[AMERICAN JOURNAL OF SCIENCE, VOL. 249, FEBRUARY, 1951, PP. 81-130]

American Journal of Science

FEBRUARY 1951

THE SYSTEM K_2O-MgO-SiO_2[1]

PART 1

EDWIN WOODS ROEDDER

ABSTRACT. The phase diagram of the more geologically significant portions of the condensed system has been determined by the quenching technique. Four new ternary compounds were found and their thermal relationships determined. Their compositions are $K_2O \cdot 5MgO \cdot 12SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, and $K_2O \cdot MgO \cdot SiO_2$(?). The first of these may occur naturally but has not been reported, possibly because of its optical similarity to quartz. The second and third appear to be isomorphous with leucite and kalsilite, respectively, and the last is of comparatively little geologic interest. Thermal, optical, and X-ray data are given for these compounds, and composition and temperature have been determined for 28 of the invariant points occurring in the system. Experimental technique, crystallization behavior, and geological application are discussed briefly.

INTRODUCTION

THE immediate purpose of this study was to aid the investigation of the four-component system K_2O-MgO-Al_2O_3-SiO_2 by Dr. J. F. Schairer,[2] which was studied because of its bearing on the stability relationships of the magnesian minerals forsterite, clinoenstatite, and cordierite, and the potash-alumina-silica minerals leucite, potash feldspar, and quartz. Four ternary systems limit the quaternary system K_2O-MgO-Al_2O_3-SiO_2. One of these, K_2O-MgO-Al_2O_3, has not been investigated because of the lack of direct geologic interest; two others, MgO-Al_2O_3-SiO_2 (Rankin and Merwin, 1918) and K_2O-Al_2O_3-SiO_2 (Schairer and Bowen, 1947a), have been studied previously; the fourth, K_2O-MgO-SiO_2, is the subject of this report. Although there is no naturally occurring mineral known consisting of K_2O, MgO, and SiO_2, during the course of the work several new ternary compounds of interest to petrology and mineralogy were found and are reported here.

[1] A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1950.

[2] Preliminary report in abstracts of papers presented at the meeting of the Geological Society of America in New York, 1948.

Potash, magnesia, and silica are among the seven most abundant constituents of igneous rocks, and Washington (1915) has shown a direct relationship between the amounts of potash and magnesia in certain rocks. The system is of interest also in the broader problem of the chemistry of silicate formation and stability. Only that portion of the condensed system higher in silica than the join $K_2O \cdot SiO_2$-MgO was studied.

In addition, the work was part of a long term project being carried on at the Geophysical Laboratory on the stability relations of the rock-forming dark micas—the biotites (Adams, 1947). As biotites are essentially hydrous, potash-magnesia-alumina silicates with a partial substitution of Fe^{++} for Mg^{++}, their compositions lie within the six-component system K_2O-MgO-FeO-Al_2O_3-SiO_2-H_2O. Since the presence of water and iron oxide causes considerable experimental difficulty, the most reasonable approach was a study of the system K_2O-MgO-Al_2O_3-SiO_2. A knowledge of the limiting system K_2O-MgO-SiO_2 is essential to an understanding of this quaternary system. The only previous work on the system K_2O-MgO-SiO_2 involved the addition of water as the fourth component to a small range of compositions with the formation of hydrated mica-like clay minerals (Noll, 1944). Another possible application of the system K_2O-MgO-SiO_2 is in the further study of the system MgO-SiO_2-H_2O (Bowen and Tuttle, 1949) where the addition of K_2O may aid the formation of a liquid phase (Adams, 1947).

This work was done at the Geophysical Laboratory of the Carnegie Institution of Washington on a one-year fellowship. The writer wishes to thank the Director of the Laboratory, Dr. L. H. Adams, for this opportunity, and Dr. J. F. Schairer, under whose direction the work was done, for his aid and encouragement. The writer is indebted also to the other members of the Laboratory for many helpful suggestions, and particularly to Drs. Schairer, Morey, and Yoder for a critical reading of the manuscript; however, the writer alone is responsible for any errors which may occur. He also expresses his appreciation for the cooperation, assistance, and advice of the members of the staff of the Geology Department of Columbia University, particularly to Professor C. H. Behre, Jr., who initiated the original discussions leading to the au-

thor's connection with the Geophysical Laboratory; to Professor Paul F. Kerr for his cooperation in making this arrangement possible; and to Professor Ralph J. Holmes for advice on X-ray diffraction techniques.

EXPERIMENTAL PROCEDURE

Raw Materials.—The starting materials for most of the compositions were $KHCO_3$, quartz, and MgO. The $KHCO_3$ was of reagent grade,[3] and was prepared by crushing to a powder and drying over KOH. The quartz used was the regular Geophysical Laboratory supply of Lake Toxaway quartz, crushed and leached with HCl. Analysis by J. W. Greig gave a residue of 0.04 per cent (using 5 grams) on evaporation with HF and H_2SO_4. It was prepared for weighing by heating for two or more hours at 1500° C.[4] This heating serves to eliminate liquid inclusions and converts the quartz to cristobalite, facilitating subsequent grinding in an agate mortar. In a few special batches Mallinckrodt "Special Bulky" silicic acid was used because of its fine grain size,[5] but in these cases a water analysis had to be made simultaneously because of its large and variable amount (15.5 per cent). The MgO used was reagent grade,[6] although analysis by J. F. Schairer showed 0.2 per

[3] J. T. Baker Chemical Co., Lot no. 12733 analysis:

	per cent
Cl	0.003
PO_4	0.001
NH_3	0.000
Fe	0.000
SO_4	0.001
Heavy metals (as Pb)	0.000
Ca, Mg, and NH_4OH ppt.	0.00

[4] All temperatures are in degrees Centigrade.

[5] The powder has a bulk density of only 0.11 grams per cc.

[6] J. T. Baker Chemical Co., Lot no. 82735 analysis:

	per cent
Insol. in HCl	0.02
Loss on ign	2.5 (10.35 E. R.)
Soluble in H_2O	0.4
Heavy metals (as Pb)	0.0035
NH_4OH ppt.	0.02
$(NH_4)_2S$ metals (as Fe)	0.008
Sulfate and sulfite	0.005
SiO_2	0.01
Cl	0.008
NO_3	0.005
Ca	0.05 (<0.2 J. F. S.)
Ba	0.005

cent total alkalies. It was prepared for weighing by heating to 1500° for one hour. This minimizes water adsorption, but corrections still had to be applied to each portion weighed, as determined by individual weight-loss measurements upon ignition of each portion weighed.

Preparation of Potassium Silicates.—In almost every case the $KHCO_3$ was first converted to a pure, completely crystalline potassium silicate compound ($K_2O \cdot 4SiO_2$, $K_2O \cdot 2SiO_2$, or $K_2O \cdot SiO_2$) before using in order to minimize volatilization of K_2O during the preparation of the various compositions. A glass of the composition of the desired potassium silicate compound is first made by mixing together on low-ash filter paper the stoichiometric amounts of $KHCO_3$ and SiO_2 to give 20 grams of the silicate. The mixture and the paper are put into a 40 cc. platinum crucible, carefully heated up to 1000° over a predetermined 48-hour heating schedule to minimize foaming and volatilization of K_2O (Kracek, 1932, p. 2529), and finally heating for two hours at 1300°. When cool it is weighed; any loss in weight in excess of the CO_2 and H_2O given off by the $KHCO_3$ is attributable only to volatilization of K_2O and must be corrected for by the addition of the calculated amount $KHCO_3$.[7] Furthermore, the batch is far from homogeneous at this stage and must be carefully removed from the crucible, crushed, replaced, and remelted again for two hours at 1300°, the process being repeated until a completely homogeneous glass is obtained. The extremely hygroscopic nature of this glass and the persistence of small amounts of CO_2 make is necessary to crystallize it, this being done by holding it at appropriate lower temperatures with occasional crushings until it remains a completely crystalline powder at the temperature of the furnace. As long as uncrystallized glass is present the powder will sinter together in the furnace. This crystallization is completed in 3 to 4 days,[8] after which the

[7] The amount of this volatilization of K_2O is small—usually less than 10-20 mg. in a 20 gm. batch—but sufficiently variable due to irregularities in the process that it must be corrected for in each batch separately. After this first fusion at 1300° further volatilization is found to be insignificant, and the volatility of silica at these temperatures is practically nil (see Sosman, 1927, p. 109). In those cases where the metasilicate, $K_2O \cdot SiO_2$, was made up, failure to eliminate all of the CO_2 caused troubles which will be considered beyond under "Alkali Losses."

[8] "Seeding" with previously obtained crystals has to be resorted to in the case of $K_2O \cdot 4SiO_2$ because of its sluggish crystallization.

crystalline powder may be kept over KOH with little gain in weight except in the case of $K_2O \cdot SiO_2$.

Preparation of Batches.—All except the high alkali compositions were determined entirely by synthesis. The calculated amounts of potassium silicate, magnesia,[9] and silica were weighed out to make the individual compositions listed in table 1. Ten grams was a convenient amount to make and should be less affected by systematic errors. Each batch was carefully mixed on low-ash filter paper and heated to 1300-1500° in a 15 cc. platinum crucible for one or more hours,[10] depending upon the viscosity of the liquid, then quenched, crushed,[11] replaced in the same crucible, and fused again. This process was repeated until a homogeneous glass was obtained. The homogeneity was checked by microscopical examination of the crushed glass when immersed in an index oil exactly matching the glass, making use of the more rapid change of the index of refraction of the oil with change in temperature to obtain a perfect match. Extremely small local variations in the composition of the glass result in index variations which are rather prominent by this method. Viscous batches may take five or even more such fusions alternating with crushings before becoming homogeneous.[12] As has been emphasized else-

[9] The small amount (0.05-0.10 per cent) of water taken up by the MgO during storage over KOH (following the 1500° ignition) was corrected for by weighing out the magnesia first into the crucible, igniting at 1300° for 15 minutes, reweighing and correcting for the loss in weight before adding the other components.

[10] Weight loss determinations on a number of such batches (using a smooth plate cut from a corundum crystal as a plaque) showed practically neglible volatilization of alkalies, as changes in weight were within the limits set by the vaporization and condensation of platinum in the furnace at such temperatures. In the high alkali portion of the system weight losses were sizable (see "Alkali Losses" beyond).

[11] The laborious process of fine grinding of many samples is made considerably easier through the use of a Plattner-type hardened steel "diamond" mortar with the crushing end of the pestle of smaller diameter than the main pestle shaft and eccentric to it. The use of a steel mortar is recommended in place of other materials because contamination of the sample can be kept to a minimum through magnetic separation after each grinding. It has been shown (Sandell, 1947) that, without magnetic separation, grinding of quartz in a Plattner-type mortar yields 0.02 to 0.03 per cent Fe in the ground material.

[12] The higher alkali glasses cannot be made perfectly homogeneous by this method as small variations in index persist indefinitely, presumably due to volatilization of alkali from the surface. The later crystallization of these glasses, however, forming crystals with individual compositions different from that of the glass, represents a far greater degree of "inhomogeneity" than occurs in the glass.

where, this homogenization is an important and essential step if true equilibrium is to be obtained in the subsequent quenching experiments with the material.

Crystallization of the Batches.—All compositions were precrystallized partially or completely before quench runs were made.[13] To do this a portion of the homogeneous glass obtained above was held at temperatures which were 50 to 100°[14] below the approximated liquidus (as predicted by experience and extrapolation from nearby points). The viscosity of the more viscous glasses increases rapidly with decrease in temperature, hence the crystallization velocity is so small as to be experimentally impractical if crystallization is attempted at much more than 100° below the actual liquidus, and, of course, no crystallization can occur if held above the liquidus temperature. Even under optimum conditions (correct temperature, frequent crushings, etc.) batches in the vicinity of the two lowest ternary eutectics did not begin to show visible crystals (1-2 microns in length) within the first month of crystallization. Such batches could not be completely crystallized in the time available for these studies, but many of the others could be, and these completely crystalline preparations were useful in determining eutectic temperatures. The viscosities of the glasses in a few cases were found to be so high that the powdered glass would not flow together to a coherent mass even when held for 24 hours at temperatures near the liquidus. Elsewhere in the system the viscosities were lower and liquidus temperatures were higher, so crystallization was usually initiated within a few days or even within a few seconds (in the very high temperature, low silica melts). Microscopical examination at frequent intervals during the crystallization provides a very rough but useful indication of the phases and temperatures to be expected during the quenching experiments. Wherever possible coarse crystallization was avoided

[13] In most silicate studies this is essential because of the sluggishness of crystallization compared with melting. In some cases it was found that compositions which required months at optimum temperatures to form the first visible crystal nuclei and weeks more, with frequent crushings, to convert even a small percentage of the glass to crystals, would attain equilibrium in less than a week in the quenching runs, where equilibrium is approached by melting rather than by crystallization.

[14] H. R. Swift (1947) found that 40-100° gave the highest rate of crystal growth for a number of silicate compounds but that there was wide variation. See also the discussion of crystallization velocity in Tammann (1925).

because of the long time necessary to attain equilibrium between crystals and liquid during the quenching experiments with such material. A few of the more viscous melts with very low liquidus temperatures had to be subjected to "hydrothermal" conditions[15] in order to induce crystallization, but in these cases subsequent "dry" crystallization was usually possible (on another portion of the glass) after the correct temperature range had been determined on the "hydrothermally" formed crystals.

Quenching Technique.—All of the equilibrium data was obtained by the quenching technique (Shepherd, Rankin, and Wright, 1909; Ferguson and Merwin, 1919; Faust, 1936; and Hill, Faust, and Reynolds, 1944). A charge of about 10 mg. of the crystalline material in a small 0.01 mm. platinum-foil envelope[16] is suspended in the hottest portion of the furnace (region of minimum thermal gradients), with a thermocouple junction about 1 mm. to the side of the center of the envelope, for a length of time sufficient to attain equilibrium

[15] The method used involved sealing two cylindrical loosely-covered, platinum-foil capsules into a fused silica tube. One capsule contained approximately 0.2 gm. of the powdered glass to be crystallized and the other about the same amount of ground obsidian. The obsidian used was that from Mono Craters, California, containing approximately 0.07 per cent F, 0.13 per cent Cl, 0.2 per cent H_2O^+, an unknown amount of H_2S, and with SiO_2 and Al_2O_3 76 and 12 per cent respectively (see Shepherd, 1938). A sample of the ground obsidian was fused and showed a 0.41 per cent weight loss when ignited over a Meker burner.

The whole tube was then put into the furnace at about 100° below the estimated liquidus of the glass to be crystallized. The heat drives some of the volatile "mineralizers" out of the obsidian and into the atmosphere of the tube, from which a portion is absorbed by the glass sample. Although the partition of these volatiles between the obsidian, the tube atmosphere, and the glass sample is not known, the glass can hardly have more than one-third of the total amount present, and may possibly have much less, but this small amount of "volatiles" dissolved in the glass is adequate to induce crystallization in extremely viscous glasses in 24 hours, where holding for one month at the correct temperature in the "dry" condition (*i.e.*, with only the partial pressure of water naturally occurring in the air in the furnace) caused no crystallization.

[16] To make these envelopes a piece of foil approximately 10 x 16 mm. is folded so that the 10 mm. edges are together. The 8 mm. sides are then folded back over themselves twice, taking about 1 mm. each time. The resultant 6 x 8 mm. envelope is spread open at the top, the charge is inserted, and the top is then folded down. A pinhole through this top fold permits hanging. If the folds are pressed tightly, they will not leak, except in the case of high-alkali compositions where a double envelope is needed.

and then dropped out of the furnace into cold mercury by suddenly melting a thin (0.2 mm.), supporting, platinum wire by an electric current. The "quenched" foil envelope is torn apart and the crushed sample examined with standard petrographic immersion methods (and X-ray where necessary and possible) to determine what crystalline phases were present at the temperature of the furnace, any liquid present having quenched to a glass. In a few cases, particularly at high temperatures and where quenching was not as rapid as desired, feathery crystals formed around each of the euhedral crystals present in the glass, or around other nuclei such as the thin platinum crystals that form on the surface of the melt from furnace vapors. Because the amount of such crystallization varied directly with the quenching time, the feathery crystals obviously formed on quenching and could be ignored.

