

5. Stability of subcalcic clinopyroxene at 30 kbars and 1500°C

There are four runs which are relevant to the problem of stability of subcalcic clinopyroxene found by Davis and Boyd [4]: runs 9 and 10 are on $\text{En}_{50}\text{Di}_{50}$, and runs 11 and 12 are on $\text{En}_{80}\text{Di}_{20}$. In runs 10 and 12, the charges were first kept at 1200°C and 30 kbars for a time considered sufficient (runs 2–4) to bring all the pyroxene compositions outside the solvus of 1500°C and 30 kbars, then temperature was increased to 1500°C. Thus, runs 9 and 10, and runs 11 and 12 can be regarded as pairs of unmixing and homogenization experiments. The results of runs 11 and 12 define the solvus very well. Run 9, however, resulted in a single-phase clinopyroxene and is inconsistent with run 10 where two pyroxenes remained and did not homogenize to a single phase. Two analyses of clinopyroxene in run 10 are slightly inconsistent with the solvus defined by runs 11 and 12, but only 15°C difference between them would explain the inconsistency. This choice of the solvus is in agreement with the data of Nehru and Wyllie [7] who carried out syn-

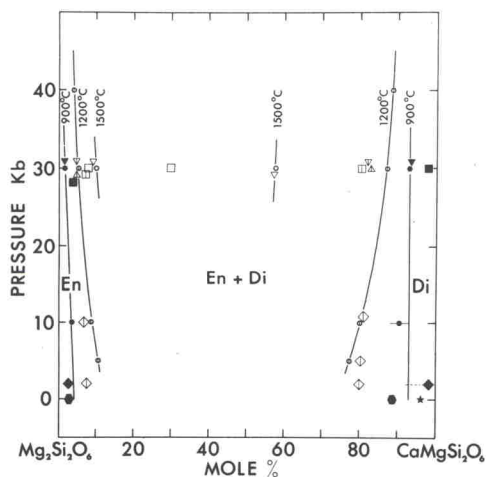


Fig. 2. Pressure-composition diagram of the enstatite–diopside solvus. Data are from Fig. 1 (circle, microprobe), Davis and Boyd [4] (square, optical), Boyd [5] (triangle, microprobe), Boyd and Schärer [1] (star, optical and X-ray), Atlas [14] (hexagon, X-ray), Warner and Luth [6] (diamond, X-ray), and Nehru and Wyllie [7] (inverted triangle, microprobe). Open symbols are at 1500°C, those with vertical line are at 1200°C, and the solid symbols are at 900°C. Some data at 10 and 30 kbars are plotted above or below the actual pressure to avoid confusion. En = enstatite, Di = diopside.

thesis experiments using sintered gel of $\text{En}_{50}\text{Di}_{50}$ as starting material (Fig. 2).

Generally, in unmixing runs yielding two pyroxenes, measured chemical ranges may be attributed to incomplete unmixing reactions, but if the single-phase pyroxene in run 9 were stable, there would be no reason for it to show such a wide chemical range as shown in Fig. 1. In run 11, two pyroxenes appeared within 3.2 hours, a slightly longer run duration than run 9, but the difference in run time appears unlikely to explain the absence of orthopyroxene. It is highly probable that $\text{En}_{50}\text{Di}_{50}$ is within the metastable composition range where Ca–Mg internal diffusion fails to occur at this P – T condition [12].

Further support for the revised position of solvus at 1500°C and 30 kbars is found in a partial melting experiment on natural garnet lherzolite [13]. In this run, clinopyroxene coexists with orthopyroxene as well as olivine, spinel and glass. The composition of the clinopyroxene ($\text{Ca}_{29.3}\text{Mg}_{66.2}\text{Fe}_{4.5}$, $\text{Al}_2\text{O}_3 = 5.3\%$) is near to the revised solvus. Since Al_2O_3 solid solution stabilizes a wider solvus [5], correction for the Al_2O_3 effect in their result will move the composition of the clinopyroxene even closer to the solvus defined above. Thus the experiment in the multicomponent system supports the stability and wide solvus between two pyroxenes at 30 kbars and 1500°C in the simple system.

6. Temperature and pressure effects on the enstatite–diopside solvus

The positions of the solvus determined in preceding sections and shown in Fig. 1 are plotted on the pressure–composition diagram (Fig. 2) and temperature–composition diagram (Fig. 3). Available data from the literature are also shown. These data were obtained by three methods: optical identification of minerals in experimental charges, X-ray calibration of pyroxene composition, and microprobe analysis of pyroxenes. It should be noted that all the data plotted in both the figures are the respective authors' ultimate selections after statistical treatment or simple curve fittings, and are not their raw data which often deviate from the selections.

