

## HIGH-PRESSURE STABILITY OF ACMITE

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**ABSTRACT.** Acmite,  $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ , continues to melt incongruently to hematite + liquid up to at least 45 kb. The equation  $T(^{\circ}\text{C}) = 988 + 20.87P(\text{kb}) - 0.155P^2(\text{kb})$  reproduces the fusion curve for acmite = hematite + magnetite + liquid over the pressure range 0 to 45 kb. The initial slope of this curve is about  $20^{\circ}\text{C}/\text{kb}$ , which is steep for silicates. An acmitic pyroxene may be stable in equilibrium with metallic iron. Under conditions of low relative oxygen fugacity, acmite melts incongruently to fayalite + liquid. Acmite and some other silicates do not exhibit a linear relation between melting temperature and compressibility and therefore do not obey the recently proposed "new law of melting".

### INTRODUCTION

The pyroxene end member acmite,  $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ , is important because it occurs as the principal constituent in pyroxenes of the late alkaline igneous rocks and because it is the second most important component of the jadeitic pyroxenes found in blue-schist facies terranes (for example, Coleman, 1965, table 2). Bowen and Schairer (1929) originally demonstrated that this compound melts incongruently at 1 atm pressure to hematite + liquid. Thus, separation of iron oxides from a magma would drive the liquid to more silica and soda-rich compositions, providing a possible fractionation mechanism for the development of the alkaline rocks. The remaining question was whether or not this incongruent melting would persist to the pressures characteristic of the lower crust and upper mantle where magmas are believed to be generated.

In the Franciscan metagraywackes of California, jadeitic pyroxenes are formed principally by the breakdown of sodic plagioclase to jadeite-rich pyroxene + quartz and have regional distribution (McKee, 1962; Ernst, 1965). In addition, pyroxenes of the eclogites occurring with the glaucophane schists of California, the Group C eclogites of Coleman and others (1965, table 5), are about equally rich in jadeite and diopside constituents, with acmite third in importance. Further reflection also indicates that a clinopyroxene phase is the most likely silicate to house ferric iron under the bulk composition-temperature-pressure conditions realized in the upper mantle. If the environment at depth had more  $\text{Fe}^{3+}$  than could be balanced by Na, then Ca- $\text{Fe}^{3+}$  phases such as garnet would be important. Ferridiopside is not likely to be significant, as it probably has no great stability at high pressure (Huckenholz, Schairer, and Yoder, 1968). Calcic amphiboles, including those Na-bearing, are not stable above  $800^{\circ}$  to  $900^{\circ}\text{C}$  at 30 kb and so may also be ruled out at depths greater than 70 to 100 km (Gilbert, 1968).

The question now raised is the effect of the acmite component on clinopyroxene stability. In order to answer these questions, acmite itself must first be studied at high pressure, and this paper reports the results of such an investigation.

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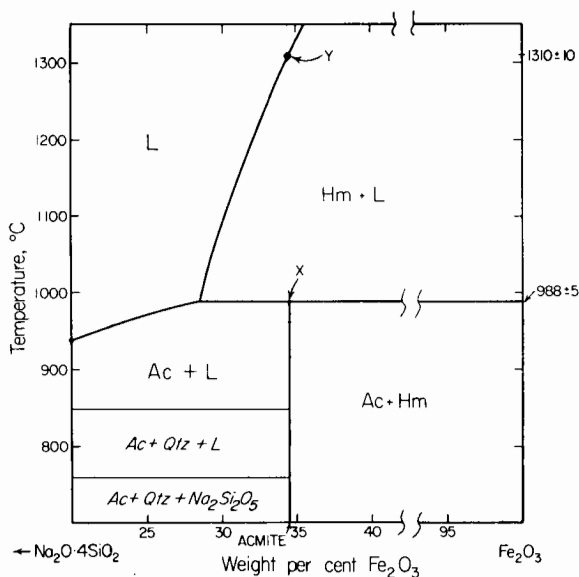


Fig. 1. One atmosphere T-X diagram featuring acmite composition. Abbreviations: Ac, acmite; L, liquid; Hm, hematite; Qtz, quartz. The form of the phase relationships was first worked out by Bowen and Schairer (1929). The temperatures of acmite melting (X) and of the liquidus for acmite compositions (Y) are from Bailey and Schairer (1966). Only the right side of the diagram, from acmite to hematite, can be considered binary. Light lines and italicized assemblages represent ternary equilibria.

#### PREVIOUS EXPERIMENTAL WORK ON ACMITE

At 1 atm and in equilibrium with air, acmite melts incongruently to hematite + liquid, as shown in figure 1 (Bowen and Schairer, 1929). Where a liquid phase is formed the system becomes nonbinary because of small amounts of ferrous iron in the liquid, the amount increasing with temperature (Bowen, Schairer, and Willems, 1930). Although ferrous iron can be neglected in a gross way, departure from a truly binary system at 1 atm is evident in the more recent experimental results on pure acmite composition in which acmite melted over a 13°C interval (Bailey and Schairer, 1966, p. 124). This melting interval implies acmite-ferrosilite solid solution during the melting.