One minor change in the usual technique permitted the heating of a larger number of different quench charges simultaneously within the same furnace.[17] Previously porcelain rings were used as separators between the platinum envelopes of such charges to prevent the welding together of the platinum surfaces. The substitution of slips of ordinary white glazed paper for these porcelain rings was found satisfactory, the ash from the paper being sufficient to keep the platinum surfaces from touching at temperatures below 1040°. Above this temperature fusion of the paper ash makes it necessary to substitute filter paper slips, dipped in a thin suspension of MgO. With this procedure 10 runs could be made simultaneously whenever desired. Even with 10 envelopes, the resultant bundle is smaller than the former maximum bundle of 4 envelopes and 3 porcelain rings, and also more thermally conductive, resulting in smaller thermal gradients throughout the bundle and more rapid quenching.

Determination of Equilibrium.—The attainment of equilibrium in the quench runs was established by several criteria:

1. Absence of rounded or corroded crystals—this is not a reliable criterion either as positive or as negative evidence but is a useful indication.

[17] Whenever possible several different charges were run simultaneously to save furnace time. The bundle of charges was sufficiently small to be entirely within the region of neglible temperature variation, a cylindrical space approximately 1 x 1 cm. By this procedure differences between batches could be detected even though they were smaller than the accuracy of the calibration of the thermocouple.

2. Agreement of data with nearby points and with other data on the same point—this is particularly useful.

3. Duplication of results by starting with the same composition in a different physical state (*e.g.*, crystalline and glassy)—this is experimentally feasible only in the more easily crystallized batches.

4. Lack of further change when held at the same temperature for a longer time—this is the best criterion.

5. Uniformity of distribution of the phases—this is useful to detect inhomogeneity in the original sample.

None of these criteria is really adequate to detect differences between stable and metastable equilibrium when the change is sluggish as in the extension of the field of tridymite over that of quartz, and the fourth is of no value in the high alkali preparations where the composition is changing during the duration of the run. The third criterion was applied in many cases but only the data for the crystalline material are given in the following tables to save space. Initiation of crystallization was so sluggish in most cases that nuclei (traces of crystalline material) were added to all quench runs starting with glassy material. As with many silicate systems the determination of the appearance of a phase at equilibrium practically requires that that phase be present, at least in traces, in the starting material, whether it be mainly crystalline or glassy. For this reason compositions having complicated crystallization paths involving the formation and subsequent disappearance of several phases during the cooling history were crystallized by various methods on separate portions, so that starting material having all the necessary phases present to establish a given phase change was available for each such determination. Obvious cases of minor local inequilibrium such as failure of a crystal to react with liquid owing to its inclosure by another crystal have been ignored in the data tables. Approximately 1300 quenching runs were made at temperatures which were not immediately adjacent to the temperature of a phase change and hence are not listed in the tables of quenching data. These served, however, as confirmatory evidence to substantiate those runs made at the more critical temperatures. In those cases in the data tables where two runs establishing a phase change have been made for different lengths of time, confirmatory runs at nearby tempera-

tures during the course of the work had established the shorter length of time as adequate to obtain equilibrium.

Temperature Measurement.—Temperatures were determined with thermocouples of Pt against Pt 90 Rh 10 measured with a shielded, double White potentiometer and galvanometer system reading directly to microvolts. The annealed thermocouples (Roeser and Wensel, 1935) were calibrated as frequently as drifting necessitated.[18] The melting points of pure NaCl (800.4°), gold (1062.6°), diopside (1391.5°), and pseudowollastonite (1544°) were used to establish the temperature scale. The NaCl was prepared for use by two precipitations with concentrated HCl from a solution of high purity reagent grade NaCl, followed by washing, drying, grinding, and final drying at 100°. It had a negligible melting range. The gold was "proof gold," obtained from the U. S. Mint, and also had a negligible melting range. This was not true of the diopside and pseudowollastonite, which, though synthesized from the purest available chemicals, had appreciable melting ranges (about 30 and 10 microvolts respectively from the first visible liquid formation to the disappearance of the last crystal). For this reason the temperature of melting of the last trace of crystals was considered to be the melting point. These four melting points are thus the basis of all of the temperature measurements, the deviation of the thermocouple from standard reference tables being used for convenience in interpolation (Sosman, 1910).

Many of the possible sources of error in the correct measurement of temperatures are eliminated or minimized by performing the calibration runs in exactly the same manner as the quenching runs,[19] so that thermal gradients within the sample

[18] The drift between calibration runs is variable and only its order of magnitude is predictable. High alkali compositions and high temperatures considerably increase the rate of drift. A platinum quench envelope sticking to a thermocouple necessitates immediate recalibration. The use of iridium-free platinum throughout the apparatus aids a great deal in stabilizing the emf of the thermocouples. (See Day, Shepherd, and Wright, 1906, p. 286.)

[19] In the case of gold calibration, a tiny sliver of gold sheet is held in a thin porcelain tube 5 mm. long with asbestos plugs. This tube is then inserted in a platinum envelope similar to those used in the quenching runs. After the calibration run the sliver is examined; if the temperature was below the melting point of gold, the sliver will be unaffected; if above, it will have coalesced to a globule. The coalescence from a white powder to a clear mass indicated melting in the case of NaCl. The diopside and pseudowollastonite runs were examined microscopically for amounts of glass and crystals.

and thermocouple are identical in both cases. The effect of inhomogeneities in the thermocouple wire away from the junction itself and differences in the temperature of the thermocouple junction and the sample itself thus become relatively insignificant. All cold junctions were kept in melting ice.

The hottest portion of the furnace varies with temperature and time and hence must be located prior to the run by exploring the furnace tube with the thermocouple; the thermal gradients and sample size are such that no portion of the sample may vary more than a few tenths of a degree from that of the thermocouple junction, the method of calibration correcting for a portion of this. The details of furnace construction and regulation have been published previously (Adams, 1924; Roberts, 1925, 1941; and Faust, 1936). Furnace temperature control can be considered to be constant to $\pm 0.3°$ approximately for runs of a few hours duration and $\pm 0.5°$ approximately for longer runs. The temperature during runs of over six hours at temperatures of over 1400° was only constant to $\pm 1.0°$.[20]

The frequency of calibration of the thermocouples, and hence the accuracy to which any given temperature determination on the following pages was made, varied with the sensitivity of the phase change being measured,[21] the temperature, and the nature of the batch (change in composition during the run makes accurate temperature measurement superfluous in the high alkali batches). Relative temperature determinations made by running several samples simultaneously in the same furnace are, of course, far more accurate than absolute determinations. By this means small differences between batches could be detected although they were less than the absolute accuracy of the temperature measurements as determined by the calibration technique. The frequency and nature of the calibration and the spacing of the quenching runs were such that most of the liquidus determinations are accurate to $\pm 3°$. Whenever possible, more careful work was done in the vicinity

[20] This is due mainly to volatilization of platinum from the winding of the furnace and consequent change in its electrical resistance, since the furnace temperature control is based on the furnace winding being one "arm" of a balanced Wheatstone bridge.

[21] Theoretically phase changes should occur with an extremely small ΔT, but in silicate systems of this type the rate of attainment of equilibrium makes such determinations experimentally impractical when ΔT approaches 1° or less, except for the more fluid batches and at the melting points of compounds.

of the invariant points, with the resultant accuracies as stated in table 5.

LIMITING BINARY SYSTEMS

Three binary systems limit a ternary system. Two of the limiting binary systems, MgO-SiO_2 (Kanolt, 1913; Ruff, 1913; Bowen and Andersen, 1914; and Greig, 1927), and K_2O-SiO_2 (Niggli, 1913; Morey, 1914; Morey and Fenner, 1917; Kracek, Bowen, and Morey, 1929, 1937; Kracek, 1930a, 1932; Goranson and Kracek, 1932; and Kröger and Fingas, 1933), have been studied and the diagrams of these are reproduced in figures 1 and 2. All of the compositions prepared in this study were ternary mixtures, hence no new data was obtained on these limiting binaries. Extrapolation from the ternary data to the sidelines, however, is concordant with the data on these two binary systems. No data on the system K_2O-MgO have been published, and since all compositions made

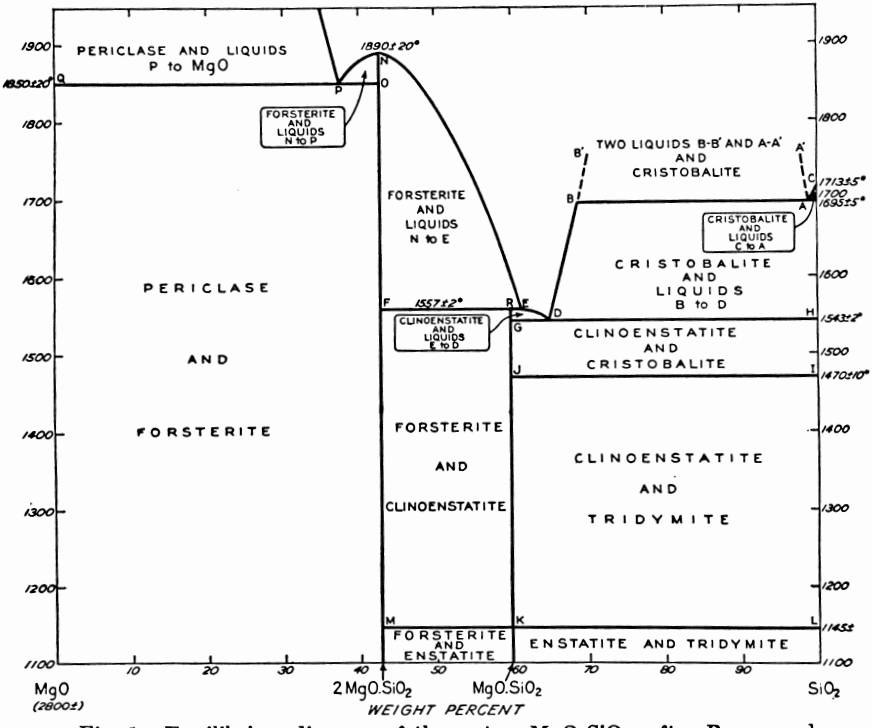

Fig. 1. Equilibrium diagram of the system MgO-SiO_2, after Bowen and Andersen (1914) as modified by Greig (1927).

in this investigation had over 30 per cent SiO_2 in them, nothing can be said here concerning it.

EXPERIMENTAL RESULTS

General Statement.—The compositions by synthesis of the 133 mixtures studied are listed in table 1 and plotted on figure 3, along with the boundary curves (heavy, solid or dashed lines), fields (primary phase areas), and tie lines (light lines). Arrows on boundary curves indicate direction of falling temperature. Figure 4 is a plot of the isofracts and curves of

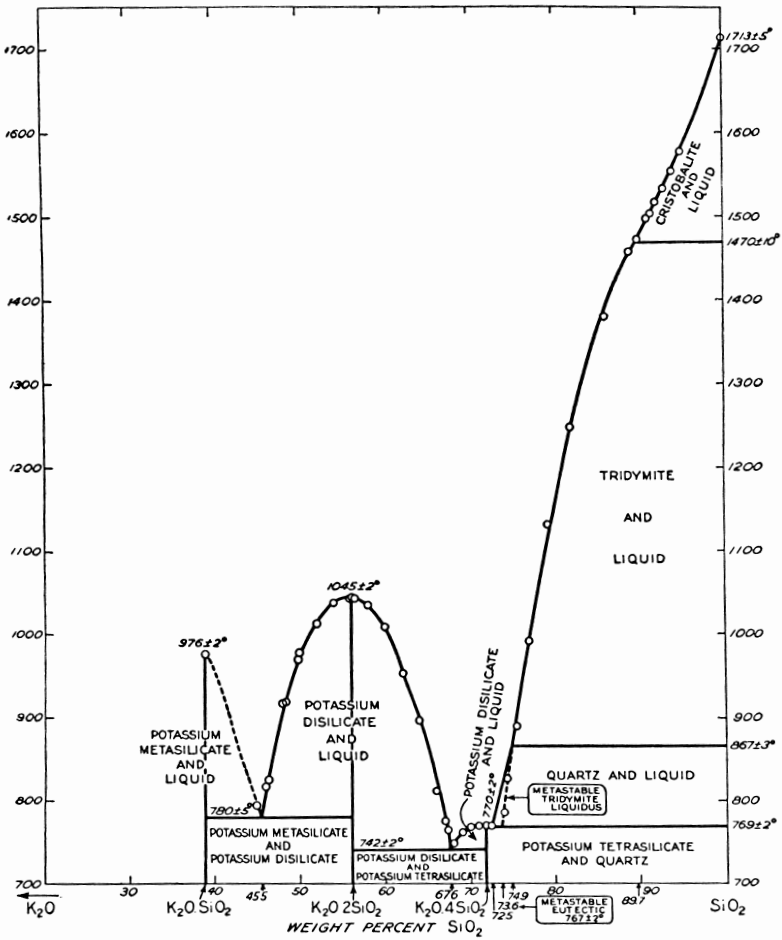

Fig. 2. Equilibrium diagram of a portion of the system K_2O-SiO_2, after Kracek, Bowen, and Morey (1937).

equal density for the various glasses obtained. The data for the indices of refraction are given in table 1. No great accuracy is claimed for these data; they were obtained by the immersion method, with white light, on the unannealed glasses quenched from temperatures above the liquidus. They were useful, however, in determining very roughly the composition of the liquid in some quench runs and as convenient checking details. Most of these indices are probably accurate to ± 0.003, although a few, particularly in the higher alkali portion where water adsorption and reaction with the index liquid causes trouble, may have less accuracy. Reaction with the index oil prevented obtaining a figure in several cases. The sharp bend

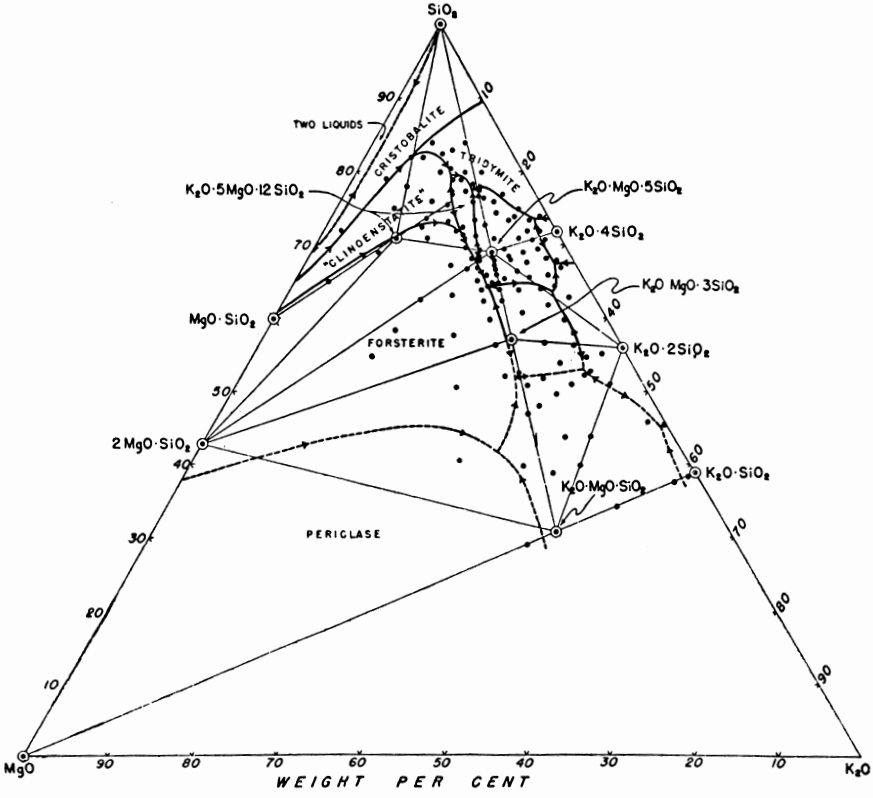

Fig. 3. Equilibrium diagram of the system K_2O-MgO-SiO_2, showing the compositions studied (plotted in weight per cent, by synthesis), compounds, boundary lines, and composition triangles (Alkemade lines). The tridymite field below 867° is metastable.

