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

C. E. NEHRU

Department of Geology Brooklyn College of the City University of New York Brooklyn, New York 11210

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 pressuredependent (*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 ironbearing 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. En₈₉ and Di₈₉ compositional data (Nehru and Wyllie, 1974) 30 kbar

Enst	comp.	(D1	mo1.%)	Dissc	omp. (Di	mo1.%)
emp. ^o C	n	x	σ	n	x	σ
1000	4	2.5	0.190	5	89.5	2.02
1100	5	3.8	0.158	6	86.0	2.31
1150	4 5 7 9	3.9	0.363	8	83.7	1.58
1200	9	4.8	0.386	10	83.8	0.71
1250	6	5.9	0.251	8	80.4	0.72
1300	4	5.9	0.359	6	78.7	1.80
1400	7	7.2	1.113	9	69.6	1.32
1500	6	9.1	1.307	9	57.3	2.93
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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 Lindsley 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 Engs coexisting with Dias 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 Lindsley 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

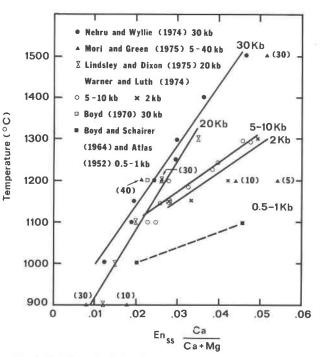


FIG. 1. Ca/(Ca + Mg) data from En_{ss} coexisting with Di_{ss} (iron-free system) from different pressures plotted against $T^{\circ}C$.

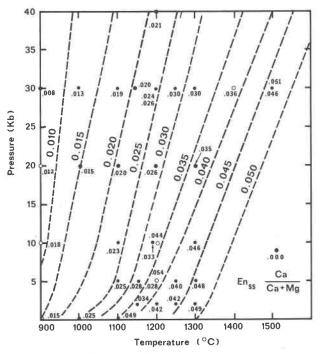


FIG. 2. *P-T* graph showing the variation of Ca/(Ca + Mg) for En_{88} coexisting with Di_{88} (iron free system). Data points clearly inconsistent with the family of curves are shown as open circles.

are also shown in the diagram. With the addition of Fe, for a given temperature and pressure, the Ca/(Ca + Mg + Fe) value tends to be higher. Also there is a progressive decrease of (Mg/Mg + 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 Ca/(Ca + Mg + Fe) at various values of Mg/(Mg + 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 ironfree counterparts. Addition of Fe thus brings about smaller variation in the Ca/(Ca + 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_{ss} compositions compared to the Di_{ss} 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_{ss} 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_{ss} 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 Ca/(Ca + 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 Mg/(Mg + Fe) increases the Ca/(Ca + Mg + 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.

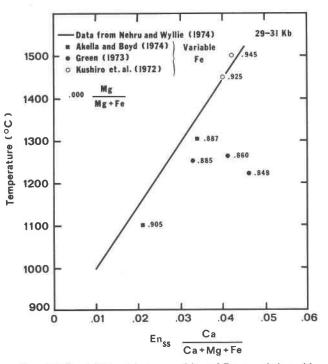


FIG. 3. Effect of Fe on the composition of En_{ss} coexisting with Di_{ss} at 29–31 kbar pressure and 900°-1500°C temperature.

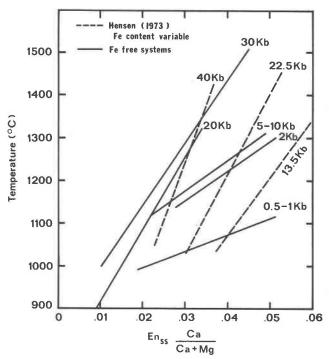


FIG. 4. Effect of Fe on the Ca/(Ca + Mg) of En_{ss} from iron freeand iron-bearing systems at 0.5–40 kbar and 1000°-1500°C.

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References

AKELLA, J. (1974) Solubility of Al₂O₃ in orthopyroxene coexisting with garnet and clinopyroxene for compositions on the diopside-pyrope join in the system CaSiO₃-MgSiO₃-Al₂O₃. *Carnegie Inst. Wash. Year Book*, **73**, 273-278.

---- AND F. R. BOYD (1972) Partitioning of Ti and Al between pyroxenes, garnets, and oxides, *Carnegie Inst. Wash. Year Book*, **71**, 378-384.

AND ——— (1974) Petrogenetic grid for garnet peridotites. Carnegie Inst. Wash. Year Book, 73, 269-373.

- ATLAS, L. (1952) The polymorphism of MgSiO₃ and solid state equilibria in the system MgSiO₃-CaMgSi₂O₆. J. Geol. 60, 125-147.
- BOYD, F. R. (1970) Garnet peridotites and the system CaSiO₃-MgSiO₃-Al₂O₃. *Mineral. Soc. Am. Spec. Pap.* **3**, 63-75. AND J. F. SCHAIRER (1964) The system MgSiO₃-CaMgSi₂O₆. *J. Petrol.* **5**, 275-309.
- DAVIS, B. T. C. AND F. R. BOYD (1966) The join Mg₂Si₂O₆-CaMgSi₂O₆ at 30 kilobars pressure and its application to pyroxenes from kimberlites. J. Geophys. Res. 71, 3567-3576.
- GREEN, D. H. (1973) Conditions of melting of basanite magma from garnet peridotite. *Earth Planet. Sci. Lett.* 17, 456-465.
- HENSEN, B. J. (1973) Pyroxenes and garnets as geothermometers and barometers. Carnegie Inst. Wash. Year Book, 72, 527-534.
- HOWELLS, S. AND M. J. O'HARA (1975) Paleogeotherms and the diopside-enstatite solvus. *Nature*, 254, 406–408.
- KUSHIRO, I. (1969) The system forsterite-diopside-silica with and without water at high pressures. Am. J. Sci. 267A, 269-294.
- ——, N. SHIMIZU, Y. NAKAMURA AND S. AKIMOTO (1972). Compositions of coexisting liquid and solid phases formed upon melting of natural garnet and spinel lherzolites at high pressures: A preliminary report. *Earth Planet Sci. Lett.* **14**, 19–25.
- LINDSLEY, D. AND S. A. DIXON (1975) Coexisting diopside and enstatite at 20 kbar and 900°-1200°C (abstr.) Geol. Soc. Am. Abstr. Progr. 7, 1171.
- MORI, T. AND D. H. GREEN (1975) Pyroxenes in the system $Mg_2Si_2O_6$ -CaMgSi₂O₆ at high pressure. *Earth Planet. Sci. Lett.* **26**, 277-286.
- MYSEN, B. O. AND A. L. BOETTCHER (1975) Melting of a hydrous mantle: II. Geochemistry of crystals and liquids formed by anatexis of mantle peridotite at high pressures and high temperatures as a function of controlled activities of water, hydrogen, and carbon dioxide. J. Petrol. 16, 549-593.
- NEHRU, C. E. AND P. J. WYLLIE (1974) Electron microprobe measurement of pyroxenes coexisting with H₂O-undersaturated liquid in the join CaMgSi₂O₆-Mg₂Si₂O₆-H₂O at 30 kilobars, with applications to geothermometry. *Contrib. Mineral. Petrol.* 48, 221-228.
- WARNER, R. D. AND W. C. LUTH (1974) The diopside-orthoenstatite two phase region in the system CaMgSi₂O₆-Mg₂Si₂O₆. Am. Mineral. 39, 98-109.