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REACTIONS INVOLVING ANORTHITE AND $CaAl_2SiO_6$ PYROXENE AT HIGH PRESSURES AND TEMPERATURES

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ABSTRACT. Phase relationships in the system $CaO–Al_2O_3–SiO_2$ have been determined in the pressure range 31 to 35 kb at temperatures of 1350° to 1450°C. The phases involved are anorthite (An), calcium tschermaks pyroxene (Cts), quartz (Q), grossular (Gro), kyanite (Ky), corundum (Cor), and liquid (L).

The reaction:

$$\text{anorthite} = \text{grossular} + \text{kyanite} + \text{quartz}$$

is joined by liquid at 1400° to 1410°C and 32 kb to form the invariant point (Cts, Cor)[1]. Four additional invariant points have been found in the vicinity of the invariant points (Cts, Cor). These are, with approximate P, T conditions: (Q, Cor) at 32 kb/1420°C, (Q, Gro) at 32 kb/1430°C, (An, Q) at 33 kb/1425°C, and (Q, L) at 31.8 kb/1410°C.

The reaction:

$$\text{anorthite} = \text{pyroxene} + \text{quartz}$$

has been deduced to lie metastably at about 33 kb at 1400°C. This position is for a non-stoichiometric clinopyroxene of approximate composition $Ca_{0.93}Al_{1.64}Si_{1.29}O_6$. Such a pyroxene is stable well outside the stability field of end-member $CaAl_2SiO_6$ clinopyroxene. The non-stoichiometry of clinopyroxene accounts, in large part, for the discrepancy between the pyroxene stability fields observed by Hays (1966) and Hariya and Kennedy (1968).

INTRODUCTION

There have been a number of experimental studies at high pressures of reactions in the systems $CaO–Al_2O_3–SiO_2$ (Hays, 1966; Hariya and Kennedy, 1968, for example) and $CaO–Al_2O_3–SiO_2–H_2O$ (Newton, 1966; Boettcher, 1970). For most of the relevant phases in these systems the different data sets are sufficiently in agreement that internally consistent thermodynamic data may be derived from them (Helgeson, Delany, Nesbitt, and Bird, 1978). A significant inconsistency in the results for $CaAl_2SiO_6$ pyroxene has, however, been apparent for some time. Hariya and Kennedy found a field of coexistence of $CaAl_2SiO_6$ pyroxene and quartz that lay partly outside the stability field of pure $CaAl_2SiO_6$ determined by Hays (fig. 1). The principal aim of this study has been to resolve this apparent discrepancy by studying appropriate melting and solid-solid reactions in the system $CaO–Al_2O_3–SiO_2$.

The discrepancy between the two sets of results shown in figure 1 could be due to disequilibrium or to inconsistencies between temperatures and pressures developed in different piston-cylinder apparatuses. A third possible explanation is that both sets of data are correct and that the stability field of clinopyroxene plus quartz is expanded by extensive solid solution of SiO_2 in the former phase. Smyth (1977) and Wood and Henderson (1978) have found excess SiO_2 in tschermakitic clinopyroxenes crystallized at high pressure, but, as will be discussed later, the amounts appear to be insufficient to account for all the differences depicted in

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[1] All invariant points are labelled with the absent phase convention.

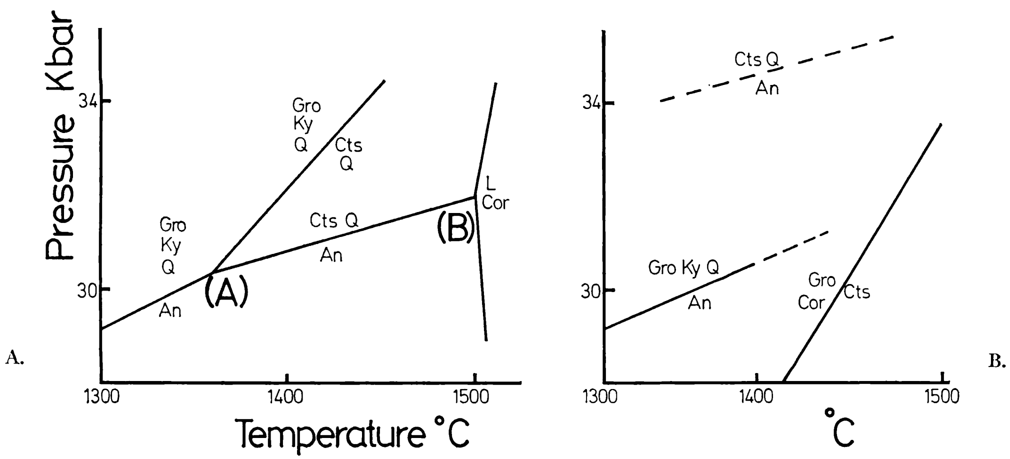

Fig. 1. A. Phase relationships for $CaAl_2Si_2O_8$ composition determined by Hariya and Kennedy (1968). B. Partial phase relationships for $CaAl_2Si_2O_8$ and $CaAl_2SiO_6$ compositions given by Hays (1966). Upper dashed curve is metastable and calculated by the method described in the text. Phase labels correspond to those used in the abstract and table 1.

