[AMERICAN JOURNAL OF SCIENCE, VOL. 276, DECEMBER, 1976, P. 1285-1301]

DIOPSIDE–ENSTATITE EQUILIBRIA AT 850° TO 1400°C, 5 TO 35 KB

DONALD H. LINDSLEY and SELENA A. DIXON*

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

ABSTRACT. Reversed experiments determine the compositions of coexisting diopside and enstatite (orthoenstatite) solid solutions from 850° to 1400°C at 15 kb and from 900° to 1400°C at 20 kb. At 1400°C, diopside solid solution is $Wo_{31\pm1.5}$ (mole percent $CaSiO_3$) at 15 kb and $Wo_{32.5\pm1.5}$ at 20 kb.

Additional experiments at 5, 30, and 35 kb, combined with recent published data, confirm the existence of a pressure effect on the diopside and enstatite solvi; over the interval 5 to 35 kb the $CaSiO_3$ content of diopside increases by 0.11 ± 0.01 mole percent per kb at 1200°C and by 0.26 ± 0.09 mole percent per kb at 1400°C. Concomitantly, the $CaSiO_3$ content of enstatite decreases by 0.06 ± 0.04 mole percent/kb at 1200°C and by 0.10 ± 0.10 mole percent/kb at 1400°C.

The Davis and Boyd diopside solvus at high temperatures gives compositions too poor in $CaSiO_3$: for example, 30.5 mole percent at 1400°C compared to 35.3 ± 0.7 mole percent based on microprobe analyses of both exsolving and dissolving experiments.

There is no effect of excess SiO_2 or of excess Mg_2SiO_4 on the diopside solvus at 1000° to 1400°C at 20 kb.

ABBREVIATIONS AND DEFINITIONS

Di_{ss} — $CaMgSi_2O_6$-rich clinopyroxene containing $MgSiO_3$ or Mg_2SiO_4 or both in solid solution.

En_{ss} — $MgSiO_3$-rich orthopyroxene containing $CaMgSi_2O_6$ in solid solution.

$Di_{ss}(En_{ss})$ — Di_{ss} in equilibrium with En_{ss} (plus any other phase that is also listed in the parentheses).

$En_{ss}(Di_{ss})$ — En_{ss} in equilibrium with Di_{ss}.

Diopside solvus — the locus of $Di_{ss}(En_{ss})$.

Enstatite solvus — the locus of $En_{ss}(Di_{ss})$.

Two-pyroxene field — the region of P-T-composition space bounded by the diopside and enstatite solvi.

$(dX/dT)_P^{Di}$ — the isobaric change in composition of $Di_{ss}(En_{ss})$ with temperature.

$(dX/dP)_T^{Di}$ — the isothermal change in composition of $Di_{ss}(En_{ss})$ with pressure.

Exsolution or exsolving experiments — those in which a single-phase pyroxene of intermediate composition breaks down to Di_{ss} and En_{ss}. Also called unmixing experiments. Establish the *maximum* Ca-content of $En_{ss}(Di_{ss})$ and the *minimum* Ca-content of $Di_{ss}(En_{ss})$.

Dissolution or dissolving experiments — those in which a mechanical mixture of Di + En reacts, the Di gaining Mg and the En gaining Ca. Establish the *minimum* Ca-content of $En_{ss}(Di_{ss})$ and the *maximum* Ca-content of $Di_{ss}(En_{ss})$. (We avoid the term "homogeniza-

* Present address: Department of Geosciences, University of Texas at Dallas, P.O. Box 688, Richardson, Texas 75080

tion experiments" since homogenization rarely takes place in this system.)

Reversal or bracket — exsolution data and dissolution data obtained at the same temperature and pressure. Establish both *maximum* and *minimum* Ca-contents of $Di_{ss}(En_{ss})$ and $En_{ss}(Di_{ss})$. The equilibrium values must lie within these limits. Compositions are expressed in mole percent $Wo(CaSiO_3)$ on the join $MgSiO_3$–$CaSiO_3$ unless otherwise noted.

INTRODUCTION AND PREVIOUS WORK

Ten years have passed since the pioneering study of the diopside–enstatite system at high pressures by Davis and Boyd (1966). Their data at 30 kb, when compared with results obtained at 1 atm (Atlas, 1952; Boyd and Schairer, 1964), suggested that the composition of $Di_{ss}(En_{ss})$ is sensitive to temperature but virtually independent of pressure. The diopside–enstatite geothermometer they proposed has been widely used; in conjunction with pressure estimates it has led to delineation of paleogeotherms based on inclusions in kimberlites (for example, Boyd, 1973).

Stimulated in part, no doubt, by the intense interest in such paleogeotherms, several recent redeterminations of subsolidus relations in the diopside–enstatite system have been made (Warner and Luth, 1974; Nehru and Wyllie, 1974; Howells and O'Hara, 1975). A drawback of all these studies is that very few data points were established by reversals. Hence, by early 1975, when we began the studies reported here, it was unclear whether there is a pressure effect on the diopside solvus and also whether that solvus is sensitive to the presence of excess SiO_2 or Mg_2SiO_4.

Warner and Luth (1974) obtained a reversal at 2 kb and 1200°C, but the rest of their results are based on dissolution experiments only, and it seemed possible that their reported pressure effect on the diopside solvus could simply reflect the effect of pressure on dissolution kinetics rather than on equilibrium.

Nehru and Wyllie (1974) experimented on gels that had been hydrothermally crystallized for 1 week at 2 kb and 800°C. Although they do not characterize the product other than as "finely intergrown crystalline starting material" (1974, p. 222), that treatment should yield coexisting nearly pure diopside and enstatite, and thus their experiments are most probably of the dissolution type. Accordingly, their data delineate the *maximum* Ca-content of the Di_{ss} and *minimum* Ca-content of the En_{ss} for each temperature at 30 kb; exsolution experiments would have verified whether or not these coincide with the *equilibrium* values.

The nature of the starting materials used by Howells and O'Hara (1975) is less certain. They were "finely ground gels which had been recrystallized at 900°C" (p. 407), but since neither duration nor water pressure of the recrystallization is specified it is impossible to guess what was produced. Accordingly one must be agnostic as to whether their

experiments were of the exsolution or dissolution type and also as to whether they reflect equilibrium. They concluded that $Di_{ss}(En_{ss})$ is sensitive to pressure as well as to silica activity (excess SiO_2 versus excess Mg_2SiO_4).