in the isofracts and in the curves of equal density[22] at the 1:1 K_2O:MgO ratio line of compounds is particularly inter-

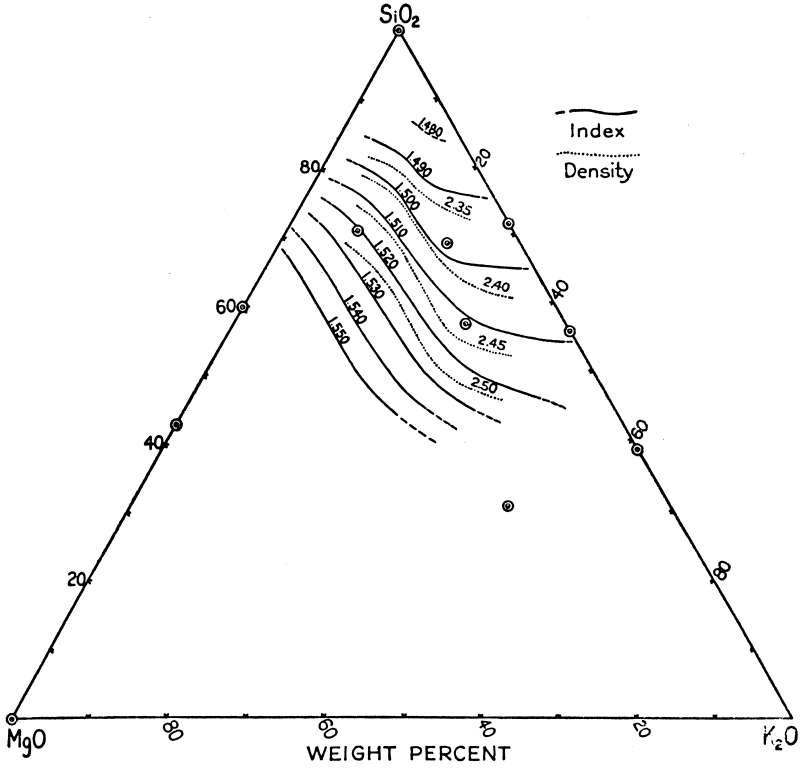

Fig. 4. Index of refraction and density of the glasses. See text for details. Circles indicate the composition of compounds.

[22] These curves of equal density are merely approximate as only 12 glass densities were determined; these data, although inaccurate for several reasons, were adequate to establish the curvature shown. The actual densities found were as follows:

Composition	*d*
2	2.44
8	2.48
10	2.54
11	2.40
17	2.50
25	2.38
28	2.41
32	2.38
58	2.44
72	2.39
75	2.36
80	2.34

esting in view of recent work on the effect of the molecular structure of glass on its properties (Lukesh, 1948), although more accurate refraction determinations as well as density measurements are needed.

In figure 5 the isotherms and temperatures of invariant points have been added. The essential data from which this diagram has been drawn are given in tables 1-5. Compositions higher in MgO or K_2O than those in the tables were not studied because of the lack of direct geologic interest and because of experimental difficulties. All data below the join $2MgO \cdot SiO_2$-$K_2O \cdot 2SiO_2$ (*LE*, fig. 5) are considered to be of a reconnais-

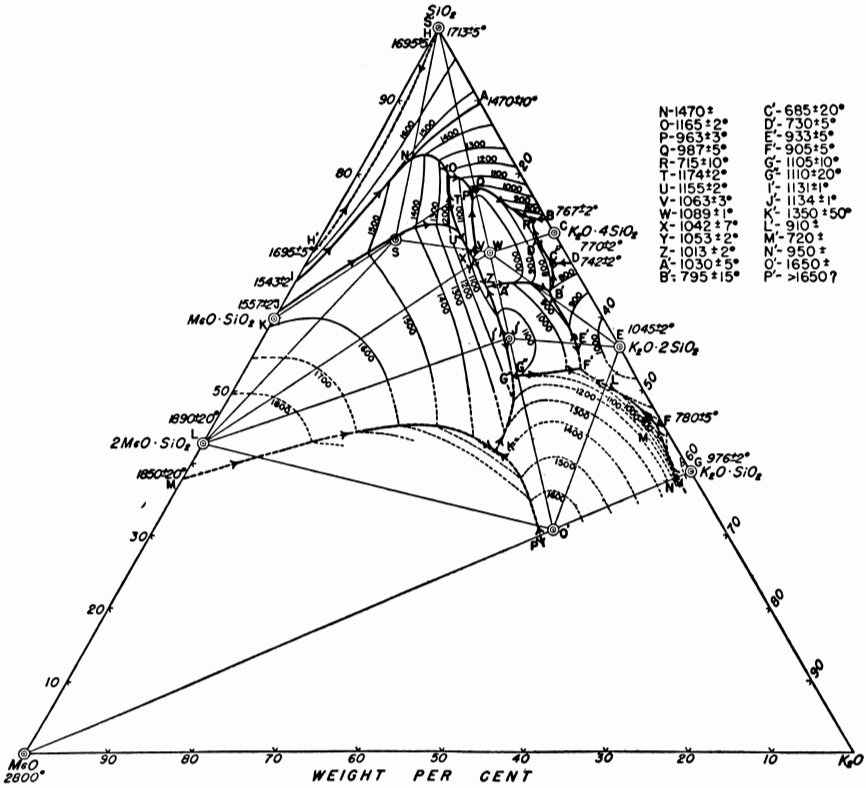

Fig. 5. Equilibrium diagram of the system K_2O-MgO-SiO_2, showing isotherms and invariant points. The tridymite field below 867° is metastable, hence binary eutectic point B and ternary eutectic point R are both metastable. For an enlarged plot of the sub-system Forsterite-$K_2O \cdot MgO \cdot 5SiO_2$-$SiO_2$ (triangle LWS′) see figure 8. Data below a line between $2MgO \cdot SiO_2$ and $K_2O \cdot 2SiO_2$ (LE) are of a reconnaissance nature; see footnote 49.

sance nature, although they are fairly concordant among themselves. In addition to the compounds already known to occur in the limiting binary systems MgO-SiO_2 and K_2O-SiO_2, four new ternary compounds were found during the course of the work. They have the compositions $K_2O \cdot MgO \cdot SiO_2$(?), $K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, and $K_2O \cdot 5MgO \cdot 12SiO_2$. A portion of figure 5 (the triangle *LWS'*, $2MgO \cdot SiO_2$-$K_2O \cdot MgO \cdot 5SiO_2$-$SiO_2$) has been recalculated in terms of these three components and replotted on a larger scale in figure 8 to show courses of crystallization, etc.

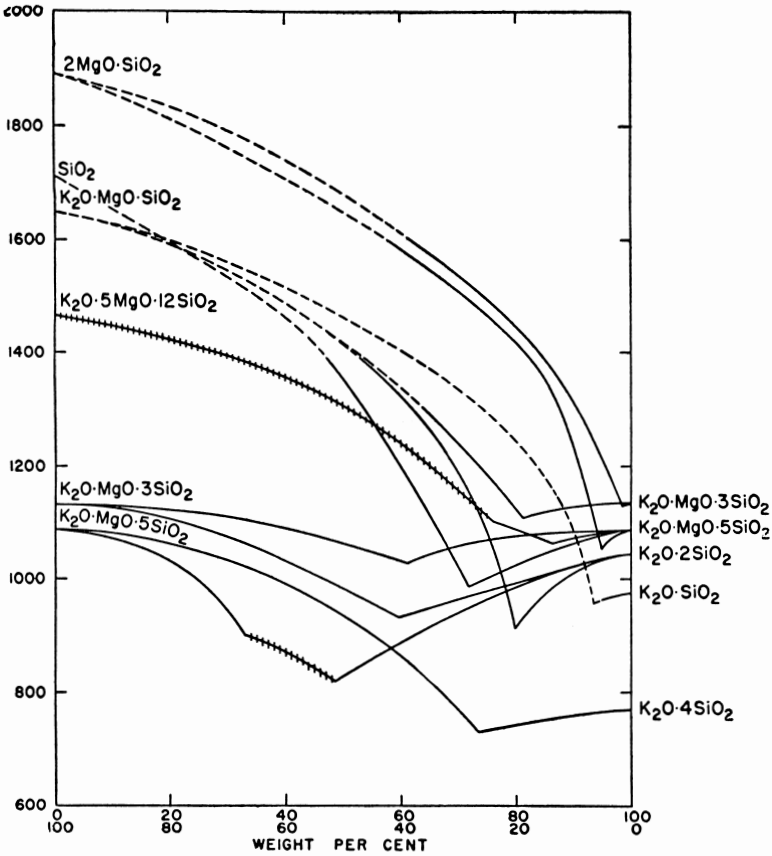

Fig. 6. Sections through the ternary system along the various binary sub-systems. The two cross-hatched lines indicate non-binary (ternary) equilibrium for those portions. Several of the binary systems that are almost wholly non-binary at liquidus temperatures have been omitted. Data taken from tables 1 to 3.

TABLE 1

COMPOSITION OF THE PREPARATIONS STUDIED

The percentages are weight per cent by synthesis (see text and table 7 for analysis of high alkali batches). The molecular weights used in the calculation were K_2O-94.20, MgO-40.32, and SiO_2-60.06. Mol ratio is the molecular ratio K_2O:MgO:SiO_2.

Mol Ratio	Prep.	Per Cent K_2O	MgO	SiO_2	n of Glass	Mol Ratio	Prep.	Per Cent K_2O	MgO	SiO_2	n of Glass
1:1:6	1	19.03	8.15	72.82	1.499		47	12.00	9.00	79.00	1.492
1:2:6	2	17.60	15.07	67.33	1.512		48	16.00	12.00	72.00	1.499
1:3:6	3	16.36	21.01	62.63	1.528		49	13.00	16.00	71.00	1.507
1:4:6	4	15.29	26.19	58.52	1.534		50	2.00	26.00	72.00	1.534
1:5:6	5	14.35	30.72	54.93	1.547		51	26.00	2.00	72.00	1.493
1:6:6	6	13.53	34.73	51.74	(1)		52	27.18	2.00	70.82	1.496
1:8:6	7	12.12	41.51	46.37	(1)		53	31.00	2.00	67.00	1.497
1:1:2	8	36.99	15.83	47.18	1.527		54	28.46	15.00	56.54	1.515
1:2:2	9	31.94	27.34	40.72	1.554	2:2:9	55	23.27	9.96	66.77	1.500
1:2:3	10	26.53	22.71	50.76	1.531		56	4.00	31.00	65.00	1.551
1:1:3(2)	11	29.93	12.81	57.26	1.510		57	31.68	16.00	52.32	1.517
	12	18.24	12.00	69.76	1.505		58	40.12	5.00	54.88	1.508
	13	37.36	8.60	54.04	1.512		59	32.00	6.00	62.00	1.503
2:1:8	14	26.57	5.68	67.75	1.501		60	31.50	4.00	64.50	1.499
1:1:4	15	25.14	10.76	64.10	1.506		61	27.50	8.50	64.00	1.500
	16	18.65	10.00	71.35	1.502		62	25.00	9.50	65.50	1.501
	17	8.00	23.00	69.00	1.524		63	24.48	7.50	68.02	1.497
2:2:5	18	33.09	14.16	52.75	1.517		64	22.50	9.50	68.00	1.498
	19	7.00	18.00	75.00	1.512		65	23.99	7.50	68.51	1.497
	20	13.00	10.00	77.00	1.495		66	20.02	10.50	69.48	1.498
2:1:4	21	40.17	8.60	51.23	1.515		67	19.50	6.00	74.50	1.493
	22	26.00	14.00	60.00	1.512		68	17.00	6.50	76.50	1.490
	23	27.87	6.41	65.72	1.503		69	22.91	7.50	69.59	1.497
	24	35.00	5.00	60.00	1.507	4:2:17	70	25.49	5.45	69.06	1.498
1:1:5(3)	25	21.67	9.27	69.06	1.498	1:2:5	71	19.83	16.97	63.20	1.515
1:2:4	26	22.69	19.43	57.88	1.522	1:2:9	72	13.17	11.27	75.56	1.498
	27	10.00	10.00	80.00	1.494		73	11.00	8.50	80.50	1.490
	28	7.00	15.00	78.00	1.502		74	15.00	7.00	78.00	1.490
	29	11.00	13.00	76.00	1.503		75	24.00	2.50	73.50	1.493
	30	19.00	4.00	77.00	1.490		76	28.61	3.20	68.19	1.497
	31	41.76	2.86	55.38	1.510		77	22.53	11.46	66.00	1.503
	32	34.00	3.00	63.00	1.506		78	21.00	12.00	67.00	1.503
	33	29.49	9.61	60.90	1.509		79	19.72	12.05	68.23	1.502
							80	5.50	12.50	82.00	1.496
	35	7.00	11.00	82.00	1.494		81	9.00	8.50	82.50	1.488
1:2:8	36	14.38	12.30	73.32	1.504		82	16.00	6.50	77.50	1.490
	37	16.00	8.00	76.00	1.493		83	18.50	5.50	76.00	1.490
	38	11.00	5.00	84.00	1.483		84	24.50	3.50	72.00	1.496
	39	7.00	9.00	84.00	1.487		85-85a	25.71	3.50	70.79	1.496
	40	4.00	17.00	79.00	1.505		86	27.00	3.50	69.50	1.497
	41	15.00	5.00	80.00	1.485		87	17.50	9.00	73.50	1.497
	42	22.00	4.00	74.00	1.495		88	16.50	11.00	72.50	1.498
	43	21.00	8.00	71.00	1.497		89	17.00	11.50	71.50	1.498
	44	24.00	5.00	71.00	1.497	1:3:10	90	11.55	14.83	73.62	1.503
	45	10.00	7.00	83.00	1.485		91	37.78	5.64	56.78	1.508
	46	13.00	7.00	80.00	1.487		92	34.14	8.97	56.89	1.508

TABLE 1 (*Continued*)

Mol Ratio	Prep.	Per Cent K_2O	Per Cent MgO	Per Cent SiO_2	n of Glass	Mol Ratio	Prep.	Per Cent K_2O	Per Cent MgO	Per Cent SiO_2	n of Glass
	93	26.00	7.50	66.50	1.500		114	30.00	2.00	68.00	1.497
	94	24.00	13.50	62.50	1.508		115	30.00	4.00	66.00	1.499
	95	23.00	13.00	64.00	1.506	3:2:6	116	39.06	11.14	49.80	1.516
	96	19.84	13.31	66.85	1.505		117	41.54	5.50	52.96	1.510
	97	20.45	11.00	68.55	1.500		118	43.03	13.00	43.97	1.522
1:5:12	98-98a(4)	9.27	19.83	70.90	1.517	2:1:3	119	46.08	9.86	44.06	1.522
	99	22.08	9.45	68.47	1.498		120	45.80	25.00	29.20	(1)
	100	22.90	9.81	67.29	1.499	1:1:1	121-121a	48.41	20.72	30.87	1.547(5)
	101	23.73	10.16	66.11	1.500	2:1:2	122	54.01	11.56	34.43	1.527
	102	24.56	10.51	64.93	1.501		123	59.23	3.00	37.77	reacts
	103	26.21	11.22	62.57	1.504		124	37.80	14.00	48.20	1.519
	104	30.00	5.81	64.19	1.501		125	41.10	6.50	52.40	1.512
	105	23.50	12.00	64.50	1.504		126	36.39	11.63	51.98	1.514
	106	14.50	8.00	77.50	1.490		127	35.00	14.00	51.00	1.517
	107	21.50	5.00	73.50	1.492		128	46.78	13.12	40.10	1.525
	108	13.00	8.00	79.00	1.490		129	60.46	1.00	38.54	reacts
	109	16.28	6.97	76.75	1.490		130	52.00	2.00	46.00	reacts
	110	22.00	3.00	75.00	1.491		131	44.81	4.00	51.19	1.515
	111	25.00	1.00	74.00	1.491		132	40.00	20.00	40.00	1.531
	112	20.77	11.25	67.98	1.501		133	44.07	16.95	38.98	1.528
	113	23.75	11.25	65.00	1.504		134	11.50	16.00	72.50	1.509

(1) These batches would not melt completely within the limit of the furnaces (1600°).
(2) This batch has the composition of the compound $K_2O \cdot MgO \cdot 3SiO_2$.
(3) This batch has the composition of the compound $K_2O \cdot MgO \cdot 5SiO_2$.
(4) This batch has the composition of the compound $K_2O \cdot 5MgO \cdot 12SiO_2$.
(5) This batch has the composition of the compound $K_2O \cdot MgO \cdot SiO_2$.

