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The melting and breakdown reactions of anorthite at high pressures and temperatures

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Abstract

The reaction 3 $CaAl_2Si_2O_8 \rightleftarrows Ca_3Al_2Si_3O_{12} + 2\ Al_2SiO_5 + SiO_2$, important to geobarometry, has been re-investigated in solid-media pressure apparatus, using very small quantities of oxalic acid dihydrate as a flux and improved pressure calibration based on runs with NaCl pressure medium at 1100° and 1150°C. The reaction was reversed at 7 temperatures between 1100° and 1400°C. The equation for the curve is $P = -2.1 + 0.0232\ T$ (P = kbar, T = °C), and the slope is 23.2 bars/°C. The curve is in good agreement with calculations using recent thermochemical data.

The (anhydrous) melting of anorthite was also investigated, and is congruent to 9 kbar where a maximum temperature of 1570°C is reached and corundum appears with the melt. With increasing pressure corundum continues to develop and the melting curve assumes an increasingly negative slope, reaching 1450°C at 29 kbar. Corundum is also produced at pressures >9 kbar by exsolution from solid anorthite by a process that is independent of the incongruent melting, and that takes place at temperatures well below melting; stoichiometric anorthite is unstable at high pressures. The presence of corundum both below and above the melting curve complicates the phase relations in the vicinity of the (virtual) intersection with the breakdown curve, and requires that, for the composition $CaAl_2Si_2O_8$, a small amount of the reaction anorthite (Al-deficient) + corundum ⇄ grossular + kyanite take place before the principal breakdown reaction.

Introduction

Knowledge of the behavior of feldspars and of the nature of their breakdown products at high pressures and temperatures is essential to an understanding of deep crustal and upper mantle petrology. The direct determination of phase relations in the laboratory does not however always result in clearly definable and unambiguously interpretable information. Many silicate reactions are very sluggish at moderate temperatures, and this is particularly true in anhydrous systems. In some cases the temperature range in which reactions can be successfully carried out is quite restricted. Accurate data are obviously necessary before good thermodynamic information can be obtained, and for the reliable extrapolation or calculation of reactions at temperatures that differ significantly from those in the range at which the experimental work was done. The direct experimental determination of the high-pressure breakdown reaction of the end-member feldspar anorthite is difficult because of slow reaction rates at temperatures below 1200°C, and although previous investigations have produced a reasonable picture of the relations, it was deemed desirable to re-examine the system using a somewhat modified technique and a new correction for "friction" in the piston–cylinder apparatus. This study is restricted to the composition $CaAl_2Si_2O_8$, and although the melting relations of the plagioclases have been examined at high pressure (Lindsley, 1968) and numerous investigations have been carried out on the albite breakdown to jadeite and quartz, little has been done on the anhydrous breakdown reaction of the intermediate plagioclases. Cohen *et al.* (1967), working with a basalt glass, observed that feldspars on the solidus become more sodic with increasing pressure, but no quantitative experiments were carried out on the plagioclase breakdown.

The melting of anorthite at high pressures has been investigated by Hariya and Kennedy (1968), and limited data have been obtained by Lindsley (1968) and by Hays (1966). The high-pressure breakdown of anorthite to grossular, kyanite, and quartz was first observed by Boyd and England (1961), and

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the reaction was studied by Hays (1966) and by Hariya and Kennedy (1968). Newton (1966) calculated the breakdown reaction 3 anorthite $\rightleftarrows$ grossular + 2 sillimanite + quartz from data on two other reactions, and corrected it for the sillimanite–kyanite inversion. Shortly after the present work was completed, a determination of the reaction anorthite $\rightleftarrows$ grossular + kyanite + quartz was published by Schmid *et al.* (1978), using a novel technique involving observations of compositional change in the garnet, which had been doped with Fe^{2+}. The results of the three experimental determinations and of the calculation by Newton will be discussed in a later section.

At the outset, however, before any data are presented, it may be helpful to point out some aspects of the behavior of anorthite at elevated pressures and temperatures, particularly in regard to reactions producing corundum. Anorthite melts congruently at one atmosphere, but at pressures above approximately 10 kbar melts incongruently to corundum plus liquid (Boyd and England, 1961; Hariya and Kennedy, 1968). There is, however, a totally different effect that also results in the development of corundum at temperatures *below* melting. Newton (1966) noted corundum in association with (alumina-deficient) anorthite in runs made with $CaAl_2Si_2O_8$ glass at elevated pressures and temperatures greater than 1200°C, and the run-tables of Lindsley (1968), who investigated the plagioclase melting relations at 10 and 20 kbar, and Hariya and Kennedy (1968), who worked with $CaAl_2Si_2O_8$, also list corundum in a number of subsolidus runs. The present work shows that the development of corundum from anorthite well below the solidus also takes place at pressures greater than approximately 9–10 kbar, the same pressure at which incongruent melting sets in.

Thus there are two distinctly different corundum-producing phenomena, which coincidentally and, perhaps, confusingly are initiated at essentially the same pressure:

(1) incongruent melting of $CaAl_2Si_2O_8$ to melt plus corundum;

(2) development of corundum by "exsolution" from solid anorthite of the composition $CaAl_2Si_2O_8$ to produce corundum plus an Al_2O_3-deficient anorthite.

The resolution of the question of the nature and composition of the anorthites at high pressure awaits further work. There are several reports in the literature of non-stoichiometry in anorthite or anorthite-like compounds, all however at low pressures. Bhatty *et al.* (1970) crystallized anorthites from glasses containing 5–10 percent excess Al_2O_3 that gave an abnormal X-ray powder diffraction pattern, and that showed no alumina-bearing phase at temperatures below *ca.* 1150°C. Reheating these anorthites to temperatures above 1200–1250°C, or crystallizing the glass above 1200–1250°C, produced a normal anorthite plus corundum. It is likely that a non-stoichiometric, metastable Al_2O_3-rich anorthite had been formed. On the other hand, the concept of excess silica in the feldspar structures accompanied by cation vacancies goes back to Schwantke (1909). Grundy and Ito (1974) crystallized stoichiometric Sr-feldspars by solvent growth using a V_2O_5 flux with an Al/Si ratio of unity, and feldspars with partially vacant "alkali" cation sites from melts with Al/Si < 1. Grundy and Ito (1974) showed that one of these non-stoichiometric feldspars had a composition corresponding to $Sr_{0.84}Na_{0.03}\square_{0.13}Si_{2.29}Al_{1.69}O_8$, clearly Al-deficient. Bruno and Facchinelli (1974) demonstrated appreciable solubility of SiO_2 in anorthite in hydrothermal experiments on the join $CaAl_2Si_2O_8$–SiO_2, and Longhi and Hays (1976) report up to 8 wt. percent excess silica in anorthite coexisting with liquid at the eutectic on the join at 1368°C.

