Rare-earth partition between allanite and glass in the obsidian of Sandy Braes, Northern Ireland

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ABSTRACT. Allanite phenocrysts and co-existing glass from the perlitic obsidian of Sandy Braes have been analysed for nine rare earths (RE), uranium, and thorium by instrumental neutron activation analysis and for the major elements by electron microprobe. The chondrite-normalized RE plot for the allanite shows a steep slope with a negative Eu anomaly. Allanite/glass partition coefficients show a smooth variation with ionic radius (except for Eu), the variation spanning two orders of magnitude. The partitioning behaviour, which is distinct from that shown by the RE in sphene, apatite, and zircon, can be explained by the allanite structure. The pronounced affinity of the light RE for allanite makes this an important mineral in considerations of RE concentrations during the evolution of granitic liquids.

THE geochemical behaviour of the rare earths (RE) has proved to be very suitable for the mathematical testing of petrogenetic models for a variety of igneous rocks including granitic ones. In some cases, accessory minerals such as zircon and apatite (Hanson, 1978) could play a significant role in the fractionation of RE by virtue of their high RE contents. Therefore it has become important to establish the partition of RE in such minerals so that the models may be more truly representative of the petrogenetic process. Allanite usually crystallizes early from granitic melts and so may have to be considered in calculations of petrogenetic modelling. In this paper we present an allanite analysis and data on the RE, Th, and U partition between the phenocrystal allanite and glass of the Sandy Braes perlitic obsidian of Northern Ireland.

Several reports already exist in the literature of phenocrystic allanite in sparsely porphyritic rhyolites (Branch, 1966; Izett and Wilcox, 1968; Duggan, 1976; Hildreth, 1979) and indeed it has been previously reported in the Sandy Braes obsidian (Cameron and Sabine, 1969; Sabine, 1970) although this occurrence apparently escaped the attention of Duggan (1976).

The Sandy Braes vent is part of the Tardree rhyolite complex of Antrim, a 26 km² outcrop of acid rocks belonging to the Interbasaltic Formation (Old, 1975). These rocks are believed to be penecontemporaneous with the tholeiitic basalts which form the Giant's Causeway of the north Antrim coast and may have been derived from such basaltic magmas by fractional crystallization. A fission track age for the Tardree rhyolite of about 65 Ma has recently been reported by Fitch and Hurford (1977).

The welded tuffs of the Sandy Braes vent have been described in detail by Cameron and Sabine (1969), and Sabine (1970) has investigated the properties of the perlitic obsidian. These rocks are black, lustrous, and porphyritic. Their textures are interpreted as extreme examples of welding during which the pyroclastic texture was largely obliterated. Phenocrysts comprise about 20% of the rock and are quartz and feldspar (respectively up to 1.5 and 3 mm in size) with trace amounts of allanite, altered fayalite, biotite, and zircon. The zircon was observed by us but not noted by Cameron and Sabine (1969). Feldspar phenocrysts make up about 4% of the rock and are both sanidine and oligoclase. A microprobe analysis of the glass in this rock is presented in Table I where it is compared with a bulk analysis from the literature. The difference is, as expected, small. There is likewise little difference from the allanite-bearing rhyolites of New South Wales described by Duggan

TABLE I. *Analyses and norms of some obsidians with allanite phenocrysts*

	1	2	3
SiO_2	72.83	74.95	73.91
TiO_2	0.06	0.12	0.27
Al_2O_3	12.41	11.77	12.25
Fe_2O_3	—	1.03	0.66
FeO	1.59	0.72	0.67
MnO	—	0.04	0.02
MgO	—	0.01	0.05
CaO	0.91	1.02	0.67
Na_2O	2.91	2.82	2.77
K_2O	5.57	4.70	5.55
H_2O	—	2.76	2.65
P_2O_5	—	0.06	0.06
Total	96.28	100.00	99.53
Q	31.38	38.36	35.08
C	—	0.32	0.61
or	32.92	27.78	32.83
ab	24.62	23.86	23.39
an	4.35	4.71	2.96
di	0.15	—	—
hy	2.22	0.35	0.41
mt	—	1.49	0.96
il	0.11	0.23	0.51
ap	—	0.14	0.14

1. Partial analysis of glass in perlitic obsidian Sandy Braes (microprobe analysis).
2. Perlitic porphyritic obsidian from borehole, Sandy Braes (Cameron and Sabine, 1969; Sabine, 1970). Original analysis reports several additional constituents.
3. Average of two analyses of allanite-bearing rhyolites from the Tweed Shield Volcano of New South Wales, Duggan (1976).

(1976), which are also regarded as being extreme differentiates of a tholeiitic magma.

Experimental methods and results. The composition of the allanite microphenocrysts was determined by microprobe techniques as described previously (Pedersen *et al.*, 1975). The *RE* were determined using CeO_2, a CaO-Al_2O_3-SiO_2 glass doped with 18 % La_2O_3, and monazite containing 12.4 % Nd_2O_3 and 4.95 % Pr_2O_3, as standards. The results of the microprobe analysis are given in Table II. Two traverses across separate allanite grains revealed no compositional zoning.

