SILICATE MELT SYSTEMS

By Edwin Roedder

INTRODUCTION

Most petrologists agree that the bulk of the rocks termed "igneous" have formed by the cooling of a hot, mobile mixture of earth materials called a "magma". There are considerable differences of opinion among these petrologists, however, as to further details of the processes of formation. For example, there is a school of thought holding that the magma from which some of the intrusive igneous rocks have formed, such as the large bodies of granite, was essentially a mass of solid crystals of various minerals, with merely a trace of liquid (or aqueous fluid) between the crystals. This liquid is considered to have been the cause of the apparent fluidity of the mass during movement into its present location, having acted both as a fluid "lubricant" for physical deformation of the mass and as a medium into which portions of crystals, more soluble as a result of being under pressure at their points of contact, dissolved and recrystallized elsewhere, thus relieving the stress. By continuation of this slow process, throughout the mass and for long periods of time, the "magma" eventually moved into an environment where the rate of heat loss to the surface exceeded the rate of heat gain from radioactivity within the mass,* or from heat flow from below, thus permitting the temperature of the mass to drop and the interstitial liquid to solidify.

Another school of thought would interpret these same granites as being the result of slow crystallization from a magma containing crystals and a sizable portion of what could best be termed a silicate melt, and in some cases a viscous but essentially crystal-free melt is envisaged as the starting magma. Although there is evidence in the form of glassy selvages, etc. that at least some magmas are essentially pure silicate melt (see Shand, 1947, p. 6), and there is also adequate evidence that other "magmas" of similar bulk composition have had very little if any silicate melt present, it appears that the end results—the final solid rocks—do not differ greatly in mineralogy in these two extreme cases.

This merely illustrates the fact, pointed out by Eskola many years ago, that many natural systems approach a condition of phase equilibrium with respect to the particular temperature and pressure existing at the time. The true equilibrium assemblage at a given temperature will be identical, whether this state was approached by slow heating during metamorphism (and perhaps movement) of a thick sequence of sediments or by slow cooling during the solidification of a large intrusive body of liquid magma. The equilibrium referred to here deals only with the mineral phases present, and does not

* A completely insulated mass of rhyolitic magma of average, present-day composition will increase in temperature approximately 32°C every 10⁶ years. The greater amount of radioactive elements present during the Precambrian would have caused this rate of evolution of heat to be significantly greater (55°C per 10⁶ years at 2 × 10⁹ years ago), under similar conditions at that time (Roedder, 1956).

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concern the textural relations of the phases, except in so far as these textures aid or hinder the attainment of the equilibrium. These textures may, however, reveal many details of the history of the rock, if they can be correctly interpreted.

Upon slow cooling from a state of equilibrium, the phase assemblage (including any liquid) continuously reacts to approach new equilibria, particularly if an appreciable amount of liquid phase is present through which these reactions may occur. In many rocks, however, a point is apparently reached where the drastic decrease in the rate at which reactions occur, with decrease in temperature, results in "freezing in" the assemblage present at that time. These are the materials with which the petrologist must work, attempting to reconstruct the thermal and compositional history of the rock from the available clues.

In this chapter the experimentally determined silicate melt systems of most interest to petrologists will be reviewed, but no attempt will be made to cover the entire broad field of silicate melt systems, and very little will be said concerning subsolidus equilibria. For a much more comprehensive survey, the reader is referred to the 1600 page treatise entitled The Physical Chemistry of the Silicates by Eitel (1954a) which includes almost all of the phase diagrams reproduced in this chapter and many others of lesser interest to petrologists. Most of the phase diagrams reproduced here will also be found in a very useful compilation of phase diagrams for ceramists, published by the American Ceramic Society (Levin et al., 1956), which indicates the importance of these phase equilibrium studies to the various ceramic industries. This compilation also contains a four-page glossary of phase equilibrium terms (pp. 5–8); for the most part, the terminology in this chapter follows this usage.

Reviews on the general subject of silicate melt systems as applied to petrology will also be found in several papers by Bowen (1935b, 1937, 1954), Morey (1936b, 1937, 1956) and Schairer (1944, 1951, 1957), to whom the author is indebted for much of the material presented here. A classic book by Bowen, published thirty years ago (Bowen, 1928), is still a standard reference for applications of melt systems to petrology.

On "wet" (i.e. containing no readily volatile substances such as H₂O or CO₂) systems at near-atmospheric pressures (published up to 1957) will be discussed quite adequately in Volume 1 of this series (Roy and Tuttle, 1956), and silicate systems at high pressure constitute a subject by themselves. As most of the silicate systems discussed beyond have been studied at the Geophysical Laboratory of the Carnegie Institution of Washington, the reader is referred also to a convenient list of systems investigated at the Geophysical Laboratory (Adams, 1952). I want to express my appreciation for the help received from various members of the Geophysical Laboratory, and in particular from J. F. Schairer, who reviewed the manuscript and offered many helpful suggestions.

**EQUIPMENT AND TECHNIQUES**

As with many fields of science, progress in the study of silicate melt systems has been closely linked with progress in a number of experimental techniques. From the standpoint of experimental techniques, there are five steps in the determination of the phase diagram of a silicate system by the "quenching" method,
as normally used at the Geophysical Laboratory: (1) synthesis, (2) homogenization, (3) equilibration, (4) quenching, and (5) identification.

1. Synthesis

The essential problem here is to weigh out appropriate amounts of suitable materials, to make the various desired compositions. This is not as simple as it appears, for although it is comparatively easy to obtain pure materials, relatively free from specific, stated impurities, it is very difficult to obtain materials of stoichiometric, or at least precisely known, composition. Analytical reagents that might be used, such as the alkali carbonates, as normally supplied, bear analyses for trace amounts of various heavy metals, insolubles, etc. but seldom have specified the much larger amounts of H₂O or other diluents, which, although harmless in most analytical applications, do cause serious deviations from stoichiometric composition.

Not only must the materials used be pure and of known composition, but they must have other desirable properties. For example, it has long been known that the alkalis are more or less volatile at elevated temperature. Losses from this cause are largest if CO₂ and H₂O are also being driven off from the mixture (Kracek, 1932). For this and other reasons, it is necessary to prepare first a crystalline alkali silicate from the alkali carbonate and silica, and then weigh the calculated amounts of this material, if the alkalis are desired in the batch. It is also desirable, and in the case of viscous melts it is imperative, to use materials that will be relatively soluble during the homogenization, although this requires a compromise, in that the fine grained, readily soluble varieties of such materials as Al₂O₃ and MgO are also hygroscopic and apt to be far from stoichiometric.

If the preparation of the batch is performed with due care, its composition, as determined by synthesis, will probably be closer to the desired composition than is possible to determine by chemical analysis of the completed batch.

2. Homogenization

The object of this step is to convert the mixture of weighed raw materials to a homogeneous glass, so that even tiny portions (a few milligrams) of the batch will be of the same gross composition as the entire batch. This homogenization usually consists of repeated fusion, quenching and crushing. A very sensitive test for homogeneity consists of observing some of the crushed glass embedded in a liquid exactly matching it in index of refraction, making use of the more rapid change of the index of refraction of the oil with change in temperature to obtain a perfect match. By this method extremely small, as well as very local, variations in the composition of the glass result in rather prominent index variations.

In many systems, particularly for subsolidus studies, sintering of the finely-ground batch is used as a method for both homogenization and equilibration.

3. Equilibration

The object here is to hold small amounts of the prepared glasses, and/or portions of them that have been crystallized previously, at a variety of constant, known, temperatures for lengths of time adequate to attain equilibrium. The technique for preparing the tiny charges, usually in platinum foil envelopes, was
first described by Shepherd et al. (1909); a number of experimental details are given by Roedder (1951a).

Two of the major problems in silicate phase equilibrium research lie in the words "constant, known, temperatures". The published information on high temperature furnaces and temperature controllers for such work is rather scattered (Adams, 1924; Roberts, 1925, 1941; Faust, 1936; Roedder, 1952). An excellent controller, using a modification of the bridge method of Roberts (1925), has been designed by Mauer and later revised by Mauer and J. England. Although this controller has not been fully described in the literature, a few details of the construction and operation of some earlier versions are given in Levin and Ugrinic (1953), and Bogue (1955, p. 311). In general, platinum-wound furnaces are used, designed to heat small diameter vertical ceramic tubes, in which the sample is hung. The normal construction involves a can of insulation (usually MgO) surrounding the furnace tubes, so that only a few hundred watts of electric power are consumed.

In the measurement of high temperatures in silicate research, the e.m.f., measured potentiometrically (White, 1941a), of thermocouples of pure platinum against a platinum alloy with 10 per cent rhodium are usually used, with the cold junction in crushed ice and water. As the e.m.f. of such thermocouples is rather small (10–12 μV/deg), considerable care must be used to isolate the thermocouple circuit from stray conducted or induced currents from the furnace heating circuit, and from stray thermal e.m.f.'s (White, 1941b). For most work the deviations of such thermocouples from the available tables of e.m.f. vs. temperature (for example, Adams, 1914), are large, even when they are newly made from the best available wire. Such thermocouples will also exhibit drift in their e.m.f., with use, due to annealing of the wire (Roeser and Wensele, 1935), and particularly from contamination with iridium (Day et al., 1906, p. 286), alkalis (Roedder, 1951a, p. 90), or iron (Bowen and Schairer, 1932, p. 181). As a consequence, the thermocouples are usually calibrated, at frequent intervals, using as reference points the melting points of various pure materials. In the publications of the Geophysical Laboratory, these melting points are specified in terms of the temperature scale based on the nitrogen gas-thermometer calibration of Day and Sosman (1911, 1912).

Representative fixed points on this scale are the melting points of zinc, 419-4°C; silver, 960-2°C; gold, 1062-6°C; synthetic diopside, 1391-5°C; palladium, 1549-5°C; and platinum, 1755°C. For convenience, certain secondary reference materials are sometimes used, such as pure NaCl, 800-4°C; synthetic Li₂O·SiO₂, 1201°C; synthetic pseudowollastonite or α CaO·SiO₂, 1544°C; and synthetic anorthite, CaO·Al₂O₃·2SiO₂, 1550°C (Roberts, 1924). The use of specific points such as these has the advantage that regardless of the changes that have already taken place in the adopted high temperature scales (Stimson, 1949; Corruccini, 1949; and Wilson, 1953), or that may take place in the future, the temperatures reported in the work can be recalculated to the scale currently adopted. For consistency, the Geophysical Laboratory has used this "Geophysical Laboratory Scale" in all their publications since 1914.* A

* Temperatures on the diagrams beyond are given as presented in the original references, and hence are not strictly comparable in all cases. The differences between the various scales are not very significant except at temperatures over 1500°C, where the differences may be up to 20°C.
discussion of the interrelationships of the various temperature scales will be found in Sosman (1952).

The specific furnace technique used will vary with the nature of the problem. The normal quenching technique, with platinum resistance furnaces, was originally described by Shepherd et al. (1909), and later by Faust (1936). Further details on the normal technique and some of the variations invoked for use with systems including FeO as a component have been described by Bowen and Schairer (1932), and by Roedder (1951a and 1952). Numerous other papers in the literature mention variations in the technique for other specific applications.

Considerably different techniques are used in special cases. The gradient furnace, wherein a long strip of the material under investigation is placed in a constant known thermal gradient, has been used as a quick reconnaissance method for determining the specific temperatures at which individual quench runs should be made (Grauer and Hamilton, 1950; Tucker and Joy, 1957). The ribbon furnace, in which a small amount of the sample is placed on an electrically heated platinum ribbon and observed telescopically, is particularly useful for high temperature studies where quenching is difficult. Temperatures in such cases are usually read with an optical pyrometer focused on the strip. Many useful variations of this device have been described, including one designed for use on a microscope stage (Roberts and Morey, 1930; Keith and Roy, 1954, p. 6). For temperatures much above 1600°C, where the platinum or platinum–rhodium resistance element begins to vaporize too much for convenient use, a variety of other furnace types are used, including electrical resistance furnaces with heating elements made of carbon tubes, spirals or granules, rare earth rods, tungsten or molybdenum ribbon or wire, electric arcs, oxy-gas and oxy-hydrogen flames, and solar energy. These high temperature furnaces are used mostly for research in the oxide systems not including SiO₂, as the presence of SiO₂ in a system brings the temperatures down into the working range of the platinum resistor in most cases.

The largest single problem, present in all silicate research, is that of establishing and verifying the existence of equilibrium in any given experiment. The methods used to verify equilibrium will be controlled by the nature of the phase assemblage, and the specific methods used for one type of assemblage, such as the metal systems (Brewer, 1950) are not necessarily applicable to another type, such as the silicate systems.

In silicate phase research, there are a number of criteria indicating that equilibrium has been established. Some of these, such as uniformity of distribution of phases and the absence of rounded or corroded crystals, are helpful criteria, but are not reliable. Lack of further change when held at the same temperature for a longer time is a necessary but not positive criterion. The existence of metastable equilibrium, even for long periods of time at high temperatures, is particularly common in the silicates and may be practically impossible to avoid. Thus in the system K₂O–MgO–SiO₂ Roedder (1951a) was unable, even with long runs, to establish equilibrium at the liquidus with the “correct” modification of silica (quartz), known from the system K₂O–SiO₂ (Kracek et al., 1929, p. 1860), and from other systems, to be the stable modification at such temperatures.

Another very valuable “proof” of equilibrium, at least with respect to a metastable process, if not the stable process, is that of duplication of results
by starting with the same composition in a different physical state (e.g. crystalline and glassy). Thus, if a glass made of components A, B and C, and a mixture of crystals of A, B and C (of the same gross composition), when heated to a given temperature, both yield crystals of B, crystals of C and liquid, one can be reasonably sure that crystals of A are not stable (they melted) and that the assemblage B, C and liquid represents at least metastable equilibrium. It does not tell us, however, that some other polymorphic form of B, or C (or even A), is not a truly stable phase under these conditions, or that some binary or ternary compound of A, B and C is not stable. For example, the binary system $K_2O\cdot SiO_2-SiO_2$ as deduced from a study of the ternary system $H_2O-K_2SiO_3-SiO_2$ (Morey and Fenner, 1917) exhibited only one intermediate compound, $K_2O\cdot 2SiO_2$, and showed a eutectic between this compound and SiO$_2$ at 525°C, at a $K_2O/SiO_2$ ratio of 1/4. This eutectic was later shown to be metastable, however (Kracek et al., 1929); if enough time is permitted, a new stable phase, coincidently of composition $K_2O\cdot 4SiO_2$, will appear. This compound is exceedingly slow to nucleate and grow in these viscous liquids. Where formerly there had been a deep, low-temperature (metastable) eutectic “valley” on the diagram, there is now a stable compound with a considerably higher melting point than the metastable eutectic (see Fig. 4).