figure 1. A substantial inconsistency in pressure or temperature calibration is virtually ruled out by the close correspondence of the results of Hays and Hariya and Kennedy for the reaction:

$$\begin{array}{ccccccc} 3CaAl_2Si_2O_8 & = & Ca_3Al_2Si_3O_{12} & + & 2Al_2SiO_5 & + & SiO_2 \\ \text{anorthite} & & \text{grossular} & & \text{kyanite} & & \text{quartz} \end{array} \qquad (1)$$

Hays determined the position of reaction (1) at pressures up to about 31 kb and temperatures up to 1400°C. At 1450°C he observed incongruent melting of anorthite to corundum plus liquid. Hariya and Kennedy found an invariant point A at about 31 kb and 1350°C where reaction (1) is joined by tschermaks clinopyroxene. They also found the temperature of anorthite melting to be substantially higher than did Hays and deduced the presence of another invariant point B at about 32 kb and 1500°C. The reaction that *stably* (according to Hariya and Kennedy) links these two invariant points is:

$$\begin{array}{ccccc} CaAl_2Si_2O_8 & = & CaAl_2SiO_6 & + & SiO_2 \\ \text{anorthite} & & \text{clinopyroxene} & & \text{quartz} \end{array} \qquad (2)$$

For comparison, Hays' results may be used to obtain a calculated *metastable* position of reaction (2). This is done by combining reaction (1) with the reaction:

$$\begin{array}{ccccc} Ca_3Al_2Si_3O_{12} & + & 2Al_2O_3 & = & 3CaAl_2SiO_6 \\ \text{grossular} & & \text{corundum} & & \text{clinopyroxene} \end{array} \qquad (3)$$

and adding free energy data (from Robie and Waldbaum, 1968) for the reaction:

$$\begin{array}{ccccc} Al_2O_3 & + & SiO_2 & = & Al_2SiO_5 \\ \text{corundum} & & \text{quartz} & & \text{kyanite} \end{array} \qquad (4)$$

As may be seen from figure 1, there is a substantial pressure difference between the positions of reaction (2) obtained from the two sets of experiments. It should be noted however that the metastable curve of Hays is for coexistence of pure $CaAl_2SiO_6$ pyroxene with anorthite and quartz. No provision has been made for the probable solid solution of pyroxene toward SiO_2. Solution of SiO_2 in the pyroxene decreases the stability of anorthite and hence, if considered, would bring the calculated metastable curve closer to Hariya and Kennedy's observed curve.

Before proceeding with a detailed discussion of this study it should be pointed out that one part of Hariya and Kennedy's phase diagram is difficult to reconcile with currently accepted thermodynamic data. At invariant point B (fig. 1) these authors found coexistence of corundum and quartz. According to the thermodynamic data of Robie and Waldbaum (1968) these two phases should be metastable with respect to kyanite by approx 1 kcal under the conditions of invariant point B. More recent data derived from phase equilibrium experiments (Essene, Boettcher, and Furst, 1972; Helgeson, Delany, Nesbitt, and Bird, 1978) also yield substantial metastability of corundum and quartz under these conditions.

EXPERIMENTAL METHODS

All experiments were performed on mixtures of synthetic crystalline phases which had been ground together under alcohol, Kyanite, anorthite, and quartz were synthesized from gel starting materials which had been prepared by the method of Hamilton and Henderson (1968). Grossular was synthesized from gel at 31 kb and 1400°C and had a unit cell edge of 11.847 (± 0.001) Å. $CaAl_2SiO_6$ pyroxene was produced from glass at 18 kb and 1300°C; the same glass yielded grossular plus corundum at 30 kb and 1300°C.

In order to minimize absorption of water, the mixtures were stored at 110°C prior to loading in platinum capsules. For the same reason, the filled capsules were heated in a bunsen for approx 2 minutes before final welding. Except where indicated in table 1, all experiments were performed in sealed capsules to prevent access of water and development of hydrous melt.

