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Li- AND F-BEARING ALKALI AMPHIBOLE FROM GRANITIC PEGMATITE AT HURRICANE MOUNTAIN, CARROLL COUNTY, NEW HAMPSHIRE

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Abstract

At Hurricane Mountain, Carroll County, New Hampshire, bodies of granitic pegmatite in riebeckite granite contain large (up to 10 cm long and 2 cm across) primary crystals of Li-bearing fluor-arfvedsonite in miarolitic cavities, grading to euhedral Li- and F-poor arfvedsonite. Fine-grained, fibrous, light blue-gray riebeckite occurs as a late-stage hydrothermal filling in the miarolitic cavities. The early, Li-rich, fluor-arfvedsonite has: *a* 9.836(5), *b* 17.997(7), *c* 5.316(4) Å, β 103.735(4)°, *V* 914.20(6) Å^3; $Z = 2$, $D_{meas.}$ 3.34 g/cm^3, $D_{calc.}$ 3.353 g/cm^3; biaxial (–), $2V_{meas.}$ 44(1)°, $2V_{calc.}$ 46°; α 1.681(2), β 1.692(2), γ 1.694(2), inclined dispersion, $r > v$; $X \wedge c$ –7°, $Y = b$, $Z \wedge a$ +7°; *X* dark blue, *Y* lavender gray, *Z* pale yellowish brown; $X > Y > Z$; *X* is opaque at 0.03 mm thickness. A structural formula, on the basis of 24 (O,OH,F) atoms is: $(Na_{0.86}K_{0.25})Na_2(Fe^{2+}_{2.54}Fe^{3+}_{1.485}Mn_{0.10}Zn_{0.02}Li_{0.49}Ti_{0.07})(Si_{7.71}Al_{0.07})O_{22}(F_{1.34}OH_{0.63})$. Arfvedsonite within the miarolitic cavities contains less Li and F than that of the earlier generation, and the still later riebeckite contains only 0.09 wt.% Li_2O and 0.3 wt.% F. The Fe^{3+}:Fe^{2+} ratio of the early Li-bearing fluor-arfvedsonite and that of the euhedral arfvedsonite crystals within miarolitic cavities is 0.58. The late, fibrous, cavity-filling riebeckite has an Fe^{3+}:Fe^{2+} ratio of 0.99. The total iron content of the three amphiboles increases with continued crystallization. These amphiboles are products of peralkaline pegmatites locally derived from peralkaline granite.

Keywords: amphibole, arfvedsonite, riebeckite, granitic pegmatite, Hurricane Mountain, New Hampshire.

Sommaire

Nous décrivons les propriétés de gros cristaux (jusqu'à 10 cm en longueur et 2 cm en largeur) de fluor-arfvedsonite à teneur élevée en Li, zonés vers une arfvedsonite appauvrie en Li et F dans une miarole, provenant d'une ségrégation pegmatitique dans un granite à riebeckite au mont Hurricane, comté de Carroll, au New Hampshire. Une riebeckite fibreuse, à granulométrie fine, de couleur bleu grisâtre pâle, remplit tardivement les cavités miarolitiques. La fluor-arfvedsonite lithique précoce a les propriétés suivantes: *a* 9.836(5), *b* 17.997(7), *c* 5.316(4) Å, β 103.735(4)°, *V* 914.20(6) Å^3; $Z = 2$, $D_{mes.}$ 3.34 g/cm^3, $D_{calc.}$ 3.353 g/cm^3; biaxe (–), $2V_{mes.}$ 44(1)°, $2V_{calc.}$ 46°; α 1.681(2), β 1.692(2), γ 1.694(2), dispersion inclinée, $r > v$; $X \wedge c$ –7°, $Y = b$, $Z \wedge a$ +7°; *X* bleu foncé, *Y* gris lavande, *Z* brun jaunâtre pâle; $X > Y > Z$; *X* est opaque à une épaisseur de 0.03 mm. Sa formule structurale, calculée sur une base de 24(O,OH,F), est: $(Na_{0.86}K_{0.25})Na_2(Fe^{2+}_{2.54}Fe^{3+}_{1.485}Mn_{0.10}Zn_{0.02}Li_{0.49}Ti_{0.07})(Si_{7.71}Al_{0.07})O_{22}(F_{1.34}OH_{0.63})$. L'arfvedsonite située dans les cavités miarolitiques contient moins de Li et de F que l'arfvedsonite précoce, et la riebeckite, plus tardive encore, ne contient que 0.09% de Li_2O et 0.3% F (poids). Le rapport de Fe^{3+} à Fe^{2+} de la fluor-arfvedsonite précoce et de l'arfvedsonite idiomorphe des cavités miarolitiques est le même, 0.58. Par contre, ce rapport est 0.99 dans la riebeckite fibreuse tardive. La teneur en fer a augmenté à mesure que la cristallisation progressait. Cette suite d'amphiboles est le produit de cristallisation d'une pegmatite hyperalcaline de dérivation locale de son encaissant, un granite hyperalcalin.