Ito (1976) extended his solvent-growth work to anorthite, and grew well-crystallized stoichiometric anorthite crystals up to 5 × 3 × 0.5 mm using a CaV_2O_6 solvent, from melts with an Al/Si ratio of close to unity. Nonstoichiometric anorthites of similar size were produced by adjusting the melt to more SiO_2-rich compositions. Anorthite of the approximate composition $Ca_{0.9}Al_{1.8}Si_{2.2}O_8$ was produced in a melt with an Al/Si ratio of 0.793. Weill *et al.* (1970) had earlier observed excess SiO_2 in some lunar plagioclases, and Wenk and Wilde (1973) also report anomalous compositions of lunar anorthite. Rather high concentrations of TiO_2 exist in the lunar anorthite-containing rocks, but the effect of TiO_2 on synthetic crystallizations is unknown, as are the inter-relations, if any, of the factors inducing the low- and high-pressure non-stoichiometry in anorthites.

Experimental methods

All the experiments were done in piston–cylinder apparatus. Those that determined the melting curve were done in 0.75″ diameter pressure chambers, using Pyrex glass pressure media with a talc outer sleeve (Newton, 1972). A number of runs at nominal pressures of 30 and 32 kbar were made with a 0.5″ diameter pressure chamber, also using Pyrex and talc parts. There was excellent agreement between the runs made with the two chamber sizes. In both size assemblies the glass parts were made from precision-bore tubing with the outer diameter ground to the desired value. Both I.D. and O.D. were held to ±0.0002″ to ensure a properly fitting pressure assembly. At pressures above 24 kbar (nominal) with the 0.75″ diameter stage, a piston with a 0.125″ bevel ground on the top was used with a matching pyrophyllite ring machined to square-off the piston. In several investigations in this laboratory, no difference in "frictional" behavior has been detected between flat and beveled pistons.

The runs that determine the high-pressure breakdown of anorthite were done in a 0.5″ diameter chamber with Pyrex glass pressure media, and at 1150° and 1200° with soft glass (Kimble R6). Calibration runs, to be discussed shortly, were made at 1100°C and 1150°C in 0.75″ diameter chambers with NaCl as the pressure medium. All runs were made with WRe_{25}–WRe_3 thermocouples, separated from the platinum capsules by a thin layer of alundum cement and 0.004″ platinum sheet.

The starting materials used to determine the melting relations were a synthetic anorthite made by reacting the oxides at approximately 1450°C with several cycles of heating and crushing, and an anorthite from the Sittampundi Complex, South India, analyzed to be An_{98}, collected by the late A. P. Subramaniam. In addition, a number of runs were made on a synthetic An_{95}, also prepared by sintering the oxides below the solidus. Optical examination and X-ray diffraction patterns indicated the plagioclases to be phase-pure and homogeneous. After loading into platinum tubes sealed at one end, the samples were heated to a red heat to eliminate moisture, then immediately sealed.

The starting materials for the reaction 3 An $\rightleftarrows$ grossular + 2 kyanite + quartz were the synthetic anorthite, a synthetic grossular prepared from the oxides by R. C. Newton by hydrothermal crystallization at 1000°C and 26 kbar, kyanite from Litchfield, Connecticut, and a pure vein quartz from near Lisbon, Maryland. The major impurity in the kyanite is 0.93 percent Fe_2O_3. The products and reactants were carefully blended in the appropriate molar proportions under acetone by mixing four times to dryness in an agate mortar and pestle. Repeated X-ray scans were made so as to be familiar with slight variations in relative intensities of the major peaks and thus to establish what constitutes a significant difference in proportions of phases. Initially runs were made in the range 1200°–1400° by carefully drying the samples at a red heat in the capsules before sealing, but as will be described shortly, a series of runs were also made in the range 1100°–1350° after adding a trace of oxalic acid to the charge before sealing.

The experimental results

The effect of small amounts of water on the anorthite breakdown reaction; the formation of zoisite

Zoisite invariably forms in the lower-temperature runs on the anorthite breakdown assemblage if any water is present. The sample as well as the components of the high-pressure assembly must be baked out and water-free. The concept of fluxing the sluggish breakdown reaction in the lower temperature range with water might seem doomed to failure for the following reasons:

1. Zoisite crystallizes very rapidly, possibly removing the water before it can have an effect on the anhydrous reaction. Once formed, the zoisite may hold the water very tenaciously, and P_{H_2O} could thus be too low to have much effect.
2. The direction of the reaction is determined by observing the relative proportions (as judged by X-ray diffraction peak intensities) of reactants and products. If zoisite is formed by selective or preferential reaction rather than by equimolar reaction of the four phases present, the reaction direction might be interpreted incorrectly. Anorthite alone contains all of the oxides and is compositionally similar to zoisite. One might assume that it is more difficult to produce zoisite by reaction between grossular, kyanite, and quartz than to convert anorthite to zoisite. If so, the development of zoisite would produce what appeared to be a reaction favoring the high-pressure assemblage.

Nevertheless, the advantages of obtaining data below 1200°C, in a P–T range where NaCl might be used as the pressure medium, were such that "hydrothermal" experiments were attempted. Very small amounts of oxalic acid dihydrate (typically one barely visible crystal) were added to the sample (approximately 7 mg) and in some cases the sample was breathed on. A minimal amount of water was desired so that as much as possible of the reactant phases other than zoisite be present. It is difficult to add traces of liquid water. In all runs below 1350°, this procedure produced zoisite, usually in very subordinate amounts, approximately 10 percent or less, although in several runs zoisite was (accidentally) predominant. In several runs, only one of which is listed, silver oxalate was added in place of oxalic acid. It is not known how effective the zoisite is in eliminating water as a fluxing agent. The activity of H_2O in the charge containing zoisite may still be adequate, at these temperatures and pressures, to promote the reaction.

Reversal runs have not been made on the zoisite-producing reaction, but it appears that zoisite is stable in the pressure range of this study to temperatures above 1300°C. This is a higher temperature than formerly assumed (Boettcher, 1970), and zoisite would be stable to an even higher temperature on its own composition.

Determination of the reaction

Table 1 contains the data on the reaction 3 anorthite $\rightleftarrows$ grossular + 2 kyanite + quartz. All pressures have been corrected for "friction," and the method will be described in the following section.

The strongest peaks in the X-ray diffraction pattern of the reactant–products mixture are the principal peaks of anorthite and grossular. The strongest kyanite peak ($\bar{1}21$), $d = 3.18$, overlaps the cluster of reflections that give the strongest peaks for anorthite. The strongest quartz peak overlaps a subsidiary kyanite peak (200), at $d = 3.35$. In addition, strong orientation effects on intensities are noted with kyanite. Most runs show an apparent reduction of intensity of the combined kyanite–quartz peak compared to a scan made from a simple smear of the original mixture, even if significant growth of grossular and depletion of anorthite is observed. Comparison with samples sprinkled on vaseline clearly shows the strong effect on the relative intensities. The sample smear of the mixture containing the raw ground Litchfield kyanite produces a (200) peak that is much stronger than the ($\bar{1}21$) peak. When the X-ray smear is made from the reacted sample, much or most of this preferred orientation is lost, and an apparent decrease in the intensity of the (200) peak is observed. In order to determine the direction of reaction, only the grossular and anorthite peaks were used, and in Table 1 no mention is made of growth or depletion of kyanite and quartz. Judgment must be exercised relative to the overlap of the kyanite and anorthite peaks, although this region of the pattern is dominated by anorthite.