High-pressure experiments were performed in a half-inch piston-cylinder apparatus of the type described by Boyd and England (1960). The pressure assemblies consisted of outer tubes of talc, Pyrex[2] glass, and graphite with 3.17 mm diameter inserts of crushable alumina. The Pt capsules were approx 3.6 mm long and 2 mm diameter. All assembly parts except the Pyrex and talc tubes were heated for several minutes in a bunsen and stored at 110°C. The Pyrex tubes were heated gently (well below red heat) for about 1 hr and then stored at 110°C.

Each experiment was brought to the desired temperature at a pressure 4 to 5 kb above the intended run pressure. Pressure was then reduced to the desired value and maintained at this value throughout the

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[2] Brand name of the Corning Glass Co.

run. Temperature control was via a $Pt_{100}/Pt_{87}\ Rh_{13}$ thermocouple situated on top of the capsule. Pressures and temperatures quoted in table 1 are nominal values and are uncorrected for possible friction effects or for pressure dependence of thermocouple emf.

Run products were investigated optically, with X-ray diffraction and, in a few cases, with the electron microprobe. The extent of reaction in subsolidus experiments was deduced from relative peak heights on X-ray

TABLE 1

Experimental results

Run no.	P (Kb)	T°C	Time (min)	Starting materials	Result
Around the invariant point (Cts, Cor)					
C102	30.0	1350	200	An, Gro, Ky, Q*	An increased
C109	30.5	1350	215	An, Gro, Ky, Q*	An increased
C97	31.0	1350	150	An, Gro, Ky, Q*	No reaction
C98	31.5	1350	200	An, Gro, Ky, Q*	Gro, Ky, Q increased
C57	32.0	1400	170	Cts, An, Q*	Gro, Ky, An, Trace Gl
C110	32.5	1415	90	An, Gro, Ky, Q	Ky + Q + Gl
C118	32.5	1415	105	An, Q	Gro, Ky, Gl
C119	32.0	1400	110	An, Q	An, Ky, Gl
C174	32.5	1415	135	An, Q	An, Ky, Gl
C175	32.3	1425	120	An, Q	An, Ky, Gl
Around the invariant point (Q, Cor)					
C114	31.3	1420	90	An	An
C170	32.5	1420	100	An, Gro, Cor	Cts formed, Cor decreased, Trace Gl
C168	32.0	1440	100	An, Gro, Cor	Cts, Cor, Gl
Around the invariant point (Q, Gro)					
C113	32.0	1430	90	An	Cor, An, Cts, Gl
C156	33.0	1430	65	An	Cor, Gl
C186	32.5	1430	95	An, Q	An, Cor, Ky, Gl
C115	32.0	1430	120	An, Ky, Q	Ky, Gl
C165	32.0	1430	75	An	An, Cor, Gl
C187	33.5	1430	90	An, Q	An, Ky, Gl
C150	33.5	1440	70	An	Cor, Gl
C190	34.0	1435	100	An, Q	Cor, Ky, Gl
C151	32.5	1445	75	An	Cor, Gl
C160	32.5	1460	30	An	Cor, Gl
The reaction Gro + Cor = Cts					
C123	31.5	1480	80	Gro, Cor	Cts, Gro, Cor
C124	31.5	1440	110	Gro, Cor*	Cts, Gro, Cor
C125	31.5	1420	120	Gro, Cor*	Gro, Cor
C126	31.5	1430	100	Cts, Gro, Cor*	No reaction
C127	31.5	1400	110	Cts, Gro, Cor*	Gro, Cor increased
Melting of An and An + Q					
C152	27.0	1480	50	An	An
C153	27.0	1500	60	An	An
C155	27.0	1525	60	An	Cor, Gl, An
C188	35.0	1440	15	An, Q	Gro, Ky, Gl, Cor
C177	35.0	1450	100	An	Cor, Ky, Gl
C190	34.0	1435	100	An, Q	Cor, Ky, Gl

An = anorthite; Q = quartz; Cts = calcium tschermaks pyroxene; Gro = grossular; Cor = corundum; Ky = kyanite; Gl = glass

Criterion of reaction in subsolidus runs was substantial (> 40 percent) increase in relative peak intensities measured on an X-ray diffractomer using Cu Kα radiation.

* Denotes unsealed capsule.

diffractograms (Cu Kα radiation). If relative peak heights had changed by less than 40 percent of the pre-run values the experiment is designated "no reaction" in table 1. Silicate liquids produced in the higher temperature experiments quenched to clear glasses. In a number of cases these glass compositions have been determined with the electron microprobe (table 2).

