

## POTASSIUM- AND FLUORINE-RICH AMPHIBOLES FROM THE GATINEAU AREA, QUEBEC

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### ABSTRACT

Certain alkali amphiboles from Proterozoic rocks of the Gatineau area, Quebec are exceedingly rich in K and F (up to 4.6% K<sub>2</sub>O and 2.8% F, corresponding to 0.8 atoms K and 1.3 atoms F per s.f.u.). Fenites near Perkins, characterized by potassium fluor-magnésio-arfvedsonite and microcline, were formed by replacement of quartzite, biotite gneiss and granite pegmatite. During growth from a hydrous carbonated fluid, temperatures ranged from above 575 to 310°C at high concentrations of CO<sub>2</sub> [ $X(\text{CO}_2) \geq 0.85$ ], and total pressure  $\geq 5$  kbar. One specimen of magnésio-arfvedsonite is characterized by the following data:  $2[(\text{K}_{0.6}\text{Na}_{0.4})(\text{Na}_{1.6}\text{Ca}_{0.4})(\text{Mg}_{3.7}\text{Fe}_{1.0}^{3+}\text{Fe}_{0.3}^{2+})(\text{Si}_{7.9}\text{Fe}_{0.1}^{3+})\text{O}_{22}(\text{F}_{1.1}\text{OH}_{0.9})]$ ;  $G = 3.14$ ;  $\alpha 1.631(2)$ ;  $\beta 1.638(2)$ ,  $\gamma 1.642(2)$ ,  $2V_X = 71^\circ$ ,  $Z \wedge c 54^\circ$ ,  $Y = b$ ;  $C2/m$ ,  $a 9.906(1)$ ,  $b 17.953(2)$ ,  $c 5.287(1)$  Å,  $\beta 104.3(1)^\circ$ . The proportion of tetrahedrally co-ordinated Fe<sup>3+</sup> is 8.5 - 9.4% Fe<sub>T</sub> for 3 specimens (Mössbauer spectroscopy). Zoned potassium richterite - potassium magnésio-arfvedsonite from a nearby site probably belonged to carbonatite or glimmerite. Associated fluorapatite and phlogopite equilibrated at 730°C,  $P_T \geq 5$  kbar, and  $f(\text{H}_2\text{O})/f(\text{HF}) = 3.8$  in equilibrium with a hydrous carbonated fluid. A fenite near Gatineau, characterized by potassium fluor-magnésio-arfvedsonite crystals with overgrowths of magnésio-riebeckite, may represent a different fault-slice and a lower pressure regime.

**Keywords:** potassium fluor-magnésio-arfvedsonite, magnésio-riebeckite, richterite, tetrahedrally co-ordinated iron, fenite, carbonatite, microcline, fluorapatite, Gatineau, Quebec.

### SOMMAIRE

On trouve, dans les roches Protérozoïques de la région de Gatineau, Québec, des exemples d'amphibole alcaline très riche en potassium et en fluor, jusqu'à 4.6% de K<sub>2</sub>O et 2.8% de F, ce qui correspond à 0.8 atomes K et 1.3 atomes F par unité formulaire. Les fénites situées près de Perkins, qui contiennent une magnésio-arfvedsonite fluorée à potassium et du microcline ont été formées par remplacement de quartzite, gneiss à biotite et pegmatite granitique. Pendant la croissance des cristaux à partir d'un fluide aqueux carbonaté, la température a varié entre plus de 575

et 310°C à haute concentration de CO<sub>2</sub> [ $X(\text{CO}_2)$  au delà de 0.85], et la pression totale a dépassé 5 kilobars. Un échantillon de magnésio-arfvedsonite possède les caractéristiques suivantes:  $2[(\text{K}_{0.6}\text{Na}_{0.4})(\text{Na}_{1.6}\text{Ca}_{0.4})(\text{Mg}_{3.7}\text{Fe}_{1.0}^{3+}\text{Fe}_{0.3}^{2+})(\text{Si}_{7.9}\text{Fe}_{0.1}^{3+})\text{O}_{22}(\text{F}_{1.1}\text{OH}_{0.9})]$ ;  $G 3.14$ ,  $\alpha 1.631(2)$ ,  $\beta 1.638(2)$ ,  $\gamma 1.642(2)$ ,  $2V_X = 71^\circ$ ,  $Z \wedge c 54^\circ$ ,  $Y = b$ ,  $C2/m$ ,  $a 9.906(1)$ ,  $b 17.953(2)$ ,  $c 5.287(1)$  Å,  $\beta 104.3(1)^\circ$ . La proportion de Fe<sup>3+</sup> tétraédrique déterminée par spectroscopie Mössbauer sur trois échantillons, varie entre 8.5 et 9.4% du fer total. Des cristaux zonés, allant de richterite à potassium à magnésio-arfvedsonite à potassium, prélevés d'un site avoisinant, proviendraient d'une carbonatite ou d'une glimmerite. La fluorapatite et la phlogopite associées ont équilibré à 730°C, à pression totale de plus de 5 kilobars, et à rapport  $f(\text{H}_2\text{O})/f(\text{HF})$  égal à 3.8, en présence d'un fluide aqueux carbonaté. Une fénite près de Gatineau, qui contient des cristaux de magnésio-arfvedsonite fluorée avec surcroissance de magnésio-riebeckite, pourrait provenir d'une écaïlle tectonique différente, équilibrée dans un régime de plus basse pression.

(Traduit par la Rédaction)

**Mots-clés:** potassium magnésio-arfvedsonite fluorée, magnésio-riebeckite, richterite, fer en position tétraédrique, fénite, carbonatite, microcline, fluorapatite, Gatineau, Québec.

### INTRODUCTION

Potassium- and fluorine-rich alkali amphiboles characterize certain fenites of the Cantley - Perkins - Gatineau region, Quebec. These were first documented by Hogarth & Lapointe (1984), who presented chemical data for "magnésio-arfvedsonite", with K<sub>2</sub>O ranging from 1.14 to 2.94% and F from 1.3 to 3.3%. During fieldwork in 1982 additional examples of alkali amphibole were collected, and some of these have recently been analyzed by electron microprobe. The first specimen studied (1093B, from locality 1093, Fig. 1) was found to contain 3.44% K<sub>2</sub>O and 2.33% F. Five additional specimens (1093A, C, D, F, G) from the same locality were found to contain even higher proportions of K. In addition, specimens from two more locali-