As may be seen in table 1, a number of the compositions were made to have integral molecular ratios of the component oxides. This procedure helped considerably to locate the composition of the compounds during the early part of the work in that it eliminated many possible combinations from further consideration. Other compositions not having simple unit weight per cent ratios were made to fall on the various binary joins within the ternary system. Of these joins, those which illustrate partial or complete binary equilibrium at liquidus temperatures have been plotted in figure 6.

Whenever possible boundary-curve determinations were made (table 3), although the optical properties and crystallization habit of some of the phases precluded experimental determinations in certain cases.[23]

[23] For example, the boundary curve *A'B'* (fig. 5) could be determined only on batches lying in the $K_2O \cdot MgO \cdot 5SiO_2$ field as the tiny isotropic crystals of this phase in a glass of almost the same index of refraction were impossible to see if much of the finely divided, higher index, birefringent $K_2O \cdot MgO \cdot 3SiO_2$ was present.

TABLE 2

DATA ON LIQUIDUS DETERMINATIONS

Abbreviations Used: L-large; M-moderate; S-small; VS-very small; R-rare; VR-very rare; VVR-exceedingly rare—right at the temperature of the phase change. These are rough visual estimates under the microscope, and are useful for comparison purposes only, as crystal habit and index of refraction may affect this estimate seriously.

Preparation	*Above Liquidus Quenched sample all glass* Temp. °C	Time	*Below Liquidus Quenched sample contained crystals in glass* Temp. °C	Time	Amount of crystals
	Primary crystal phase—Cristobalite, SiO_2				
40	1535	5 hrs.	1530	4 hrs.	R
50	1590	2 "	1580	2 "	S
	Primary crystal phase—Tridymite, SiO_2				
30	930	5 days	925	3 days	R
38	1325	48 hrs.	1320	20 hrs.	S
39	1435	5 "	1430	19 "	VR
41	1115	6 days	1110	5 days	VR
45	1320	20 hrs.	1315	2 "	S
46	1135	3 days	1130	2 "	S
73	1210	24 hrs.	1205	24 hrs.	R
74	985	5 days	980	5 days	R
81	1340	24 hrs.	1335	54 hrs.	VR
110	785	6 days	780	3 days	VR(1)
111	760	6 "	755	2 " (2)	VR(1)
	Primary crystal phase—"Clinoenstatite," $MgO \cdot SiO_2$ (3)				
19	1480	2 hrs.	1475	5 hrs.	R
27	1310	6 "	1305	4 days	R
28	1465	5 "	1460	6 hrs.	R
29	1360	18 "	1355	17 "	VR
35	1420	6 "	1415	17 "	S
36	1265	4 days	1260	4 days	VR
72	1245	6 hrs.	1240	22 hrs.	VR
90	1380	23 "	1375	19 "	S
	Primary crystal phase—Forsterite, $2MgO \cdot SiO_2$				
2	1305	5 hrs.	1300	5 hrs.	R
3	1465(4)	3 "	1460	3 "	VR
4	1545	1 "	1540	1 "	R
5	1600(4)	1 "	1590	1 "	S
8	1215	3 "	1210	24 "	R
10	1480	3 "	1475	2 "	S
12	1130	24 "	1125	4 days	R
17	1495	6 "	1490	6 hrs.	R
22	1135	2 days	1130	2 days	VVR
26	1450	4 hrs.	1445	6 hrs.	R
49	1385	48 hrs.	1380	20 "	R
54	1170	6 "	1165	15 "	S
56	1535	5 "	1530	4 "	S

TABLE 2 (*Continued*)

Preparation	*Above Liquidus Quenched sample all glass* Temp. °C	Time	*Below Liquidus Quenched sample contained crystals in glass* Temp. °C	Time	Amount of crystals
57	1200	5½ hrs.	1195	5 hrs.	R
71	1355	3 days	1350	14 "	R
78	1065	2 "	1060	5 days	VR
79	1095	4 "	1090	2 "	R
94	1125	2 days	1120	5 days	VR
95	1110	2 "	1105	4 "	VVR
96	1190	21 hrs.	1185	21 hrs.	R
(5)98	1470	6 "	1465	6 "	R
(5)98a	1465	2 "	1460	10 "	S
(6)121a	1540	1 "	1530	1 "	R
132	1410	1 "	1400	1 "	R
133	1365	1 "	1355	1 "	S
134	1395	14 "	1390	10 "	R
	Primary crystal phase—$K_2O \cdot 5MgO \cdot 12SiO_2$				
20	1175	1 day	1170	5 days	S
37	1020	4½ "	1015	5 "	S
47	1165	7 "	1160	7 "	VR
88	1135	4 "	1130	2 "	S
89	1140	4 "	1135	4 "	VR
106	1055	4 "	1050	3 "	S
108	1100	48 hrs.	1095	12 hrs.(7)	R
	Primary crystal phase—$K_2O \cdot MgO \cdot 5SiO_2$				
1	1060	7 days	1055	4 days	S
14	980	5 "	975	4 "	S
23	980	5 "	975	4 "	S
25	1090	11 hrs.	1088	1 "(8)	80%
42	885	6 days	880	3 "	S
43	1080	2 "	1075	2 "	S
44	970	5 "	965	3 "	S
55	1080	2 "	1075	3 "	R
60	790	8 "	785	6 "	R
62	1055	3 "	1050	3 "	S
63	1055	3 "	1050	3 "	S
64	1085	2 "	1084	2 "	R
65	1060	3 "	1055	3 "	S
66	1070	4 "	1065	7 "	S
67	1010	4 "	1005	4 "	S
68	1005	5 "	1000	2½ "	S
69	1065	2 "	1060	3 "	S
70	985	5 "	980	5 "	S
75	765	7 "	760	7 "(9)	VR
76	835	6 "	830	7 "	R
77	1050	4 "	1045	5 "	S
82	995	6 "	990	6 "	R
83	975	5 "	970	4 "	R
84	860	5 "	855	4 "	R
85	865	4 "	860	4 "	S
85a	865	4 "	860	4 "	S
86	860	5 "	855	4 "	R
87	1045	3 "	1040	3 "	S
93	1030	5 "	1025	2 "	S

TABLE 2 (*Continued*)

Preparation	*Above Liquidus Quenched sample all glass* Temp. °C	Time	*Below Liquidus Quenched sample contained crystals in glass* Temp. °C	Time	Amount of crystals
97	1065	6 days	1060	5 days	S
99	1084	2 "	1082	4 "	S
100	1080	2 "	1075	3 "	S
101	1070	2 "	1065	2 "	VR
102	1050	4 "	1045	3 "	S
105	1035	4 "	1030	2 "	S
107	955	2 "	950	5 "	S
109	1005	3 "	1000	2 "	R
112	1075	3 "	1070	2 "	VR
113	1045	2 "	1040	4 "	S
115	845	2 "	840	4 "	S
	Primary crystal phase—$K_2O \cdot MgO \cdot 3SiO_2$				
11	1135	2 days	1133.5	2 days(10)	80%
13	1055	3 hrs.	1050	20 hrs.	M
15	1035	5 days	1030	5 days	S
18	1133.5	2 "	1130	2 "	M
24	885	2 "	880	2 "	VR
33	1095	2 "	1090	20 hrs.	M
59	935	17 hrs.	930	5 days	S
61	1000	2 days	995	4 "	S
91	965	5 "	960	20 hrs.	R
92	1080	3 "	1078	2 days	M
103	1080	3 "	1075	3 "	R
104	885	5 "	880	3 "	S
	Primary crystal phase—$K_2O \cdot MgO \cdot SiO_2$(?)				
21	1090	4 days	1088	5 days	R
116	1270	1 hr.	1265	1 hr.	R
118	1385	30 min.	1380	15 min.	R
119	1385	30	1380	15 "	R
122	1470	15 "	1465	15 "	M
123	1220	1 hr.	1210	1 hr.	R
124	1310	15 min.	1305	15 min.	S
125	985	1 hr.	980	10 hrs.	R
126	1140	1 day	1135	1 day	S
127	1210	1 hr.	1200	1 hr.	R
128	1450	15 min.	1440	15 min.	S
130	905	1 hr.	900	1 hr.	VR
	Primary crystal phase—Periclase, MgO				
9	1600	1 hr.	1595	1 hr.	R
	Primary crystal phase—$K_2O \cdot 4SiO_2$				
51	740	12 days	735	7 days	S
52	739	9 "	735	7 "	S
75	725	2 "	720	2 "	S(11)
114	710	5 "	705	5 "	M

TABLE 2 (*Continued*)

Preparation	*Above Liquidus Quenched sample all glass* Temp. °C	Time	*Below Liquidus Quenched sample contained crystals in glass* Temp. °C	Time	Amount of crystals
		Primary crystal phase—$K_2O \cdot 2SiO_2$			
31	995	3 hrs.	990	3 hrs.	S
32	860	5 days	855	4 days	R
53	739	9 "	735	7 "	R
58	945	2½hrs.	940	17 hrs.	S
117	930	14½ "	925	4 "	S
131	920(4)	1 hr.	910	1 hr.	S
		Primary crystal phase—$K_2O \cdot SiO_2$			
129	980	10 hrs.	970	1 hr.	L

(1) Metastable, only tridymite in the starting material.
(2) Held 4 days at 740° first.
(3) May include other modifications—see discussion in text.
(4) Quenched glass contained exceedingly rare crystals; right at the liquidus temperature.
(5) These preparations have the composition $K_2O \cdot 5MgO \cdot 12SiO_2$.
(6) This preparation was originally of the composition $K_2O \cdot MgO \cdot SiO_2$ —see data on alkali losses.
(7) This result was duplicated in a run at 1090° for 4 days.
(8) This preparation has the composition $K_2O \cdot MgO \cdot 5SiO_2$.
(9) "Hydrothermally" crystallized material used. "Dry" crystallization yielded only $K_2O \cdot 4SiO_2$ crystals and hence a metastable liquidus determination.
(10) This preparation has the composition $K_2O \cdot MgO \cdot 3SiO_2$.
(11) Metastable; see footnote (9) above.

Stability Fields for the Various Crystalline Phases of the Limiting Binary Systems.—The fields of stability of the primary crystalline phases within the ternary system are shown in figures 3 and 5 and are labeled in figure 3.

Cristobalite.—The field of cristobalite (*IS'ANI*, fig. 5) extends from 1470° up to the melting point of cristobalite at 1713 ± 5° (Greig, 1927, p. 12). The crystals obtained at higher temperatures were usually rounded, though occasionally facetted masses showing very low birefringence and the characteristic complex twinning caused by the $\beta \rightarrow \alpha$ inversion were formed. The smaller crysals formed at lower temperatures appeared sensibly isotropic because of their size.

In that portion of the cristobalite field lying between *H'H* and the dashed curve in figure 5 two conjugate immiscible liquids are in equilibrium with cristobalite at appropriate temperatures between the temperature of *H'H* and that of the

TABLE 3

DATA ON BOUNDARY CURVES

Abbreviations used:

Phases—		Amounts—	
Cris	Cristobalite, SiO_2		
Trid	Tridymite, SiO_2	L	large
Clino	Clinoenstatite, $MgO \cdot SiO_2$ (1)	M	moderate
Forst	Forsterite, $2MgO \cdot SiO_2$	S	small
Peric	Periclase, MgO	VS	very small
1:1:1	$K_2O \cdot MgO \cdot SiO_2$	R	rare
1:1:3	$K_2O \cdot MgO \cdot 3SiO_2$	VR	very rare
1:1:5	$K_2O \cdot MgO \cdot 5SiO_2$	VVR	exceedingly rare, right at the temperature of the phase change
1:5:12	$K_2O \cdot 5MgO \cdot 12SiO_2$		
KS_4	$K_2O \cdot 4SiO_2$		
KS_2	$K_2O \cdot 2SiO_2$		
KS	$K_2O \cdot SiO_2$		
gl	glass		

Preparation	*Temperature*	*Time*	*Phases present in quenched sample* (2)
	Between Cristobalite and Clinoenstatite		
40	1510	6 hrs.	M cris
	1505	6 "	M cris and VR clino
50	1535	3 "	M cris
	1530	5 "	M cris and S clino
80	1475	6 "	All gl
	1470	6 "	S cris and R clino
	Between Tridymite and Clinoenstatite		
27	1240	4 days	L clino
	1235	2 "	L clino and R trid
35	1400	5 hrs.	M clino
	1395	26 "	L clino and R cris (metastable)
39	1380	20 "	L trid
	1375	20 "	L trid and R clino
73	1175	7 days	M trid
	1170	7 "	M trid and VVR clino
81	1275	3 "	M trid
	1270	6 "	M trid and S clino
	Between Tridymite and $K_2O \cdot 5MgO \cdot 12SiO_2$		
45	1140	2 days	L trid
	1135	3 "	L trid and S 1:5:12
46	1050	3 "	L trid
	1045	4 "	L trid and VR 1:5:12
47	1135	3 "	L 1:5:12
	1130	2 "	L 1:5:12 and R trid
106	975	4 "	L 1:5:12
	970	4 "	L 1:5:12 and R trid
108	1075	3 "	L 1:5:12
	1070	2 "	L 1:5:12 and VR trid
	Between Tridymite and $K_2O \cdot MgO \cdot 5SiO_2$		
41	965	5 days	L trid
	960	6 "	L trid and R 1:1:5
67	930	5 "	L 1:1:5
	925	3 "	L 1:1:5 and R trid

TABLE 3 (*Continued*)

