

THE RARE-EARTH-ELEMENT CHEMISTRY OF ALLANITE FROM THE GRENVILLE PROVINCE

RONALD C. PETERSON AND DARRYL B. MACFARLANE*

Department of Geological Sciences, Queen's University, Kingston, Ontario K7L 3N6

ABSTRACT

The results of electron-microprobe analyses of 38 samples of allanite from granitic rocks and calcite veins in the Grenville Province of southeastern Ontario and southwestern Quebec are presented. Allanite from granitic rocks show a wider range of REE contents than those from carbonate veins. The samples of allanite studied exhibit the coupled solid-solution $\text{Ca}^{2+} + \text{Al}^{3+} + \text{Fe}^{3+} = \text{REE}^{3+} + \text{M}^{2+}$ as well as an omission solid-solution of the form $3\text{Ca}^{2+} = 2\text{REE}^{3+} + \square$.

Keywords: allanite, epidote group, electron-microprobe analysis, solid solution, Grenville Province, Ontario, Quebec.

SOMMAIRE

Nous présentons les résultats d'analyses à la microsonde électronique de trente-huit échantillons d'allanite provenant de roches granitiques et de filons de calcite dans la province du Grenville, dans le sud-est de l'Ontario et le sud-ouest du Québec. L'allanite prélevée des roches granitiques montre une plus grande variabilité en teneurs de terres rares (TR) que celle des filons de carbonate. La solution solide couplée $\text{Ca}^{2+} + \text{Al}^{3+} + \text{Fe}^{3+} = \text{TR}^{3+} + \text{M}^{2+}$ et un mécanisme impliquant une lacune, comme $3\text{Ca}^{2+} = 2\text{TR}^{3+} + \square$, rendent compte de la composition des échantillons.

(Traduit par la Rédaction)

Mots-clés: allanite, groupe de l'épidote, analyses à la microsonde électronique, solution solide, province du Grenville, Ontario, Québec.

INTRODUCTION

Allanite-(Ce), which has, as idealized formula, $(\text{Ce,Ca,Y})_2(\text{Al,Fe}^{3+})_3(\text{SiO}_4)_3(\text{OH})$, is the most abundant and widespread rare-earth-element-bearing mineral found in the Grenville Province of the Canadian Shield. The allanite, which is commonly metamict, is an accessory mineral in many rock types including: granite, granitic pegmatite, syenite, syenitic pegmatite and calcite skarns and veins. Allanite generally is associated with radioactive minerals, and its mode of occurrence is well documented (Ellsworth 1932, Hewitt 1955, Satterly 1957, Shaw 1958, Rose 1960, Lang *et al.* 1962, Masson & Gordon 1981).

In the Grenville Province of southern Ontario and southwestern Quebec, allanite most commonly occurs as an accessory mineral in granitic pegmatites. From textural, mineralogical and structural features, Masson & Gordon (1981) divided these pegmatites into four types: 1) simple zoned pegmatites, 2) complex zoned pegmatites, 3) simple unzoned pegmatites, and 4) com-

plex unzoned pegmatites. Although allanite is found in all four types, it is particularly abundant in simple zoned pegmatites in the vicinity of Bancroft and Madawaska, Ontario. In this area, individual crystals up to 60 cm in length and 15 cm in width have been reported (Hogarth *et al.* 1983). Allanite also occurs as an accessory mineral in some of the calcite veins of the Grenville Province (Hogarth *et al.* 1983). Masson & Gordon (1981) divided the uraniferous carbonate veins into two types based on their mineralogy and internal structure. These are the fluorite-apatite-rich pink carbonate veins, which Satterly (1957) referred to as the "fission type", and "Cardiff or Eagle's Nest type" veins, which contain calcite, fluorite, apatite, biotite, diopside, hornblende and scapolite.

The purpose of the present study is to investigate the detailed chemistry of Grenville allanite by electron-microprobe analysis and to compare the compositions of allanite from granitic pegmatites with those obtained from calcite veins.

PREVIOUS STUDIES OF DISTRIBUTION OF RARE-EARTH ELEMENTS IN ALLANITE

The distribution of the rare-earth elements (REE) in

* Present address: Grenville Minerals, P.O. Box 453, Kingston, Ontario K7L 4W5.

allanite was first described by Goldschmidt & Thomas-sen (1924), who noted that allanite, like monazite, concentrates the light rare-earth elements (*LREE*). Semenov (1958) attributed the preference for *LREE* to a