The use of small quantities of water appears justified, and the development of some zoisite as an extraneous phase can be tolerated. Anhydrous runs were made at 1250°, 1350°, and 1400°C, and runs with added oxalic acid at 1100°, 1150°, 1200°, 1300°, and 1350°C, with consistent results. The results are shown in Figure 1; the brackets for the two types of runs are not differentiated. Both types of runs were carried out at 1350°C, and the curve was bracketed in both cases between 28 and 30 kbar. There is however what appears to be a difference in the anhydrous and "hydrous" runs at 29 kbar (AN43 and AN52). The curve comes so close to passing through this point that slight pressure variation, within the limit of error, could produce either anorthite or grossular growth.

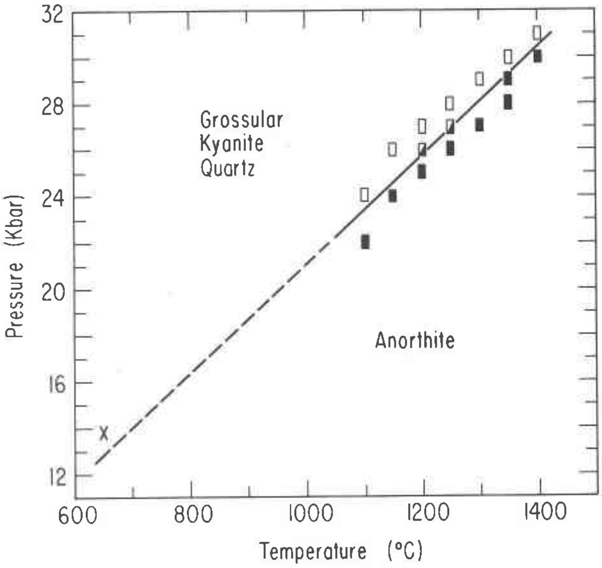

Fig. 1. Experimental data and the *P-T* curve for the anorthite breakdown reaction, 3 $CaAl_2Si_2O_8 \rightleftarrows Ca_3Al_2Si_3O_{12} + 2\ Al_2SiO_5 + SiO_2$. Open rectangles products grew, closed rectangles reactants grew. Diagonally-divided rectangles indicate no reaction. Table 1 contains complete set of data. The runs at 1200°C and above, done in glass pressure media, are corrected for "friction" (see text). The symbol at 650°C and 13.8 kbar is the point calculated by Newton (1966). See text for discussion of the presence of some corundum and the non-stoichiometric nature of the anorthite.

Fears relative to preferential or selective conversion of part of the reversal mix to zoisite appear to have been unjustified. Runs such as AN59 (25 kbar, 1200°C) and AN60 (27 kbar, 1200°C), each containing zoisite, clearly indicate that both anorthite and grossular can grow along with zoisite, and that if any preferential development of zoisite from one of them takes place, the effect is inadequate to mask the direction of the equilibrium.

It also appears that H_2O can be effectively held in a glass assembly. Goldsmith and Newton (1977) were successful in fluxing scapolite reactions, using oxalic acid in soft-glass pressure assemblies, but reaction

Table 1. High-pressure breakdown in anorthite

(3 anorthite $\rightleftharpoons$ grossularite + 2 kyanite + quartz)
Starting materials are above reactants and products,
± oxalic acid (OX), as indicated

Run No.	Starting Material	P, kbar	T, °C	Time, hrs.	Results
AN 62	Dry	31	1400	2	Gros grew
AN 61	Dry	30	1400	2	An grew
AN 35	Dry	30	1350	6	Almost all gros, etc.
AN 43	Dry	29	1350	6	Slight gros growth
AN 36	Dry	28	1350	1 3/4	Strong An growth
AN 37	Dry	28	1350	2 1/2	Almost all An
AN 53	Trace OX	30	1350	1/2	Almost all gros, etc.
AN 52	Trace OX	29	1350	1/2	An grew
AN 51	Trace OX	29	1300	1/2	Gros grew, Zo present
AN 50	Trace OX	27	1300	1/2	An grew, gros gone, Zo present
AN 58	Trace OX	27	1300	1/2	An grew, Zo present
AN 42	Dry	28	1250	6	Gros grew
AN 39	Dry	27	1250	24	No reaction
AN 41	Dry	26	1250	23	Strong An growth
AN 40	Dry	25	1250	21	Strong An growth
AN 49	Trace OX	27	1250	1	Zo, other phases depleted
AN 48	Trace OX	27	1200	4 1/2	Zo, gros and An depleted
AN 60*	Trace OX	27	1200	2 2/3	Gros grew, Zo present
AN 38	Dry	26	1200	21 3/4	No reaction
AN 59*	Trace OX	25	1200	2 1/2	An grew, Zo present
AN 72*	Trace OX	26	1150	94	Strong gros growth, trace Zo
AN 71*	Trace OX	24	1150	98	Strong An growth, trace Zo
AN 63**	Trace OX	26	1150	18	Gros grew, Zo present
AN 64**	Trace OX	24	1150	19	No reaction, Zo present
AN 70**	Trace OX	24	1150	48	An grew, Zo present
AN 54**	Trace OX	26	1100	2	Gros grew, Zo present
AN 45	12% AgOX	25	1100	18	An depleted, gros, etc. + Zo present
AN 55**	Trace OX	24	1100	2 1/6	Slight gros growth, Zo present
AN 68**	Trace OX	24	1100	143	Slight gros growth, Zo present
AN 56**	Trace OX	22	1100	3 1/3	Gros depleted, chiefly Zo
AN 57**	Trace OX	22	1100	2	Slight An growth, Zo present
AN 66**	Trace OX	22	1100	24	No reaction
AN 67**	Trace OX	22	1100	97	An growth, Zo present

* = Soft glass assembly, 1/2"
All others Pyrex, 1/2"

** = Salt assembly, 3/4"

Pressures for all glass runs corrected for "friction" (3 kbar) as determined from salt runs (see text).

An = Anorthite, Gros = grossulante, Ky - kyanite, Q = quartz, Zo = zoisite, OX = oxalic acid, AgOX = silver oxalate.

temperatures were for the most part below 1100°C. Run AN46 in the current series, not listed in Table 1, contained silver oxalate (8 percent by weight) in the reversal mix, and was run at 1100°C, 22 kbar, for 17.5 hrs. Silver oxalate releases CO_2 upon decomposition. The principal run products were scapolite, some zoisite, and residual grossular. The zoisite undoubtedly formed from adsorbed moisture in the (undried) silver oxalate, but the presence of scapolite is clear evidence that CO_2 was retained in the capsule long enough to react with the anorthite. I believe this is the first synthesis of meionite, $3CaAl_2Si_2O_8 \cdot CaCO_3$, by reaction with CO_2. Prior syntheses (Newton and Goldsmith, 1975; Goldsmith and Newton, 1977) were carried out by reacting feldspar with $CaCO_3$.

