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The reaction pigeonite = diopside$_{ss}$ + enstatite$_{ss}$ at 15 kbar

ELAINE SCHWEITZER[1]

Department of Earth and Space Sciences
State University of New York
Stony Brook, N. Y. 11794

Abstract

On the join enstatite–diopside at 15 kbar, the reaction pigeonite = diopside$_{ss}$ + enstatite$_{ss}$ is in equilibrium at 1465±10° C. The compositions of the three coexisting phases are (mole percent): pigeonite = $Wo_{18.3}En_{81.7}$ (±1.5); enstatite = $Wo_{5.5}En_{94.5}$ (±1.0); diopside = $Wo_{28.5}En_{70.5}$ (±3.5). Experiments were done in a piston cylinder apparatus using trace amounts of water as a flux, and were reversed to establish equilibrium compositions.

Introduction

Relations along the join enstatite (En, $Mg_2Si_2O_6$)–diopside (Di, $CaMgSi_2O_6$) at 15 kbar and above 1400° C have been investigated in order to characterize the reaction En_{ss} + Di_{ss} = Pig (iron-free pigeonite), particularly the temperature and the compositions of the three coexisting phases. A major purpose of the experiments was to provide constraints on thermodynamic solution models of the Di–En system, and also to extend the 15 kbar phase diagram of Lindsley and Dixon (1976).

Throughout this paper three main phases are discussed: enstatite$_{ss}$, diopside$_{ss}$, and pigeonite. Enstatite$_{ss}$(En_{ss}) is used to indicate an orthopyroxene solid solution with a composition of about $Wo_{5-6}En_{95-94}$ (mole percent, except where noted). Diopside solid solution (Di_{ss}) refers to a clinopyroxene with a wollastonite content of approximately Wo_{27}. The term pigeonite (Pig) is used for an iron-free clinopyroxene with composition near $Wo_{18}En_{82}$. Room temperature X-ray diffraction patterns of this pyroxene show a (231) peak at approximately 37.5°2θ (Cu$K\alpha_1$) which is not present in either the En_{ss} or Di_{ss} patterns, and which is diagnostic of the $P2_1/c$ space group of pigeonite.

Two types of reactions were used as reversals in the experiments: pigeonite-forming reactions (Di_{ss} + En_{ss} = Pig) and pigeonite breakdown reactions (Pig = Di_{ss} + En_{ss}). These define the univariant curve Pig = Di_{ss} + En_{ss}, which becomes invariant when constrained to a single pressure. If the *direction* of reaction (*i.e.*, forming or breaking down pigeonite) can be determined, even when the reaction is incomplete, its position relative to the (isobaric) invariant line is determined.

Previous work

Iron-free pigeonite has been, and is, the subject of some controversy in the literature. Kushiro (1964) synthesized a clinopyroxene with an X-ray reflection (231) compatible with the $P2_1/c$ clinoenstatite structure but not with $C2/c$ diopside. On the basis of the X-ray powder diffraction pattern, in particular the (231) peak and the Ca content, Kushiro (1968) called this clinopyroxene an "iron-free pigeonite". At 20 kbar, for anhydrous runs, Kushiro (1968; 1969) suggested a stability field for "cpx" or iron-free pigeonite. Kushiro and Yoder (1970) reported pigeonite breaking down to Di_{ss} + En_{ss} at 1425° C at 15 kbar. These experiments were done using glass starting materials and were mainly synthesis runs, so they may not represent equilibrium results. Based mainly on research of others, Mori and Green (1975) also concluded that pigeonite forms at about 1425° C at 15 kbar. The temperature reported by the above investigators is about 40° lower than that found in the present study.

There is controversy, however, over whether iron-free pigeonite exists as a stable phase at all. Howells and O'Hara (1975) state that the existence of iron-free pigeonite was not confirmed in their experiments at 20 and 30 kbar. Since their experiments used dehydrated gels, were primarily synthesis experiments and were analyzed with optical and X-ray techniques, the system should be considered

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[1] Present Address: Elaine Schweitzer McGee, U.S. Geological Survey, National Center, Mail Stop 951, Reston, Virginia 22092.

