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nepheline-anorthite-silica; see Schairer, 1957, p. 232, Fig. 35). In $Jd_{95}An_5$ the crystalline assemblage nepheline+plagioclase began to melt at 1048° ±5°C and the nepheline liquidus was at 1153° ±5°C. In $Jd_{85}An_{15}$, $Jd_{75}An_5$, and $Jd_{65}An_{35}$, respectively, nepheline+plagioclase began to melt at 1058°, 1073°, and 1085°C, the temperature shift being in response to the changing compositions of plagioclase. The plagioclase liquidus temperatures for these compositions were 1268°, 1333°, and 1378°C; nepheline appeared as a second solid phase at 1168°, 1197°, and 1213°C.

Experiments on the liquidus and in the subsolidus region in the range 10–50 kb have been started for all of the compositions prepared at 1 atm. It is hoped that an understanding of the influence of anorthite and forsterite on the behavior of jadeite at high pressure will be gained from these experiments. Combinations of anorthite, forsterite, and jadeite will clarify the roles of anorthite, calcium Tschermak's molecule, and diopside in the pressure-temperature stabilization of omphacite.

Diopside Solid Solutions in the System Diopside-Anorthite-Albite at 1 Atm and at High Pressures

I. Kushiro and J. F. Schairer

The liquidus relations in the system diopside-anorthite-albite were studied by Bowen (1915) at 1 atm for an understanding of the crystallization behavior of basaltic and dioritic magmas. Bowen (1928) described this system as the simplest example of a ternary system with a binary series of solid solutions. Osborn (1942) found, however, that the join diopside-anorthite is not binary and showed that diopside crystallizing from this join is not pure diopside but a solid solution containing some alumina. This result was confirmed by Hytönen and Schairer (*Year Book 60*, pp. 125–141) and Clark, Schairer, and de Neufville (*Year Book 61*, pp. 59–68). Schairer and Yoder (1960) also found that the join diopside-albite is not binary and showed that the feldspar crystallizing from this join is not pure albite but is a solid solution containing a small amount of the anorthite component and that the diopside is also a solid solution. These results suggest that the system diopside-anorthite-albite is not ternary and that the diopside crystallizing within this system is not pure diopside but a solid solution. The join diopside-plagioclase ($An_{50}Ab_{50}$ wt %) has been studied carefully to ascertain and define the nature of the diopside solid solution. Four compositions were selected along this join: (1) $Di_{70}An_{15}Ab_{15}$, (2) $Di_{50}An_{25}Ab_{25}$, (3) $Di_{42}An_{29}Ab_{29}$ and (4) $Di_{40}An_{30}Ab_{30}$ (wt %). Starting materials were glasses crystallized at temperatures between 1050° and 1175°C for 10 to 22 days.

The liquidus temperatures are 1318°, 1268°, 1237°, and 1233°C for compositions 1, 2, 3, and 4, respectively. Diopside solid solution is the liquidus phase for compositions 1, 2, and 3, and both diopside solid solution and plagioclase are the liquidus phases for composition 4. Composition 4 is, therefore, at the liquidus boundary between diospide solid solution and plagioclase. These liquidus results are nearly the same as those obtained by Bowen (1915); the temperatures at which diopside solid solution and plagioclase began to crystallize simultaneously, however, are 1251°, 1246°, 1237°, and 1233°C for compositions 1, 2, 3, and 4, respectively. Since the uncertainties of these temperatures are ±3°, these differences are significant. If diopside is of pure $CaMgSi_2O_6$ composition, diopside should be joined by plagioclase at the same temperature for all of these mixtures. The present results indicate, therefore, that diopside crystallizing in this system is not pure $CaMgSi_2O_6$ but a solid solution.

Determination of the temperature of beginning of melting was not easy because of the difficulty of detecting a small amount of glass in the fine-grained products. In the present experiments, the temperature of beginning of melting has been estimated by whether the products are loose powder or fritted. If the products are barely fritted or fritted, the temperature of the run is considered to be above the beginning of melting. It is noted that temperatures estimated by this method could be slightly different from the temperature of beginning of melting. The glasses for these experiments were crystallized at 1080°C, a little below the beginning of melting, for 7 to 15 days. The temperatures of "beginning of melting" thus estimated are 1103°, 1115°, 1140°, and 1145°C for mixtures 1, 2, 3, and 4, respectively. They are considerably lower than 1200°C, the temperature of beginning of melting given by Bowen (1915) for the composition $Di_{50}(An_1Ab_1)_{50}$ (mole %), which lies very close to the present join. The temperature of "beginning of melting" increases systematically from composition 1 to composition 4. This evidence also indicates that diopside crystallizing in this system is a solid solution whose composition is off the plane diopside-anorthite-albite. The composition of liquids formed at temperatures at or near the "beginning of melting" (1100°–1150°C) should be very rich in albite, on the basis of the liquidus diagram of Bowen (1915). As suggested below, however, the liquid may be enriched in silica and off the plane diopside-anorthite-albite.

