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MELTING RELATIONS IN THE SYSTEMS Na_2O—Al_2O_3—SiO_2 AND K_2O—Al_2O_3—SiO_2.

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PHASE equilibrium relations in the ternary systems Na_2O—Al_2O_3—SiO_2 and K_2O—Al_2O_3—SiO_2 were studied concurrently during the years between 1929 and 1941. These studies were completed before the war and some of the very numerous data assembled, and the preparation of manuscripts for publication was started. Work on these articles was interrupted by the war and only recently has been resumed. Two forthcoming papers will give complete details of the studies. Because of the wide usefulness of the results in petrology and silicate technology, however, it seems desirable to make the final diagrams available at once. They are presented in this preliminary paper. The data on which the diagrams are based and a full discussion of the preparation of the compositions studied, quenching data, the results and some of the applications will appear later.

These studies are a part of the program at the Geophysical Laboratory for the determination of the mutual melting and crystallization relations in silicate systems of broad fundamental interest to petrology. The systems Na_2O—Al_2O_3—SiO_2 and K_2O—Al_2O_3—SiO_2 depict the mutual melting relations between two important groups of rock-forming minerals, the soda and potash feldspars, respectively, and the corresponding feldspathoids, and the relations of these minerals to corundum, mullite, alkali silicates, and the several forms of silica. The results have a direct bearing on the origin of rocks containing leucite, potash feldspar, albite, and nepheline and show the courses of crystallization of these minerals when excess of one or another of the component oxides is present in molten

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mixtures. A knowledge of the phase relations in these alkali—alumina—silica systems was essential to an attack on the problems of the late stages in the crystallization of igneous rocks, because of their relation* to the system $KAlSiO_4$—$NaAlSiO_4$—SiO_2[1], "petrogeny's residua system," investigation of which is well along towards completion. Moreover, the information gained on these systems provides the necessary basis for extension of the studies to systems having water as an additional component, in other words, to aqueo-igneous

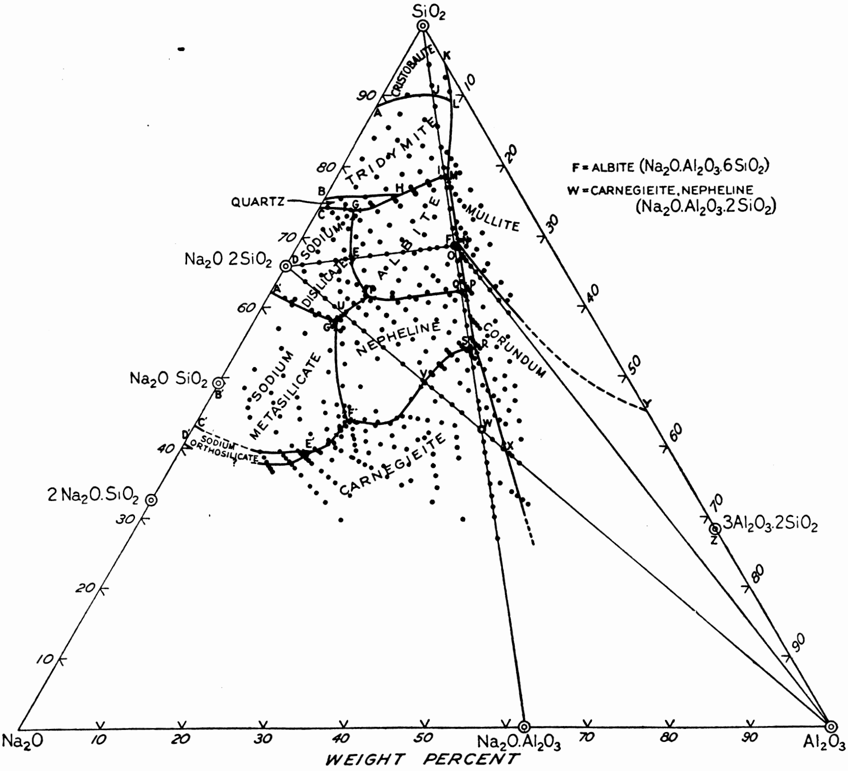

Fig. 1. Equilibrium diagram of the system Na_2O—Al_2O_3—SiO_2 showing compositions studied and the fields of the primary crystalline phases.