Preparation	*Temperature*	*Time*	*Phases present in quenched sample* (2)
68	980	5 days	L 1:1:5
	975	4 "	L 1:1:5 and VR trid
74	980	5 "	R trid
	975	5 "	M trid and M 1:1:5
82	990(3)	6 "	R 1:1:5
	985(3)	5 "	M 1:1:5 and M trid
83	925	16 hrs.	L 1:1:5
	920	4 days	L 1:1:5 and S trid
Between Tridymite (metastable) and $K_2O \cdot 4SiO_2$			
111	750	4 days	R trid
	745	4 "	R trid and R KS_4
Between Clinoenstatite and $K_2O \cdot 5MgO \cdot 12SiO_2$ (Reaction curve)			
17	1175(4)	7 days	L clino and VR 1:5:12
	1172(4)	7 "	M clino and M 1:5:12
29	1170	7 "	L clino
	1165	7 "	L clino and VR 1:5:12
	1160	7 "	L 1:5:12
36	1175	7 "	L clino
	1170	7 "	R clino and L 1:5:12
	1165	7 "	L 1:5:12
49	1165	7 "	L clino
	1160	7 "	L clino and M 1:5:12
72	1175(4)	7 "	L clino
	1172(4)	7 "	R clino and L 1:5:12
	1170(4)	7 "	L 1:5:12
98	1175(4)	2 "	L clino
	1170(4)	3 "	L clino and VR 1:5:12 } Starting material "bombed" 1:5:12 crystals
Between Forsterite and Clinoenstatite (Reaction curve)			
17	1460	6 hrs.	L forst and VVR clino
	1455	6 "	L forst and S clino
	1395	26 "	L clino and R forst
	1390	4 days	L clino
48	1180	7 "	All glass
	1175	7 "	S clino and R forst
	1160	7 "	M clino and R forst
49	1285	3 "	L forst
	1280	3 "	L forst and L clino
	1200	6 "	L clino and VR forst
	1195	4 "	L clino
56	1530	4 hrs.	S forst
	1525	4 "	M forst and S clino
	1485	5 "	VR forst and L clino
	1480	4 "	L clino
98	1455	6 "	S forst
	1450	6 "	M forst and R clino
	1400	24 "	L clino and VR forst
	1395	12 "	L clino

TABLE 3 (*Continued*)

Preparation	*Temperature*	*Time*	*Phases present in quenched sample* (2)
98a	1445	7 hrs.	M forst
	1440	19 "	M forst and M clino
	1400	15 "	L clino and VVR forst
	1390	10 "	L clino
134	1390	10 "	R forst
	1385	4 days	S clino
Between Forsterite and $K_2O \cdot 5MgO \cdot 12SiO_2$ (Reaction curve)			
2	1100	7 days	L forst
	1095	7 "	L forst and R 1:5:12
12	1120	5 "	R forst
	1115	5 "	VR forst and S 1:5:12
	1110	5 "	VR forst and M 1:5:12
	1105	4 "	M 1:5:12
49	1120	5 "	L 1:5:12 and S forst
	1115	7 "	L 1:5:12
79	1070	7 "	M forst
	1065	7 "	S forst and M 1:5:12
	1057	4 "	L 1:5:12
Between Forsterite and $K_2O \cdot MgO \cdot 5SiO_2$			
77	1035	3 days	L 1:1:5
	1030	3 "	L 1:1:5 and M forst
78	1055	4 "	R forst
	1050	3 "	M forst and M 1:1:5
96	1055(5)	4 "	M forst and L glass
	1050(5)	4 "	L forst, L 1:1:5, and no gl
105	1030	2 "	S 1:1:5
	1025	2 "	L 1:1:5 and S forst
112	1057(5)	4 "	L 1:1:5 and L glass
	1055(5)	4 "	L 1:1:5, R forst, and L gl
	1050(5)	4 "	L 1:1:5, L forst, and VVR gl
Between Forsterite and $K_2O \cdot MgO \cdot 3SiO_2$			
10	1125	19 hrs.	L forst
	1120	2 days	L forst and M 1:1:3
18	1115	7 "	L 1:1:3
	1110	5 "	L 1:1:3 and L forst
22	1100	21 hrs.	M forst
	1095	18 "	M forst and R 1:1:3
54	1132(6)	2 days	L forst
	1130(6)	7 "	L forst and L 1:1:3
57	1125	19 hrs.	L forst
	1120	2 days	L forst and M 1:1:3
94	1050	2 "	L forst
	1045	3 "	L forst and S 1:1:3
Between Forsterite and $K_2O \cdot MgO \cdot SiO_2$ (6a)			
8	1110	4 days	L forst
	1100	5 "	L forst and L 1:1:1
9	1260	7 "	L forst
	1255	7 "	L forst and L 1:1:1
Between Periclase and Forsterite (Reaction curve)			
9	1525	2 hrs.	M peric and VR forst
	1490	1 "	R peric and R forst
	1480	3 "	M forst

TABLE 3 (*Continued*)

Preparation	*Temperature*	*Time*	*Phases present in quenched sample* (2)
	Between $K_2O \cdot MgO \cdot SiO_2$ and $K_2O \cdot SiO_2$ (6a)		
122	920	1 hr.	L 1:1:1
	910	2 days	L 1:1:1 and R KS
123	935	1 hr.	L 1:1:1
	925	4 hrs.	L 1:1:1 and S KS
	Between $K_2O \cdot MgO \cdot SiO_2$ and $K_2O \cdot 2SiO_2$ (6a)		
119	910(7)	2 days	L 1:1:1 and L gl
	905(7)	3 "	L 1:1:1, S KS_2, and S gl
125	910	2 "	L 1:1:1
	905	1 hr.	L 1:1:1 and L KS_2
130	730	1 "	L 1:1:1
	720	1 "	L 1:1:1 and S KS_2
131	910(7)	1 "	S KS_2
	905(7)	1 "	L KS_2 and R 1:1:1
	Between $K_2O \cdot MgO \cdot SiO_2$ and $K_2O \cdot MgO \cdot 3SiO_2$ (6a)		
116	1045	2 days	L 1:1:1
	1040	4 "	L 1:1:1: and L 1:1:3
118	995	6 "	L 1:1:1
	990	6 "	L 1:1:1 and M 1:1:3
124	1125	1 "	L 1:1:1
	1120	1 "	L 1:1:1 and R 1:1:3
127	1140	1 "	L 1:1:1
	1135	1 "	L 1:1:1 and L 1:1:3
	Between $K_2O \cdot MgO \cdot 3SiO_2$ and $K_2O \cdot 2SiO_2$		
13	915	2 days	L 1:1:3
	910	42 hrs.	L 1:1:3 and S KS_2
24	875	3 days	M 1:1:3
	870	3 "	L 1:1:3 and R KS_2
31	920	24 hrs.	L KS_2
	915	20 "	L KS_2 and R 1:1:3
58	915	2 days	L KS_2
	910	42 hrs.	L KS_2 and R 1:1:3
59	820	7 days	L 1:1:3
	815	4 "	L 1:1:3 and R KS_2
91	935(8)	17 hrs.	S 1:1:3
	931(8)	17 "	L 1:1:3, L KS_2, and R gl
92	935(8)	17 "	L 1:1:3 and M gl
	931(8)	17 "	L 1:1:3, L KS_2, and R gl
	Between $K_2O \cdot MgO \cdot 3SiO_2$ and $K_2O \cdot MgO \cdot 5SiO_2$		
55	1035(9)	4 days	L 1:1:5 and L gl
	1030(9)	5 "	L 1:1:5, M 1:1:3, and R gl
62	1030(9)	3 "	L 1:1:5
	1025(9)	3 "	L 1:1:5 and S 1:1:3
64	1025	3 "	L 1:1:5 and R gl
	1020	10 "	L 1:1:5, S 1:1:3, and R gl
93	860	5 "	L 1:1:5
	855	4 "	L 1:1:5 and R 1:1:3
100	1025	6 "	L 1:1:5 and S gl
	1020	10 "	L 1:1:5, L 1:1:3, and R gl
101	1030(9)	5 "	L 1:1:5 and L gl
	1025(9)	6 "	L 1:1:5, S 1:1:3, and L gl

TABLE 3 (*Continued*)

Preparation	*Temperature*	*Time*	*Phases present in quenched sample* (2)
102	1030(9)	5 days	L 1:1:5 and L gl
	1025(9)	6 "	L 1:1:5, R 1:1:3, and L gl
113	1025	2 "	S 1:1:5
	1020	10 "	L 1:1:5 and L 1:1:3
	Between $K_2O \cdot MgO \cdot 5SiO_2$ and $K_2O \cdot 2SiO_2$		
23	810	7 days	L 1:1:5
	805	9 "	L 1:1:5 and R KS_2
60	785	6 "	R 1:1:5
	780	3 "	S 1:1:5 and VR KS_2
115	745	2 "	S 1:1:5
	740	2 "	S 1:1:5 and R KS_2
	Between $K_2O \cdot 2SiO_2$ and $K_2O \cdot 4SiO_2$		
53	710	5 days	S KS_2
	705	5 "	S KS_2 and R KS_4
114	695	3 "	L KS_4
	690	5 "	L KS_4 and S KS_2
	Between $K_2O \cdot MgO \cdot 5SiO_2$ and $K_2O \cdot 5MgO \cdot 12SiO_2$		
12	1060	5 days	L 1:5:12
	1055	3 "	L 1:5:12 and S 1:1:5
16	1055	7 "	All glass
	1050	7 "	S 1:1:5 and S 1:5:12
37	1000	2½ "	S 1:5:12
	995	4 "	S 1:5:12 and S 1:1:5
66	1065(10)	7 "	L 1:1:5
	1060(10)	5 "	L 1:1:5 and S 1:5:12
87	1040	3 "	S 1:1:5
	1035	5 "	M 1:1:5 and VR 1:5:12
88	1040	4 "	L 1:5:12
	1035	4 "	L 1:5:12 and VR 1:1:5
89	1050	3 "	L 1:5:12
	1045	3 "	L 1:5:12 and M 1:1:5
97	1060	3 "	L 1:1:5
	1058	3 "	L 1:1:5 and S 1:5:12

(1) May include other modifications—see discussion in text.
(2) Glass is present in all cases unless otherwise stated.
(3) These runs determine binary eutectic point Q.
(4) These runs determine binary reaction point T.
(5) These runs determine binary eutectic point Y.
(6) These runs determine binary eutectic point I′.
(6a) The isotropic crystals obtained in some of these runs may not be the compound $K_2O \cdot MgO \cdot SiO_2$, see footnote 49.
(7) These runs determine the minimum temperature of the binary eutectic point L′.
(8) These runs determine binary eutectic point E′.
(9) These runs determine binary eutectic point A′.
(10) These runs determine binary eutectic point V.

TABLE 4

DATA ON TERNARY INVARIANT POINTS

(Abbreviations given at heads of tables 2 and 3. The compositions of the ternary points are given in table 5.)

Preparation	*Temperature °C*	*Time*	*Phases present in quenched sample* (1)
Reaction Point N—Cristobalite, Tridymite, Clinoenstatite, and liquid			
80	1475	6 hrs.	All glass
	1470	6 "	S cris, R clino, and gl
Reaction Point O—Tridymite, Clinoenstatite, $K_2O \cdot 5MgO \cdot 12SiO_2$, and liquid			
27	1170	7 days	L clino, S trid, and gl
	1165	7 "	S clino, M trid, L 1:5:12, and gl
	1160	7 "	VVR clino, M trid, L 1:5:12, and gl
45	1140	2 "	L trid
	1135	3 "	L trid and S 1:5:12
47	1165	7 "	All glass
	1160	7 "	VR 1:5:12
	1135	3 "	L 1:5:12
	1130	2 "	M 1:5:12 and R trid
73	1170	7 "	M trid, VVR clino, and gl
	1165	7 "	M trid, M clino, R 1:5:12, and gl
	1160	6 "	M trid, S 1:5:12, and gl
Eutectic Point P—Tridymite, $K_2O \cdot 5MgO \cdot 12SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, and liquid			
37	965	4 days	L 1:1:5, R 1:5:12, and M gl
	960	6 "	L 1:1:5, R 1:5:12, (M trid?), and no gl
74	975	5 "	M 1:1:5, M trid, and L gl
	960	4 "	L 1:1:5, L trid, R 1:5:12, and S gl
106	965	4 "	M 1:5:12, R trid, and L gl
	960	4 "	M 1:5:12, M(?) trid, (L 1:1:5?), and S-R gl
Eutectic Point R—Tridymite, $K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot 4SiO_2$, and liquid (metastable)			
75	765	7 days	All glass
	760	7 "	VR 1:1:5
	725(2)	2 "	All glass
	720(2)	2 "	S $K_2O \cdot 4SiO_2$ (metastable)
111	720	5 "	L KS_4, L trid, and L glass
	710	5 "	L KS, L trid, S(?) 1:1:5, and R gl
Reaction Point U—Forsterite, Clinoenstatite, $K_2O \cdot 5MgO \cdot 12SiO_2$, and liquid			
48	1160	7 days	R forst, M clino, and glass
	1155	7 "	S forst, S clino, S 1:5:12, and gl
	1150	5 "	M 1:5:12 and glass
49	1160	7 "	L clino, M 1:5:12, and gl
	1155	7 "	L clino, VR forst, L 1:5:12, and gl
	1150	7 "	R forst, L 1:5:12, and gl
88	1135	4 "	All glass
	1130	2 "	S 1:5:12
89	1140	4 "	All glass
	1135	4 "	VR 1:5:12

TABLE 4 (*Continued*)

Preparation	*Temperature °C*	*Time*	*Phases present in quenched sample* (1)
	Eutectic Point X—Forsterite, $K_2O \cdot 5MgO \cdot 12SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, and liquid		
79	1040	4 days	L 1:5:12, S forst, L(?) 1:1:5, and L gl
	1035	4 "	L 1:5:12, S forst, L(?) 1:1:5, and R gl
97	1050	4 "	S 1:5:12, L 1:1:5, and S gl
	1045	3 "	S 1:5:12, L 1:1:5, R(?) forst, and no gl
	Eutectic Point Z—Forsterite, $K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, and liquid		
77	1015	3 days	L forst, L 1:1:5, and L gl
	1010	2 "	L forst, L 1:1:5, L 1:1:3, and VR gl
95	1015	3 "	L forst, and L gl
	1010	3 "	L forst, L 1:1:3, L 1:1:5, and no gl
105	1015	2 "	M forst, L 1:1:5, and L gl
	1010	3 "	M forst, L 1:1:5, L 1:1:3, and R gl
113	1015	10 "	S forst, L 1:1:5, L 1:1:3, and L gl
	1010	3 "	S forst, L 1:1:5, L 1:1:3, and R gl
	Reaction Point B′—$K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot 2SiO_2$, and liquid		
59	810	7 days	L 1:1:3, S KS_2, and M gl
	805	9 "	L 1:1:3, S KS_2, (M 1:1:5?), and S gl
	800	8 "	L 1:1:3, S KS_2, (L 1:1:5?), and R gl
	790	8 "	L 1:1:3, S KS_2, (L 1:1:5?), and no gl
60	785	6 "	R 1:1:5
	780	3 "	S 1:1:5 and VR KS_2
93	815	4 "	L 1:1:5, R 1:1:3, and L gl
	805	9 "	L 1:1:5, R 1:1:3, and R KS_2
104	885	5 "	All gl
	880	3 "	S 1:1:3 in gl
	Eutectic Point C′—$K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot 4SiO_2$, $K_2O \cdot 2SiO_2$, and liquid		
53	710	5 days	S KS_2
	705	5 "	S KS_2 and R KS_4
76	835	6 "	All glass
	830	7 "	R 1:1:5 in gl
114	695	3 "	L KS_4
	690	5 "	L KS_4 and S KS_2
115	705	4 "	L KS_2 and R 1:1:5
	700	2 "	L KS_2, R KS_4, and R 1:1:5
	Eutectic Point F′—$K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot MgO \cdot SiO_2$, $K_2O \cdot 2SiO_2$, and liquid (3)		
13	910	42 hrs.	L 1:1:3, S KS_2(?),1:1:1(?), and S gl
	905	48 "	L 1:1:3, S KS_2(?), 1:1:1(?), and R gl
31	910	48 "	S 1:1:3, L KS_2, and M gl
	905	48 "	S 1:1:3, L KS_2, (S 1:1:1?), and no gl
58	910	42 "	L KS_2, S 1:1:3, and S gl
	905	48 "	L KS_2, M 1:1:3, (S 1:1:1?), and no gl
116	910	2 days	L 1:1:1, L 1:1:3, and L gl
	905	3 "	L 1:1:1, L 1:1:3, M KS_2, and M gl
	900	12 hrs.	L 1:1:1, L 1:1:3, L KS_2, and R gl
117	905	3 days	M KS_2, (1:1:1?), and M gl
	900	16 hrs.	No glass
124	905	3 days	L 1:1:1, L 1:1:3, and R gl
	900	12 hrs.	L 1:1:1, L 1:1:3, R KS_2, and VR gl

TABLE 4 (*Continued*)

Preparation	*Temperature °C*	*Time*	*Phases present in quenched sample* (1)
125	905	1 hr.	L 1:1:1, L KS_2, and L gl
	900	1 "	L 1:1:1, L KS_2, (L 1:1:3?), and R gl
	Eutectic Point G′—$K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot MgO \cdot SiO_2$, Forsterite, and liquid (3)		
8	1110	4 days	L forst and L gl
	1100	5 "	L forst, L 1:1:1, and VR gl
10	1110	5 "	L forst, L 1:1:3, and L gl
	1105	2 "	L forst, L 1:1:3, (S 1:1:1?), and no gl
18	1110	5 "	L forst, L 1:1:3, and S gl
	1105	1 day	L forst, L 1:1:3, (S 1:1:1?), and R gl
	1095	4 days	L forst, L 1:1:3, (S 1:1:1?), and no gl
57	1110	2 "	L forst, L 1:1:3, and S-R gl
	1105	2 "	L forst, L 1:1:3, (S 1:1:1?), and no gl

(1) Most of these results were obtained by starting with the all-crystalline material. The intergrowths of very minute crystals with insufficiently distinctive optical properties prevented accurate determination of the presence of one of the three crystal phases at the ternary point in some cases. Reliance then had to be placed on sharp differences in the amounts of liquid (glass) formed in samples of the all-crystalline material held at various temperatures.

