MINERALOGICAL MAGAZINE, MARCH 1976, VOL. 40, PP. 473-9

The chemistry of riebeckites of Massachusetts and Rhode Island

PAUL C. LYONS[1]

Boston University, College of Basic Studies, Boston, Massachusetts 02215, U.S.A.

SUMMARY. Four new chemical analyses are reported for riebeckites of the hypersolvus granites of Massachusetts and Rhode Island. Riebeckites of southern New England are enriched in Li^+, which appears to substitute for Fe^{2+}, with additional Na^+ coming in to compensate for the charge imbalance.

FOUR new chemical analyses are presented (Table II, analyses 2, 6, 7, and 8) for riebeckites from the alkali granites of southern New England. Although early chemical analyses of riebeckites were provided by Chester and Cairns (1887) and Warren and Palache (1911), little additional data have been added. Lyons (1972) discussed amphiboles from this area and reported an analysis of riebeckite from the Quincy Granite proper.

General geology. The areal distribution of the hypersolvus granites of Massachusetts and Rhode Island is shown in fig. 1. The alkali granite plutons of this area are aligned in a north-east direction following the structural trend of the Appalachians. The Cape Ann and Peabody Granites to the north are characteristically ferrohastingsite granites, although some riebeckite granite has been reported from the Cape Ann pluton (Zartman and Marvin, 1971, p. 955). The alkali granites to the south are riebeckite granites; the Quincy Granite and the alkali granite from the north-east corner of Rhode Island are riebeckite–aegirine granites and the Rattlesnake granite is a riebeckite granite. Modal data on these granites are presented in Table I.

These alkali granite plutons are distinguished by a relatively high percentage of amphibole granite compared with biotite granite, syenite, and quartz syenite, and by the absence of the ring structures that are typical of similar rocks of other areas such as New Hampshire (Billings, 1956), Greenland, (Puklen complex, Pulvertaft, 1961), and Nigeria (Jacobson *et al.*, 1958).

The age (ages?) of these Palaeozoic granites has not been finally resolved. They are almost certainly post-Cambrian and most likely Silurian to Devonian in age (Zartman and Marvin, 1971; Krueger and Lyons, 1972).

Definitions of riebeckite and arfvedsonite. It is impossible to reliably separate riebeckite from arfvedsonite on the presently available X-ray and optical data because of lack of correlation with accurate chemical compositions for specific species in the riebeckite–arfvedsonite series. In view of this problem, chemical data will be used in this paper to distinguish riebeckite and arfvedsonite. Analyses reported as arfvedsonite almost always show higher M_4+A values and lower Fe^{3+} values in comparison with

---

[1] Present address: 18 Northwood Drive, Walpole, Mass. 02081

TABLE I. *Modes of selected hypersolvus granites of Massachusetts and Rhode Island*

	RP	RV	RG	RI-G	QP	QG	CA
Microperthite*	56·5	23·4	67·7	54·5	57·5‖	62·7	66·0
Quartz	31·1	67·7	26·8	37·4	26·1	29·0	27·0
Riebeckite	12·2	08·9	04·9	04·7	x	06·2	tr
Ferrohastingsite	—	—	—	—	—	—	07·0
Grunerite	tr	—	—	—	—	—	tr
Astrophyllite	—	—	—	tr	—	tr	x
Katophorite	—	—	—	—	—	tr	—
Aenigmatite	—	—	—	—	—	tr	—
Hedenbergite	—	—	—	—	—	—	tr
Aegirine	—	—	—	03·4	14·2	01·8	—
Augite/aegir.-augite	—	—	tr	—	—	tr	x
Fayalite	—	—	—	—	—	—	tr
Biotite	—	—	00·1	x	—	00·1	x
Opaque Oxides†	00·2	x	00·4	x	x	00·2	x
Zircon	tr	tr?	tr	00·1	x	tr	tr
Fluorite	—	—	tr	—	x	x	tr
Allanite	—	—	—	—	x	tr	tr
Sphene	—	—	—	x?	x	x	x
Carbonates‡	—	—	—	x	x	x	x
Sulphides	—	—	—	tr	tr¶	tr	tr**
Muscovite	tr	tr?	tr	tr	x	tr	tr
Epidote	—	—	—	—	—	—	x
Chlorite	—	—	—	—	—	tr	—
Apatite	—	—	—	—	—	—	tr
Other Minerals	—	—	—	—	x††	—	x‡‡
Ab content of Microperthite§	34	—	53	—	—	53	55

* Microcline microperthite, includes small amounts of albite.