After most of the experiments reported here had been completed, the study of Mori and Green (1975) was published. Their starting materials were of two main types: glasses and mixtures of synthetic diopside plus clinoenstatite. Based on experiments with Fe-bearing pyroxene glasses (but not confirmed for the Fe-free glasses), these authors interpret that their glasses crystallize rapidly to single-phase clinopyroxenes which then begin to exsolve Di_{ss} and En_{ss} and are thus exsolution experiments. This interpretation is supported by the fact that Boyd and Schairer found it to be true for glasses crystallized at 1 atm and by Mori and Green's demonstration that the width of the two-pyroxene field in such experiments increases with time. The mixture of diopside and clinoenstatite are homogenization experiments in a *chemical* sense; the use of *clino*-enstatite rather than the more stable enstatite provides a starting assemblage of slightly higher free energy and thus a small but real chance of producing metastable phases. The general compatibility of their results with our own (which used orthorhombic enstatite) suggests that no serious problems stemmed from their use of clinoenstatite. Furthermore, the clinoenstatite to orthoenstatite inversion is complete in 5 min at 1200°C and 30 kb (Mori, written commun. from D. H. Green, 1976). Our data for the most part support the conclusions of Mori and Green, but we present them because we have reversals at additional temperatures and at different pressures.

Prior to the study of Mori and Green (1975) none of the available data on diopside–enstatite seemed compatible with experiments on Fe-bearing pyroxenes at temperatures below 1000°C (Lindsley, King, and Turnock, 1974a,b); it appeared that $Di_{ss}(En_{ss})$ contained considerably more $CaSiO_3$ than do Fe-bearing augites at the same pressure and temperature. Furthermore, thermodynamic solution models for the diopside–enstatite system (Warner and Luth, 1974; Saxena and Nehru, 1975) have been derived mainly from unreversed data and were thus of dubious significance. Accordingly, we embarked on a reinvestigation of this system with an emphasis on obtaining reversals using well-characterized crystalline starting material. Our goals were several: (1) to obtain reliable data at and below 1000°C so as to complete our isothermal sections for Ca, Mg, Fe pyroxenes at 810°, 900°, and 980°C at 15 kb; (2) to examine the pressure effect on the diopside solvus; (3) to test the conclusion by Howells and O'Hara (1975) that $Di_{ss}(En_{ss})$ is different depending on the presence of excess SiO_2 or Mg_2SiO_4; (4) to obtain reversed data over a sufficiently wide temperature range so as to permit calculation of a meaningful thermodynamic solution model. We chose to work mainly at 15 kb and at 20 kb but also obtained data from 5 to 35 kb.

PRESENT WORK

Starting Material

An essential aspect of our study is that all experiments were performed on previously synthesized and well-characterized crystalline pyroxene starting material (table 1). The desired compositions were weighed out using MgO (Johnson Matthey Batch S50068D, purity 99.998 percent), SiO_2 (Johnson Matthey Batch S50389B, purity 99.999 percent), and $CaSiO_3$ made from the SiO_2 and $CaCO_3$ (Bakers Lot #10641, purity 99.98 percent). After grinding for several hours in an agate mortar, each composition was initially reacted for 1 to 6 days at 1 atm and 1300° to 1440°C to yield a mixture of forsterite, amorphous SiO_2, incipient pyroxene phases, and (for Ca-bearing compositions) one or more polymorphs of $CaSiO_3$. At this stage the partially reacted mixes were divided and 1 to 5 wt percent excess SiO_2 or Mg_2SiO_4 was added to each subgroup to assure that the final starting pyroxenes to be synthesized were saturated with one of those components. Approximately 0.4 g of this material was then reacted in piston-cylinder pressure apparatus at the conditions shown in table 1. The products of this final synthesis step were examined by optics, X-ray diffraction, and electron microprobe and were found to be single-phase pyroxenes plus 1 to 5 percent quartz or forsterite. To provide starting material for dissolution experiments, crystalline diopside and enstatite were then weighed together and thoroughly mixed.

Use of the agate mortar contributed small (< 1 wt percent) amounts of additional SiO_2 to each mixture. For SiO_2-saturated phases, this merely produced a minor increase in the amount of quartz present. For Mg_2SiO_4-saturated phases, the SiO_2 contributed by the mortar reacted with a portion of the excess Mg_2SiO_4 to produce additional $MgSiO_3$ component, thereby biasing the final composition of the synthesized phases by 1 percent or less toward $MgSiO_3$. Thus, a Mg_2SiO_4-saturated clinopyroxene with nominal composition $Wo_{30}En_{70}$ (mole percent) had an actual composition of $Wo_{29}En_{71}$ as shown by electron microprobe. We used as

TABLE 1
Starting materials

Composition	Excess phase	Conditions of final synthesis T,°C	P,kb	H_2O	Duration, hr	Products
$Wo_{37.5}En_{62.5}$	Q	1450	20	—	1.7	Cpx ($Wo_{38\pm1}$) + minor Q
$Wo_{30}En_{70}$	Q	1500	20	—	0.6	Cpx ($Wo_{31\pm1}$) + minor Q
$Wo_{30}En_{70}$	Fo	1500	20	—	1.5	Cpx ($Wo_{28\pm1}$) + minor Fo
$Wo_{50}En_{50}$	Q	1000	20	7%	3.5	Di + minor Q } Mixed to make bulk
En_{100}	Q	1000	20	7%	7	En + minor Q } $Wo_{30}En_{70}$
$Wo_{50}En_{50}$	Fo	1450	20	—	2	Di } Mixed to make bulk
En_{100}	Fo	1000	20	5%	5.5	En + minor Fo } $Wo_{30}En_{70}$

Mg_2SiO_4-saturated starting materials only those pyroxenes that contained excess crystalline forsterite after the final synthesis.

We made no effort to prepare starting materials whose bulk compositions lay directly on the Di–En join, that is, materials with neither excess SiO_2 nor excess Mg_2SiO_4. This is because many previous workers (for example, Kushiro, Yoder, and Nishikawa, 1968; Lindsley and Munoz, 1969; Warner and Luth, 1974) performing high-pressure hydrothermal experiments on stoichiometric pyroxenes have observed that small amounts of pyroxene dissociate, SiO_2 being enriched in the fluid phase, and leave behind trace amounts of olivine in the crystalline material. Thus, stoichiometric metasilicate starting materials tend to become olivine-saturated when reacted hydrothermally at high pressures.