A preliminary report on the system  $\text{Na}_2\text{O}-\text{FeO}-\text{SiO}_2$  at 1 atm, which includes "reduced" acmite composition, was made available several years ago (Schairer, Yoder, and Keene, 1954). Although pyroxene was not positively identified at that time, one of the phases retrieved on quenching appeared to be acmite pyroxene (H. S. Yoder, Jr., personal commun.).

Bailey (1969) has investigated the melting relations of acmite in the presence of water under conditions of controlled oxygen fugacity, at fluid (= total) pressures of 2 and 5 kb. He also made unbuffered runs up to 10 kb and was able to show that incongruent melting persists to at least

that pressure. The melting curve was also found to be sensitive to variations in oxygen fugacity.

Yagi (1962, 1966) has investigated the 1-atm relations in the acmite-diopside system. Nolan and Edgar (1963) synthesized acmite hydrothermally along with other members of the acmite-diopside series. They presented the first well indexed powder pattern of acmite and calculated the cell parameters of their synthetic material. Their values are listed in table 1.

Work bearing on the relationship of acmite in more complicated chemical systems has been published by Bailey and Schairer (1966), who studied the anhydrous system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$  at 1 atm, and by Nolan (1966), who studied part of the  $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system at a pressure of 1000 kg/cm<sup>2</sup>. Ernst (1960, 1962) encountered acmite as a decomposition product in studying the stability relations of the amphiboles magnesioriebeckite and riebeckite-arfvedsonite.

#### EXPERIMENTAL PROCEDURES

Starting material was fine-grained crystalline acmite (conditions of formation are listed in table 1) and hematite + glass of acmite composition, both obtained from J. F. Schairer. Values of  $2\theta$  of the crystalline acmite were measured for ten reflections with high-intensity copper  $K\alpha$  X-radiation and a NaF internal standard. Indexing was done by comparison with Nolan and Edgar (1963). Cell parameters were then calculated with the use of the least-squares refinement program of Burnham (1962), and the results are listed in table 1 as Ac SM.

Experiments were carried out on the single-stage, piston-cylinder device described by Boyd and England (1960). The furnace-cell arrangement currently employed is shown in figure 1 of Bell and England (1967). Problems of pressure calibration in piston-cylinder apparatus have recently received much attention. Boyd and others (1967) showed how the sign of any pressure discrepancy due to frictional effects may be determined by the history of piston motion during a run. In essence, three types of run are possible in a piston-cylinder device: (1) piston-out, where piston motion during the run is always out-stroke, resulting in a *higher* pressure on the furnace cell than calculated from the gauge pressure; (2) piston-in, where piston motion is always in-stroke, resulting in a *lower* pressure on the cell; and (3) to temperature at pressure where the nature of piston travel is unknown throughout the run. Although the first two types of run maximize friction, an advantage is gained in knowledge of the sense of the frictional correction. Details on performance of these two types of experiment are now available (Boyd and others, 1967; Richardson, Bell and Gilbert, 1968).

Pressure discrepancy due to strength of the solid pressure media is a separate factor which is not easily evaluated. Green, Ringwood, and Major (1966) advocate applying a -11 percent correction to the calculated run pressure, supposedly to take into account the strength of

TABLE 1  
Cell parameters of synthetic acmite

|        | a, Å           | b, Å            | c, Å            | $\beta$ , degrees | Vol., Å <sup>3</sup> | T, °C | P, kb | Duration, hours | Capsule  |
|--------|----------------|-----------------|-----------------|-------------------|----------------------|-------|-------|-----------------|----------|
| N & E* | 9.658          | 8.795           | 5.294           | 107.42            | 429.1                | 750   | 1     | 120             | Au       |
| Ac SM† | 9.660 ± 0.003  | 8.804 ± 0.003   | 5.2891 ± 0.0010 | 107.33 ± 0.03     | 429.4 ± 0.3          | 825   | 1 atm | 26              | Pt       |
| A22    | 9.657 ± 0.001  | 8.793 ± 0.001   | 5.2951 ± 0.0003 | 107.44 ± 0.01     | 429.0 ± 0.1          | 1300  | 20    | 1/2             | Pt70Rh30 |
| A5     | 9.659 ± 0.002  | 8.803 ± 0.002   | 5.2916 ± 0.0007 | 107.57 ± 0.02     | 428.9 ± 0.2          | 1000  | 20    | 1/2             | Fe       |
| A84    | 9.660 ± 0.002  | 8.798 ± 0.002   | 5.2925 ± 0.0007 | 107.54 ± 0.02     | 428.9 ± 0.2          | 1000  | 30    | 8-1/2           | Fe       |
| A58    | 9.655 ± 0.001  | 8.794 ± 0.001   | 5.2932 ± 0.0005 | 107.45 ± 0.01     | 428.7 ± 0.1          | 900   | 20    | 24              | C        |
| A77    | 9.660 ± 0.001  | 8.802 ± 0.001   | 5.2924 ± 0.0004 | 107.47 ± 0.01     | 429.2 ± 0.1          | 1050  | 30    | 12              | C        |
| Cfs‡   | 9.708 ± 0.0008 | 9.0872 ± 0.0011 | 5.2284 ± 0.0006 | 108.43 ± 0.004    | 437.6 ± 0.1          | 1150  | 20    | 24              | Fe       |

\*Nolan and Edgar (1963, table II and p. 627).

