RARE-EARTH DISTRIBUTIONS
IN SOME ROCKS AND ASSOCIATED MINERALS
OF THE BATHOLITH OF SOUTHERN CALIFORNIA

by

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Thesis Supervisor

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Chairman, Departmental Committee
on Graduate Students

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ABSTRACT

The rare-earth and yttrium abundances in four whole-rock samples and eight associated mineral fractions from the batholith of Southern California have been determined by means of neutron activation and partition chromatography. It is shown that, on a whole-rock basis, an increase in total rare-earth content in the sequence gabbro-tonalite-granodiorite-quartz monzonite is paralleled by an increase in relative fractionation favoring the lighter rare earths. In the same sequence, there is an apparently systematic increased relative removal of Eu which is attributed to the existence of Eu(II). Analyses of feldspar, pyroxene, amphibole, mica, and apatite mineral fractions also indicate that divalent Eu was an important constituent during the evolution of the rocks studied. The feldspar mineral fractions were invariably enriched in Eu relative to the adjacent rare earths, whereas the ferromagnesian minerals were relatively depleted.

A procedure for determination of the rare-earth elements and yttrium, applicable over a wide range in concentrations and to silicates as well as other rocks and minerals, has been developed. The procedure utilizes chromatographic separation of neutron induced, low-level radioactivities. Two analysts working jointly can analyze up to three samples per week which is faster than methods commonly used. Self-shielding errors are eliminated by irradiating all samples and standards in aqueous solution. After dissolution of the sample by classical methods, the rare earths were separated from the ammonia-soluble elements by two ammonia precipitations. The rare earths were then isolated by ion exchange.

The pure rare-earth fraction was irradiated in a thermal neutron flux of approximately 8 x 10^{12} neutrons/cm^2-sec for a period of time (1-20 hours) proportional to the amount of rare earths expected. The irradiated solution was chromatographed by gradient elution with hydrochloric acid on a column of refined diatomaceous silica coated with di-(2-ethylhexyl)orthophosphoric acid. Precision and accuracy were approximately $\pm 10\%$. They were determined by comparison of a series of duplicate runs on different samples, comparison of results with those of other analysts on the same samples, and a spiking test made on a silicate sample. A majority of the chemical yields were $\geq 97\%$ (monitored by Y^{88} and Ce^{139} carrier-free tracers). Gadolinium and erbium were not determined.

As an additional study, the rare-earth contents (exclusive of Gd and Er) of the standard granite G-1 and standard diabase W-1 have been determined. The results are, for the most part, in rather close agreement with the data of Haskin and Gehl (1963). The most significant discrepancy is between the Eu values in G-1. The abundance of this analytically-sensitive element was found to be approximately 20% higher in this study.

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CHAPTER I

RARE-EARTH DISTRIBUTIONS IN SOME ROCKS AND ASSOCIATED MINERALS OF THE BATHOLITH OF SOUTHERN CALIFORNIA

by

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ABSTRACT

The rare-earth and yttrium abundances in four whole-rock samples and eight associated mineral fractions from the batholith of Southern California have been determined by means of neutron activation and partition chromatography. It is shown that, on a whole-rock basis, an increase in total rare-earth content in the sequence gabbro-tonalite-granodiorite-quartz monzonite is paralleled by an increase in relative fractionation favoring the lighter rare earths. In the same sequence, there is an apparently systematic, increased relative removal of Eu which is attributed to the existence of Eu(II). Analyses of feldspar, pyroxene, amphibole, mica, and apatite mineral fractions also indicate that divalent Eu was an important constituent during the evolution of the rocks studied. The feldspar mineral fractions were invariably enriched in Eu relative to the adjacent rare earths, whereas the ferromagnesian minerals were relatively depleted.

INTRODUCTION

The rare-earth elements have attracted the interest of geochemists for many years. Their very similar chemical properties, which nevertheless vary quite smoothly with atomic number, prompted Goldschmidt (1954) to suggest that the rare earths behave as a geochemical "entity." The most notable exceptions to the common trivalency of the rare earths (and the non-lanthanide but chemically very similar element yttrium) are the presence of divalent Eu and tetravalent Ce. Differences in relative distributions of the rare-earth elements and yttrium in rocks and minerals should serve as indicators of differences in the physico-chemico conditions of formation of those rocks and minerals.

By far, most rare-earth analyses have been carried out on rare-earth minerals and rare-earth-concentrating accessory minerals found in pegmatites, granophyres, and alkaline igneous rocks. Some of the more recent of these investigations are those of Vainshtein et al. (1956), Butler (1957a, 1957b), Butler (1958), Seminov and Barinskii (1958), Vainshtein et al. (1958), Murata et al. (1959), Borodin and Barinskii (1960, 1961), Balashov and Turanskaya (1961), Zhirov et al. (1961), and Lyakhovich (1962).

Whole-rock analyses of rare earths in igneous rocks have been much more limited in number. These include, among others, the works of Sahama (1945) on Finnish granites and gabbros; Schmitt (1963), and Schmitt and Smith (1961, 1962, 1963) on two basalts, two eclogites, and a peridotite; and

Balashov (1962) on differentiated alkaline rocks. Haskin and Gehl (1963) have published complete rare-earth data on the standard granite G-1 and standard diabase W-1.

To the authors' knowledge, at this time the only complete rare-earth study of coexisting rock-forming minerals in igneous rocks classified compositionally between gabbro and granite is the work of Gavrilova and Turanskaya (1958) on some Russian granites. Since there is very little data available on the behavior of the rare earths during the evolution of the most common igneous rocks, a study has been made of the rare-earth distributions in a suite of genetically-related igneous rocks ranging from gabbroic to granitic in composition. In addition to whole-rock analyses, selected coexisting mineral fractions have been studied. Samples were chosen from the batholith of Southern California because such large plutonic bodies represent quantitatively-significant portions of the earth's crust. A study of the rare-earth abundances in various members of one of these batholiths should yield information regarding the evolution of these bodies since changing rare-earth distributions should reflect changing geochemical conditions.

The batholith of Southern California has been quite extensively studied. Larsen (1948) believed that these Cretaceous rocks were the result of magmatic differentiation of gabbroic magma at depth, followed by successive intrusions by means of magmatic stoping (rather than forceful injection). As evidence of magmatic differentiation, he cited the smooth variation curves obtained from the chemical analyses and the systematic changes in mineral percentages found in the series from the gabbros to granites. Most contacts between the intrusive bodies were found to be sharp.

Taylor and Epstein (1962a, 1962b) have made an oxygen isotopic study of four rocks and their associated minerals from this batholith: the San Marcos gabbro, Bonsall tonalite, Woodson Mountain granodiorite, and Rubidoux Mountain leucogranite (quartz monzonite). The same samples have been used for this rare-earth study. For sample descriptions, including modal analyses and petrographic descriptions, the reader is referred to the papers by Taylor and Epstein.

The above authors emphasize that obvious caution is required when trying to relate the results on four specimens to the genesis of a body of batholithic size. Nevertheless, they found that the systematic changes in the O^{18}/O^{16} ratios of these four samples were consistent with the origin by magmatic differentiation advanced by Larsen (1948). The reader, however, must be cautious in using the results of this study since they represent but a small sampling of a large plutonic body whose petrology is by no means completely understood. It is hoped that the rare-earth data will shed some light on this problem.

EXPERIMENTAL PROCEDURE

The analytical procedure used for this study employed group isolation of the rare earths and yttrium followed by neutron activation and partition chromatography. Gadolinium and erbium were not determined. Accuracy and precision were approximately ±10%. The details of this procedure will appear elsewhere (Volfovsky et al., 1963).

Samples weighing up to 0.500 g were dissolved using a mixture of perchloric and hydrofluoric acids. Following precipitation by ammonia, the rare earths were isolated as a group by ion exchange. Chemical yields were measured at this stage using Ce^{139} and Y^{88} carrier-free tracers. Two aliquots of each sample and two solutions of rare earths in known concentrations were irradiated by pile neutrons at thermal neutron fluxes of approximately 8×10^{12} n/cm^2-sec. The irradiated sample and standard solutions were chromatographed by gradient elution with hydrochloric acid on columns of refined diatomaceous silica coated with di-(2-ethylhexyl) orthophosphoric acid.

Induced gamma radioactivities were counted by means of a 400-channel pulse height analyzer and a well-type, 1-3/4 inch by 2-inch NaI(Tl) scintillation crystal. Betas were counted as thin sources on 2-inch watch glasses with a standard end-window flow-proportional counting system.

RESULTS AND DISCUSSION

Analytical Results

The analytical results are presented in Table I-1 and Table I-2. The precision for each concentration was calculated from the precision observed in a series of duplicate runs on other samples; precision and accuracy were found to be comparable (Volfovsky et al., 1963).

Whole-rock rare-earth abundances in the San Marcos gabbro, Bonsall tonalite, Woodson Mountain granodiorite, and Rubidoux Mountain leucogranite (quartz monzonite) are given in Table I-1. Also given are the average rare-earth abundances in a series of 12 chondritic meteorites analyzed by Schmitt and Smith (1962). The chondrite data will be used for geochemical interpretation of the rare-earth abundance patterns in the manner of Coryell et al. (1963).

Mineral fractions were analyzed from three of the rocks, and the results are tabulated in Table I-2. These include plagioclase feldspar (An_{55}), augite, hornblende, and apatite from the San Marcos gabbro; plagioclase feldspar (An_{20}), K-feldspar, and biotite from the Rubidoux Mountain leucogranite; and apatite from the Bonsall tonalite. Since there were limited amounts of most mineral fractions and some of these had relatively low rare-earth contents, there are some missing values for those rare earths with poorer sensitivities. No results are given for gadolinium and erbium since neither

Table I-1

Rare-Earth Abundances in the Batholith of Southern California* and in Chondritic Meteorites**

Element	San Marcos gabbro	Bonsall tonalite	Woodson Mountain granodiorite	Rubidoux Mountain leucogranite	Average in 12 chondrites
La	4.011 ± 0.160	13.4 ± 0.7	25.3 ± 1.0	24.5 ± 1.0	0.32 ± 0.01
Ce	14.5 ± 2.3	22.5 ± 4.0	34.2 ± 5.5	87.6 ±14.0	0.90 ± 0.08
Pr	2.15 ± 0.24	5.66 ± 0.62	6.96 ± 0.77	5.64 ± 0.62	0.13 ± 0.01
Nd	7.68 ± 0.77	17.2 ± 1.72	22.3 ± 2.2	23.5 ± 2.4	0.57 ± 0.04
Sm	2.17 ± 0.02	3.65 ± 0.04	3.96 ± 0.04	3.78 ± 0.04	0.21 ± 0.01
Eu	1.05 ± 0.04	1.06 ± 0.04	0.795 ± 0.032	0.629 ± 0.025	0.074 ± 0.003
Gd	- - -	- - -	- - -	- - -	0.31 ± 0.02
Tb	0.478 ± 0.043	0.839 ± 0.076	0.826 ± 0.074	0.633 ± 0.057	0.051 ± 0.002
Dy	2.79 ± 0.11	2.60 ± 0.10	2.99 ± 0.12	3.08 ± 0.12	0.30 ± 0.02
Ho	0.569 ± 0.023	0.752 ± 0.030	0.898 ± 0.036	0.742 ± 0.030	0.074 ± 0.003
Er	- - -	- - -	- - -	- - -	0.21 ± 0.01
Tm	0.248 ± 0.017	0.386 ± 0.027	0.373 ± 0.026	0.263 ± 0.018	0.032 ± 0.002
Yb	1.70 ± 0.14	2.00 ± 0.16	2.93 ± 0.23	1.30 ± 0.10	0.18 ± 0.01
Lu	0.256 ± 0.015	0.298 ± 0.018	0.385 ± 0.023	0.198 ± 0.012	0.032 ± 0.002
Y	15.5 ± 1.9	21.5 ± 2.6	24.6 ± 3.0	17.3 ± 2.1	1.9 ± 0.1
Total	53	92	127	169	5.3

* Values are given in parts per million ± analytical precision.

** Schmitt and Smith (1962).

Table I-2

Rare-Earth Abundances in Selected Mineral Fractions*

	San Marcos gabbro			
Element	plagioclase feldspar (An_{55})	hornblende	augite	apatite
La	2.28 ± 0.09	2.38 ± 0.10	0.409 ± 0.016	392 ± 16
Ce	3.57 ± 0.57	- - -	- - -	- - -
Pr	- - -	- - -	- - -	172 ± 19
Nd	- - -	- - -	- - -	534 ± 53
Sm	0.264 ± 0.026	8.97 ± 0.90	4.39 ± 0.44	97.4 ± 9.7
Eu	0.808 ± 0.032	2.11 ± 0.84	0.922 ± 0.037	17.3 ± 0.7
Gd	- - -	- - -	- - -	- - -
Tb	- - -	1.77 ± 0.16	1.32 ± 0.12	12.5 ± 1.1
Dy	0.173 ± 0.007	13.1 ± 0.5	7.84 ± 0.31	66.5 ± 2.7
Ho	0.048 ± 0.002	2.48 ± 0.10	1.52 ± 0.06	13.5 ± 0.5
Er	- - -	- - -	- - -	- - -
Tm	0.022 ± 0.002	1.20 ± 0.08	0.687 ± 0.048	3.25 ± 0.23
Yb	0.150 ± 0.012	7.74 ± 0.62	4.01 ± 0.32	19.9 ± 1.6
Lu	0.023 ± 0.001	1.07 ± 0.06	0.741 ± 0.044	3.10 ± 0.19
Y	1.08 ± 0.13	73.1 ± 8.8	44.4 ± 5.3	327 ± 39

Table I-2 (continued)

	Rubidoux Mountain leucogranite			Bonsall tonalite
Element	plagioclase feldspar (An_{20})	K-feldspar	biotite	apatite
La	10.7 ± 0.4	9.68 ± 0.39	225 ± 9	171 ± 7
Ce	- - -	- - -	- - -	- - -
Pr	- - -	- - -	68.2 ± 7.5	110 ± 12
Nd	- - -	- - -	222 ± 22	603 ± 60
Sm	1.68 ± 0.17	1.07 ± 0.11	48.0 ± 4.8	157 ± 16
Eu	0.965 ± 0.039	0.938 ± 0.038	0.359 ± 0.014	19.5 ± 0.8
Gd	- - -	- - -	- - -	- - -
Tb	- - -	- - -	7.29 ± 0.66	23.6 ± 2.1
Dy	1.72 ± 0.07	0.743 ± 0.030	43.1 ± 1.7	140 ± 6
Ho	0.452 ± 0.018	0.166 ± 0.004	9.58 ± 0.38	31.0 ± 1.2
Er	- - -	- - -	- - -	- - -
Tm	- - -	0.078 ± 0.005	3.23 ± 0.23	9.27 ± 0.65
Yb	0.898 ± 0.072	0.510 ± 0.041	22.3 ± 1.8	59.3 ± 4.7
Lu	0.129 ± 0.008	0.068 ± 0.004	2.69 ± 0.16	9.23 ± 0.55
Y	8.45 ± 1.01	4.72 ± 0.57	226 ± 27	878 ± 105

* Values are given in parts per million ± analytical precision.

was determined in the analytical method as developed for this study. Nevertheless, because no fewer than eight rare earths (including yttrium) have been determined for any sample, it is felt that the rare-earth distributions of all samples have been well-established. Data is presented for all rare earths except Gd and Er in the four rocks. Inspection of Table I-1 reveals that the total rare-earth content (including yttrium) found in the rocks from the batholith increases progressively from a minimum value in the gabbro (53 ppm) to intermediate values in the tonalite (92 ppm) and granodiorite (127 ppm) to a maximum value in the leucogranite (169 ppm).

Data Presentation

Coryell et al. (1963) and Masuda (1962) have independently proposed very similar methods for the geochemical interpretation of terrestrial rare-earth abundance patterns. They observed increased regularity when the absolute rare-earth abundances in terrestrial samples were divided by the corresponding abundances in chondritic meteorites. The normalized values were then plotted as a function of atomic number. This normalization technique removes most of the natural irregularities in absolute abundances arising from the original cosmo-chemical production of the elements. In this way, the relatively small differences between adjacent rare earths produced by geochemical processes are readily apparent. In addition, evidence has been given by Taylor (1962) and Masuda and Matsui (1963) to suggest that the mean relative rare-earth abundances of the chondrites are representative of the relative rare-earth abundances in the earth as a whole. The essential uniformity in the rare-earth abundances in chondrites has been well-established (Schmitt and Smith, 1962; Schmitt, 1963). As of this writing, 17 different chondrites have been analyzed by Schmitt and his co-workers. In this study, their data on 12 chondrites (Schmitt and Smith, 1962) have been used. The authors believe that the chondrite rare-earth abundances represent the best presently-available reference for normalization of terrestrial rare-earth data.

Several modifications and extensions of the chondrite-normalization technique have been made by different authors. These include an additional normalization of all data to La = 1.00 or Yb = 1.00 . Some authors have preferred to use ionic radius rather than atomic number as the abscissa of the normalization plot. The authors of this paper, however, prefer to use atomic number since there are some major discrepancies between different sets of published rare-earth ionic radii. In addition, it seems to be somewhat risky to use published radii based upon a combination of measurements in simple crystal structures, theoretical calculations, and rough interpolations. Effective radii in complex silicate structures may be quite different from the simple ionic radii reported in the literature. The use of atomic number expresses the true qualitative nature of the normalization method, and at the same time may somewhat better facilitate rapid inspection of the data. The authors also prefer to plot the normalized abundances on a logarithmic scale since relative differences will show up equally well at all absolute values. When a linear scale is used, the relative differences at small absolute values tend to be obscurred.

The absolute rare-earth abundances given in Table I-1 and Table I-2 have been used to compile Table I-3 and Table I-4. The latter two tables consist of the chondrite-normalized abundances (both absolute ratios and ratios with La = 1.00) of the whole rocks and mineral fractions, respectively, from the batholith.

The absolute, chondrite-normalized ratios for each rock along with the corresponding mineral fractions have been plotted in Figures I-1 through I-4. The curves have been drawn by a visual best-fit. The convention of Coryell et al. (1963) has been used, except that the yttrium ratios have been plotted at atomic number 68 (corresponding to Er). This has been done because in the partition chromatography employed in this study, Y and Er showed essentially identical behavior. The published ionic radii indicate values for Y as large as the radius of Dy and as small as that of Lu. Therefore, an intermediate value corresponding to Er, although somewhat arbitrary, may be a satisfactory choice.

In plotting the data on the mineral fractions, each distribution has been weighted by its modal abundance in the corresponding whole-rock sample. The modal analyses of these

Table I-3

Normalized Rare-Earth Abundances in the Batholith of Southern California

Element	San Marcos gabbro		Bonsall tonalite		Woodson Mountain granodiorite		Rubidoux Mountain leucogranite	
	a	b	a	b	a	b	a	b
La	12.5	1.00	41.9	1.00	79.1	1.00	76.6	1.00
Ce	16.1	1.29	25.0	0.597	38.0	0.480	97.3	1.27
Pr	16.5	1.32	43.5	1.04	53.5	0.676	43.4	0.566
Nd	13.5	1.08	30.2	0.721	39.1	0.494	41.2	0.538
Sm	10.3	0.824	17.4	0.415	18.9	0.239	18.0	0.235
Eu	14.2	1.14	14.3	0.341	10.7	0.135	8.50	0.111
Gd	-	-	-	-	-	-	-	-
Tb	9.37	0.750	16.5	0.394	16.2	0.205	12.4	0.162
Dy	9.30	0.744	8.67	0.207	9.97	0.126	10.3	0.131
Ho	7.69	0.615	10.2	0.243	12.1	0.153	10.0	0.134
Er	-	-	-	-	-	-	-	-
Tm	7.75	0.620	12.0	0.286	11.7	0.148	8.22	0.107
Yb	9.44	0.755	11.1	0.265	16.3	0.206	7.22	0.094
Lu	8.00	0.640	9.31	0.222	12.0	0.152	6.19	0.081
Y	8.16	0.653	11.3	0.270	12.9	0.163	9.11	0.119

a. Absolute abundance divided by average chondrite abundance (from Table I-1).

b. Chondrite-normalized abundance (column a) re-normalized to La = 1.00 .

Table I-4

Normalized Rare-Earth Abundances in Selected Mineral Fractions

San Marcos gabbro

Element	plagioclase feldspar (An_{55})		hornblende		augite		apatite	
	a	b	a	b	a	b	a	b
La	7.13	1.00	7.44	1.00	1.28	1.00	1230	1.00
Ce	3.97	0.557	-	-	-	-	-	-
Pr	-	-	-	-	-	-	1346	1.09
Nd	-	-	-	-	-	-	937	0.762
Sm	1.26	0.177	42.7	5.74	20.9	16.3	464	0.411
Eu	10.9	1.53	28.5	3.83	12.5	9.77	234	0.190
Gd	-	-	-	-	-	-	-	-
Tb	-	-	34.7	4.66	26.0	20.3	245	0.199
Dy	0.577	0.860	43.7	5.87	26.1	20.4	222	0.180
Ho	0.654	0.092	33.5	4.50	20.5	16.0	182	0.148
Er	-	-	-	-	-	-	-	-
Tm	0.681	0.096	37.5	5.04	21.5	16.8	102	0.083
Yb	0.833	0.117	43.0	5.78	22.3	17.4	111	0.090
Lu	0.706	0.099	33.4	4.49	23.2	18.1	96.9	0.079
Y	0.568	0.080	38.5	5.17	23.4	18.3	172	0.140

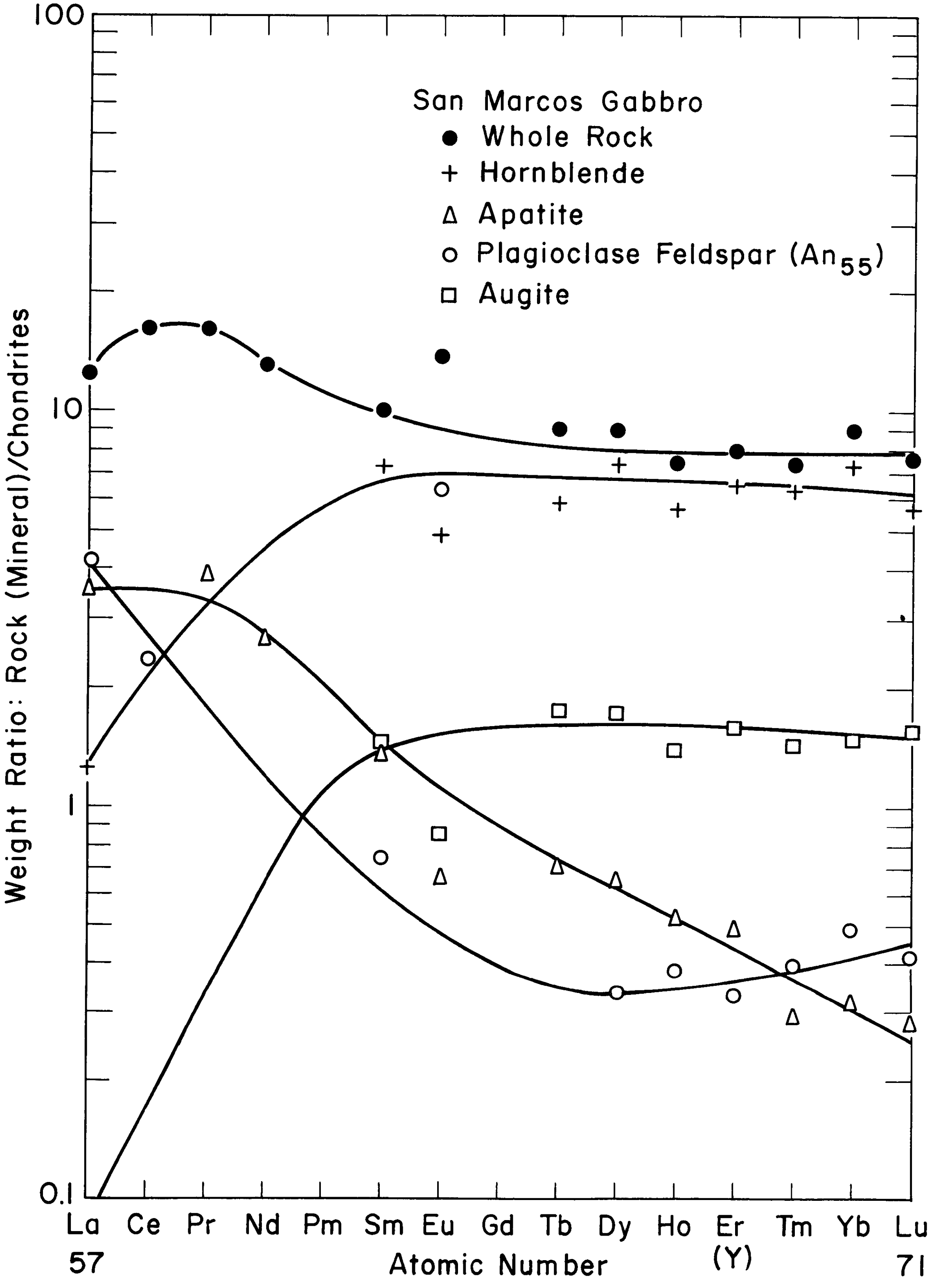
Table I-4 (continued)

	Rubidoux Mountain leucogranite						Bonsall tonalite	
Element	plagioclase feldspar (An_{20})		K-feldspar		biotite		apatite	
	a	b	a	b	a	b	a	b
La	33.4	1.00	30.3	1.00	703	1.00	534	1.00
Ce	-	-	-	-	-	-	-	-
Pr	-	-	-	-	525	0.747	846	1.58
Nd	-	-	-	-	389	0.553	1060	1.99
Sm	8.00	0.240	5.10	0.168	229	0.326	748	1.40
Eu	13.0	0.389	12.7	0.419	4.85	0.007	264	0.494
Gd	-	-	-	-	-	-	-	-
Tb	-	-	-	-	143	0.203	463	0.867
Dy	5.73	0.172	2.48	0.082	144	0.205	467	0.875
Ho	6.11	0.183	2.24	0.074	129	0.183	419	0.785
Er	-	-	-	-	-	-	-	-
Tm	-	-	2.43	0.080	101	0.144	290	0.543
Yb	4.99	0.149	2.83	0.093	124	0.176	329	0.616
Lu	4.03	0.121	2.11	0.070	84.1	0.120	288	0.539
Y	4.45	0.133	2.48	0.082	119	0.169	462	0.865

a. Absolute abundance divided by average chondrite abundance (from Table I-1).

b. Chondrite-normalized abundance (column a) re-normalized to La = 1.00 .

