YTTRIAN ANDRADITE FROM THE GATINEAU PARK, QUEBEC

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Abstract

Yttrian andradite is a common accessory mineral in granite pegmatites from the southern Gatineau Park, Quebec. Samples from three separate occurrences showed 2.65, 1.23 and 0.74% yttrium. These garnets are unusual in being virtually the sole rare earth minerals in the pegmatites and in their lack of cerium and neodynium. Andradite itself is rare in pegmatites. Possible mechanisms of ionic substitution are $Y^{3+} + (Fe^{3+}, Al^{3+}) \rightarrow Ca^{2+} + Si^{4+}$ and $Mn^{2+} \rightarrow Ca^{2+}$.

Introduction

Yttrian andradite is a common accessory mineral in granitic rocks about 15 miles north-west of Ottawa. Previously the mineral at this location has received only passing reference (Rose 1960, p. 40 and Hogarth 1962, p. 19). In view of its unusual composition and occurrence it was considered worthy of further investigation.

Black andradite was noted from an area 4 miles long and 3 miles wide in the Gatineau Park, Quebec. Figure 1 is a generalization from an unpublished geological map drawn to a scale of 1,000 feet to the inch. Geological data was collected during traverses spaced at 400-foot intervals. Garnet was mainly identified visually in the field and the "approximate limit of Y-andradite" (Fig. 1) was established from field observations.

Samples were selected for detailed study from three easily accessible areas. Two localities are in roadside outcrops on the Gatineau Parkway (Champlain Lookout: CL-1 and Fortune Lake: FL-1). The third locality (Camp Fortune: CF-1) is on a road leading from the Gatineau Parkway to the Camp Fortune Ski Club property. One or two fresh crystals from each of the three occurrences were selected for detailed work and crushed. Grains were then hand-picked under the binocular microscope. Material for chemical analysis was further crushed, screened, and cleaned by magnetic and heavy-liquid separations.

Much of this work was done by Mrs. Kasowski (Hobart 1964) as a Bachelor of Science thesis project at the University of Ottawa. Mrs. D. J. Reed of the Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, kindly scanned the samples with an x-ray spectrometer in search of rare earth elements. Dr. P. G. Manning, also

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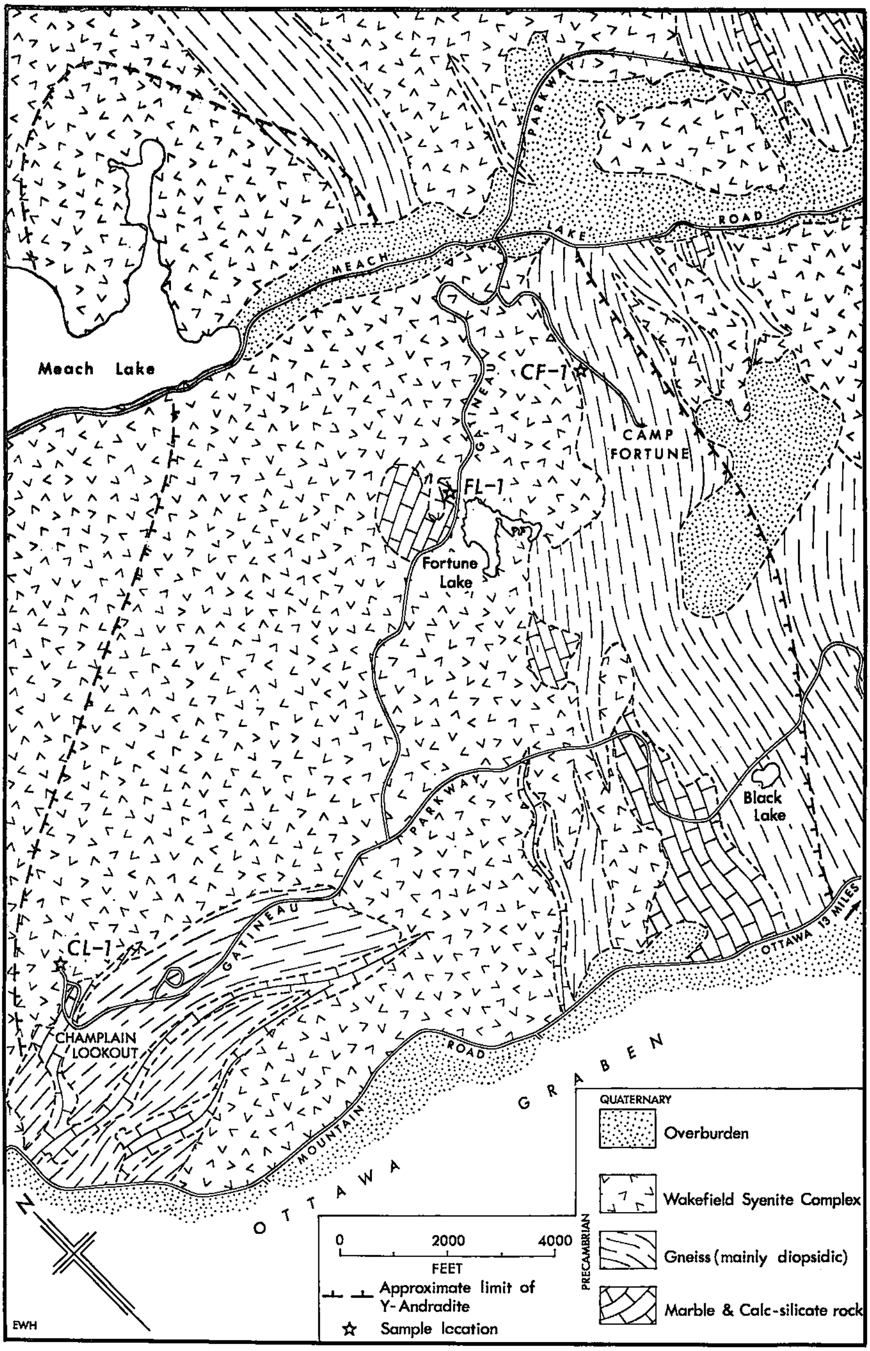

