Table 1. Molar concentrations of cations in calibrating solutions and in standard I.A.P.O. sea water of chlorinity 19.373 parts per thousand.

Solution (No.)	Ion concentration (M)			
	Na	K	Ca	Mg
1	0.469	0.0097	0.0088	0.0248
2	.469	.0097	.0088	.0496
3	.469	.0097	.0088	.0465
Sea water	.469	.0097	.0102	.0534

magnesium ion in sea water by calibrating it in solutions that have the competing cations already present, varying only the concentration of magnesium ion. In sea water some of the magnesium is complexed by bicarbonate, carbonate, and sulfate ions, but as far as is known there is no complexing of magnesium, calcium, or sodium ion by chloride ion (*2*). The calibrating solutions were made up from the chloride salts of the several cations; their compositions, and the composition of standard sea water from data of Sverdrup *et al.* (*3*), appear in Table 1. Calcium concentration in the calibrating solutions is 86 percent of that in the sea water—about as much as is considered to be ionized in sea water (*2*). The sea water used was standard I.A.P.O. (International Association of Physical Oceanography) sea water; chlorinity, 19.373 parts per thousand.

The electrode-potential measurements were made against a saturated KCl-calomel reference electrode with an expanded-scale voltmeter (10 mv, full scale) and a strip-chart recorder. The solutions were stirred magnetically, and temperature was controlled at 25° ± 0.1°C. The potential measurements were repeated several times; reproducibility was about ± 0.1 mv.

The best values for the four solutions were, in millivolts: solution 1, − 56.2; solution 2, − 50.6; solution 3, − 51.2; and sea water, − 50.9. The potential for sea water lies halfway between the potentials for solutions 2 and 3, which have, respectively, 0.0496 and 0.0465M magnesium; ionized magnesium in sea water may be taken as the average of these two concentrations, 0.048M. The total magnesium present in the sea water being 0.0534M (Table 1), it is apparent that only about 90 percent of the magnesium in sea water is ionized; this finding is in fair agreement with the data of Garrels and Thompson who calculated that about 87 percent is ionized (*2*).

To convert the electrode-potential measurements to activities of magnesium ion one must use an individual ion activity coefficient. The ionic strengths of the calibrating solutions are nearly the same as that of the sea water, so I shall use the activity coefficient for magnesium ion used by Garrels and Thompson in their model. (I realize that I have combined a molal-activity coefficient with a molar concentration, but the differences between molal and molar magnesium in these solutions are less than 1 percent.)

With the use of this activity coefficient, 0.36, the calculated activities for magnesium ion in the calibrating solutions are: solution 1, 0.0089; solution 2, 0.0179; and solution 3, 0.0167. Because the potential in standard sea water lies midway between the potentials for solutions 2 and 3, the activity of magnesium ion in sea water may be taken as their average—0.0173, which also is in fair agreement with the value calculated by Garrels and Thompson, 0.0169.

Recently another value for the activity of magnesium ion in sea water was reported by Pytkowicz *et al.* (*4*); they measured the *p*H of sea water that was presumably saturated with brucite, $Mg(OH)_2$, obtaining 0.0084 for the activity of magnesium, a value about half as great as the one I report. It is difficult to reconcile their measurement with the assumptions used in constructing the chemical model of Garrels and Thompson. If, as Pytkowicz *et al.* suggest, 39 to 53 percent of the magnesium in sea water forms $MgSO_4^0$-ion pairs, virtually all the sulfate present in sea water must be combined with magnesium, because sulfate is less than 53 percent as abundant as magnesium.

But the dissociation constants compiled by Garrels and Thompson indicate that about as much $NaSO_4^-$-ion pair is formed as is $MgSO_4^0$. Possibly the different result may be explained by assumption that the solubility of brucite is not known closely enough, or that in their experiment equilibrium was really attained with a hydroxy carbonate of magnesium, such as hydromagnesite $[Mg_4(CO_3)_3(OH)_2]$.

On the other hand, the good agreement between the values obtained by this electrode measurement and the calculations of Garrels and Thompson tends to support the assumptions on which construction of their model for sea water was based: that estimated values for individual ion activity coefficients, used in conjunction with thermodynamic dissociation constants involving the eight major species in sea water, yield at least a first approximation of the extent of interaction among those species. If the activity coefficients used in the model were not reasonably correct, the calculated amount of ionized magnesium would probably not agree so well with the measured value.