Fig. I-1. Chondrite-normalized rare-earth abundances in the San Marcos gabbro plotted on a logarithmic scale as a function of atomic number.



San Marcos Gabbro
● Whole Rock
+ Hornblende
Δ Apatite
○ Plagioclase Feldspar (An_{55})
□ Augite
Weight Ratio: Rock (Mineral)/Chondrites
100
10
1
0.1
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
(Y)
Tm
Yb
Lu
57
Atomic Number
71

Fig. I-2. Chondrite-normalized rare-earth abundances in the Rubidoux Mountain leucogranite plotted on a logarithmic scale as a function of atomic number.

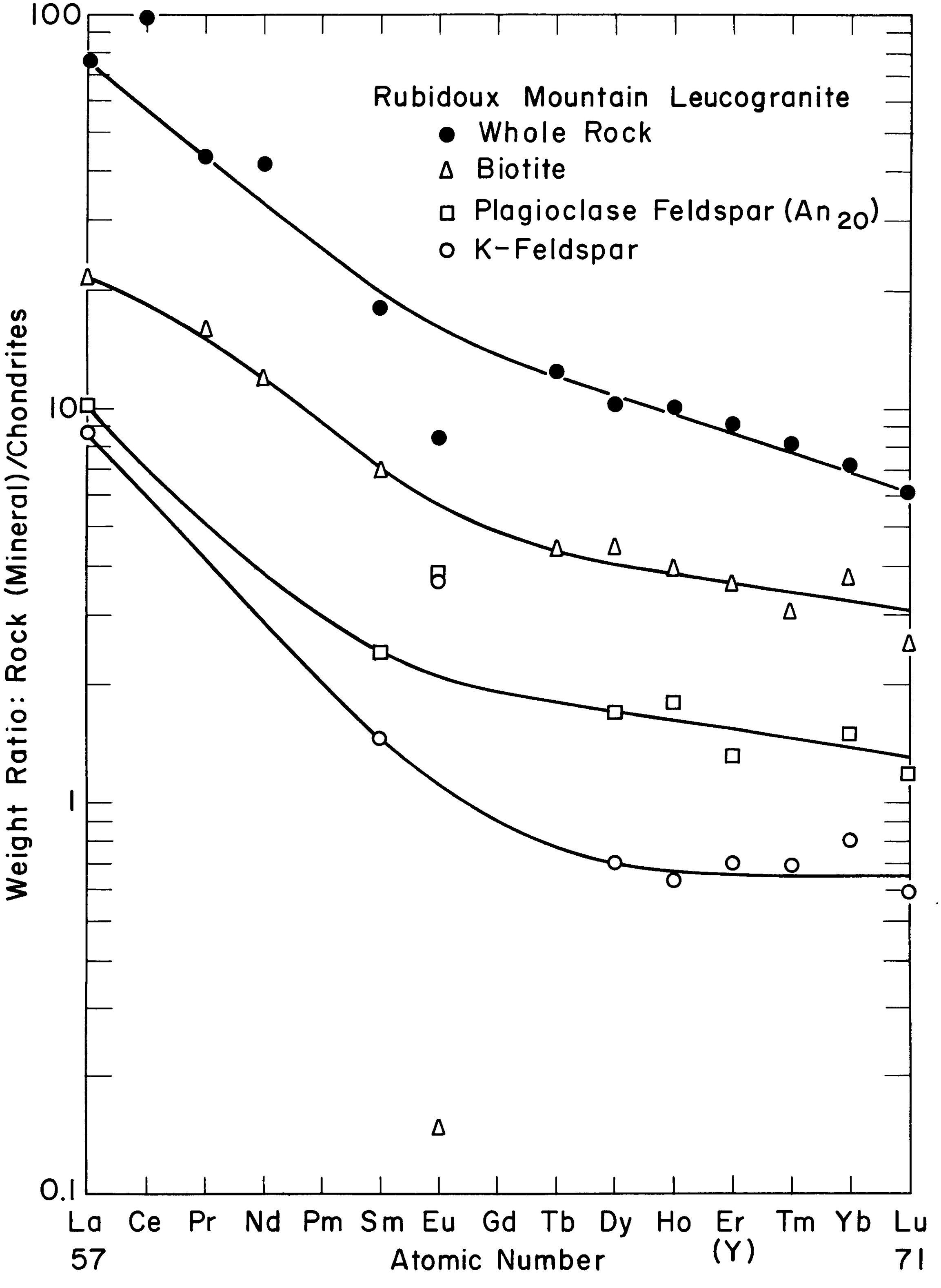
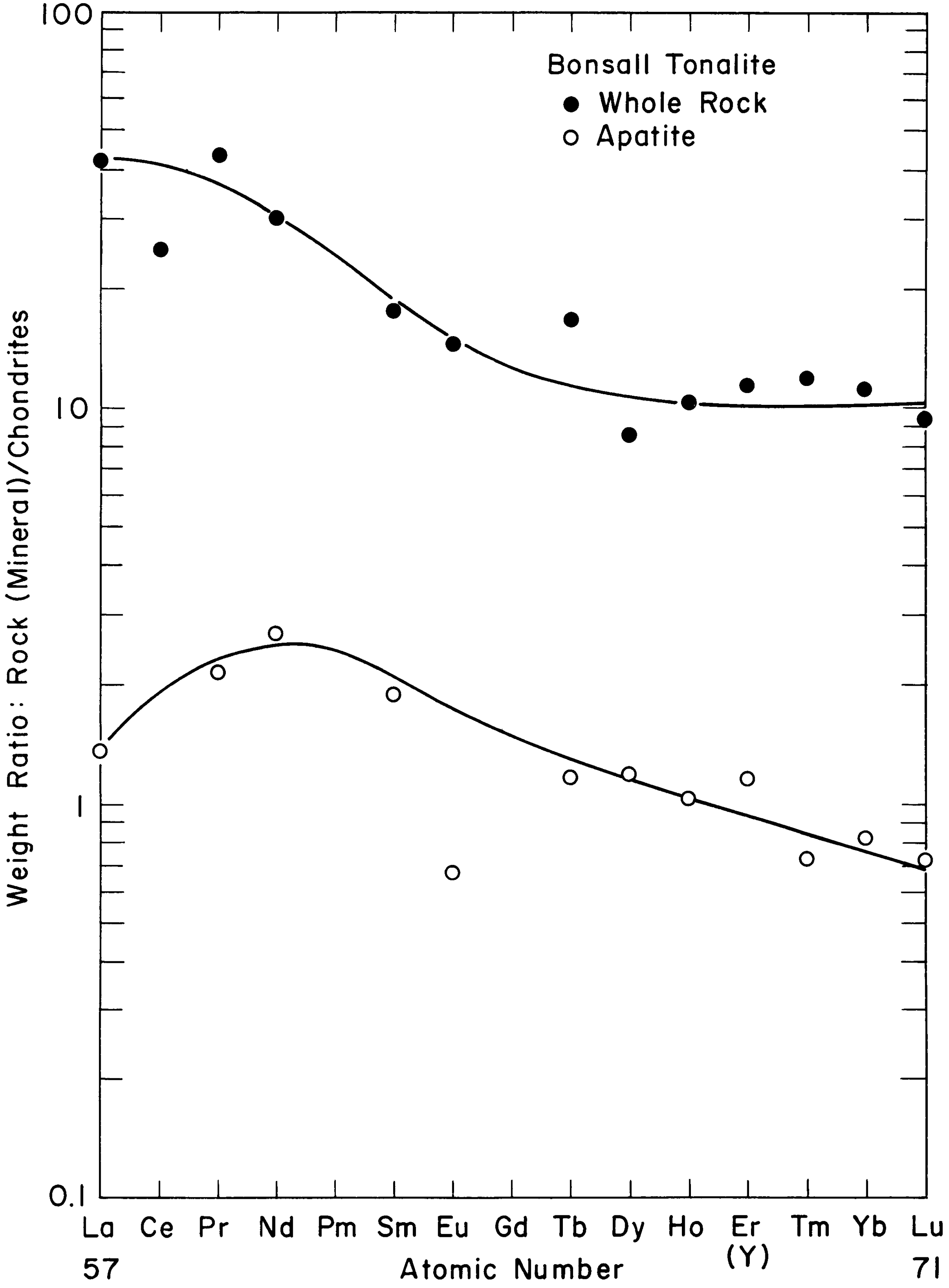
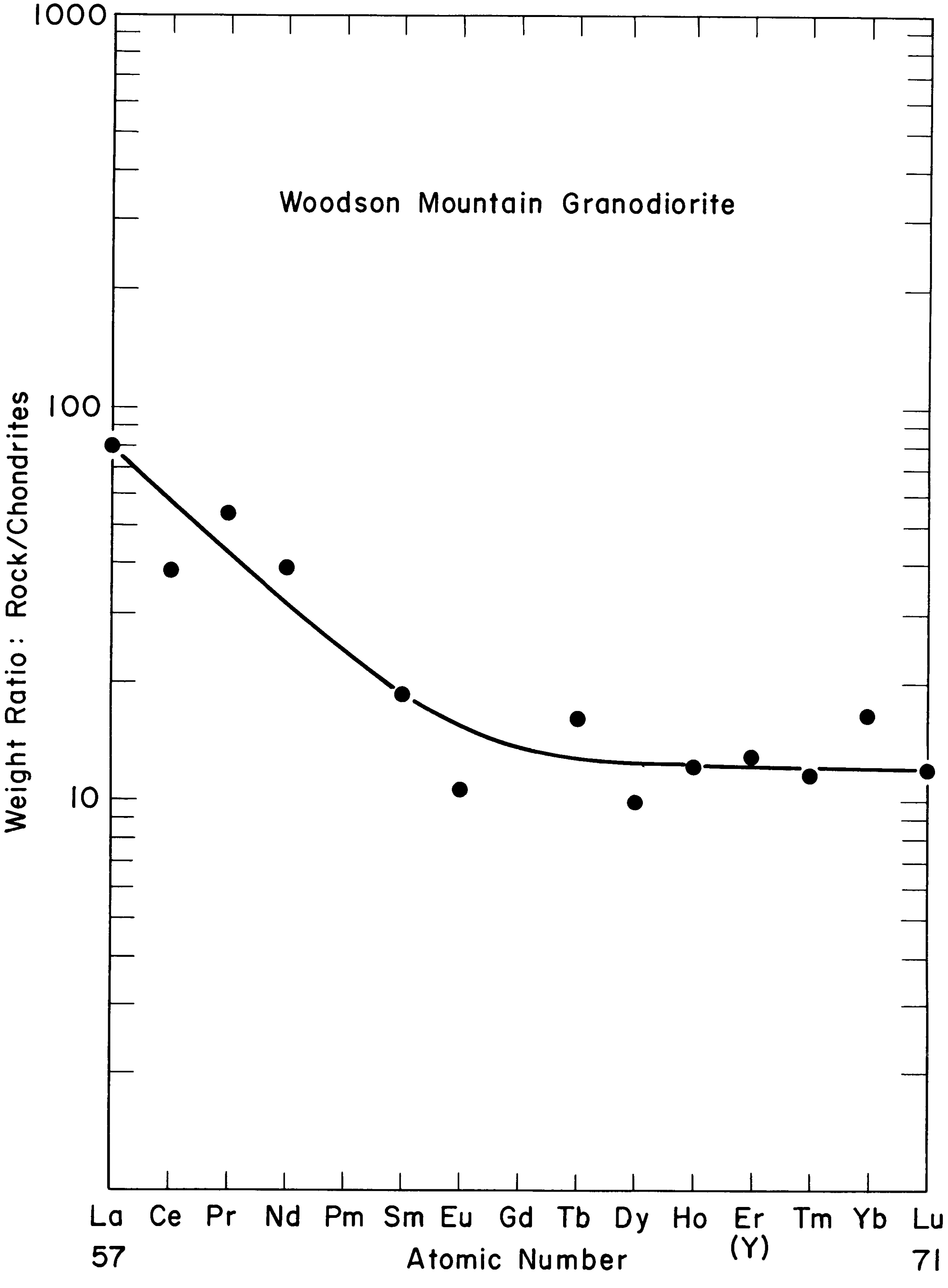

Rubidoux Mountain Leucogranite
● Whole Rock
Δ Biotite
□ Plagioclase Feldspar (An20)
○ K-Feldspar
Weight Ratio: Rock (Mineral)/Chondrites
100
10
1
0.1
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
(Y)
Tm
Yb
Lu
57
Atomic Number
71

Fig. I-3. Chondrite-normalized rare-earth abundances in the Bonsall tonalite plotted on a logarithmic scale as a function of atomic number.



Bonsall Tonalite
● Whole Rock
○ Apatite
Weight Ratio: Rock (Mineral)/Chondrites
100
10
1
0.1
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
(Y)
Tm
Yb
Lu
57
Atomic Number
71

Fig. I-4. Chondrite-normalized rare-earth abundances in the Woodson Mountain granodiorite plotted on a logarithmic scale as a function of atomic number.


Woodson Mountain Granodiorite
1000
100
10
Weight Ratio: Rock/Chondrites
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
(Y)
Tm
Yb
Lu
57
Atomic Number
71

samples have been given by Taylor and Epstein (1962a). Ideally, if all minerals were analyzed from a rock, their sums would approximate the whole-rock distribution. However, all fractions were not analyzed from each rock, and the presence of trace amounts of rare-earth-concentrating accessory minerals cannot be ruled out. Therefore, a mass balance of the rare earths could not be made.

Whole-Rock Distributions

Caution again must be emphasized when interpreting the rare-earth abundances in but four hand specimens. Taylor and Epstein (1962a) indicate that the samples of tonalite, granodiorite, and leucogranite are adequate representatives of their respective units. The gabbro, however, is variable in composition and texture throughout its outcrop area. The sample analyzed in this study is a noritic hornblende gabbro.

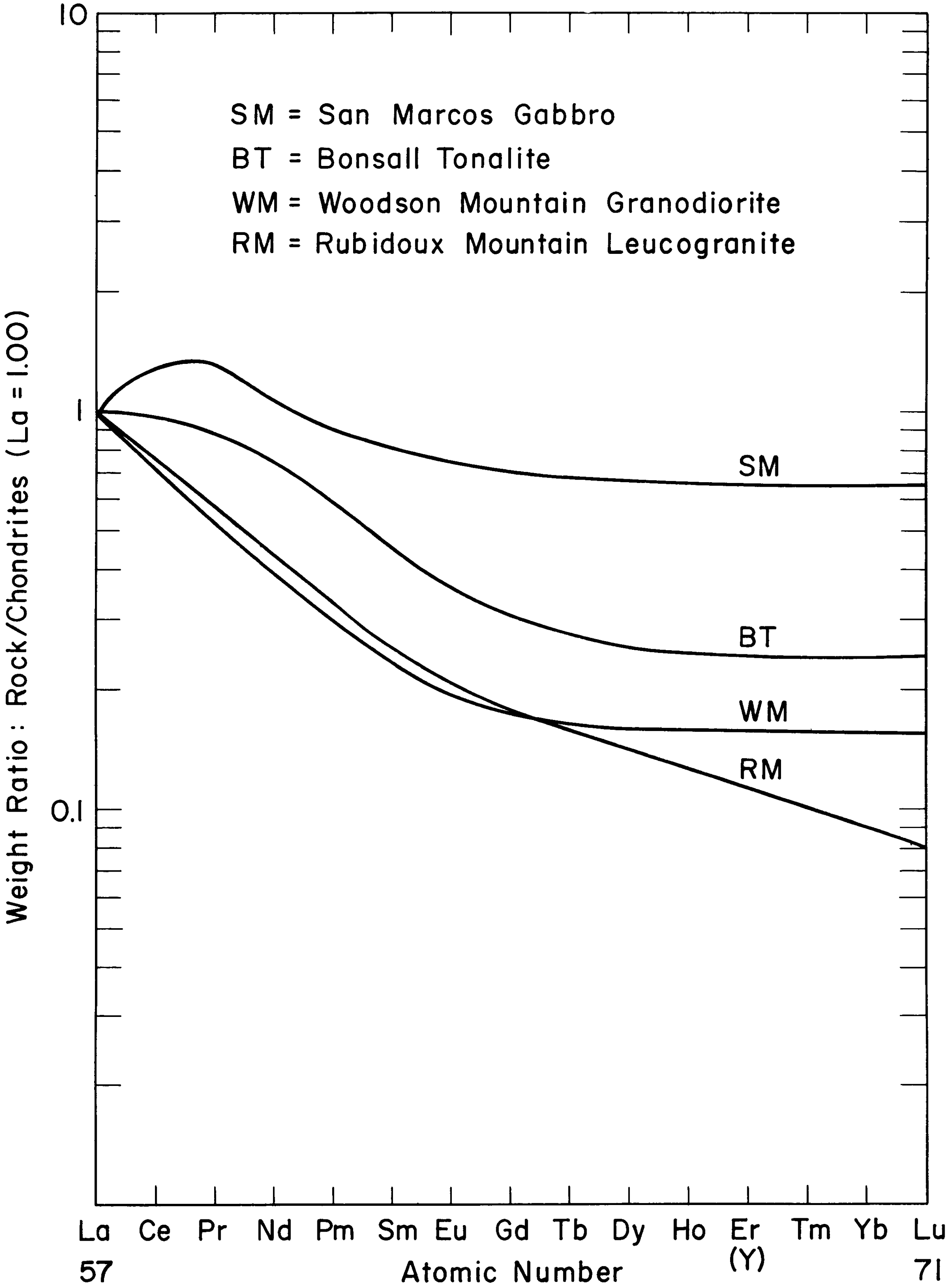
Figures I-1 through I-4 show that in the sequence gabbro-tonalite-granodiorite-leucogranite, there is an increase in absolute rare-earth content paralleled by an increase in fractionation favoring the lighter rare earths. The San Marcos gabbro is only very mildly fractionated versus the chondrites and actually shows an apparent maximum at Ce-Pr. It is observed that Eu is high compared to the abundance predicted by its near-neighbors and the overall distribution of the gabbro in the Eu region. The ratio of the observed Eu abundance to the predicted Eu abundance is approximately 1.6 . This ratio will be defined as Eu/Eu^*.

Inspection of the Bonsall tonalite distribution indicates that Eu apparently is "normal" compared to its neighbors, and therefore Eu/Eu^* for this rock is approximately 1.0 . Both of the granitic rocks have apparent Eu deficiencies. The Eu anomaly is somewhat more apparent in the Rubidoux Mountain leucogranite. Inspection of Figures I-2 and I-4 yields values for Eu/Eu^* of about 0.5 in the Rubidoux Mountain leucogranite and 0.7 in the Woodson Mountain granodiorite.

Cerium may be somewhat high in the leucogranite and low in the tonalite, but no estimate has been made because the accuracy and precision of the analytical method is poorest for this element.

Figure I-5 is a superposition of the whole-rock, chondrite-normalized distributions which have been re-normalized to La = 1.00 . It clearly reveals the relative changes in the rare earths independent of absolute abundances. Relative fractionation of the rare earths heavier than Tb is essentially absent in all rocks except the Rubidoux Mountain leucogranite. The leucogranite (quartz monzonite) and granodiorite have essentially-identical relative distributions from La through Gd or Tb. The chemical compositions of these two rocks are quite similar. However, Taylor and Epstein (1962b) note that the granodiorite falls within the field of primary

Fig. I-5. Chondrite-normalized rare-earth abundances in the four principal rock types from the batholith of Southern California. The abundances are re-normalized to La = 1.00 and plotted on a logarithmic scale as a function of atomic number.



