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A Calorimetric Investigation of the Stability of Anhydrous Magnesium Cordierite with Application to Granulite Facies Metamorphism

R. C. Newton
The Department of the Geophysical Sciences, The University of Chicago
T. V. Charlu
James Franck Institute
O. J. Kleppa
James Franck Institute and The Department of the Geophysical Sciences,
The University of Chicago

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Abstract. The heats of solution of synthetic anhydrous Mg-cordierite and of its high-pressure breakdown assemblage sapphirine + quartz (+ enstatite ?) have been measured in a lead borate melt at 694° C. The ΔH of this reaction at this temperature and one atmosphere is 6.1 ± 1 kilocalorie per mole of cordierite.

A P-T stability diagram of cordierite relative to other synthetic phases in the system $MgO—Al_2O_3—SiO_2$ was constructed which satisfies the heat of reaction data and all other reliable observations pertaining to the stability of anhydrous cordierite. The stability field of cordierite is limited by boundaries of very small dP/dT slopes. The maximum pressure of cordierite stability is about 8 kilobars. Above an invariant point near 950° C the sapphirine-bearing assemblage is the stable breakdown product of cordierite. Below 950° C the stable breakdown assemblage is enstatite + sillimanite + quartz. New heat of solution data for orthorhombic enstatite are presented which allow a calculation of the lower-temperature breakdown boundary. This calculation is in good agreement with the boundary deduced above. The calculated breakdown pressure of cordierite at 700° C is 5.6 ± 1.5 kilobars. This is much lower than estimates of earlier workers and shows that cordierite stability is greatly restricted under very dry conditions.

Heat of solution data of natural low-iron cordierite and sapphirine samples are presented. These indicate that synthetic cordierite is energetically close to natural cordierite and is therefore an adequate stability model to apply to natural occurrences but that the synthetic sapphirine prepared by the breakdown of cordierite is quite different from natural sapphirine. An estimate of the breakdown relations of cordierite relative to natural sapphirine is presented, which looks quite like the diagram of the synthetic system except that the invariant point is shifted to considerably lower temperatures.

A consequence of the present work is that if conditions of metamorphism were very dry, pressures of only six to eight kilobars would have been necessary to produce the dense anhydrous assemblages equivalent to natural cordierite which are found in some ancient granulites. The subcrustal pressures considered necessary by some workers should not be regarded as established by presently available evidence.

Introduction

The application of experimental work on cordierite stability to granulites containing high pressure magnesian assemblages alternative to cordierite has resulted in some very high temperature and high pressure estimates for the genesis of rocks containing the assemblages orthopyroxene-aluminum silicate and sapphirine-quartz. Recent discoveries of these dense magnesian assemblages from Rhodesia (Chinner and Sweatman, 1968), Antarctica (Dallwitz, 1968) and Labrador (Morse and Talley, 1971; Meng and Moore, 1972) has given rise to estimates of 900–1200°C and 10–12 kilobars for conditions of recrystallization of some granulite terrains (c.f. Chatterjee and Schreyer, 1970). The very deep-seated, perhaps subcrustal, conditions of metamorphism inferred from experimental studies deserve close scrutiny. Some of the rocks described appear to be metasediments. Some mechanism for great vertical transport of rocks must be invoked if the above estimates give a valid picture of the metamorphism; high-grade metamorphism of this profound character has not been reported from younger terrains.

The experimental difficulties which could bias estimates of the upper pressure stability limits of cordierite have been discussed by Newton (1972). They include extreme sluggishness of the breakdown reaction below 1200°C in very dry systems (which might best represent many actual granulite metamorphic conditions) and the probability that water available to enter the cordierite structure could stabilize it by as much as four kilobars above the dry breakdown limit. It was suggested by Newton (1972) that these biasing factors could account for the negative dP/dT slopes reported for the breakdown of Mg-cordierite (Schreyer and Yoder, 1964; Hensen and Green, 1970; Schreyer and Seifert, 1969a) and for a tendency to overestimate the pressure of cordierite breakdown at temperatures below 1000°C.

The recently developed method of oxide-melt solution calorimetry has provided heat of formation and heat of reaction data in several important systems of minerals which do not dissolve readily in HF and which cannot be investigated by older techniques (Yokokawa and Kleppa, 1964; Navrotsky and Kleppa, 1967; Anderson and Kleppa, 1969; Navrotsky and Kleppa, 1973). The present study makes use of the new method to derive heat of reaction data, and hence, stability data for the high pressure breakdown reactions of Mg-cordierite to enstatite, sillimanite and quartz, and, at higher temperatures, to sapphirine and quartz. These data are used to extrapolate reliable high temperature experimental data to the probable conditions of granulite metamorphism. Measurements on synthetic and natural materials are presented and compared in order to examine possible effects of compositional variation and cation ordering which are impossible to duplicate in synthetic material but which might be of quantitative importance to the stability of cordierite in nature.

Experimental Methods and Results

Preparation of Calorimeter Materials

Synthetic Mg-Cordierite. Two samples of synthetic cordierite were used in the calorimeter. Phase-pure anhydrous Mg-cordierite was obtained from Tem Pres Co., State College, Pa. This material had an X-ray "distortion index" (Miyashiro, 1957) of about $\Delta = 0.10° \, 2\theta$. Another sample of Mg-cordierite was prepared by crystallizing a glass at 1380°C for 3 days. The glass was prepared by an arc-fusion method by the Muscle Shoals Electro-Chemical Co., Tuscumbia, Ala. According to the manufacturer, the glass composition corresponded to that of the Mg-cordierite formula with maximum departures of ± 0.3 wt. %. The crystallized cordierite had $\Delta = 0.15° \, 2\theta$. Details of the preparation of these and the other calorimeter materials used here are on file with the authors and will be made available upon request.

Table 1. Unit cell constants of sapphirine and quartz

	A (Å)	B (Å)	C (Å)	β (Deg.)	V (Å^3)
Sapphirine (2:2:1 comp ?)					
Synthetic 1390° C, 12.5 kb from Mg-cordierite	11.287 ±0.006	14.444 ±0.006	9.957 ±0.007	125.48 ±0.03	1321.965 ±1.861
Sapphirine[a] (2:2:1 comp ?)					
synthetic 900° C, 13 kb hydrothermal	11.284 ±0.010	14.452 ±0.004	9.951 ±0.013	125.46 ±0.04	1321.822 ±3.159
Sapphirine (7:9:3 comp.)					
Fiskenaesset, Greenland, No. 7563 Herd (1972)	11.276 ±0.002	14.409 ±0.002	9.941 ±0.001	125.44 ±0.01	1316.091 ±0.415
Quartz					
Synthetic, with sapphirine from cordierite 1390° C, 12.5 kb	4.937 ±0.004		5.396 ±0.004		113.894 ±0.119
Quartz					
Natural-Lake Toxaway, N.Y. Swanson, Fuyat and Ugrinic (1964)	4.913		5.405		113.060

[a] Refinement performed by us with listed X-ray data of Schreyer and Seifert (1969b).