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more thoroughly before their conclusions are accepted. Mori and Green (1976) suggested that a Pig–Di$_{ss}$ field, if present at 20 kbar was much smaller than that proposed by Kushiro. Lindsley, Grover, and Davidson (1981) have recently developed a solution model for the Di–En join that reconciles most of these results.

Procedures

Experimental techniques

All experiments used a solid-media piston-cylinder apparatus and a piston-out technique. The temperature was controlled throughout the run by an automatic set point system and was not corrected for pressure effects on the thermocouples, which were Pt, Pt_{90}–Rh_{10} for preliminary runs and W/3%Re–W/25%Re for all phase-equilibrium runs.

Materials used for the runs were synthesized from pure MgO, SiO_2, and $CaCO_3$ (Johnson Mathey Lot S.50068.D; Johnson Mathey Lot S50389B; and Baker Lot 10641, respectively). The MgO was dried for several days at approximately 1100° C, the SiO_2 was dried for about 30 hours at 1100° C, and the $CaCO_3$ was dried for 4 hours at 400° C before using. $CaSiO_3$ was synthesized first from $CaCO_3$ and SiO_2 by heating them in a stepwise fashion to drive off CO_2. Amounts of MgO, SiO_2, and $CaSiO_3$ needed for a composition were calculated, weighed out, and ground under alcohol in an agate mortar for 5–6 hours. Mixes were then prereacted in a platinum foil bucket and heated at approximately 1100° C and 1 atm, for 3–4 days. This prereaction aided in the synthesis of starting materials at high temperatures and pressures; it produced olivine, $CaSiO_3$, various forms of SiO_2, and in some cases small amounts of pyroxene.

The prereacted mixes were ground for 1 hour and then loaded into capsules 0.25 in. (0.64 cm) in diameter and 0.50 in. (1.27 cm) long, for final synthesis of starting phases. Ca-bearing mixes used platinum capsules; these were dried after loading for one-half hour at 900° C. Enstatite mix was loaded into silver capsules with 7.5 wt.% H_2O and approximately 0.1 wt.% excess SiO_2 added to the prereacted mix to permit hydrothermal synthesis. Synthesis runs were made under the conditions shown in Table 1. In some cases it was necessary to regrind and rerun the material to produce a single-phase starting material. Phases synthesized in this manner were used in the final phase-equilibrium runs as single phases (Cpx, $Wo_{20}En_{80}$ and $Wo_{24}En_{76}$) or as a mechanical mixture of $Di_{ss}(Wo_{37.5}En_{62.5})$ + En having the bulk composition $Wo_{20}En_{80}$ or $Wo_{24}En_{76}$.

Platinum capsules used for the phase-equilibrium runs were smaller (0.094 in., 0.24 cm in diameter; 0.150 in., 0.381 cm, long). The most successful procedure for phase-equilibrium experiments consisted of running samples for 1½–3 hours at pressure and temperature, then quenching and examining the sample optically and by X-ray diffraction. If the reaction appeared to be inconclusive, the sample was rerun under the same conditions.

Although the phase-equilibrium experiments were not deliberately hydrothermal, the presence of a small amount of water in the capsules was important to the success of a run. Thoroughly dried samples reacted poorly if at all, and produced products with a very fine grain size. Small amounts of water adsorbed by the sample seemed to aid reaction and increase grain size, a distinct aid in microprobe analysis. If too much water was present, however, appreciable melting occurred, sufficient to bias the composition of the remaining solids. Experiments using starting materials that were not dried after loading into the Pt capsules, allowing the adsorbed moisture to work as a catalyst, were the most successful.

Run products were examined in several ways. Mounts of powder in index oils were examined optically to look for glass or quench crystals. Powder diffraction X-ray patterns were made to identify phases present and to determine approximate changes in composition. If these results were satisfactory, a polished mount of grains in epoxy was prepared for electron microprobe analysis.

X-ray techniques

Powder X-ray analysis of experimental results was used to indicate reaction direction. The defini-

Table 1. Synthesis of starting materials

Composition	T(°C)	P(kb)	t(hrs)	Product
$Wo_{24}En_{76}$	1430-1480	10	2.25	Cpx
$Wo_{20}En_{80}$	1440-1490	10	2 + 3*	Cpx ($Wo_{19} \pm 4$)
$Wo_{37.5}En_{62.5}$	1440-1450	15	3	Cpx ($Wo_{38} \pm 2$)
Enstatite$_{100}$**	950-980	20	3	Opx (Wo_0)

* sample was run, ground, and then rerun for the times shown.

