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SOME ASPECTS OF THE MELTING AND CRYSTALLIZATION OF ROCK-FORMING MINERALS*

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INTRODUCTION

Minerals are interesting because of the story they tell of those complex physical and chemical processes that have operated in the building and modification of our earth and its crust. One of the most fascinating problems of earth science is the delineation of the physical chemistry of the crystallization of rock-forming minerals from magmas.

The rock magma—a molten solution of complex silicates—is the parent source of the igneous rocks and their minerals. Many igneous rock types may result from the cooling and crystallization of this magma.

Much information on the processes involved in igneous-rock origin has been obtained from detailed petrographic examinations of samples of igneous rocks and from geological field data on the interrelations of the various rocks. However, in order to understand and interpret the complex phenomena of crystallization, with changing mineral assemblages responding to changes in thermodynamic environment brought about by cooling or by changes in pressure, it has been necessary to study the phase equilibrium relations in a large number of silicate systems. Fundamental information concerning the mode of origin of the minerals of the igneous rocks has been obtained through the preparation of silicate melts (simplified artificial magmas) in the laboratory with controlled variations of chemical composition, and a study of the behavior of these melts at equilibrium under a wide variety of temperature and pressure conditions.

We have been particularly interested in the mutual melting and crystallization relations, which cause changes in chemical composition and crystal system in response to changing temperature conditions, of the olivines, the pyroxenes and pyroxenoids (especially those containing

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* At the request of the Council, Dr. J. F. Schairer has prepared this Presidential address, which because of the cancellation of the annual meeting was not presented orally. Although heavily burdened with war work the author has kindly consented to prepare, on short notice, this general survey article which we are pleased to present at this time. The Editors.

FeO) and the melilites. We have also been interested in the direction of change of chemical composition of the residual liquid phase as crystallization proceeds in artificial melts that may approach the compositions of natural magmas.

All of the important rock-forming minerals of the igneous rocks, with the exception of quartz, have a variable composition. They are solid solutions which undergo progressive changes in chemical composition during cooling and crystallization of the magma. Even when there are no interruptions in the cooling cycle, there are continuous or discontinuous changes in the compositions of individual minerals and in the kinds of minerals crystallizing from the liquid phase. A mineral or assemblage of minerals stable at an early stage in the crystallization process may become unstable at a later stage and undergo transformation to new mineral assemblages with changes in both chemical composition and crystal system.

Of the various oxides that enter into the composition of the minerals of the igneous rocks, SiO_2, Al_2O_3, iron oxides, MgO, CaO, Na_2O and K_2O are of greatest importance. In order to obtain the desired information concerning the processes involved in the crystallization of a rock magma, one by one the fundamental unary, binary and ternary systems of rock-forming oxides have been studied in the laboratory. Studies of four of the quaternary systems which include these oxides are in progress. We propose to review briefly what progress has been made from a study of artificial silicate melts towards the understanding of the crystallization chemistry of three groups of rock-forming minerals—the olivines, the pyroxenes and related pyroxenoids and the melilites.

OLIVINES

The olivines are a series of polycomponent orthosilicate solid solutions. Most rock-forming olivines consist essentially of the two molecules forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). Other molecules which may be present in rock-forming olivines are Ca_2SiO_4 (which exists in at least two crystalline modifications, one of which is the monoclinic mineral larnite), merwinite ($Ca_3Mg(SiO_4)_2$, monoclinic), monticellite ($CaMgSiO_4$), Fe-monticellite ($CaFeSiO_4$), tephroite (Mn_2SiO_4) and glaucochroite ($CaMnSiO_4$).

Bowen and Schairer[1] studied the system MgO–FeO–SiO_2. By means of a series of isothermal planes they showed in detail the compositions of all liquid and solid phases from the liquidus temperatures to below 955°C. and discussed the paths of crystallization of typical liquids. Their

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[1] Bowen, N. L., and Schairer, J. F., The system MgO–FeO–SiO_2: *Am. Jour. Sci.*, **29**, 151–217 (1935).

studies on this system showed the chemical compositions, optical properties and mutual melting and stability relations of three sets of solid solutions—the magnesia-iron olivines, the magnesia-iron pyroxenes and the magnesio-wüstites (MgO–FeO solid solutions). Their equilibrium diagram for the magnesia-iron olivines is given here as Fig. 1.

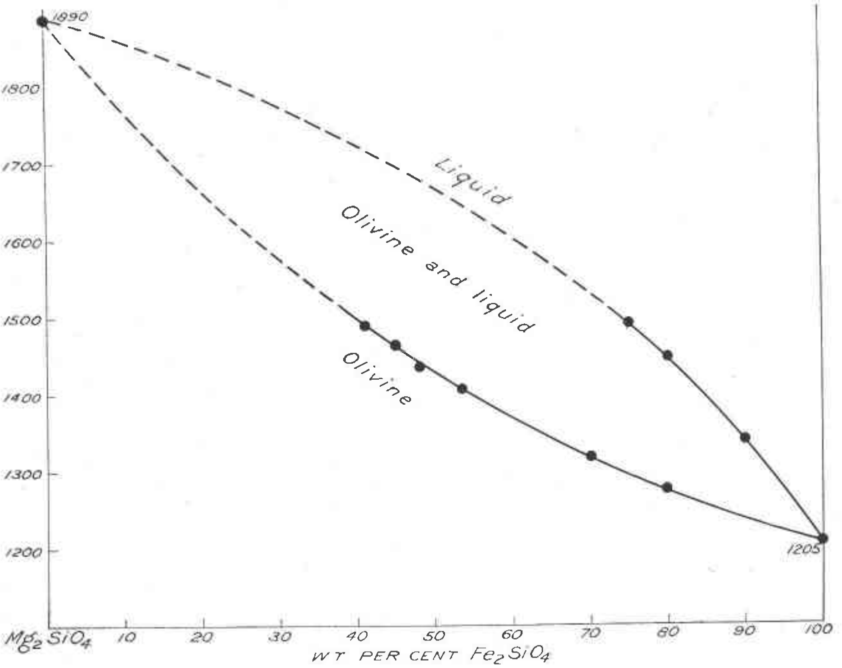

FIG. 1. Equilibrium diagram of the binary system Mg_2SiO_4–Fe_2SiO_4. (Diagram of Bowen and Schairer.)