TABLE 1. LOCATION AND DESCRIPTION OF SAMPLES OF ALLANITE

SAMPLE	DEPOSIT NAME	LOCATION	HOST ROCK	REFERENCE	SOURCE
R1002	---	Champagne Twp., Que. (Riviere Serpent-near outlet of Lac Bois Franc)	GP	---	GSC(07974)
R1005	Moly. Corp. Cheddar Road Occur.	N 1/2 Lot 11, Conc. 11, Cardiff Twp., Ont.	GP	Satterly (1957)	ROM(24628)
R1006	Fission (Richardson) Mine	Lots 4-6, Conc. 11, Cardiff Twp., Ont.	CV	Ellsworth (1932), Rowe (1952)	ROM(29754)
R1008	---	Lot 7, Conc. 11, Armour Twp., Ont. (North side of Pickeral and Jack Lake Road)	GP	Satterly (1977)	ROM(34034)
R1010	Cardiff Mine	Lot A, Conc. 17, Cardiff Twp., Ont.	CV	Satterly (1957)	NMC(42755)
R1011	---	Lot 27, Conc. 15, Glamorgan Twp., Ont.	CV	---	NMC(42758)
R1012	Gole Quarry	Lots 14 and 15, Conc. 4, Murchison Twp., Ont.	SZGP	Hogarth et al. (1983)	NMC(42759)
R1013	Rosenthal Occur.	Lot 34, Conc. 4, Brudenell Twp., Ont.	GP	Hewitt (1954)	NMC(42760)
R1014	Guts Farm Occur.	Lot 34, Conc. 5, Brudenell Twp., Ont.	GP	---	NMC(42764)
R1015	---	S 1/2 Lot 26, Conc. 19, Raglan Twp., Ont.	SG	Hewitt (1954)	NMC(42766)
R1018	Giroux Prop (Bear Lake Mine)	Litchfield Twp., Que.	CV	---	NMC(42772)
R1019	Five Mile Lake Mine	Lot 17, Conc. 7, Dickens Twp., Ont.	SZGP	Sabina (1971)	NMC(43347)
R1020	---	West of Maynooth, approx. 8 km from railway - McClure or Herschel Twp., Ont.	GP	---	NMC(43348)
R1023	Craigmont Mine	Lots 3 and 4, Conc. 18, Raglan Twp., Ont.	SP	Ellsworth (1932)	NMC(47504)
R1024	Wal Gem East Quarry	Lot 23, Conc. 15, Lyndoch Twp., Ont.	CZGP	Hewitt (1967)	NMC(47550)
R1025	Jewellville Cuts	Lot 25, Conc. 19, Raglan Twp., Ont.	SP	Hewitt (1954)	NMC(47615)
R1026	Madawaska (Faraday) Mine	Lots 16 and 17, Conc. 11, Faraday Twp., Ont.	CZGP	Satterly (1957), Bullis (1965)	NMC(47681)
R1027	---	Lot 1, Conc. 14, Lutterworth Twp., (Pit 20m NE of where Hwys 35 and 121 cross)	GP	---	NMC(48133)
R1028	---	Minden Twp., Ont.	CV	---	NMC(48186)
R1029	---	Lot 6, Conc. 2, Dudley Twp., Ont. (Hwy 121 roadcut near Loon (Dudman) Lake)	GP	---	NMC(48188)
R1030	Atlin-Ruffner Allanite Prop.	N 1/2 Lot 2, Conc. 16, Cardiff Twp., Ont.	CZGP	Satterly (1957)	GSC(60956)
R1032	---	Lytton Twp., Que.	U	---	GSC(60963)
R1033	Bicroft (Centre Lake) Mine	Lots 27 and 28, Conc. 11, Cardiff Twp., Ont.	CUGP	Satterly (1957)	GSC(60986)
R1034	Rare Earth Mine Shaft #1	Lot 20, Conc. 8, Monmouth Twp., Ont.	CUGP	Satterly (1957)	GSC(60987)
R1035	Lac a Baude Occur.	Normand Twp., Que. (East short of Lac a Baude)	SUGP	Harvie (1921)	GSC(60994)
R1037	Watson #1 Mine	Lot 21, Conc. 6, Monteagle Twp., Ont.	GP	Hewitt (1955)	GSC(60998)
R1038	MacDonald Mine-North Dike	Lot 18, Conc. 7, Monteagle Twp., Ont.	SZGP	Hewitt (1955), Ellsworth (1932)	GSC(62545)
R1039	---	Lot 27, Conc. 18, Brougham Twp., Ont. (Hwy 41, roadcut near Tooys Lake)	CV	---	GSC(63009)
R1040	---	Mitchell Twp., Que. (300m west of Gatineau River - SE corner of twp.)	GP	---	GSC(64446)
R1041	---	Clapham Twp., Que. (Roadcut on Picanoc Road 11.4 km north of Otter Lake)	GP	Sabina (1971)	GSC(64447)
R1042	Fry Lake Occur (Seguin Falls)	Lot 21, Conc. B, Monteith Twp., Ont.	SUGP	Ellsworth (1932)	QMM(N1538)
R1043	MacDonald Mine - South Dike	Lots 18 and 19, Conc. 7, Monteagle Twp., Ont.	SUGP	Hewitt (1955), Ellsworth (1932)	QMM(N8617)
R1044	Yates Mine - Matte Zone	Lots 16 and 17, Range 5, Huddersfield Twp., Que.	CV	Lafontaine (1979)	QMM(N8618)
R1045	Parham Occur.	W 1/2 Lot 2, Conc. 8, Olden Twp., Ont.	CV	Satterly (1977)	QMM(N8619)
R1046	Universal Light Metals Occur.	Lot 25, Conc. 15, Lyndoch Twp., Ont.	SUGP	Masson & Gordon (1981)	QMM(N8620)
R1048	Miller Lake Occur.	W 1/2 Lot 2, Conc. 7, Olden Twp., Ont.	CV	---	QMM(N8621)
R1052	Welsh Farm Occur.	Lot 8, Conc. 10, Monteagle Twp., Ont.	GP	Masson & Gordon (1981)	QMM(N8622)
R1054	Sundstrom North Occur.	N1/2 LOT 18, Conc. 12, Carlow Twp.	GP	Masson & Gordon (1981)	QMM(N8623)