MARY E. THOMPSON

Department of Geology, University of South Carolina, Columbia 29208

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31 May 1966

Rare Earths in Hawaiian Basalts

Abstract. *Rare-earth elements have been determined by neutron activation analysis in 20 basalts from the Hawaiian Islands. The abundance patterns of these elements form groups coinciding closely with groupings based on other evidence, and a fractional crystallization mechanism for change in rare earth abundance is implied.*

Volcanic rocks of the Hawaiian Islands have been under intensive study, from the standpoint of petrology and major-element chemical composition, by a number of investigators (*1–5*) who seek answers to the questions of the origin of these rocks and differentiation of the earth. We have analyzed some of these rocks for rare-earth elements by means of a neutron activation procedure used in previous work (*6*). In this preliminary report we present some of the relations revealed by abundance patterns of the rare earths.

In Table 1 we describe the samples analyzed and group them according to the similarity of rare earth abundance patterns given below. Following the practice of this laboratory (*7*), we compared the rare earth abundance pattern of each rock, element by element, with a common reference, for example, the average of ordinary chondritic meteorites (*8*). The relative abundance of each rare earth (that is, enrichment factor relative to the reference) is plotted logarithmically versus a linear scale of the atomic numbers of the rare earths. These elements decrease in size with increasing atomic number, and an ap-

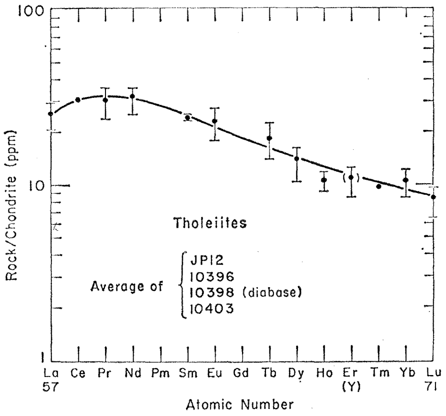

Fig. 1. Average abundance of rare earths of four tholeiites relative to chondrites. Vertical bars represent extreme deviations of each element from the mean.

proximately linear relation exists between atomic number and reciprocal ionic radius (*9*).

Figure 1 is such a plot for the average of four tholeiitic basalts analyzed relative to the chondrite reference. Extreme deviations of each element for any of the tholeiites in the group, as shown by the vertical bars, indicate that the rare earth abundances are very similar in the four rocks. Individual rocks in any one of the other groups in Table 1 are also very similar in the concentrations of rare earths, although the groups are distinct from each other. These groups coincide closely with groupings based on mineralogy and major-element composition. Patterns in all groups are fractionated relative to chondrites in the regions of the heavy as well as the light elements, but to different degrees in the different groups of lavas.

Figure 2 presents, element by element, the rare earth concentrations of each rock group relative to the olivine tholeiite sample No. 9948 as a reference. This sample is the lowest in K_2O and rare earths of any analyzed and contains normative olivine. Its composition has often been identified as the primary magna for the tholeiite series in Hawaii. The other tholeiites have the same rare earth abundance pattern but are somewhat enriched in total rare earth compared to sample 9948. Alkali olivine basalts, basanites, hawaiites, and mugearite all show a remarkable break near gadolinium. The heavy rare earths are in the same relative abundance as in the tholeiite and give nearly horizontal trends in Fig. 2, but in the lighter-element region the relative abundance of these rare earths is progressively strongly enriched as the atomic number decreases. Nepheline melilite basalts do not show such a break, but the progressive enrichment with decreasing atomic number extends over the entire range and is approximately linear on these semilogarithmic graphs. Trachyte shows a minimum near gadolinium and a slow rise in the region of heavy elements. If fractional crystallization is an important part of the evolutionary mechanism (*1–5, 10*), we may draw some inferences from these patterns.

Similar patterns are observed in other related igneous rocks. Using data for the rare earths in the Southern California batholith (*6*), we have compared Bonsall tonalite and Woodson Mountain granodiorite with San Marcos gabbro in this element-by-element way. The result is a similar pattern for both cases, with a negative slope from lanthanum to the middle of the rare earth series and a horizontal trend of the relative abundances in the region of the heavy elements. (The Rubidoux