In like manner, Bowen, Schairer and Posnjak[2] in two papers presented their study of the system CaO–FeO–SiO_2 with data on the chemical compositions, optical properties and mutual melting and stability relations of two sets of solid solutions—the lime-iron olivines with compositions between Ca_2SiO_4 and Fe_2SiO_4 and the lime-iron pyroxenes and pyroxenoids with compositions between $CaSiO_3$ and $FeSiO_3$. By means of a series of isothermal planes, they showed in detail the compositions of all liquid and solid phases from the liquidus temperatures to 700°C. and discussed the paths of crystallization of typical liquids. Their equilibrium diagram for the system Ca_2SiO_4–Fe_2SiO_4 is given here as Fig. 2.

[2] (a) Bowen, N. L., Schairer, J. F., and Posnjak, E., The system Ca_2SiO_4–Fe_2SiO_4: *Am. Jour. Sci.*, **25**, 273–297 (1933); (b) The system CaO–FeO–SiO_2: *ibid.*, **26**, 193–284 (1933).

Some years ago, Ferguson and Merwin[3] presented data for the system CaO–MgO–SiO_2. The composition join Ca_2SiO_4–Mg_2SiO_4 cuts this system. They established the incongruent nature of the melting of monticellite ($CaMgSiO_4$) and show a field of monticellite solid solutions on the liquidus surface in the ternary system. Recently, Osborn[4] has made some corrections to the diagram for CaO–MgO–SiO_2, including stability data on the orthosilicate merwinite which melts incongruently and has a field on the liquidus surface in the ternary system. Preliminary data suggest that there is limited solid solution extending from Ca_2SiO_4 toward merwinite. His diagrams for Ca_2SiO_4–akermanite and merwinite–akermanite are reproduced here as Figs. 3 and 4, respectively.

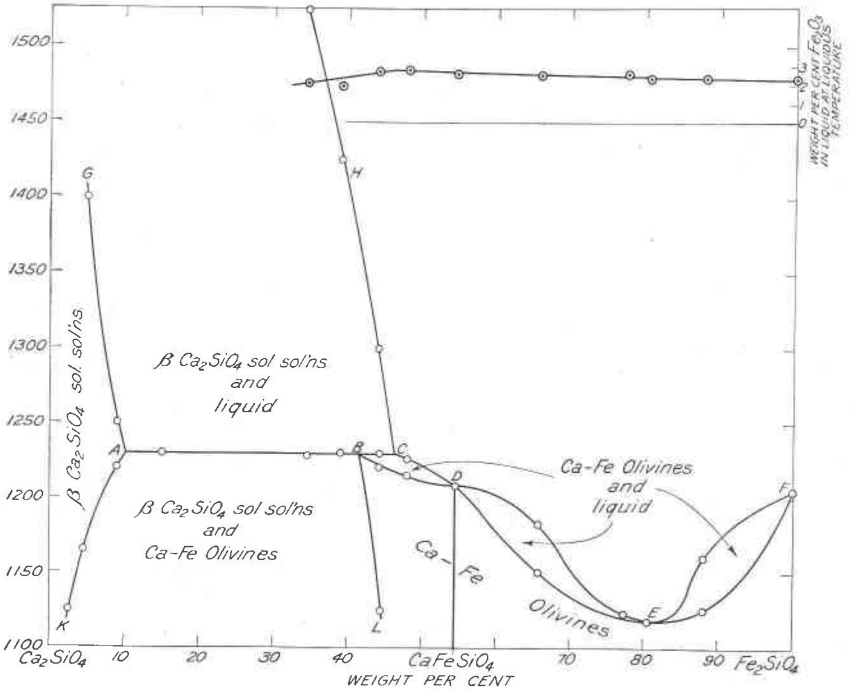

FIG. 2. Equilibrium diagram of the binary system Ca_2SiO_4–Fe_2SiO_4. (Diagram of Bowen, Schairer and Posnjak.)

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[3] Ferguson, J. B., and Merwin, H. E., The ternary system CaO–MgO–SiO_2: *Am. Jour. Sci.*, **48**, 81–123 (1919).

[4] Osborn, E. F., The compound merwinite (3CaO · MgO · $2SiO_2$) and its stability relations within the system CaO–MgO–SiO_2. (Preliminary report.): *Jour. Am. Ceram. Soc.*, **26**, 321–332 (1943).

