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THE FUSION RELATIONS OF ACMITE.

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Acmite or aegirite ($NaFeSi_2O_6$) is one of the end members of that complicated and important group of rock-forming minerals, the pyroxenes. It is found in a great variety of alkaline rocks whether these are feldspathoid-bearing or quartz-bearing, plutonic or effusive. The natural mineral is never the pure theoretical end member but always contains some of the other pyroxene molecules in solid solution, thus passing through aegirite-augite to the more common pyroxenes.[1] We have been carrying on a synthetic study of this group of minerals and present here our findings with the pure end member, acmite.

SYNTHESES OF ACMITE.

Acmite has been prepared by Weyberg[2] and by Washington and Merwin[3] by fusing its constituents with an excess of NaCl. An attempt by Bäckström to make acmite by simple fusion of its constituents gave a product which was partly acmite but contained also some hematite.[4] The reason for this result will appear in the sequel; in fact we have found that pure acmite can not be made by simple melting of its constituents on account of its complicated fusion relations.

When a mixture of the composition of acmite is melted and allowed to cool slowly, hematite is the first crystalline phase to separate. We accordingly started to investigate the whole ternary system, Na_2O-Fe_2O_3-SiO_2, and this study is now well advanced. As it proceeded we found that the fusion relations of acmite can be adequately described in terms of the

[1] For a general discussion of acmitic pyroxenes see H. S. Washington and H. E. Merwin, Am. Mineralogist, 12, 233-252, 1927.
[2] Centralbl. Min., 1905, p. 717.
[3] Op. cit., pp. 238-9.
[4] Bull. Soc. Min. France, 16, 130, 1893.

join Fe_2O_3-$Na_2O.4SiO_2$ and the results of determinations along this join are now presented.

EXPERIMENTAL METHODS.

The methods were those commonly employed in such work in this Laboratory. The mixtures were made up from a pure ferric oxide, sodium carbonate and selected quartz. In practice we found it advantageous to make up the mixture $Na_2O.4SiO_2$[5] as a basic material and then to add to this the various amounts of Fe_2O_3 required for the ternary mixtures. The making of the mixture $Na_2O.4SiO_2$ requires, as is true of all silicates of the alkalies, the careful weighing of each charge after fusion and the addition of a further amount of soda to replace that volatilized during fusion. After 5 fusions complete combination to a homogeneous glass is obtained and thereafter further loss of Na_2O is negligible, nor is there appreciable loss when Fe_2O_3 is fused with this glass in order to prepare the ternary mixtures.

The thermal investigation of the mixtures was carried on by the method of quenching. This consists in suspending a small charge nearly in contact with the junction of a thermo-element in an electric furnace. After exposure for a period of time sufficient to insure equilibrium the charge is caused to drop into a dish of mercury at room temperature. Upon examination with the petrographic microscope the phases that were present at the temperature of the furnace can be determined.

The thermoelement was calibrated at fixed points defined as follows:

NaCl	melting-point	800.4° C.
Au	melting-point	1062.6° C.
$CaMgSi_2O_6$	melting-point	1391.5° C.

RESULTS.

The results of the quenching experiments are given in Table I and are shown graphically in Fig. 1.

[5] It should be emphasized that no compound of soda and silica in the 1:4 ratio is known, the dissilicate being the most siliceous compound. The above form of designation is used here merely as a convenient way of referring to the 1:4 mixture.

TABLE I.

Results of Quenching Experiments on the
($Na_2O.4SiO_2$)—(Fe_2O_3) Join.