Experimental Procedures

Approximately 15 mg of pre-synthesized starting material plus water (ranging from trace amounts to 7 wt percent) were loaded into platinum capsules (finished outer dimensions 3.81 mm long by 2.39 mm diameter) which were then sealed by welding. A few experiments at temperatures below 1000°C used silver capsules. The samples were run in piston-cylinder pressure apparatus using a talc-boron nitride pressure cell in a 12.7 mm bore. Temperatures were measured using platinum versus $platinum_{90}$ $rhodium_{10}$ thermocouples* and were not corrected for effects of pressure. From the data of Getting and Kennedy (1970), we can estimate the *maximum* pressure effects at 1400°C: 9°C at 15 kb, 11°C at 20 kb, and 18°C at 35 kb; all values would be added to the reported temperatures. These corrections assume a pressure-seal temperature of 20°C. The temperature of our seal is higher (although unknown), and hence the actual corrections are smaller than listed. Except for 5 kb experiments, pressure was achieved by pumping to 1 kb above the desired pressure, then bringing the sample to temperature. The gauge pressure initially drops as temperature is increased; up to 1200°C it falls very close to the desired nominal value. At temperatures above 1200°C, it is usually necessary to bleed off some excess pressure when using this procedure. For 5 kb runs we used piston-instroke + 10 percent friction correction, so as to compare with the results of Mori and Green (1975). We chose run durations for each pressure and temperature such that powder X-ray diffraction patterns of exsolution and dissolution experiments were indistinguishable. After quenching, each sample was carefully tested for the presence of water (the opened capsule was placed at the bottom of a glass shell vial on a hot plate at approximately 130°C; water driven off from the sample condensed on the walls of the vial) and studied optically and by powderX-ray diffraction. Those samples that appeared to have reached equilibrium on the basis of the X-ray patterns (that is, similar or identical

* To test the possibility that the output of Pt versus $Pt_{90}Rh_{10}$ thermocouples may have drifted at 1400° (see, for example, Nehru and Wyllie, 1974), we duplicated the dissolving run at 1400°C, 20 kb, excess SiO_2 using a $W_{97}Re_3$ versus $W_{75}Re_{25}$ thermocouple. The latter experiment showed a tighter clustering of $Di_{ss}(En_{ss})$ data points but otherwise no significant difference.

patterns for exsolving and dissolving runs) were then analyzed by electron microprobe (an automated ARL-EMX model using 15 kv and 0.015 microamp specimen current on brass, with an effective spot size of one to two micrometers). We used as working standard a natural diopside ($Wo_{49.6}En_{50.4}$) from Twin Lakes, Calif. (Smith, 1966). Because of the fine grain size of some samples (5-10 μm), it was not always possible to obtain good analyses. We rejected all analyses yielding sums (MgO + CaO + SiO_2) less than 98 percent or greater than 102 percent and also those for which the mineral formula showed fewer than 1.98 or more than 2.02 Si per six oxygens. Approximately 10 percent of the analyses were rejected on the basis of these criteria, which were established before the analyses were made and which permitted us to reject questionable analyses without regard to the CaO and MgO values.

Some grains in some dissolution experiments were zoned, the rims approaching the equilibrium compositions, but the cores ranging toward the initial composition of the starting phases. We emphasize that the actual volume of such incompletely reacted material is considerably exaggerated by the microprobe data because of the tendency of the operator to position the electron beam as close as possible to the center of small grains. Thus, if *any* incompletely reacted material is present, it will tend to be included in the analysis, even though the volume percentage of such material may be small. Sharp X-ray diffraction peaks corresponding to the equilibrium compositions and skewed only slightly, if at all, toward the starting compositions confirm that reaction has been essentially complete in the experiments reported here. Apparent zoning or incomplete reaction in exsolving runs may simply reflect finely intergrown phases.

In common with most recent investigators in this system, we used water as a catalyst to promote reaction rates and increase grain size in our samples. A drawback to this technique is that water also enhances the formation of silicate liquids. For example, at $P_{H_2O} = 20$ kb (Kushiro, 1969, fig. 7, p. 283), En_{ss} + Di_{ss} + quartz + vapor coexist with an SiO_2-rich liquid at 960 ± 15°C. At the same P_{H_2O} and at 1220 ± 15°C, En_{ss} + Di_{ss} + Fo_{ss} + vapor coexist with a liquid close to but on the SiO_2 side of the Di-En join; and all vapor-saturated compositions on the Di–En join have melted by 1340 ± 10°C. Clearly, the experimenter who wishes to use water to aid in determining what are essentially subsolidus relations must walk a tight-rope, using enough water to be effective but not so much as to form excessive amounts of silicate liquid. The problem is more severe for SiO_2-excess than for Mg_2SiO_4-excess compositions: a few of our SiO_2-excess samples contain several percent SiO_2-rich glass instead of primary quartz in the final run products. We do not consider this a serious problem in that the pyroxene products were still saturated with respect to a silica-rich phase. We tried to avoid the quenched liquids when analyzing those samples with the electron microprobe, but since the liquids are greatly enriched in SiO_2 relative to pyroxenes (Si >> 2.00 per six oxygens) any analyses of quench phases were easily spotted and

discarded. It should be noted that our conclusions regarding the effect of silica activity are based on those runs that contained crystalline quartz in the run products.

Use of water as a catalyst becomes particularly important for experiments below 900°C. Unfortunately, the water may also result in the formation of amphibole. The presence of amphibole does not invalidate the experiment so long as two pyroxenes are also present.