Synthetic Sapphirine + Quartz + Enstatite (?). Two different samples of this assemblage were prepared from the two synthetic cordierite samples by pressing at 12.5 kb at 1390° C for 6 hours.

The unit cell constants of the sapphirine and quartz produced were determined from X-ray diffractograms run at 1/8° 2θ per minute using National Bureau of Standards $MgAl_2O_4$ spinel and $KBrO_3$ as internal standards. The unit cell constants of the sapphirine produced from the two cordierite samples were indistinguishable and not significantly different from those of a sapphirine synthesized hydrothermally at 900° C and 13 kb by Schreyer and Seifert (1969b). These authors offered arguments that their synthetic sapphirine has nearly the 2:2:1 composition. The unit cell constants were computed with the least squares refinement program of Burnham (1962). The 2θ values for their sapphirine listed by Schreyer and Seifert (1969b) were used in the Burnham program to compute the cell constants for that material. The cell constants are listed in Table 1.

The quartz had d-spacings which were slightly but definitely longer than those of natural quartz (see Table 1). This is undoubtedly due to the presence of a small amount of $MgAl_2O_4$ contained in solid solution in the quartz (Schreyer and Schairer, 1961). The diagram of unit cell constants versus composition for the solid solution of $MgAl_2O_4$ in quartz of Schreyer and Schairer yield about 2.5 wt. % for the synthetic (α-)quartz. The $MgAl_2O_4$ content of synthetic quartz found by Schreyer and Schairer was shown by them to be mostly metastable. This is probably true in the present case.

No enstatite could be identified in these charges either in the diffractograms or optically as crushed particles in immersion oil. If the sapphirine has indeed the 2:2:1 composition, no enstatite would be formed by breakdown of cordierite. An electron microprobe analysis of synthetic sapphirine produced at high temperatures and pressures by Taylor (1973) yielded the average composition 23.2 ± 0.5% MgO, 58.3 ± 1.2 Al_2O_3 and 18.5 ± 0.4% SiO_2. This composition is quite near the 2:2:1 composition (Fig. 1). The available evidence indicates,

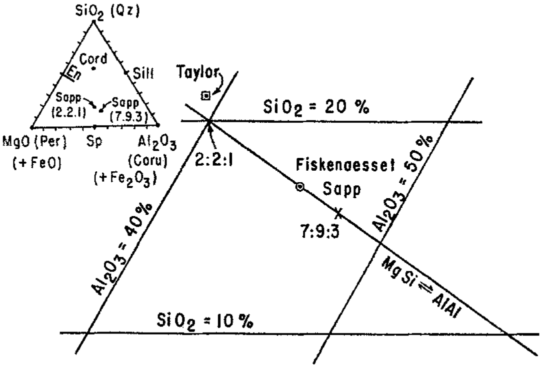

Fig. 1. Mol % plot of the system $MgO—Al_2O_3—SiO_2$ showing location of phases referred to in this study. *Qz* quartz; *Sill* sillimanite; *Sapp* sapphirine; *En* enstatite; *Per* periclase; *Sp* spinel; *Coru* corundum; *Cord* cordierite. The composition of the natural sapphirine specimen (1.7% FeO) used in this study is shown, as well as the theoretical 2:2:1 and 7:9:3 compositions as related by the possible cation substitution scheme for sapphirine: MgSi ⇌ AlAl. The measured composition of a sapphirine prepared at about 1400°C and 15 kb by Taylor (1973) is shown. The Fiskenaesset sapphirine contains small amounts of iron oxides, and these are added to the MgO and Al_2O_3 contents in the expanded diagram

therefore, that enstatite may be ignored in considering the experimental breakdown of Mg-cordierite to a sapphirine-bearing assemblage.

Synthetic Enstatite. A phase-pure orthorhombic $MgSiO_3$ pyroxene was prepared by treating a dehydrated gel at 1500°C and 20 kb for 6 hours. The X-ray diffraction pattern was identical to that of synthetic enstatite given by Stephenson, Sclar and Smith (1966).

Natural Cordierite. Low-iron natural cordierite was hand-picked from a nearly monomineralic cordierite rock from Fiskenaesset, West Greenland (Herd, 1972, Specimen No. 128554). The cordierite was meshed to the calorimeter size range and heated in air at 800°C for 14 hours to drive off the zeolitic water. The apparent water loss was 2.34 wt. %. An electron microprobe analysis by E. J. Olsen showed 1.1 wt. % FeO as the only noteworthy departure from the ideal composition.

Natural Sapphirine. A sample of low-iron natural sapphirine was hand-picked from a sapphirine-enstatite-phlogopite rock from Fiskenaesset, West Greenland (Herd, 1972, Specimen No. 7563). A microprobe analysis of this material given in Herd (1972) shows 1.6 to 1.7 wt. % FeO as the only significant compositional departure from the system $MgO—Al_2O_3—SiO_2$.

Natural sapphirine is invariably more aluminous than the 2:2:1 composition inferred for the high-pressure synthetic product. The theoretical crystallographic composition deduced by Moore (1969) is $7MgO:9Al_2O_3:3SiO_2$, based on a crystal structure analysis of the Fiskenaesset sapphirine used in this work. This composition may be derived from the 2:2:1 formula by substitution of 2Al for Mg + Si, a substitution series characteristic of several magnesium-aluminum silicates. The chemical analysis of Herd (1972) plots on the join between the 2:2:1 and 7:9:3 compositions and fairly close to the latter (Fig. 1). The ideal 7:9:3 composition for the Fiskenaesset sapphirine will be used in the theoretical discussion of the present calorimetric results.

Calorimetric Techniques

The calorimetric measurements carried out in the course of the present work were performed in a Calvet-type twin microcalorimeter of a design which has been described previously (Kleppa, 1960). The calorimeter has a 300 lbs. Ni-block thermostat and has occasionally been operated at temperatures up to

800°C. In the present investigation it was maintained at 695 ± 1°C, as determined by a Pt-Pt13Rh thermocouple which had been checked against a Bureau of Standards calibrated couple.