The unit-cell dimensions of diopside solid solutions crystallized from the mixtures $Di_{70}An_{15}Ab_{15}$ and $Di_{50}An_{25}Ab_{25}$ (wt %) have been determined to ascertain the nature of the solid solution. Least-squares refinement of the data from the powder X-ray diffraction patterns was carried out on the basis of $C2/c$ symmetry, with a program for the IBM 7094 digital computer by Burnham (*Year Book 61*, pp. 132–135). The reflections measured against the internal silicon standard were $\bar{2}23$, 150, 510, $\bar{4}02$, 041, $\bar{4}21$, $\bar{3}31$, 330, 311, 221, 002, $\bar{1}31$, $\bar{3}11$, 310, $\bar{2}21$, 220, and 021. The results are shown in Table 16, with the unit-cell dimensions of pure diopside determined by Clark, Schairer, and de Neufville (*Year Book 61*, pp. 59–68) and diopsides crystallized at high pressures from the mixtures $Di_{70}An_{15}Ab_{15}$ and $Di_{50}An_{25}Ab_{25}$. As

TABLE 16. Unit-Cell Dimensions of Diopside Solid Solutions Crystallized in the System Diopside-Anorthite-Albite at 1 Atm and at High Pressures

		a, Å	b, Å	c, Å	β, deg.	V, Å^3
	Pure diopside (Clark, Schairer, and de Neufville, *Year Book 61*)	9.745 ±0.001	8.925 ±0.001	5.248 ±0.001	105.87 ±0.01	439.08 ±0.07
a	$Di_{70}An_{15}Ab_{15}$ 1 atm, 1250°C, 3 days	9.741 ±0.002	8.918 ±0.001	5.253 ±0.001	105.98 ±0.02	438.72 ±0.19
b	$Di_{70}An_{15}Ab_{15}$ 1 atm, 1080°C, 8 days	9.722 ±0.003	8.905 ±0.002	5.254 ±0.003	106.12 ±0.03	436.96 ±0.38
c	$Di_{50}An_{25}Ab_{25}$ 1 atm, 1235°C, 7 days	9.738 ±0.002	8.914 ±0.001	5.253 ±0.001	106.06 ±0.02	438.19 ±0.20
d	$Di_{50}An_{25}Ab_{25}$ 1 atm, 1080°C, 8 days	9.715 ±0.004	8.884 ±0.003	5.265 ±0.003	106.23 ±0.03	436.31 ±0.38
e	$Di_{70}An_{15}Ab_{15}$ 25 kb, 1350°C, 2 hours	9.672 ±0.005	8.855 ±0.004	5.263 ±0.004	106.28 ±0.06	432.67 ±0.53
f	$Di_{50}An_{25}Ab_{25}$ 30 kb, 1350°C, 2 hours	9.622 ±0.007	8.787 ±0.004	5.267 ±0.004	106.52 ±0.06	426.93 ±0.55

shown in the table, the unit-cell dimensions of the diopsides crystallized at 1 atm are significantly different from that of pure diopside; *a, b,* and unit-cell volume *V* of these four diopsides are smaller and *c* and β are slightly larger than those of pure diopside. Particularly, the diopsides crystallized at 1080°C for 8 days show greater differences of unit-cell parameters from those of pure diopside. The diopsides crystallized at 1240°C from the mixture $Di_{70}An_{15}Ab_{15}$ and at 1235°C from the mixture $Di_{50}An_{25}Ab_{25}$ coexisted only with liquid, whereas those crystallized at a subsolidus temperature of 1080°C coexisted with plagioclase. The variation in the unit-cell parameters is similar to those observed for the clinopyroxenes formed in the joins diopside-$CaAl_2SiO_6$ and diopside-anorthite at high pressures (Clark, Schairer, and de Neufville, *Year Book 61,* pp. 59–68; Kushiro, 1969), suggesting that the differences between the unit-cell dimensions of these diopside solid solutions and those of pure diopside are mainly due to the presence of Ca-Tschermak's component. However, the $MgSiO_3$ component would also be present in these clinopyroxenes, since the diopside solid solutions in the join diopside-anorthite contain measurable amounts of excess $MgSiO_3$ at about 1150°C, as shown by Hytönen and Schairer (*Year Book 60,* pp. 125–141). Jadeite solid solution is also possible but would not be significant at 1 atm. On the assumption that the differences in the unit-cell dimensions of these diopsides are essentially due to the presence of the Ca-Tschermak's component, the contents of the Ca-Tschermak's component can be estimated roughly from the relations between the unit-cell parameters and compositions of the clinopyroxenes crystallized from the join diopside-$CaAl_2SiO_6$ (Clark, Schairer, and de Neufville, *Year Book 61,* pp. 59–68). The contents thus estimated are about 3, 10, 5, and 13 wt % $CaAl_2SiO_6$ for diopsides *a, b, c,* and *d* in Table 16, respectively. The content of $CaAl_2SiO_6$ is larger for the clinopyroxene crystallized from the more plagioclase-rich mixture and also at lower temperatures. If the relation between composition and *d* values of the (510) and (150) planes of diopside solid solutions given by Hytönen and Schairer is used, the present diopside solid solutions contain about 3 to 7% Al_2O_3 and up to about 8% excess $MgSiO_3$.