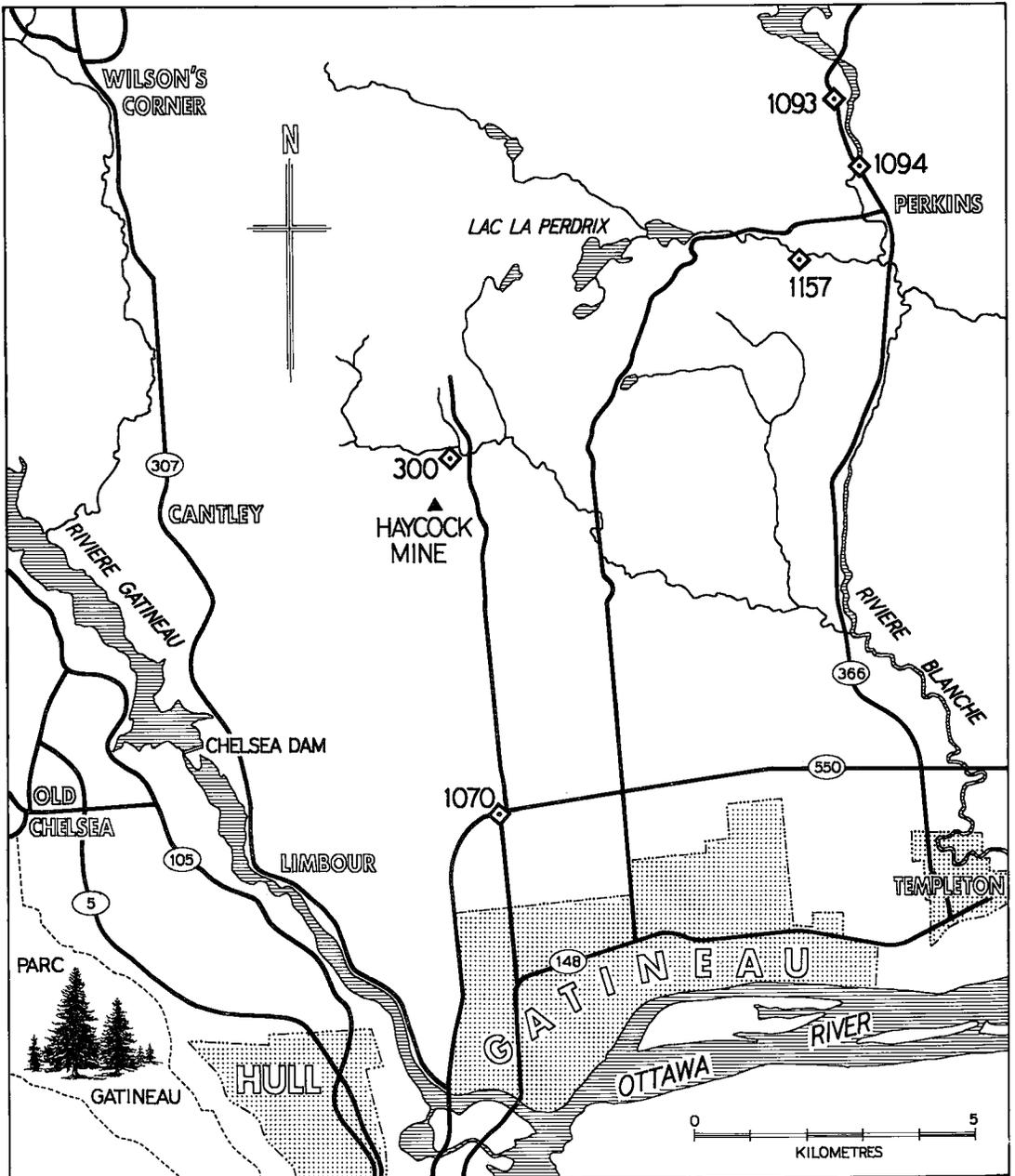


FIG. 1. Location of the five occurrences from which the amphiboles were collected, Gatineau area, Quebec.

ties (1070 and 1094), contain potassium- and fluorine-rich amphiboles. During the 1983 field season, a specimen from another locality (1157) yielded more potassium- and fluorine-rich amphibole. The four localities, as well as locality 300, the site of the most potassium-enriched amphibole encountered by Hogarth & Lapointe (1984), are shown in

Figure 1. The 10 specimens derived from these sites constitute the object of this research.

#### GEOLOGICAL CONTEXT

The area of Figure 1 is characterized by metamorphic rocks of assumed Proterozoic age (Wynne-

Edwards 1972). Especially common are metasedimentary types, which include biotite gneiss, feldspathic quartzite, calcitic marble and calc-silicate rock ("skarn"). These rocks have been metamorphosed during the Grenville Orogeny under granulite-facies conditions, intruded by granite pegmatite sills and dykes, folded into NNE-plunging isoclinal folds, and refolded into NE-plunging open folds. Post-tectonic, Proterozoic intrusive bodies include lamprophyre (minette and kersantite) and syenite dykes, none of which are common. With the exception of marble, all of the above-mentioned rocks have been locally fenitized and intruded by carbonatite during late Grenvillian time (Hogarth *et al.* 1985, Hogarth & Rushforth 1986). In some places, such as the Templeton carbonatite (Hogarth & Rushforth 1986), fenites can be definitely linked with carbonatite, but nowhere was fenitization observed to proceed from syenite or any other igneous rock.

The Proterozoic rocks are cut by several sets of faults, the result of repeated activation of the Ottawa - Bonnechère graben. The system originated in the Precambrian, and fault activity persisted at least into the Ordovician (Kumarapeli 1978, Kumarapeli & Saull 1966). The fenites are synchronous with an early episode of faulting.

A few vertical, E - W, post-tectonic (possibly Ordovician) diabase dykes transect the Proterozoic rocks in the vicinity of localities 1070, 1093 and 1094. They have effects on adjacent quartzite, gneiss and granite pegmatite, but an intrusive contact with fenite was not observed. Cambro-Ordovician (Nepean Fm) sandstone appears as small outliers on Proterozoic rocks, 3.5 km E of locality 300, 2 km ESE of locality 1070, and 4 km SW of locality 1070. Additional information on the local geology can be obtained

from Hogarth (1981), Hogarth & Rushforth (1986) and Hogarth & Steacy (1986).

#### DESCRIPTION OF OCCURRENCES

##### *Locality 300*

Fenitized layers of quartz-rich biotite gneiss, individually up to 25 cm thick, are exposed in a small outcrop. Specimen 300 contained about 20% secondary microcline, 20% alkali amphibole, 15% aegirine, 10% hematite, 5% calcite, and minor phlogopite, albite, barite and fluorapatite, with the remainder being quartz and altered feldspar of the host rock (Hogarth & Lapointe 1984). Amphibole occurs as prisms or, more rarely, as fans of fibres, some of which taper on phlogopite crystals or terminate on the divergent ends to prisms of amphibole. Paragenetic relationships suggest that the prisms postdate the fibres. Secondary, twinned microcline, believed to belong to the fenite suite, is unaltered (clear) compared to the altered (cloudy) microcline of the wall rock. It is most apparent under the electron beam, where it luminesces bright red and forms patches and veinlets in the microcline of the wall rock, similar to the replacement features described by Mariano (1978) from Kangankunde, Malawi and Cerro Impacto, Venezuela. The closest known carbonatite is a small lens of calcite - barite - parisite 840 m southwest ('site 3' of Hogarth *et al.* 1985).

##### *Locality 1070*

This occurrence is now almost completely covered over after completion of Highway 550. Several

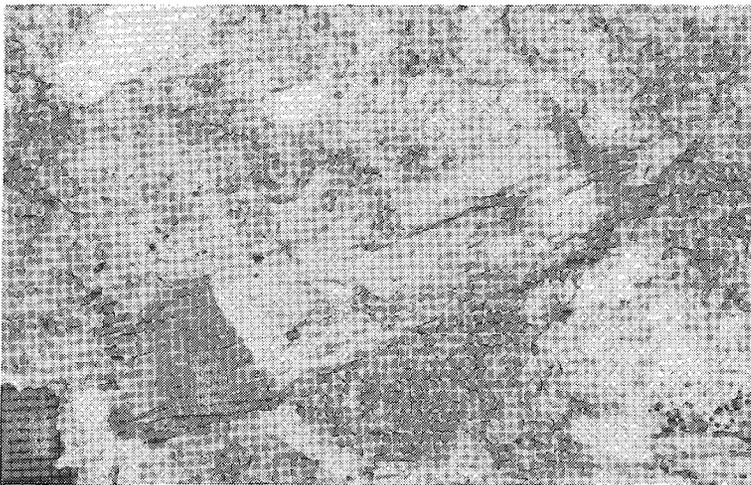


FIG. 2. Grain of pale magnesio-arfvedsonite (central part), overgrown with darker magnesio-riebeckite (both ends of the crystal; composite length 0.60 mm). Plane-polarized light. Locality 1070.

steeply dipping, parallel veins of blue amphibole cut feldspathic quartzite. They were exposed over a total width of 1.5 m and traced 15 m across the floor of a shallow road-cut. The largest vein was up to 30 cm thick and cored with calcite.