SM = San Marcos Gabbro
BT = Bonsall Tonalite
WM = Woodson Mountain Granodiorite
RM = Rubidoux Mountain Leucogranite
10
1
0.1
Weight Ratio: Rock/Chondrites (La = 1.00)
SM
BT
WM
RM
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
(Y)
Tm
Yb
Lu
57
Atomic Number
71

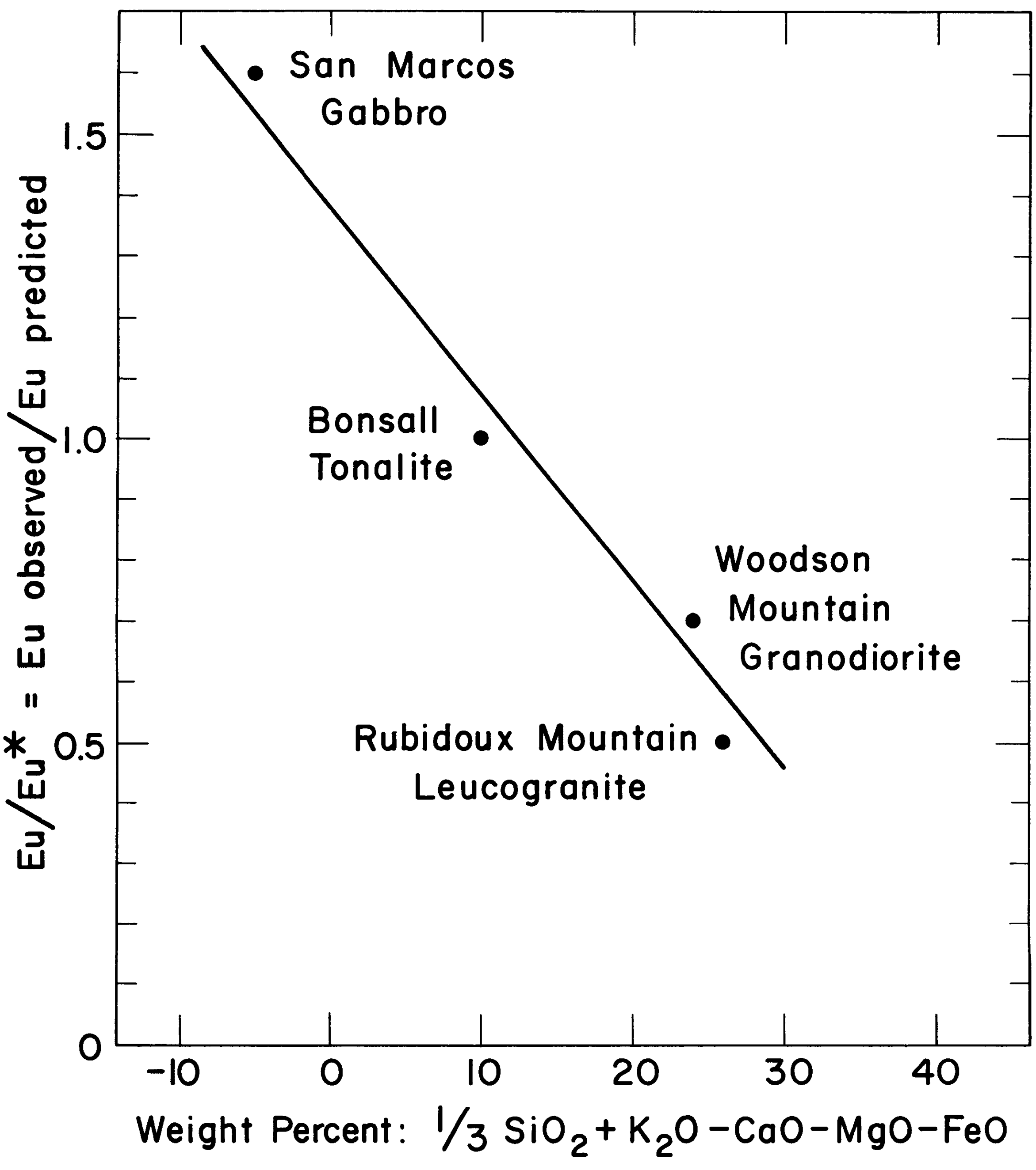
quartz crystallization in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O (Tuttle and Bowen, 1958, p 56). The oxygen isotopic measurements indicate that, indeed, quartz began to crystallize early in the granodiorite. They also indicate that simple fractional crystallization of Woodson Mountain granodiorite magma would have yielded progressively lighter (isotopically) melts. A resulting melt having the composition of the Rubidoux Mountain leucogranite would have been significantly lighter than the isotopic composition found in the leucogranite sample. Therefore, Taylor and Epstein conclude that it is unlikely that the leucogranite could have originated by simple fractional crystallization of a Woodson Mountain granodiorite magma. They suggest that it is conceivable that both the granodiorite and leucogranite were derived by direct differentiation of a Bonsall tonalite magma.

It would seem that the differences in behavior of the heavy rare earths between the granodiorite and leucogranite could be related to the preceding discussion. These two rocks may represent two different trends in magmatic differentiation. Taylor and Epstein (1962b) also cite evidence which suggests that the Rubidoux Mountain leucogranite may have formed from a magma which was quite "dry" relative to those for the other three rocks. Relative mobilities of the rare earths may very well be related to the P_{H_2O} in a silicate melt.

It is worth taking a closer look at the Eu distributions in these rocks. In Figure I-6, the Eu/Eu* ratios are plotted in a variation diagram as a function of weight percent 1/3 SiO_2 + K_2O - CaO - MgO - FeO. The latter are taken directly from a variation diagram given by Taylor and Epstein (1962b, p. 684). It can be seen that the deviation of Eu from its predicted behavior bears an approximately linear relationship with the chemical composition of the rocks expressed in this manner. Although the distribution curves were drawn by means of a visual best-fit, and consequently the values of Eu/Eu* are only approximate, Figure I-6 suggests an important observation. If the four rocks studied have been derived by magmatic differentiation of gabbroic magma, then Eu was continually depleted in the successive residual melts.

Anomalous behavior of Eu suggests that it has been divalent at some stage during the evolution of these rocks. The ionic radius of Eu^{+2} approximates that of Sr^{+2}. Consequently, if present, Eu^{+2} would be expected to geochemically follow Sr. Strontium is known to be associated with the feldspars in igneous rocks. If the magmatic sources at depth postulated by Larsen (1948) indeed existed, they may have had sufficiently-reducing redox potentials to reduce Eu^{+3} to Eu^{+2}. Europium would then tend to follow Sr with the early-forming feldspars, whereas the remaining trivalent rare earths would follow their usual trend of being concentrated in the residual melts.

Fig. I-6. Variation diagram showing the relationship between chemical composition and Eu/Eu^* ratios in the four principal rock types from the batholith of Southern California.



San Marcos Gabbro
Bonsall Tonalite
Woodson Mountain Granodiorite
Rubidoux Mountain Leucogranite
0
0.5
1.0
1.5
-10
0
10
20
30
40
Weight Percent: $\frac{1}{3}$ $SiO_2+K_2O-CaO-MgO-FeO$
$Eu/Eu^* = $ Eu observed/Eu predicted

Before discussing the rare-earth distributions associated with the mineral fractions, it should be pointed out that the highly-reducing conditions required to convert Eu^{+3} to the simple Eu^{+2} divalent state may not actually be necessary. The observed Eu anomalies may possibly be the result of a mechanism proposed by Coryell and Chase (1961). These authors observed that in a highly-simplified aqueous system, available thermodynamic data indicates that Eu reduction could be greatly enhanced in the presence of sufficient sulfate to yield a precipitate. If the solubility product of $SrSO_4$ or $BaSO_4$ should be exceeded, Eu^{+3} could be rather easily reduced and incorporated into a mixed $(Sr,Ba)SO_4$ precipitate as Eu(II). In other words, in this simplified system, the presence of a sulfate precipitate will greatly reduce the range of stability of Eu^{+3} in solution. It is worthwhile to note that Ricke (1960) reports that significant amounts of sulfate are present in most igneous rocks. The proportion of sulfate to total sulfur was observed to generally increase from basic to acid igneous rocks. Ricke also found that in a study of three granites and one basalt, sulfate was preferentially associated with the feldspars.

Distributions in Mineral Fractions

In discussing the rare-earth distributions found in the mineral fractions, it must be pointed out that no conclusive judgment can be made from this study regarding the crystal chemistry of the rare earths. Although the purity of the mineral fractions was checked by microscopic observation, small amounts of accessory minerals which might concentrate relatively large amounts of rare earths could be present. Likewise, the rare earths might also be present in significant proportions over the mineral grain boundaries in addition to their incorporation within the crystal lattices of the rock-forming and accessory minerals. Nevertheless, the rare-earth abundances in mineral fractions should yield significant information regarding the behavior of the rare earths during the formation of a given rock.

Because of the time-consuming and financially-expensive nature of the analytical method, only eight mineral fractions were studied. Except for an analysis of the apatite fraction in the tonalite, all mineral analyses were restricted to the gabbro and leucogranite.

Figure I-1 reveals that although the San Marcos gabbro as a unit is very mildly fractionated versus the chondrites when compared to fractionation in most other rocks, there are some markedly-different distributions in the analyzed mineral fractions. By far, the highest absolute rare-earth abundances were found in the apatite fraction which, in turn, has the lowest modal abundance.

The lighter rare-earths in the gabbro are favored in both the plagioclase feldspar (labradorite) and apatite fractions. The augite and hornblende, on the other hand, are markedly depleted at the La end of the rare-earth series.

Unfortunately, abundances are not available for Ce, Pr, and Nd in the latter two fractions. However, the La abundances anchor the light end of the series. The sample of San Marcos gabbro contains hypersthene, but only the clinopyroxene was analyzed. Taylor and Epstein (1962a) state that the two pyroxenes are both in obvious reaction relationship with the hornblende which encloses them. It is interesting to note that both the hornblende and augite fractions show identical relative distributions with apparent absence of fractionation of the heavier rare earths.

The most striking observation is that Eu is very high in the feldspar fraction of the gabbro. The value of Eu/Eu^* is approximately 10. This is in sharp contrast to the corresponding values of about 0.6 in the augite, 0.7 in the hornblende, and 0.6 in the apatite. The latter fractions, therefore, are somewhat depleted in Eu. The association of positive Eu anomalies with the feldspar fraction was predicted by the earlier discussion of these anomalies in the whole-rock distributions.

A check of Figure I-3 reveals that the apatite fraction from the Bonsall tonalite has a different distribution than the corresponding fraction from the gabbro. In the tonalite, the apatite is much less strongly fractionated favoring the lighter rare earths, especially when compared to the whole-rock distribution. Europium is somewhat lower in the tonalite apatite than in the apatite from the gabbro.

Figure I-2 indicates that all three analyzed mineral fractions from the Rubidoux Mountain leucogranite show roughly the same overall relative rare-earth distribution as the whole rock. The K-feldspar fraction exhibits a somewhat greater degree of fractionation favoring the lighter rare earths than the plagioclase (oligoclase) fraction. This is perhaps attributable to the fact that the K-feldspar probably began crystallizing slightly later than the plagioclase. At later stages it is to be expected that the residual melt would be somewhat more strongly fractionated favoring the lighter rare earths. Crystallization of biotite, in fact, might tend to bring this about since the biotite fraction is observed to be slightly fractionated favoring the heavy rare earths when compared to the whole-rock distribution.

Anomalous behavior of Eu is indicated in all three mineral fractions from the leucogranite. Again, as in the gabbro, the feldspars have significantly high relative Eu abundances. The K-feldspar fraction yields a Eu/Eu^* value of about 3, and the plagioclase is enriched in Eu by approximately a factor of 2. The biotite fraction, on the other hand, exhibits an astonishing Eu depletion. Its Eu/Eu^* ratio is only about 0.03 .

Europium anomalies in mica and feldspar mineral concentrates from three granites have been indicated by Chase et al. (1963). Although their estimates are based entirely upon La, Eu, and Dy abundances, their observations are quite similar to those made in this study on the

Rubidoux Mountain leucogranite. They found that invariably the feldspars were enriched in Eu relative to the micas and suggested that divalent Eu might possibly be stabilized in granites by the presence of sulfate.

In summary, this study indicates that, on a whole-rock basis, the four samples analyzed from the batholith of Southern California show progressively increased relative fractionation favoring the lighter rare earths in the sequence of gabbro, tonalite, and granodiorite-quartz monzonite. Paralleling this overall rare-earth fractionation, Eu seems to have suffered a systematic relative removal which increases in the same sequence. Further, the existence of significant Eu anomalies in mineral fractions from the San Marcos gabbro, Rubidoux Mountain leucogranite, and Bonsall tonalite suggests that divalent Eu was an important constituent during the evolution of all of the rocks studied.

It is hoped that a study will soon be made of the rare earths in a differentiated sill or some other igneous body of apparent magmatic origin in which a material balance can be attempted. In this case, a more quantitative study of rare-earth behavior would be possible. It also would be highly desirable to look at the rare earths in selected minerals from a suite of volcanic rocks. Schmitt (1963) indicates that a Kilauea basalt and Columbia Plateau basalt show very similar rare-earth fractionation and apparent normal behavior of Eu. Chase et al. (1963) suggest similar uniformity in fractionation and normal behavior of Eu in three oceanic basalts. It should, therefore, be informative to look at rare-earth distributions in a series of compositionally-different but genetically-related volcanics. The present study suggests that systematic differences in overall rare-earth fractionation as well as anomalous behavior of Eu in the associated mineral fractions may exist in such a suite of samples. Future study of Eu distributions may eventually be useful in making estimates of redox potentials.

ACKNOWLEDGMENTS

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CHAPTER II

DETERMINATION OF THE RARE-EARTH ELEMENTS AND YTTRIUM USING GROUP ISOLATION FOLLOWED BY NEUTRON ACTIVATION AND PARTITION CHROMATOGRAPHY

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ABSTRACT

A procedure for determination of the rare-earth elements and yttrium, applicable over a wide range in concentrations and to silicates as well as other rocks and minerals, has been developed. The procedure utilizes chromatographic separation of neutron induced, low-level radioactivities. Two analysts working jointly can analyze up to three samples per week which is faster than methods commonly used. Self-shielding errors are eliminated by irradiating all samples and standards in aqueous solution.

After dissolution of the sample by classical methods, the rare earths were separated from the ammonia-soluble elements by two ammonia precipitations. The rare earths were then isolated by ion exchange. The pure rare-earth fraction was irradiated in a thermal neutron flux of approximately 8×10^{12} neutrons/cm^2-sec for a period of time (1-20 hours) proportional to the amount of rare earths expected. The irradiated solution was chromatographed by gradient elution with hydrochloric acid on a column of refined diatomaceous silica coated with di-(2-ethylhexyl)orthophosphoric acid.

Precision and accuracy were approximately $\pm 10\%$. A majority of the chemical yields were $\geq 97\%$ (monitored by Y^{88} and Ce^{139} carrier-free tracers). Gadolinium and erbium were not determined.

INTRODUCTION

A procedure for the determination of the rare-earth elements (hereafter referred to as the RE) has been developed which offers several advantages over other methods. After dissolution of samples (e.g. silicates), the rare earths were isolated by hydroxide precipitation and ion exchange. Aqueous solutions containing essentially only the RE were irradiated in the pneumatic tube of a nuclear reactor in thermal neutron fluxes of approximately 8 x 10^{12} neutrons/cm^2-sec. Subsequently, the individual RE were separated by reversed-phase partition chromatography with di-(2-ethylhexyl)orthophosphoric acid (hereafter referred to as DEP) as described by Winchester (7). The induced radioactivities of the RE were then counted along with those of a simultaneously-irradiated and chromatographed standard rare-earth mixture.

Neutron activation and rare-earth chromatography have been employed by other investigators (2,3) in methods which are both accurate and highly sensitive and applicable to the parts per million to fractional parts per billion concentration range. In these procedures, samples are irradiated prior to any chemical processing to avoid reagent contamination. In the procedure herein described, it was found that for most geological materials, the reagent contamination was negligible, and therefore, pre-irradiation isolation of the RE was possible. This obviated the necessity of using remote manipulation and the heavy shielding required in handling the extremely radioactive materials resulting when many samples (e.g. silicates) are irradiated directly. An additional important advantage is that all samples were irradiated in homogeneous solutions. In many solids, the RE may be irregularly dispersed throughout the sample and self-shielding problems may arise, particularly since many RE have high thermal neutron cross sections.

In this investigation it has been assumed that the relative isotopic abundances of each RE are identical in all samples and standards. This isotopic constancy was confirmed by Mosen et al. (3) who measured six different isotopic ratios in a series of terrestrial and meteoritic samples.

EXPERIMENTAL

REAGENTS AND APPARATUS

In the pre-irradiation rare-earth group separation, all chemicals used were reagent grade, and all distilled water was obtained from a tin-lined Barnstead No. ELO-1 1/2 still. Dowex 50W-X8 (200-400 mesh or 100-200 mesh) and Dowex 1-X8 (50-100 mesh) cation and anion exchange resins, respectively, were employed for group separations. Chemical yields were monitored by carrier-free 140-day Ce^{139} and 108-day Y^{88} tracers furnished by Nuclear Science and Engineering Corporation.

Post-irradiation partition chromatography was carried out using columns of Johns-Manville Celite, rendered hydrophobic by prior treatment with vapors of dimethyldichlorosilane and coated with high purity di-(2-ethylhexyl)orthophosphoric acid (DEP). A weight ratio of DEP to Celite of about 1:5 was employed (7). The lower ends of the inner tubes of micro Liebig condensers (with water jackets approximately 8 cm in length) were drawn to capillary tips (1.5 cm from end of jacket to tip) and packed with about 2 cm^3 of the DEP-Celite preparation (column length 6 cm, diameter 6 mm). The water jackets were connected to circulating, constant-temperature water baths.

Individual stock solutions of rare earths in 3$\underline{N}$ HNO_3 were prepared using high purity (99.9%) rare-earth oxides purchased from the Lindsay Chemical Division, American Potash and Chemical Corporation and stored in polyethylene bottles.

Concentrations of the standard stock solutions ranged from approximately 0.75 mg/ml to 15 mg/ml. These concentrations were chosen such that small aliquots of each solution could be combined and accurately diluted to yield a rare-earth mixture roughly approximating the rare-earth distributions of the samples to be analyzed. The exact concentrations of the rare-earth stock solutions were determined by EDTA titration with Alizarin Red S as indicator, according to a procedure by Bril et al. (1), modified by using a visual end point. The precision obtained was 0.2% or better. A mixture with concentrations 10 times greater than required was made from the stock solutions every one-two months. From this solution, a 10-fold dilution was made prior to each irradiation. The amounts of the RE in the final irradiated solution which serves as a standard are given (in μg/100λ) in column S="known" of Table II-3.

Chemical yield determinations and post-irradiation gamma-ray scintillation spectrometry were performed with a Technical Measurement Corporation system. This included a TMC 400-Channel Pulse Height Analyzer Model 402, TMC Resolver-Integrator Model 522, TMC Paper Tape Printer Model 500, TMC SG-3A Scaler, and a Harshaw Chemical Company 1-3/4 in. by 2-in. thallium-activated sodium iodide well-type scintillation crystal and photomultiplier tube (integral line assembly) housed in a lead shield. Beta counting was done with a standard flow-proportional counting system manufactured by Baird-Atomic, Inc.

PROCEDURE

Rare-Earth Group Isolation

I. Dissolution of Sample and Isolation of Ammonia Group

a. Silicates.

Up to 500 mg of powdered sample were placed in a platinum dish and known amounts of 108d Y^{88} and 140d Ce^{139} tracers, about 50,000 cpm each, were added. Exactly the same amounts of each tracer were mixed with 2<u>N</u> acid (to prevent adsorption on the walls) in 1-ml volumetric tubes to serve as references for determination of chemical yields. For 500-mg samples, 25 ml of 48% HF and 5 ml of 70% $HClO_4$ were added and heated strongly with occasional stirring on a hot plate until a clear solution was obtained (two-three hours). Up to 15 ml of HF were added gradually, if necessary, to complete the dissolution. The solution was taken to dryness and most of the $HClO_4$ fumes were driven off, taking care not to convert the perchlorates to oxides (one hour). The residue was dissolved in 10 ml of 2N HCl, adding occasionally 5-10 ml of H_2O to aid in dissolving the salts (up to one hour).

The solution was transferred to a 50-ml centrifuge tube and precipitated twice with 1:1 ammonia, heating each time for 20 minutes or more to complete coagulation. The supernatants were discarded after checking for unprecipitated activity (it was usually negligible). The precipitate was dissolved in a minimum amount of 6N HCl, added dropwise with heating, to obtain a solution not exceeding 5 ml in volume and less than 1N in acid concentration. The solution was then loaded on a cation exchange column.

b. Other Non-Refractory Solids.

Samples largely soluble in HCl (marine shells, a carbonatite, a manganese nodule) were dissolved; then, after addition of the tracers, the insoluble fraction was centrifuged out and, if siliceous, was treated as in (a). Organic material was wet-washed with HNO_3. When the insoluble fraction was not of interest, it was filtered out on filter paper instead of centrifuged, and washed with acid until no activity remained on the paper.

To samples containing less than milligram amounts of Fe, Al, or both, 3-5 mg of spectrographically-pure Fe in HCl solution were added to serve as a carrier for the RE. Further processing was the same as in (a).

c. Refractory Minerals.

For samples containing minerals which are not decomposed by the HF + $HClO_4$ treatment, a fusion with NaOH was employed. It should be used only after making sure that procedure (a) is unsatisfactory for a given sample (see DISCUSSION).

NaOH and the finely-powdered sample were placed in a 5:1 weight ratio in a nickel crucible and tracer solutions were added. The liquid was evaporated with a low Bunsen flame, avoiding spattering upon the crucible lid. The sample was then fused in a muffle furnace at 500°C (red heat) for 15 minutes. After cooling, the solid was loosened by moistening with 5 ml of H_2O, acidified with 6N HCl and transferred to a 600-ml beaker. After adding 10-ml portions of 1N HCl to the crucible, they were heated until hydrogen was evolved, and then added to the rest of the sample. This was repeated until the crucible was inactive, or its activity remained constant. The sample solution was precipitated with

1:1 ammonia, coagulated, and filtered through Whatman No. 41 filter paper to remove the large excess of NaCl. The precipitate was washed with 2N HCl into a platinum dish, evaporated to 2-3 ml, and treated with HF + $HClO_4$, etc. as in (a).

II. Ion Exchange

Columns of 200-400 mesh Dowex 50W-X8 cation exchange resin were used for 0.5-g silicate samples and were about 37 cm long (in 2N HCl) and 13 mm in diameter. Elutions were run under applied air pressure to obtain flow rates of about 1 ml per minute and total elution times of about nine hours. For samples containing distinctly less Al + Fe, smaller columns (8 mm in diameter and 18 to 25 cm in length) of 100-200 mesh resin were used and pressure was not applied. In these cases, a complete elution took about 12 hours. Coarser resin or shorter columns gave insufficient separation of Al from Lu.

Before packing a column, the resin was soaked in 6N HCl for at least half an hour. After settling in the column, the resin was washed with 6N HCl until the effluent was colorless, and then conditioned with 0.5N HCl. Columns operated under pressure were loosened with a glass rod after each run.

All cations held less strongly by the resin than the RE (this includes all but Ba, Zr, and Th) are eluted with 2N HCl. The RE were eluted with 8N HCl, coming off the column in the order of Lu to La+Ce. The amounts of eluents to be used were determined individually for each column. A solution containing Y^{88} and Ce^{139} tracers and the maximum amounts of Al, Fe, and RE expected in the samples to be used on a given column was loaded on the column and eluted with 2N HCl. Fractions of 5 or 10 ml were collected and tested colorimetrically for Al with aluminon; alternatively, Ca^{45} tracer was added to the test solution to find the end of the Al (the distribution constants of Al and Ca are essentially equal in 2N HCl according to Strelow (6)).

Elution with 2N HCl was continued until Y^{88} appeared in the effluent. Columns were considered satisfactory when there were at least 50 ml of 2N HCl between the last positive aluminum test and the first appearance of Y^{88} tracer. A total volume of 2N HCl, 10-15 ml in excess of that required to bring off all the Al from a given column was used with successive samples on that column. Similarly, the amount of 8N HCl required to bring off all the Ce^{139} activity was determined. Reproducibility of column performance was maintained over a 6-month period of repeated use. The large columns required about 250 ml of 2N HCl and 200 ml of 8N HCl; the small columns required about 155 ml of 2N HCl and 65 ml of 6N HCl. Separation of Lu from Al on the large columns exceeded 100 ml.

Samples were loaded on columns conditioned with 0.5N HCl. Loading under pressure at roughly one-half the elution flow rate gave a satisfactory initial band. Checks for absence of Y^{88} in the last few milliliters of 2N HCl and absence of Ce^{139} activity in the last few milliliters of the 8N HCl insured complete collection of all the RE. The large columns were reconditioned with 100 ml of 0.5N HCl.

The effluent containing the RE was evaporated to about 5 ml using a stream of air (filtered through glass wool) to speed up the evaporation, and passed through a Dowex 1-X8, 50-100 mesh, 7 cm x 5 mm anion exchange column, previously conditioned with 6N HCl. This removed any Fe re-introduced in the large volume of HCl eluent, and filtered out a very thin, inactive suspension usually present at this stage (consisting presumably, of silica, resin material previously dissolved but coagulated during the evaporation, or both). In this step, 5-7 free-column volumes of 6N HCl (7-10 ml) were sufficient to recover all the activity. This effluent was collected in a 50-ml Pyrex centrifuge tube. The column was washed with 0.01N HCl and reconditioned with 6N HCl before re-use.

Reduction of Sample to 1.0 ml in Chloride-Free 1N HNO_3

The centrifuge tube was placed in a sand bath and the solution evaporated to less than 0.5 ml in a stream of air (to prevent bumping). The chlorides were driven off by evaporation with two 5-ml portions of concentrated HNO_3, which also destroyed dissolved resin material. The first portion was evaporated to a few drops, the second to 0.2-0.5 ml. Then 1-2 ml of 0.05N HNO_3 were added and complete transfer was made to a 10-ml test tube, checking that no significant activity remained in the large tube. The solution was evaporated to almost dryness, and baking was avoided. Following this, 4-5 drops of 0.05N HNO_3 were added with heating to dissolve the residue. The solution was centrifuged and the supernatant transferred to a 1-ml volumetric tube. This was repeated several times to transfer all activity. The tube was then filled to the 1.00-ml mark with 0.05N HNO_3. The solution was mixed thoroughly with a small teflon rod to obtain a homogeneous solution prior to determination of chemical yields.