Accuracy of the first method depends on the quality of identification of minerals and the spacing of the

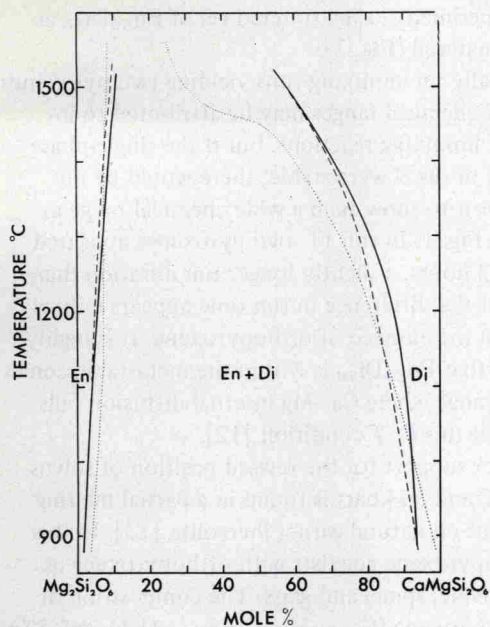


Fig. 3. The enstatite–diopside solvus at 30 kbars. Solid line: our data, dotted line: Davis and Boyd [4], and dashed line: Nehru and Wyllie [7].

composition grid employed, and that of X-ray method is ± 1 to ± 3 mole % end member [6,14]. The inconsistency seen among the data including ours should be viewed in relation to the accuracy of the method employed and the type of reaction, i.e. homogenization or unmixing. Particularly, it should be noted that determination of pyroxene composition from homogenization experiments using the X-ray calibration is very uncertain. This is because, in those experiments, chemical hysteresis can hardly be avoided, and the X-ray method will bias towards compositions outside the solvus.

The differences between the various data plotted in Fig. 2 are not entirely within analytical or method-derived error. We will examine particularly the data for the clinopyroxene limb at 1200°C and 30 kbars and at 900°C , 30 kbars to 1 atmosphere. Our reversal experiments at 30 kbars and 1200°C yielded overlapping compositional ranges with the unmixing experiment (run 4) giving strongly clustered data. We consider that the spread of the homogenization (run 5) data to lower diopside contents is due to greater temperature uncertainty in this run (see Table 1). In Fig. 2 we have drawn the solvus at 1200°C as a func-

tion of pressure as defined by our own data.

At 900°C and 30 kbars our closely bracketted reversal gives a clinopyroxene composition coincident with that predicted by extrapolation of Nehru and Wyllie's [7] data (1500 – 1000°C) and this composition is less calcic than that previously accepted [4]. At 900°C and 10 kbars our data bracket the clinopyroxene limb of the solvus within 5 mole % end member. At 900°C and 2 kbars earlier data [6] led to selection of a more calcic composition but it should be noted that in their unmixing experiments, Warner and Luth [6] did not obtain clinopyroxene more calcic than $\text{En}_8\text{Di}_{92}$ (Fig. 2). The clinopyroxene limb at 900°C has been drawn through the reversal brackets at 30, 10 and 2 kbars but its extrapolation is then inconsistent with 1-atmosphere data [1,14]. Boyd and Schairer's [1] determination was based on optical identification of phases and some of the crucial phase identifications at and below 900°C were reported as doubtful (queried) [1, table 5]. Their data thus permit the interpretation that the clinopyroxene limb at one atmosphere lies between $\text{En}_{5.3}\text{Di}_{94.7}$ and $\text{En}_{10.7}\text{Di}_{89.3}$. We conclude, in the light of this and earlier studies, that there is little or no pressure effect on the diopside limb of the pyroxene solvus at 900°C from 0 to 30 kbars.

To summarize (Fig. 2), at higher temperature ($\geq 1200^{\circ}\text{C}$) the pyroxene solvus widens considerably as pressure increases, and at low temperature ($\leq 900^{\circ}\text{C}$) there is no perceptible pressure effect on the clinopyroxene limb and a slight pressure effect on the orthopyroxene limb. The pressure dependence of the orthopyroxene limb is of the same character as inferred in the Fe-bearing system [11]. Although pressure effects on emf of the thermocouple have not been corrected for and remain uncertain, the correction would raise indicated temperature to higher real values and would thus enhance the widening of the solvus with increasing pressure.

The temperature dependence of the solvus is shown in Figs. 2 and 3 which reaffirm the well-established increase of mutual solubility with increasing temperature. At 30 kbars, however, the shape of the re-determined solvus is very different from that of Davis and Boyd [4] and similar to that of Nehru and Wyllie [7]. Our new data show that the clinopyroxene limb is less sensitively dependent on temperature between 900 and 1200°C . This means that the