RESULTS

Reversal experiments on reaction (1) (table 1) yielded an equilibrium pressure of 31.0 ± 0.5 kb at 1350°C. This observed pressure is similar to, but slightly higher than, those obtained by Hays (29.7 kb approx) and Hariya and Kennedy (30.3 kb). Identical experimental techniques and pressure cell have been used in Manchester to study the reaction:

$$\begin{array}{ccccc} NaAlSi_3O_8 & = & NaAlSi_2O_6 & + & SiO_2 \\ \text{albite} & & \text{jadeite} & & \text{quartz} \end{array}$$

At 600°C an equilibrium pressure of 16.6 kb was obtained; this is 0.3 kb higher than the value "preferred" by Johannes and others (1971). The reader must bear in mind, therefore, that the absolute pressures quoted in this paper may be small overestimates, but that internal consistency should enable deduction of the correct form of the phase diagram for the system $CaO–Al_2O_3–SiO_2$.

Experiments on mixtures of anorthite, grossular, kyanite, and quartz indicate that reaction (1) is joined by liquid at about 1400°C and 32 kb. In view of the general rapidity of melting, all melting reactions were studied with crystalline starting materials *only*. The breakdown of anorthite and quartz to kyanite plus liquid demonstrates that the liquid composition lies on the CaO-side of the join $CaAl_2O_4–SiO_2$. This observation, corroborated by analyses of quenched liquids (table 2) indicates that $CaAl_2SiO_6$ pyroxene cannot be stable together with quartz at temperatures above 1400°C. Stable tie lines crossing the join $CaAl_2O_4–SiO_2$

TABLE 2

Analyses of product glasses

Run no.	C174	C175	C156	C168	C188
P/T	32.3/1415	32.3/1425	33/1430	32/1440	35/1440
Coexisting Phases	An, Ky	An, Ky	Cor	Cts, Cor	Gro, Ky, Cor
SiO_2	51.68 (1.22)	51.27 (1.34)	51.61 (1.42)	46.83 (1.81)	51.75 (1.53)
Al_2O_3	27.83 (1.20)	28.20 (0.61)	24.56 (0.80)	27.70 (2.14)	24.41 (1.10)
CaO	21.04 (0.25)	20.75 (0.31)	24.34 (0.45)	24.75 (0.57)	23.77 (1.75)
	100.6	100.2	100.5	99.3	99.9
			Molecular proportions		
SiO_2	0.570	0.569	0.560	0.522	0.565
Al_2O_3	0.181	0.184	0.157	0.182	0.157
CaO	0.249	0.247	0.283	0.296	0.278

Six to eight analyses were performed in each case. Value in brackets is one standard deviation.

which preclude clinopyroxene plus quartz are kyanite-liquid and, at higher temperatures, corundum-liquid. The stable portions of univariant reactions that radiate from the invariant point (Cts, Cor) were deduced by the method of Schreinemakers and are shown in figure 2B.

Between 1400° and 1430°C at pressures of 32 to 33 kb, the incongruent melting reaction of anorthite changes from:

$$\text{anorthite} = \text{grossular} + \text{kyanite} + \text{liquid} \qquad (5)$$

to reactions involving calcium tschermaks pyroxene and corundum. Hence, two additional invariant points must lie between 1400° and 1430°C at about 32.5 kb. It has proved somewhat difficult to deduce which of the phases corundum and pyroxene joins reaction (5) to form the lower temperature of the two additional invariant points.

At temperatures of 1430°C and above anorthite melts incongruently according to the degenerate reaction:

