SIGNIFICANCE OF RIEBECKITE AND FERROHASTINGSITE IN MICROPERTHITE GRANITES

Paul C. Lyons, *Boston University, College of Basic Studies, Boston, Massachusetts 02215*

Abstract

Riebeckite and ferrohastingsite occur separately in closely related hypersolvus granites of eastern Massachusetts. Mineralogical, chemical, and phase equilibria data suggest that the Quincy riebeckite granite and the Peabody ferrohastingsite granite crystallized at similar temperatures, most likely 650–750°C. The chemical composition of the parent magma and oxygen fugacity played important roles in determining the composition of the amphibole. Parent composition favored a calcium–iron–aluminum amphibole, ferrohastingsite, $NaCa_2Fe^{2+}{}_4Fe^{3+}Al_2Si_6O_{22}(OH)_2$, in the Peabody, and a soda-iron amphibole, riebeckite, $Na_2Fe^{2+}{}_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$, in the Quincy. Higher oxygen fugacities favored the ferric-rich amphibole, in the Quincy; lower oxygen fugacities favored the ferric-poor amphibole, ferrohastingsite, in the Peabody. Mineral relations in the Quincy suggest an increase in oxygen fugacity with decrease in temperature. Two new chemical analyses, one of the Quincy granite riebeckite and one of the Peabody granite ferrohastingsite, are reported.

Introduction

Riebeckite (or arfvedsonite) and ferrohastingsite are found in one-feldspar granites of Nigeria, New Hampshire, and eastern Massachusetts. The riebeckite and ferrohastingsite granites typically occur in separate plutons. In New Hampshire and Massachusetts, a small amount of riebeckite granite is associated with ferrohastingsite granite in the same pluton.

The Quincy and Peabody granites of eastern Massachusetts will be used to address the problem of the spatial independence of riebeckite and ferrohastingsite. New chemical data are presented for the Quincy riebeckite and the Peabody ferrohastingsite. This paper will attempt to explain the field relations of these amphiboles in light of their chemistry, mineralogical and whole-rock chemical data, and phase equilibria studies.

The spatial relations of the alkali granite plutons of eastern Massachusetts are shown in Figure 1. The Quincy[1] and Rattlesnake Hill are riebeckite granites, and the Peabody and Cape Ann are ferrohastingsite granites.

---

[1] Investigators should clearly state whether they are referring to the Quincy, Peabody, or Cape Ann granites, because using Quincy granite for all three has caused confusion in the literature (see Toulmin, 1964).
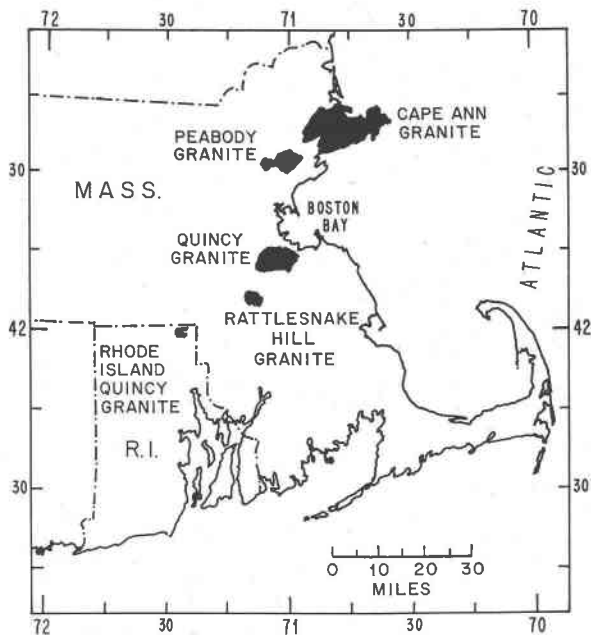
Fig. 1. Location of the granite plutons.

