Contrib. Mineral. Petrol. 56, 289–295 (1976)

LEE-SM 76-0453

Petrology

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Cordierite Breakdown under High-Pressure Hydrous Conditions

A Comment

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Abstract. Green and Vernon (1974) have experimentally determined a divariant field of cordierite-orthoamphibole-kyanite-quartz with a slope of 12 ± 4 bars per °C occurring between 8.0 and 10.4 kbar at 750° C and between 9.5 and 11.3 kbar at 850° C. However, the writers' thermodynamic calculation of the divariant band indicates a more limited range of 0.65 and 0.7 kbar at 750° C and 850° C respectively, with an estimated error of ± 0.2 kbar.

Introduction

Green and Vernon (1974) (see also Vernon, 1972a, b) present experimental results based on a natural cordierite-aluminous anthophyllite-kyanite assemblage with an average composition of about Mg_{87}[1]. Their results suggest a field of cordierite-gedrite-kyanite-quartz which is about 2.4 kbar wide at 750° C and 1.8 kbar wide at 850° C. Green and Vernon interpret this field as a reasonable approach to divariant equilibrium but suggest the possibility that the field may have been enlarged due to incomplete reaction. Unfortunately, they did not estimate relative changes in experimental products.

It occurred to us that it would be worthwhile to calculate the width of the divariant field to test the importance of incomplete reaction to their results.

Basic Relations

For the calculations discussed below, the following assumptions were made: (1) orthoamphibole solid solution best fits the multi-site ionic solution model,

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[1] Mg_{87} refers to the ratio 100 Mg/Mg + Fe in atomic %

while the octahedral positions in cordierite are energetically equal; (2) activity coefficients remain constant over the range of composition, pressure, and temperature being considered, and therefore may be ingnored; (3) tetrahedral Al ions reside near octahedral Al to maintain charge balance, and thus tetrahedral ions do not contribute to amphibole disorder (Wood and Banno, 1973); (4) gedrite, identified as anthophyllite II in Green and Vernon's experiments, represents the stable amphibole; (5) over the limited pressure-temperature range being considered pressure and temperature effects on Al content of gedrite may be ignored.

The following relations exist between the gedrite sites (M 1, M 2, M 3, M 4) and between gedrite and cordierite sites (X_{Mg}^{M1} indicates mole fraction of Mg in site M 1).

$$\frac{X_{Mg}^{M1}}{X_{Fe}^{M1}}=\frac{X_{Mg}^{M2}}{X_{Fe}^{M2}}=\frac{X_{Mg}^{M3}}{X_{Fe}^{M3}}, \tag{1}$$

$$X_{Mg}^{M2}+X_{Fe}^{M2}+X_{Al}^{M2}=1, \tag{2}$$

$$X_{Al}^{M1}=X_{Al}^{M3}=X_{Al}^{M4}=0, \tag{3}$$

$$\frac{X_{Mg}^{M4}}{X_{Fe}^{M4}}\frac{X_{Mg}^{M1}}{X_{Fe}^{M1}}=0.29=K_{D1}, \tag{4}$$

$$\frac{X_{Mg}^{M1}}{X_{Fe}^{M1}}\frac{X_{Mg}^{Cd}}{X_{Fe}^{Cd}}=0.52=K_{D2}. \tag{5}$$

Equations (1)–(4) follow from Ross and Papike (1970), who show that in gedrite M 2 contains all octahedral Al and M 4 concentrates Fe relative to other sites. Their K_{D1} values of 0.16 and 0.23 are increased to account for probable higher temperatures of Green and Vernon's experiments relative to natural minerals and possibility of slight ordering on cooling in the natural specimens. For coexisting cordierite and orthoamphibole in the experiments compositions average $Mg_{92.5}$ and Mg_{80} respectively. This and Equations (1)–(4) allow determination of K_{D2}.