Experimental Results

Our results are given in table 2 and in figure 1. Following the commendable lead of Nehru and Wyllie (1974), we have plotted as data points all pyroxene compositions that meet the criteria listed above. We believe that there are three main causes of scatter among these data points: (1) Compositional zoning that produces skewness toward the composition(s) of the original starting phase(s), as discussed above. (2) Grain-overlap between Ca-rich and Ca-poor pyroxenes, yielding apparent compositions lying within the two-pyroxene (Di_{ss} + En_{ss}) field and thus also resulting in skewness. We tried to avoid such regions of overlap during microprobe analysis but were not always successful. (3) Random scatter resulting from counting statistics. Replicate analyses on the diopside standard indicate that this random scatter rarely exceeds ± 1 mole percent $CaSiO_3$ and typically lies within ± 0.5 mole percent. If (3) were the only cause of scatter, it would be appropriate to use the mean of data points for each phase as the best value for the composition of that phase, as was done, for example, by Nehru and Wyllie (1974, p. 224). We consider that neither the mean nor the median value is appropriate where the data points are skewed as in cases (1) and (2). Probably the best values in such cases are essentially modal, and accordingly we have drawn our data symbols in the summary diagrams (figs. 2, 3), so as to encompass the majority of the individual data points but omitting the obviously skewed "tails." We emphasize once again that the analytical procedure greatly exaggerates the volumetric importance of incompletely reacted material (see discussion above) and that there is not so much zoned material as the "tails" would suggest. Note that we are *not* saying that the "best" or equilibrium composition is necessarily given by the mode of the combined exsolving and dissolving data; we argue only that the data symbol ("half-bracket") for each experiment should be modal. The equilibrium composition is then constrained to lie within the brackets, but there is no *a priori* reason to choose a "best" value at a particular point within the limits imposed by the brackets. Thus, although we have drawn the solvi as *lines* in figure 1, they might be represented as *bands* 1 to 3 mole percent wide. The true solvi should lie within those bands, but again there is no *a priori* reason to favor any particular position within these bands as the "best" value.

20-kb results.—We have obtained close brackets for $En_{ss}(Di_{ss})$ and somewhat less close brackets for $Di_{ss}(En_{ss})$ from 900° to 1400°C at 20 kb for SiO_2-excess pyroxenes and from 1000° to 1400°C for Mg_2SiO_4-excess

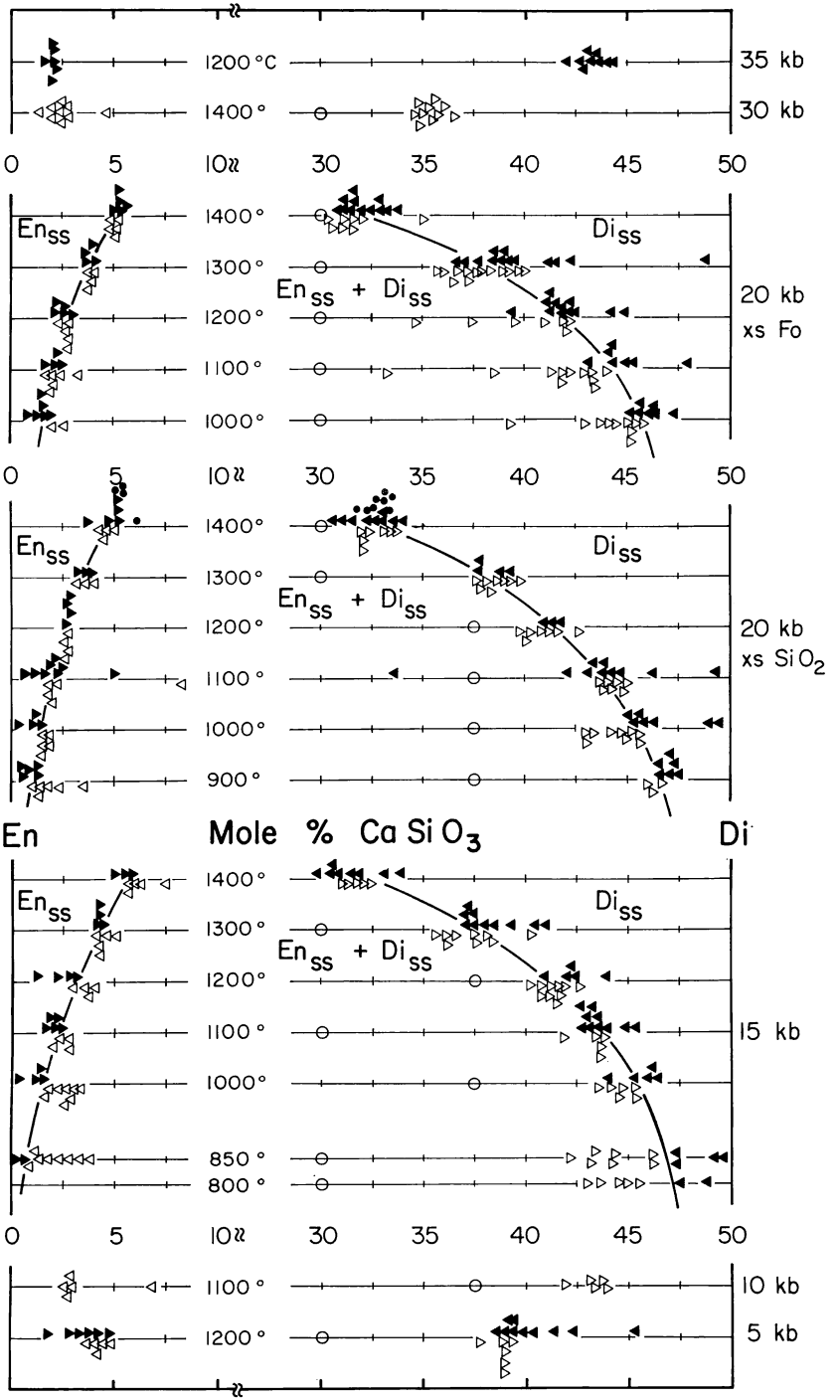
1200 °C
1400 °
35 kb
30 kb
0
5
10
30
35
40
45
50
Enss
Diss
Enss + Diss
1400 °
1300 °
1200 °
1100 °
1000 °
20 kb
xs Fo
900 °
20 kb
xs SiO2
En
Mole % CaSiO3
Di
850 °
800 °
15 kb
10 kb
5 kb