Amphibole is interlayered with hematite and calcite. The amphibole is long prismatic, with prisms tending to grow perpendicular to the vein walls and to the hematite – calcite layers. Most crystals are pale (almost colorless) greenish blue in thin section, but some are tipped with indigo blue and others are entirely indigo blue. The contact between the indigo and greenish blue parts is sharp (Fig. 2), even under high-power magnification. Other minerals are quartz, barite, phlogopite and fluorite (especially in the calcite-rich assemblage), and microcline, fluorapatite and chalcopryrite (especially in the amphibole-rich assemblage).

The calcite – ankerite – barite core to these veins may represent a late-stage carbonatite. The barium and REE contents of the core material (Ba 37600 ppm, Ce 755 ppm, La/Yb 190) are similar to those from late ankeritic carbonatites (Samoylov 1984) and are reflected in the composition of the amphibole-rich exteriors (Ba 8200 ppm, Ce 430 ppm, La/Yb 110; Ba analyses by XRF, Ce and Yb analyses by DCP).

#### Locality 1093

A steeply dipping vein of alkali amphibole is exposed in a rock-cut on the west side of Highway 366. It transects quartzite and biotite gneiss, seals a NNE-trending fault, and attains a maximum thickness of 1.7 m. The vein was once cored with calcite and less common dolomite but these have been mostly dissolved by groundwater. Some large rutile crystals, weighing up to 670 g, were collected from the partly dissolved calcite rubble. The amphibole is blue-black in hand specimen and accounts for 70 to 95% of specimens 1093C, D, F, G. It forms long (up to 2 cm) prismatic crystals, which tend to grow perpendicular to the vein wall and be separated by a "felt" of asbestiform amphibole. Secondary microcline ( $Or_{98}Ab_2$ ), strontian fluorapatite and end-member albite virtually account for the remainder of the vein. Pyroxene is associated with amphibole in the fenitized wall rock only; phlogopite is rare.

Our specimens were collected from the following locations: 1093A, from a patch of fenite in quartzite, ca. 1.5 m from the vein; 1093B, from a patch of fenite in quartzite, ca. 0.5 m from the vein; 1093C, from the vein, 5 cm from the contact, and 1093D, F, G, from the vein, near the calcite core. Carbonatites are not known near locality 1093, but the geology of this area has not been mapped.

#### Locality 1094

The exposure is a road-cut on the east side of Highway 366. Twelve amphibole veins cut feldspathic quartzite, biotite – almandine – sillimanite gneiss and granite pegmatite, within a length of 100 m (Fig. 3). Our specimen was collected from a vertical, E – W-trending vein, 40 cm wide at its base, that seals a fault, separating quartzite from gneiss. Each vein is made up of layers of amphibole prisms, oriented approximately perpendicular to the vein contact and separated by randomly oriented amphibole fibres. Minor associated minerals are strontian fluorapatite, microcline ( $Or_{97}Ab_3$ ), calcite, dolomite, albite, rutile, allanite, barite and pyrite. A few reaction rims of phlogopite are evident at the contact of microcline and cross-cutting veinlets of calcite. Around some veins are envelopes of metasomatically altered rock with local concentrations of

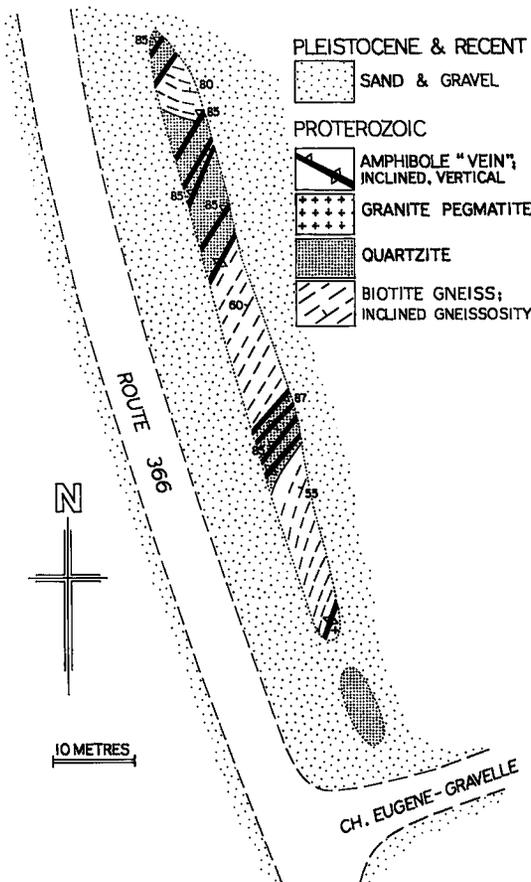


FIG. 3. Geology of locality 1094. Specimen 1094A was collected from the third "vein" from the north. Reproduced from Hogarth & Steacy (1986) with permission of the Geological Association of Canada – Mineralogical Association of Canada, Ottawa '86 Committee.

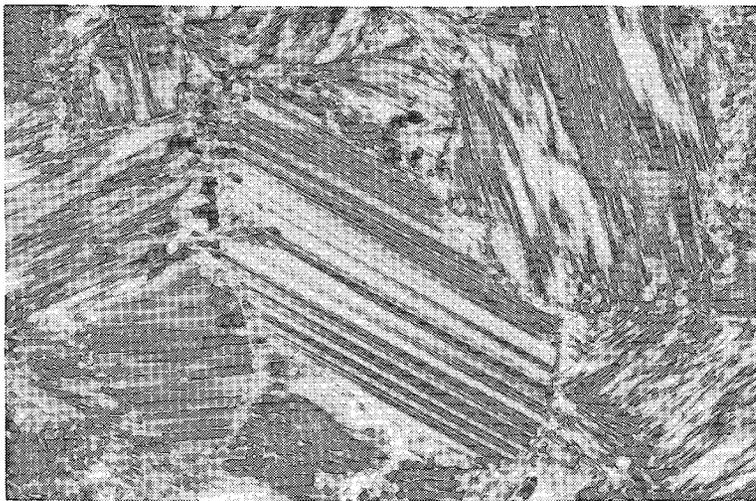


FIG. 4. Polysynthetically twinned amphibole grain (central part of photograph; length through the centre 1.75 mm) and asbestiform amphibole (surrounding). Amphibole grains and packets are separated by fine-grained phlogopite. Crossed polars. Locality 1157.

alkali amphibole, aegirine-augite, calcite and microcline. Additional information on this occurrence is given by Hogarth & Rushforth (1986) and Hogarth & Steacy (1986). A number of small carbonatites are known in the area, including a calcite - ankerite - barite lens on the opposite (west) side of the road-cut.

#### Locality 1157

This is the upper "Miller pit" of the Rainville mine, which was tested for apatite in 1877 (Spence 1920, p. 89-90). Clean walls are no longer exposed, and field relations are obscured, although, by analogy to an occurrence 100 m north, the sampled assemblage represents a carbonatite lens or perhaps glimmerite related to carbonatite, cutting calc-silicate rock ("pyroxenite" of Spence 1920). Our specimen was collected from the old mine dump. Randomly oriented fibres and interspersed crystals of alkali amphibole (some twinned polysynthetically on {100}; (Fig. 4) are associated with major amounts of coarse-grained calcite, fine-grained (fluor-) phlogopite and fine-grained strontian fluorapatite. Quartz is minor, and barite and monazite are rare.

#### CHEMICAL COMPOSITION

##### Methods of investigation

Most minerals were analyzed at Carleton University (by P. Jones) by wavelength dispersion with a Cambridge Geoscan Mk5 microprobe, operated with an accelerating voltage of 15 kV and a beam cur-

rent of 10 nA. Amphiboles and associated minerals in specimens 1093B and 1157A were analyzed (by D.D.H. and T.N. Solberg) at Virginia Polytechnic Institute by wavelength dispersion, using a 9-channel ARL - SEMQ microprobe, with standards and methodology as outlined by Solberg (1982), Solberg & Speer (1982), and Hogarth *et al.* (1985).