(Traduit par la Rédaction)

Mots-clés: amphibole, arfvedsonite, riebeckite, pegmatite granitique, mont Hurricane, New Hampshire.

Introduction

Bodies of miarolitic granitic pegmatite (Creasy & Eby 1993) occur at Hurricane Mountain, 3 km northeast of North Conway, Carroll County, New Hampshire, within an arcuate rib-shaped mass of riebeckite granite (Table 1) that is enclosed by the Conway Granite of the Early Jurassic (~180 Ma) White Mountain plutonic-volcanic series. These bodies of pegmatite, perhaps better termed "pegmatitic segregations" because of their small size, typically range from 1 to 20 cm thick and from 0.1 to 2 m long. They have been extensively prospected (Fig. 1) for euhedral crystals of quartz (generally smoky), feldspar, amphibole and astrophyllite. Partial chemical analysis (by VTK) of large (>7 cm long) prisms of alkali amphibole and the geological environment (*i.e.*, alkaline igneous rocks) suggested that significant amounts of Li might be present in the amphibole. The importance of Li as a component in igneous alkali amphiboles has been emphasized by Hawthorne *et al.* (1993, 1996). The importance of Fe^{3+}/Fe^{2+} determinations also was noted to be significant if amphibole compositions are to be used to derive information on redox conditions of crystallization. Primary, tapering, black, prismatic crystals of amphibole occur in feldspar–quartz pegmatite adjacent to sporadic miarolitic cavities, and project into the miarolitic cavities. A total of three different amphiboles were characterized: 1) basal portion of the primary, tapering amphibole crystals (*i.e.*, portion not within an open miarolitic cavity; 2) euhedral terminations of the primary, tapering amphibole crystals (portion projecting into an open miarolitic cavity), and 3) late-stage fine-grained, blue-gray riebeckite coating and interstitial crystals to primary minerals within miarolitic cavities.

TABLE 1. BULK COMPOSITION* OF FOUR SAMPLES OF RIEBECKITE-BEARING ALKALI GRANITE FROM HURRICANE MOUNTAIN, NEW HAMPSHIRE

SiO_2 wt.%	74.1	73.1	75.2	74.5
Al_2O_3	12.5	12.1	11.4	12.0
Fe_2O_3	3.43	4.11	3.46	3.53
MgO	<0.02	<0.02	<0.02	<0.02
CaO	0.44	0.54	0.55	0.35
Na_2O	4.35	4.38	4.21	4.26
K_2O	4.88	4.73	4.36	4.60
TiO_2	0.19	0.21	0.11	0.15
P_2O_5	0.07	0.07	0.06	0.08
MnO	0.06	0.09	0.06	0.06
LOI	–0.04	–0.02	–0.09	–0.06
Total	99.96	99.35	99.32	99.47

* X-ray-fluorescence data. Total iron expressed as Fe_2O_3.

Experimental

Chemical analytical methods used included: wavelength-dispersion spectrometry (WDS) electron-microprobe (JEOL 8900) analysis (EMPA) for the early Li-bearing fluor-arfvedsonite, X-ray fluorescence (XRF) analysis (PW 1606 instrument, using Li-tetraborate fusion disks) for all three amphiboles (Taggart *et al.* 1987), and laser-ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS) analysis (VG Plasmaquad II+ instrument equipped with a Spectron Inc. Nd:YAG laser) for all three amphiboles. Unit-cell data were determined using X-ray powder-diffraction methods.