TABLE 2

Phase equilibria

Starting* material	H_2O wt %	T,°C	P,kb	Duration d	Duration h	Products** Di_{ss},%Wo	Products** En_{ss},%Wo	Other
Cpx(Q)	7	1200	5	0	9	39-39.5	3.5-5	Q
Di + En(Q)	7	1200	5	0	17	38.5-39.5	3-4.5	Q
Cpx(Q)	7	1100	10	2	17	43-44	2.5-3	Q
Cpx(Q)	7	800	15	12	0	43-45.5	(present)	Amph
Di + En(Q)	7	800	15	12	0	(47.5-49)	(present)	Amph
Cpx(Q)	7	850	15	13	6	43-46.5	0.5-4	Amph
Di + En(Q)	7	850	15	13	6	47	0.5	Amph
Cpx(Q)	7	1000	15	3	1	44.5-45.5	1.5-3.5	Q
Di + En(Q)	7	1000	15	3	1	45-46.5	1-1.5	Q
Cpx(Q)	7	1100	15	3	13	43.5-44	2-3	Q
Di + En(Q)	7	1100	15	2	7	42.5-44	1.5-2.5	Q
Cpx(Q)	7	1200	15	0	9	40-42.5	3-4	Gl
Di + En(Q)	7	1200	15	0	16	42-42.5	2.5-3	Gl
Cpx(Q)	3	1300	15	0	4	36-38.5	4-5	Gl
Di + En(Q)	3	1300	15	0	4	37-39	4-4.5	Gl
Cpx(Q)	tr	1400	15	0	4	31-32.5	5.5-6.5	Q;Gl
Di + En(Q)	tr	1400	15	0	4	29.5-32	5-5.5	Q;Gl
Cpx(Q)	7	900	20	7	0	46-47	1.2	Q
Di + En(Q)	7	900	20	9	6	46.5-47.5	.25-1.25	Q
Cpx(Q)	7	1000	20	2	19	44.5-46	1.5-2.0	Q
Di + En(Q)	7	1000	20	3	4	45-46	1-1.5	Q
Cpx(Fo)	7	1000	20	3	16	44-46	2-2.5	Fo
Di + En(Fo)	7	1000	20	3	16	45-46.5	1.25-1.75	Tr Fo
Cpx(Q)	7	1100	20	2	14	43.5-45	1.75-2.5	Q
Di + En(Q)	7	1100	20	1	18	43-45	1-2.5	Q
Cpx(Fo)	7	1100	20	2	1	41.5-44	1.5-2.5	Fo
Di + En(Fo)	7	1100	20	1	22	43-45	1.5-2	Tr Fo
Cpx(Q)	7	1200	20	0	8	39.5-42	2.5-3	Q
Di + En(Q)	7	1200	20	0	8	41-42	2-3	Gl;TrQ
Cpx(Fo)	7	1200	20	0	7	41-42	2-3	Fo
Di + En(Fo)	7	1200	20	0	7	41-42.5	2-3	Tr Fo
Cpx(Q)	3	1300	20	0	4	37.5-40	3-4	Q
Di + En(Q)	3	1300	20	0	3	37.5-39.5	3-4	Gl
Cpx(Fo)	3	1300	20	0	4	36-40	3.5-4	Fo
Di + En(Fo)	3	1300	20	0	4	37-39.5	3.5-4	TrGl,Fo
Cpx(Q)	tr	1400	20	0	5	32-34	4-5	Q
Di + En(Q)	tr	1400	20	0	4	30.5-34	4.5-5.5	Q
Di + En(Q)	tr	1400***	20	0	4	32-33.5	5-5.5	Q
Cpx(Fo)	tr	1400	20	0	5	31-32.5	4.5-5.5	Fo
Di + En(Fo)	tr	1400	20	0	5	31-33	4.5-5	Fo
Cpx(Q)	tr	1400	30	0	5	34.5-36	4-5.5	Q
Di + En(Q)	tr	1200	35	0	22	42.5-44	1.5-2	Q

* (Q) means excess quartz, (Fo) means excess forsterite present in starting material; see table 1.

** Compositions show the range in mole % Wo($CaSiO_3$) as determined by electron microprobe. These ranges omit extreme values interpreted to represent incompletely reacted starting material or grain overlap. Gl, glass, does not exceed 5% by visual estimate in any run; Amph, tremolitic amphibole; Q, quartz; Fo, forsterite.

*** This experiment used a $W_{97}Re_3$ versus $W_{75}Re_{25}$ thermocouple.

← Fig. 1. Microprobe analyses of coexisting Di_{ss} and En_{ss} for pressures from 5 to 35 kb and temperatures from 850° to 1400°C. Note break in composition scale. All experiments had excess SiO_2 except the set at 20 kb labelled "xs Fo" (excess Mg_2SiO_4). Data from dissolution runs, solid triangles plotted on or above each temperature line; data from exsolution runs, open triangles mainly plotted below each appropriate temperature line. Large open circles show composition of starting pyroxene (either Wo_{30} or $Wo_{37.5}$) for exsolution runs; dissolution runs started with mechanical mixtures of enstatite plus diopside (bulk composition Wo_{30}). Small closed circles show compositions of coexisting pyroxenes in a dissolving run at 1400°C, 20 kb using $W_{97}Re_3$ versus $W_{75}Re_{25}$ thermocouple.

pyroxenes. There is no systematic or significant effect of excess SiO_2 versus Mg_2SiO_4 under these conditions (fig. 2).

Diopsides coexisting with forsterite contain approximately 5 wt percent Mg_2SiO_4 in solid solution at 1387°C and 1 atm (Kushiro and Schairer, 1963; Kushiro, 1972) and at 1600° to 1625°C at 20 kb (Kushiro, 1964). Deviations from the ideal 1:1 metasilicate ratio (Ca + Mg):Si were invoked by Howells and O'Hara (1975, p. 407) to explain apparent differences in $Di_{ss}(En_{ss})$ reported by them for SiO_2-excess and Mg_2SiO_4-excess compositions. Five wt percent Mg_2SiO_4 in $CaMgSi_2O_6$ would correspond to the formula $Ca_{0.949}Mg_{1.103}Si_{1.974}O_6$. To test for such silica-deficiency, we made a careful study of the SiO_2 content of the pyroxenes produced at 1400° and 20 kb for Mg_2SiO_4-excess compositions. The mean of 24 analyses of the Mg_2SiO_4-saturated Di_{ss} is 1.993 (S.D. = 0.005) Si per six oxygens; this is not significantly different from the mean of 1.996 (S.D. = 0.009) Si per six oxygens obtained for Di_{ss} made at 1400°C in