The presence of the $CaAl_2SiO_6$ and excess $MgSiO_3$ components (and possibly a very small amount of $NaAlSi_2O_6$) in diopside solid solutions crystallizing from the present system indicates that the liquids coexisting with the diopside solid solutions must be off the plane diopside-anorthite-albite and contain excess silica and $CaSiO_3$ components, and that free silica must exist at temperatures below the solidus at 1 atm. No reflections of silica minerals were detected, however, in the powder X-ray diffraction patterns of the mixtures crystallized at subsolidus temperatures. This could be explained by a diopside solid solution containing a small amount of excess silica, suggested by Schairer and Kushiro (*Year Book 63,* pp. 130–132), but the amount of excess silica would be very small at temperatures below 1300°C, as they suggested. Even if the silica mineral is present in the products, it may be in too small amount to be detected by X ray. Under the microscope, crystals formed at subsolidus temperatures are very fine grained and the presence of the silica mineral was not confirmed.

The subsolidus phase relations in the join diopside-plagioclase ($An_{50}Ab_{50}$ wt %) have been studied in the pressure range 15 to 31 kb at 1150° and 1350°C with the solid-media, piston-cylinder apparatus. The starting materials were glass and glass crystallized at 1 atm. At 1150°C, only glass was used because the crystalline mixtures did not react at this temperature even in long runs. At 1350°C, it was shown that the results obtained from glass are identical with those obtained from the crystalline mixtures. The subsolidus phase relations at

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1150°C are shown in Fig. 17. As shown in the figure, the range of the clinopyroxene (diopside solid solution) + quartz assemblage expands to about 30 wt % $CaAl_2Si_2O_8 + NaAlSi_3O_8$ at 20 kb and 1150°C, indicating that the clinopyroxene contains about 25 wt % $CaAl_2SiO_6$ and $NaAlSi_2O_6$ components at 20 kb and 1150°C. The range of the solid solution may attain its maximum at about 25 kb and 1150°C. More detailed subsolidus phase relations are described elsewhere (Kushiro, 1969).

The unit-cell dimensions of diopside solid solutions crystallized from the mixtures $Di_{70}An_{15}Ab_{15}$ and $Di_{50}An_{25}Ab_{25}$ at 25 and 30 kb at a subsolidus temperature of 1350°C are shown in Table 16. The parameters *a*, *b*, and *V* of these clinopyroxenes are much smaller than those of pure diopside and the diopside solid solutions crystallized at 1 atm. These high-pressure diopside solid solutions, which coexist only with quartz, must contain jadeite as well as Ca-Tschermak's component.

The results of the present experiments indicate that diopside or augite crystallizing from silica-saturated basaltic magmas at 1 atm would contain small amounts (up to several weight percent) of $CaAl_2SiO_6$ and excess $MgSiO_3$ components. Those crystallizing from silica-undersaturated basaltic magmas would contain more $CaAl_2SiO_6$ and less $MgSiO_3$ components, on the basis of the results of Hytönen and Schairer (*Year Book 60*, pp. 125–141) and de Neufville and Schairer (*Year Book 61*, pp. 56–59). Present results also indicate that the plane

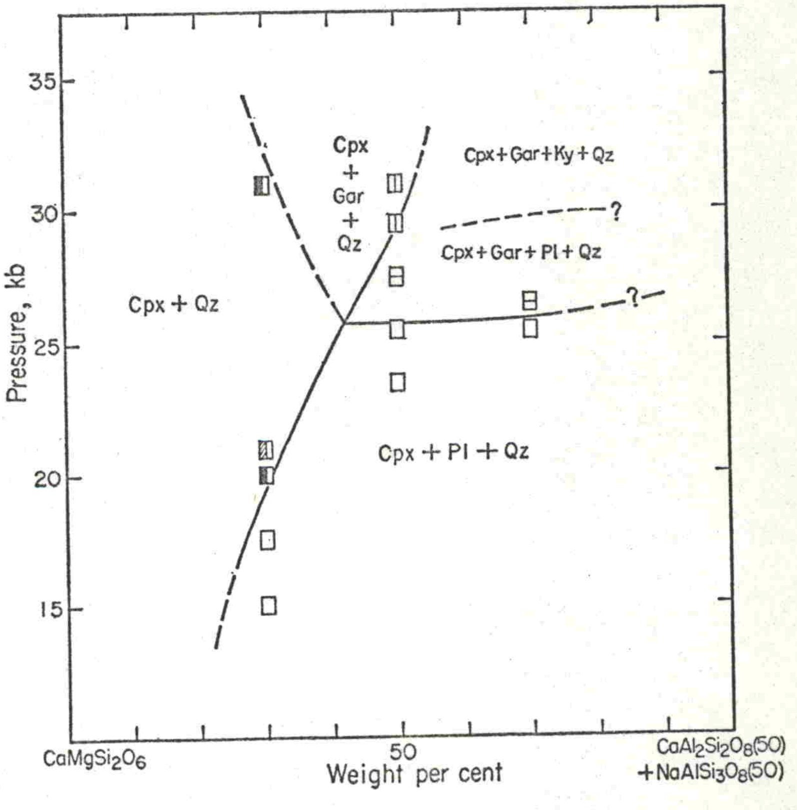

Fig. 17. Subsolidus phase-equilibrium relations on the join diopside-plagioclase ($An_{50}Ab_{50}$ wt %) at 1150°C. Abbreviations: Cpx, clinopyroxene (diopside solid solution); Gar, garnet; Ky, kyanite; Pl, plagioclase; Qz, quartz.

diopside-anorthite-albite is not ternary and is not a thermal barrier between silica-saturated and silica-undersaturated compositions at 1 atm nor at high pressures.