Chemical Yield Determination and Irradiation

Chemical yields were determined for cerium and yttrium by selective gamma-counting of the Ce^{139} and Y^{88} tracer radioactivity. The sample and the two reference tracer solutions were counted in 1-ml volumetric tubes to maintain reproducible geometry. The two energy ranges of 0.75 Mev to 2.00 Mev and 0.10 Mev to 0.22 Mev were counted separately with the aid of the pulse height analyzer. The high range included the Y^{88} γ's = 0.90 Mev and 1.83 Mev; the low range included the Ce^{139} γ = 0.166 Mev. The Ce^{139} contribution in the high range is negligible, and therefore the chemical yield of yttrium was the ratio of the high-energy range gamma activity of the sample to that of the reference Y^{88} tracer. Similarly, the cerium yield was determined from the low-energy range counting data, except that the Y^{88} contribution had to be subtracted from the sample count (the number to be subtracted was calculated by multiplying the measured yttrium yield of the sample by the observed activity of the Y^{88} reference solution in the low energy range). The two yields were almost invariably greater than 90% (frequently 98-99%, and the difference between the cerium and yttrium yields was usually less than 3% (never exceeded 6%). Therefore, the cerium and yttrium chemical yields were assumed to represent those of all rare-earth elements of the cerium- and yttrium-earth groups, respectively. Approximately one half of each processed sample was packaged in polyethylene tubing for irradiation. An aliquot of a standard mixture of rare earths in roughly similar proportions to the sample rare-earth contents and prepared by dilution of the standard rare-earth stock solutions was also packaged. A maximum of three samples and one standard were then packaged together in a 4-dram polyethylene vial and irradiated in a thermal neutron flux of approximately 8 x 10^{12} neutrons/cm^2-sec. Samples were irradiated for one hour or five hours (except a sea water sample and a reagent blank which had very low total rare-earth contents and were irradiated approximately twenty hours each).

Chromatographic Separation of the Rare Earths

After irradiation, aliquots of each sample and the standard mixture were chromatographed on the columns of

DEP-Celite described under REAGENTS AND APPARATUS. In loading a sample on a column, an approximately equal volume of 2M HSO_3^- solution was included to adjust the final mixture to a pH = 2 and reduce any tetravalent cerium to the cerrous state. The columns were previously conditioned with 10-15 ml of 6N HCl followed by the same volume of 0.01N HCl prior to sample loading. Elutions were carried out under applied nitrogen pressures up to 8 lbs/in^2 so as to maintain flow rates of approximately 3 seconds per drop. Column operating temperatures were maintained at 60-65°C by connecting the outside jacket of the micro Liebig condenser to an external constant-temperature water bath. Pressure was applied in loading samples only after they had been heated sufficiently to drive off dissolved air. A stepwise gradient elution with hot, outgassed hydrochloric acid, ranging in concentration from 0.05N to 6N , was carried out with each sample and the standard. The concentration and volume of each acid used are listed in Table II-1. Figure II-1 is a plot of radioactivity versus fraction number. As can be seen, the sequence of elution is from La to Lu. Acid concentrations were such that each acid would bring one rare earth off the DEP-Celite column in two free-column volumes (70% of the geometrical volume) (7).

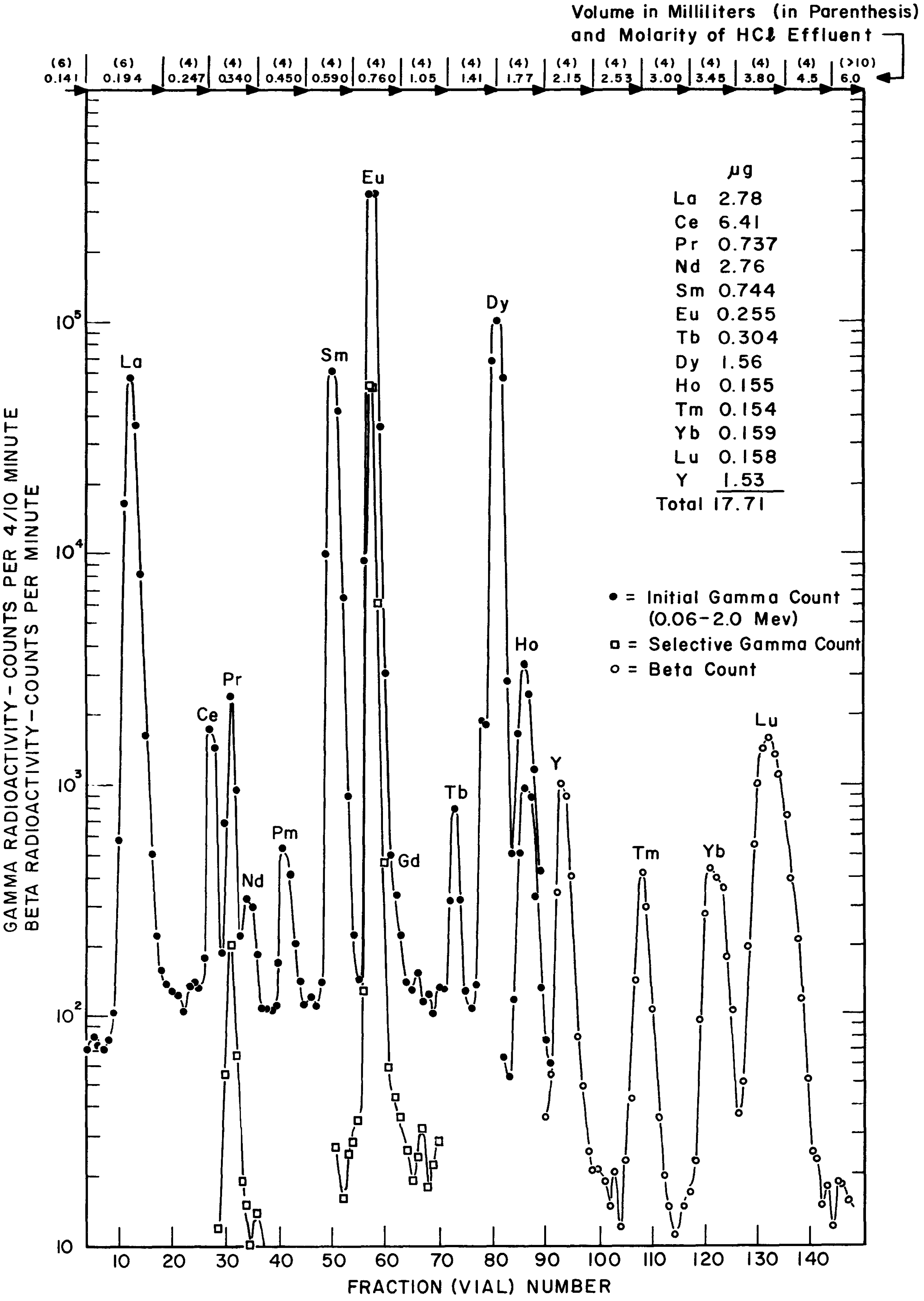
Two fraction collectors and drop counters were used simultaneously and a total of four elutions (three samples and the standard mixture) could be made by two people in an 8-10 hour day. Approximately 150 fractions of 0.5 ml each

Table II-1

Concentrations and Volumes of HCl Used for Chromatography of the Rare Earths

Rare earth eluted	Acid concentration, moles/liter	Volume, ml
--	0.05	6
La	0.141	6
Ce	0.194	6
Pr	0.247	6
Nd	0.340	4
(Pm)	0.450	4
Sm	0.590	4
Eu	0.760	4
Gd	1.05	4
Tb	1.41	4
Dy	1.77	4
Ho	2.15	4
Er	2.53	4
Tm	3.00	4
Yb	3.45	4
Lu	3.80	4
--	4.5	4
--	6.0	12
Column reconditioning	0.01	12

Fig. II-1. Typical elution of a rare-earth mixture irradiated for one hour in a thermal neutron flux of 8 x 10^{12} n/cm^{2}-sec.


Volume in Milliliters (in Parenthesis)
and Molarity of HCℓ Effluent
(6) 0.141
(6) 0.194
(4) 0.247
(4) 0.340
(4) 0.450
(4) 0.590
(4) 0.760
(4) 1.05
(4) 1.41
(4) 1.77
(4) 2.15
(4) 2.53
(4) 3.00
(4) 3.45
(4) 3.80
(4) 4.5
(>10) 6.0
GAMMA RADIOACTIVITY - COUNTS PER 4/10 MINUTE
BETA RADIOACTIVITY - COUNTS PER MINUTE
10
10^2
10^3
10^4
10^5
10
20
30
40
50
60
70
80
90
100
110
120
130
140
FRACTION (VIAL) NUMBER
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Y
Tm
Yb
Lu
µg
La 2.78
Ce 6.41
Pr 0.737
Nd 2.76
Sm 0.744
Eu 0.255
Tb 0.304
Dy 1.56
Ho 0.155
Tm 0.154
Yb 0.159
Lu 0.158
Y 1.53
Total 17.71
● = Initial Gamma Count (0.06-2.0 Mev)
□ = Selective Gamma Count
○ = Beta Count

were collected in 1-dram glass vials during each elution. The first 100-110 vials were half-filled with 2N HCl to provide better geometry for gamma counting. The remaining fractions were later transferred directly to 2-in. watch glasses, evaporated to dryness by an infra-red lamp and hot-plate combination, and saved for subsequent beta counting. After the first two elutions were completed and all activity removed from the columns, the latter were reconditioned with about 10 ml of 0.01N HCl, loaded with the remaining two samples, and the final two elutions performed.

The following manipulative details required special attention. Aliquots of samples and the standard RE mixture were taken from the irradiated solutions and loaded on the DEP-Celite columns (volumes, in general, were between 100 and 500 microliters and were accurately measured by λ-pipets). Prior to sample loading, a small volume of the 2M HSO_3^- buffer was added above the column. The irradiated solution was added immediately, and following this, an equal volume of the buffer was rapidly added so as to thoroughly mix with the sample and the buffer below the sample. In order to prevent dissolved gases from being forced into the columns, the sample-buffer mixture was allowed to soak at least partially into the column while being heated by the external water jacket. When caution was not exercised in sample loading, channeling appeared in the columns during the subsequent elution, and poor results were obtained.

In raising the temperature of columns from room temperature to the operating temperature (60-65°C), it was found necessary to pass hot outgassed 0.01N HCl through the columns while the latter were still at room temperature, and to continue adding hot acid as the columns were being gradually heated. Failure to do this usually resulted in the appearance of channeling in the columns. Approximately 20 minutes were required to bring a DEP-Celite column to the operating temperature.

Counting of Radioactivity

The pulse height analyzer was calibrated to accept gammas ranging in energy between 0.06 Mev and 2.0 Mev. The scaler was modified to accept only those pulses accepted by the analyzer. Therefore, scaler readings on a given vial corresponded to the total integrated activity recorded in the memory of the analyzer for that count (i.e. from 0.06 Mev to 2.0 Mev).

All gamma counts were for 0.4 live-minutes (the analyzer timer measures live-time rather than elapsed-time, thereby eliminating dead-time corrections for high-activity fractions). For some fractions, selective integration with the integrator-resolver (starting at energies above 0.06 Mev) was used to resolve adjacent RE which might be present in the same fraction. The four corresponding fractions of the three sample elutions and one standard elution were counted before proceeding to the next four fractions, thereby eliminating the necessity of making decay corrections in sample-standard comparisons. The gamma spectrum of each fraction was inspected for positive identification of the radionuclide being counted.

In Table II-2 are the important rare-earth radionuclides produced by irradiation with thermal neutrons at a flux equal to 8 x 10^{12} neutrons/cm^2-sec. The elution curve in Figure II-1 is for the standard rare-earth mixture (one-hour irradiation). The elution curves of samples were the same except that the Ce and Y fractions were also selectively counted to distinguish between the reactor-induced activities and the Ce^{139} and Y^{88} tracer activities used to measure chemical yields. With the pulse height analyzer, resolver-integrator, and scaler it was possible to simultaneously determine both the "total activity" (0.06 - 2.0 Mev) and the integrated activities of selected ranges. The latter were stored in a portion of the analyzer memory not used for accumulation of activity and were later printed out on paper tape. The fractions containing Ce were integrated from 0.25-2.0 Mev (to eliminate the 0.166 Mev γ of tracer Ce^{139}). The Ce and Pr fractions were integrated from 0.8 Mev to 2.0 Mev to eliminate all Ce and Nd activity. This method of measuring Pr activity also provided an accurate method for detection of any Pr contamination in the Ce fractions.

The activity used to calculate the Nd concentration was the sum of the Pm^{149} and Pm^{151} activities (daughter activities from parent Nd^{149} and Nd^{151}). This is possible

Table II-2

Principal Induced Rare-Earth Radionuclides

Parent element	Radionuclide	Half-life
La	La^{140}	40.2 h
Ce	Ce^{141}	33.1 d
	Ce^{143}	33 h
Pr	Pr^{142}	19.2 h
Nd	Nd^{147}	11.1 d
	Nd^{149}	1.8 h
	Pm^{149}	50 h
	Nd^{151}	12 m
	Pm^{151}	27.5 h
Sm	Sm^{153}	47.1 h
Eu	Eu^{152m}	9.2 h
Gd	Gd^{159}	18.0 h
	Gd^{161}	3.7 m
	Tb^{161}	7.0 d
Tb	Tb^{160}	72.3 d
Dy	Dy^{165}	2.3 h
Ho	Ho^{166}	27.2 h
Er	Er^{169}	9.4 d
	Er^{171}	7.5 h

Table II-2 (continued)

Parent element	Radionuclide	Half-life
Tm	Tm^{170}	129 d
Yb	Yb^{169}	32 d
	Yb^{175}	4.2 d
	Yb^{177}	1.9 h
Lu	Lu^{176}	3.7 h
	Lu^{177}	6.8 d
Y	Y^{90}	64.2 h

because there are no stable isotopes of Pm (and, consequently, no primary Pm activity).

The Eu fractions were integrated from 0.75 - 2.0 Mev to eliminate both Sm and Gd. This also provided a method of measuring any Eu contamination of Sm fractions. The induced Gd activity was very low compared to the Eu activity, and since the two elements could not be separated by the chromatographic procedure, Gd was not determined.

Since Dy^{165} has a 2.3-hour half-life (and is the only induced Dy activity) it was counted on the day of the irradiation. It generally was the most active rare-earth nuclide at the end of each elution and its location (range of fractions) could quickly be found and the fractions counted. A day later the Dy^{165} had decayed sufficiently to determine 27.2-hour Ho^{166} without interference from the Dy activity (see Figure II-1). The later determination of Ho could be used to estimate the Ho contamination of the earlier Dy count. The Y fractions were gamma counted from 0.75 - 2.0 Mev. This was used both as a check on the post-irradiation chemical yields of Y^{88} tracer (the induced 64.2-hour Y^{90} decays 99.98% of the time by pure beta emission), and for later subtraction from the beta count.

All fractions past Ho were evaporated on 2-in. watch glasses and counted for one minute each by the flow-proportional beta counter. Since Y and Er could not be separated by the chromatographic procedure, it was decided not to determine the latter. The Y content of samples generally was about ten times greater than the Er content, and at the time these fractions were counted (50-75 hours after the irradiation) the Er^{171} beta activity was less than 1% of the Y^{90} beta activity. It was determined that 0.08% of the Y^{88} tracer gamma activity was recorded by the beta counter, and consequently this was subtracted from the gross Y^{90} beta count.

The Dy fractions were counted immediately after finishing the elutions (i.e. on the day of the irradiation). The remainder of the gamma counting was completed on the following day. Beta counting was done a day or two later. In later runs, the 127-day Tm^{170} and 73-day Tb^{160} were not counted until a week or two after irradiations. In this way, resolution between their adjacent rare earths was improved, and background activities were markedly reduced.

Calculations

The total activity of a given rare earth in a sample (or standard) was determined by integration of the counting data over the corresponding fractions (as determined from the elution diagram, e.g. Figure II-1). The individual rare-earth concentrations of a sample were calculated from the summed sample and standard activities, the known rare-earth concentrations in the standard mixture, the chemical yields, and the known proportion of the original sample which was chromatographed. Decay corrections were generally unnecessary because corresponding fractions from the four elutions were counted at essentially identical times .

RESULTS

Precision Test with a Pure Rare-Earth Mixture

A freshly-diluted portion of the standard mixed-RE solution also containing the usual Y^{88} and Ce^{139} yield monitors was loaded on the cation exchange column and processed further using the previously-described procedure. The chemical yields (determined directly before irradiation) were $Y^{88} = 98\%$ and $Ce^{139} = 96\%$. This solution was irradiated with an identical amount of unprocessed standard solution. The two solutions were chromatographed simultaneously on two DEP-Celite columns and counted as usual.

The net summed activity of each rare earth in the two solutions is recorded in Table II-3. The amounts of RE found in the processed solution (SP) were calculated by the usual procedure, which assumes that the activity of each fraction in the unprocessed reference solution (S) represents a known amount of that RE (previously determined by titration of the individual stock solutions). This, of course, is correct only within the limit of error introduced by the chromatography and counting statistics. The values of the ratios RE(SP)/RE(S) which appear in the last column of Table II-3 would be unity if the reproducibility were 100%.

Table II-3

Precision Test on Processed (SP) and Unprocessed (S) Pure Rare-Earth Mixtures

Element	Activity, cpm S	Activity, cpm SP	Rare-earth content (RE), µg S="known"	Rare-earth content (RE), µg SP= $\frac{cpm_{SP}}{cpm_S} \times \frac{\mu g_S}{yield}$	$\frac{SP}{S} = \frac{RE\ found}{RE\ taken}$
La	83,985 ± 0.3%	78,129 ± 0.4%	2.778	2.694	0.97 ± 0.5%
Ce	743 ± 4.5%	630 ± 6.0%	6.408	5.639	0.88 ± 7.5%
Pr	315 ± 7.5%	315 ± 7.5%	0.736	0.765	1.04 ± 10.5%
Nd (Pm)	572 ± 7.2%	564 ± 7.5%	2.760	2.843	1.03 ± 10.5%
Sm	82,380 ± 0.3%	79,760 ± 0.4%	0.744	0.751	1.01 ± 0.5%
Eu	31,316 ± 0.6%	31,685 ± 0.6%	0.255	0.268	1.05 ± 0.9%
Tb	2,148 ± 3.0%	2,182 ± 3.0%	0.303	0.312	1.03 ± 4.5%
Dy	184,826 ± 0.2%	183,717 ± 0.2%	1.560	1.575	1.01 ± 0.3%
Ho	3,845 ± 2.1%	3,799 ± 2.2%	0.155	0.156	1.01 ± 2.8%
Tm	1,599 ± 3.0%	1,594 ± 3.6%	0.154	0.157	1.02 ± 4.7%
Yb+Lu	15,669 ± 1.0%	14,690 ± 1.1%	0.316	0.303	0.96 ± 1.5%
Y	5,262 ± 1.5%	5,012 ± 1.5%	1.525	1.479	0.97 ± 2.0%

Their departures from unity represent the combined effect of the errors introduced in chromatographing the solutions and the statistical errors inherent in measuring the induced radioactivities. The separation of Yb from Lu in the SP (processed) sample was unsatisfactory, so that only Yb + Lu values are reported.

It is seen that, except for Ce, the deviations of these ratios from unity do not exceed 0.05, and they are randomly positive and negative. This indicates that no systematic errors are introduced, either by comparing a processed RE mixture to an unprocessed one, or by chromatographing them on different columns. It also shows that the chemical processing does not effect the completeness of recovery from the DEP-Celite columns.

The percentage error recorded with each activity in Table II-3 is the statistical counting error (67% confidence level) and is a function of the total-to-background ratio. The value of the percentage error in the last column was obtained by combining the corresponding preceding errors according to the usual statistical procedure. It is seen that in 5 cases the deviation from unity can be accounted for by the counting statistics alone. Where the counting statistics are appreciably better than the observed precision (e.g. in the cases of La, Eu, and Yb + Lu), this precision is a direct measure of the reproducibility of the chromatographic separation of these elements, and is believed to represent the overall quality of the separation attainable using the DEP columns. The precision of the Ce values is regarded as ±15%.

Precision Test on Duplicate Runs Taken from the Same Sample Solutions

Two aliquots of each of 4 sample solutions were irradiated and analyzed. The results are given in Table II-4. In the case of a quartz-feldspar mixture, both aliquots came from one batch of irradiated solution. They were chromatographed on different DEP-Celite columns and assayed with reference to the standard solution irradiated along with them. This test measures the effect of using different columns, everything else being kept identical.

The duplicates of the other 3 samples were irradiated on different days and assayed with reference to different standards; i.e. each was compared to the standard irradiated with it. This tests the precision of the overall procedure.

The RE content of the quartz-feldspar sample turned out to be too low for the one-hour irradiation used, and it was possible to determine only the elements for which the procedure is most sensitive (La, Sm, Eu, and Dy). The observed precision spread in this case was better than for the runs of different irradiations with different standards, but to a rather insignificant degree.

The simple arithmetic deviations of each 2 determinations from their mean are expressed in percentages of

Table II-4

Duplicate Runs Taken from the Same Sample Solutions

Sample		Rare-earth concentration, µg/g (ppm)						
		La	Ce	Pr	Nd	Sm	Eu	Tb
San Marcos gabbro	A	4.1_0	$16._9$	1.9_1	7.2_8	2.1_4	0.99	0.50_7
	B	3.9_2	$12._1$	2.3_9	8.0_8	2.2_0	1.1_1	0.44_9
	mean	4.0_1	$14._5$	2.1_5	7.6_8	2.1_7	1.0_5	0.47_8
		±2%	±16%	±11%	±5%	±1%	±5%	±6%
Standard diabase W-1	A	9.9_0	$15._1$	3.5_1	$16._7$	3.4_0	1.3_2	0.85_1
	B	8.7_2	--	--	$23._7$	3.5_2	1.2_6	0.76_3
	mean	9.3_1			$20._2$	3.4_6	1.2_9	0.80_7
		±6%			±17%	±2%	±2%	±6%
Standard granite G-1	A	$95._5$	15_0	$12._9$	$53._4$	8.1_4	1.4_1	0.72_6
	B	$89._3$	--	--	$57._0$	8.3_6	1.3_1	0.54_8
	mean	$92._4$			$55._2$	8.2_5	1.3_6	0.63_7
		±3%			±3%	±1%	±4%	±14%
Quartz-feldspar mixture	A	0.30_4				0.12_0	0.012_2	
	B	0.30_2				0.11_8	0.012_9	
	mean	0.30_3				0.11_9	0.012_6	
		±0.3%				±1%	±3%	
Root-mean-square-deviation		±4%	(±16%)	(±11%)	±10%	±1%	±4%	±9%

Table II-4 (continued)

Sample		Dy	Ho	Tm	Yb	Lu	Y
San Marcos gabbro	A	2.8_8	0.56_0	0.24_0	1.9_2	0.27_4	$17._2$
	B	2.7_0	0.57_8	0.25_6	1.4_8	0.23_8	$13._8$
	mean	2.7_9 ±3%	0.56_9 ±2%	0.24_8 ±3%	1.7_0 ±13%	0.25_6 ±7%	$15._5$ ±11%
Standard diabase W-1	A	4.0_7	0.87_8	--	2.2_9	0.33_6	$27._4$
	B	4.6_9	0.83_2	0.33_2	2.1_7	0.36_0	$28._6$
	mean	4.3_8 ±7%	0.85_5 ±3%		2.2_3 ±3%	0.34_8 ±3%	$28._0$ ±3%
Standard granite G-1	A	2.4_4	0.38_7	0.16_9	0.97_8	0.13_0	$15._7$
	B	2.6_0	0.42_9	0.14_3	0.89_6	0.11_6	$10._9$
	mean	2.5_2 ±3%	0.40_8 ±5%	0.15_6 ±9%	0.93_7 ±4%	0.12_3 ±6%	$13._3$ ±18%
Quartz-feldspar mixture	A	0.11_9					
	B	0.12_6					
	mean	0.12_3 ±3%					
Root-mean-square-deviation		±4%	±4%	±7%	±8%	±6%	±12%

the mean value. The root-mean-square of these percentages is listed as the root-mean-square deviation for each element. These compare well with the larger of the two deviations listed for each element in the last column of Table II-4. The precision is seen to be within ±12% for all elements except Ce.