For such reasons as this, it is important to obtain as many different phases as possible in the precrystallization of the batches, to use as “seeds” in the equilibration runs, so that the reluctance of the system to initiate the formation of a new phase—the major cause of metastability—may be avoided. When nucleation is very difficult in the precrystallization, it is sometimes desirable to subject the samples to a mild “hydrothermal” treatment to induce crystallization. One such method involves sealing the sample, in a loose capsule, in an evacuated tube, along with another capsule containing a small amount of a natural water-bearing glass, such as obsidian (Gregg and Barth, 1938, p. 98). At the temperature of the crystallization this yields a small water vapour pressure in the tube which increases the rate of nucleation and growth of crystals in the sample many orders of magnitude. With this technique one must be careful not to grow crystals so large that equilibration, by melting of the crystals, will be slow. In general, crystal size should be kept under 20 $\mu$. If only a very small percentage of tiny crystals is formed in this manner, their behaviour can give a sensitive indication of the equilibrium even in exceedingly viscous glasses; thus if they grow slightly at one temperature, and become corroded at a higher temperature, the melting point of the crystals must lie between (Gregg and Barth, 1938, p. 97). Ordinarily, if viscosities are low, nucleation is fast and seeding is not necessary. In some cases it appears that the transformation of an early-formed disordered to an ordered phase is the rate-limiting step in the attainment of equilibrium, as in the aluminium-silicon ordering in the feldspars (Goldsmit, 1953).

There is one further check on the existence of equilibrium, in the form of agreement of the data on a given point with data from nearby points. This is a powerful tool to detect disequilibrium. Unfortunately, however, no method of experimental or theoretical determination of phase relationships in a heterogeneous system can completely exclude the possible existence of other, more stable phases. Metastable phase diagrams can appear perfectly normal in all respects, and unless the possibility of the existence of other modifications or compounds can be deduced from crystal chemical considerations or from the
occurrence of such phases in other systems, or in nature, the diagrams will appear to represent true equilibrium conditions. Phases have been found in nature that do not show up on the appropriate silicate melt systems; some of these phases are apparently monotropic, and have no stability field, and others apparently form and are stable only under high pressures. In a few cases, however, it is apparent that the reactions forming them (usually in the solid state) have activation energies which are prohibitive of laboratory synthesis, but are permissive if geological time is available.

4. Quenching

The purpose of quenching is to bring the sample from the high temperatures, at which it was equilibrated, down to room temperature at such a rate that phase changes do not occur. The main reason for this is that it is generally inconvenient or even impossible to identify the phases present while the temperature is high. Quenching is done in a variety of ways, depending upon the ease with which the particular phase changes involved may occur. Highly viscous silicate melts may be cooled in air without fear of crystallization, as some of these take months or even years to crystallize even at optimum temperatures. On the other hand, liquids of low viscosity may crystallize, at least partly, even in the few tenths of a second during which they cool when suddenly submerged in cool mercury (as by the use of a platinum weight as a sinker, Roedder, 1952, p. 442), and of course the "snap" inversions in some crystalline phases will occur regardless of the cooling rate.

One problem developed in quenching is that of recognizing phases "formed on quench" from those present in the equilibrated batch at the furnace temperature. In some cases a few feathery, dendritic spines form on quench at the corners of the large solid euhedral crystals present at equilibrium. In other cases all liquid present in the charge in the furnace crystallizes on quench to a fine feathery mass, in which are embedded the large solid euhedral crystals that were present at the temperature of the furnace. If this sort of ambiguity cannot be eliminated by the obvious procedure of faster quenching, then it is quite possible that one of the other methods of recognition of phase change, such as differential thermal analysis (DTA), or heating or cooling curves (Morey, 1923; 1936a, p. 1–3), might be used to advantage. Most silicates crystallize so sluggishly, however, and with such small heats of crystallization, that these dynamic methods are not very applicable (Kräcek, 1951).

5. Identification*

The identification of the phases present and the determination of their composition is sometimes one of the most difficult aspects of phase equilibrium studies. As any of the characteristic properties of a phase may be measured to prove its existence or to discern a phase change (Brewer, 1950), recent developments in instrumentation, and a wider use of older techniques, have done much to aid phase identification.

Although in general a combination of thermal, X-ray and microscopic data is used to determine the composition and interrelationships of phases, the petrographic microscope is still the most useful tool in silicate studies, even when the

* This section is taken, with some modification, almost directly from Christensen and Roedder (1952).
optical properties of the phases are unknown at the start of the investigation. Petrographic methods are particularly useful with the quenching technique, as the quantity of sample required for a complete optical determination is very small. As many as seven distinct optical properties, any one or combination of which may be definitive of a phase, may, if necessary, be measured on a single crystal grain less than 10 µ in diameter (i.e. down to 0-001 µg) without destroying the grain. In the system pseudowollastonite–akermanite–gehlenite, for example, OSBORN and SCHAIRER (1941) used the interference colour of the melilite solid solution to establish its composition between akermanite and gehlenite, and hence determine conjugation lines and crystallization curves in the large solid solution field. It is far more convenient, however, to use different portions of the sample for each such determination, and hence 1 mg or more of sample is desirable. As most of the procedures used in the quenching technique provide samples of approximately 10 mg, there is adequate material left for other techniques such as the X-ray diffraction.

Determination of the amount and composition of liquid present at high temperatures (or glass, its quenched equivalent) has been a considerable problem in many silicate systems, as glass does not have many of the properties so characteristic of crystalline solids. Centrifuging at high temperatures to separate liquid from crystals works rather well, as an adaptation of the well-known "wet-rest" method used so frequently in soluble salt–water systems at lower temperatures, but experimentally this method presents serious problems at high temperatures (see BIRCH, 1955; DØRGE and SHEGOG, 1955; BOGUE, 1955). Heat-of-solution calorimetry has been used to determine the amount of liquid (glass) present in Portland cement clinker, in consequence of the differences in heat of solution of crystals and that of the glass (LERCH and BROWNMILLER, 1937), but this requires a knowledge of the latent heat of crystallization of all possible glass compositions in the system. A less elegant but exceedingly simple and convenient procedure involves the use of a porous relatively nonreactive material (e.g. sintered Al₂O₃), to remove the liquid from the batch by capillarity. The determination of the approximate amount of liquid present by the "quenching" technique is usually based on microscopic examination for glass in the quenched product. A more accurate method is available, however, when the index of refraction of the glass in the mixture of glass plus crystals can be obtained. If one knows the total composition of the mixture (by synthesis) and the composition of the crystal phase present (from petrographic examination), by the use of a previously determined plot of composition versus index of refraction for glasses in the system, one can determine both the composition of the glass and the relative amounts of crystals and glass present in the quenched sample. In silicate systems these determinations of amounts of liquid and crystal phases are usually used only as a guide to further work, and seldom as data on which to base an equilibrium diagram. For the determination of the temperature of eutectic points by observing the start of melting of all-crystalline material, microscopic examination for the presence of glass is not so sensitive a test sometimes as is the sintering of the powdered crystalline material.

Next to the petrographic microscope, the most useful tool in the identification of the phases in silicate work is the diffraction of X-rays. X-ray techniques are not a panacea, however, and some of the limitations have been discussed by BREWER (1950). Because of the minute percentage of crystalline phase
present, such techniques are useless for determining the crystal phase at the liquidus unless such crystals can be determined by petrographic methods to be identical with other crystals occurring in larger amounts in samples equilibrated at lower temperatures. Of particular significance is the limitation of X-ray techniques in systems involving solid solution series between “end members” whose unit cells are practically identical in size and shape.

One very important technique, which should have even greater application in the future, is the use of the high temperature X-ray camera for identification of the phases present while the sample is still in the furnace. Although experimentally difficult, this technique has the great advantage of being a direct method, and thus avoiding ambiguity resulting from crystallization or rapid inversions on quench. Many designs of high temperature X-ray cameras are described in the literature, but most of these are made for detecting phase changes in single crystals or powdered solids (for example, BASSETT and LAPHAM, 1957), and hence are not readily applicable to solid–liquid equilibria.

Method of Presentation of Data

The phase rule of Willard Gibbs, stated simply, is that for a system in equilibrium, the number of degrees of freedom must equal the sum of the number of components, plus two, minus the number of phases. The degrees of freedom are taken in the definition of MACDOUGALL (1939, p. 136): “The number of intensive variables which can be altered independently and arbitrarily (within certain limits) without bringing about the disappearance of a phase or the formation of a new phase is called (in the thermodynamic sense) the number of degrees of freedom of a system.” (Another widely-quoted definition of degrees of freedom involving the number of variables “which must be arbitrarily fixed in order to define the system”, results in serious ambiguity and should be avoided.) A phase diagram is merely a graphical expression of the limits to which these variables can be independently and arbitrarily altered. As such it is usually a plot of one variable against another, with the limits indicated for given phase assemblages. In the diagrams presented beyond, pressure is not considered as a variable.

In unary (single-component) systems, the convention is to plot T as abscissa and P (vapour pressure or total pressure on the system) as ordinate.

In binary (two-component) systems, the convention in condensed systems is to plot composition as the abscissa (usually in weight per cent but occasionally mole per cent) against T as the ordinate. Most silicate melt systems can be considered to be condensed systems, in that the vapour pressures of the phases involved are negligible, and so no vapour phase appears and the effect of 1 atm external pressure is nil. An exception to this will be found in the systems bearing FeO. Here a variation from an essentially zero partial pressure of oxygen (as with a flow of carefully purified nitrogen) to even a small part of the 0.2 atm partial pressure of oxygen in air can change the phase assemblage drastically. In many cases such systems, although they are usually considered as “condensed” systems, are actually determined under some fixed, very low, but significant partial pressure of oxygen, such as that determined by the efficiency of the oxygen-removing train used to purify the nitrogen atmosphere.

In ternary (three-component) systems, the convention is to plot two compositional variables (per cent A and per cent B, per cent C being implicit in the
statement of the other two) on an equilateral triangle, and represent the temperatures of a given surface, such as the liquidus, by contours (isotherms) representing the height above the base of a three-dimensional triangular prism figure. The figure is projected onto the base along the temperature axis, as only two variables can be rigorously plotted on a two-dimensional diagram, and the compositions are most important.

One of the fortunate aspects of this type of plot, which is seldom used to the extent that it might be, lies in the fact that these diagrams can be used to determine quantitatively the amount and composition of each phase present, for any

![Diagram showing the phases present, at equilibrium, in a mixture of composition “a”, (Fig. 26) between liquidus and solidus, in the system K₂O–MgO–SiO₂. The temperatures of phase changes were obtained experimentally; the percentages were obtained by scaling Fig. 26. Letters in parentheses refer to points on Fig. 26 and Table 1. (After ROEDDER, 1951a, p. 227.)](image)

composition in the system at any temperature. The methods for such operations are given, rather cursorily, in most phase rule texts. A short but rather lucid review of the principles will be found in LEVIN et al. (1956, pp. 9–29). Although graphical methods are customarily used in working with these diagrams, rigorous analytical methods have been described (MOREY, 1930). Quantitative information obtained by such methods reveals that some compositions have surprisingly abrupt changes in the total quantity of the various phases present during their cooling (or heating) history. These abrupt changes can usually be seen in a qualitative way, of course, by simple inspection of the diagram, but their rapidity and magnitude become much more apparent when a plot is made of the amounts of the various phases present in per cent of the total, vs. the temperature. Figure 1 is an example of such a plot, made from the graphically determined data of Table 1, showing the change in phase assemblage with temperature for a certain composition in the system K₂O–MgO–SiO₂ (Fig. 26). This composition shows, incidentally, one type of recurrent crystallization of forsterite, 2MgO·SiO₂. This means that forsterite is stable in two different temperature ranges, separated by a temperature range in which it cannot exist as a stable phase. Other compositions near to point “a”, in the triangle SV’V’ of Fig. 26, have three separate stability ranges for forsterite (see ROEDDER, 1951a, pp. 228 and 243).
Table 1. Phase Changes Occurring between the Liquidus and Solidus for a Mixture of Composition “a”, Fig. 26
(See text and Fig. 1)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Phases present at equilibrium</th>
<th>Composition of the liquid lies</th>
<th>Composition of the solid lies</th>
<th>Weight per cent</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Liquid</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>2MgO·SiO₂</td>
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<td></td>
<td>MgO·SiO₂</td>
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<td></td>
<td></td>
<td>K₂O·5MgO·12SiO₃</td>
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<td></td>
<td>K₂O·MgO·5SiO₃</td>
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<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>&gt; 1383</td>
<td>All liquid</td>
<td>at a</td>
<td>none present</td>
<td>100</td>
</tr>
<tr>
<td>1383–1283</td>
<td>Forsterite + liquid</td>
<td>at L</td>
<td>100</td>
<td></td>
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<tr>
<td>1283–1198</td>
<td>Forsterite + protoenstatite + liquid</td>
<td>along a–b'</td>
<td>100–95</td>
<td></td>
</tr>
<tr>
<td>1198–1163</td>
<td>Protoenstatite + liquid</td>
<td>at b'</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>1163–1155</td>
<td>Proto. + K₂O·5MgO·12SiO₃ + liquid</td>
<td>along b''b'''</td>
<td>95–88</td>
<td></td>
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<tr>
<td>1155–1118</td>
<td>Forst. + K₂O·5MgO·12SiO₃ + liquid</td>
<td>along b''–c</td>
<td>88</td>
<td></td>
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<tr>
<td>1116–1053±</td>
<td>K₂O·5MgO·12SiO₃ + liquid</td>
<td>at c</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>± 1053±–963</td>
<td>+ liquid + Tridymite (no liquid)</td>
<td>along cU</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>± 963</td>
<td></td>
<td>at U</td>
<td>84–58</td>
<td></td>
</tr>
<tr>
<td>± 1053±–963</td>
<td>K₂O·5MgO·12SiO₃ + liquid</td>
<td>along Ud</td>
<td>58–55</td>
<td></td>
</tr>
<tr>
<td>± 963</td>
<td>+ liquid + Tridymite (no liquid)</td>
<td>along ud'</td>
<td>55–47</td>
<td></td>
</tr>
<tr>
<td>&lt; 963</td>
<td>K₂O·5MgO·12SiO₃ + K₂O·MgO·5SiO₃</td>
<td>along de</td>
<td>55–47</td>
<td></td>
</tr>
</tbody>
</table>

1. Experimentally determined points—for data see Preparation 49 in Tables 1–5 of RÖDECKER, 1951.
2. Not determined directly on this composition due to the large percentage of crystals present causing experimental difficulties. Data obtained from other points in the diagram.
Table 2. Phase Changes Occurring between the Liquidus and Solidus for a Mixture of Composition “a”, Fig. 10
(See text and Fig. 2)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Phases present at equilibrium</th>
<th>Weight per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Liquid</td>
</tr>
<tr>
<td>&gt; 1600 at 1600</td>
<td>All liquid</td>
<td>100</td>
</tr>
<tr>
<td>1600–1500 at 1500</td>
<td>CaO + liquid</td>
<td>100-95</td>
</tr>
<tr>
<td>1500–1470 at 1470</td>
<td>CaO + 3CaO·SiO₂ + liquid</td>
<td>95</td>
</tr>
<tr>
<td>1470–1455 at 1455</td>
<td>3CaO·SiO₂ + 3CaO·Al₂O₃ + liquid</td>
<td>95-92</td>
</tr>
<tr>
<td>1455–1335 at 1335</td>
<td>3CaO·Al₂O₃ + 2CaO·SiO₂ + liquid</td>
<td>58-43</td>
</tr>
<tr>
<td>&lt; 1335</td>
<td>(2CaO·SiO₂ inverts at 1420°)</td>
<td>43-12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5-0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>
Another similar plot is shown in Fig. 2, made from the data of Table 2, for a composition "a" in the system CaO–Al₂O₃–SiO₂ (Fig. 10). Obviously there will be abrupt breaks in the amounts of phases present while the particular composition chosen goes through invariant points (points c and e for Fig. 1, and points A and B for Fig. 2), but the tremendous changes in the phase composition of these examples with very minor drops in temperature, particularly Fig. 2, are noteworthy. They are strictly a result of the geometric relations of the gross composition of the batch to the pertinent boundary curves, and their corresponding Alkemade lines, but crystallization paths such as these must

certainly have their counterparts in the multicomponent systems representing rock magmas. It is difficult, in fact, to visualize such a complex system where there will not be rather abrupt changes in the amounts, and ratios, of the crystallizing phases on cooling.