Mössbauer spectra of a mineral concentrate from the same sample site as 1093B were recorded (by M.G.T.) on a constant-acceleration Mössbauer spectrometer with a  $^{57}\text{Co}$  source in Rh matrix. Velocities were recorded directly by laser interferometry. For analysis, the spectra were computer-fitted, using a least-squares derivative procedure with a preselected number of absorption lines of Lorentzian shape.

##### Chemical characterization

The compositions of the amphibole specimen are given in Table 1, and chemical and optical data are summarized in Table 2. In deriving formulae, we used 13 (C + Z) cations, 46 positive charges, and assumed that F + Cl + OH is equal to 2, which permitted calculation of FeO, Fe<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O. However, FeO was determined by titration in a concentrate from 1093B. Atoms were assigned to the various atomic sites in the sequence recommended by Leake (1978); in these assignments, some Fe<sup>3+</sup> was placed in tetrahedral sites for most of our samples, including all those from locality 1093. This assignment will be discussed further under Mössbauer spectroscopy.

TABLE 1. CHEMICAL COMPOSITION\* OF TYPICAL AMPHIBOLES OF THE CANTLEY-PERKINS-GATINEAU AREA

	1070D(k)	1070D(i)	1093B(p)	1093F(p)	1094A(p)	1094A(f)	1157A(k)	1157A(r)
SiO <sub>2</sub>	55.77	55.01	54.80	55.21	55.42	55.23	55.86	54.52
TiO <sub>2</sub>	0.18	0.20	0.15	0.16	0.21	0.14	0.07	0.10
Al <sub>2</sub> O <sub>3</sub>	0.37	0.38	0.17	0.14	0.32	0.64	0.10	0.43
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.02	0.07	0.00	0.00	0.00	n.a.	n.a.
Fe <sub>2</sub> O <sub>3</sub>	7.23	20.50	9.84	9.41	8.57	11.51	7.12	5.13
FeO	5.89	4.08	2.61	3.61	3.20	3.18	0.00	0.55
MnO	0.14	0.18	0.11	0.09	0.07	0.06	0.07	0.07
MgO	15.72	11.31	17.44	16.57	17.18	15.45	20.42	21.16
BaO	n.a.	n.a.	0.03	n.a.	n.a.	n.a.	0.00	0.00
SrO	n.a.	n.a.	0.02	n.a.	n.a.	n.a.	0.06	0.01
CaO	1.30	0.48	2.37	0.79	0.85	0.60	3.32	5.07
Na <sub>2</sub> O	7.22	6.86	6.37	7.00	7.22	7.60	5.88	6.17
K <sub>2</sub> O	3.44	0.15	3.44	4.59	4.55	2.44	4.27	2.84
F <sub>2</sub>	2.54	0.47	2.33	2.42	2.84	2.34	2.05	1.70
Cl	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.01
H <sub>2</sub> O	0.88	1.88	0.99	0.94	0.75	0.98	1.15	1.29
O=F, Cl	100.68	101.55	100.74	100.93	101.18	100.17	100.37	99.05
O=F, Cl	1.07	0.21	0.98	1.02	1.20	0.99	0.86	0.72
Total	99.61	101.34	99.76	99.91	99.98	99.18	99.51	98.33
Ions per 13 (C + Z) and 46 positive charges (except specimen 1093B, see text)								
Si	8.032	7.818	7.852	7.943	7.939	7.934	7.904	7.787
Al	0.000	0.064	0.029	0.024	0.054	0.066	0.016	0.073
Fe <sup>3+</sup>	0.000	0.116	0.111	0.033	0.007	0.000	0.080	0.140
Cr	0.000	0.002	0.008	0.000	0.000	0.000		
Σ	8.03	8	8	8	8	8	8	8
Al	0.063	0.000	0.000	0.000	0.000	0.042	0.000	0.000
Ti	0.019	0.021	0.016	0.018	0.023	0.015	0.007	0.011
Cr	0.000	0.000	0.000	0.000	0.000	0.000		
Fe <sup>3+</sup>	0.784	2.076	0.950	0.985	0.917	1.244	0.678	0.411
Fe <sup>2+</sup>	0.709	0.485	0.309	0.435	0.383	0.382	0.000	0.065
Mn	0.017	0.022	0.000	0.011	0.008	0.007	0.009	0.009
Mg	3.375	2.396	3.725	3.552	3.668	3.308	4.306	4.504
Σ	4.97	5	5	5	5	5	5	5
Fe <sup>2+</sup>	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.000	0.013	0.000	0.000	0.000	0.000	0.000
Ca	0.201	0.073	0.364	0.122	0.130	0.092	0.504	0.775
Na	1.799	1.890	1.619	1.878	1.870	1.908	1.496	1.225
Σ	2	2	2	2	2	2	2	2
Na	0.217	0.000	0.151	0.073	0.136	0.209	0.118	0.485
Sr			0.002				0.005	0.001
Ba			0.002				0.000	0.000
K	0.632	0.027	0.629	0.842	0.831	0.447	0.770	0.517
Σ	0.85	0.03	0.78	0.92	0.97	0.66	0.89	1.00
F	1.157	0.211	1.056	1.103	1.287	1.063	0.916	0.766
Cl	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.002
OH	0.843	1.782	0.944	0.897	0.713	0.937	1.084	1.232
Σ	2	2	2	2	2	2	2	2

\*Electron microprobe analyses. H<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, FeO derived by calculation, except in 1093B, where FeO was found by titration.  
Abbreviations: (f) fibrous, (i) indigo, (k) core, (p) prismatic, (r) rim, n.a. not analyzed.

According to the nomenclature of Leake (1978), most of the amphibole samples consist of *magnesioarfvedsonite*, but the colored tip of amphibole 1070D is *magnesio-riebeckite*, and the rim of 1157A is *richterite*. The relationship between the amphiboles is shown in the A-site plot of Figure 5. It should be emphasized that tie lines in this diagram join "associated" amphiboles in the same thin section, and do not necessarily represent equilibrium pairs. Our amphiboles tend to be higher in potassium than those of fenites from Cantley described by Hogarth

& Lapointe (1984), but there are some low-potassium varieties in amphibole from localities 1070, 1093 and 1157, which will be described below.

Notable variation was found in the composition of the amphibole from a single polished thin section, although tests for zoned crystals, by positioned microprobe analyses, proved negative (except in specimens 1070D and 1157A). An interesting feature is the dual composition encountered in the prismatic amphibole in 1093D and 1093G (Table 2). These compositions belonged to individual crystals, and

TABLE 2. CHARACTERISTICS OF AMPHIBOLES IN THE TEN SPECIMENS EXAMINED

Spec. No.	Type	Anal.*	Atomic constants**						Pleochr. †			Bref.	Zlc
			Na <sub>B</sub>	K	F	Fe <sup>2+</sup>	Fe <sup>3+</sup>	X	Y	Z			
300G	fibrous	6	1.88	0.54	1.2	0.04	0.99	C1	C1	C1	0.01	ca.70°	
1070D	pale core	5	1.80	0.63	1.2	0.17	0.93	B	B	C1	0.011	66°	
	coloured tip	2	1.89	0.03	0.2	0.17	1.00	I	V	C1	indet.	ca.80°	
1093A	prismatic	6	1.83	0.80	1.1	0.09	1.00	B	M	Y	0.01	ca.70°	
	fibrous	5	1.62	0.63	1.1	0.07	1.00						
1093B	prismatic	4	1.62	0.63	1.1	0.08	1.00	B	B-V	G	0.011	55°	
1093C	prismatic	8	1.64	0.68	1.1	0.10	1.00	B	B-V	C1	0.011	55°	
	fibrous	2	1.73	0.53	1.2	0.05	1.00						
1093D	prismatic	6	1.86	0.79	1.1	0.08	1.00	G	B	G	0.012	61°	
	prismatic	3	1.57	0.58	1.1	0.07	1.00						
1093F	prismatic	10	1.88	0.84	1.1	0.11	1.00						
1093G	prismatic	7	1.81	0.81	1.2	0.06	1.00						
	prismatic	2	1.67	0.67	1.1	0.08	1.00						
1094A	prismatic	5	1.87	0.83	1.3	0.09	1.00	C1	C1	C1	0.013	61°	
	fibrous	2	1.91	0.45	1.1	0.10	0.97						
1157A	prism core	4	1.50	0.77	0.92	0.00	1.00	C1	C1	C1	0.010	48°	
	prism rim	4	1.22	0.52	0.77	0.01	1.00	C1	C1	C1	0.005	45°	

\* Anal. = number of microprobe analyses averaged.