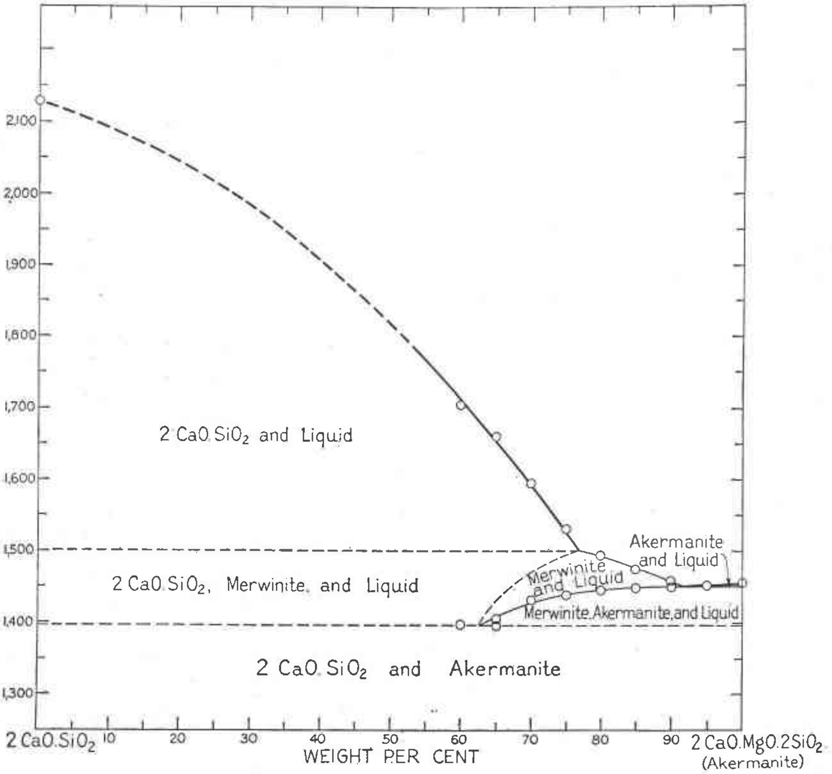

FIG. 3. Equilibrium diagram of the join Ca_2SiO_4–akermanite, heavy lines represent binary equilibrium relations, light lines illustrate relations lying outside the plane of this diagram in the ternary system $CaO–MgO–SiO_2$. (Diagram of Osborn.)

PYROXENES AND RELATED PYROXENOIDS

The pyroxenes and related pyroxenoids present exceptional complexity both of crystalline modifications and chemical composition. They are a series of polycomponent solid solutions, some of the molecules of which are completely miscible and others only partly so. The important mineral molecules which enter into the composition of the rock-forming pyroxenes are given in Table 1.

The three most important molecules are the metasilicate molecules $CaSiO_3$, $MgSiO_3$ and $FeSiO_3$. The composition triangle, which is given as Fig. 5, shows the chemical relations between diopside and hedenbergite and the simple metasilicates.

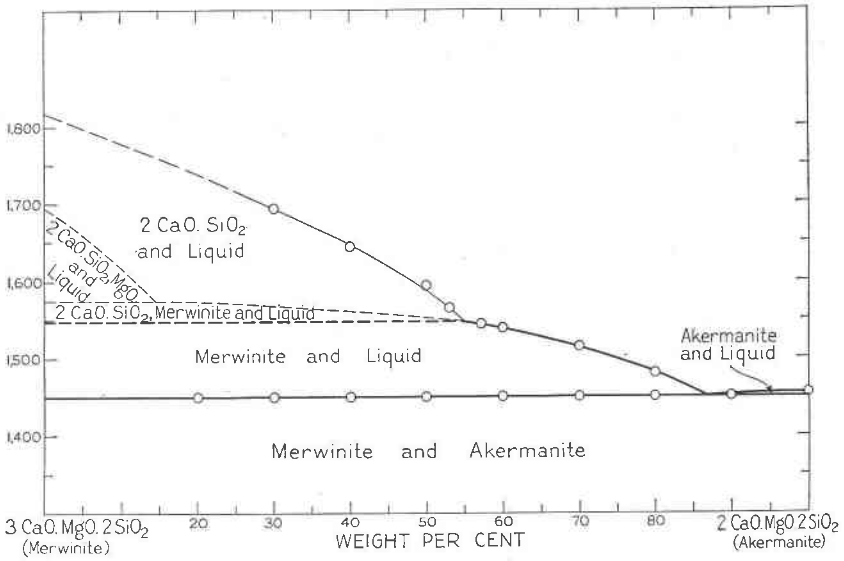

FIG. 4. Equilibrium diagram of the join merwinite–akermanite; heavy lines represent binary equilibrium; light lines illustrate relations lying outside the plane of this diagram in the system CaO–MgO–SiO$_2$. (Diagram of Osborn.)

TABLE 1. MOLECULES OF THE ROCK-FORMING PYROXENES

$CaSiO_3$	Wollastonite, pseudowollastonite
$MgSiO_3$	Enstatite, clinoenstatite
$CaSiO_3 \cdot MgSiO_3$	Diopside
$FeSiO_3$	Ferrosilite, clinoferrosilite
$CaSiO_3 \cdot FeSiO_3$	Hedenbergite
$MnSiO_3$	Rhodonite, bustamite
$CaSiO_3 \cdot MnSiO_3$	Johannsenite
Molecules containing	
Al_2O_3	Augites
Fe_2O_3	Augites and babingtonite
TiO_2	Titaniferous augites
$Na_2O \cdot Al_2O_3 \cdot 4SiO_2$	Jadeite
$Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$	Acmite, aegirite

As already mentioned, Bowen, Schairer and Posnjak[2b] studied the system CaO–FeO–SiO_2. Their studies showed the chemical compositions, optical properties, and mutual melting and stability relations of the lime-iron pyroxenes and pyroxenoids (all compositions between $CaSiO_3$ and $FeSiO_3$), including pseudowollastonite (α–$CaSiO_3$), wollastonite (β–$CaSiO_3$ solid solutions with up to 76 per cent $FeSiO_3$), hedenbergite (with hedenbergite solid solutions containing up to 80 per cent $FeSiO_3$), and the lime-iron olivines. Their diagram for the join $CaSiO_3$–$FeSiO_3$ is given here as Fig. 6.