Analytical conditions for the EPMA analyses were: 15 kV and 20 nA beam current, 20-second count times

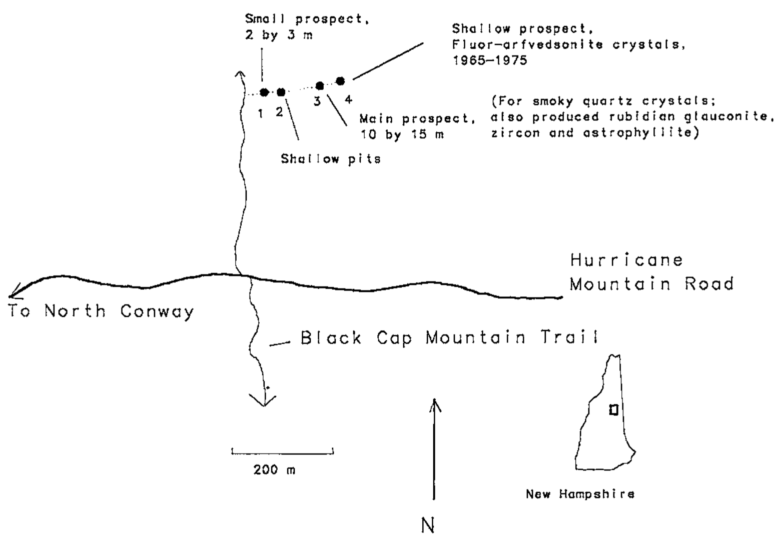

FIG. 1. Location map of granitic pegmatite occurrence at Hurricane Mountain, Carroll County, New Hampshire.

on peak positions, and 10-second count times on background positions. On the basis of counting statistics, the accuracy of the major element determinations is ±1%, and that of the minor elements is ±3%. Both natural and synthetic standards were used (minerals and oxides).

For the LA–ICP–MS analyses, the Nd:YAG laser was operated at the primary wavelength (1064 nm). A single mineral grain was glued onto a white polypropylene surface and placed into an enclosed sample-cell. The power and frequency of laser firings were adjusted to ablate material from the surface of the mineral grain at a controlled rate. A typical protocol used 350 mJoules per laser shot at 5 Hz in the fixed-switch mode. The power was increased in 50-mJoule increments to ablate more material until an adequate mass spectrometric signal was obtained. If the coupling efficiency between sample and laser energy was low, the process was repeated under Q-switched conditions. The instrument was calibrated from a glass standard containing all of the elements of interest, using laser conditions that were similar to those used for the mineral grain.

Total water was determined by heating about 40 mg of sample with 300 mg of lead chromate, lead oxide, and calcium carbonate flux at 900–950°C. The evolved water was quantified by using a Mitsubishi CA–05 coulometric Karl Fischer titrator (Jackson *et al.* 1987).

The empirical formula for the late, fibrous riebeckite was calculated on the basis of 7 total cations. This basis was used because of excess water (adsorbed) (Σ4.51 wt.%) is present.

TABLE 2. CHEMICAL COMPOSITION OF FLUOR–FERRO–LEAKEITE AND AMPHIBOLES FROM ALKALINE GRANITIC PEGMATITES, HURRICANE MOUNTAIN, CARROLL COUNTY, NEW HAMPSHIRE

	A	B	C	D
SiO_2 wt.%	51.12	50.8	50.1	48.9
Al_2O_3	1.13	0.4	0.5	0.5
FeO	8.87	20.0*	21.8	18.2
Fe_2O_3	16.73	13.0	14.2	20.0
MgO	2.02	<0.03	0.03	0.1
CaO	0.15	0.03	0.1	0.03
Na_2O	9.22	9.7	7.8	5.85
K_2O	1.19	1.3	1.45	0.25
TiO_2	0.68	0.65	0.3	0.85
P_2O_5	—	<0.01	<0.01	0.1
MnO	4.51	0.8	0.9	0.1
ZnO	0.57	0.2	0.1	0.07
Li_2O	0.99	0.8	0.34	0.09
SnO_2	—	0.02	0.05	0.08
ZrO_2	—	0.08	0.03	0.23
B_2O_3	—	<0.01	<0.01	0.01
BeO	—	0.01	0.02	0.05
Nb_2O_5	—	0.01	0.008	0.07
H_2O (total)	0.60(calc.)	0.62	1.07	4.51
F	2.87	2.8	1.8	0.3
Total	100.65	101.23	100.62	100.3
O for F	1.21	1.16	0.76	0.13
Total	99.44	100.04	99.84	100.17
Fe^{3+}/Fe^{2+}	1.69	0.58	0.58	0.99

