An occurrence of rare-earth-rich eudialyte from Ascension Island, South Atlantic

C. Harris, G. Cressey, J. D. Bell, F. B. Atkins, and S. Beswetherick

Department of Geology and Mineralogy, Parks Road, Oxford

ABSTRACT. A mineral closely resembling eudialyte in single crystal X-ray pattern and chemistry has been found in one granite block from the 5 Mile Post area on Ascension Island. To our knowledge, eudialyte has not previously been recognized in this suite of granites although they contain two other rare zirconium silicates, dalyite and vlasovite. Textural evidence suggests that the eudialyte, which is remarkable for its high yttrium and REE content, crystallized from very late-stage magmatic fluids. Rare-earth patterns are only slightly fractionated ($Ce_N/Y_N = 1.8–2.5$) compared with those of allanites and sphenes from Skye granites which presumably have similar parageneses. In contrast, the whole-rock REE pattern shows greater enrichment of light REE ($Ce_N/Y_N \sim 10$). This difference in REE pattern is considered to be due to the effects of REE and other element complexing related to the peralkalinity of the granite liquid.

COARSE-GRAINED peralkaline granite blocks have long been known from Ascension Island, situated at 8° S. 14° W., 120 km west of the Mid-Atlantic Ridge. They occur in trachytic breccias at numerous localities around Green Mountain, towards the centre of the island. The most notable of these is 5 Mile Post where the suite of granite blocks has been the subject of several papers (van Tassel, 1952; Fleet and Cann, 1967; Roedder and Coombs, 1967). An apparently identical suite of granites has been found nearby at the base of the Middletons Ridge pyroclastic sequence and presumably represents part of the same eruption. It should be noted that these blocks are free from any lava coating or matrix and may therefore be considered as fragments torn from the walls of a conduit during an explosive phase of eruption.

Petrography of the 5 Mile Post suite. Three texturally similar types which appear to be intergradational can be recognized (see Roedder and Coombs, 1967, for a more complete description). Possible end members are: (i) hornblende non-perthitic granites; (ii) arfvedsonite/aegirine ± oligoclase granites, generally non-perthitic; (iii) arfvedsonite/aegirine perthite granites. The only specimen found to contain eudialyte [spec. H 30(1)] falls within group (iii).

Petrographically, this last group of granites consists of perthite and quartz (often showing coarse granophyric texture) together with about 10 modal % of mafic minerals (arfvedsonite and aegirine). Rarer accessories are dalyite, vlasovite, aenigmatite, zircon, and fayalite (in the cores of some of the other mafic minerals). These blocks show prominent miarolitic cavities which were probably once fluid filled.

Granite blocks of this group are remarkable for the presence of the rare zirconium silicates dalyite (van Tassel, 1952) and vlasovite (Fleet and Cann, 1967). Vlasovite ($Na_2ZrSi_4O_{11}$) may be interstitial and anhedral or well formed with one good cleavage visible in thin section. It is sometimes rather altered. Dalyite ($K_2ZrSi_6O_{15}$) is unaltered, invariably interstitial in texture and displays no cleavage. It very closely resembles quartz in thin section but has a slightly higher birefringence. Vlasovite is much more common than dalyite in these rocks but was unaccountably discovered much later.

Dalyite and vlasovite have not so far been found together in the same block (although some fifty specimens with either mineral are available). Dalyite blocks tend to be slightly more miarolitic but otherwise the two groups are petrographically identical. Block H 30(1), the subject of this paper was collected by one of us (C.H.) in December 1979. This block is dalyite-bearing and indistinguishable in mineralogy and texture from other members of its group and its whole-rock chemistry and modal proportions are shown in Table I. A light brown to colourless, low birefringence mineral infrequently occurs between quartz, mafic, and perthite grains. Fig. 1 shows a typical grain in rock H 30(1) also in contact with dalyite with which there is no apparent reaction. It must be noted that only small amounts of the eudialyte are available and therefore a complete X-ray and chemical investigation