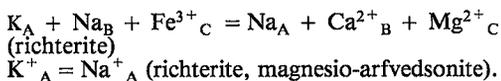
\*\* Atomic constants based on 13(C +Z) cations and 46 positive charges, except for 1093B (see text). Fe<sup>2+</sup> = Fe<sup>2+</sup> / (Fe<sup>2+</sup> + Mg); Fe<sup>3+</sup> = Fe<sup>3+</sup> / (Fe<sup>3+</sup> + <sup>VI</sup>Al).

† Color abbreviations: B = blue, B-V = blue-violet, C1 = colorless, G = green, I = indigo blue, M = mauve, V = greyish violet, Y = greenish yellow.

transitions between the two were not found. Asbestiform varieties, present in all specimens, are characterized by lower K than their prismatic counterparts. This is especially marked in 1094A (Table 1). Figure 5 does not consider F, which is generally high in these amphiboles.

Magnesio-riebeckite, containing little F and K, is associated with an alkali amphibole rich in F and K, in specimen 1070D. Two similar types of amphibole, occurring in fenite near Cantley, are suggested by data presented by Hogarth & Lapointe (1984).

Amphibole 1157A also differs from typical alkali amphibole. By definition (Leake 1978), it varies from magnesio-arfvedsonite [1157A(k)] to richterite [1157A(r)], but contains significant quantities of K and F (Tables 1, 2). A step-count across a grain (Fig. 6) showed sympathetic variation of K with Fe, and antipathetic variation of K with Ca and, less pronouncedly, with Na, all consistent with the substitutions:



However, F shows poor correlation with other elements, tending to mimic both Na and K (in different parts of the same crystal).

A diagram with  $R^+ + {}^{VI}R^{3+}$  and  $R^{2+}$  as coordinates (Fig. 7) indicates that the Quebec amphiboles can be expressed in terms of three end-member components, richterite, magnesio-arfvedsonite and

magnesio-riebeckite, and that 16 of our compositions define a single series extending from richterite to a magnesio-arfvedsonite, undersaturated in C-site, divalent cations (such as Mg).

#### Mössbauer spectroscopy

The positioning of Fe<sup>3+</sup> in the tetrahedral site in our amphiboles, as dictated by most of our calculations of the structural formula and particularly in 1093, where all amphiboles gave formulae with tetrahedral Fe<sup>3+</sup>, prompted us to test the role of Fe<sup>3+</sup> by Mössbauer spectroscopy. Accordingly we separated amphibole from 1093B, 1093D and 1093F. In preparation for Mössbauer spectroscopy, the concentrates were dispersed in icing sugar to ensure random orientation.

The ratio of Fe<sup>2+</sup> to Fe<sup>3+</sup> and site populations are based on the relative proportion of areas under the absorption peaks pertaining to Fe<sup>2+</sup> and Fe<sup>3+</sup>. The assumption is made that the Mössbauer fraction (f) is equal for Fe<sup>2+</sup> and Fe<sup>3+</sup> and is independent of site symmetry.

Three specimens from occurrence 1093 were tested by Mössbauer spectroscopy. Specimen 1093B showed  ${}^{IV}Fe^{3+}/Fe_T = 8.5\%$  (collected at ca.  $\pm 13 \text{ mm s}^{-1}$ ). This compares with 8.1% by chemical analysis and 10.9% by calculation from microprobe data. Unfortunately, this specimen was lost in the preliminary Mössbauer trial. The spectra of specimen 1093F were collected at ca.  $5 \text{ mm s}^{-1}$  (Table 3, Fig. 8). The

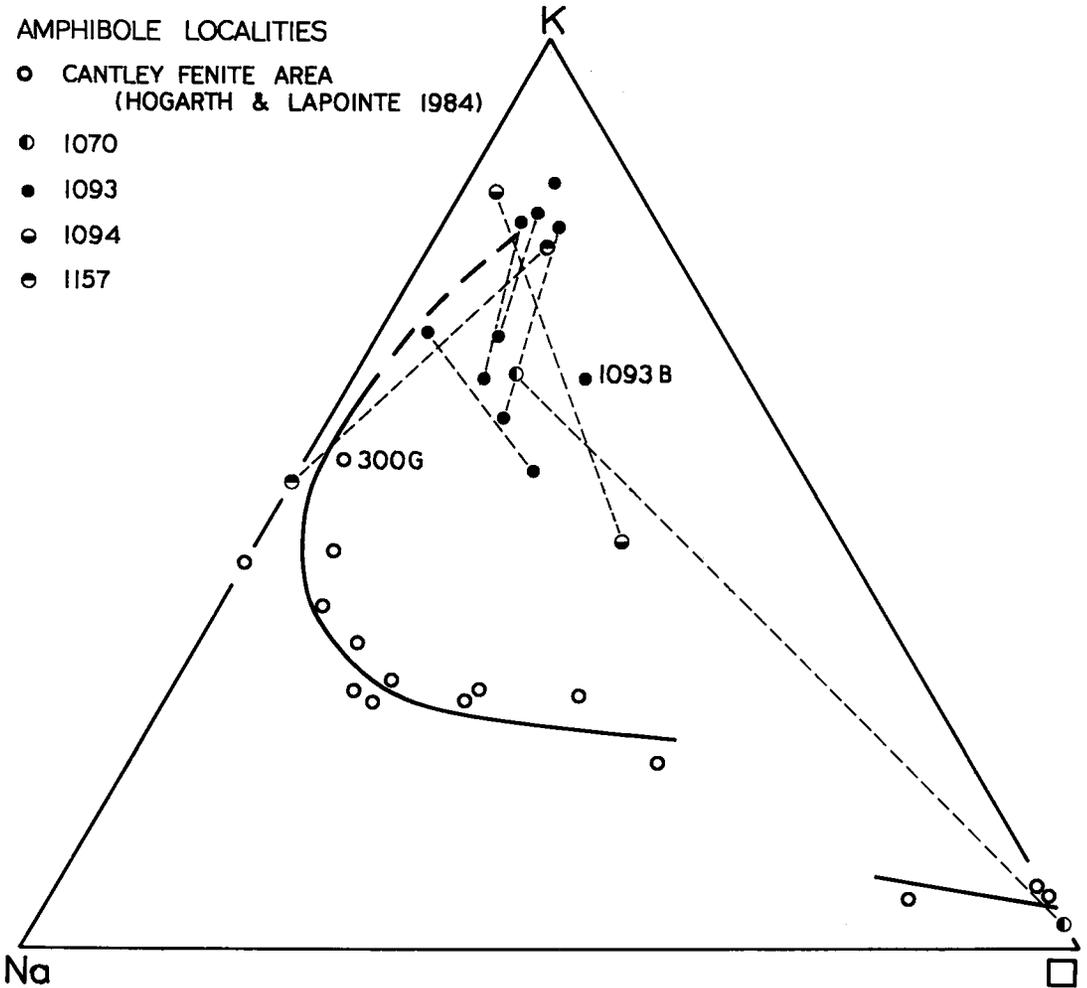


FIG. 5. Plot showing occupancy of the *A* site. Associated amphiboles in the same thin section are linked by a broken line. The trend for amphiboles from the Cantley fenites is shown by a broad line.

proportion of  $^{54}\text{Fe}^{3+}$  in this test (9.4%) is higher than that calculated from microprobe data (2.3%). Specimen 1093D gave similar results (9% Möss. versus 2.8% calc.).