STABILITY FIELD OF IRON-FREE PIGEONITE IN THE SYSTEM $MgSiO_3$-$CaMgSi_2O_6$

I. Kushiro and H. S. Yoder, Jr.

Iron-free "pigeonite" has been synthesized on the join diopside-enstatite at 20 kb, and its stability field at 20 kb has been outlined (Kushiro, *Year Book 67*, pp. 80–83; 1969). Since pigeonite occurs in igneous rocks crystallized on or near the surface of the earth's crust, it is important to understand the stability field of pigeonite at lower pressures. Therefore, additional experiments have been undertaken to determine the stability field of iron-free "pigeonite" at lower pressures. The starting materials used in the present experiments were several different crystalline mixtures and glass of the composition $Di_{20}En_{80}$ (wt %) whose Ca/(Ca+Mg) atomic ratio is very close to the $Ca/(Ca+Mg+Fe^{2+})$ ratios of natural pigeonites. In the previous experiments a mixture of this composition was crystallized to a single-phase pigeonitic clinopyroxene at 1630°C and 20 kb. In the present experiments a solid-media, piston-cylinder apparatus was used for the runs at pressures higher than 10.5 kb and a gas-media, internally heated apparatus for those at and below 10 kb. The gas-media apparatus is considered to generate hydrostatic pressure, whereas the piston-cylinder apparatus has some shearing effects.

The experimental results are shown in the pressure-temperature diagram (Fig. 18). The boundary between the field of a single-phase pigeonitic clinopyroxene and that of orthoenstatite solid solution +pigeonitic clinopyroxene for the composition $Di_{20}En_{80}$ is about 1540°C at 20 kb, about 1480°C at 15 kb, and about 1430°C at 12.5 kb. The lower stability limit of the pigeonitic clinopyroxene, which is more important, may be a little below 1480°C at 20 kb, about 1450°C at 17.5 kb, and a little above 1400°C at 12.5 kb. At 17.5 and 20 kb, the amount or orthoenstatite solid solution relative to that of pigeonitic clinopyroxene in the $Pig+En_{ss}$ field decreases with increasing temperature. These relations are interpreted in a schematic diagram of the enstatite-rich part of the join diopside-enstatite at 17.5 kb (Fig. 19).

At and below 10 kb, three or four different starting materials were used in a single run. Many of the results are different for different starting material, and they are described below in more detail. At 10 kb, clinoenstatite and diopside solid solutions were not reacted but converted to a mixture of orthoenstatite and diopside solid solutions, held for 4 hours at 1350° and 1375°C and for 2 hours at 1400° and 1425°C. Orthoenstatite solid solution grew from a single-phase pigeonitic clinopyroxene, and glass was crystallized to orthoenstatite and diopside solid solutions at 1350° and 1375°C. The results indicate that pigeonitic clinopyroxene is not stable but orthoenstatite and diopside solid solutions are stable at 1350° and 1375°C at 10 kb. At 1450°C, neither the mixtures of clinoenstatite and diopside solid solutions nor orthoenstatite and diopside solid solutions were reacted, and mixtures of orthoenstatite and diopside solid solutions were obtained in the 4-hour run; however, glass was crystallized into a single-phase pigeonitic clinopyroxene under the same conditions. The temperatures at least above 1400°C would be in the stability field of pigeonitic clinopyroxene at 10 kb if the stability field determined at pressures higher than 12.5 kb can be extrapolated to 10 kb. Therefore, three runs made on the crystalline mixtures at 1400°, 1425°, and 1450°C do not agree with the phase relations determined at higher pressures, although the runs made on glass at 1350°, 1375°, and 1450°C are consistent with those at higher pressure. In the