Another possible method of representation of the data of a ternary system such as K₂O–MgO–SiO₂ would involve for example tracing the changes in composition, and temperature, of the system MgO–SiO₂, with small additions of K₂O. This is, in effect, viewing from the K₂O corner a series of non-binary sections through the diagram, each at constant K₂O content. This is illustrated in Fig. 3 (see also Krácek, 1939, p. 2873). A variant of this was used by Morey (1932), in which he showed on a composition plot the lateral displacement of boundary curves in the system Na₂O–CaO–SiO₂ with additions of B₂O₃, by superimposing the new boundary curves for 1 per cent and 5 per cent added B₂O₃ on those for the pure system. A variety of other methods have been developed for representing ternary systems, but these are not as generally convenient as the usual equilateral composition plot.

In some instances a four-component system, containing only small amounts of one of the four components, is represented simply as a three-component system, with a plot or merely a statement of the amount of the fourth component.
Examples of this are common in systems containing FeO as a component; these, even though run in a pure nitrogen atmosphere, in containers of pure iron, always contain small, equilibrium amounts of ferric iron. This is really another component, but as its concentration is insufficient to form significant amounts of independent ferric iron phases, the system is presented as though it contained one less component, and lines are drawn to show the Fe₂O₃ content in the various compositions, under some specified conditions (see Fig. 15).

![Equilibrium diagram of the system MgO-SiO₂](image)

Fig. 3. Equilibrium diagram of the system MgO-SiO₂, after Bowen and Andersen, and Gregg (solid lines), showing the effects of various additions of K₂O on the MgO-SiO₂-SiO₂ eutectic I, as recalculated from the system K₂O-MgO-SiO₂ (broken lines). The letters refer to points on Fig. 25.

One very useful type of diagram, particularly for complex ternary systems, is the isothermal section. This is in effect a plane through the triangular prism model of the system, and shows the phase assemblage for any composition, at the specified temperature. On it can be represented the tie lines connecting the compositions of coexisting phases, for example solid solutions and liquid solutions; this information cannot be represented rigorously on the general (non-isothermal) ternary diagram, as there will be an infinite array of such lines. The isothermal section has long been used by the chemists to represent the phase relations in ternary systems including two salts and water, as this type of diagram is particularly suited to represent the data which, for convenience in the laboratory work, are usually obtained under isothermal conditions. A simple example is given in Fig. 31, showing an isothermal section through the system Na₂O-Fe₂O₃-SiO₂ at 825°C (Bowen et al., 1930). This figure shows areas representing four types of equilibria in the condensed system: trivariant (liquid only); divariant (one crystal phase and liquid, joined by radial tie lines); monovariant (two crystal phases and a coexisting liquid, making a “three-phase triangle”); and invariant (three crystal phases and liquid). The three-phase
triangles in a simple system such as Na₂O–Fe₂O₃–SiO₂ can be drawn by inspection of the liquidus phase diagram (Fig. 30). In a system involving solid solutions, however, the three-phase triangles must be established by experimental measurements of the compositions of coexisting phases. As there are infinite numbers of such three-phase triangles in any system involving solid solutions, it is conventional to represent only a few of them on the diagram, either as triangles or as tie lines connecting two coexisting phases, to illustrate their general shape and direction (see, for example, Fig. 47).

In quaternary (four-component) systems, the problems of representation of the data become severe, as three dimensions are needed to represent composition alone, unless simplifying restrictions are made, or “line-symbols” are used in place of points for the representation of compositions, (Reimers, 1946; Dolar-Mantuani, 1957). Thus a three-dimensional model (usually a regular tetrahedron) is needed to represent the compositions, and the other variable, temperature, can only be represented by spot figures, written in on the solid model. As three dimensions are needed to represent unambiguously the three independent compositional variables, any attempt to represent a quaternary system on a two-dimensional sheet of paper must, of necessity, be far from rigorous.

A number of different techniques are used to reduce quaternary phase diagrams to two-dimensional drawings. If the system is simple, a perspective drawing of an apparently transparent model showing the univariant boundary lines can be made, or a plan view of the four limiting ternary systems comprising the four sides of the tetrahedron is shown, folding down three of the sides to the plane of the paper on which the fourth sits. In other examples, a transparent tetrahedron is drawn, with cross-cutting triangular planes representing the ternary subsystems that separate the diagram into smaller individual quaternary subsystems (Fig. 58).

The most satisfactory method of representing the phase equilibria within a quaternary system is the use of a series of sections through the system. In most cases these constitute ternary, or at least partially ternary, sections joining the composition points of three compounds or components (for example, see Fig. 53). Although these diagrams may appear as normal ternary systems, they frequently contain portions representing non-ternary (quaternary) equilibrium, and cannot be “read” in the usual fashion (for example, see Fig. 41, and discussion in Schairer, 1942). Thus, where four-phase univariant lines in the quaternary system, representing equilibria between a liquid and three solids, are cut by any arbitrary triangular planes, the points appear as ternary invariant points; to distinguish them Schairer has given them the name “piercing points” (Schairer, 1942, p. 253). If the compositions of all four phases at the point may be expressed in terms of the three compositions at the apices of the triangle, then the point is a true ternary invariant point, and the section, or at least this part of it, represents a ternary subsystem. In some quaternary systems, where there are no convenient ternary sections to be drawn, a series of sections at different fixed percentages of one component are used to illustrate the equilibria within the tetrahedron.

One further graphical method for representing quaternary equilibria in two dimensions deserves mention. This has come to be known as a “Schairer diagram,” as it is a procedure first described by Schairer (1942) for representing
the univariant lines (three solid phases and liquid) within a quaternary. It shows their relationships to the quaternary invariant points, and to the ternary invariant points on the four limiting ternary faces of the tetrahedron as well as on ternary subsystems within the quaternary. An example of the use of this device for illustrating equilibria in the system $K_2O-MgO-Al_2O_3-SiO_2$ is shown in Fig. 59. The phases coexisting in equilibrium are indicated, the direction of drop in temperature on univariant lines is apparent, and spot temperatures can be written in at invariant points.

**SILICATE MELT SYSTEMS OF PETROLOGICAL IMPORTANCE**

**Scope**

In a review of this length, it is obvious that only a few of the many hundreds of diagrams may be presented and discussed. Levin et al. (1956), list over 800 diagrams of interest to ceramicists, and the bulk of these contain silica and are of interest to petrologists.

The following discussion will hence be limited essentially to diagrams in the eight-component "system" $K_2O-Na_2O-CaO-FeO-MgO-Fe_2O_3-Al_2O_3-SiO_2$. This "system" has been chosen as it represents, in only eight components, a reasonably close approach to the composition of most ordinary igneous rocks.

**Table 3. Average Composition of Igneous Rocks**
*(from Clarke, 1924, p. 29)*

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>59.14</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15.34</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.08</td>
</tr>
<tr>
<td>FeO</td>
<td>3.80</td>
</tr>
<tr>
<td>MgO</td>
<td>3.49</td>
</tr>
<tr>
<td>CaO</td>
<td>5.08</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>3.84</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>3.13</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.15</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.05</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.039</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.101</td>
</tr>
<tr>
<td>Cl</td>
<td>0.048</td>
</tr>
<tr>
<td>F</td>
<td>0.030</td>
</tr>
<tr>
<td>S</td>
<td>0.052</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.299</td>
</tr>
<tr>
<td>MnO</td>
<td>0.124</td>
</tr>
<tr>
<td>BaO</td>
<td>0.055</td>
</tr>
</tbody>
</table>

---

Table 3 lists Clarke’s (1924) data for the average composition of igneous rocks as sampled from the crust of the earth. From this table it will be seen that over 99 per cent of the average igneous rock consists of the top ten oxides, and the top eight make up nearly 97 per cent. TiO$_2$ and all the constituents below it on the table will be omitted in the following discussion as they are present in small amounts and have comparatively little effect on the bulk phase assemblage obtained. H$_2$O is different, however. Although it is merely another component,
in the strict sense, it raises special experimental problems, and has considerable
effect on the bulk phase assemblage. As systems involving $\text{H}_2\text{O}$ have been
discussed in the first volume of this series (Roy and Tuttle, 1956), they will be
omitted here, but it should be remembered that $\text{H}_2\text{O}$ is present in significant
amounts in most, if not all, magmas. The diagrams presented beyond will be
affected by this extra component in several qualitatively predictable ways.
Although some of the hydrous minerals that might form under these conditions,
such as certain amphiboles, can be considered to approximate the hydrous equi-
valents of well-known anhydrous phases, there are other hydrous phases, such as
muscovite, for which there are no single anhydrous equivalents. In this latter
case, the presence or absence of $\text{H}_2\text{O}$ may have rather drastic effects on the
phase diagrams. In addition to causing the formation of new phases, the presence
of even a small amount of water will cause a considerable lowering of the liquidus
(and solidus), as well as a drastic lowering of the viscosity, of most silicate melts.
These effects are readily explained, mechanistically, in the breaking of $\text{Si-O}$
bonds by the entrance of hydrogen ions. As a consequence, anhydrous phases
that are not stable at the temperatures of the liquidus in the anhydrous system,
may crystallize from the liquid phase where the liquidus has been lowered
sufficiently, and the lowered viscosity results in easier diffusion and nucleation,
as well as more rapid flow under a given pressure differential.

There have been no direct studies of equilibria in this eight-component
system. Although it would be experimentally simple to add all eight components
to a given batch, identification of the phases obtained (particularly the solid
solutions), would be exceedingly difficult, and there would still be the problem of
representation. Just to represent the composition variables alone, with no
dimension for representing the temperature variable, would require a diagram
drawn in seven dimensions. Obviously, limiting assumptions must be made,
to simplify the system to a manageable number of variables, and the work of the
Geophysical Laboratory since its inception in 1907, and of many other
laboratories studying phase equilibria of interest to petrology, has been along
these lines. The approach has been to start with simple binary systems between
individual pairs of these components, followed by the ternary systems, then the
quaternary systems, etc. Although there are fifty-six possible ternary combina-
tions and seventy possible quaternary combinations in an eight-component
system, not all of these need be determined. This is fortunate, in that up to the
present time, not even one single quaternary silicate system has been completely
determined. As the work is aimed at the elucidation of rocks, simplifying
assumptions may be made based on the composition of rocks. Thus, as silica
is present in practically all rocks, systems not including silica need not be
considered essential. They cannot be ignored, in that the phases formed in
these systems may occur also in the systems with silica, and they represent
limiting cases for the equilibria involving silica, but as most rocks contain
forty or more per cent silica, these considerations are not very important. Other
possible compositional limitations that may be assumed, in order to simplify
the system, stem from the fact that igneous rocks, although containing signi-
ficant amounts of all eight of the oxides mentioned, usually contain at least
some of these in amounts corresponding to simple ratios. This is merely a
logical consequence of the fact that rocks are made of a comparatively few
minerals, but it does make it possible to represent the petrologically important
portions of relatively complex systems with far fewer components. Thus a saturated basalt, the bulk composition of which can be reasonably approximated by the six-component system CaO–MgO–FeO–Na₂O–Al₂O₃–SiO₂, can also be represented, with little loss in rigour, by the four-component system diopside (CaO·MgO·2SiO₂)–ferrosilite (FeO·SiO₂)–albite (Na₂O·Al₂O₃·6SiO₂)–anorthite (CaO·Al₂O₃·2SiO₂). Still further simplification lies in the similarity with which certain pairs of elements behave. Thus small amounts of ferrous iron can be lumped with magnesium, with comparatively little stretching of the facts. In actual practice, there has been sufficient study of the relative behaviour of Mg++] and Fe++] in silicate melts, that the concentration of iron relative to magnesium in the residual liquids from the basalt “system” above can be predicted, qualitatively, with a fair degree of certainty. Thus the basalt “system” diopside–ferrosilite–albite–anorthite can be further simplified, with additional but still minor losses in accuracy, by the ternary system diopside–albite–anorthite.

This type of simplification is necessary if the complex natural systems are to be placed on a rational basis. The simplifying assumptions made would be very hazardous, however, were it not for the fact that the results of the more complex systems—the rocks themselves—are always at hand, and provide a framework of facts and observations, obtained by the study of rocks in the field and in the laboratory, into which the experimental work must fit. When contradictions occur, further work in the field, or in the laboratory, is needed. By this process, in which each discipline nicely supplements the other, we may hope to obtain an understanding of the processes whereby rocks have formed in nature.

Specific Systems in the More General System \( \text{K}_2\text{O–Na}_2\text{O–CaO–FeO–MgO–Fe}_2\text{O}_3–\text{Al}_2\text{O}_3–\text{SiO}_2 \)

For a complete understanding of any complex system, all limiting simpler systems should be determined first. In order to limit the presentation to those diagrams of most direct interest to petrology, however, only systems with SiO₂ will be given here, and although the subsolidus relations are of great importance to petrology, space prevents their being covered. A number of other possible systems, involving only oxides other than SiO₂, have been determined and are given by Levin et al. (1956). In the diagrams which follow, it is particularly instructive to observe in each the composition and temperature of the last residual liquids to solidify. If ferrous iron is present, it will become concentrated in the residual liquids under equilibrium or disequilibrium crystallization, unless the alkalis and alumina are also present. In this case, the residual liquids, without exception, are seen to approach a composition corresponding to quartz plus alkali feldspar. The liquidus temperatures for such residual mixtures are very low unless no ferrous iron, or alkalis plus alumina, are present.