Notes: n.d. means "not detected"

H_2O^+ was calculated on the basis of 1 OH per formula

Fe^{2+}/Fe^{3+} was calculated by normalizing on fixed cation and anion sums of $Si+M1+M2+M3=6$ and $(O,OH)=13$, respectively.

Host Rock Codes:

GP - granite pegmatite

CV - calcite vein

SZGP - simple zoned granite pegmatite

SUGP - simple unzoned granite pegmatite

SG - syenite gneiss

U - unknown

CZGP - complex zoned granite pegmatite

CUGP - complex unzoned granite pegmatite

The following notation is used to describe the source of the specimens:

GSC - Geological Survey of Canada, Ottawa, Ontario

ROM - Royal Ontario Museum, Toronto, Ontario

NMC - Canadian Museum of Nature, Ottawa, Ontario

QMM - Queen's University, Miller Museum, Kingston, Ontario

crystal-chemical control. He showed that mineral structures having a cation site with a high coordination number (10–12) are *LREE*-selective, and those with low-coordination cationic sites prefer the heavy rare-earths. Allanite, which has an 11-fold-coordinated site (Dollase 1971), would therefore be expected to contain a large proportion of *LREE*.

Several investigators have noted that the *REE* content of allanite depends on the bulk chemistry of the host rock (Vainshtein *et al.* 1956, Murata *et al.* 1957, Kosterin *et al.* 1961, Fleischer 1965, 1985), Murata *et al.* (1957) defined Σ as the ratio $(La+Ce+Pr)/(\text{total } REE)$, a numerical index to assess degree of fractionation of *REE* in allanite from different sources. They showed that the relative *LREE* enrichment of allanite increases progressively from granitic pegmatite to granodiorite to carbonatite to alkaline rocks to alkaline pegmatites. Fleischer (1985) used the Σ value of Murata *et al.* (1957) to compare data for 330 samples of allanite from a variety of rock types. Lee & Bastron (1967) showed the variation and relative abundance of *REE* in allanite to be related to the calcium content of the host rock. In a study of accessory allanite and monazite in the granitic rocks of the Mount Wheeler mine area, Nevada, they discovered that: 1) there is a direct correlation between proximity to limestone and Ca content of the granitic rocks, 2) the Ca content of the granitic rocks influences the type of accessory minerals that developed, and 3) there is a direct correlation between Ca content of the host rock and the Σ of the constituent allanite and monazite.

It has been common in the past to report results of partial analyses of allanite. Furthermore, the frequent presence of alteration products and inclusions in allanite (Robinson & Abbey 1957, Withers 1976, Rimsaite 1978, Lafontaine 1979, Masson & Gordon 1981, Habib 1982) makes most of the unpublished analytical data suspect because all but a few have been based on wet-chemical or bulk X-ray spectrographic methods. In the present study, the use of the electron microprobe to study a wide range of elements allows a much more complete study of the composition of allanite.

SAMPLE DESCRIPTION AND ELECTRON-MICROPROBE DATA

The chemical composition of 38 grains of allanite was determined by wavelength-dispersion electron-microprobe analysis. The microprobe data were collected on an ARL-SEM-Q electron microprobe (take-off angle 52.5°) equipped with Tracor Northern automation and data reduction. Analytical conditions for quantitative analysis include: an excitation voltage of 15 kV, beam current of approximately 20 nA measured with a Faraday cup, mean beam diameter of approximately 0.5 to 1.0 μm , and a counting time of 100 seconds (50 seconds on the peak and 25 seconds on each back-

ground). More specific instrumental settings for each element are given by MacFarlane (1987).

Initial wavelength-dispersion scans of the *REE* and trace elements were conducted at 20 kV for eight representative samples, to determine which elements are present and their approximate relative abundance, and to select appropriate background positions. As a result, the concentration of six *REE* (La, Ce, Pr, Nd, Sm and Gd) and two other trace elements (Y and Th) were found to be above background. The scans were then superimposed and, with the aid of the wavelength tables of White & Johnson (1979), background positions above and below the various peaks were chosen. During the quantitative wavelength-dispersion analysis, the upper and lower background counts for these elements were carefully monitored, and the difference was found to be negligible. The *K* series of X-ray spectra was used for the major elements, the *M* series for Th, and the *L* series for Y and the *REE*. Lines were chosen to minimize interference. By choosing the $\text{La}\alpha_1$ line for La, Ce and Nd, and the $\text{Pr}\beta_1$ line for Pr and Sm, no peak-overlap corrections were needed. By assuming that there was no Ho present, the $\text{Pr}\beta_1$ line for Gd could be used without correction (Roeder 1985). This assumption is supported, as no Ho was observed in the spectral scans.

