

Pressure dependence of the enstatite limb of the enstatite–diopside solvus

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Abstract

A critical evaluation of the data on the compositional variation of En_{ss} (orthoenstatite solid solution) coexisting with Di_{ss} (diopside solid solution) with temperature, now available at different pressures up to 40 kbar, strongly indicates that the En_{ss} composition is pressure-dependent (*cf.* Hensen, 1973, and Mysen and Boettcher, 1975).

The smaller spread in the En_{ss} compositions at each temperature (between 1000 and 1300°C) experimentally obtained by Nehru and Wyllie (1974), compared to the Di_{ss} compositional spread, defines the enstatite limb of the solvus more precisely than the diopside limb. Assuming this to be true of the data available at other pressures in the iron-free system, the En_{ss} data are ideally suitable for testing the effect of pressure or the lack of it on the enstatite limb of the solvus.

Available experimental data on the compositions of En_{ss} from the iron-free En–Di system, when plotted on a P - T graph, show variation of the $Ca/(Ca + Mg)$ ratio not only with temperature but also with pressure. Curves of constant $Ca/(Ca + Mg)$ ratio have a positive slope on the P - T graph. For a given value of the ratio, pressure variation (between 1 and 40 kbar) can cause discrepancies of up to 250°C in temperature estimation.

The addition of iron to the system further complicates the picture. An evaluation of the available En_{ss} compositional data from experimentally determined synthetic and natural iron-bearing systems indicates that the slopes of the constant $Ca/(Ca + Mg)$ ratio lines change with the addition of iron. Until such time as we have more data on this important system to precisely define the effect of this variable as well, the geothermometric applications to naturally occurring rocks have to be used with caution.

Introduction

The experimental work of Boyd and Schairer (1964) and Davis and Boyd (1966) brought recognition to the enstatite–diopside (En–Di) solvus as a geothermometer. Davis and Boyd showed that the diopside limb of the solvus was pressure-insensitive. Experimental work on this system at different pressures is now available (Lindsley and Dixon, 1975; Mori and Green, 1975; Howells and O'Hara, 1975; Nehru and Wyllie, 1974; Akella, 1974; Akella and Boyd, 1972, 1974; Kushiro, 1969; Warner and Luth, 1974; Boyd, 1970) along with some electron microprobe data on coexisting phases. Hensen (1973), on the basis of experimental work on natural pyroxenes between 22.5–40.5 kbar and 1100°–1410°C, concluded that the behavior of the orthopyroxene limb of the solvus with varying pressure, temperature, and Fe/Mg ratio is complicated and that the $Ca/(Ca +$

Mg) ratio of orthopyroxene increases with temperature and decreases with pressure. A critical evaluation of all the available data on the enstatite limb of the solvus strongly points toward not only its dependence on temperature but also on pressure and supports the findings of Hensen (1973), Akella (1974), and Mysen and Boettcher (1975).

Data and discussion

Data available in the literature on the compositions of coexisting pyroxene pairs are used. The electron microprobe data on the En–Di solvus at 30 kbar (Nehru and Wyllie, 1974) along with the standard deviation for each set of data are given in Table 1. The smaller spread in compositions on En_{ss} at each temperature (particularly between 1000–1300°C) compared to the Di_{ss} compositional spreads is reflected in the standard deviations. Thus the enstatite

TABLE 1. En_{ss} and Di_{ss} compositional data (Nehru and Wyllie, 1974) 30 kbar

Temp. °C	En_{ss} comp. (Di mol.%)			Di_{ss} comp. (Di mol.%)		
	n	\bar{x}	σ	n	\bar{x}	σ
1000	4	2.5	0.190	5	89.5	2.029
1100	5	3.8	0.158	6	86.0	2.316
1150	7	3.9	0.363	8	83.7	1.585
1200	9	4.8	0.386	10	83.8	0.710
1250	6	5.9	0.251	8	80.4	0.721
1300	4	5.9	0.359	6	78.7	1.808
1400	7	7.2	1.113	9	69.6	1.321
1500	6	9.1	1.307	9	57.3	2.934

n = Number of grains analyzed
 \bar{x} = Mean
 σ = Standard deviation

limb of the solvus is more precisely defined (despite its steep slope) than the diopside limb. Assuming this to be true of the data available from the iron-free system at other pressures also (investigated by Lindley and Dixon, 1975; Mori and Green, 1975; Warner and Luth 1974; Boyd and Schairer, 1964; and Atlas, 1952), the En_{ss} data are ideally suitable for testing the effect of pressure or the lack of it on the enstatite limb of the solvus.