TABLE I. *Chemistry and modal proportions of H 30(1)*

Analysis of H 30(1)		Modal proportions H 30(1)	
Na$_2$O	5.01	Perthite	59
MgO	0.04	Quartz	30
Al$_2$O$_3$	11.48	Mafics (including aegirine	
SiO$_2$	74.00	arfvedsonite)	10
P$_2$O$_5$	0.01	Dalyite	< 1
K$_2$O	4.65	Eudialyte	< 1
CaO	0.27		
TiO$_2$	0.21		
MnO	0.16	* Total Fe as FeO.	
*FeO	4.33	Analysis by microprobe on fused	
ZrO$_2$	0.12	rock/flux beads by the method of	
	————	Dickin and Exley, 1981.	
	100.28	*REE* analysed by standard isotope	
		dilution techniques, Y by XRF.	
Y	86 ppm		
REE abundances ppm			
Ce	220		
Nd	108		
Sm	21.5		
Eu	1.86		
Gd	17.7		
Dy	17.5		
Er	7.38		
Yb	1.99		

has not been possible. The data presented below confirm this mineral as eudialyte.

Optical properties of H 30(1). The mineral studied has moderate relief and is irregularly fractured, but no cleavage is visible in the section available (see fig. 1). It is optically biaxial with 2V$_\gamma$ ~ 70° and shows very weak pleochroism with β slightly brownish and α colourless. Birefringence is low and often slightly anomalous in patches. Zoning is also visible but restricted to small areas.

X-ray study. The eudialyte was identified by X-ray diffraction methods using a 114.6 mm diameter Gandolfi camera. A powder-type diffraction pattern was obtained from a single crystal measuring 0.03 mm across using Ni-filtered Cu-$K\alpha$ radiation and was indexed with the aid of the Powder Diffraction File (card nos. 8-355 and 25-814). The cell dimensions, based on hexagonal indexing, are $a = 14.16$ (± 0.01) and $c = 30.15$ (± 0.03) Å and were calculated by least squares from twenty-eight lines. This unit cell is slightly larger than that of the eudialyte described by Edgar and Blackburn (1972) from Kipawa Lake with $a = 13.95$ (± 0.02) and $c = 30.10$ (± 0.02) Å. The difference in cell size is probably attributable to the higher (Y + *REE*) content of the Ascension eudialyte (see Table III).

Chemistry. Analyses of the eudialyte were performed using a Cambridge Scientific Instruments Microscan 9, operating at 20 kV with a probe current of 5×10^{-8} A. The beam was rastered over an area of 10 μm^2. For Y and *REE* the synthetic glass standards of Drake and Weill (1972) were used. Details of the analytical procedure may be found in Exley (1980). A further check on the validity of the *REE* results was made by analysing the synthetic glass standards for *REE* at the same time as performing the analyses of eudialyte. This was found to give very good agreement with the published results (Drake and Weill, 1972) and also demonstrated the lack of interference between the analytical lines chosen for *REE*, since in no cases were significant amounts of a *REE* detected in a standard in which the element was not present.

The analysis of Eu has proved impossible because of its low abundance and the severity of interferences on both Eu-Lα_1, from Pr-Lα_2 and Sm-Lβ_2 (Exley, 1980). However the probe detection limit is well below the level of the Sm–Gd join. Since there is no observable Eu-Lα peak, there
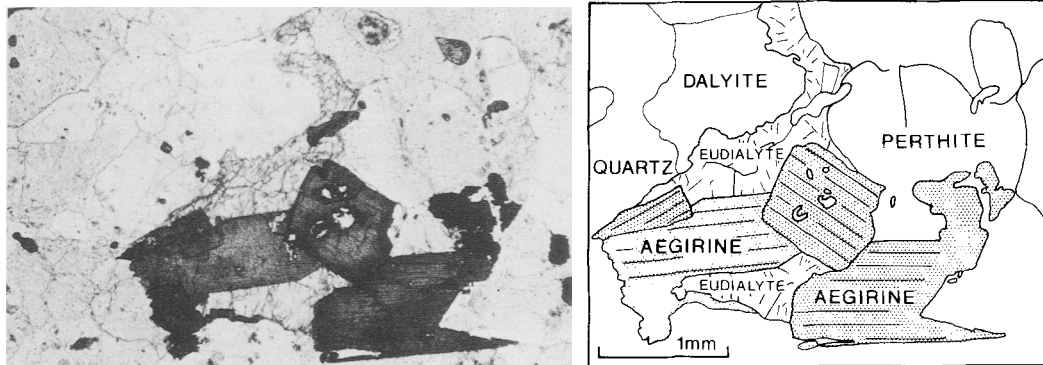

