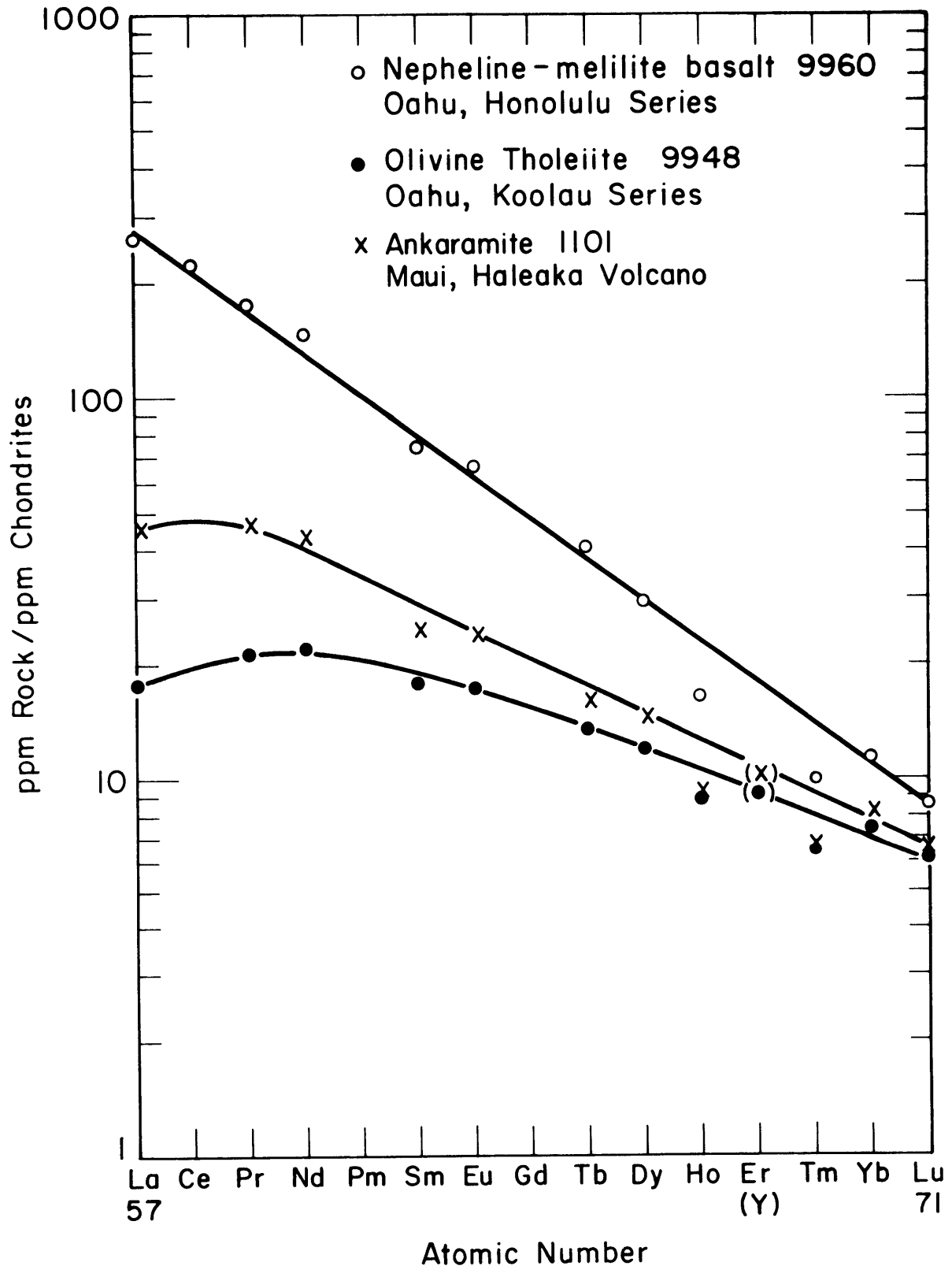
Figure 3-5. Abundances of the rare-earth elements rel-
ative to 20 chondrites (Schmitt et al., 1963, 1964) in
2 Mid-Atlantic Ridge tholeiites, plotted on a logarith-
mic scale as a function of the atomic number. Data
from F. A. Frey and L. A. Haskin (1964) and Haskin
et al. (1965).

Mid Atlantic Ridge Tholeiitic basalts

• GE60
○ D-2-l-b

Data from Frey + Haskin 1964
Frey + Haskin + Poetz 1965
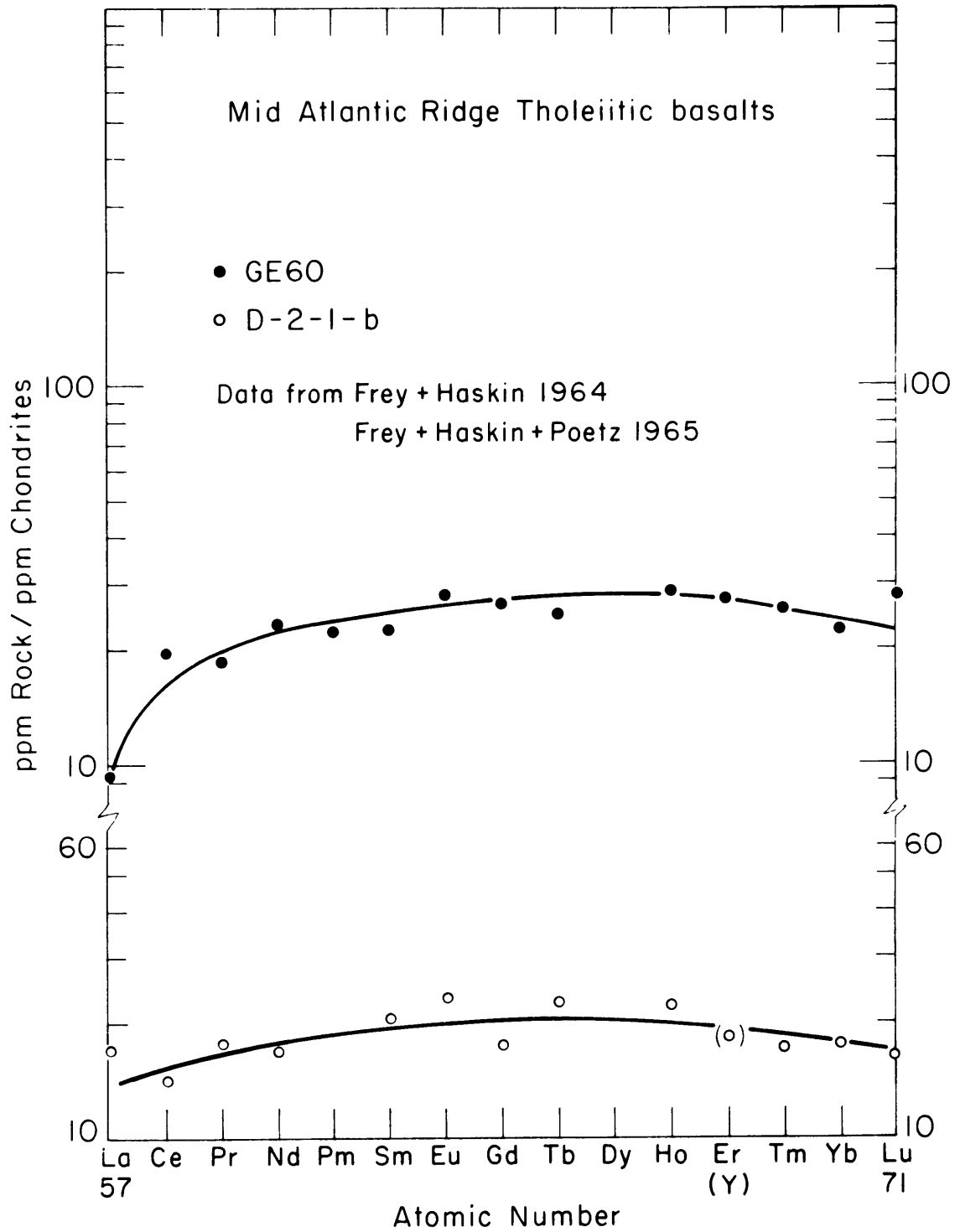
Figure 3-6. Abundances of the rare-earth elements rel-
ative to 20 chondrites (Schmitt et al., 1963, 1964) in
three peridotites, plotted on logarithmic scale as a
function of the atomic number. Data from L. A. Haskin
et al. (1965).

Peridotites

ppm Rock / ppm Chondrites

o Tinaquillo, Venezuela

● Lizard, Cornwall

△ Mt Albert, Quebec

Data from Frey + Haskin 1966

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
57   (Y)   71
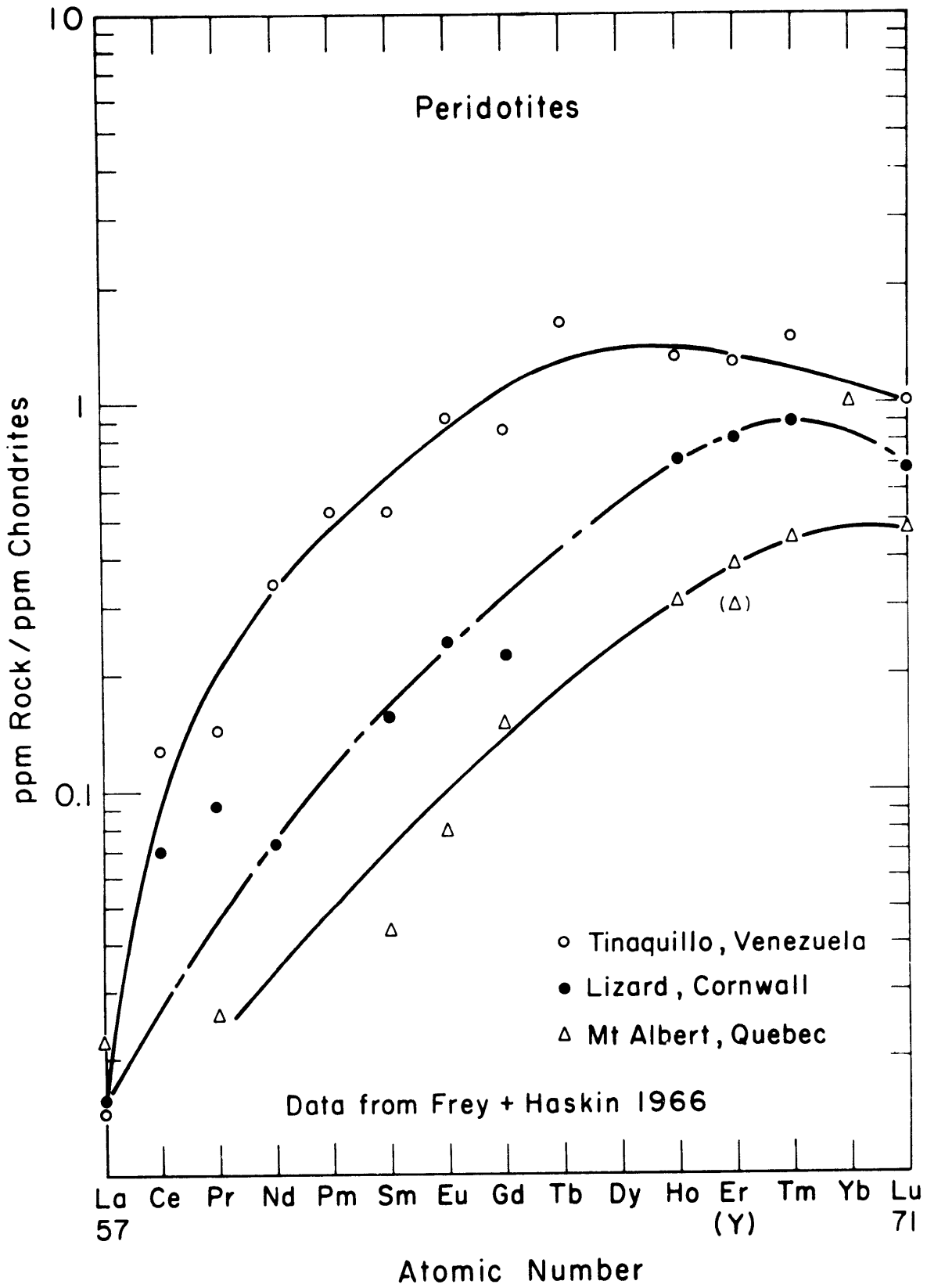
Atomic Number

Figure 3-7. Abundances of the rare-earth elements rel-
ative to 17 chondrites in three meteorites, plotted on
logarithmic scale as a function of the atomic number.
Data from R. A. Schmitt, et al. (1963, 1964).

Pasamonte – Ca – rich Achondrite
Estherville – Mesosiderite (silicate phase)
Orgueuil – Carbonaceous Chondrite

Data from R.A. Schmitt 1963 & 1964

ppm Rock / ppm Chondrites

La 57   Ce   Pr   Nd   Pm   Sm   Eu   Gd   Tb   Dy   Ho   Er (Y)   Tm   Yb   Lu 71

Atomic Number
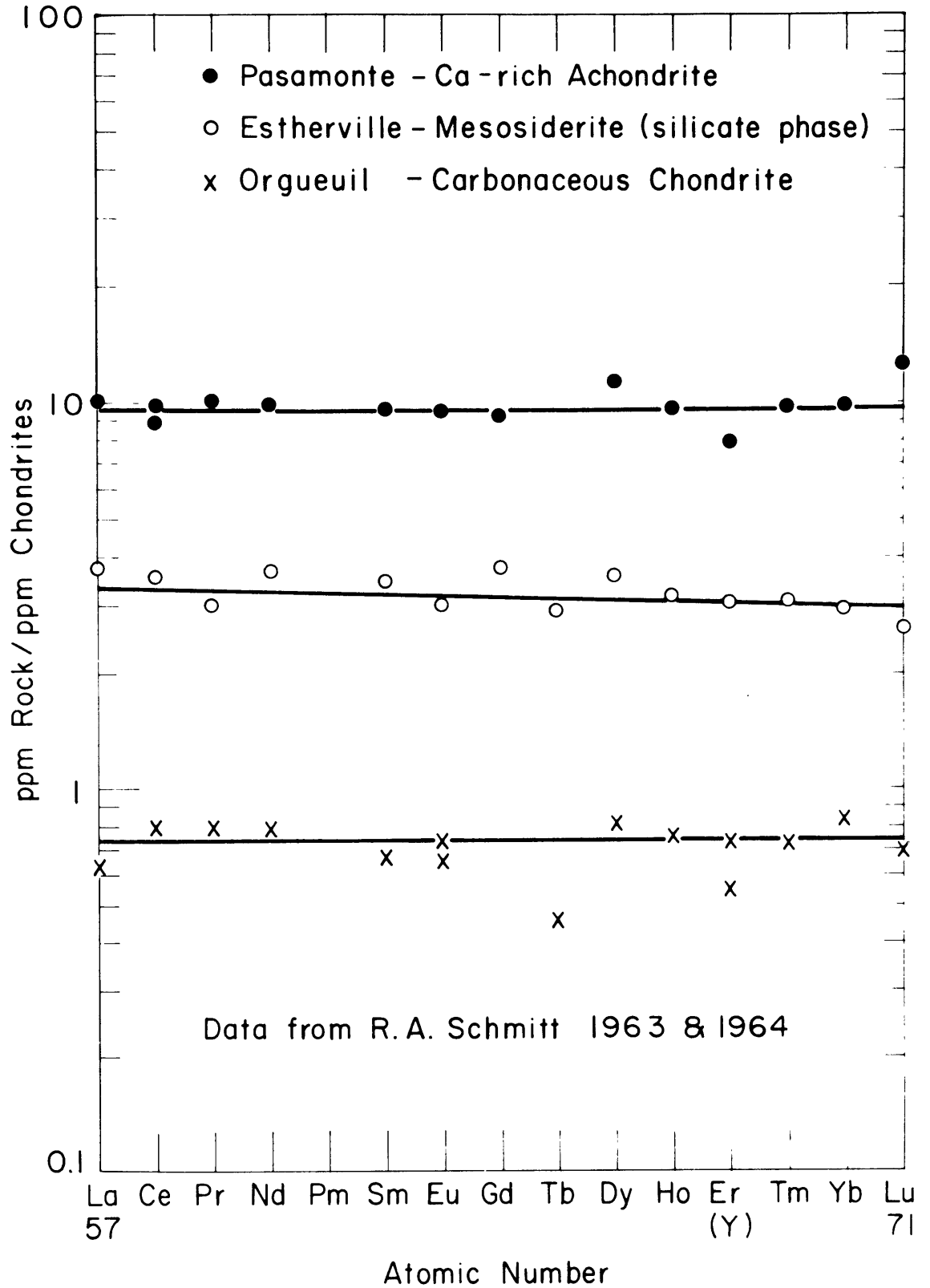
patterns obtained in terrestrial material are shown in Figures 3-1, 2, 3, 4, 5, and 6, and for some meteorites in Figure 3-7. Invariably smooth and regular curves are observed for the variation of the rare earth enrichment factors relative to chondrites. These patterns show that indeed the rare earths form a coherent group and that only slowly and progressively do they separate from each other. Apparently this must be the result of small but real differences of the intrinsic properties of individual rare earths and of the conditions imposed upon them.

Despite the intricacy in the evolutionary history of the earth to form the crust, it is remarkable that the rare earths in crustal lavas (Figures 3-1, 3-4, and 3-5) are so regularly fractionated. This paradox remains to be explained and will be our main concern in this paper.

Presumably, the rare earth fractionation patterns must be a direct reflection of the physico-chemical processes involved in the evolution of the earth, and certain meteorites from more primitive matter. We will proceed with this assumption in mind.

Masuda and Matsui (1963, 1966) noting especially the linear patterns obtained by Minami (1935) and Schmitt et al. (1964) developed a mathematical model for fractional crystallization to explain such features. They concluded that the rare earth partition coefficients between liquid and solid must vary as an arithmetical progression with the atomic number Z, if linear patterns are to be obtained

in the residual liquid, and that fractional crystallization is the most important process in the differentiation history of the earth.

Although such mathematical development may be an oversimplification, the consequences are highly significant, namely that crystal-liquid equilibria may explain the rare earth fractionation rather well.

Nevertheless from a geophysical point of view, it is not realistic to suppose that fractional crystallization is the only process responsible for the differentiation of the earth and meteorites. Apart from large-scale mass transfer and gravitational differentiation other processes such as partial melting, fractional melting (Bowen, 1956), zone refining (Harris, 1957), selective volatilization (Edward and Urey, 1955), gaseous transfer, diffusion and mixing processes are known or suspected to be in operation during the chemical differentiation of the earth and meteorites.

We will focus our attention in this paper on the processes involving crystal-liquid equilibria. Simple models will be considered for the following processes: fractional crystallization, partial melting, fractional melting, zone melting and mixing processes. We will limit ourselves to the cases where the rare earths occur mostly in trace amounts, thus always undersaturated in any melt, and incorporated in lattice sites smaller than Lu. These limitations permit us to use the well established Berthelot (1872) and Nernst (1891) and Doerner-Hoskins (1925) distribution laws derived from copreci-

Although our models are oversimplified, they at least permit us:

1. To get a qualitative understanding of the rare earth fractionation in general.

2. To stress the importance of major physico-chemical parameters involved in the distribution and relative fractionation of the rare earths and for that matter of other trace elements such as U, Th, Rb, Sr, Ba, Zr, Hf and Ta, etc.

3. To emphasize the effect of the dynamics of differentiation processes on the relative rare earth fractionation.

4. And finally to demonstrate, with all the necessary precautions, the potentiality of using rare earth fractionations to study the physico-chemical processes in operation during the evolution of the earth and cosmic matter, and their relative importance.

The following mathematical developments will be kept intentionally as general and as open as possible, so that these models can be expanded easily in subsequent work.

I. DISTRIBUTION LAWS

The partitioning of a component between two phases is governed by the chemical potential of this component in both phases. At equilibrium:

$$\mu_1^a (T,P,X_1) = \mu_1^\theta (T,P,X_1) \qquad (3-1)$$

μ_1^a is the chemical potential of component 1 in the phase a, and μ_1^θ in the phase θ.

Assuming that the component 1 is sufficiently dilute in each phase a and θ, it can behave ideally in both of them (Denbigh, 1961), Equation 3-1 becomes:

for $X_1 \to 0$

$$\mu_1^{a*} (T,P) + RT \ln X_1^a = \mu_1^{\theta*} (T,P) + RT \ln X_1^\theta$$

or

$$\ln \frac{X_1^a}{X_1^\theta} = \frac{\mu_1^{\theta*} - \mu_1^{a*}}{RT}$$

$$K_1 (T,P) = \frac{X_1^a}{X_1^\theta} = \exp. \frac{\mu_1^{\theta*} - \mu_1^{a*}}{RT} \qquad (3-2)$$

Where μ_1^{a*} and $\mu_1^{\theta*}$ represent the chemical potential of pure 1, in a physically unattainable state a or θ, respectively (Denbigh, 1961, pp. 247 and 255). X_1^a and X_1^θ are the mole fraction of component 1 in the phase a and the phase θ, respectively. K_1 is defined as the partition coefficient. Equation 3-2 is the Berthelot-Nernst distribution law. It should be noted that K_1 is a function of T and P only and not of the concentration in the region where each solution is ideal or as long

as $X_i \rightarrow 0$.

The principles governing the distribution of trace element impurities in minerals have been intensively studied. The fundamentals were already established by Goldschmidt (1937). Ahrens (1953, 1953), Ramberg (1952), De Vore (1955, 1957), Ringwood (1955, a,b), Wickman (1943), and Shaw (1932), extended somewhat this early work. Much of the emphasis was on parameters such as ionic radius, electronegativity and ionization potential, as a measure of polarization etc. MacIntyre (1963) reviewed the use of partition coefficients in geochemistry. In the following discussion we will be considering only liquid-solid equilibria. Although Equation 3-1 is a sufficient condition for describing the partitioning of a trace element between a melt and a solid crystallizing from this melt, it does not specify anything on how and to what extent the equilibrium is attained. Since the concentration of a trace component i in the solid separating from the melt is directly proportional by a factor K to the concentration in the melt, it is important to know to what scale this relation applies.

Can the interior of the crystal re-equilibrate with the constantly changing composition of the melt?

This is the domain of kinetics. The degree of equilibration is controlled by the physical conditions of crystallization and by the dynamical conditions of the processes. Physical parameters such as those enumerated below will be important:

diffusion rates in the phases involved, the rate of growth
and nucleation of the solid crystallizing, degree of mix-
ing in the liquid, lattice characteristics of the min-
erals crystallizing and, their surface energies, viscos-
ity of the melt, primary composition of the melt, its
cooling rate, and temperature and pressure conditions.

Two limiting cases have generally been considered
in coprecipitation studies (Berthelot, 1872; Nernst,
1891; Doerner and Hoskins, 1925; and McFee, 1947):
The homogeneous law or the Berthelot-Nernst law, and the
logarithmic distribution law or the Doerner-Hoskins law.
Applications to magmatic crystallization have been dis-
cussed by Neumann (1948), Holland (1949), Neumann et al.
(1954), Ryabchikov (1960, 1965) and reviewed by MacIntyre
(1963).

DOERNER-HOSKINS OR LOGARITHMIC LAW

The assumptions are: a. Practically no diffusion
of the trace component is allowed in the solid. b. Com-
plete mixing and rapid diffusion in the melt. Thus, only
the surface of the solid is in equilibrium with the melt.

The segregation caused by such a crystallization
process for a binary solute-solvent system is described
by:

$$C_L = C_o \, (1-x)^{D_i - 1} \qquad (3\text{-}3)$$

and

$$C_S = D_i C_L = D_i C_o \, (1-x)^{D_i - 1} \qquad (3\text{-}3')$$

with $0 \leq x \leq 1$

where C_S = instantaneous concentration of a trace component "i" in the solid.

C_L = concentration of a trace component "i" in the melt.

C_O = initial concentration of a trace component "i" in the melt.

$x = \dfrac{\text{Amount of crystal}}{\text{Total amount of melt originally present.}}$, and $0 \leq x \leq 1$

D_i = effective partition coefficient.[*]

The partition coefficient "D_i" is assumed constant and the density does not change on freezing.

Equation 3-3 in one form or another has been derived by several workers. (Doerner and Hoskins, 1925; and McFee, 1947). Figure 3-8 shows, for different values of D_i, the change of the relative concentration versus the degree of solidification, X, in the solid and in the liquid. For D less than 1 the relative concentration increases only slowly till much of the solid has crystallized, and then increases very rapidly.

[*] We have used D_i rather than K_i to indicate the small difference between the theoretical K_i value which can be obtained from the phase diagram of solute-solvent system and the effective partition coefficient whose value depends on the physical conditions of freezing and certain properties of the material. For a good discussion of this problem see Pfann (1966).

BERTHELOT-NERNST OR HOMOGENEOUS LAW

In this other limiting case, for a two phase system, one assumes rapid diffusion rates in both phases and complete equilibration between the solid crystallizing from the melt and the melt itself. Thus, the entire crystal is in equilibrium with the melt, and the concentrations are given by the expression:

$$K_1 = \frac{C_s}{C_L} \qquad (3\text{-}4)$$

If the crystals at a certain moment become separated from the melt, one can easily derive the change of concentration as function of the degree of solidification in both phases and the original concentration of the melt. In addition to the Nernst law a material balance requires that:

$$C_L (1\text{-}x) + C_s x = C_o \qquad (3\text{-}5)$$

combining Equation 3-4 and Equation 3-5 and rearranging:

$$C_L = \frac{C_o}{1 + (K_1\text{-}1)x} \qquad (3\text{-}6)$$

where the same notation as previously described is used. The changes of the relative concentration in the melt and in the solid versus degree of solidification are shown on Figure 3-9.

The application of this limiting law to crystallization from a melt is questioned. Diffusion of ions

Figure 3-8. (Left diagram) Variation of the relative concentration C/C_0 of a trace element in a melt (upper left diagram) and in a solid (lower left diagram) with degree of solidification x of the melt, for the logarithmic distribution law (Doerner-Hoskins, 1925), and different values of D. $C_0 = 1$ for all curves.

(Right diagram) Variation of the relative concentration C/C_0 initial of certain trace elements in the Skaergaard magma (upper diagram) and in the Skaergaard rock (lower right diagram) with degree of solidification (after McIntyre, 1963; data from Wager and Mitchell, 1951).
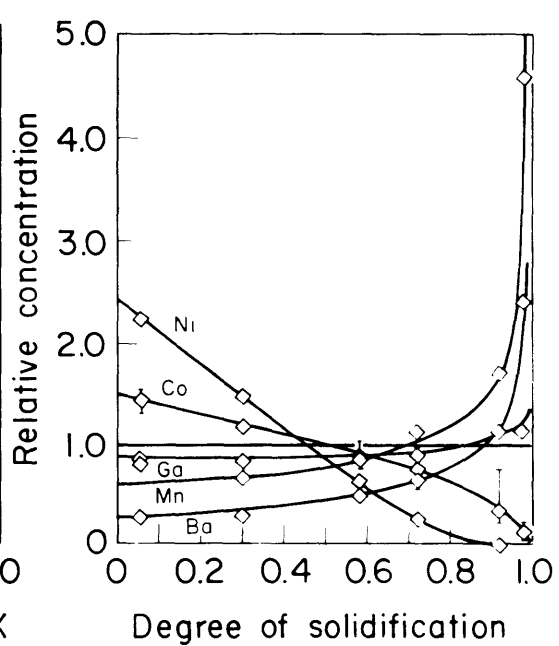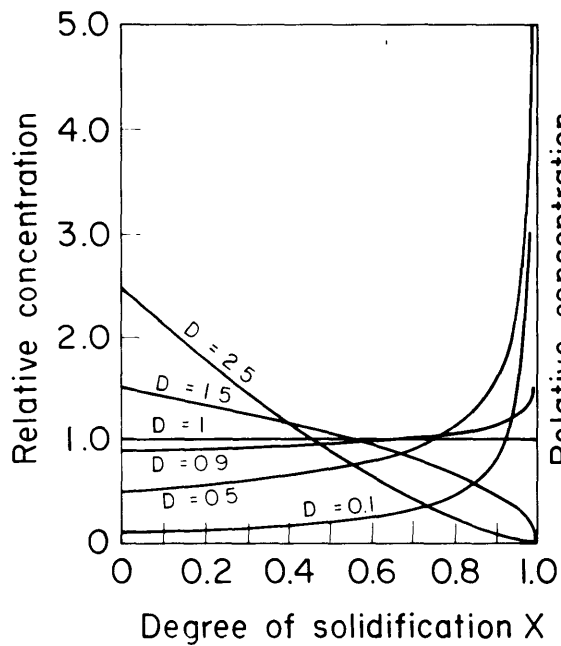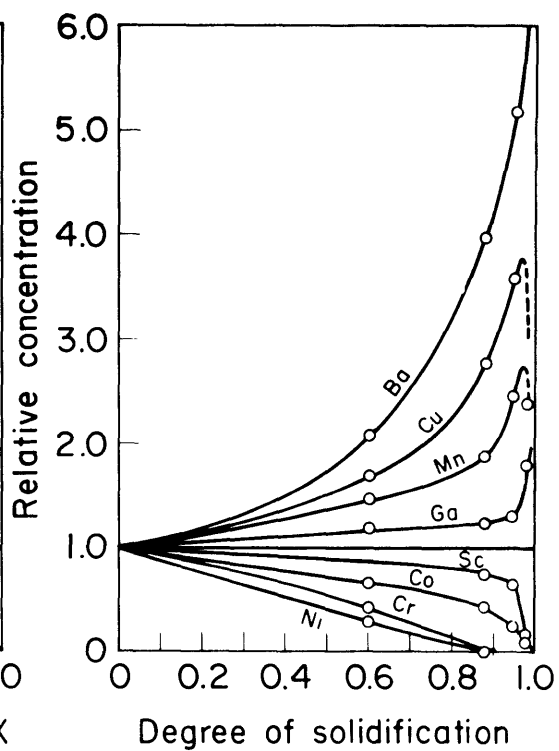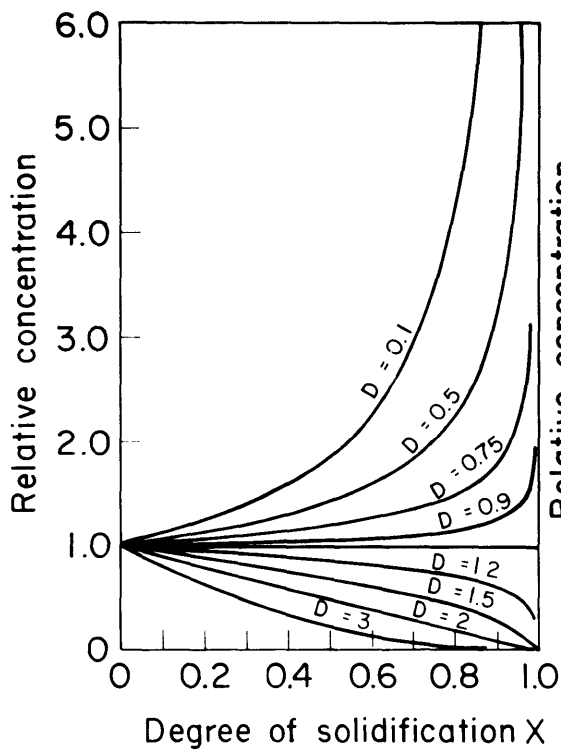
Figure 3-9. Variation diagram of the relative concen-
tration C/C_0 of a trace element in a melt (left diagram)
and in a solid (right diagram) with degree of solidi-
fication x, for the homogeneous distribution law (Berthelot,
1872; Nernst, 1891) and for different values of K.
C_0 = 1 for all curves.

Left plot — x-axis: Degree of solidification X, y-axis: Relative concentration. Curves labeled $K_i = 0.1$, 0.2, 0.4, 0.9, 1, 1.5, 2, 2.5.

Right plot — x-axis: Degree of solidification X, y-axis: Relative concentration. Curves labeled $K_i = 3$, 2.5, 2, 1.5, 1, 0.9, 0.4, 0.2, 0.1.

in silicate minerals are too small for complete equili-
bration to be attained.

Intermediate cases between these two extreme condi-
tions are probably the rule.[*]

---

[*] Ryabchikov (1960, 1965) has derived a more general
expression $C_s = C_o D \ (PDx + 1 - x)^{D-1/1-PD}$, where P is
the ratio of the finite fraction of solid continuously
in equilibrium with the melt. P=0 represents the log-
arithmic case and P=1 the homogeneous law. Neumann et al.
(1954) has derived another expression taking into account
the possible resorption of earlier crystallized solids.

Crystal growth in a melt free of convection of mixing,
where transport is entirely by diffusion has been examin-
ed by Burton and Slichter (1953, a,b).

II FRACTIONAL CRYSTALLIZATION AND THE RARE EARTHS

Fractional crystallization is an important process in the differentiation of crustal rocks. (Bowen, 1956; Turner and Verhoogen, 1962). In the case of the formation of the mantle it is not yet clear if this process has been effective. This problem will be discussed in Section VI.

There is much supporting evidence that during fractional crystallization of silicate melts, the logarithmic distribution law tends to be approached. This is not so surprising. The diffusivity in silicate minerals is lower by a factor of 10^4 to 10^5 than the values obtained in basic silicate melts (Gupta, 1963). In addition, the differential movements of the crystals relative to the melt influenced by gravity will accentuate the disequilibrium effect. Therefore one would expect some zoning in the concentration of trace elements to occur in the minerals separating from the melt.