The smaller spread in the En_{ss} compositions compared to the Di_{ss} compositions has to do with the differences in kinetics of equilibration of these two minerals. Therefore, use of En_{ss} compositions in temperature estimations should yield values of greater accuracy than those obtained from Di_{ss} compositional measurements. However, the smaller variation in the En_{ss} compositions with temperature, as compared to those of Di_{ss} , offsets this accuracy.

Compositional data of the En_{ss} coexisting with Di_{ss} in the pure (Fe, Al, and Ti free) system from different temperatures and pressures are plotted in Figure 1. Isobaric lines shown in this diagram are fitted, by inspection, to data points available at each pressure. The lines for the 30 kbar electron microprobe data from Nehru and Wyllie (1974) and the 2 kbar data from Warner and Luth (1974) clearly display a large separation, indicating the pressure dependence of the data. The other data support this conclusion. The 20 kbar data from Lindley and Dixon (1975) show a trend parallel to the 30 kbar data. The 500 bar data from Boyd and Schairer (1964) and Atlas (1952) are insufficient (only two data points for orthoenstatite in this temperature range) to draw significant conclusions but are in the correct direction and lend support to the argument. The 5 and 10 kbar data

from Warner and Luth are indistinguishable in terms of variation in pressure and are close to the 2 kbar data. The 2 and 5–10 kbar lines are not parallel to the 30 and 20 kbar lines. The 30 and 20 kbar lines are based on electron microprobe data and are considered more reliable.

Data on En_{ss} coexisting with Di_{ss} are plotted on a P - T diagram with $Ca/(Ca + Mg)$ as the variable and are shown in Figure 2. A family of curves with equal $Ca/(Ca + Mg)$ ratios at 0.005 intervals are visually fitted to the data. The data points used in Figure 2 are the same as those used in Figure 1. The curves clearly show a positive slope and are useful for estimating the temperature, once the composition of the En_{ss} is accurately determined and the pressure is determined or assumed. However, these curves are not applicable to natural iron-bearing systems where the situation becomes more complex due to the addition of one more variable, namely iron.

Figure 3 shows the effect of iron. $Ca/(Ca + Mg + Fe)$ compositions of En_{ss} coexisting with Di_{ss} from synthetic and natural systems are plotted against temperature for pressures of 29, 30, and 31 kbar (data from Akella and Boyd, 1974; Green, 1973; and Kushiro *et al.*, 1972) and compared with the line obtained from the data of Nehru and Wyllie (1974) at 30 kbar. The $Mg/(Mg + Fe)$ values of the individual points