Notes: * average of two determinations, 19.8 and 20.2, respectively. SiO_2, Al_2O_3, total iron (as Fe_2O_3), MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, and MnO determined by X–ray–fluorescence spectrometry on 0.4–g samples. Analysts: David Siems and Steve Mee (USGS). FeO and F determined by titration and selective–ion electrode, respectively. Analysts: C.S. Papp and J.E. Curry. SnO_2, ZrO_2, ZnO, B_2O_3, BeO, Li_2O, Rb_2O, Cs_2O, and Nb_2O_5 determined by LA–ICP–MS. Analyst: Frederick E. Lichte. Rb_2O and Cs_2O are both 0.01 wt.% or less. Other trace elements were sought by LA–ICP–MS and found to be less than 0.01 wt.%. H_2O (total) determinations by Larry L. Jackson (USGS). Samples: A: Bluish black to black fluor–ferro–leakeite from the Canada Pinabete pluton, Questa, New Mexico (Hawthorne *et al.* 1996); B: Early, black large prisms of lithium–bearing fluor–arfvedsonite in pegmatite; C: Euhedral, black fluor–arfvedsonite crystals in miarolitic cavities; D: Late, fine–grained medium blue–gray riebeckite partially filling miarolitic cavities.

Results and Discussion

Within the pegmatite, the basal parts of the prismatic crystals are Li-bearing fluor-arfvedsonite closely approaching the compositional boundary with fluor-ferro-leakeite (Hawthorne *et al.* 1996). The composition grades along the length of the crystals, from base to termination, into Li- and F-poor arfvedsonite, of similar composition to that from the miarolitic cavities. A minor amount of Zn (0.2 wt.% ZnO) is present in the early amphibole, typical for alkali amphibole from alkaline igneous rocks. Younger, secondary, hydrothermal, fibrous, light-blue masses of Li-free and F-poor riebeckite partly fill some of the miarolitic cavities, forming casts over quartz and feldspar. The riebeckite contains trace to minor amounts of elements not present in the primary fluor-arfvedsonite crystals (Table 2); these are elements characteristically found in the final differentiates of granitic pegmatite systems and in secondary minerals derived or altering from the final differentiates. The total iron content of the three amphiboles (pre-miarolitic cavity, miarolitic-cavity, and late hydrothermal) increases from early to late, again emphasizing the Fe-enrichment trend that is commonly found in alkali pegmatite systems.

The Fe^{3+}:Fe^{2+} ratio of the early Li-bearing fluor-arfvedsonite and of the euhedral miarolitic-cavity-filling crystals is 0.58. Apparently, little or no change in the Fe^{3+}:Fe^{2+} ratio occurred during crystallization of the amphibole-bearing pegmatites. The late riebeckite has an Fe^{3+}:Fe^{2+} ratio of 0.99 and is significantly richer in Fe than the arfvedsonite.

Optical data (Table 3) for the early Li-bearing fluor-arfvedsonite are ususual compared to regular arfvedsonite. The optical orientation is that of riebeckite rather than arfvedsonite, but the indices of refraction are in the range reported for arfvedsonite. The optical properties for fluor-ferro-leakeite (Hawthorne *et al.* 1996) are included for comparison. Using the determined unit-cell volume and the average index of refraction, a "superior" Gladstone–Dale compatibility index of –0.0127 was calculated. The calculated density, using the chemical analysis from Table 2 and the unit-cell volume, is 3.353 g/cm^3, similar to the measured density of 3.34(2) g/cm^3.

Unit-cell parameters (Table 3) and chemical composition for the early Li-bearing fluor-arfvedsonite are similar to values for analogous amphiboles from

TABLE 3. OPTICAL PROPERTIES AND UNIT-CELL DATA FOR Li- AND F-BEARING FLUOR-ARFVEDSONITE FROM HURRICANE MOUNTAIN, NEW HAMPSHIRE, AND COMPARISON WITH FLUOR-FERRO-LEAKEITE, RIEBECKITE AND ARFVEDSONITE

	A	B
Index of refraction α	1.681(2)	1.675(2)
β	1.692(2)	1.683(2)
γ	1.694(2)	1.694(1)
	$2V_x$ = 46° (calc.)	$2V_z$ = 81° (calc.)
	$2V_x$ = 44(1)° (obs.)	$2V_z$ = 87(2)° (obs.)
Dispersion	inclined, $r > v$	not given
$X \wedge c$	–7°	10° (in obtuse β)
Orientation	$Y = b$	$Y = b$
$Z \wedge a$	+7°	4° (in obtuse β)
X	dark blue	very dark indigo blue
Y	lavender gray	gray blue
Z	pale yellowish brown	yellow green
	$X > Y >> Z$	$X > Y > Z$
	X is opaque at 0.03 mm thickness	——