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* The system $KAlSiO_4$—$NaAlSiO_4$—SiO_2 is a ternary system within the quaternary system Na_2O—K_2O—Al_2O_3—SiO_2, two of whose limiting systems are the ternary systems Na_2O—Al_2O_3—SiO_2 and K_2O—Al_2O_3—SiO_2.

[1] Schairer, J. F., and Bowen, N. L.: 1935, Preliminary report on equilibrium relations between feldspathoids, alkali-feldspars, and silica. Trans. Amer. Geophys. Union, pp. 325-328.

fusion. These extended studies should furnish useful knowledge concerning the natural processes operative in the crystallization of igneous magmas, the development of pegmatites and veins, and the hydrothermal alteration of minerals.

THE SYSTEM—Na_2O—Al_2O_3—SiO_2.

The phase equilibrium relations in this ternary system are presented here by means of two phase equilibrium diagrams (Figs. 1 and 2) and two tables (Tables I and II).

Figure 1 shows the fields of the several crystalline phases which appear on the liquidus surface. These fields are separated by boundary curves which have arrows indicating falling temperature. These arrows show the positions of maxima on certain boundary curves. Dots represent the compositions which have been investigated. Tie lines joining coexistent solid phases divide the ternary system into sub-systems and constitute binary systems within the ternary system.* That portion of the system Na_2O—Al_2O_3—SiO_2 limited by Na_2SiO_3, $Na_2Si_2O_5$, and $NaAlSiO_4$ has already been reported[2] from this Laboratory.

There are seven binary systems within the ternary system Na_2O—Al_2O_3—SiO_2 as follows:

(1) Albite—silica
(2) Sodium disilicate—albite
(3) Albite—corundum
(4) Nepheline, carnegieite—albite
(5) Sodium disilicate—nepheline, carnegieite
(6) Carnegieite—corundum
(7) Carnegieite—$Na_2O.Al_2O_3$

Data on two of these; nepheline, carnegieite—albite[3] and sodium disilicate—nepheline, carnegieite,[4] have already been reported from this Laboratory.

Two ternary compounds appear in the system Na_2O—Al_2O_3—SiO_2 in addition to the solid phases, which were found in

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*Some of these tie lines are not shown in Figs. 1 and 2.

[2] Tilley, C. E.: 1933, Mineralog. petrog. Mitt., **43**, 406-421.

[3] Greig, J. W., and Barth, T. F. W.: 1938, AMER. JOUR. SCI., (5) **35**A, 93-112.

[4] See ref. 2.

the limiting binary systems $Na_2O—SiO_2$[5] and $Al_2O_3—SiO_2$.[6] Albite ($Na_2O.Al_2O_3.6SiO_2$ or $NaAlSi_3O_8$) has a congruent melting point at 1118±3° C. and shows little or no solid solution. The compound $Na_2O.Al_2O_3.2SiO_2$ (or $NaAlSiO_4$) has two crystalline forms, nepheline stable below 1254±5° C.