Pressure calibration

The data in Table 1 and Figure 1 have been corrected for "friction" of the glass assemblies by subtracting 3 kbar from the nominal gauge pressure based on comparison with runs made with NaCl pressure medium. The curve representing the anorthite breakdown reaction was located by reversal runs in Pyrex assemblies from 1250° to 1400°C, and with soft-glass assemblies at 1150° and 1200°. Results with the two types of glass are consistent, and a straight line can be cleanly drawn through all the brackets. It would thus appear that at the temperatures of this investigation the value of "friction" for the two assemblies is the same.

The curve was bracketed at 1100° and 1150°C with "piston-out" runs made in NaCl assemblies. At temperatures as low as 600°C the correction due to "friction" in these assemblies in "piston-out" runs is very small (Johannes *et al.,* 1971; Mirwald *et al.,* 1975). It was not possible to work with salt at temperatures above 1150°, and in fact several runs failed at this temperature. As the melting curve of NaCl is approached, it becomes so weak that it is difficult to avoid mechanical disruption, usually expressed as penetration of the graphite "furnace" sleeve by sheets or dikes of salt. The slope of the curve of the breakdown reaction to be discussed shortly is close to 23 bars/°C, whereas the slope of the melting curve of NaCl is approximately 64 bars/°C (Clark, 1959). The NaCl melting curve intersects the anorthite breakdown curve at slightly over 1250°C and 27 kbar. In a number of investigations in this laboratory it appears that NaCl becomes too weak to maintain the integrity of the high-pressure assembly at about 100°C from its melting point.

Eight runs were made with NaCl assemblies at

1100°C, and although the curve is pinned between 22 and 24 kbar, data (Table 1) indicate that the curve is probably closer to the upper pressure range of the bracket. Three runs were made at 1150°C, and there is no evidence to indicate that the curve should be shifted from the center of the bracketing runs at 24 and 26 kbar. Accordingly, for the purpose of pressure calibration, the curve is considered to pass through the point at 1150°C and 25 kbar. The curve as finally drawn is however modified slightly.

The nominal or gauge pressure for all runs made in glass assemblies was 3 kbar higher than the values listed. The nominal pressure brackets defined a curve that when lowered 3 kbar passed through the 1150° and 25 kbar point. Even if one ignores the runs at temperatures greater than 1150°C, the same 3 kbar correction is obtained by considering the difference between the 1150°C glass run (nominal brackets at 27 and 29 kbar, or 28 kbar point) and the NaCl point. This gives a value for the "friction" of 10.7 percent for the glass assemblies at 1150°C. The question then arises as to whether the 3 kbar correction should also be applied at higher temperatures; if it is assumed that with increasing temperature the "frictional" effect lessens, then the slope of the curve would be somewhat greater than the apparent experimental slope. If on the other hand the experimental slope is assumed correct, some relative decrease in "friction" is intrinsically accepted, for the percentage correction at 1400°C is 9 percent compared to the 10.7 percent at 1150°. There is no real justification for changing the slope in favor of untested assumptions about "friction," so the correction is made here by simply dropping the entire curve 3 kbar. Furthermore, if the mechanical support of a cool outer column of glass is the correct explanation for the "frictional" effect, it could not be greatly decreased with increasing temperature because of the large radial temperature gradient inherent in the piston–cylinder device. The outer layer of glass adjacent to the talc is always below 825°C, the dehydration temperature of talc at these pressures (unpublished data of T. J. B. Holland, this laboratory). From the point of view of resolution of these problems it is unfortunate that the NaCl pressure medium cannot be used at temperatures above 1150°C, and that reaction rates are so slow below 1100°C.

The melting relations

Boyd and England (1961) noted that at pressures up to about 10 kbar the anorthite melting curve has a positive slope, but that above about 10 kbar the melting of anorthite becomes incongruent, with corundum and liquid as the products, and the slope of the melting curve becomes negative. Hays (1966) also observed the incongruent melting products of anorthite to be corundum and liquid at 1450°C and at pressures of approximately 28 and 34 kbar.

The congruent melting point of anorthite at one atmosphere is 1553°C (Rankin and Wright, 1915). Hariya and Kennedy (1968) show congruent melting behavior to about 9 kbar, and their melting curve has a positive slope of 2.7°C/bar. Above 9 kbar they represent the incongruent melting curve as a straight line with a negative slope of −3.5°C/kbar to pressures of 31.6 kbar, and state that the boundary between anorthite and the corundum + liquid region is defined quite sharply. A triple point between the fields of anorthite, liquid, and liquid plus corundum is shown in approximately 1575° and 9 kbar. The authors do not speculate on what becomes of the boundary between the fields of liquid and liquid plus corundum at higher temperatures and pressures; their data are limited to runs at two temperatures at 12.3 kbar. At about 1620°C very small amounts of corundum are seen, and corundum is not present above 1640°C. Lindsley (1968) indicates corundum disappears from the melt at ~1625°C at 10 kbar, and ~1765°C at 20 kbar.

Table 2 contains the data delineating the melting curve, shown in Figure 2, plus some runs at lower temperatures that relate to the behavior of anorthite in the solid state. All pressures have been corrected by 9 percent, the amount of "friction" correction used at the highest temperature portion of the anorthite breakdown reaction. Although data are lacking in the region between 1 atmosphere and 7 kbar, there is no evidence for anything but a continuous curve with a temperature maximum of approximately 1570°C at 9 kbar. The curve could be approximated up to about 22 kbar by two straight lines of positive and negative slope, but to attempt to do so beyond this pressure would seriously violate the data.

Discussion of results

The anorthite breakdown reaction

Figure 1 represents the reaction:

$$\underset{\text{anorthite}}{3\ CaAl_2Si_2O_8} \rightleftarrows \underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{kyanite}}{2\ Al_2SiO_5} + \underset{\text{quartz}}{SiO_2}$$

as determined in this investigation. The brackets from 1100° to 1400° represent the appropriate runs from Table 1, and the straight line is a least-squares fit calculated from the center point of the bracketing runs. The equation for the curve is $P = -2.1 +$

