

## Rare Earth Element Patterns of Rocks from the Centre 3 Igneous Complex, Ardnamurchan, Argyllshire

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**Abstract.** Systematic differences in absolute abundancies and distribution patterns of rare earth elements are shown to exist for the main rock types of the third and final phase of the Tertiary igneous complex of Ardnamurchan. Published partition coefficients of the rare earth elements between crystals and host magmas of extrusive rocks have been used, together with modes of the Ardnamurchan rocks, to estimate the rare earth element patterns of the parent magmas. The results confirm that the basic rocks formed by crystal fractionation but that continued crystal fractionation from a single parent magma could not have formed the intermediate rocks.

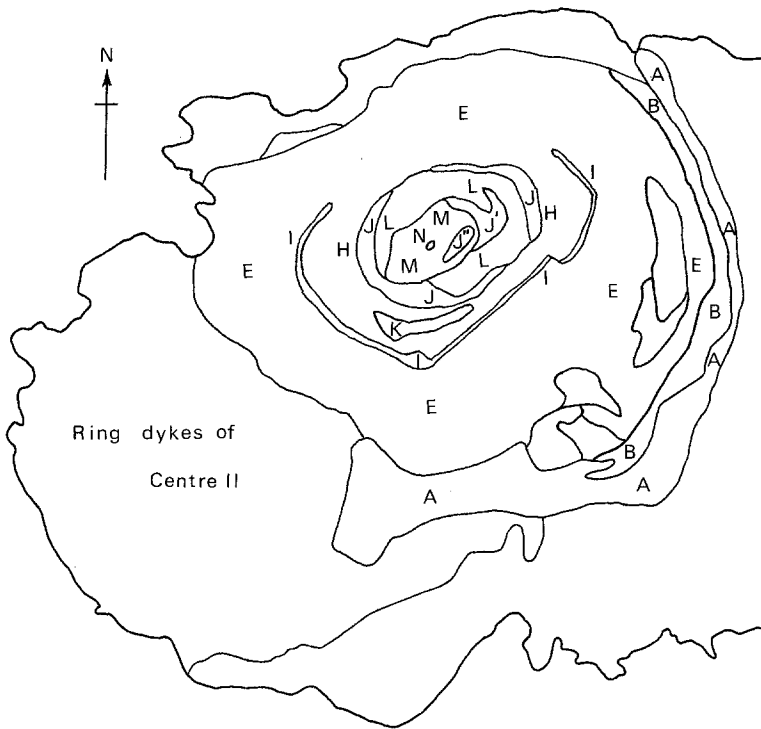
### Introduction

The igneous rocks of the Ardnamurchan peninsula in western Scotland form one of the major central intrusive complexes of the British Tertiary province. The final phase in the evolution of the complex was the formation of the third Centre which cuts the two previous centres to form the largest and most complete set of ring intrusions in the British Isles.

Centre 3 is a plutonic complex of ring and arcuate intrusions of rock types ranging from olivine-rich gabbros, through intermediate rocks to granophyres. The distribution of the main intrusions of the Centre is shown in Figure 1. The details of the petrography and petrology of the area have been discussed in several publications, including Richey et al. (1930) and Deer (1969).

Studies of the clinopyroxene and biotite compositions (Walsh, 1975) and also of the rock chemistry (Walsh, 1971) have suggested that the basic intrusions of Centre 3 may be divided into three main groups, the eucrites, the gabbros (all the gabbro intrusions being closely related) and the dolerites. Furthermore, on the basis of changes in Fe/Mg ratios in the minerals, and other chemical changes, all these basic rocks could represent three successive stages in the

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**Fig. 1.** Simplified sketch map showing the location of the more important members of Centre 3, Ardnamurchan. (After Richey et al., 1930). (A) Quartz-gabbro of Faskadale (earliest 'ring-dyke'). (B) Fluxion Gabbro of Faskadale. (E) Great Eucrite. (H) Inner Eucrite. (I) Quartz-dolerite veined with granophyre (*I D* and *I G*). (J) Quartz-biotite-gabbros. (K) Fluxion Biotite-gabbro of Sithean Mor. (L) Fluxion Biotite-gabbro of Glendrian. (M) Tonalite. (N) Quartz-monzonite. Intrusions of Centre 3, with smaller members omitted. (Letters also refer to sample numbers in Tables 1 and 2)

fractionation of basic magma. The Fe/Mg ratios of the minerals from the intermediate rocks show that these rocks cannot have formed by a continuation of the fractionation process that formed the basic rocks.