$$\text{anorthite} = \text{corundum} + \text{liquid} \qquad (6)$$

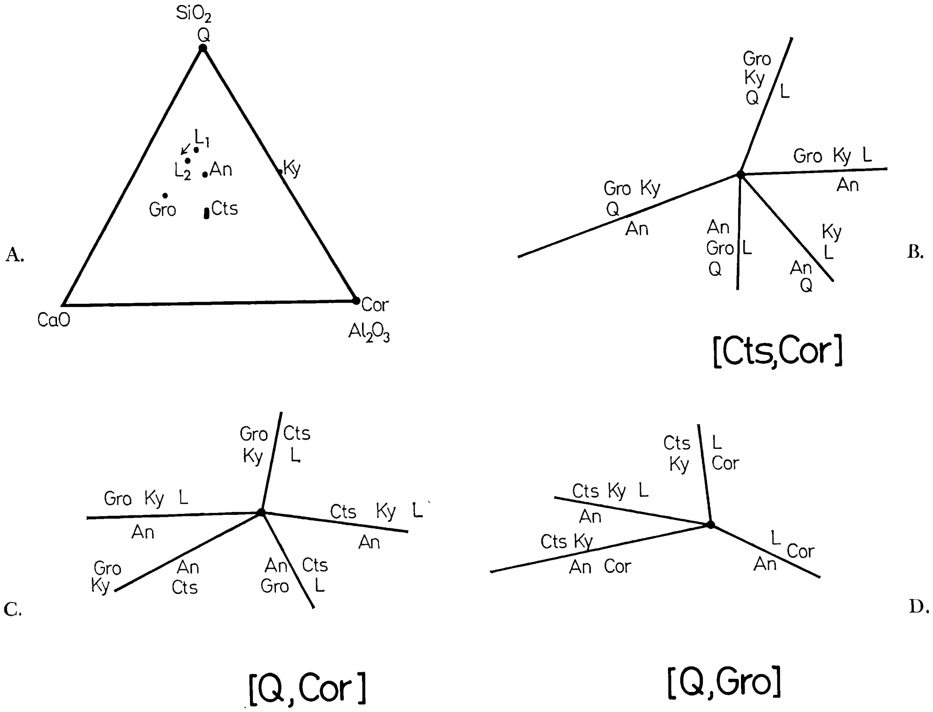

Fig. 2. A. Compositions of relevant phases in the system $CaO–Al_2O_3–SiO_2$ (mol percent). Note that pyroxene (Cts) is a solid solution. The lowest melting composition produces a liquid near L_1. The liquid field expands toward L_2 with increasing temperature. B. C. D. Distribution of univariant curves about the invariant points (Cts, Cor), (Q, Cor), and (Q, Gro).

The degenerate reaction:

$$\text{grossular} + \text{corundum} = \text{pyroxene}$$

was experimentally reversed at between 1400° and 1440°C at 31.5 kb. These data do not, in themselves, enable the sequence of invariant points to be deduced. The experimental data of table 1 show, however, that corundum did not appear at temperatures below 1430°C in the pressure-range 32 to 33 kb. Pyroxene did, however, form in one run at 32.5 kb/1420°C (C170) from a mixture of anorthite, grossular, and corundum. Hence figures 2C, D have been constructed for the situation in which reaction (5) is joined by pyroxene to form the invariant point (Q, Cor). The higher temperature invariant point (Q, Cor) is thus deduced to occur at the point where one of the melting reactions originating at (Q, Cor):

$$\text{anorthite} = \text{pyroxene} + \text{kyanite} + \text{liquid} \tag{7}$$

is joined by corundum.

In figure 2D it has been assumed that, at temperatures above 1430°C, anorthite melts incongruently to corundum plus liquid. This implies that, as temperature increases from 1400° to 1430°C (at 32-33 kb), the liquid composition in equilibrium with anorthite shifts from the SiO_2-rich side of the join Al_2O_3–$CaSi_2O_5$ (on which anorthite lies) to become colinear with anorthite and corundum. This is confirmed by microprobe analyses of glasses (table 2) and by the observed melting relations of anorthite under these P-T conditions (table 1). One experiment (C113), involving anorthite melting, resulted in pyroxene together with corundum and glass. This may simply reflect straddling of the P-T conditions of the invariant point within the capsule. A duplicate experiment, (C165), under the same nominal conditions yielded only corundum and glass in addition to unreacted anorthite.

ADDITIONAL INVARIANT POINTS

If one joins the three invariant points (Cts, Cor), (Q, Cor), and (Q, Gro) by the reactions they have in common, it becomes apparent (fig. 3) that at least one and probably two additional invariant points are present in the P-T region of interest.

Two solid-solid reactions which originate at (Q, Cor) and (Q, Gro) have P-T slopes that imply that they must meet at about 31.8 kb and 1410°C. The two reactions are:

$$\text{grossular} + \text{kyanite} = \text{anorthite} + \text{pyroxene} \tag{8}$$

$$\frac{dP}{dT} \cong 27.6 \text{ bar deg}^{-1} \text{ (from Robie and Waldbaum, 1968)}$$

and

$$\text{pyroxene} + \text{kyanite} = \text{anorthite} + \text{corundum} \tag{9}$$