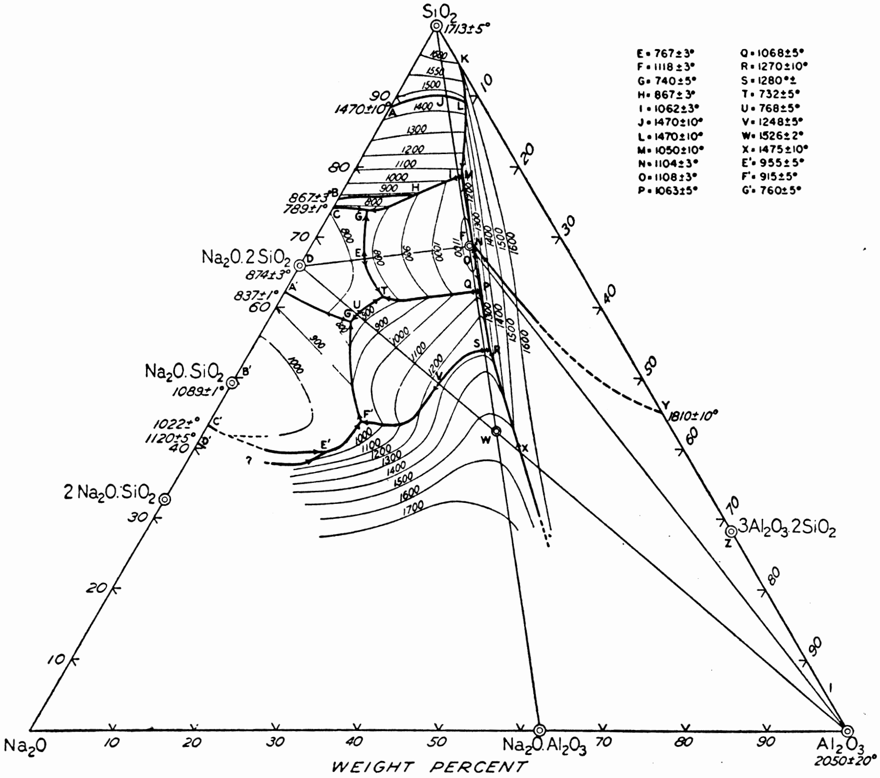

Fig. 2. Equilibrium diagram of the system $Na_2O—Al_2O_3—SiO_2$ with isotherms.

and carnegieite stable from this temperature to its congruent melting point at 1526±2° C. Greig and Barth[7] have shown that both nepheline and carnegieite take up limited amounts of albite in solid solution. Tilley[8] has shown that, in

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[5] Kracek, F. C.: 1930, Jour. Phys. Chem., **34**, 1583-1598 and 1939, Jour. Amer. Chem. Soc., **61**, 2868-2870.

[6] Bowen, N. L., and Greig, J. W.: 1924, Jour. Amer. Ceram. Soc., **7**, 238-254.

[7] See ref. 3.

[8] See ref. 2.

the binary system sodium disilicate—nepheline, carnegieite, neither nepheline nor carnegieite shows any solid solution. There is a series of solid solutions from carnegieite towards $Na_2O.Al_2O_3$ which was investigated only in part because of the high melting temperatures encountered in compositions of low silica content. These solid solutions occur as the primary phase in portions of the field labeled carnegieite (Fig. 1). The several forms of silica (cristobalite, tridymite, and quartz) were encountered in their respective temperature ranges of stability except for compositions in and near the binary system albite—silica, which compositions are very viscous and sluggish and only cristobalite crystals were encountered even with long runs. In compositions which lie in the field where Al_2O_3 is the primary phase only corundum was present at liquidus temperatures. In some compositions

TABLE I.

Binary Invariant Points within the Ternary System Na_2O—Al_2O_3—SiO_2.

Letter (Figures 1 and 2)	Temperature °C.	Solid and Liquid Phases
I	1062 ± 3	Albite, tridymite and liquid (Na_2O 8.1 Al_2O_3 13.3 SiO_2 78.6 or albite 68.5 silica 31.5)
J	1470 + 10	Tridymite, cristobalite and liquid (Na_2O 3.7 Al_2O_3 6.1 SiO_2 90.2 or albite 31.5 silica 68.5)
E	767 ± 3	Albite, sodium disilicate and liquid (Na_2O 25.6 Al_2O_3 7.4 SiO_2 67.0 or albite 38 sodium disilicate 62)
O	1108 ± 3	Albite, corundum and liquid (Na_2O 11.6 Al_2O_3 20.7 SiO_2 67.7 or albite 98.5 corundum 1.5)
X	1475 ± 10	Carnegieite, corundum and liquid (Na_2O 20.3 Al_2O_3 40.4 SiO_2 39.3 or carnegieite 93 corundum 7)
Q	1068 ± 5	Albite, nepheline and liquid (Na_2O 14.2 Al_2O_3 23.4 SiO_2 62.4 or albite 76 nepheline 24) (Greig and Barth)
S	1280	Nepheline, carnegieite and liquid Na_2O 17.5 Al_2O_3 28.8 SiO_2 53.7 or albite 43 nepheline 57) (Greig and Barth)
U	768 ± 5	Nepheline, sodium disilicate and liquid (Na_2O 30.5 Al_2O_3 10.4 SiO_2 59.1 or nepheline 29 sodium disilicate 71) (Tilley)
V	1248 ± 5	Nepheline, carnegieite and liquid (Na_2O 25.3 Al_2O_3 25.6 SiO_2 49.1 or nepheline 71.4 sodium disilicate 28.6) (Tilley)

TABLE II.

Ternary Invariant Points in the System $Na_2O—Al_2O_3—SiO_2$.