Actually, many of the systems presented beyond have little resemblance to any igneous rock composition, but they are necessary to an understanding of the equilibria in the more complex systems that do approach igneous rock compositions. A phase diagram is an exceedingly concise method of reporting, in a graphical “short hand”, a tremendous amount of data. Only a few of the more significant petrological aspects can be mentioned in the descriptions; for further discussions of the diagrams given, the reader is directed to the original references. A recent paper by Schairer (1957) gives a more complete
coverage of most of the systems discussed beyond. All diagrams are in terms of weight per cent and degrees Centigrade, and unless stated otherwise, all are given essentially as published. On the ternary diagrams the direction of decreasing temperature is indicated by arrows on the boundary curves, and light lines (Alkemade lines) dividing the system up into composition triangles have been drawn.

**Binary Oxide Systems**

$\text{K}_2\text{O} - \text{SiO}_2$. The portion of the system $\text{K}_2\text{O} - \text{SiO}_2$ from $\text{SiO}_2$ to the compound $\text{K}_2\text{O} - \text{SiO}_2$ was studied by Kracek et al. (1929), and by Kracek (1930a). These studies showed the existence of two intermediate compounds, $\text{K}_2\text{O} - 2\text{SiO}_2$ and

![Equilibrium diagram of the system $\text{K}_2\text{O} - \text{SiO}_2 - \text{K}_2\text{O}$](image-url)

*Fig. 4. Equilibrium diagram of the system $\text{K}_2\text{O} - \text{SiO}_2 - \text{K}_2\text{O}$. (After Kracek et al.)*
K₂O·4SiO₂. The revised diagram, as given by Kracek et al., (1937) is reproduced in Fig. 4, with the addition of the metastable eutectic between K₂O·2SiO₂ and SiO₂, as deduced by Morey and Fenner (1917). It should be noted also how the addition of K₂O to SiO₂, to the extent of 27.5 per cent, brings the liquidus of SiO₂ down from the melting point (1713°C) to 770°C—averaging 34° drop for each per cent K₂O.

Na₂O–SiO₂. The high-silica portion of this system (above the compound Na₂O·SiO₂), was investigated by Morey and Bowen (1924), and additional data were added by Bowen and Schairer (1929b) and by Bowen et al. (1930). The system was restudied and extended to include the compound 2Na₂O·SiO₂, by Kracek (1930a, b and 1939). His phase diagram for the system is given as Fig. 5. The addition of Na₂O is seen to lower the liquidus of SiO₂ 36° for each per cent Na₂O. The low-melting mixtures in the vicinity of the compound Na₂O·2SiO₂ are sluggish to crystallize and are rather viscous.

CaO–SiO₂. This rather complex system (Fig. 6) was reported by Rankin and Wright in their study of the system CaO–Al₂O₃–SiO₂ (1915), and various
portions of their diagram have been revised by numerous later investigators (see Levin et al., 1956, p. 48 and Schairer, 1957). There are four binary compounds in the system, and at least two of these have two or more modifications. The lowest liquidus temperature in the system is still rather high (1436°), in spite of the very abrupt drop from 2CaO·SiO₂ to the rankinite-pseudowollastonite

![Equilibrium diagram of the system CaO–SiO₂](image)

Fig. 6. Equilibrium diagram of the system CaO–SiO₂. (After Rankin and Wright, Greig, and others.)

eutectic (see Fig. 6). The decrease in the liquidus of silica is not as abrupt as with the alkalis K₂O and Na₂O, in that a field of liquid immiscibility intersects the liquidus surface from 0.6 per cent CaO to 27.5 per cent CaO. This has the effect of negating the drop in the SiO₂ liquidus that would have taken place for CaO additions in this range, if no immiscibility had occurred.

MgO–SiO₂. The system MgO–SiO₂ is considerably simpler than the system CaO–SiO₂. It is shown in Fig. 7 as reported by Bowen and Andersen (1914)
and modified by Greig (1927). There are only two compounds in the system, a pyroxene \((\text{MgO} \cdot \text{SiO}_2)\) and an olivine \((2\text{MgO} \cdot \text{SiO}_2)\), and the liquidus temperatures are high throughout, never falling below that of the eutectic between \(\text{MgO} \cdot \text{SiO}_2\) and \(\text{SiO}_2\) at 1543°C. A region of liquid immiscibility, similar to that in the system \(\text{CaO} \cdot \text{SiO}_2\), extends (at the liquidus) from 0·8 per cent to 30·5 per cent \(\text{MgO}\), causing the rate of drop, in the range from \(B\) to \(D\) (Fig. 7) to be 38° for each \(°/\text{o}\) \(\text{MgO}\). This system also illustrates the incongruent melting of

![Equilibrium diagram of the system \(\text{MgO} \cdot \text{SiO}_2\). (After Bowen and Andersen, and Greig.)](image)

the pyroxene \(\text{MgO} \cdot \text{SiO}_2\) to form crystals of the olivine \(2\text{MgO} \cdot \text{SiO}_2\) (forsterite) and a more siliceous liquid. As will be shown beyond, many silicate compounds melt incongruently, and with a few exceptions, always to form a more siliceous liquid.

This and other diagrams involving the compound \(\text{MgO} \cdot \text{SiO}_2\) have been relabelled to indicate the relationships found by Schairer (1954) for the various forms of this compound. He showed that enstatite, the low-temperature form, inverts at 1125, + 0 − 25°, to protoenstatite, which is stable to the liquidus; on quenching protoenstatite goes through a snap inversion to clinoenstatite.

\(\text{FeO} \cdot \text{SiO}_2\). The phase diagram for this system is even simpler than the foregoing, but the variable valence of iron resulted in experimental difficulties that were not solved until much later. Bowen and Schairer (1932) found that it was possible to melt ferrous iron-bearing batches in pure metallic iron crucibles in an inert (nitrogen) atmosphere. There was always a small amount of ferric iron present (usually stated in terms of weight per cent \(\text{Fe}_2\text{O}_3\)), representing an equilibrium between the ferrous, ferric and metallic iron species. Such systems
should therefore be considered to lie in a more general system with Fe and Fe₃O₄ as components. There is only one compound in the system, the iron olivine fayalite (2FeO·SiO₂). The hypothetical iron ortho-pyroxene FeO·SiO₂, named ferrosilite, does not occur in this system and has not been synthesized, although a clino-pyroxene of this composition has been found in nature (Bowen, 1935a) and Kurtsева (1953) has reported slag pyroxenes containing up to 76 per cent ferrosilite "molecule". The diagram for the system, with all iron calculated as FeO, is given in Fig. 8 from Bowen and Schairer (1932). The actual amounts of Fe₃O₄ found are indicated on the upper figure, which shows the manner in which the amount of Fe₃O₄ is strongly influenced by the total amount of iron, as FeO, in the batch. This relationship holds true in all systems with FeO. The high-silica portion, showing liquid immiscibility, has been taken from the work of Greig (1927b).

Although similar in many ways to the systems CaO–SiO₂ and MgO–SiO₂, several features of the system FeO–SiO₂ contrast strongly with the other two. Thus the addition of FeO is not very effective in lowering the liquidus of silica, until approximately 50 per cent has been added (a point of great importance in the use of refractories in the steel industry). The iron olivine, fayalite, melts at 685° lower than its magnesian equivalent, forsterite, and this results in very much lower liquidus temperatures here (the two eutectics occur at 1177° and
1178°) than in the systems with CaO and MgO. Viscosity, which is not indicated on the diagram as it is a rate property, is low throughout most of the system, resulting in rapid crystallization and very short (< 1 hr) equilibration times, even with the low-temperature melts.

Fe₂O₃–SiO₂. The available data indicate that this system would require large oxygen pressures to maintain the iron in the ferric state (Muan, 1955). Apparently it would consist of a large region of immiscible liquids, and small fields of hematite and silica (Greig, 1927a).

Al₂O₃–SiO₂. The phase diagram for this system (Fig. 9) is from Bowen and Greig (1924), with a modification of the eutectic temperature based on the work of Schairer and Bowen in the systems K₂O–Al₂O₃–SiO₂ (1955) and Na₂O–Al₂O₃–SiO₂ (1956). The eutectic, originally given as 1545°C, has been raised to 1595° ± 10°C. The original figure was too low probably because of small amounts of alkalies as impurities (Schairer, 1957, p. 217). Even at these temperatures the viscosities are high. There is still some disagreement among various workers concerning the melting of the compound mullite (3Al₂O₃·2SiO₂). Bowen and Greig (1924) found this to be an incongruently-melting compound (see Fig. 9), but Bauer et al. (1950), report synthesis of the compound by flame fusion, and Toropov and Galakhov (1951 and 1953) report that it melts congruently at 1890°C, and has a eutectic with Al₂O₃ at 1850° and 78 per cent Al₂O₃. They explain the evidence of incongruent melting, found by Bowen and Greig, on the basis of rapid volatilization of silica, leaving excess Al₂O₃ behind to form corundum. The data on the boundary line between the fields of corundum and mullite in the systems with K₂O and Na₂O (Schairer and Bowen, 1955 and 1956) appear to point toward an incongruent melting for mullite, however. The compound also takes excess Al₂O₃ in solid solution, but the limits of this are still in question (see Shears and Archibald, 1954; Schairer and Bowen, 1955, p. 690).
Ternary Oxide Systems

CaO–Al₂O₃–SiO₂. The equilibrium diagram for this system is given in Fig. 10. It is taken from the work of Rankin and Wright (1915), as modified by the work of Bowen and Greig (1924), Greig (1927b), Bowen et al. (1933b), and others. The diagram, in this form, first appeared in Schairer (1942).

The system is complicated by two series of binary compounds, four in each of the systems CaO–SiO₂ and CaO–Al₂O₃, plus the compound mullite (3Al₂O₃·2SiO₂), and two ternary compounds 2CaO·Al₂O₃·SiO₂ (gehlenite) and CaO·Al₆O₁₇·2SiO₂ (anorthite).

Although some of the composition triangles drawn on the diagram outline simple ternary subsystems with a ternary eutectic point located within each (e.g., CaO·SiO₂·CaO·Al₂O₃·2SiO₂·SiO₂), six of the composition triangles shown have their corresponding ternary points outside of their respective triangles, i.e. they have ternary peritectic points (or ternary reaction points). This can result in rather unusual crystallization paths, and very erratic amounts of crystallization with a steadily decreasing temperature, as illustrated by Fig. 2 for the point “a” at 62.2 per cent CaO, 30.2 per cent Al₂O₃ and 7.6 per cent SiO₂. On cooling, the liquid in this composition passes through two ternary peritectic
points, \( A \) and \( B \), very close to each other (see points \( A \) and \( B \) on Fig. 10), at which points the bulk of the crystallization takes place. At point \( A \), at 1470°, all of the early-formed CaO crystals (5 per cent) react with liquid of composition \( A \) to form \( 3\text{CaO} \cdot \text{SiO}_2 \) and \( 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \) (along with simultaneous additional, direct crystallization from the liquid). At point \( B \), at 1455°, all the \( 3\text{CaO} \cdot \text{SiO}_2 \) crystals react with liquid of composition \( B \) (and there is additional direct crystallization from the liquid) to form \( 2\text{CaO} \cdot \text{SiO}_2 \) and \( 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \). At this point there is only 12 per cent liquid left, the last 5 per cent of which crystallizes at the ternary eutectic point \( C \). (As with all the diagrams of phase per cent vs. temperature presented here, the percentages are best obtained by scaling a much larger copy of the diagram.)

\( \text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2 \). This system is shown in Fig. 11, taken from the work of BOWEN et al. (1933a and b). There are several important solid–solution series in this system, occurring along binary (or practically binary) subsystems through the ternary system. Diagrams for these are given in Figs. 12 and 13, for the system \( 2\text{CaO} \cdot \text{SiO}_2 \cdot \text{FeO} \cdot \text{SiO}_2 \) (the orthosilicate or “olivine” join), and the system \( \text{CaO} \cdot \text{SiO}_2 \cdot \text{FeO} \cdot \text{SiO}_2 \) (the metasilicate or “pyroxene” join). In each of these two systems, there is an intermediate compound with a 1:1 mole ratio of \( \text{Ca} : \text{Fe} \). In the system \( 2\text{CaO} \cdot \text{SiO}_2 \cdot \text{FeO} \cdot \text{SiO}_2 \) the compound \( \text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2 \) (point \( D \) in Fig. 12) melts congruently and forms a solid solution on both the Ca-rich and Fe-rich sides. Between \( \text{CaO} \cdot \text{FeO} \cdot \text{SiO}_2 \) and \( 2\text{FeO} \cdot \text{SiO}_2 \) there is a
Continuous series of solid solutions with a low-temperature minimum at point $E$, rich in iron. In the system CaO·SiO$_2$–FeO·SiO$_2$, the compound CaO·FeO·2SiO$_2$ (hedenbergite) breaks down, upon heating, at 965° (point $H'$ Fig. 13) to form a wollastonite ($\beta$CaO·SiO$_2$) solid solution, of the same composition, which starts to melt incongruently at about 1120° to form tridymite and liquid (ternary equilibria). The progress of crystallization in this system is complex, due to these two solid solution series, and has been outlined by a series of fifteen isothermal planes (Bowen et al., 1933b). The very marked drop in liquidus temperatures toward the iron silicate fayalite should be noted.

MgO–FeO·SiO$_2$. This system was studied by Bowen and Schaerer (1935), and their phase diagram is presented in Fig. 14. As with all systems including FeO as a component, a small amount of Fe$_2$O$_3$ is present in all liquids, representing equilibrium between the melt and the metallic iron crucible (see Fig. 15). The system is rather closely related to that for the system CaO–FeO–SiO$_2$, in that the metasilicate and orthosilicate binary (or partially binary) subsystems also show solid solution series. As in the system CaO–FeO–SiO$_2$, the precise melting relations in this system are best seen with the aid of a series of isothermal sections, as given by Bowen and Schaerer (1935). The orthosilicate system forsterite–fayalite, a simple binary solid solution series (see Fig. 16), was first presented and its application to the intrusion of dunite given by Bowen and Schaerer (1933). The metasilicate (pyroxene) system is complicated by virtue
o, considerable areas of ternary (i.e. non-binary) equilibrium (see Fig. 17), and by the inversion between ortho- and clino-pyroxene. Although synthetic pyroxenes containing up to nearly 90 per cent of the FeO·SiO$_2$ "molecule" have been made in the laboratory, and crystals with as much as 76 per cent have been found in slags (KURTSEVA, 1953), the pure ortho-pyroxene ferrosilite has not been found in nature. BOWEN (1935a) reported the occurrence of apparently pure clinoferroilite in the lithophysae of obsidians.

CaO-MgO-SiO$_2$. The diagram for this system, with isotherms, is given as Fig. 18. The system shows four ternary compounds, the metasilicate pyroxene diopside (CaO·MgO·2SiO$_2$), the orthosilicates monticellite (CaO·MgO·SiO$_2$), and merwinite (3CaO·MgO·2SiO$_2$), and the compound akermanite (2CaO·MgO·2SiO$_2$). This diagram is based on the general study of the system by FERGUSON and MERWIN (1919), and on the work of BOWEN (1914) on the subsystem diopside–forsterite–silica, GREIG (1927) on the high-silica region of immiscibility, SCHAIRER and BOWEN (1942), and OSBORN (1942), on the subsystem CaO·SiO$_2$–diopside, and OSBORN (1943) on the stability of merwinite.
Fig. 14. Equilibrium diagram of the system, MgO–FeO–SiO₂. There is a small amount of Fe₂O₃ in all liquids in this system, as shown in Fig. 15. (From Bowen and Schairer.)

