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THE STABILITY OF ACMITE IN THE PRESENCE OF H_2O

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ABSTRACT. In the pressure range 2 to 5 kb and in the presence of excess H_2O, acmite is stable within the range of partial pressures of oxygen provided by the hematite-magnetite and quartz-fayalite-magnetite buffers. Under hematite-magnetite conditions, acmite melts incongruently to hematite + magnetite + liquid at 870°C and 2 kb total pressure. At the same pressure, under quartz-fayalite-magnetite conditions, acmite melts at 780°C to magnetite + liquid. But, while acmite melting is very sensitive to the oxidation conditions, it is relatively insensitive to total pressure in the 2 to 5 kb range. The dT/dP of melting under hematite-magnetite conditions is —5°C/kb; as the partial pressure of oxygen is reduced the melting temperature becomes even less dependent on total pressure until, under quartz-fayalite-magnetite conditions, $dT/dP \approx 0$°C/kb. Under all experimental conditions studied, acmite crystallizes only from liquids containing excess sodium silicate, and this condition seems to be paralleled in some rock series where the modes and chemistry are well known.

At partial pressures of oxygen controlled by wustite-magnetite and iron-wustite, acmite is unstable in the presence of excess H_2O at least between 1 and 4 kb. It is replaced below the solidus by arfvedsonitic amphibole, which melts around 700°C over a short temperature interval to fayalite + liquid. Examples in rocks of fluctuating crystallization of aegirine and arfvedsonite may have been controlled simply by fluctuating oxidation conditions in the magma. The melting temperature of arfvedsonitic amphibole is relatively insensitive to total pressure and also to oxidation conditions below wustite-magnetite. It appears to be insensitive to bulk chemical composition, too, in the range arfvedsonite-acmite, and this mineral may provide useful upper limits of temperature and oxygen partial pressure in magmas from which it crystallizes.

The broad range of melting of the acmite composition (700°-870°C) under different buffer conditions raises the possibility that partial metling of peralkaline rocks could be achieved at constant temperature and pressure merely by reduction of the partial pressure of oxygen in the coexisting vapor phase.

INTRODUCTION

On a small rocky islet in a fiord in southern Norway we stood in the sun, eating raw mussels and marvelling at the prodigious crystals of aegirine in the pegmatite. Later that evening, with the help of some Yugoslavian plum-brandy, we wondered again about the petrologic significance of aegirine and talked of its phase relations. The incongruity of the situation somehow enhanced that of the mineral, and I was impatient to learn more about the stability of this pyroxene. Thus, in his own amiable way J. Frank Schairer gave the present study its initial shove. His encouragement and enthusiasm have helped it along ever since. It is a happy circumstance, indeed, to set down the results in tribute to him.

Aegirine, or acmite, have long been regarded as the modal and normative hall-marks of peralkalinity in rocks. Knowledge of the conditions of formation and stability are essential to the understanding of peralkaline granites, syenites, nepheline-syenites, and ijolites. The first aim of the present investigation was to discover if the incongruent melting of acmite (Bowen and Schairer, 1929) persisted at higher pressures in the presence of H_2O. This is an essential preliminary to the study of more complex peralkaline systems under hydrous conditions.

It was tacitly assumed, from incidental evidence such as the formation of acmite in boiler-scale, that acmite might be stable at solidus temperatures in the presence of H_2O, even under severely reducing conditions.[1]

This assumption proved erroneous in the pressure range 2 to 5 kb. Crystalline acmite has a stable solidus at petrologically moderate to high oxidation conditions, but the temperature of melting is strongly dependent on the oxygen fugacity (Bailey, 1963). At low oxygen fugacities acmite is replaced in the solidus by the assemblage arfvedsonite-riebeckite plus sodium silicate. The amphibole melts incongruently with the appearance of fayalite. In this region the investigation could be more appropriately described in terms of $Na_2O.FeO_x.\ 4SiO_2$ + excess H_2O, and the most relevant previous work is that of Ernst (1962) on the synthesis and stability of riebeckite-arfvedsonite solid solutions.

METHOD

All experiments up to 5 kb pressure were made in cold-seal, pressure-vessels made from Stellite 25, René 41, or Nimonic 105 rods. The vessels were held in the vertical position, closed-end uppermost, to minimize convection in the hot zone in the top of the vessel, the charge capsule being supported on a steel filler-rod of appropriate length. In oxygen buffered runs the charge plus an excess of water were sealed in a platinum or silver-palladium tube, which in turn was enclosed with the buffer mixture in a sealed, thick-walled, gold tube (Eugster, 1957). Pressure was transmitted to the charge by ductile collapse of the tubes, using water as the external applied pressure medium. Pressure was measured with a Bourdon-tube gauge with an uncertainty of $\pm$ 10 bars. Temperatures were measured by a chromel-alumel couple inserted into a well in the hot-zone of the pressure-vessel and continuously recorded on a Honeywell recorder. Each spool of thermocouple wire was calibrated at intervals against the melting point of sodium chloride, and the recorder readings adjusted accordingly. Temperature values are quoted at $\pm$ 5°C to take account of uncertainties of temperature gradients through the pressure vessel wall rather than the accuracy of the measured temperature. Actual variations during the experiments, as registered on the recorder, are generally less than $\pm$ 2°C.