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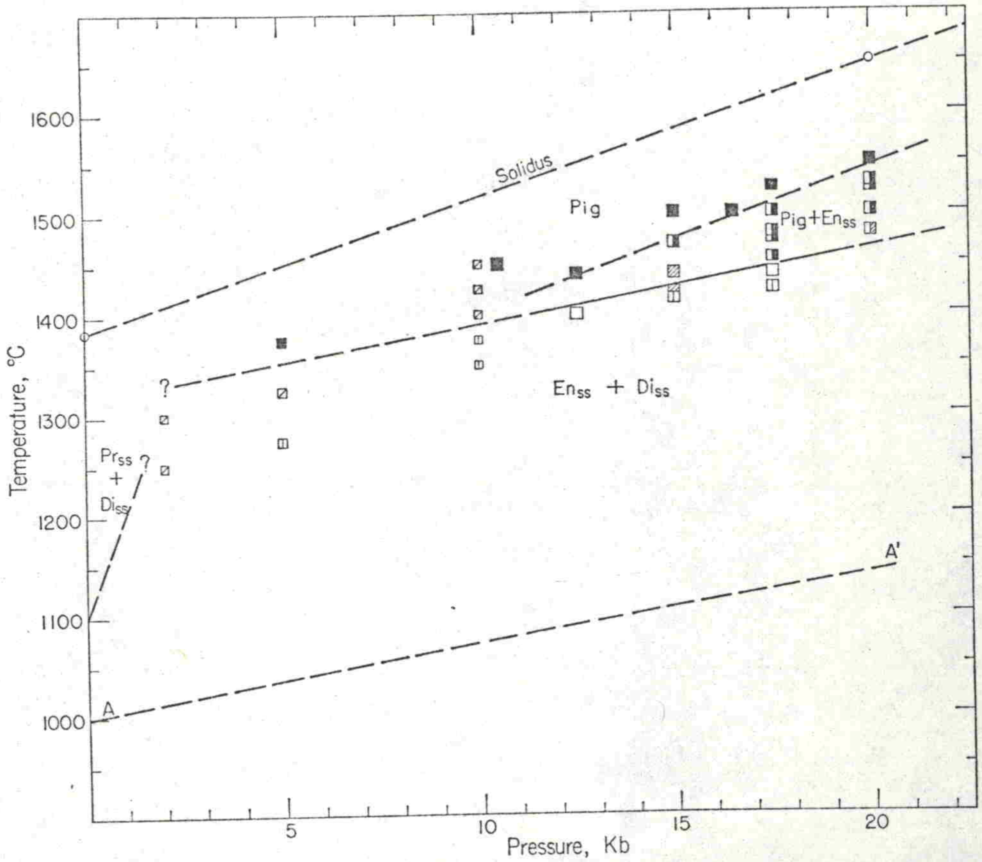


Fig. 18. Pressure-temperature plane for composition $Di_{20}En_{80}$ (wt %). Abbreviations: Pig, pigeonitic clinopyroxene; Di_{ss}, diopside solid solution; En_{ss}, orthoenstatite solid solution; *L*, liquid; Pr_{ss}, protoenstatite solid solution. Symbols: solid square, Pig formed from En_{ss} + Di_{ss} or clinoenstatite$_{ss}$ + Di_{ss}; half-solid square, Pig + En_{ss} formed from En_{ss} + Di_{ss} or clinoenstatite$_{ss}$ + Di_{ss}; shaded square, Pig unchanged; half-shaded square, Pig + En_{ss} formed from Pig; square with vertical line, En_{ss} + Di_{ss} formed from clinoenstatite$_{ss}$ + Di_{ss}; open square, En_{ss} + Di_{ss} formed from Pig; square with diagonal line, run that is not satisfactorily interpreted (see text). Dashed line *A–A'* is the lower stability limit of pigeonite ($Wo_{7.6}En_{40.7}$-$Fs_{51.7}$ mole %) determined by Brown (*Year Book 66,* pp. 347–353).

solid-media apparatus, orthoenstatite and diopside solid solutions were reacted to form a single-phase pigeonitic clinopyroxene at 10.5 kb and 1450°C in the 3-hour run, whereas they were not reacted at 10 kb and 1450°C in the 4-hour run made with the gas-media apparatus. The discrepancy between the results obtained by the gas-media and the solid-media apparatus suggests that the nonhydrostatic pressure in the solid-media apparatus stabilizes the pigeonitic clinopyroxene in wider *P-T* ranges or the reaction rate is greater in the solid-media apparatus than in the gas-media apparatus.

At 5 kb and 1375°C, a mixture of orthoenstatite and diopside solid solutions was reacted to form orthoenstatite solid solution and pigeonitic clinopyroxene, and glass crystallized to pigeonitic clinopyroxene in the 6-hour run. These results indicate that the composition $Di_{20}En_{80}$ is in the field of pigeonitic clinopyroxene or of pigeonitic clinopyroxene+orthoenstatite solid solution at 1375°C. At 1325°C, glass was crystallized to pigeonitic clinopyroxene, and