The locations and descriptions of the occurrences are given in Table 1. A list of the primary and secondary standards used in this study is presented in Table 2. A

TABLE 2. STANDARDS USED FOR WAVELENGTH-DISPERSION ELECTRON-MICROPROBE ANALYSES

Standard Element	Standard Number	Name	Composition	Reference
Si, Ti, Al, Fe, Mg, Ca	S205	Kaersutite	Si(18.86), Ti(2.83), Al(7.89), Fe(8.49), Mn(0.07), Mg(7.72), Ca(7.36), Na(1.93), K(1.70), O(41.90)	1
Mn	S207	Rhodonite	Si(22.21), Al(0.13), Fe(8.81), Mn(25.58), Mg(0.20), Ca(5.39), O(37.69)	1
La	S241	Synthetic LaPO ₄	La(58.39), P(13.24), O(27.36)	2
Ce	S242	Synthetic CePO ₄	Ce(59.20), P(13.17), O(27.22)	2
Pr	S245	Synthetic PrPO ₄	Pr(59.74), P(13.13), O(27.13)	2
Nd	S244	Synthetic NdPO ₄	Nd(60.30), P(12.95), O(26.75)	2
Sm	S243	Synthetic SmPO ₄	Sm(61.29), P(12.63), O(26.09)	2
Gd	S261	Synthetic GdPO ₄	Gd(62.35), P(12.29), O(25.37)	2
Y	S248	Synthetic YPO ₄	Y(48.35), P(12.94), O(34.60)	2
Th	S304	Fused ThO ₂	Th(77.89), O(12.12)	2
U	S155	Fused UO ₂	U(68.15), O(11.85)	2
Secondary Standards				
Si, Ti, Al, Fe, Mn, Mg, Ca	S195	VG-2 Glass	Si(23.75), Ti(1.11), Al(7.44), Fe(9.20), Mn(0.17), Mg(4.05), Ca(7.85), Na(1.94), K(0.16), O(43.65)	1
La, Ce, Pr	S153	REE Glass #3	Si(12.69), Al(16.26), Ca(18.10), Y(3.21), La(2.65), Ce(3.410) Pr(3.79), O(38.89)	3
Nd, Sm	S152	REE Glass #2	Si(12.65), Al(16.21), Ca(18.05), Nd(3.85), Sm(3.67), Yb(3.74), Lu(3.75), O(38.28)	3
Gd	S151	REE Glass #1	Si(12.60), Al(16.15), Ca(17.98), Eu(3.80), Gd(3.87), Tb(3.78), Tm(3.81), O(38.01)	

Note: All standards are from the Queen's Department of Geological Sciences Microprobe

Lab. 1. Jeroszewich *et al.* (1979) 2. Boatner *et al.* (1980) 3. Drake & Well (1972)