$$\frac{dP}{dT} \cong 13.7 \text{ bar deg}^{-1}$$

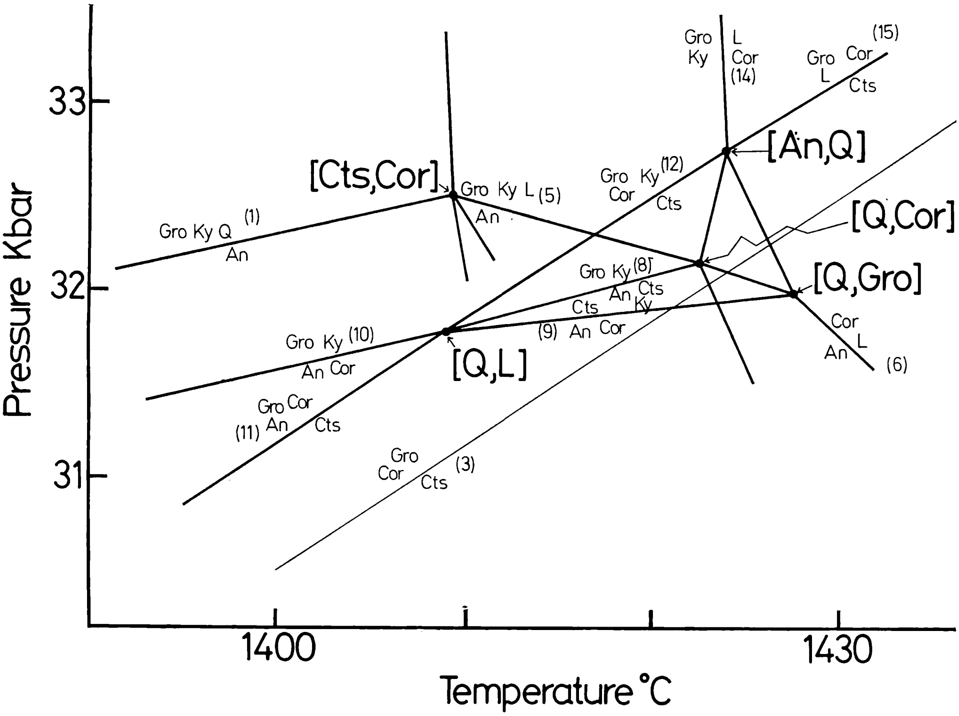

Fig. 3. Phase relationships in the pressure-temperature ranges 31 to 33 kb and 1400° to 1440°C for bulk compositions bounded by the triangle grossular–corundum–quartz. Numbers in brackets refer to reaction numbers in the text.

At the invariant point (Q, L), (8) and (9) are joined by the reaction:

$$\text{anorthite} + \text{corundum} = \text{grossular} + \text{kyanite} \qquad (10)$$

On the basis of thermodynamic data for quartz, kyanite, and corundum (Robie and Waldbaum) reaction (10), may be readily calculated to lie at a pressure approx 0.7 kb below reaction (1) (see also Boettcher, 1970).

At the invariant point (Q, L), reactions (8), (9), and (10) *should* be joined by the degenerate reaction (3).

$$\text{grossular} + \text{corundum} = \text{pyroxene}$$

It has been found, however (Wood and Henderson, 1978), that tschermakitic pyroxenes coexisting with anorthite have small amounts of SiO_2 in solid solution. This solid solution must make the stability field of pyroxene slightly larger than is implied by the equilibrium conditions for reaction (3). A confirmation of this observation is provided by the fact that pyroxene formed from anorthite, grossular, and corundum at 32.5 kb/1420°C, whereas it did not grow from grossular and corundum alone at 31.5 kb/1430°C. Since there are differences in the pyroxene compositions involved, reaction (3) must cross (8) and (9) indifferently. Instead, therefore, of meeting (3) at the invariant point (Q, L) reactions (8), (9), and (10) are joined by the following two reactions:

grossular + corundum + anorthite = pyroxene (11)

grossular + corundum + kyanite = pyroxene (12)

Let us now consider the possible high pressure invariant point (An, Q). Evidence for the existence of this invariant point is, in part, negative. At pressures above the invariant point (Q, Gro), anorthite melts incongruently via the reaction:

anorthite = pyroxene + kyanite + liquid (13)

Pyroxene, kyanite, and liquid have not, however, been observed, and anorthite always melts to corundum plus liquid in the region where the above assemblage might occur. It seems likely, therefore, that reaction (13) has a P-T slope such as that shown in figure 3 which would restrict stable occurrence of the assemblage pyroxene, kyanite, liquid to an extremely small range of pressures and temperatures. An infinite or negative P-T slope would generate the invariant point (An, Q) at a pressure of about 33 kb and a temperature of approx 1425°C. Additional support for the existence of this invariant point is provided by experiment C188 in which the products were grossular, kyanite, corundum, and glass. Generation of these phases from anorthite and quartz implies stable existence of the univariant reaction:

grossular + kyanite = corundum + liquid (14)

Reaction (14) emanates from the high-pressure side of the invariant point (An, Q).