Aluminum in Gedrite

An attempt to calculate the effect of Mg-Fe variation on cordierite breakdown should include the Al content of the gedrite and the possibility of variation in Al content with Mg/Fe ratio. Reaction of cordierite with the anthophyllite end member produces the gedrite end member:

$$3\,Mg_7Si_8O_{22}(OH)_2+7\,Mg_2Al_4Si_5O_{18}\cdot 0.7\,H_2O$$
$$\rightleftharpoons 7\,Mg_5Al_2Si_6Al_2O_{22}(OH)_2+17\,SiO_2+0.9\,H_2O. \tag{6}$$

Cordierite containing $0.7\,H_2O$ is consistent with results of Schreyer and Yoder (1964). The equilibrium constant for Equation (6) becomes:

$$K_1=\frac{X_{Mg}^{M1^8}\,X_{Mg}^{M3^4}\,X_{Mg}^{M4^8}\,X_{Al}^{M2^{14}}}{X_{Mg}^{Cd^{14}}\,X_{Mg}^{M2^6}}=2.9\times 10^{-5}. \tag{7}$$

Table 1. Site occupancies for coexisting gedrite and cordierite at compositions of interest

	Cordierite	Gedrite	$X_{Mg}^{M1}=X_{Mg}^{M3}$	X_{Mg}^{M4}	X_{Mg}^{M2}	$X_{Al}^{M2}=x$
a)	Mg_{100}	Mg_{100}	1.000	1.000	0.615	0.385
b)	$Mg_{95.6}$	Mg_{87}	0.919	0.768	0.524	0.430
c)	Mg_{87}	$Mg_{68.5}$	0.777	0.503	0.385	0.504

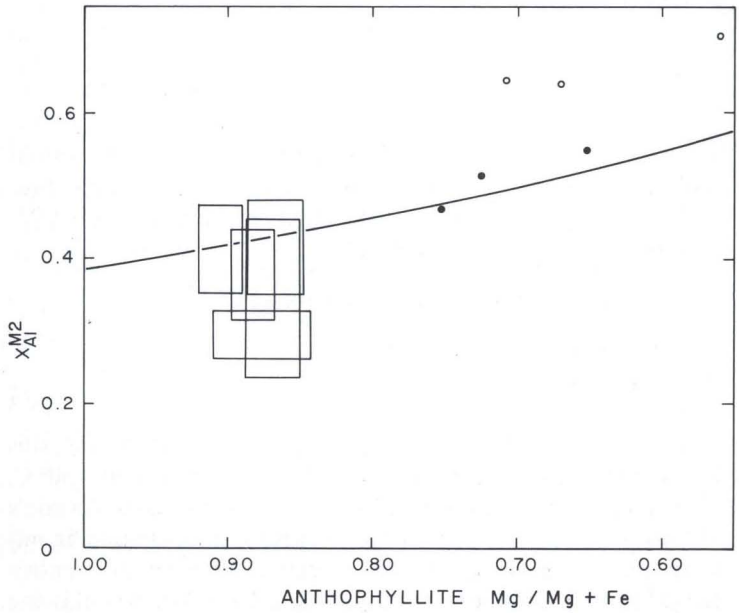


Fig. 1. Calculated effect of gedrite composition on X_{Al}^{M2}. Boxes: range for anthophyllite II (Green and Vernon, 1974); closed symbol: gedrite with cordierite at high pressure (Robinson and Jaffe, 1969); open symbol: gedrite with kyanite (Deer et al., 1963; Robinson and Jaffe, 1969)

To formulate this constant each mole fraction involved in Equation (6) is raised to a power equal to the site multiplicity (M 1 = M 2 = M 4 = 2, M 3 = 1) times the number of moles. Appearance of Mg in M 1, M 3, and M 4 on both sides of the equation results in powers of 8 and 4 for these mole fractions.

Once evaluated, Equation (7) can be used to determine X_{Al}^{M2} for any gedrite composition coexisting with cordierite. Equation (7) was evaluated at Mg_{87} gedrite composition using $X_{Al}^{M2}=0.43$ (11.0 weight % Al_2O_3). The other Al contents were calculated (Table 1) using Equations (1)–(5) and (7). Plotted in Figure 1, these compositions pass through the lower portion of the field of high pressure gedrites. For a given temperature, gedrite should contain its maximum Al at the upper pressure limit of cordierite as indicated by negative ΔV of Equation (6) and positive ΔV for the analogous reaction using kyanite instead of cordierite. The calculated curve may be low for one or more of the following reasons: (1) Green and Vernon's (1974) anthophyllite II may be below the equi-

librium Al content; (2) the kyanite-gedrite assemblages in Figure 1 may represent significantly lower temperatures under compositional conditions where talc is not likely; or (3) the assumption of constancy of activity coefficients for gedrite was not entirely correct.