Composition Weight per cent ($Na_2O.4SiO_2$)	(Fe_2O_3)	Time hrs.	Temperature ° C.	Final Condition of Charge*
100	0	1	1105	Tridymite in glass
100	0	1	1114	Very rare tridymite in glass
95	5	¾	1000	Very rare tridymite in glass
90	10	1	882	Quartz, tridymite in glass
90	10	1	893	Very rare quartz and tridymite in glass
88¼	11¾	1½	861	Quartz in glass
88¼	11¾	1½	865	Very rare quartz in glass
87½	12½	¾	845	Rare quartz and acmite in glass
87½	12½	¾	850	Very rare quartz and acmite in glass
85	15	1	880	Rare acmite in glass
85	15	¾	889	Very rare acmite in glass
80	20	¾	873	Large amount of acmite in glass
80	20	¾	937	Very rare acmite in glass
75	25	¾	968	Acmite in glass
75	25	¾	970	Very rare acmite in glass
75	25	¾	973	All glass
71½	28½	1	978	Acmite and hematite in glass
71½	28½	1	986	Rare acmite and hematite in glass
71½	28½	¾	990	Very rare acmite and hematite in glass
71½	28½	1	995	Very rare hematite in glass
71½	28½	¾	1000	All glass
70¾	29¼	1	1049	Very rare hematite in glass
70¾	29¼	1	1060	All glass
70	30	1	1090	Rare hematite in glass
70	30	¾	1093	Very rare hematite in glass
70	30	1	1100	All glass

* All charges were initially crystalline.

DISCUSSION OF RESULTS.

The Invariant Point: Acmite-Hematite-Liquid.

The point *R* of Fig. 1 represents the liquid which is in equilibrium with acmite and hematite. The composition of the liquid is 28.5 per cent Fe_2O_3; 71.5 per cent $Na_2O.4SiO_2$ or Na_2O 14.6, Fe_2O_3 28.5, SiO_2 56.9.

The point is a reaction point; with falling temperature hematite reacts with liquid to produce acmite.

The temperature is 990°.

It may be seen from Fig. 1 that if pure crystalline acmite is heated it remains unchanged until a temperature of 990°

is reached, at which temperature it melts incongruently giving a liquid of the composition *R* and crystals of hematite. The temperature must then be raised to about 1275°, or nearly 300°, before all the hematite disappears.

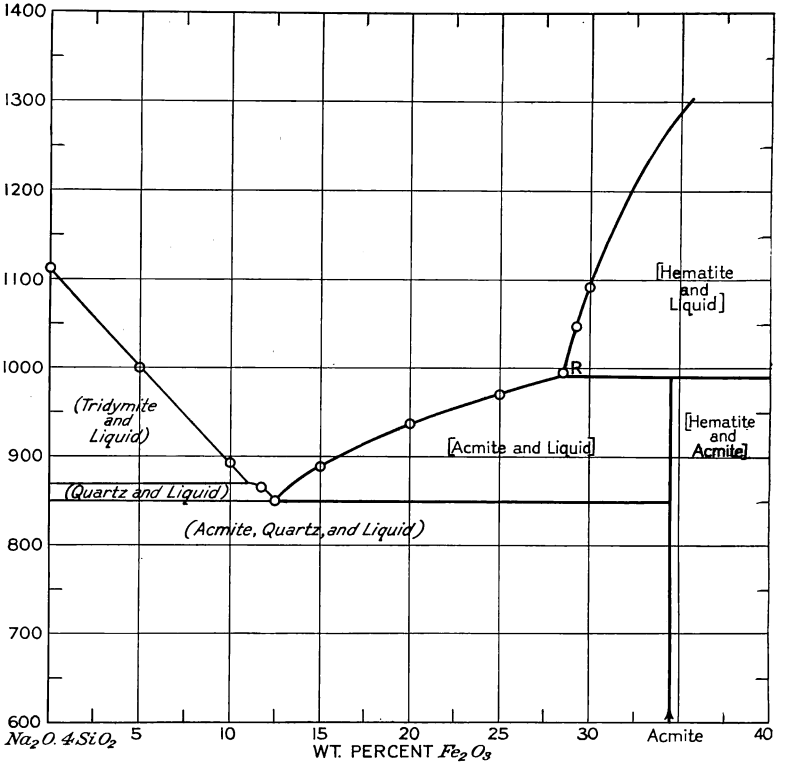

Fig. 1. Equilibrium diagram for mixtures on the join $Na_2O.4SiO_2$—Fe_2O_3. All equilibrium to the right of the liquidus minimum is truly binary (except for the effects of small amounts of ferrous oxide—see text—), and is designated by heavy curves and lettering enclosed in square brackets. All equilibrium to the left of the liquidus minimum is merely a linear section of ternary equilibrium and is designated by lighter curves and lettering enclosed in parentheses.