† Mainly magnetite, less commonly ilmenite, rarely hematite.

‡ Mainly calcite, less commonly siderite.

§ Lyons (1969), Toulmin (1964).

‖ 22·5 % microcline, 35·0 % albite (central pocket of Fallon pegmatite).

¶ Galena, sphalerite, chalcopyrite, and molybdenite.

** In pegmatites, molybdenite, galena, sphalerite, pyrite, pyrrhotine, and danalite.

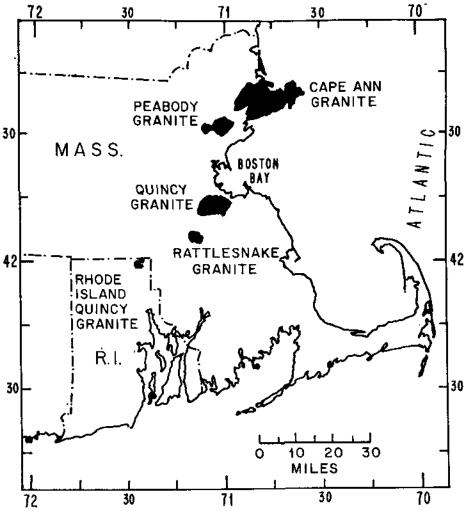
†† Parisite, anatase, beckelite, wulfenite.

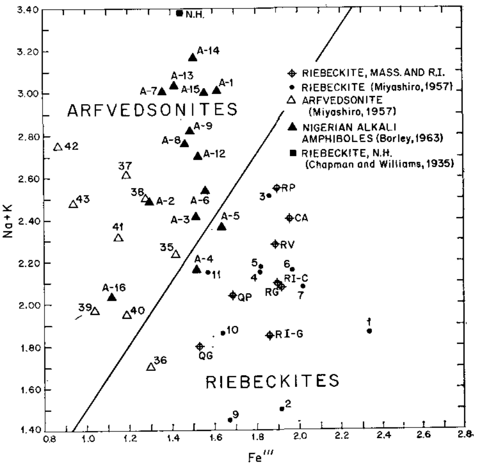
‡‡ In pegmatites, a variety of rare-earth minerals, including cyrtolite, fergusonite, yttrocerite, tantalite, thorite, and gadolinite; cryophyllite (lithium mica).

RP	Rattlesnake pegmatite, Lyons (1969).
RV	Rattlesnake quartz vein, Lyons (1969).
RG	Rattlesnake granite, Lyons (1969).
RI-G	Rhode Island Quincy granite, Quinn (1971; written communication, 1972).
QP	Quincy pegmatite, Warren and Palache (1911).
QG	Quincy granite, Warren (1913).
CA	Cape Ann granite, Warren and McKinstry (1924); Toulmin (1964).
x	Indicates present, but amount not known; x's total 2·2 in QP.

reported riebeckite analyses. For the purpose of this paper, the writer separates riebeckites and arfvedsonites on the basis of the atomic ratios of $(Na+K)/Fe^{3+}$ as follows: riebeckite: $(Na+K)/Fe^{3+} < 1{\cdot}50$; arfvedsonite: $(Na+K)/Fe^{3+} \geqslant 1{\cdot}50$.

Fig. 2 shows a plot of representative riebeckites and arfvedsonites based on this criterion. Such a classification scheme causes a 'riebeckite' of Chapman and Williams (1935) to be renamed arfvedsonite and one of the arfvedsonites of Miyashiro (1957) to be reclassified as riebeckite. Fig. 2 also shows that all the soda-iron amphiboles of Massachusetts and Rhode Island fall into the category of riebeckite.





FIGS. 1 and 2: FIG. 1 (left). Areal distribution of hypersolvus granites of eastern Massachusetts and Rhode Island. FIG. 2 (right). $(Na+K)/Fe^{3+}$ atomic ratios of selected riebeckites and arfvedsonites.

Preparation and purity of concentrates. Riebeckite samples (Table II, analyses 2, 6, 7, and 8) were hand-picked and concentrated by heavy liquids and magnetic separation. The purity of the samples, based on 500 grain counts for each concentrate, ranged from 93·5 to 98·8 wt. % riebeckite. The only impurities observed were quartz and alkali feldspar, except for grunerite in analysis 8. Estimates of the impurities and their probable compositions are shown at the bottom of Table II. Compositions of impurities, except for grunerite, are known with a great deal of certainty as K and Na determinations by atomic absorption were made on the alkali feldspars and quartz has a composition very close to 100 % SiO_2.