Starting materials were homogeneous glass, free from hematite but of undetermined FeO/Fe_2O_3 ratio, and crystalline acmite prepared from the glass at atmospheric pressure (Bailey and Schairer, 1966). These two starting materials enabled equilibrium to be approached in two ways, even to the extent of differing oxidation states in the initial charges. Duplicate runs with these two starting materials have invariably yielded the same products. Silver-palladium tubes were used to hold the charges whenever there were problems of platinum alloying with the buffer

[1] In nitrogen, at 1 atm pressure, acmite forms in the system Na_2O–FeO–SiO_2, even in an iron crucible (Schairer, Yoder, and Keene, 1954, p. 126; personal commun., H. S. Yoder, Jr., 1968).

materials, for example, metallic nickel or iron, but in general platinum suffers less embrittlement during buffered experiments and was used in the absence of nickel and iron. No difference was detected in the run-products when both types of capsule were used under identical conditions, and loss of Fe from the charge to a platinum capsule appears to have no appreciable effect and may be neglected.

In addition to a preliminary series of unbuffered runs, five different buffers were employed to control the oxygen fugacity in the charge capsule. These were (1) Fe_2O_3–Fe_3O_4; (2) Ni–NiO; (3) Fe_3O_4–SiO_2–Fe_2SiO_4; (4) Fe_3O_4–FeO; and (5) Fe–FeO. Each of these mixtures in the presence of H_2O establishes an equilibrium with the dissociated hydrogen and oxygen in the vapor at a given elevated temperature. The resulting atmosphere buffers that of the charge by reason of the permeability of platinum or silver-palladium to H_2 and the large excess of buffer mixture providing the external atmosphere. These five buffers cover the reasonably expected range of petrological oxidation conditions.

Charges were examined immediately on opening the tube with a binocular microscope and variations along the length of the tube, for example, meniscus, condensates, grain size, and mineralogy, were noted. Any major differences were examined separately with a polarizing microscope and, if necessary, by X-ray diffraction. When possible, and when necessary, thin sections of the main body of the charge were used to examine textures and quench products.

TABLE 1

Experiments using magnetite-hematite buffer

Starting material (+ H_2O)	Total pressure, bars (± 10)	Temperature, °C (± 5)	Time, hours	Products (condensed)*
Acmite	2040	880	17	Glass + M + H
Acmite	2040	864	18	Ac
Acmite	2040	870	17	Ac + partial melt
Acmite	5000	862	4.6	Ac + partial melt
Acmite	5000	850	5	Ac + trace M and H
(The following previously unpublished data on the magnetite-hematite buffer at lower pressures were kindly provided by W. G. Ernst.)				
Oxide mix	1447	880	5	Ac
Oxide mix	1447	892	5	Glass + M + H
Oxide mix	1042	874	6	Ac
Oxide mix	1050	888	2	Ac + M + H + glass
Oxide mix	740	891	3	Ac
Oxide mix	750	90[illegible]	2	Ac + M + H + glass
Oxide mix	502	904	2	Ac (+ M + H)
Oxide mix	502	913	3	Ac + glass + M + H
Oxide mix	273	910	4	Ac
Oxide mix	274	925	2	Ac (+ glass + M + H)
Oxide mix	143	940	3	Ac (+ glass?)
Oxide mix	145	949	2	Ac + glass + M + H

*Symbols: Ac, crystalline acmite; H, hematite; M, magnetite.

TABLE 2

Experiments using nickel-nickel-oxide buffer

Starting material (+ H_2O)	Total pressure, bars (± 10)	Temperature, °C (± 5)	Time, hours	Products (condensed)*
Acmite	2040	800	5	Ac + incipient melting
Acmite	2040	800	19	Acmite
Acmite	2040	800	22	Ac + incipient melting
Acmite	2040	810	19	Glass + M
Acmite	2040	820	5-1/4	Glass + M
Acmite	4830	780	19	Ac
Acmite	5090	790	19	Ac
Acmite	4830	800	18-1/3	Glass + M

*Symbols: Ac, crystalline acmite; M, magnetite.

TABLE 3

Experiments using fayalite-magnetite-quartz buffer

Starting material (+ H_2O)	Total pressure, bars (± 10)	Temperature, °C (± 5)	Time, hours	Products (condensed)*
Glass**	1007	780	19	Ac
Acmite	2010	790	22-2/3	Glass + M
Acmite	2010	780	23-1/3	Ac + glass + M
Acmite	2010	770	21-1/2	Ac (+ trace glass)
Acmite	2010	750	20-1/2	Ac
Acmite	2010	700	7	Ac
Glass**	2040	780	19-1/2	Glass + M
Acmite**	3950	775	25-1/2	Ac
Glass**	3980	785	19-1/4	Glass + M

*Symbols: Ac, crystalline acmite; M, magnetite.