Letter (Figures 1 and 2)	Temperature °C.	Solid and Liquid Phases
G	740 ± 5	Albite, quartz, sodium disilicate and liquid (Na_2O 21.5 Al_2O_3 4.7 SiO_2 73.8)
H	867 ± 3	Quartz, tridymite, albite and liquid (Na_2O 15 Al_2O_3 9 SiO_2 76)
M	1050 ± 10	Albite, tridymite, mullite and liquid (Na_2O 7.8 Al_2O_3 13.5 SiO_2 78.7)
L	1470 ± 10	Tridymite, cristobalite, mullite and liquid (Na_2O 2 Al_2O_3 9 SiO_2 89)
N	1104 ± 3	Albite, mullite, corundum and liquid (Na_2O 11.2 Al_2O_3 20.0 SiO_2 68.8)
P	1063 ± 5	Albite, nepheline, corundum and liquid (Na_2O 13.8 Al_2O_3 23.8 SiO_2 62.4)
R	1270 ± 10	Nepheline, carnegieite, corundum and liquid (Na_2O 17.0 Al_2O_3 29.5 SiO_2 53.5)
T	732 ± 5	Albite, nepheline, sodium disilicate and liquid (Na_2O 26.0 Al_2O_3 12.5 SiO_2 61.5)
G′	760 ± 5	Nepheline, sodium disilicate, sodium metasilicate and liquid (Na_2O 32.0 Al_2O_3 10.1 SiO_2 57.9) (Tilley)
F′	915 ± 5	Nepheline, carnegieite, sodium metasilicate and liquid (Na_2O 37.4 Al_2O_3 18.7 SiO_2 43.9)
E′	955 ± 5	Carnegieite, sodium metasilicate, sodium orthosilicate (?) and Liquid (Na_2O 44.0 Al_2O_3 16.5 SiO_2 39.5)

"β-Al_2O_3" was present as crystals in addition to corundum but the former (whatever may be its composition) was always metastable and disappeared on long heatings. Difficulties were encountered in studying compositions in the region of the field labeled "sodium orthosilicate?" in Fig. 1. Owing to the volatility of soda in this region, difficulty in removing CO_2 from melts (made from Na_2CO_3, Al_2O_3 and SiO_2), and attack of the platinum containers by the melts, no precise phase-equilibrium measurements were possible. Close determination of the optical properties of the crystals was impossible and we could not demonstrate that the crystals obtained were undoubtedly sodium orthosilicate.

Figure 2 shows the system $Na_2O—Al_2O_3—SiO_2$ with isotherms. The temperatures and compositions of the binary invariant points within the ternary system are given in Table I and similar data for the ternary invariant points are given in Table II.

THE SYSTEM K_2O—Al_2O_3—SiO_2.

The phase equilibrium relations in this ternary system are presented here by means of two diagrams (Figs. 3 and 4) and two tables (Tables III and IV).