Besides major element zonings observed by common optical means, electron microprobe data on unmetamor phosed minerals also show zoning of trace elements. Electron fluorescence (Smith and Stenstrom, 1965; and Glover, 1965), fission track data (Maurette et al., 1964; Fleischer, 1965; Fleischer and Price, 1964) are also informative of the distribution of trace elements in silicate minerals. These data show that surface adsorption and occlusion are also important factors superimposed on the normal substitution in solid solution.

Although the matter is by no means clear cut, there seems to be a definite tendency for trace elements to approach on the average the logarithmic distribution law in silicate minerals crystallizing from a melt.

This tendency is best shown by some trace element data obtained by Wager and Mitchell (1951) on the Skaergaard intrusion, and first pointed out by Shimazu (1959) and MacIntyre (1963). Figure 3-8 shows the variation of the relative concentration of some trace elements in the "whole rock" as function of the estimated degree of solidification. There is a striking similarity between these curves and the theoretical one obtained from the logarithmic distribution law shown on Figure 3-8.

The fact that a given trace element tends to follow the logarithmic law in "whole rock" analyses is intriguing. If the various minerals present in the Skaergaard intrusion precipitated from the liquid one after the other (Wager and Mitchell, 1951), one would expect discontinuities in the relative concentration curves each time a new phase appears on the solidus, because of different partition coefficients for each mineral. The fact that smooth curves are obtained would indicate that most minerals of different lattice types separated more or less simultaneously. This is somewhat supported by Yoder and Tilley's work (1962) on the Origin of Basalt Magma. They show that over the greater part of the crystallization path of basaltic magma all phases (mainly olivine, augite, hypersthene, plagioclase and titanium and iron ore)

crystallize together, over a narrow range of temperature. Thus the partition coefficient obtained from these experimental curves would represent an overall effective distribution coefficient between the mineral phases crystallizing simultaneously and the melt.

Holland and Kulp (1949) have discussed this possibility in detail. They give the following expression for the effective joint distribution coefficient, D, assuming that individual phases are separating simultaneously.

$$D = p_1 D_1 + p_2 D_2 + p_3 D_3 + \ldots\ldots p_n D_n$$

or

$$D = \sum_{n=1}^{n} p_n D_n$$

but

$$D = \sum_{n=1}^{n} p_n D_n = \frac{C_{s1} p_1}{C_L} + \frac{C_{s2} p_2}{C_L} + \frac{C_{s3} p_3}{C_L} + \ldots\ldots \frac{C_{sn} p_n}{C_L}$$

or

$$D = \frac{1}{C_L} \sum_{n=1}^{n} p_n C_{sn}$$

Equation 3-3' becomes

$$\sum_{n=1}^{n} p_n C_{sn} = C_o (1-x)^{\sum_{n=1}^{n} p_n D_n} \sum_{n=1}^{n} p_n D_n \qquad (3\text{-}7)$$

where D is the effective <u>joint</u> partition coefficient. D_1, D_2, D_3 $\ldots\ldots D_n$ are the effective partition coefficients for mineral type 1, 2, 3 $\ldots\ldots$n, respectively, which are separating simultaneously. p_1, p_2, p_3 $\ldots\ldots p_n$ represent the modal abundances of mineral type 1, 2, 3 $\ldots\ldots$n, and $\sum_{n=1}^{n} p_n = 1$.

If all the individual D_n are either > 2 or < 1, or $1 \leq D_n \leq 2$, then the "whole rock" relative concentration curves will have the same forms as they are shown on Figure 3-8. On the other hand, if two or more phases are crystallizing together, with one phase or more having a distribution coefficient > 1, Holland and Kulp (1949) have shown that the relative concentration in the phase with $D < 1$ can either decrease or increase depending on the other values of D which are greater than 1.

Obviously in the case of the Skaergaard intrusion, there are not enough analytical points available to decide, from trace element evidence alone, whether the different minerals such as pyroxenes olivines and plagioclase feldspars crystallized simultaneously or in a step-wise manner. Intermediate cases where neither step-wise nor complete simultaneous crystallization of different minerals occur, must be the most common. Nevertheless, Equation 3-7 can be applied over small ranges where simultaneous crystallization of different minerals occurs. As we will see later neither case will affect very much our arguments for rare earth fractionation.

In the further developments on the fractionation of rare earths during fractional crystallization, we will assume that the logarithmic distribution law is obeyed. We will consider only whole rock concentrations and assume that D is a joint effective partition coefficient and stays constant during crystallization of phases with cations sites smaller than Lu, the smallest rare earth. Thus mainly

orthopyroxenes, Fe and Mg garnets, olivine and spinels
are involved but not Ca-rich mineral phases. We will
limit our discussion to concentrations much below sat-
uration point of any rare earths. In the following
derivations the late differentiates will be omitted, the
concentrations increasing too rapidly and departure from
the ideal limiting laws of thermodynamics becomes ap-
parent. This is especially true for the heavy rare
earths which can complex easily and show different be-
havior at low and high concentrations. Thus Equation 3-7
becomes:

$$C_s = C_o \ D \ (1-x)^{D-1} \qquad (3-8)$$

and

$$C_L = C_o \ (1-x)^{D-1} \qquad (3-9)$$

C_s = concentration of trace component I in whole rock,
and is equal to $\sum_{n=1}^{n} P_n C_{sn}$

C_L = concentration of component i in the melt

C_o = initial concentration of component i in the melt

x = degree of solidification

D = <u>effective</u> <u>joint</u> <u>partition</u> <u>coefficient</u> and is equal
to $\sum_{n=1}^{n} P_n D_n$

Taking the logarithm on both sides of Equation 3-9:

$$\text{Log} \ \frac{C_L}{C_o} = (D-1) \ \text{Log} \ (1-x) \qquad (3-10)$$

The rare earth patterns of Figures 3-2, 3-3, and 3-4
show the change of the Log conc. whole rock/conc. chondrite

Figure 3-10. Variation of the apparent equilibrium constants for extraction of M^{3+} rare earth tracers from aq. HCl by HDEHP-Toluene plotted versus the atomic number Z. Data from D. F. Peppard et al., J. Inorg. Nucl. Chem. 4, 334 (1957).

DEPENDENCE OF K_{eq} (app.) ON Z
FOR EXTRACTION OF M^{3+}
TRACERS FROM AQ. HCl
BY HDEHP-TOLUENE.*

* As determined by D. F. Peppard et al.,
J. Inorg. Nucl. Chem. 4 334 (1957)
Data taken at 0.5 M HCl and 0.75 M HDEHP
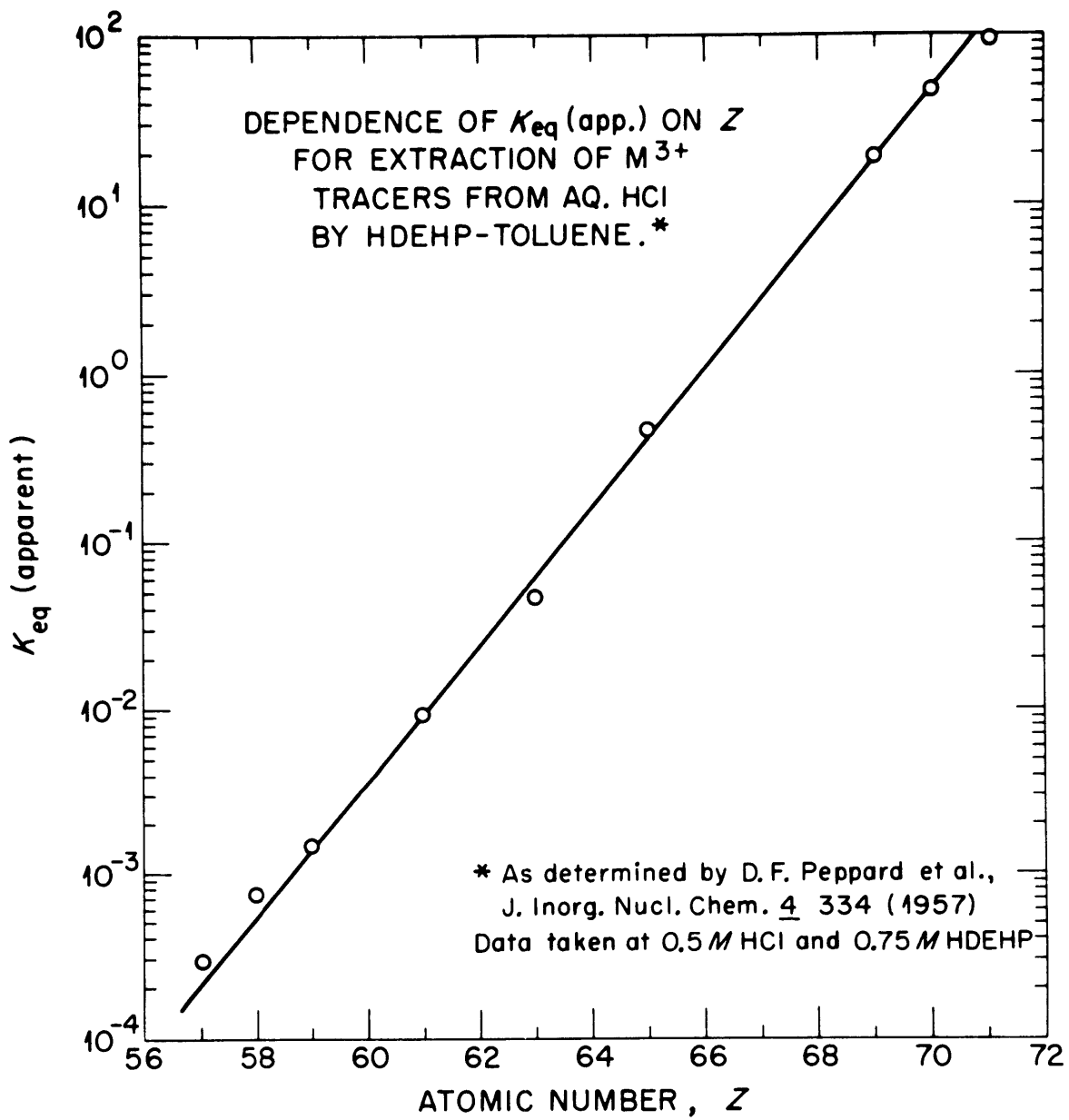
as function of the inverse rare earth ionic radii or the atomic number Z (1/r is a linear function of Z). This stresses the importance of the ionic radii in controlling the concentration of the rare earths. We will assume for a moment that these patterns are the result of fractional crystallization and represent some residual liquids for some values of x. Also we will assume that the chondrite values represent an earlier stage of differentiation, possibly equal to C_0 for each individual rare earth in Equation 3-9.

Therefore, in order to get a smooth continuous fractionation as function of the atomic number Z, D, the effective joint partition coefficient in Equation 3-10, must also be a smooth continuous function of the atomic number Z or the inverse ionic radi radius. Dividing both sides of Equation 3-10 by Log U(z), the logarithm of the rare earth chondritic concentrations, one obtains:

$$\text{Log } \frac{C_L(z)}{U(z)} = \text{Log } \frac{C_O(z)}{U(z)} + (D(z)-1) \text{ Log } (1-x) \qquad (3-11)$$

It is interesting at this moment to see how some equilibrium constants of some rare earth complexing agents vary with the atomic number Z for the rare earth series. Figure 3-10 shows the dependence of the apparent equilibrium constant K_{eq} on Z, the atomic number of M^{3+} tracer rare earths from aqueous hydrochloric solution by HDEHP-toluene (Powell, 1961). There is a linear relationship between the logarithm of the apparent equilibrium constant and the atomic number. Also, smooth dependence on Z of the

stability constant of other rare earth complexing agents is often observed. For instance, Powell (1961) shows that for DCTA, EDTA, and NTA, the logarithm of K increases regularly with Z. Therefore the Gibbs free energy of these partition reactions is linear or increases smoothly with Z.

No data are available for D in silicate systems. Therefore we will have to assume some kind of dependence of D on Z. Masuda and Matsui (1963, 1966) have assumed that D forms an arithmetic progression with increasing atomic number for the rare earth series: $D_1 = D_o + \Delta D$, $D_2 = D_o + 2 \cdot \Delta D$, ...$D(z) = D_o + z \cdot \Delta D$, with $0 \leq z \leq 14$

thus:
$$D(z) = D_o + z \Delta D \qquad (3-12)$$

Where the subscript number refers to La for 0, Ce for 1, ... to Lu for 14. ΔD is the difference of two adjacent rare earth partition coefficients.

Introducing Equation 3-12 into Equation 3-11 and rearranging one obtains:

$$\text{Log} \frac{C_L(z)}{U(z)} = \text{Log} \frac{C_o(z)}{U(z)} + (D_o - 1) \text{ Log } (1-x) + z \Delta D \text{ Log } (1-x)$$
$$(3-13)$$

If the logarithm of the ratio $C_o(z)/U(z)$ is independent of z or varies linearly with z, then the relative liquid concentration, $C_L(z)/U(z)$, is a straight line when plotted logarithmically against z. The slope is given by $\Delta D \cdot \text{Log } (1-x)$, and the intercept by $\text{Log } \frac{C_o(z)}{U(z)} + (D_o - 1) \text{ Log}(1-x)$.

Any multiple of chondritic concentrations, as for example, in eucritic achondrites, would affect only the intercept and lead to the same slope of the residual liquid. Any linear variation of Log $C_O(z)/U(z)$ with z would lead to a residual liquid trend of different slope on the semi-logarithmic plots.

If $U(z) = C_O(z)$ for all values of z, with $0 \leq z \leq 14$, Equation 3-13 becomes:

$$\text{Log } \frac{C_L(z)}{C_O(z)} = (D_O-1) \text{ Log } (1-x) + z \Delta D \text{ Log } (1-x) \qquad (3-14)$$

The concentration in the solid is easily found since: $C_S(z) = D(z) \; C_L(z)$. Equation 3-14 confirms Masuda and Matsui's[*] earlier derivation that fractional crystallization can produce linear patterns in the residual liquid. This is true within the limits of the assumptions made. That is to say: only if the trace rare earth elements follow the logarithmic distribution law; that the joint effective partition coefficient is constant for all values of x, $0 \leq x \leq 1$; that the solid phases separate simultaneously and that the individual partition coefficient D_i are constant for the same range of x values: and finally, that D increases linearly with z.

This theoretical development shows that in the

[*] Since Equation 3-14 was derived, Masuda and Matsui (1966), independently, starting also from the Doerner-Hoskins law, derived the same expression.

residual liquid:

1. The degree of rare earth fractionation is only a function of the product of the logarithm of the liquid fraction $(1-x)$ times ΔD, the change of the joint effective partition coefficient.

2. The degree of absolute enrichment is a function of $D_o \cdot, \Delta D$ and the liquid fraction $(1-x)$, and of course, the original rare earth concentrations.

It is possible to calculate the average rare earth concentrations for certain range of crystallization, limited by two values of x.

$$\overline{C}_s(z) = \frac{\displaystyle\int_{x_1}^{x_2} C_s(z) \, dx}{\displaystyle\int_{x_1}^{x_2} dx} \qquad \text{for } x_1 < x < x_2 \qquad (3\text{-}15)$$

$C_s(z)$ is given by the expression 3-8, and introducing the limits, Equation 3-15 becomes:

$$x_1 < x < x_2 \qquad \overline{C}_s(z) = \frac{C_o(z)}{(x_2 - x_1)} \left[(1-x_1)^{D(z)} - (1-x_2)^{D(z)} \right]$$

$$(3\text{-}16)$$

For $0 < x < x_1$, Equation 3-15 becomes:

$$\overline{C}_s(z) = \frac{C_o(z)}{x_1} \left[1 - (1-x_1)^{D(z)} \right] \qquad (3\text{-}17$$

Where $D(z)$ is given by $D = D_o + z \Delta D$. The concentration after rehomogenization of a zone previously formed by fractional crystallization would also be given by Equation 3-16 and Equation 3-17.

Possible applications of this process will now be considered in the following section.

APPLICATION II-A   MANTLE-CRUST FORMATION

Much of what is following in this section is a summary of Masuda & Matsui's (1963, 1966) earlier papers; but for the sake of completeness we will extend their discussions somewhat.

Very briefly, geophysical and geochemical consideration (Birch, 1965; Ringwood, 1966, 1960, 1959; MacDonald, 1964; Urey, 1962) tend to indicate that the earth must have passed through a stage of complete or partial melting very early in its history. During this stage the earth differentiated. Elements with ions too large to be incorporated in the dense lattice structures, mainly Fe, Mg silicates and spinels, would tend to get enriched in the melt which would migrate upwards. Thus elements such as U, Th, K, Rb, Sr, Hf, Ta, the rare earths and others would get enriched towards the upper zone of the earth forming a protocontinental layer (Patterson 1963) or the upper mantle.

Masuda & Matsui (1963, 1964) have assumed that this chemical segregation was produced by fractional crystallization of the mantle from a molten earth. Based on rare earth evidences they made the following assumptions:

1. The crust represents the residual liquid after the mantle formed by crystallization. The rare earth content

of Minami composite shale is taken as the average rare
earth concentration of the crust.

2. The average rare earth content of the mantle, after
it had produced the crust by fractional crystallization,
is represented by the rare earth content of Norton-County
achondrite (Schmitt et al., 1963). See Figure 3-2.

3. The initial rare earth concentration of the whole
earth is represented by chondritic rare earth composi-
tion (increased by 30% for correction due to loss of re-
duced iron to form the core).

4. Bullen's value 1/82 is assumed for the mass ratio,
crust to mantle + crust.

5. The rare earths are distributed according to the log-
arithmic distribution law. The joint distribution co-
efficient D (Z) is constant for the range $0 \leq x \leq 1$ and
increases linearly with Z.

Following these five assumptions and using Equa-
tion 3-14 to describe the rare earth pattern obtained
for Minami composite shale (assumption 1), Equation 3-17
to describe the rare earth concentration of Norton County
achondrites (assumption 2), D_0 and ΔD were determined
by a least squares fit through this set of values (Top-
ping, 1965). The results are shown in Table 3-1. They
are compared with Masuda & Matsui's (1963) values.

Thus, with these D and ΔD values, it is possible to
compute the rare earth patterns in some hypothetical
shells in the earth, assuming that the mantle is formed
by fractional crystallization. The rare earth patterns
for the following zones have been computed:

TABLE 3-1.

Computed rare-earth partition coefficients based on Masuda & Matsui's (1963) assumptions. For different values of $F = (1-x)$, the mass ratio of crust over crust + mantle are shown. The partition coefficient is assumed to vary linearly. Only La and Lu values and $D = (D_{z+1} - D_z)$ are given.

	F=.0122[*]	F=0.0122[**]	F=0.0105	F=0.0087	F=.004[***]
D_{La}	.12	.195	.205	.217	.257
D_{Lu}	.62	.562	.562	.561	.558
$\triangle D$	.035	.0262	.0255	.0246	.0215

[*]Masuda & Matsui (1963), [**]Bullen's value, [***]MacDonald's value.

TABLE 3-2.

Distribution of rare earths with depth in a
fractionally crystallized earth

Depth in km	D_M	F_{La}	F_{Lu}
0-10	0.0056	0.53	0.029
0-35	0.020	0.62	0.069
10-175	0.090	0.22	0.17
10-400	0.205	0.29	0 31
400-1000	0.267	0.086	0.26
1000-2898	0.522	0.084	0 39

1. Protocrustal nuclei, represented by the residual liq-
uids using Equation 3-14 with (1-x) = 0.0087.

2. The uppermost part of the upper mantle, or the last
solid C_s to have crystallized, using Equation 3-14. This
corresponds to 1-x = 0.0087.

3. Rehomogenized zones at various depths after the mantle
crystallized, using Equation 3-16.

Figure 3-11 shows these patterns. D_o was assumed equal
to 0.12. (Masuda's value). "x" was calculated from the
intercept of Minami's shales, and λD = 0.04 was computed
from the slope of the shale's line. $C_o(z)$ were assumed
equal to U (z) (i.e. the chondrite values).

These curves can give us some qualitative ideas on
what kind of rare earth fractionation patterns one could
expect in the mantle regions:

In the lower part of the mantle, below 400 km., the
lighter rare earths are depleted relative to the heavy
rare earths as well as to the primary earth composition,
the partition coefficient being smaller than one. A posi-
tive slope results. In other words, the dense solids dis-
criminate strongly against all rare earths but progressively
less as the size of the ions decrease from La to Lu.

Consequently, as crystallization proceeds in the
lower mantle, the rare earths are still largely excluded
from the solid phases. Only by the time one is well within
the upper-mantle are the rare earths enriched relative to
the original rare earth level. In this region the middle

part of the rare earth series is preferentially en-
riched, producing a broad maximum near the middle of
the series. At progressively shallower depths of the
upper mantle, the lighter rare earths are progressive-
ly and preferentially enriched relative to the heavi-
er ones. This results in a narrowing of the broad
maximum, its shift towards the lighter rare earth end
and a progressive increase of the negative slope for
the heavy end of the series. Ultimately, if the frac-
tionation process would continue, one would expect
only a slight inflexion in the light end of the series,
which would tend to a straight line with strong neg-
ative slope.

Thus, the rare earth concentration would change
from the lower mantle to the upper part by a factor of
about 50 for La $(r^{3+} = 1.22\ \overset{o}{A})$ and 5 for Lu $(r^{3+} = 0.99\ \overset{o}{A})$.

On this basis, it is expected that the uppermost
part of the mantle developed a rare earth pattern lying
between the extreme curve C_s for $(1-x) = 0.0087$ and the
curve $\overline{C}_s = 10\text{-}175$ km. in Figure 3-11; i.e., a broad maxi-
mum near Nd and a smooth regular decrease of the heavy
rare earths with increasing z, i.e., a nagative slope.
This pattern is not unfamiliar. Since these calcula-
tions were made, similar patterns with a maximum in the
lighter rare earth end have been observed in one eclogite
(Schmitt et al., 1964), and in several tholeiites lavas
from Hawaii (part I). The significance of such patterns
will be discussed in Section VI.

Figure 3-11. Fractional crystallization earth model with relative abundances of the rare-earth elements. The straight line C_L $(1-x)$ = 0.0087 represents the last residual liquid after fractional crystallization forming presumably protocrustal nuclei. $\bar{C}_s$ curve represents average relative rare earth abundance for shells at various depths. C_s $(1-x)$ = 0.0087 represents the last solid to have crystallized which is in equilibrium with the residual liquid. These curves are calculated for D_0 = 0.12 and D = 0.04 and the Masuda and Matsui (1963, 1966) assumption $D = D_0 + z\ D$. C_0 = 1 for all curves.

Fractional Crystallization

C_L

$(I-x) = 0.0087$

C_s

$(I-x) = 0.0087$

$\bar{C}_s$ 10-175 km

$\bar{C}_s$ 10-400 km

$\bar{C}_s$ 400-1000 km

$\bar{C}_s$ 1000-2898 km

$$C_L(z) = C_0(z)(I-x)^{(D(z)-1)}$$

$$\frac{C_s(z)}{C_L(z)} = D(z)$$

C/C_0

z
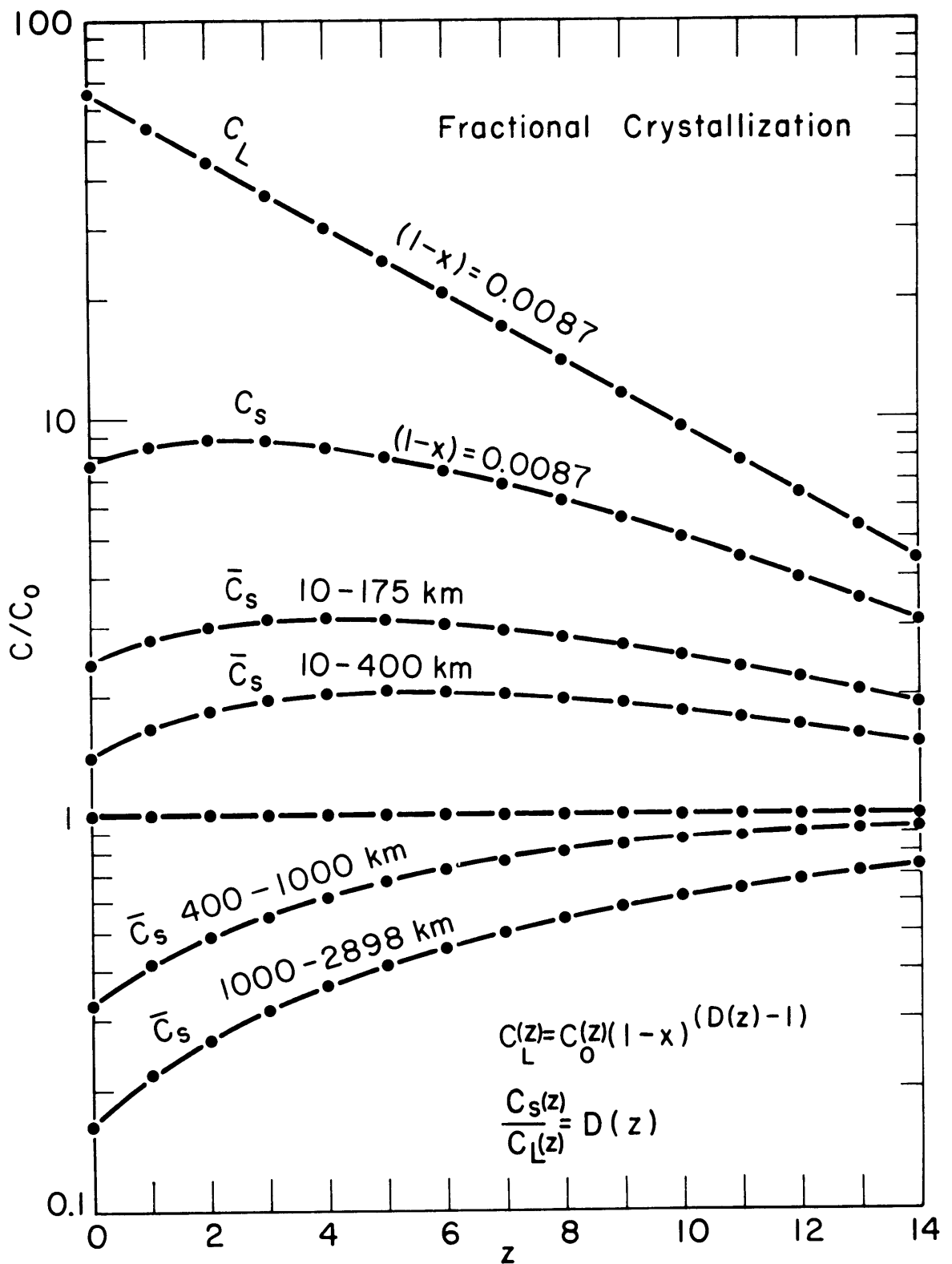
While keeping in mind all the hazards of speculating too far on such a contrived model, it may still be instructive to compute the amounts of the various rare earths in shells of the earth at different depths of a fractionally crystallized earth. Using values of $D_0 = 0.12$ and

$D = 0.04$, and assuming that the primordial crust of residual liquid comprised 0.56% of the silicate mass of the earth, Table 3-2 has been drawn up for the two end member rare earths La and Lu. F_M is the fraction of the mass of the mantle + crust contained in the zone, and F_{La} and F_{Lu} are the fractions of the earth's inventory of La and Lu in the same zone. Thus half the La but only 3% of the Lu are contained in the uppermost 10 km. but about equal amounts of La and Lu are in the upper mantle to a depth of 400 km.

III   PARTIAL MELTING AND THE RARE EARTHS

The production of basaltic melts by selective fusion of peridotites was first suggested and discussed in some detail by Bowen (1956). Recent growing interest in the upper-mantle and developments in high pressure research have revived Bowen's idea. For example see Boyd and England (1961), Kushiro (1961), Kushiro and Kuno (1963), Yoder and Tilley (1962), Reay and Harris (1964), and O'Hara and Yoder (1963). These authors and others have discussed the partial melting of peridotites of one kind or another to produce basaltic melts, in the light of experimental data and

theoretical considerations.

That partial melting is an important process need not be emphasized. Bowen says: "Geologic evidence shows that from Keewatin time to the present, a source of basaltic magma has been available, perhaps not continuously but certainly at very frequent intervals."...... "Whether it is currently produced or whether it was produced long ago by earth differentiation, we have no means of deciding." Since Bowen much effort has been made in geochronology to resolve these problems.

It is likely that during the partial melting of a polycrystalline silicate rock the homogeneous distribution law tends to be approached for the partition of trace elements between the residual crystals and the interstitial melt produced. Nevertheless this is not by all means clear cut as no direct experimental evidence is available yet.

Criteria to ascertain whether a true equilibrium has been attained for trace element partitioning in some geologic systems are meager and difficult to obtain. On the other hand there is considerable textural and mineralogical evidence that many rocks represent a state of chemical equilibrium in general, or at least a close approximation thereto during metamorphism (Eskola, 1915; Filley, 1924; Turner, 1948; and Thompson, 1955).

If basalts are to form by partial melting of some kind of ultrabasic rocks in the upper-mantle, one can assume that previous to this event, the major phases

were in chemical equilibrium at the high temperature and pressure conditions that must exist in this region of the earth (gabbroic, eclogitic facies, etc.).

Kretz's (1959, 1960, 1961) studies on element partitioning among phases in regionally metamorphosed terrain show that, at least for some trace elements which are in low enough concentrations, a true equilibrium is attained and that the Nernst law is approached.

It is well to remember at this point that for the ideal dilute solutions the chemical potential of a component i is given by: $\mu_i = \mu_i^* + RT \ln X_i$, and thus for small concentrations, $X_i \rightarrow 0$, the chemical potential approaches rapidly $-\infty$. Small differences in concentrations of a trace element in a phase will therefore correspond to a much greater gradient of the chemical potentials or the molar Gibbs free energies: the motor for self diffusion.

Electron probe data give interesting clues. Van Schmus (1966) has shown that the dispersion of the Fe/Fe+Mg ratio in olivine and pyroxene of some chondrites decreases rapidly with increasing degree of metamorphism. The degree of metamorphism was evaluated on a textural basis. Similar results were obtained by Keil and Fredrikson (1964) but were interpreted differently. Forbes and Banno (1965) in an electron probe study of Fe/Ni ratios in olivines from basalts and peridotites inclusions show that in Ross Island basalts, this ratio is homogeneous in olivine grains of inclusion aggregates. No zonation was detected. On

the other hand, the Fe/Ni ratios of cognate olivine grains, phenocrystal, microphenocrystal and groundmass olivine are compositionally zoned. The same homogeneity was observed for olivine grains in some dunites, indicating that these and the homogeneous aggregates could not have formed by crystallization from a melt, but were rather of a residual nature after basaltic liquid was formed in the upper-mantle.

These few facts tend to indicate that equilibrium is attained between the complex residual solid solution phases and the interstitial, low melting, basaltic melt portion formed by partial melting of the upper-mantle material.

The diffusion coefficients of cations in silicates are strongly dependent on temperature:

$$J = J_o \exp - E/RT \qquad (3-18)$$

where J is the diffusion coefficient, J_o the diffusion coefficient at some standard temperature, and E is the effective activation energy. Not much data is available for the diffusion coefficient of cations in silicate minerals. The activation energies are of the order of 1.5 to 4 e.v. The greater E is, the greater the dependence of J is on temperature. A small increase in temperature corresponds to a large variation in J: e.g., for $E = 2$ e.v., a change from $800°$ to $1000°$ C J increases by 3 order of magnitude (1.6×10^{-11} to 1.6×10^{-8}). There is a discontinuity in the intrinsic diffusion of pure

compounds at the melting point. The diffusion coefficients increase by several orders of magnitude, the exact amount depending on the viscosity of the liquid. Nevertheless, it is not known how J varies for the trace components when the liquidus temperature of complex multicomponent solid solutions is reached, as is the case for complex silicate systems, and especially when the temperature is moving slowly along the liquidus surface. The diffusion coefficients of the trace components in the solids will certainly be of the same order of magnitude as for the major cations of the same charge in the solid, and possibly intermediate between values for liquid and solid.

This is the condition of partial melting. The complex silicate solid solutions will change their composition with the appearing interstitial melt. The solid solutions are reorganized and the trace elements such as the rare earths have all the opportunities to partition between the residual crystals and the interstitial melt.

Thus, the effect of partial melting on trace element distributions can be considered as an extreme case of metamorphism. Before melting the solid phases will tend to be already in equilibrium. Upon appearance of interstitial basaltic melt the trace elements will partition between the residual solid solution phases and the interstitial melt according to the Nernst homogeneous law. This, of course, presupposes that the interstitial melt is in contact long enough with the residual

crystals.

Assuming the Nernst law to be obeyed in such conditions:

$$\frac{C_R}{C_L} = D \tag{3-19}$$

Mass balance requires:

$$C_L\, y + C_R\, (1-y) = C_p \tag{3-20}$$

Where: C_p = initial composition of trace component i in whole rock previous to partial melting.

C_L = concentration of component i in interstitial melt.

C_R = concentration of component i in residual solid.

$D = \sum_{n=1}^{n} P_n D_n$ = effective joint partition coefficient.

y = degree of melting = $\dfrac{\text{mass of interstitial melt}}{\text{mass of primary solid}}$, $0 \leq y \leq 1$.