(2) Only $K_2O \cdot 4SiO_2$ crystals present in the glass at the start.

(3) The isotropic crystals obtained may not be the compound $K_2O \cdot MgO \cdot SiO_2$, see footnote 49.

TABLE 5

SUMMARY OF INVARIANT POINTS

Point (1)		Equilibrium type	Crystal phases in equilibrium with liquid at point
W	UNARY	Melting	$K_2O \cdot MgO \cdot 5SiO_2$
J′		"	$K_2O \cdot MgO \cdot 3SiO_2$
O′		"	$K_2O \cdot MgO \cdot SiO_2$ (?)
Q	BINARY	Eutectic	Tridymite + $K_2O \cdot MgO \cdot 5SiO_2$
T		Reaction	Clinoenstatite + $K_2O \cdot 5MgO \cdot 12SiO_2$
V		Eutectic	$K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 5MgO \cdot 12SiO_2$
Y		"	$K_2O \cdot MgO \cdot 5SiO_2$ + Forsterite
A′		"	$K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot MgO \cdot 3SiO_2$
D′		"	$K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 4SiO_2$
E′		"	$K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot 2SiO_2$
I′		"	$K_2O \cdot MgO \cdot 3SiO_2$ + Forsterite
L′		"	$K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot 2SiO_2$
N′		"	$K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot SiO_2$
P′		?	$K_2O \cdot MgO \cdot SiO_2$ (?) + Periclase
G″		Eutectic?	$K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot MgO \cdot 3SiO_2$
N	TERNARY	Inversion	Clinoenstatite + Cristobalite + Tridymite
O		Reaction	Clinoenstatite + Tridymite + $K_2O \cdot 5MgO \cdot 12SiO_2$
P		Eutectic	Tridymite + $K_2O \cdot 5MgO \cdot 12SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$
R		" (3)	Tridymite + $K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 4SiO_2$
U		Reaction	Forsterite + Clinoenstatite + $K_2O \cdot 5MgO \cdot 12SiO_2$
X		Eutectic	Forsterite + $K_2O \cdot 5MgO \cdot 12SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$
Z		"	Forsterite + $K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$
B′		Reaction	$K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 2SiO_2$
C′		Eutectic	$K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 2SiO_2$ + $K_2O \cdot 4SiO_2$
F′		"	$K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot 2SiO_2$
G′		"	$K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot MgO \cdot SiO_2$ (?) + Forsterite
K′		Reaction	$K_2O \cdot MgO \cdot SiO_2$ (?) + Forsterite + Periclase
M′		Eutectic	$K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot 2SiO_2$ + $K_2O \cdot SiO_2$

(1) See figure 5.

(2) The compositions of the invariant points were obtained mainly by extension of the established boundary curves to intersection. The compositions are in weight per cent, as are the approximate limits. In those cases where one component is present in considerably smaller quantities than the others, the limit of error is probably less than the figure given for that component.

(3) Metastable.

TABLE 5 (*Continued*)

SUMMARY OF INVARIANT POINTS

Point (1)	Composition (2) K_2O per cent	MgO per cent	SiO_2 per cent	Approx. limits ± per cent	Temperature °C
W	21.66	9.27	69.06	—	1089 ± 1
J′	29.93	12.81	57.25	—	1134 ± 1
O′	48.41	20.72	30.87	—	(1650 ±)
Q	15.5	6.7	77.8	0.3	987 ± 5
T	13.5	10.5	76.0	0.3	1174 ± 2
V	20.0	10.7	69.3	0.2	1063 ± 3
Y	20.5	11.8	67.7	0.2	1053 ± 2
A′	24.8	10.7	64.5	0.2	1030 ± 5
D′	26.5	2.4	71.1	0.3	730 ± 5
E′	38.3	5.2	56.5	0.5	933 ± 5
I′	29.5	13.5	57.0	0.2	1131 ± 1
L′	44.8	4.2	51.0	1.0	910 ± ?
N′	60.1	1.7	38.2	0.5	950 ± ?
P′	—	—	—	—	>1650 ± ?
G″	33.0	14.0	53.0	1.0	1110 ± 20?
N	5.7	12.3	82.0	0.5	1470 ± ?
O	11.6	8.8	79.6	0.3	1165 ± 2
P	15.1	7.2	77.7	0.3	963 ± 3
R	24.5	2.0	73.5	0.3	715 ± 10
U	16.4	11.5	72.1	0.3	1155 ± 2
X	20.2	11.8	68.0	0.2	1042 ± 7
Z	23.9	12.0	64.1	0.2	1013 ± 3
B′	31.6	4.8	63.6	0.5	795 ± 15
C′	30.0	2.5	67.5	0.3	685 ± 20
F′	40.5	6.0	53.5	0.5	905 ± 5
G′	33.0	15.0	52.0	1.0	1105 ± 10
K′	36.0	22.0	42.0	4.0	1350 ± 50
M′	54.2	0.5	45.3	1.0	720 ± ?

minimum temperature on the dashed curve. No data are available on the extent of this two-liquid field into the ternary system from the MgO-SiO_2 side other than that by interpolation of isotherms from points on the sidelines and compositions 39, 40, 50, and 80. To these must be added Greig's point at 4.4 per cent K_2O, 10.6 per cent MgO, and 85.0 per cent SiO_2[24] which had a cristobalite liquidus at 1541 ± 9°,

[24] All per cent figures refer to weight per cent.

and melted to one liquid (Greig, 1927, p. 40). The above data make any extension of the two-liquid field beyond 2 per cent K_2O improbable, and the agreement of the isotherms drawn from the above with the data on the system Na_2O-MgO-SiO_2 (Greig, 1927, p. 35) is sufficiently good to warrant the assumption that the field of two liquids extends about the same amount or even less into the K_2O system (*i.e.*, to about 1.5 per cent K_2O or less). This is to be expected in view of the weakly polarizing nature of the K^+ ion which aids the formation of oxygen bridges and hence tends to eliminate liquid immiscibility (Barth and Rosenqvist, 1949).

Tridymite.—The field of tridymite extends from 1470° down to the eutectic point *R* (*NABRQPON*, fig. 5) at 715 ± 10°. Thus it extends metastably over an area where quartz should be the stable form. Since K_2O and MgO are not known to enter the quartz lattice, but may well be present in appreciable quantities in the tridymite lattice (Lukesh, 1942, found approximately 21 per cent CaO, Na_2O, and Al_2O_3 in tridymite from Plumas Co., this tridymite having the empirical formula $NaCaAl_3Si_{15}O_{36}$), the inversion, under equilibrium conditions, should be lowered an appreciable amount below 867° wherever it can occur in the ternary system. No quartz formed in any of the mixtures, although a number were crystallized at temperatures below the 867° (Kracek, 1939) inversion of tridymite to quartz, and two had their metastable tridymite liquidus considerably below 867° (110 and 111). Presumably these would have a higher temperature stable quartz liquidus if held for a longer period, but as these glasses are exceedingly viscous they might require excessive time.[25]

The difference between the metastable tridymite and the higher temperature stable quartz liquidus is unknown in this system, but its magnitude may be judged from several experimental determinations of it in binary systems. In the system K_2O-SiO_2 the metastable tridymite-$K_2O \cdot 4SiO_2$ eutectic is only 2° lower than the stable quartz-$K_2O \cdot 4SiO_2$ eutectic (Kracek, Bowen, and Morey, 1937), and in the system Na_2O-SiO_2 the metastable eutectic of $Na_2O \cdot 2SiO_2$ with tridymite is 11° below the stable eutectic with quartz (Kracek, 1930b). These small differences in the eutectic temperature may be

[25] Three-month crystallization of 110 at temperatures of 800° and 720° failed to yield quartz crystals.

misleading, however, as the difference between the stable liquidus temperature of quartz and the metastable one of tridymite for a given composition is much greater because of the steep slope of the silica liquidus and lateral shift in the eutectic point. When the data for these two systems are plotted on an enlarged scale, the metastable tridymite liquidus is found to be lower than that of stable quartz by amounts varying from 0° (at the 870° inversion point) to as much as 50° for compositions at the metastable eutectic.

The tridymite crystals formed were exceedingly thin hexagonal flakes; the size and speed of crystallization varied with the temperature of formation.

Clinoenstatite.—The field of the pyroxene clinoenstatite (*INOTUJI*, fig. 5) is unusual in the degree to which it encroaches upon the area where silica might be expected. A composition to the right of *N* (fig. 5) can have over 82.5 per cent SiO_2 and only 10 per cent MgO in it and still form the pyroxene clinoenstatite (composition 59.9 per cent SiO_2 and 40.1 per cent MgO) as the primary phase. Three of the other alkali-alkaline earth-silica systems, Na_2O-CaO-SiO_2 (Morey and Bowen, 1925), K_2O-CaO-SiO_2 (Morey, Kracek, and Bowen, 1930), and Na_2O-MgO-SiO_2 (Botvinkin and Popova, 1937; Manuilova, 1937), are similar, but the most siliceous liquid from which the pyroxenoid pseudowollastonite ($CaO \cdot SiO_2$) can form as the the primary phase is only 75 per cent SiO_2 in the first and 76 per cent in the second; the pyroxene clinoenstatite separates out from certain compositions with as much as 77 per cent SiO_2 in the third of these systems. Other ternary systems of silica with K_2O and Na_2O (Kracek, 1932), with diopside and leucite (Schairer and Bowen, 1938), with anorthite and leucite (Schairer and Bowen, 1947b), and with forsterite and leucite (Schairer, 1948) show similar tendencies but to a lesser degree.

The field of clinoenstatite is rather narrow, as may be seen from figure 5 and the following example: a mixture of the composition 68 per cent SiO_2, 32 per cent MgO (on the MgO-SiO_2 binary) has a cristobalite liquidus at 1660° (Greig, 1927, p. 17). The addition of 1 per cent K_2O to this composition will cause it to form clinoenstatite as the primary phase, with a liquidus of 1540°, and the addition of 2.7 per cent more K_2O (3.7 per cent total) will cause it to form forsterite as

the primary phase, with a liquidus of 1533°. Compositions near to the clinoenstatite-silica eutectic on the MgO-SiO_2 binary (at 65 per cent SiO_2, 35 per cent MgO) need the addition of only about 2 per cent K_2O to change them from a cristobalite to a forsterite liquidus.

The strong curvature of the clinoenstatite-tridymite boundary curve (fig. 5) results in a rapid change in the bulk composition of the crystals forming at any given $-\Delta T$ along this boundary curve, *e.g.*, from 87 per cent clinoenstatite, 13 per cent tridymite at point N to 13 per cent clinoenstatite, 87 per cent tridymite just above point O, as shown by the intersection of the tangent to the boundary curve with KS'.

The crystal habit of the clinoenstatite varied widely. In the high-temperature compositions (>1300° ±) the crystals were short, stubby prisms (almost equant) with the forms (100), (010), (110), and (111), an extinction angle ($Z \wedge c$) of 22°, the characteristic multiple twinning on (100) (Allen, Wright, and Clement, 1906), and pronounced rough cracks parallel to (001) (Bowen and Andersen, 1914). At lower temperatures (875-1300 ±) those compositions which lie in the "Clinoenstatite" field of figure 3 crystallized to extremely thin needles elongated parallel to the slow vibration direction (+ elongation) with parallel extinction, and with multiple twinning absent throughout.[26] In a number of preparations these acicular crystals were formed metastably in the first few minutes at the start of crystallization, only to disappear after a few weeks in the furnace.

It might appear that this system would offer good possibilities of clarifying the confusion that exists concerning the various forms of the compound $MgO \cdot SiO_2$, but up to the present it has not done so. The monoclinic form clinoenstatite has been obtained from melts with various fluxes in good crystals suitable for goniometry (Allen, Wright and Clement, 1906). Good crystals of the orthorhombic form enstatite have not been obtained in the laboratory.[27] Grigor'ev (1935) found

[26] In the system MgO-Al_2O_3-SiO_2 the clinoenstatite crystals formed were "seldom twinned" although 1345° was the lowest liquidus temperature involved. See Rankin and Merwin, 1918, footnote 2, p. 302.

[27] The second orthorhombic form of $MgO \cdot SiO_2$ obtained by Allen *et al.*, p. 400 and 433, similar to Kupfferite, was later shown to be a submicroscopic intergrowth of forsterite crystals and a siliceous glass, the mass having the composition $MgO \cdot SiO_2$ and the optical properties of a homogeneous substance. See Bowen and Posnjak, 1931.

that the addition of CaF_2 was necessary to cause enstatite to form on cooling a mixture of the composition $3MgO \cdot CaO \cdot 3SiO_2$. Bowen and Schairer (1935) caused new crystals of orthorhombic $(Mg, Fe)O \cdot SiO_2$ to form by the recrystallization of natural bronzites, but only with the aid of a small amount of NaF. Thilo (1937) converted "metatalc" (from the thermal decomposition of talc) to enstatite at 790° by the addition of LiF. The only syntheses of enstatite not involving the use of a flux seem to be formation both from a glass of the composition $MgO \cdot SiO_2$ at 1000-1100° (Allen, Wright, and Clement, 1906, p. 400) and from thermal decomposition of natural anthophyllite and talc (Thilo and Rogge, 1939; Rigterink, 1947). The former "enstatite" occurred as acicular crystals in the glass and had definitely parallel extinction in all orientations,[28] this being the only criterion then available to identify it as enstatite. Some of the preparations in the present study formed similar length-slow (*i.e.*, with *Z* vibration direction parallel to the long axis) acicular crystals with definitely parallel extinction, but as the temperatures were considerably above the 1140° inversion, these crystals cannot be enstatite. In those cases where thicker crystals grew (mostly above 1300°) they usually were of inclined extinction and hence presumably clinoenstatite. Bowen and Schairer (1935) give some evidence for an enantiotropic relation between enstatite and clinoenstatite with an inversion at about 1140°, enstatite being the stable form at $<1140°$. The reaction rate at temperatures near the inversion temperature is small. Four hours at 1150° were required to effect even a partial transformation. This inversion temperature is for the pure compound; the possibility is not excluded that small amounts of K_2O may enter the pyroxene lattice in the present system and affect the inversion temperature slightly.