The operating procedures used in oxide melt calorimetry recently have been discussed by Kleppa (1972), who also gives references to earlier work. These procedures were adopted with only minor modifications in the present work. Most of these modifications relate to the preparation and treatment of the lead borate solvent: A well-homogenized mixture of lead (II) oxide and orthoboric acid (Baker Analyzed Reagents) in the stoichiometric proportions $2PbO:B_2O_3$ were melted together in 50 g portions in a Pt crucible at 800°C and poured onto a silver plate. The entire (500 g) batch of glassy melt was crushed to small fragments in a mullite mortar. After intimate mixing of the fragments, 80 g portions were remelted for $1\text{–}^1/_2$ hours at 1050 ± 20°C, again poured onto the silver plate and crushed into small fragments. All fragments from the same batch were again mixed intimately and 30 g samples of the glassy solvent mixture withdrawn to be used for heat of solution experiments.

The first calorimetric experiment in each 30 g sample of melt still showed some experimental scatter from one sample to the other. These experiments were rejected. Subsequent to this six or seven consecutive calorimetric measurements were carried out in the same 30 g sample of melt with good precision. The heats of solution showed no evidence of a dependence on solute concentration. In the course of the present work it was found that the heats of solution in a specific 500 g batch of melt were internally consistent, but that small variations sometimes were obersved when different batches were used. This could possibly be due to the retention of small (but different) amounts of water in the lead borate glass. All measurements reported in the present paper were performed on samples drawn from the same 500 g batch of lead borate.

All mineral samples were powders in the size range —150 to —325 mesh. The amount of sample used in each experiment was adjusted so as to produce a heat effect of about 2 cal, and ranged from 25 mg to 40 mg. Among the minerals studied the dissolution of enstatite proved to be rather slow. Otherwise no special problems were encountered. The calorimetric experiments lasted from 36 to 60 minutes before the temperature signal had returned completely to its baseline. Most calorimetric experiments were performed in air. However, natural samples which contained small amounts of iron in the ferrous state were run in a dry, inert atmosphere of argon.

Calibration of the calorimeter was by the Pt-drop method, based on the heat content of Pt reported by Kelley (1960). Weighed pieces of pure 2 mm Pt-wire (about 0.25 g) were dropped into the calorimeter from room temperature. A correction of 1% was applied for the heat pick-up of the platinum wire during its drop into the calorimeter.

Results of Experiments

Synthetic Cordierite. Table 2 shows the measured heats of solution of the two samples of synthetic cordierite. The results for the Tem Pres cordierite sample are in good agreement with the earlier value of 28.1 ± 1.5 kcal/mole for the same

Table 2. Heat of solution of synthetic materials

Material and preparation	Additional heat treatment	Wt. sample (mg)	ΔH Sol'n (Kcal/mole)
Mg-cordierite I			
Tem Pres Co.	800°C	40.05	27.52
1325°C, 7.5 kb	5 hr	43.03	27.56[a]
6 hr (unless otherwise noted)	1 atm.	43.53	27.92[b]
		40.67	28.08
			28.23[b]
			28.56
			28.76
			Avg. 28.09 ± 0.49
Mg-cordierite II from glass			
(Muscle Shoals Electrochem Corp.)			
1380°C	None	40.80	27.38
1 atm.		40.30	27.62
3 days		42.37	28.00
		39.06	28.60
		41.96	28.68
		42.91	28.72
		40.67	28.76
		39.31	28.89
		42.87	29.02
		40.77	29.32
		41.21	29.34
		40.94	29.47
			Avg. 28.65 ± 0.68
Sapphirine (2:2:1)			
+quartz I from Tem Pres			21.87[c]
cordierite, 1390°C,	800°C	40.72	21.99
12.5 kb, 6 hrs	1 atm	38.81	22.01
	5 hrs	42.82	22.04
		41.16	22.22
		38.92	22.27
			Avg. 22.07 ± 0.14
Sapphirine (2:2:1)			
+quartz II from cord. II,	800°C	41.63	21.05
1390°C, 12.5 kb, 6 hrs	1 atm	40.10	21.74
	5 hrs	40.57	22.38
		39.28	22.54
		43.22	22.65
		40.56	22.94
		47.34	22.96
		40.99	22.97
		39.39	23.07
			Avg. 22.48 ± 0.68

Table 2 (continued)

Material and preparation	Additional heat treatment	Wt. sample (mg)	ΔH Sol'n (Kcal/mole)
Enstatite			
from gel (see text)	800° C	26.73	8.50
1500° C, 20.0 kb, 4 hrs	1 atm	25.18	8.73
	5 hrs	25.01	8.84
		24.61	8.92
		26.45	8.96
		28.18	9.14
		20.30	9.53
			Avg. 8.95 ± 0.33

[a] Treated at 1370° C, 7.5 kb, 5.5 hrs. Performed by A. Navrotsky, quoted in Newton (1972).
[b] Untreated Tem Pres Cordierite. Performed by A. Navrotsky, quoted in Newton (1972).
[c] Performed by A. Navrotsky, quoted in Newton (1972).

cordierite by Navrotsky and Kleppa (1973). The heat of solution of the second sample of synthetic condierite does not seem to be significantly different.

Synthetic Sapphirine + Quartz (+ Enstatite ?). The heats of solution for the two samples of the high temperature, high pressure breakdown products of synthetic cordierite were not significantly different. The results, listed in Table 2, are in agreement with the one run performed earlier by A. Navrotsky and quoted in Newton (1972).

Natural Cordierite and Sapphirine. The average value of the heat of solution for the specimen of natural cordierite is slightly but significantly higher than for the synthetic samples (Table 2). The heat of solution per gram of the natural sapphirine is considerably higher than for synthetic sapphirine (calculated from the results on the breakdown products of cordierite allowing a molar heat of solution of − 1.04 kilocalories for quartz). This effect cannot be due to the iron content which, by analogy with iron garnet and olivine (Shearer, 1973) would be expected to shift the heats of solution to lower values, but must be due to an essential difference between synthetic and natural sapphirine. This point will be considered in the Interpretations section.