Combining Equation 3-19 and Equation 3-20, and rearranging:

$$C_L = \frac{C_p}{y + D\,(1-y)} \tag{3-21}$$

Equation 3-21 shows that the concentration of a trace element in the interstitial melt is a function of its partition coefficient, of the initial concentration of

the trace element in the source material, and of the degree of melting. The greater the degree of melting, the smaller the concentration is in the interstitial melt. Reay and Harris (1964) in their experiment on partial fusion of peridotite have confirmed this point very fully.

Thus "y", the degree of melting, is an important parameter in trying to reconstitute the composition of the mantle from rare earths, U, Th, Pb, Rb and Sr data in lavas, as well as for interpretation of heat flow data.

Even if D is very small, that is to say that the particular trace element i strongly prefers the melt, Equation 3-21 shows that the concentration of i in the interstitial melt will never be equal to the initial concentration, unless near complete melting occurs. Thus the concentration ratio of two trace element pair will tend to be equal in both the primary source material and in the basaltic melt only if the partition coefficients of these two trace elements are nearly equal.

For the rare earths, Equation 3-21 can be written as follows:

$$C_L(z) = \frac{C_p(z)}{y + D(z)\ (1-y)} \qquad (3-22)$$

APPLICATION III-A: PARTIAL MELTING OF UPPER MANTLE

MATERIAL AND THE RARE EARTHS

We will assume that $D(z)$ varies linearly with z, as done previously. Combining Equation 3-22 and Equation 3-12, and dividing both sides by $U(z)$, the rare earth chondritic composition, one obtains:

$$\frac{C_L(z)}{U(z)} = \frac{C_p(z)/U(z)}{y + (D_o + z\Delta D)\,(1-y)} \qquad (3\text{-}23)$$

This Equation gives the relative change of the rare earth concentration in the interstitial melt as a function of the concentration of the source material and the degree of melting.

We have discussed in Application II-A possible rare earth patterns for the upper mantle. A simple model which might work for basalts, would be to assume a pattern with a broad maximum near Nd and a smooth negative slope in the heavy rare earth region for the source rock in the upper-mantle, e.g., curve C_s $(1-x) = 0.0087$, in Figure 3-11. Upon partial melting of such pattern to different degrees "y", one can compute the rare earths patterns in the interstitial melt formed, such as basalts, and in the residual refractory crystalline material left over. This is shown in Figure 3-12. We used $D_o = 0.12$, $\Delta D = 0.04$ and values of "y" equal to 0.01, 0.1, and 0.5. A linear dependence for D on z was also assumed.

Figure 3-12. Partial melting model for formation of ba-
salts. The primary material of composition shown in Fig-
ure 3-11 is curve C_s 1-x = 0.0087 is used for thé upper
mantle. The relative rare earth composition for melts
formed by 1%, 10% and 50% melting of the primary material are
shown, L-0.01, L-0.1 and L-0.5, and the residual material,
R-0.01, R-0.1 and R-0.5, respectively are plotted on a
logarithmic scale as a function of the atomic number z.
Thus a two step model is implied. 1. Formation of the
upper mantle by fractional crystallization-primary curve.
2. Partial melting of the upper mantle to produce ba-
saltic melts - L. and residual solids - R. These curves
are calculated for D_0 = 0.12 and D = 0.04 and the
Masuda and Matsui (1963, 1966) assumption D = D_0 + z ΔD.
C_0 = 1 for all curves.

Partial melting

$$\frac{C_L(z)}{C_0(z)} = \frac{C_p(z)/C_0(z)}{\left[y + D(z)(1-y)\right]}$$

$$C_R(z) = D(z)\, C_L(z)$$
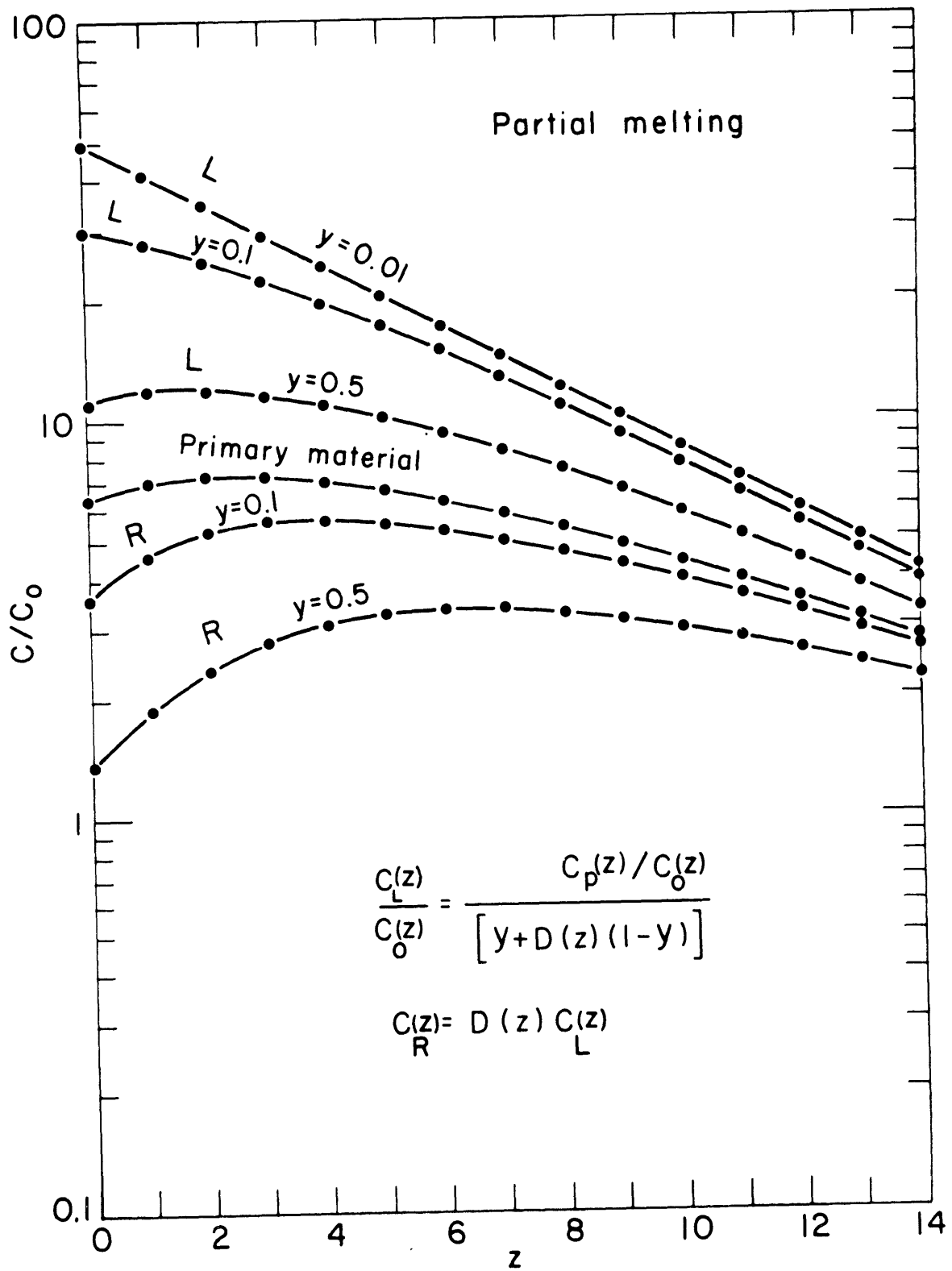
For small degrees of melting, a maximum enrichment is obtained in the melt. The linear pattern with a negative slope is approached. For greater degrees of melting, say 10%, moderate enrichment relative to the source material is expected in the melt. Patterns with a small inflection in the lighter rare earths is obtained. For more complete melting, the primary pattern is approached.

For the residual solid, as the degree of melting increases the lighter rare earths become more rapidly and preferentially depleted, and one observed a broadening of the maximum and a progressive shift toward the heavy rare earth end.

One might consider the differentiation of the earth as a two step process, (Application II-A and III-A, combined).

1. Formation of the mantle by fractional crystallization in the early history of the earth, and production of protocrustal nuclei from the residual liquids (linear patterns).

2. Partial melting of the upper mantle material (maximum near Nd and a negative slope for the heavy rare earths) to produce basaltic melts during later geologic time.

The following remarks can be made:

a. The sporadic addition to the so called protocrustal nuclei, of basalts produced by small degrees of melting, 1 to 10%, should not change appreciably the average rare earth concentration and the original characteristic pattern

of the primordial continental nuclei. Kushiro and Kuno
(1963) estimated that 2 to 9% melting of peridotites
could produce melts of basaltic composition. Ringwood
(1962, 1966) estimated a ratio of 4:1 or 3:1 for the
peridotite to basalt for the upper mantle composition.

b. Patterns produced by partial melting to different
degrees cannot be distinguished from patterns produced by
fractional crystallization to different extents of a
melt derived by complete melting of localized area of
the upper mantle. Neither can these patterns be distin-
guished from patterns produced from early residual liquids
after the mantle formed by fractional crystallization.
This was observed and clearly pointed out by Reay
and Harris (1964) in their experiment on partial fusion
of perodotites.

c. An interesting possibility is the study of ultramafic
inclusions in basalts and their relations with the host
basalts. If a geologic situation could be found where the
lava and some pieces of the residual refractory crystals
represent the two subsystems derived from partial melting
of the upper mantle, then the rare earth composition of
the latter and the degree of melting could be derived.

d. Partial melting at different depths will, of course,
change the effective partition coefficient due to the ef-
fect of pressure. Within a mineralogical facies, the ab-
solute value will be changed, but the relative rare earth
partition coefficient will not change appreciably. The
pressure dependence of the rare earth partition coefficient

is related to their molar volume or to their compressibility. The relative dependence of the rare earth compressibility factors upon pressure is small and can be considered as a second order effect. The principal effect of partial melting at different depths upon the joint effective partition coefficient, will be produced by changes of fields of mineral stabilities of the primary source material with depth. Thus appearance and disappearance of phases may influence drastically the effective joint partition coefficient, $D = \sum_{n=1}^{n} p_n D_n$. O'Hara (1965) has emphasized that diopside, olivine and orthopyroxene coexist with melts, formed by partial melting, over a wide range of pressure. On the other hand, the alumina-rich phases, plagioclase, spinel and garnet are sensitive to depth, and disappear with depth in the order mentioned above. Thus abrupt changes of the joint effective partition coefficient would be expected depending in what facies partial melting occurs. The change of $D = \sum_{n=1}^{n} p_n D_n$ with pressure, from one facies to the next, will be mainly due to the change of the alumina-rich phases, as well as the change of the modal proportions p_n. The significance to the rare earth patterns of changes of facies is discussed in some detail in Part I.

APPLICATION III-B: PARTIAL MELTING OF CRUSTAL ROCKS

Partial or nearly complete melting of deeply buried
sediments or rocks to produce granitic or syenitic rocks
has been often considered as a possible source of crustal
melts. In this case the primary material would be rep-
resented by possibly a linear pattern and a negative
slope. The rare earth pattern in the melt can be com-
puted from Equation 3-23. The pattern in the melt is
concave upwards, with the lighter rare earth more en-
riched relative to the primary material. Figure 3-13
shows some patterns in the melt for 0.1%, 1% and 30%
melting. $D_o = 0.12$, $\Delta D = 0.04$ and a linear dependence
of D on z, was assumed.

Nevertheless such a process is much more complex
and the melting is probably produced in the presence
of fluid phases. The heavy rare earths are easily com-
plexed and may change the picture drastically. Neumann
(1948) and Mineyev (1963) have discussed this problem
in some detail. Despite all this, upwards patterns can
possibly give some qualitative feeling about the genesis
of some rocks. Many granites show this tendency. Cir-
cumoceanic and continental basalts also sometimes ex-
hibit this feature: e.g., an alkali olivine basalt from
Ross Island, Antartica (unpublished). Melting of the
lower part of the crust could eventually produce ba-
saltic melts. This problem will be discussed more fully
in the section on mixing processes.

Figure 3-13. Model for formation of crustal rocks by partial melting of pre-existing crustal rocks. The relative rare earth composition C_L for melts formed by melting 1%, 10%, 30% and 50% of initial crustal material (straight line) are plotted on a logarithmic scale as a function of the atomic number z. These curves are calculated for D_o = 0.12 and $\triangle D$ = 0.04 and the Masuda and Matsui (1963, 1966) assumption $D = D_o + z \triangle D$. C_o = 1 for all curves.

Partial melting

C_L

$y = 0.01$

0.1

0.3

0.5

Initial

C/C_0

$D_0 = .12$ $\Delta D = .04$

Z
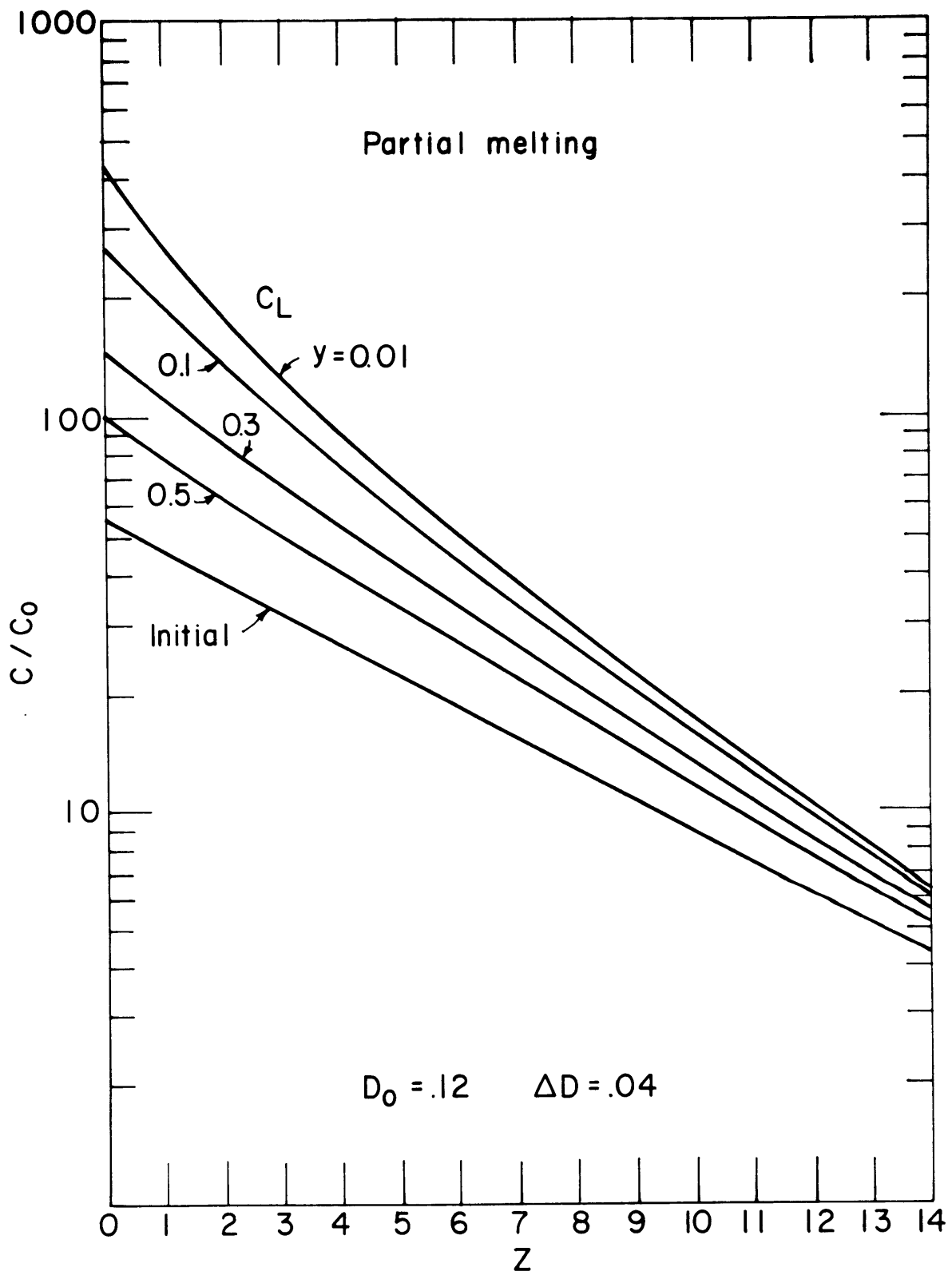
APPLICATION III-C: FRACTIONAL MELTING OF THE UPPER MANTLE

A process of possible physical significance is successive partial meltings and removal of the melt each time, where the homogeneous distribution law is assumed for each step. Keeping in mind the step-wise process, after n stages Equation 3-22 becomes:

$$\frac{C_{Ln}(z)}{U(z)} = \frac{C_p(z)}{U(z)} \cdot \frac{\prod_{j=1}^{n-1} D_j(z)}{\prod_{j=1}^{n} \left[y_j + D_j(z)(1-y_j) \right]} \qquad (3\text{-}24)$$

and for the residual solid after the nth partial melting event:

$$\frac{C_{Rn}(z)}{U(z)} = \frac{C_p(z)}{U(z)} \cdot \frac{\prod_{j=1}^{n} D_j(z)}{\prod_{j=1}^{n} \left[y_j + D_j(z)(1-y_j) \right]} \qquad (3\text{-}25)$$

The same notation is used as for Equation 3-21. The index n refers to the n partial melting event, and for j the values of individual events.

Assume for a moment that y_j = constant for the n events, and the individual rare earth partition coefficient D_j = constant for the n steps. Equation 3-24 and Equation 3-25 can be combined with Equation 3-12. Dividing both sides by the chondritic rare earth composition, $U(z)$,

$$\frac{C_{Ln}(z)}{U(z)} = \frac{C_p(z)}{U(z)} \cdot \frac{(D + z\,\Delta D)^{n-1}}{\left[y + (D+z\,\Delta D)(1-y) \right]^n} = \frac{C_{R1}^n}{D \cdot C_p^{n-1}} \qquad (3\text{-}26)$$

and
$$\frac{C_{Rn}(z)}{U(z)} = \frac{C_P(z)}{U(z)} \cdot \frac{(D + z \, \Delta D)^n}{\left[y + (D+z \, \Delta D)(1-y)\right]^n} = \frac{C_{Rl}^n}{C_P^{n-1}}$$

(3-27)

Figure 3-14 shows some computed curves, considering again the curve C_s $(1-x) = 0.0087$ of Figure 3-11 for the primary upper-mantle material. Curves for degrees of melting $y = 0.01$, 0.1, and 0.3 are shown for $n = 1$ and $n = 5$. We have assumed again a linear dependence of D on z, and used $D_o = 0.12$ and $\Delta D = 0.04$.

As Bowen (1956) pointed out, the process of successive partial melting often repeated corresponds to the inverse of fractional crystallization if small enough degrees of melting are considered at each step.

The successive melts produced at each step are less and less concentrated in rare earths. For small degrees of melting ($y = 0.01$), the rare earth composition of the successive melts does not change appreciably. For 10% melting, after 5 successive extractions, only La and Ce are depleted relative to the primary material. The successive residual solid shows an increased depletion of the lighter rare earths at each step. If melting is repeated often, the broad maximum disappears and a positive slope results.

Of course, variation in the degree of melting from one step to another complicates the matter very much.

If such a process was important in the evolution of basalts from upper mantle material, it seems necessary

Figure 3-14. Fractional melting model for formation of
basalts. The initial material C_p of composition shown
in Figure 11 is curve C_s 1-x = 0.0087 is used for the
upper mantle. The relative rare earth composition for
melts formed by 1%, 10% and 50%, after one step melting
(n=1) and 5 step melting (n=5) events are shown in left
diagram and for the corresponding residual solid in
right diagram. Thus a n+1 step model is implied:
1. Formation of the upper mantle by fractional crystal-
lization-initial curve. 2. n successive partial melt-
ing events of the upper mantle to produce basaltic melts.
These curves are calculated for D_0 = 0.12 and ΔD = 0.04
and the Masuda and Matsui (1963, 1966) assumption
$D = D_0 + z \Delta D$. C_0 = 1 for all curves.

Left panel:

Fractional melting

$y = 0.01\ n = 5$

$y = 0.01\ n = 1$

$y = 0.1\ n = 1$

$y = 0.3\ n = 1$

$y = 0.1\ n = 5$

Initial Cp

$y = 0.3\ n = 5$

Melt fraction

$$\frac{C_{Ln}(z)}{C_o(z)} = \frac{[D(z)]^{n-1}\, C_p(z)/C_o(z)}{[y + D(z)(1-y)]^n}$$

C_L / C_o

Z

100
10
1
.1

0 2 4 6 8 10 12 14

Right panel:

Fractional melting

Initial Cp

$y = 0.01\ n = 5$

$y = 0.1\ n = 1$

$y = 0.3\ n = 1$

$y = 0.1\ n = 5$

$y = 0.3\ n = 5$

Residual solid fraction

$$\frac{C_{Rn}(z)}{C_o(z)} = \frac{[D(z)]^{n}\, C_p(z)/C_o(z)}{[y + D(z)(1-y)]^n}$$

C_R / C_o

Z

100
10
1
.1

0 2 4 6 8 10 12 14
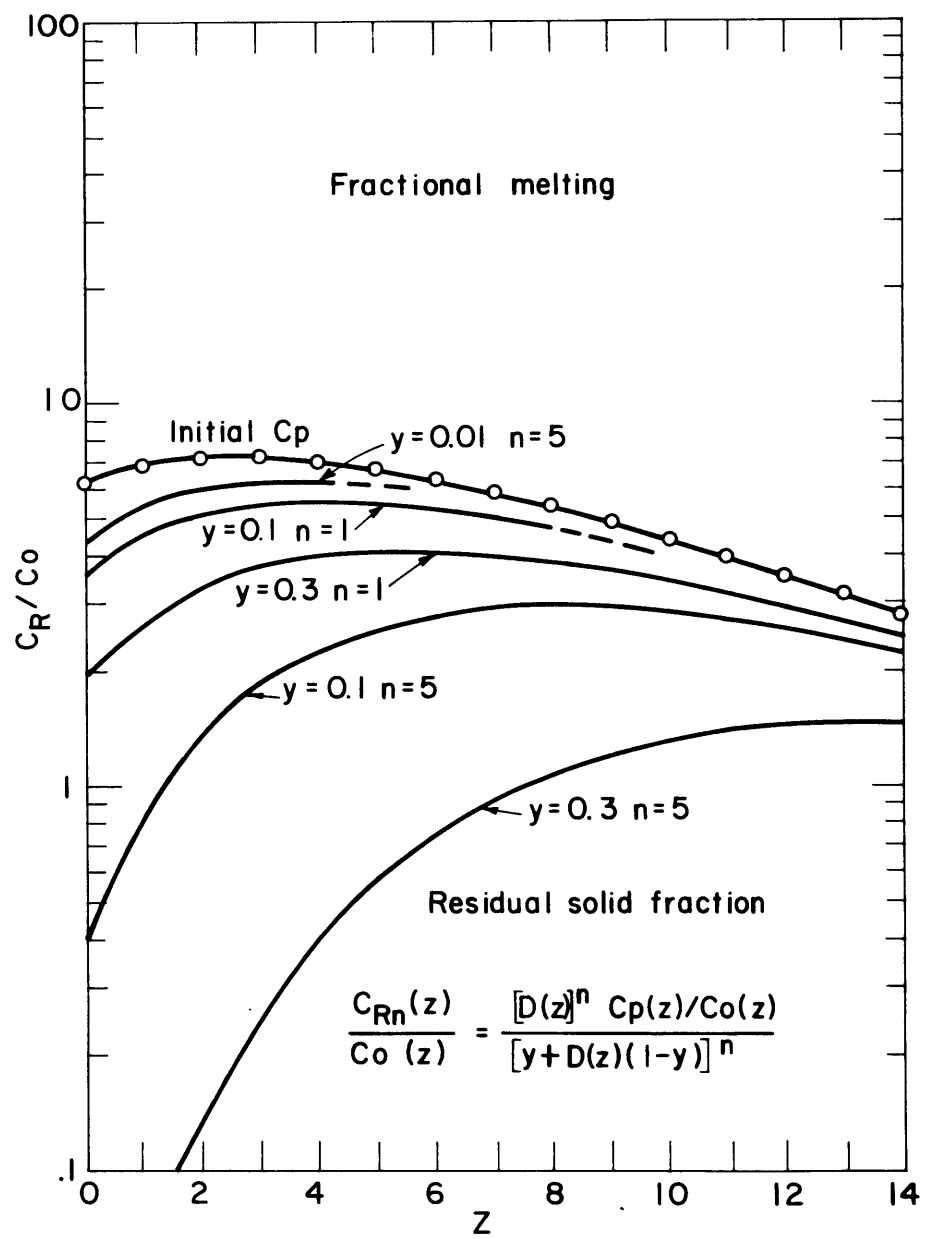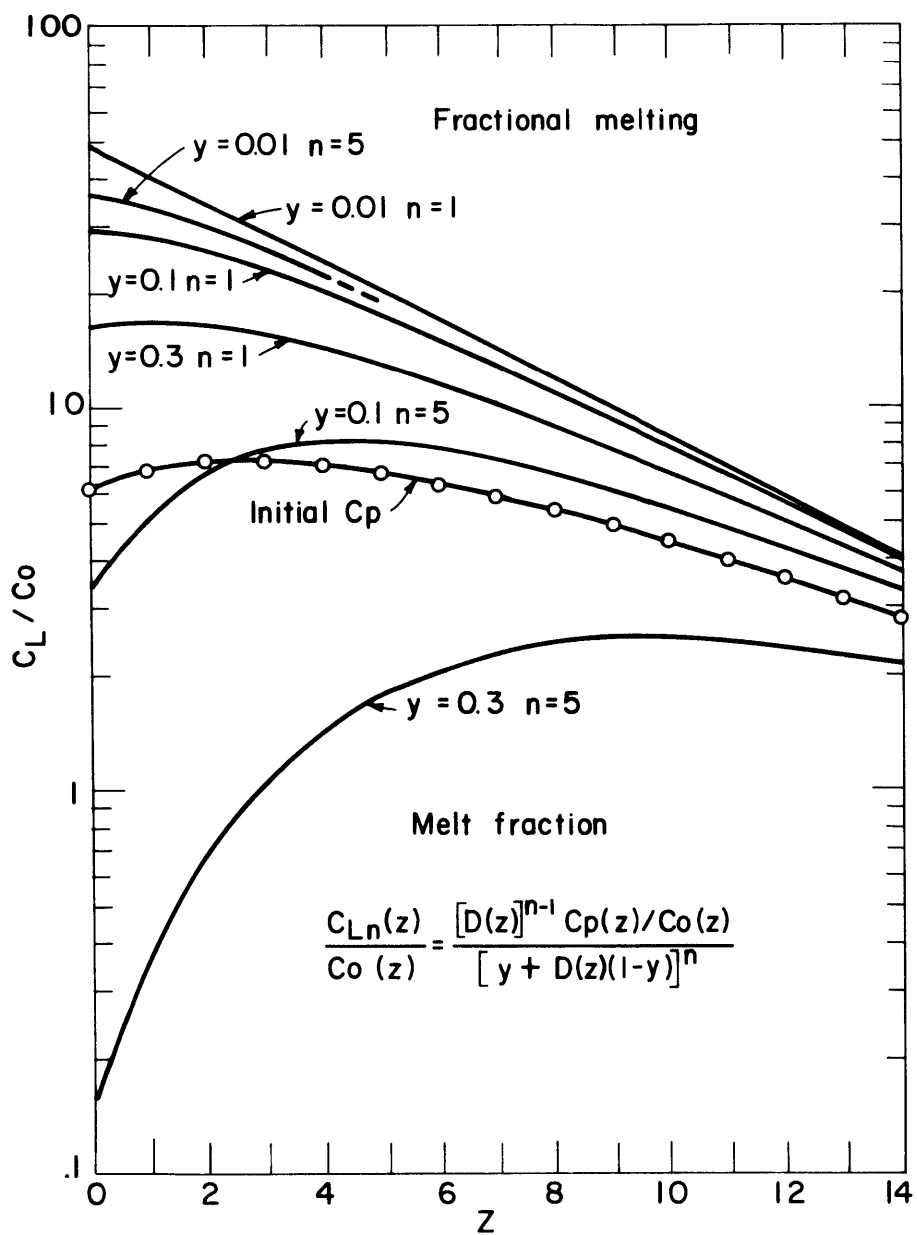
that the total fraction of melting and the number of steps
involved were small if all the successive melts are to
have major element compositions typical of basalts. There-
fore, in practice, the rare earth patterns obtained by
this process cannot be distinguished from patterns formed
by fractional crystallization (different values of x) or
by partial melting to different degrees (different values
of y) as applied to basalt formation.

IV.   ZONE MELTING AND THE RARE EARTHS

The first paper on zone melting was published by Pfann
(1952). During the next 14 years a great many other papers
treating the mathematical formalism of the process and its
applications to semiconductor technology, metallurgy, solid
state physics and organic chemistry, appeared in the liter-
ature. Harris (1957) discussed the geological possibi-
lity of the process and its possible application to the
origin of potassic basalts and the differentiation of the
earth. Vinogradov (1958, 1959, 1961) did some zone melt-
ing experiments on non magnetic silicate fractions of
Saratov chondrite meteorite. Shimazu (1959a, 1959c,
1960, 1961) in a series of papers discussed the physics
of zone melting as applied to the differentiation of the
earth. Recently, Magnitski (1964) reconsidered the problem.

It is not our purpose to evaluate the plausibility
of this process for the differentiation of the earth and
formation of the crust, but merely to point out the dif-
ference that such a process would have on the fractionation

of the rare earth and trace elements in general. Three
books published recently on zone melting (Shaskov,
1961; Schidknecht, 1966), and in particular Pfann's
(1966) book pointed out clearly the relative dif-
ferences between zone melting and normal freezing
on the fractionation of impurities.

Pfann's (1966) description of the process in some-
what modified terms is as follows:

Consider a column of material forming a solid sol-
ution, whose cross section is unity and whose composi-
tion C_0 is constant along the length L of the column.
By some means a zone of length ($\ell \ll$ L) is fused and
is allowed to move slowly along the column. The course
of segregation during this process is the following:

As the molten zone advances it freezes out a
layer dx of solid behind and melts a layer dx of the
column in front of it. The first solid to freeze,
at x = 0, is of concentration DC_0. For D < 1, DC_0 is
less than C_0 and hence the melt is enriched in the trace
element. As the zone progresses the melt continues to
be enriched, although at a decreasing rate, until it
attains concentration C_0/D. When this steady state condi-
tion is attained the concentration of solids entering
and leaving the zone are the same and hence no further
change of concentration occurs, until the zone reaches
the end of the column. The remaining melt then solidi-
fies by normal freezing or in another way depending on
the conditions.

Figure 3-15. Approximate concentration of a trace element after passage of one molten zone through a column of uniform mean concentration C_0 (after Pfann, 1966).
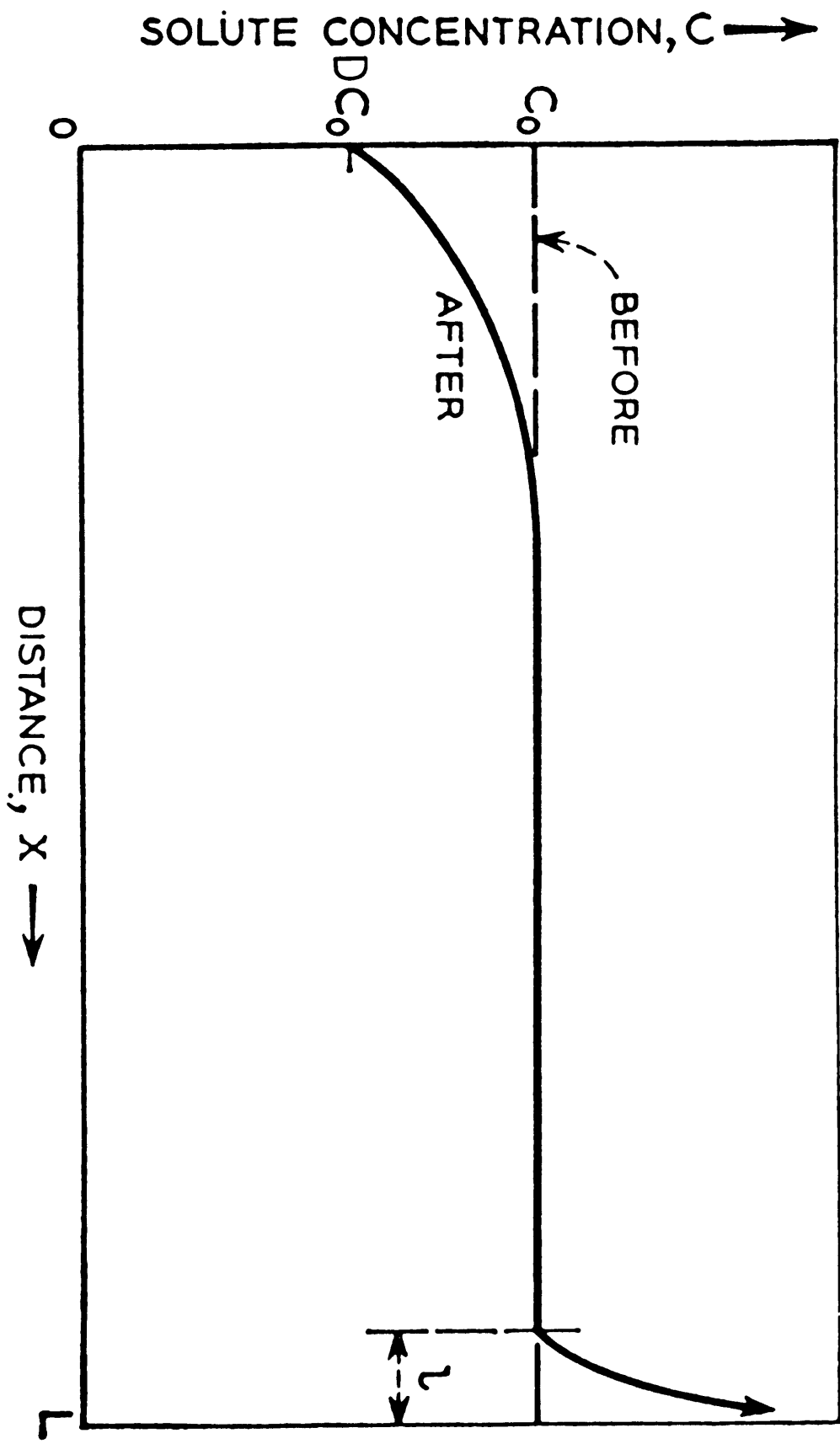
Figure 3-16. (Left diagram) Curves for normal freezing (fractional crystallization, logarithmic distribution law, Doerner and Hoskins, 1925) showing relative trace element concentration C_s/C_0 in the solid versus fraction solidified x, for various values of the partition coefficient D (after Pfann, 1966).