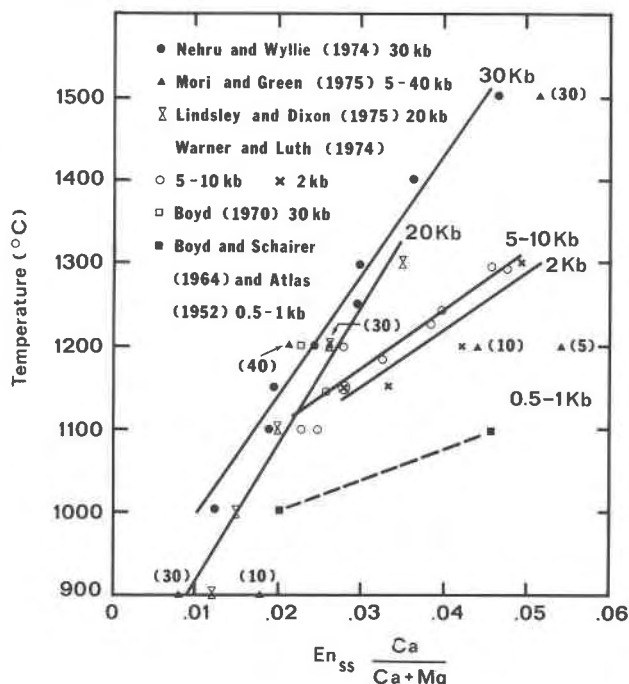


FIG. 1. $Ca/(Ca + Mg)$ data from En_{ss} coexisting with Di_{ss} (iron-free system) from different pressures plotted against $T^{\circ}C$.

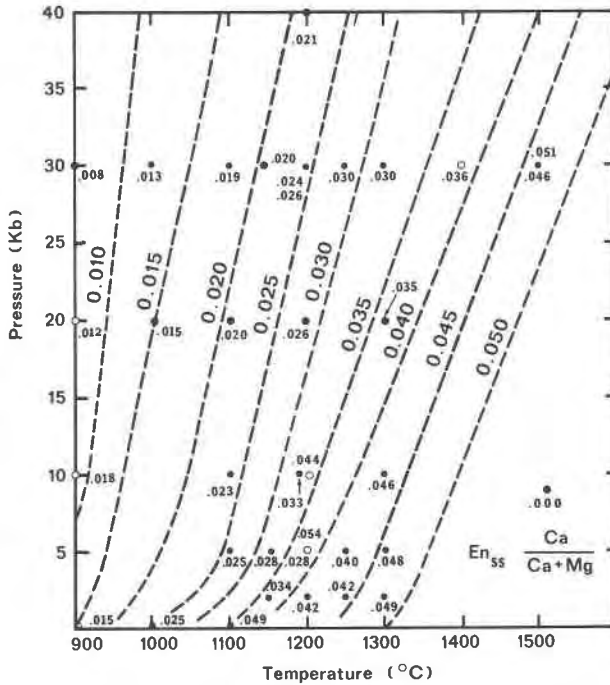


FIG. 2. P - T graph showing the variation of $\text{Ca}/(\text{Ca} + \text{Mg})$ for En_{88} coexisting with Di_{88} (iron free system). Data points clearly inconsistent with the family of curves are shown as open circles.

are also shown in the diagram. With the addition of Fe, for a given temperature and pressure, the $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})$ value tends to be higher. Also there is a progressive decrease of $(\text{Mg}/\text{Mg} + \text{Fe})$ values away from the line drawn for the iron-free data. It is conceivable that a systematic relationship exists, and a family of lines relating temperature and $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})$ at various values of $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio could be drawn. However, it is premature to draw such lines on this plot because of the paucity of data. Attempts at determining the effect of Fe on this plot at other pressures also yield results similar to the ones obtained at 30 kbar. Figure 4 compares the lines presented in Figure 1 from iron-free systems with those of Hensen (1973) for iron-bearing systems. Isobaric lines on this diagram from the iron-bearing systems show steeper slopes compared to their iron-free counterparts. Addition of Fe thus brings about smaller variation in the $\text{Ca}/(\text{Ca} + \text{Mg})$ value, and any errors in the measurement of this value lead to larger errors in the temperature estimates.

Conclusions

The smaller spread in the En_{88} compositions compared to the Di_{88} compositions (Nehru and Wyllie, 1974) defines the enstatite limb of the En - Di solvus more precisely. Assuming this to be true of the data

available at other pressures also, the En_{88} data are ideally suitable for testing the effect of pressure on the enstatite limb of the solvus.

A critical evaluation of the data on the compositional variation of En_{88} with temperature and pressure in the interval 900–1500°C and 0.5 kbar to 40 kbar respectively shows temperature as well as pressure dependence and supports the contention of Hensen (1973) Akella (1974), and Mysen and Boettcher (1975). A family of $\text{Ca}/(\text{Ca} + \text{Mg})$ curves fitted to available data on the iron-free En - Di system on a P - T graph has positive slopes. Errors up to 250°C can result in temperature estimates if the pressure effect is neglected in the range 0.5 bar–40 kbar. However, in the pressure range 20 to 30 kbar and temperature range 1000–1300°C, the temperatures determined using the enstatite limb of the solvus are not drastically affected (error range 30 to 65°C).