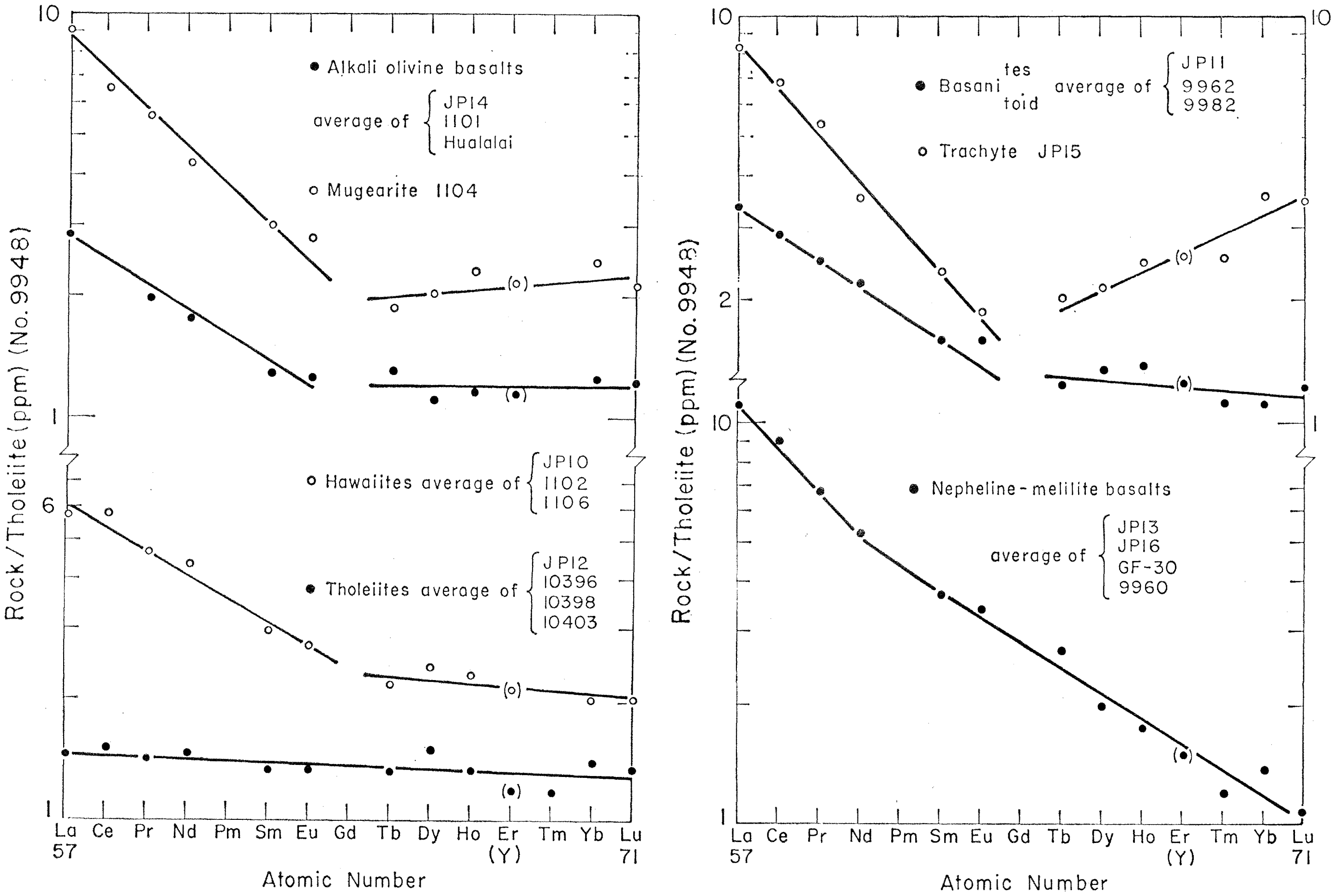

Fig. 2. Average abundance of rare earths of rock groups relative to the low-potassium olivine tholeiite sample No. 9948.

Table 1. List of samples analyzed, grouped according to rare earth patterns and showing SiO_2 and K_2O contents. JP and GF samples are discussed in (*4*) and the other samples in (*1*), (*2*), or (*3*), except for No. 1801. Values for the SiO_2 and K_2O contents are those given in these references.