FIG. 1. Geological map showing the location of yttrian andradite in the Gatineau Park, Quebec.

of the Mineral Sciences Division, studied optical absorption of Fortune Lake andradite. The *x*-ray patterns were checked by Michele Fratta and Ulrich Mayr of the University of Ottawa.

Occurrence

Yttrian andradite is especially common in pegmatite and aplite dykes and sills which cut foliated syenite in the Fortune Lake-Champlain Lookout area but it is also present in granitic interlayers in diopside-oligoclase gneiss to the south. All occurrences are at or near the southern boundary of the Wakefield syenite batholith (Fig. 1).

Characteristically the pegmatites of this area are mineralogically simple being composed almost exclusively of microcline-perthite, oligoclase (An_{10}–An_{15}), quartz, and andradite. Most crystals of andradite are found in areas enriched in coarse plagioclase (some grains peristeritic) and quartz. Other minerals in the dykes include very small amounts of pyrite, magnetite, ilmenite, zircon, sphene, fluorite, biotite, chlorite and epidote. Allanite, thorite, monazite, and euxenite can be found with difficulty in some of the dykes. The common occurrence of yttrian garnets and the extreme rarity of other yttrium minerals is remarkable.

Normally the pegmatites of this area show very little internal zoning, as for example those at Champlain Lookout and Camp Fortune, but there is a tendency for garnets to be concentrated near the borders of the dykes. Some of the larger dykes, like that at Fortune Lake, have a narrow border zone of graphic granite but this is nearly devoid of garnet, abundant coarse garnet appearing in pegmatite just inside the border zone. An interesting occurrence is at Champlain Lookout where crystals of black garnet are scattered abundantly through the dyke. Coarse pegmatitic portions contain crystals to several inches diameter whereas aplitic seams show grains ($\sim$ 1 mm) liberally peppered through the rock.

Andradite crystals may be very large, attaining diameters of 4 inches at Fortune Lake. Exterior forms are poorly developed and only where small crystals have been freed from quartz is a rounded dodecahedral form discernible. Many crystals enclose quartz and feldspar poikilitically. The colour is jet black with crevices coated by limonite. Broken surfaces commonly show dodecahedral parting.

Under the microscope the garnet is brown and isotropic. Garnets from Camp Fortune and Champlain Lookout were noticeably zoned greenish brown in the centre and yellowish near the periphery and along cracks. This zoning is diffuse and may be due to leaching. Garnet from Fortune Lake is more homogeneous. A fine-grained rim of chlorite separates garnet from other mineral grains.

Chemical Composition

Tables 1 and 2 represent analyses made on clean garnet samples from lots weighing 4 to 6 grams. If the garnets are plotted on Winchell's charts (Winchell 1958) using refractive index and cell edge data, the specific gravities are always too high for the plots. This may be due to the role of yttrium and the somewhat doubtful structural position of iron and certain other constituents. However the optical absorption curve of a thin section of Fortune Lake andradite is not unlike those of other andradites and the magnitude of the 4,400 Å peak suggests that at least 3/4 of the ferric iron is in octahedral coordination (P. G. Manning, Mines Branch, personal communication). Regardless of quantitative uncertainty the physical and chemical data suggest these garnets are andradite: CL-1 and FL-1 appear to be close to end-member composition.