FIG. 1. Photomicrograph of eudialyte. Note the presence of dalyite. Specimen H 30(1).

must be a strong Eu anomaly. Fig. 2 shows the position of the Eu detection limit (chondrite-normalized).

Analyses of eudialyte in H 30(1) are given in Table II. Table III shows the structural formula of one analysis assuming the formula $Na_4(Ca,Fe^{2+}$, REE, $Y)_2ZrSi_6O_{17}(OH,Cl)_2$ proposed by Gossner (1930) and Hey (1962). This is compared with the eudialyte from Kipawa Lake, Canada (Edgar and Blackburn, 1972). The Ascension example fits the formula well although as with the Kipawa Lake eudialyte, Si is rather high. It is possible that some of the REE substitute for Zr as well as (Ca,Fe) since in the analyses with highest REE, Zr is always rather low. The determination of Fe^{3+}, OH, Cl, and F has not been possible. It is probable that only a small amount of the total Fe is Fe^{3+} since (Zr,Al,Ti) is only 0.04 formula units deficient.

This eudialyte is remarkable for the presence of 10–12% REE and Y. The rare-earth content of this and other minor phases such as apatite and zircon is to be the subject of a later paper (C. Harris, work in progress) and only brief consideration of its significance will be given here.

TABLE III. *Structural formula of eudialyte from H 30(1) assuming nineteen oxygens compared with Kipawa Lake eudialyte*

Ascension (rim)	wt. %	19(O)	Kipawa Lake*	wt. %	19(O)
Na_2O	13.48	} 3.48	Na_2O	12.53	} 3.08
K_2O	0.52		K_2O	0.43	
CaO	3.92		CaO	9.74	
FeO	5.97		FeO	2.41	
MnO	2.19	} 2.01	MnO	1.34	} 2.08
MgO	0.02		MgO	0.13	
Y_2O_3	3.61		RE+Y	6.40	
REE_2O_3	7.16		SrO	0.11	
ZrO_2	14.39	} 0.96	ZrO_2	11.80	
Al_2O_3	0.09		Al_2O_3	0.44	
TiO_2	0.50		Fe_2O_3	0.19	} 0.87
SiO_2	49.36	6.48	TiO_2	0.38	
			Nb_2O_5	0.69	
			SiO_2	50.35	6.23
Total	100.96	12.98	Total	99.88	12.26

* Edgar and Blackburn (1972).

TABLE II. *Chemical analysis of eudialyte from H 30(1)*

	Rim	Rim–core	Core
SiO_2	49.36	47.76	46.64
Al_2O_3	0.09	0.02	0.02
*FeO	5.97	5.92	6.24
MgO	0.02	0.02	0.02
CaO	3.92	4.29	4.04
Na_2O	13.48	12.74	12.82
K_2O	0.52	0.42	0.37
TiO_2	0.50	0.43	0.41
MnO	2.19	2.45	2.69
ZrO_2	14.39	13.39	13.39
Y_2O_3	3.61	4.18	3.58
La_2O_3	1.13	1.31	1.50
Ce_2O_3	2.37	2.48	2.93
Pr_2O_3	0.27	0.25	0.25
Nd_2O_3	1.12	1.05	1.30
Sm_2O_3	0.29	0.28	0.35
Gd_2O_3	0.69	0.72	0.75
Dy_2O_3	0.52	0.68	0.69
Er_2O_3	0.48	0.45	0.45
Yb_2O_3	0.18	0.16	0.17
Total	100.96	99.03	98.62
RE+Y	10.77	11.55	11.78
Ce_N/Y_N	1.86	1.87	2.49

* All Fe represented as Fe^{2+}.