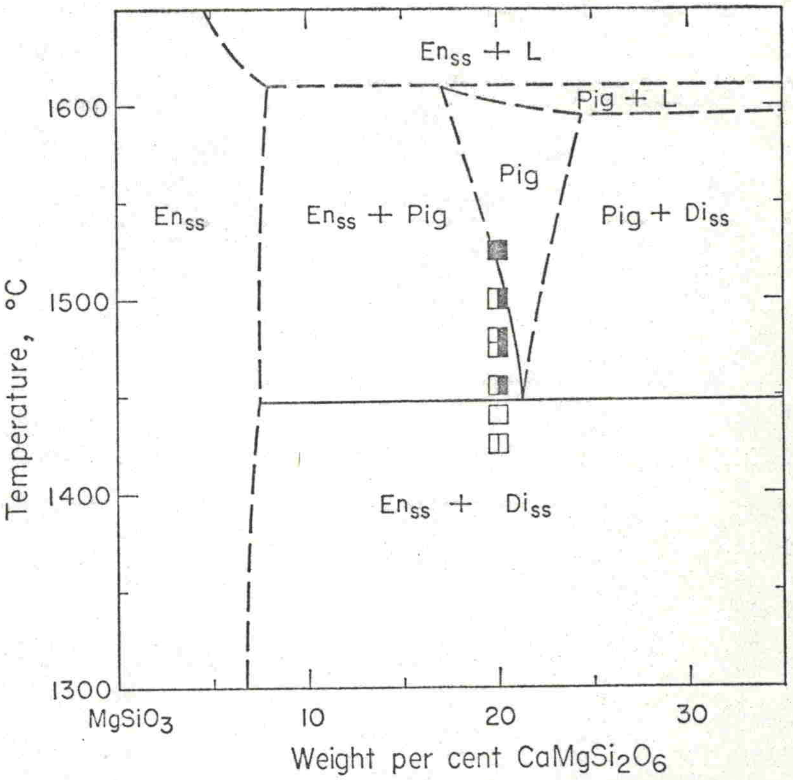


Fig. 19. Schematic diagram showing the phase relations for composition $Di_{20}En_{80}$ (wt %) at 17.5 kb. Abbreviations as in Fig. 18.

pigeonitic clinopyroxene was unchanged; however, a mixture of clinoenstatite and diopside solid solutions was converted to a mixture of orthoenstatite and diopside solid solutions in the 24-hour run. These results are ambiguous, presumably because of the different starting materials. The results obtained from glass and pigeonitic clinopyroxene suggest the stability of pigeonitic clinopyroxene at 1325°C, but the result obtained from the mixture of clinoenstatite and diopside solid solutions fails to confirm this possibility. This same problem is encountered at 10 kb and 1450°C. At 2 kb, the results obtained at 1300° and 1250°C are nearly the same as those obtained at 5 kb and 1325°C. These results strongly suggest that the reaction rates, particularly those of the homogenization of two pyroxenes and the breakdown of a single pyroxene, are very slow at relatively low pressures and temperatures.

Although there are problems with reaction rates and a discrepancy in the results between the solid-media and gas-media apparatus, the present experiments indicate that the stability field of pigeonitic clinopyroxene exists near the composition $Di_{20}En_{80}$ in the pressure range at least between 20 and 5 kb and near the solidus temperatures. It is likely that the stability field of pigeonitic clinopyroxene extends to lower pressures and possibly to 1 atm. At pressures lower than 2 kb, however, the field of protoenstatite solid solution may appear even near the composition $Di_{20}En_{80}$ and the phase relations may be more complicated. In the iron-bearing system the stability field of pigeonite will be more easily determined because of a more favorable reaction rate. For the compositions $Wo_{7.6}En_{40.7}Fs_{51.7}$ (mole %), Brown (*Year Book 66*, pp. 347–353) determined the lower stability limit of pigeonite in the pressure range 1 atm to 20 kb, shown for comparison in Fig. 18. Comparison of the present results and those of Brown suggests that the lower stability limit of pigeonite drops about 300°C from the iron-free composition to the composition having the ratio $Fe/(Mg+Fe)=0.56$ in the pressure range from near 1 atm to 20 kb. It should be mentioned that temperatures of basaltic and andesitic magmas (1250°–1100°C) are between the lower stability limit of pigeonite estimated in the iron-free system and that in the ratio $Fe/(Mg+Fe)=0.56$ at pressures lower than 5 kb. The evidence that the natural pigeonites have $Fe^{2+}/(Mg+Fe^{2+})$ ratios larger than 0.3 can be explained by the magma temperatures crossing the lower stability limit of pigeonite at the $Fe^{2+}/(Mg+Fe^{2+})$ ratio near 0.3, as first suggested by Hess (1941).

STABILITY OF IRON-RICH ORTHOPYROXENE

Douglas Smith

Orthopyroxene occurs in most rocks instead of the compositionally equivalent assemblage of olivine+quartz. In rocks with high Fe/Mg ratios, however, the assemblage olivine+quartz is more common than orthopyroxene. The iron end member of the orthopyroxene series, ferrosilite, was shown to be stable at high pressures relative to fayalite and quartz by Lindsley, MacGregor, and Davis (*Year Book 63*, pp. 174–176) and by Akimoto, Fujisawa, and Katsura (1964). The purposes of this investigation were (1) to establish limits of orthopyroxene stability as a function of pressure and composition for possible use as a barometer for rocks of crustal origin and (2) to provide a basis for subsolidus investigations in the iron-rich portion of the pyroxene quadrilateral. The only previous comprehensive investigation of the relative stabilities of orthopyroxene and olivine in the system FeO-MgO-SiO_2 was made by Bowen and Schairer (1935); experimental limitations at that time precluded studies with iron-rich synthetic phases at temperatures much below 1000°C.

The relative stabilities of these minerals were investigated over a range of pressures and temperatures. Either orthopyroxene or olivine+silica was used as a starting material for each experiment. Equimolar mixtures of silica and olivine of the desired compositions were made from oxide mixes in evacuated silica glass tubes and in controlled gas mixtures. Silica was present as glass, quartz, and tridymite in various starting materials. Orthopyroxenes were synthesized at 20 kb from mixtures of olivine+silica in a large volume, piston-cylinder apparatus. All hydrothermal runs were conducted in the presence of excess silica, added to saturate the fluid phase.