**hydrothermal: 30mg H_2O, 0.5 mg excess SiO_2 in approximately 400mg sample, Ag capsule.

tive (231) pigeonite peak is very small but unlike most other pigeonite peaks it is unobstructed by diopside$_{ss}$ or enstatite$_{ss}$ peaks. However, the sample must be nearly all pigeonite for the (231) peak to be observed above background. Two distinct and fairly strong enstatite peaks, (421) and (511) are easily distinguished from the pigeonite or diopside patterns. For bulk compositions that were at least as calcic as the pigeonite, the appearance or disappearance of the (421) and (511) peaks of En$_{ss}$ signalled the disappearance or formation of pigeonite, and therefore indicated reaction direction.

Microprobe techniques

Mineral grains were analyzed for CaO, MgO, and SiO_2 using an automated ARL-EMX SM electron microprobe. The data were reduced using an on-line computer program based on the Bence–Albee (1968) correction procedures. Many points were analyzed for one sample in order to get a good statistical base. Histograms of analyses were plotted to determine the composition of a sample. Satisfactory probe analyses were selected using the following criteria: (1) total oxide weight percent sums to 100±2%; (2) sum of Si cations per 6 oxygens = 2.00±0.02; and (3) sum of total cations = 4.00±0.02. These criteria were applied to analyses of starting materials and products.

Results

Two experiments show that the reaction Pig = Di$_{ss}$ + En$_{ss}$ takes place at 1465±10° C at 15 kbar (Table 2). One experiment, starting with Wo$_{20}$ pigeonite, produced a small amount of En$_{ss}$ indicating that pigeonite was breaking down. In another experiment, run under the same nominal conditions but using the product from the first experiment as a starting material, the orthopyroxene peaks disappeared, indicating that pigeonite had grown. This set of experiments is interpreted as a reversal that occurred within the ±10° C uncertainty inherent in each experiment. Pigeonite was both broken down and formed at separate times under similar conditions. The three coexisting pyroxenes from these experiments were not analyzed because small grain sizes and the problem of distinguishing remaining "starting material" would make analysis difficult to do and to interpret. Recycling run products by running them under the same conditions normally enhances grain size, but because in this case a different reaction occurred under the same nominal conditions grain size was not enhanced.

Table 2. Critical experiments at 15 kbar

Comp^n (Mole %)	Starting Phase(s)	T°C	Duration (hours)	Results X-ray	Microprobe
Wo$_{20}$	M.M.*	1470	3	Pig. grew	see fig. 1a
Wo$_{20}$	Cpx	1465	3+3**	Opx grew	****
Wo$_{20}$	***	1465	3	Opx disap.	****
Wo$_{20}$	Cpx	1460	7+2	Opx + Di	see fig. 1b
Wo$_{24}$	M.M*	1460	7+2.3	Opx + Di	see fig. 1c

* M.M = Mechanical mixture of En$_{100}$Opx+Wo$_{37.5}$Cpx

** Two cycles of 3 hours each, with grinding of the charge between cycles

*** Product of previous experiment

**** Too fine grained for microprobe analysis

Compositions of the three coexisting pyroxenes were approximated from experiments that were run 5° above and below 1465°, where that reaction was more nearly complete. Pigeonite broke down at 1460° C and it was formed from diopside$_{ss}$ and enstatite at 1470° C. The microprobe results of the three experiments are shown in Figures 1a, 1b, and 1c. The composition of the product pigeonite is Wo$_{18.3}$ En$_{81.7}$ (±1.5). The compositional limits on the diopside$_{ss}$–enstatite$_{ss}$ miscibility gap at 1460° C are approximately Wo$_5$En$_{95}$–Wo$_6$En$_{94}$ and Wo$_{25}$En$_{75}$–Wo$_{32}$En$_{68}$ as illustrated by the arrowheads in Figures 1b and 1c. The compositions of Di$_{ss}$ and En$_{ss}$ are compatible with the data of Lindsley and Dixon (1976) for experiments up to 1400° at 15 kbar.