**Runs at different pressures in same apparatus and under same conditions.

TABLE 4

Experiments using FeO-Fe_3O_4 buffer

Starting material (+ H_2O)	Total pressure, bars (± 10)	Temperature, °C (± 5)	Time, hours	Products (condensed)*
Acmite	2010	710	5	Glass + Fay + A-R
Acmite	2010	700	4-2/3	Fay + A-R + glass
Acmite	2010	690	8-2/3	A-R + glass
Acmite	1000	700	7	A-R + Fay + glass
Acmite	4080	720	6-1/4	Glass + Fay (+ A-R)
Acmite	4040	708	5-1/2	Fay + A-R + glass
Acmite	4040	700	6	A-R + Fay + glass
Acmite	4080	690	4-1/4	A-R (+ Fay) + glass

*Symbols: Fay, fayalite; A-R, arfvedsonite-riebeckite.

TABLE 5

Experiments using Fe-FeO buffer

Starting material (+ H_2O)	Total pressure, bars (± 10)	Temperature, °C (± 5)	Time, hours	Products (condensed)*
Glass	2040	750	5-1/2	Glass + Fay
Glass	2040	730	4-1/2	Glass + Fay
Glass	2040	710	4-1/2	Glass + Fay
Acmite	2010	700	6-1/3	Fay + A-R + glass
Acmite	2010	690	5-2/3	A-R + Fay + glass
Acmite	2010	690	5-1/2	A-R + Fay + glass
Acmite	2010	680	5-3/4	A-R + glass
Glass	2040	670	6	A-R + glass
Glass	2040	630	5-1/2	A-R + glass
Acmite	4000	700	1	Fay + A-R + glass

*Symbols: Fay, fayalite; A-R, arfvedsonite-riebeckite.

TABLE 6

Unbuffered experiments in R41 bombs

Starting material (+ H_2O)	Total pressure, bars (± 10)	Temperature, °C (± 5)	Time, hours	Products (condensed)*
Natural acmite (Quincy, Mass.)	2040	800	1	Ac + slight melting
Glass (Schairer)	2040	800	1	Ac + slight melting
Glass 300	2040	800	1	Ac + incipient melting
Glass (Schairer)	2040	900	1	Glass
Glass 300	2040	900	1	Glass
Glass (Fenner)	2040	900	1	Glass
Glass	2040	850	1-1/4	Glass
Acmite	2040	850	1-1/4	Glass + M
Glass	2040	825	1-1/2	Glass + M
Acmite	2040	825	1-1/2	Glass + M
Glass	2040	810	3-1/2	Glass + M
Acmite	2040	810	3-1/2	Glass + M
Glass	2040	812	2-3/4	Ac (+ trace of glass)
Acmite	2040	812	2-3/4	Ac (+ trace of glass)
Acmite	2040	827	2-1/2	Glass + M
(A-R + M + glass)**	1000	450	285	Ac
Glass	5100	725	1/2	Ac
Acmite	5100	725	1/2	Ac
Glass	5100	750	1	Ac
Acmite	5100	750	1	Ac
Glass	5100	775	3/4	Ac (+ glass + M)
Acmite	5100	775	3/4	Ac + incipient melting
Glass	5100	775	5	Ac (+ ? glass)
Acmite	5100	775	5	Ac
Glass	5100	785	4	Ac (+ trace glass)
Acmite	5100	785	4	Ac (+ trace glass)
Acmite	5100	800	3	Glass + M (+ Ac)
Acmite	5100	800	4-1/2	Glass + M

*Ac, crystalline acmite; M, magnetite; A-R, arfvedsonite-riebeckite.

**Rerun of previous run products (including quench amphibole).

EXPERIMENTAL RESULTS

Tables 1 to 5 contain the results from which the text figures 1 to 4 were constructed. Table 6 brings together the results of unbuffered runs: most of these were the early exploratory runs at 2 kb and 5 kb which correspond closely with the results obtained using Ni-NiO buffer. A few results are unbuffered runs at 10 kb using the internally-heated, gas-media apparatus of H. S. Yoder, Jr., to check the persistence of incongruent melting to this pressure. The pressure medium at 10 kb was argon, but the acmite melted incongruently to magnetite + liquid, suggesting that the external atmosphere was effectively a reducing one: the reason for this is not clear, but it may be due to breakdown of hydrocarbon impurities finding access into the hot zone. One result in table 6 refers to an experiment with an earlier charge that had melted to magnetite + liquid and formed amphibole during the quench. This was held for 12 days at 450°C and 1 kb pressure in a Pt capsule and yielded crystalline acmite. These conditions are well within the expected stability range for riebeckite-arfvedsonite (Ernst, 1962), and the result indicates that acmite is the stable solidus phase in this oxidation range (approximately equivalent to Ni-NiO).