Formula calculation method and cation assignment scheme. The chemical formulae of the new analyses were calculated following the methods of Deer *et al.* (1966) on the basis of 24(O, OH, F).

Cations in Table III were assigned in the order of Z, M_4, and Y sites. Si, Al, and Fe^{3+} (if needed) were assigned to the Z sites until they totalled 8·00 cations. The Y cations were not specifically assigned to M_1, M_2, and M_3 sites in Table III because of lack of

TABLE II. *Chemical compositions of riebeckites of southern New England and selected riebeckites*

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	52·13	48·50	50·62	47·06	49·65	48·47	50·01	49·20	43·46	47·70	51·90	44·45
Al_2O_3	n.d.	3·74	0·68	2·36	1·34	1·75	2·07	2·28	1·18	1·15	1·25	4·28
TiO_2	n.d.	0·80	1·28	1·53	n.d.	1·06	1·39	0·94	0·54	1·04	0·55	1·06
Fe_2O_3	15·53	16·13	14·51	12·91	17·66	16·38	16·51	16·39	19·57	12·90	15·00	17·74
FeO	21·25	18·97	21·43	20·92	19·55	19·20	17·90	17·21	18·00	22·57	16·10	17·50
MgO	0·22	0·32	0·10	0·30	n.d.	0·10	0·14	0·09	0·32	0·44	0·35	1·00
MnO	n.d.	0·59	1·15	0·76	n.d.	0·76	0·55	0·72	0·29	0·54	3·10	0·42
CaO	n.d.	1·29	1·28	3·76	3·16	0·87	0·27	0·15	5·83	2·22	0·45	0·32
Na_2O	6·26	5·91	6·15	5·96	7·61	6·70	6·23	7·48	4·75	6·36	7·60	7·22
K_2O	n.d.	0·55	1·10	1·22	n.d.	1·42	1·22	1·65	0·42	1·14	1·25	1·24
Li_2O	n.d.	0·56	n.d.	0·38	n.d.	0·96	0·75	1·16	0·26	0·52	n.d.	0·83
H_2O+	3·95	2·23	1·30	1·64	1·67	1·55	1·83	1·85	2·01	1·70	2·07	n.d.
H_2O-	0·00	0·41	0·10	0·28	n.d.	0·20	0·43	0·27	—	0·12	—	1·69
F	n.d.	0·74	0·20	1·16	n.d.	1·45	1·08	1·49	3·50	1·31	n.d.	1·00
Total	99·34	100·74	99·90	100·64	100·24	100·87	100·38	100·88	100·13	101·20*	99·62	98:75
$O=F$	0·00	0·31	0·09	0·49	0·00	0·57	0·45	0·60	1·46	0·56	0·00	0·42
	99·34	100·43	99·81	99·75	100·64	100·30	99·93	100·28	98·67	100·64	99·62	98·33

1 Crocidolite, Cumberland, Rhode Island (RI-G), Chester & Cairns (1887).
2 From granite, Cumberland, Rhode Island (RI-G), Lat. 41° 59′ 38″, Long. 71° 27′ 17″, (123F).
3 From pegmatite, Quincy, Mass. (QP), Warren and Palache (1911), Fallon Quarry.
4 From granite, Quincy, Mass. (QG), Lyons (1972), Lat. 42° 14′ 36″, Long. 71° 1′ 52″, (123G).
5 From granite, Cape Ann, Mass. (CA), Warren and Palache (1911).
6 From quartz vein, Rattlesnake Hill, (RC), Sharon, Mass., Lat. 42° 5′ 40″, Long. 71° 8′ 28″, (118).
7 From granite, Rattlesnake Hill, (RG), Sharon, Mass., Lat. 42° 5′ 17″, Long. 71° 8′ 58″ (74K).
8 From pegmatite, Rattlesnake Hill, (RP), Sharon, Mass., Lat. 42° 5′ 40″, Long. 71° 8′ 28″ (118C).
9 Calciriebeckite, Tuva, U.S.S.R., Kovalenko *et al.*, (1966).
10 Arfvedsonitic riebeckite, Nigeria, Borley (1963). *Includes: ZrO_2, 0·87; ZnO, 0·50; P_2O_5, 0·07; Cl, 0·05.
11 From granite, Fort-Trinquet, Mauretania, N.W. Africa, Fabriès and Rocci (1972).
12 Riebeckite, Ulkan Pluton, U.S.S.R., Gamaleya (1970).