The purpose of the present paper is to present rare earth element (REE) data for some Ardnamurchan Centre 3 rocks in order to establish the genetic relationships between the various rock types.

### Analytical Methods

Instrumental neutron activation analysis (INAA) was used for the determination of REE concentrations (Gordon et al., 1968). About 250 mg of powder of each rock sample, together with elemental standards and a rock standard, were irradiated in the University of London reactor for a period of about 25 h at an approximate flux of  $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . The elemental standards were prepared by making a standard solution from an ultra-pure metal or compound of each element (supplied by Koch Light) and evaporating a known volume of the solution to dryness in an irradiation ampoule.

Table 1. Approximate modal percentages (volume) and chemical analyses (wt. %) for the Ardnamurchan Centre 3 rocks

	Eucrites				Gabbros					Dolerite	Tonalite	Quartz Monzonite	Granophyre	
	E1	E5	H4	A2	B5	J12	K5	L1	I12D				M3	N2
Plagioclase	62	75	75	52	48	56	50	60	57	39	44	<5		
Alkali Felspar	-	-	-	-	-	An 50-60		-	An 30	26	An 20-30	70		
Quartz	-	-	-	Tr	Tr	1-2	Tr	Tr	3	16	12	25+		
Pyroxene	20	6	10	35	40	30	31	25	27	4	6	Tr		
Olivine	14	16	12	-	-	-	-	-	-	-	-	-		
Biotite	-	-	-	-	-	1-2	2	Tr	4	8	9	-		
Opaques	2	2	2	8	7	7	13	10	6	4	4	1		
Alteration + Accessories	2	1	1	5	5	5	4	5	2	3	3	Tr		
SiO <sub>2</sub>	47.71	48.30	45.34	46.97	49.36	49.97	45.13	49.30	51.21	58.75	58.65	71.59	73.49	
TiO <sub>2</sub>	0.26	0.36	0.18	2.36	1.28	1.65	2.24	0.90	1.82	1.12	1.23	0.25	0.26	
Al <sub>2</sub> O <sub>3</sub>	17.17	20.11	21.18	14.50	13.66	15.67	13.17	19.88	14.19	16.31	15.29	15.56	13.70	
Fe <sub>2</sub> O <sub>3</sub>	2.44	1.84	1.80	7.87	6.56	6.79	9.59	4.85	6.92	3.88	5.42	1.41	1.30	
FeO	5.15	6.10	5.59	8.37	7.38	6.36	8.41	4.13	7.67	3.25	3.11	0.97	1.07	
MnO	0.14	0.12	0.12	0.27	0.24	0.16	0.20	0.11	0.17	0.13	0.14	0.02	0.03	
MgO	10.05	7.63	10.06	5.05	5.69	4.45	6.28	4.03	3.68	2.14	2.50	0.01	0.35	
CaO	13.64	11.44	12.17	9.68	9.58	8.72	10.97	12.03	7.80	4.60	4.82	0.71	0.58	
Na <sub>2</sub> O	1.99	2.85	1.87	3.23	3.92	3.23	2.75	3.54	3.67	4.58	4.24	3.70	3.53	
K <sub>2</sub> O	0.18	0.24	0.15	0.55	0.72	0.89	0.42	0.55	1.47	3.33	3.28	5.43	5.27	
H <sub>2</sub> O <sup>+</sup>	0.48	0.85	0.83	0.42	1.22	1.30	0.72	0.78	0.51	0.67	0.56	0.11	0.22	
H <sub>2</sub> O <sup>-</sup>	0.26	0.12	0.21	0.23	0.30	0.09	0.21	0.11	0.29	0.51	0.36	0.11	0.46	
P <sub>2</sub> O <sub>5</sub>	0.02	0.03	0.02	0.14	0.15	0.28	0.16	0.07	0.26	0.52	0.62	0.03	0.03	
Total	99.49	99.99	99.52	99.64	100.06	99.56	100.25	100.28	99.66	99.79	100.22	99.90	100.29	