Fig. 15. Diagram showing the approximate Fe₂O₃ content of liquid mixtures of MgO, SiO₂, and Fe oxide, in equilibrium with metallic iron. The position of the figure in the general triangle is readily made out by comparison with Fig. 14. (After Bowen and Schairer.)
Fig. 16. Equilibrium diagram of the system $2\text{MgO} \cdot \text{SiO}_2 - 2\text{FeO} \cdot \text{SiO}_2$ (orthosilicate join in the system $\text{MgO} - \text{FeO} - \text{SiO}_2$). (After Bowen and Schairer.)

Fig. 17. Equilibrium diagram of mixtures of metasilicate ratio in the system $\text{MgO} - \text{FeO} - \text{SiO}_2$. Heavy curves refer to binary equilibrium and light curves to ternary equilibrium (binary and ternary respectively only when small amounts of $\text{Fe}_2\text{O}_3$ present in liquids are treated as FeO). “Clino-pyroxene” here refers to protoenstatite (Schairer, 1954). (After Bowen and Schairer.)
Additional portions were restudied by Ricker and Osborn (1954), and Fig. 18 is taken from their work. The lowest eutectic in the system is that between $\beta$CaO·SiO$_2$ solid solutions, a diopsidic pyroxene and tridymite, at 1320$^\circ$. The odd-shaped field for the pyroxenes is particularly interesting. Between MgO·SiO$_2$ (clinoenstatite and protoenstatite) and CaO·MgO·2SiO$_2$ (diopside) there is a series of solid solutions, almost continuous at high temperature, with a minimum near diopside, and unmixing at lower temperatures (Atlas, 1952; Boyd and Schairer, 1957). In addition, one end of this system (MgO·SiO$_2$) melts incongruently to form forsterite plus a more siliceous liquid, whereas the other end (diopside) melts congruently. The liquidus surface for diopside in the ternary system is exceedingly flat over the composition point of the compound, indicating extensive dissociation in the melt. This is one reason why the melting, of synthetic diopside provides a good temperature calibration point, as deviations from the stoichiometric composition are not serious in their effect. There are ten binary and ternary compounds in this system, and a number show two or more modifications and extensive but partial solid solution. For a fuller discussion of these complexities and the extensive literature, see the original references and Eitel (1954a, pp. 656–667).

MgO–Al$_2$O$_3$–SiO$_2$. The system MgO–Al$_2$O$_3$–SiO$_2$ is complicated by the
presence of two ternary compounds cordierite (2MgO·2Al₂O₃·5SiO₂), and sapphireine (4MgO·5Al₂O₃·2SiO₂). In the original work by RANKIN and MERWIN (1918), only cordierite was found at the liquidus surface. FOSTER (1950) predicted that the compound sapphireine should occur at the liquidus surface in the system, and this was verified by KEITH and SCHAIRER (1952), whose diagram

Fig. 19. Equilibrium diagram of the system MgO–Al₂O₃–SiO₂. (Diagram of RANKIN and MERWIN as modified by BOWEN and GREIG, GREIG, SCHAIRER, FOSTER, and KEITH and SCHAIRER.)

is presented (Fig. 19). This shows the liquidus relations between the ten phases found in the system, all of which occur in nature.

FeO–Al₂O₃–SiO₂. This system, as drawn by SCHAIRER and YAGI (1952), is presented as Fig. 20. There is a considerable similarity to the system MgO–Al₂O₃–SiO₂, in that there are iron analogs of the binary compounds forsterite and spinel, and of the ternary compound cordierite. The field of FeO is considerably smaller than that of MgO in the other system, as might be expected from the large difference (1420°) in the melting points. As with all silicate systems, the substitution of FeO for MgO lowers the liquidus throughout. Thus the lowest liquidus temperature in the system MgO–Al₂O₃–SiO₂, at the eutectic between silica, Mg–cordierite, and MgO·SiO₂ is 1345° (point S, Fig. 19), whereas the lowest liquidus in the iron system is at the eutectic between silica,
Fe–cordierite, and 2FeO·SiO₂ at 1083° (point N, Fig. 20). The large effect of oxygen pressure in the gas with which this system is equilibrated is shown by Muan (1957).

FeO–Fe₂O₃–SiO₂. This system will be discussed here, not for its particular pertinence to igneous rock compositions, but for the important principles which it demonstrates. The system at 1600°C was sketched by Gurry and Darken (1950), and the entire liquidus surface below 1600° was determined by Muan (1955). Fig. 21 (from Muan) shows the liquidus relations. In particular, it shows the incongruent melting of FeO, and 2FeO·SiO₂, to form metallic iron and a liquid enriched in oxygen, as indicated by the field of iron over the composition points for FeO and 2FeO·SiO₂. This field probably should extend up to the SiO₂ corner, indicating that all mixtures of FeO and SiO₂ will form some “Fe₂O₃”, plus metallic iron, at equilibrium. This figure also shows the wide band of immiscibility in the silica-rich corner of the system and the low minimum temperature on the liquidus, 1140°, for the eutectic magnetite–fayalite–tridymite. Figure 22, also from Muan, is a plot of the oxygen pressures in the gas over the melts whose phase equilibria are recorded in Fig. 21. It is important to note the vast range in oxygen pressures involved in this system—over twelve orders of magnitude. Kennedy (1948) made use of such relationships in an attempt to estimate the amount of hydrogen in the gas with respect
to which some Halemaumau basalts had presumably been equilibrated, using
the ferrous/ferric ratio and the known dissociation of water. It is apparent from
Fig. 22, however, that the isobars are not solely dependent on the FeO/Fe₂O₃
ratio, in this particular system.

K₂O-CaO-SiO₂ and Na₂O-CaO-SiO₂. The high liquidus temperatures
characteristic of the binary system CaO-SiO₂ are brought down rapidly by the
addition of K₂O, as shown in Fig. 23 from Morey et al. (1930, 1931). Practically

Fig. 21. Equilibrium diagram of the system FeO–Fe₂O₃–SiO₂. Circles represent
compositions as shown by analysis, of mixtures at liquidus temperature. The tridymite–cristobalite boundary curve is dashed. (After Muan.)

the entire high-silica portion of the ternary system has liquidus temperatures
well under the lowest liquidus in the binary system CaO–SiO₂ (1355°C). There
are six ternary compounds in this part of the system K₂O–CaO–SiO₂, none of
which are known in nature. Information on such phases is necessary, however, to
understand phase equilibria in the more complex quaternary and quinary systems
involving these three oxides. The viscosities are very high in the portions of
this system having low liquidus temperatures, and crystallization is extremely
sluggish. The lowest eutectic occurs at 720°C.

The system Na₂O–CaO–SiO₂ (Fig. 24) is similar, in its grosser aspects, to the
system K₂O–CaO–SiO₂, but has only three ternary compounds in the portion
studied (Morey and Bowen, 1925; Morey, 1930), of which two, having ratios
of 2:1:3 and 1:3:6, are also found in the system with potassia. Also as with
the other system, the lowest liquidus temperatures (725°C), between Na₂O–2SiO₂,
Fig. 22. Equilibrium diagram of the system FeO–Fe₂O₃–SiO₂. Heavy lines are boundary curves and light lines are lines of equal O₂ pressure for points on liquidus surface. (After Muñoz.)

Fig. 23. Equilibrium diagram of part of the system K₂O–CaO–SiO₂. (Revised, after Morey, Kräcek and Bowen.)
Fig. 24. Equilibrium diagram of part of the system Na₂O–CaO–SiO₂.
(After Morey and Bowen.)

\[ a = \text{K}_2\text{O-MgO-SiO}_2 \]
\[ w = \text{K}_2\text{O-MgO-0.5SiO}_2 \]
\[ j = \text{K}_2\text{O-MgO-0.3SiO}_2 \]
\[ s = \text{K}_2\text{O-MgO-1.2SiO}_2 \]

Fig. 25. Equilibrium diagram of the system K₂O-MgO-SiO₂. The tridymite field below 867° is metastable. (After Roedder.)
Na$_2$O·3CaO·6SiO$_2$ and quartz, occur in an area having exceedingly high viscosity.

K$_2$O–MgO–SiO$_2$ and Na$_2$O–MgO–SiO$_2$. The system K$_2$O–MgO–SiO$_2$ is shown in Fig. 25, after Roedder (1951a). It also shows a very rapid lowering of the liquidus temperatures of the binary system MgO–SiO$_2$ upon addition of K$_2$O (Fig. 3). Only one of the four ternary compounds in the system has the same ratios of alkali to alkaline earth to silica as were found in the systems with

![Equilibrium diagram of the system 2MgO·SiO$_2$–K$_2$O·MgO·5SiO$_2$–SiO$_2$.](image)

Fig. 26. Equilibrium diagram of the system 2MgO·SiO$_2$–K$_2$O·MgO·5SiO$_2$–SiO$_2$. This is a portion of the general system K$_2$O–MgO–SiO$_2$, the oblique triangle LWS' in Fig. 25. See text for description of crystallization path. (After Roedder.)

lime above. A compound of rather unusual formula, K$_2$O·5MgO·12SiO$_2$, appears in this system, and may be expected to occur in nature; its recognition may be difficult, however, as its optical properties are very similar to those of the quartz with which it might well occur. This compound occurs in the ternary subsystem 2MgO·SiO$_2$–K$_2$O·MgO·5SiO$_2$–SiO$_2$, seen enlarged in Fig. 26. The crystallization of composition "a" in this subsystem has been discussed earlier (see Fig. 1 and Table 1). The two ternary compounds K$_2$O·MgO·5SiO$_2$, and K$_2$O·MgO·3SiO$_2$, found in this system, are also petrologically interesting. They are, in effect leucite (K$_2$O·Al$_2$O$_3$·4SiO$_2$) and kalsilite–kaliophilite (K$_2$O·Al$_2$O$_3$·2SiO$_2$), respectively, each with the two atoms of aluminium replaced by one magnesium and one silicon. In each case X-ray diffraction shows that they are apparently isostructural with their alumina analogues, and the striking similarity of the phase transitions observed, as well as the optical and crystallographic data, support this view. This would require, however, that
the Mg\(^{++}\) ion be in four-fold co-ordination in the two magnesium compounds, as it is substituting for a four-co-ordinated aluminium. Although the aluminium "end members" apparently crystallize at times in high-magnesium natural environments, magnesium does not seem to enter the natural minerals. The lowest temperature eutectic is near the compound K\(_2\)O·4SiO\(_2\), at 685\(^\circ\).

The system Na\(_2\)O–MgO–SiO\(_2\) was studied by Botvinkin and Popova (1937), and Manuilova (1937), and later was re-examined by Schairer et al. (1953, 1954), with considerably different results. The preliminary diagram presented by Schairer et al. (1954), is shown as Fig. 27. An additional compound, Na\(_2\)O·MgO·SiO\(_2\), is reported by Schairer (1957), but is not shown on Fig. 27. It is seen that although only the high-silica portion (> approximately 50 per cent SiO\(_2\)) has been studied, nine ternary compounds have been found. Three of these (1:1:1, 1:1:3 and 1:5:12) have counterparts in the system K\(_2\)O–MgO–SiO\(_2\), but the other six do not. The large field of forsterite, the large distortion of the protoenstatite field toward the SiO\(_2\) apex, and the low temperatures toward the alkali-silica side are all quite similar to the results found for the system K\(_2\)O–MgO–SiO\(_2\). The lowest eutectics in the system Na\(_2\)O–MgO–SiO\(_2\) occur near the compound Na\(_2\)O·2SiO\(_2\), at 713\(^\circ\).

K\(_2\)O–FeO–SiO\(_2\) and Na\(_2\)O–FeO–SiO\(_2\). These two systems show striking similarities to the equivalent systems with MgO described above, and in fact, the study of the magnesia-bearing systems aided considerably in understanding

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Fig. 27. Preliminary equilibrium diagram of the system Na\(_2\)O–MgO–SiO\(_2\). (After Schairer, Yoder and Keene.)
the experimentally more difficult iron systems. A preliminary diagram for
the system K₂O·2SiO₂–FeO–SiO₂, the high-silica portion of the system
K₂O–FeO–SiO₂, as given by Roedder (1952), is shown in Fig. 28, and a pre-
liminary diagram for the system Na₂O–FeO–SiO₂ as given by Schairer et al.
(1953, 1954), is shown in Fig. 29. A previous study of the soda system by
Carter and Ibrahim (1952) shows only one ternary compound, Na₂O·FeO·SiO₂,
but Schairer’s preliminary diagram indicates that the system is perhaps as

Fig. 28. Preliminary equilibrium diagram of the system K₂O·2SiO₂–FeO–SiO₂,
subject to revision, showing liquidus relationships in equilibrium with metallic iron.
Fe₂O₃ is present in all liquids. The insert shows the position of this system (shaded
area) in the more general system K₂O–FeO–SiO₂. (After Roedder.)

complex as the analogous system Na₂O–MgO–SiO₂. Only two ternary com-
ounds were found in the preliminary study of the system K₂O–FeO–SiO₂,
having the ratios 1:1:3 and 1:1:5, just as in the system K₂O–MgO–SiO₂.
These are the ferrous iron counterparts of the potassium aluminium silicates,
kalsilite–kaliophilitie and leucite, exactly as with the magnesium compounds
above. As the iron compounds are apparently isostructural with the aluminium
ones which have tetrahedrally co-ordinated aluminium ions, the Fe²⁺ ion must
occur in tetrahedral co-ordination in the iron compounds. Although none of
the numerous ternary compounds found in the system with Na₂O have been
specifically identified as to composition, several of these occur in the equivalent
area of the system as the above potassium iron silicates. In both cases the lowest
eutectics occur relatively near to the alkali–silica sideline, at temperatures
< 800°C, and at low-iron compositions. Carter and Ibrahim (1952) report the
eutetic between Na₂O·2SiO₂, 2FeO·SiO₂ and SiO₂ to be at < 500°C. Also in
both systems the field of fayalite extends to very high silica compositions.
Fig. 29. Preliminary equilibrium diagram of the system Na$_2$O–FeO–SiO$_2$.
(After Schairer, Yoder and Keene.)