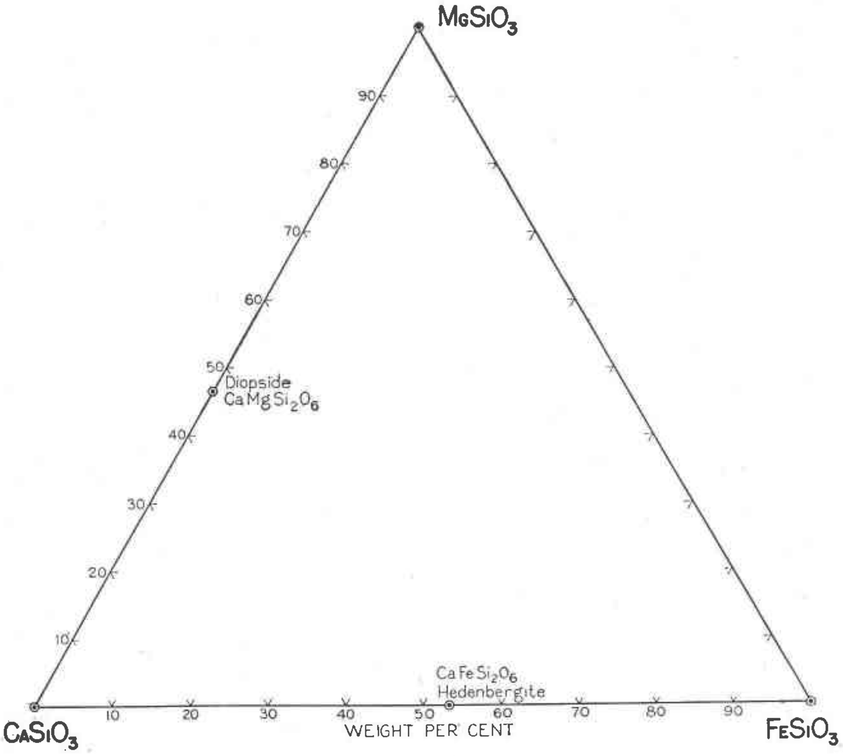

FIG. 5. Composition triangle $CaSiO_3$–$MgSiO_3$–$FeSiO_3$ showing the chemical relations between diopside, hedenbergite, and the three simple metasilicates.

In like manner, in their study of the system MgO–FeO–SiO_2, Bowen and Schairer[1] presented complete data on chemical compositions, optical properties, and mutual melting and stability relations of the $MgSiO_3$–$FeSiO_3$ pyroxenes, including both the clino-pyroxenes and the ortho-pyroxenes, and their relations to the magnesia-iron olivines. Their diagram for the join $MgSiO_3$–$FeSiO_3$ is reproduced here as Fig. 7.

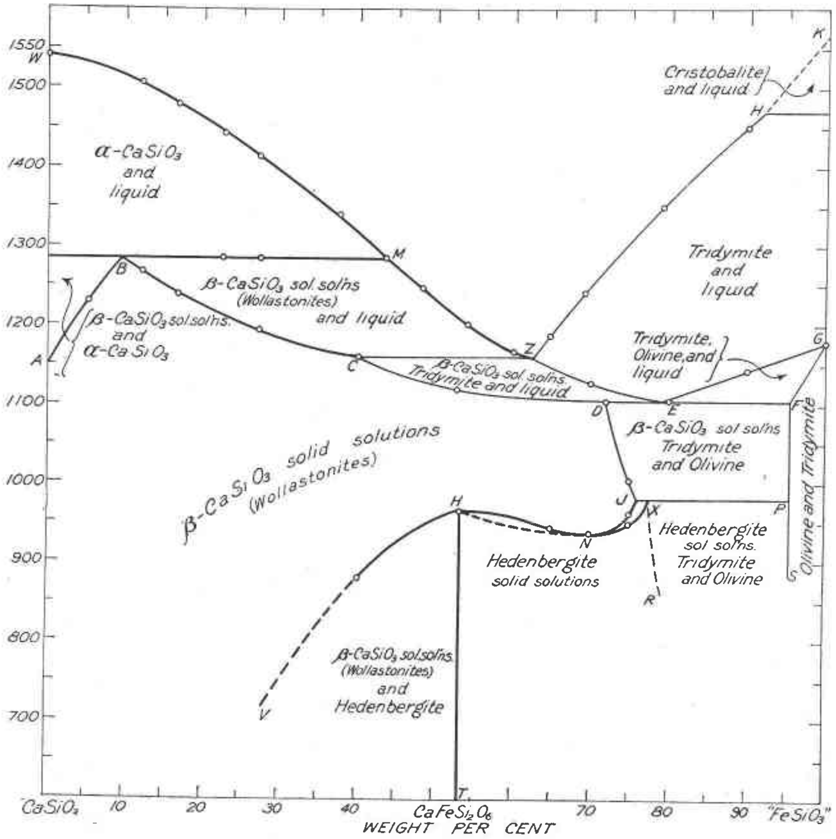

FIG. 6. Equilibrium diagram of the join $CaSiO_3$–$FeSiO_3$ in the system CaO–FeO–SiO_2. Heavy curves refer to binary equilibrium and light curves to ternary equilibrium. (Diagram of Bowen, Schairer and Posnjak.)

Bowen,[5] in his study of the system diopside–forsterite–silica, showed

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[5] Bowen, N. L., The ternary system: diopside–forsterite–silica: *Am. Jour. Sci.*, **38**, 207–264 (1914).

the presence of a complete series of solid solutions between diopside and clinoenstatite and gave their optical properties and complete melting relations. His equilibrium diagram is reproduced here as Fig. 8.