(Right diagram) Curves for single-pass zone melting showing relative trace element concentration C/C_0 in the solid versus distance in zone lengths x/l from the beginning of column, for various values of the partition coefficient D (after Pfann, 1966). $C_0 = 1$ for all curves.

$$C = kC_0 (1-D)^{D-1}$$

$C_0 = 1$ FOR ALL CURVES

$$C/C_0 = 1-(1-D)e^{-Dx/l}$$

$C_0 = 1$ FOR ALL CURVES
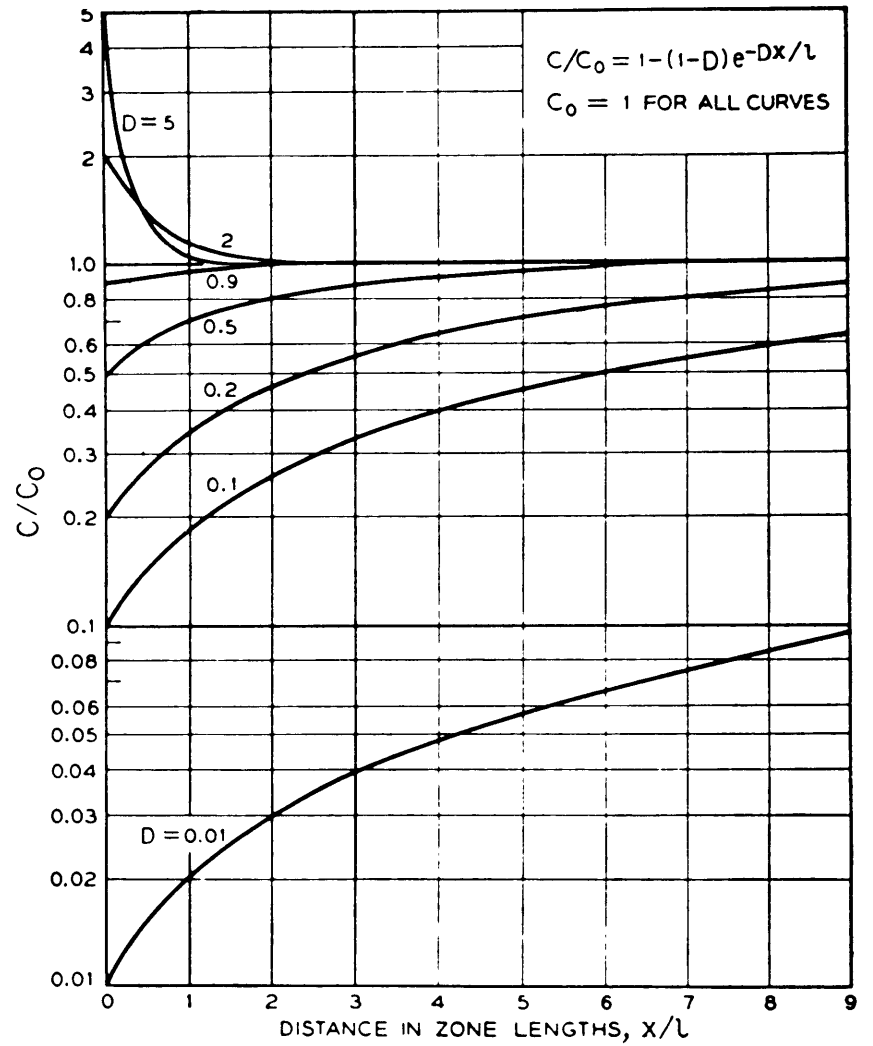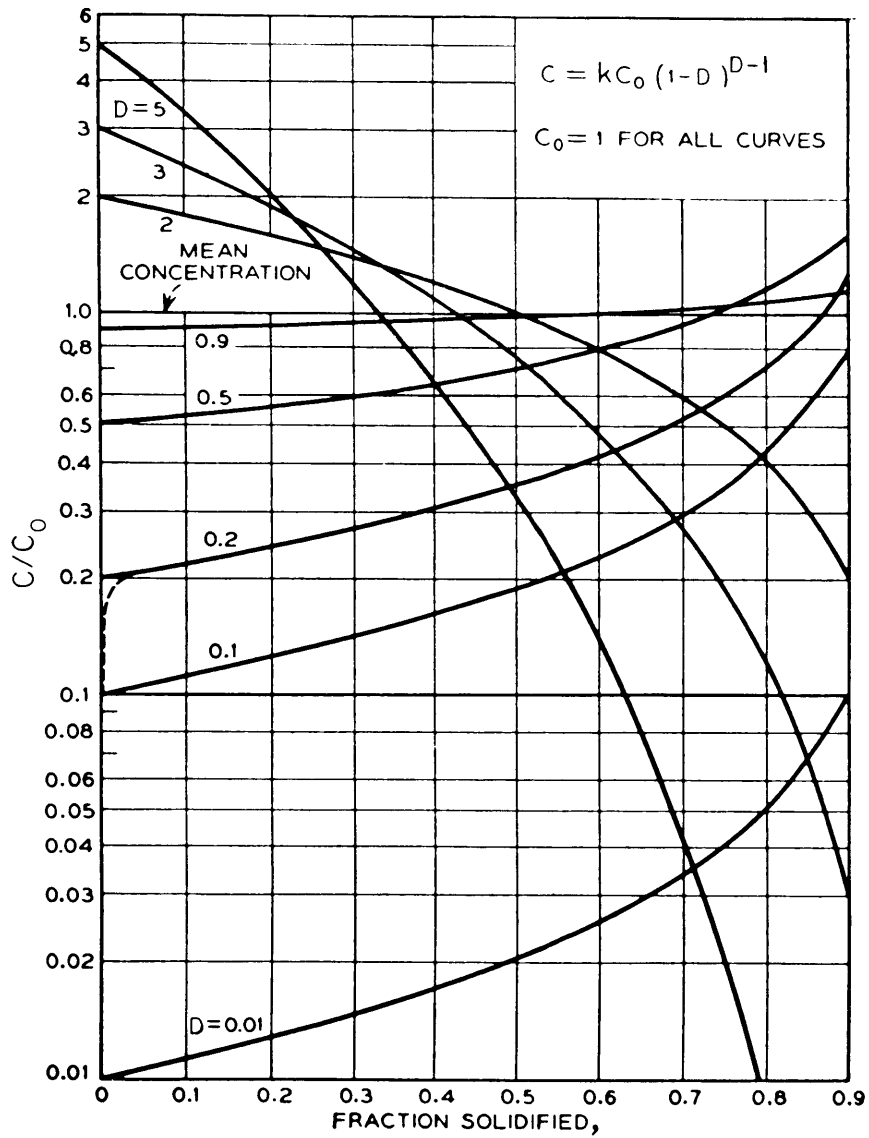
Thus as shown in Figure 3-15, zone melting of a uniform column results in an initial transition region, a region of uniform concentration and an end region of length equal to one zone.

The concentration C_s at any length x along the zone melted column (except in the last zone) is given by:

$$\frac{C_s}{C_o} = 1 - (1-D) \exp. - Dx/\ell \qquad (3-28)$$

Where x is the length solidified, measured from the starting end, (not to be confused with x the fraction solidified). The assumptions for the derivation of Equation 3-28 are the following:

1. Uniform composition of the liquid phase

2. No diffusion in the solid phase

3. Constant partition coefficient D

4. Constant zone length

5. Concentration of the impurity less than its solubility (trace level).

Curves of C_s versus x/ℓ, the distance expressed in zone lengths, calculated from Equation 3-28 for $C_o = 1$, are plotted in Figure 3-16, (right) for different values of D where $D = \sum_{n=1}^{n} p_n D_n$ for a column composed of mixed crystals (Pfann, 1966).

It is interesting to compare the zone melting curves with those obtained by fractional crystallization. Figure 3-16 (left) shows the solute concentration in the crystal-

lizing solid as a function of the fraction solidified x.
The curves for D<1 are concave upwards. In contrast,
the curve for D < 1 for zone melting is concave down-
ward. Hence, less segregation is achieved by one zone
pass than by one normal freezing step. This is due to
the fact that only a portion of the column is liquid
at any time; an ultimate case would be to make the zone
length equal to the column length, which is, of course,
the case of normal freezing.

Thus a maximum segregation or fractionation is ob-
tained by fractional crystallization.

It may be difficult to discriminate which of the
two processes may have been operative in some geo-
logical situations when only one trace element is con-
sidered at a time. The Skaergaard intrusion is a rare
case, representing an ideal geological situation (see
Section III). Nevertheless, when a group of trace
elements such as the rare earth series with D values
smoothly related to each other, is considered, and
the systematic fractionation patterns developed among
the group is examined, the difference between the two
processes becomes much more evident.

For the different rare earths Equation 3-28
becomes:

$$\frac{C_s(z)}{C_o(z)} = 1 - (1-D(z)) \exp. -D(z)x/\ell \qquad (3-29)$$

Where $C_o(z)$ is taken to be equal to $U(z)$, the rare earth chondrite composition, for all rare earths. This equation describes the rare earth concentrations in the solid along the column for a single pass operation.

APPLICATION IV-A   ZONE MELTING IN THE EARLY DIFFERENTI-

ATION OF THE EARTH AND THE RARE EARTHS.[*]

Any discussion of the early history of the earth and attempts to solve the problems involved is, and will remain, for a long time, highly speculative and may approach what may be called Geopoetry (Hess, 1962). Nevertheless it may be interesting to see how the rare earth fractionation may be related to these problems.

In solution II-A, we have considered the formation of the mantle and the protocrustal nuclei by fractional

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[*] The reason we have limited our discussion to the early differentiation of the earth is that zone melting requires a delicate balance between the heat of melting and the heat of fusion in P, T gradients. The heat energy available at this time must have been much greater than now. If zone melting would occur presently, superheated melts would certainly activate the process. Nevertheless Bowen (1956) and Turner & Verhoogen (1962) have shown that appreciably superheated magmas are very unprobable in the earth.

crystallization. This implied that the earth was com-
pletely molten at one stage (Masuda & Matsui, 1963).
There is no agreement among earth scientists on whether
the earth has passed through a completely molten stage
or only partially molten stage early in the history of
the earth. This depends on the mode of formation of
our solar system, which is not known. Earlier belief
was that the earth and the planets formed from condens-
ation of a hot gas mixture implying that the earth must
have passed through a completely molten stage (Lord
Kelvin & Thomson, 1862). Even if one follows the
current tendencies to believe that the planets of our
solar system formed by accretions from a complex con-
densed cold gas-dust nebula, it is not yet clear whether
the earth has been completely or only partially molten
early in its evolution.

The problem lies in the models proposed for the
early thermal history of the earth. These models de-
pend mainly on the mode of accretion of the dust-grains;
the physico-chemical state of the elements composing the
dust-grain particles, in particular iron; the mode of
formation of the core; and finally, the mode of dissip-
ation of the potential energy released and of latent heat
of chemical reactions.

Depending on whether the accreting dust-grains were
composed mainly of a mixture of metallic iron and Mg, Fe
silicates (the iron being already reduced) as proposed

by Urey (1952, 1962), or of complex oxides and ices, (the
iron being reduced during the accretion stage) as suggested
by Ringwood (1966a and b, 1960, 1959), very different
thermal models are deduced.

Even in these last two possibilities, as it was dis-
cussed by Birch (1965), the potential energy alone re-
leased during the formation of the core is great enough
to melt the entire earth.

Thus if one likes to keep the earth partially molten
at any time, complex physico-chemical models including
convective, conductive, radiative and mechanical proces-
ses are required to take into account the necessary dis-
sipation of excess heat energy.

Zone melting has the advantage that only a fraction
of the system is molten at any time during the process
of fractionation. Thus a process akin to zone melting
may have been operative early in the differentiation of
the earth. Pfann (1955) has shown that if a temperature
gradient is imposed on the column, the zone movement is
to a certain extent self generating. In this case the
molten zone will climb along the liquidus surface. The
length of molten zone can either increase or decrease to
$\ell = 0$, depending on the conditions. Zone of unusually
small dimentions upbline or dot zones can be maintained.
A pressure gradient will have the opposite effect of the
temperature gradient on the self generating movement of
the zone. Thus, a delicate balance must be maintained

between the heat of melting, the heat of crystallization
and the pressure and temperature gradients, for the zone
to be maintained and self generating. Shimazu (1959 a
and c, 1960, 1961) and Magnitskii (1964) have examined
in detail the optimum conditions for zone melting to
occur in the earth.

Thus the process can be visualized either as
slowly ascending molten zones with dissolution at the
front and crystallization behind or perhaps should be
looked upon as small multicell systems in which localized
excess heat would produce interstitial melts. These
interstitial melts would heat their way up by dissolution
and redeposition, sweeping out in this way the trace
elements. The zone die and the process is repeated
many times. The superimposition of large scale mass move-
ments by convective means, would by mixing, have the same
effect of integration of the small subsystems in mathemat-
ical language. The convective mass movements would transfer
the interstitial melts to the upper part of the mantle,
where by buancy they would reach the surface and form the
protocrustal nuclei.

Zone melting has the advantage of concentrating
undesirable   trace elements in the last molten
zone without changing appreciably the major composition
of the column through which the molten zone has passed.
The heat flow between the oceanic and continental areas
being roughly the same and considering the known

differences of U, Th and K concentrations, Birch (1965) has shown much of these elements must be concentrated in the upper-mantle under the oceanic crust. Thus a process which does not severely fractionate the major elements (Ringwood, 1966 a and b), but yet concentrate U, Th, the rare earths and other trace elements, near the upper zone of the earth is needed. A process akin to zone melting may well be the answer.

MULTIPASS ZONE MELTING AND THE RARE EARTHS

Assume that the trace elements were segregated in the earth early in its differentiation by a process similar to that described above, and that this complex process has the same mathematical formalism as multipass zone melting.

No general equation that express the solute concentration as a function of distance, for any number of pass through a crystalline column of specified length, has been derived. While the concept of zone melting are simple it is difficult to describe the multipass process mathematically. Reiss (1954) and Lord (1953) have derived the basic differential equation. It relates the change in solute concentration in the moving zone to the difference between fluxes of solute entering and leaving the zone.

$$\frac{1}{D}\, dC_n(x) = \left[C_{n-1}(x+\ell) - C_n(x) \right] dx \qquad (3\text{-}30)$$

The same assumptions made in deriving Equation 3-28 were used. $C_n(x)$ denotes the solute concentration freezing out of the zone at distance x in the nth pass.

When the zone reaches the end of the column, at $x = L-\ell$, the length is no longer constant and the solute is no longer taken in. Equation 3-30 becomes:

$$dC_n(x) = \frac{(1-D)}{(L-x)} \; C_n(x) \; dx \qquad (3-31)$$

No exact solution of these two differential equations has been derived. Only approximate solutions have been described, but with the aid of computers, curves relating the solute concentration along the column length, measured in zone length x/ℓ , for different values of D and n number of passes have been published. A qualitative picture of what is happening during multipass process can easily be described (Pfann, 1966, p. 32):

Consider the second pass through a first pass distribution like that of Figure 3-15. As the zone passes through the initial region, it accumulates solute and leaves behind it a lower somewhat longer initial region. When the front of the zone reaches the beginning of the normal freezing region the slope of the curve rises sharply. Thus the pile up at the column end is reflected back one zone length during the second pass. Additional passes, therefore, lower the initial region, raise the end region, and decrease the length of the intermediate

region. Ultimately all three regions blend into a relatively smooth curve. For the 14 rare earths Equation 3-30 and 3-31 become respectively:

$$\frac{1}{D(z)} \, dC_n(x,z) = \left[C_{n-1}(z) \, (x+\ell) - C_n(x,z) \right] \, dx \qquad (3\text{-}32)$$

for $0 \le x \le L-\ell$

and

$$\frac{1}{D(z)} \, dC_n(x,z) = \frac{(1-D(z))}{(L-x)} \, C_n(x,z) \, dx \qquad (3\text{-}33)$$

for $L-\ell \le x \le L$

Using the same notation as in Figure 3-28 and Figure 3-30. Solution of differential Equation 3-32 would describe the concentration C(z) of the rare earth in the mantle after n passes.

Solution of differential Equation 3-33 would describe the concentration $C_L(z)$ of rare earth in the last piling up zone to form the protocrustal nuclear after n passes.

Obviously, the parameters L, ℓ, x and n cannot be estimated for geological cases considered earlier in this section. Nevertheless, with the aid of computed curves published by Pfann (1966), rare earth fractionation patterns can be computed for different values of L, ℓ, x and n. To be self consistent with the other solutions presented previously the distribution coefficients were assumed to

vary with z as in Equation 3-12. Values D_o = 0.12, ΔD = 0.04 were used. Some of these patterns are shown on Figure 3-17, for x/ℓ = 10 and C_o = 1 for all values of z.

It is interesting to note that there is an ultimate distribution of $C_n(x,z)$ for n approaching infinity (n $=\infty$). This solution is given by Pfann (1966, p. 42) who discusses its consequence. The very existence of an ultimate distribution signifies that the traveling zone is in equilibrium of all points with the adjacent material. Put in another way, an overall steady state condition of gradually increasing concentration with height has been established. Unless a drastically different process is superimposed, the overall distribution cannot be altered significantly. This condition will give a minimum value for $C_n(x,z)$ in the limits $0 \leq x \leq (L-\ell)$, or a maximum value for $C_n(x,z)$ in the limits $(L-\ell) \leq x \leq L$. For finite values of x, L, ℓ and D<1, the concentration $C_n(x,z)$ for n $=\infty$ is not zero. For D values 1 < D > 0.7 and $L/\ell \rightarrow \infty$, the ultimate distribution is rapidly attained and not much fractionation appears. Figure 3-17 shows that all the rare earths fractionation patterns are concave downwards.

At half of the length (x/ℓ = 5), after one pass (n=1), La is depleted by 50% and the heavy rare earths are almost unfractionated. By increasing the number of passes, the depletion of La and light rare earths increases

Figure 3-17. Zone melting model. The relative rare
earth abundances at different depths measured in units
of the zone length for a model earth differentiated by
multipass zone melting is plotted on logarithmic scale
as a function of the atomic number z. The curves are
computed for $n=1$, 4, and ∞ and at height $x/\ell = 5$, 8
and 9 which would correspond approximately to depths of
1500 km, 600 km and 300 km. The relative rare earth con-
centrations in the last piling up zone after four passes
is also shown on the top. $C_0 = 1$ for all curves.

Residual liquid for $n = 4$

$n = \infty$ $x = 9\ell$

$n = 4$ $x = 9\ell$

Primary material

$n = 1$ $x = 8\ell$

$n = 1$ $x = 5\ell$

$n = 4$ $x = 8\ell$

$n = 4$ $x = 8\ell$

$n = 4$ $x = 5\ell$

Zone melting

$$\frac{C(z)}{C_0(z)} = 1 - \left(1 - D(z)\right) e^{\frac{-D(z)X}{\ell}}$$

for $n = 1$

$$\frac{L}{\ell} = 10$$

$n = \infty$ $x = 5\ell$

C/C_0

z
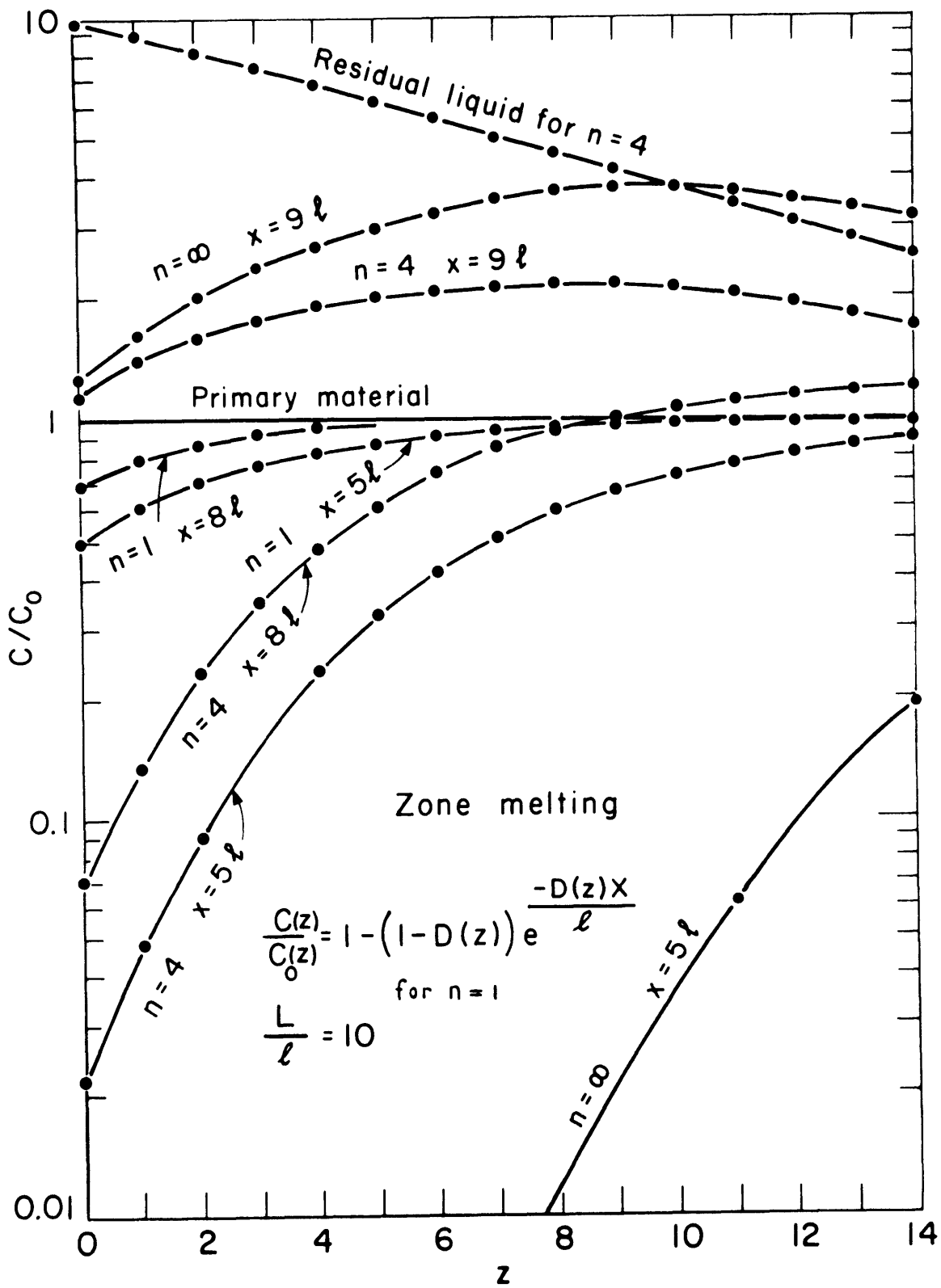
rapidly. After 4 passes (n=4) La (z=0) is already depleted by a factor of 50. The ultimate La depletion after an infinite number of passes would be $10^{-5} \cdot C_o$ or 5 orders of magnitude lower. On the other hand, Lu after 4 passes is depleted by only 10%, and the ultimate depletion for Lu (z=14) would be only by a factor of 5.

At the higher level in the column $x/\ell = 8$. The La depletion is not severe. For n=1, La is depleted by only 30% and Lu has not changed appreciably. After 4 passes La is depleted by a factor of 14 only. Lu is now not depleted anymore but enriched by 20%. For the ultimate distribution at this height, La is depleted by a factor of 50 and Lu is enriched by 50%.

The slight depletion followed by a small increase of the heavy rare earths as the number of passes is increased at this level, is due to the piling up of the traces is the last zone length, $x = L-9$ (for $L/\ell = 10$). After the second pass, this is reflected in 2 zone lengths below, after 3 passes, 3 zone lengths below and after n passes n zone lengths below. Thus for intermediate to high levels in the column the heavy rare earths concentrations will pass through a minimum as n increases.

Therefore, even if the partition coefficients are lower than 1, after a certain number of passes the rare earths can be slightly enriched if they are piled up in the last zone length of the refined column. This phenomena is much more pronounced and apparent at the highest level of the column.

At the height $x/\ell = 9$, which is the maximum height for our chosen case, $L/\ell = 10$, La is depleted by only 20% after one pass and Lu has not changed. After 4 passes La is now enriched by 15% and Lu 70%.

The ultimate La enrichment is about 25 to 30% and Lu in enriched by a factor of 3.

Since the level $x/\ell = 9$ represents the highest point of the column these last two values correspond to the maximum permissible enrichment for these two elements. But since the curves are concave downwards the intermediate to heavy rare earths will be slightly more enriched than Lu. Thus there is a maximum enrichment of the rare earths near Dy or Ho, which are enriched by a factor of 4.

Contrary to fractional crystallization, multipass zone melting produces a maximum in the fractionation patterns near the heavy end of the rare earths.

Another interesting point is that at intermediate to low levels of the column the depletion increases rapidly with the number of passes n, and much greater depletion of the lighter rare earths can be obtained by multipass zone melting than by normal freezing.

If a zone melting process took place over a great range of depth in the earth, we may ask how effectively the rare earths would be removed from the lower mantle. Table 3-3 is a calculation of the fractions, F_{La} and F_{Lu}, of La and Lu remaining in each of the depth ranges

TABLE 3-3.

Distribution of rare earths with depth in a
zone refined column of silicate rock.[*]

Depth in km	F_M	F_{La}	F_{Lu}
400-1000	0.2	1.4×10^{-3}	0.25
1000-2898	0.655	3.3×10^{-9}	0.04

[*] Steady state values after infinite zone re-
fining of a 2898 km column of uniform cross
section assuming a zone height of 10% of the
total height.

indicated after an infinite number of passes of the zone

melting, assuming ℓ/L = 0.1. It is seen that La is

especially well extracted from the deeper layers, but

both La and Lu are lower in abundance than in a fraction-

ally crystallized earth   (Table 3-2). Thus, Table 3-3

points out clearly that multipass zone melting can be

a much more powerfull way of cleaning up trace elements

from the lower mantle of the earth. We may also sug-

gest that the radioactive elements U, Th and K should be moved

more effectively from deep layers by multipass zone

melting than by fractional crystallization, a point of

interest in the problem of heat flow from the earth.

Assuming that the mantle formed by fractional crystal-

lization, Masuda (1964) estimated the partition coefficients

of D_U = 0.073, D_{Th} = 0.18 and D_K = 0.55. The fraction of

these elements left in the zone of 400 to 1000 km. depth,

relative to the total mantle + crust abundance would be

F_U = 7%, F_{Th} = 12% and F_K = 24%. For multipass zone melt-

ing only F_U = 0.5 10^{-3} %, F_{Th} = 0.5 10^{-2} % and F_K = 16 %

would be present in this zone. For the heat flow to be

roughly equal in the oceanic and continental areas Birch

(1965) has shown that virtually all the U, Th and K

should be concentrated in the continents and in the upper

mantle under the oceanic areas. Therefore, if the mantle

had formed by fractional crystallization, too much U,

Th and K would be left in the lower part of the mantle,

assuming Masuda's values to be correct. Thus multipass

zone melting seems to be a better "broom" for collecting

trace element near the upper zones of the earth than fractional crystallization. This last statement should not be misinterpreted. We have seen that compared to a single pass zone melting, fractional crystallization is definitely a more efficient process to fractionate trace elements. Nevertheless, it is extremely inprobable that repeated fractional crystallization has occurred to form the present mantle. This would imply that the earth would have been molten and had recrystallized several times. On the other hand, multipass zone melting could have occurred in a single event early in the differentiation of the earth. This, of course, does not preclude the partial melting of the upper-mantle later during geological time to produce basaltic melts.

Finally, all the curves shown in Figure 3-17 were calculated for L/ℓ = 10. This corresponds roughly to a depth of 250-300 km. for the last zone length where the trace elements are piling up. This can be considered as a protocrust (Patterson, 1963). It is interesting to note that this zone includes the low velocity zone of the upper mantle. It has been suggested that interstitial liquids could be responsible for the decrease of the S wave velocities. The temperature and pressure gradient in the earth seem to be such that the low melting point of ultrabasic to basic rocks is best approached in this region. Thus, if interstitial melts were present already early in the history of the earth, these melts could either subsist, or slowly differentiate by crystallizing, with some of the residual

melts escaping to the surface adding to the expansion of the primordial continents.

Is this not what one would expect if multipass zone melting had been an operative process?

V.   MIXING PROCESSES AND THE RARE EARTHS

Many tupes of mixing processes can be considered in magmatism. Bowen (1956) discussed in detail the principles of assimilation of country rocks by a crystallizing melt. He emphasized that:

No saturated magma can dissolve in inclusions consisting of phases or components with which the magma is already saturated, (reactive solution). It can only react with these phases and convert them into the phases or components which are just saturated, (reactive precipitation). Thus, only phases which belong to the later stages of saturation of the crystallizing magma can be dissolved. This is only true for melts which are not superheated. However, it has been already been mentioned earlier that appreciably superheated magma are very improbable (Bowen, 1956; Turner and Verhoogen, 1962; and O'Hara, 1965).

In the range of concentrations with which we are concerned in this discussion, the rare earths and other trace elements will be always undersaturated in the melt. Thus, there always will be a tendency for equilibration of the rare earths between the melt and the foreign material.

The degree of equilibration, of course, will again be dependent on the physico-chemical conditions of the two systems to be mixed and the dynamical conditions of mixing and of crystallization. Obviously, the diffusivities and the chemical potential of the rare earths in the melt and in the different phases to be incorporated will be two important parameters.

Several mixing processes can be considered based on the two types of reactions given by Bowen (1956), namely: reactive solution, and reactive precipitation. Some of these processes will be considered but only briefly. Mixing and alteration processes are very complex and little is known about these problems. This section is only an attempt to point out the complexities of these processes.

APPLICATION V-A.   REACTIVE SOLUTIONS AND THE RARE EARTHS

a. Pure mixing:

The foreign material is completely soluble and is entirely incorporated in the melt as a whole. No equilibration is thus established between the two systems. Conservation of mass requires:

$$\bar{C}_c(z) \ (1-q) + C_L(z) \ q = C(z) \qquad (3\text{-}34)$$

Where $\bar{C}_c$ = average rare earth concentration of the assimilated material

C_L = rare earth concentration in the melt before
assimilation

C = final rare earth concentration in the melt
after assimilation

q = melt fraction = amount of melt/amount of melt +
amount of assimilated material

Thus, $C(z)$, the final rare earth concentration, will always be intermediate between $\overline{C}_c$ and C_L:

for $\overline{C}_c > C_L$ $\overline{C}_c(z) \geq C(z) \geq C_L$,   and

for $\overline{C}_c < C_L$ $C_L(z) \geq C(z) \geq \overline{C}_c$. The final patterns

will always be included in the envelope formed by the

two patterns to be mixed. This also is the case of pure

mechanical mixing.

It has been suggested that some meteorites are the

product of mechanical mixing during collisions in space.

This problem could be investigated profitably with the

rare earth patterns. Taylor (1964, 1965) has also made

attempts to estimate the different proportions of major

components of the crust from the rare earth patterns of

some average crustal rocks. A further application of such

a process as applied to volcanism will be considered in

the last general discussion, and was also presented

in Part I.

b. Mixing as the magma is crystallizing:

The country rock or some other phases are assimil-

ated at a constant rate. This is the case of complete

resorption of one or more phases. The change of the

32

concentration of a trace component i in the melt has been
derived by Neumann et al. (1954).

$$C_L(z) = \left[1 - x\,(1-q)\right]^{\frac{D(z)}{(1-q)}} \cdot \left[C_0(z) + \frac{C_c(z)\,q}{1-q-D(z)}\right] - \frac{\overline{C}_c(z)\,q}{1-q-D(z)} \quad (3\text{-}35)$$

This equation is valid for all values of D except for $D = (1-q)$,
which involves an indeterminate. For this particular case
Equation 3-35 becomes:

$$C_L(z) = \frac{\overline{C}_c(z)\,q}{(1-q)}\,\ln\left[1 - (1-q)\,x\right] + C_0(z) \quad (3\text{-}36)$$

Where $C_L(z)$, $C_c(z)$ and q are defined as in Equation 3-34,
and x, and $D = p_n D_n$ = constant, are defined as in Equation 3-3.
This equation can be used only in the range where D is
constant. For a detail discussion of its application, the
reader is referred to the original work by Neumann et al. (1954).
c. Magma stopping:

The magma is heating its way up by dissolving the country
rock and recrystallizing at the bottom in a gradient of
temperature and pressure. This is the ideal case of zone
melting for n = 1, and has been intensively discussed in
Section IV.