Petrogenesis. Eudialyte is most commonly found in pegmatite and syenitic peralkaline rocks of both over- and under-saturated types. Ascension Island granites are rather peralkaline (with a small amount of normative sodium metasilicate) and very over-saturated (see analysis of H 30(1) and modal proportions Table I). It is obvious on textural grounds (fig. 1) that eudialyte formed at a very late stage in the rock's crystallization history. It is possible that the mineral formed from hydro-thermal fluids after the rock had solidified but the lack of alteration in the rock as a whole seems to preclude this. It is also possible that the eudialyte formed as an alteration of dalyite but in fig. 1 eudialyte occurs adjacent to dalyite with no evidence of reaction.

The high rare earth content of this eudialyte seems, therefore, to be due to its late-stage crystallization from the residual magmatic fluid. The chondrite-normalized REE patterns for the core, the rim, and a point mid-way between are shown in fig. 2. Y is plotted in place of Ho on ionic radius considerations, as recommended by Eby (1975). The Ascension eudialyte is seen to be very slightly LREE enriched (Ce_N/Y_N 1.86–2.49 and Ce_N/Yb_N 3.5–4.2). This can be contrasted with Exley's data on rare-earth-enriched sphenes and allanites from the Skye epigranites, also considered to be the late crystallization products of residual magmatic fluids. The two Skye examples illustrated show highly fractionated REE patterns (Ce_N/Y_N = 40–100).
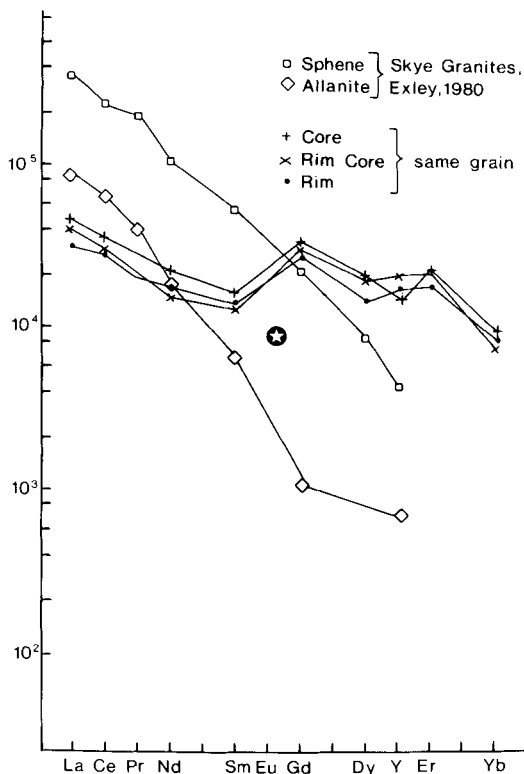
FIG. 2. Chondrite-normalized *REE* profiles of eudialyte
from H 30(1). Shown for comparison are *REE* profiles
of sphene and allanite from Skye granites (Exley, 1980).
Circle = Eu detection unit. Chondritic values from
Nakamura (1974), Y and Pr from Frey *et al.* (1968).

Zoning is seen in the Ascension eudialyte in thin
section and has been investigated for any difference
in *REE* content between rims and cores of grains.
The cores of analysed grains are found to be slightly
more *REE* enriched (this is also seen in grains not
represented by analyses in this paper). There seems
to be no noticeable change in fractionation of the
REE pattern from rim to core, the three *REE*
patterns in fig. 2 remaining approximately parallel.