Sample No.	Rock type and description	SiO_2 (wt. %)	K_2O (wt. %)
9948	Olivine tholeiite, Koolau series, Oahu	49.62	0.15
10396	Tholeiite, Koolau series, Oahu	48.76	.22
10398	Diabase, Koolau series, Oahu	52.30	.60
10403	Tholeiite, Koolau series, Oahu	51.94	.35
JP12	Tholeiite, Mauna Loa, 1881 flow, Hawaii	51.85	.37
JP14	Akali olivine basalt, Hualalai, Hawaii	46.53	.84
1101	Picrite basalt, Haleakala, Maui	42.30	.42
1801	Alkali basalt, 1801 flow, Hualalai, Hawaii		
JP10	Hawaiite, Mauna Kea, Hawaii	47.99	1.82
1102	Hawaiite, Haleakala, Maui	47.64	1.60
1106	Hawaiite, Haleakala, Maui	47.78	1.30
1104	Mugearite, Haleakala, Maui	54.14	2.72
JP15	Trachyte, Puu Anahulu, Hawaii	62.02	4.93
JP11	Basanitoid, Honolulu series, Oahu	43.12	0.60
9962	Linosaite, Honolulu series, Oahu	45.13	1.02
9982	Nepheline basanite, Honolulu series, Oahu	42.86	0.93
JP16	Melilite nepheline basalt, Honolulu series	36.34	1.78
GF30	Melilite nepheline basalt, Honolulu series	37.16	1.95
9961	Nepheline basalt, Honolulu series	38.57	1.20
9960	Nepheline melilite basalt, Honolulu series	36.75	0.91

Mountain leucogranite pattern also shows a break in the middle, but the trend of the heavy elements still has a negative slope.) Furthermore, separated mineral data for San Marcos gabbro [Fig. 1 in (*6*)] shows that augite (and hornblende which is an alteration product of augite) contains heavy rare earths with the abundance pattern of whole rock, but light elements are sharply discriminated against. Although one should be cautious about interpretation based on an assumed paragenesis of minerals, subtraction of reasonable amounts of augite from whole-rock San Marcos gabbro leads to a rare earth pattern of the residual liquid that shows the horizontal trend of heavy elements, the break in the middle, and increasing concentrations of rare earths in the region of light elements. It therefore appears that development of a distribution of rare earths with a break in the middle and a horizontal trend for heavy elements may be produced in the residual liquid by calcium mineral crystallization.

Substitution of trivalent rare earths for calcium with a preference for the heavier elements is plausible in the light of ionic radii. Goldschmidt (*11*) gives the following radii: La^{+++} 1.22, Gd^{+++} 1.11, Lu^{+++} 0.99, Ca^{++} 1.06, Mg^{++} 0.78, and Fe^{++} 0.83 Ångstrom units. Rare earths with radii similar to and smaller than the radii of calcium may substitute for Ca^{++} without fractionation, but larger ions may be discriminated against to a degree increasing with increasing radius. As crystallization proceeds and clinopyroxenes, olivine, and limited amounts of plagioclase are removed from the liquid, the residual liquid should develop the pattern of basanites, alkali olivine basalts, hawaiites, and mugearite and show the break in the middle and the horizontal trend for heavy elements, according to this simple model. The trachyte pattern seems to be a modified form, particularly in having a positive slope in the region of heavy elements, perhaps because of crystallization of new phases or the presence of volatiles late in differentiation.

The calcium crystallization model does not account for the nepheline melilite basalt pattern which shows no break in the middle. Following suggestions (*10, 12*) that removal of orthopyroxene from olivine tholeiitic magma may produce silica undersaturated, nepheline normative, residual liquid, we may ask how fractional crystallization of Mg^{++} and Fe^{++} minerals will affect the rare earth pattern of the residual liquid. Because cation sites of orthopyroxene are smaller than the radius of the smallest rare earth, progressive discrimination against rare earths with increasing radii may be expected over the entire range from lutecium to lanthanum. We may expect the residual liquid to be enriched with rare earths to a degree which increases with increasing ionic radius. The observed nepheline melilite basalt pattern is consistent with this model.

It is noteworthy that patterns show the greatest steepness in the region of light elements for rock types which have apparently undergone the greatest degree of differentiation. Futhermore, absolute concentrations of rare earths increase progressively with degree of differentiation from tholeiite to alkali olivine basalt to hawaiite and mugearite-trachyte. Although none of these lavas show rare earth patterns that would probably be identical with the composition of magma produced in the upper mantle by partial or total melting, tholeiite appears to be the least differentiated of the group studied. In contrast, the alkali series including nepheline melilite basalts are residual liquid fractions. We suspect that rare earth distribution patterns may contribute significantly to our understanding of the mineralogical and chemical history of these lavas and their relation to the upper mantle, to our formulation of models related to isotopic measurement of strontium and lead, and to the thermal history of the earth.

JEAN-GUY SCHILLING
JOHN W. WINCHESTER

Department of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge 02139

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13 May 1966