For the case where the molten zone of length ℓ is
constant, and rapid diffusion in the melt and no diffusion
in the solid take place above the liquid front; the concentra-
tion in the melt is described by:

$$C(z) = D(z) \, \overline{C}_c(z) \left[1 - (1-mD(z)) \exp. - D(z)x/\ell \right] \quad (3\text{-}37)$$

For $0 < x < L-\ell$

The same notation as defined in Equation 3-34 is used
for C, $\overline{C}_c$, C_L and

$x =$ the distance traveled by the zone

$m = \dfrac{\overline{C}_c}{C_L} =$ average rare earth concentration of the
country rock/concentration of the melt before
assimilation

If the original magma was formed by complete melting
of the country rock, m becomes equal to 1, $m = 1$. If
$\overline{C}_c \ll C_L$, and $D(z) < 1$, as is the case for the rare earths,
Equation 3-37 becomes:

$$C(z) = D(z) \, \overline{C}_c \, (1 - \exp. - D(z) \, x/\ell) \quad (3\text{-}38)$$

With $0 < x < L-\ell$.

Shimazu (1959 a and c, 1960, 1961), Harris (1957) and
Magnitskii (1964) have discussed some geological situ-
ations such as sill or other magma bodies working their
way up by melting and recrystallization. As we already
emphasized, the advantage of such process is that, al-
though the bulk chemistry and mineralogy is not changed
very much, it can fractionate and change the trace el-
ement composition of the rocks to a considerable extent.
Thus, the great variation in trace element content of
some basalts with bulk chemistry varying only in a

narrow range could be explained by such process.

APPLICATION V-B   REACTIVE PRECIPITATION AND THE RARE EARTHS

Only a part of the country rock is incorporated into
the magma crystallizing. This is the case of incomplete
assimilation. The rare earth in the melt tends to equili-
brate with the phases of the country rock, which also
contains some trace of rare earths. The equilibrium re-
action can be described by a joint partition coefficient
$\lambda = \sum_{n=1}^{n} p_n \lambda_n$. The equilibration will tend to approach
the homogeneous law. Meanwhile, the saturated magma is
crystallizing and separating minerals which incorporate
some rare earths according to the logarithmic law. The
partition of the rare earths will be described by a joint
partition coefficient, $D = \sum_{n=1}^{n} p_n D_n$. Thus the rare earth
concentration in the melt will change in rather delicate
and complex manner, which is difficult to formalize
mathematically. This case will not be developed here.

A simplified case can be considered, however, when the
assimilation occurs at a certain stage and no phases
are separating from the melt during this partial assimila-
tion process. This includes reequilibration of the rare
earths between the melt and the undigested phases.
Analytically, this process of partial assimilation has a
mathematical formalism very similar to partial melting
considered in Section III.

Mass conservation requires that:

$$\overline{C}_c(z)\ (1-q) + C_L(z)\ q = C(z)$$

and
$$\lambda(z) = \frac{\overline{C}_c(z)}{C_L(z)}\ ,$$

combining:
$$C(z) = C_L(z) \left[\lambda(1-q) + q \right] \qquad (3\text{-}39)$$

Where $C_c(z)$, $C_L(z)$, $C(z)$ and q are defined as in Equation 3-34 and $\lambda = \sum\limits_{n=1}^{n} p_n \lambda_n =$ constant during the partial assimilation.

Obviously, except for some very simple cases, these models are unsatisfactory. The effect on the rare earths by mixing and alteration processes are very complex and little is known about these problems (Mineyev, 1962). No direct application will be considered.

VI.   SOME POSSIBLE GENETIC RELATIONSHIPS IN THE LIGHT OF EXPERIMENTAL AND THEORETICAL RARE EARTH PATTERNS

RARE EARTHS IN HAWAIIAN VOLCANIC ROCKS

Twenty basalts from the Hawaiian Islands have been analyzed for rare earths by neutron activation. The results and their implication are discussed in Part I. The major element chemistry and mineralogy and other trace element data are available for these particular specimen (Macdonald, 1946; Winchell, 1947; Wentworth and Winchell, 1947; Muir and Tilley, 1961; Macdonald and Katsura, 1964; and Powell et al., 1965). The

classification of these basalts based on the absolute
abundance and the type of rare earth pattern coincide close-
ly with other classifications based on chemistry and miner-
alogy.

Figure 3-4 shows three individual patterns. The
olivine tholeiite 9948, with a maximum near Nd and a
smooth negative slope for the heavy rare earths, represents
the pattern with the lowest rare earth enrichment and the
least internal fractionation. It has also the lowest pot-
assium content of the suite of sample analyzed. The nephe-
line basalt, with a straight line and a negative slope,
shows the maximum enrichment of the lighter rare earths
and the greatest negative slope obtained in the suite.
All other rocks analyzed in the suite: Toleiite,-basanite-
basanitoid, nepheline-melilite basalts show rare earth
patterns in between the envelope (Figure 3-4) formed by
these two lavas.

There is a progressive enrichment for all the rare
earths, although to different degrees for the suite of
lavas in the order mentioned above. The lighter rare
earths get enriched at a faster rate. Thus, there is a
progressively faster rate of enrichment with increasing
rare earth trionic radii or decreasing atomic number
from Lu to La.

It is remarkable that these experimental patterns
resemble the theoretical curves given in Figures 3-11
and 3-12. The origin of Hawaiian volcanic rocks has been
discussed intensively (Kuno, 1957; Powers, 1955). Many

different processes have been proposed, some of which
we have discussed in this section and Part I. In
the light of this theoretical rare earth discussion,
and in particular referring to Applications II, III,
IV and V, we see that several possibilities are avail-
able. These lavas could have either been differentiated
from each other or derived from the upper-mantle sep-
arately, by fractional crystallization to different
degrees; by different degrees of partial melting; by
successive fractional melting; or by mixing processes,
depending on which lava is considered as the precusor.
Other unexplored or undreamed mechanisms are, of course,
possible.

The olivine tholeiite, considering II-A, could
represent the complete low melting portion of the
upper-mantle. On the other hand, if application
III-A is considered, it could represent the residual
solid left after partial melting of a material of inter-
mediate rare earth composition lying in the envelope of
Figure 3-4. Similarly, the straight line pattern of
the nepheline-melilite basalt could either be an ex-
treme case of differentiation from a melt of tholeiitic
composition, and therefore represent a residual liquid
(O'Hara, 1965); or it could also well be the melt
fraction produced by a very small degree of partial
melting in the upper mantle with a tholeiitic rare
earth type pattern. Finally, the intermediate cases

could be either the primary melts formed by different degrees of partial melting of the upper mantle (Application III-A), or successive fractional melting of a pattern like alkali basalts, or simple mechanical mixing in different proportions of the nepheline-melilite basalt and tholeiite basalt patterns. Thus, as we have already emphasized, fractional crystallization, partial and fractional melting cannot be differentiated in practice on the basis of the light of this theoretical consideration only.

Nevertheless, some possibilities are more likely than others, and other geological and geochemical evidence can help in deciding which process has been operative in Hawaii.

The correlation of geochronological order of eruptions, the chemistry and petrology of these lavas are important factors. Detailed discussion of the genesis of these rocks is given in Part I.

Silica and alkali enriched lavas of the series Hawaiite, Mugearite Trachyte have also been analyzed. One pattern for a trachyte is shown in Figure 3-18. Its relation with the "nepheline-melilite-tholeiite" envelope is easily observed. The lighter rare earth end for this suite shows patterns characteristic of the other suite, and lies within the envelope. There is a progressive enrichment of the lighter and of the series with the increase of alkalinity, but this time with an increase in SiO_2 content as well. On the other hand, there is a tendency for

the heavy rare-earths to depart from the envelope. A slight progressive leveling out, followed by a progressive enrichment of the smallest rare earths from Lu to Dy, in the order Hawaiite-Mugearite-Trachyte is observed. The maximum effect is produced in the trachyte. This heavy rare earth end effect is not yet explained and cannot be accounted for on the basis of our theoretical considerations. The viscosity of silicate melts increases rapidly with alkali and SiO_2 content. Moreover, these lavas are known to contain more volatiles than the more basic lavas. The heavy rare earths have greater complexing stability constants than the lighter ones (Mineyev, 1963). Thus, departure from the ideal dilute ionic melts, high diffusivities in the melt, and changes in the partition coefficients may be some of the reasons for this behavior. Other possibilities for the origin of trachyte have been discussed in Part I. Mixing may be another possibility of explaining the slight enrichment of the heavy rare earth with SiO_2 increase. The rare earths in some deep-seated sedimentary material as well as in calcareous sediments are shown in Figure 3-18. It is interesting to note that the trachyte lies in the envelope formed by the red clay and the tholeiite or some intermediate basalts. Thus a magma of these compositions assimilating some red clay material could produce a trachyte as far as the rare earth content is concerned. To the author's knowledge this possibility has

Figure 3-18. Abundances of the rare-earth elements rel-
ative to 20 chondrites (Schmitt et al. 1963, 1964) in
three sedimentary materials and one trachyte from Hawaii
plotted on logarithmic scale as a function of the atomic
number. The two dashed curves represent two basalts from
the Hawaiian Islands shown on Figure 4. Data for the red
clay and globigerina tests are from R. Volfovsky Spirn
(1965), for the Florida Bay from L. Haskin and M. A. Gehl
(1962) and for the trachyte (this work).
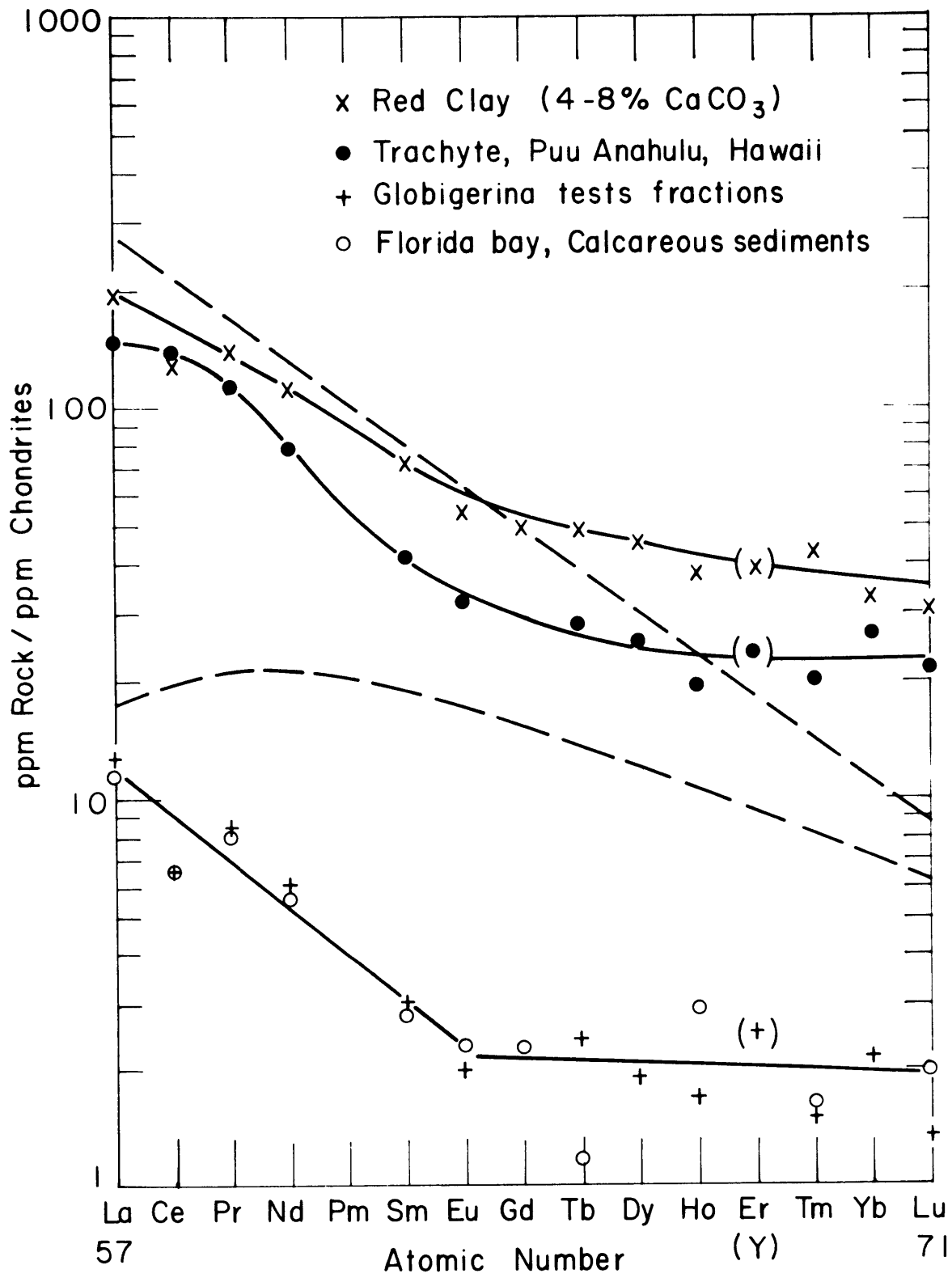
not been seriously considered in the past. The major element
chemistry of these two mixing components is not incompatible
with this possibility. Arguments against this possibility
are presented in Part I. Of course this does not preclude
some further fractionation as was discussed in Section V.
In general, the greater the degree of fractionation, the
more enriched are the rare earths. This would mean that
a smaller amount of red clay would have been incorporated.
The geochronological order of extrusion of these lavas is
not in disagreement with such a possibility (Macdonald &
Katsura, 1964; Stearns, 1946, 1940).

It has also been suggested (Daly, 1944) that the ne-
pheline normative alkali basalts (Nepheline-melilite basalts)
could be produced by assimilation of calcareous sediments.
The rare earths in calcareous sediments and one limestone
shown in Figure 3-18 are characteristic of many other simi-
lar sediments (Haskin & Gehl, 1962; Volfovsky Spirn, 1965;
and Wildemann & Haskin, 1965). Assimilation of such sedi-
ments in any proportions by Hawaiian basalts could hardly
produce the extreme differentiation and high enrichment
found in nepheline-melilite basalts. This is in good agree-
ment with Sr^{87}/Sr^{86} isotopic ratios determined on the very
same samples   (Powell et al., 1965).

It has been suggested (Powers, 1935; Tilley, 1950;
Macdonald, 1949; and Green & Ringwood, 1964) that nepheline-
melilite basalts melts could be produced as residual liquids
by crystallization and removal of hypersthene from the primary
melt. This is not at all in disagreement with the rare earth

patterns obtained for these lavas. This problem has
been discussed in greater detail in Part I.

RARE EARTHS IN OCEANIC BASALTS:

Frey and Haskin (1964) determined rare earths
in some dredged basalts from the Mid-Atlantic ridge
and one sample from the experimental Mohole from the
Guadalupe site. Two representative rare earth patterns
of these basalts are shown in Figure 3-5.

The oceanic lavas form a very consistant group
(Nicholls, 1965; Nicholls et al., 1964; Engel et al.,
1965) with rare earths patterns quite different from ba-
salts of oceanic islands and continental plateau ba-
salts. This surprising finding led Frey & Haskin
(1964) to believe that these basalts are "nearly un-
disturbed chondritic rare earth distribution patterns"
and "decidedly primitive".

This statement which is somewhat misleading brought
Frey & Haskin into a polemic with Lovering & Morgan
(1965) (See Lovering & Morgan, 1965; Haskin & Frey,
1965) for replies). As Frey & Haskin pointed out and
as also observed from Figure 3-5, the lighter rare
earths seem to be depleted relatively to the heavy
rare earths. Nevertheless it should be pointed out that
when absolute abundance relative to the Hawaiian
tholeiites are considered, this depletion is almost non-
existant. On the contrary, the heavy rare earths are

not only "not depleted" but are enriched relative to the
Hawaiian tholeiites from Sm to Lu. So great is the
heavy rare earth enrichment in these oceanic tholeiites
that they reach in absolute abundance those found in the
Hawaiian trachyte and even many granites which are both
characteristic of quite differentiated rocks. This is
rather surprising and troublesome, especially if one con-
siders that these lavas are rather basic in character.
Thus, for the oceanic tholeiites one finds a definite
enrichment of the heavy rare earths (small radii) and a
tendency for a broad maximum near the middle to the end
of the rare earth series.

In the light of our theoretical discussion, the origin
of these patterns cannot be accounted for by partial melt-
ing or fractional melting of a mantle formed by fractional
crystallizatôon. Contamination by sedimentary material
is also not a possibility.

When these patterns are compared with those computed
from multipass zone melting discussed in Application V-A
(Figure 3-17), in particular for x/ℓ = 9 and n = 4 to
n = ∞, a striking resemblance is observed. These 2 com-
puted curves represent the rare earth patterns expected
in the uppermost solid part of the column, just underneath
the last piling zone. The maximum enrichment varies from
2 for n = 4 to 4 for n = ∞, the ultimate enrichment.

The rare earth in oceanic tholeiites are enriched by
a factor of 2 to 3 relative to the average calcium-rich
achondrites, which in turn are enriched by a factor of 10

relative to the average rare earth content of chondrites.

Does this mean that the oceanic basalts were the result of multipass zone melting?

If so, then material with rare earth similar in content to the calcium-rich achondrites would have been the primary material for this earth model. (Gast, 1960). It is interesting at this time to look at rare earth patterns obtained in 3 peridotites analyzed by Haskin et al. (1965) Figure 3-6 shows these 3 patterns plotted relative to average chondrite rare earth content.

The striking features are: a. the rare earth content in Lizard and Mt. Albert peridotite are all lower than rare earth chondritic concentrations. For Tinaquillo peridotite, the lighter rare earth up to Gd are also lower than chondrite values. b. There is a strong depletion of the lighter rare earth, particularly La, which is lower by 2 orders of magnitude relative to the heavy rare earths. This produces a positive slope for the lighter rare earths and a slight inflection near the heavy end of the series.

Again there is a striking similarity between these 3 patterns and those obtained by zone melting (Figure 3-17). But, this time, for lower levels in the column, $x/\ell = 5$ for $n = 4$.

We have seen in solution IIIA and IVA, that if basalts are produced by partial or fractional melting of an upper mantle formed by fractional crystallization, depletion of the lighter rare earths is expected, but not

to such an extent. The production of such unusual patterns is hardly expected from such an earth model.

Again, does this mean that these peridotites were the result of multipass zone melting?

If so, then material with rare earth content as in chondrites would have been the primary material for this earth model. Thus in the case of peridotites, chondrites seem to be the primary material from which the mantle would have been formed by multipass zone melting. On the other hand, for oceanic tholeiites, the primary material would have been like Ca-rich achondrites. This is not quite impossible as enrichment up to a factor 10 without internal fractionation of the rare earths is also observed in meteorites.

Variations in the amount of reduced iron or other elements (e.g. silicon) and its removal from a previously homogeneous source to form the core, for instance, could change by appreciable amount the rare earth concentration in silicates. Ringwood's manipulation on chemical analysis of carbonaceous chondrites (1966 a and b) to produce a mantle to core ratio of 69/31, shows that the estimated chemical composition of the mantle could be increased by a factor of 1.38 to 2.74 for most oxides relative to chondrites, depending on whether a value of 0.1 or 0.2 is taken for the estimated $\frac{FeO}{FeO+MgO}$ molecular ratio of the mantle (Clarke & Ringwood, 1964). This, of course, would not fractionate the rare earths.

If the earth's core is made mostly of iron (with some

silicon), and there are geophysical indications that it is so, the rather high content of oxidized iron (FeO) present in silicate minerals of the mantle tends to indicate that the core is not in equilibrium with the mantle (Ringwood, 1966, 1960, 1959; Urey, 1962). Thus variations in the amount of reduction in different regions of the earth could be expected. This in turn would be reflected in the absolute rare earth concentration of silicates in these regions, without internally fractionating the rare earths. We have already mentioned that zone melting has the advantage of not changing appreciably the major element composition of the material through which the molten zone is passing. Like a broom it only sweeps out the trace element impurities with partition coefficients less than 1. Thus, these major inhomogeneities would not be appreciably changed by multipass zone melting.

By analogy, it is interesting to look at some of the rare earth patterns obtained by Schmitt (1963, 1964) in some meteorites. Figure 3-7 shows 3 types of meteorites with almost no relative fractionation, but all enriched to different degrees relative to the average rare earth content in chondrites. The rare earths in Ca-rich achondrites are higher by an order of magnitude than in the average chondrites. The mesosiderites (silicate phase) are higher by a factor of 3.

Could the primary average rare-earth composition of the mantle and crust system have been higher than that

of chondrites by a factor of $\sim$ 3?

Better fits between the absolute concentration of rare earths computed in our models and the observed rare earth patterns in general would tend to support such a possibility.

ADDITIONAL REMARKS

A principal objective of this part has been to demonstrate the importance of dynamical processes upon the relative fractionation of the rare earth series.

Despite the oversimplifications a multitude of possibilities have emerged.

The study of processes operative in the interior of the earth to bring about its differentiation, and the study of its present chemical composition, can only be made from samples available to us on its surface. The theoretical development shows that identical rare earth patterns can be produced by different processes.

It is important to realize that the rare earth patterns reflect differences of thermodynamical functions. Thus, the partition coefficient is related to the Gibbs free energy. The variation of the partition coefficient with temperature is related to differences in enthalpy. Variations of enthalpy with temperature is related to the heat capacity. The heat capacity at high temperature (several Debyes) approaches a constant value for crystalline solids. Only the change of enthalpy in the melt.

has to be considered. Nevertheless, the delta varia-
tion of the partition coefficient ΔD from two adjacent
rare earths with change of temperature will be related
to the change of enthalpies $\Delta H = H_{z+1} - H_z$ of the
melt with temperature, a second order effect. The
pressure dependence of the rare earth partition coef-
ficients will be related to their molar volume or to
their compressibility. But again the change of such
parameters between two adjacent rare earths with P is a
second order effect.

The change of P,T conditions will certainly change
the stability of the major phases. Thus rather drastic
changes of the rare earth partition coefficients and
their values are expected on the appearance of such new
phases on the liquidus for crystallization or in the pri-
mary material for partial melting at different depths.
Only experimental work at high T and P, approximating
the conditions of the mantle can possibly resolve such
problems.

Thus it cannot be denied that a great number of
factors and many complexities can be introduced by dif-
ferent processes during the differentiation of the earth.
Individual rock-forming minerals are very selective in
their uptake of rare earths. (Towell et al., 1965).
They show very different rare earth patterns. Yet whole
rock show continuous rare-earth patterns with the inverse
of the ionic radii. The only discontinuities are observed
for Eu and Ce. These elements can, in nature, be easily

reduced or oxidized, respectively. Despite all this, the fact remains that rare earth in whole rocks are smoothly and regularly fractionated and some systematic differences are preserved in crustal rocks.

This needs explanation!

The answer may lie in the mode of differentiation of the earth early in its history. Whether the earth has been completely or partially molten is of fundamental importance. Completely different processes for the formation of the mantle and the crust are expected. These differences may well be reflected in the rare earth composition of basalts and some related ultramafic rocks. This despite the fact that secondary processes, such as partial or fractional melting may change their patterns somewhat. Thus, possibly some of the problems of single stage (Ringwood, 1966 a and b) versus multistage models (Urey, 1952, 1962) for the origin of the earth could be partially resolved.

The rare earths in Hawaiian basalts or the large shield volcanoes of oceanic islands seem to indicate that the mantle formed by fractional crystallization. On the other hand, the few samples dredged from the bottom of the ocean near ridges seem to indicate that if multipass zone melting has been an operative process, the earth has been only partially molten at any one time. Although large, the shield volcanoes of oceanic island apparently represent only a small fraction of the wide spread up welling volcanism of the ocean (Engel et al., 1965).

Could these factual differences in the rare earth patterns between shield volcanoes of the islands and upwelling volcanism near the ridge reflect large scale differences of dynamical processes such as convective currents in subcrustal regions?

An interesting analogy can be drawn between the rare earth patterns of granites and granitic pegmatites and the tholeiites from shield volcanoes and oceanic ridge tholeiites. The major chemistry of granites and pegmatites is roughly identical. The only difference lies in the amount of volatiles, particularly water. The rare earth patterns show a reversal in the slope: strongly negative for granites to slightly positive for pegmatites (Sahama and Vä hätalo, 1939). The major chemistry of tholeiites from shield volcanoes and oceanic ridge basalts is roughly the same (except for minor and trace elements and perhaps Al (Nicholls, 1965; Nicholls et al., 1964; Engel et al., 1965). The oceanic ridge basalts are extruded under large columns of water, preventing escape of volatiles to a certain extent. The rare earths in tholeiite from shield volcanoes show somewhat negative slopes. The ridge basalts show the reverse tendency, a slightly positive slope.

Could this be due to the effect of volatiles or water?

Hawaiian lavas seem to have their source at a depth of 45 to 60 km. in the upper mantle. (Eaton & Murata, 1960).

They must have been produced by partial melting of relatively dry ultramafic rocks. The oceanic basalts may be produced from serpentinite or amphibolites (Nicholls, 1965; Nicholls et al., 1964) by partial melting of shallower depths (Heezen, 1960). Partial or complete melting of such materials would produce not only basaltic melts but also dehydration with production of volatiles and water. It is well known that the heavy rare earths are preferentially complexed relative to the lighter ones. Thus the heavy rare earths could be preferentially enriched in the melts. Finally, although the mathematical form of these different processes seems to indicate that in some geological situations these processes may have been operative, it is possible that the same patterns could be produced by completely different mechanism, although with the same mathematical formalism.

CONCLUSIONS

At the present time perhaps the most useful con-
clusions to reach are to decide what the interesting
questions are which should be asked about the rare
earth elements in basic igneous rocks and their bear-
ing on the upper mantle and the differentiation of the
earth.

1. To what extent can the dynamics of physically
different processes be revealed by rare earth abundance
measurements? The theoretical treatment worked out
here depends quantitatively on assumed values of joint
effective partition ratios of the rare earth elements,
and some ability to discriminate between processes was
demonstrated. It may be that different partition
ratios would make further distinctions, although it may
also be that new ambiguities arise. The rare earths
are instructive for they show the relative inadequacy
of single trace elements or trace element pairs to be
sensitive indicators of the history of chemical dif-
ferentiation. However, direct measurements of rare
earth partitions in interesting mineralogical systems
are clearly needed.

2. Can it be that the very simple models of frac-
tional crystallization, zone melting, etc., considered
here are essentially good approximations to what has
actually happened in the upper mantle and the crust?
Or is there an accidental mathematical similarity be-
tween reality and the models? Given the many assumptions

in the theoretical treatment here, any serious attempt to answer these questions would be dangerous. However, the great smoothness of rare earth abundance curves relative to chondrites and the relative freedom from points of inflection suggests simplicity.

3. Do the rare earths reveal inhomogeneity in the upper mantle and different chemical differentiation processes of the crust from the upper mantle for different regions of the earth? From a rare earth standpoint, Hawaiian basalts suggest that partial melting of a solid derived ultimately from a fractionally crystallized chondritic earth may have been operative. The peridotites indicate zone melting of chondritic matter, but the Mid-Atlantic Ridge basalts point more to Ca-rich achondrites as the primitive material.

4. More profoundly, do rare earth abundances reflect processes which took place during the early differentiation of the earth? Already evidence for a completely molten earth and one which at most was only partially molten is indicated, and both an initially chondritic earth and one of higher rare earth concentrations approaching 10 times chondritic are implied. The alternatives may not be mutually exclusive, depending on inhomogeneities and the extent of equilibrium in the early differentiation of the earth.

5. In spite of the selectivity demonstrated for small rare earth ions by some rock-forming minerals, how can we account for the simplicity of most rare earth patterns for whole rocks compared with chondrites? The chemical

histories since primeval times have most certainly been complex, and such things as formation of different minerals at different stages and crystal settling may be expected to produce irregularities in rare earth patterns for individual rocks. It may be thát processes within the mantle are simpler than this.

6. What additional chemical factors have influenced rare earth abundance patterns? Oxidation-reduction conditions are critical for Ce and Eu, and the similarity of these elemental abundances to the other rare earths in whole rock suggests that both assume the 3+ state in the equilibria of basic rocks. However, without separate mineral data one cannot say for sure. Furthermore, the role of water may be important in determining the partition of rare earths inasmuch as the smaller ions form stronger complexes in solution. Pegmatites have been observed to have a strong enrichment of the heavy rare earths, in contrast to granites which are frequently La-enriched, and the difference may reflect the presence of volatiles in the late stages of differentiation.

7. In view of the generality of our understanding at the present time, can we still suggest specifically how the basic igneous rocks we have been discussing here originated? The tholeiites of Hawaii and of the Mid-Atlantic Ridge, for example, are very different in their rare earth abundances. The Hawaiian tholeiites conform

surprisingly well to the fractionally crystallized earth model, and the _relative_ rare earth patterns in the Mid-Atlantic Ridge basalts are "flat" as if they were "nearly undisturbed chondritic rare earth distribution patterns" (Frey and Haskin, 1964). Closer examination of these latter tholeiites, however, indicates the heavy rare earth concentrations to be very high, some 30 times chondritic and 3 times achondritic concentrations and as high as Hawaiian trachyte, Figure 3-18, and many granites (Towell et al., 1965). Rather than being primitive and unaltered, it seems more likely that these tholeiites are quite differentiated but such that the relative rare earth patterns are only slightly fractionated. In addition to zone melting, another possible process, in analogy to pegmatites, would involve water which may complex the heavy rare earths preferentially in solution. Partial melting of serpentinites and amphibolites at shallow depth with evolution of volatiles may have been important in the Mid-Atlantic Ridge, whereas in Hawaii, where earthquake foci are at greater depth,silicate melts may have been relatively dry.

In the long run, any satisfactory explanation of rare earth abundance patterns will have to be according to models in agreement with geophysical observations, and it may be that satisfactory geophysical models for the differentiation of the earth will have to agree with rare earth geochemistry.

NOTATION USED:

μ_i^a = chemical potential of trace component i in phase a

μ_i^θ = chemical potential of trace component i in phase θ

μ_i^{a*} = chemical potential of pure component i in a physically unattainable state a

$\mu_i^{\theta*}$ = chemical potential of pure component i in a physically unattainable state θ

X_i^a = mole fraction of trace component i in phase a

X_i^θ = mole fraction of trace component i in phase θ.

C = final concentration of trace component i in the melt after assimilation, (mixing)

C_L = concentration of trace component i in the melt, (fractional crystallization, partial melting)

C_s = concentration of trace component i in solid, (fractional crystallization)

C_0 = initial concentration of trace component i in the melt for Doerner-Hoskins law: and in the original column (zone melting)

C_p = primary concentration of trace component i of source rock, (partial melting)

C_R = concentration of trace component i in residual solid, (partial melting)

$\overline{C}_c$ = average concentration of trace component i in the material to be assimilated (mixing).

C_{Ln} = concentration of trace component i in the liquid formed after the nth partial melting event, (fractional melting)

C_{Rn} = concentration of trace component i in the residual solid after n partial melting events.

D_i = effective partition coefficient of trace component i between solid and melt

D = $\sum_{n=1}^{n} P_n D_n$ = effective **joint** partition coefficient of trace component i between the melt and crystalline phases present.

D_0 = effective joint partition coefficient for La

D_1 = effective joint partition coefficient for Ce

D_2, D_3, ...D_{14} = effective joint partition coefficient for Pr, Nd, ...Lu, respectively.

D = $D_{z+1}-D_z$ = difference between adjacent rare earth joint partition coefficient

E = effective activation energy (diffusion).

J = diffusion coefficient

J_0 = Diffusion coefficient at a reference state.

K_i = partition coefficient of solute component i between phases a and θ

ℓ = lenght of molten zone

L = total length of column to be refined by zone melting

m = $\overline{C}_c / C_L$

P_1, P_2, P_3, ...P_n = modal abundance of mineral 1, 2, 3,......n, respectively, with $0 \leq p \leq 1$, $\sum_{n=1}^{n} P_n = 1$

P = pressure

q = melt fraction = amount of melt/amount of melt + amount of assimilated material

λ = effective joint partition coefficient of trace component i between melt and unassimilated wall rock material, (mixing)

$U(z)$ = chondritic rare earth concentrations

y = degree of melting = amount of melt/amount of melt + amount of residual solid, $0 \leq y \leq 1$

x = degree of solidification, $0 \leq x \leq 1$, (fractional crystallization)

x = distance of the molten along the column from the origin

Z = atomic number

z = fictive atomic number for the rare earths, $0 \leq z \leq 14$

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APPENDIX A AND B

DESCRIPTION OF THE SAMPLES ANALYZED

APPENDIX A

SPECIMEN 9948:   Olivine tholeiite, Koolau basalt series.