After irradiation, suitable decay times were adopted to allow for the differences in the half-lives of the various isotopes. Activities were determined by means of a large coaxial Ge(Li) detector (for La) and an intrinsic Ge detector (for the other REE) with the following measured specification: FWHM at 122 keV = 538 eV; active area 200 mm<sup>2</sup>. Each detector was coupled via a pre-amplifier and amplifier to a Link system 4000 channel analyser based on a small computer. Peak integrals were recorded directly and 'dead-time' and half-life corrections were made. Estimates of both the precision, based on counting statistics, and accuracy, based on results for an internal rock standard matched against U.S.G.S. BCR-1, are 5% or better, at the two sigma level.

Major element oxide percentages were determined by gravimetric, atomic absorption and colorimetric methods. The modal percentages, given as volume percentages in Table 1, were determined by point counting.

## Results

The modal and major element compositions of the analysed rocks are given in Table 1. The REE abundances are given in Table 2 and the chondrite-normalised (Haskin et al., 1968) distribution patterns for these rocks are given in Figure 2. All the rocks are enriched in REE relative to chondrites and the lowest absolute abundances are shown by the eucrites (E1, E5 and H4 in Fig. 2), two of which have a small, but distinct, positive Eu anomaly, in an otherwise almost flat pattern.

The gabbro samples (A2, B5, J12, K5 and L1) have higher absolute abundances of REE than the eucrites. They show a generally similar distribution pattern with a small light to heavy REE relative enrichment (normalised Ce/Yb ~ 2 to 3). Dolerite (I12D) also shows a similar pattern to the gabbros, but unlike the majority of the gabbro samples, has a small negative Eu anomaly. There is evidence from the Eu anomalies of some accumulation of plagioclase in the eucrites and of some plagioclase depletion in the dolerites.

The intermediate rocks of Centre 3 (M3 and N2 in Fig. 2) show substantial differences to the basic rocks, both in REE absolute abundances and in the

**Table 2.** Concentration of rare earth elements in the Ardnamurchan Centre 3 rocks ( $\mu\text{g./g.}$ ).

Rock No.	Type	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
H4	Eucrite	2.4	—	3.0	0.67	0.40	0.10	0.45	0.09
E5	Eucrite	2.0	4.3	1.6	0.52	0.36	0.10	0.29	0.05
E1 <sup>b</sup>	Eucrite	—	5.7	2.6	0.90	0.41	0.24	0.59	0.08
L1 <sup>a</sup>	Gabbro	—	12	9.7	2.0	0.70	0.38	1.3	0.18
K5 <sup>b</sup>	Gabbro	—	20	14	3.3	1.14	0.57	1.7	0.25
J12 <sup>b</sup>	Gabbro	—	40	25	5.1	1.33	0.83	2.5	0.30
B5 <sup>a</sup>	Gabbro	22	30	22	5.0	1.67	1.0	2.9	0.46
A2 <sup>b</sup>	Gabbro	—	22	20	4.5	1.92	0.73	2.7	0.42
I12D <sup>b</sup>	Dolerite	—	46	30	7.3	2.09	1.4	4.3	0.72
N2 <sup>b</sup>	Q. Monzonite	—	118	71	11	2.44	1.7	3.5	0.59
M3 <sup>a</sup>	Tonalite	77	130	75	12	2.44	1.9	3.5	0.40
I21G <sup>a</sup>	Granophyre	77	135	66	13	1.54	2.9	7.0	0.99
I12G <sup>a</sup>	Granophyre	66	112	56	11	1.52	2.4	6.7	0.89