The position of invariant point (An, Q) shown in figure 3 is, of course, subject to considerable uncertainty. The invariant point has, in addition, the unusual feature of having a reaction that involves melting on *decrease* of temperature:

grossular + corundum + liquid = pyroxene (15)

Fortunately, there are important constraints on the slope of this reaction.

Because of the small amount of liquid involved it must be virtually parallel to the degenerate reaction:

grossular + corundum = pyroxene (3)

In addition, reaction (15) cannot cross reaction (3) and can only become tangent to it if the nonstoichiometry of the pyroxene decreases. It is not yet known if the small (see below) pyroxene nonstoichiometry is a function of pressure and temperature, but it is unlikely to change sufficiently rapidly for the illustrated form of reaction (15) to be substantially in error.

CALCULATED METASTABLE REACTIONS

The data presented in this paper may be used to deduce the position of the reaction:

$$\text{anorthite} = \text{pyroxene} + \text{quartz} \qquad (2)$$

This reaction occurs metastably at the point where the reaction:

$$\text{anorthite} = \text{grossular} + \text{kyanite} + \text{quartz} \qquad (1)$$

$$\frac{dP}{dT} \cong 22.2 \text{ bar deg}^{-1}$$

meets:

$$\text{grossular} + \text{kyanite} = \text{anorthite} + \text{pyroxene} \qquad (8)$$

The stable parts of reactions (1) and (8) lie, respectively, on the low temperature sides of the invariant points (Cts, Cor) and (Q, Cor). The location of reaction (1) has been fixed by the subsolidus experiments discussed earlier, whereas the position of (8) is fixed by the invariant point (Q, Cor). The latter invariant point is constrained to lie in a P-T area close to 32.2 kb and 1420°C. Metastable extrapolation of (8) and (1) using high temperature entropy and 298 K/1 bar volume data (Robie and Waldbaum, 1968) yields the point of intersection at about 37 kb (with an uncertainty of 1.5 kb) and 1600°C.

It should be noted that the above estimate provides only for the fixed pyroxene composition at the invariant point (Q, Cor). Wood and Henderson (1978) found that such a pyroxene coexisting with anorthite would contain about 1.7 wt percent SiO_2 in excess of the stoichiometric amount. It was demonstrated, however, that as a_{SiO_2} increases the excess SiO_2 content of the pyroxene rises dramatically. Thus, a pyroxene on the join: $(CaMg_{0.3}Al_{1.4}Si_{1.3}O_6)$–$SiO_2$ may, when coexisting with quartz, dissolve about 6 percent SiO_2 in excess of the stoichiometric amount. Extrapolating this result to pyroxenes on the join $CaAl_2SiO_6$–SiO_2 implies that tschermakitic clinopyroxene actually coexisting with quartz would have approximate formula $Ca_{0.93}Al_{1.64}Si_{1.29}O_6$.

The calculated point of intersection of (1) and (8) has been corrected for nonstoichiometry of the clinopyroxene by assuming that this phase behaves as an ideal ionic solution. This assumption yields the following result for activity of the $CaAl_2SiO_6$ component, relative to a standard state of the pure phase at the pressure and temperature of interest:

$$a_{CaAl_2SiO_6}{}^{cpx} = 4(X_{Ca}{}^{M2})\,(X_{Al}{}^{M1})\,(X_{Al}{}^{T})\,(X_{Si}{}^{T})$$

The point of intersection of reactions (1) and (8) has therefore been corrected upward in pressure by 0.2 kb to take account of an activity of $CaAl_2SiO_6$ in the clinopyroxene (at the invariant point (Q, Cor)) of 0.98. The calculated metastable curve is thus for pure $CaAl_2SiO_6$ clinopyroxene.

Figure 4 shows the calculated metastable curve for reaction (2) extrapolated down in temperature assuming dP/dT of 10 bar deg^{-1}. This latter figure is consistent wtih recent high temperature calorimetric data