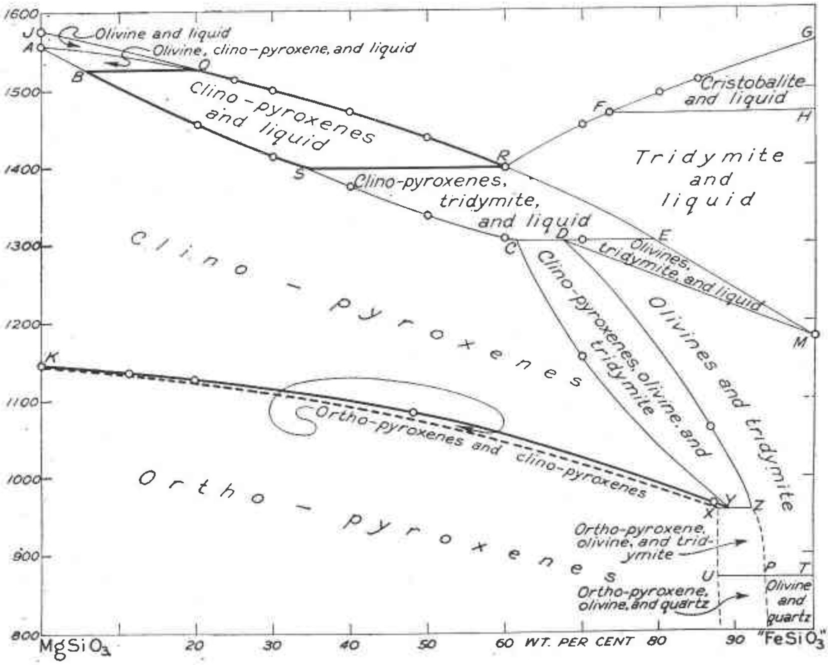

FIG. 7. Equilibrium diagram of the join $MgSiO_3$–$FeSiO_3$ in the system MgO–FeO–SiO_2 Heavy curves refer to binary equilibrium and light curves to ternary equilibrium. (Diagram of Bowen and Schairer.)

Recently, Schairer and Bowen[6] showed that in the system $CaSiO_3$–diopside there is little or no solid solution of diopside in pseudowollastonite (α–$CaSiO_3$) or of $CaSiO_3$ in diopside, but that wollastonite (β–$CaSiO_3$) may take up to a maximum of 22 per cent of diopside in solid solution. Their equilibrium diagram is reproduced here as Fig. 9.

Bowen and Schairer[7] showed that acmite ($Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$) melts

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[6] Schairer, J. F., and Bowen, N. L., The binary system $CaSiO_3$–diopside and the relations between $CaSiO_3$ and akermanite: *Am. Jour. Sci.*, **240**, 725–742 (1935).

[7] Bowen, N. L., and Schairer, J. F., The fusion relations of acmite: *Am. Jour. Sci.*, **18**, 365–374 (1929).

incongruently at 990°C. to hematite and liquid. In a later paper, Bowen, Schairer and Willems[8] described the melting relations of acmite in the presence of an excess of any of its component oxides. Their equilibrium diagram is given here as Fig. 10.

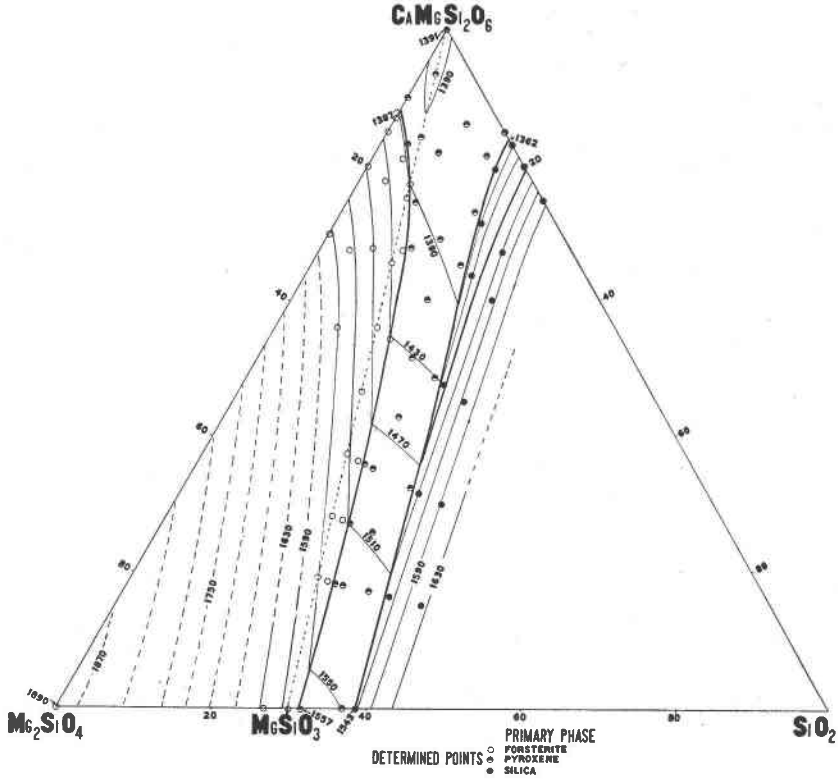

FIG. 8. Equilibrium diagram of the ternary system forsterite–diopside–silica showing the melting relations of pyroxenes between diopside and clinoenstatite ($MgSiO_3$). (Diagram of Bowen.)

Greig and Barth[9] in studies of the system nepheline–albite, and Schairer and Bowen in unpublished studies of the system Na_2O–Al_2O_3–SiO_2, found that there was no field of jadeite on the liquidus surface and

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[8] Bowen, N. L., Schairer, J. F., and Willems, H. W. V., The ternary system Na_2SiO_3–Fe_2O_3–SiO_2: *Am. Jour. Sci.*, **20,** 405–455 (1930).

[9] Greig, J. W., and Barth, T. F. W., The system, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ (nephelite, carnegieite)–$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ (albite): *Am. Jour. Sci.*, **35-A,** 93–112 (1938).

that no crystals of jadeite ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2$) appeared at any of the temperatures studied. A crystallized charge of the composition $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$ consisted of crystals of nepheline and albite. Jadeite might be a stable phase only at low temperatures or at pressures above atmospheric pressure or it might only be stable in solid solution with other pyroxene molecules. More experimental work is necessary.