Separately-Processed Duplicates

In Table II-5 are listed the results of repeated analyses of whole-rock samples, each analysis made on a separately-weighed out amount of material taken from the same vial. The Kilauea Iki-22 sample was ground to < 100-mesh; the 3 others were ground to < 200-mesh.

Values are given for La, Sm, Eu, and Dy, for which analytical precision of ±4% or better has been shown in the preceding section. Here the spread of results is much larger, indicating that it reflects actual inhomogeneities in the sample powders. This should be remembered when comparing data of different authors on assumedly-identical silicate samples.

Spiking Test

This experiment consisted of an addition of known amounts of RE to a silicate sample. Two 0.500-g samples of Kilauea Iki basalt (powdered to < 100-mesh) were taken from the same vial. To one of them were added 100 λ of freshly-

Table II-5
Separately-Processed Duplicates

		Rare-earth concentration, µg/g (ppm)			
Sample		La	Sm	Eu	Dy
Rubidoux	A	$24._4$	4.0_0	0.71_4	3.8_3
Mountain	B	$29._6$	--	0.83_4	4.4_4
leucogranite	C	$27._4$	4.1_7	0.74_8	--
	D	$24._5$	3.7_8	0.62_9	3.0_8
	mean	$26._5$	3.9_8	0.73_1	3.7_8
	range	20%	10%	28%	36%
San Marcos gabbro	A	4.7_2		1.1_4	
	B	4.0_1		1.0_5	
	mean	4.3_7		1.1_0	
	range	16%		8%	
Bonsall tonalite	A	$16._7$	4.0_0	1.1_8	
	B	$13._4$	3.6_5	1.0_6	
	mean	$15._1$	3.8_3	1.1_2	
	range	22%	9%	11%	
Kilauea Iki-22	A	$13._2$	4.4_7	1.5_0	--
basalt	B	$11._3$	4.3_2	1.4_3	3.5_5
Schmitt et al. (1962)	=	$10._5$	4.2_0	1.3_4	3.0_0
	mean	$11._7$	4.3_3	1.4_2	3.2_8
	range	23%	6%	11%	17%

diluted, mixed-RE solution (the same as used for standards). The amounts of RE added are listed in Table II-6. The additions varied widely in absolute amounts of the various RE (from 0.08 to 3.20 μg) and constituted varying percentages of the RE in the sample (18% to 140%). This one experiment thus simulated 11 experiments with different additions of one element. The sample without addition was labelled "K", that with the addition was "L". Samples K and L were processed simultaneously, keeping all conditions identical. The yields of Ce^{139} and Y^{88}, measured just before irradiation, were 99% and 98%, respectively, in L and 99% of both tracers in K. Both samples were irradiated and chromatographed simultaneously, along with a standard to which their activities were later compared.

The results obtained are listed in columns (K) and (L) in Table II-6. Listed errors are based on counting statistics. They are functions of the total activities and the ratios of total to background activities.

If the RE content of the two powdered samples were identical and the recoveries of all RE were complete, the equality $L = K + \Delta$ should hold. Values of $\frac{L}{K+\Delta}$ are listed in Table II-6 and are seen to be less than unity (with the single exception of Ce); their mean is 0.96 . This can be due to either incomplete recovery of the RE, or due to a smaller RE content in the powder taken for the "L" sample. To see which of the two possibilities was more likely, values of $\frac{L-K}{\Delta}$ (which measure the recovery of the addition, assuming the

Table II-6
Spiking Test*

Element	μg measured no addition (K)	μg added (Δ)	$(\frac{\Delta}{K}\cdot 10^2)$	μg measured with addition (L)	$(\frac{L}{K+\Delta})$
La	2.81 ± 0.01	1.39	49%	3.75 ± 0.01	0.89
Ce	7.42 ± 0.23	3.20	43%	10.77 ± 0.30	1.01
Pr	0.950 ± 0.036	0.368	39%	1.228 ± 0.044	0.93
Nd	4.83 ± 0.20	1.38	29%	6.03 ± 0.24	0.97
Sm	1.080 ± 0.004	0.372	34%	1.380 ± 0.005	0.95
Eu	0.358 ± 0.001	0.128	36%	0.465 ± 0.001	0.96
Tb	0.157 ± 0.008	0.152	97%	0.283 ± 0.010	0.92
Dy	0.887 ± 0.002	0.780	88%	1.603 ± 0.002	0.96
Ho	0.167 ± 0.003	0.078	47%	0.233 ± 0.003	0.95
Tm	0.055 ± 0.002	0.077	140%	0.131 ± 0.004	0.99
Yb	---	0.080	--	0.517 ± 0.010	--
Lu	---	0.079	--	0.122 ± 0.001	--
Y	4.29 ± 0.05	0.760	18%	5.00 ± 0.07	0.99
				mean:	0.96 ±0.03

Table II-6 (continued)

Element	Difference (L-K)	Addition recovery $\left(\frac{L-K}{\Delta}\right)$	(L-Δ)	Sample comparison $\left(\frac{L-\Delta}{K}\right)$
La	0.94 ± 0.01	0.68 ± 0.01	2.36 ± 0.01	$0.84 \pm 0.00_3$
Ce	3.35 ± 0.38	1.05 ± 0.12	7.57 ± 0.30	1.02 ± 0.04
Pr	0.278 ± 0.057	0.76 ± 0.15	0.860 ± 0.044	0.91 ± 0.05
Nd	1.20 ± 0.31	0.87 ± 0.22	4.65 ± 0.24	0.96 ± 0.05
Sm	0.300 ± 0.006	0.806 ± 0.016	1.008 ± 0.005	0.94 ± 0.01
Eu	0.107 ± 0.001	0.836 ± 0.008	0.337 ± 0.001	$0.94 \pm 0.00_4$
Tb	0.126 ± 0.013	0.83 ± 0.09	0.131 ± 0.010	0.83 ± 0.05
Dy	0.716 ± 0.003	0.918 ± 0.004	0.823 ± 0.002	$0.93 \pm 0.00_2$
Ho	0.066 ± 0.004	0.85 ± 0.05	0.155 ± 0.003	0.93 ± 0.02
Tm	0.076 ± 0.005	0.99 ± 0.06	0.054 ± 0.004	0.98 ± 0.05
Yb	---	---	0.437 ± 0.010	---
Lu	---	---	0.043 ± 0.001	---
Y	0.71 ± 0.09	0.93 ± 0.12	4.24 ± 0.07	0.99 ± 0.02
			mean, 11 elements:	0.93 ± 0.11
			mean, La, Sm, Eu, Dy :	0.91 ± 0.01

* Estimates of errors are calculated from the radioactivity counting statistics.

powders were identical) and values of $\frac{L-\Delta}{K}$ (which compare the RE contents of the two powdered samples, assuming complete revovery) are also listed in Table II-6.

Because of the chemical similarity of the RE, both incomplete recovery and a difference in sample content should exhibit similar, or smoothly-varying effects over the lanthanide series. The $\frac{L-K}{\Delta}$ values are seen to be much more scattered than the $\frac{L-\Delta}{K}$ values, even in cases where the addition roughly equalled or exceeded the initial amount (i.e. Tb, Dy, and Tm); this, along with the inhomogeneities observed in other powdered samples in the previous section, indicates that a real difference in the RE content of the powder rather than incomplete recovery of the RE is responsible for the discrepancies.

An additional indication in favor of the assumption that the powder in L really contained only about 0.93 times as much RE as K can be shown. The elements Sm, Eu, and Dy, which have the smallest counting uncertainties, were found in the previously-described experiments to give the best precision. They agree very closely in their $\frac{L-\Delta}{K}$ values of 0.93-0.94, whereas their $\frac{L-K}{\Delta}$ values vary from 0.81 to 0.92 . Holmium, with the next best counting statistics (La will be dealt with separately) also has the 0.93 value. The largest deviations from the mean of 0.93 occur in the elements with the largest counting errors, precision uncertainties, or both (Ce, Y, and Tb), and their deviations are therefore less significant in discerning sample inhomogeneities. The values of K and those of L-Δ are larger and smaller, respectively, than those found by Schmitt and Smith (4) on a sample taken from the same vial. This again suggests that inhomogeneities were present.

An exception is La, whose precision is usually good, and which is conspicuously low in sample L. A slight depletion of La in this sample is still possible, but without additional evidence on special La variability, a selective loss of La in processing sample L must be suspected.

The scatter of the values of $\frac{L-\Delta}{K}$ about 0.93 is within the ±10% precision claimed for this analytical method.

Reagent Blanks

The reagents used in chemical processing were analyzed for their combined RE content. The blank corresponding to procedure (a) for silicates, included the yield-monitor tracers, HF, $HClO_4$, HCl, H_2O, and the NH_3 employed in the double precipitation (in the amounts used for 0.500-g silicate samples). This solution was evaporated to dryness and the large excess of ammonium chloride was sublimed (the rare-earth chlorides and perchlorates are not appreciably volatile). The residue was dissolved in water and subsequently processed in the usual manner (i.e. loaded on the large cation exchange column, etc.).

One blank (RB1) was irradiated for 18 hours, to obtain detectible activities from the largest possible number of RE. A second, separately-prepared blank (RB2) was irradiated for 5 hours, since this was the longest time actually used for irradiation of silicate samples. The eight elements which were not detected in the shorter irradiation were assigned blank values of zero. For the five elements which were detected in both runs (i.e. La, Sm, Eu, Dy, and Y), the two blank values agree well in order of magnitude, even though the blanks were prepared on different days, and irradiated for different periods of time. The results are shown in Table II-7.

The blank values of the five detectible RE in RB2 do not exceed 3% of their respective amounts founds in basalts, which are relatively low in RE. Hence, contamination of the samples by processing them before (rather than after) the irradiation, is seen to be negligible for eight elements and small, but reproducibly determinable for the other five elements.

The NaOH-fusion blank was prepared by dissolving and acidifying the NaOH, adding 5 mg of spectrographically-pure iron chloride (in solution), precipitating with ammonia, proceeding as in procedure (a), and irradiating for 1 hour. The amount of La found was similar to that in the combined acids, but all the heavier RE are about an order of magnitude higher, with Dy 60-times higher than in the acid dissolution. In natural samples, the content of the heavier RE are usually the lowest. For this reason, their relatively high content in NaOH makes the fusion procedure acceptable only

Table II-7

Reagent Blanks, μg / 0.500-g sample

	Acid dissolution				
Element	RB1*	RB2#	Mean	NaOH Fusion°	Sea water" blank
La	0.13	0.10	0.11_5	0.11	0.07
Ce	0.05	n.d.	---	n.d.	n.d.
Pr	0.03	n.d.	---	n.d.	n.d.
Nd	0.23	n.d.	---	n.d.	n.d.
Sm	0.0045	0.0024	0.0035	0.022	0.005
Eu	0.0007	0.0008	0.0007_5	0.035	0.002
Tb	0.003	n.d.	---	0.07	n.d.
Dy	0.0031	0.0047	0.0039	0.18	0.028
Ho	0.0008	n.d.	---	0.06	0.052
Tm	n.d.	n.d.	---	0.01	n.d.
Yb	n.d.	n.d.	---	0.02	n.d.
Lu	n.d.	n.d.	---	0.06	n.d.
Y	0.020	0.005	0.013	n.d.	n.d.

* irradiated 18 hours.

irradiated 5 hours.

° irradiated 1 hour.

" with reagents used to process a 4-liter sample and irradiated 1 hour.

n.d. not detected.

when procedure (a) is impracticable.

The sea water blank included 30 mg of spectrographically-pure iron (the amount that was added to the sea-water samples to isolate the RE), as well as the acids and ammonia. It was passed through one of the smaller cation exchange columns, so that less HCl was used in the elution. It is seen to contain less La than the other blanks, but much more Ho and Dy, presumably from the iron. The values comprise up to 20% of the RE in 4-liter sea-water samples; this amount will be reduced in future work. The iron will be examined, and if found to be significantly contaminated, the ammonia precipitation step may be replaced by using a larger cation exchange column. Higher purity HCl will be required in this case, since much larger volumes will be used.

DISCUSSION

Sample Size and Analytical Sensitivity

In determining the required sample size and irradiation period, the expected content of the less abundant RE (i.e. Sm through Lu) should be considered. A total of at least 3 μg of these elements was desirable for one-hour irradiations in a thermal neutron flux of 8×10^{12} n/cm^2-sec. Most crustal rocks contain this amount of Sm through Lu in 0.250 g of sample. In strongly fractionated rocks (e.g. most granites), this is associated with about 80 μg of total RE;

in basalts and sedimentary rocks, this corresponds to about 40 μg of total RE. Samples of double this size were processed, and 50% aliquots were irradiated, thus providing material for duplicates if necessary.

For smaller amounts of RE or a lower neutron flux, correspondingly longer irradiations should be used. Since the material actually irradiated contains virtually only the RE, increase of irradiation time does not produce highly increased sample activities. This is an important advantage over methods currently used, in which an unprocessed sample is irradiated directly. Therefore, in practice, the limit of detection depends for the most part upon the irradiation facilities.

Fractionation Effects

The ammonia precipitation step was tested for fractionation effects. In silicate samples, where only small volumes of liquid are involved, the tracer activities of the supernatants from well-coagulated ammonia precipitates were invariably negligible, indicating complete precipitation of all RE In sea water samples (4 liters each), the supernatant was slightly active, and it was tested for fractionation of Ce and Y by reacidifying, adding iron, and precipitating again. This precipitate was found to contain 0.5% of the initial Y^{88} activity and 0.8% of the initial Ce^{139} activity. This indicated that if fractionation does occur in the solid, it is proportionally very small, since recovery is nearly complete (99.5% for Y versus 99.2% for Ce). The fractionation was sufficiently small between these two elements (or, alternatively, recoveries sufficiently complete) to justify the assumption that no RE were lost during the ammonia precipitation.

Sample Fusion with NaOH

Fusion with NaOH should be employed only if procedure (a) proves unsatisfactory. The main disadvantage of the fusion is the relatively high, heavy-RE content (ppm range) of the purest NaOH commercially available (0.02% material precipitable by ammonia is permitted by ACS specifications for Reagent Grade NaOH). Using the lowest possible ratio of NaOH to sample, 0.250 g of silicate require 1.25 g of NaOH, which results in a blank as high as 10% of the RE content in the sample. An additional problem is present with Na_2O_2, which besides having the same impurity problem, also reacts violently with the tracer solution added prior to the fusion.

In the basic fusion, the RE (especially Ce) tend to adhere tenaciously to the crucible walls. Repeated attack with strong acid was necessary to recover 99% of the Y^{88}, and the Ce^{139} recovery was always at least 5% lower.

Zirconium crucibles were used at first, but they were found to introduce milligram quantities of Zr, which is not readily separable from the RE and interferes by its bulk. The amounts of Zr commonly occurring in rocks are harmless. Use of nickel crucibles is preferred, since the Ni introduced is eliminated by the ammonia precipitation and also by the cation exchange.

Cation Exchange

In principle, the RE could be isolated from nearly all elements usually present in most samples by cation exchange alone, omitting the ammonia precipitation. Barium would remain with them, but it would be eliminated later on the DEP column by the initial 0.05N HCl eluent. The same applies to Sr which might be incompletely separated by cation exchange. The behavior of traces of Zr and Th was not investigated, since even if they remained with the RE, their radioactivities would be negligible.

However, if the large amounts of Ca, Mg, K, and Na commonly present in rocks were left in solution, much larger exchange capacities and hence larger columns and correspondingly larger amounts of HCl eluent would be necessary. Excessive increase of the already large HCl volumes was avoided in order to keep to a minimum the RE contamination introduced by reagents. The double ammonia precipitation requires only a small amount of reagent and removes practically all Na, K, Ca, Mg, Sr, and Ba. The small amounts conceivably remaining are removed in the cation exchange step, and if necessary, later by the 0.05N HCl eluent added initially in the post-irradiation DEP chromatography. Essentially complete elimination of aluminum is the most critical function of the cation exchange step, because Al resembles the RE in its behavior on the DEP column, and it might overload it, since the total exchange capacity of this column is rather small. Of all elements that are precipitated with ammonia, Al is closest to the RE in the sequence of elution from the cation exchange column, and therefore the performance of these columns is evaluated on the basis of their capability to separate Al from the RE.

Removal of Chlorides

The M.I.T. Nuclear Reactor staff required removal of chlorides before all irradiations in order to eliminate any possibility of halogen spillage inside the pneumatic tube facility. This possibility is remote when proper packaging is employed.

Determination of Chemical Yields

Chemical yields were determined directly only for Y and Ce. However, the yields of both were invariably above 90%, and fractionation between these two elements (which differ chemically more than any other rare-earth pair) was usually about ±3% and indicated no consistent trend. Differences in yields of the other RE should therefore be even smaller, and considering that the precision of the method is approximately ±10%, such differences are not significant.

Post-Irradiation Chromatography

The chromatographic columns were found to give quantitative recovery of Ce^{139} and Y^{88} added to a carrier solution containing all of the RE. As an additional check, the Ce and Y fractions from two irradiated sample solutions were saved until the reactor-induced activities had decayed completely. The fractions were then combined and reduced to the 1-ml volumes of the reference tracer solutions. The yields were found to be 96±2%. When the possible losses in combining these fractions were considered, it was decided that the pre-irradiation chemical yields were a satisfactory measure of the overall yields for the procedure. Determination of post-irradiation yields was more time-consuming. The additional laboratory time required was undesirable since fewer samples could be analyzed, and only a relatively minor improvement would be obtained in the overall accuracy and precision of the procedure.

Counting

It was a definite advantage to gamma count the lighter RE and beta count the heavier ones. Selective gamma counting with the pulse height analyzer markedly improved resolution of some neighboring RE (e.g. Ce-Pr). In addition, spectra could be inspected for positive identification.

The much smaller amounts of induced activities of the heavy lanthanides made beta counting desirable because of the markedly lower backgrounds (particularly important for Tm).

Precision and Accuracy

The precision of the method varied from about ±4% to ±12% for the different RE as can be seen in Table II-4. Two independent sources contribute to the random error: the DEP-Celite columns and the counting statistics. The reproducibility of the columns is ±3-5% for all elements (except Ce) as indicated by the precision test on identical elutions of pure RE (Table II-3, last column). The same test shows that monitoring the chemical yields of only Ce and Y, rather than that of each RE individually, is not a source of any considerable error.

Since equal counting times were used regardless of sample activity, the counting errors depended on the absolute amount of each element, the abundances of its isotopes which capture thermal neutrons as well as the corresponding cross sections, and the half-lives of the resulting radionuclides. Thus the counting errors ranged from 0.3% to greater than 10%. They could be improved by taking longer counts, but this was not necessary for the purposes of this study.

The overall errors are a combination of the chromatographic separation errors and the counting errors; they can partly cancel or add up at random.

The estimate of precision is based entirely upon duplicate analyses of identical sample solutions. The spread of results on duplicates of powdered rocks was so much larger than with the identical solutions, that it was evident that these "duplicates" were actually not identical. The RE can be distributed very unevenly among the minerals in a rock (particularly among the accessory minerals), and therefore a lack of complete homogeneity, even in < 200-mesh powder, is quite plausible. When the general relative distribution pattern of all the RE in a sample is of greater interest than their absolute concentrations, even ±20-30% errors on individual RE are quite tolerable, and therefore no additional effort was expended to grind the samples to complete homogeneity.

Comparison of the processed and unprocessed RE solutions (Table II-3) as well as the spiking test (Table II-6), and comparison of the results on the same samples analyzed Schmitt (Kilauea Iki basalt, 4), Haskin (G-1 granite, 8), and by the authors indicate that the accuracy of the method is comparable to its precision.

Sensitivity and Applicability

The sensitivity of the method is, for practical purposes, determined largely by the available amounts of samples and the reactor facilities. Prolonging the irradiation does not require working with excessive total activities, since the solution which is irradiated contains essentially only the RE (and blank impurities). The limits of detection for a one-hour irradiation in the neutron fluxes used for this study are given in Table II-8. From these data, the required irradiation time in any flux and for any sample size can be calculated. Activities 100 to 10,000 times the limits of detection are convenient when 0.4-1.0 minute counting times per fraction are used. This range gives satisfactory counting statistics at the lower limit, and its higher limit is set by DEP column-overload considerations.

Practical considerations, such as the expenses involved and the reactor facilities, will determine the limit of detection attainable in an individual case. Prolonged irradiations are costly, and very large initial samples will require more time for the chemical processing, as well as larger amounts of reagents. The latter will result in higher reagent blanks. The blanks are, therefore, the chemical limiting factors on the lowest concentration of RE that can be determined. As can be seen from Table II-7, blanks in this work were quite low, even though ordinary distilled water and commercial reagent grade HCl were used. Both could readily be purified further and yield much lower blanks. Obtaining lower reagent blanks became necessary in the present authors' work only with sea water samples, where the RE concentrations were in the 10^{-10} to 10^{-11} g/liter range, and the blank values approached 20% of the total RE.

Table II-8
Limits of Detection* Using a 1-Hour Irradiation in a Thermal Neutron Flux of 8 x 10^{12} n/cm^2-sec

Element	Atomic number	Limit of detection, μg
La	57	0.005
Ce	58	0.8
Pr	59	0.06
Nd	60	0.6
Pm	61	---
Sm	62	0.001
Eu	63	0.0005
Gd	64	---
Tb	65	0.02
Dy	66	0.0005
Ho	67	0.006
Er	68	---
Tm	69	0.01
Yb	70	0.01
Lu	71	0.003
Y	39	0.03

* Limit of detection is defined as net count = background.

Thorium and zirconium are only partly separated from the RE by this method, and a means of removing them would be required when milligram quantities of either were present in a sample.

The procedure is applicable to most materials, including all kinds of rocks, organic matter, and natural waters.

Advantages of the Method

1) Irradiation of samples and standards in aqueous solutions

Since all solutions are homogeneous, there can be no self-shielding errors introduced during the irradiation. Such errors could be very serious in samples in which the RE (with many nuclides having high thermal cross sections) are inhomogeneously distributed.

2) Overall speed

Concurrent chemical processing of three samples took three days (about one third in actual working time). Post-irradiation chromatography of three samples and one standard required the full-time work of two analysts for 8-10 hours. Preparation of beta sources and subsequent counting required the work of two analysts for two days. Another 10-15 hours were used to resolve the raw data. In practice, two analysts working jointly could complete a maximum of three RE analyses per week (apparently about half the time required by similar methods currently in use). Counting the column effluent directly in flow by continuous recording (see below) could reduce the working time appreciably.

3) Fast RE separation

A complete separation of the RE took 3-4 hours. Under these conditions, even the 2.3-hour Dy^{165} was ready for counting when a considerable part of its activity remained. Other methods of RE separation take much longer, and correspondingly larger total amounts of RE must be used in order to obtain sufficient Dy activity at the time when it can be counted.

4) Chemical separation of the RE before irradiation

This gives the advantage of working with only low-level radioactivities. It is also a basis for the extension of the method to more varied sample types, since the post-irradiation procedures will remain unchanged.

5) Positive identification of the individual RE and checks for cross-contamination

These are rapidly made for all the elements which are gamma counted with the pulse height analyzer.

Some Possible Improvements

1) Determination of Gd

The gadolinium content can be calculated from the counting data. The ratio of the high-energy gamma activity (> 0.75 Mev) to total gammas of irradiated pure Eu should be determined. Then the total gamma activity contributed by the Eu in any sample can be calculated from the observed high-energy gammas (emitted only by Eu^{152m}). This would be subtracted from the total gamma activity actually recorded in all fractions containing Eu and Gd. The difference is contributed by Gd only, and it will be a rather small difference between two large numbers. However, it should still give a precision no worse than ±30%. It was not done in this study since the major application was in the establishment of over-all group trends. The time saved was considered more important than the additional information on one isolated rare-earth element.