Locality: Long. 157° 39' 42" W., Lat. 21° 18' 46" N.,
Elevation 120 feet. Road cut on north side, main highway
pass, Makapuu Point, Oahu; at road level 50 feet south-
east from lower and northwest end cut, near manhole
cover.

Megascopic description: Gray fine grained, with large
vesicles.   Probably aa.   Considerable number of pheno-
crysts visible.

Microscopic description: Olivine and orthorombic pyroxene
phenocrysts, in an interstitial groundmass containing
labradorite crystals (An_{60}, An_{40}) and pigeonitic pyroxene
grains, with ore minerals, held together by glassy
material, 5 to 20%.

Chemical analysis: Wentworth and Winchell, 1947, Table 4,
column 9, p. 47.

SPECIMEN 10396:   Tholeiite, Koolau series.

Locality: Long. 157° 58' 18" W., Lat. 21° 28' 29" N.,
Waiahole Valley, elevation 890', in channel on north side
of portal to the tunnel through the Koolau Range.

Megascopic description: Medium gray rock of very fine
grain, with few phenocrysts and few vesicles.

Microscopic description: Intergranular porphyritic
texture, with rather abundant (10%) plagioclase pheno-
crysts and almost as much hypersthene.   Some olivine
phenocrysts with brown iddingsite rims.   Groundmass

contains at least 30% feldspar (labradorite), pigeonite, and fine grains of magnetite and ilmenite. Several per cent of glassy material.

Chemical analysis: Wentworth and Winchell (1947), Table 4, column 4, p. 71.

SPECIMEN 10398: Diabase, Koolau (intrusive) volcanic series.

Locality: Long. 157° 47' 15" W., Lat. 21° 18' 15" N., Palolo quarry, central zone of the complex dike near the inland end of the upper workings, June 1940. Elevation 600 feet.

Megascopic description: Greenish-gray rock of millimeter or larger grain size, without noticeable phenocrysts.

Microscopic description: The texture is intergranular and locally diabasic. The rock consists of plagioclase, augite, hypersthene, a little olivine, ore minerals, and interstitial alkalic feldspar which in part is a microperthitic intergrowth. Small acicular grains of apatite are enclosed in the feldspar. The ore minerals are partly ilmenite and partly magnetite. A few hypersthene grains contain cores of olivine; others are enclosed in thin jacket of augite. The plagioclase is zoned from intermediate labradorite in the center to andesite to the outside.

Chemical analysis: Wentworth and Winchell, (1947), Table 4, column 1, p. 71.

SPECIMEN 10403: Tholeiite, Kooalu volcanic series.

Locality: Long. 157° 39' 19" w., Lat. 21° 18' 38" N., 100 feet south of Makapuu Head triangulation station. Elevation about 647 feet.

Megascopic description: Nonporphyritic, light-gray basalt from the ledge of aa. Irregular vesicles in highly variable proportions in different parts of the same ledge.

Microscopic description: A few phenocrysts of olivine are present. They are partly resorbed and altered around the edges to iddingsite. The groundmass is interstitial, composed of plagioclase, pyroxene, ore minerals, and interstitial glass. Both magnetite and ilmenite are present. The plagioclase is medium labradorite. The pyroxene is predominantly pigeonite, but a few phenocrysts of hypersthene are present, enclosed in a thin shell of pigeonite. Minute grains of apatite are enclosed in the feldspar.

Chemical analysis: Wentworth and Winchell, (1947), Table 4, column 2, p. 71.

SPECIMEN JP.12: Tholeiite

Locality: Lava of 1881 eruption of Mauna Loa, at Kaumann, Hawaii.

No megascopic and microscopic descriptions are available for this sample.

Chemical analysis: Macdonald and Katsura, (1964), Table 8, column 6, p. 123.

PELE HAIR.

Locality: Around Halemaumau pit, Kilauea, Hawaii; collected by H. O. Wood, and sent to R. A. Daly.

Megascopic description: Mainly glass.

Chemical analysis: For similar hair from this locality see: Daly, R. A., (1944), Table 7, 1370.

Tilley, (1960), Table 4, column 4, p. 50.

SPECIMEN JP.14: Alkali olivine basalt.

Locality: Keauhou Beach, Hawaii. Collected by G. A. Macdonald.

No megascopic and microscopic description is available.

Chemical analysis: For similar samples from this locality see: Muir and Tilley, (1961), Table 2, column 1, p. 189.

HUALALAI 1801 FLOW: Alkali basalt.

Locality: Hualalai, Hawaii. This flow contains numerous xenolitiths of dunite, iherzolite and gabbro.

Megascopic description: Washington's description of this flow is the following: Porphyritic with well shaped fresh olivine phenocrysts are present in variable amounts. Groundmass is very fine-grained and composed of slightly brownish augite with subordinate grains of olivine, small laths of labradorite, many grains of magnetite, and small amounts of glass; contains several tents of a percent of spinel.

Chemical analysis: For analysis of the same flow see Washington, (1913) Table , column 3, p. 102.

SPECIMEN 1101: Ankaramite, Haleakala Crater, Maui.

Locality: From lowest point of the east facing cliff,
at 9500 feet altitude, 0.3 mile north of Pakaoa Hill,
at the southwestern corner of Haleakala Crater, Maui.

Megascopic description: Dark gray aa, numberous pheno-
crysts of brownish green olivine and black augite up
to one cm. long.

Microscopic description: 21% augite and 20.5% olivine
phenocrysts, both type are partly resorbed. Intersti-
tial to intergranular groundmass composed of: 25%
plagioclase, 18% pigeonite pyroxene, 5% olivine,
9% iron ore, 1% glass and apatite < 1%.

Chemical analysis: Macdonald and Powers, (1946),
Table 1, column 1, p. 119.

SPECIMEN 1102: Hawaiite, Haleakala, Maui.

Locality: From 6-foot dike in face of Kalahaku cliff,
0.45 mile N. 80° E. of Kilohana triangulation station.
F. Haleakala, Maui.

Megascopic description: Nonporphyritic, few vesicles (1mm),
intergranular, grain size about 0.2mm.

Microscopic description: Volumetric percentage of miner-
al are: plagioclase 74.1%, pyroxene 11.1%, olivine 3.9%,
iron ore 8.0%, biotite 1.1% and apatite 1.8%. Feldspar
are on the average sodic andesine, the pyroxene is
augite.

Chemical analysis: Macdonald and Powers (1946),
Table 1, column 4, p. 119.

SPECIMEN 1106: Hawaiite, Haleakala, Maui.

Locality: From Hawaiian Commercial and Sugar Co. quarry near the road from Kahului to the summit of Haleakala, at about 250 feet altitude, 3.6 miles southeast of Kahului, Maui.

Megascopic description: Medium gray and dense, essentially nonporphyritic, with very rare phenocrysts of olivine up to 1 mm long. Intergranular texture, grain size about .07 mm.

Microscopic description: The approximate mineral compsition is: plagioclase (sodic andesine) 53%, pyroxene (augite) 24%, olivine 24%, iron ore 12%, apatite 1% and biotite 1%. Chemical analysis: Macdonald and Powers (1946), Table 1, column 5, p. 119.

SPECIMEN JP.10: Hawaiite, Laupahoehoe series, Mauna Kea, Hawaii.

Locality: Road cut on Kamuela-Kona road, 1.6 miles southwest of Popoo Gulch.

No megascopic and microscopic description are available for this sample.

Chemical analysis: Macdonald, and T. Katsura, Table 4, column 8, p. 118.

SPECIMEN 1104: Mugearite, Haleakala Crater, Maui.

Locality: From the western rim of Haleakala Crater, at an altitude of 8700 feet of the top of Leleiwi Pali Cliff, 0.6 mile northwest of the summit Rest House.

Megascopic description: Medium gray and dense, with a few tabular phenocrysts of feldspar up to 7mm long (1%) and rare small phenocrysts of hornblende (riebeckite like amphibole, < 1%).

Microscopic description: Poikilitic grains of feldspar, 50%, (oligoclase), containing small included grains of monoclinic pyroxene, 28%, olivine 4%, iron ore 12%, apatite 1% and biotite 1%.

Chemical analysis: Macdonald, G. A., and Powers (1946), Table 1, column 6, 119.

SPECIMEN JP.15: Trachyte, Puu Anahulu, Hawaii.

No megascopic and microscopic description is available for this sample.

Chemical analysis: For analysis of similar rocks from this locality see: Washington, (1923), Table III, column 2, p. 108.

SPECIMEN 9962: Linosaiite, Honolulu series.

Locality: From southwest edge of flow in gulch north of Hanauma Bay, Koko Head, elevation about 130 feet.

Long. 157° 41' 38" W., Lat. 21° 16' 33" N. Ohau.

Megascopic description: Dark gray, vesicular, practically nonporphyritic basaltic rock.

Microscopic description: Very fine grained groundmass containing 50% feldspar, 35% pyroxenes, 2% olivine, 5% iron ore, analcime 2% and apatite 1%.

Chemical analysis: Winchell, (1947) Table 7, column 12,

SPECIMEN 9982: Nepheline basanite, Honolulu series.

Locality: From south tip of Black Point (Kupikipikio),
near foot of steps on public right-of-way from shore to
Black Point Road. Long. 157° 47' 45" W., Lat. 21° 15'
30" N., Oahu.

Megascopic description: Very dark-gray (nearly black),
vesicular basaltic rock with inconspicuous olivine pheno-
crysts.

Microscopic description: Porphyritic, 15% olivine pheno-
crysts, and trace of augite phenocrysts. Fine-grained
groundmass containing olivine + pyroxene 40%, plagioclase
30%, iron ore 6%, glass 2%, and zeolite 15%.

Chemical analysis: Winchell, (1947), Table 7, column
13, p. 30.

SPECIMEN JP.11 (C-32): Basanitoid, Honolulu series.

Locality: Lava of Kaimuki shield, 18th and Kilauea Avenue,
Honolulu, Oahu.

No megascopic description is available.

Microscopic description: No nepheline was observed.

Chemical analysis: Macdonald, G. A., and T. Katsura (1964),
Table 8, column 12, p. 123.

SPECIMEN 9961, (JP.13): Nepheline basalt, Honolulu series.

Locality: From lower Nuuanu (Luakaha flow, northwest bank
of Nuuanu Stream above Kapana Pool. Long. 157° 50' 50" W.,
Lat. 21° 19' 43" N. Oahu.

Megascopic description: Very dark-gray, fine-grained,

scattered sparsely throughout.

Almost no vesicles.

Microscopic description: Porphyritic, 15% olivine
and 2% augite phenocrysts. The groundmass composi-
tion is 34% combined olivine and pyroxene, 36%
analcime, 5% melilite, 7% iron ore and 1% apatite.
Chemical analysis: Winchell, H. (1947), Table 7,
column 15, p. 30.

SPECIMEN 9960: Nepheline-melilite basalt, Honolulu
series.

Locality: From Kalihi flow in kalihi stream channel
at Water Reserve boundary. Elevation 600 feet.
Long. 157° 50' 10" E., Lat. 21° 22' 12" N. Oahu.
Megascopic description: Specimen for analysis con-
sisted of chips of 2-inch diameter, hand picked to
eliminate olivine segragation (dunite) common in this
flow. Dark-gray, massive basaltic rock visible grains.
Besides the dunite nodules, some olivine phenocrysts
may be identified in hand specimen. Such grains were
not removed in sorting.

Microscopic description: Porphyritic, 16% olivine and
1% augite phenocrysts. The groundmass composition is:
30% combined olivine + pyroxene, 23% nepheline, 18%
melilite, 9% iron ore and 3% anacilme.

Chemical analysis: Winchell (1947), Table 7, column 18,
p. 30.

SPECIMEN JP.16: Melilite-nepheline basalt, Honolulu series.

Locality: Moiliili quarry, Honolulu, Oahu. Collected by G. A. Macdonald.

For megascopic, microscopic description and chemical analysis of rocks from this locality see: Cross, W., (1915), pp. 21-22.

SPECIMEN GF.30: Melilite-nepheline basalt, Honolulu series.

Locality: Sugar Loaf Crater, North Wall of Moiliili Quarry, Honolulu, Oahu.

For description of rocks from this locality see: Cross (1915),pp. 21-22.

HUALALAI OLIVINE NODULE:

Locality: Occurs as xenolith in the 1801 flow from Hualalai, Hawaii.

Megascopic description: Light-green, sugar granular texture, very friable, grain sizes 1.5 mm. Composed of olivine, 98%, with unconspicuous dark green grains (dioside?), and opaque mineral (spinel), 1%.

For description of other nodules from the same locality see: Macdonald, (1949a), p. 1553; Macdonald (1949b), p. 76; and Cross (1919), p. 35.

For chemical analysis of mineral phases of similar nodules from this locality see: Ross et al., (1954), Tables 4 to 11, column 11, pp. 707-714.

SALT LAKE CRATER NODULE:

Locality: Salt Lake Crater, Oahu.   Occurs in tuffaceous bed.

Megascopic description: Light-green olivine, 70-75%, dark bottle green enstatite (determined by the X-ray powder method), irregularly distributed.   Both grain types average 3 mm. in diameter.   Small calcite veinlets were observed in altered region, but were avoided for analysis.

For description of other nodules from this locality see: Macdonald (1949a), p. 1553; Winchell (1947), p. 13.; Macdonald and Kasura, (1964) p. 102; and Ross et al., (1954), pp.697-698.

For chemical analysis of mineral phases of similar nodules from this locality see: Ross et al., (19540, Tables 4 to 11, column 8, pp. 707-714.

APPENDIX B: CHEMICAL ANALYSES AND NORMS

	Ol.Tholeiite 9948[*]	Tholeiite 10396[*]	Diabase 10398[*]	Tholeiite 10403[*]	Tholeiite JP.12 [†] (2201)
SiO_2	49.62	48.74	52.30	51.94	51.85
TiO_2	1.51	2.42	1.68	2.58	1.93
Al_2O_3	12.68	15.98	14.80	14.18	14.04
Fe_2O_3	3.21	4.14	3.12	2.81	1.56
FeO	7.60	7.16	7.30	8.14	9.16
MnO	.09	.06	.05	.08	.17
MgO	13.86	6.96	6.72	7.21	7.85
CaO	7.48	9.90	7.98	9.24	10.45
Na_2O	2.36	2.77	3.78	2.52	2.07
K_2O	.15	.22	.60	.35	.37
H_2O^-	.34	.70	.23	.12	.27
H_2O^+	.67	1.19	.64	.59	.24
P_2O_5	.04	.08	.66	.35	.22
Cr_2O_3	.19	.04	-	.04	-
CO_2	-	-	-	-	-
SO_3	.05	.09	-	-	-
Sum	99.85	100.45	99.86	100.15	100.18
Q		1.62	2.16	6.24	3.42
Or	1.11	1.11	3.34	2.22	2.22
ab	19.91	23.58	31.96	20.96	18.34
an	23.63	30.58	21.68	26.41	27.24
di ⎰ wo	5.68	7.42	5.57	7.31	9.78
di ⎱ en	4.10	5.10	3.50	4.60	5.80
di ⎱ fs	1.06	1.72	1.52	2.24	3.70
hy ⎰ en	22.90	12.30	13.30	13.40	13.80
hy ⎱ fs	5.94	4.22	6.47	6.34	8.84
ol ⎰ fo	5.32				
ol ⎱ fa	1.43				
mt	4.64	6.03	4.41	4.18	2.32
cm	.22				
hm					
il	2.89	4.56	3.19	4.86	3.65
Ru					
ap		.34	1.68	.67	.34
Ne					
lc					
cs					
cc					
Ak					
Rest					
Sum	98.83	98.58	98.78	99.43	

Analyst. F.A.Gonyer F.A.Gonyer F.A.Gonyer F.A.Gon. T.Katsura

APPENDIX B (Continued)

	Pele's [††]	Hair [†††]	Alk.ol.basalt JP.14[x]	Alk.Basalt 1801Flow[xx] Hualalai	Ankaramite 1101[†]
SiO_2	50.04	49.23	46.53	46.43	42.30
TiO_2	3.02	2.75	2.28	2.59	2.41
Al_2O_3	14.02	12.94	14.31	10.91	10.52
Fe_2O_3	1.72	1.76	3.16	3.15	4.22
FeO	9.45	9.28	9.81	10.26	9.70
MnO	.17	.08	.18	.09	.06
MgO	6.93	7.42	9.54	11.08	14.90
CaO	11.54	11.28	10.32	10.09	12.08
Na_2O	2.42	2.64	2.85	3.16	1.56
K_2O	.57	.59	.84	.54	.42
H_2O^-		.08	-	.15	.45
H_2O^+	.10	.74	-	.66	.87
P_2O_5	.26	1.21	.28	.67	.33
Cr_2O_3	-	-	-	-	.11
CO_2	-	-	-		-
SO_3				.07	
Sum	100.31	100.0		99.85	99.93
Q	.87	.18	-	-	-
Or	3.34	3.34	5.28	3.34	2.22
ab	20.44	22.57	20.04	23.84	7.34
an	25.58	21.45	23.63	13.90	20.57
di {wo, en, fs}	} 24.46	} 22.87	} 20.89	} 25.31	15.66 / 11.10 / 3.17
hy	16.52	18.42	-	-	-
ol {fo, fa}	- / -	- / -	18.48	19.97	18.27 / 5.61
mt	2.55	2.55	4.53	4.64	6.03
cm					
hm	5.78	5.32	4.41	4.86	4.56
Ru					
ap	.67	2.48	.67	1.68	.67
Ne			2.20	1.56	3.12
lc					
cs					
cc					
Ak					
Rest	.10	.82			
Sum	100.31	100.00		99.85	

Analyst. J.H.Scoon   J.H.Scoon H.S.Washington F.A.Gonyer

APPENDIX B (Continued)

	Linosaite 9962[**]	Ne.basanite 9982[**]	Basanitoid JP.11 [†] (C-32)	Hawaiite 1102 [†]	Hawaiite 1106 [†]
SiO_2	45.13	42.86	43.12	47.64	47.78
TiO_2	2.94	2.94	2.11	3.44	4.11
Al_2O_3	16.40	11.46	13.36	17.62	16.32
Fe_2O_3	3.42	3.34	2.45	5.62	4.37
FeO	8.17	9.03	10.53	5.48	8.43
MnO	.07	.13	.19	.08	–
MgO	5.52	13.61	13.07	4.19	5.06
CaO	11.30	11.24	11.02	7.90	7.58
Na_2O	3.62	3.02	2.55	4.72	4.18
K_2O	1.02	.93	.60	1.60	1.30
H_2O^-	.42	.12	.40	.09	.06
H_2O^+	1.16	.44	.38	.45	.37
P_2O_5	.66	.52	.38	.87	.61
Cr_2O_3	–	.04	–	–	.02
CO_2	.05	–	–	–	–
SO_3	.17	.22	–	.03	–
Sum	100.11	99.94	100.16	99.73	100.27
Q	–	–	–	–	–
Or	6.12	5.56	3.34	9.45	7.78
ab	19.91	5.76	10.48	34.06	35.11
an	25.58	15.29	23.35	25.85	21.68
di { wo	10.67	15.43	11.83	3.25	5.22
di { en	6.50	11.10	7.70	2.80	3.50
di { fs	3.56	2.90	3.30	–	1.32
hy { en	–	–	–	–	–
hy { fs	–	–	–	–	–
ol { fo	5.04	16.10	17.50	5.39	6.37
ol { fa	3.06	4.69	8.46	–	2.86
mt	4.87	4.87	3.48	7.66	6.50
cm	–	–	–	–	–
hm	–	–	–	.32	–
il	5.62	5.62	3.95	6.54	7.75
ap	1.68	1.34	1.01	2.02	1.34
Ne	5.68	10.51	5.96	3.12	.28
lc	–	–	–	–	–
cs	–	–	–	–	–
cc	.08	–	–	–	–
Ak					
Rest					
Sum	98.29	99.17			

Analyst. F.A.Gonyer   FAGonyer T.Katsura   FAGonyer FAGonyer

APPENDIX B (Continued)

	Hawaiite JP.10[†] (C-72)	Mugearite 1104[†]	Trachyte JP.15[xx]	Ne.-mel.basalt 9960[**]	Ne.basalt. 9961[**] (JP.13)
SiO_2	47.99	54.14	62.02	36.75	38.57
TiO_2	2.62	1.81	.31	2.41	2.79
Al_2O_3	19.36	17.82	18.71	11.98	11.71
Fe_2O_3	5.83	3.90	4.30	6.05	5.21
FeO	5.17	5.34	.10	7.45	7.78
MnO	.21	.08	.15	.08	.11
MgO	4.39	1.88	.40	12.08	13.08
CaO	6.54	4.94	.86	13.81	12.84
Na_2O	4.58	6.24	6.90	4.75	4.22
K_2O	1.82	2.72	4.93	.91	1.20
H_2O^-	.17	.03	.31	.36	.19
H_2O^+	.33	.24	.80	1.61	.59
P_2O_5	.63	.61	.24	1.41	1.11
Cr_2O_3	-	-	-	.03	.06
CO_2	-	-	-	-	.27
SO_3	-	.04	.02	.17	.17
Sum	99.64	99.79	100.13	99.98	99.98
Q	-	-	1.80	-	-
Or	10.56	16.12	28.91	-	-
ab	36.15	46.11	58.16	-	-
an	26.97	12.51	2.22	8.90	9.45
di ⎰ wo	.81	3.48	-	11.14	14.15
di ⎱ en	.60	1.90	-	8.60	10.80
di ⎱ fs	.13	1.45	-	1.32	1.85
hy ⎰ en	-	-	⎱ 1.00	-	-
hy ⎱ fs					
ol ⎰ fo	7.28	1.96	-	13.86	15.12
ol ⎱ fa	.51	1.63	-	4.49	2.86
mt	8.35	5.57	-	8.82	7.66
cm	-	-	-	-	-
hm	-	-	4.30	-	-
il	5.02	3.50	.15	4.56	5.32
Ru	-	-	.24	-	-
ap	1.34	1.34	.67	3.36	2.69
Ne	1.42	3.69	-	21.58	19.31
lc	-	-	c=1.22	4.36	5.67
cs	-	-	-	7.40	3.44
cc	-	-	-	-	.60
Ak	-	-	-	-	-
Rest					
Sum				98.39	98.32

Analyst. T.Katsura F.A.Gonyer H.S. Wash. F.A.Gonyer F.A.Gonyer

APPENDIX B (Continued)

	Ne.-mel.basalt JP.16	Ne.-mel.basalt GF.30
SiO_2	36.34	37.16
TiO_2	2.87	2.17
Al_2O_3	10.14	11.57
Fe_2O_3	6.53	8.89
FeO	10.66	8.63
MnO	.20	-
MgO	10.68	11.75
CaO	13.10	12.26
Na_2O	4.54	5.11
K_2O	1.78	1.95
H_2O^-	1.00	
H_2O^+	1.00	.15
P_2O_5	1.02	-
Cr_2O_3	-	
CO_2	.15	-
SO_3	.04	-
Sum	100.05	99.64

Q	-	
Or	-	
ab	-	
an	1.67	
di {wo, en, fs}	17.39	
hy {en, fs}	-	
ol {fo, fa}	20.23	
mt	9.51	
cm	-	
hm	-	
il	5.47	
Ru	-	
ap	2.35	
Ne	21.02	
lc	8.28	
cs	-	
cc	.31	
AK	11.95	
Rest	-	
Sum	100.13	

Analyst.G.Steiger Andrew S.
McCreath & Son, Inc.

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APPENDIX C

ESTIMATION OF PRECISION AND ACCURACY

J-G. Schilling

Precision:

The estimation of precision was made on the basis
of 9 samples with two reference solutions, combination
of 5 sets of duplicates, 3 sets of triplicates and one
quadruplicate of the same or different sample solutions.
The standard deviation rfom the mean of the results
are reported in Table C-1. The estimated precision
for individual rare earths is arrived at by computing
the average of all standard deviations of each individual
element. Calculated averages and generalized estimates
of standard deviations for all elements are shown in
the last two columns of Table C-1.

Accuracy:

In order to estimate the accuracy of the analytical
procedure used the rock standards G-1 and W-1 were analy-
zed for the rare earths. The results are shown in Table
C-2 and Figures C-1 and C-2. The values obtained by
Towell et al.(1965) and Haskin and Gehl (1963), both using
neutron activation, are also listed for comparison. The
concentrations given for G-1 are averages of duplicate
analyses of two different solutions. The values for
W-1 are averages of triplicate analyses of the same
solution. The values compare reasonably well with
Haskin and Gehl and Towell et al. values. For most
rare earths the concentrations are intermediate between
the values given by these different analysts. Ho and
Tm are slightly lower for G-1 and definitely lower for

TABLE C-1.

Standard deviations from the mean on a percent basis
for 2 or more analyses.

	9948	10398	JP.12	10396	10403
La	.94	.30	9.0	.2	2.3
Ce	-	-	20	-	-
Pr	2.0	2.6	.2	3.0	-
Nd	.5	3.0	3.0	2.2	-
Sm	6.4	-	11	6.5	-
Eu	-	-	9.0	15.	1.0
Gd	-	-	-	-	-
Tb	2.0	7.3	-	18.7	5.4
Dy	2.5	2.6	-	2.5	-
Ho	16	1.5	7.0	1.5	-
Er	-	-	-	-	-
Tm	-	-	3.0	-	-
Yb	.3	1.0	28	.3	-
Lu	2.0	1.5	19	2.	-
Y	.6	.7	16	1.0	9.0

$$\sigma = \sqrt{\frac{\sum_{n=1}^{A}(X-\overline{X})^2}{n-1}}$$

TABLE C-1 (Continued)

	Pele Hair	1801 Flow	1101	JP.14	JP.11
La	–	3.6	–	13.	3.0
Ce	–	–	–	–	–
Pr	–	8.0	–	3.0	–
Nd	–	21.	–	2.0	–
Sm	–	9.0	–	5.0	.80
Eu	2.0	2.5	–	7.0	4.0
Gd	–	–	–	–	–
Tb	–	–	29.	–	11
Dy	–	13.	–	16.	–
Ho	–	3.0	–	–	2.0
Er	–	–	–	–	–
Tm	–	–	–	–	4.0
Yb	–	6.0	–	12.	1.0
Lu	–	18.	–	6.0	7.0
Y	–	3.0	3.0	3.5	3.0

TABLE C-1 (Continued)

	9982	9962	1106	JP.10	1104
La	1.0	-	-	9.0	4.5
Ce	-	-	-	-	-
Pr	2.5	-	3.0	3.0	-
Nd	4.0	-	4.0	2.8	1.0
Sm	2.3	-	2.5	2.0	2.0
Eu	1.0	2.0	5.0	1.0	2.0
Gd	-	-	-	-	-
Tb	2.6	9.0	6.0	3.0	-
Dy	-	-	-	-	-
Ho	-	-	-	-	2.5
Er	-	-	-	-	-
Tm	-	-	-	5.0	-
Yb	.50	-	.50	-	4.0
Lu	4.4	-	4.0	7.0	-
Y	.50	2.5	.50	8.2	-

TABLE C-1 (Continued)

	JP.15	JP.13	JP.16	9960	S.Lake C.Nod.
La	-	-	2.6	-	5.0
Ce	-	-	-	3.0	-
Pr	-	-	9.0	-	1.0
Nd	-	-	13.0	-	9.0
Sm	-	2.5	9.0	1.0	5.0
Eu	4.0	7.0	11	-	8.0
Gd	-	-	-	-	-
Tb	3.5	11	16	13.	2.0
Dy	.10	-	-	10	-
Ho	1.0	7.0	3.0	-	18.
Er	-	-	-	-	-
Tm	5.0	8.0	9.4	-	6.0
Yb	3.0	7.0	19	-	14.
Lu	2.0	7.0	6.0	-	1.0
Y	.40	-	21.	-	13.

TABLE C-1 (Continued)

	Hual.ol.	JC1-18-62	G-1	W-1	Average	Final Estimate
La	2.0	-	8.7	1.1	4.1	4
Ce	-	-	1.1	7.0	7.8	10
Pr	-	-	3.5	1.0	3.2	4
Nd	-	-	12	6.0	6.0	6
Sm	12	-	2.0	6.0	5.0	5
Eu	7.0	-	5.0	13	5.5	6
Gd	-	-	-	-	-	15
Tb	-	-	6.8	1.0	8.7	9
Dy	-	-	-	.5	5.9	6
Ho	18	-	-	7.0	6.7	7
Er	-	-	-	-	-	-
Tm	-	-	-	1.2	5.2	8
Yb	31	-	19	8.5	9.1	9
Lu	38	9.3	-	13	8.6	9
Y	13	1.0	-	3.0	5.4	6

TABLE C-2a.

Rare concentration, in ppm., for standard granite G-1.

	This work[*]			Towell et al.[†]			Haskin & Gehl[‡]		
La	89.0	±	7.8	92.4	±	3.1	102	±	7.7
Ce	207.	±	2.4	150	±	24	134	±	13
Pr	20.0	±	.71	12.9	±	1.4	20.9	±	.32
Nd	57.6	±	7.2	55.2	±	5.5	54.6	±	1.5
Sm	6.85	±	.14	8.25	±	.08	8.6	±	.56
Eu	1.20	±	.06	1.36	±	.05	1.04	±	.11
Gd	3.57			–			4.88	±	.13
Tb	.573	±	.039	.637	±	.057	.50	±	.01
Dy	2.88			2.52	±	.10	–		
Ho	.487			.408	±	.016	.50	±	.01
Er	–			–			1.40	±	.14
Tm	.153			.156	±	.011	.20	±	.02
Yb	1.04	±	.20	.937	±	.075	.625	±	.06
Lu	.165			.123	±	.007	.17	±	.02
Y	13.14			13.3	±	1.6	12.5	±	.25

[*] Standard deviation $\sigma = \sqrt{\dfrac{\sum\limits_{i=1}^{n}(X_i-\bar{X})^2}{n-1}}$

[†] Towell, D. G., R. Volfovsky, and J. W. Winchester, Geochim et Cosmochim. Acta 29, 569-572, 1965.

[‡] Haskin, L, and M. A. Gehl, J. Geophys. Res. 68, 2037-2042, 1963.

TABLE C-2b.

Rare earth concentration, in ppm., for standard diabase W-1.

	This work [*]	Towell et al. [†]	Haskin & Gehl [‡]
La	8.54 ± .09	9.31 ± .37	11.7 ± 1.21
Ce	26.8 ± 1.8	15.1 ± 2.4	24.3 ± 2.4
Pr	2.90 ± .024	3.51 ± .39	3.68 ± .19
Nd	12.1 ± .75	20.2 ± 2.0	15.1 ± 1.4
Sm	3.15 ± .20	3.46 ± .03	3.79 ± .32
Eu	1.03 ± .14	1.29 ± .05	1.09 ± .12
Gd	—	—	4.2 ± .35
Tb	.595 ± .005	.807 ± .073	0.75 ± .075
Dy	3.76 ± .017	4.38 ± .18	—
Ho	.687 ± .047	.855 ± .034	1.35 ± .11
Er	—	—	2.57 ± .26
Tm	.257 ± .003	.332 ± .023	.355 ± .005
Yb	2.18 ± .18	2.23 ± .18	2.10 ± .01
Lu	.320 ± .041	.348 ± .021	.325 ± .033
Y	22.4 ± .59	28.0 ± 3.4	23.8 ± .12

[*] Standard deviation $\sigma = \sqrt{\dfrac{\sum\limits_{i}^{n}(X-\bar{X})^2}{n-1}}$

W-1. In almost all the analyses we have undertaken, Ho and Tm were found consistently lower by about 20% relative to the expected value estimated from the smooth fractionation curve on a chondritic normalized plot. Possible causes of these two systematic discrepancies are explored below.

Source of errors:

Several independent sources of errors can be introduced during the different steps involved in the procedure described in Part II. Besides errors due to weighing and pipetting, five major sources of errors are recognized.

1. Chemical yield determination: Internal rare earth fractionation during the pre-irradiation chemistry is always possible. In order to have a close control on such phenomena Ce-139 and Y-88 monitors are used to control the light and heavy end of the series respectively. The two chemical yield determinations never deviated more than 5% from the mean value. Usually they were found to vary by less than 3%.

2. Loading: During irradiation, the rare earths were found to be adsorbed to a certain extent to the wall of the polyethylene tubes. Thus incomplete transfer of the radioactivity from the polyethylene container and the chromatographic column during the loading operation could produce appreciable loss and possibly internal fractionation. To avoid such errors, the tubes were

Figure C-1. Abundances of the rare earth elements in
the standard granite G-1 relative to 20 chondrites
(Schmitt et al., 1963, 1964) are plotted on a logarith-
mic scale as a function of atomic number. Averages of
duplicate analyses. The vertical bars represent extreme
deviation of each element from the mean.