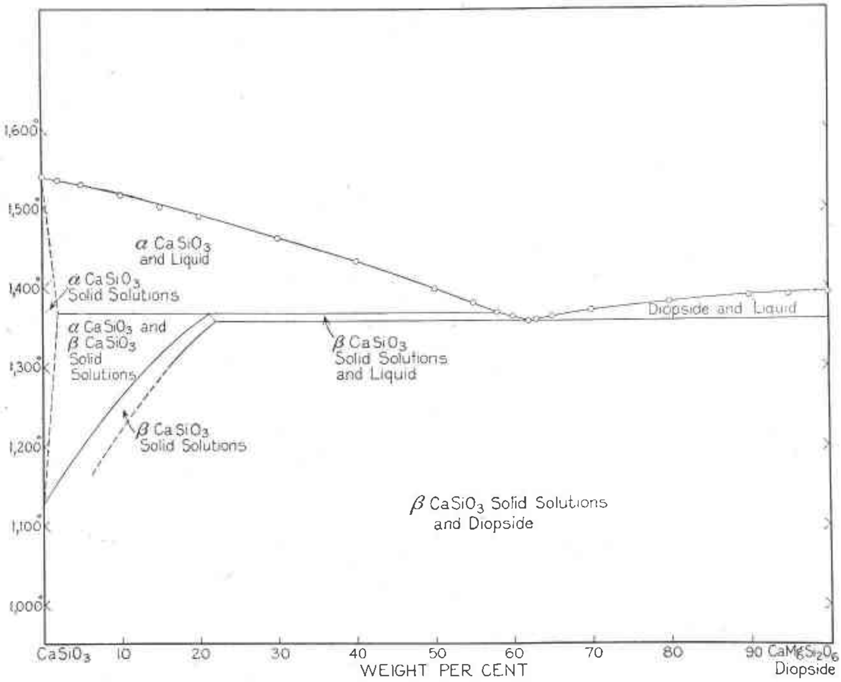

FIG. 9. Equilibrium diagram of the binary system $CaSiO_3$ (wollastonite, pseudowollastonite)-$CaMgSi_2O_6$ (diopside). (Diagram of Schairer and Bowen.)

Recently, Schairer[10] presented an equilibrium diagram showing the liquidus relations in the system $FeO–Al_2O_3–SiO_2$. No compound of FeO, Al_2O_3 and SiO_2 was encountered which might enter into solid solution with other pyroxene or pyroxenoid molecules in the aluminous pyroxenes. Experiments at sub-liquidus temperatures are not yet com-

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[10] Schairer, J. F., The system $CaO–FeO–Al_2O_3–SiO_2$: I, Results of quenching experiments on five joins. *Jour. Am. Ceram. Soc.*, **25**, 241–274 (1942); see page 245.

pleted. In this same paper, the results of quenching experiments on five joins through the tetrahedron representing the quaternary system CaO–FeO–Al_2O_3–SiO_2 were presented. The mutual melting relations between olivines, pyroxenoids and melilites whose compositions lie in this system were given. Exact data on the chemical composition of the several solid phases of variable composition (solid solutions) have not yet been obtained.

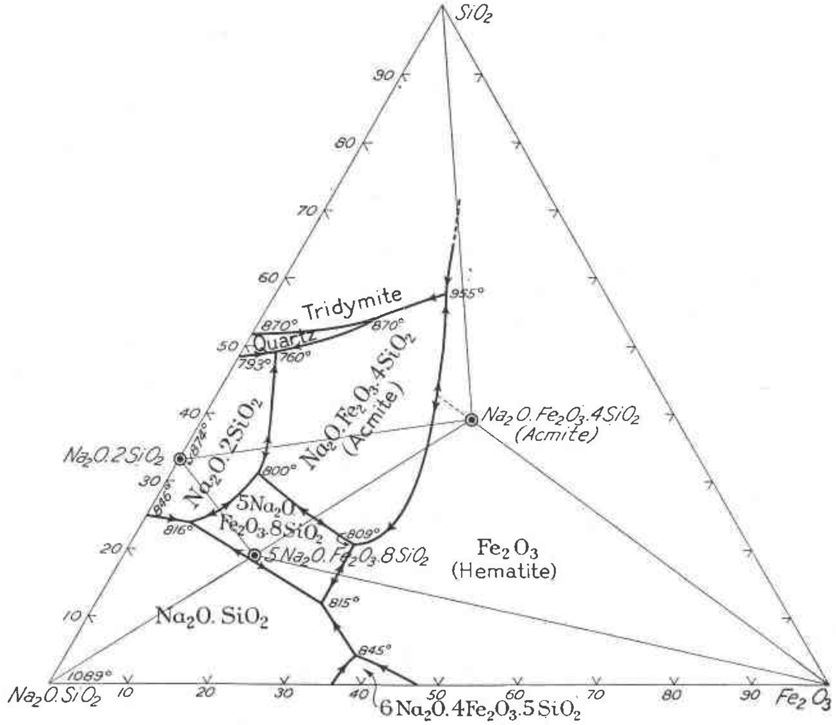

FIG. 10. Equilibrium diagram of Na_2SiO_3–Fe_2O_3–SiO_2, a portion of the ternary system Na_2O–Fe_2O_3–SiO_2 without isotherms but showing the fields of stability and the incongruent nature of the melting of the pyroxene, acmite. (Diagram of Bowen, Schairer and Willems.)

MELILITES

The melilites are complex solid solutions of several different molecules which are wholly or partially miscible in the solid state and form well crystallized tetragonal crystals. From studies of the analyses of melilite it has been shown that akermanite ($2CaO \cdot MgO \cdot 2SiO_2$) and gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) are the dominant molecules.