Fig. 30. Equilibrium diagram of the portion of the system Na$_2$O–Fe$_2$O$_3$–SiO$_2$ between Na$_2$O–SiO$_2$, Fe$_2$O$_3$ and SiO$_2$. Equilibria along the sideline Fe$_3$O$_4$–SiO$_2$ are not known.
(After Bowen et al.)
Na₂O–Fe₂O₃–SiO₂. This system is of interest in that one of the ternary compounds found in it, Na₂O·Fe₂O₃·4SiO₂, occurs also in nature as the pyroxene mineral acmite. The high-soda portion of the system Na₂O·SiO₂–Fe₂O₃–SiO₂ has been studied by Bowen and Schairer (1929) and by Bowen et al. (1930). The latter workers found two other ternary compounds, 5Na₂O·Fe₂O₃·8SiO₂, and 6Na₂O·4Fe₂O₃·5SiO₂, as well as some evidence for the existence of the compound 2Na₂O·Fe₂O₃·SiO₂. Their diagram is reproduced as Fig. 30, in

Fig. 31. Isothermal section at 825°C in the system Na₂O–Fe₂O₃–SiO₂.
(After Bowen et al.)

which small amounts of iron as Fe⁺⁺ have been considered as Fe⁺⁺⁺. An isothermal section through this system at 825°, from the same authors, is given as Fig. 31. The low temperature trough near to the Na₂O–SiO₂ sideline is notable; although the differentiation of most igneous rocks results in a concentration of Fe relative to Mg, the lowest melting liquids in this system, as in the equivalent systems with K₂O and with FeO, are still rich in silica and alkali, and relatively poor in iron. Thus one can assume that of the two arms of Bowen’s reaction series (Bowen, 1922), the one that results in a net enrichment in alkalis in the residual liquids dominates over the one that results in a net enrichment in iron (Bowen et al., 1930, p. 450–454). Another significant consequence of the work on the system Na₂O–Fe₂O₃–SiO₂ is the discovery of the incongruent
melting of acmite, at 990°, to form hematite plus liquid. This requires that the acmite in rocks must have crystallized at this or lower temperatures, barring significant pressure effects and impurities.

K$_2$O–Al$_2$O$_3$–SiO$_2$ and Na$_2$O–Al$_2$O$_3$–SiO$_2$. These two diagrams are of considerable significance in petrology, as they include a number of important rock-forming minerals, the most important of which are the feldspars. The diagrams for both of these, with a brief discussion, were published by Schairer and Bowen (1947b), and a full discussion of them will be found in Schairer and Bowen (1955 and 1956), from which Figs. 32 and 33 were taken. Only a few of the many features of these diagrams that should be pointed out can be considered here. The lowest temperature eutectics occur at 710° and 732°, respectively. In particular, the line of ternary compounds in each, including feldspathoids and feldspars, should be noted. The binary system between leucite and silica (line X–SiO$_2$ on Fig. 32) is shown in detail in Fig. 34, also from Schairer and Bowen (1955). From this it is seen that the incongruently melting compound potassium feldspar, and tridymite, form a eutectic at 990° ± 20° (point I, Fig. 32). The liquidus lines going down to this eutectic are dashed in Fig. 34, however, having been extrapolated from data in the ternary system, as the viscosities of the melts in this range of composition made precise determinations
Fig. 33. Equilibrium diagram of the system Na₂O–Al₂O₃–SiO₂.
(After Schairer and Bowen.)

Fig. 34. Equilibrium diagram of the binary system leucite–silica.
(After Schairer and Bowen.)
practically impossible. Glasses of these compositions would not crystallize "dry" (i.e. without addition of water) even during periods as long as five years (SCHAIRER and BOWEN, 1955, p. 715). Yet a short distance from this line, in the ternary system, viscosities were considerably lower. These data, along with the sharp bend in the isotherms at the 1:1 K₂O:Al₂O₃ line, and the similar sharp bend in the lines of equal index of refraction (isoelastics) for the glasses in this system (SCHAIRER and BOWEN, 1955, p. 714), indicate a strong dependence of the liquid properties on the molecular ratio of K₂O:Al₂O₃. Identical behaviour,

![Equilibrium diagram of the binary system albite-silica.](image)

**Fig. 35.** Equilibrium diagram of the binary system albite-silica. (After SCHAIRER and BOWEN.)

but with lower viscosities, was noted in the system Na₂O–Al₂O₃–SiO₂ (SCHAIRER and BOWEN, 1956, p. 158), and a similar but much less obvious break was found in the isoelastics and lines of equal glass density in the system K₂O–MgO–SiO₂, at the 1:1 molecular ratio of K₂O: MgO (ROEDDER, 1951a, p. 95). These phenomena are presumably related to the structure of the liquids, which must show maximum polymerization at the 1:1 molecular ratio.

The system Na₂O–Al₂O₃–SiO₂, from SCHAIRER and BOWEN (1956), is shown in Fig. 33. It has many things in common with the system K₂O–Al₂O₃–SiO₂. The most significant difference is in the lack of a sodium compound chemically equivalent to leucite (K₂O·Al₂O₃·4SiO₂). Although such a compound exists in nature (jadeite) and has been synthesized, it is not stable under the conditions of high temperature and one atmosphere pressure used in the determination of the system. The system albite–silica, line F–SiO₂ on Fig. 33, is shown in Fig. 35, also from SCHAIRER and BOWEN (1956). It is seen from this that the compound albite (Na₂O·Al₂O₃·6SiO₂) melts congruently, and the eutectic with silica occurs at a lower ratio of silica/feldspar than occurs between potassium.
feldspar and silica. Note also that the entire binary diagram was determined—no part of the liquidus has to be obtained by extrapolation, as was the case in the system with potassium. This is in consequence of the lower viscosities in the system with sodium, although a sharp rise in the viscosities of the liquids in the vicinity of the line albite–silica did occur.

One very unusual feature of this system is the subsystem albite–corundum. This is given in Fig. 36, from Schairer and Bowen (1956). It shows the exceedingly small solubility of “excess” $\text{Al}_2\text{O}_3$ in albite melts; this is also apparent from the steep slope of the corundum, and mullite, fields in Fig. 33, where they approach the line representing a 1:1 molecular ratio of $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$.

Another unusual feature of the system $\text{Na}_2\text{O}–\text{Al}_2\text{O}_3–\text{SiO}_2$ is the interrelationships of the two forms of the compound $\text{Na}_2\text{O}·\text{Al}_2\text{O}_3·2\text{SiO}_2$. The two forms, nepheline (low-temperature), and carnegieite (high-temperature), have an inversion at $1254^\circ \pm 5^\circ$ when pure but have widely differing tolerances for solid solution of various other substances. The curving inversion line $SVT’F’$ (Fig. 33) shows the behaviour of this inversion depending upon the nature of the substance entering into solid solution. Thus point $S$, at $1280^\circ$, indicates that solid solution of albite raises the inversion temperature, and $I’$ at $1163^\circ$, indicates that solid solution of $\text{Na}_2\text{O}·\text{SiO}_2$ lowers the inversion temperature. Point

Fig. 36. Equilibrium diagram of the binary system albite–corundum. (After Schairer and Bowen.)
Fig. 37. Effect of various added materials on the inversion nepheline–carnegieite. (After various sources as indicated.)

Fig. 38. Equilibrium diagram of the binary system Na₂O·SiO₂ (sodium metasilicate)—Na₂O·Al₂O₃·2SiO₂ (nepheline, carnegieite) after Tilley (1933), as given by Schairer and Bowen (1956). The value 900° ± 2° for the eutectic temperature is from Spivak (1944).
inversion temperature varies from 1163° (91° below) to 1404° (150° above) the inversion of the pure compound. The most unusual case is that of the system with Na₂O·SiO₂; this is shown in its entirety as Fig. 38, from Tilley (1933), and Spivak (1944), as given by Schairer and Bowen (1956). As the low-temperature phase takes less in solid solution, the inversion temperature is lowered. However, as a result of the large difference in the amounts of solid solution (24 per cent for carnegiite vs. essentially none for nepheline), it is possible to have a solid mass of carnegiite crystals of composition Q (Fig. 38), at 1163°, which will melt to form 20 per cent crystals of nepheline and 80 per cent liquid of composition I', upon cooling one degree, to 1162°. Although this particular inversion may not take place in nature, carnegiite being unknown as a natural mineral, the phenomenon of melting of crystals upon cooling through an inversion may well occur in natural systems.

Incongruent Melting of Silicates

Before taking up the more complex quaternary and quinary systems, a few generalizations on the preceding diagrams should be made. It has long been known that certain silicates melt incongruently, i.e. upon heating they decompose to form another crystalline phase plus a liquid, neither of which has the same composition as the original silicate. The fact that this incongruent melting usually results in an enrichment in silica was pointed out by Bowen (1928, particularly p. 298), who also discussed the consequences of this fact to igneous petrogenesis. As a number of new diagrams have been published since 1928, the following tabulation is presented.

Of the twenty-nine binary silicate compounds shown in Levin et al. (1956), twenty melt congruently, i.e. to a liquid of their own composition, and only nine melt incongruently. Eight of these nine melt to form a liquid more silica-rich than the original compound, but the amount of silica enrichment varies widely. Five yield liquids having only a fraction of a per cent to 3 per cent more silica than the original crystals, and one (ZrSiO₄) yields a liquid having approximately 50 per cent by weight silica over that of the crystals (Levin et al., 1956, p. 67). In only one case does an incongruently melting binary compound yield a liquid poorer in silica than the original crystals. This is the compound MnO·SiO₂, which melts to form crystals of silica and a liquid containing about 3 per cent less silica than the crystals (White et al., 1934; Glasser and Osborn, 1957). This is presumably a result of the region of liquid immiscibility in this system, which “pushes” the silica liquidus over the composition point of the metasilicate compound.

Of the sixty-eight ternary silicate compounds shown in the diagrams given in Levin et al. (1956), and the present paper, thirty-seven show congruent melting, and thirty-one melt incongruently. Of these thirty-one, only one—the compound sapphire (4MgO·5Al₂O₃·2SiO₂) in the system MgO·Al₂O₃·SiO₂—shows more than 10 per cent enrichment in silica in the liquid formed, and most of the rest show from zero to 5 per cent enrichment. Five of the thirty-one show slightly less silica in the liquid than in the original crystals. These five are as follows: 2Na₂O·CaO·3SiO₂ (Morey and Bowen, 1925), Na₂O·2PbO·4SiO₂ and Na₂O·3PbO·7SiO₂ (Krakau et al., 1937, 1949), and Na₂O·2MgO·6SiO₂ and Na₂O·MgO·4SiO₂ (Schairer et al., 1953). As these five have little petrologic significance, it can be said that Bowen’s statement of thirty years ago is still
valid; in general, silicate compounds with incongruent melting points melt to form liquids richer in silica than the original crystals.

Any solid solution series actually represents an infinite series of incongruently melting compounds; although these have not been included above, they may have great significance in petrogenesis, as for example, the olivines, the pyroxenes and the plagioclases. In these the enrichment in the liquid on melting is toward higher iron and alkalies, rather than toward high silica.

In the above data, 31 per cent of the binary compounds melt incongruently, and 46 per cent of the ternary compounds melt incongruently, indicating an increase in incongruent character with increase in complexity of the compound. A crude parallel to this is found in the nature of the invariant points in binary, ternary and quaternary systems. In the systems described in this review, 22 per cent of the invariant points in binary systems, 51 per cent of the invariant points in ternary systems, and 72 per cent of the invariant points in quaternary systems are peritectics (reaction points), indicating a strong increase in peritectic behaviour with increasing complexity of the melt. Thus one might expect that peritectic relations will be the rule in natural, complex, magmas.

Crystallization of Silica

Bowen pointed out that, "...in spite of the high melting-point of silica, every dry system investigated in which SiO₂ is one of the components, whether the system is binary, ternary or quaternary, has shown free silica as one of the solid phases separating at the lowermost eutectic." (1928, p. 298.) As shown above, the additional diagrams that have been determined still bear out this statement, if it is changed to read "one of the lowermost eutectics."

One interesting aspect of these systems is the size and shape of the field of silica on the various diagrams. The boundary of the field of the various silica minerals, in each of the fifteen different ternary oxide systems described above, has been sketched in Fig. 39. Minor differences, as between the metastable tridymite and stable quartz boundary curves, have been ignored. Although it is obvious that the terminations of the boundary curves are controlled by equilibria in the individual binary systems, it is equally obvious that these boundary curves could not be determined by simple interpolation from the limiting binary systems. The five systems with Al₂O₃ all show a similar rapid increase in the Al₂O₃-SiO₂ ratio of liquids along the boundary line originating at the Al₂O₃-SiO₂ eutectic, with increasing amounts of the third component; the system Na₂O-Fe₂O₃-SiO₂ apparently shows a similar behaviour with respect to Fe₂O₃, although the extrapolations to this sideline from the data on the systems Na₂O-Fe₂O₃-SiO₂ (Bowen et al., 1930) and FeO-Fe₂O₃-SiO₂ (Muñ, 1955) do not agree (see Figs. 21 and 30). The shape of the silica boundary curve, and particularly its position near the centre line of the triangle (Fig. 39) are strongly affected by the composition of the most siliceous ternary compound in the system. Thus six of the seven systems whose silica boundary curves cross below point X on Fig. 39 have, for their most siliceous ternary compounds, ratios of Si/O ranging from 1/3-0 to 1/4-0, whereas the eight that cross above point X have for their most siliceous ternary compounds, ratios of Si/O ranging from 1/3-0 to 1/2-33. One system, (MgO-FeO-SiO₂), whose boundary also crosses below point X, has no ternary compound as such. Other factors must also be involved in the explanation of these boundary curves, however. Thus in
the system $K_2O-MgO-SiO_2$ (Fig. 25), the field for the binary compound protoenstatite extends considerably further toward the $SiO_2$ apex (up to approximately 83 per cent $SiO_2$) than the fields of any of the ternary compounds in this or other systems (see Fig. 39).

![Fig. 39. Boundary curves limiting the field of the silica minerals in various systems, from various references as given in text. Each individual line represents the limits of the fields of the silica minerals, quartz, tridymite, and cristobalite, in the system between $SiO_2$ and the two oxides named at the ends of the line. The line ending at $a$ is for the system $Na_2O-Fe_2O_3-SiO_2$; its termination on the binary system $Fe_2O_3-SiO_2$ is not known.]

**Ternary Subsystems from Four- and Five-component Oxide Systems**

As mentioned above, the fact that a comparatively few minerals make up the bulk of igneous rocks makes it possible to choose very limited portions of four- and five-component systems which will, however, closely approach the ranges of igneous rock composition. Thus the very complex five-component system $K_2O-CaO-MgO-Al_2O_3-SiO_2$ has not been worked out, but the relatively simple system diopside–potassium feldspar represents a petrologically significant "binary" system in the quinary system. The following pages show twelve of the petrologically most significant subsystems containing four and five oxides from the general system $K_2O-Na_2O-CaO-FeO-MgO-Fe_2O_3-Al_2O_3-SiO_2$. These all have as their components, or as intermediate compounds, the following common rock-forming minerals in addition to silica:*

* There are many combinations of these minerals that can be found as subsystems in the ternary-oxide systems described above. Thus the classic system forsterite–diopside–silica (Bowen, 1914) falls in the system CaO–MgO–SiO$_2$ (Fig. 18).
Olivines—Forsterite and fayalite
Pyroxenes—Diopside, enstatite (including clinoenstatite and protoenstatite) and the pyroxenoid wollastonite (and pseudowollastonite)
Feldspars—Anorthite, albite and “orthoclase” (potassium feldspar)
Feldspathoids—Leucite, nepheline, “K-nepheline” (kaliophilite and kalsilite).