†Starting material.

‡Clinoferrosilite: Burnham (1965, table 22) and D. H. Lindsley (personal communication).

Uncertainties shown for the cell parameters are those generated by the least-squares solution.

A5 contained Ac + trace (opaques + Na silicate + quartz + glass). A84 contained Ac + trace (amphibole + Na silicate + quartz). A58 contained Ac. A77 contained Ac.

the pressure media. But this approach fails to recognize the possible large frictional effects, which may be either additive or subtractive, and also the fact that the "strength" varies as a function of pressure, temperature, materials, and design of cell. On the basis of studies of the kyanite-sillimanite transition in both piston-cylinder and gas-media apparatus, Richardson, Bell, and Gilbert (1968) have conclusively shown that the true sample pressure is at least 1 kb lower than the nominal (calculated) pressure at 12 to 13 kb and 850°C, for the present cell arrangement, due entirely to strength of media. However, no way is now known to extrapolate this finding to any other very different P and T condition. Pressures given in this report have not been corrected, but the frictional sense is indicated where known.

Most runs in this study were piston-out, for two reasons. First, this insured that the melting curve would be approached from the solid field as the run pressure was attained. Second, most of the pressure cylinders used in this study were steel lined. Boyd and others (1967) noted that pressure discrepancies due to frictional effects were smaller in piston-out runs where steel liners were employed.

Temperatures presented for runs were determined with Pt-Pt<sub>90</sub>Rh<sub>10</sub> thermocouples and have an uncertainty of  $\pm 10^\circ\text{C}$  (Bell and England, 1967), with no correction applied for pressure. The containers for most of the charges were Pt<sub>70</sub>Rh<sub>30</sub> capsules. Since iron is least soluble in platinum when in the ferric state, it appeared that there would be no serious loss of iron to the container. To check this assumption, a capsule and charge, which had been run at 1400°C and 10 kb for 30 minutes (table 3, A45) was examined with a Material Analysis Company model-400 electron microprobe. The entire capsule was mounted in epoxy and ground down until a longitudinal section half way through the capsule was exposed. Scans across the quenched glass showed no detectable variation in iron content, either in the center of the charge or near the container walls. Scans from the glassy part of the charge across the interface into the wall showed a smooth drop in X-ray emission to a constant background level within 3 to 5  $\mu\text{m}$ . For a beam size of about 1 to 2  $\mu\text{m}$  this drop corresponds to the simple effect of moving across an edge. Thus, no diffusion gradient was detected.

This ferric silicate is one of the first to be studied at very high pressure. Because the environment in the furnace assembly is reducing with respect to ferric iron owing to the graphite heater, a difficulty arose in the piston-cylinder device with the type of charge container used. This container is sealed mechanically with a lid. Some recrystallization of the Pt<sub>70</sub>Rh<sub>30</sub> alloy during the run should act to tighten the seal and is normally adequate to hold and isolate liquids and solids. However, reduction of some hematite to magnetite during runs of even a few minutes is evidence of the fact that the capsule is not completely closed to gas (namely, CO/CO<sub>2</sub> from the graphite heater).

All parts of the pressure cell (except the talc sleeve) were dried at 1000° to 1100°C in N<sub>2</sub> for 30 minutes to 1 hour before use. The loaded

capsule was also dried at 850° to 925°C for several hours before use. In some experiments, both the dried assembly and charge were stored in a desiccator until the run was made. The onset of melting is lowered distinctly if the sample is not moisture free. From Bailey's (1969) data, it can be seen that the lowering would be about 350°C at 10 kb for H<sub>2</sub>O-saturated samples.

A series of experiments designed to check the stability of acmite under conditions of lowered relative oxygen fugacity was also carried out, employing graphite and iron capsules. Some of the graphite capsules (plus charges) were dried at 850° to 925°C in N<sub>2</sub>. The iron capsules plus charges were dried at 160° to 170°C in vacuum for 24 to 48 hours. As will be discussed later, this procedure was inadequate.

#### EXPERIMENTAL RESULTS

The intention of this study was to determine the pressure effect on the incongruent melting of acmite (point X in fig. 1) and the liquidus