Enstatite would not be expected to appear at the liquidus surface in the present system on the basis of this inversion to clinoenstatite, as all liquids from which $MgO \cdot SiO_2$ can crystallize complete their crystallization above that temperature (*i.e.*, at *O*, 1165 ± 2°, or at *U*, 1155 ± 2°, see fig. 5). Under equilibrium conditions this inversion should take place in the solid state when these compositions are held at temperatures

[28] Allen *et al.* (1906), have shown that this precaution is necessary due to the occasional tabular habit of clinoenstatite crystals parallel to (100) yielding parallel extinction.

below 1140°, but no unequivocal evidence was found here to prove it, probably due to the slow rate.

Above 1400° there seems to be little doubt that clinoenstatite is the only stable phase, and all other forms, regardless of their source, invert to it, the differences being due to different starting materials, the rate factor (Allen, Wright, and Clement, 1906, above 1300°; Haraldsen, 1930, above 1400°?; Ewell, Bunting, and Geller, 1935, between 1200° and 1300°; Büssem and Schusterius, 1938, above 1400°; Thilo, 1939, above 1270°; Thilo and Rogge, 1939, above 1270°; and Eitel, 1943, above 1200°), and impurities (Rigterink, 1947; Haraldsen, 1930, reported rather large amounts of impurities in the SiO_2 and MgO used). Below these temperatures there appear to be forms of $MgO \cdot SiO_2$ other than enstatite and clinoenstatite. Haraldsen (1930) found, on the basis of X-ray data, that by heating talc a new form of $MgO \cdot SiO_2$ developed. Ewell, Bunting, and Geller (1935) did not duplicate the results of Haraldsen, but Thilo (1939) and Büssem and Schusterius (1938) did verify them, and in later work (1939) on anthophyllite and talc Thilo and Rogge discovered two other new forms, "M_1" and "M_2," in addition to the form found by Haraldsen.[29] There seems to be little doubt that at least some of these forms are metastable. Mesoenstatite is not stable at room temperatures, as Büssem *et al.* (1939) and later workers (Thurnauer and Rodriguez, 1942) found that grinding to prepare samples for X-ray work will cause mesoenstatite (protoenstatite) to invert to clinoenstatite unless 25 to 50 per cent of glass is present to stabilize it. Clark (1946) reports that mesoenstatite inverts spontaneously within two months at room temperature to form clinoenstatite with a volume change sufficient to crumble a fired briquette. Büssem and Schusterius (1938) found that various fluxes, such as H_2O, Li_2O, CaF_2, H_3BO_3, and borax, aided the change to clinoenstatite, and the inversion seems to be irreversible (Eitel, 1943).

In the present investigation a number of the samples which showed parallel extinction needles were X-rayed by the powder technique, but because of the distance between the composition points of the mixtures and that of $MgO \cdot SiO_2$ the necessarily small percentage of crystals present in the glass in each case

[29] The original form found by Haraldsen and the "metatalc" of Thilo appear to be identical with the "protoenstatite" of Büssem and of Eitel, and the "mesoenstatite" of Thilo and Rogge, and of later workers.

yielded rather poor patterns, and unfortunately the patterns of all forms of $MgO \cdot SiO_2$—clinoenstatite, enstatite, mesoenstatite, M_1, and M_2—are rather similar in some respects. However, several of the patterns obtained were very much more like that given by Clark for mesoenstatite than those for clinoenstatite or enstatite. A more thorough check on the optical properties of the $MgO \cdot SiO_2$ crystals obtained in the various preparations and more detailed X-ray work are planned. Recently, while the present paper was in press, W. R. Foster presented a paper on X-ray and thermal data at the meeting of the Geological Society of America in Washington, D. C., November 1950, indicating that protoenstatite (mesoenstatite) is the stable form at moderate and high temperatures but that it inverts during the cooling cycle to clinoenstatite in a manner similar to the inversion of high to low cristobalite.

Forsterite.—The field of forsterite covers a large part of the diagram (*LJUYI'G'K'ML*, fig. 5). Its extension toward the SiO_2 apex (up to 72.7 per cent SiO_2 near *U*, fig. 5) is similar to that of clinoenstatite but not as pronounced. The isotherms on the forsterite field above 1600° are only approximations up to the melting point of forsterite at 1890° ± 20° (Bowen and Andersen, 1914), as excessive volatilization of the platinum winding at higher temperatures makes 1600° the useful working limit of the furnaces.

The crystals of forsterite formed at high temperatures were nearly equant, sharp prisms, usually showing the forms (100), (010), (101), (021), (001), and (111). At lower temperatures (near the line *UZI'G'*, fig. 5) the forsterite crystals are usually very thin plates, blades, or needles, with the *Z* vibration direction parallel to the elongation (length-slow, or + elongation). Although many of these plates and blades were elongated to five times their width, the direction of elongation was frequently not parallel to any one of the crystallographic axes, resulting in inclined extinction of as much as 40°. Although these crystals were very thin, the elongation appeared to be due to excessive development of diagonally opposite faces of (011) or (101).

Periclase.—Only one composition was situated on the periclase liquidus surface (9), although indirect evidence from 120 and 121 is concordant with the data from it. Both of these

latter compositions yielded tiny sharp octahedra of periclase, an unusual habit for this mineral since it normally crystallizes from melts as completely rounded grains.[30] X-ray examination of this material verified the petrographic examination. In certain mixtures in this system periclase will form as the primary phase with as much as 45 to 46 per cent SiO_2 present. Presumably there is a smooth rise in the liquidus surface of periclase up to its melting point at 2800° (Kanolt, 1913; Ruff, 1913, melting point >2500°).

Potassium Silicates.—The fields of the potassium silicates $K_2O{\cdot}4SiO_2$, $K_2O{\cdot}2SiO_2$, and $K_2O{\cdot}SiO_2$ are small, extending out into the ternary system to only 2½, 6, and 2 per cent MgO respectively, because of the low melting points of these three silicates and the formation of three ternary compounds with a 1:1 ratio of K_2O:MgO. Compositions having $K_2O{\cdot}4SiO_2$ as the primary phase (area *CBRD'C'DC*, fig. 5) were very reluctant to crystallize, although they eventually formed thin blades and needles of $K_2O{\cdot}4SiO_2$ characterized by their low indices and low birefringence. Compositions having a $K_2O{\cdot}2SiO_2$ liquidus (area *EDC'B'F'M'FE*, fig. 5) crystallized readily (in a few hours or days) to yield booklets of plates, occasionally of parallelogram outline with the optic plane in the plane of the tablet and the Z vibration direction bisecting the acute angle. Similar crystals have been described by Niggli (1913) and by Morey (1914). The $K_2O{\cdot}SiO_2$ field is very narrow and only one composition was made in it. As no composition was made with a K_2O:SiO_2 ratio >1, nothing can be said about the appearance of the orthosilicate $2K_2O{\cdot}SiO_2$ in the system (Kröger and Fingas, 1933).

Stability Fields of the Ternary Compounds.

$K_2O{\cdot}MgO{\cdot}SiO_2$ (?).

The field of this compound occupies a rather large area in the lower portion of the diagram (*P'K'G'G''F'L'M'N'*,

[30] This rounded growth of crystals seems to be most frequently found in very slightly undercooled melts; perhaps the slight oscillation in temperature due to the normal regulator action is sufficient to result in repeated minor solution and redeposition, with very slight undercooling. The preparations yielding the euhedral crystals of periclase were heated in a gas-fired furnace, not controlled by a regulator. For a discussion of this rounded growth of crystals see Naken (1915, 1917) and Tammann (1925). Sharp octahedra of MgO have been obtained from melts containing no silica (Rankin and Merwin, 1916).

fig. 5). It occurs usually as colorless transparent rounded grains, isotropic, with n = approximately 1.54, and a strong, distinctive X-ray powder pattern. Many of these grains possessed a small gas-filled cavity at the center, and occasionally sharp octahedra or skeletal growths consisting of three thin, mutually perpendicular dendrites were formed. There were some discrepancies in the measurement of the index of refraction from sample to sample; these may be due mainly to reaction of these high alkali materials with the index liquid, or they may be connected with the observed variation in the unit cell dimensions (see under X-ray Data). Another possibility is that some of these crystals were the compound $K_2O \cdot MgO$ $2SiO_2$ (see footnote 49).

The evidence is in favor of the composition of most of these isotropic crystals being $K_2O \cdot MgO \cdot SiO_2$, but is not adequate to state so definitely because of the high melting temperatures and the high alkali losses in this area of the diagram. When a mixture of the composition $K_2O \cdot MgO \cdot SiO_2$ was made up and held at 1620° for 30 minutes,[31] the batch was found to consist of a mass of round, clear, isotropic crystals with a small amount of interstitial glass and undissolved MgO. Remelting at 1650° for 10 minutes resulted in fusion and on cooling a dendritic mass of the same isotropic crystals with more glass was found. MgO was present also but had recrystallized to the sharp octahedra mentioned under "Periclase." Further fusion of a small sample of this batch for 5 seconds in an oxy-gas flame resulted in visible alkali fumes and the appearance of an appreciable quantity of forsterite crystals in the melt, along with the MgO and isotropic crystals. This behavior is caused by the loss of alkali changing the composition of the batch. In one case one 15 minute fusion in air at 1600° resulted in a drop of the K_2O content from the weighed 48.4 per cent down to 28.1 per cent (determined by weight loss). Other attempts to synthesize this compound gave similar results. Batch 120, calculated to give approximately 95 per cent $K_2O \cdot MgO \cdot SiO_2$, 5 per cent MgO, showed the same behavior, but the amount of periclase in the fused material was definitely greater than in 121.

The above data indicate $K_2O \cdot MgO \cdot SiO_2$ to be the probable

[31] Using a gas-fired furnace and a Leeds and Northrup disappearing filament-type optical pyrometer.

composition of the compound and 1650° its approximate melting point, although the possibility of incongruent melting to MgO and liquid is not excluded. More accurate work will presumably require the control of the rather high alkali vapor pressures. Several other batches of integral molecular composition in the general area (with the ratios 2:1:2, 2:1:3, 2:1:4, 1:1:2, and 3:2:6 potash to magnesia to silica) were made up but cannot be the isotropic compound since they gave much lower liquidus determinations with the isotropic crystals as the primary phase, wide melting ranges, and definitely heterogeneous crystalline products. One of these ratios (2:1:3) occurs as an isometric compound in the systems K_2O-CaO-SiO_2 (Morey, Kracek, and Bowen, 1930), Na_2O-CaO-SiO_2 (Morey and Bowen, 1925), and possibly K_2O-ZnO-SiO_2 (Ingerson, Morey, and Tuttle, 1948), but the data on a batch of that composition (119) and neighboring points would seem to preclude both the possibility that that is the composition of the isotropic crystals in the present system and the possibility that such a compound occurs above the solidus in this system.

Apparently the counterpart of $K_2O \cdot MgO \cdot SiO_2$ does occur in the potash-zinc oxide-silica system in which an isotropic compound tentatively identfied as $K_2O \cdot ZnO \cdot SiO_2$ was found (Ingerson, Morey, and Tuttle, 1948, p. 33). The similarity of ionic size of Zn^{++} and Mg^{++} (0.83 and 0.78 Å) should result in similar structures for these two compounds. The substitution of the larger Ca^{++} ion (1.06 Å) for Mg^{++} cannot be made without changing the lattice, however, as the compound $K_2O \cdot CaO \cdot SiO_2$ is hexagonal (Morey, Kracek, and Bowen, 1930), and the substitution of the still larger Pb^{++} ion (1.32 Å) apparently cannot be made at all (Geller and Bunting, 1936; McMurdie, 1941). The smaller sodium ion (0.98 Å) can presumably replace the larger potassium (1.33 Å), as the compound $Na_2O \cdot MgO \cdot SiO_2$ is isometric also (Botvinkin and Popova, 1937; Manuilova, 1937) and the substitution of $2Al^{+++}$ for Mg^{++} and Si^{++++} results in the compound $K_2O \cdot Al_2O_3$ which is also isometric (Brownmiller, 1935), and apparently isostructural with $K_2O \cdot MgO \cdot SiO_2$.

$K_2O \cdot MgO \cdot SiO_2$ forms binary systems with $K_2O \cdot SiO_2$, $K_2O \cdot 2SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, and probably with MgO (see figs. 5 and 6). The system with forsterite is only partially binary, as the field of periclase covers most of it.

$K_2O \cdot MgO \cdot 3SiO_2$.—The field of this compound is outlined on figure 5 by the line *I'Z B'F'G''G'I'*. The compound melts congruently and sharply to a rather thin liquid at 1134° ± 1°, which crystallizes readily upon cooling (within several minutes) to a granular mass. Very slow cooling of a liquid of this composition through the liquidus temperature yields large, sharp hexagonal tablets, uniaxial negative, with $n_o = 1.530 \pm .002$, $n_e = 1.524 \pm .002$ ($Na_D^{36°}$). In batches of other compositions and less often in the pure material, it crystallizes occasionally as trillings with hexagonal outline or fourlings with a rectangular or circular outline, but these twin crystals appeared to be almost optically continuous across the "twinning planes." In some cases a series of grooves were seen on the (0001) face of the hexagonal tablets, perpendicular to each edge exactly as in the pseudo-hexagonal cyclic twins of aragonite, but such crystals gave sharp, definitely uniaxial interference figures and uniform extinction throughout. Several runs yielded long, rectangular cross-section crystals of the compound with a twinning plane running the length of the crystal, the two halves showing 27° extinction against this plane. All of the above types of crystals are presumed to be the same phase and are here called $\alpha K_2O \cdot MgO \cdot 3SiO_2$. This is the form which occurred in those quenching runs where sufficiently large crystals were obtained to differentiate, but usually this was not possible. The compound has a definite inversion to a finely fibrous appearing, spherulitic form having an "extinction cross" parallel to the vibration directions of the nichols, usually with the fast ray parallel to the radius of the spherulite, although the reverse was found. The gross index of refraction of this material lies between the two indices of the other form (*i.e.*, approximately 1.527), and there appears to be a fairly large dispersion, but further data on the optical properties could not be obtained from these samples. As this form is apparently the stable one, it is called "$\beta K_2O \cdot MgO \cdot 3SiO_2$" here. The differences between the two forms under the microscope are not great, particularly in fine materials, and hence the inversion was not found until X-ray patterns were obtained. The nature of this inversion is unknown, as no quenching data could be found to indicate it, and high sensitivity differential thermal analysis run on a preparation consisting of the β form showed no thermal activity from 20° to 1080°.

The hexagonal crystals seem to form first in any crystallization, and later slowly invert to the other form, even at temperatures just below the melting point. Optically the change seems to be gradual, but one series of X-ray patterns showed a rather abrupt change between samples held for 2 and 3 days at 1100°. Density measurements were not made of the α form, but there appears to be a volume change upon inversion. For additional data on this compound see "X-ray Data" section.

The compound $K_2O \cdot MgO \cdot 3SiO_2$ forms binary systems with the compounds $K_2O \cdot MgO \cdot SiO_2$(?), $K_2O \cdot 2SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, and forsterite, as shown in figure 6. Glass of the composition $K_2O \cdot MgO \cdot 3SiO_2$ has a density of 2.40 and an index of 1.510, and crystals of the β form have a density of 2.56.