Mineralogical Data

Modal data for the Quincy and Peabody granites are summarized in Table 1. Pyrochlore in the Peabody and fluorite in the Quincy suggest that mineralizers were present during the crystallization of the magmas. The similar younger granites of Nigeria (Borley, 1963) contain, in addition, cryolite and topaz, again indicating the presence of mineralizers, particularly fluorine. The alkali amphiboles of Nigeria (Borley, 1963) and of Massachusetts and Rhode Island (Lyons, unpublished data) also contain considerable amounts of fluorine substituting for OH. The absence of aegirine and aenigmatite from the Peabody and fayalite from the Quincy are noteworthy. Fayalite has not been reported from the Peabody, although it does occur in the closely-related Cape Ann granite and is common to the ferrohastingsite granites of New Hampshire and Nigeria.

The Peabody and Quincy granites have counterparts in New Hampshire and Nigeria; all three areas have ferrohastingsite and riebeckite (or arfvedsonite) granites with strikingly similar mineralogical compositions. Typically one granite is a riebeckite– or arfvedsonite–aegirine granite and the other is a ferrohastingsite–fayalite granite.

Table 1

MODAL AND CHEMICAL DATA FOR QUINCY AND PEABODY GRANITES

MODAL DATA			CHEMICAL DATA							
	Quincy[1]	Peabody[2]		Quincy				Peabody	[3]	[4]
Perthite*	62.7	67.2	SiO_2	75.08	75.58	73.93	74.86	71.90	72.26	72.08
Quartz	29.0	25.0	ZrO_2	.20	.20	(.20)	.20	.12	n.d.	.12
Ferrohastingsite	0.0	6.4	Al_2O_3	11.57	11.17	12.09	11.61	12.98	13.18	13.08
Riebeckite	6.2**	tr	Fe_2O_3	2.25	1.71	2.91	2.29	.81	.24	.53
Aegirine	1.8	0.0	FeO	.93	1.26	1.55	1.25	2.85	2.77	2.81
Pyroxene	Tr	.2	MgO	.03	.04	.08	.05	.02	.20	.11
Biotite	.1	.3	MnO	tr	.05	tr	.02	.08	.10	.09
Magnetite	.2	.7	CaO	.44	.49	.31	.41	1.04	1.10	1.07
Hematite	tr	0.0	Na_2O	4.21	4.03	4.66	4.30	4.19	3.99	4.09
Ilmenite	tr	tr	K_2O	4.62	4.68	4.63	4.64	5.60	5.01	5.30
Sulphides	tr	tr	H_2O^+	.19	.34	.41	.31	.20	.20	.20
Zircon	tr	.2	H_2O^-	.04	.10	0.0	.04	n.d.	.08	.08
Sphene	tr	tr	P_2O_5	tr	tr	tr	tr	n.d.	.07	.07
Allanite	0.0	tr	TiO_2	.20	.22	.18	.20	.34	.36	.35
Calcite	tr	0.0	Total	99.76	99.87	100.95	100.18	100.13	99.56	99.98
Apatite	0.0	tr								
Aenigmatite	tr	0.0								
Astrophyllite	tr	?								
Fluorite	tr	0.0								
Pyrochlore	0.0	tr								
Fayalite	0.0	?								
Sericite	tr	tr								

[1] Mean of 12 analyses; minor constituents are approximate (Warren, 1913; Lyons, unpub.).
[2] Mean of 14 analyses; minor constituents are approximate (Toulmin, 1964; Lyons, unpub.).
[3] Mean of 3 analyses (Warren, 1913).
[4] Mean of 2 analyses (Toulmin, 1964).
*Consists of microcline and albite; includes minor amounts of separate albite.
**In places, partly katophorite.

The ferrohastingsite granites of the Northwest Adirondacks (Buddington, 1948) contain similar minerals to the comparable granites of New Hampshire (Billings, 1956) such as microperthite, minor plagioclase, quartz, biotite, and apatite. The New Hampshire ferrohastingsite granites have, in addition, traces of fayalite.