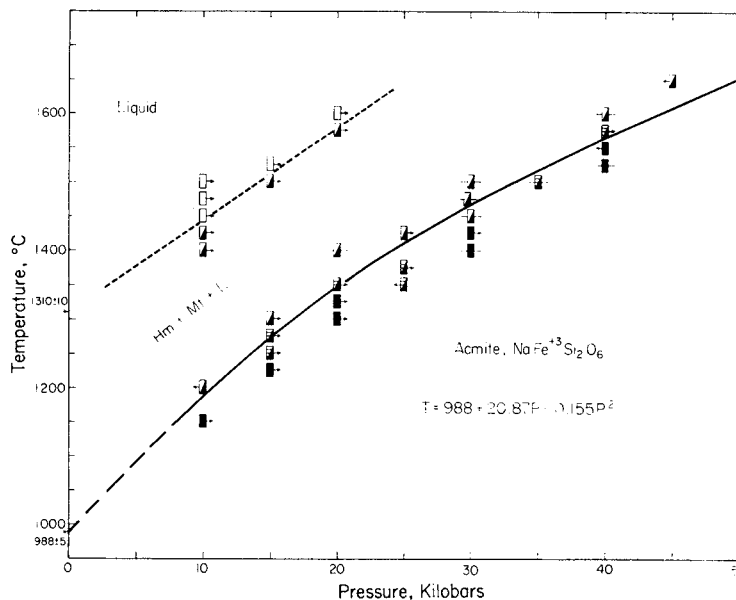


Fig. 2. Acmite composition Na<sub>2</sub>O•Fe<sub>2</sub>O<sub>3</sub>•4SiO<sub>2</sub>. All runs were performed in Pt<sub>70</sub>Rh<sub>30</sub> capsules. Solid rectangles represent acmite; half-solid rectangles with horizontal lines represent acmite + hematite + magnetite + liquid; half-solid rectangles represent hematite + magnetite + liquid; open rectangles represent all liquid. A right-directed arrow indicates a piston-out run (any pressure deviations due to frictional effects would shift pressure to a higher value); a left-directed arrow indicates a piston-in run. Bars extending both directions indicate that history of piston travel during run is unknown. The acmite melting curve is drawn into the 1-atm point (where P<sub>O<sub>2</sub></sub> = 0.2 atm) determined by Bailey and Schairer (1966). Strictly, the curve should be drawn to a temperature at 1 atm where acmite would melt in equilibrium with hematite + magnetite (P<sub>O<sub>2</sub></sub> ≈ 10<sup>-6</sup> bars). This temperature is probably not significantly lower than that determined in equilibrium with the atmosphere. Similarly, the curve tentatively suggested as the liquidus should not be drawn to the 1310°C point, but to some lower temperature.

for acmite composition (point Y in fig. 1). The results are shown in figure 2, and the limiting run data are given in tables 2 and 3.

Incongruent melting to hematite (+ magnetite) + liquid persists to at least 45 kb (for example, see table 2, A86). The fact that acmite continues to melt at high pressure to hematite (+ magnetite) + liquid suggested that excess hematite could be added to the charge as an oxygen reservoir without influencing the solidus. Accordingly, hematite was added to most charges when the acmite solidus was being investigated. Since both hematite and magnetite were products of the runs, the system was buffered with respect to oxygen fugacity.

The equation  $T(^{\circ}\text{C}) = 988 + 20.87P(\text{kb}) - 0.155P^2(\text{kb})$  reproduces the melting curve over the range of data shown in figure 2. Both melting and crystallization appeared to be rapid, and most run times in table 2 are now thought to be needlessly long.

There appears to be a small melting interval over which acmite coexists with hematite + magnetite + liquid, similar to that found in the 1 atm melting. The width of the temperature interval of melting is not known precisely because either infinitesimal amounts of water (from

TABLE 2  
Critical runs determining acmite melting

| Run no. | T, $^{\circ}\text{C}$ | P, kb | Friction*   | Duration, minutes | Starting material† |                            | Results‡ |
|---------|-----------------------|-------|-------------|-------------------|--------------------|----------------------------|----------|
| A36     | 1150                  | 10    | O (NSL)     | 30                | Ac                 | Ac                         |          |
| A37     | 1200                  | 10    | I (NSL)     | 60                | Ac + Hm            | Hm + Mt + gl               |          |
| A38     | 1225                  | 15    | O (NSL)     | 60                | Ac + Hm            | Ac + Hm + Mt               |          |
| A40     | 1250                  | 15    | O (NSL)     | 60                | Ac + Hm            | Ac + Hm + Mt + tr gl       |          |
| A39     | 1275                  | 15    | O (NSL)     | 60                | Ac + Hm            | Ac + Hm + Mt + gl          |          |
| A41     | 1300                  | 15    | O (NSL)     | 60                | Ac + Hm            | Hm + Mt + gl               |          |
| A22     | 1300                  | 20    | O (OC)      | 30                | Ac                 | Ac                         |          |
| A42     | 1325                  | 20    | O (NSL)     | 30                | Ac + Hm            | Ac + Hm + Mt               |          |
| A43     | 1350                  | 20    | O (NSL)     | 30                | Ac + Hm            | Ac + QAc + Hm + Mt         |          |
| A3      | 1400                  | 20    | T at P (SL) | 30                | Ac                 | QAc + Hm + gl              |          |
| A82     | 1350                  | 25    | I (MC)      | 30                | Ac + Hm            | Ac + QAc + Hm + Mt + tr LI |          |
| A57     | 1375                  | 25    | O (OSL)     | 30                | Ac + Hm            | Ac + QAc + Hm + Mt         |          |
| A44     | 1425                  | 25    | O (NSL)     | 30                | Ac + Hm            | QAc + Hm + Mt + gl         |          |
| A16     | 1400                  | 30    | T at P (SL) | 30                | Ac                 | Ac                         |          |
| A56     | 1425                  | 30    | O (OSL)     | 30                | Ac + Hm            | Ac + Hm + Mt               |          |
| A55     | 1450                  | 30    | ? (MSL)     | 30                | Ac + Hm            | QAc + Hm + Mt + gl         |          |
| A49     | 1475                  | 29.7  | ? (MSL)     | 30                | Ac + Hm            | QAc + Hm + Mt + tr LI      |          |
| A17     | 1500                  | 30    | T at P (SL) | 30                | Ac                 | QAc + Hm + Mt + tr LI      |          |
| A50     | 1500                  | 35    | ? (MSL)     | 30                | Ac + Hm            | Ac + QAc + Mt + Hm + tr LI |          |
| A61     | 1525                  | 40    | ? (C)       | 30                | Ac + Hm            | Ac + Hm + Mt               |          |
| A63     | 1550                  | 40    | I (C)       | 20                | Ac + Hm            | Ac + Hm + Mt               |          |
| A67     | 1575                  | 40    | O (MC)      | 23                | Ac + Hm            | Ac + QAc + Hm + Mt         |          |
| A47     | 1600                  | 40    | ? (MSL)     | 20                | Ac                 | QAc + Mt + tr LI           |          |
| A86     | 1650                  | 45    | I (MSL)     | 5                 | Ac                 | QAc + Hm + Mt              |          |