Discussion

Since very few runs went to completion, one difficulty encountered in analyzing run products was distinguishing unreacted or zoned starting materials from new material produced during the run. Even when only small grains were analyzed, some analyses yielded compositions of the starting materials. Similar analytical problems were discussed by Lindsley and Dixon (1976) for the diopside–enstatite miscibility gap. The problems include: (1) overlap between Ca-rich and Ca-poor phases; (2) grains with cores of unreacted starting material and rims of equilibrium compositions; (3) fine intergrowths of the starting material and product; and (4) counting statistics. The problems cause the analyses to be scattered and skewed toward starting compositions. By analyzing many grains and avoiding the larger grains which might be unreacted starting materials, the problems could be minimized.

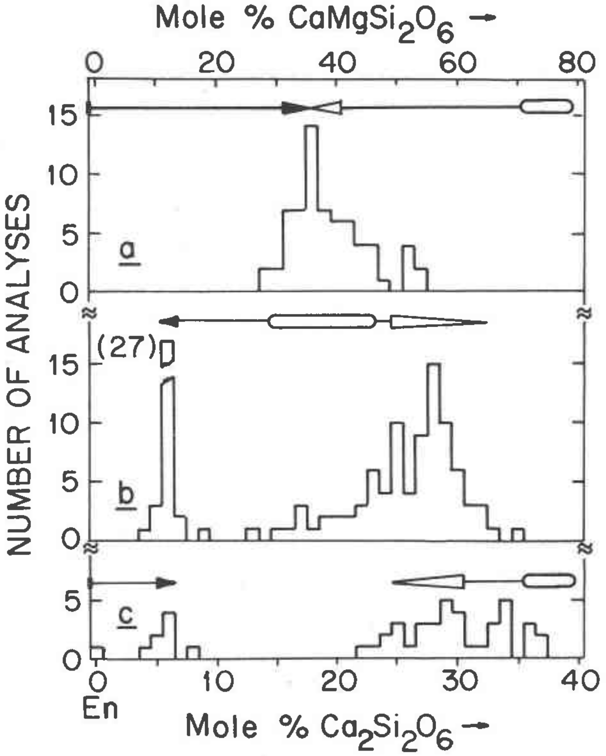

Fig. 1. Histograms of microprobe analyses of critical run products defining compositions of coexisting Opx + Pig + Di$_{ss}$ at 15 kbar. Compositions of initial Cpx are given by ovals; initial opx was pure Mg$_2$Si$_2$O$_6$. (a) Pigeonite-forming experiment at 1470° C. Length of adjacent arrowheads shows interpreted range of the pigeonite; analyses falling outside this range are presumed to reflect incomplete reaction; (b) Pigeonite-breakdown experiment at 1460° C. Length of arrowheads show ranges of preferred compositions for the Opx and Di$_{ss}$ produced; (c) Dissolving reaction En + Ca-rich Di$_{ss}$ = En$_{ss}$ + Ca-poor Di$_{ss}$ at 1460° C. Length of arrowheads show ranges of preferred compositions; these ranges define the maximum width of the Opx–Di$_{ss}$ field.

The composition of pigeonite (Wo$_{18.3}$En$_{81.7}$±1.5) is an average over the area indicated by the arrow in Figure 1. The entire compositional range was not used because of scatter problems such as those discussed by Lindsley and Dixon (1976) on the diopside–enstatite miscibility gap. Although areas were selected for analysis on the basis of their Ca content to avoid analyzing starting material, some starting material may have been within the area of the analyzing beam. This and the uncertainty about zoning in the grains results in the observed spread in composition.

The ranges given for the enstatite$_{ss}$ and diopside$_{ss}$ compositions have been chosen in light of the probable skewness towards relic starting compositions and the zoning problems as discussed above. The compositions of the two limbs fall within the limits: Wo$_{5-6}$ for En$_{ss}$ and Wo$_{25-32}$ for Di$_{ss}$. The composition range on the En$_{ss}$ limb is limited to Wo$_{5-6}$ because the single analyses at Wo$_4$ and Wo$_8$ might be attributed to counting statistics. The problems of zoning and of distinguishing products from starting materials are much more severe in the case of the Di$_{ss}$ limb, so the composition range selected is much wider. Figure 2 is a summary diagram of the data presented above and the Lindsley and Dixon (1976) diopside–enstatite miscibility gap, with calculated phase boundaries from Lindsley *et al.* (1981).