New Analyses: Analyst, Tadashi Asari; Methods of analysis—gravimetric: SiO_2, Al_2O_3, MgO, CaO, $H_2O(+)$, $H_2O(-)$; Volumetric: Fe_2O_3, FeO; Colorimetric: TiO_2, MnO, F; Flame Photometric: Na_2O, K_2O, Li; Standard Deviations: SiO_2, 0·55 %; Al_2O_3, 2·20 %; Fe_2O_3, 6·13 %; FeO, 2·09 %; CaO, 2·16 %; MgO, 3·40 %; Na_2O, 4·45 %; K_2O, 10·40 %; H_2O+, 21·3 %; H_2O-, 25·0 %; TiO_2, 5·85 %; F, 15·0 %; Li, 10·0 %.

New analyses corrected for impurities (wt. %) as follows, anal. 2: quartz, 2·6 %, feldspar ($Or_{50}Ab_{50}$), 3·0 %; anal. 6: quartz 4·4 %, feldspar ($Or_{65}Ab_{35}$), 2·1 %; anal, 7: quartz 0·8 %, feldspar ($Or_{47}Ab_{53}$), 0·4 %; anal. 8: quartz, 0·7 %, grunerite [$Fe_7^{+2}Si_8O_{22}(OH)_2$], 3·6 %.

precise information on their distribution in riebeckites and arfvedsonites. Ca, K, and Na were assigned to the M_4 sites until they totalled 2·00 cations; the remaining Na was assigned to the A site. In one case (4, Table III) octahedral Na, as predicted from the Na and Li relations to be discussed later, was assigned to the Y positions. The remaining cations were assigned to the Y positions.

Crystal chemistry of riebeckites

The chemical compositions of riebeckites of Massachusetts and Rhode Island and some selected riebeckites from other areas are presented in Table II. Formulae are given in Table III.

A-site occupancy varies from zero in riebeckites of ironstones, through intermediate values in arfvedsonites, to a maximum in magnesioriebeckites and magnesioarfvedsonites, which indicates that higher temperatures favour the filling of the A site.

One of the most unusual cations that occurs in the Y sites of riebeckite is Li.

TABLE III. *Atomic ratios of riebeckites of Table II*

	1	2	3	4	5	6	7	8	9	10	11	12
Si	781	743	784	741	765	752	766	754	735	749	801	695
Al^{iv}	(19)	57	14	44	23	31	34	41	24	21	00	92
$(Fe^{3+})^{iv}$	00	00	02	15	12	17	00	05	41	30	00	13
Z	800	800	800	800	800	800	800	800	800	800	801	800
Al^{vi}	00	10	00	00	00	00	03	00	00	00	23	00
$(Fe^{3+})^{vi}$	191	185	167	138	183	172	190	184	208	122	174	217
Ti	(14)	09	15	18	12	12	16	11	07	12	06	08
Fe^{2+}	266	242	277	276	243	249	230	220	254	296	208	235
Mn	(10)	07	15	10	(10)	10	07	09	04	07	40	06
Mg	(03)	07	02	07	(04)	02	03	02	08	11	08	14
Li	(44)	34	(44)	24	(67)	60	46	72	18	33	(41)	20
Na^{vi}	00	00	00	27	00	00	00	00	00	00	00	00
Y	528	494	520	500	519	505	495	498	499	481	500	500
Ca	(13)	21	21	63	51	14	05	04	106	38	07	05
Na^{viii}	163	168	157	112	125	158	171	112	86	139	168	173
K	(24)	11	22	25	(24)	28	24	34	08	23	25	22
M_4	200	200	200	200	200	200	200	200	200	200	200	200
A (Na)	21	07	27	43	92	44	15	60	69	55	59	42
OH	380	228	134	173	174	160	188	189	124	178	207	(150)
F	(71)	36	12	58	(58)	71	53	72	(185)	65	—	50

Value divided by 100 equals the number of ions per formula unit.
Formulas 2, 6, 7, and 8 were calculated on the basis of 24(O, OH, F).
Values in parentheses are estimates.

Previously, Sundius (1946) suggested that Li (0·65 cations per formula unit) substitutes for Mg in the *Y* positions in eckermannite, $Na_3Mg_4AlSi_8O_{22}(OH)_2$, from a nepheline syenite of southern Sweden. He also suggested that Li (1·12 cations per formula unit) substitutes for Na in the M_4 site of holmquistite (glaucophane) of Üto, Sweden (Sundius, 1946).