Charges were contained in Pt<sub>70</sub>Rh<sub>30</sub> capsules.

\*First symbol denotes piston travel during run as follows: O, piston-out run; I, piston-in run; ?, direction of piston motion not constant; T at P, to temperature at pressure (direction of piston motion not held constant during run).

Symbols in parentheses denote cylinder condition as follows: O, old, cracked; M, cracks beginning to show but no significant spalling; N, new, no cracks. The symbols also denote cylinder type: SL, steel liner; C, carbide.

†Symbols for phases are Ac, acmite; Q, quench phase; Hm, hematite; Mt, magnetite; gl, glass; LI, low refractive index phases; tr, trace.

TABLE 3  
Liquidus runs for acmite composition

| Run no. | T, °C | P, kb | Friction* | Duration, minutes | Starting material* | Results*            |
|---------|-------|-------|-----------|-------------------|--------------------|---------------------|
| A45     | 1400  | 10    | 0 (NSL)   | 30                | Ac                 | Hm + Mt + gl        |
| A51     | 1425  | 10    | 0 (MSL)   | 15                | Ac                 | Hm + Mt + gl        |
| A52     | 1450  | 10    | 0 (MSL)   | 20                | Ac                 | Qhm + Qmt + gl + LI |
| A53     | 1475  | 10    | 0 (MSL)   | 15                | Ac                 | Qhm + Qmt + gl + LI |
| A54     | 1500  | 10    | 0 (MSL)   | 15                | Ac                 | Qhm + Qmt + gl + LI |
| A60     | 1500  | 15    | 0 (C)     | 15                | Ac                 | Hm + Mt + gl        |
| A64     | 1525  | 15    | 0 (C)     | 15                | Ac                 | Qhm + Qmt + gl      |
| A65     | 1575  | 20    | 0 (MC)    | 1                 | Ac                 | Hm + Mt + gl        |
| A70     | 1600  | 20    | 0 (MC)    | 18                | Ac                 | tr QAc + Qmt + gl   |

\*See legend of table 2.

incomplete sample drying or from the dehydrating talc sleeve) or the reducing atmosphere of the furnace would tend to lower the beginning of melting. The incongruent melting curve shown in figure 2 is drawn on the disappearance of acmite.

Liquids just above the acmite solidus can easily be quenched to glass at pressures below 20 kb. At 20 kb and higher, however, liquids stable at the conditions of the run quench to acmite + glass. Above 30 kb only quench acmite is obtained above the solidus. Fortunately, there is no difficulty in distinguishing acmite held stably at the conditions of the run and that formed on quenching, as the quench pyroxene is, microscopically, in large sheaves with sweeping extinction.

A few of the runs in which melting occurred produced trace amounts of phases with low refractive index, presumably a Na-silicate and quartz. These phases apparently result from a fractional crystallization during the quench, in which crystalline hematite and magnetite fail to react with the liquid, causing the composition of the liquid to become enriched in soda and silica and thus quenching to acmite plus Na silicate and quartz (compare fig. 1). No phases with low refractive index were observed where crystalline acmite was held in its own stability field. Cell parameters of such an acmite from run A22 (table 2) are given in table 1 and are comparable to the starting material.

Determination of the liquidus for acmite composition poses some serious difficulties. First, hematite can no longer be added to help maintain a high oxygen potential, since the liquidus temperature obviously depends on bulk composition. Second, the liquid at high temperatures cannot be quenched. As expected, runs at successively higher temperatures in the region up to 150° to 200°C above the incongruent melting curve in the hematite + magnetite + liquid field show a decrease in the proportion of oxide crystals to glass. Above these temperatures, the quenched glasses contain abundant oxides (dominantly magnetite), commonly evenly distributed, which are interpreted as having been grown on the quench. The suggestion is made here that the development of this phenomenon approximately marks the true liquidus curve. The dashed



curve for the liquidus in figure 2 (table 3) is drawn on this basis. A complication might arise because hematite is known to dissociate to magnetite plus oxygen at 1457°C at 1 atm (Darken and Gurry, 1946) so that an additional reaction could be involved. However, it is likely that the effect of pressure on this transition is to increase the temperature stability of hematite even though the P-T slope is unknown.