In all runs in which there was no melting, where acmite + fluid was the stable assemblage, the resulting charge was a very pale green mesh of well formed prisms of clear acmite, up to 0.5 mm in length, with optical and X-ray properties corresponding to pure $NaFeSi_2O_6$. Incomplete melting was seen in several runs, and is easily detected by the appearance of dark spots of glass + iron oxide in the pale acmite mesh. The melting interval is small and cannot be defined accurately within the limits of the experiment; complete melting occurs 10°C higher and no melting 10° lower. This melting interval is of similar magnitude to that found in the melting of acmite at 1 atm (975-988° ± 5°C, Bailey and Schairer, 1963). The departure from univariance is largely attributed to the presence of FeO in the liquid and, in the present experiments, the magnetite. Complete melting produces a dark glass bead, usually with a deep concave meniscus at temperatures well above the melting interval. Primary, euhedral magnetite crystals (plus hematite in experiments with the magnetite-hematite buffer) are well distributed in the glass and are commonly fringed with quench amphibole or quench acmite sheathed in quench amphibole. The amphibole, in long, well formed prisms, is strongly pleochroic (X, brown; Y, light green; Z, green; see Bailey, 1963) and gives an X-ray diffraction pattern corresponding to synthetic arfvedsonite-riebeckite (Ernst, 1962). Another noteworthy change after melting occurs in the fluid phase. On opening the capsule the condensed fluid phase is found to be a thin, clear liquid that congeals rapidly on exposure to a clear glass of low refractive index. It is apparent that the melting acmite $\rightarrow$ liquid + iron oxide + O_2 also results in some sodium silicate being expelled into the vapor. All runs in this system involving melting result in greatly increased vapor activity, and it is usual to find

magnetite, fayalite, acmite, and amphibole in cavities where they have grown (frequently to large size) from the vapor.

Under oxidation conditions defined by the iron-wustite and wustite-magnetite buffers the run-products were entirely different. Even when crystalline acmite was used as starting material it failed to survive in any runs, even those of 1 hour duration, under these conditions. Instead arfvedsonite-riebeckite solid solution appears as the major solidus phase, yielding greenish-black charges cemented by a sparse clear glass of low refractive index. This is assumed to be a hydrous sodium silicate glass. The charge is also coated with a similar glass that congeals rapidly from a thin, clear liquid when the capsule is opened. The formation of the amphibole can be simply represented by the following reactions:

$$\underset{\text{acmite}}{10Na_2Fe_2Si_4O_{12}} + 4H_2O = \underset{\text{riebeckite}}{4Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2} + 4(Na_2O\cdot SiO_2) + 2(Na_2O\cdot 2SiO_2) + 3O_2$$

$$\underset{\text{acmite}}{5Na_2Fe_2Si_4O_{12}} + 2H_2O = \underset{\text{arfvedsonite}}{2Na_3Fe_4^{2+}Fe_3^{+}Si_8O_{22}(OH)_2} + 2(Na_2O\cdot 2SiO_2) + 2O_2$$

At higher temperatures, the amphibole melts incongruently to fayalite plus liquid. Fayalite is easily recognizable and discernible at the onset of melting, because it forms comparatively large, golden-yellow, blocky euhedral crystals.

VARIATION OF ACMITE STABILITY WITH P_{Total}, P_{O_2}, and T

The variation of the melting temperature of acmite in the presence of water, in terms of total pressure and temperature, is shown in figures 1 to 3 for conditions defined by the magnetite-hematite, nickel-nickel oxide, and quartz-fayalite-magnetite buffers, respectively. The melting curves are drawn either through those conditions at which unequivocal partial melting had occurred or between runs showing no melting on one side and complete melting on the other. Complete melting at high pressures using the magnetite-hematite buffer was not attained, because the time-temperature range is beyond the failure range of R41 pressure vessels. Extensive melting was observed in the run at 862°C, and judging from experiments under other conditions a longer run would probably have produced complete melting. Rate of melting is presumably controlled by the rate of diffusion of hydrogen through the capsule, because melting involves formation of magnetite and an Fe^{2+}-bearing liquid from the completely oxidized acmite composition.

The most noticeable feature of the melting curves is their low dT/dP values, which decrease with decreasing P_{O_2}. From $-5°$ per kb under magnetite-hematite buffer conditions, the value becomes zero (possibly even slightly positive) in the 2 to 5 kb range under quartz-fayalite-magnetite conditions. Even under high P_{O_2} conditions the dT/dP is much smaller than for other anhydrous silicates (see fig. 5) in which melting produces a large reduction of total volume by solution of H_2O in the melt. When acmite melts, H_2O enters the melt, but the reduction