G-1 Granite

ppm Rock / ppm Chondrites

Average of 2 analyses

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
57   (Y)   71
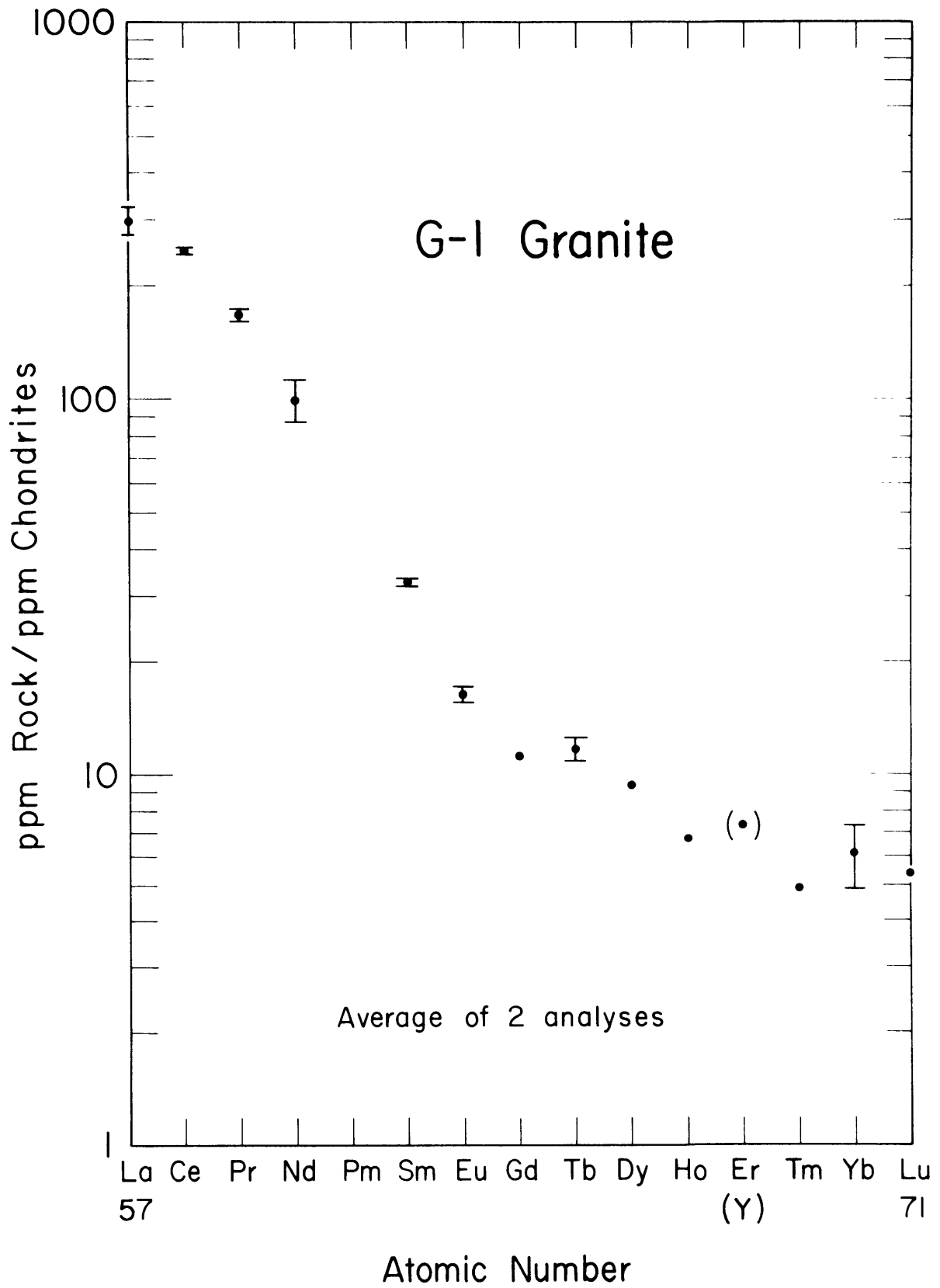
Atomic Number

Figure C-2. Abundances of the rare earth elements in the
standard diabase W-1 relative to 20 chondrites (Schmitt
et al., 1963, 1964) are plotted on a logarithmic scale
as a function of atomic number. Averages of triplicate
analyses of the same solution. The vertical bars represent
extreme deviation of each element from the mean.
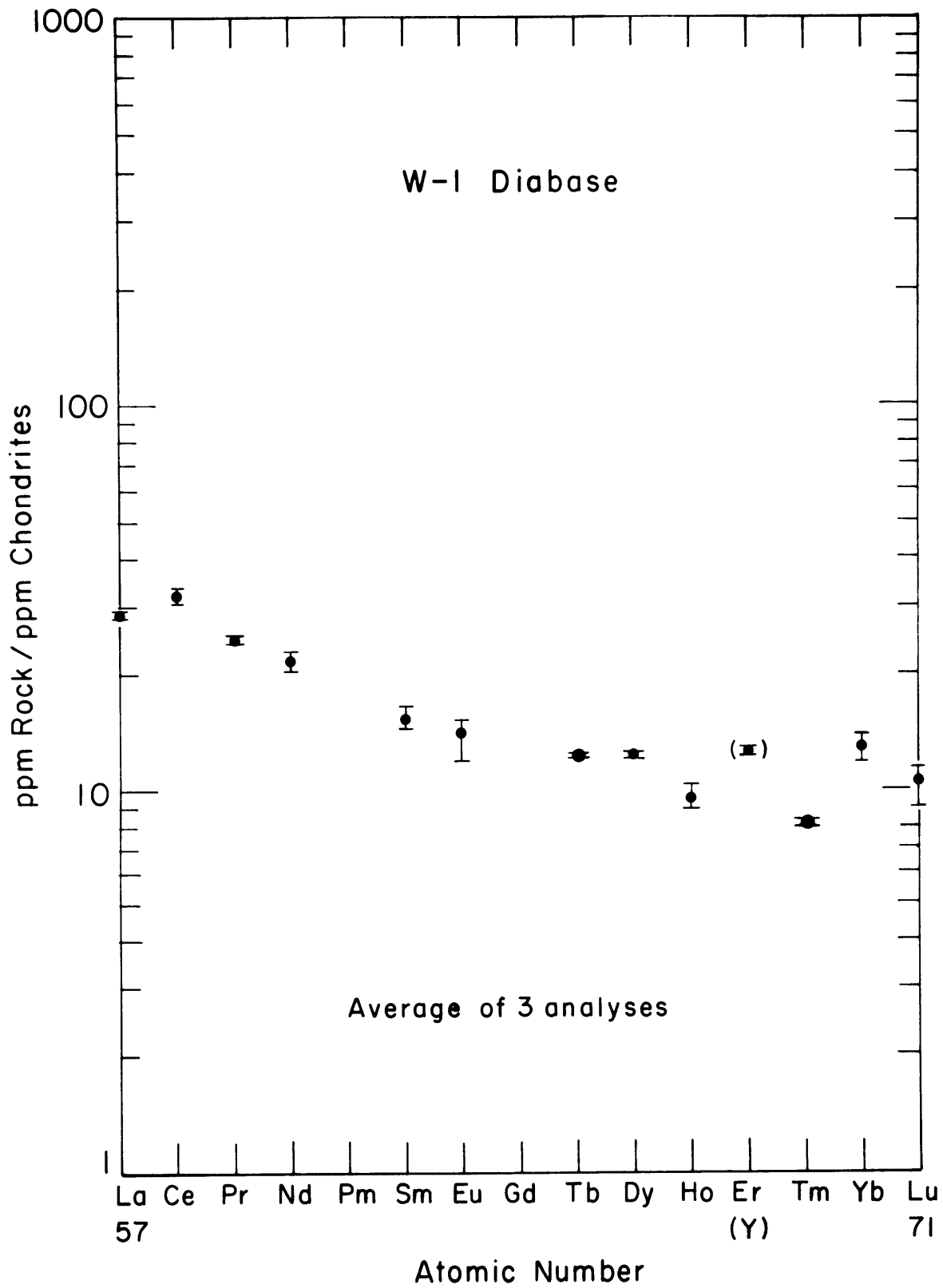
Figure C-3. Typical elution of a rock sample irradiated for three hours in a thermal neutron flux of 2×10^3 n/cm^2/sec. 6 ml volume is used per acid.
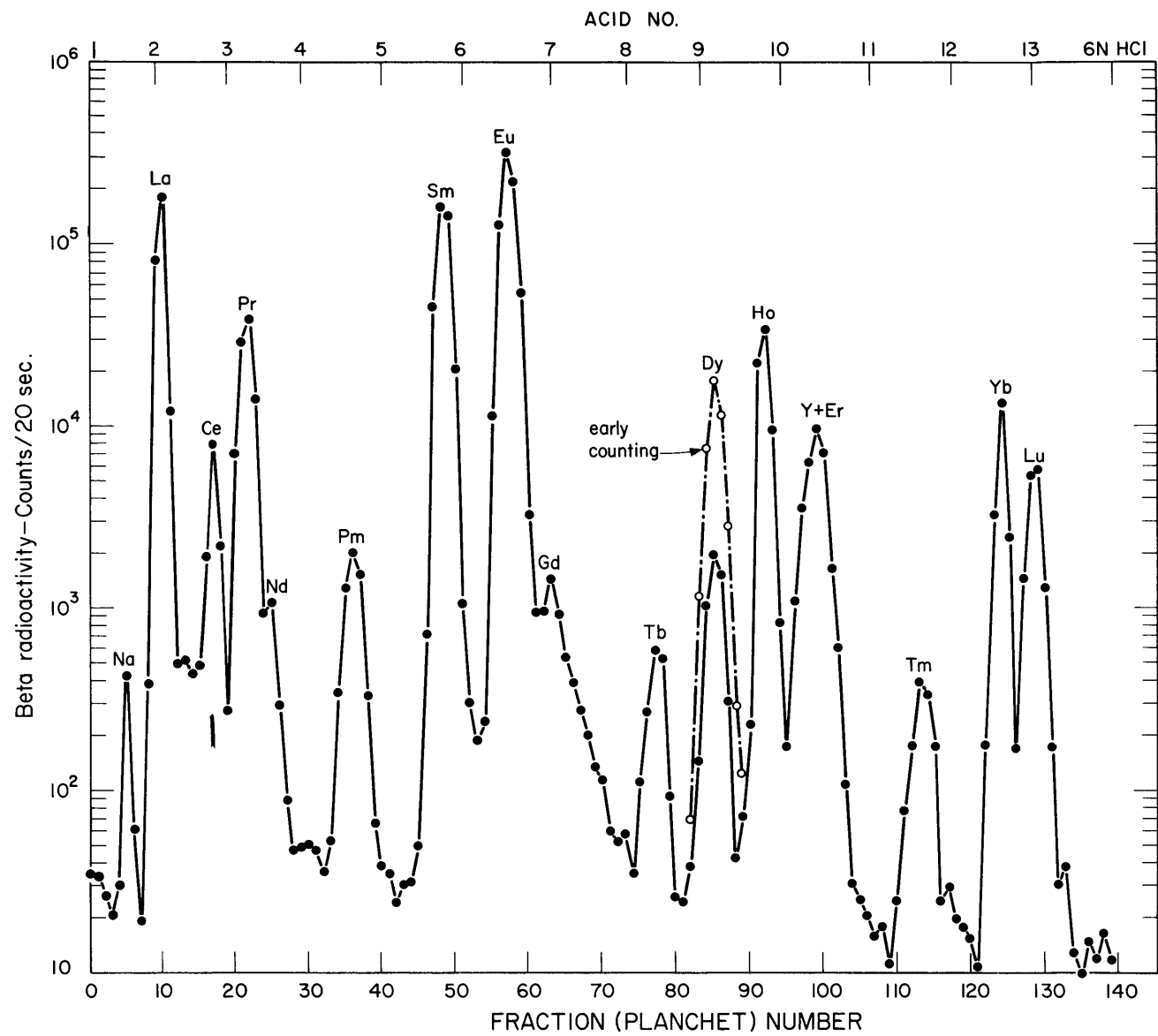
washed 4 to 5 times till more than 99% of the total radio-
activity had been transferred. The activity remaining
in the vial was found to be due, by γ-ray spectroscopy, to
Na-24 which was always present, and in some cases possibly
to Mn-56.

3. Chromatography: Incomplete separation of the rare
earths during the chromatographic step is the most serious
source of errors. However, one of the advantages of this
procedure is that a complete elution spectrum is available.
Figure C-3 shows that the rare earths occur in character-
istic patterns in this elution curve. The first group-
ing involves La, Ce, Pr, and Nd with La having a very
high activity, Ce and Pr moderately high and Nd low. Pm
stands alone. The second grouping contains Sm, Eu, and
Gd. Sm and Eu have very high activity whereas Gd activi-
ity is low. Tb then stands alone. The third group-
ing involves Dy, Ho, and Er and Y superimposed on each
other. The Dy is low by the time the entire curve is
counted; Ho and Y are high (Er is only about 1% of the
beta activity in the Er-Y peak). Tm then stands alone
and the last grouping involves Yb and Lu. This allows
assigning more confidence to the higher activity peaks,
e.g. La, Sm, Eu, Ho, Y, and make corrections, whenever
necessary, for interference in poorly separated pairs,
e.g. Ce-Pr, Pr-Nd, Eu-Gd, and Yb-Lu. In general errors
due to incomplete separation was less than 3% for La,
Sm, Eu, Ho, and Y, and varied up to 10% for the poorly
separated pairs Ce-Pr, Eu-Gd and Yb-Lu.

4. Counting: The high quality rare earth separation of the chromatographic step and its high reproducibility allows the use of unsophisticated gross beta counting. Radioactivity in reference and the sample fractions was counted alternatively. Except for Dy-165, with a 2.3 hrs half life, all the other rare earths were counted a day after the irradiation and chromatographic separation were performed. The activities were high enough to operate with 20 seconds count duration only, except for Tb and Tm, both having low abundances and sensitivities. Fortunately Tb-160 and Tm-170 isotopes have long half-lives, 73 days and 125 days respectively and can be counted 3 to 6 months later when the activities from the adjacent elements have decayed away. These two elements were counted for 10 minutes.

The standard deviation of replicate counts of the same fraction were found to be about 3%. But since each peak corresponding to one rare earth is composed of about 7 fractions out of which 3 to 4 carry most of the activity, these errors tend to cancel out and improve the statistics somewhat. Thus, 3% error should be considered as a maximum value for the counting errors.

5. Reference stock solutions: These solutions were prepared by Towell (1963) and stored in polyethylene bottles. They were retitrated recently by Ehrlich (1966). The solutions were prepared by dissolving high

purity rare earth oxides (Lindsay, 99.9%) in 3N HNO_3.
The purity of Lindsay rare earth oxides was not checked
until it was found that Ho and Tm were consistently low-
er by about 20% than the expected value obtained from
the smooth fractionation curve on semi logarithmic chon-
dritic plots. Most of the impuritites contained in
given rare earth oxide are expected to be from the two
adjacent rare earths. The reference solutions were
tailored to approximate the concentrations of rare earths
expected in the rock sample analyzed. Therefore the re-
ference solutions of even rare earth atomic number are
about 3 to 6 times higher than those of the adjacent odd
rare earths, except for Yttrium. Yttrium concentration
of the reference solution is about 75 times higher than for
Tm and 28 times higher than for Ho. Y was found always
to elute between Ho and Tm and was superimposed on Er;
but Er contribution to the activity peak was only a few
percent of the total peak.

Assuming 99.9% purity for Y oxide, and that the
remaining 0.1% impurities are evenly distributed between
Ho and Tm, one computes that Tm reference peak will be
increased by 3.8% and Ho peak by 1.4%, due to the Y im-
purities. Yet, if Y oxide has 1% impurities these two
values will be increased 10 fold, a significant contribu-
tion.

Thus, the consistently lower Ho and Tm values would
be explained if impurities in Lindsay rare earth oxides

were of the order of 0.5-1%. In order to check this impurity problem, a reference solution containing only Y and Er in the proportions used ordinarily and two separate solutions of Ho and Tm alone were irradiated in duplicates. The Ho and Tm impurities contained in the Y reference solution on a percentage basis relative to Ho and Tm and Y reference peak are listed in Table C-3:

$$
\begin{array}{lll}
\text{Ho} & .0177\% & \pm\ 8\% \\
\text{Tm} & 2.05\ \% & \pm\ 40\% \\
\text{Y} & .0411\% & \pm\ 59\%
\end{array}
$$

Thus, these values give an upper limit for the contamination of reference peaks from adjacent rare earths, Y being much more abundant relative to any other rare earths. The consistently low values of Ho and Tm cannot be attributed to impurities of the Lindsay rare earth oxides. When the 20 analyses are plotted relative to the olivine tholeiite on a semilogarithmic plot against the atomic number, Tm and Ho fall on the smooth fractionation curve. This indicates that the Tm and Ho anomaly is due either to a systematic error in this procedure or that the chondrite values for these two elements are slightly too high (Smitt et al., 1963 and 1964). However, our Tm and Ho concentrations of W-1 were found also definitely lower than values given by Towell et al. (1965) and Haskin and Gehl (1963). Other possibilities were explored to explain this two anomalies, but were found unsatisfactory. The reasons

remain obscure and further work is indicated to elucidate this problem.

Chromatographic reproducibility:

A good estimate of the reproducibility of rare earth separation can be obtained by comparing the activity ratio of two reference solutions irradiated, chromatographed and counted at the same time. Table C-4 shows this ratio for each rare earth. This ratio includes errors type 3 (loading) and type 4 (counting). Thus these values represent maximum deviations for the estimate of the chromatographic reproducibility. The position of valleys and peaks with respect to the acid numbers (Figure 2-1) on the elution curve was found to be highly reproducible.

Reagent blanks:

The reagents were analyzed for their combined rare earth content. This includes the following reagents: HF, $HClO_3$, HCl, H_2O, NH_4OH, HNO_3, $(NH_4)_2C_2O_4 \cdot H_2O$, $H_2C_2O_4 \cdot 2H_2O$, $NaHSO_3$, and Ca^{++} and Fe^{+++} carriers in HCl solution. Two blanks irradiated for 8 hrs. were processed. The average values for individual rare earths given in $\mu gm/\approx.500gm$. sample are given in Table C-5. No corrections for reagent blank were applied since they are smaller than other experimental errors.

Purification of reagents:

HF was of AR quality (Transist AR).

$HClO_3$ double vacuum distilled from vycor and shipped in vycor ampules was used (G. Frederic and Smith).

TABLE C-4.

Activity ratios for individual rare earths of two
reference solutions irradiated, chromatographed and
counted at the same time.

	Nov. 11/65 irradiation	Dec. 16/65 irradiation	Feb. 3/65 irradiation	Feb.10/65 irradiation
La	-	1.292	.995	1.013
Ce	-	-	1.271	1.001
Pr	1.056	1.066	.959	1.052
Nd	1.095	1.039	.942	1.076
Sm	1.042	1.006	.878	1.049
Eu	.958	1.056	.747	.910
Gd	-	-	-	-
Tb	1.064	-	1.097	.949
Dy	-	1.026	.953	-
Ho	-	1.025	.970	-
Er	-	-	-	-
Tm	1.058	-	1.013	1.024
Yb	1.019	1.193	1.009	1.009
Lu	1.152	.920	.972	.925
Y	1.059	.995	1.014	.990

TABLE C-5.

Rare earth content of reagent blanks, average of two analyses.

$\mathcal{M}$ gm/$\approx$0.500 gm. sample	
La	.065
Ce	.78
Pr	.016
Nd	< .24
Sm	.0073
Eu	.0015
Gd	-
Tb	.032
Dy	.0040
Ho	.0012
Er	-
Tm	< .006
Yb	< .004
Lu	< .00068
Y	.077

HCl was prepared by passing HCl gas (Matheson Co.) through distilled and demineralized water in a plastic bottle until saturation. The acid was then distilled using vycor apparatus.

NH_4OH was prepared by passing NH_3 gas through distilled and deminaralized water in a plastic bottle until saturation.

HNO_3, AR grade, was redistilled using: vycor aparatus.

Fe^{+++} in HCl solution was prepared from spec-pure iron (Jarrel-Ash) and further purified by anion exchange chromatography using Dowex 1-X8, 50-100 mesh resin.

Ca^{++} in HCl solution was prepared dissolving AR grade $CaCl_2$ and then purified twice by cation exchange chromatography using Dowex 50W-X8, 200-400 mesh resin.

AR grade ammonium oxalate, oxalic acid and sodium bisulfite were used.

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APPENDIX D

FULLY AUTOMATED STEP-WISE CONCENTRATION
GRADIENT ELUTION CHROMATOGRAPHY FOR
RARE EARTH SEPARATIONS

Jean-Guy Schilling, Pierre U. Jaillet,
and George S. Cichocki

Purpose:

A neutron activation procedure for analysis of micro-amounts of rare earths (from La_{57} to Lu_{71} and including Y_{39}) has been developed in this laboratory by Volfovsky et al. (1963) and amended by Ehrlich et al. (1966). This method involves a pre-irradiation separation of the rare earth group followed by post-irradiation separation of individual rare earths by reversed phase chromatography. In this latter step the rare earths are chromatographed by successive addition of 13 different concentrations of hydrochloric acid each of 6ml volume. To accelerate the kinetics of separation the columns are kept at $70^{o}C$. and the acid pushed through under approximately 14 psig. pressure of nitrogen gas. To avoid bubble formations in the column, the acid had to be degassed by heating and kept at the same temperature until used. Great attention is required to avoid drying the column bed and in practice only two elutions can be operated by one person at a time.

System:

A fully automated system was designed to make this technique a routine operation. The acids are poured into small tubes and kept in a hot bath. The acid containers are joined to 13 small solenoid valves whose outlets are connected to the main exchange column by means of small tygon tubings. One small pair of electrodes referred to as "bottom electrodes" is placed in a centimeter above the top of the column bed. A second pair of electrodes referred to as "top electrodes" is placed further above.

The two pairs of electrodes are separated by a 6 ml column volume, corresponding to the volume used for each acid. These electrodes are connected to an electronic valve control unit, all solid state designed. When the washing acid reaches the bottom electrode, valve #1 opens and lets acid #1 flow to fill the tube between the two electrodes, till it reaches the top electrode which upon signal closes valve #1 and advances the circuit to preselect valve #2. The acid is then pushed through the column slowly. When the liquid again reaches the bottom electrode, valve #2 opens. This sequence is repeated thirteen times until valve #14 is reached and opens the system to the atmosphere thus preventing any further flow. The liquid eluants are collected in fractions with a standard fraction collector. A schematic drawing of the system is shown in Figure D-1.

Description of the electronic system:

The purpose of this electronic system is to control the successive addition of the different acids. Manual control of all electronic functions is provided for maintenance purposes: solenoid valve control, electrode test etc.

Opening and closing of the valves is controlled by two level electrodes placed above the chromatographic column. To avoid electrolysis and formation of bubbles by DC current a 1000 Hertz wave generator is used.

When the level of the acid in the column gets below the "bottom electrodes", a pulse is generated by an amplifier-rectifier-pulse shaper-differentiation circuit. See block diagram in Figure D-2. This pulse opens the valve which is selected by a binary counter decoder combination. Now the acid is filling the tube. When the level reaches the "top electrodes" a similar amplifier-rectifier-pulse shaper-differentiation circuit produces a pulse which resets the valve and advances the counter to the next position. The counter is a 4 flip-flops binary counter built using Amperex modules. Display of the states of the flip-flops is provided using neon bulbs. A diode AND gate preforms the function of decimal decoding to operate one solenoid at a time for the sixteen positions, providing the ON-OFF flip-flop is in the ON position (set). A diode OR gate allows manual selection of any solenoid driver by push button. A manual advance counter by push button is provided for control. A reset button is also provided to reset the counter to zero at the beginning of the cycle.

The solenoid driver uses a Darlington circuit, driving a saturated power transistor. The switch valve current is in the order of 500 mA with a 24 volts supply. Diode transient supressor is used to protect the power transistor. Each solenoid driver and decoder is mounted on a plug in PC board for easy replacement.

Figure D-1. Schematic representation of the electrode controlled automated step-wise elution device.

PRESSURE

O-RING JOINTS

N2 CYLINDER

WATER BATH

PRESSURE

ACID CONTAINER

VALVES

O-RING JOINTS

TOP ELECTRODES

O-RING JOINTS

BOTTOM ELECTRODES

DEP-CELITE

WATER JACKET

MAGIC EYE

PLANCHET

FRACTION COLLECTOR
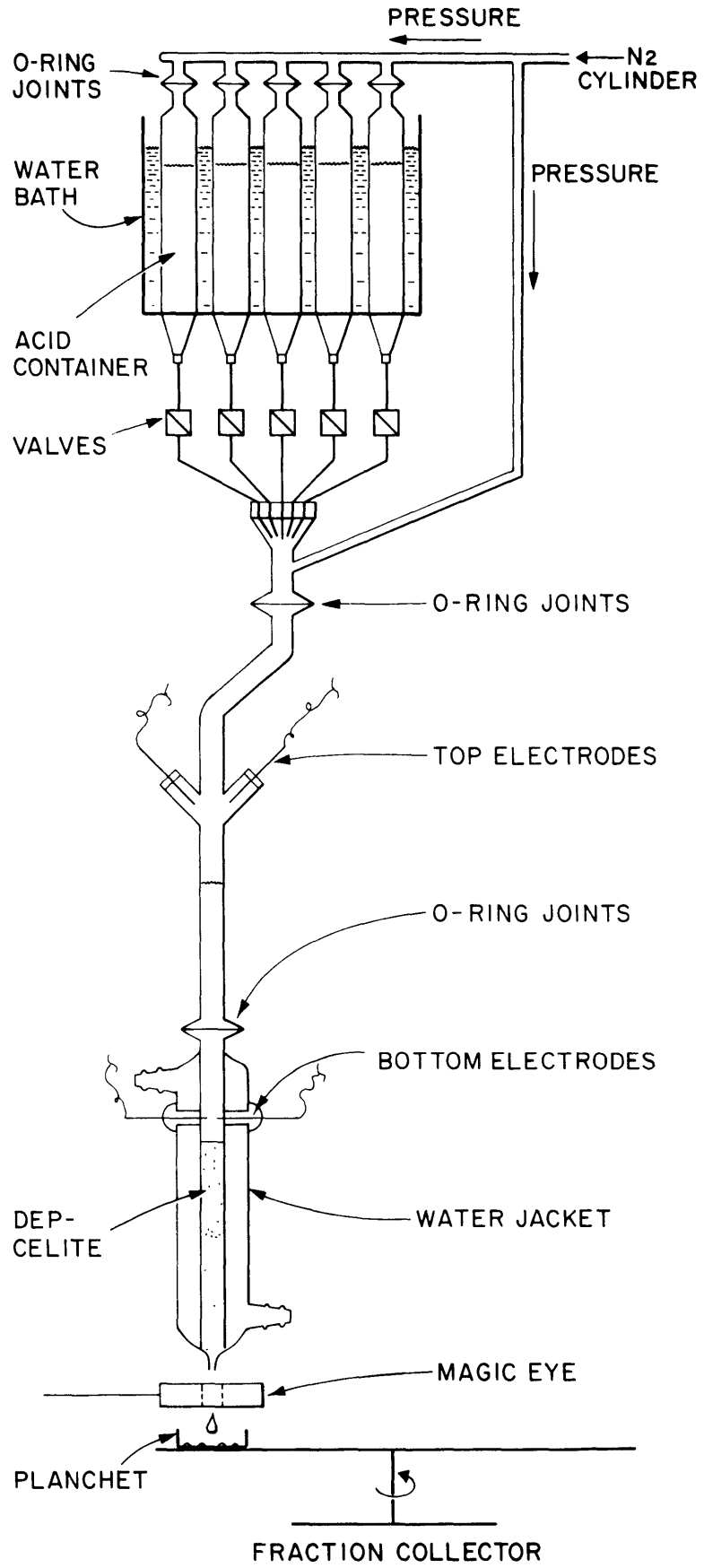
Figure D-2. Block diagram of the valve control system.
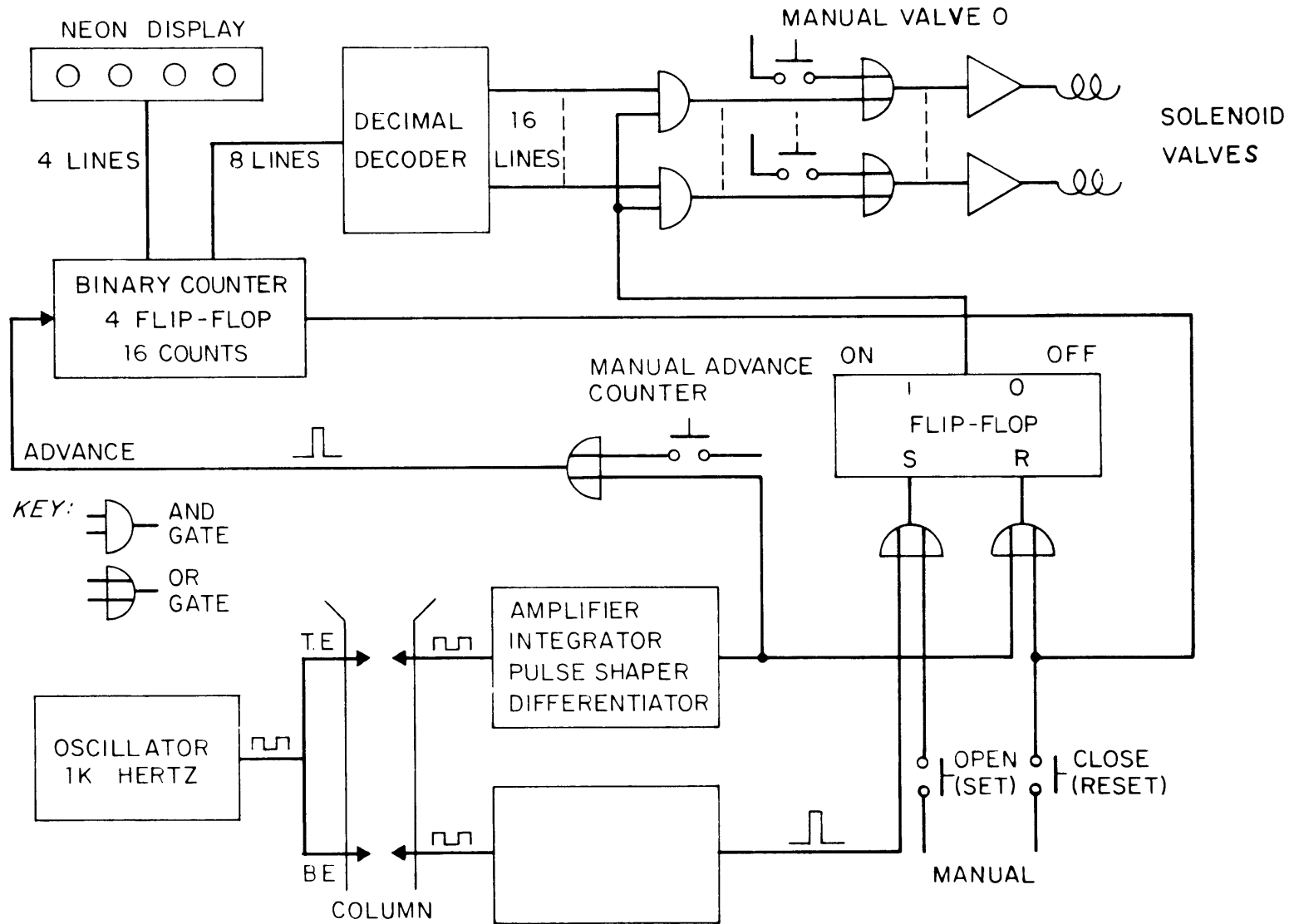
The circuit is powered from the 115 VAC 60 cycles line. Transistor stabilized ± 6 volts supply is used for the logic circuit and Amperex modules. A 100 volts supply is used for the neon display, The 24 volts solenoid power is not stabilized. All the elctronic circuit is fully transistorized. The prototype was built in this laboratory. The production units were manufactured under a contract by Salco Electronics, Salisbury Massachusetts. Additional information:

Special glass columns were designed in order to isolate the electrodes which had to pass through the water jacket. Only the tip of the electrodes, which was in contact with the acid was made of platinum The rest of the lead was made of tungsten carbide which matches better the thermal expansion of glass. The columns were built by Ryan and Velutto, Cambridge, Massachusetts.

The top electrodes had to be protected from acid descending from the outlet valve which could produce an accidental contact, Thus closing the valve before the tube was filled with the proper volume of acid. For this purpose the electrodes were placed in small satellite tubes which formed a downward pointing "V". Therefore only the ascending liquid filling the tube could produce the necessary contact and close the valve after the proper volume of acid was poured into the system.

Special valves were built for this purpose. They are composed of a small lever pressing upon flexible

siliconized rubber tubing by means of a small spring.
The lever is attached to a small solenoid cone which
is pulled by the solenoid upon signal.

Conclusions:

This system allows as many simultaneous elutions
as required. In our laboratory five set-ups have
been built and it is routine to run five elutions
of any combination of reference standards, rock mineral
samples or blanks, at the same time.

ACKNOWLEDGMENTS

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APPENDIX E

RARE EARTH AND RUBIDIUM-STRONTIUM

RELATIONSHIPS IN HAWAIIAN BASALTS

J-G. Schilling,& A. E. Bence

Introduction:

Rubidium/strontium ratios and strontium isotopic compositions have proven to be important research tools in studying the chemical evolution of the earth. They put constraints upon the composition of the source material and upon the time of differentiation processes. Nevertheless due to the lack of complete understanding of trace element distribution and the factors influencing them the applications of this method are limited. On the other hand, recent progress in rare earth geochemistry indicates that rare earth fractionation patterns may be sensitive indicators of the physico-chemical processes of differentiation. Thus a combination of the rare earth and rubidium-strontium methods would have the attributes of both methods and a more complete picture of the evolutionary history of the earth may be attained.