— Not determined

<sup>a</sup> Results averaged from two determinations

<sup>b</sup> Results averaged from three determinations

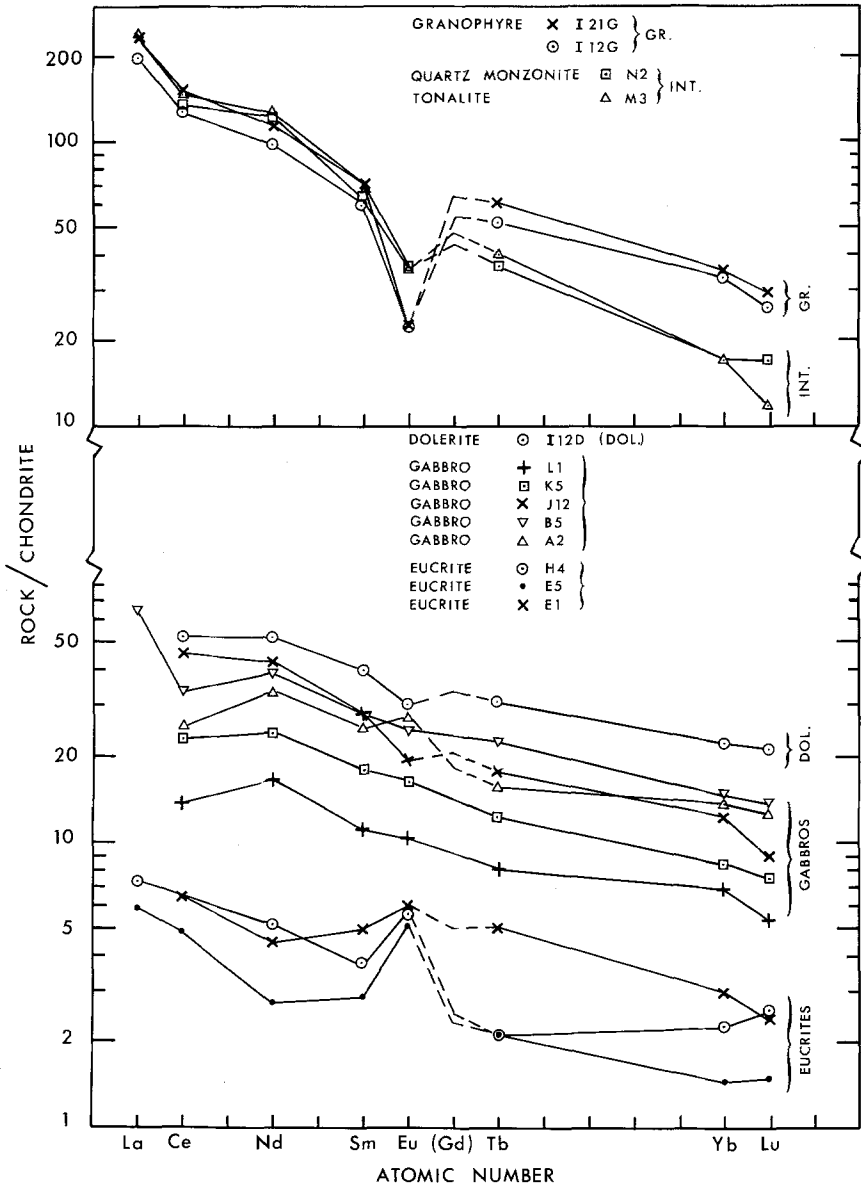


Fig. 2. Chondrite-normalised rare earth element abundances v atomic number for the major rock types from Centre 3, Ardnamurchan. (Chondrite abundances from Haskin et al., 1968)

normalised patterns. The two samples show almost identical REE abundances to each other and a negative Eu anomaly of similar magnitude. However the extent of the relative enrichment of the light to heavy REE is much greater (normalised Ce/Yb  $\approx$  8) than in the basic rocks.

The most acid of the Ardnamurchan Centre 3 rocks (the granophyre I12G and I21G in Fig. 1) have high REE abundances (150 times chondrite for Ce)

and large negative Eu anomalies. Higher absolute abundances of REE, large Eu anomalies and light REE enrichment distinguish them from the basic rocks. They differ from the intermediate rocks in the larger negative Eu anomaly and greater amount of the heavy REE.