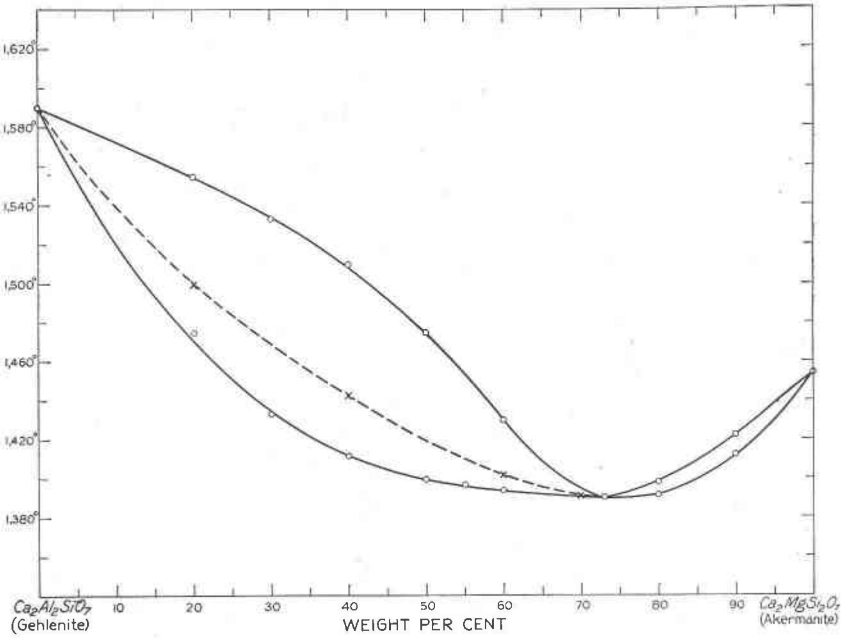

FIG. 11. Equilibrium diagram of the binary system gehlenite–akermanite. Dashed line is solidus curve of Ferguson and Buddington. (Diagram of Osborn and Schairer.)

Ferguson and Buddington[11] showed that akermanite and gehlenite form a complete series of solid solutions with a temperature minimum on the liquidus surface. They recorded the optical properties of these solid solutions. Further optical and thermal data were given by Buddington[12] on more complex artificial melilite solid solutions. Recently, Osborn and Schairer[13] corrected the position of the solidus curve for the system akermanite–gehlenite. Their diagram is given here as Fig. 11.

[11] Ferguson, J. B., and Buddington, A. F., The binary system åkermanite–gehlenite: *Am. Jour. Sci.*, **50,** 131–140 (1920).

[12] Buddington, A. F., On some natural and synthetic melilites: *Am. Jour. Sci.*, **3,** 35–87 (1922).

[13] Osborn, E. F., and Schairer, J. F., The ternary system pseudowollastonite–akermanite–gehlenite: *Am. Jour. Sci.*, **239,** 715–763 (1941).

Bowen, Schairer and Posnjak[14] described the iron analogue of akermanite, $2CaO \cdot FeO \cdot 2SiO_2$, and gave its optical properties. This compound is stable only below 775°C. and above this temperature breaks up into a pyroxenoid, wollastonite (β–$CaSiO_3$) and an olivine, Fe-monticellite ($CaFeSiO_4$). Their diagram for $CaSiO_3$–$CaFeSiO_4$ is reproduced here as Fig. 12. They also call attention to the fact that in attempts to prepare crystalline akermanite from a glass of that composition, a single phase, akermanite was obtained at 1375°C. while this same glass crystallized at 1050°C. gave a crystal complex with Ca_2SiO_4 as one of the phases.

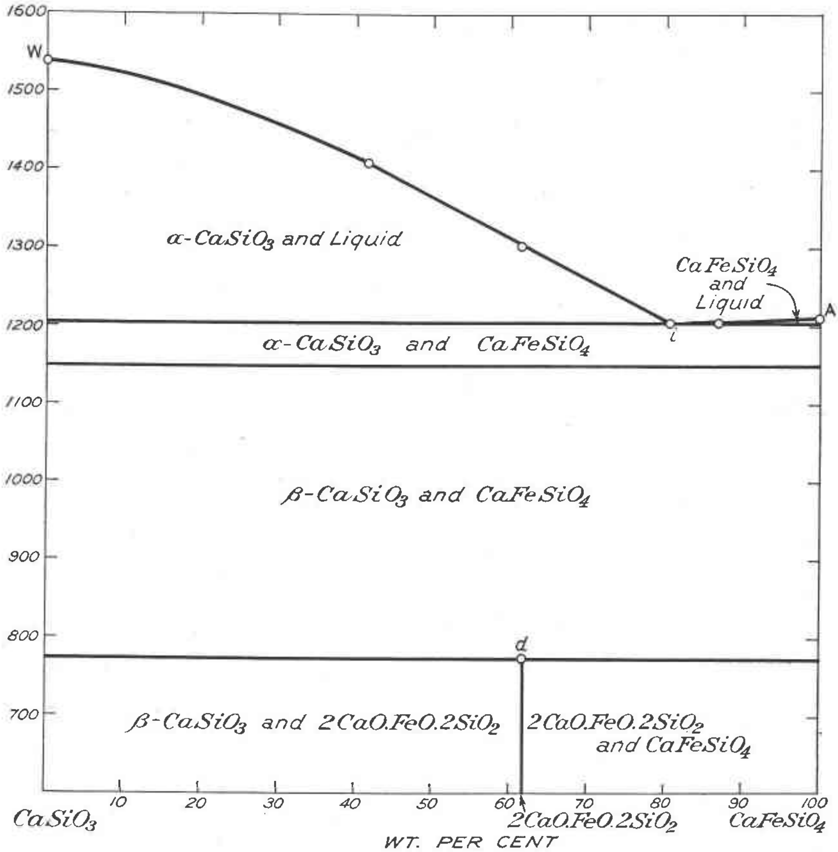

FIG. 12. Equilibrium diagram of the binary system $CaSiO_3$–$CaFeSiO_4$ showing stability relations of the melilite, Fe-akermanite. (Diagram of Bowen, Schairer and Posnjak.)

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[14] See ref. 2*b*, pp. 211 and 276.

Recently, Osborn and Schairer[15] observed by heating pure artificial akermanite crystals that they remain homogeneous above 1325°C., but at temperatures below 1325°C., very small euhedral crystals (not positively identified) grow within the akermanite crystals. Investigation of the stability relations of akermanite and related compositions is continuing.