Rock Chemistry

The chemical compositions of the Quincy and Peabody granites are given in Table 1. The Quincy is higher in silica and soda, but lower in alumina, potash, and lime than is the Peabody. There is no significant difference between the total iron contents of the two granites; the major difference is in the oxidation state of the iron: the Quincy is ferric–rich and the Peabody is ferric–poor. Obviously, the oxidation state of the iron partly conditioned the nature of the amphibole which crystallized from the magmas. This will be discussed later in the paper.

The ferric–rich nature of the Quincy is consistent with its mineralogy, riebeckite and aegirine. The three chemical analyses of the Quincy granite consistently show ferric ion dominant over ferrous ion. The ferric/ferrous ion ratio of the riebeckite in the Quincy pegmatite (Warren and Palache, 1911) is nearly identical to that of the riebeckite of the Quincy granite proper, which suggests that similar oxygen fugacities prevailed during their crystallization.

The higher silica content of the Quincy is reflected by more quartz in its mode. The higher alumina and potash contents of the Peabody are shown by a greater modal amount of perthite and a more aluminous amphibole. The amphibole compositions (Table 2) indicate the differences in lime and soda; the Peabody has a calcium amphibole and the Quincy has a soda amphibole. The marked distinction in the ferric and ferrous iron contents is clearly revealed by the amphiboles; the Quincy has riebeckite, $Na_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$; the Peabody has ferrohastingsite, $NaCa_2Fe^{2+}_4Fe^{3+}Al_2Si_6O_{22}(OH)_2$.

Amphibole Chemistry

A summary of the chemical compositions of the two amphiboles is given in Table 2. The chemical composition of the Peabody amphibole is very similar to the compositions of the ferrohastingsites of Northern Nigeria (Borley and Frost, 1963) and the hastingsites of the Adirondack hornblende granites (Buddington and Leonard, 1953).

The atomic proportions of the various constituents in the two amphiboles are shown in columns (7) and (8) of Table 2. The formula of the Peabody ferrohastingsite is: $Na_{0.80}K_{0.24}Ca_{1.70}$, $Fe^{2+}_{3.62}Mg_{0.47}Mn_{0.13}Li_{0.03}$, $Fe^{3+}_{0.79}Ti_{0.23}Al_{0.06}$, $Al_{1.59}Si_{6.41}$, $(OH)_{0.91}F_{0.24}$. The data for the Quincy amphibole indicates an arfvedsonitic riebeckite, or, if you prefer, a riebeckitic arfvedsonite. The formula is: $Na_{1.82}K_{0.25}Ca_{0.63}$, $Fe^{2+}_{2.76}Mg_{0.07}Mn_{0.10}$, $Fe^{3+}_{1.53}Li_{0.24}Ti_{0.03}$, $Al_{0.44}Ti_{0.15}Si_{7.41}$, $(OH)_{1.73}F_{0.58}$.

In contrasting the chemical compositions of the amphiboles of the Quincy and Peabody granites, note that the major differences indicated