The absence of other rare earths was demonstrated by Mercy who spectrographically determined only traces of ytterbium. Scans for rare earths in the L spectra were made for all three samples by x-ray spectrometer at the University of Ottawa. The procedure was repeated for the K spectra, but with a more powerful spectrometer, by Mrs. Reed at the Mines branch, but no additional rare earth elements were detected. The pattern of rare earths thus appears to differ markedly from that in andradite described by Semenov (1963, pp. 169–171) where cerium and neodymium are important rare earth constituents.

No systematic determinations of yttrium were made in garnets taken at several locations within a single pegmatite as was done by Dudykina (1959) who showed that spessartine from pegmatites in the U.S.S.R. has the highest yttrium content in the contact zone. It is known, however, that the yttrium content varies markedly for garnets within a single occurrence, samples from the Fortune Lake pegmatite showing variations from 2.2% to 1.0%Y (analyses by x-ray fluorescence).

Discussion

Yttrian-garnets from pegmatite are not rare but are commonly spessartine-almandine (Jaffe, 1951; Dudykina, 1959). Bodenbenderite from Argentina, a mixture of spessartine, fluorite, albite and chlorite, contains 13.2%Y_2O_3 (Milton & Myers 1949). Presumably the yttrium mainly belongs to the garnet. Three specimens of spessartine from the Kola peninsula show 3.02, 2.95 and 1.55% Y_2O_3 (Belkov 1958). Spessartine from New Mexico (Jaffe 1961) and U.S.S.R. (Dudykina 1959) contain about 2% yttrium.

Jaffe (1951) postulated that the substitution of yttrium in pegmatitic

TABLE 1. YTTRIAN ANDRADITE: CHEMICAL COMPOSITION OF SAMPLE CF-1

	Wt. per cent (1)	Ions per 24(0) (2)			Atomic per cent (3)	
Na_2O	0.16					
K_2O	0.02				$Y_3Fe_2^{3+}Fe^{3+}{}_3O_{12}$	4.95
					Andradite	52.55
CaO	24.79	Ca	4.558	6.204	Grossular	20.92
MnO	5.86	Mn	0.851		Almandine	7.67
FeO	3.32	Fe^{2+}	0.476		Spessartine	13.72
Y_2O_3	3.36	Y	0.307		Pyrope	0.19
MgO	0.05	Mg	0.012			
						100.00
TiO_2	0.10	Ti	0.013	4.000		
Fe_2O_3	20.69	Fe^{3+}	2.364			
Al_2O_3	8.43	Al	1.623			
SiO_2	33.40	Al	0.025	5.946		
H_2O+	0.05	Fe^{3+}	0.307			
		Si	5.557			
	100.23	H	0.057			

Analyst: E. L. P. Mercy, University of Edinburgh, 1965.
Notes:
1 Analysis on material dried at 100°C for 2 hours. H_2O+ determined at 900°C in presence of $PbCrO_4$ flux. Spectrographic analysis showed rare earths to be mainly yttrium with only small traces of ytterbium; all other rare earths appeared to be absent. Indium was also noted in trace amounts.
2 Na_2O and K_2O deducted as feldspar.
3 Constituents calculated in the order listed.

TABLE 2. YTTRIAN ANDRADITE: PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION

Samples (1)	CF-1	FL-1	CL-1
Fe (2)	17%	19%	19%
Ca	18%	21%	24%
Mn	4.54%	2.61%	1.70%
Y	2.65%	1.23%	0.74%
n	1.86	1.88	1.87%
G (Berman balance)	3.95±0.03	4.08±0.03	4.07±0.03
a (115 mm powder camera)	11.957±0.003 Å	12.022±0.002 Å	12.024±0.002 Å

Notes:
1 CF-1 from small concordant pegmatite in diopside-oligoclase gneiss. FL-1 from footwall of discordant pegmatite, about 25 feet thick, which cuts syenite, calc-silicate rock and biotite breccia. CL-1 from small concordant pegmatite cutting syenite.
2 Weight per cent values of Fe, Ca, Mn, Y. For CF-1 per cent derived from Mercy's analysis (Table 1). Values for FL-1 and CL-1 from x-ray fluorescence; Fe and Ca by comparison with CF-1 (vacuum path, EDDT crystal), Y and Mn using artificial external standards (air path, LiF crystal).