One of the most important features of the interrelationships of these rock-forming minerals in silicate melts is the trend in composition of the liquids, with either normal equilibrium crystallization, or particularly with the geologically inevitable crystal fractionation, toward low-melting eutectic liquids rich in alkali aluminosilicates and silica, extremely poor in CaO, MgO, Fe₂O₃, Al₂O₃ over a 1:1 ratio with total alkalis, and to a lesser degree, poor in FeO. This trend was very apparent in some of the systems described above, such as Na₂O–CaO–SiO₂ (Fig. 24), but becomes even more apparent in the diagrams of the various systems between the above rock-forming minerals.

*Pseudowollastonite–Diopside–Anorthite* (CaO·SiO₂–CaO·MgO·2SiO₂–CaO·Al₂O₃·2SiO₂). The liquidus phase diagram for this system is given in Fig. 40, from Osborn (1942). It is apparent from this diagram that although there is a decided lowering of the eutectic below the melting points of the components, the final eutectic E, between anorthite, wollastonite solid solution (βCaO·SiO₂
with Mg) and diopside (slightly aluminous) lies practically in the middle of the diagram, and occurs at a relatively high temperature (1236°).

Anorthite–Forsterite–Silica (CaO·Al₂O₃·2SiO₂–2MgO·SiO₂–SiO₂). This system, also from the quaternary CaO–MgO–Al₂O₃–SiO₂, is similar to the foregoing one in that no alkali is present, and temperatures, even at the lowest eutectic, are relatively high. The diagram for this system (Fig. 41) was one of the

![Equilibrium diagram of the system anorthite–forsterite–silica. (After Andersen.)](image)

rather early products of the Geophysical Laboratory, having been published by Andersen in 1915. It shows the incongruent melting of MgO·SiO₂, yielding a reaction line from 1557° to the ternary reaction point or peritectic at 1260°, which has been a pedagogical stand-by for countless professors of petrology. Another interesting feature of the system is the field of spinel, representing non-ternary (quaternary) equilibrium, as the composition of spinel cannot be represented in terms of the three components. Forsterite and anorthite cannot coexist, with liquid, in binary mixtures of the two, as they will react to form spinel. However, if there is excess silica present in the liquid (i.e. the composition lies inside the triangle), these two phases can coexist with liquid.

Anorthite–Leucite–Silica (CaO·Al₂O₃·2SiO₂–K₂O·Al₂O₃·4SiO₂–SiO₂). This system is shown in Fig. 42, from Schairer and Bowen (1947a). It is readily apparent that the lowest-melting liquid in this system, point V, is essentially the eutectic mixture of potash feldspar and silica, point U, with very little added anorthite. Conversely, anorthite can be said to be highly insoluble in potash feldspar–silica melts, except at elevated temperatures. The incongruent melting of potash feldspar to form leucite plus liquid is also readily visible.
Silicate Melt Systems

Anorthite–Nepheline–Silica (CaO·Al₂O₃·2SiO₂–Na₂O·Al₂O₃·2SiO₂). A preliminary diagram for this system from Schairer (1957) is shown in Fig. 43. There are two low-melting liquids in this system, at 1062° and 1068°, on either side of albite along the nepheline–silica sideline. All crystallization trends toward these two points. The large "plagioclase" field across the centre of the diagram represents the solid solution series between anorthite and albite. The

field for alumina represents quaternary equilibria in the more general system Na₂O–CaO–Al₂O₃–SiO₂.

Anorthite–Potassium Feldspar–Sodium Feldspar (CaO·Al₂O₃·2SiO₂–K₂O·Al₂O₃·6SiO₂–Na₂O·Al₂O₃·6SiO₂). This system, shown in Fig. 44, was determined by Franco and Schairer (1951). It appears to be a simple ternary solid solution series, at liquidus temperatures, with the exception of the potassium feldspar corner, where the incongruent melting of this material results in a field of leucite. As leucite is a very low density phase, this incongruent melting is eliminated by adequate pressure, further simplifying the system. Below the liquidus, however, this system is far from simple, and as this system and the quaternary one between the three feldspars and silica have very great petrologic significance, considerable effort is being put into unravelling the intricacies of the three feldspars,

Fig. 42. Equilibrium diagram of the system anorthite–leucite–silica.
(After Schairer and Bowen.)
Fig. 43. Preliminary equilibrium diagram of the system anorthite-nepheline-silica. (After Schairer.)

Fig. 44. Equilibrium diagram for the system sodium feldspar-potassium feldspar-calcium feldspar. (After Franco and Schairer.)
their modifications, solid solution limits and equilibria, particularly under hydrothermal conditions.

Diopside–Leucite–Silica \((\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2 \cdot \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdots \text{SiO}_2)\). This diagram, published by Schairer and Bowen (1938), is reproduced in Fig. 45. The very flat field of diopside, extending practically to the potassium feldspar–silica sideline, attests to the insolubility of diopside in such melts. The low

slope of this liquidus becomes particularly apparent when a point such as \(Q\) is considered. This point, consisting of 12 per cent diopside, 88 per cent mixture \(Q'\), has a diopside liquidus only 100° lower than pure diopside. The lowest-melting liquid is at point \(P\), and consists essentially of the potassium feldspar–silica eutectic liquid \(P'\), with an unknown but necessarily very small amount of diopside.

Diopside–Nepheline–Silica \((\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2 \cdot \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdots \text{SiO}_2)\). The diagram for this system, as determined by Schairer, was first given by Yoder (1950, p. 318), and is reproduced here as Fig. 46. It shows that diopside is rather insoluble in albite–silica melts, the lowest-melting liquid from which diopside can crystallize being at 1075°, and only a few per cent diopside. The system nepheline–diopside is not binary, in that forsterite appears on it, and the field that normally would be for albite alone is instead a field for plagioclase, i.e.
melts in this portion of the system crystallize a feldspar containing some calcium, and the equilibria are quaternary, not ternary.

Diopside–Albite–Anorthite (CaO·MgO·2SiO₂–Na₂O·Al₂O₃·6SiO₂–CaO·Al₂O₃·2SiO₂). This system, a ternary plane through the more general quinary system, Na₂O–CaO–MgO–Al₂O₃–SiO₂, was the first ternary system to be studied that approached igneous rock compositions rather closely. The diagram,

Fig. 46. Equilibrium diagram of the system diopside–nepheline–silica. (After Schairer.)

which is surprisingly simple considering its significance, is shown in Fig. 47, after Bowen (1915). Each point on the boundary line between the two fields represents a liquid in equilibrium with diopside and a plagioclase. Thus liquid a is in equilibrium with diopside d and plagioclase b, as shown by the three phase triangle abd. The composition of the crystals forming from liquid a (i.e. the gross composition of the material being extracted from the liquid by crystallization and by reaction), must lie along the tangent to the boundary line at a. The manner in which the position and shape of these three phase triangles controls the crystallization paths in a system including a solid solution has been discussed by Osborn and Schairer (1941) for the system pseudowollastonite–akermanite–gehlenite.

As pointed out above, compositions in the system diopside–albite–anorthite are such that they approach that of basalt. Thus a mixture of composition G (Fig. 47), consists of diopside, 40 per cent, and labradorite (An₅₀), 60 per cent.
This composition is not far removed from that of the average Deccan trap (Bowen, 1928, p. 66), particularly if some Fe is substituted for the Mg in the pyroxene, a change which should have relatively little effect on this equilibrium. One important feature of such compositions is that upon cooling they become saturated with respect to plagioclase and pyroxene simultaneously, as Bowen has pointed out is characteristic of natural basaltic liquids. Another interesting feature is the short range of temperature between liquidus and solidus for such compositions. Mixture $G$, for example, starts forming crystals of pyroxene and plagioclase (about An$_{89}$), at about 1240°, and at equilibrium the last liquid, having composition $H$, solidifies only 40° lower (at about 1200°). This equilibrium crystallization behaviour is illustrated by the solid lines on Fig. 48. With crystal fractionation, as by the settling of crystals, the crystallization range is increased considerably, but is still rather narrow (155°), and the last liquid, at 1085°, has the composition $I$ (Fig. 47), consisting of albite plus a very little diopside, as the diagram was drawn by Bowen in 1915. Point $I$, which could only be estimated by Bowen, due to the high viscosities, probably should be placed at a
Fig. 48. Diagram showing the phases present at equilibrium (solid lines) in a mixture of composition G (Fig. 47). The dashed lines show the behaviour of the same composition under conditions of crystal fractionation.

Fig. 49. Equilibrium diagram of a part of the system nepheline–FeO–SiO₂, showing the relations between nepheline, albite, and fayalite. (After Bowen and Schairer.)
somewhat higher per cent diopside (see Fig. 46); the actual relations in this area, though of great importance, are not yet thoroughly understood. On Fig. 48 the dashed lines correspond to crystallization with crystal fractionation (i.e. non-equilibrium), calculated by assuming that 10 per cent of the residual liquid from the previous step crystallizes, and the crystals are separated, at each of a series of steps. Note that even in this case, the bulk of the liquid crystallizes

![Fig. 50. Preliminary equilibrium diagram for the system fayalite–leucite–silica, showing the fields of the several crystalline phases and the intersection of the new area of immiscibility with the liquidus surface (shaded). In the area AA'CA two liquids are in equilibrium with silica crystals, and in the area AA'B'DBA two liquids are in equilibrium with fayalite crystals. Along the line AA' two liquids (A and A') are in equilibrium with each other and with crystals of both silica and fayalite. The tie line between conjugate liquids B' and B, extended, goes through the composition point for fayalite, making this line a true binary system and the points B and B' a maximum on the line ABDB'A'. All melts contain Fe$_2$O$_3$ in amounts representing equilibrium with pure metallic iron. (After Roedder.)](image)

in the first 50 degrees drop in temperature below the liquidus. The differences between the results with and without fractionation have been discussed in detail for another system (Osborn and Schairer, 1941), but are equally applicable here.

*Fayalite–Nepheline–Silica* (2FeO·SiO$_2$–Na$_2$O·Al$_2$O$_3$·2SiO$_2$–SiO$_2$). The phase diagram for this system, as presented by Bowen and Schairer (1938), is given in Fig. 49, where it is plotted as a subsystem in the system FeO–nepheline–SiO$_2$. Although fayalite is a low-melting compound (m.p. 1205°) it is still relatively insoluble in alkali-alumino-silicate melts, as shown by the positions of the two eutectics, near to the composition of albite. The eutectic with silica, fayalite, and albite at 980° corresponds roughly to a fayalite soda-granite, with about 6 per cent fayalite.
Fayalite–Leucite–Silica (2FeO·SiO₂–K₂O·Al₂O₃·4SiO₂–SiO₂). A preliminary diagram of this system, after Roedder (1951b), is given in Fig. 50. This system is interesting in that it shows that fayalite is relatively insoluble in potash feldspar–silica melts. Point E has not been determined accurately, but can hardly contain more than a few per cent fayalite, and may contain much less. The liquidus on the fayalite field in this system has a strong inverse curvature, and one portion is actually isothermal over a range of compositions, i.e. liquid immiscibility is involved. This immiscibility occurs at considerably lower temperatures (to less than 1100°C), and considerably higher alkali and alumina contents (to over 16 per cent K₂O + Al₂O₃), than in all other silicate systems showing immiscibility. The area in which this low temperature immiscibility intersects the liquidus surface in this system is shaded in Fig. 50, and overlies the boundary curve for the fields of fayalite and silica, yielding very unusual crystallization histories (see Fig. 51). This area represents a section through a two-liquid immiscibility phase volume in the system K₂O–FeO–Al₂O₃–SiO₂, the general shape of which has been determined (Roedder, 1953) but the full data have not been published. There is some evidence that the low temperature immiscible liquid field in the system fayalite–leucite–silica is connected, metastably under the silica liquidus surface, with the high temperature two liquid field along the fayalite–silica sideline, and also that it extends, metastably, under the practically flat fayalite field. This introduces the problems of the possible presence of a field of two immiscible liquids in various other systems showing practically flat and even inverse curvatures to the field for some phase. This region of immiscibility can either occur, stably, just above the liquidus, or else it can occur, metastably, just beneath the liquidus. In either case there will be a similar, nearly flat portion on the liquidus surface. Among the systems presented in this review, this type of liquidus is approached mostly in combinations of a silicate containing a divalent element (Ca, Mg, Fe), with alkali–aluminosilicate mixtures approaching the composition of the eutectics sodium feldspar–silica, and potassium feldspar–silica. Several of these binary and semibinary systems are sketched in Fig. 52, as plotted graphically from the various

Fig. 51. Diagram showing the phases present, at equilibrium, in a mixture of composition a, Fig. 50 (leucite 14, fayalite 46, silica 40). The phase change at 1140° is shown to take place over an assumed small temperature interval, as there is some Fe₂O₃ present in these liquids, precluding truly invariant conditions when four phases are present. This interval has not been measured experimentally.
sources given above. The existence of a low two-liquid "dome," cutting the liquidus from below, in the system fayalite–(potash feldspar–silica), would suggest that the reverse curvature in the system fayalite–(albite–silica), and perhaps the shape of some of the other liquidus curves, may reflect fields of immiscibility occurring metastably below the liquidus.

Forsterite–Leucite–Silica ($2\text{MgO} \cdot \text{SiO}_2 – \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 – 4\text{SiO}_2 – \text{SiO}_2$). This system

Fig. 52. Composite diagram showing the binary systems between a series of silicates of divalent ions (forsterite, “enstatite” ($\text{MgO} \cdot \text{SiO}_2$), anorthite, diopside and fayalite), and alkali–aluminosilicate liquids of the eutectic composition potassium feldspar–silica ("Or–SiO$_2$", point I in Fig. 34) and sodium feldspar–silica ("Ab–SiO$_2$", point I in Fig. 35). All of these curves represent binary equilibria except for the portions cross hatched. All have been sketched by graphical methods, from the appropriate ternary systems given above, except the dotted line for the system forsterite–albite, which represents unpublished data furnished through the courtesy of Mr. Robert Insley.

was studied by Schairer (1954) as one of the ternary planes in the general system $\text{K}_4\text{O} – \text{MgO} – \text{Al}_2\text{O}_3 – \text{SiO}_2$ (see Fig. 58). The phase diagram for this ternary, as given by Schairer (1957), is shown in Fig. 53. The potash feldspar field is vanishingly small in this system—only 0.2 per cent by weight forsterite results in the elimination of feldspar as the primary phase, i.e. magnesium silicates are exceedingly insoluble in these liquids. (The analogous system with nepheline in place of leucite has been studied by Greig at the Geophysical Laboratory, but the results have not been published.) The strong curvature of the boundary line between the fields of protoenstatite and silica, and the very small slope to the upper part of the protoenstatite liquidus surface results in very unusual crystallization histories, two of which are shown in Figs. 54 and 55, for
compositions $A$ and $B$ in the protoenstatite field of Fig. 53. Although both of these compositions are made of the same three materials, and there is comparatively little difference in the temperature of their protoenstatite liquidus, their general behaviours on crystallization are diametrically opposite. If magmas such as these occurred in nature, it is obvious that phenomena resulting from the formation and distribution of pyroxene phenocrysts should be quite different in the two cases.