Synthetic Enstatite. The average value reported here of 8.95 ± 0.33 kilocalories per mole is significantly higher than the value of 8.36 ± 0.19 reported for $MgSiO_3$ by Shearer and Kleppa (1973). However, their material was probably a mixture of clinoenstatite and protoenstatite, and probably was of very fine grain size owing to decrepitation in passing through the protoenstatite-clinoenstatite inversion in cooling.

Interpretation of Results

Invariant Point Relations

Many previous experimental workers on cordierite stability have inferred the existence of an invariant point in the P-T stability diagram for anhydrous Mg-cordierite composition in the neighborhood of 1000° C and 10 kilobars, in-

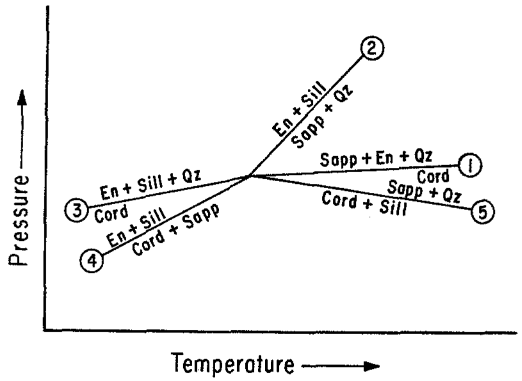

Fig. 2. Schematic *P-T* diagram of the univariant reactions considered in this paper. Phase designations are the same as in Fig. 1

volving the simultaneous presence of the five phases cordierite, sapphirine, enstatite, sillimanite and quartz. From the invariant point there must, in general, radiate five equilibrium *P-T* curves, the reaction of each of which lacks one of these five phases. In the following discussions, reference to these five reactions will be made with the use of the schematic diagram of Fig. 2 (see also Chatterjee and Schreyer, 1972, p. 51). If, in the synthetic system, the breakdown products of cordierite at temperatures above the invariant point lack enstatite (that is, if the resulting sapphirine has the composition $2MgO \cdot 2Al_2O_3 \cdot SiO_2$), then reactions I and V below coincide. The phase relations for the synthetic and natural systems must be considered separately because the kind of sapphirine produced in synthetic work is somewhat different from the typical natural variety.

Synthetic System

Reaction I. Cordierite = Sapphirine + Quartz (+ Enstatite ?). Since enstatite was not detected in the breakdown products of synthetic cordierite it is assumed that Reaction I may be approximated by

$$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2 = 2MgO \cdot 2Al_2O_3 \cdot SiO_2 + 4SiO_2.$$

The equilibrium pressure of this reaction has been determined experimentally to be 8.2 ± 0.4 kb in the range 1300–1400°C (Newton, 1972); however, the relatively short temperature range over which reversals may be secured does not permit an accurate experimental determination of dP/dT. The most important information stemming from the present study is a knowledge of this slope. Indirect thermodynamic reasoning suggests that the slope should be quite small (Newton, 1972).

Comparison of the measured enthalpies of solution of the Tem Pres synthetic cordierite and its breakdown products at 700°C gives a standard enthalpy change of Reaction I at this temperature [$\Delta H^\circ(973)$] of 6.02 ± 0.63 kcal/gfw cordierite (Table 2). The measurements for the other synthetic cordierite and its breakdown products give 6.17 ± 1.36 kcal/gfw. Heat capacity data are not available which allow a precise calculation of $\Delta H^\circ(1600)$. Even so, no significant additional error should be incurred if we set $\Delta H^\circ(1600) = \Delta H^\circ(973) = 6.10$ kcal/gfw. The volume

Table 3. Heat of solution of natural materials[a]

Material	Heat-treating	Wt. Sample Milligrams	ΔH Sol'n (Kcal/mole)
Cordierite			
1.1 wt.% FeO	800°C	36.20	29.40[b]
Fiskenaesset,	24 hrs in air	30.67	29.55[b]
West Greenland		36.98	29.62
		37.67	29.92
		40.15	30.03
		40.04	31.72
		Avg.	30.04 ± 0.86
Sapphirine			
7:9:3 composition			
1.7 wt.% FeO	800°C	26.18	117.33
Fiskenaesset,	24 hrs in air	28.46	119.61[b]
West Greenland		26.96	121.62
		33.16	122.26
		28.53	123.30
		24.06	126.54
		Avg.	121.78 ± 3.15

[a] Experiments carried out under argon atmosphere unless otherwise noted.

[b] Experiment carried out in air.

data listed in Table 4 give $\Delta^\circ V(1600) = 38.3\ \mathrm{cm}^3 = -0.915$ cal/bar gfw. Neglecting the slight dependence of ΔV° on pressure we accordingly have

$$\Delta G^\circ(1600) \cong -V^\circ P_{\mathrm{eq}} = 7.5 \pm 0.4\ \mathrm{kcal}.$$

Thus

$$\Delta S^\circ(1600) = \frac{\Delta H^\circ - \Delta G^\circ}{1600} = -0.9 \pm 1.0\ \mathrm{cal/deg}$$

and

$$\frac{dP}{dT} \simeq \frac{\Delta S^\circ}{\Delta V^\circ} = 1 \pm 1\ \mathrm{bar/deg}.$$

The expectation of an essentially flat slope for this reaction, rather than the steep negative slope supposed by other investigators, is accordingly substantiated.

Since the standard entropies of cordierite and quartz are known our approximate value of ΔS° (I) allows an estimate of the standard entropy of synthetic (2:2:1) sapphirine: $\Delta S^\circ\ (\mathrm{I}) = -0.9\ (\pm 1) = S^\circ_{\mathrm{sapph}} + 4S^\circ_{\mathrm{qtz}} - S^\circ_{\mathrm{cord}}$. Again neglecting temperature dependence we get at 700°C

$$S^\circ_{\mathrm{sapph}}(973) = -0.9 + 264.58 - (27.34 \times 4) + S_{\mathrm{conf.,\ cord}}.$$

If $S_{\mathrm{conf.,\ cord}} = 1.22$ cal/deg gfw (see Table 4) we obtain $S^\circ_{\mathrm{sapph}}(973) = 155.54$ cal/deg gfw with an estimated uncertainty of the order of ± 1.5 cal/deg gfw.

According to the method of estimation of Fyfe, Turner and Verhoogen (1958), the calculated value of $S^\circ_{\mathrm{sapph}}(973)$ is 151.38 cal/deg gfw, using the data of Table 4.