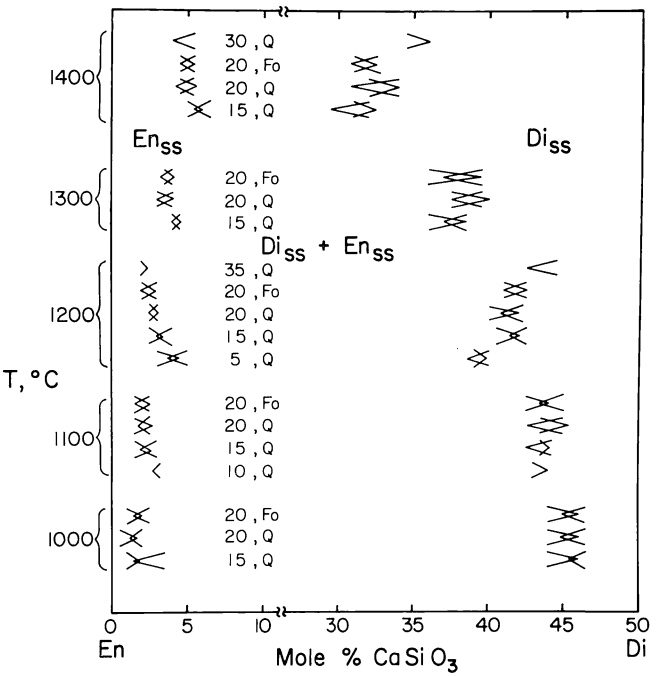

Fig. 2. Summary of microprobe data from figure 1. Note break in composition scale. Data symbols exclude those analyses considered to represent overlapping grains or incompletely reacted grains; width of symbols is, therefore, our best estimate of the composition for each run product. Arrowheads pointing toward Di_{ss} + En_{ss} field are for dissolution experiments; those pointing away from that field are for exsolution experiments. The number and letter on line with each set of symbols shows the pressure in kb and the *component* (Q = SiO_2, Fo = Mg_2SiO_4) in excess for that experiment. The *phase* quartz or forsterite was also present in excess in the products of all runs except for a dissolving run at 20 kb, 1300°C, excess Q, which contained several percent of SiO_2-rich glass but no free quartz.

SiO_2-excess compositions. (No individual analysis for these samples fell below 1.980 Si per six oxygens, and thus none was rejected in accordance with that criterion for acceptability.) Replicate analyses of the diopside standard run immediately before and after the experimental samples yielded means of 1.996 ± 0.006 and 1.997 ± 0.005 — almost identical with the value 1.998 Si per six oxygens obtained by wet chemical analysis (Smith, 1966). While our results show little significant solubility of Mg_2SiO_2 in Di_{ss}(En_{ss}, Fo) at 1400°, 20 kb, they are not necessarily in conflict with Kushiro's data, which were obtained at 1600°C. Note that Kushiro's Di_{ss} coexisted with Fo but not also with En_{ss}. We suggest that Mg_2SiO_4 solubility in Di_{ss} may be significant only in the absence of a silica-saturated phase such as En_{ss}.

15-kb results.—Brackets for 15 kb experiments (excess SiO_2 only) are good from 1400° to 1000°C. The runs at 850°C yielded poorer brac-

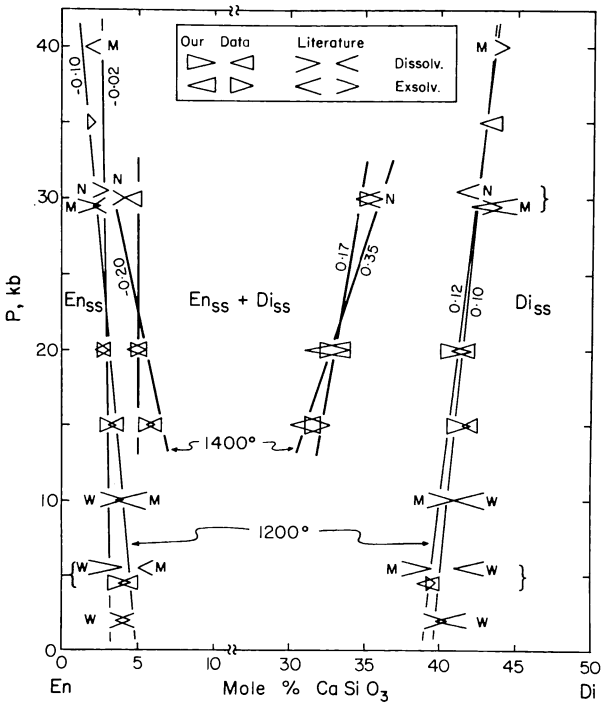

Fig. 3. Compositions of coexisting Di_{ss} and En_{ss} as functions of pressure at 1200° and 1400°C, as constrained by exsolution and dissolution experiments. Note break in composition scale. Our data are from figures 1 and 2; literature data are labelled W (Warner and Luth, 1974), N (Nehru and Wyllie, 1974), and M (Mori and Green, 1975). Width of each symbol shows estimated uncertainty in composition, based on the scatter of microprobe data or the precision of X-ray determinations. The straight lines show the minimum and maximum values of $(dX/dP)_T$ allowed by the data; their slopes are labelled in mole percent $CaSiO_3$/kb. Some data symbols at 5 and 30 kb are plotted above or below the actual pressures for clarity.

kets and minor Ca, Mg amphibole, and those at 800°C gave much amphibole and little useful pyroxene information. There is permissive, but only marginally significant, evidence that at 1300° and 1400°C, the two-pyroxene field is narrower at 15 kb than it is at 20 kb (fig. 2).

5-kb results.—Mori and Green (1975, fig. 3) show a distinct curvature for $(dX/dP)_{1200°}^{Di}$. This curvature results in part from their decision to draw the solvus through their data point ($Wo_{38.7 \pm 1}$) at 1200°C and 5 kb. However, since this point is for an exsolution experiment only, it places a minimum but not a maximum value for the Ca-content of $Di_{ss}(En_{ss})$ at those conditions. A maximum value is shown by the dissolution data of Warner and Luth (1974): $Wo_{42 \pm 1}$. Together these data constrain the equilibrium composition rather loosely between the extremes $Wo_{37.7}$ and Wo_{43}.