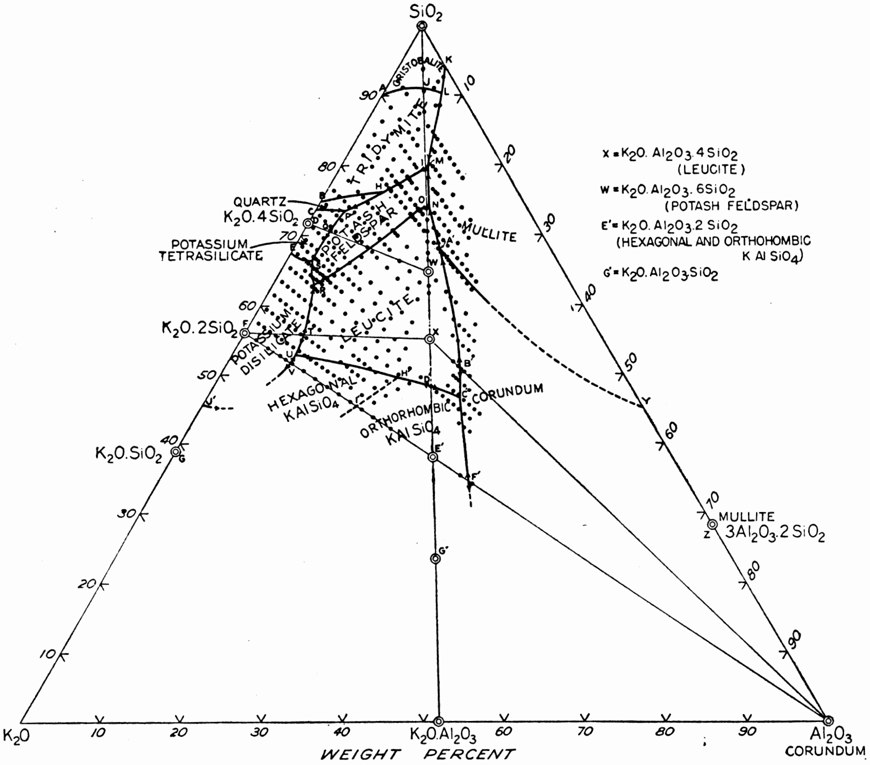

Fig. 3. Equilibrium diagram of the system K_2O—Al_2O_3—SiO_2 showing compositions studied and the fields of the primary crystalline phases.

Figure 3 shows the fields of the several crystalline phases which appear on the liquidus surface. These fields are separated by boundary curves. Arrows on these curves indicate falling temperature and show the positions of maxima. Dots represent the comparisons which have been investigated. Tie lines divide the ternary system into sub-systems and are binary systems (at least in part) within the ternary system. Not all of the tie lines are shown in Figs. 3 and 4.

There are six binary systems within the ternary system and one tie line is shown which is partially binary. They are as follows:

(1) Leucite—silica
(2) Leucite—corundum
(3) Potassium disilicate—leucite
(4) $KAlSiO_4$—leucite
(5) Potassium disilicate—$KAlSiO_4$
(6) $KAlSiO_4$—corundum
(7) Potassium tetrasilicate—potash feldspar (partially binary)

Four ternary compounds appear in the system K_2O—Al_2O_3—SiO_2 in addition to the solid phases which were found in the limiting binary systems K_2SiO_3—SiO_2[9] and Al_2O_3—SiO_2.[10] Potash feldspar ($K_2O.Al_2O_3.6SiO_2$ or $KAlSi_3O_8$) melts incongruently at 1150±20° C. to leucite (*X* of Fig. 3) and a liquid of composition *O* (Fig. 3) and therefore its composition *W* (Fig. 3) does not lie in its own field (*RSQPHIMNO* of Fig. 3). The tiny crystals of potash feldspar obtained in melts in these studies did not permit a decision as to whether they are orthoclase or microcline. Leucite ($K_2O.Al_2O_3.4SiO_2$ or $KAlSi_2O_6$) melts congruently at 1686±5° C. and shows an inversion somewhat above 600° C.[11] The compound $K_2O.Al_2O_3.2SiO_2$ (or $KAlSiO_4$) has several crystalline forms. Only two were encountered at the temperatures between the beginning of melting and the liquidus in this system, a hexagonal form stable below about 1540° C[12] and an orthorhombic form stable from this temperature to its congruent melting point not located exactly because of the high temperature but probably somewhat above 1750° C. The compound $K_2O.Al_2O_3.SiO_2$ (or $K_2Al_2SiO_6$) has been prepared by Weyberg,[13] using kaolin and potassium chromate as a flux. Because of

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[9] Kracek, F. C., Bowen, N. L., and Morey, G. W.: 1937, J. Phys. Chem., 41, 1183-1193.

[10] Bowen, N. L., and Greig, J. W.: 1924, J. Amer. Ceram. Soc., 7, 238-254.

[11] Bowen, N. L., and Schairer, J. F.: 1929, AMER. JOUR. SCI., (5) 18, 301-312.

[12] Bowen, N. L.: 1917, AMER. JOUR. SCI., (4) 43, 116-119.

[13] Weyberg, Z.: 1908, Centralblatt Min., pp. 326-330.

its high melting point, an attempt to prepare this compound in homogeneous form from a melt of its own composition was not successful. When the composition (made by mixing $KHCO_3$, Al_2O_3, and SiO_2) after several preliminary alternate