Table 4. Volumes and entropies of minerals at selected temperatures and 1 atm. Entropy data from Robie and Waldbaum (1968). Thermal expansions from B. J. Skinner in S. P. Clark (ed.) (1966)

Mineral	*Volume* cm^3/gfw			*Entropy* cal/deg gfw	
	25°C	700°C	1327°C	25°C	700°C
Cordierite[a]					
2 MgO·2 Al_2O_3·5 SiO_2 gfw = 584.969	233.22	234.01	235.67	97.33	264.58
Sapphirine[b]					
7 MgO·9 Al_2O_3·3 SiO_2 gfw = 1380.081	395.89	402.26	—	—	605.86
2 MgO·2 $Al_2O_3SiO_2$ gfw = 344.629	98.86	100.55	102.91	—	151.38
Enstatite					
$MgSiO_3$ gfw = 100.396	31.30	31.93	—	16.22	45.28
Sillimanite[c]					
Al_2SiO_5 gfw = 162.046	49.90	50.45	—	22.97	69.22
Quartz					
SiO_2 gfw = 60.085	22.69	23.72	23.61	9.88	27.34
Corundum					
Al_2O_3 gfw = 101.961	25.58	26.01	—	12.18	42.24
Periclase					
MgO gfw = 40.311	11.25	11.55	—	6.44	19.33

[a] In our calculations the entropy of cordierite is corrected for network disorder of $+1.22$ cal/deg gfw. This estimate is based on the structural data of Gibbs (1966).

[b] The room temperature volume values are based on the d-spacings of the synthetic sapphirine used. In referring the volume data to higher temperatures, the thermal expansions of spinel have been assumed. The entropy estimates at 700°C were obtained by the method of Fyfe, Turner and Verhoogen (1958). In calculations these values are corrected for the entropies of cation disorder. In natural sapphirine (7:9:3) this entropy is estimated at $+9.98$ cal/deg gfw according to the site populations given by Moore (1969). In synthetic sapphirine (2:2:1) the correction is about $+4.2$ cal/deg gfw (see text).

[c] In our calculations the entropy of sillimanite at 700°C has been corrected for a disordering entropy of $+0.42$ cal/deg gfw according to the calculations of Holdaway (1971).

Hence $S^{\circ}_{\text{sapph}}(973, \text{expt}) - S'_{\text{sapph}}(973, \text{FTV}) = 4.16$ cal/deg gfw. This difference represents the entropy of disorder in the synthetic (2:2:1) sapphirine. While the estimated uncertainty in this value clearly is large, perhaps ± 2–3 cal/deg gfw, it nevertheless represents an entirely plausible result. Note, for example, that on a per gram basis this estimate of the disordering entropy is roughly twice as large as for the natural (7:9:3) mineral (Table 4), which presumably is more highly ordered.

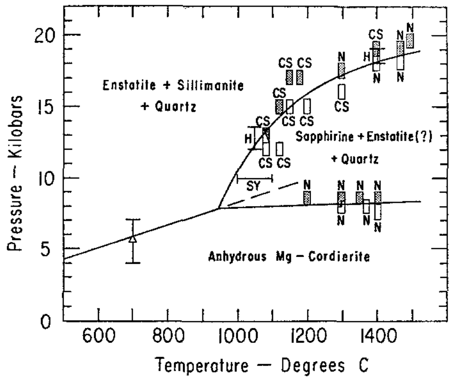

Fig. 3. Experimental reversal data which, along with the present thermodynamic data, determine the stability *P-T* curves and invariant point for the synthetic system (system with synthetic sapphirine of nearly 2:2:1 composition). "*N*" refers to runs of Newton (1972). "*CS*" refers to those of Chatterjee and Schreyer (1972). "*SY*" with horizontal bracket refers to breakdown of synthetic anhydrous Mg-cordierite to enstatite + sillimanite + quartz in a gas-pressure apparatus (Schreyer and Yoder, 1960). "*H*" refers to the experimental brackets for Reaction II of Hensen (1972). A triangle shows the pressure of Reaction III at 700° C calculated from the present heat of solution data, with estimated uncertainty bracket ($\pm$ 1.5 kb)

Reactions II. *Enstatite + sillimanite ⇌ sapphirine + quartz*

$$2MgSiO_3 + 2Al_2SiO_5 \rightleftharpoons 2MgO \cdot 2Al_2O_3 \cdot SiO_2 + 3SiO_2$$

and III. *Cordierite ⇌ enstatite + sillimanite + quartz*

$$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2 \rightleftharpoons 2MgSiO_3 + 2Al_2SiO_5 + SiO_2.$$

Experimental reversal data for Reaction II over the temperature range 1100–1500° C are available (Chatterjee and Schreyer, 1972; Newton, 1972), and are plotted in Fig. 3. A further constraint on the course of the equilibrium is given by a calculation of the slope dP/dT where Reaction II intersects Reaction I. It was shown by Chatterjee and Schreyer (1972) and by Newton (1972) that this intersection must be somewhere in the neighborhood of 1000° C and 10 kb.

The intersection of Reaction I and II determines III. If we neglect the slight solubility of Al_2O_3 in enstatite, a Clausius-Clapeyron calculation of dP/dT for Reaction III may be made by using the measured volumes and third law entropies of the phases (Robie and Waldbaum, 1968). We get

$$\Delta S^\circ(\text{III, } 1300) \approx \Delta S^\circ(\text{III, } 973) \cong -8.2_4 \text{ cal/deg.}$$

This value can be somewhat refined if allowance is made for the framework disorder in cordierite (+1.22 cal/deg gfw) and for Al-Si disorder in sillimanite which, according to Holdaway (1971), would be 0.42 cal/deg gfw at 700° C. Thus we have ΔS° (III, 973, corrected) $= -8.6_2$ cal/deg gfw. The slope of the *P-T* curve for Reaction III estimated on this basis will be about 8 bar/deg. Any further configurational entropy in cordierite would result in a steeper slope, more disorder in sillimanite and substitution of Al_2O_3 into enstatite would give a somewhat less steep slope.