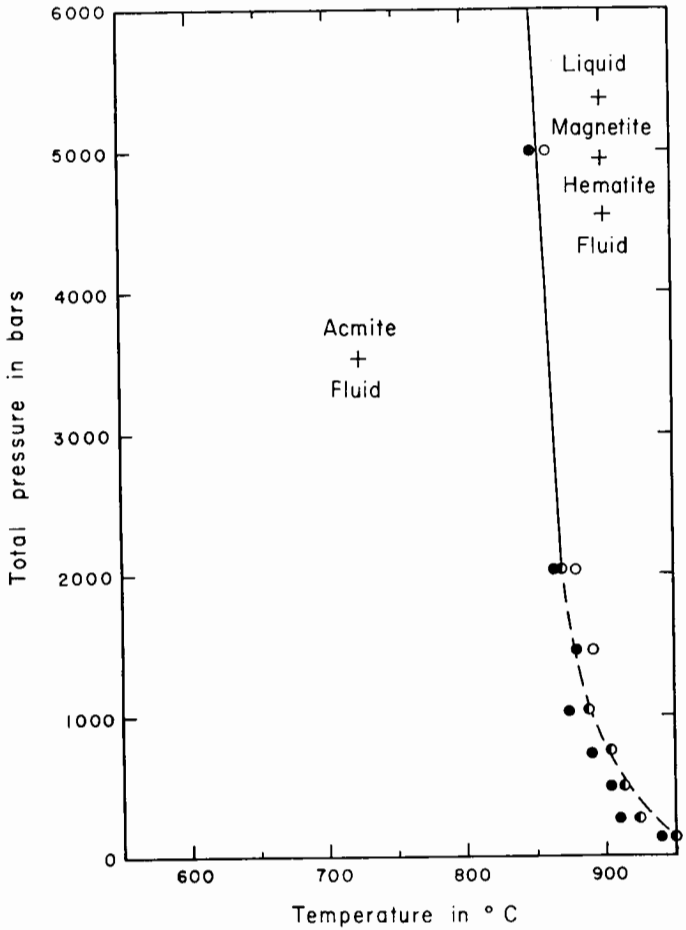

Fig. 1. Total pressure-temperature diagram for acmite + excess water under conditions controlled by the magnetite-hematite buffer. Open symbols, complete melting; divided symbols, acmite + melt.

of total volume is partly counteracted by the effective loss of oxygen from liquid and crystals to the fluid phase. Under oxidation conditions lower than the quartz-fayalite-magnetite buffer the effective gain in O_2 by the fluid is greater than loss of H_2O to the melt.

Although the effect of total pressure on the melting temperature is small for any given oxidation condition, lowering the partial pressure of oxygen produces a drastic lowering of the high temperature stability of acmite, resulting from the greater disparity between the oxygen content of the acmite crystals and the reduced melt. Melting of acmite involves liberation of O_2, and this process must be favored by decreased P_{O_2} in the coexisting vapor. This effect might be expected in an iron-rich

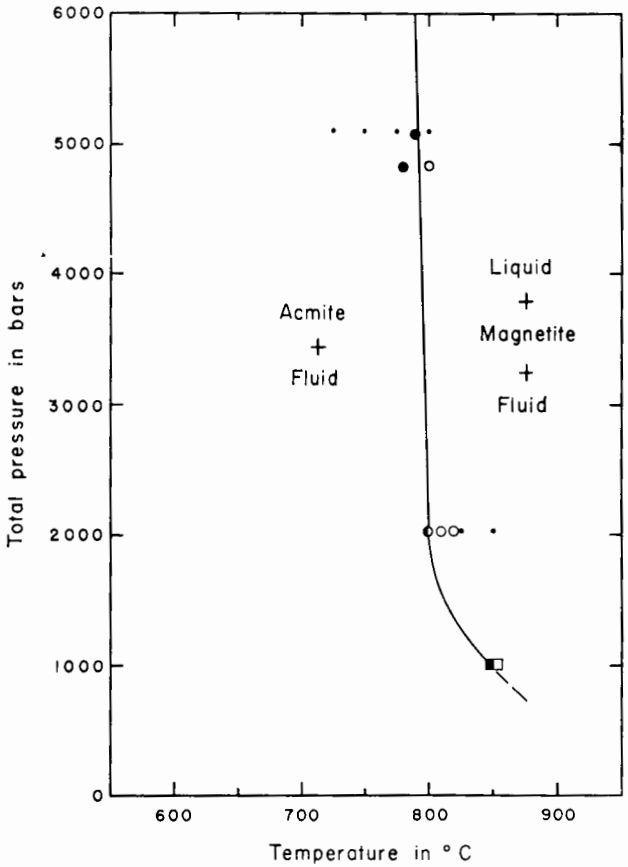

Fig. 2. Total pressure-temperature diagram for acmite + excess water under conditions controlled by the nickel-nickel oxide buffer. Open symbols, complete melting, divided symbols, acmite + melt. Single dots indicate some of the unbuffered runs used to delimit the fields prior to buffered experiments. The points at 1 kb total pressure are from Nolan, 1966.

system, but the lowering of the melting point by nearly 100°C between the magnetite-hematite and the quartz-fayalite-magnetite buffer conditions is none-the-less remarkable. A similar reduction in the stability range of acmite, as part of the higher temperature assemblage, was found by Ernst (1962) in the riebeckite-arfvedsonite system. With a temperature range of this order the paragenesis of acmite in nature must be profoundly influenced by the oxidation conditions.