Table 2

AMPHIBOLE DATA

	(1)*	(2)	(3)	(4)*	(5)	(6)		(7)	(8)
SiO$_2$	48.74	47.06	41.15	41.02	36.66	38.91	Si	7.409	6.41
Al$_2$O$_3$	2.31	2.36	7.29	9.08	9.74	8.51	Al^{IV}	.439	1.59
TiO$_2$	1.48	1.53	.67	2.88	3.10	1.89	Al^{VI}	.000	.06
Fe$_2$O$_3$	13.22	12.91	5.75	6.59	7.06	6.41	Ti	.152	.00
FeO	19.95	20.92	27.78	23.09	24.82	26.30	Ti	.028	.23
MnO	.74	.76	.97	.77	.83	.90	Fe(III)	1.532	.79
MgO	.29	.30	1.90	1.83	1.96	1.93	Fe(II)	2.755	3.62
Li$_2$O	.35	.38	n.d.	.04	.04	.04	Mg	.070	.47
CaO	3.61	3.76	9.54	9.03	9.73	9.64	Mn	.101	.13
Na$_2$O	6.01	5.96	2.86	1.99	2.15	2.51	Li	.240	.03
K$_2$O	1.17	1.22	.99	1.20	1.29	1.14	Ca	.634	1.70
F	1.11	1.16	.05	.42	.45	.45	Na	1.820	.80
H$_2$O$^+$	1.56	1.64	1.05	.56	.60	.83	K	.246	.24
H$_2$O$^-$	.27	.28	—	.88	.95	.95	OH	1.728	.91
Total	100.81	100.24	100.00	99.38	99.38	100.41	F	.578	.24
-O=F	.47	.49	.02	.18	.19	.19			
	100.34	99.75	99.98	99.20	99.19	100.22			

(1) Riebeckite, Quincy granite, new analysis; Tadashi Asari, analyst.
(2) Riebeckite, Quincy granite, corrected for impurities (3.0% quartz, 2.8% aegirine).
(3) Ferrohastingsite, Peabody granite, Toulmin (1964); corrected for impurities.
(4) Ferrohastingsite, Peabody granite, new analysis; Tadashi Asari, analyst .
(5) Ferrohastingsite, Peabody granite, corrected for impurities (8.6% qtz, .3% biotite).
(6) Mean of (3) and (5).
(7) Riebeckite, Quincy granite (2); No. of ions on basis of 24 (O,OH,F)
(8) Ferrohastingsite, Peabody granite (6); No. of ions on basis of 24 (O,OH,F).

*The precision of the data for the major constituents of the two new analyses
is 1-2 percent. The precision in the H$_2$O+ concentrations is poor and may be
as high as 50% deviation from the mean. The precision for the aluminum is
10% deviation from the mean.

in the whole-rock chemical compositions are reflected in the amphibole compositions; that is, the Quincy riebeckite is higher in Si and Na but lower in Al and Ca than the Peabody amphibole. It appears that the composition of the amphibole was partly controlled by the chemical composition of the parent granite magma.

STABILITY RELATIONS

The separate occurrence of riebeckite (or arfvedsonite) and ferro-hastingsite in granites of Nigeria, New Hampshire, and eastern Massachusetts suggests either that riebeckite (or arfvedsonite) and ferrohast-

ingsite do not occur together in equilibrium or that they have a very limited field where both coexist in equilibrium. Toulmin (1964) has found traces of riebeckite(?) associated with the ferrohastingsite of the Peabody and Cape Ann granites. These traces are closely associated with pyroxene and, probably, are secondary crystallizations. Huang (1958) reported riebeckite from a peculiar riebeckite-aegirine melagranite from the Wichita Mountains, Oklahoma. The riebeckite occurs with "hornblende" which has a β too low to be consistent with ferrohastingsite. Ernst (1968) suggests that these two amphiboles represent an equilibrium association.

Ernst (1962) has investigated the phase relations of synthetic soda-iron amphiboles. Riebeckite is stable to about 500°C under oxidizing conditions defined by the hematite–magnetite buffer. The solid solution riebeckite–arfvedsonite is stable to temperatures of about 700°C, with oxygen fugacities defined by the wüstite–iron buffer. Below about 900 bars fluid pressure with oxygen fugacities defined by the wüstite–iron buffer, the assemblage quartz–aenigmatite–aegirine is stable between 650–750°C, except for fluid pressures below about 200 bars where the temperature stability range is 600–800°C. At temperatures below 650°C to 675°C, this assemblage is unstable relative to quartz + riebeckite–arfvedsonite. At fluid pressures of 700–900 bars, there is a field for fayalite + quartz + aegirine separating these two fields. The fayalite–bearing field also separates the same two fields at higher oxygen fugacities (magnetite–wüstite buffer). The absence of fayalite in the Quincy granite therefore suggests either fluid pressures below 700 bars or oxygen fugacities lower than those defined by the magnetite–wüstite buffer, or, most likely, both.