The approach used here is comparable to that used by Wood and Banno (1973) on orthopyroxene with garnet. If these results are correct, the scarcity of Mg-rich gedrites may result from the fact that most magnesian rocks have low Al. Finally, if tetrahedral disorder were also allowed, it would further reduce the Mg-Fe dependence of gedrite Al with cordierite.

Divariant Field

For calculating the effect of Mg/Fe ratio on cordierite equilibria, the initial equation is the sum of a gedrite-producing equation and an anthophyllite-producing equation. The ratio of gedrite to anthophyllite is fixed by $x = X_{Al}^{M2}$. The equation is balanced for one mole of amphibole.

$$(3.5-x)\,Mg_2Al_4Si_5O_{18}\cdot 0.7\,H_2O \rightleftharpoons x\,Mg_5Al_2Si_6Al_2O_{22}(OH)_2$$
$$+(1-x)\,Mg_7Si_8O_{22}(OH)_2+(7-4x)\,Al_2SiO_5$$
$$+(2.5+x)\,SiO_2+(1.45-0.7x)\,H_2O. \qquad (8)$$

At Mg_{100} composition $x=0.385$ (Table 2a). A phase boundary for this reaction was chosen to pass through points at 750° C, 10.2 kbar, and 830° C, 11.2 kbar. The line was drawn parallel to the average slope of Green and Vernon's divariant field and through the cordierite-talc-enstatite-sillimanite-quartz invariant point in the Fe-free system (Fig. 2) approximately established by Newton (1972). The somewhat arbitrary estimate of this boundary is based on the following evidence: (1) if the boundary were significantly lower, gedrite would have appeared in some of Newton's runs near the invariant point; (2) if the boundary were significantly higher, presence of Fe would not have stabilized gedrite as a cordierite breakdown product as shown experimentally and in nature by Green and Vernon (1974); (3) the assumed boundary gives a calculated divariant field within the field experimentally discovered by Green and Vernon. Estimated error in the positioning of this initial reaction boundary is ± 1 kbar.

For the calculations molar volumes of minerals are from Robie and Waldbaum (1968), except the values for gedrite were calculated from anthophyllite cell dimensions given by Greenwood (1963) and corrected for Al by analogy with data of Skinner and Boyd (1964) on aluminous enstatite. Molar volumes of water are from Burnham, Holloway, and Davis (1969), extrapolating values beyond 10 kbar. By iteration ΔV was evaluated at about the pressure at which the reaction occurs (Table 2).

Green and Vernon (1974) used a composition of about Mg_{87} in their experiments. The composition limits for cordierite and gedrite in the divariant field determined from relations 1–5 and 7 are given in Table 1(b, c). At the top of the divariant field cordierite $Mg_{95.6}$ begins to form from gedrite Mg_{87}, and at the bottom, the last gedrite ($Mg_{68.5}$) disappears leaving only cordierite Mg_{87}. Green

Table 2. Molar volumes for reaction 8

	Applicable Gedrite composition	$X_{Al}^{M2} = x$	Evaluated at (kbar)	$-\Delta V$ (cal/bar)
a)	Mg_{100}	0.385	10.2	3.24
b)	Mg_{87}	0.430	9.8	3.17
c)	$Mg_{68.5}$	0.504	9.1	3.00
d)	Any	0.000	9.7	3.76