An attempt to check the position of the suggested liquidus boundary was made by the following method: By reference to the 1-atm relations depicted in figure 1, it may be seen that with increasing temperature, and for the bulk composition of acmite, the composition of the liquid changes in a regular manner from the onset of incongruent melting to point Y. The refractive index of the quenched glasses representing these liquids should change with composition also. The total iron content of the liquid will remain constant (for acmite composition) after the temperature is raised beyond point Y, and the refractive index of the glass should no longer change appreciably (or, at least, in the same way as before). Thus a series of isobaric runs (15 kb) at increasing temperature above the incongruent melting curve was made to follow the change in index of the quench glasses (table 4). Unfortunately, at 1400°C the glass exhibited a variable index of refraction, and at 1450°C the values spread over more than 0.01. The index was lower in glass fragments that contained abundant oxides, supporting a possible quench origin for some of the oxides. These data would nevertheless indicate that the position of the liquidus is probably approximately as shown in figure 2.

In order to investigate the effect of oxygen fugacity on acmite stability, some runs were made in graphite and in iron crucibles. If the gas phase inside the graphite capsule contains only the species CO<sub>2</sub>, CO, and O<sub>2</sub>, then  $f_{O_2}$  is defined (French and Eugster, 1965). In the iron capsules, the equilibrium  $Fe + 1/2 O_2 = FeO$  should prevail and fix  $f_{O_2}$ . Experiments in these capsules gave erratic and nonreproducible results regarding temperature of melting. Variations in the drying procedure did not lead to consistency in the results. Nevertheless, some interesting observa-

TABLE 4  
Refractive index measurements of glasses at 15 kb

| Run no.* | T, °C | Duration, minutes | Starting material | Index, $\pm 0.002$            |
|----------|-------|-------------------|-------------------|-------------------------------|
| A105     | 1300  | 5                 | Hm + gl           | 1.646                         |
| A106     | 1350  | 5                 | Hm + gl           | 1.654                         |
| A107     | 1400  | 5                 | Hm + gl           | 1.666, ranges above and below |
| A108     | 1450  | 5                 | Hm + gl           | <1.670 to 1.682               |

\*Isobarically quenched.

Yagi (1966, table 1) gives 1.643 as the index of a glass of acmite composition at 1 atmosphere.

TABLE 5

Summary of results with graphite and iron capsules, showing highest temperature (°C) at which pyroxene was obtained as a run product

|          | 10 Kb |     | 20 Kb |      | 30 Kb |      | 40 Kb |
|----------|-------|-----|-------|------|-------|------|-------|
|          | C     | Fe  | C     | Fe   | C     | Fe   | Fe    |
| Pyroxene | 900   | 800 | 1025  | 1050 | 1100  | 1100 | 1200  |

tions were obtained (table 5). Melting temperatures seem to be lowered by 200° to 300°C or more compared to that found when oxygen fugacity is defined by hematite + magnetite. An amphibole, presumably arfvedsonitic because of the low relative oxygen fugacity and high temperature (see Ernst, 1962), appeared in a number of the runs. The amphibole may have been a quench product in some runs, although no "quench texture" was observed. Only rarely was it present in sufficient amounts to be detected by means of powder X-ray diffraction. Evidently, water either found its way into the charge from the dehydrating talc sleeve or was not eliminated during drying.

An acmitic pyroxene does appear to be stable at low oxygen fugacity (that is, in equilibrium with iron) in an anhydrous environment. This clearly points up the importance of H<sub>2</sub>O because Bailey (1969) showed that acmite in the presence of water had no stability field at fluid pressures of 1 kb or more at oxygen fugacities defined by the wustite-magnetite and iron-wustite buffers. Instead, an arfvedsonitic amphibole was the stable solid phase. These results appear to be confirmed in this study, where amphibole crystallized readily when the environment became hydrous.

Cell parameters for acmites held in graphite or iron capsules are listed in table 1 and seem to indicate little solid solution toward ferrosilite. However, almost all runs at low relative  $f_{O_2}$  contained small amounts of phases of low refractive index, presumably Na silicate and quartz (especially if opaques, glass, or amphibole were present), possibly indicating some deviation away from ferric acmite. Ernst (1962, p. 715), on the basis of refractive index, noted that the acmitic pyroxene formed at oxygen fugacities defined by the iron-wustite buffer (and  $\leq 1000$  bars fluid pressure) showed possible solid solution toward ferrosilite ( $11 \pm 9$  mole percent).

Incongruent melting behavior is retained up to 40 kb in iron capsules where acmite melts to fayalite + liquid. This is consistent with the 1-atm relations in the system Na<sub>2</sub>O-FeO-SiO<sub>2</sub>, where a field of fayalite exists on the liquidus over reduced "acmite" composition (Schaerer, Yoder, and Keene, 1954).