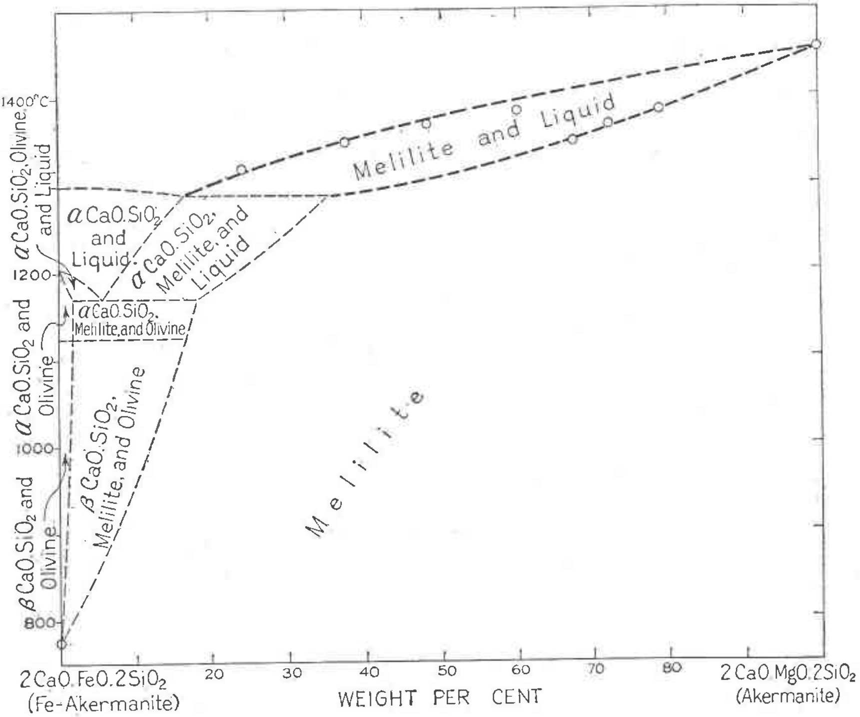

FIG. 13. Preliminary equilibrium diagram of the join Fe-akermanite-akermanite; a portion of the join $CaSiO_3$–MgO–FeO in the quaternary system CaO–MgO–FeO–SiO_2. (Unpublished diagram of Schairer and Osborn.)

As a part of the study of the quaternary system CaO–MgO–FeO–SiO_2 now in progress, Schairer and Osborn[16] have obtained some data for the join $CaSiO_3$–MgO–FeO. The line akermanite–Fe-akermanite

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[15] Osborn, E. F., and Schairer, J. F., The ternary system pseudowollastonite–akermanite–gehlenite: *Am. Jour. Sci.*, **239**, 715–763 (1941); see page 718.

[16] These preliminary data were presented by J. F. Schairer and E. F. Osborn at the 44th Annual Meeting of the American Ceramic Society April 22, 1942, at Cincinnati, Ohio, in order to make the information immediately available while progress on the investigation was temporarily interrupted by other work.

lies in this join. The preliminary data for this line, which have not yet been published, are reproduced here as Figs. 13 and 14, with the kind permission of Dr. E. F. Osborn.

The complex crystallization relations in the system $CaSiO_3$–akermanite–gehlenite, which combines simple melilites and a pyroxenoid are given by Osborn and Schairer.[17] There is no ternary eutectic. The lowest temperature at which liquid is present is at the ternary minimum (1302°C.) on the boundary curve between the fields of melilite and α–$CaSiO_3$. It is shown that zoned solid solution crystals possessing one or more reversals in the direction of zoning (oscillatory zoning) may be produced by normal processes of crystallization with continuously decreasing temperature.

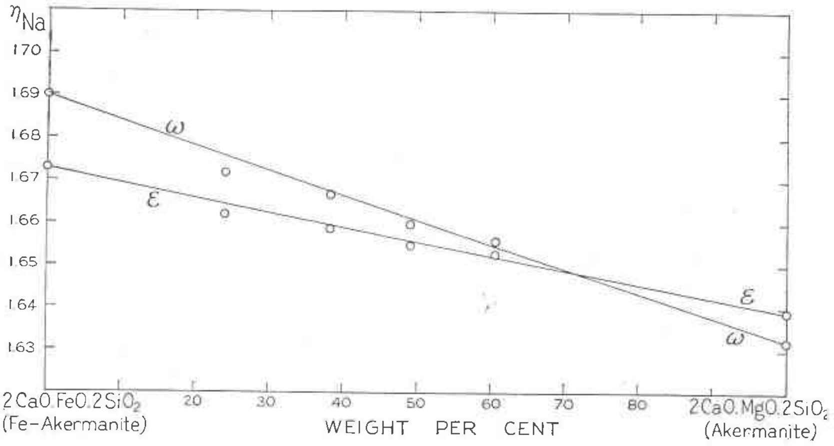

FIG. 14. Diagram showing indices of refraction of artificial melilites lying between Fe-akermanite and akermanite in chemical composition. (Unpublished diagram of Schairer and Osborn.)

CONCLUDING REMARKS

The foregoing brief discussion is perhaps sufficient to indicate that substantial progress has been made on determining the exact chemical compositions and range of compositions and the temperature stability relations of the various rock-forming olivines, pyroxenes (and related

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[17] Osborn, E. F., and Schairer, J. F., The ternary system pseudowollastonite–akermanite–gehlenite: *Am. Jour. Sci.*, **239**, 715–763 (1941).

pyroxenoids), and melilites. Some progress has been made on determination of the mutual melting relations of these groups of minerals and of these minerals with other rock-forming species. More progress on both aspects of the problem may be expected from studies of four quaternary systems now in progress: $CaO–FeO–Al_2O_3–SiO_2$, $CaO–MgO–Al_2O_3–SiO_2$ and $CaO–MgO–FeO–SiO_2$ at the Geophysical Laboratory, and $CaO–Na_2O–Al_2O_3–SiO_2$ by Bowen and his students at the University of Chicago.