	Arfvedsonite	Li- and F-bearing arfvedsonite	Fluor-ferro-leakeite	Riebeckite	Riebeckite
α	1.700–1.672	1.681	1.675	1.690	1.702
β	1.710–1.677	1.692	1.683	1.690	1.712
γ	1.715–1.684	1.694	1.694	1.702	1.719
$2V_x$	0–70°	44°	93°	0–90°	0–50°
sign	(–)	(–)	(+)	(+)	(–)
	$Z = b$	$Y = b$	$Y = b$	$Y = b$	$Y = b$
	$X \wedge c$ = +5–30°	$X \wedge c$ = –7°		$X \wedge c$ = –8°	$X \wedge c$ = –7°
	$Y \wedge a$ = +20–45°	$Z \wedge a$ = +7°		$Z \wedge a$ = +6°	$Z \wedge a$ = +7°
dispersion	$r > v$	$r > v$	——	$v > r$	$r > v$
	very strong	moderate		strong	strong

Optical data for arfvedsonite and riebeckite from Phillips & Griffen (1981). Unit-cell data for fluor-arfvedsonite from Hurricane Mountain, New Hampshire: *a* 9.836(5), *b* 17.997(7), *c* 5.316(4) Å, β 103.735(4)°, *V* 914.20(6) Å^3. Data were collected on a Scintag XDS-2000 system with a normal-focus Cu X-ray tube running at 45 kV, 40 mA. Step scans were made from 2 to 80° 2θ, with a step size of 0.02° and a dwell time of 5–10 seconds. Column A: Li- and F-bearing arfvedsonite; column B: fluor-ferro-leakeite.

Hawthorne *et al.* (1993, 1996). The structural formula, on the basis of 24 (O,OH,F) atoms, for the early, Li-bearing fluor-arfvedsonite is: $(Na_{0.86}K_{0.25})_{\Sigma 1.11}Na_2(Fe^{2+}_{2.54}Fe^{3+}_{1.485}Mn_{0.10}Zn_{0.02}Li_{0.49}Ti_{0.07})_{\Sigma 4.705}(Si_{7.71}Al_{0.07})_{\Sigma 7.78}O_{22.03}(F_{1.34}OH_{0.63})_{\Sigma 1.97}$. Li enters the arfvedsonite structure primarily by means of the substitution: $^{[M3]}Li + Fe^{3+} \rightarrow {}^{[M3]}Fe^{2+} + Fe^{2+}$ (Hawthorne *et al.* 1993, 1994).

Likewise, a structural formula (also on the basis of 24(O,OH,F) atoms) for the euhedral, miarolitic-cavity-filling fluor-arfvedsonite is: $(Na_{0.28}K_{0.28})_{\Sigma 0.56}(Na_{2.00}Ca_{0.02})_{\Sigma 2.02}(Fe^{2+}_{2.74}Fe^{3+}_{1.61}Li_{0.21}Mn_{0.11}Ti_{0.03}Mg_{0.01}Zn_{0.01})_{\Sigma 4.71}(Si_{7.54}Al_{0.09})_{\Sigma 7.63}O_{22.07}(OH_{1.07}F_{0.86})_{\Sigma 1.93}$. The principal differences noted between the early and late fluor-arfvedsonite crystals are in the amounts of Na, Li and total Fe.

A formula for the late, fibrous riebeckite, calculated on the basis of seven total cations, is: $(Na_{1.82}K_{0.05}Ca_{0.01})_{\Sigma 1.88}(Fe^{2+}_{2.44}Li_{0.06}Mg_{0.02}BeO_{0.02}Mn_{0.01}ZnO_{0.01})_{\Sigma 2.56}(Fe^{3+}_{2.42}Ti_{0.10}Zr_{0.02}Sn_{0.01}Nb_{0.01})_{\Sigma 2.56}(Si_{7.85}Al_{0.10}P_{0.01})_{\Sigma 7.96}O_{23.2}$.

The importance of Li in igneous amphiboles is clearly supported by the occurrence of Li-bearing amphibole in alkaline granitic pegmatites at Hurricane Mountain. Furthermore, it is interesting to note that the ferrous:ferric ratio remained constant throughout the crystallization of the pegmatite and that oxidation and chemical conditions changed significantly after final crystallization of the primary minerals in the miarolitic cavities. The fine-grained riebeckite is a product of final low-temperature hydrothermal solutions that were present in the miarolitic cavities.

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