garnets can be represented as $Y^{3+} + Al^{3+} \rightarrow Mn^{2+} + Si^{4+}$. That this is possible has been shown experimentally by Yoder & Keith (1951) who demonstrated a complete solid solution series $Mn_3Al_2Si_3O_{12}$-$Y_3Al_2Al_3O_{12}$. Semenov (1963, pp. 169–170) considered Belkov's analyses of Kola spessartine, with surplus Si and deficient Al, and suggested an alternate mechanism: $Na^+ + Y^{3+} \rightarrow 2Mn^{2+}$. Dudykina (1959) suggested that at least part of the yttrium may be due to submicroscopic inclusions of other minerals.

Yttrian andradites are also described in the literature but from different environments. Andradite from nepheline syenite from Stöcko, southern Norway, contains 6.66% Y_2O_3 (Brøgger 1890). Black andradite from skarn in western Transbaikalia contain 2.73% rare earth oxides (Nechaeva & Borneman-Starynkevich, 1956). Individual rare earths in this sample and those from 3 other localities in the U.S.S.R. are quoted by Semenov (1963 table 93).

The pegmatitic yttrian garnets from Quebec are unusual because they contain minor amounts of Mn (less than 5%) and major amounts of Ca. However the term "pegmatitic" may be misleading as these garnets, while always occurring in pegmatites, possibly derive their calcium from the wall rocks. Calcium-rich rocks (marbles and calc-silicate rocks) are found with or near all the pegmatites where garnet was observed but the plagioclase (oligoclase), associated with garnet in pegmatite, is rather poor in calcium.

The mechanisms of coupled substitution proposed by Jaffe (1951) and Semenov (1963) seem to have limited applications for our specimens of andradite from Quebec. Y does not vary antipathetically with Mn but one element tends to follow the other, Y being about half the value of Mn (Fig. 2). A possible mechanism might be as follows: Y^{3+} replaces Ca^{2+}, the extra charge being compensated by Fe^{3+} and Al^{3+} which replace

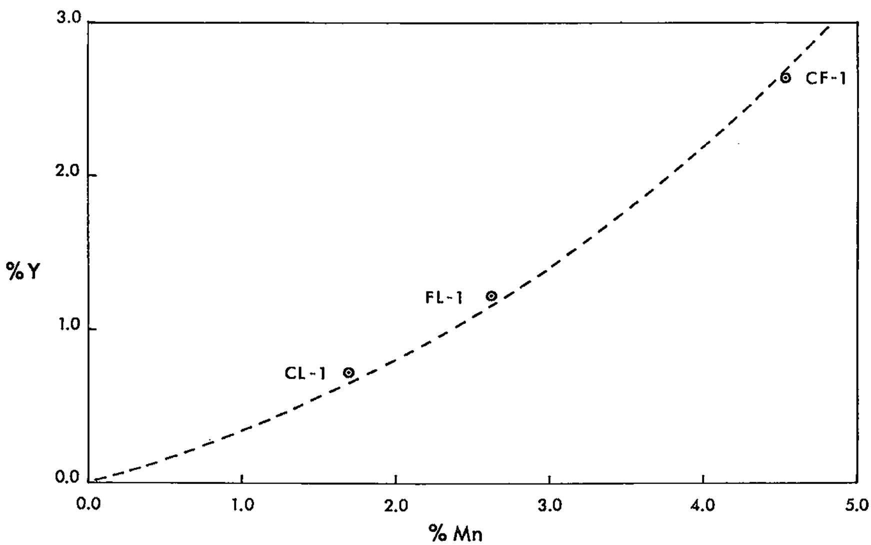

FIG. 2. Yttrian and manganese content of andradite from the Gatineau Park, Quebec.

Si^{4+}. Mn^{2+} is supplied with Y^{3+} and replaces Ca^{2+}. These possibilities can be represented as:

$$(1) \qquad Y^{3+} + (Fe^{3+}, Al^{3+}) \rightarrow Ca^{2+} + Si^{4+}$$

$$(2) \qquad Mn^{2+} \rightarrow Ca^{2+}$$

Ionic radii of Ca^{2+} and Y^{3+} are similar (Ca = 1.03 Å, Y = 0.95 Å in 8-fold coordination: Green 1959) and the experimental work of Gentile & Roy (1960) suggests extensive solid solution between andradite and $Y_3Fe_5O_{12}$.

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