2) Determination of Er

Erbium, which is eluted with yttrium, could be determined in a manner very similar to Gd. Total beta activity of Y and Er and the high-energy betas emitted only by Y^{90} would be counted. The precision here would be poorer, however, because the picture is complicated by the high-energy gammas emitted by the Y^{88} tracer (about 1% of which are recorded as betas).

3) Improvement of precision

Better resolution in the DEP chromatography can be obtained by increasing the volume of each acid used in the elution; this will most probably improve the precision of the chromatographic step. Fractions containing elements with low specific activity can be counted longer to obtain better counting statistics. These measures were not taken in the present work since the precision actually obtained was satisfactory for its purpose and additional time would be required.

4) Reduction of working time

Elimination of much of the manual counting and calculations can be attained. The eluent could be pumped into the column by a precision pump delivering the liquid at an accurately-controlled rate. The effluent could be passed into a 1/32-in. teflon tube (thin enough to prevent mixing) coiled in the well of a scintillation crystal. The tube would then run from the crystal to the fraction collector. The radioactivity could then be continuously counted by a precision ratemeter and recorded on a chart recorder. The area of each peak would be proportional to the amount of the corresponding element. The fractions which were counted selectively in this study could then be combined and counted as one fraction; the same could be done with the beta-counted elements. In this way, the manual summations will be eliminated. The automation will cut the working time approximately in half and remove the most tedious part of it. It will also give an immediate check on column performance (i.e. while an elution is in progress).

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CHAPTER III

RARE-EARTH ABUNDANCES IN THE STANDARD GRANITE G-1 AND STANDARD DIABASE W-1

Abstract. The rare-earth contents (exclusive of Gd and Er) of the standard granite G-1 and standard diabase W-1 have been determined by neutron activation and partition chromatography. The results are, for the most part, in rather close agreement with the data of Haskin and Gehl (1). The most significant discrepancy is between the Eu values in G-1. The abundance of this analytically-sensitive element was found to be approximately 20% higher in this study.

The first essentially-complete determinations of rare-earth abundances in the standard granite G-1 and standard diabase W-1 have been made recently by Haskin and Gehl (1) who employed neutron activation analysis. Prior to this, the published rare-earth abundances (2) in these two standard rocks consisted primarily of optical spectrographic determinations of La and Y. Chase et al. (3) determined La, Eu, and Dy by neutron activation analysis , and Hamaguchi et al. (4) have reported values for La, Sm, and Eu using a similar technique.

In this study, a quite different analytical procedure has been employed using group isolation of the rare earths and yttrium, followed by neutron activation and partition chromatography. Gadolinium and erbium were not determined. Accuracy and precision were approximately ±10%. The details of this procedure will appear elsewhere (5).

A 0.500-g sample of each rock was dissolved using a mixture of perchloric and hydrofluoric acids. Following ammonia precipitation, the rare earths were isolated as a group by ion exchange. Chemical yields were measured at this stage using Ce^{139} and Y^{88} carrier-free tracers. Two aliquots of each sample solution and two solutions of rare earths in known concentrations were irradiated by pile neutrons in thermal fluxes of approximately 8 x 10^{12} n/cm^2-sec. The irradiated sample and standard solutions were chromatographed by gradient elution with hydrochloric acid on columns of refined diatomaceous silica coated with di-(2-ethylhexyl)-orthophosphoric acid. Induced gamma radioactivities were counted by means of a 400-channel pulse height analyzer and a well-type, 1-$^3/_4$ inch by 2-inch NaI(Tl) scintillation crystal. Betas were counted with a standard end-window flow-proportional counter.

Rare-earth concentrations determined from duplicate irradiations of aliquots of the G-1 and W-1 sample solutions (corresponding to known proportions of the original 0.500-g samples of each) are shown in Table III-1 and Table III-2, respectively. The analytical precision for each rare earth has been calculated from the precision observed in a series of duplicate runs on other samples; accuracy and precision were found to be comparable (5). For comparison, the results of Haskin and Gehl are also shown.

The agreement between this work and that of Haskin and Gehl, who used a quite different analytical procedure,

Table III-1
Rare-Earth Content (ppm) of Standard Granite G-1

Element	This study	Haskin and Gehl (1)
La	92.4 ± 3.1	102 ± 7.7
Ce	150 ± 24	134 ± 13
Pr	12.9 ± 1.4	20.9 ± 0.32
Nd	55.2 ± 5.5	54.6 ± 1.5
Sm	8.25 ± 0.01	8.6 ± 0.56
Eu	1.36 ± 0.05	1.04 ± 0.11
Gd	- - -	4.88 ± 0.13
Tb	0.637 ± 0.057	0.50 ± 0.01
Dy	2.52 ± 0.10	- - -
Ho	0.408 ± 0.016	0.50 ± 0.01
Er	- - -	1.40 ± 0.14
Tm	0.156 ± 0.011	0.20 ± 0.02
Yb	0.937 ± 0.075	0.625 ± 0.06
Lu	0.123 ± 0.007	0.17 ± 0.02
Y	13.3 ± 1.6	12.5 ± 0.25

Table III-2
Rare-Earth Content (ppm) of Standard Diabase W-1

Element	This study	Haskin and Gehl (1)
La	9.31 ± 0.37	11.7 ± 1.21
Ce	15.1 ± 2.4	24.3 ± 0.24
Pr	3.51 ± 0.39	3.68 ± 0.19
Nd	20.2 ± 2.0	15.1 ± 1.4
Sm	3.46 ± 0.03	3.79 ± 0.32
Eu	1.29 ± 0.05	1.09 ± 0.12
Gd	- - -	4.2 ± 0.35
Tb	0.807 ± 0.073	0.75 ± 0.075
Dy	4.38 ± 0.18	- - -
Ho	0.855 ± 0.034	1.35 ± 0.11
Er	- - -	2.57 ± 0.26
Tm	0.332 ± 0.023	0.355 ± 0.005
Yb	2.23 ± 0.18	2.10 ± 0.01
Lu	0.348 ± 0.021	0.325 ± 0.033
Y	28.0 ± 3.4	23.8 ± 0.12

is quite remarkable when the wide differences between other published results are considered. The results of this study and those of Haskin and Gehl are statistically the same for La, Ce, Nd, Sm, and Y in G-1 and likewise are essentially identical for Pr, Sm, Tb, Tm, Yb, and Lu in W-1. For most other rare earths, the agreement is excellent. The only really significant differences are with Pr, Eu, and Yb in G-1 and with Ce and Ho in W-1. Although the absolute discrepancy between the Ce values in W-1 may seem large, it must be remembered that the Ce precision in this study was worse than for any other rare earth.

The most notable discrepancy is between the Eu values in G-1. Analytically, the Eu data should be among the most accurate by both methods. Chase et al. (3) found La = 142 ppm and Eu = 1.42 ppm in G-1 which yields the same La/Eu ratio as obtained by Haskin and Gehl. The latter believe that Eu is about 20% low versus the behavior predicted when the rare-earth abundances are normalized to those in chondritic meteorites (6) or the assumed crustal average found in sediments (7). Since the Eu value of Haskin and Gehl is also approximately 20% lower than the value obtained in this study and the Sm values are identical, the authors conclude that Eu is normal in the sample of G-1 analyzed.

Haskin and Gehl (1) have pointed out that the large differences in the reported rare-earth contents of G-1 and W-1 may indicate sample inhomogeneities with respect to the rare earths. The authors believe that this, indeed, may be true.

Consequently, the excellent agreement observed between the rare-earth concentrations in these two studies may be somewhat fortuitous. The relative concentrations, however, may be rather constant from sample to sample, provided sample sizes are not too small. In such cases, an excess of a specific rare-earth-concentrating accessory mineral might produce a non-representative distribution. With this in mind, it would be profitable to look at rare-earth distributions (and distributions of other trace elements as well) of individual minerals from G-1 and W-1 (8,9).

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8. W. H. Pinson, Jr. donated the samples of G-1 and W-1.

9. This investigation was supported by the U. S. Office of Naval Research under Contract Nonr 1841 (74).

PART II

APPENDIX A

A REVIEW OF PERTINENT LITERATURE ON RARE-EARTH DISTRIBUTIONS

Introduction

The rare-earth elements have stimulated the interest of geochemists for many years. In addition to the lanthanides, La through Lu (atomic numbers 57 through 71), yttrium (atomic number Z = 39) has also been studied with the rare earths because of its close geochemical affinity to the latter.

Outline of Previous Work

Outlines of rare-earth geochemistry have been presented by Goldschmidt (1954) and Rankama and Sahama (1950). The first author assumed that the rare earths migrated as a geochemical "entity" because of their very similar chemical properties.

Under most geological conditions, the rare earths are trivalent, although under reducing conditions Eu may be divalent and in highly oxidizing environments Ce may be tetravalent. The successive filling of the 4f electron shell results in a progressive decrease in ionic radius from La to Lu which is commonly referred to as the "lanthanide contraction". The essential uniformity in oxidation state and the systematic change in ionic radii make rare-earth distributions extremely useful as geochemical indicators.

Rare-earth geochemistry has actually been studied from two aspects. By far, most work has been in the field of rare-earth distributions in coexisting minerals, and more specifically, in relatively rare, accessory minerals which concentrate large amounts of rare earths. The reasons are partly due to the early absence of analytical methods with the necessary sensitivity to study common rock-forming and accessory minerals, and partly economic; the rare, naturally-occurring rare-earth minerals and other minerals which are enriched in the rare earths are of high commercial value. Studies of minerals which concentrate rare earths have been made by numerous authors including Goldschmidt and Thomassen (1924), Bjørlykke (1935), Sahama and Vähätalo (1939a, 1939b), Vainshtein et al. (1956), Butler (1957a, 1957b), Butler (1958), Seminov and Barinskii (1958), Vainshtein et al. (1958), Murata et al. (1959), Borodin and Barinskii (1960), Balashov and Turanskaya (1961), Borodin and Barinskii (1961), Zhirov et al. (1961), and Lyakhovich (1962).

The study of rare earths in the normal rock-forming minerals has been extremely limited. Apparently the first complete rare-earth study of the coexisting rock-forming and accessory minerals of granites was made by Gavrilova and Turanskaya (1958). Also of interest are the results of Chase et al. (1963), who determined La, Eu, and Dy distributions of coexisting feldspars and micas from three northeastern North American granites.

The second and much less extensively studied aspect of rare-earth geochemistry has been with respect to rocks and meteorites. This was largely because of analytical problems. By far, the most important early works were those of Noddack (1935) on composite mixtures of chondritic and achondritic meteorites (12 parts chondrite to 1 part achondrite) and Minami (1935) on Japanese and European shales. Both authors used X-ray spectrographic methods of analysis. Comparison of their results indicates that the relative abundances of the light rare earths compared to the heavy rare earths are approximately six times greater in the shales than in the meteoritic composite.

Twenty-five years later, Schmitt et al. (1960), employing neutron activation analysis, found that the relative rare-earth abundances of two chondrites agreed with the results of Noddack to within 30%, although the absolute values of these authors were about six times smaller. Subsequently, Schmitt (1963) and his co-workers have analyzed 17 chondrites and a wide variety of other meteorites. The rare-earth contents of the chondrites were found to vary within a relatively small range on both an absolute scale (factor of 3) and a relative scale (30%).

Haskin and Gehl (1962) determined the rare-earth abundances in a series of sandstones, limestones, and shales by a method very similar to that used by Schmitt et al. Haskin's and Gehl's results were in essential agreement with those of Minami (1935).

Goldschmidt (1954) interpreted the results of Minami to indicate that, although fractionation of the rare earths may occur during igneous processes, these elements are subsequently homogenized by the processes of weathering, erosion, and sedimentation. He believed that the average rare-earth content of sediments was a true measure of their average relative crustal abundances. Goldschmidt observed, in fact, that although europium was frequently low in pegmatitic environments (apparently due to reduction at some stage to the divalent state), it was not low (compared to its near-neighbor rare earths) in Minami's shales.

Suess and Urey (1956) tabulated the solar abundances of all the elements based to a large extent on chondritic meteorites. The latter are believed by many to represent the best-available sources of the undifferentiated, nonvolatile material from which the solar system was formed. Suess and Urey based their rare-earth abundances largely upon the results of Minami, which were more generally accepted as the true rare-earth distribution. Burbidge et al. (1957) have studied the formation of the elements by different processes in stars, and in addition discuss synthesis of the rare earths in terms of the abundances given by Suess and Urey. Cameron (1959a), however, adopted the results of Noddack on chondrites and published a revised set of rare-earth abundances. Taylor (1960, 1962) has discussed these differences between meteorites and terrestrial rare-earth abundance patterns. Schmitt et al. (1960, 1962) experimentally confirmed that the relative rare-earth abundances of Noddack were indeed the true chondritic abundances (although the absolute abundances were reduced by factors of about 6). Haskin and Gehl (1962) also demonstrated that if sediments are a true average of crustal rare-earth distributions, then the rare earths are nearly an order of magnitude more abundant in the crust than in the chondritic meteorites, and at the same time they are quite strongly fractionated (up to a factor of 6) favoring the lighter rare earths when compared to chondrites. Taylor (1962) has concluded that the earth as a whole contains similar relative amounts of rare earths to those found in chondrites, and that those of lower atomic number have been selectively enriched in crustal rocks. He paid particular attention to the data of Sahama (1945) on calcic igneous rocks which showed relative rare-earth abundance patterns similar to the chondritic patterns.

There are practically no available data on rare-earth distributions in suites of genetically-related differentiated igneous rocks. Sahama and Våhätalo (1939a) studied the rare earths in acid dikes and pegmatoids in the diabases of Säppi and Walamo, Finland. However, some uncertainty in the quality of the analyses and in the geologic field relationships makes interpretation of their results difficult. Some differentiated alkaline massifs of the Soviet Union have been quite extensively studied in recent years. The reader is referred to the studies of the Lovozero alkalic massif of the Kola Peninsula by Balashov and Turanskaya (1961) and Balashov (1962). Zlobin and Balashov (1961) have also investigated rare-earth distributions in the five different rock types of the Sandyk alkalic massif of northern Tien Shan.

In summary, the published rare-earth data show that individual minerals may be extremely selective or non-selective in their rare-earth assemblages, whereas the rare-earth distributions found in rocks vary between much smaller limits. The major bulk of the rare earths tend to be concentrated in the final stages of magmatic differentiation. Consequently, most rare-earth minerals and accessory minerals which concentrate large amounts of rare earths are found in pegmatites or highly-alkaline rocks. Nearly all crustal rocks are fractionated rather smoothly favoring the rare earths of lower atomic number when compared to a chondritic rare-earth model of the earth (or mantle). Basic rocks exhibit more-uniform distributions and generally are least fractionated. Granites are extremely variable and the light rare earths may be fractionated by as much as two orders of magnitude compared to chondrites, whereas basic rocks are generally fractionated by factors of less than five.

Europium and cerium may be in some instances anomalous when compared to adjoining rare earths. This may be attributed to the presence of Eu^{+2} and Ce^{+4} as opposed to the common trivalency of the rare earths. Europium is commonly low in pegmatites and in many granites. In such granites, the micas are relatively depleted in europium versus the feldspars. Diadochic replacement of Sr^{+2} by Eu^{+2} has been noted in minerals high in strontium.

Interpretation of Rare-Earth Abundances

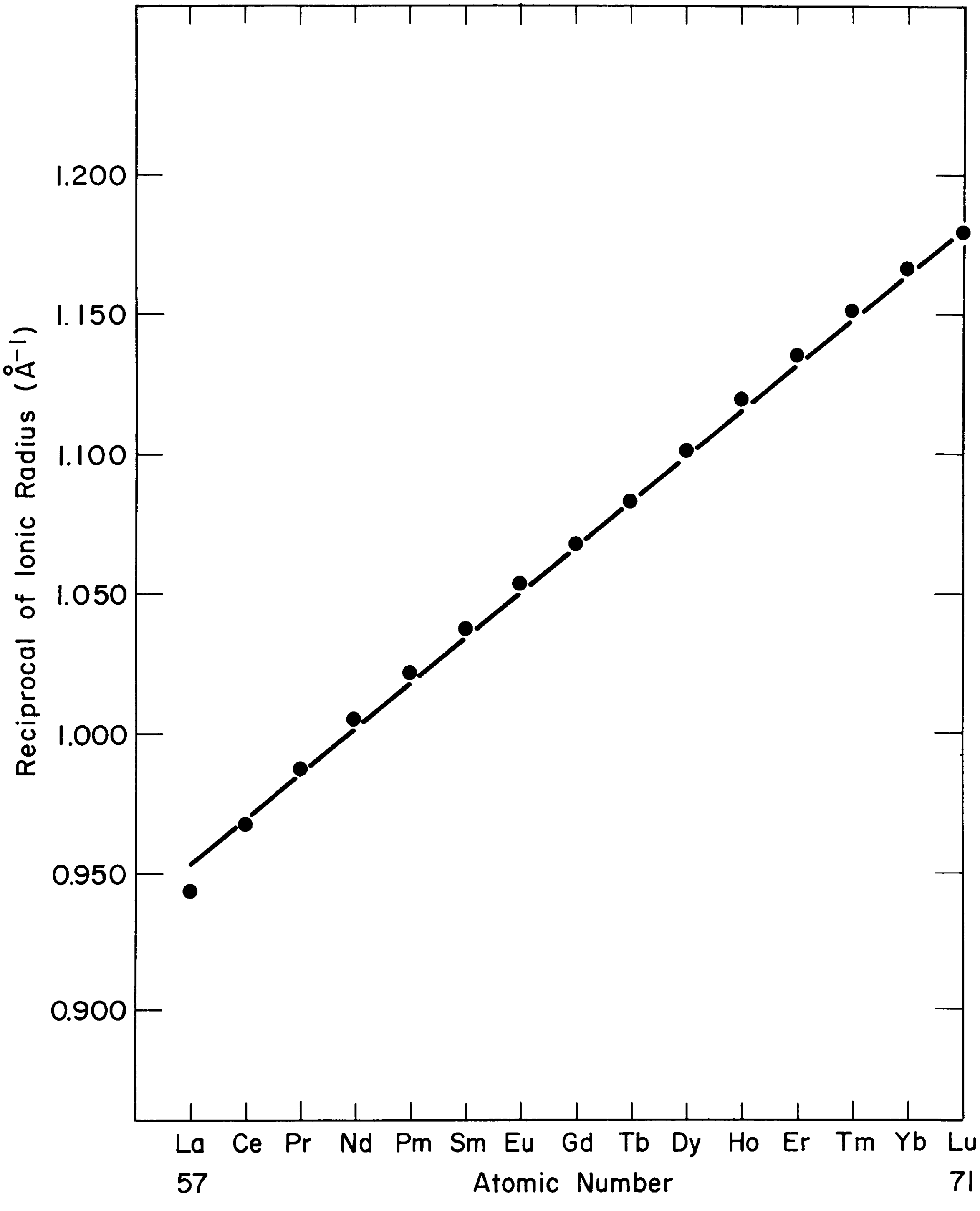
Most explanations of rare-earth abundances in rocks and minerals have been based upon the essential constancy of charge (trivalent, with possible exceptions being Eu^{+2} and Ce^{+4}) and the quite smooth decrease in ionic radius with increasing atomic number (lanthanide contraction). Several authors have given ionic radii for the rare-earth elements including Goldschmidt (1926), Ahrens (1952), Templeton and Dauben (1954), and Pauling (1960). Pauling based his radii directly upon those of Templeton and Dauben, but there is an unexplained systematic difference between these two sources. There are also non-systematic differences between the ionic radii of different authors. In Table A-1 are shown the rare-earth radii of Templeton and Dauben (1954). The inverse radii are also given. A plot of these reciprocal ionic radii versus atomic number is given in Figure A-1 and is essentially the same as given by Masuda (1963b). The plot is approximately linear and clearly demonstrates the effect of the lanthanide contraction. The radius of Eu^{+2} is essentially the same as La^{+3} and Sr^{+2}, while the radius of Ce^{+4} is about the same as Eu^{+3}.

There are, of course, many other considerations besides ionic radius and charge. In fact, the concept of ionic

Table A-1
Rare-Earth Ionic Radii and Reciprocal Ionic Radii
(after Templeton and Dauben, 1954)

Element	Atomic number	Ionic radius (Å)	Reciprocal ionic radius ($Å^{-1}$)
La	57	1.061	0.943
Ce	58	1.034	0.967
Pr	59	1.013	0.987
Nd	60	0.995	1.005
Pm	61	0.979	1.021
Sm	62	0.964	1.037
Eu	63	0.950	1.053
Gd	64	0.938	1.067
Tb	65	0.923	1.083
Dy	66	0.908	1.101
Ho	67	0.894	1.119
Er	68	0.881	1.135
Tm	69	0.869	1.151
Yb	70	0.858	1.166
Lu	71	0.848	1.179

Fig. A-1. Reciprocal ionic radii of the rare earths plotted as a function of atomic number (after Masuda, 1963b).



Reciprocal of Ionic Radius (Å⁻¹)
1.200
1.150
1.100
1.050
1.000
0.950
0.900
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
57
Atomic Number
71

radius tends to lose its meaning when dealing with highly-polymerized melts which are so complex in nature. Certainly many elements which can be simply ionic under ordinary aqueous conditions may be bound in complexes when present in silicate melts. Balashov (1962), in discussing the Lovozero massif, pointed out that during differentiation of the alkaline magma, the complexes of the heavier rare earths (i.e. the "yttrium earths") became progressively more stable in the melt. Consequently, the later phases are less-strongly fractionated (in contrast to the observation made in Part I, Chapter I, that fractionation increases during normal differentiation of basaltic magma). The concept of the increased role of complex formation of elements with higher valency in alkaline magmas has been discussed by Ringwood (1955) on the basis of electronegativities.

Rare-earth distributions in minerals will, of course, also depend upon the coordination number of the rare earth positions in the crystal structures. The polarizability of the nearest-neighbor anion likewise will influence diadochic substitution, as will the polarizing power of the cations. In addition, it should be remembered that the nature of the bonding will vary from one silicate structure to another.

Coryell and Chase (1961) have recently proposed an intriguing mechanism capable of producing the observed anomalous europium distributions found in many granites, most pegmatites, and numerous minerals. Using a highly-simplified aqueous system, calculations from published thermodynamic data showed that in a sulfate redox system, europium could be removed as the divalent sulfate according to the following half-cell reaction:

$$EuSO_4(s) \rightleftharpoons Eu^{+3} + SO_4^{-2} + e^- \qquad E^o = -0.04 \text{ volts} \quad \text{(Latimer convention)} \qquad (A-1)$$

Also relevant is the half-cell reaction:

$$Eu^{+2} \rightleftharpoons Eu^{+3} + e^- \qquad E^o = 0.43 \text{ volts} \quad \text{(Latimer convention)} \qquad (A-2)$$

It can be seen from the above expressions that in the presence of excess sulfate (i.e. the presence of a sulfate precipitate) Eu^{+3} will be reduced and removed as the divalent sulfate much more easily than it can be reduced from Eu^{+3} to Eu^{+2}. This is equivalent to saying that in the sulfate system, the stability field of Eu^{+3} is markedly reduced, so much so in fact, that it can be reduced under conditions which might be considered geologically as being weakly oxidizing. Coryell and Chase (1961) estimate that the solubility product of $EuSO_4$ is intermediate between the values of $10^{-6.1}$ for $SrSO_4$ and $10^{-8.8}$ for $BaSO_4$. Should Eu(II) be in solid solution in $(Sr,Ba)SO_4$, the resulting E^o of the half-cell corresponding to expression (A-1) will even be lowered slightly more.

The above considerations begin to carry added significance when it is realized that during magmatic processes barium tends to be concentrated in the later stages. Also, it has been found by Ricke (1960) that significant amounts of sulfate are present in most rocks. The proportion of sulfate to total sulfur generally increases in proceeding from basic to acidic igneous rocks. Ricke also found that in a study of three granites and one basalt, the feldspars were the preferred hosts for sulfate sulfur.