The composition of the iron-free pigeonite (Wo$_{18.3}$En$_{81.7}$±1.5) in this study is higher in calcium than most Fe-containing pigeonites, and also than previously reported iron-free pigeonites. The solution model of Lindsley *et al.* (1981) helps explain the calcium content. They calculate that the Pig–Di$_{ss}$ consolute point at 15 kbar lies only 15–25° above the temperature (1465±10° C) reported here for the three-pyroxene field; hence the pigeonite and Di$_{ss}$ must be relatively close in composition. At lower pressures the gap on the diopside–enstatite join is wider, and the pigeonite is therefore lower in calcium. Likewise, the gap is wider for most Fe-bearing pigeonites because they formed at temperatures much lower than those of this study.

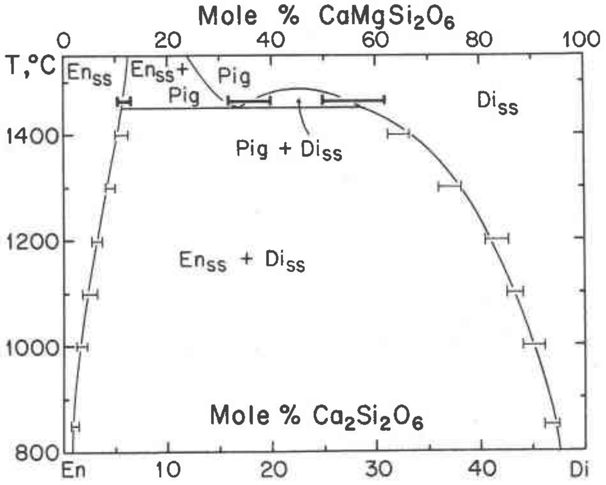

Fig. 2. Summary diagram for subsolidus relations on the Di–En join at 15 kbar. Data from this paper are shown as heavy symbols. The remainder are from Lindsley and Dixon (1976). The phase boundaries are those calculated by Lindsley *et al.* (1981).

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References

Bence, A. E. and Albee, A. L. (1968) Empirical correction factors for electron microanalysis of silicates and oxides. Journal of Geology, 76, 382–403.

Howells, S. and O'Hara, M. J. (1975) Paleogeotherms and the diopside enstatite solvus. Nature, 254, 406–408.

Kushiro, I. (1964) The system diopside–forsterite–enstatite at 20 kilobars. Carnegie Institution of Washington Year Book, 63, 101–108.

Kushiro, I. (1968) Synthesis and stability of iron-free pigeonite in the system $MgSiO_3$–$CaMgSi_2O_6$ at high pressures. Carnegie Institution of Washington Year Book, 67, 80–83.

Kushiro, I. (1969) The system forsterite–diopside–silica with and without water at high pressures. American Journal of Science, 267-A, 269–294.

Kushiro, I. and Yoder, H. S., Jr., (1970) Stability field of iron-free pigeonite in the system $MgSiO_3$–$CaMgSi_2O_6$. Carnegie Institution of Washington Year Book, 68, 226–229.

Lindsley, D. H. and Dixon, S. A. (1976) Diopside–enstatite equilibria at 850° to 1400° C, 5 to 35 kb. American Journal of Science, 276, 1285–1301.

Lindsley, D. H., Grover, J. E., and Davidson, P. M. (1981) The thermodynamics of the $Mg_2Si_2O_6$–$CaMgSi_2O_6$ join: A review and an improved model. In S. K. Saxena, Ed., Advances in Physical Geochemistry, V. 1, p. 146–172. Springer-Verlag, New York.

Mori, T. and Green, D. H. (1975) Pyroxenes in the system $Mg_2Si_2O_6$–$CaMgSi_2O_6$ at high pressure. Earth and Planetary Science Letters, 26, 177–286.

Mori, T. and Green, D. H. (1976) Subsolidus equilibria between pyroxenes in the CaO–MgO–SiO_2 system at high pressures and temperatures. American Mineralogist, 61, 616–625.

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