Fig. 3 shows the chrondrite-normalized *REE*
pattern for H 30(1) whole rock. A strong negative
Eu anomaly is present which suggests that the
suspicion of an Eu anomaly in the eudialyte is
justified. This type of anomaly is strongly sug-
gestive of feldspar fractionation at some time
during the earlier history of this magma. It can
also be seen that the whole-rock *REE* profile is
rather different in shape from the profile exhibited
by the eudialyte contained within it, showing a
much stronger enrichment of light *REE*. This type
of relationship is seen in a number of peralkaline

rocks where eudialyte, despite being the major
REE-bearing mineral, has a heavy *REE*-enriched
pattern, and the whole rock a light-*REE*-enriched
pattern (Fryer and Edgar, 1977).

Fryer and Edgar (1977) suggest that this late-
stage enrichment of heavy *REE* does not occur
because of the preferential concentration of these
elements by the eudialyte, but is due to complexing
involving Na and F in late-stage magma and
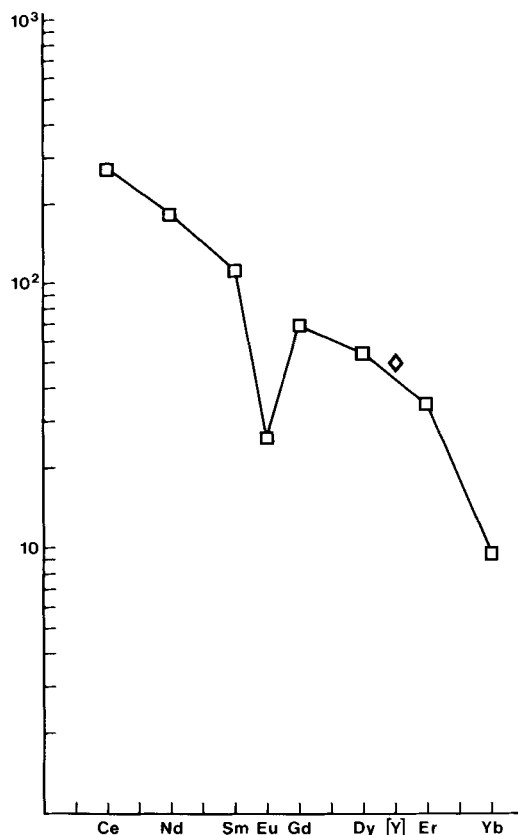postmagmatic fluids. Complexes involving heavy

FIG. 3. Chondrite-normalized *REE* profile of H 30(1)
whole rock. *REE* values obtained by standard isotope
dilution methods, Y by XRF.

REE are more stable than those with light *REE*
and hence the liquids left at the last stages will be
enriched in heavy *REE*. Consequently the last
mineral to crystallize, which in the case of H 30(1)
is eudialyte, will be much richer in heavy *REE* than
the whole rock.

Late-stage sphenes and allanites from the Skye
granites do not show any heavy *REE* enrichment
(fig. 2) and consequent indication of *REE* complex-
ing. It is presumably the extreme peralkaline nature

of the Ascension granites which makes the *REE* behaviour in late-stage fluids so different from that of the Skye granites.

Conclusions. (i) A late-stage crystallization product of residual magmatic fluids has been identified as eudialyte from X-ray and chemical evidence. (ii) Since only one block of fifty examined contained this mineral, the fluid concerned was not widely distributed throughout the parental coarse-grained body (assuming random sampling by eruption). (iii) Eudialyte shows a heavy-*REE*-enriched pattern relative to that of its whole rock. This is considered to be due to the effect of the relative stability of heavy *REE* complexes compared with those of light *REE* in the final stages of crystallization. (iv) This example is very similar to the type of *REE* distribution seen in various peralkaline undersaturated rocks and shows that oversaturated peralkaline rocks show similar complexing effects. Late-stage minerals from Skye show no such *REE* distribution which presumably reflects the importance of peralkalinity in this type of complexing.

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