Recent chemical data indicate major quantities of Li (up to 1·31 cations per formula unit) in riebeckites and arfvedsonites (Borley, 1963; Kovalenko *et al.*, 1966; Afonina *et al.*, 1969; Gamaleya, 1970; and Lyons, 1972). Older chemical analyses of riebeckites do not give Li and further analyses of these riebeckites will probably reveal, in many cases, appreciable quantities of Li.

Addison and White (1968) offer spectroscopic evidence that Li substitutes for Fe^{2+} in riebeckites, but this is only supported by limited chemical data. Li may also substitute for Fe^{3+} as in the riebeckites of the metasomatic zones between granites and gabbro in Tuva, U.S.S.R. (Kovalenko *et al.*, 1966).

Li increases as Fe^{2+} decreases in riebeckites of Nigeria, the Ulkan pluton (U.S.S.R.), and southern New England. This inverse relation between Li and Fe^{2+} is strong evidence that Li substitutes for Fe^{2+} in riebeckites of these areas. Coupled with this fact is one of the major findings of this paper: Li and Na correlate positively in riebeckites of southern New England. This is shown graphically in fig. 3. This relation is also shown in data from other regions (Borley, 1963; Gamaleya, 1970), although the lines have different slopes, probably indicating varying oxygen fugacities and bulk chemistries. The more arfvedsonitic amphiboles of Nigeria depart from this relation,

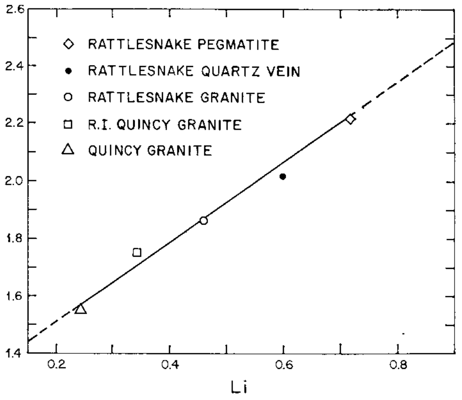


FIG. 3. Relation of atomic non-octahedral Na to Li in riebeckites of Massachusetts and Rhode Island. Na value for riebeckite of Quincy Granite is predicted.

probably due to substitution of Li^+ for Fe^{3+} in M_2 sites, thus requiring two additional Na^+ to maintain the charge balance.

Li is most likely preferred in the M_3 site (Whittaker, 1971) or M_1 site, as opposed to the M_2 site, as these are the preferred sites of Fe^{2+} (Bancroft and Burns, 1969; Burns and Prentice, 1968). It is suggested that for every Fe^{2+} replaced by Li^+, one Na^+ comes into the A site to balance the charge difference between Li^+ and Fe^{2+}.

Fluorine values increase with the values M_4+A in the riebeckites and arfvedsonites of the U.S.S.R. and Nigeria (Afonina *et al.*, 1969). This relation also holds for the riebeckites of southern New England. It is not clear whether this is due to NaF being one of the reactants involved or to some other mechanism.

Phase relations and paragenesis

The phase relations of riebeckite and riebeckite–arfvedsonite solid solutions have been determined by Ernst (1962). Riebeckite is stable to a maximum temperature of 515 °C under high oxygen fugacities (hematite–magnetite buffer); under more reducing conditions (wüstite–iron buffer) riebeckite–arfvedsonite solid solutions are stable to a maximum temperature of about 710 °C. The phase relations indicate that the absence of fayalite and the occurrence of quartz, aenigmatite, and aegirine (acmite) in the Quincy Granite are consistent with magmatic temperatures of 650 to 750 °C, low oxygen fugacities, and fluid pressures below 700 bars (Lyons, 1972).

Riebeckites of alkali granites probably crystallized at temperatures much higher than 515 °C as indicated by their association with hypersolvus feldspar that crystallized above 660 °C (Tuttle and Bowen, 1958). The occurrence of fibrous riebeckites (crocidolites) in hematite–magnetite (ironstone) formations indicates crystallization below 500 °C, and authigenic riebeckite(?) in the Green River Formation of Utah (Milton and Eugster, 1959) may indicate crystallization as low as 100 °C.

Acknowledgements. This research was supported by Boston University grants UG123-CBS and UG151-CBS. Thanks are given to W. G. Ernst, A. Miyashiro, D. R. Wones, and C. W. Burnham for critical review of the manuscript. They do not necessarily agree with the classification scheme used or with the significance of the chemical relations expressed in this paper. Paul Cook and Robert Harris served as laboratory and field assistants and their help is gratefully acknowledged. Many thanks to M. M. Albanese for preparing the illustrations and to Barbara Boughman for typing assistance.