Empirical Methods

Various authors have observed empirical relationships in rare-earth distributions and have attempted to use them in interpreting rare-earth behavior. Masuda (1957) formulated an expression based upon the data of Vainshtein et al. (1956) on cerium minerals. A recent modification of the expression by Masuda (1962) yields the following empirical equation:

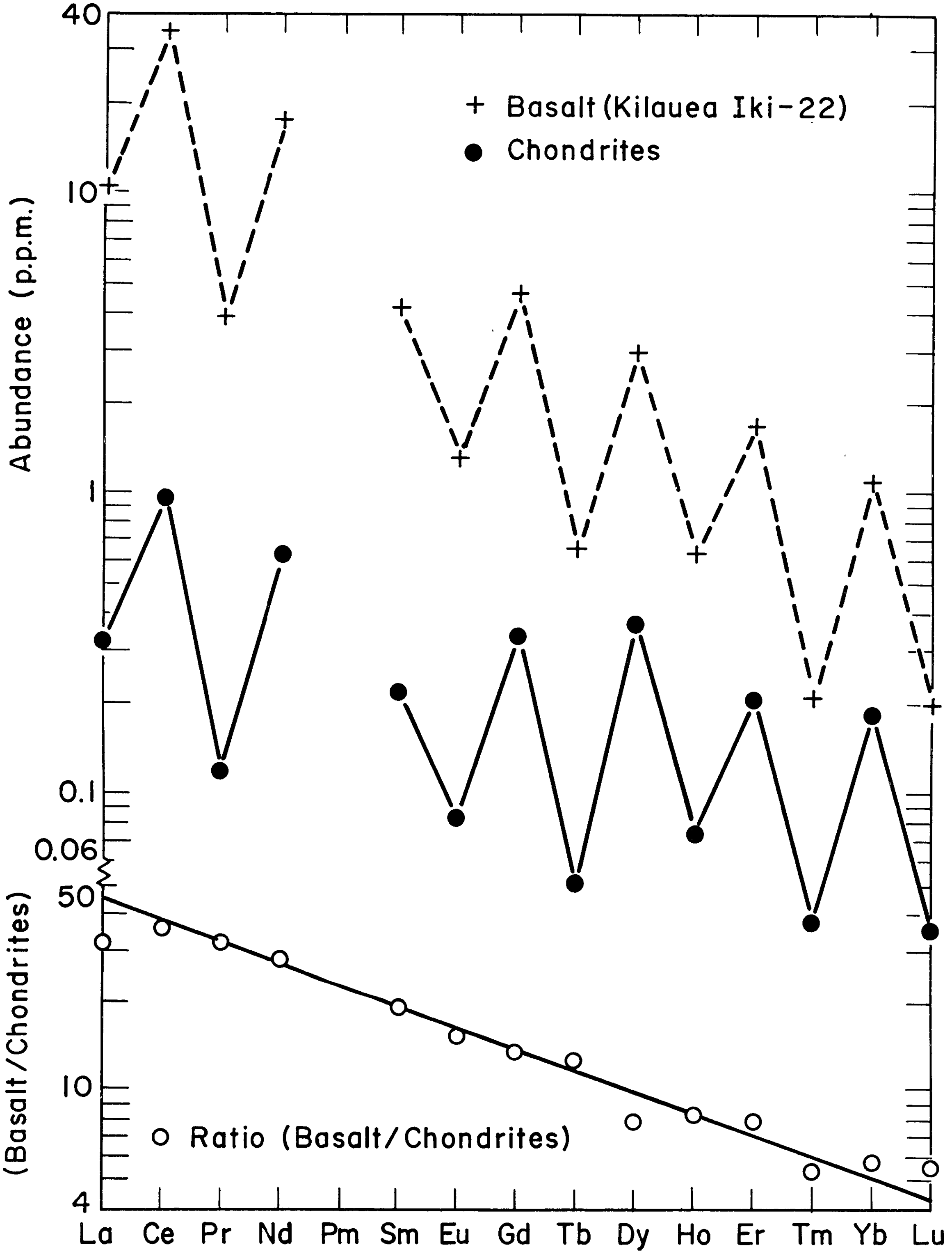
$$\log\ (E_i/\mathrm{La}) = \frac{i}{7} \log\ (\mathrm{Gd}/\mathrm{La}) + c_i \qquad \text{(A-3)}$$

where E_i is the abundance of the i-th element from La in the periodic table (e.g. E_3 = Nd, E_8 = Tb) and c_i is a constant of integration, characteristic of E_i .

Matsui and Masuda (1963) have applied expression (A-3) to some selected rocks and meteorites with reasonable success. The data of Schmitt et al. (1961) on chondrites were used along with the latter's results on Kilauea Iki-22 basalt, Minami's (1935) abundances in shales, Gavrilova's and Turanskaya's (1958) data on the Kirovograd granite, and the rare-earth abundances in Black Sea sediments (average) given by Ostroumov (1953). Matsui and Masuda point out that their formulation was applied only to the lighter rare earths, and that extension to the yttrium earths is still a matter of conjecture. It was their observation (in accordance with those of other authors) that crustal rare-earth distributions could be derived from chondritic distributions by magmatic differentiation. The amount of fractionation of the lighter rare earths seemed to parallel increase in acidity.

Coryell et al. (1963) and Masuda (1962) have independently proposed a very useful procedure for geochemical interpretation of terrestrial rare-earth abundance patterns. The systematic behavior of the rare earths is somewhat obscurred when absolute abundances are considered. This is because of the natural irregularities inherited from their original cosmochemical production. The reader is referred to papers by Burbidge et al. (1957), Cameron (1959b), Taylor (1960), and Coryell (1961) for discussions of these irregularities. Figure A-2 is taken directly from Coryell et al. (1963). In the upper portion of this figure, the absolute rare-earth abundances of Kilauea Iki-22 basalt (Schmitt and Smith, 1961) and mean of two bronzitic chondrites (Schmitt et al., 1960) are plotted on logarithmic scale versus atomic number. The zig-zag pattern is quite apparent. However, when the ratio of the basalt-to-chondrite abundance for each rare earth is plotted on the same scale, there is increased order (there is no point for promethium since this

Fig. A-2. Abundances of the rare-earth elements in the basalt Kilauea Iki-22 (broken line) and mean of two chondrites (solid line) plotted on a logarithmic scale as a function of atomic number. The lower curve gives the ratios of the rare-earth abundances in the basalt to the corresponding abundances in chondrites (after Coryell et al., 1963).



40
10
1
0.1
0.06
50
10
4
Abundance (p.p.m.)
(Basalt/Chondrites)
+ Basalt (Kilauea Iki-22)
● Chondrites
○ Ratio (Basalt/Chondrites)
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

element has no stable isotope). The smooth distribution, thus obtained, was approximated by a straight line. In making plots such as these, the relatively small enrichments and depletions of individual rare earths can be spotted much more readily (e.g. Eu and Ce). The chondrites serve as perhaps the best choice for normalization of terrestrial samples since (1) they are considered by many authors to represent the best presently-available sources of the undifferentiated, nonvolatile primary material of the solar system; and (2) as of this writing, 17 different chondrites have been analyzed for rare earths (see Schmitt, 1963), and their essential uniformity in relative rare-earth abundances has been statistically well-established.

Coryell et al. (1963) applied this chondrite-normalization technique to a large number of published analyses of rare-earth minerals. They also applied this method of analysis to the data of Gavrilova and Turanskaya (1958) on the coexisting minerals in the Kirovograd granite of the Ukraine. By adding the normalized rare-earth abundances of all the various minerals (each mineral weighted according to its modal abundance) the apparent whole-rock distribution of the Kirovograd granite was obtained. This distribution approximated a straight line.

Assuming that approximately straight-line distributions (such as observed in Kilauea Iki-22 and the Kirovograd granite) were common in other igneous rocks, Chase et al. (1963) plotted normalized La, Eu, and Dy abundances in the above manner for three oceanic basalts, one diabase, and four granites. The authors used the La/Dy ratios as measures of overall rare-earth fractionation. They estimated Eu anomalies by the amounts which the Eu values deviated from arbitrary straight lines between La and Dy. On this basis, it was concluded that the oceanic basalts were substantially fractionated by similar amounts favoring the lighter rare earths versus the chondrites (e.g. La/Dy ppm ratios were observed to be 7.2, 6.7, and 4.5). Europium appeared to be normal. The implication was that the basalts were formed by similar processes from source materials with similar rare-earth distributions.

The granites analyzed by Chase et al.(1963), however, had widely-different La/Dy ratios, ranging from 1.3 to 63 . The suggestion was that different processes are operative in the origin of different granites (which is consistent with geologic observation). Europium was found (using the straight-line criterion) to be low in all four granites, suggesting divalent behavior. In feldspar and mica concentrates from the granites, it was found that Eu was invariably enriched in the feldspars relative to the coexisting micas. Chase et al. nevertheless pointed out that the apparent Eu anomalies in the granites could be significantly reduced if the overall rare-earth distribution exhibited a flattening-out over those elements past Eu.

More-recent complete rare-earth analyses have shown, indeed, that in many rocks, fractionation of the heavier rare earths versus chondrites is absent and sometimes even shows a reversed trend. Thus the normalization curve may bend smoothly through Eu, indicating that Eu is normal with respect to the adjacent rare earths, even though it would fall below an arbitrary straight line between La and Dy. Haskin and Gehl (1963) have emphasized that caution must be observed when deducing Eu or Ce anomalies without some knowledge of the overall shape of the distribution curve (i.e. numerous rare earths must be determined, especially those nearest to Eu and Ce).

Haskin and Gehl (1962, 1963), Schmitt and Smith (1962), and Schmitt (1963) have preferred to plot the chondrite-normalized data versus ionic radius rather than atomic number. Because of the discrepancies between the ionic (or "crystal") radii of different authors, and because the actual effective radii in silicates may be quite different, this author has chosen to use atomic number as the abscissa. In addition, it has been shown that atomic number and reciprocal ionic radius are approximately linear. The latter parameter is a measure of relative energy and perhaps for this reason alone, bears greater significance than the ionic radius.

Two Recent Models of Rare-Earth Differentiation

Schmitt (1963) has adopted a shell model for a single-parent meteoritic body based upon earlier models by Fish et al. (1960) and Ringwood (1961). Schmitt and his co-workers have obtained complete rare-earth, yttrium, and scandium abundances for a total of 32 meteorites (including all major classes). All chondrites (except one class of carbonaceous chondrites) and Ca-rich achondrites showed the same rare-earth distribution. Over 90% of observed falls can be classified into these two categories. Each shell was weighted according to the proportion of its members in the total number of falls. The model consists of an inner Fe-Ni core followed outward by a pallasitic layer (0.6%), Ca-poor achondritic layer (2.5%), chondritic layer (86%), Ca-rich achondritic layer (4.8%), and a carbonaceous chondritic layer (2.5%) at the surface. Scattered over the surface are nakhlitic achondrites. The absolute rare-earth abundances increase progressively outward from the core. The iron meteorites (core) analyzed were found to contain only about 10^{-4} as much of each rare earth compared to the chondrites.

Below the chondritic shell, the lighter rare earths were generally unfractionated or else progressively depleted versus the chondrites. The heavier rare earths were generally unfractionated or else progressively enriched versus the chondritic layer. The Ca-rich achondrites had relative rare-earth distributions indistinguishable from the chondrites, but the absolute concentrations were approximately one order of magnitude greater. The nakhlites had relative rare-earth distributions indistinguishable from two terrestrial basalts, and were therefore considered to be of volcanic origin (petrographic observations also supported this conclusion).

Masuda and Matsui (1963) have recently proposed what they call a "geometrically progressional residual model as the explanation of lanthanide pattern variation." This model is conceived as applying to the development of a "proto-crust" and mantle and is to be distinguished from subordinate crustal differentiation. The authors assume that: (1) the earth's lithosphere was molten at some period; (2) the mantle and crust have been formed by successive solidification of the melt; (3) the partition coefficients for the lanthanide series elements were constant during all of the solidification stages (or if not constant, they must have maintained an arithmetically-progressional relationship); and (4) the initial terrestrial abundance ratios of the rare earths are given by the chondrite abundances. The latter two assumptions implicitly require that the chondrite-normalized abundances maintain logarithmically-linear patterns (e.g. Kilauea Iki-22). Using (1) Minami's (1935) abundance for La = 18.3 ppm in shales as the average crustal abundance of that element; (2) a "slope coefficient" = 1.17 (average ratio of chondrite-normalized values between adjacent rare earths in Minami's shales); and (3) a mass ratio of the lithosphere to the crust of 82 (after Bullen), the authors calculated the La content of the initial molten material to be 0.38 ppm. The agreement between this value and the 0.30 ppm found by Schmitt (1963) from the average of 17 chondrites is striking. Masuda and Matsui take this as strong evidence that the initial terrestrial material was chondritic with respect to its rare-earth distribution. However, they have not (as of this writing) attempted to quantitatively apply their model to the entire lanthanide series, apparently out of uncertainty as to the true average rare-earth abundances in the crust.

APPENDIX B

RELATED GEOLOGY AND SAMPLE DESCRIPTIONS

Geology of the Batholith of Southern California

The batholith of Southern California was chosen for this study of rare-earth distributions in differentiated igneous rocks for several reasons. First, it represents a large, geologically important, suite of plutonic rocks which has similar counterparts in other parts of the world. Prior to this investigation, the only reported studies of complete rare-earth distributions in differentiated igneous rocks were those relating to highly alkaline plutons in the Soviet Union; see, for example, the works of Zlobin and Balashov (1961) and Balashov (1962). The early work by Sahama and Vähätalo (1939) on the acid dikes and pegmatoids of Säppi and Walamo, Finland is suspect of analytical errors. All of the above authors used X-ray spectrographic methods of analysis.

An additional reason for choosing the batholith of Southern California is that it has been extensively studied. The most frequently quoted description of its geology is given in the classic work by Larsen (1948). The abstract of his Geological Society of America Memoir 29 is given below as an excellent summary of the general relationships.

> The batholith of Southern and Lower California is exposed continuously from near Riverside, California, southward for a distance of

about 350 miles. In central Lower California it is covered in part by younger rocks, but discontinuous bodies extend to the southern end of Lower California, and hence the batholith is probably over 1000 miles long. Its width is about 60 miles. A strip across the northern part of the batholith about 70 miles wide has been studied; the western half was mapped in detail, and the eastern half was covered in rapid reconnaissance.

In the area studied the batholith intrudes Triassic sediments and Jurassic(?) volcanic rocks along its western border and Paleozoic sediments along its eastern border. Screens and roof pendants are common within the batholith. The Triassic rocks are mildly metamorphosed in the western part of the area but become progressively more coarsely crystalline toward the east. The Paleozoic rocks are rather coarsely crystalline. The metamorphism in large part preceded the intrusion of the batholith and only locally was there appreciable contact metamorphism. The batholith and older rocks are overlain by Upper Cretaceous and younger sediments. Small bodies of andesite and basalt are associated with the Tertiary sediments, and small bodies of nepheline basalt of Quaternary age are present in the area. The batholith was intruded in early Upper Cretaceous time.

The batholith in the area studied was emplaced by over 20 separate injections. Most of the resulting rock types are found in only one or a few small bodies which are confined to a small area. In the area studied in detail five types are present in many large, widely separated bodies, making up about 88 percent of the area underlain by the batholith. In the eastern half of the batholith three more widespread types are present. In the western half of the body the rocks range from gabbro to granite, but in the eastern half several tonalites constitute nearly the whole of the mass. The gabbro is composed of many related rocks. Some have hornblende, some pyroxene; in some the plagioclase is anorthite, in others it is as sodic as andesine-labradorite. Some of the tonalites contain abundant inclusions that have been almost completely reworked by the magma and have been softened and stretched into thin disks. These inclusions are well oriented and near the contacts with older rocks they parallel the contacts, but elsewhere they strike about N.30°W. and dip steeply to the east. One tonalite, whose feldspar is andesine, has scattered crystals with cores of bytownite, and has well-crystallized hornblende with cores of pale uralitic hornblende and remnants of augite. Hornblende and biotite are the predominant mafic minerals of the tonalites and granodiorites. The iron content of the mafic minerals of the gabbros is moderate, and it increases as the rocks become richer in silica. The norms and the modes are shown on a variation diagram. The chemical analyses of the rocks fall near smooth variation curves.

The general strike of the structures of the area have been about N.30°W. from Paleozoic to the present time. The Paleozoic and Triassic sediments, the orientation of the inclusions and other structures of the batholith, the elongation of the batholith and the mountain ranges, and the strike of the major faults are in about the same direction. In the batholith and the older sediments the dips are steep to the east.

The batholith must have been emplaced by stoping and not by forceful injection. Calculations show that the cooling of a large batholith is chiefly through the roof and not through the walls. Crystallization to a depth of 3 kilometers takes place in about half a million years. The different rocks of the batholith were formed from the intermediate gabbro by crystal differentiation and assimilation in depth.

In early Upper Cretaceous time diastrophism folded the older rocks and formed, in depth, a strip of gabbroic magma about 1000 miles long. A small amount of this magma was intruded nearly to the surface. The deep magma differentiated quietly until its upper part attained the composite of a tonalite. Earth movements then occurred at least five times in rapid succession and caused the injection of the different tonalites. Some of these carry abundant inclusions, indicating a widespread shattering of the rock wall shortly before final emplacement. From time to time local movements caused the injections of the different granodiorites. When the deep-seated

> magma reached the composition of a light-colored granodiorite, widespread diastrophism moved the main granodiorite upward. Further local movement caused the emplacement of the many local granodiorites and granites.

Taylor and Epstein (1962a, 1962b) have recently studied oxygen isotopic variations in the batholith. They have furnished the majority of samples for this investigation. L. T. Silver collected the actual hand specimens and furnished both chemical and modal analyses for Taylor and Epstein. Description of these samples are given later in this section.

Taylor and Epstein (1962b) emphasized that caution was necessary when using their results to draw conclusions regarding the genetic relationships among the rock types of the batholith. Their data was based on but four hand specimens. However, their results were quite consistent with the geological observations and conclusions of Larsen (1948) A plot of O^{18}/O^{16} ratios versus the chemical composition of the four samples (using Larsen's variation index of weight percent $1/3\ SiO_2 + K_2O - CaO - MgO - FeO$) shows that the ratios progressively increase with increasing silica content. One might legitimately suggest that the observations are the results of temperature effects alone (the larger ratios indicating lower final temperatures of formation); however, the consistent sequence is also compatible with a mode of origin by magmatic differentiation at depth as advanced by Larsen. Taylor and Epstein have shown that the

San Marcos gabbro magma became enriched in O^{18} as the early-formed, O^{16}-poor, mafic minerals settled from the melt. This process would lead to successively higher O^{18}/O^{16} ratios in the more acidic differentiates.

On the basis of O^{18}/O^{16} ratios, Taylor and Epstein (1962b) suggested that both the Rubidoux Mountain leucogranite and Woodson Mountain granodiorite could represent direct differentiates from the Bonsall tonalite. At the same time, they emphasized that it is unlikely that the leucogranite could have been derived by simple fractional crystallization of Woodson Mountain granodiorite magma. This conclusion was supported by their observation that the granodiorite melt became isotopically lighter as solidification progressed. The melt which compositionally corresponded to the leucogranite (quartz monzonite) would have been 1 per mil or more lighter than observed in the Rubidoux Mountain sample. The authors also noted that the most O^{18}-rich rock of the batholith was the Ramona pegmatite which intrudes the Bonsall tonalite. However, it was significantly poorer in O^{18} than observed in pegmatites associated with granodiorites and quartz monzonites from other areas. For this reason, it was suggested that the Ramona pegmatite might conceivably represent a direct differentiate of Bonsall tonalite magma.

One of the most important uses of oxygen isotopic variations is in determining the order of crystallization of minerals from a magma. Although the mode of origin of the rocks studied may still be open to question, the isotopic data showed excellent agreement with the common geologic criteria that indicate a mode of origin by magmatic differentiation (fractional crystallization with incomplete reaction).

In the San Marcos gabbro, the first minerals to crystallize were calcic plagioclase, two pyroxenes and magnetite. The pyroxenes were isotopically lighter than the plagioclase, the latter having approximately the same isotopic composition as the magma (Taylor and Epstein, 1962b). The later hornblende and tiny amounts of quartz were heavier relative to the plagioclase than in the tonalite and quartz monzonite. Since augite was observed to be 0.7 per mil lighter than hypersthene, it was suggested that this was a clear indication that clinopyroxene was the first to begin crystallization. In a similar manner, it was shown that the apatite in the San Marcos gabbro began crystallizing at an earlier stage than it did in the Bonsall tonalite.

In the Bonsall tonalite, Taylor and Epstein found that the O^{18}/O^{16} ratios indicated that plagioclase, hornblende, and biotite were relatively early in forming, whereas quartz began to crystallize later. This is in close agreement with the probable sequence derived from textural criteria.

The Woodson Mountain granodiorite showed very interesting results. Taylor and Epstein noted that on the basis of composition, this rock falls inside the field of primary crystallization of quartz in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O (Tuttle and Bowen, 1958). Quartz and plagioclase would most likely have begun to crystallize first. Plagioclase contained an isotopic oxygen composition approximately that of the melt, while quartz was heavier. Consequently, the melt would have become progressively depleted in O^{18} in contrast to the usual trend of increasing O^{18}/O^{16} ratios in residual melts. Subsequent crystallization of biotite and K-feldspar might then reduce this effect but should at the same time reflect it. The authors, in fact, found that the O^{18}/O^{16} ratios of K-feldspar in the granodiorite were smaller than the associated plagioclase ratios, as opposed to the reverse in all four quartz monzonites studied (from different geographical areas). The oxygen isotopic composition of the Rubidoux Mountain leucogranite (quartz monzonite) indicated that oligoclase and quartz crystallized early, whereas K-feldspar formed later. However, all major phases apparently crystallized at nearly the same time, and as a result, Taylor and Epstein suggest that the isotopic composition of this melt remained essentially constant.

Description of Samples

In the following descriptions, those for samples from the batholith of Southern California are taken directly from Taylor and Epstein (1962a).

San Marcos gabbro. Collected from Emil Johnson & Son quarry 3 miles northeast of Pala, California, by L. T. Silver, who provided the following mode for this rock: quartz-0.24, plagioclase(An_{55})-59.4, biotite-0.21, hornblende-17.2, hypersthene-10.8, augite-6.9, apatite-0.29, chlorite-0.03, opaques-5.0 . This is a noritic hornblende gabbro, not representative of the San Marcos gabbro as a unit, because that rock type is variable in composition and texture. Medium-grained and equigranular, with zoned, subhedral laths of plagioclase. The two pyroxenes occur both as separate grains and together in finer-grained clusters, invariably with abundant included magnetite grains. Hornblende is deep green and is in obvious reaction relationship to the pyroxenes enclosed by it. Both pyroxenes are replaced by hornblende, but augite preferentially so. Quartz and biotite occur as rare, anhedral grains interstitial to plagioclase. Apatite occurs in uniformly-distributed euhedral grains, and more is probably present than is listed in mode, on the basis of quantities obtained in mineral separations (L. T. Silver, personal communication).

Bonsall tonalite. Collected 2 miles west of Val Verde, California, by L. T. Silver, who provided a mode for the rock as follows: quartz-25.2, plagioclase(An_{40})-48.3, orthoclase-0.5, biotite-14.2, hornblende-10.0, apatite-0.25, opaques-0.14, accessories-0.78, epidote-0.65. Fairly representative of the Bonsall tonalite as a unit, medium- to coarse-grained and inequigranular, with strongly zoned, subhedral, well-twinned laths of plagioclase 0.5-5 mm in length. Hornblende subhedral, commonly twinned, deep green, zoned. Biotite averages 2 mm, as does hornblende, and occurs as independent grains with ragged borders. Although biotite and hornblende locally occur clustered together, they are never in reaction relationship. Quartz averages 2-3 mm, is anhedral, and is interstitial to plagioclase laths. Rare K-feldspar interstitial to quartz and plagioclase.

