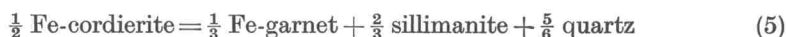


Information on the value of K may be obtained by study of the reaction



which has been realized by Richardson (1968). This reaction is at equilibrium along a given curve in the P - T plane, at any point of which

$$\left(\frac{1}{2} F_{\text{f}}^{\text{c}} - \frac{1}{3} F_{\text{f}}^{\text{g}}\right) = \left(\frac{2}{3} F_{\text{sill}} + \frac{5}{6} F_{\text{quartz}}\right) \quad (6)$$

Now for a given temperature T , if the equilibrium pressure for Eq. (5) is P_{e}^{a} , then at any other pressure, P

$$\left(\frac{1}{2} F_{\text{f}}^{\text{c}} - \frac{1}{3} F_{\text{f}}^{\text{g}}\right) = \frac{2}{3} F_{\text{sill}} + \frac{5}{6} F_{\text{quartz}} + (P - P_{\text{e}}^{\text{a}}) dV \quad (7a)$$

where the possible difference in compressibility between phases is ignored. dV is the volume change in reaction (5).

Now an exactly analogous equation to (7) holds for the conversion of magnesian cordierite. Using the data of Robie and Waldbaum (1968), Iiyama (1956), Schreyer (1965), Deer *et al.* (1963, vol. 1) and Rickwood (1968), the change in volume of this reaction (26.35 cc per mol) is virtually identical to that of the iron analogue, (26.49 cc per mol). The equation analogous to (7a) is therefore

$$\left(\frac{1}{2} F_{\text{m}}^{\text{c}} - \frac{1}{3} F_{\text{m}}^{\text{g}}\right) = \frac{2}{3} F_{\text{sill}} + \frac{5}{6} F_{\text{quartz}} + (P - P_{\text{e}}^{\text{m}}) dV \quad (7b)$$

subtracting (7a) from (7b) and substituting in (4) we obtain

$$\begin{aligned} \left(\frac{1}{2} F_{\text{m}}^{\text{c}} - \frac{1}{3} F_{\text{m}}^{\text{g}}\right) - \left(\frac{1}{2} F_{\text{f}}^{\text{c}} - \frac{1}{3} F_{\text{f}}^{\text{g}}\right) &= -(P_{\text{e}}^{\text{p}} - P_{\text{e}}^{\text{a}}) dV \\ &= -RT \ln (X_{\text{m}}^{\text{c}}/1 - X_{\text{m}}^{\text{c}}) (X_{\text{f}}^{\text{g}}/1 - X_{\text{f}}^{\text{g}}). \end{aligned} \quad (8)$$

From Eq. (8) it is clear that if the composition of coexisting garnet and cordierite are known, and the pressures at which pure cordierite end members are converted to garnet are known, the temperature can be found. (8) may be rearranged to give

$$T = (dP \cdot dV/R) (1/\ln K) \quad (9)$$

where dP is $(P_{\text{e}}^{\text{p}} - P_{\text{e}}^{\text{a}})$.

It may also be shown, given ideal solution in garnet and cordierite, that the pressure is fixed for a particular coexisting pair. Consider pure Fe-cordierite in equilibrium with pure almandine. Now suppose that magnesium is added to the system. The magnesian component of the cordierite and garnet would be in equilibrium with each other at P_{e}^{p} . Thus for garnet to remain in equilibrium with cordierite in the magnesium bearing system, the pressure must rise in such a way that the change in free energy due to the magnesium components is balanced by the change in free energy of the iron components. Since the volume change for conversion of cordierite to garnet is invariant with composition, this condition may be expressed by

$$(P_{\text{e}}^{\text{p}} - P) (X_{\text{m}}^{\text{g}} + X_{\text{m}}^{\text{c}}) dV = (P - P_{\text{e}}^{\text{a}}) (X_{\text{f}}^{\text{g}} + X_{\text{f}}^{\text{c}}) dV$$

By algebraic rearrangement, and substitution of $(1 - X_{\text{m}}^{\text{g}})$ for X_{f}^{g} and $(1 - X_{\text{m}}^{\text{c}})$ for X_{f}^{c} , this may be reduced to

$$P = P_{\text{e}}^{\text{a}} + (dP/2) (X_{\text{m}}^{\text{g}} + X_{\text{m}}^{\text{c}}) \quad (10b)$$

Given appropriate experimental data, it is thus possible to determine both temperature and pressure from the compositions of coexisting garnet and cordierite.

Experimental Considerations

The variation with temperature of the equilibrium pressure between Fe-cordierite and almandine is known from the work of Richardson (1968), but similar data is not available for pyrope. In fact the work of Schreyer (1970) and Henson and Green (1970) strongly suggests that the direct breakdown of magnesian cordierite to pyrope can not be experimentally realized because of the appearance of hypersthene and/or sapphirine as a breakdown product of cordierite. This difficulty does not invalidate Eq. (9), but it requires experimental work to establish the value of dP . From Eq. (9), it may be seen that for a given T , one value for K would establish dP . Other values of K at the same temperature would serve to demonstrate the internal consistency of the model, that is the validity of the ideal solution assumption for garnet and cordierite, and the neglect of compressibilities in calculating dP .

An experimental program was undertaken to establish the value of dP for various temperatures in the metamorphic range. Gels with the stoichiometric composition of cordierite with Fe/Fe + Mg ratios 0.8, 0.6, 0.4 and 0.2 were prepared by dissolving appropriate amounts of standardized ferrous oxalate, magnesium oxalate, and aluminum wire in nitric acid, and gelling with tetraethyl orthosilicate. After dessication, the iron in the products was reduced to the ferrous state by passing CH_4 over it at 800°C for 8 hours. Analysis of the products after this treatment showed that they were 100% cordierite and that the ferrous/ferric ratio exceeded 20 in all materials. Pure cordierite with Fe/Fe + Mg > 0.8 can not be prepared by this method due to appearance of a spinel phase.

The experiments were carried out in an internally heated pressure vessel similar to that described by Goldsmith and Heard (1961), using methane as a pressure medium. Temperatures were measured with 3 Pt - Pt/10% Rh thermocouples, placed at 0.5 cm intervals along the sample capsules, and pressure was measured by a resistance piezometer standardized against a dead-weight tester. The specimens were welded into 3 mm diameter by 0.1 mm wall Pt tube with about 5 weight percent H_2O , and four samples of different Fe/Fe + Mg ratio were run at one time, permitting the simultaneous determination of the garnet cordierite equilibrium over a range of compositions. The empty space in the furnace was filled by graphite rods, assuring maintenance of the oxygen fugacity at the graphite-methane buffer. Quoted temperature are believed to be accurate within $\pm 4^\circ$, and pressure within 0.1 kilobar.

All runs in this apparatus were 48 hours in length. Sixty day runs in standard Tuttle bombs, using the graphite-methane buffer, gave results identical within measurement errors to the 48 hour runs at 600° , 6 kilobars, 40 mol per cent magnesium molecule, and 800° , 5 kilobars, 20 mol percent magnesium molecule.

The experimental products were X-rayed in 114.6 mm. Debye-Scherrer cameras using silica as an internal standard, and examined in immersion oils. The first appearance of garnet was more easily detected optically. The composition of the garnet was determined by assuming that the cell edge and refractive index were