$K_2O \cdot MgO \cdot 5SiO_2$.—The field of this compound is outlined by the line A′ZXVPQRC′B′A′ on figure 5. This compound melts congruently and sharply, though slowly, to a viscous liquid at 1089° ± 1°, and will start to crystallize from a melt of its own composition within a few hours at optimum temperatures. It occurs in two modifications; an isotropic form called "α $K_2O \cdot MgO \cdot 5SiO_2$," as tetrahexahedra and occasional octahedra and cubes with an index of 1.501 ± .002 ($Na_D^{32°}$); and a very weakly birefringent (estimated birefringence 0.001-0.002) spherulitic, almost fibrous form called "β $K_2O \cdot MgO \cdot 5SiO_2$," showing wavy, irregular extinction, and an index of 1.505 ± .002 ($Na_D^{32°}$). The isotropic α form always seems to crystallize first, and, if sufficient time is allowed in the furnace, it slowly inverts to the anisotropic β form, regardless of the temperature. The isotropic form has not been obtained free from both glass and the anisotropic form; whether this is due to the necessity of having glass present to prevent a "snap" inversion to the anisotropic form on cooling, or whether it is merely a result of inversion proceeding almost as fast as the crystallization of the isotropic form, is not known. It is very apparent, however, that the glass surrounding crystals of the isotropic form, and even that around those crystals that have inverted to the anisotropic one, is under strain indicating compression along the tangent and tension along the radius from each grain. This might be due to a shrinkage of the crystal upon inversion as would be indicated by the increase in index, but this would not explain similar strains around each seemingly perfectly isotropic crystal unless there is a

partial inversion that is not visible. Possibly these strains are attributable merely to large differences between the thermal expansions of the crystalline material and the glass. The strains in the glass frequently made it impossible to distinguish the two forms in the quenching runs, but in general the anisotropic β form seemed far more common, the occurrence of the isotropic form being irregular. The inversion with time can be followed easily by X-ray methods (see beyond), but high sensitivity differential thermal analysis of a preparation consisting of the β form showed no thermal activity from 20° to 1080°.

$K_2O \cdot MgO \cdot 5SiO_2$ forms binary systems with the compounds $K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot 4SiO_2$, SiO_2, and forsterite, and partially binary systems with $K_2O \cdot 2SiO_2$ and $K_2O \cdot 5MgO \cdot 12SiO_2$, as indicated in figure 6. Glass of the composition $K_2O \cdot MgO \cdot 5SiO_2$ has a density of 2.38 and an index of 1.498, and crystals of the β form have a density of 2.39_5.

$K_2O \cdot 5MgO \cdot 12SiO_2$.—This is the most interesting of the new ternary compounds, and was the most difficult to prove as to composition because of its incongruent melting and very small field on the liquidus surface (see fig. 5, area *TOPVXUT*). Although the field is small, it forms as one of the stable phases in all compositions in the triangle *LWS′* (figs. 5 and 8), and occasionally is formed metastably in compositions outside of that triangle. It generally crystallizes within a few days to sharp, thin, hexagonal tablets, frequently with the second-order prism and first- and second-order pyramids as modifying forms. The small crystals obtained here have no visible cleavage. Optically it is uniaxial positive, $n_o = 1.543$, $n_e = 1.550 \pm .002$ ($Na_D^{36°}$), $n_o - n_e = 0.008 \pm .002$. It should be noted that these optical properties are very similar to those of quartz. Crystals of the compound containing small amounts of glass and clinoenstatite (see beyond) had a density of 2.58.

The thermal behavior of this compound is illustrated by figure 7. Upon heating the pure crystals, they melt incongruently at 1174° ± 2° to form clinoenstatite (31.3 per cent) and liquid *T* (68.7 per cent). Above 1174° this clinoenstatite goes into solution, but at 1398° the liquid composition touches the forsterite-clinoenstatite reaction curve (*JU*, figs. 5 and 8) and thus the remaining clinoenstatite begins to break up to form forsterite and more liquid. At 1453° this reaction is

completed with the decomposition of the last trace of clinoenstatite; with further heating the remaining forsterite crystals start to dissolve and the liquid composition leaves the curve *JU* and approaches point *S*, where the last of the forsterite crystals dissolve at the forsterite liquidus temperature of 1467°.

As the composition $K_2O \cdot 5MgO \cdot 12SiO_2$ is a little unusual, the following discussion is offered in its support. The best method of proving the composition of a compound in this type of work would be to synthesize an optically homogeneous crystalline phase of integral molecular ratio of constituents possessing the thermal behavior of a compound. From detailed work on the reaction curve *OTU* between the fields of clinoenstatite and $K_2O \cdot 5MgO \cdot 12SiO_2$ (see fig. 8), it was possible to locate the maximum point *T* with fair certainty although the temperature differences are small. On a theoretical basis the

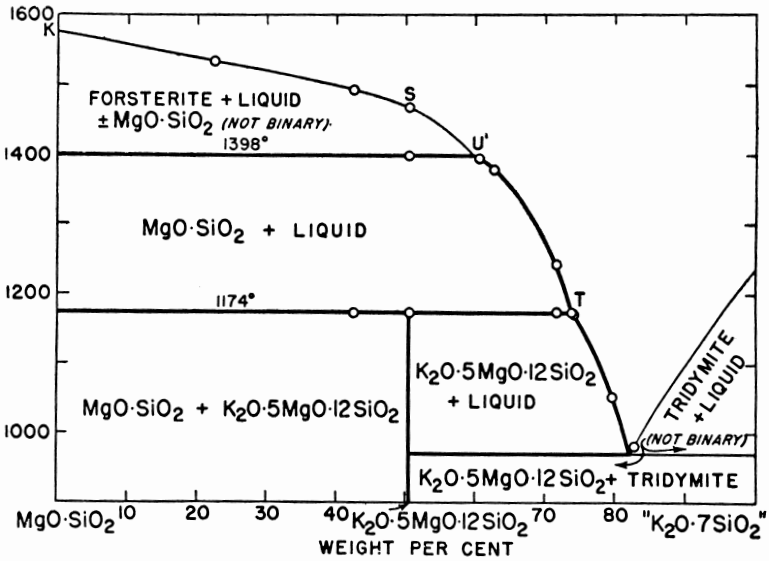

Fig. 7. Equilibrium diagram for the partially binary system $MgO \cdot SiO_2$-$K_2O \cdot 5MgO \cdot 12SiO_2$. This represents a cross section through the ternary system along the line KST (fig. 5), extended to its intersection with the K_2O-SiO_2 side at the molecular ratio $1K_2O:7SiO_2$ (not a compound). The letters used for the points are the same as those on figures 5 and 8. Heavy lines refer to binary equilibrium, light lines to non-binary (ternary) equilibrium. The small circles are experimentally determined points, mostly projected short distances ($<$0.5 per cent) along the isotherms in the ternary system.

composition of the (at that time) unknown phase would thus lie along the line connecting T with the composition of clinoenstatite (K). On the same basis the small maximum at V on the boundary curve XVP (between $K_2O \cdot MgO \cdot 5SiO_2$ and the unknown phase) would require that the composition of the unknown phase lie on the extension of the line WV. If the maxima T and V could be located with complete accuracy, this would be adequate to establish the composition of the phase, which must lie at the intersection of WV produced and TK in order to satisfy both requirements. Experimentally, however, this accuracy was not feasible. When the possible errors in location of T and V were taken into account a small area in the vicinity of point S was found to be the most likely. The only

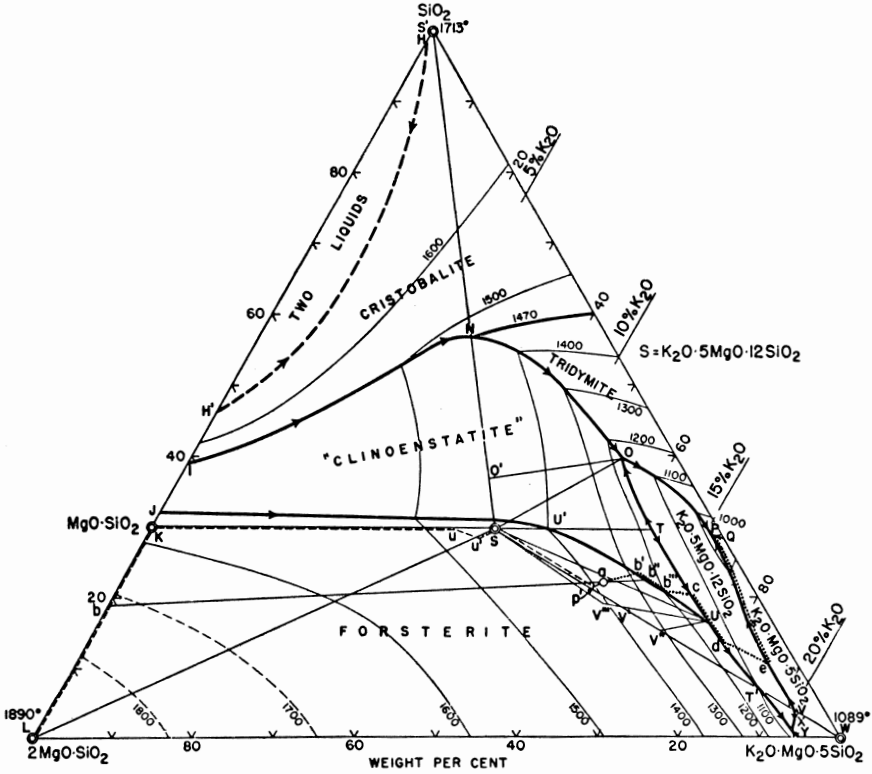

Fig. 8. Equilibrium diagram for the system Forsterite-$K_2O \cdot MgO \cdot 5SiO_2$-$SiO_2$. This represents a portion of the more general system K_2O-MgO-SiO_2 (the oblique triangle LWS′ on figure 5). See text for description of crystallization paths.

integral molecular ratio that fell within this area that was at all rational was the composition $K_2O \cdot 5MgO \cdot 12SiO_2$.

The next step would be to produce a homogeneous crystalline product of this molecular ratio. A number of methods were tried unsuccessfully in an attempt to obtain such a product. When a glass of that composition (98 and 98a) was held at any temperature below the 1174° incongruent melting point, the first crystals to form were metastable "clinoenstatite" needles. This occurred within a few hours when held at 1100° and within a few days at temperatures around 875°. Within a day (or more at the lower temperatures) large hexagonal plates of the new compound started to grow in the glass surrounding the clinoenstatite needles and to enclose some of them. With further crystallization of these plates the clinoenstatite in the surrounding glass gradually decreased in amount until finally a mass of crystals of the new phase was obtained, surrounded by films of glass and enclosing a small precentage of fine needles of clinoenstatite, after about three days at 1100°. Actually this glass was of composition *T* (figs. 5 and 8) and was in the stoichiometrically correct amount to combine with all of the clinoenstatite remaining to form more of the new phase, but as the glass-new phase interface and the new phase-clinoenstatite interface are each in themselves stable at these temperatures, the clinoenstatite is effectively removed from further reaction with the glass and solid diffusion through the lattice of the new phase is the only way that the reaction can continue. The rate of this diffusion at 1100° is apparently slow enough to be experimentally negligible, as an additional 17 days at 1100° failed to produce any further visible change, particles of the new phase only a few microns in diameter still possessing their films of glass and enclosed clinoenstatite needles. Fluxes such as potassium tungstate were tried, but unsuccessfully. Even when a glass of the composition $K_2O \cdot 5MgO \cdot 12SiO_2$ was carefully "seeded" before crystallization with crystals of the compound containing no clinoenstatite, the metastable clinoenstatite still formed. Since the composition of the glass cannot be independently determined with any accuracy, and the relative amounts of glass and metastable clinoenstatite cannot be measured with any certainty in material of this type, the composition of the compound has not been proven by these data.

In order to prevent this formation of metastable clinoenstatite, crystallization of glasses of the composition $K_2O \cdot 5MgO \cdot 12SiO_2$ (98 and 98a) was attempted at 500° for 14 hours under a pressure of 6000 psi water in a bomb of the Morey type (Morey and Ingerson, 1937). The result was a mixture of two phases, containing approximately 10 per cent of large crystals of a hydrous prismatic material, and 90 per cent of a hydrous, fibrous, highly birefringent material with indices approximately 1.565 and 1.585. Both of these decomposed to an isotropic, low index material on being heated to 950° for three minutes. When this heated material was held in air at 1100° for one day, it yielded a mass of metastable clinoenstatite needles in glass.

As higher temperatures tend to prevent the formation of hydrous phases in bomb runs, samples were run at 900° and 15,000 psi water pressure for 1 hour in O. F. Tuttle's (1948) hydrothermal quenching apparatus. These runs were successful, yielding a product which was a mass of interlocking crystals with optical properties and X-ray powder patterns identical with those of the crystals formed in the "dry" manner but without the clinoenstatite. A small fraction of 1 per cent of some low index, extraneous material was present, presumably because slight impurities in the starting material (particularly the MgO) caused divergence of the batch from the theoretical composition. If the actual composition of the compound were such that it differed from 98 in having only 0.5 per cent more MgO, the crystalline material obtained here from 98 should contain only 94.5 per cent crystals of the compound, the other 5.5 per cent being either glass or crystals of $K_2O \cdot MgO \cdot 5SiO_2$ and SiO_2. This amount of such low index materials should be visible readily under the microscope when immersed in a liquid having the mean index of $K_2O \cdot 5MgO \cdot 12SiO_2$ crystals; if the compound contained 0.5 per cent less MgO than 98, the crystalline material obtained should consist of approximately 97.5 per cent of the compound and 2.5 per cent clinoenstatite, and the latter should be even more visible under the microscope as a result of its high index. Furthermore, even these differences in composition from that of 98 would not be sufficient to yield any rational formulas for the composition of the compound. The closest integral ratio of any simplicity and probability according to present knowledge of

silicate structure[32] is $K_2O \cdot 4MgO \cdot 10SiO_2$, but this composition is so far removed from 98 (it would have 11.0 per cent K_2O, 18.8 per cent MgO, and 70.2 per cent SiO_2) that, although the quenching data might possibly be interpreted in this light, the crystallization of 98 to a homogeneous crystalline phase prohibits it.

In order to prove that there was not a range of compositions that would have behavior similar to that of 98 upon crystallization, two other batches were given the same treatment at 900° and 15,000 psi water pressure. They were 17 (approximately 3.2 per cent more MgO) and 134 (approximately 3.8 per cent less MgO). The former yielded a mass of $K_2O \cdot 5MgO \cdot 12SiO_2$ crystals containing a mat of tiny clinoenstatite needles (theoretically 16 per cent by weight), and the latter a mass of $K_2O \cdot 5MgO \cdot 12SiO_2$ crystals coated with films of a low index material, presumably $K_2O \cdot MgO \cdot 5SiO_2$ and SiO_2 or glass.[33] The above data are considered adequate to establish with fair certainty that $K_2O \cdot 5MgO \cdot 12SiO_2$ is the composition of the compound. It is stable in equilibrium with $K_2O \cdot MgO \cdot 5SiO_2$, forsterite, clinoenstatite, and silica, although most of these sub-systems are not binary at liquidus temperatures due to the incongruent melting of the compound.

[32] *E.g.*, see Hendricks (1944). A series of infinite sheets of $(Si_4O_{10})_n^{-4n}$ as in the micas, bonded with K and Mg, would satisfy either $K_2O \cdot 4MgO \cdot 10SiO_2$ or $K_2O \cdot 5MgO \cdot 12SiO_2$, but layers of 12 coordination K^+ cannot exist as they do in the micas, as the crushed crystals showed no sign of the perfect cleavage of the micas.

[33] X-ray examination of these examples was not very satisfactory due to the overlap of strong $K_2O \cdot 5MgO \cdot 12SiO_2$ lines upon weak clinoenstatite and $K_2O \cdot MgO \cdot 5SiO_2$ lines.

(*To be continued*)