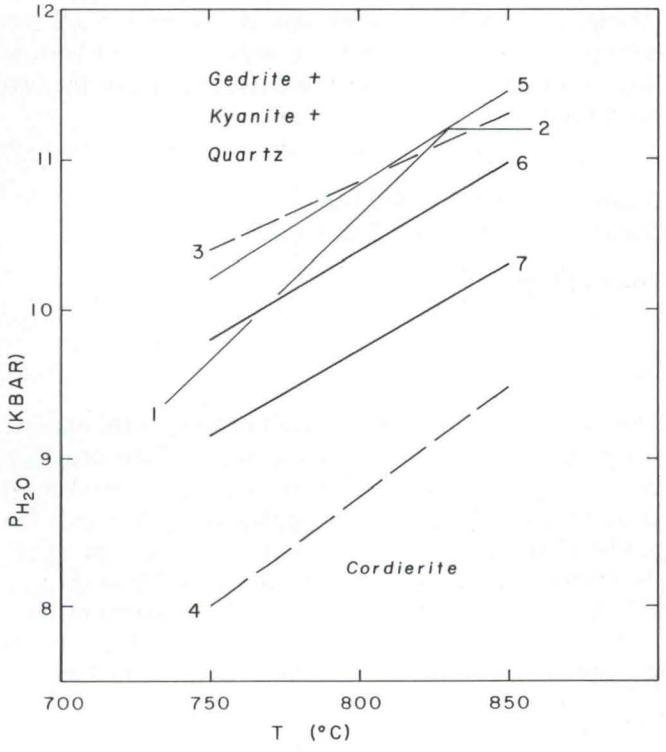


Fig. 2. Illustration of cordierite-gedrite-quartz-kyanite divariant field. *1* Cordierite⇌Talc – Sillimanite – Quartz (Newton, 1972); *2* Cordierite⇌Enstatite – sillimanite – Quartz (Newton, 1972). *3–4* Cordierite-Gedrite-Quartz-Kyanite divariant field (Green and Vernon, 1973); *5* initial boundary assumed for Fe-free Cordierite ⇌ Gedrite + Quartz + Kyanite; *6–7* Cordierite-Gedrite-Quartz-Kyanite divariant field calculated

and Vernon obtained cordierite as magnesian as $Mg_{94.4}$ and orthoamphibole as iron-rich as $Mg_{76.1}$.

Equation (8) with $x = 0.385$ (Table 2, a) applies only to the first increment of pressure shift from the initial boundary. As Fe content increases, gedrite Al increases slightly, thus changing reaction coefficients and ΔV. The pressure shift

with composition is given by the relation:

$$-\frac{\overline{\Delta V}\Delta P}{RT} = \ln K_2(\text{final}) - \ln K_2(\text{initial}) \tag{9}$$

K_2, based on Equation (8), is given by:

$$K_2 = \frac{X_{Mg}^{M1\,3}\, X_{Mg}^{M4\,2}\, X_{Mg}^{M2\,(2-2x)}\, X_{Al}^{M2\,2x}}{X_{Mg}^{Cd\,(7-2x)}}. \tag{10}$$

The ΔP from this initial reaction to the top of the divariant field is evaluated using data of Table 1(a) for initial K_2 and Table 1(b) for final K_2. Because the reaction is continually changing along the pressure shift $\overline{\Delta V}$ is the average ΔV from Table 2(a, b). A similar procedure may be used to calculate ΔP to the bottom of the divariant field using data from Table 1(a, c) and Table 2(a, c). For the two temperatures used, the results are:

	750° C	850° C
Top	$\Delta P = -$ 403 bars	$\Delta P = -$ 442 bars
Bottom	$\Delta P = -1043$ bars	$\Delta P = -1145$ bars.

These boundaries are shown in Figure 2.

Discussion of Error

Estimating maximum error of these calculations is difficult because of the number of assumptions and relations involved. Recall that the position of the divariant field has a ± 1 kbar error. A few additional calculations were undertaken at 750° C in an effort to evaluate error in the *width* of the calculated field. A calculation made with no Al in gedrite (Table 2, d) narrows the divariant field by about 85 bars. Doubling the compositional affect of gedrite Al ($x = 0.260$ at Mg_{100}, 0.356 at Mg_{87}, 0.504 at $Mg_{68.5}$) narrows the calculated field by about 60 bars. Considering possible errors and pressure-temperature effects in K_{D1}, K_{D2}, and Al content total error in the width of the divariant field is estimated at ± 200 bars.

Conclusion

Thermodynamic calculations suggest that the equilibrium divariant field for Green and Vernon's (1974) experiments should have been 640 ± 200 bars wide at 750° C and 700 ± 200 bars wide at 850° C. Study of their diagram shows that at least five of their experimental runs between 700° and 780° C must represent incomplete reaction rather than divariant equilibrium. Experiments at 820° and 860° C may well represent equilibrium in that they indicate field widths of $\gtrsim 900$ bars at 820° C and between 0 and 1800 bars at 860° C.

These results emphasize the importance of thermodynamic analysis in interpretation of experimental results.

Acknowledgements. We thank B. J. Wood for his constructive review.

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Received June 20, 1975/Accepted January 10, 1976