TABLE 3. CHEMICAL COMPOSITION (OBTAINED BY ELECTRON-MICROPROBE ANALYSIS) OF ALLANITE FROM THE GRENVILLE PROVINCE

	R1002	R1005	R1006*	R1008	R1010	R1011	R1012*	R1013	R1014	R1015	R1018	R1019	R1020	R1023	R1024	R1025	R1026	R1027	R1028
SiO ₂	32.92	31.06	30.21	33.20	32.65	31.62	33.84	32.05	33.24	31.68	32.50	31.73	33.63	33.12	31.11	32.45	30.40	32.88	32.69
TiO ₂	.95	.75	.72	.17	.68	.65	.35	.40	.68	.48	.33	1.02	.42	.28	.75	.50	1.28	.58	.48
Al ₂ O ₃	16.65	13.87	13.21	18.67	13.57	14.13	17.91	16.80	14.85	15.87	17.53	15.91	16.40	16.61	16.10	15.72	9.62	17.12	17.00
Fe ₂ O ₃	11.84	15.54	14.47	5.79	13.66	17.75	15.58	7.71	12.96	13.36	9.88	13.33	15.10	12.03	10.32	13.53	17.73	7.81	7.19
FeO	2.66	2.72	.00	3.77	5.45	.79	.00	5.51	3.83	3.15	2.11	1.07	1.76	4.36	2.41	3.73	5.01	3.70	3.20
MnO	.28	.48	.59	.55	2.46	.37	2.35	.40	.27	.30	.12	.27	.27	.31	.81	.34	.63	.27	.14
MgO	.80	.28	.83	.23	.60	.58	.41	.46	1.03	.83	1.99	1.38	.71	.45	.17	.80	.51	2.15	2.59
CaO	11.11	10.62	7.75	11.77	11.96	10.20	12.45	12.21	11.77	12.09	12.03	9.78	13.01	11.35	10.02	12.48	9.98	11.26	11.43
La ₂ O ₃	6.65	6.90	7.70	3.87	7.70	6.66	1.36	5.68	6.17	6.09	7.26	6.14	5.23	7.28	5.59	6.24	8.47	8.74	8.70
Ce ₂ O ₃	9.73	10.03	10.10	8.13	10.08	10.52	3.21	9.78	10.69	10.24	10.33	11.30	8.82	10.29	10.28	10.25	11.29	11.62	11.34
Pr ₂ O ₃	.99	.80	.75	.84	.82	.82	.48	1.03	1.05	1.01	.92	1.11	.92	1.06	.94	.99	.80	1.01	.84
Nd ₂ O ₃	2.66	1.87	1.63	3.51	1.78	2.30	2.10	2.78	2.90	2.64	2.37	3.45	2.88	3.06	2.36	2.74	1.74	2.27	1.98
Sm ₂ O ₃	.22	n.d.	n.d.	.52	n.d.	n.d.	.86	n.d.	n.d.	n.d.	n.d.	.29	n.d.	.45	n.d.	n.d.	n.d.	n.d.	n.d.
Gd ₂ O ₃	.24	n.d.	n.d.	.36	n.d.	.20	1.41	n.d.	n.d.	n.d.	n.d.	.21	n.d.	.29	n.d.	n.d.	n.d.	n.d.	n.d.
Y ₂ O ₃	n.d.	n.d.	n.d.	.41	n.d.	n.d.	4.47	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ThO ₂	1.22	.89	1.13	.51	1.00	n.d.	2.10	.37	.33	n.d.	n.d.	.69	n.d.	n.d.	.80	n.d.	n.d.	n.d.	n.d.
H ₂ O ⁺	1.64	1.57	1.47	1.59	1.63	1.60	1.71	1.59	1.65	1.62	1.64	1.61	1.68	1.66	1.53	1.65	1.54	1.65	1.63
Total	100.56	97.37	90.56	93.89	101.85	98.19	100.59	96.77	101.43	99.36	99.01	99.30	100.84	102.60	93.19	101.42	98.99	101.06	99.21
	R1029	R1030	R1032	R1033	R1034	R1035	R1037*	R1038	R1039	R1040	R1041	R1042*	R1043*	R1044	R1045	R1046	R1048	R1052	R1054
SiO ₂	30.63	34.06	32.28	32.35	30.48	31.62	31.88	34.51	30.59	31.53	30.53	33.12	32.77	32.50	31.11	31.06	31.02	32.50	30.2
TiO ₂	1.63	.18	.60	.78	1.98	1.25	.57	.23	.80	1.68	.88	.80	.22	.42	.63	.85	.70	.78	1.15
Al ₂ O ₃	12.89	17.59	15.81	15.70	14.19	14.53	15.40	18.21	13.96	8.80	14.74	16.55	17.68	16.23	11.90	13.47	12.21	15.34	13.02
Fe ₂ O ₃	10.12	12.50	14.09	9.76	11.04	15.67	17.61	15.20	9.16	18.01	4.69	18.58	13.44	10.27	13.71	8.85	5.77	12.98	6.44
FeO	7.97	3.70	2.51	6.57	4.80	1.71	.00	.64	6.18	6.26	7.91	.00	.00	3.99	5.01	6.04	8.64	3.13	7.81
MnO	.31	.34	.17	.22	.28	.55	.74	.21	.48	.31	.36	.54	.32	.17	.36	.68	.31	.44	.48
MgO	.26	.31	1.04	.33	.31	.96	.46	.36	.20	.45	.43	1.29	.10	1.38	.75	.36	.65	1.01	.41
CaO	9.82	15.12	12.87	11.25	9.29	9.63	13.24	14.95	10.76	9.26	11.36	11.61	11.70	11.71	9.61	10.27	10.27	12.33	9.78
La ₂ O ₃	10.67	3.69	7.36	6.94	9.06	6.40	2.59	3.42	7.41	12.11	5.78	5.30	3.12	7.34	9.17	7.39	8.07	7.62	7.94
Ce ₂ O ₃	11.60	6.99	8.68	11.50	10.78	11.44	6.17	6.91	9.99	10.93	9.72	9.39	6.80	10.85	11.31	10.14	10.58	9.37	10.78
Pr ₂ O ₃	.70	.80	.63	1.12	.78	1.16	.81	.76	.74	.48	.88	1.10	.83	.89	.70	.88	.69	.71	.85
Nd ₂ O ₃	1.31	2.44	1.42	2.85	1.59	3.77	2.88	2.26	1.57	.91	2.65	3.08	2.90	2.26	1.43	1.80	1.81	1.49	2.03
Sm ₂ O ₃	n.d.	.35	n.d.	n.d.	n.d.	.28	.49	.30	n.d.	n.d.	n.d.	.28	.45	n.d.	n.d.	.20	n.d.	n.d.	n.d.
Gd ₂ O ₃	n.d.	.25	n.d.	n.d.	n.d.	.29	.25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Y ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ThO ₂	n.d.	2.04	.70	.70	.93	.45	4.16	1.30	.99	n.d.	1.65	.50	1.15	.63	.81	1.14	.43	.50	.92
H ₂ O ⁺	1.55	1.70	1.64	1.62	1.54	1.62	1.62	1.73	1.51	1.57	1.49	1.72	1.60	1.63	1.56	1.51	1.47	1.63	1.47
Total	99.45	102.07	99.80	101.69	97.06	101.33	98.87	101.17	94.35	102.30	93.07	104.04	93.08	100.28	98.04	94.65	92.63	99.83	93.34