Woodson Mountain granodiorite. Collected 3 miles south of Temecula, California, by L. T. Silver, who supplied the following mode for this rock: quartz-36.8, plagioclase (An_{25})-39.5, K-feldspar-15.2, myrmekite-1.8, biotite-5.8, hornblende-0.17, opaques-0.17, accessories-0.52, alteration products-0.02. Fairly representative of Woodson Mountain unit throughout its outcrop area. Moderately coarse-grained, almost equigranular; contains subhedral plagioclase grains that are zoned, well-twinned, and average 3 mm. Microcline microperthite and quartz occur as slightly smaller, anhedral grains. Rarely, K-feldspar grains are larger than 6 mm. Much of the quartz occurs in clusters of grains and in small amounts as myrmekitic intergrowths. Biotite averages 3 mm in length and occurs in irregular, ragged grains, some interstitial to plagioclase.

Rubidoux Mountain leucogranite. Collected from Mount Rubidoux near Riverside, California, by L. T. Silver, who supplied a mode as follows: quartz-34.4, plagioclase (An_{20})-30.3, microperthite-27.9, biotite-3.03, hornblende-1.39, myrmekite-2.5, hypersthene-0.05, accessories-0.32, opaques-0.10. Typical of the coarse-grained leucogranite, pale greenish gray, with grains averaging about 8 mm. Microperthite contains stringers of albite. Quartz grains large and anhedral. Plagioclase unzoned and contains blebs of quartz near grain borders. Minor biotite, dark-green hornblende, and iron-rich hypersthene are fine-grained and tend to occur interstitially. This should properly be called a leuco-quartz monzonite.

Ramona pegmatite. Collected by D. R. Simpson from a pegmatite body near Ramona, California. Besides quartz, albite, and perthite, this pegmatite contains minor amounts of tourmaline and spessartitic garnet (a quartz-feldspar mixture from this pegmatite was processed and used in the precision test on duplicate runs of sample solutions--see Part I, Chapter II of this study).

Kilauea Iki-22. Hawaiian basalt from the November 18, 1959 eruption of Kilauea Iki. Collected by K. Murata and donated by R. A. Schmitt.

Standard granite, G-1. Westerly, Rhode Island. Donated to the author by W. H. Pinson, Jr. This interlaboratory standard is discussed in U. S. Geol. Surv. Bulls. 980 and 1113.

Standard diabase, W-1. Centerville, Virginia. Donated to the author by W. H. Pinson, Jr. This interlaboratory standard is discussed in U. S. Geol. Surv. Bulls. 980 and 1113.

APPENDIX C

ADDITIONAL NOTES ON THE ANALYTICAL PROCEDURE

Introduction

Figure C-1 is an outline of the rare-earth analytical procedure. Most aspects of the procedure are extensively discussed in Part I, Chapter II. However, it is useful to add some additional notes here.

Determination of Chemical Yields

As an example, the calculation of the chemical yields on sample AuSM (augite from the San Marcos gabbro) is given below.

TMC Pulse Height Analyzer Model 402
Input No. 1
High voltage = 1100 volts
Amplifier gain = 1.16
Base line = 0.20
Upper level = 10.0
Accumulation : channels 1-199

On February 18, 1963, the above settings were observed to place the Y^{88} γ's = 0.90 Mev and 1.83 Mev in channels 78 and 170, respectively. Channels 63-199

Fig. C-1. Outline of the analytical method.

ACTIVATION ANALYSIS - CHROMATOGRAPHY PROCEDURE FOR RARE EARTHS

I. Pre-irradiation Chemistry

A. Sample

Weigh Samples (100 to 500 mg)

Add Ce^{139}, Y^{88} Tracers (carrier free)

Dissolution with $HF+HClO_4$

Alternative Fusion with NaOH

Repeated Hydroxide Scavenge of the Rare Earths

Cation Exchange

Anion Exchange

Conversion to 1N HNO_3 Solution

Determination of Chemical Yields

Package for Irradiation

B. Standard Mixture of Rare Earths Packaged

II. Irradiation by Pile Neutrons

III. Post-irradiation Chemistry

Samples and Standard Loaded on DEP-Celite Columns

Gradient Elution with HCl

Collect Fractions

Count Induced Radioactivity

Calculations

included both of these peaks, and channels 3-17 included essentially all Ce^{139} activity ($\gamma = 0.166$ Mev). The sample and two reference tracer solutions were each counted (in 1-ml volumetrics) for 0.4 live minutes. After accumulation in channels 1-199, the analyzer memory was integrated over channels 63-199 and channels 3-17 by the TMC Integrator-Resolver Model 522 and the results printed out on paper tape.

The chemical yields of Y and Ce were calculated as follows:

Activity (counts per 0.4 minutes)

	AuSM	Y^{88} Reference Solution	Ce^{139} Reference Solution
Y^{88} range (63-199)	7,501	7,777	13
Ce^{139} range (3-17)	14,315	2,685	12,076

Yttrium yield in AuSM = $\frac{7501-13}{7777} \times 10^2 = 96\%$

Y^{88} contribution in channels 3-17
for AuSM = $2685 \times 0.96 = 2578$

Cerium yield in AuSM = $\frac{14315-2578}{12,076} \times 10^2 = 97\%$

Packaging for Irradiation

In general, three samples and one standard rare-earth solution were packaged in separate polyethylene tubes for simultaneous irradiation in a 4-dram polyethylene vial ("polyvial"). Approximately one-half of each processed solution was packaged (the remainder was saved in case a duplicate was needed). Polyethylene tubing of 1/4-in., 5/16-in., and 3/8-in. outside diameter was used as sample containers. The smallest tubing was always used for the standard solution. The tubing was cut to approximately the length of the polyethylene vial. It was then soaked in hot 1:1 HNO_3 for about an hour, rinsed with distilled water, dried, and stored for later use. In packaging samples for irradiation, one end of a tube was sealed by heating it over a bunsen burner until the end was clear, and then closing it with a pair of tweezers. The sample was added, and the other end closed in the same manner. The ends were carefully fused to ensure that no cracks were present which would lead to leakage during the irradiation.

Standard Rare-Earth Solutions

Table C-1 provides the basic information for the preparation of rare-earth standard solutions for irradiation. The stock solutions were prepared by dissolving high-purity rare earth oxides (Lindsay, 99.9%) in 3N HNO_3. The nominal concentrations (calculated from the weights of

Table C-1

Rare-Earth Standard Solutions

	(1) Nominal conc. of stock sol'ns. mg/ml	(2) This volume of (1) taken λ(10^{-6}ml)	(3) Conc. after dilution to 10 ml μg/100λ	(4) Conc. after 10-fold dilution μg/100λ
La	6.00	500	30.0	3.00
Ce	6.00	1000	60.0	6.00
Pr	0.75	1000	7.50	0.75
Nd	15.0	200	30.0	3.00
Sm	1.50	500	7.50	0.75
Eu	3.00	100	3.00	0.30
Tb	3.00	100	3.00	0.30
Dy	15.0	100	15.0	1.50
Ho	1.50	100	1.50	0.15
Tm	1.50	100	1.50	0.15
Yb	0.75	200	1.50	0.15
Lu	1.50	100	1.50	0.15
Y	7.50	200	15.0	1.50

each oxide used) are shown in column (1). These stock solutions were stored in polyethylene bottles. In preparing a working solution, volumes of each stock solution, corresponding to the values listed in column (2) were taken and combined. This mixture was then diluted to 10.00 ml with distilled water. The resulting concentrations of individual rare earths are shown in column (3). This solution was approximately 1N in HNO_3. An aliquot of the latter was diluted exactly ten-fold with water, and the resulting solution was packaged for irradiation with samples. The nominal concentrations in the final rare-earth standard mixture are shown in column (4) of Table C-1. The final dilution was made just prior to each irradiation. The solutions shown in column (3) were used for a month or two before preparing a new mixture from the individual stock solutions. The actual concentration of each rare-earth stock solution was accurately determined by titration with ethylenediaminetetraacetic acid (commonly known as EDTA). The method was essentially that of Bril, et al. (1959), modified by a visual end point.

An EDTA solution, whose concentration had been accurately determined by titration against dried $CaCO_3$ (for use in calcium isotopic studies), was provided by Dr. James T. Corless.

For visual end-point determination, a solution was prepared as follows: Into a 50-ml beaker were pipeted 5 ml of 1$\underline{N}$ HCl, 25 ml of H_2O, and 1 ml of a 1$\underline{M}$ sodium acetate - 1$\underline{M}$ acetic acid buffer solution. To this were added 12-15 ml of 0.5$\underline{N}$ NH_4OH, followed by dropwise addition to a pH = 4.60 (measured by a Beckman Model G, pH meter). Fifteen drops of a 0.05% solution of Alizarin Red S indicator were then added. The resulting solution was used for comparison with titrated aliquots of the rare-earth stock solutions.

The titration results are shown in Table C-2. Duplicate titrations were performed on each stock solution. As can be seen, the end points were reproducible to better than 1%. From the 1:1 equivalence between the rare earths and the EDTA, the true concentrations of the stock solutions can be readily calculated as follows:

$$\text{True conc. (mg/ml)} = \frac{\text{Volume EDTA(ml)}}{\text{Volume stock sol'n(ml)}} \times \text{Conc. EDTA(M/L)} \times \frac{\text{Nominal conc. (mg/ml)}}{\text{Nominal conc. (M/L)}}$$

e.g. the concentration of the holmium (Ho) stock solution is equal to:

$$\frac{4.51 \text{ ml}}{5.00 \text{ ml}} \times 1.045 \times 10^{-2} \text{ M/L} \times \frac{1.50 \text{ mg/ml}}{0.910 \times 10^{-2} \text{ M/L}} = 1.55 \text{ mg/ml}$$

Table C-2

Titration of Rare-Earth Stock Solutions

EDTA concentration: 1.045 x 10^{-2} ($\pm$0.005 x 10^{-2}) molar

Element	Nominal conc. mg/ml	Nominal conc. x 10^{-2}M	Volume titrated ml	EDTA ml	True conc. mg/ml
La	6.00	4.32	1.00	3.83, 3.81	5.56
Ce	6.00	4.28	1.00	4.38, 4.38	6.41
Pr	0.75	0.532	10.0	5.00, 4.99	0.736
Nd	15.0	10.4	0.500	4.42, 4.42	13.8
Sm	1.50	0.980	5.00	4.64, 4.65	1.49
Eu	3.00	1.98	3.00	4.78, 4.79	2.55
Tb	3.00	1.89	3.00	5.44, 5.47	3.07
Dy	15.0	9.23	0.500	4.60, 4.59	15.6
Ho	1.50	0.910	5.00	4.52, 4.50	1.55
Tm	1.50	0.888	5.00	4.36, 4.35	1.54
Yb	0.75	0.433	10.0	4.39, 4.39	0.795
Lu	1.50	0.858	5.00	4.28, 4.30	1.58
Y	7.50	8.44	0.500	4.11, 4.11	7.62

In practice, the true concentrations of the stock solutions were not determined until late in the investigation. Consequently, the nominal values were used in all preliminary calculations, and then the results for each rare earth were multiplied by the ratio of the true concentration to the nominal concentration of each standard.

Neutron Activation

Radioactivation analysis is one of the most versatile analytical methods developed in recent years. Of high importance are the extremely high sensitivities which are obtained for many elements. The most recent extensive review of the basic considerations in activation analysis is presented by Koch (1960). Winchester (1960) has discussed its application to inorganic geochemistry.

By far, the most commonly-used activation involves neutron irradiation. The least-complicated case is the irradiation of samples with slow (thermal) neutrons in a nuclear reactor. The slow neutrons produce initial (n,γ) reactions, thus giving rise to induced initial activities solely in the parent element (subsequent decay, however, may lead to daughter activities in adjacent elements of the periodic table). In practice, however, pile-neutron fluxes are a mixture of slow and fast neutrons. The ratio can vary quite widely between different irradiation facilities of the same reactor. Initial nuclear reactions from bombardment with fast neutrons are much more complicated since a variety of initial reactions are possible, e.g. (n,p), (n,2n), (n,α), etc. In this study, pneumatic tubes were employed which had associated neutron fluxes with high ratios of thermal neutrons to fast neutrons (e.g. as high as 10:1). Side reactions produced by fast neutrons were considered to be unimportant, since even though they might be present to a small, but significant extent, the close similarity between sample and standard solutions would result in effective cancellation of any influence on the analytical results.

Methods employing neutron activation of the rare earths in silicates have been developed by several investigators including Mosen, et al. (1961) and Chase (1962). The basic nuclear considerations in this study are essentially the same as those discussed in detail by Mosen et al. (1961). However, this study represents a somewhat simpler case, since the self-shielding effects investigated in detail by Mosen et al. are eliminated by irradiating all samples and standards in aqueous solutions.

The basic principle behind measurement of concentrations by the comparison method of neutron activation analysis is quite simple. In the simplest case, the following relation holds true:

$$\frac{A_{sa}}{A_{std}} = \frac{M_{sa}}{M_{std}}$$

where

A_{sa} = induced activity of the element in the sample

A_{std} = induced activity of the element in the standard

M_{sa} = mass of the element in the sample

M_{std} = mass of the element in the standard

The implicit assumption is made that the relative isotopic composition of a particular element under consideration is identical in the sample and standard. Following irradiation, this element is isolated by chemical means from the other elements (and their radioactivities), its radioactivity isolated by counting techniques, or both. In this study, individual rare earths were isolated from each other by partition chromatography. Where chromatographic separation was not complete, selective counting of the radioactivities was employed. From the induced activities in the sample and standard, and the separately-determined chemical yields, the actual concentrations in the sample could be readily calculated. An example of these calculations is given later in Appendix C.

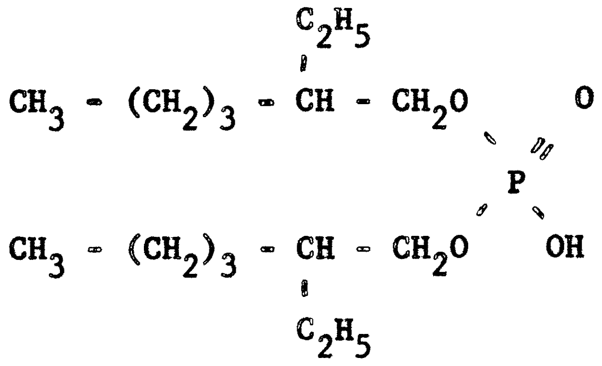
In cases where the post-irradiation chromatographic separation of certain rare earths in the standard solution was poor, it was an advantage to use the activities of the standard from another irradiation. Caution, however, was necessary when comparing a sample and standard irradiated at different times. In general, the induced activities of the standard mixtures (corrected to the same time after identical irradiations) were constant to about ±10% between different irradiations. A notable exception was dysprosium, which exhibited a large resonance effect (up to 50%). Apparently slight changes in the energy distribution within the neutron beam produced large differences in the effective cross section of Dy^{164}.

Partition Chromatography

The post-irradiation chromatography with di-(2-ethylhexyl)orthophosphoric acid (DEP) has been discussed in detail by Winchester (1963). Prior to this, Peppard et al. (1957) had found in solvent extraction studies that the rare earths formed highly selective complexes with DEP. The separation factors were observed to change systematically by a factor of approximately 2.5 between adjacent rare earths.

Chromatographic separation of rare earths was carried out by Siekierski and Fidelis (1960, 1961) on columns of refined diatomaceous silica coated with tributylphosphate. The silica was rendered hydrophobic by treatment with vapors of dimethyldichlorosilane. Winchester (1963) used the same technique to prepare DEP-Celite columns. Also of interest is a recent paper by Cerrai and Testa (1962) in which the paper-chromatographic separation of rare earths by DEP is discussed.

The structural formula of the monobasic acid di-(2-ethylhexyl)orthophosphoric acid is:



Peppard et al. (1957) report the following equilibrium, applicable to a system with a large excess of DEP:

$$3DEP + M^{+3} \rightleftharpoons M(DEP)_3 + 3H^+ \tag{1}$$

where DEP represents the free acid, M^{+3} the rare-earth cation, $M(DEP)_3$ the rare earth-DEP complex, and H^+ the hydrogen ion. The equilibrium constant for this reaction is therefore

$$K = \frac{(M(DEP)_3)(H^+)^3}{(DEP)^3(M^{+3})} \tag{2}$$

The extraction coefficient is defined as

$$E_a^o = \frac{(M(DEP)_3)}{(M^{+3})} \tag{3}$$

Consequently

$$E_a^o = K \frac{(DEP)^3}{(H^+)^3} \tag{4}$$

The value of K increases by a factor of approximately 2.5 per unit increase in rare earth atomic number. Peppard et al. (1957) found that at a (DEP) $\approx$ 0.75M and an (HCl) = 0.5M the values of E_a^o ranged from 1.0×10^{-3} for lanthanum to $3.2 \times 10^{+2}$ for lutetium.

In the stepwise gradient elution with HCl employed by Winchester (1963) and also in this study, a series of acids were used such that each acid would bring one rare earth off the column in about two free-column volumes, if that acid were used alone (the free-column volumes of the DEP-Celite columns are approximately 70% of their geometrical volumes). It can be seen from (4) that higher hydrochloric acid concentrations decrease the value of E_a^o and consequently will favor removal of rare earths by the aqueous phase. The actual concentrations of HCl used and the sequence of addition are shown in Table II-1, Chapter II, Part I.

Details regarding preparation of column material are given by Winchester (1963). The following paragraph is taken directly from his paper:

> Column substrate material is Johns-Manville Celite Analytical Filter Aid, used directly as supplied by the manufacturer. The surface is made hydrophobic by placing several grams of Celite in a desiccator containing an open bottle of dichlorodimethylsilane, allowing about two days of contact time, and heating briefly and washing with methanol to remove hydrogen chloride released during the reaction. The dried product is slurred with an acetone solution of DEP such that the weight ratio of DEP to Celite is about 1:5. After a few minutes, the acetone is evaporated with gentle heating until the odor of acetone is gone. The dry-looking product is then slurried with 0.01M HCl containing a wetting agent (0.1% of the polyester Tergitol Nonionic NPX, manufactured by the Union Carbide Co., Inc., is satisfactory) and held at 90°C for two days until all particles settle out easily and no air bubbles remain. Removal of air bubbles is critical for subsequent column operation.

A small glass wool plug was inserted in the bottom of the columns before packing them with the treated DEP-Celite material. However, glass wool was not placed above the top of the column beds. During sample loading and the subsequent chromatographic elution, acids were added carefully so as not to disturb the top bed.

The pH 2 buffer used in adjusting acid concentration prior to sample loading was prepared by dissolving 9.5 g of $Na_2S_2O_5$ (sodium metabisulfite) in 50 ml of H_2O. The resulting solution was 2$\underline{M}$ in $NaHSO_3$.

Calculation of Rare-Earth Concentrations in Samples

The determination of the concentration of each rare-earth element was made from the following information:

(1) net activities of the rare-earth element in the sample and standard at identical times after the irradiation; (2) amount of the rare earth in the standard; (3) chemical yield of the sample; and (4) amount of the sample chromatographed on the DEP-Celite column. In addition, where necessary, the reagent blank contribution was subtracted from the apparent rare-earth content of the sample.

The calculation may be expressed in this form:

$$\mathrm{RE}_{\mathrm{conc}}(\mathrm{ppm}) = \frac{A_{\mathrm{REsa}}}{A_{\mathrm{REstd}}} \times \frac{\mu g_{\mathrm{REstd}}}{Y_{\mathrm{REsa}} \times W_{\mathrm{sa(g)}}} - \mathrm{Reag(ppm)} \qquad (5)$$

where

$\mathrm{RE}_{\mathrm{conc}}$ = concentration of the rare earth in the sample (ppm)

A_{REsa} = net induced activity of the rare earth in the sample

A_{REstd} = net induced activity of the rare earth in the standard

μg_{REstd} = micrograms of the rare earth in the standard

Y_{REsa} = chemical yield of the rare earth in the sample

$W_{\mathrm{sa(g)}}$ = corresponding weight of the sample chromatographed

Reag(ppm) = reagent contribution of the rare earth

As an actual example, the determination of La in sample W-1A is chosen. The following information is given:

(a) weight of sample processed - 0.500 g

(b) chemical yield on Ce^{139} - 95%

(c) proportion of sample chromatographed with DEP - 50% (500λ out of 1.00 ml)

(d) amount of standard solution chromatographed - 100λ

from Table C-1 and Table C-2 this is seen to correspond to

$$100\lambda \times \frac{3.00\ \mu g}{100\lambda} \times \frac{5.56\ mg/ml}{6.00\ mg/ml} = 2.78\ \mu g\ La$$

(e) for a 0.500-g sample, Reag(ppm) = 0.230 (a constant, see Table II-7, Chapter II, Part I)

(f) A_{REsa} = 78,004 counts per 4/10 minute

A_{REstd} = 89,794 counts per 4/10 minute

Therefore, using (5):

Conc. La in W-1A =

$$= \frac{78{,}004}{89{,}794} \times \frac{2.78\ \mu g}{0.95(0.500\ g \times 0.500)} - 0.23\ ppm$$

$$= 10.17\ \mu g/g - 0.23\ ppm$$

$$= 10.17\ ppm - 0.23\ ppm = 9.94\ ppm$$

Table C-3 summarizes the pertinent information on sample designations, weights, chemical yields, irradiation periods, standards, etc.

Table C-3

Samples Processed and Irradiated

1	2	3	4	5		6	7	8
			(mg)	Ce(%)	Y(%)	(hrs)	(%)	(λ)
KI1	Kilauea Iki-22 basalt	whole rock*	100	77	85	1	60	100
KI2	" " "	whole rock	500	98	97	1	30	100
KI3 (K)	" " "	" "	500	99	99	1	50	100
KI3A (L)	" " "	whole rock plus 100λ of standard	500	98	99	1	50	100
RM1	Rubidoux Mountain leucogranite	whole rock*	100	--	60	1	40	200
RM2	" " "	whole rock	100	92	91	1	40	200
RM3	" " "	" "	100	53	56	1	90	200
RM4	" " "	" "	500	97	97	1	50	100
RM5	" " "	" "	500	97	99	1	40	100
SM1	San Marcos gabbro	whole rock	100	93	95	1	90	200
SM2	" " "	" "	500	95	97	1	40	100
SM3	" " "	" "	500	95	97	5	45	50

Table C-3 (continued)

1	2	3	4	5		6	7	8
			(mg)	Ce(%)	Y(%)	(hrs)	(%)	(λ)
BT1	Bonsall tonalite	whole rock	100	81	86	1	40	200
BT2	" "	" "	500	100	100	1	40	100
WM1	Woodson Mountain granodiorite	whole rock	500	93	95	1	40	100
AuSM	San Marcos gabbro	augite	142	97	97	5	50	25
PlSM	" " "	labradorite	318	94	99	5	50	50
ApSM	" " "	apatite	60.5	100	99	5	30	25
HoSM	" " "	hornblende	255	97	97	5	50	50
BiRM	Rubidoux Mountain leucogranite	biotite	51.9	98	94	5	50	25
PlRM	" " "	oligoclase	36.2	97	98	5	50	25
MiRM	" " "	microcline	125	98	99	5	50	50
ApBT	Bonsall tonalite	apatite	115	96	99	5	10	25

Table C-3 (continued)

1	2	3	4	5		6	7	8
			(mg)	Ce(%)	Y(%)	(hrs)	(%)	(λ)
RP1	Ramona pegmatite	quartz + feldspar (random mixture)	500	97	92	1	40	100
RP2	" "	" " " (proportions different from RP1)	515	92	88	5	50	25
G-1A	Standard granite G-1	whole rock	500	99	98	1	10	100
G-1B	" " "	" "	500	99	98	5	55	50
W-1A	Standard diabase W-1	whole rock	500	95	96	1	50	100
W-1B	" " "	" "	500	95	96	5	29	50
B	NaOH reagent blank	NaOH	4000	87	85	1	40	100
RB1	HF + $HClO_4$ acid treatment blank	HF, $HClO_4$, NH_3, HCl	(1000)	88	90	18	50	10
RB2	" " "	" " " "	(500)	94	90	5	40	50

1 Sample designation.

2 Source of sample.

Table C-3 (continued)

3 Type of sample.

4 Weight of sample processed (mg).

5 Chemical yields on Ce^{139} and Y^{88} (%).

6 Period of irradiation (hours).

7 Proportion of total sample solution (1.00 ml) chromatographed (%).

8 Volume of standard rare-earth mixture chromatographed (λ).

* NaOH fusion (acid dissolution where unspecified).

APPENDIX D

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BIOGRAPHICAL NOTE

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