Figure 4 shows the results of experiments on the acmite composition (+ H_2O) under conditions controlled by the wustite-magnetite equilibrium. No figure is presented specifically for the experiments using the iron-wustite buffer, because the results with this buffer do not differ significantly from those obtained under wustite-magnetite conditions. It may be noted in passing that Ernst's results for arfvedsonite-riebeckite

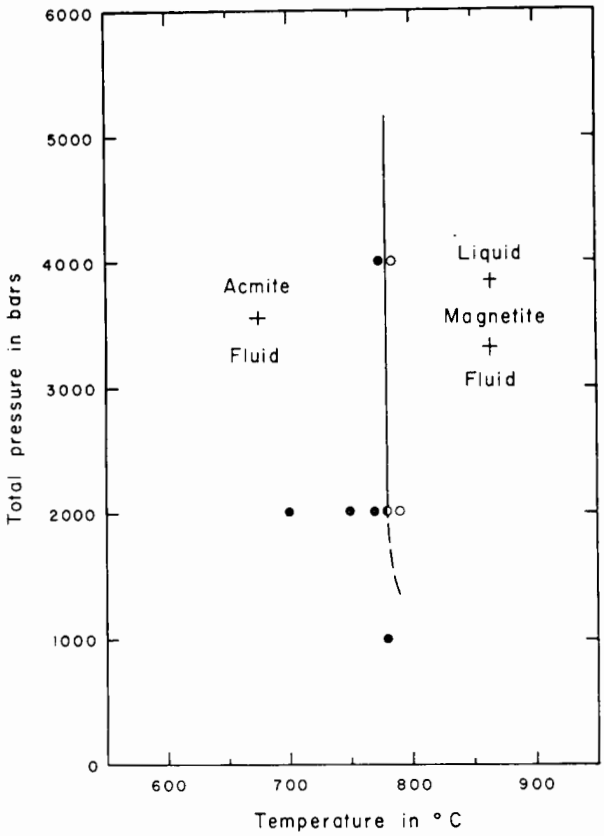

Fig. 3. Total pressure-temperature diagram for acmite + excess water under conditions controlled by the quartz-fayalite-magnetite buffer. Open symbols, complete melting; divided symbols, acmite + melt.

decomposition at 2 kb are also the same within experimental error for those two buffers (Ernst, 1962, table 14). The resemblance to Ernst's results is even more remarkable in that the acmite composition yields amphibole as the major solidus phase under these conditions, and the range of thermal decomposition of the amphibole is virtually the same as that found by Ernst working on the amphibole composition. Ernst recognized the existence of a decomposition interval for the amphibole in his experiments, but it was not possible to define the limits. With acmite composition, however, the interval is clearly discernible—the amphibole melts incongruently to fayalite plus liquid over an interval of approximately 20°C. Progressive melting is seen particularly well by the increase in fayalite in the charges at successively higher temperatures. It is possible that the melting interval is better defined using the acmite composition because of the small amount of sodium silicate-rich liquid accompanying the amphibole.

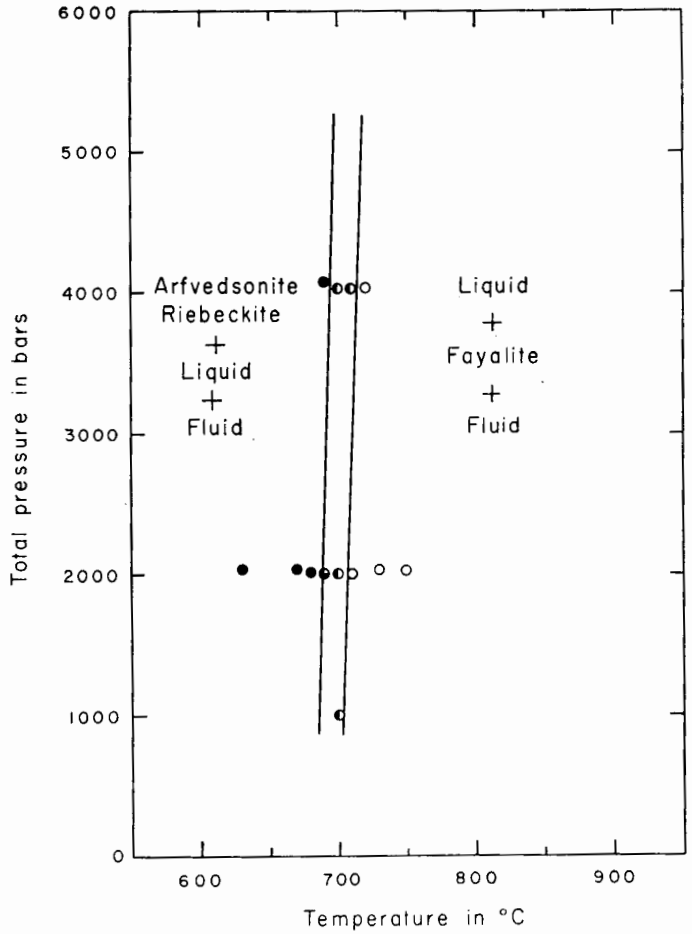

Fig. 4. Total pressure-temperature diagram for the acmite composition + excess water under conditions controlled by the wustite-magnetite and iron-wustite buffers. Open symbols complete melting; divided symbols, arfvedsonite-riebeckite + fayalite + melt.

One result shown in figure 4 was an exploratory run at 1 kb to check any inflection in the melting curve. The result was surprising for two reasons (1) the melting curve shows little sign of inflection, and (2) under the same conditions, using the riebeckite-arfvedsonite composition, Ernst (1962) obtained the assemblage Fay + Q + Ac + Fluid. The reason for the difference is not yet clear but may be resolved when this study is extended to lower pressures.