kaersutite standard (Jarosewich *et al.* 1979) was used for the major elements, as no suitable epidote or allanite standard was available. All the data were corrected with a "ZAF" matrix-correction program provided by Tracor Northern. The resulting compositions are listed in Table 3. Secondary standards were analyzed as unknowns at the beginning, middle and end of each analytical session. Each time the secondary standards were run, 5, 10 or 15 spots were analyzed and averaged. If the average varied by more than 5% of the expected value for the major elements, or 7.5% for the minor elements in the secondary standard, the data were rejected. The term "major element" refers to those elements with a concentration greater than 5% in the secondary standard. Table 4 compares the range and mean of the concentrations (in atomic %) determined in this study with the results of Hasegawa (1960). The two sets of results are very similar, with the smaller ranges of the present study consistent with the smaller set of samples and restricted types of occurrence. Figures 1a and 1b show the chondrite-normalized concentrations of the REE in allanite in granitic rocks and calcite veins, respectively. The REE enrichment trends for the two groups are very

close. Although the relative slopes are very similar, the spread of chondrite-normalized values, for a particular REE, is smaller for the nine samples of allanite from calcite veins than that for the 29 samples of allanite from granitic rocks.

In a study of uranothorite from eastern Ontario, Robinson & Abbey (1957) showed that thorite from calcite veins is greatly enriched in the REE relative to thorite from granitic pegmatites. No such difference in enrichment in REE was found in the allanite specimens studied here.

COUPLED SUBSTITUTIONS IN ALLANITE

A chemical substitution that takes place in allanite is the replacement of Ca²⁺ by trivalent REE in the A sites, coupled with a substitution of divalent species (predominantly Fe²⁺ and Mg²⁺) for trivalent species (predominantly Al³⁺ and Fe³⁺) in the M sites (Fig. 2):

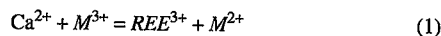


TABLE 4. COMPOSITIONAL RANGES OBSERVED IN ALLANITE

Element	Standard		
	Range(atomic %)	Mean	Deviation
Si	14.12-16.13	14.96	0.52
Ti	0.10- 1.19	0.44	0.25
Al	4.66- 9.88	7.98	1.17
Fe	6.98-17.47	11.37	2.12
Mn	0.09- 0.63	0.29	0.13
Mg	0.06- 1.56	0.45	0.34
Ca	5.54-10.81	8.03	1.09
La	2.21-10.33	5.82	1.69
Ce	5.27- 9.92	8.51	1.20
Pr	0.41- 0.99	0.74	0.13
Nd	0.78- 3.23	1.98	0.58
Sm	0.00- 0.45	0.09	0.15
Gd	0.00- 0.31	0.05	0.10
Y	0.00- 0.32	0.01	0.06
Th	0.00- 3.66	0.62	0.69
REE	11.28-20.85	17.20	2.38

Compositional Ranges Observed in 126 samples of Allanite from World-wide Localities (Hasegawa 1960)

Element	Range (atomic %)	Standard	
		Mean	Deviation
Si	13.56-16.36	14.83	1.86
Ti	0.00- 2.10	0.47	0.07
Al	3.70-12.17	8.25	0.56
Fe ²⁺	2.33-14.77	8.18	0.60
Fe ³⁺	0.00- 7.69	2.32	0.10
Mn	0.00- 5.42	1.66	0.06
Mg	0.00- 2.11	0.61	0.05
Ca	2.14-12.15	7.30	0.49
REE	11.11-27.35	19.69	1.10

This coupled substitution allows all sites to remain filled, and charge balance to be maintained.

The low *A*-site occupancies of some of the samples suggest another mechanism of substitution, of the form



which also would maintain charge neutrality. Figure 3 shows the sum of all cations in the *A* site versus *REE* minus divalent cations in the *M* sites. $\Sigma REE - M^{2+}$ is the amount of *REE* not participating in the coupled substitution [mechanism (1)]. The omission-style substitution [mechanism (2)] results in a correspondence between the deficiency in the *A* site and the amount of *REE* not participating in the coupled substitution. Figure 3 shows this correspondence; the intercept in *A*-site occupancy of 1.92 is close to the expected value of 2 (full *A* sites) expected where all the *REE* are attributed to the coupled substitution [mechanism (1)] discussed above. Figure 3 shows that most of the allanite samples studied exhibit vacancy on the *A* site to varying degrees, indicating that the omission-style substitution is not unusual in these samples. It is possible that the omission-style substitution may be common in other epidote-group minerals that have lesser amounts of *REE* than allanite. Further work is required to test this hypothesis.