In summary, the occurrence of quartz, aegirine, and aenigmatite, and absence of fayalite in the Quincy granite suggests temperatures of 650–750°C, fluid pressures below 700 bars, and oxygen fugacities lower than those defined by the magnetite–wüstite buffer. The association of riebeckite and magnetite in the Quincy (Warren, 1913) suggests a change to higher oxygen fugacities as crystallization continued at lower temperatures.

Ernst (1968) suggested that the temperature of crystallization of riebeckite in the pegmatite phase of the Quincy granite was 500 ± 50°C. In the Quincy granite proper, the association of riebeckite with alkali feldspars, which probably crystallized above the solvus (660°C) in the system Ab–Or–H_2O (Tuttle and Bowen, 1958), indicates a temperature of riebeckite crystallization perhaps as high as 700°C. The pegmatite riebeckite (Warren and Palache, 1911) has significantly lower concentrations of Ca, Al, and F when compared with the Quincy

riebeckite of the main body. Ernst (personal communication, 1971) suggests that the high concentrations of these constituents in the Quincy riebeckite would probably stabilize this amphibole to near-solidus magmatic temperatures.

Phase relations of hastingsite minerals have not been determined (Ernst, 1968). However, Ernst (1968) suggests that the $P-T$ relations of the ferrohastingsites are probably similar to ferropargasite, but with a more extensive $f_{O_2}-T$ stability range. The ferrohastingsite of the Beverly syenite, which is associated with the Peabody granite, has inclusions of euhedral microperthite crystals (Toulmin, 1964), suggesting crystallization of the amphibole above 660°C. Tuttle and Bowen (1958) have shown that the Peabody ferrohastingsite (presumably their Quincy granite riebeckite) is unstable in the presence of excess water at a temperature of 625°C. This amphibole may be stable to higher temperatures at lower water fugacities, as suggested by the above mineral relations for the Beverly syenite.

The soda/potash ratios of the microcline microperthites of the Quincy and Peabody granites are nearly identical (Lyons and Wolfe, 1971). These ratios and their similar feldspar Ca content (chemical data of Toulmin, 1964; optical work of Warren, 1913) indicate a close temperature correspondence between the two granites. The feldspars indicate crystalization above 660°C.

DEVELOPMENT OF OXIDIZING CONDITIONS

The factors that led to a development of more oxidizing conditions in the Quincy magma, as compared to the Peabody magma, are a matter of speculation. However, a clue is given in the iron contents of the granite porphyries associated with the Quincy granite in the Blue Hills area.

Warren (1913) showed that the normal granite porphyry has a different Fe^{3+}/Fe^{2+} ratio as compared to the porphyries near rhyolite contacts. This is shown below:

	Normal Granite Porphyry	Contact Porphyry	Contact Porphyry
wt. percent Fe^{3+}	1.17	1.53	1.87
wt. percent Fe^{2+}	1.63	1.33	1.18
Total Fe^{3+}, Fe^{2+}	2.80	2.86	3.05

Note that the total iron contents in the three rocks are similar. However, in the normal granite porphyry Fe^{2+} is dominant, whereas in

the contact type Fe^{3+} is dominant. This suggests more oxidizing conditions near the contact (Warren, 1913) where, presumably, Fe^{2+} was oxidized to Fe^{3+}. It may be that some external factor, similarly, triggered higher oxygen fugacities in the Quincy magma. Some possible mechanisms for changing f_{O_2} are given in Eugster and Wones (1962).

Conclusions

The chemistry of their alkali feldspars and the amphibole phase equilibria data suggest that the Quincy and Peabody magmas crystallized at similar temperatures, probably between 650–750°C. Both amphiboles, riebeckite and ferrohastingsite, apparently crystallized at magmatic or near-magmatic temperatures.