The experimental results shown in Fig. 20 clearly establish that the most iron-rich orthopyroxene stable at temperatures of 800° to 950°C and pressures of 0.3 to 1 kb is more magnesian than $En_{25}Fs_{75}$. The results suggest that the actual composition of the most iron-rich orthopyroxene stable under these conditions is close to $En_{30}Fs_{70}$. In runs at 1000°C in evacuated silica glass tubes, orthopyroxenes of compositions $En_{30}Fs_{70}$ and $En_{25}Fs_{75}$ broke down to yield orthopyroxene, olivine, silica, and minor multiply twinned clinopyroxene in the quench product. The clinopyroxene presumably inverted from a proto form (Boyd and Schairer, 1964, p. 297).

In hydrothermal experiments at 1 kb and 800°C, olivine ($Fo_{20}Fa_{80}$) reacted with silica to form some orthopyroxene, whereas orthopyroxene ($En_{20}Fs_{80}$) partially broke down to olivine and silica. These results establish a point in the three-phase field orthopyroxene-olivine-silica in the system FeO-MgO-SiO_2. The hydrothermal experiments at 800°C in which olivine reacted with silica lasted about 80 days. In contrast, the hydrothermal experiments at 900° and 950°C lasted only a few days, and olivine as magnesian as $Fo_{35}Fa_{65}$ failed to react

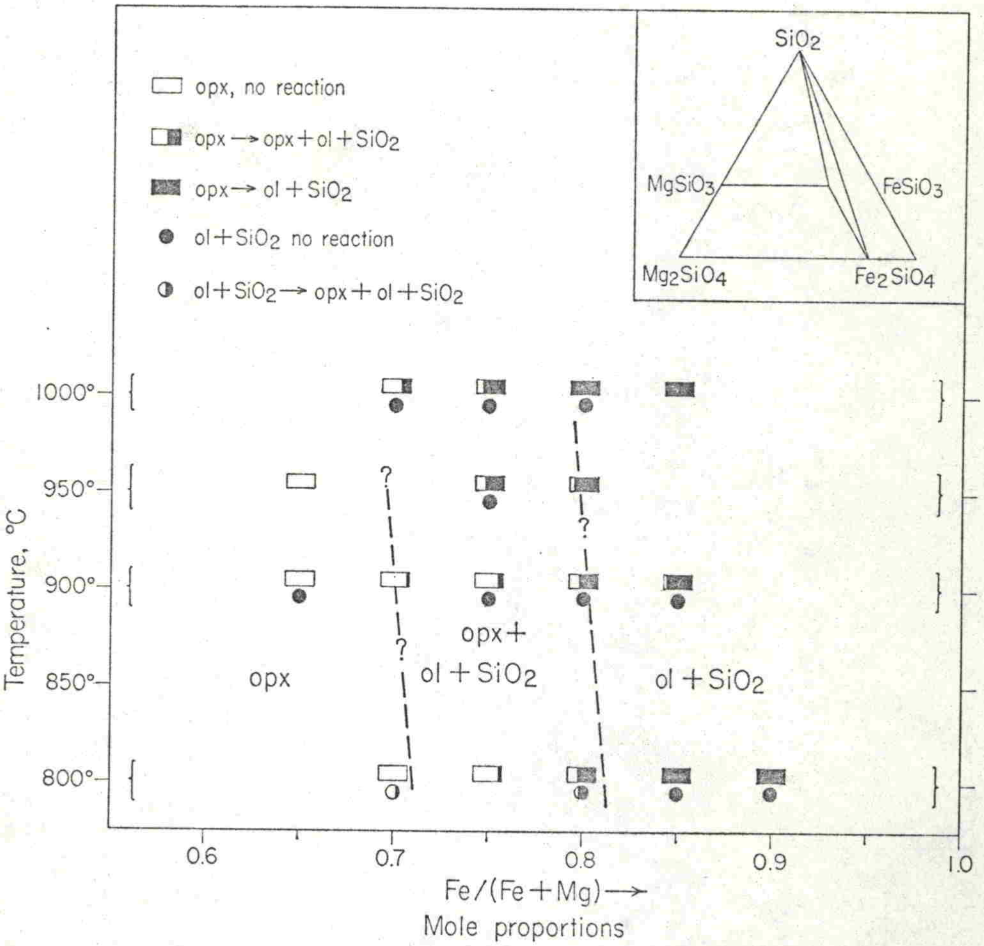
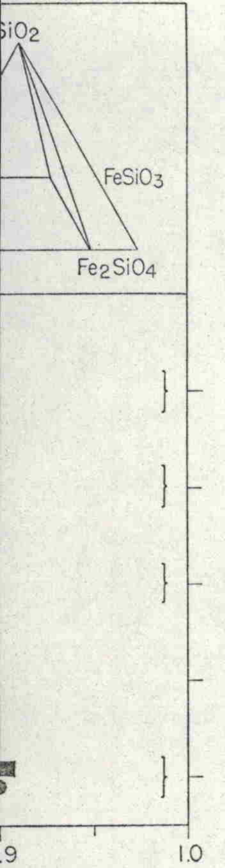