PETROLOGIC APPLICATIONS

Acmite and aegirine form in nature under widely varying conditions, from primary magmatic crystallization in the plutonic and volcanic states, through hydrothermal, deuteric, metasomatic, devitrification, metamor-

phic, and diagenetic conditions. It appears to be stable under hydrous and anhydrous conditions (Gilbert, 1967, 1969) up to the highest pressures to which it has been tested, 10 kb and 45 kb, respectively. As a ferric compound its most remarkable property is its stability under strongly reducing hydrous conditions. The chief effect of reducing the oxygen fugacity to conditions governed by the quartz-fayalite-magnetite buffer, is to depress strongly the melting temperature.

One outstanding result of all experimental studies is that acmite crystallizes only from a liquid containing excess sodium silicate. This is seen in its simplest form as a reaction relationship between iron oxide and liquid, but this is not invariable. In the system Na_2O–Al_2O_3–Fe_2O_3–SiO_2 (Bailey and Schairer, 1966) acmite crystallizes directly from liquids with excess sodium silicate, and this result is perhaps more relevant to natural conditions. It is important to distinguish the condition of excess alkali silicate in a liquid from peralkalinity, which implies simply molecular excess of alkalis over alumina. Excess alkali silicate refers to the condition where molecular alkalis exceed molecular alumina and iron oxide. In most peralkaline igneous rocks acmite does not appear to be forming as a reaction product between magma and earlier formed ore minerals. Instead it appears in many cases as a late crystallizing pyroxene, post dating and frequently mantling earlier aegirine-augite. This indicates that if excess sodium silicate in the melt is necessary under all conditions, it has been achieved by the continuous crystallization of other phases such as pyroxene and feldspar, rather than by separation of iron oxide from a melt that had already achieved peralkalinity.

A better understanding of conditions in peralkaline rocks will emerge when more attention is given to acmite paragenesis. At the present time, petrographic evidence, even on the coexistence of iron ores and primary aegirine in rocks, is meager. In the rocks of Sakhalin (Yagi, 1953) aegirine and ore are listed as coexisting phases in the syenites and are presumably compatible. In the Kûngnât series, however, Upton (1960) shows the disappearance of ore from the mode immediately prior to the appearance of aegirine. In the nearby Tugtutôq suite, Macdonald (1966) finds that aegirine appears in the mode simultaneously with the appearance of *ns* in the norm and states (personal commun., 1968) that ore disappears as a modal mineral in the series at the same point. In these rocks it would seem that excess sodium silicate is necessary for the formation of aegirine and that iron ore is unstable under these conditions. Much more detailed petrography and petrochemistry of this type are needed before we can evaluate properly the role of acmite in igneous rocks. The problem is complicated by the ease with which acmite forms metasomatically, and it is vital that primary and secondary crystallization should be distinguished. Metasomatic or deuteric formation of acmite is less feasible when it forms large crystals in an igneous rock. The problem is most acute when acmite occurs interstitially, commonly as mossy aggregates between larger and presumably earlier-formed crystals of feldspar and quartz or feldspar and nepheline.

In lavas, aegirine is rare as a phenocryst mineral. Examination of the various melting curves in figure 5 offers one explanation of this. At low pressures acmite melts at temperatures well below those of silica, alkali feldspars (especially the minimum melting curve S), and nepheline which form the major constituents of rhyolites, trachytes, and phonolites. It is unlikely therefore that acmite would appear on the liquidus of such compositions in the low pressure region. Phenocrysts of aegirine, if they occur in lavas, may have been carried from depth and should be examined for signs of resorbtion or mantling with iron oxide. I am inclined to the view that most unaltered, green pyroxene phenocrysts in such lavas will prove to be aegirine-augites or aegirine-hedenbergites. Because the dT/dP for acmite melting is very small the melting curve