Mössbauer data indicate that appreciable tetrahedral  $\text{Fe}^{3+}$ , corresponding to the doublet 'a' in Figure 8 and Table 3, is required for a good fit. The isomer shift I.S. for  $^{54}\text{Fe}$  is equal to  $0.21 \text{ mm s}^{-1}$ , relative to Fe metal (Table 3). This is in the lower range expected for  $^{54}\text{Fe}^{3+}$  (Bancroft 1973, p. 157). Above  $0.21 \text{ mm s}^{-1}$  the fit for this component deteriorates appreciably.

In all, some 30 fits were tried on 1093F. The best fit gave  $\chi^2 = 460$  for 500 channels (goodness-of-fit 0.92).

#### PHYSICAL PROPERTIES AND X-RAY-DIFFRACTION DATA OF THE AMPHIBOLES

##### *Physical properties*

All crystals are biaxial negative and have the optical-crystallographic orientation  $Y = b$ , with strongly inclined dispersion and  $r \approx v$ . The {110} cleavage is perfect, twinning is common, as simple or lamellar (1157A) on {100}, crystal elongation and striations parallel *c*, parting on {001} (1070D, indigo type),  $H = 6$ ,  $G_{\text{meas.}}$  (1093B) = 3.14. The color in hand specimen varies from blue-black (1093C, D, F, G) to purplish blue (1094A), to pale greyish blue (the remaining specimens).

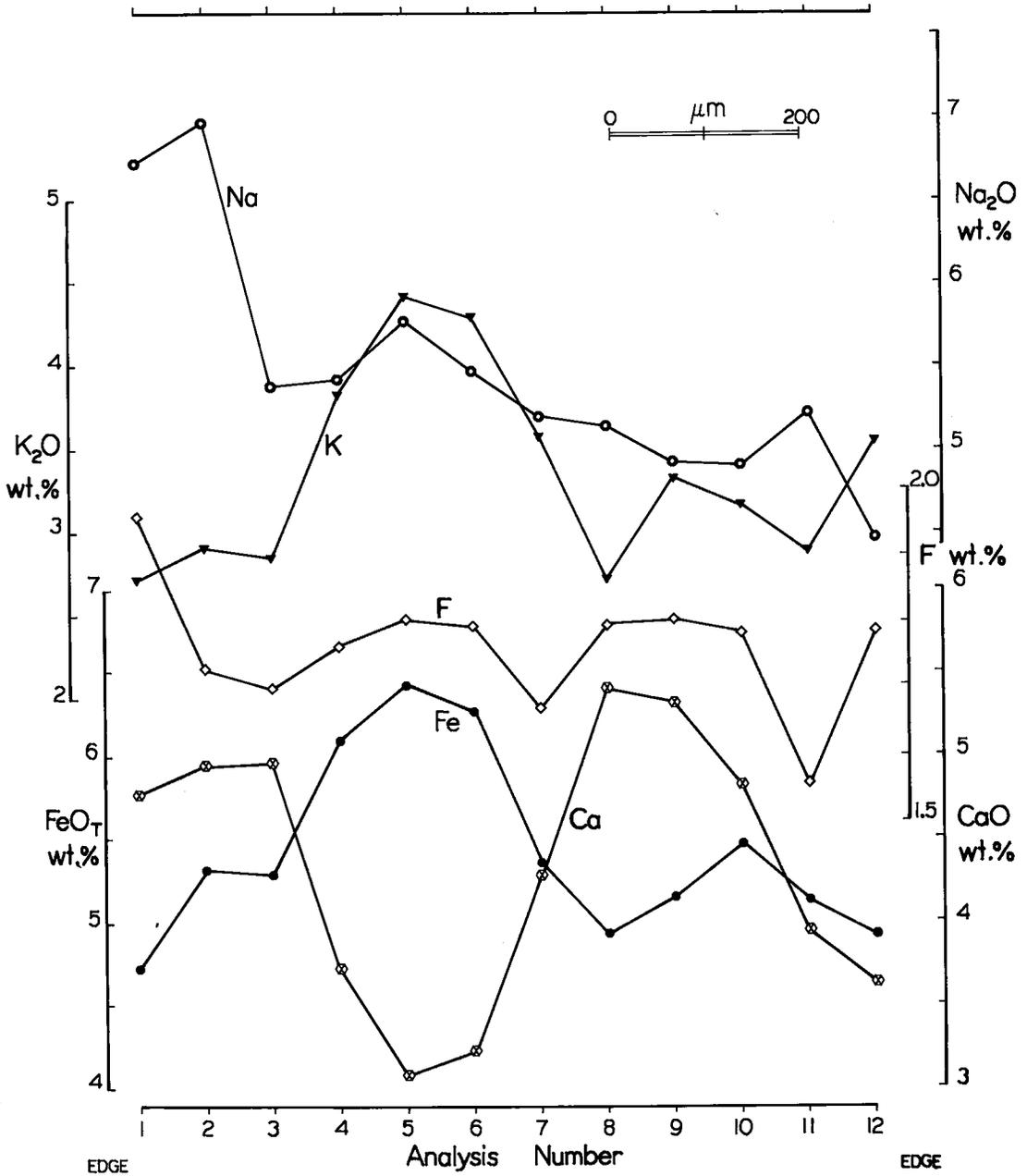


FIG. 6. Results of step analyses across a zoned amphibole grain in specimen 1157A.

Optical properties for 1093B (measured on a spindle stage in Na<sub>D</sub> by G.Y.C.) are as follows:  $\alpha$  1.631(2),  $\beta$  1.638(2),  $\gamma$  1.642(2),  $2V_x$  meas. 71°;  $2V_x$  calc. 74.2°.  $Z \wedge c = 54^\circ$  in obtuse  $\beta$  angle;  $Y = b$ . Compatibility Index (Mandarino 1981) 0.023. In

white light, the sample shows inclined dispersion;  $v > r$  (wk).

Pleochroic colors, birefringence and extinction angles, measured from thin sections in white light, are listed in Table 2 for the 8 specimens from which