## Discussion

It has been suggested (Walsh, 1975) that the Centre 3 basic rocks represent three stages in the fractionation of one basic magma. The REE distribution patterns are compatible with this conclusion, as they are similar in the three basic rock types and, when account is taken of the modal proportions of the minerals, are likely to have been similar in the parent liquids.

From a knowledge of the partition coefficients for the REE between a magma and rock forming minerals together with the modal and REE data given in Tables 1 and 2, it is possible to establish the natures of the rare earth element distribution patterns for the various parent magmas of the major rock types of Centre 3.

Data on the partition of rare earth elements between plagioclase and magma are more extensive than for the partition between clinopyroxene and magma (e.g. Drake and Weill, 1975; Schnetzler and Philpotts, 1970; Higuchi and Nagasawa, 1969; Onuma et al., 1968). However, from published results it is evident that the partition coefficients  $(M)_{\text{pyrox.}}/(M)_{\text{magma}}$  for most of the REE (excluding La and Eu) are larger than for plagioclase and the differential increases with increasing atomic number of the REE. This is shown, for example, by minerals from the lower zone of the Skaergaard intrusion where the concentrations of La and Yb are respectively 1.6 and about 41 times greater in the clinopyroxene than in the coexisting plagioclase (Paster et al., 1974).

If the partition coefficients determined by Schnetzler and Philpotts (1970) for feldspar and clinopyroxene (sample number GSFC 271) can be applied to the Ardnamurchan rocks, then the normalised Ce/Yb ratio for the parent magma of the gabbros may be calculated to have been of the order of 4. This result is obtained by using the modal proportions of plagioclase and pyroxene from Table 1, the results in Table 2 and the published partition coefficients in a simple mass balance equation. The calculated (Ce/Yb) normalised values for the magma from the five gabbro samples range from 2.8 to 5.7, with a mean of 4.1 (standard deviation = 1.2). The calculations assume an absence of accessory minerals which accept a significant amount of REE. The bulk of the alteration + accessories denoted in Table 1 is made up of chlorite. However some trace amounts of apatite (which would accept REE) might be present in these rocks, but it is clear from the  $P_2O_5$  values given that its modal proportion must be low in all the gabbros (maximum 0.6%).

The normalised Ce/Yb ratio of the granophyre rocks is also about 4, so it could be concluded that these rocks were derived from the same parent magma as that of the basic rocks, provided that the granophyre is not a cumulate. However, this conclusion is inconsistent with the Eu anomalies shown by the gabbros, two samples have small negative anomalies, two have virtually no

anomaly, and only one shows a small positive anomaly (see Fig. 2). There is no petrographic or geological evidence (Walsh, 1971) to suggest that the granophyre is an igneous cumulate and it may be inferred that the major element and REE compositions for these rocks are those of the granophyric magma.

The intermediate rocks have a marked negative Eu anomaly and the normalised Ce/Yb ratio is about 8. Hence the relative fractionation of the light from the heavy REE is more extreme in these rocks compared with either the basic or acid members. There is no simple fractional crystallisation process involving the rocks of Centre 3 that could produce these differences in REE distribution patterns. Although the evidence from the rare earth element distributions is somewhat equivocal, it does not appear to support a simple fractional crystallisation genesis for the acid and intermediate rocks from the same parent of the basic rocks.

The slight enrichment of the light REE relative to the heavy REE in the parent magma of the Ardnamurchan basic rocks is shown also by the magmas of the Skaergaard and Rhum layered intrusions. Paster et al. (1974) estimate that the parent liquid of Lower Zone b (LZb) of the Skaergaard intrusion had a normalised Ce/Yb  $\approx$  2.6, and a similar ratio existed in the Rhum magma (Henderson and Gijbels, in preparation). The Ce/Yb ratio in the Ardnamurchan basic magma is estimated to have been about 4. Furthermore the REE absolute abundances initially for the Ardnamurchan magma were at a similar level to those in the Skaergaard magma (e.g. at LZb) (see Paster et al., 1974).

A study of the REE and other incompatible element geochemistry of rocks from the Mull and Skye basic intrusions would help to elucidate the relationships between the parent magmas of the different intrusive centres of the Hebridean Tertiary igneous province.

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