Rare earths, Rb, and Sr concentrations and Sr^{87}/Sr^{86} ratios are determined for the same sample powders of a suite of Hawaiian basalts. The results and interpretations are reported separately (Schilling and Winchester 1966c; Bence, 1966). Moreover these samples have been analyzed for major oxides and petrographic characteristics and geological occurrences have been discussed in great detail (Washington 1923; Macdonald & Powers 1946; Winchell 1947; Wentworth and Winchell 1947; Muir and Tilley 1961; Macdonald & Katsura 1964). Additional

Figure E-1. Variation diagram of La vs. Rb in Hawaiian
volcanic rocks.

+ Tholeiite
● Alkali olivine basalt and ankaramite
○ Basanite-basanitoid
□ Hawaiite
✶ Mugearite
▲ Trachyte
△ Nepheline-melilite basalt
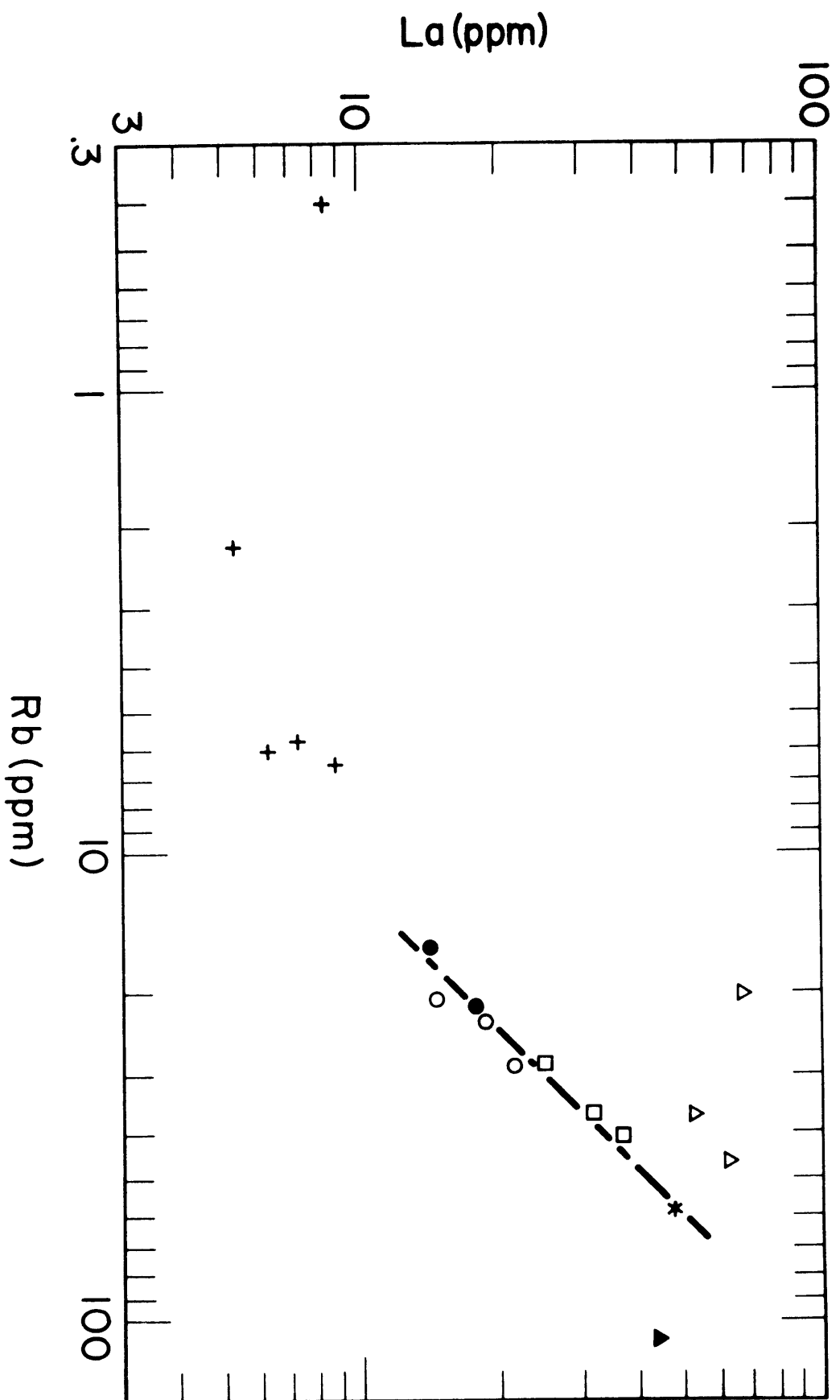
Figure E-2. Variation diagram of La vs. Sr in Hawaiian
volcanic rocks.

+ Tholeiite
● Alkali olivine basalt and ankaramite
○ Basanite-basanitoid
□ Hawaiite
✳ Mugearite
▲ Trachyte
△ Nepheline-melilite basalt
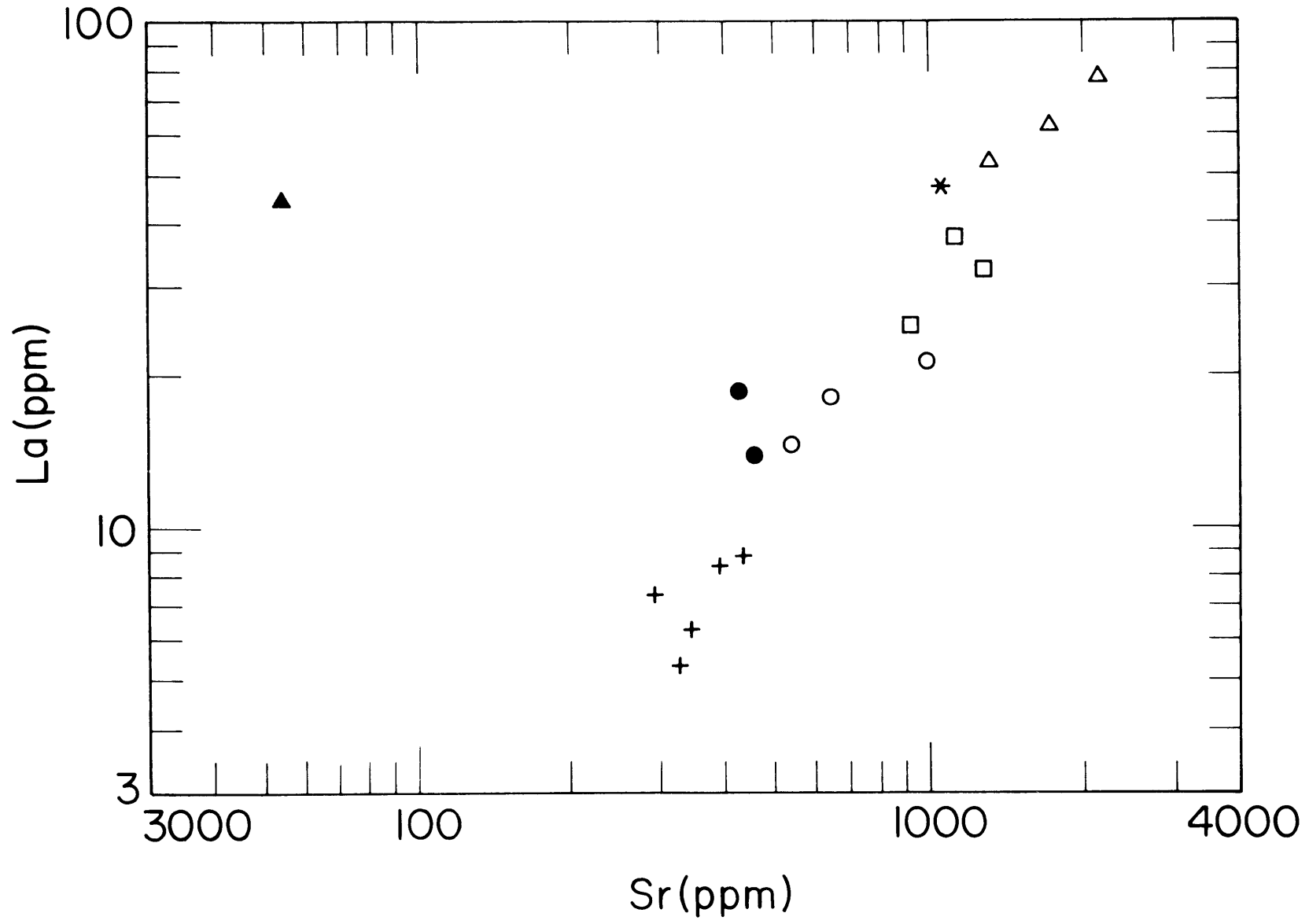
Figure E-3. Variation diagram of Rb vs. Sr in Hawaiian volcanic rocks.

+ Tholeiite
● Alkali olivine basalt and ankaramite
○ Basanite-basanitoid
□ Hawaiite
✳ Mugearite
▲ Trachyte
△ Nepheline-melilite basalt
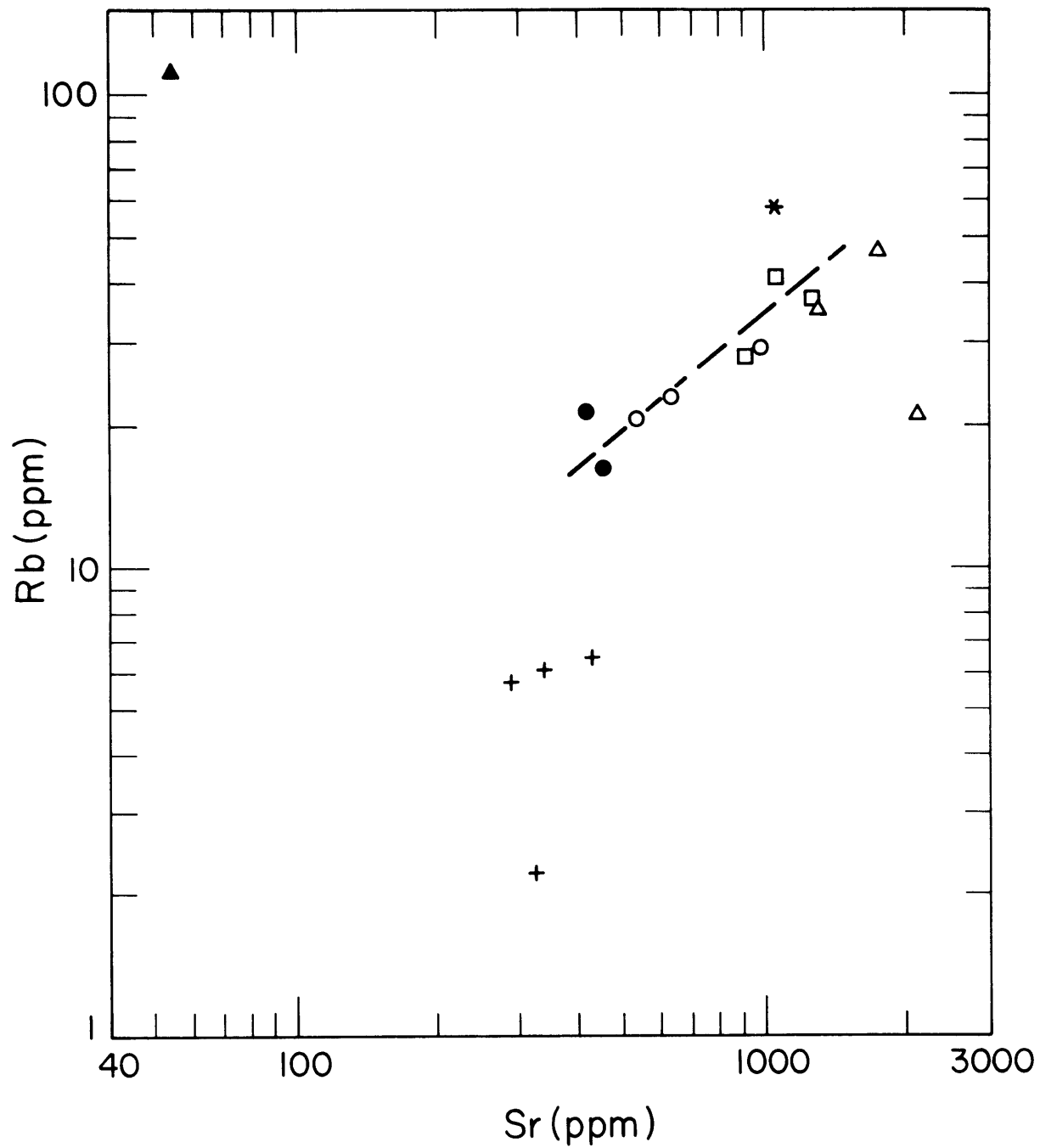
information on U, Th. and Pb abundances and Pb isotopic composition are available for several of the samples (Tatsumoto, 1966). The samples numbered "J.P." were previously analyzed for Sr^{87}/Sr^{86} ratios by Powell, Faure, & Hurley (1965).

Discussion:

The Rb, Sr, La, and Yb concentrations and sr^{87}/sr^{86} ratios for each sample analyzed are given in Table E-1. The concentrations of the other rare earths are available elsewhere (Schilling and Winchester 1966c). On the basis of the Rb, Sr, and La concentrations, the basalts are divided into four groups. Figures E-1,2, and 3 are the variation diagrams of La vs Rb, La vs Sr, and Rb vs Sr respectively. The four groupings are particularly evident on the La-Rb variation diagram. The groupings are: the tholeiites which include a diabase from the Palolo quarry; the alkali series comprising an ankaramite, alkali-olivine basalts, basanite-basanitoids,hawaiites, and a mugearite; the nepheline-melilite basalts; and finally a trachyte which stands by itself because of its high rubidium content. Although less evident the other two diagrams show the same groupings. Schilling and Winchester (1966c) observed these same groupings independently, from the relative rare earth patterns and from other variation diagrams of La against major oxides. It is remarkable that these groups based on trace element data alone correspond closely to well recognized petrological classifications. Moreover these groupings also

TABLE E-1.

K, Rb, Sr, La and Yb Abundances in ppm and Sr^{87}/Sr^{86} Ratios in Hawaiian Basalts.

Group	Sample Number	K	Sr	Rb	La	Yb	Sr^{87}/Sr^{86}
Tholeiite basalt	9948	1245	329	2.18	5.30	1.26	.7048
	JP.12	3070	290	5.73	7.22	1.85	.7038
	10396	1826	396	0.48	8.41	1.81	.7048
	10403	2905	432	6.43	8.78	2.06	.7046
	10398	4980	346	5.99	6.24	1.45	.7043
Alkali basalt	1101	3480	453	16.3	13.91	1.40	.7040
	JP.14	6970	419	21.4	17.76	1.63	.7030
	JP.11	4980	539	20.6	14.49	1.14	.7028
	9962	8460	992	28.9	21.29	1.82	.7037
	9982	7720	635	22.9	18.08	1.23	.7035
	JP.10	15100	1260	36.6	31.65	2.74	.7035
	1102	13280	1107	40.2	36.09	2.44	.7044
	1106	10790	908	28.3	24.59	2.40	.7031
	1104	22580	1061	58.4	47.98	3.08	.7046
Trachyte	JP.15	40900	5415	113.80	44.13	4.56	.7033
Nepheline basalt	JP.16	14780	1752	46.6	62.61	.899	.7027
	JP.13	9960	1303	36.2	51.96	2.01	.7030
	9960	7550	2150	20.9	78.07	1.96	.7043

correspond closely with groupings based upon the Sr^{87}/Sr^{86} ratios with the exception of the trachyte, which cannot be distinguished from the alkali series on this basis along (Bence, 1966), and the somewhat anomalous nepheline-melilite basalt #9960.

No systematic variation of La with Rb within the tholeiite suite or the nepheline-melilite basalt group is observed. In the alkali series, there is a sympathetic increase of La with Rb from the ankaramite to the mugearite. This coherence of two quite dissimilar elements may reflect simple mechanisms of differentiation for this series. The La-Rb variations suggest identical behavior for these two elements in the series. Many lines of evidence point to this series being the product of fractional crystallization, involving mainly olivine, augite, and plagioclase, in a magma originally of alkali-olivine composition.

Although the two ions are quite different in size ($La^{+++} = 1.14\text{Å}$ and $Rb^* = 1.47\text{Å}$) both are larger than the largest major cation sites in the minerals involved. Thus, in addition to filling of vacancies, if diadochic replacement of major cations by these ions has taken place, one would expect an increasing difficulty in replacing major cations by ions with increasing ionic radius. Rubidium should therefore increase more rapidly in the residual melt than lanthanum. This is not the case and it indicates that other parameters must influence the relative partitioning of these elements. (Adsorption, charge differences,

or bonding, etc.). The relatively larger scatter in the alkali series for La-Sr (Fig. E-2), produced mainly by Strontium variations, may be due to the fact that Strontium has a close affinity for Calcium sites and small variations in the proportions of Ca-bearing phenocrysts (augite, plagioclase) will influence noticeably the Strontium abundances of the rocks.

A better coherence of Sr-La than Rb-La is observed for the tholeiitic and nepheline-melilite groups but there is a much greater dispersion of data for the alkali series.

Using the published K_2O analyses we have observed that the K/Rb ratios seem to increase slightly with increasing K_2O content for the alkali series. Lessing et al. (1963), Gast (1965), and Taubeneck (1965) show clearly that the K/Rb ratios for this series remain constant or slightly decrease with increasing K_2O. A redetermination of K_2O in these rocks seems advisable.

The data by Lessing et al. (1963) show a marked decrease of K/Rb ratios with increasing K for lavas with K content higher than ~2%. This corresponds to lavas grading from mugearite to trachyte. They attributed this decrease to some other process than crystal settling. Although this is quite possible for the trachyte it should be remembered that anorthoclase is reported for lavas in the range hawaiite to mugearite (Muir & Tilley, 1961). This indicates clearly that the Potassium

Figure E-4. Relationships of K/Rb, K/Sr, K/U, K/La K/Yb
and K/Sr ratios in basalts from oceanic areas.
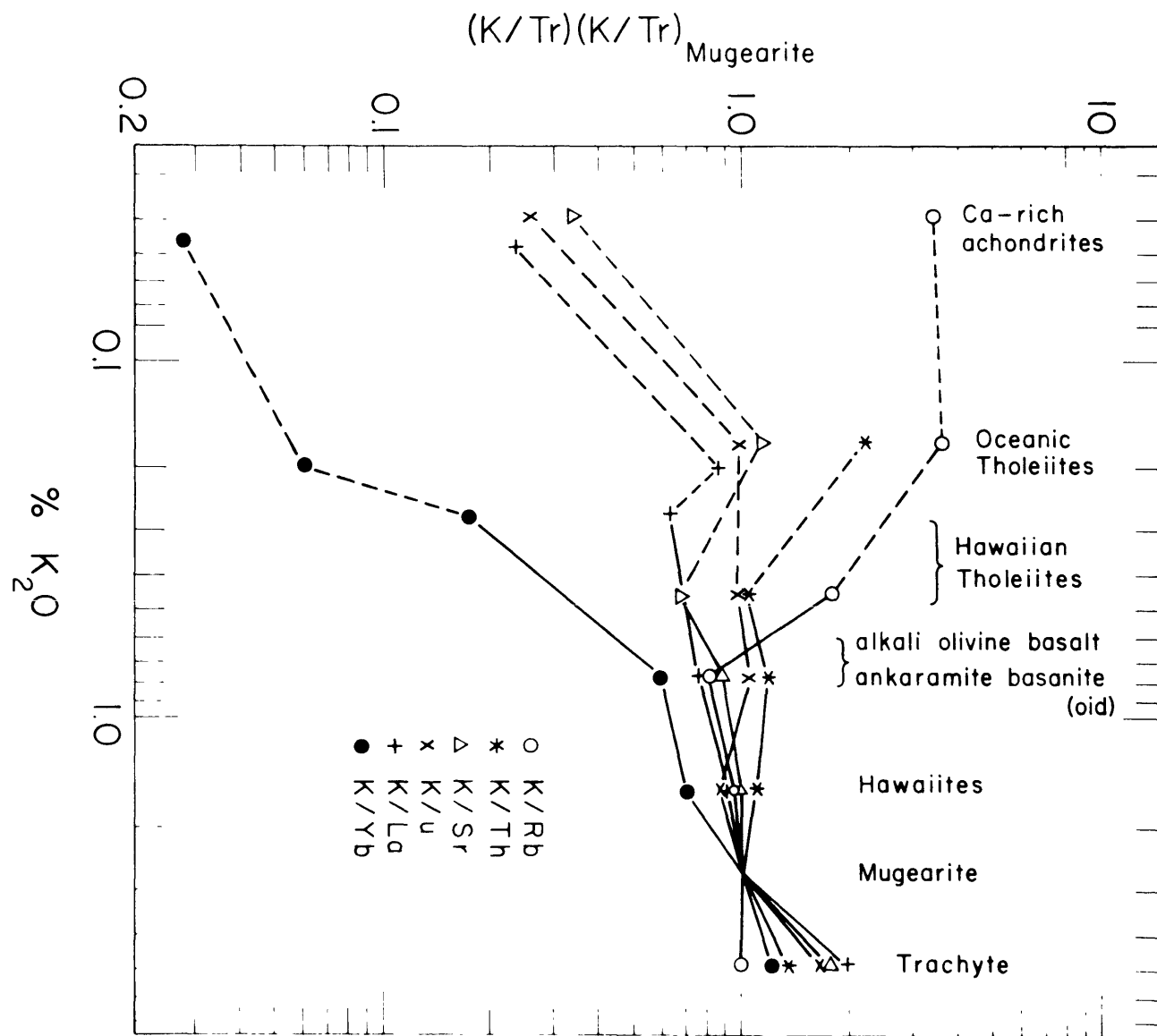
content has reached its saturation point and, if equilibrium is maintained, the Potassium concentration in the residual melt should stay constant or slightly decrease but certainly not increase. On the other hand, Rubidium continues to be increasingly concentrated in the residual melt. Thus the K/Rb ratio is expected to decrease.

Special conditions for the origin of trachyte have been postulated (Turner & Verhoogen, 1960; Chayes, 1963; and Bailey & Schairer, 1966) where the importance of volatiles for the formation of these lavas is stressed. A marked increase of the heavy rare earths, which complex easily in solutions, has been noted by Schilling and Winchester (1966c) and in this respect confirms the importance of volatiles. If gaseous transfer is an important process for the formation of trachytic melt, one would expect a preferential enrichment of the more volatile trace alkali metals relative to the trace alkaline earths, the rare earths, Th, and U. Figure E-4 illustrates the K/Rb, K/Sr, K/La, K/Yb, K/Th, and K/U ratios as functions of the K_2O content for the samples listed in Table E-1. These ratios are normalized to the same ratios obtained for the mugearite in order to compare the relative behavior of the elements. The ratios are average values for the anchondrites, oceanic tholeiites, Hawaiian tholeiites, Hawaiian alkaline series (excluding the hawaiite and mugearite), Hawaiian hawaiite, trachyte and mugearite. A horizontal line on this diagram indicates similar behavior

for the element pairs. Thus from Figure E-4 and
Table E-2, the K/Rb ratio from the mugearite to the
trachyte remains constant indicating similar be-
havior for K and Rb. On the other hand, K/Sr, K/U,
K/La, K/Yb, and K/Th all increase markedly from
the mugearite to the trachyte indicating a prefer-
ential increase of Potassium and, by inference,
other alkali metals relative to Sr, U, Th, and the
rare earths. Table E-2 also shows how Rb is pre-
ferentially enriched in the trachyte relative to the
alkaline earths, rare earths, U, and Th. In the alkali
series one finds that Rb is slightly preferred to
Potassium in the trachyte which is in the same direc-
tion as emphasized by Gast (1960. 1965) for the loss
of alkalis from the privitive earth. Thus these data
support the possibility that the trachyte may have
formed by gaseous transfer.

The increasing activities in oceanographic re-
search have resulted in the recovery of many interest-
ing samples from the ocean depths especially from the
oceanic ridges and rises (Engel and Engel, 1964 ab;
Nicholls 1964; Nicholls, Nalwalk and Hays, 1964;
Muir and Tilley, 1964; Engel, Engel, and Havens,
1965; and others). Chemical studies of these basalts
have revealed important differences between these so-
called "oceanic tholeiites" and the shield building
tholeiites from large volcanoes such as the Hawaiian

TABLE E-2.

K/Tr and Rb/Tr ratios in Hawaiian mugearite and trachyte.

	Mugearite	Trachyte	Trachyte Mugearite
K/Rb	387	259	.93
K/Sr	21.3	751	35.2
K/Th	3670	5350	1.46
K/U	9900	26950	2.72
K/La	471	927	1.97
K/Yb	7330	8973	1.22
Rb/Sr	.055	2.09	38.0
Rb/Th	9.85	14.9	1.51
Rb/U	26.5	75	2.83
Rb/La	1.22	2.58	2.11
Rb/Yb	19.0	25.0	1.31

Islands. These results have been interpreted in different ways by geochemists. Engel, Engel, and Havens, (1965) suggest that the oceanic ridge basalts are the principal or only primary magma generated in the upper mantle under the oceans. They have argued that the shield-building tholeiites are derivatives of these primary melts followed by thin capping of alkaline basalts. Grey and Haskin (1964) on the basis of relative rare earth patterns suggest that these basalts are "nearly undisturbed rare earth distribution patterns" and these "oceanic basalts are decidedly primitive". Further scrutiny of the rare earth abundance patterns of the oceanic and Hawaiian lavas have lead Schilling & Winchester (1966b and c) to object to such suggestions.

Figure E-4 shows the change of K/Rb, K/Sr, K/Th, K/U, K/La, and K/Yb ratios between oceanic tholeiites and the Hawaiian tholeiites. Except for K/Rb and K/Yb ratios, which behave as expected from geochemical reasoning, the change of K/Th K/U K/La and K/Sr ratios is anomalous. The ratios change in the opposite direction from what is expected for fractional crystallization from the observation of the alkali series. Although from the absolute abundances of Rb, Sr, La, U, Th in the two types of tholeiites, it cannot be denied that the Hawaiian tholeiite (Engel et al's intermediate type) could be derived from the oceanic tholeiitic magma. The change of these ratios indicates that fractional

crystallization apparently cannot be the operative process.
The high abundances of the heavy rare earths (those with
the smallest ionic radii), which are as high as their
abundances in trachyte-mugearite differentiates and many
granites, also strongly indicate that processes other than
fractional crystallization must be considered if shield-
building tholeiites need to be derived from the oceanic
tholeiites.

The Strontium isotope data for the Hawaiian tholeiites
and the ridge basalts (Bence 1966) show that there are
small but marked differences in the Sr^{87}/Sr^{86} ratios for
the two types of tholeiite. The Hawaiian tholeiites
tend to have higher Sr^{87}/Sr^{86} ratios than their ridge
counterparts. This may be an indication that the two are
derived from different depths in an upper mantle that has
a decreasing Rb/Sr with depth or it may be a reflection
of latteral variations of Rb/Sr ratios in the upper mantle.
Whatever the explanation, it is obvious that one cannot
be a derivative of the other and they must originate from
different source regions, which are characterized by dif-
ferent Rb/Sr ratios. The Rb/Sr ratios for the two tholeiite
magmas are identical within the limits of precision; but
the absolute abundances of both elements are lower in
the oceanic tholeiites. This needs explanation.

Therefore on the basis of the heavy rare earth data
and the other ratios discussed above and possibly Sr^{87}/Sr^{86}
ratios, it seems more reasonable to assume independent

origins for the oceanic ridge and shield-building tholei-
ites. Thus, it appears that different fractionation
processes must have been operative for the formation
of these two lava types; or alternatively, that they
are derived from different source regions. One of
us (JGS) has emphasized the possible effects of vola-
tiles and environmental pressures during the extrusion
of the oceanic lavas, and the possible presence of
hornblende within the source region of the upper
mantle (Schilling and Winchester, 1966b, and Nicholls
1965) Zone melting as an alternative process was
also considered.

Finally generalizations on relative partition
coefficients and ionic size (Masuda, 1965), although
interesting should be made with care. The reversal
of the relative behaviours of some trace elements
indicate that physico-chemical processes of differenti-
ation, other than fractional crystallization, may
affect the relative fractionation of these trace
elements in very different ways than are predicted on
the basis of ionic size and charge alone (Schilling
and Winchester, 1966b).

ACKNOWLEDGEMENTS

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APPENDIX F

GRAPHICAL REPRESENTATION OF THE RARE EARTH

DATA FOR THE SAMPLES ANALYZED

The abundances of the rare earth elements relative to 20 chondrites (Schmitt et al., 1963, 1964) in the samples analyzed are plotted on a logarithmic scale as a function of atomic number.

Tholeiite
Oahu, Koolau Series

9948

Diabase
Oahu, Koolau Series

10398

10396

Tholeiite
Oahu, Koolau Series

ppm Rock / ppm Chondrites

1000

100

10

1

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
57   (Y)   71

Atomic Number

Tholeiite
Oahu, Koolau Series

10403

Pelé's hair
Hawaii – Kilauea Volcano

1101

Ankaramite
Maui, Haleakala Volcano

ppm Rock / ppm Chondrites

1000

100

10

1

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
57   (Y)   71

Atomic Number

Basanitoid
Oahu, Honolulu Series

JP11

Nepheline basanite
Oahu, Honolulu Series

9982

Linosaite
Oahu, Honolulu Series

Hawaiite
Maui, Haleakala Volcano

1106

Hawaiite
Maui, Haleakala Volcano

1102

ppm Rock / ppm Chondrites

Atomic Number

Trachyte
Hawaii, Puu Anahulu

JP15

Nepheline-melilite basalt
Oahu, Honolulu Series

9960

Figure. Plot of ppm Rock / ppm Chondrites versus Atomic Number for olivine nodules.

Legend:
- ● Olivine Nodule, Salt Lake Crater, Oahu (Average of 2 analyses)
- ○ Olivine Nodule, Hualalai, Hawaii (Average of 2 analyses)

X-axis: Atomic Number — La 57, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er (Y), Tm, Yb, Lu 71

Y-axis: ppm Rock / ppm Chondrites (10, 1, 0.1, 0.01)

G-I Granite

Average of 2 analyses

ppm Rock / ppm Chondrites

1000

100

10

1

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
57   (Y)   71

Atomic Number

ACKNOWLEDGEMENTS

recasting it into better English.

Fellow graduates of the Geochemistry and Geochronology Laboratories for many helpful discussions, with particular thanks to Alan Ehrlich for his ready close cooperation and valuable suggestions, Lester Walters for kindly writing several computer programs and processing the data, and to Alfred Bence for interesting discussions.

Mr. George Cichocki, Miss Mary Untz and Peter Foley for their most valuable technical assistance and their impassive patience working with an often "too difficult" boss.

Miss Charlotte Emery for performing the tedious operations of counting and calculating.

Mrs. Narda Ehrlich for kindly editing part of this manuscript.

Miss Ida M. De Toma for typing the manuscript intelligently, meticulously and patiently.

Ken Harper's Geology Shop, for their ingeneous suggestions and for building equipment which worked.

The M.I.T. Nuclear Reactor and Radiation Protection personnel for their excellent cooperation throughout the duration of this work.

J. L. Powell, G. Faure, J. B. Thompson, J. H. Crocket, G. Tilton for generously furnishing the samples analyzed.

This work has been made possible by the generous financial support of the Office of Naval Research,

BIOGRAPHICAL SKETCH

The writing of a biographical sketch is a difficult task, because what may be of interest to the reader may be of little significance to the author or vice versa.

The author was born in Geneva, Switzerland on 5 August 1936 to Jeanne Uzel and Jean Schilling. Lazy by nature, he struggled through primary and secondary schools. Finally thanks to the "stubbornness" of his parents, rather than ending as jazz musicien in Spain, he graduated in 1956 from the Ecole Supérieure Technique, Geneva, with an Electrical Engineering degree. A day after his 20th birthday, he left for "la grande aventure" and ended in Finland teaching French for about a year. "D'un concours de circonstances" he landed in New York to visit the New World on a beautiful morning of spring, 1957. After a few months through the United States, he arrived in Montreal, again broke, dug ditches for a month and finally worked as a city planner for almost two years. Unsatisfied and thirsting for knowledge, he went back to the academic world and, to the great surprise of his family and friends, graduated "magna cum laude" from the Ecole Polytechnique, Universite de Montreal, with a B. Sc and Engineering degree in Geology in 1961.

In September 1961 he entered the Department of Geology and Geophysics, M.I.T., as a graduate student, having been awarded a 3-year Canadian Imperial Oil Scholarship, another scholarship from the Ministry of Education of the Province of Quebec, Canada, (three times renewed), and a scholarship from the Canadian National Research Council, which unfortunately he had to refuse.

He spent five summers learning to appreciate the Eskimo's philosophy of life while doing mining exploration for private companies and geological reconnaissance work for the Ministry of Natural Resources of the Province of Quebec, Canada.

While at M.I.T., he was scientific French instructor in the Department of Languages for two years. He held a research assistantship from the spring term of 1964 onward.

The author was elected to Sigma Xi while at M.I.T. and is a member of the Geochemical Society of America, the American Geophysical Union, and the American Association for the Advancement of Science.

In the fall of 1964 he was sent to the University

of California at La Jolla, to deliver a paper entitled
" A model for rare earth fractionation during partial melt-
ing" at a special conference on the origin of volcanic rocks.

In the spring of 1966 he was awarded a NATO travel
grant to participate at a conference on "The mantles of the
earth and terrestrial planets" at the NATO Advanced Study
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and to deliver a paper entitled "Rare earth fractionation
and magmatic processes."

He has published two papers: "Rare earth in Hawaiian
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