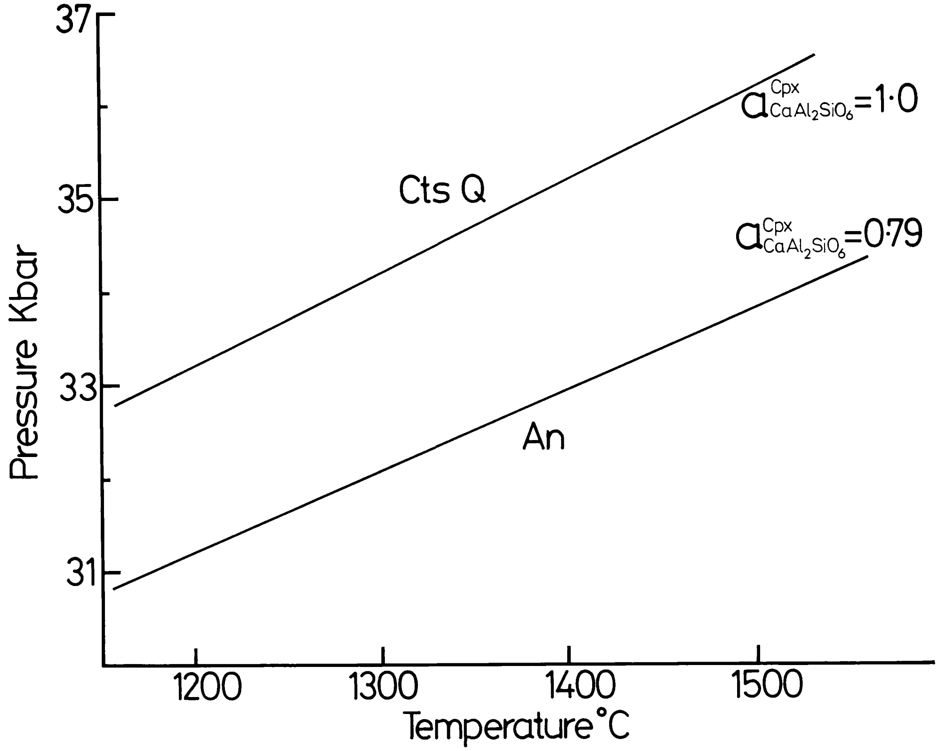

Fig. 4. Calculated curves for the reaction: An = Cts + Q. The upper curve is hypothetical in that the pyroxene is taken to be pure $CaAl_2SiO_6$. The lower curve approximates the true metastable position of the reaction because the nonstoichiometry of the pyroxene has been taken into consideration.

(R. C. Newton, personal commun.). An additional point on reaction (2) may be constructed at 35.7 (+1.5/−1.0) kb and 1450°C from a combination of reaction (1), degenerate reaction (3), and thermodynamic data of Robie and Waldbaum for reaction (4).

Also shown in figure 4 is the *true* metastable position of reaction (2) taking account of the maximum solubility of SiO_2 in the clinopyroxene phase. The estimated composition of tschermakitic clinopyroxene coexisting with quartz which is given above yields an activity of $CaAl_2SiO_6$ component of 0.79. This lowering of $CaAl_2SiO_6$ activity relative to the pure phase shifts the metastable curve for reaction (2) downward by about 2 kb. The observation that reaction (2) is not stable necessitates that the pressures of the reactions shown in figure 4 are not more than 1 kb too high. The *upper* limits on pressure are approx 1.5 kb above the illustrated curves.

The true metastable position of reaction (2) determined in this study is approx 2 kb above the stable position given by Hariya and Kennedy (1968). The data presented here appear, therefore, to be consistent with those of Hays (1966) rather than those of Hariya and Kennedy (fig. 1). It is of interest to note, however, that the calculated true metastable position of reaction (2) is virtually coincident with the melting reactions of anorthite (5 and 7) which were discussed earlier. Thus any additional nonstoichiometry of clinopyroxene (over that obtained by Wood and Henderson) would lower reaction (2) in pressure so that it would appear to be stable. A lowering in pressure of 500 to 1000 bars (175-350 cal) would be sufficient for this purpose. Thus, Hariya and Kennedy's results on reaction (2) may have been due to synthesis of a pyroxene with a slightly higher degree of nonstoichiometry than that obtained in this study. Such an explanation could not, however, provide for coexistence of quartz and corundum at invariant point B shown in figure 1.

CONCLUSIONS

Anorthite melts incongruently above about 1400°C at a pressure of 32 kb. The anorthite melting relations and the stability of $CaAl_2SiO_6$ clinopyroxene obtained in this study are in general agreement with those of Hays (1966). The stability field of pyroxene expands in anorthite- or quartz-bearing assemblages due to solution of excess SiO_2 in the former phase. This nonstoichiometry of the pyroxene is sufficient to explain in large part the differences between the results of Hays and those of Hariya and Kennedy (1968). The invariant point involving corundum and quartz (at 32 kb/1500°C) which was reported by the latter authors appears, however, to be incorrect. It is precluded by thermodynamic data on corundum, quartz, and kyanite and by the observed melting of anorthite at substantially lower temperatures.

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