REFERENCES

ADDISON (W. E.) and WHITE (A. D.), 1968. *Min. Mag.* **36,** 743.

[AFONINA (G. G.), KOVALENKO (V. I.), and PISARSKAYA (V. A.)] Афонина (Г. Г.), Коваленко (В. И.) и Писарская (В. А.) 1969. Докл. акад. наук СССР (*Compt. Rend. Acad. Sci. URSS*), **187,** 1371.

BANCROFT (G. M.), and BURNS (R. G.), 1969. *Min. Soc. Amer. Spec. Paper No.* 2, 137.

BILLINGS (M. P.), 1956. *The Geology of New Hampshire, Part II, Bedrock Geology,* New Hampshire State Planning and Development Comm.

BORLEY (G. D.), 1963. *Min. Mag.* **33,** 358.

BURNS (R. G.) and GREAVES (C.), 1971. *Amer. Min.* **56,** 2010.

—— and PRENTICE (E. J.), 1968. Ibid. **53,** 770.

CHAPMAN (R. W.) and WILLIAMS (C. R.), 1935. Ibid. **20,** 502.

CHESTER (A. H.) and CAIRNS (F. I.), 1887. *Amer. Journ. Sci.* **34,** 108.

DEER (W. A.), HOWIE (R. A.), and ZUSSMAN (J.), 1966. *An Introduction to the Rock-Forming Minerals.* John Wiley, New York.

ERNST (W. G.), 1962. *Journ. Geol.* **70,** 689.

FABRIÈS (J.) and ROCCI (G.), 1972. *Contr. Min. Petrol.* **35,** 215.

[GAMALEYA (YU. N.)] Гамалея (Ю. Н.), 1970. Изв. акад. наук СССР (*Bull. Acad. Sci. U.S.S.R., ser. geol.*), 39.

JACOBSON (R. R. E.), MACLEOD (W. N.), and BLACK (R.), 1958. *Geol. Soc. London,* Mem. **1.**

[KOVALENKO (V. I.), PISARSKAYA (V. A.), and MIKOLAEVA (D. K.)] Коваленко (В. И.), Писарская (В. А.), и Миколаева (Д. К.), 1966. Докл. акад. наук СССР (*Compt. Rend. Acad. Sci. URSS*), **169,** 1162.

KRUEGER (H. W.), and LYONS (P. C.), 1972. *Geol. Soc. Amer., N.E. Sect. 7th Ann. Meet., Abs. Programs,* **4,** no. 1, 26.

LYONS (P. C.), 1969. *Bedrock Geology of the Mansfield Quadrangle, Massachusetts,* Boston Univ. Ph.D. thesis.

—— 1972. *Amer. Min.* **57,** 1404.

MILTON (C.) and EUGSTER (H. P.), 1959. *Mineral assemblages of the Green River Formation,* pp. 118–50, in *Researches in Geochemistry,* P. H. ABELSON, ed., John Wiley, New York.

MIYASHIRO (A.), 1957. *Journ. Fac. Sci., Univ. Tokyo,* **11,** sect. 2, 57.

PULVERTAFT (T. C. R.), 1961. *Bull. Grønlands Geol. Unders.* **29.**

QUINN (A. W.), 1971. *U.S. Geol. Surv. Bull.* **1295.**

SUNDIUS (N.), 1946. *Geol. Unders., Ser. C, No. 48* (Årsbok 40), 1.

TOULMIN (P.), 1964. *U.S. Geol. Surv. Bull.* **1163–A.**

TUTTLE (O. F.) and BOWEN (N. L.), 1958. *Geol. Soc. Amer. Mem.* **74.**

WARREN (C. H.), 1913. *Proc. Amer. Acad. Arts and Sci.* **49,** 203.

—— and MCKINSTRY (H. E.), 1924. Ibid. **59,** 314.

—— and PALACHE (C.), 1911. Ibid. **47,** 126.

WHITTAKER (E. J. W.), 1971. *Amer. Min.* **56,** 980.

ZARTMAN (R. E.) and MARVIN (R. F.), 1971. *Geol. Soc. Amer. Bull.* **82,** 937.

[*Manuscript received 10 January 1975; revised 6 February 1975*]

Note added in proof: A recently reported chemical analysis of the authigenic riebeckite (?) of the Green River Formation indicates magnesioarfvedsonite (Milton *et. al.*, 1974, *Amer. Min.* **59,** 830.