## DISCUSSION OF RESULTS

The initial slope of the acmite fusion curve, under conditions where oxygen fugacity is specified by hematite + magnetite, is about  $20^{\circ}/\text{kb}$ , one of the steepest of any silicate yet investigated. From the Clapeyron relation,  $dT/dP = \Delta V/\Delta S$ , it is clear that either  $\Delta V$  is unusually large relative to  $\Delta S$ , compared to other silicates, or  $\Delta S$  is unusually small relative to  $\Delta V$ . Since acmite melts incongruently to relatively dense solids (oxides) + liquid,  $\Delta V$  could not be unusually large. It is probable, instead, that  $\Delta S$  is unusually small relative to  $\Delta V$ . This may be in part due to the low entropy of the oxides and also may indicate that coordination of the ions in the liquid is similar to that in acmite itself, contributing to the small change in entropy on melting.

In figure 3 the melting curves of diopside, jadeite, and acmite are compared. Substitution of  $\text{Fe}^{3+}$  for Al in jadeite to make acmite raises the melting temperature about  $100^{\circ}\text{C}$  at 30 kb and  $50^{\circ}\text{C}$  at 50 kb. However, acmite still melts about  $250^{\circ}\text{C}$  lower than diopside over most of the pressure range to 50 kb. Thus the presence of Na, Al, and  $\text{Fe}^{3+}$  in pyroxenes of possible mantle assemblages can have an appreciable effect on pyroxene stability. At first glance, the acmite and jadeite curves might be thought a model for the minimum temperatures of melting in the upper mantle. But two effects will work to lower these temperatures drastically, low relative values of oxygen fugacity and trace amounts of  $\text{H}_2\text{O}$ .

The continued incongruent melting of acmitic pyroxene over a wide range of oxygen fugacity and to high pressure indicates that in magmas

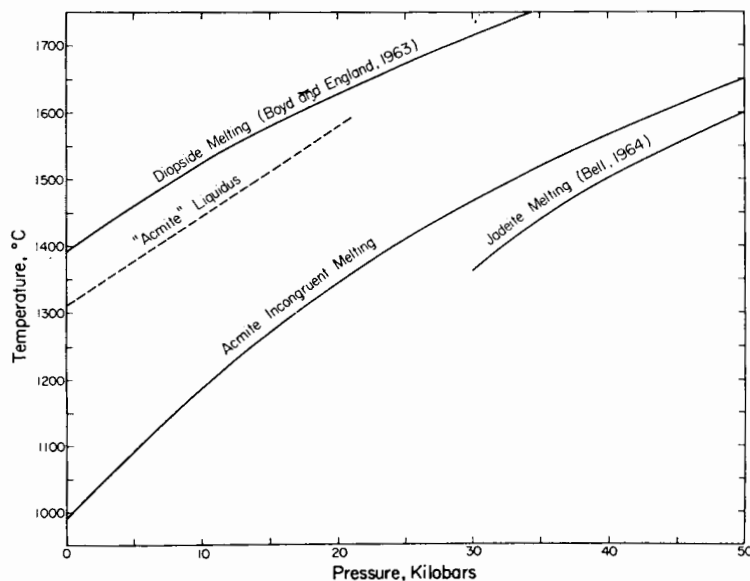


Fig. 3. Fusion curves of several related end-member clinopyroxenes.

with initial peralkaline tendencies, fractional crystallization due to separation of early-formed iron oxides or olivine could easily bring about a change in liquid composition toward a general enrichment of sodium and silica. Such a development of a peralkaline trend was postulated many years ago by Bowen, Schairer, and Willemms (1930) and more recently by Bailey and Schairer (1966) on the basis of experimental work at 1 atm. The importance of this study is that pressures equivalent to depths of 120 to 140 km do not change the incongruent relationship discovered at 1 atm, which is basic to that theory. Indeed, partial melting of lower crust and upper mantle material, possibly involving several stages, would help generate the initial peralkaline trend. Mobile melts rich in Na and Si (also Al from jadeite "component"), compared to the crystalline residue, once formed, could work their way to the surface, leaving behind spinel-olivine assemblages. Spinel peridotite inclusions commonly found in association with alkali olivine basalts may partially reflect such a process.

Preliminary experiments on the join acmite-jadeite indicate that incongruent melting of pyroxene to hematite + liquid continues across to jadeite-rich compositions. In the 1-atm study of these compositions, although these jadeite-rich pyroxenes are not stable, hematite is stable at the liquidus to near jadeite composition (Bailey and Schairer, 1966). Yagi (1966) showed that, on the diopside-acmite join at 1 atm, pyroxenes from acmite<sub>100</sub> to acmite<sub>10</sub>-diopside<sub>90</sub> (wt percent) also melt incongruently. Thus incongruent melting of soda-rich pyroxenes to oxides is a general phenomenon of some importance.