Fig. 20. Experimental results on orthopyroxene and on olivine plus quartz at low pressures. The brackets by the temperature axis of the figure indicate that the plotted experiments were conducted at 800°, 900°, 950°, and 1000°C, *not* at temperatures slightly above and below these values. Hydrothermal experiments at 800°C were conducted at 1 kb, and those at 900° and 950°C were conducted at 0.3 kb. Experiments at 1000°C were performed in evacuated silica-glass tubes. The amount of shading is approximately proportional to the amount of olivine + silica in the reaction products. The quartz-tridymite inversion and the inversion of orthopyroxene to a proto form have been ignored in drawing this diagram.

with silica during these time periods. Likewise, olivine and silica failed to react in evacuated tube experiments at 1000°C. Medaris (1969) has studied the partition of Fe and Mg between coexisting orthopyroxene and olivine at temperatures from 700° to 900°C. The Fe/(Fe+Mg) ratios of the two phases coexisting with silica should lie on the boundaries of the three-phase field as drawn in Fig. 20. The studies of Medaris show that the field (Fig. 20) should extend over an interval of Fe/(Fe+Mg) of about 0.1. Further experiments are being carried out to define more precisely the position of the three-phase field.

Experiments at high pressure at 900°C (Fig. 21) bracket at least part of the three-phase field orthopyroxene-olivine-silica within the pressure interval 10 to 11 kb for a bulk composition with Fe/(Fe+Mg) = 0.9 and within the interval 12 to 13 kb for Fe/(Fe+Mg) = 0.95. At



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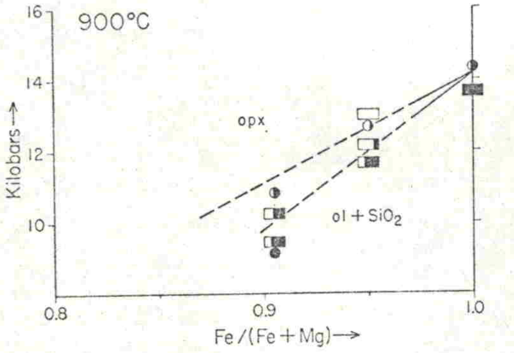

Fig. 21. Experimental results on orthopyroxene and on olivine + quartz at 900°C and high pressures. Symbols are the same as in Fig. 20.

900°C, pure orthorhombic ferrosilite was found to be stable above 14.5 kb. These experiments were conducted in a solid-media piston-cylinder apparatus by the modified piston-out procedure of Richardson, Bell, and Gilbert (1968, p. 517), and nominal, uncorrected pressures are reported here.

The experimental results establish that the most iron-rich orthopyroxene stable from 800° to 950°C at pressures lower than 1 kb is somewhat more magnesian than $En_{25}Fs_{75}$. This value contrasts with the limit of about $En_{15}Fs_{85}$ suggested by Bowen and Schairer (1935, Fig. 8). The present results also show that with increasing pressure, orthopyroxenes of progressively greater iron enrichment become stable, pure ferrosilite being stable at 900°C above 14.5 kb. Natural orthopyroxenes more iron-rich than $En_{25}Fs_{75}$ have been described (e.g., Henry, 1935; Kuno, 1954). Some such orthopyroxenes may have been stabilized by the presence of minor elements like calcium and manganese. Some may have formed at low pressure but at temperatures considerably below 800°C in a possible low-temperature expansion of the orthopyroxene field. Others may have been stabilized by high pressure. For instance, Wheeler (1965) described an olivine adamellite with complex intergrowths of calcic pyroxene, orthopyroxene, fayalitic olivine, and quartz in which the olivine and quartz apparently formed by the breakdown of orthopyroxene. Lindsley and Munoz (1969, p. 319) suggested that the orthopyroxene was initially stabilized by pressure. In this and other instances, the presence of high-iron orthopyroxene may serve as a useful geobarometer. At a given temperature and neglecting minor elements, the composition of orthopyroxene in the three-phase assemblage orthopyroxene-olivine-quartz uniquely characterizes the pressure of equilibration. The occurrence of iron-rich orthopyroxene alone may be useful in establishing a minimum pressure of formation if the temperature can be estimated by other means.

STABILITY OF POTASSIC RICHTERITE

*I. Kushiro and A. J. Erlank**

The occurrence of potassic richterite, a member of the alkali amphiboles, in a diopside-phlogopite nodule in the Wesselton kimberlite pipe, South Africa, is described in the preceding section. This discovery suggests that potassic richterite is a possible amphibole in the upper mantle. To examine this possibility, preliminary experiments have been conducted on the stability of potassic richterite at high pressures.

The starting material was a potassic richterite from a leucite lamprophyre from Wolgidee, Australia, collected by B. Mason. Partial analysis (Table 17) shows that it is similar in composition to that described originally by Wade and Prider (1940). The chemical composition of this richterite indicates that its chemical formula is close to $KNaCa(Mg,Fe,Ti)_5Si_8O_{22}(OH)_2$. Mixtures of this richterite and synthetic minerals were also used. The experiments were conducted in solid-media, piston-cylinder apparatus in sealed Pt capsules with water contents varying from 4.7 to 10.5 wt %.

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* Department of Terrestrial Magnetism.