Table 2. Melting relations and associated phenomena

Run No.	Starting Material	P, kbar	T, °C	Time, hrs.	Results
AN 1a	Syn An	7.3	1575	1/4	Glass
AN 1b	Syn An	7.3	1575	1/4	Glass
AN 2a	Syn An	7.3	1560	1/4	An
AN 2b	Syn An$_{95}$	7.3	1560	1/4	Plag
AN 7a	Syn An	9.1	1575	1/4	Glass + Cor
AN 7b	C-50	9.1	1575	1/4	Glass + Cor
AN 6a	Syn An	9.1	1560	1/4	An, some Cor
AN 6b	C-50	9.1	1560	1/4	An, some Cor
AN 5a	Syn An	10.9	1575	1/4	Glass + Cor
AN 5b	Syn An$_{95}$	10.9	1575	1/4	Glass + Cor
AN 4a	Syn An	10.9	1560	1/4	An + Cor
AN 4b	Syn An$_{95}$	10.9	1560	1/4	Plag + Cor
AN 9a	Syn An	14.6	1575	1/4	Glass + Cor
AN 9b	C-50	14.6	1575	1/4	Glass + Cor
AN 8a	Syn An	14.6	1560	1/4	An + Cor
AN 8b	Syn An$_{95}$	14.6	1560	1/4	Glass + some Plag + Cor
AN 10a	Syn An	18.2	1550	1/4	Glass + Cor
AN 10b	Syn An$_{95}$	18.2	1550	1/4	Glass + Cor
AN 11a	Syn An	18.2	1540	1/4	An + Cor
AN 11b	Syn An$_{95}$	18.2	1540	1/4	Plag + Cor
AN 12a	Syn An	21.8	1540	1/4	Glass + Cor
AN 12b	C-50	21.8	1540	1/4	An + Glass + Cor
AN 13a	Syn An	21.8	1530	1/4	An + Glass + Cor
AN 13b	C-50	21.8	1530	1/4	An + Glass + Cor
AN 14a	Syn An	21.8	1520	1/4	An + Cor
AN 14b	C-50	21.8	1520	1/4	An + Cor
AN 15a	Syn An	25.5	1510	1/4	Glass + Cor
AN 15b	C-50	25.5	1510	1/4	Glass + Cor
AN 16a	Syn An	25.5	1500	1/4	Glass + Cor
AN 16b	C-50	25.5	1500	1/4	An + glass + Cor
AN 17a	Syn An	25.5	1490	1/4	An + Cor
AN 17b	C-50	25.5	1490	1/4	An + Cor
AN 27a	Syn An	27.2	1490	1/4	Glass + Cor
AN 27b	C-50	27.3	1490	1/4	Glass + An + Cor
AN 26a	Syn An	27.3	1480	1/4	An + glass + Cor
AN 26b	C-50	27.3	1480	1/4	An + Cor + Glass
AN 29*	Syn An	27.3	1475	1/4	An + glass + Cor
AN 25a	Syn An	27.3	1470	1/4	An + Cor + some glass
AN 25b	C-50	27.3	1470	1/4	An + Cor + rare glass
AN 30*	Syn An	27.3	1460	1/4	An + Cor
AN 31*	Syn An	29.1	1450	1/4	Glass + Cor + some An
AN 32*	Syn An	29.1	1435	1/3	An + Cor + sparse glass
Runs at lower temperatures					
AN 18a	Syn An	10.9	1500	1 1/2	An + very small Cor(?) xls
AN 18b	C-50	10.9	1500	1 1/2	An + Cor (spotty distribution)
AN 23	C-50	13.6	1200	3 1/2	An + Cor
AN 19a	Syn An	18.2	1500	1/2	An + Cor (small xls)
AN 19b	C-50	18.2	1500	1/2	An + Cor (spotty distribution)
AN 20a	Syn An	18.2	1450	7	An + very small xls (Cor?)
AN 20b	C-50	18.2	1450	7	An + Cor (spotty distribution)
AN 24a	Syn An	27.3	1420	1/4	An + Cor
AN 24b	C-50	27.3	1420	1/4	An + come Cor

Pressures in Table 1 are corrected 9% for "friction" (see text).

Syn = synthetic, An = anorthite, Cor = corundum, C-50 = anorthite from Sittampundi, India.

* 1/2" chamber (all others 3/4" chamber)

0.0232 *T*, where P = kbar and T = °C. The slope is 23.2 bars/°C.

Hays (1966) indicated a dP/dT slope of 23.9 bars/°C, and Hariya and Kennedy (1968) one of 23.3 bars/°C. Their linear formulae for the reaction give pressures at 700°C of 14.2 and 15.2 kbar respectively; the Hays value falls directly on the line in Figure 1. Schmid and Wood (1976) showed that a single line can be drawn through the data of Hays and of Hariya and Kennedy, with the expression $P = (37.73T - 13740 \pm 1060)/1.582$ where T is in Kelvins and P is in bars, corresponding to a slope of 23.85 bars, and a pressure of 14.5 kbar at 700°C. Charlu *et al.* (1978) also have calculated the slope of the breakdown reaction, using newly obtained enthalpy of solution data on synthetic grossular and anorthite, and an average value from Hays and Hariya and Kennedy of 14.7 kbar for $\Delta G = 0$ at 1000K, and obtain a value of 22.9 bars/°C. The average value of the slope obtained by Schmid *et al.* (1978) was 22.5 bars/°C; all of the slopes are in good agreement.

Newton (1966) had earlier calculated the anorthite breakdown curve, using two other equilibria that he experimentally determined:

$$\text{(a)}\quad 4\ \underset{\text{zoisite}}{Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{quartz}}{SiO_2} \rightleftarrows 5\ \underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + 2\ H_2O$$

$$\text{(b)}\quad 4\ \underset{\text{anorthite}}{CaAl_2Si_2O_8} + H_2O \rightleftarrows 2\ \underset{\text{zoisite}}{Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{sillimanite}}{Al_2SiO_5} + \underset{\text{quartz}}{SiO_2}$$

Subtracting reaction (a) from reaction (b) gives the reaction 3 anorthite ⇄ grossular + 2 sillimanite + quartz, and Newton calculated the breakdown pressure of anorthite at 650°C to be 14720 bars; neglecting the effect of (unknown) compressibilities on ΔV and entropy he obtained a slope of 21.8 bars/°C. Also, by using his provisional kyanite–sillimanite inversion data at 650°C, Newton made a correction of 1.1 kbar downward in pressure, and got a value of 13.8 kbar for the anorthite breakdown curve. This point is plotted on Figure 1. In Schmid *et al.* (1978) the uncorrected 1968 point of Newton is plotted in their illustration.

Calculations made by T. J. B. Holland of this laboratory, based on data on high-temperature entropies and volumes [isothermal compressibilities from Birch (1966), except kyanite compressibility from Brace *et al.* (1969); thermal expansion data from Skinner (1966); and high-temperature entropies from Robie *et al.* (1978) adjusted to high pressures using the above data], give a slope ($\Delta S_{P,T}/\Delta V_{P,T}$) in the *P–T* range of the experiments of 22.8 bars/°C if the standard entropy of anorthite is that given by Robie and Waldbaum (1968), but is lowered to 20.9 bars/°C if anorthite data from Robie *et al.* (1978) are accepted. However, Charlu *et al.* (1978) found that the enthalpy of solution of synthetic anorthite was about 0.8 kcal/gfw lower than that of natural anorthites. If it is assumed that this difference is due to some disorder in the synthetic anorthite, and Robie *et al.* (1978) suggest that the Al/Si order is incomplete in the synthetic anorthite they used, then by analogy with albite (Holm and Kleppa, 1967) this enthalpy would correspond to an entropy difference (increase) of approximately 1 cal (R. C. Newton, personal communication). Smith (1974, p. 139) concludes, from several lines of evidence, that "some Al,Si disorder occurs even in pure anorthite." The calculated higher slope (22.8 bars/°C) is very close to the value of 22.9 obtained by Charlu *et al.* (1978), and lends credence to the use of a higher entropy of anorthite. The experimental reversals are in excellent agreement not only with the calculations of Holland and of Charlu *et al.* (1978) based on thermochemistry, but also with the experimental determinations of Hays (1966), Hariya and Kennedy (1966), and Schmid *et al.* (1978).