ALLANITE FROM THE GOLE QUARRY

The allanite-(Y) (R1012) from the Gole quarry was

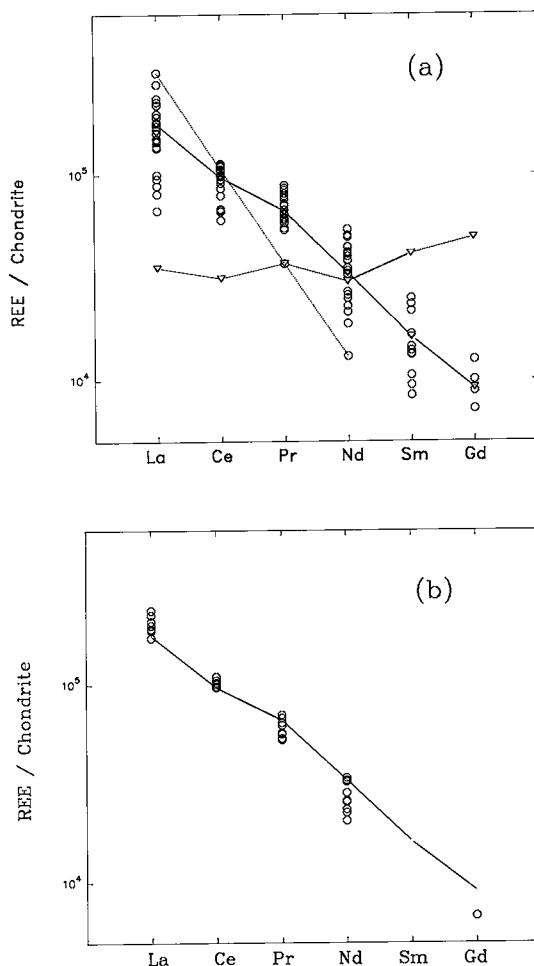


FIG. 1. Chondrite-normalized concentrations of the *REE* in allanite a) from granitic pegmatites, and b) from calcite veins. The triangles represent the values for the sample from the Gole quarry. The dashed line in a) connects the values for the allanite from Mitchell Township, Quebec (R1040). A solid line connects the triangles, which are the averages for the samples studied.

previously analyzed by Frondel (1964). She noted that this material contains Y as the dominant *A*-site trivalent species instead of Ce, as is common in most cases. After studying two heat-treated samples by X-ray diffraction, however, Frondel concluded that this material is not allanite at all but possibly a new species. We have studied this high-Y, metamict material from the Gole quarry and find it to have a chemical composition consistent with allanite and to contain appreciable amounts of the intermediate *REE*, as is common in yttrium-rich allanite. This material contains the highest atomic percentage of Y (3.52%), Sm (0.74%), Gd

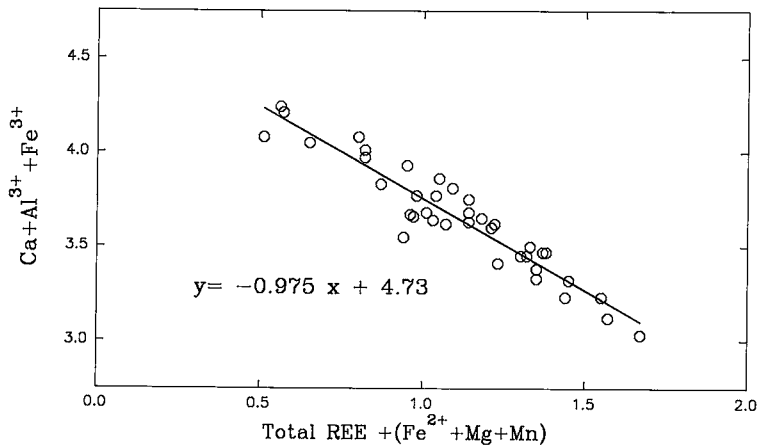


FIG. 2. The coupled substitution of $\text{Ca}^{2+} + (\text{Al}^{3+}, \text{Fe}^{3+}) = \text{REE} + \text{M}^{2+}$ is the dominant mechanism of solid solution in allanite.

(1.22%) and Mn (1.82%), and the lowest atomic percentage of La (1.82%) and Ce (2.74%) observed in the present study. Figure 1a shows the very different *REE* abundances in this material. In addition to containing allanite-(Y), the Gole quarry contains abundant fergusonite, YNbO_4 , which suggests that the pegmatite itself represents a unique Y-rich geological environment.