A "new melting law" of the form  $T_M = T_M^\circ (1 + C \Delta V/V_0)$ , for application at high pressures, has recently been proposed by Kraut and Kennedy (1966a). It was based on the observation that plots of melting temperature at pressure against isothermal (room-temperature) compression of the solid phase appeared to give a linear relation. These authors originally suggested that "this result seems to apply to all substances examined which melt with an increase in volume . . .". Shortly thereafter Kraut and Kennedy (1966b) indicated that some solidified gases did not obey this relationship. More recent work by Luedemann and Kennedy (1968) has shown that the linear relation also breaks down for the alkali metals as melting maxima are approached, and compression of the solid reaches 35 to 40 percent. The latter authors speculated that the results may indicate that, at equivalent compressions for silicates (in the deep mantle and core), fusion maxima would also be encountered. In the light of these arguments it seemed of interest to examine such a plot for acmite, which melts incongruently (fig. 4). Compressibility values are derived from ultrasonic measurements on a specimen of aegirite, which was not chemically analyzed (Birch 1966, tables 7-10 and 7-12; Alexandrov and Ryzhova, 1961).

It is clear that no linear relation between  $\Delta V/V_0$  and melting temperature exists for acmite. In fact, the resulting curve is similar in form to the fusion curve itself. It was thought possible that deviation from

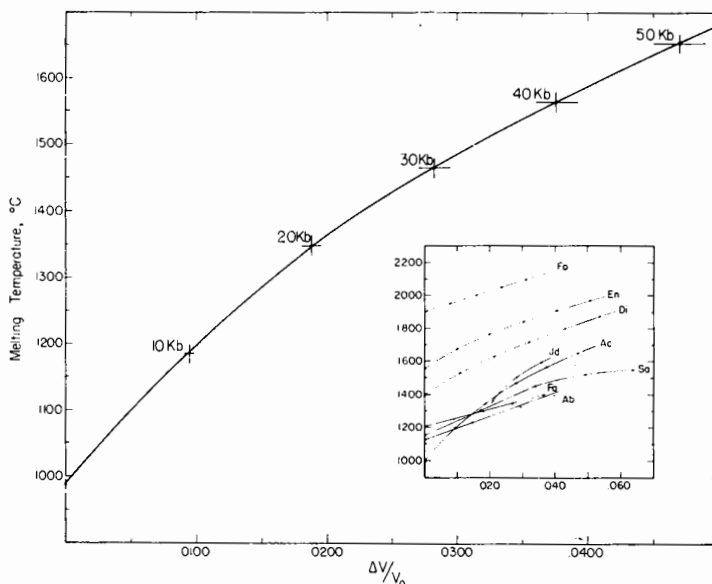


Fig. 4. Melting temperature of acmite versus compression at room temperature. Inset shows similar plots for other silicates. Compression data summarized in Birch (1966, table 7-10). Melting curves are Fo, forsterite,  $\text{Mg}_2\text{SiO}_4$  (Davis and England, 1964); En, enstatite,  $\text{MgSiO}_3$  (Boyd, England, and Davis, 1964); Di, diopside,  $\text{CaMgSi}_2\text{O}_6$ , and Ab, albite,  $\text{NaAlSi}_3\text{O}_8$  (Boyd and England, 1963); Jd, jadeite,  $\text{NaAlSi}_2\text{O}_6$  (Bell, 1964); Ac, acmite; Sa, sanidine,  $\text{KAlSi}_3\text{O}_8$  (Lindsley, 1966); Fa, fayalite,  $\text{Fe}_2\text{SiO}_4$  (Hsu, 1967).

linearity might be due to incongruent melting. For comparison, plots of melting temperature versus compressibility for other silicates are shown in the inset of figure 4. Fayalite ( $\text{Fe}_2\text{SiO}_4$ ), which melts incongruently up to 40 kb (Hsu, 1967), and sanidine ( $\text{KAlSi}_3\text{O}_8$ ), which melts incongruently up to 20 kb (Lindsley, 1966), show linear relationships over that region; thus, incongruent behavior cannot be used to explain curvature. In contrast, diopside, which melts congruently (Boyd and England, 1963), and sanidine, which melts congruently above 20 kb (Lindsley, 1966), do not show linear relations. On the whole, the relationships for silicates shown in figure 4 reflect the form of the fusion curves: linear fusion curves result in linear  $T_M$  versus  $\Delta V/V_0$  curves; fusions with marked curvature result in curved  $T_M$  versus  $\Delta V/V_0$  relations, with the exception of albite.

A pressure effect on the emf of thermocouples cannot be used to account for the nonlinear  $T_M$ — $\Delta V/V_0$  curves presented here, because all curves shown are plotted without this correction so that differences between curves are real. Nothing in the experimental techniques used to determine the melting curves can be appealed to since all these curves were determined with the same type of apparatus and technique. It is possible that the compressibility measurements at lower pressures for silicates may have larger uncertainties than expected and that extrapola-

tion to higher pressure of low-pressure measurements is unwarranted. As previously noted, difficulties in the simple temperature-compression relation are not limited to silicates. Whatever the reasons, the "new law of melting" does not seem to be substantiated by silicates over the pressure range thus far investigated.

In summary, the more significant features of the work are: (1) incongruent melting of acmite persists to 45 kb; (2) oxygen fugacity has a strong influence on acmite melting; (3) incongruency is maintained from high to low oxygen fugacity; (4) the initial slope of the incongruent melting curve is surprisingly steep—about 20°C/kb, one of the steepest of any silicate yet investigated. These observations clearly support the key role of acmite in the genesis of alkaline rocks.

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