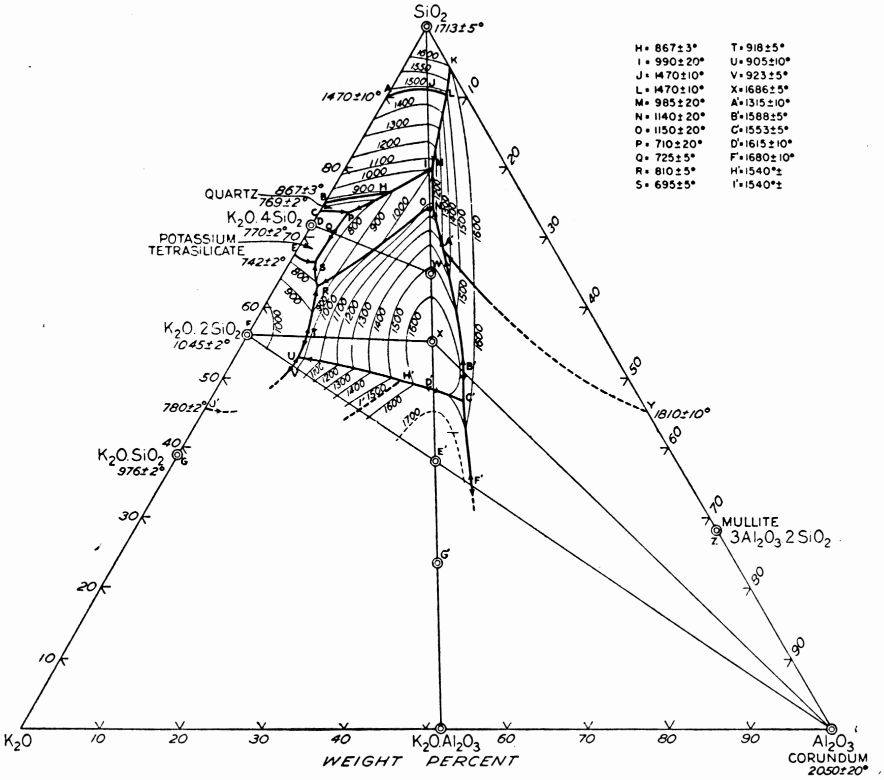

Fig. 4. Equilibrium diagram of the system K_2O—Al_2O_3—SiO_2 with isotherms. (This supersedes a preliminary diagram given by Bowen: 1943, Jour. Amer. Ceram. Soc., **26**, 296).

heatings at 1650° and crushing was heated to about 1710° C., it did not even sinter. Microscopic examination showed a large amount of this isotropic compound but the mixture still contained much undissolved alumina.

No solid solutions were encountered in the system K_2O—Al_2O_3—SiO_2. Some difficulties were experienced in obtaining the several forms of silica (cristobalite, tridymite, and quartz) in their respective temperature ranges of stability. In compositions in and near the binary system leucite—silica, no crystals of tridymite were obtained and only cristobalite was formed; indeed, in all of the compositions in this binary system whose silica liquidus was below 1345°C. no crystallization could be achieved in anhydrous melts, but the relations could be readily obtained by extrapolation from data on ternary compositions not too close to this tie line, which is a locus of viscous melts. Unlike our experience in connection with the system $Na_2O—Al_2O_3—SiO_2$, where quartz crystallizes readily from appropriate compositions at appropriate temperatures, we were not able to crystallize quartz in the system $K_2O—Al_2O_3—SiO_2$ from anhydrous melts of compositions which should show quartz as the primary phase. We always

TABLE III.

Binary Invariant Points within the Ternary System $K_2O—Al_2O_3—SiO_2$.

Letter (Figures 3 and 4)	Temperature °C.	Solid and Liquid Phases
I	990 ± 20	Potash feldspar, tridymite and liquid (K_2O 9.8 Al_2O_3 10.7 SiO_2 79.5 or leucite 45.6 silica 54.4)
J	1470 ± 10	Tridymite, cristobalite and liquid (K_2O 4.3 Al_2O_3 4.7 SiO_2 91.0 or leucite 20.0 silica 80.0)
O	1150 ± 20	Leucite, potash feldspar and liquid (K_2O 12.5 Al_2O_3 13.5 SiO_2 74.0 or leucite 57.8 silica 42.2)
Q	725 ± 5	Potassium tetrasilicate, potash feldspar and liquid (K_2O 26.1 Al_2O_3 3.3 SiO_2 70.6 or potassium tetrasilicate 82 potash feldspar 18)
T	918 ± 5	Potassium disilicate, leucite and liquid (K_2O 36.9 Al_2O_3 7.4 SiO_2 55.7 or potassium disilicate 68.3 leucite 31.7)
V	923 ± 5	Potassium disilicate, hexagonal $KAlSiO_4$ and liquid (K_2O 40.6 Al_2O_3 7.7 SiO_2 51.7 or potassium disilicate 76.1 $KAlSiO_4$ 23.9)
I′	about 1540	Hexagonal $KAlSiO_4$, orthorhombic $KAlSiO_4$ and liquid (approximately K_2O 35.6 Al_2O_3 19.0 SiO_2 45.4 or potassium disilicate 41 $KAlSiO_4$ 59)
B′	1588 ± 5	Leucite, corundum and liquid (K_2O 19.9 Al_2O_3 29.3 SiO_2 50.8 or leucite 92.2 corundum 7.8)
F′	1680 ± 10	Orthorhombic $KAlSiO_4$, corundum and liquid (K_2O 27.4 Al_2O_3 37.7 SiO_2 34.9 or $KAlSiO_4$ 92 corundum 8)
D′	1615 ± 10	Leucite, orthorhombic $KAlSiO_4$ and liquid (K_2O 24.8 Al_2O_3 27.0 SiO_2 48.2 or leucite 58.9 $KAlSiO_4$ 41.1)