Univariant and invariant relations between the anorthite breakdown and melting curves

No attempt was made to examine the complex region where the univariant curve of the anorthite breakdown reaction is ultimately replaced by the anorthite melting curve. This has been done by Wood (1978). The phases encountered in the current work are anorthite, grossular, kyanite, quartz, corundum, and liquid. Hays (1966) outlined the stability field of $CaAl_2SiO_6$ (calcium Tschermak's pyroxene) in the system $CaO–Al_2O_3–SiO_2$, but did not encounter it in runs on the anorthite composition. However, Hariya and Kennedy (1968) reported a stable reaction at high temperatures and pressures of anorthite going to $CaAl_2SiO_6$ pyroxene and quartz. Wood (1978) made a series of runs in this region of the system, between 1350° and 1450°C and at stated pressures of 31 to 38 kbars, and shows 5 invariant points for the greatly expanded composition range in the system $CaO–Al_2O_3–SiO_2$, bounded by the compositional triangle grossular–corundum–quartz. There are three invariant points if the composition is restricted to $CaAl_2Si_2O_8$, but none associated with a univariant reaction of anorthite to $CaAl_2SiO_6$ pyroxene plus quartz. Wood (1978) also points out the incompatibility of corundum and quartz as represented in Hariya and Kennedy's (1968) paper, and indicates that the discrepancy between the results of Hays (1966) and Hariya and Kennedy (1968) is a consequence of the non-stoichiometry of the Ca-Tschermak's pyroxene, which like anorthite also takes up "excess" SiO_2 if it is available.

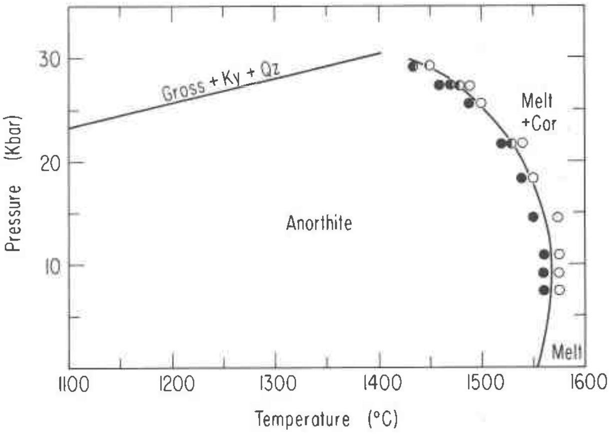

Fig. 2. The melting curve of anorthite, and the breakdown curve of Fig. 1. Open circles, all melt (below 9 kbar), or melt + corundum (above 9 kbar). Solid circles, all anorthite (below 9 kbar) or anorthite + some corundum (above 9 kbar). Partially filled circles indicate anorthite and melt (+ cor). The region between the breakdown curve and the melting curve is treated by Wood (1978). See text for discussion of anorthite–corundum association below the melting curve.

The nature of the anorthite breakdown curve

All runs that delineate the anorthite melting curve at approximately 9 kbar and above (Table 2) show corundum associated with anorthite on the low-temperature (solid) side of the curve. Although at the onset of melting the concentration of corundum increases significantly, its appearance in crystalline anorthite below the temperature at which any melt is observable indicates that it is more than just a product of the incongruent melting process. Table 2 also lists a number of runs made at temperatures well below melting; all of them contain exsolved corundum. Run AN23, made on an initially homogeneous natural anorthite, has exsolved corundum at more than 350°C below the solidus.

Thus at pressures above approximately 9 kbar there are two distinct processes that produce corundum: incongruent melting, and exsolution in the solid state with the development of non-stoichiometric anorthite. Newton (1966, p. 216) states, "Runs on anorthite glass at higher temperatures (>1200°C) often crystallize to an alumina-deficient anorthite plus corundum." Hariya and Kennedy (1968) state, "Runs on synthetic anorthite below the temperature of the incongruent melting curve often crystallize to an alumina-deficient anorthite plus small amounts of corundum." Lindsley (1968) also shows corundum + plagioclase in the absence of glass in his tabulated data, yet does not mention these observations in the text. Lindsley, in discussing reversal difficulties because of persistence of corundum once formed, does say, "Furthermore, corundum would crystallize metastably in experiments held outside the probable corundum field." At 10 kbar, his data show "3% cor, rest plag" at 1570°C, and "2% cor, rest plag" at 1525°C, and An_{80} gave "2% cor, rest plag" at 1520°C. Hariya and Kennedy (1968), at both 14.5 kbar and 1550°C and at 21 kbar and 1500°C show "An + small amount Cor."

Newton and Goldsmith (1975) observed a similar exsolution of corundum in the solid state from the scapolite meionite at pressures above 15 kbar, and found a significantly smaller *a* axis in the meionites crystallized at high pressures as compared to corundum-free material synthesized at lower pressure. Thus, as with anorthite, the high-pressure product is non-stoichiometric and Al_2O_3-deficient. The Al_2O_3 content of sapphirines is also related to pressure and temperature (Schreyer and Siefert, 1970); alumina-poor sapphirines form at the lowest temperatures at pressures near 10 kbar. None of the anorthite samples has been examined for variation in lattice constants.

The exsolution of corundum below the solidus is observed in all three starting materials of this investigation: synthetic anorthite, the anorthite from Sittampundi (C-50), and the synthetic An_{95}. The corundum that appears in the natural plagioclase generally shows a "spotty" or irregular distribution. The Sittampundi samples were loaded into capsules as rather coarsely crushed crystals (approximately 0.05–0.1 mm), and although the grains tended to break down somewhat during the runs, sizeable crystals remained. Some of the grains showed no exsolved corundum, others contained quite a bit, and the distribution is even irregular within some grains. There tends to be more exsolution (clustering) in the larger grains. In addition, the natural anorthite appears to contain more and larger crystals of corundum than the synthetic anorthite, although this may in part be a "visibility" effect in the coarse-grained and clearer natural material. R. C. Newton (personal communication) feels that it may be due to the more extensive Al_2O_3 "source" within the larger crystals. On the other hand, the Sittampundi material has a slightly different initial composition than the synthetic anorthite. Table 2 indicates that there are very slight differences in melting behavior in the two samples, the natural plagioclase being somewhat more refractory.

It thus appears that at elevated pressures stoichiometric anorthite is unstable. This tendency may extend to low temperatures, although it is very likely that at moderate or low temperatures exsolution may not be observed because of kinetic restraints. The presence of corundum and the non-stoichiometric nature of the anorthite have repercussions on the phase relations relating to the breakdown of anorthite to the high-pressure phases. The univariant curve for the reaction anorthite + corundum $\rightleftarrows$ grossular + kyanite lies slightly below the anorthite $\rightleftarrows$ grossular + 2 kyanite + quartz curve (Boettcher, 1970), and Wood (1978) calculates it at a pressure approximately 0.7 kbar lower. Thus at the composition of stoichiometric anorthite, the feldspar breakdown reaction begins in fact as a reaction between an Al-deficient anorthite and corundum, and although at the onset of the reaction it closely approximates the ("normal") anorthite + corundum breakdown, there is a small difference due to the unknown difference in thermochemical properties between stoichiometric and Al-deficient anorthites.