Addition of iron (lower $\text{Mg}/(\text{Mg} + \text{Fe})$) increases the $\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe})$ value at a given temperature and pressure, and available data are insufficient to draw conclusions of compositional variations in a P - T grid.

Until such time as we have more data on this important system to precisely define this variable as well, the geothermometric applications to naturally occurring rocks have to be used with caution.

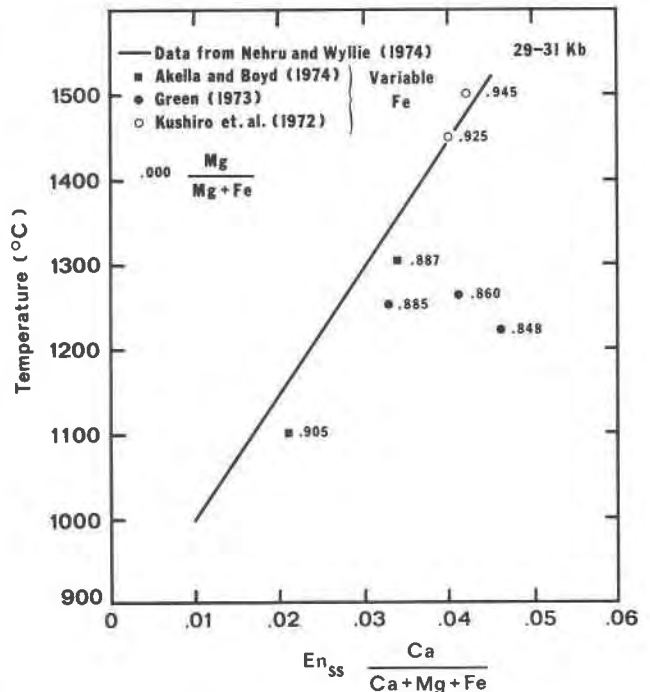


FIG. 3. Effect of Fe on the composition of En_{88} coexisting with Di_{88} at 29–31 kbar pressure and 900°–1500°C temperature.

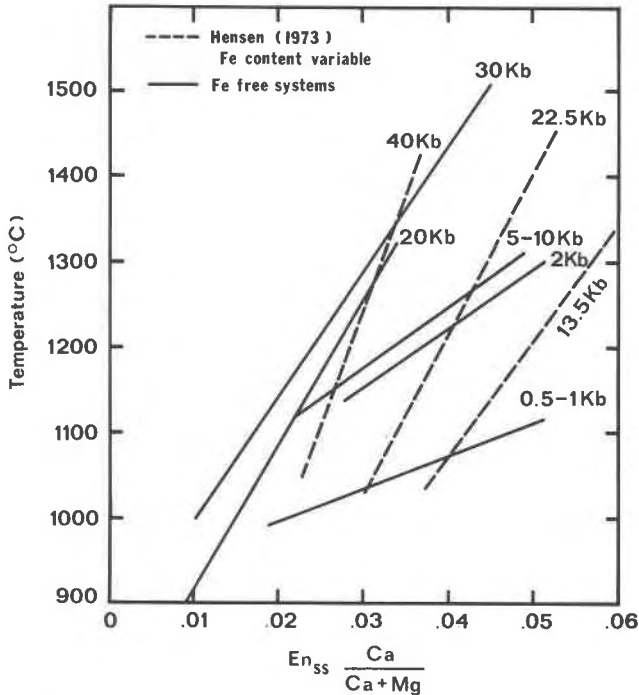


FIG. 4. Effect of Fe on the $\text{Ca}/(\text{Ca} + \text{Mg})$ of En_{ss} from iron free and iron-bearing systems at 0.5–40 kbar and 1000°–1500°C.

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