The slope of Reaction II at the intersection of I and III may now be calculated. Since

$$\Delta S^\circ(\text{II}) = \Delta S^\circ(1) - \Delta S^\circ(\text{III}) \cong 7.7 \text{ cal/deg}$$

and

$$\Delta V^\circ(\text{II}) = \Delta V^\circ(1) - \Delta V^\circ(\text{III}) \cong 0.165 \text{ cal/bar}$$

we have

$$\frac{dP}{dT}(\text{II}) = \frac{7.7}{0.165} = 47 \text{ bar/deg.}$$

This value clearly is associated with very considerable uncertainty, perhaps as much as ± 15 bars/° C. Even so, the relatively large initial slope of Reaction II and the reversal data at higher temperatures define the course of the equilibrium in the temperature range 900–1 500° C as shown in Fig. 3. The rather significant curvature for Reaction II is, in fact, a consequence of the increasing amounts of Al_2O_3 in solid solution in enstatite with increasing temperature and pressure, in conjunction with the small volume change of the reaction as discussed by Chatterjee and Schreyer (1972) and by Newton (1972). An invariant point near 950° C and 8 kilobar is indicated. Reaction III continues stably to lower temperatures with a slope of about 8 bars/° C.

A calculation of the pressure of Reaction III using the heat of solution data provides independent confirmation of the position of Reaction III deduced above. The enthalpies of solution of synthetic cordierite and enstatite were used in this calculation along with a value of − 1.04 kcal/gfw for quartz (Shearer and Kleppa, 1973), and a value of 6.93 kcal/gfw for sillimanite (Anderson and Kleppa, 1969). We calculate the enthalpy change for Reaction III to be

$$\begin{aligned}\Delta H^\circ(\text{III}, 973) &= [-2\times 8.95 + 2\times 6.93 - 1.04 - 28.39] \\ &= -2.33 \text{ kcal/gfw cordierite.}\end{aligned}$$

From these results we calculate

$$\begin{aligned}\Delta G^\circ(\text{III}, 973) &= -2.33 + 973\times 8.62 = 6.06 \text{ kcal} \\ &\cong -\Delta V^\circ(\text{III})\, P_{\text{eq}}.\end{aligned}$$

If $\Delta V^\circ(\text{III}) = -1.088$ cal/bar, we obtain

$$P_{\text{eq}} \cong 5.6 \text{ kb at } 700^\circ\text{C}$$

with an estimated uncertainty of the order of ± 1.5 kb, largely due to the errors in the enthalpies of solution.

Reaction IV. *Enstatite + sillimanite = sapphirine + cordierite*

$$8MgSiO_3 + 8Al_2SiO_5 = 2MgO\cdot 2Al_2O_3\cdot SiO_2 + 3(2MgO\cdot 2Al_2O_3\cdot 5SiO_2)$$

and V. *Cordierite + sillimanite = sapphirine + quartz.*

These are the two remaining equilibria which emanate from the invariant point generated by the intersections of I, II, and III. Among these, V will coincide with I if the sapphirine has the composition 2:2:1. In any event, it is expected to be located fairly close to I.

The slope for Reaction IV follows immediately from the data for I and III: Reaction IV = Reaction I — 4 × Reaction III i.e.

$$\Delta S^\circ(\text{IV}) = \Delta S^\circ(\text{I}) - 4\Delta S^\circ(\text{III}) = 33.58\ \text{cal/deg}$$
$$\Delta V^\circ(\text{IV}) = \Delta V^\circ(\text{I}) - 4\Delta V^\circ(\text{III}) = 3.48\ \text{cal/bar.}$$

Thus

$$\frac{dP}{dT}(\text{IV}) \cong 10\ \text{bar/deg}$$

with an estimated uncertainty of about ± 1 bar/deg.

Natural System

The thermodynamic properties of synthetic minerals differ somewhat from their natural analogs because of differences in composition and cationic ordering state. These properties will in general be reflected in the stability relations. While small differences in composition usually may be neglected, this is not the case with cation disorder. Where cation disordering is possible in a mineral structure a synthetic product will commonly be more disordered than its natural analog, and thus will be metastable with respect to the natural mineral at lower temperatures. As the temperature is increased, the metastability of the synthetic sample will become less significant, and will be eliminated at temperatures when comparable disorder can be produced in the natural sample. Some justification is needed, therefore, when an attempt is made to use experimentally-determined stability relations of synthetic minerals as models for the behavior of the natural substances.

Cordierite has its Al and Si tetrahedrally coordinated and there is the consequent possibility of framework order-disorder relations, as in the feldspars. Some disordering among Al and Si atoms probably is associated with the observed polymorphic gradation from orthorhombic to hexagonal symmetry (Gibbs, 1966), which involves quite minor variations in the positions and intensities of X-ray reflections of natural and synthetic specimens. However, evidence from calorimetry (Navrotsky and Kleppa, 1973) and from IR absorption spectroscopy (Langer and Schreyer, 1968) indicates that the distortional polymorphism is not produced by a cation-site variation as profound as thorough frame-work disordering. Therefore, we believe that synthetic Mg-cordierite should be a reasonably good stability model for its natural counterpart.

Synthetic sapphirine is, in contrast, conspicuously different from natural specimens. In addition to the difference in composition previously noted, the several types of cation disorder possible both in tetrahedral and octahedral sites (Moore, 1969) make it seem likely that synthetic samples will have comparatively large amounts of configurational entropy. Evidence presented above indicates that synthetic sapphirine prepared by the breakdown of cordierite has about twice the configurational entropy per gram of the natural sapphirine. The differences in composition and ordering state between synthetic and natural sapphirine produce considerable differences in the positions and intensities of the X-ray reflections. Thus, synthetic sapphirine cannot be used as a stability model for natural sapphirine with the same confidence as in the case of cordierite.

The above conjectures are supported by the measured heats of solution. While the difference between the heats of solution per gram of natural and synthetic cordierite is only about 5%, the natural sapphirine has a heat of solution per gram which is about 15% higher than the synthetic material.

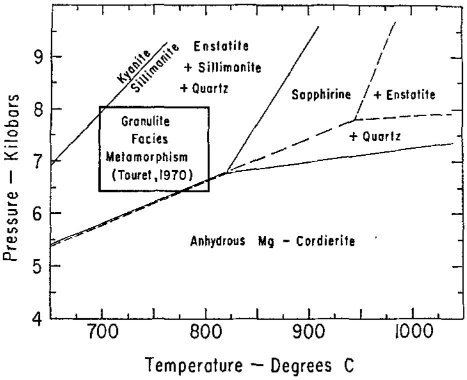

Fig. 4. Invariant point and Mg-cordierite stability limits in the system $MgO—Al_2O_3—SiO_2$ determined for the synthetic system (dashed lines) and for the natural system (solid lines). Rectangular area is estimate of Touret (1970) of conditions of granulite metamorphism. Kyanite-sillimanite *P-T* stability boundary from Holdaway (1971). The figure indicates that the anhydrous breakdown products of magnesian cordierite could be produced under conditions of crustal metamorphism if P_{H_2O} was very low