Inasmuch as the amount of corundum exsolved and available for this reaction is quite limited, it is soon reacted out, and the principal reaction, the breakdown of Al-deficient anorthite in the absence of corundum, goes on. The kyanite and grossular produced by the initial reaction with corundum is probably too small in amount and the reaction pressure too close to the anorthite breakdown in the absence of corundum to be detected experimentally. This view is supported by the excellent agreement between the calculated and observed reaction.

On the composition $CaAl_2Si_2O_8$ the amount of corundum in equilibrium with Al-deficient anorthite as a function of pressure and temperature is unknown. In this region the composition of the anorthite is buffered by the presence of Al_2O_3. In Figure 3 lines of equivalent corundum content are shown below the solidus in a totally arbitrary way. It is likely that they have a positive slope, for increasing temperature should favor 4-coordinated Al.

Similarly, on the composition $CaAl_2Si_2O_8$ the amount of corundum in equilibrium with melt is not really known, although a few data points are at hand. Lindsley (1968) determined the boundary between the field of liquid and liquid + corundum at 10 and

20 kbar along the join albite–anorthite, and for the end-member anorthite the respective temperatures are approximately 1625° and 1765°C. These points are plotted in Figure 3 and lie on the line of zero percent corundum. At 12.3 kbar, Hariya and Kennedy (1968) show some corundum at "about 1620°C," and none above 1640°C. Their point (at 1630°C) is also plotted on Figure 3. Another point, on the melting curve, is the singular point at approximately 9 kbar, where incongruent melting begins. The line of zero percent corundum is drawn through the Lindsley points for consistency. Additional totally schematic lines of increasing corundum content are also shown. There is no obvious reason why the subsolidus lines should be related in any way to those in the liquid field.

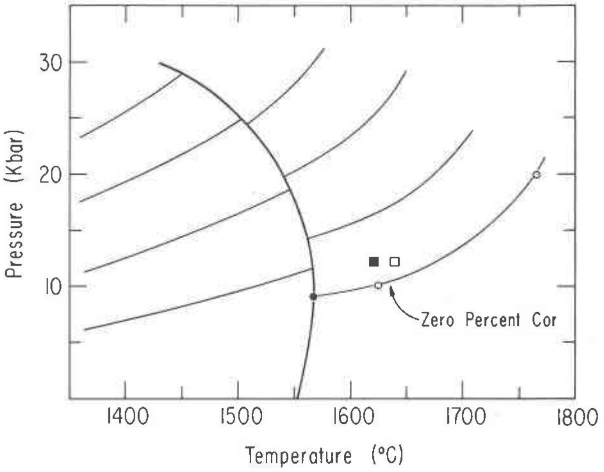

Fig. 3. The melting curve of anorthite, and diagrammatic lines of equivalent corundum content (percent corundum coexisting with non-stoichiometric anorthite for a $CaAl_2Si_2O_8$ bulk composition) in both the liquid region and solid region are indicated. The zero percent corundum line in the region of liquid is drawn through two points (open circles) separating the fields of liquid and liquid + corundum at 10 and 20 kbar determined by Lindsley (1968), and the solid circle where corundum appears on the melting curve. The squares are from Hariya and Kennedy (1968), the open symbol indicating all liquid, the solid symbol indicating liquid plus corundum. The remaining lines, in both fields, are completely arbitrarily drawn; slopes and curvatures are unknown. There is no necessary relationship between the lines in the two fields.

The nature of the melting curve

Both the curvature of the melting curve and the development of incongruent behavior are the result of the effect of pressure on anorthite and its melt product. Increased pressure obviously induces an increase in density, and therefore tends to promote 6- rather than 4-coordination in Al. One of the ways in which densification can take place with increasing pressure is by the separation of corundum, with aluminum in 6-coordination. The anorthite in equilibrium with the melt plus corundum at pressures above that at which incongruency develops is Al-deficient and becomes increasingly so as the pressure is increased. The high degree of Al–Si order that exists even near the melting point in anorthite at one atmosphere is in part a consequence of the ideal 1:1 Al:Si ratio (Laves and Goldsmith, 1955), and must necessarily be reduced as pressure increases and the Al:Si ratio increasingly deviates from unity. The pronounced curvature and the development of a negative slope are the result of the two pressure-dependent factors, the increase in δV due to the exsolution of 6-coordinated corundum, and the increase in δS due to the associated deviation from the stoichiometry that favors a high degree of Al–Si order. The δV effect is obviously the dominant one. The "squeezing out" of corundum from both solid and melt and the development of a similarly shaped melting curve was also noted in the case of the scapolite meionite by Newton and Goldsmith (1975), although the phase relations in the case of the scapolite are more complex.

The onset of incongruent melting appears to coincide with the maximum on the melting curve, but this may be just a coincidence. This "point" is probably a singular point on a smooth curve, rather than a triple point as shown by Hariya and Kennedy (1968). Examination of the $CaO–Al_2O_3–SiO_2$ phase diagram (Rankin and Wright, 1915) shows that the boundary curve between the fields of anorthite and corundum lies close to the composition of anorthite. The join $Al_2O_3–CaAl_2Si_2O_8$ crosses this boundary at 1547°C, and at this point the boundary curve defines the eutectic point on the binary join $Al_2O_3–CaAl_2Si_2O_8$, at approximately 94.5 percent $CaAl_2Si_2O_8$. The effect of pressure on this anorthite–corundum eutectic assemblage is shown diagrammatically in Figure 4. With increasing pressure the composition of the eutectic liquid between anorthite and corundum approaches $CaAl_2Si_2O_8$ in composition (stoichiometric anorthite). When it crosses the composition of the anorthite that is stable at that pressure and temperature, the melting relations become incongruent, for anorthite now lies in the field of corundum. Thus the anorthite melting curve becomes coincident and indistinguishable from the *P–T* curve of the corundum–anorthite eutectic (now turned peritectic) at this singular point. The shift in the composition of anorthite away from the Al_2O_3

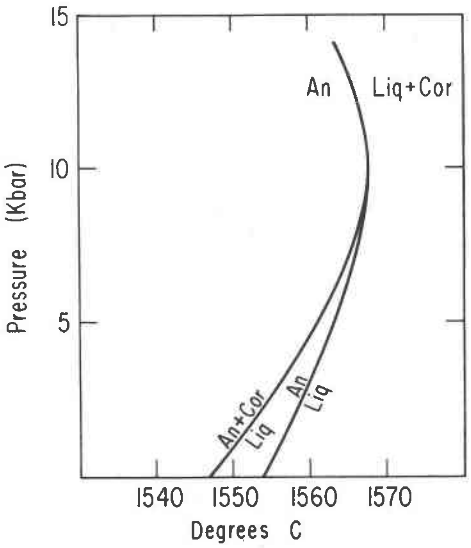

Fig. 4. A portion of the anorthite melting curve, and diagrammatic representation of the *P-T* melting relations of the anorthite–corundum eutectic composition along the join Al_2O_3–$CaAl_2Si_2O_8$ in the system CaO–Al_2O_3–SiO_2. The two curves join at a singular point, at approximately 9 kbar, at which point the melting of anorthite becomes incongruent (see text).

corner of the ternary system with pressure is a much smaller effect than the movement of the boundary curve that produces incongruency.