The *RE*, Th, and U contents of allanite (1.8 mg) and glass (13 mg) were determined by instrumental neutron activation analysis (INAA) by the technique described by Henderson and Williams (in press). One intrinsic Ge detector of a measured resolution of 560 eV at 122 keV was used. The results are given in Table III. Accuracy and precision are estimated to be better than 5 % for La and

TABLE II. *Microprobe analysis of allanite microphenocryst in obsidian from Sandy Braes, Antrim*

		Number of cations	
SiO_2	31.20	Si	3.037
Al_2O_3	14.32	Al	1.644
TiO_2	1.69	Ti	0.124
FeO	15.52	Fe	1.263
MnO	0.27	Mn	0.022
MgO	0.17	Mg	0.025
CaO	10.11	Ca	1.055
La_2O_3	5.83	La	0.209
Ce_2O_3	12.26	Ce	0.436
Nd_2O_3	4.28	Nd	0.149
Pr_2O_3	1.00	Pr	0.035
ZrO_2	0.03	Zr	0.001
	96.68		8.000
*FeO	13.03	Fe^{2+}	1.060
*Fe_2O_3	2.77	Fe^{3+}	0.203

* Oxidation state of Fe estimated on basis of 13(O,OH) in the formula unit which is taken to be of the type: $(Ca,Ce)_2(Fe^{3+},Fe^{2+})Al_2O \cdot OH[Si_2O_7][SiO_4]$.

Lu and better than 2 % for the other determined *RE*. There is close agreement between the results obtained by microprobe analysis and by activation analysis. Chondrite-normalized *RE* plots of the allanite and glass are shown in fig. 1. The allanite
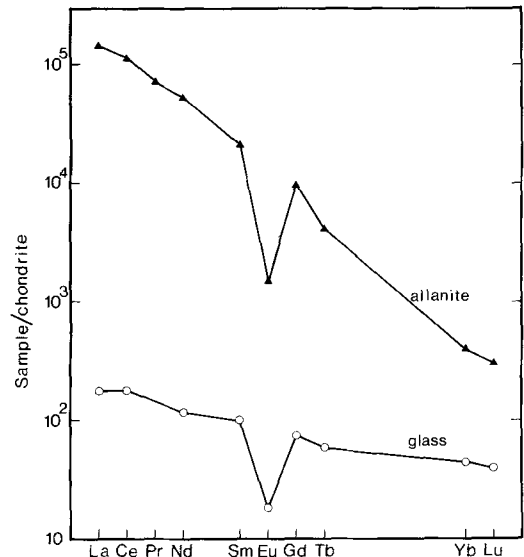

FIG. 1. Chondrite-normalized *RE* abundances of the allanite and co-existing glass plotted against atomic number. *RE* chondrite values from Wakita *et al.* (1971). The INAA data are used for all elements except Pr, the value for which is from the microprobe analysis.

plot demonstrates the extreme fractionation of the RE by this mineral, with a chondrite-normalized La/Lu ratio of 473. Allanite from the rhyolitic Bishop Tuff, California has a similar RE pattern with chondrite-normalized La abundance of 1.85×10^5 and a La/Lu ratio of 1050 (Hildreth, 1979). Likewise, similar RE patterns were reported for allanites from the Tertiary granites of Skye by Exley (1980), although Eu was not determined.

The composition of the allanite from Sandy Braes is fairly typical of the mineral as indicated from analyses quoted by Deer et al. (1962, pp. 214–15), despite the fact that most analysed allanites have come from granite pegmatites and similar rocks which probably formed in an environment richer in RE than that of the Sandy Braes obsidian.

TABLE III. Activation analyses for RE, U, and Th in allanite and co-existing glass, and calculated partition coefficients

	Allanite	Glass (ppm)	Partition coefficient
La	4.92%	60	820
Ce	10.45%	165	635
Nd	3.47%	75	463
Sm	0.41%	20	205
Eu	108 ppm	1.33	81
Gd	2590 ppm	20	130
Tb	195 ppm	2.75	71
Yb	87 ppm	9.8	8.9
Lu	10 ppm	1.3	7.7
U	<62 ppm	9.3	<6.7
Th	7600 ppm	45.2	168

Phenocryst/glass partition coefficients (k) are given for the RE, Th, and U in Table III; they confirm the great affinity of allanite for these elements, especially the light RE. The highest partition coefficient is shown by La and then there is a rapid decrease with atomic number of the RE. The partition coefficient values show a smooth variation with ionic radius (fig. 2) except for europium which lies off the depicted curve most probably because it exists partly in the 2 + oxidation state.

The marked variation in partition coefficient values, even for the light RE, recorded here contradicts earlier statements (e.g. Jensen, 1967) that allanite incorporates the larger RE without appreciable fractionation. However, the variation is dissimilar to that shown by apatite (Nagasawa, 1970) or sphene (Hellman and Green, 1979; Henderson, 1980) in that these two latter minerals show a preference for the middle group of RE and without such an extreme fractionation.