In the cooling of a liquid of the composition of acmite, hematite begins to separate at about 1275° and this continues until a temperature of 990° is reached. At this temperature, if perfect equilibrium is attained, the liquid and the hematite both disappear by interaction to produce acmite and the whole mass is composed of acmite only. In actual practice it has

not proved possible to bring this reaction to completion. Some hematite remains unattacked and therefore some liquid is left in excess. From this liquid acmite continues to crystallize with falling temperature until at 850° it is joined by quartz. Further crystallization can be accurately described only in terms of the full ternary system which is not pictured in our present diagram. Suffice it to say here that crystallization then proceeds to the ternary eutectic: quartz-acmite-sodium disilicate. There is thus a great difference in the possible product obtained by the crystallization of a mixture whose total composition is acmite. With excessively slow cooling and perfect equilibrium only acmite is obtained and liquid disappears completely at 990°. With failure of complete equilibrium a product consisting of hematite, acmite, quartz and sodium dissilicate is obtained and crystallization is complete only at a temperature far below 990° (about 750°). The alternative results are made possible by the incongruent melting of acmite.

The Fields of Quartz and Tridymite.

The field of quartz, where it is intersected by the join under investigation, is very narrow, extending only from 11 per cent to 12.5 per cent Fe_2O_3, with temperatures from 870 to 850°. From these liquids quartz separates fairly readily in small but sharply defined bipyramids characteristic of high quartz. It is always accompanied by some tridymite formed metastably. In all other mixtures from which silica separates it appears dominantly as tridymite, which is, however, often accompanied by some cristobalite formed metastably. The field of tridymite extends from 11 per cent Fe_2O_3 to pure $Na_2O.4SiO_2$ and the temperatures from 870 to 1114°. Quartz was never formed in any mixture at a temperature above 870°, but quartz formed below that temperature may persist for a considerable period at temperatures above 870°. These results are in accord with the universal finding that a high temperature form may crystallize metastably at temperatures below its stability range but a low temperature form never crystallizes at temperatures above its stability range. Thus the formation of quartz in nature must be taken as occurring below 870°, but the formation of tridymite or cristobalite does not necessarily indicate a temperature above 870°.[6]

[6] N. L. Bowen, Geologic Thermometry. Chapter 10 in Fairbanks' Laboratory Investigations of Ores, New York, 1928.

The Field of Acmite.

The field of acmite has notable width on this join, extending from 12.5 per cent Fe_2O_3 to 28.5 per cent Fe_2O_3. It is cut off on the low temperature side by the quartz field and on the high temperature side by the hematite field. The temperature range of stability of acmite in contact with liquid on this join is from 850 to 990°. Acmite never forms or persists metastably above the temperature 990°.

The Field of Hematite.

The field of hematite, beginning at 28.5 per cent Fe_2O_3, must extend to 100 per cent Fe_2O_3. The hematite liquidus rises very steeply. Only a short portion of it is given because at higher temperatures notable amounts of ferrous iron are formed in the liquid under the ordinary pressure of oxygen in the atmosphere. The mixture then ceases to lie in the ternary system whose section we are here discussing. Indeed, it should be emphasized that in all our mixtures there is some ferrous iron and its amount increases with increasing temperature. A full discussion of this factor will be reserved until publication of the paper on the ternary system. Suffice it to say here that the mixture plotted as 28.5 per cent Fe_2O_3 (*R* of Fig. 1) when held in an open crucible for one hour at 1015° C. is found to contain 1.54 per cent FeO. In other words somewhat more than 5 per cent of the iron is in the ferrous state at that temperature. Most of the liquidus temperatures of our diagram are lower than 1000° C. so that this proportion of ferrous oxide may be regarded as more than the average proportion present in the liquids at the points determined for complete disappearance of crystals.

PROPERTIES OF THE CRYSTALLINE PHASES.

Hematite.