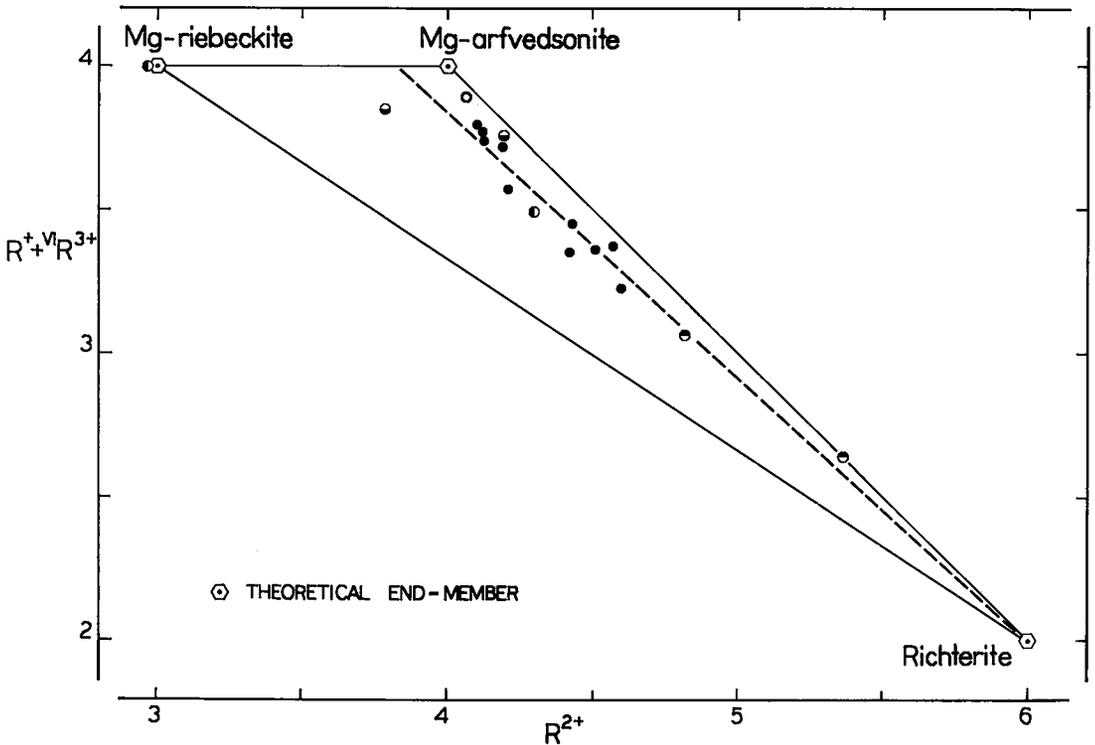


FIG. 7.  $(R^{2+} + VI R^{3+})/R^{2+}$  plot, after Samoylov & Gormasheva (1975), for 17 amphibole compositions described in this study. The richterite - magnesio-arfvedsonite trend of the 16 amphiboles is shown by a broken line. Locality symbols are given in Figure 5.

standard thin sections were cut. The color is normally pale, inclining to colorless, although *X* and *Y* for the colored tips of certain crystals in 1070D are, respectively, indigo and deep violet. A characteristic of all specimens is a distinct purple tinge in *Y* and an absorption that can best be described as  $X \approx Y > Z$ . With the exception of specimen 300G, no attempt was made to determine the optical properties of the fibrous variety, although it may be said that the fibrous aggregates are always more deeply colored than their prismatic counterparts.

Some crystals in 1157A are strongly zoned, and the birefringence and extinction angles quoted in

Table 1 are averages from three crystals. The "core" corresponds to the high-potassium portion of the crystals, whereas the "rim", a low-birefringence zone near the periphery of the crystal, corresponds to the low-potassium zone (Tables 1, 2, Fig. 6). The extreme edges of strongly zoned crystals could not be extinguished in white or monochromatic light, and possibly represent a high-sodium rim of the type shown in Figure 6.

#### *X-ray-diffraction data*

An untwinned crystal from specimen 1093B was selected under the polarizing microscope for X-ray study (by G. Y. C.) using a precession camera. Precession photographs (0-, 1- and 2-levels) were prepared about the *a* and *b* axes. Systematic extinctions observed on these photographs are consistent with the space group  $C2/m$ , common to most clin amphiboles. The cell parameters of 1093B, determined from a single-crystal photograph, were refined by a least-squares program using powder-diffraction data (Table 4). The indexing of the diffraction pattern is based on the data for potassic richterite

TABLE 3. MÖSSBAUER PARAMETERS AND SITE OCCUPANCY OF IRON SPECIES IN SPECIMEN 1093F

Peak*	I.S.	Quad. Split. (# e <sup>2</sup> q Q)	§ width	% Fe (Mössbauer)	Assignment	% Fe (calc.#)
a	0.21	0.45	0.30	9.4	Tetrah. Fe <sup>3+</sup>	2.3
b	0.40	0.57	0.34	60.5	Octah. Fe <sup>3+</sup>	67.8
c	1.13	1.84	0.26	4.2	Octah. Fe <sup>2+</sup>	29.9
d	1.13	2.25	0.31	5.7	Octah. Fe <sup>2+</sup>	
e	1.13	2.76	0.26	20.2	Octah. Fe <sup>2+</sup>	
				100.0		100.0

\* Spectral peak as indicated in Fig. 8. mm.s<sup>-1</sup> with respect to metallic iron. § Calculated from microprobe data.

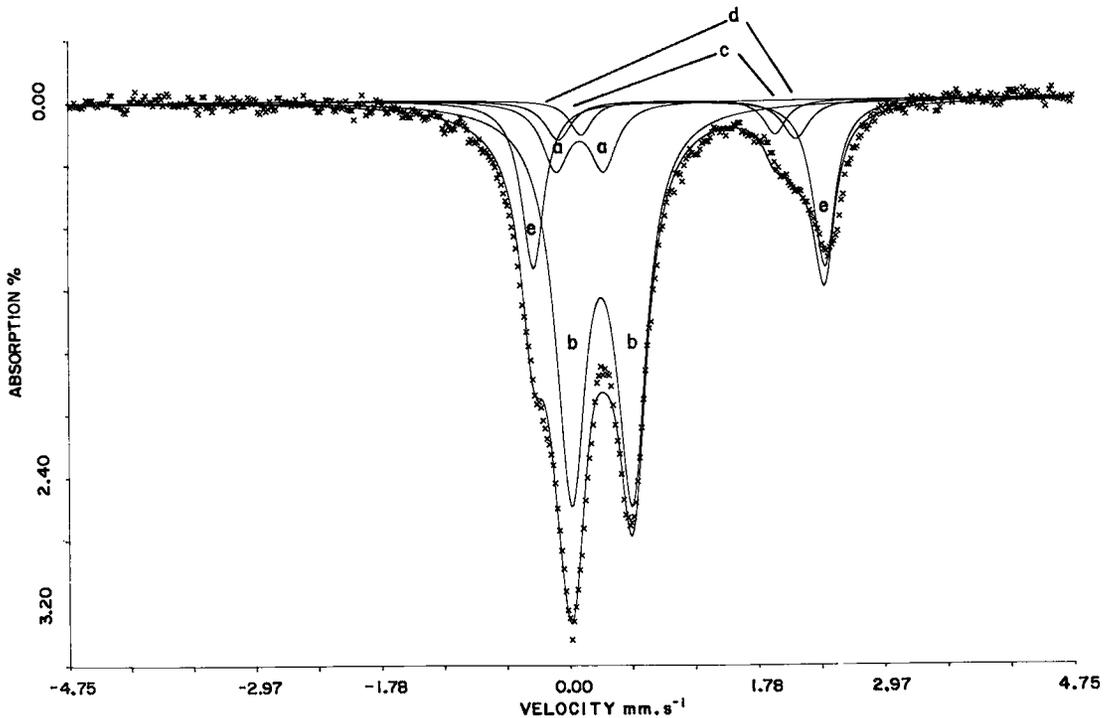


FIG. 8. Mössbauer spectrum of Fe in specimen 1093F; a, b, c, d and e represent coupled peaks of Table 3.

(Huebner & Papike 1970). The refined values are  $a$  9.906(1),  $b$  17.953(2),  $c$  5.287(1) Å,  $\beta$  104.3(1)°. Cell contents are  $2[(K_{0.6}Na_{0.2})(Na_{1.6}Ca_{0.4})(Mg_{3.7}Fe^{3+}Fe^{2+}_{0.3})(Si_{7.9}Fe^{3+}_{0.1})O_{22}(F_{1.1}OH_{0.9})]$ .

#### CONDITIONS OF FORMATION

The well-developed veins and rare patches of fenite in the wall rock at localities 1070, 1093 and 1094, suggest that fenitizing fluids proceeded mainly along fractures (some of which had been the loci of faults, see Fig. 3). These fluids were rich in F, as shown by the composition of amphibole (Table 1, 2), apatite (Table 4) and phlogopite (specimen 1157A, contrasted with zoned biotite 1093 from country-rock gneiss; Table 5). Overfilling of the OH site with F in apatite has been noted elsewhere [discussed in McConnell (1973), Chapter 7] and may be the result of some F co-ordinated with C in the P site, which would also account for the low totals of S + P + Si atoms in some of our apatite formulae. On the other hand, Cl must have been low, as Cl is at the detection limit (*ca.* 0.02%) in some of our apatite and phlogopite samples. Sulfate is eliminated as an important component of the fluid because it would precipitate BaSO<sub>4</sub> near the source, rather than transport Ba to the fenites.