In an attempt to obtain a tighter bracket, we ran dissolving and exsolving experiments at 5 kb and 1200°. Our data constrain the equilibrium value for $Di_{ss}(En_{ss})$ to between $Wo_{38.5}$ and Wo_{40} (fig. 1), a tighter bracket than provided by the previous experiments.

10-kb, 30-kb, and 35-kb results.—We made an exsolving run at 30 kb and 1400° to complement the Nehru-Wyllie dissolving run; together they provide a tight bracket on $Di_{ss}(En_{ss})$ at those conditions. A dissolving run at 35 kb, 1200°, helps constrain $(dX/dP)_{1200°}^{Di}$ at high pressures (fig. 3), even though it is not paired with an exsolving run at those conditions. We also include data for an exsolving run at 1100°C, 10 kb.

DISCUSSION AND CONCLUSIONS

Our data bear on several important questions regarding the use of coexisting Di_{ss} and En_{ss} as a geothermometer: (1) the existence of a pressure effect on the compositions of Di_{ss} and En_{ss}; (2) the effect of excess SiO_2 or Mg_2SiO_4 on $Di_{ss}(En_{ss})$; (3) the calibration of $En_{ss}(Di_{ss})$ as a geothermometer, as proposed by Boyd and Nixon (1973), Hensen (1973), and Mysen (1973); and (4) the validity of the Warner-Luth solution model for coexisting Di_{ss} and En_{ss}.

Pressure Effect on compositions of Coexisting $Di_{ss} + En_{ss}$

Most recent investigations have concluded that there is a pressure effect on the composition of $Di_{ss}(En_{ss})$, particularly at higher temperatures; Mori and Green (1975) show, in addition, a pressure effect on $En_{ss}(Di_{ss})$. Mori and Green have also pointed out the difficulties in comparing compositions from different investigations as determined by three methods: optical identification, X-ray diffraction, and microprobe analysis. We restrict this discussion only to those experiments where the direction of reaction — exsolution or dissolution — is apparent and where X-ray or microprobe was employed. Only at 1200° and 1400°C are there adequate data at a sufficient range of pressures to provide a realistic test of pressure effects. Reversed data at 1200°C are available for 2 kb (Warner and Luth, 1974); 5, 15, and 20 kb (our data); and 30 kb (Mori and Green, 1975). In addition, unreversed data exist for exsolution

at 5, 10, and 40 kb (Mori and Green, 1975) and 30 kb (our data); and for dissolution at 5 and 10 kb (Warner and Luth, 1974; the 10 kb data were actually obtained at 1190°C), 30 kb (Nehru and Wyllie, 1974), and 35 kb (our data). In plotting these data on a pressure-composition diagram (fig. 3), we have taken pains to include the uncertainties in composition associated with each measurement — the reported range of microprobe analyses or the precision of X-ray determinative methods — for we consider this to be more realistic than treating each data set as a point. For reversals, the "true" (that is, equilibrium) composition need only lie within the total range of uncertainty for both the exsolving and dissolving runs. It is important to recall that unreversed data are not so restrictive: the "true" composition *may* lie within the range of uncertainty of the analysis but may also lie at any value that is further removed from that of the starting phase, since there is no *a priori* proof that the equilibrium composition has been obtained. For example, Nehru and Wyllie (1974) give data for $Di_{ss}(En_{ss})$ at 1200°C, 30 kb with a range $Wo_{41}En_{59}$ to $Wo_{43}En_{57}$. Because it was dissolution experiment, the equilibrium composition cannot be *more* calcic than Wo_{43}, but, based on this experiment alone, it could be *less* calcic than Wo_{41}. Mori and Green (1975), on the other hand, report an exsolution experiment at the same conditions that shows that the equilibrium composition cannot be *less* calcic than $Wo_{42.5}$. These data sets appear to be almost mutually contradictory; however, consideration of the ± 10°C temperature uncertainty inherent in piston-cylinder experiments allows for considerable overlap of these data, and together they provide a close bracket on the equilibrium value.

Pressure effect on $Di_{ss}(En_{ss})$.—Visual inspection of figure 3 shows that in general $Di_{ss}(En_{ss})$ at 1200°C becomes more calcic with increasing pressure. But note that since the brackets have finite width at each pressure, there is no unique line that gives $(dX/dP)_{1200°}^{Di}$, the change in composition of Di_{ss} with pressure. One can, however, construct the maximum and minimum values of $(dX/dP)_{1200°}^{Di}$ that are compatible with all the data. The data neither require nor justify the use of other than straight lines for this construction. The maximum value of $(dX/dP)_{1200°}^{Di}$ is 0.12 mole percent Wo/kb; it is constrained by the Warner-Luth exsolving run at 2 kb, our exsolving run at 5 kb, and the Nehru-Wyllie dissolving run at 30 kb. The minimum value of 0.10 mole percent wo/kb is constrained by our dissolving run at 5 kb and the Mori-Green exsolving runs at 30 and 40 kb. Thus, the effect of a 20 kb pressure difference on $Di_{ss}(En_{ss})$ is 2.0 to 2.4 mole percent Wa, or an error of 60° to 80° in the geothermometer for temperatures near 1200°C.

The pressure effect on $Di_{ss}(En_{ss})$ appears to increase with temperature. Brackets at 15, 20, and 30 kb constrain $(dX/dP)_{1400°C}^{Di}$ to between 0.17 and 0.35 mole percent Wo/kb (fig. 3). A pressure difference of 20 kb at 1400°C would change $Di_{ss}(En_{ss})$ by 3.4 to 7 mole percent Wo, corresponding to a temperature error of 50° to 120°C. Further experi-

ments at 40 or 50 kb should aid in decreasing the uncertainty of $(dX/dP)_{1400°C}^{Di}$.

Pressure effect on $En_{ss}(Di_{ss})$.—The data of figure 3 indicate that En_{ss} becomes less calcic with increasing pressure. The values of $(dX/dP)_{1200°C}^{En}$ consistent with the data range from −0.02 to −0.10 mole percent Wo/kb; the range at 1400°C is from 0 to −0.20 mole percent Wo/kb. Thus, while a pressure effect on $En_{ss}(Di_{ss})$ probably exists, it may be small.