![Equilibrium diagram of the system forsterite-leucite-silica](image)

**Fig. 53.** Equilibrium diagram of the system forsterite-leucite-silica. (After Schairer.)

**Potash Nepheline–Nepheline–Silica** ($K_{2}O \cdot Al_{2}O_{3} \cdot 2SiO_{3} \cdot Na_{2}O \cdot Al_{2}O_{3} \cdot 2SiO_{3} \cdot SiO_{2}$). Although no one has attempted a rigorous laboratory approach to the eight-component system $K_{2}O \cdot Na_{2}O \cdot CaO \cdot FeO \cdot MgO \cdot Fe_{2}O_{3} \cdot Al_{2}O_{3} \cdot SiO_{2}$, for the reasons discussed earlier, it is obvious from the numerous possible 3-, 4- and 5-component systems, and in particular from the specific subsystems discussed above, that there are certain crystallization trends in common, which may logically be assumed to occur in mixtures of all eight components. In all of the subsystems discussed above, the general crystallization trends, for liquids resembling igneous rocks in composition, are toward the crystallization of phases that will deplete the melt of most of its CaO, MgO, FeO, and most of the $Al_{2}O_{3}$ molecularly in excess of the amount of alkalis present. This yields a net enrichment in $K_{2}O$, Na$_2$O and FeO, and usually in $Al_{2}O_{3}$ and SiO$_2$ as well.
Further crystallization results in the depletion of even the FeO, so that the residual liquids from this process will be essentially compositions in the system \( \text{K}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 \). Obviously, the reverse process of selective fusion of a polycrystalline mixture of these oxides will give similar liquids, in the reverse order, except for any effects specifically caused by disequilibrium on cooling. Although some phenomena resulting from disequilibrium on cooling may be

![Diagram showing the phases present, at equilibrium, in a mixture of composition \( \text{A} \), Fig. 53. Note that 72 per cent of the melt crystallizes in the first 30° drop from the liquidus, but that the remaining liquid does not crystallize completely until 510° lower.](image1)

![Diagram showing the phases present, at equilibrium, in a mixture of composition \( \text{B} \), Fig. 53. Note that although this point falls in the same field as point \( \text{A} \) (Fig. 52), only 7.5 per cent is solid at 990°, 410° below the liquidus.](image2)

reversed on heating, this is not necessarily true, particularly where there has been a physical separation of phases. Reaction with inclusions of wall rocks, as discussed by Bowen (1922) represents in effect a reversal of the equilibria on cooling.

As most igneous rocks that even approach the system \( \text{K}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 \) in composition are at least 50 per cent \( \text{SiO}_2 \), and have the sum of \( \text{K}_2\text{O} + \text{Na}_2\text{O} \) approximately equal to \( \text{Al}_2\text{O}_3 \) (on a molecular basis), the section \( \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{SiO}_2 \) through this quaternary system should come close to representing their compositions. This system was very aptly termed "petrogeny’s residua system" by Bowen (1937), as it represents the goal for
the compositions of the residual liquids, not only in the synthetic systems, but also in the natural systems, wherever evidence of natural residual liquids is available.

Wherever the evidence permits evaluation of the sequence of crystallization, the rocks show that the oxide ores, olivines, pyroxenes and calcic plagioclase separate early and almost quantitatively from magmas (i.e. they become highly insoluble under lowered temperatures), eventually resulting in low-melting, liquid alkali–aluminosilicate residua. This will take place under conditions of equilibrium crystallization, and even more so under conditions of fractional crystallization, although there are some differences of opinion as to the specific results of fractional crystallization.

The diagram for the system $K_2O \cdot Al_2O_3 \cdot 2SiO_2-Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ was first given by Schairer and Bowen (1935), and later was given in a revised form, as shown in Fig. 56, by Schairer (1950). It is apparent that the last residual liquids in most of the systems discussed above, neglecting relatively insignificant amounts of silicates of Ca, Mg and Fe, would fall on the sidelines of this system, in the vicinity of the binary eutectics of the feldspars with silica (points $A$ and $B$) or in a few cases at the eutectic with nepheline (point $C$). Mixtures containing both potassium and sodium can be expected to fall in the area between these points. One can think of rock magmas as multicomponent systems, plotted in
polydimensional space above this diagram, which simplify themselves, by quantitative crystallization of various components, until they finally come funnelling out of polydimensional space to land in this ternary system. Regardless of where they start in this system, however, the results will be similar. The residual liquid compositions for this system lie in a saddle-like trough of low liquidus temperatures, centered about the points X, Y and Z, and thus corresponding in composition to leucocratic nepheline syenite, syenite and granite, respectively, or to their effusive equivalents. Crystallization paths in the feldspar field are strongly curved as a consequence of the solid solution series with a

![Diagram](image-url)

Fig. 57. The alkali–feldspar join K₂O·Al₂O₃·6SiO₂–Na₂O·Al₂O₃·6SiO₂. Heavy solid or dashed curves refer to binary equilibrium. Light solid or dashed curves refer to ternary equilibrium. Open circles indicate determined points. (After Schairer.)

minimum between albite and orthoclase (shown in Fig. 57 from Schairer, 1950). There has been an intensive study of these crystallization paths, under various water pressures, in order to understand the derivation of granitic and rhyolitic magmas (for example Tuttle, 1955).

Throughout this process, there has been an ever-increasing amount of water, carbon dioxide, and various trace elements including sulphur and the ore elements, in the residual liquid, as small amounts of all of these materials are present in the original magma, and as the bulk of the phases that can form under the conditions that must obtain up to this point, both in the laboratory and the earth, are free of these materials. The behaviour of trace elements during magmatic differentiation has been discussed by numerous writers, and has been summarized by Osborn (1950). Other than the occasional formation of small amounts of early hornblende and biotite in some rocks, and the general lowering of the liquidus, these components have had very little effect on the equilibria up to this point, and the phase equilibria for the anhydrous systems represent a reasonably close approach to the actual conditions. Further crystallization of the anhydrous phases in this system results in still greater concentration of
water (and other materials) into the residual liquid, however, and from here on these residual liquids behave in a manner controlled more by these volatile materials than by the non-volatile components. (See Roy and Tuttle, 1956, volume 1 of this series.)

Other Systems of Petrological Interest

Many other systems of petrological interest have been studied, only a few of which can be mentioned here. In particular, many other ternary or partially ternary planes through the tetrahedrons representing four-component systems have been reported in the literature. Much of this work was done for its pertinence to industrial problems involving slags, cements and refractories (see Levin et al., 1956). The four systems in which the most work of petrological significance has been done are the four-component systems combining Al₂O₃ and SiO₂ with K₂O + MgO (see below), Na₂O + CaO (see Greene and Bogue, 1946; Goldsmith, 1947), CaO + FeO (see Schairer, 1942; Muan and Osborn, 1951), and CaO + MgO (see Osborn and Tait, 1954; DeVries and Osborn, 1957). Extensive studies have also been made in the system MgO–FeO–Fe₂O₃–SiO₂ (Muan and Osborn, 1956). Although several dozen ternary or partially ternary planes in the first four systems alone have been studied and published in recent years, and smaller portions of many other systems have been studied, only one of the systems can be given here as an illustration.

The system K₂O–MgO–Al₂O₃–SiO₂ was studied by Schairer (1954, 1955). Three of the four limiting ternary systems making the faces of the tetrahedron representing this system had been studied previously (see above) and as most of the interest lay in the higher silica mixtures, the fourth ternary K₂O–MgO–Al₂O₃, was not studied. A number of binary and ternary compounds were known, and these were chosen as the components for a series of seven 3-component systems.
published by Schairer (see Fig. 58), and data have been obtained but are yet to be published on a large number of additional triangular joins in the system, connecting these and other compounds (Schairer, 1955, 1957). One of these seven joins, the system forsterite–leucite–silica, has been presented above as Fig. 53.

A study of this type is aimed at understanding the mutual relationships of the various phases in the system, the trends taken by liquids upon crystallization, and the temperatures involved, and at providing the necessary base for experiment or extrapolation into more complex systems, in this particular instance.

Fig. 59. Diagram showing univalent lines and their relation to ternary invariant points (small black dots and letters a through o) in limiting systems and to quaternary invariant points (large black dots and capital letters). All univalent lines are 3-dimensionally curved lines but for simplicity are shown as straight lines. These lines and points do not lie in a plane. Only their relations to one another are shown in this diagram, which is not intended to depict their angular spatial relations. The lengths of the lines and the position of a temperature maximum on a line are arbitrary and without significance. Arrows indicate the direction of falling temperature. Abbreviations for crystalline solid phases along the lines and at the points: LC = leucite, COR = corundum, MU = mullite, SP = spinel, CORD = cordierite, SAP = sapphire, FEL = potassium feldspar, TR = tridymite, CR = cristobalite, FO = forsterite, PR = protoenstatite, EN = enstatite. (After Schairer.)
with $\text{H}_2\text{O}$ and FeO. Furthermore the actual compositions themselves are useful as a basis for addition of other components, such as $\text{H}_2\text{O}$. Thus certain limited portions of the system $\text{K}_2\text{O}$–$\text{MgO}$–FeO–$\text{Al}_2\text{O}_3$–SiO$_2$–H$_2$O might be studied, and reveal the stability relations of a large group of minerals occurring in igneous and metamorphic rocks. The most important results on this series of joins is best given by a single “Schaerer diagram” (Fig. 59). Inspection of this diagram shows that as a result of a number of quaternary peritectic points, crystallization in this portion of the system trends, particularly with crystal fractionation, toward two low-temperature eutectics, points $E$ and $K$, which correspond essentially to potash granites, with very minor amounts of cordierite, and mullite or pyroxene (enstatite). This illustrates what will probably be found to be a general phenomenon in complex silicate systems; there will probably be far more peritectic (reaction) invariant points than eutectic points. This of course results in far greater effects for any crystal fractionation, as a liquid must stop at a eutectic, with or without fractionation, but with fractionation it will go right on past a reaction point where it should stop, at equilibrium. One other important fact, apparent from Fig. 59, is that certain planes in such a system act as barriers to liquids changing with crystallization, whether at equilibrium or with fractionation, and hence partition the diagram into regions, each with its own residual liquid goal.

CONCLUSION

The major purpose of the silicate phase equilibrium research covered in this review was to aid in the understanding of igneous rocks, and in this respect it has been eminently successful. In addition, it has been of great help in the study of slags, refractories and cements. The systems described have immediate application to many problems in igneous petrology, and with the addition of volatiles under pressure, or pressure alone, they may be extended to cover rather closely the conditions of formation of most igneous and many metamorphic rocks in the crust of the earth. Obviously, the greater the difference in composition, or pressure, from the conditions under which the diagram was determined, the greater the possible errors in extrapolation, but the “dry” systems presented here still provide the necessary firm base on which experimental or theoretical extensions must be built.

As for the future, there are many important additional dry silicate melt systems that have not been determined. Some of the more important of these, such as the pyroxene quadrilateral, MgO·SiO$_2$–CaO·MgO·2SiO$_2$–CaO·FeO·2SiO$_2$–FeO·SiO$_2$, are currently under investigation, but others have not even been started. The procedure described by Muñoz (1955, 1957) for controlling the oxygen pressure over melts, and hence the state of oxidation of variable valence elements in the melt, should be applied to a variety of complex systems to aid in understanding the great influence of oxidation state on differentiation trends in iron-rich magmas such as basalt, as well as to study the geochemistry of other variable-valence elements such as manganese, titanium, sulphur, etc. Much work is needed on the distribution of all trace elements between liquid and various crystallizing phases under various conditions of temperature and composition. Radioactive tracer techniques should be particularly useful here.

Much of the silicate phase research up to the present has been in the area between the liquidus and solidus; this is admittedly the most significant part for
igneous petrology, but when effects such as inversion or exsolution appear on cooling, studies of the subsolidus region are obviously needed, and may yield much information on the thermal history of the rock as well as on metamorphic processes. These subsolidus reactions are slow to equilibrate and hence experimentally difficult, but are gradually being unravelled by a variety of techniques including sintering, high temperature X-ray diffraction, and thermochemical measurements and calculations (see, for example, SAHAMA and TORGESON, 1949, and KRACEK and NEUVONEN, 1952).

One particularly important purpose of silicate research, in which considerable advances can be expected in the future, is to gain an understanding of the liquid phase. Knowledge of the liquid phase has lagged behind that of the solid, crystalline phase and there are many phenomena involving silicate glasses that are not fully understood at this time. A good example is the "acclimation" of a non-crystallizable glass of albite composition, formed at 1600°, by successive lower heat treatments, to permit ready crystallization at subliquidus temperatures (SCHÄFER, 1951, p. 282). The liquidus curves for substances may have a variety of shapes, depending on the thermal properties of the crystals and liquid and the effects of any interactions in the liquid causing deviation from ideality (see, for example, BOWEN and SCHÄFER, 1929a). The ionic species present in liquid silicate melts may be investigated by electrical methods, but the experimental techniques are difficult (EITEL, 1954b). KNAPP and FLOOD (1957) have calculated the activities in borosilicate melts to evaluate various structural models, and have extended their work to melts between CaO·SiO₂ and SiO₂.

Viscosity, density and X-ray measurements on silicate melts have also provided considerable information about their nature. Most density determinations have been made on the quenched glasses at room temperature, from which partial molar volumes may be calculated (CALLOW, 1952); precision determinations of the density of glasses by the density gradient method (HORN, 1955) should aid these studies. A short but excellent review of the crystal chemical explanation of magmatic differentiation is given by OSBORN (1950), and further studies of this nature are in order. Investigations such as these provide a better understanding of the nature of the bonding in silicate melts and may actually permit prediction of phenomena such as immiscibility (LEVIN and BLOCK, 1957; BLOCK and LEVIN, 1957).

In general, however, it is safe to say that silicate systems must still be determined experimentally as this is usually less difficult than obtaining the experimental data needed to calculate them, particularly where the deviations from ideality are large. In this connexion a quotation from N. L. Bowen is apropos. In a presidential address in 1937 (BOWEN, 1938, p. 124) he wrote the following concerning the status of the calculation of silicate phase diagrams when he first joined the Geophysical Laboratory in 1912:

"There were then enthusiastic thermodynamicians who wagered that within five years such advance would occur in thermodynamic theory and in the measurement of fundamental thermodynamic quantities for silicates that it would no longer be necessary to determine silicate equilibrium relations experimentally; instead they would be determined by a few simple calculations. Five times five years have passed since those sanguine days yet it is still necessary to determine silicate equilibrium diagrams by means of experiment."
Although considerable progress has been made in the twenty years since Bowen wrote this, it appears that silicate diagrams must still be determined experimentally.

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