Hematite occurs in the mixture here investigated as very thin hexagonal plates. We have made no measurements of its optical constants. It is readily distinguished by its red color (yellowish when very thin) and excessively high refringence and birefringence.

Acmite.

The properties of pure acmite have been measured by Merwin and found to be as follows:

$\alpha = 1.776 \pm .003$, $\gamma = 1.836 \pm .004$, $\beta = 1.819 \pm .004$
$\gamma \wedge \dot{c} = 8°$ for red, 10° for blue.[7]

In routine determinations in our mixtures acmite was distinguished by its high refringence and birefringence, nearly parallel extinction and negative elongation. The crystals have a notable tendency to occur in radiate groups as is so often true of this mineral in rocks.

Quartz.

The properties of quartz as crystallized from these liquids are those ordinarily given for that mineral. It always forms, as already noted, sharply defined bipyramids analogous to the quartz crystals of many rhyolites. In the present examples prism faces appear to be entirely lacking.

Tridymite.

Tridymite forms thin hexagonal plates either as individuals or in groups. They are too thin for the twinning to be made out under crossed nicols. Only in the needle-shaped cross sections of the plates can birefringence be made out. The extinction is then seen to be parallel and the elongation negative.

THE MELTING OF NATURAL ACMITE.

Natural acmite may, in some occurrences, approach the theoretical composition very closely. The purest natural acmite at our disposal was that from Quincy, Massachusetts, described by Palache and Warren[8] and by Washington and Merwin.[9] Analyses given by these investigators show it to be about 90 per cent acmite. We have determined the melting temperature of a small crystal of this material selected under the microscope.

This small crystal, weighing a few milligrams, probably contained somewhat less impurity than the material analyzed since it is possible to select more carefully than can be done with the larger amount required for analysis. The melting

[7] Washington and Merwin, op. cit., p. 239.
[8] This Journal, 31, 550, 1911.
[9] Op. cit., pp. 239-40 and 250.

temperature found was 975°, only about 15° lower than the melting of the pure compound. The melting takes place incongruently, hematite separating from the liquid just as in the synthetic material.

Several earlier workers have determined the fusion temperature of natural acmite. For all of the early determinations Norwegian acmites were used. Brun, by comparison with Segar cones, obtained the value of 970° C.[10] Doelter found 960°.[11] Schumoff-Deleano and Dittler give the values 970-1020°.[12] Leitmeier gives the somewhat lower figures 940-950°.[13]

These results of different observers agree with each other and with our results on natural and synthetic acmite better than is usually found to be true in such work with silicates. The agreement is no doubt to be referred to the moderate temperatures involved and consequent ease of measurement together with the ready melting of acmite to a comparatively thin fluid unlike that obtained with many silicates. All of the earlier workers have, however, missed the incongruent character of the melting. This fact is not surprising because no method but the method of quenching can be depended upon to reveal melting of that character.

PETROLOGIC CONSIDERATIONS.

Acmites or pyroxenes rich in the acmite molecule are a common constituent of alkaline granites, feldspathoidal syenites, the intermediate alkaline syenites, and of the dike and flow rocks related to all these. The low melting temperature of acmite, 990°, sets a definite upper limit to the temperature at which acmite can have formed in these rocks. This incongruent melting point is affected by the presence of other substances in the same manner as is a congruent melting point. If the substance enters in greater quantity into the liquid phase the melting point is lowered. If it enters more abundantly into the solid phase the melting point is raised. The alkaline feldspars and the feldspathoids that are associated with acmite in rocks plainly enter into the liquid and not appreciably into the crystalline acmite. In the presence of these minerals acmite can, therefore, form only at temperatures well below 990°. It should be noted that these low

[10] Ann. Sc. phys. et nat. Genève, 1902-4.
[11] T. M. P. M., **22**, 311, 1903.
[12] Centralbl. Min., 1911, p. 756.
[13] Z. anorg. Chem., **81**, 225, 1913.

temperatures of crystallization are necessitated by the properties of perfectly dry melts. In corresponding natural magmas there is, no doubt, a somewhat increased lowering as a result of the presence of volatile constituents.