The RE partitioning behaviour can be explained in terms of the structural characteristics of allanite. The Ca atoms are located in two large polyhedra, designated $A(1)$ and $A(2)$. Site $A(2)$ is the larger and has a co-ordination number of eleven and is mostly occupied by the RE (Dollase, 1971). Site $A(1)$ is 9-fold co-ordinated. The cation–oxygen bond distances associated with the $A(2)$ site show wide variation, being dependent upon the size of the occupying cation (Dollase, op. cit.). The largest RE ions are readily accommodated in the large $A(2)$ site but the heavier RE, such as Yb and Lu, are too small for their exchange between allanite and melt to be energetically very favourable (Henderson, 1979). The effect of the size of the available sites on crystal/liquid partition of the RE is well exemplified by consideration of the three minerals, allanite, apatite, and zircon. Fig. 3 shows selected data on partition coefficients of the RE for these minerals and their host volcanic matrices. Allanite has the largest available site and the highest RE partition coefficient is shown by La.
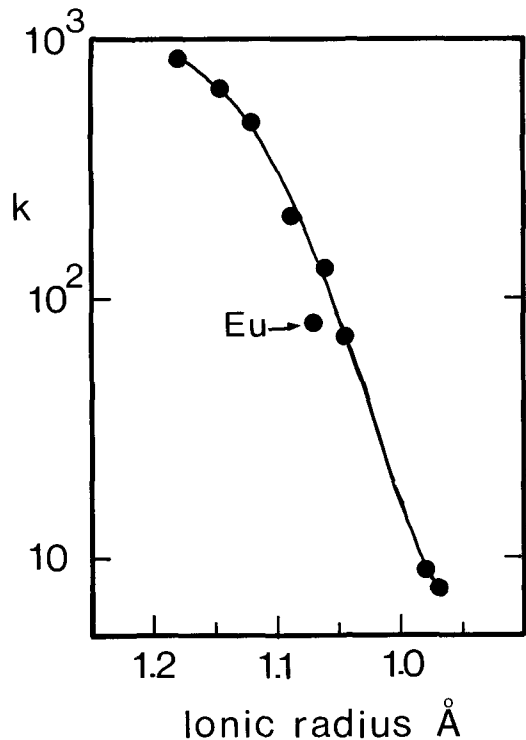

FIG. 2. Rare earth partition coefficients, k, for allanite/glass versus ionic radius. Ionic radii values from Shannon and Prewitt (1969) for 3 + cations in 8-fold co-ordination (data for higher co-ordinations not always available).
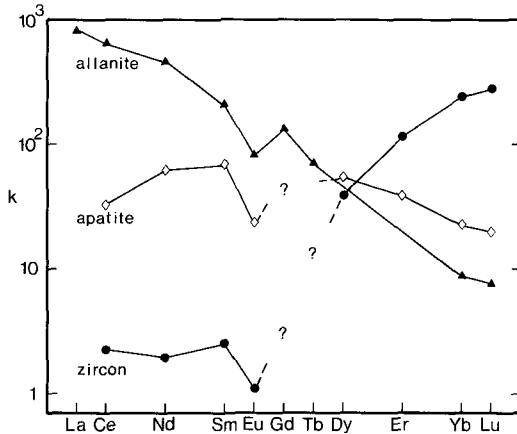
FIG. 3. Rare earth, mineral/matrix partition coefficients, *k*, versus atomic number for allanite (this work), apatite and zircon (Nagasawa, 1970).

Zircon has the smallest available site, the substituted cation Zr^{4+} is relatively small, and the highest partition coefficient is shown by Lu. Apatite, with available cation sites intermediate in size between those of allanite and zircon has high partition coefficients shown by the middle group of *RE*, especially Sm. Fig. 3 shows the nature of the differences in partitioning behaviour but direct comparison of the values is precluded as the allanite was separated from a rock different in composition from that giving apatite and zircon.

Despite its high charge, Th^{4+} shows a similar partition coefficient to Gd^{3+} and Sm^{3+} (Table III). However, the partition coefficient of uranium, although determined only as a possible upper limit, is less than that of any of the *RE*. This suggests that the uranium is present predominantly in a high oxidation state (U^{6+}?) in both phases. Hence allanite crystallization tends to fractionate thorium from uranium.

The high partition coefficients for the light *RE* recorded here mean that the crystallization of the approximately 0.1 % allanite present in the Sandy Braes rock leads to a decrease in La by a factor of nearly two and a 45 % change in the La/Lu ratio of the supernatant melt. Thus the presence of allanite, although readily overlooked, could be a very significant factor in the evolution of granitic liquids and any attempt to model this evolution must take into account the possible crystallization of allanite as well as other accessories such as zircon and apatite. However, the high viscosities associated with acid magmas will reduce the extent of any fractional crystallization. Chekinite and

perrierite may also be significant phases controlling the *RE* in some cases and have, for example, been reported as phenocrysts in peralkaline ignimbrites (Schmincke, 1976). An analysis of chevkinite from a similar chemical environment as the Sandy Braes rock has been provided by Brooks and Rucklidge (1976).

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