TABLE 4. X-RAY POWDER-DIFFRACTION DATA OF AMPHIBOLE SPECIMEN 1093B

<i>hkl</i>	$d_{calc}$	$d_{obs}$	<i>I</i>	<i>hkl</i>	$d_{calc}$	$d_{obs}$	<i>I</i>
020	8.976	8.98	3	$\bar{3}32$	2.143	2.142	1
110	8.465	8.49	58	202	2.058	2.057	3
130	5.078	5.09	1	351	2.026	2.026	4
$\bar{1}11$	4.879	4.88	2	370	2.001	2.001	1
200	4.799	4.80	4	421	1.945	1.946	2
040	4.488	4.49	10	510	1.909	1.909	11
111	4.013	4.01	1	461	1.878	1.879	1
$\bar{1}31$	3.868	3.872	1	191	1.856	1.856	1
131	3.392	3.393	13	530	1.828	1.828	2
240	3.278	3.279	28	0.10.0	1.795	1.794	2
310	3.150	3.151	100	191	1.795	1.794	2
$\bar{3}11$	3.032	3.034	2	512	1.750	1.751	1
221	2.961	2.962	9	282	1.680	1.680	1
330	2.821	2.822	23	461	1.658	1.658	9
$\bar{3}31$	2.736	2.735	9	480	1.639	1.638	4
151	2.706	2.707	19	1.11.0	1.609	1.609	2
061	2.583	2.584	5	600	1.5999	1.5995	5
202	2.535	2.535	5	153	1.5789	1.5775	2
170	2.477	2.478	1	602	1.5384	1.5383	2
350	2.388	2.390	4	551	1.5124	1.5125	4
351	2.366	2.333	9	263	1.5115	1.5115	2
421	2.331	2.331	3	0.12.0	1.4961	1.4964	2
171	2.288	2.287	3	442	1.4808	1.4813	1
242	2.207	2.207	1	3.11.0	1.4539	1.4539	1
261	2.165	2.165	10	661	1.4430	1.4425	8

CuK<sub>α</sub> radiation,  $\lambda = 1.5418$  Å, diffractometer calibrated with NBS Si standard.

If the age of the Haycock fenites [920 ± 60 Ma; Hogarth (1981)] can be applied to all our occurrences, then Grenvillian metamorphism, resulting in



Munoz & Ludington (1974)] intersect at 730°C, with  $\log f(\text{H}_2\text{O})/f(\text{HF}) = 3.8$ . These values, when combined with the fugacity coefficients of Burnham *et al.* (1969) at phlogopite – apatite equilibrium and  $X(\text{H}_2\text{O}) \geq 0.10$  (Berman *et al.* 1985) at  $P_{\text{total}} = 5$  kbar, yield a minimum  $f(\text{H}_2\text{O})$  of 400 bars and  $f(\text{HF})$  of 0.07 bars. The remainder of the fluid was assumed to be essentially  $\text{CO}_2$  in these calculations. It is known that fluorine is partitioned almost equally between phlogopite and clin amphibole in equilibrium with a high-temperature fluid (Westrich 1981) and, therefore, the high-F, low-Ca portion of the crystals of amphibole 1157A (composition 1157Ar, Table 1 and Fig. 4;  $F/(F + \text{OH}) = 0.38$ ) may approach equilibrium with phlogopite (Table 5;  $F/(F + \text{OH}) = 0.33$ ).

Stringers of late calcite in occurrence 1094, possibly in manifestation of carbonatite activity, are separated from microcline in the amphibole veins by a narrow reaction-rim of phlogopite. Here, the control of the appearance of phlogopite in place of microcline may be  $X(\text{CO}_2)$ , owing to escape of  $\text{CO}_2$  through the fracture system, thus driving the reaction  $\text{Or} + 3 \text{Dol} + \text{H}_2\text{O} \rightleftharpoons \text{Phl} + 3 \text{Cal} + \text{CO}_2$  toward phlogopite and calcite (Bailey 1966).

Locality 1070 may represent a comparatively low-pressure regime. Granulite assemblages are lacking in this area, and diabase dykes, which appear to taper toward the surface, here attain a width of 1.5 m maximum (*versus* 60 m at Perkins). However, lack of good exposure prevents verification of this possibility. The occurrence of K- and F-depleted magnesio-riebeckite ( $\text{Fe}^{2+} : \text{Fe}^{3+} = 1 : 1.11$ ) indicates a marked drop in K and F activity and a sharp increase in oxidation during the growth of late-stage amphibole at this locality.

#### RELATED AMPHIBOLES

*Potassium magnesio-arfvedsonite* with a composition similar to that from the Gatineau area has been described from carbonatite in the Loe Shilman complex, Pakistan (Mian & Le Bas 1986) and Firesand River, Ontario (Teal 1979, p. 63–64, compositions 6, 49, 54). Potassium magnesio-arfvedsonite from lamproite (Velde 1971, Scott 1981, Hall 1982, Wagner & Velde 1986) is characteristically rich in Ti ( $\text{TiO}_2$  1–5%, commonly *ca.* 4%). Fluorine appears to be low [0.5% calc. from Velde (1971)]. Potassium-rich ( $\text{K}_2\text{O}$  1.72%) *fluor-magnesio-arfvedsonite* from fenitized granite of the Čistá massif, Czechoslovakia, is unusually rich in Mn ( $\text{MnO}$  1.48%: Ulrych 1978) for an occurrence lacking manganese minerals.

*Potassium fluor-richterite*, almost iron-free but otherwise similar in composition to richterite at occurrence 1157 (composition 1157Ar, Table 1), has

been described from marble ejecta at Monte Somma, Italy (Della Ventura *et al.* 1983). Potassium fluor-richterite from lamproite, “magnophorite” of Prider (1939), is rich in Ti ( $\text{TiO}_2$  2–8.5%, commonly *ca.* 5%: Wagner & Velde 1986, Jaques *et al.* 1986). MARID (mica – amphibole – rutile – ilmenite – diopside) and similar xenoliths in kimberlite contain *potassium richterite*, with less Ti and F ( $\text{TiO}_2$  0.3–2%, F 0.2–0.6%: Dawson & Smith 1977, Jones *et al.* 1982). Potassium richterite from skarn associated with manganese silicates contains considerable Mn ( $\text{MnO}_T$  0.5–0.6% at St. Marcel, Italy, 4.9–6.4% at Långban, Sweden: Mottana & Griffin 1986, Magnusson 1930).

*Zoned amphibole* in lamproite is characterized by a pale core of potassium richterite and a more deeply colored rim of potassium magnesio-arfvedsonite or potassium arfvedsonite (Velde 1975, Thy 1982, Jaques *et al.* 1986). This zonation differs markedly from carbonatite amphibole 1157, with a potassium-rich magnesio-arfvedsonite core and a potassium-depleted richterite zone near the rim. In some respects, it is similar to amphibole from fenite 1070, in which Fe is enriched and F is depleted on the more deeply colored rim.

Typical compositions of potassium-rich *arfvedsonite* from peralkaline intrusive rocks are given by Deer *et al.* (1963, p. 367–368, compositions 9 and 12), Nickel & Mark (1965), and Singh (1972). These compositions tend to be somewhat more aluminous and lower in sodium and fluorine than ours. They bridge the gap between arfvedsonite – ferro-eckermannite, on the one hand, and arfvedsonite – richterite on the other.

Amphibole compositions (particularly those of magnesio-arfvedsonite) from the Gatineau area, appear to be unusual if compared with those of igneous rocks from world-wide localities. They are rare, if not unique, for amphibole from metasomatic rocks.

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