A simple but straightforward analysis may be made of the *P-T* position of the natural analog (I′) of Reaction I: the breakdown of cordierite to sapphirine (assumed 7:9:3 composition), enstatite and quartz, as follows. For the reaction (I) cordierite ⇌ sapphirine (synthetic) + quartz (+ enstatite ?) we have shown above that ΔG (I) (1600) is about + 7.5 kcal/gfw. However, for the ordering reaction

sapphirine (synthetic) ⇌ sapphirine (natural)

we generally (except at the very highest temperatures) expect $\Delta G < 0$. Thus, for

(I′) cordierite ⇌ sapphirine (natural) + quartz + enstatite

we predict $\Delta G°(\mathrm{I}') < \Delta G°(\mathrm{I})$. Accordingly, since $\Delta V°$ does not depend strongly on cation disorder, $P_{eq}(\mathrm{I}') < P_{eq}(\mathrm{I})$. This lowering of the equilibrium pressure will be the least at the highest temperatures, where sufficiently high kinetics will allow the determination of the true equilibrium pressure of the most stable breakdown reaction.

At 700°C the data of Table 4 may be used to estimate a dP/dT slope of about 3 bars/deg for the breakdown of cordierite to natural 7:9:3 sapphirine. An approximate boundary for this reaction was constructed by making it coincide with the experimental boundary at 1500°C and curving it continuously downward in pressure with decreasing temperature so that the 3 bar/deg slope at 700°C is achieved. This graphical estimate is shown in Fig. 4. The difference in pressure between the natural and experimental breakdown curves is only a few hundred bars. The important point is raised that the invariant point will be shifted to considerably lower temperature. If natural cordierite is more stable than synthetic cordierite relative to enstatite, sillimanite and quartz by even a few hundred bars, the invariant point will undergo a significant further shift to lower temperatures.

Geological Application

The present results permit a reevaluation of the evidence on granulite facies metamorphism based on cordierite stability. Fig. 4 shows the invariant points in the system $MgO—Al_2O_3—SiO_2$ deduced for the synthetic and natural systems. The pressure stability limit of cordierite relative to more aluminous, better-ordered natural sapphirine, is not much different than relative to the more siliceous, more disordered synthetic sapphirine, but the invariant point in the former case must lie at considerably lower temperature, perhaps near 800°C. The presence of iron in the natural system will bring the stability limit of cordierite to lower pressures and probably will move the invariant point to still lower temperatures.

A qualitative conclusion which follows from the present work is that subcrustal conditions of metamorphism are not necessarily demanded by the presence of the assemblages enstatite-sillimanite-quartz or sapphirine-enstatite-quartz, which are equivalent to anhydrous cordierite in composition, if very dry conditions prevailed during metamorphism. Fig. 4 shows the *P-T* area inferred for granulite facies metamorphism by Touret (1970). Touret argued cogently on the basis of fluid inclusion composition and other evidence that water pressures were extremely low during the metamorphism. Fig. 4 strongly suggests that Touret's *P-T* estimates are compatible with the high pressure magnesian assemblages enstatite-sillimanite and sapphirine-quartz and that the physical conditions of the metamorphism need not have been as extreme as inferred by Chinner and Sweatman (1968), Chatterjee and Schreyer (1970) and Morse and Talley (1971).

Newton (1972) showed that water pressures approaching load pressures could stabilize cordierite relative to the high pressure breakdown assemblages by as much as four kilobars, but would produce melting in these assemblages over most of the *P-T* ranges in which they would be stable relative to cordierite. The effect of small amounts of water present during the metamorphism would probably be as Chatterjee and Schreyer (1972, p. 59) indicate; namely, that cordierite together with its high pressure breakdown products would coexist together over an interval of temperature and pressure bounded by the stability limits for the cases $P_{H_2O}=0$ and $P_{H_2O}=P_{total}$. Such co-occurrence of cordierite with enstatite-sillimanite and sapphirine-quartz is indeed the more frequently encountered situation (Dallwitz, 1968; Marakushev and Kudryatsev, 1965; Rabkin, 1968; Moore and Leong, 1971). A viewpoint which diverges from this one is expressed by Hensen (1972) who states that even very small amounts of water, which (he infers) must be present in granulite-type metamorphism, would stabilize cordierite to nearly the pressure limits for the case of $P_{H_2O}=P_{total}$. Thus he concludes that the experimental results for $P_{H_2O}=P_{total}$ should apply more closely to granulite metamorphism than the results for the dry system.

The effect of iron in the system will be to produce a similar divariancy and to reduce the pressures at which the assemblages enstatite and sillimanite and sapphirine-quartz can exist. The pressure lowering is small for moderate amounts of iron as shown by the experimental data of Hensen and Green (1970) for a bulk composition having (Mg)/(Mg+Fe)=0.7. This is consistent with ideal mixing of Mg and Fe in the cordierite structure (Newton, 1972). The effect of the large Fe_2O_3 content of hypersthene coexisting with sillimanite in some localities (Lutts and Kopaneva, 1968) may not be negligible.

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References

Anderson, P. A. M., Kleppa, O. J.: The thermochemistry of the kyanite-sillimanite equilibrium. Am. J. Sci. **267**, 285–290 (1969)

Burnham, C. W.: Lattice constant refinement. Ann Rept. of the Dir. of the Geophysical Lab., Carnegie Inst. Washington Yearbook **61**, 132–135 (1962)

Chatterjee, N. D., Schreyer, W.: Stabilitätsbeziehungen der Paragenese Sapphirin + Quartz. Fortschr. Mineral. **47**, Suppl. 1, 9–10 (1970)

Chatterjee, N. D., Schreyer, W.: The reaction enstatite + sillimanite = sapphirine + quartz in the system $MgO—Al_2O_3—SiO_2$. Contr. Mineral. and Petrol. **36**, 49–62 (1972)

Chinner, G. A., Sweatman, T. R.: A former association of enstatite and kyanite. Mineral. Mag. **36**, 1052–1060 (1968)

Clark, S. P. (ed.): Handbook of Physical Constants. Geol. Soc. Am. Mem. **97**, 567 pp. (1966)

Dallwitz, W. B.: Coexisting sapphirine and quartz in granulite from Enderby Land, Antarctica. Nature **219**, 476–477 (1968)

Fyfe, W. S., Turner, F. J., Verhoogen, J.: Metamorphic reactions and metamorphic facies. Geol. Soc. Am. Mem. **73**, 259 pp. (1958)