The chemical compositions of the Peabody and Quincy amphiboles were controlled by at least two variables: composition of the parent magma and oxygen fugacity. Composition favored a calcium-iron-aluminum amphibole, ferrohastingsite, $NaCa_2Fe^{2+}_4Fe^{3+}Al_2Si_6O_{22}(OH)_2$, in the Peabody; and a soda-iron amphibole, riebeckite $Na_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$, in the Quincy. Higher oxygen fugacities in the Quincy, as compared to the Peabody, favored a ferric-rich amphibole, riebeckite; lower oxygen fugacities in the Peabody, as compared to the Quincy, favored a ferric-poor amphibole, ferrohastingsite.

The mineral relations in the Quincy granite suggest an increase in oxygen fugacity with decrease in temperature. Buma and others (1971) have explained the Eu depletion in the Quincy feldspar, as compared to the Peabody feldspar, as the result of higher oxidizing conditions in the Quincy, which prevented the acceptance of Eu^{3+} into the feldspar structure. Their conclusion about oxygen fugacity agrees with that of the writer, which is based on amphibole and rock chemical compositions.

References

BILLINGS, M. P. (1956) The geology of New Hamsphire, Part II, Bedrock geology. *N.H. State Plann. Develop. Comm.*, 203 p.

BORLEY, G. D. (1963) Amphiboles from the younger granites of Nigeria, part 1, chemical classification. *Mineral. Mag.* 33, 358–376.

———, AND M. T. FROST (1963) Some observations on igneous ferrohastingsites. *Mineral. Mag.* 33, 646–662.

BUDDINGTON, A. F. (1948) Origin of granitic rocks of the Northwest Adirondacks. *Geol. Soc. Amer. Mem.* **28**, 21–43.

———, AND B. F. LEONARD (1953) Chemical petrology and mineralogy of hornblendes in northwest Adirondack granitic rocks. *Amer. Mineral.* **33**, 891–902.

BUMA, G., F. A. FREY, AND D. R. WONES (1971) New England granites: Trace element evidence regarding their origin and differentiation. *Contrib. Mineral. Petrology* **31**, 300–320.

ERNST, W. G. (1962) Synthesis, stability relations, and occurrence of riebeckite and riebeckite-arfvedsonite solid solutions. *J. Geol.* **70**, 689–736.

——— (1968), *Amphiboles,* Springer-Verlag, New York, 125 p.

EUGSTER, H. P., AND D. R. WONES (1962) Stability relations of the ferruginous biotite, annite. *J. Petrology,* **3**, 82–125.

HUANG, W. T. (1958) Riebeckite granite in the Wichita Mountains, Oklahoma. *Geol. Soc. Amer. Bull.* **69**, 1191–1192.

LYONS, P. C., AND C. WROE WOLFE (1971) Correlation of granites by soda/potash ratios. *Geol. Soc. Amer. Bull.* **82**, 2023–2026.

TOULMIN, P. 3d (1964) Bedrock geology of the Salem Quadrangle and vicinity, Massachusetts. *U.S. Geol. Surv. Bull.* 1163-A, 79 p.

TUTTLE, O. F., AND N. L. BOWEN (1958) Origin of granite in light of experimental studies in the system $NaAlSi_3O_8–KAlSi_3–O_8–SiO_2–H_2O$, *Geol. Soc. Amer. Mem.* **74**, 153 p.

WARREN, C. H. (1913) Petrology of the alkali-granites and porphyries of Quincy and the Blue Hills, Massachusetts, U.S.A. *Amer. Acad. Arts Sci., Proc.* **49**, 203–331.

WARREN, C. H., AND C. PALACHE (1911) The pegmatites of the riebeckite-aegerite granite of Quincy, Mass., U.S.A.: Their structure, minerals, and origin. *Amer. Acad. Arts Sci., Proc.* **47**, 126–168.