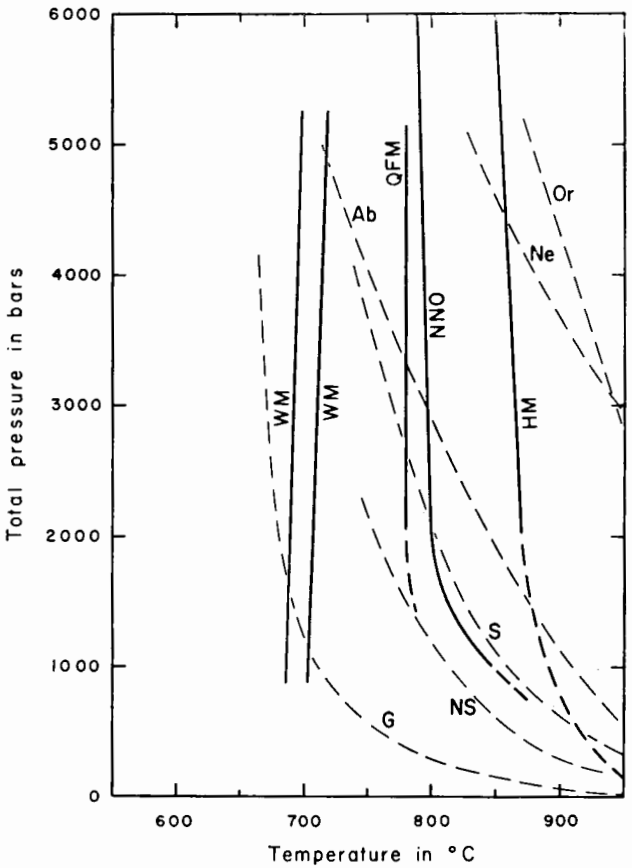

Fig. 5. Composite pressure-temperature diagram showing the variation of acmite stability with different partial pressures of oxygen. Buffers indicated by capital initials on curves taken from figures 1 to 4. The melting curves (dashed lines) for albite (Ab), K-feldspar (Or), "granite minimum" (G), and Ab-Or minimum (S) are taken from Tuttle and Bowen, 1958; the curve for nepheline (Ne) from Yoder, 1958; and the curve for nepheline syenite (NS) from Barker, 1965.

crosses the melting curves for the other common minerals (fig. 5) at moderate pressures and becomes a possible phenocryst mineral in magmas crystallized at depth. Under such conditions the appearance of acmite phenocrysts will depend essentially on the bulk composition of the magma. By the same reasoning the order of crystallization of nepheline and acmite in malignites and ijolites might be reversed according to the depths of crystallization. Variable parageneses are recorded from this group of rocks, but until more is known about the stability of aegirine-augite, this possibility can be considered for the hypersodic members only.

In many peralkaline rocks acmite is accompanied by riebeckite or arfvedsonite, or the amphibole occurs alone. The present study indicates that an arfvedsonitic amphibole is the stable phase in equilibrium with liquid instead of acmite under severely reducing conditions. Rocks containing arfvedsonite only, especially if they show *ns* in the norm, undoubtedly crystallized under very low partial pressures of oxygen. Mixed assemblages of arfvedsonite-acmite may indicate a lower degree of peralkalinity in the magma or a slightly higher P_{O_2}. In the Younger Granites of Northern Nigeria the acmite is found forming both rims and cores to arfvedsonite crystals (Jacobson, Macleod, and Black, 1958). The authors ascribe this to a fluctuating chemical composition of the magma: it is possible that this could be due solely to fluctuating P_{O_2} during crystallization. This type of chemical change has the advantages of being simple, rapid, and easily reversible.

The evidence from the present experiments supports the view of Ernst (1962) that a primary igneous paragenesis for riebeckite is doubtful. Arfvedsonitic amphibole is found in equilibrium with liquid in the present experiments and those of Ernst (1962) on the Na-Fe amphibole composition. In Ernst's experiments at higher P_{O_2} the riebeckite-arfvedsonite underwent dehydration decomposition at temperatures considerably below the melting curve. It appears extremely unlikely that riebeckite can coexist with magma unless it is a magnesio-riebeckite (Ernst, 1960), and the appearance of riebeckite in igneous rocks must invite suspicion of a late-stage deuteric or metasomatic crystallization. Although riebeckite contains ferrous iron it is stable over the same range of P_{O_2}, in the presence of excess H_2O, as acmite. The difference in their chemistry, apart from the oxidation state of the iron, can be expressed by a higher sodium silicate content in the acmite. Formation of riebeckite therefore reflects a lower degree of peralkalinity in the bulk composition. It seems probable that riebeckite and acmite reflect different degrees of peralkalinity in rocks, but until more is known about the influence of fluorine on the stability of these two minerals it would be unwise to accept this without reservation.

Consideration of the chemical equations presented earlier gives a further insight into the preferential formation of arfvedsonite, rather than riebeckite from the acmite composition. Decomposition of acmite to form riebeckite would require the release of sodium disilicate plus

sodium metasilicate, that is, an extremely hyperalkaline liquid. Formation of arfvedsonite releases only sodium disilicate, and it may be that this factor, as well as P_{O_2} governs the type of amphibole that forms from the acmite composition. Riebeckite has a vacant structural site that is progressively filled by Na^+ in the transition to arfvedsonite, and riebeckite may be unstable in the presence of excess soda.

A noteworthy feature of the melting of arfvedsonite is its comparative insensitivity to composition (at least from the Na-Fe amphibole composition to the acmite composition) and pressure above 1 kb P_{H_2O}. This sets useful upper limits on both the temperature and partial pressure of oxygen at which rocks containing arfvedsonite have crystallized. A maximum temperature of 700°C and a P_{O_2} in the range defined by the wustite-magnetite and fayalite-magnetite-quartz buffers are indicated.

Finally, attention must be drawn again to the very large temperature span of melting of the acmite composition with variation in P_{O_2}. From the melting under wustite-magnetite conditions (700°C) there is an interval of 170°C to the melting curve for hematite-magnetite (870°C). Possibly this interval will be reduced by increasing total pressure and almost certainly diminished in a more complex rock assemblage where the melting of other phases will be involved. There remains however the real possibility of the generation of peralkaline magmas at constant pressure and temperature merely by reduction of the partial pressure of oxygen in the vapor phase. Partial melting of rocks such as alkali basalt, which would be expected to have a peralkaline end-stage of crystallization, could yield peralkaline liquids by this mechanism.

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