Mori and Green plot the enstatite and diopside solvi for 1200°C as curves on a pressure-composition diagram (1975, fig. 2). This curvature results partly from their exsolution data at 5 kb; our 5-kb bracket and the Warner-Luth 2-kb bracket show this curvature is unnecessary, especially when the uncertainties in all the data are considered. Extrapolation of our 1200°C curves to 1 atm yields (metastable) values for $Di_{ss}(En_{ss})$ of $Wo_{38.5}$ and $Wo_{39.5}$, somewhat more calcic than the value for Di_{ss}(protoenstatite) reported by Boyd and Schairer (1964, p. 280) of $Wo_{37.6}$. D. H. Green (written commun., 1976) has correctly pointed out that metastable $Di_{ss}(En_{ss})$ at 1200°C, 1 atm, should be less calcic than is Di_{ss} (protoenstatite). However, the Boyd and Schairer value is based on exsolving runs and thus gives only a minimum value for the Wo content of the Di_{ss}. Thus our values for $Di_{ss}(En_{ss})$ at 1200°C are not in conflict with the 1 atm data. Some curvature may well exist above 40 kb, for otherwise the 1200°C solvi would intersect the end-member compositions.

Calibration of the Enstatite Solvus as a Geothermometer

Boyd and Nixon (1973) showed small but consistent variations of the Ca content of $En_{ss}(Di_{ss})$ with temperature *as inferred from the coexisting Di_{ss}* for approximately 30 lherzolites from kimberlites of northern Lesotho. Hensen (1973) and Mysen (1973) provided a partial calibration for this solvus with dissolving experiments on natural pyroxenes but did not reverse it with corresponding exsolving experiments. We have obtained tight brackets on this solvus from 1000° to 1400°C at 15 kb and from 900° to 1400°C at 20 kb (figs. 1 and 2). For several temperatures our data lie within the range of scatter to be expected for replicate microprobe analyses on homogeneous material. Unfortunately, however, the solvus is so steep that our brackets taken 100°C apart tend to overlap. This means that our calibration of this solvus cannot be used to determine temperatures to better than ± 100°C. We seriously doubt that it can be calibrated more closely by standard methods of experimental phase equilibria. Pressure effects at 1200°C and above may result in still greater uncertainties.

Effect of Excess SiO_2 or Mg_2SiO_4 on $Di_{ss}(En_{ss})$

The work of Kushiro (1964; 1972; Kushiro and Schairer, 1963) shows that diopside coexisting with forsterite can contain up to 5 wt percent Mg_2SiO_4 in solid solution at near-solidus temperatures. The effect of such solid solution is to increase (Ca + Mg)/Si and also Mg/(Ca + Mg), thus

increasing the apparent En content of the Di_{ss}. But to our knowledge it has not been demonstrated that Di_{ss} simultaneously coexisting with forsterite *and* a more siliceous phase such as En_{ss} also shows pronounced silica deficiency. It seems plausible on crystal chemical grounds that when sufficient SiO_2 is present the pyroxenes will approach metasilicate compositions. Indeed, Kushiro's analysis of Di_{ss} coexisting with forsterite + pigeonite + liquid at 1385°C, 1 atm (1972, p. 1265) shows, if anything, a slight *excess* of SiO_2!

Our careful analyses of $Di_{ss}(En_{ss} + Fo)$ formed at 1400°C, 20 kb show a SiO_2 deficiency that can be reckoned as 1.05 ± 0.75 mole percent (0.7 ± 0.5 wt percent) Mg_2SiO_4 in solid solution. There is no significant difference in Mg/(Ca + Mg) between this Di_{ss} and $Di_{ss}(En_{ss}$ + excess $SiO_2)$ reacted at the same conditions. Thus, our data do not support the conclusion by Howells and O'Hara (1975) that a difference in SiO_2 content also changes the apparent Wo content. It should be noted that their experiments were at higher temperature and pressure (1550°C, 30 kb) than our own and that our results do not disprove their conclusion for those conditions. But in the absence of reversals in their experiments we consider their conclusion as unproved. In view of the high temperatures of their experiments and their use of X-ray determinative methods, we tentatively suggest the possibility that the differences reported by Howells and O'Hara might reflect different amounts of quench pyroxene in SiO_2- and Mg_2SiO_4-excess experiments. Small to moderate amounts of liquid would form if their gel starting materials were not completely dehydrated.

Evaluation of the Warner-Luth Solution Model for Coexisting Di_{ss} and En_{ss}

On the basis of their reversal at 1200°C and 2 kb, plus various dissolving experiments at 2 to 10 kb, Warner and Luth (1974) formulated a solution model for coexisting Di_{ss} and En_{ss}. This model predicts Di_{ss} (En_{ss}) at 900°C and 20 kb as $Wo_{49.1}$; the range of values permitted by our data is Wo_{46}-$Wo_{47.5}$. Likewise, the model predicts Wo_{31} for $Di_{ss}(En_{ss})$ at 1400°C and 30 kb, compared to the experimentally determined $Wo_{34.5}$-Wo_{36}. Because of its failure to predict these values, the Warner-Luth model should be discarded.

SUMMARY

There is clearly a pressure effect on the composition of $Di_{ss}(En_{ss})$ at 1200°C, although the effect at low pressures is smaller than that reported by Mori and Green (1975). The pressure effect increases with increasing temperature.

There is no significant difference in the Mg/(Ca + Mg) of $Di_{ss}(En_{ss})$ for SiO_2-excess and Mg_2SiO_4-excess compositions at 20 kb and 1400°C. We consider suggestions that there is a difference at higher pressures and temperatures (Howells and O'Hara, 1975) as not yet proved.

The composition of $En_{ss}(Di_{ss})$ varies with temperature. The enstatite solvus is so steep, however, that the small compositional range permitted by our tight brackets corresponds to temperature uncertainties of ± 100°C. The data at 1200°C also indicate a pressure effect that would add a further uncertainty as large as ± 100°C for a 10 kb change in pressure at that temperature.

ACKNOWLEDGMENTS

This work was supported by Earth Sciences Section, National Science Foundation, N.S.F. Grant #DES74-21891. The final version was improved by the comments of F. R. Boyd, D. H. Green, T. Mori, and D. C. Presnall, but they should not be held responsible for some of the conclusions we draw. To them all go our deep thanks.

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