TABLE IV.

Ternary Invariant Points in the System K_2O—Al_2O_3—SiO_2.

Letter (Figures 3 and 4)	Temperature °C.	Solid and Liquid Phases
P	710 ± 20	Potash feldspar, quartz, potassium tetrasilicate and liquid (K_2O 22.8 Al_2O_3 3.7 SiO_2 73.5)
H	867 ± 3	Quartz, tridymite, potash feldspar and liquid (K_2O 17.0 Al_2O_3 6.8 SiO_2 76.2)
M	985 ± 20	Potash feldspar, tridymite, mullite and liquid (K_2O 9.5 Al_2O_3 10.9 SiO_2 79.6)
L	1470 ± 10	Tridymite, cristobalite, mullite and liquid (K_2O 2.4 Al_2O_3 7.3 SiO_2 90.3)
N	1140 ± 20	Potash feldspar, leucite, mullite and liquid (K_2O 12.2 Al_2O_3 13.7 SiO_2 74.1)
A′	1315 ± 10	Leucite, mullite, corundum and liquid (K_2O 13.9 Al_2O_3 18.5 SiO_2 67.6)
R	810 ± 5	Potash feldspar, leucite, potassium disilicate and liquid (K_2O 32.1 Al_2O_3 5.3 SiO_2 62.6)
S	695 ± 5	Potash feldspar, potassium tetrasilicate, potassium disilicate and liquid (K_2O 30.4 Al_2O_3 3.2 SiO_2 66.4)
U	905 ± 10	Leucite, hexagonal $KAlSiO_4$, potassium disilicate and liquid (K_2O 39.3 Al_2O_3 7.8 SiO_2 52.9)
H′	about 1540	Hexagonal $KAlSiO_4$, orthorhombic $KAlSiO_4$, leucite and liquid (approximately K_2O 28.5 Al_2O_3 22.0 SiO_2 49.5)
C′	1553 ± 5	Leucite, orthorhombic $KAlSiO_4$, corundum and liquid (K_2O 22.1 Al_2O_3 31.3 SiO_2 46.6)

obtained the metastable tridymite liquidus. As in the system Na_2O—Al_2O_3—SiO_2, we found that, in compositions in the system K_2O—Al_2O_3—SiO_2 which lie in the field where Al_2O_3 is the primary phase, only corundum was present at liquidus temperatures. In some compositions "β-Al_2O_3" was present as crystals in addition to corundum, but the former (whatever may be its composition) was always metastable and disappeared on long heatings.

Figure 4 shows the system K_2O—Al_2O_3—SiO_2 with isotherms. The temperatures and compositions of the binary invariant points within the ternary system are given in Table III and similar data for the ternary invariant points are given in Table IV.

SUMMARY.

The phase equilibrium relations in the ternary systems Na_2O—Al_2O_3—SiO_2 and K_2O—Al_2O_3—SiO_2 are presented by means of four diagrams. Temperature and composition data are given for eleven ternary invariant points and nine binary invariant points in the system Na_2O—Al_2O_3—SiO_2 and for eleven ternary invariant points and ten binary invariant points in the system K_2O—Al_2O_3—SiO_2. The outstanding features of the two ternary systems are briefly presented. The very numerous data on which the diagrams are based and a full discussion of the preparation of the compositions studied, quenching data, the results and some of the applications will appear later.

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