Table 3 contains electron microprobe data on the synthetic anorthite used in the runs, compared with analyses made on the anorthite from run AN17a (1490°C, 25.5 kbar) and on glass (containing corundum) from runs AN5a (1575°C, 10.9 kbar) and AN16a (1500°C, 25.5 kbar). The decrease in Al_2O_3 in the anorthite of AN17a appears to be real. Although the CaO content has increased, no increase in SiO_2 is shown. If the compositional change in the anorthite were due entirely to removal of Al_2O_3, an increase in SiO_2 content would be quantitatively greater than the increase in CaO. On the other hand the increase in both CaO and SiO_2 shown by the glass in run 16A (1500°C, 25.5 kbar) is more in line with the compositional trend of a liquid away from the Al_2O_3 corner of the ternary system.

Petrologic interpretation

The breakdown of plagioclase feldspar to garnet and jadeitic pyroxene is one of the essential reactions in the conversion of a crustal rock to its high-pressure equivalent, such as basalt to eclogite. The breakdown curves of anorthite and albite (Holland, 1980) are now well delineated, but little is known of the relations in the intermediate plagioclase compositions. The albite curve lies about 4.5 kbar above the anorthite breakdown at 700°C, and the spread increases with temperature, to about 6 kbar at 1200°C. Boettcher (1971) has calculated the breakdown pressures of the intermediate plagioclases assuming an ideal solution, and finds that at 800K the maximum breakdown pressure is for a composition of approximately Ab_{80}, at approximately 1 kbar above the curve for pure albite; thus the breakdown "bandwidth" is not greatly increased beyond the confines of the end-member curves.

A number of investigations have been concerned with the nature of the basalt–eclogite transformation, and these are summarized by Ringwood (1975). The latest data on a tholeiitic basalt (Ito and Kennedy, 1971) indicate a transition zone of garnet granulite of approximately 15 kbar bandwidth between basalt and eclogite, whereas earlier work (Cohen *et al.*, 1967) had indicated a transition zone of only 3 to 4 kbar. Cohen *et al.* have also indicated that the feldspar becomes more albitic with increasing pressure, and state that because Na can only be taken by the clinopyroxene, and calcic feldspar disappears by reaction to garnet or solid solution in clinopyroxene, the upper pressure limit of plagioclase feldspar of any composition is close to that of albite.

The eclogite reaction in nature is very complex, involving additional components, and can even be affected by the structural state of the feldspars (Hlabse and Kleppa, 1968; Holland, 1980). The presence of elements such as Mg and Fe that are incorporated into the minerals of the reaction (pyroxene and garnet) lowers the pressure of the reaction and also enlarges the pressure range over which the reaction occurs. The "garnet-in" curve is significantly below the anorthite breakdown curve. These effects are in-

Table 3. Electron microprobe analyses of anorthite and glass

	Stoichiometric An	Synthetic An_{100}	Run AN17a (2 analyses)	
Na_2O	0.00	0.46	--	0.08
CaO	20.16	19.92	23.20	22.91
Al_2O_3	36.65	36.65	34.12	34.42
SiO_2	43.19	43.12	43.14	42.81
	100.00	100.14	100.46	100.23
	Run AN5a (2 analyses)		Run AN16a (2 analyses)	
Na_2O	--	--	0.12	--
CaO	22.57	22.56	25.47	25.31
Al_2O_3	35.01	34.92	27.16	27.11
SiO_2	42.22	42.31	47.11	46.31
	99.80	99.79	99.85	99.01

dicated in the wide pressure band shown in the results of Ito and Kennedy (1971); the "plagioclase-out" curve in their experiments lies between the anorthite and albite breakdown curves, with a somewhat lower dP/dT slope than either. Ringwood (1975) considers in some detail the effect of rock composition on the development of garnet and the elimination of plagioclase.

The presence of H_2O introduces an additional complicating factor. Anorthite breaks down to zoisite, kyanite, and quartz in the reaction:

$$\underset{\text{anorthite}}{4\ CaAl_2Si_2O_8} + H_2O \rightleftarrows \underset{\text{zoisite}}{2\ Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{kyanite}}{Al_2SiO_5} + \underset{\text{quartz}}{SiO_2}$$

approximately 4 kbar below the anhydrous anorthite breakdown (Newton, 1966; Goldsmith, unpublished data), thus expanding the reaction zone of plagioclase even further. A more complex reaction in the intermediate plagioclases that produces zoisite plus a more sodic plagioclase is initiated at the same pressure, independently of composition, in the range An_{30}–An_{100} (Goldsmith, 1978). It is unlikely, however, that aside from subduction zones there is enough water in the deep crust to have a zoisite-bearing rock replacing garnet granulite.

It is tempting to suggest that the pressure effect on anorthite might be responsible for some associations of corundum with calcic plagioclase, such as in the corundum anorthosite at Sittampundi. It is also risky to do so, for in the absence of detailed data on the composition of the natural plagioclases we would have to assume them to be non-stoichiometric. A chemical analysis of the Sittampundi anorthite (C-50) used in this investigation, given to the author by the late A. P. Subramaniam in 1951, is shown in Table 4. This composition is that of An_{98}, although a careful spectrographic analysis for Na_2O by O. Joensuu (personal communication) indicates Na_2O = 0.16–0.19 percent, even closer to pure An. Comparison with Table 3 shows however that C-50 is certainly not far from stoichiometric An, and it is not likely that corundum has ever been exsolved from this particular sample. Compositional re-adjustment with the development of small amounts of other phases is of course possible.

Table 4. Chemical composition of anorthite C-50

SiO_2	43.88	CaO	19.37
TiO_2	0.00	SrO	0.01
Al_2O_3	36.18	Na_2O	0.22
Fe_2O_3	0.08	K_2O	0.00
FeO	0.00	P_2O_5	–
MnO	0.00	H_2O+	0.28
MgO	0.00	H_2O-	0.08
			100.10

Analysts: S. S. Goldich and E. K. Oslund

Perhaps the potentially most useful aspect of the high-pressure reaction of anorthite to grossular, kyanite, and quartz has to do with thermodynamic considerations relating to geobarometry, and to experimental measurements of garnet activities. Ghent (1976) has shown that the reaction, modified for the presence of sillimanite or andalusite as the Al_2SiO_5 polymorph, applies to the assemblage plagioclase–garnet–Al_2SiO_5–quartz, one potentially useful for determining pressures and temperatures of metamorphism. His equations, containing terms for activity of anorthite solid solution in plagioclase and activity of grossular solid solution in garnet, were tested with calculations on data from several metamorphic localities. The calculated pressures were entirely consistent with the Al_2SiO_5 phase diagram (Holdaway, 1971), and show a clear separation of garnet and plagioclase assemblages into the appropriate "facies region" of the diagram. Ghent suggests that the critical experiments to provide data on the activities of grossular in garnet solid solutions be carried out. The only available study of this kind is that of Hensen *et al.* (1975) for pyrope–grossular compositions, but as similar future studies become available, it will be essential that they be referred to the most accurate end-member breakdown reaction.

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