There has long been an opinion among petrologists that the presence of volatile constituents is necessary to the formation of quartz. It is not improbable that many petrologists have held a similar opinion of acmite. In the melts here investigated, dry melts of course, quartz and acmite crystallize side by side, the quartz in the bipyramids characteristic of the high temperature form and the acmite often in radiate groups similar to those in rocks. Plainly all that is necessary to the formation of quartz is that the temperature at which silica separates lie within the stability range of quartz. Any materials that adequately reduce the temperature of crystallization may induce the crystallization of silica as quartz.

The general results accruing from the incongruent melting[14] of acmite have already been discussed, especially the alternative courses of crystallization and the corresponding alternative products. The exact character of the incongruent melting of acmite is a matter of some importance. During cooling hematite first forms and, if complete reaction fails, an excess of Na_2O and SiO_2 in the ratio 1.4 is thrown into the liquid. This leads to the formation of quartz and $Na_2O.2SiO_2$. We have, then, in this system another illustration of the condition that has been found to obtain universally in silicate systems, viz. that when there is an incongruent melting of a silicate compound it is always of such a nature as to throw excess silica into the liquid.[15] In the present instance the temperature is low enough so that quartz itself is formed.

Another feature of this incongruent melting of acmite is of some interest in connection with a common chemical peculiarity of some rocks bearing acmite and closely related sodic amphiboles. It is a nearly universal character of igneous rocks that there is more than enough Al_2O_3 and Fe_2O_3 to form with the alkalies the common compounds that contain these in the 1:1 ratio, expressed in a generalized way $R_2'O.R_2'''O_3.nSiO_2$. In the acmitic and related rocks above noted there may, however, be an actual excess of alkalies and in such a system of recalculation of rock analyses as the

[14] A general discussion of the importance of incongruent melting in these respects is given in N. L. Bowen, The Evolution of the Igneous Rocks, Princeton, 1928, pp. 54-62.

[15] For a fuller discussion of this point see N. L. Bowen, The Evolution of the Igneous Rocks, Princeton, 1928, pp. 298-9.

"norm system" it has been necessary to calculate the proportion of a sodium silicate, for which purpose the normative mineral sodium metasilicate has been chosen.[16] This throwing of a sodium silicate into the liquid is exactly what the incongruent relation of acmite accomplishes in the cooling direction. The deficiency of sesquioxides in the magmas noted and their derivation from magmas which have an excess of sesquioxides would therefore appear to be susceptible of explanation in terms of fractional crystallization. In most magmas the availability of oxygen is such that iron oxide appears as magnetite instead of the hematite of our preparations. No doubt, the reaction relation obtains between acmite and the ferric oxide of magnetite in the natural examples.

SUMMARY.

Acmite is found to melt incongruently with separation of hematite and its melting or crystallization, with perfect equilibrium, can be expressed in terms of the join $Na_2O.4SiO_2$-Fe_2O_3. The results of investigation of this join are given in the present paper. This investigation shows that the incongruent melting of acmite occurs at 990° hematite separating and the liquid having the composition $Na_2O.4SiO_2$ 71.5, Fe_2O_3 28.5, acmite itself having 34.5 per cent Fe_2O_3. The temperature must then be raised to about 1275° (nearly 300°) before complete solution of hematite occurs. Crystallization of a liquid of the composition of acmite is, with perfect equilibrium, the reverse of the above. Hematite reacts with liquid at 990° to produce acmite.

If the reaction is incomplete some liquid remains in excess. Upon lowering of temperature acmite separates from this liquid, and at 850° it is joined by *quartz*, which forms sharp bipyramids analogous to the phenocrysts of many rhyolites. With further cooling the crystallization passes into the ternary system and is complete only at the ternary eutectic acmite-quartz-sodium disilicate. It is suggested that the excess sodium silicate in many rocks bearing acmite and related sodic amphiboles is the result of crystal fractionation of the above type, controlled by the incongruent melting of acmite.

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[16] H. S. Washington, Chemical Analyses of Igneous Rocks, U. S. Geol. Survey Prof. Paper 99, 1917, p. 1163.