Gibbs, G. V.: The polymorphism of cordierite I: The crystal structure of low cordierite. Am. Mineralogist **51**, 1068–1087 (1966)

Hensen, B. J.: Experimental metamorphic petrology: Cordierite-garnet equilibrium as a function of pressure, temperature, and iron-magnesium ratio. Ann. Rept. of the Dir. of the Geophys. Lab., Carnegie Inst. Washington Yearbook **71** (1972)

Hensen, B. J., Green, D. H.: Experimental data on coexisting cordierite and garnet under high-grade metamorphic conditions. Phys. Earth Planet. Sci. Interiors **3**, 431–440 (1970)

Herd, R. K.: The petrology of the sapphirine-bearing associated rocks of the Fiskenaesset Complex, West Greenland. Unpub. Ph. D. thesis, University of London, England (1972)

Holdaway, M. J.: Stability of andalusite and the aluminum silicate phase diagram. Am. J. Sci. **271**, 97–131 (1971)

Kelley, K. K.: Contributions to the data on theoretical metallurgy XIII. High-temperature heat content, heat capacity, and entropy data for elements and inorganic compounds. U. S. Bur. Mines No. **584**, U. S. Government Printing Office (1960)

Kleppa, O. J.: A new twin high-temperature reaction calorimeter. The heats of mixing in liquid sodium-potassium nitrates. J. Phys. Chem. **64**, 1937–1940 (1960)

Kleppa, O. J.: Oxide-melt solution calorimetry. Calloques Internationaux du C. N. R. S. No. **201**. Thermochimie 119–127 (1972)

Langer, K., Schreyer, W.: Infrared and powder X-ray diffraction studies of the polymorphism of cordierite, $Mg_2Al_4Si_5O_{18}$. Am. Mineralogist **54**, 1442–1459 (1969)

Marakushev, A. A., Kudryatsev, V. A.: Hypersthene-sillimanite paragenesis and its petrologic implication. Dokl. Akad. Nauk SSR **164**, 145–148 (1965)

Miyashiro, A.: Cordierite-indialite relations. Am. J. Sci. **255**, 43–62 (1957)

Meng, L. K., Moore, J. M.: Sapphirine-bearing rocks from Wilson Lake, Labrador. Can. Mineralogist **II**, 777–790 (1972)

Moore, J. M., Leong, K. M.: Comments on "Sapphirine reactions in deep-seated granulites near Wilson Lake, Central Labrador, Canada" by A. Morse and J. H. Talley. Earth Planet. Sci. Letters **10**, 355–356 (1971)

Moore, P. B.: The crystal structure of sapphirine. Am. Mineralogist **54**, 31–49 (1969)

Morse, S. A., Talley, J. H.: Sapphirine reactions in deep-seated granulites near Wilson Lake, Central Labrador, Canada. Earth Planet. Sci. Letters **10**, 325–328 (1971)

Navrotsky, A., Kleppa, O. J.: The thermodynamics of formation of simple spinels. J. Inorg. Chem. **30**, 479–498 (1967)

Navrotsky, A., Kleppa, O. J.: Estimate of enthalpies of fusion and formation of cordierite. J. Am. Ceram. Soc. **56**, 198–199 (1973)

Newton, R. C.: An experimental determination of the high pressure stability limits of magnesian cordierite under wet and dry conditions. J. Geol. **80**, 398–420 (1972)

Rabkin, M. I.: Depth conditions of regional metamorphism of the Anabar Sheild. Int. Geol. Congr. 23rd Sess. Prague, Sec. 4, 215–223 (1968)

Robie, R. A., Waldbaum, D. R.: Thermodynamic properties of minerals and related substances at 298.15 K (25.0 C) and one atmosphere (1.013 bars) pressure and at higher temperatures. U. S. Geol. Surv. Bull. **1259**, 256 pp. (1968)

Schreyer, W., Schairer, J. F.: Metastable solid solutions with quartz-type structures on the join SiO_2—$MgAl_2O_4$. Z. Krist. **116**, 60–82 (1961)

Schreyer, W., Seifert, F.: Compatibility relations of the aluminum silicates in the systems MgO—Al_2O_3—H_2O and K_2O—MgO—Al_2O_3—SiO_2—H_2O at high pressures. Am. J. Sci. **267**, 371–388 (1969a)

Schreyer, W., Seifert, F.: High pressure phases in the system MgO—Al_2O_3—SiO_2—H_2O. Am. J. Sci. Schairer Vol., 407–443 (1969b)

Schreyer, W., Yoder, H. S.: Instability of anhydrous Mg-cordierite at high pressures. Ann. Rept. of the Dir. of the Geophysical Lab., Carnegie Inst. Washington Yearbook **59**, 90–91 (1960)

Schreyer, W., Yoder, H. S.: The system Mg-cordierite-H_2O and related rocks. Neues Jahrb. Mineral. Abhandl. **101**, 271–342 (1964)

Shearer, J. A.: Thermochemistry of the garnets and some related compounds. Unpub. Ph.D. thesis, University of Chicago (1973)

Shearer, J. A., Kleppa, O. J.: The enthalpies of formation of $MgAl_2O_4$, $MgSiO_3$, $MgSiO_4$ and Al_2SiO_5 by oxide melt solution calorimetry. J. Inorg. Nucl. Chem. **35**, 1073–1078 (1973)

Stephenson, D. A., Sclar, C. B., Smith, J. V.: Unit cell volumes of synthetic orthoenstatite and low clinoenstatite. Mineral. Mag. **35**, 834–846 (1966)

Swanson, H. E., Fuyat, R. K., Ugrinic, G. M.: Standard X-ray diffraction powder patterns. U. S. Bur. Stds. Circ. **539**, 24–26 (1954)

Taylor, H. C. J.: Melting relations in the system MgO—Al_2O_3—SiO_2 at 15 kb. Geol. Soc. Am. Bull. **84**, 1335–1438 (1973)

Touret, M. J.: Le facies granulite, metamorphisme en milieu carbonique. Compt. Rend. **271**, 2228–2231 (1970)

Yokokawa, T., Kleppa, O. J.: A calorimetric study of the transformation of some metastable modifications of alumina to α-alumina. J. Phys. Chem. **68**, 3246–3248 (1964)

R. C. Newton
Department of Geophysical Sciences
University of Chicago
Chicago, Illinois 60637
U.S.A.