ALLANITE FROM MITCHELL TOWNSHIP

A sample of allanite from Mitchell Township, Quebec (R1040) contains more La than Ce. In addition, it contains the highest atomic percentage of total *REE* (20.85%) and total iron (17.47%), and the lowest aluminum (4.66%), Pr (0.41%) and Nd (0.78%) ob-

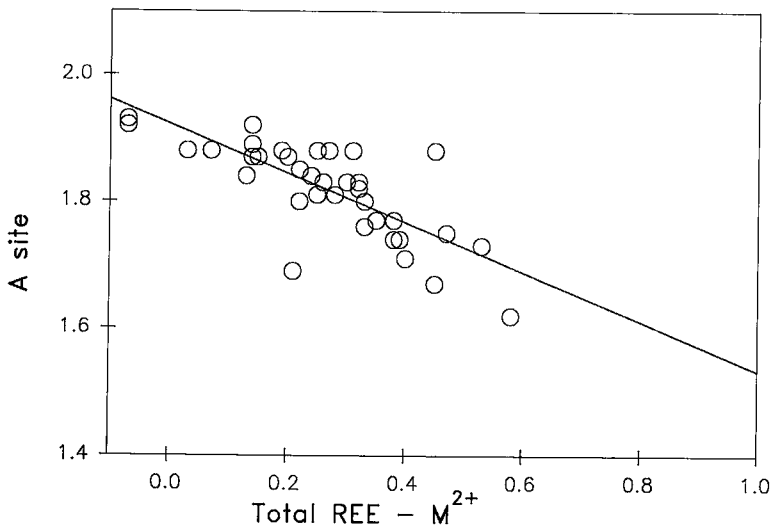


FIG. 3. If the only mechanism of substitution operating in allanite is $\text{Ca}^{2+} + \text{Al}^{3+} + \text{Fe}^{3+} = \text{REE} + \text{M}^{2+}$, then *REE* and M^{2+} should be in equal abundance ($\text{REE} - \text{M}^{2+} = 0$). However, as $\text{REE} - \text{M}^{2+}$ increases, the sum of cations in the A site is seen to decrease in order to maintain charge neutrality, indicating that the substitution of $3\text{Ca}^{2+} = 2\text{REE}^{3+} + \square$ operates in allanite.

TABLE 5. SUMMARY OF PHYSICAL DATA FOR ALLANITE-(La)

a 8.934(3) b 5.760(2) c 10.236(3) β 114.9(2) $^\circ$
 Sp. Grp. $P2_1/m$ $Z=2$

colour black streak brown H. 5 - 5 1/2
 cleavage- {100} poor fracture conchoidal
 Density 3.69-4.02 g/cm³ meas. 4.06 g/cm³ calc.

optical properties

biaxial +ve α 1.730(5) β 1.740(5) γ 1.770(5)
 $2V = 129(2)^\circ$ (meas.) 119° (calc.)

(Ca_{0.95}La_{0.45}Ce_{0.38}Pr_{0.02}Nd_{0.03})Zr₁

(Fe³⁺_{1.26}Al_{0.89}Fe²⁺_{0.50}Ti_{0.12}Mn_{0.06}Mg_{0.02})Zr_{0.98}Si_{3.01}O₁₂(OH)

one H per formula assumed.

three strongest lines:	2.944 ₁₀₀ ,	2.73 ₅₅ ,	3.24 ₅₁
hkl	d(obs.)Å	I/I ₀	
001	9.242	16	
$\bar{1}01$	7.957	19	
$\bar{1}02$	5.053	18	
110	4.740	21	
200	4.062	10	
111	3.818	13	
012	3.623	17	
$\bar{2}11$	3.541	35	
210	3.311	16	
201	3.243	51	
$\bar{2}03$	3.191	24	
$\bar{1}13$	2.944	100	
020	2.897	33	
013	2.730	55	
$\bar{3}03$	2.642	39	
202	2.576	21	

The powder data were collected on a Picker X-ray diffractometer using CuK α (Ni) radiation and the d values and intensities were estimated from the diffractogram.

served in the present study. Table 5 lists the various properties of allanite R1040. Optical data were collected using a detent spindle stage (Bloss 1981), and the program EXCALIBUR (Bloss 1981) was used to calculate $2V$ and crystal orientation so that indices of refraction could be determined with Becke line tests using the appropriate oils. The crystal structure of R1040 has been determined by X-ray diffraction and will be reported elsewhere.

It is not clear why this particular sample of allanite has La greater than Ce. The plot of chondrite-normalized concentrations (Fig. 1a) shows a smooth trend of *LREE* enrichment, as is commonly seen in granitic rocks. La is significantly lower in abundance than Ce in chondrites; therefore, if La is to exceed Ce in absolute abundance, the slope of the sample in a plot of chondrite-normalized concentrations must be very steep in the La and Ce region, as it is for R1040.

CONCLUSIONS

Allanite from the Grenville Province show a well-developed substitution of the form $Ca^{2+} + Al^{3+} + Fe^{3+} = REE^{3+} + M^{2+}$ as well as an omission substitution $3Ca^{2+} = 2REE^{3+} + \square$.

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