[American Journal of Science, Vol. 266, March 1968, P. 193-203]

EQUILIBRIUM STUDY OF ANORTHITE UNDER HIGH PRESSURE AND HIGH TEMPERATURE*

Y. HARIYA and G. C. KENNEDY

Institute of Geophysics and Planetary Physics,
University of California, Los Angeles, California 90024

ABSTRACT. The stability field of anorthite has been determined in the temperature range 950° to 1640°C and in the pressure range 6 to 37 kilobars. The breakdown of anorthite under high pressure is shown for the following:

(1) 3 anorthite ⇄ grossularite + 2 kyanite + quartz

(2) 3 anorthite ⇄ 3 Ca-Tschermak's molecule + 3 quartz ⇄ grossularite + 2 kyanite + quartz

The equilibrium boundary of reaction (2) takes place at higher temperatures than that of reaction (1). The boundary of the anorthite breakdown to grossularite + 2 kyanite + quartz lies at a lower pressure but rather close to that of albite, as determined by Birch and Le Conte (1960).

Anorthite melts incongruently at pressures above 9 kilobars to corundum + liquid.

INTRODUCTION

The open framework structure of anorthite, in which aluminum exists in 4-fold coordination with oxygen, must collapse under elevated pressure to a denser assemblage of minerals with 6-coordinated aluminum.

Previous studies have been made on the stability of anorthite under very high pressure and temperature by Boyd and England (1961), Newton (1966b), and Hays (1966a). Boyd and England first found that the reaction of anorthite to grossularite, kyanite, and quartz took place at 1350° C and 30.0 kilobars, and they also found that anorthite melted above 10 kilobars to corundum and liquid. Hays (1966a) gives the equation for the upper limit of the stability field of anorthite as:

$$P_{(bars)} = 28{,}500 + 23.9\,(T_{(°C)} - 1300)$$

This curve also passes through the 1350°C, 30 kilobars point cited by Boyd and England (1961). Newton (1966b) observed that the breakdown curve of anorthite lies at a lower pressure but close to that of albite, as determined by Birch and Le Conte (1960). These experimentally determined boundaries also agree reasonably well with the curves calculated by Newton (1966b).

Clark, Schairer, and de Neufville (1962) reported the synthesis of a clinopyroxene having the composition $CaAl_2SiO_6$, which they refer to as "Ca-Tschermak's molecule" (Tschermak, 1914). This composition has long been recognized as a component in certain natural aluminous pyroxenes. Recently, a stability field for this synthetic mineral was reported by Hays. However, the formation of Ca-Tschermak's molecule + quartz from anorthite takes place at a pressure above the breakdown of pure Ca-Tschermak's molecule.

One hypothesis is that calcic feldspar, which is characteristic of near surface basic rocks, is replaced by garnet below the Mohorovicic

* Publication 624, Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California 90024.

discontinuity. The breakdown of anorthite at high pressure may be one of the principal factors that limit the thickness of the Earth's crust if the "phase change" mechanism of the crust-mantle boundary is effective. The large change in density of the rock may account for the increase in seismic velocity at the crustal base.

In the present work, the stability field of anorthite was investigated over a wide range of pressure and temperature.

EXPERIMENTAL METHODS

All experiments in the present study were carried out in the single-stage piston- and cylinder apparatus. The particular piston- and cylinder apparatus has been described by Boyd and England (1960a), Kennedy and La Mori (1962), Kennedy and Newton (1962), and Jayaraman and others (1963). The working volume was of half an inch diameter and 2 inch length.

Artificial and natural minerals were used as starting materials. Artificial anorthite was crystallized from glass (n = 1.575) of anorthite composition prepared from quartz, aluminum oxide, and calcium carbonate at 1600°C. The pure "Ca-Tschermak's molecule" does not occur as a natural mineral. The stability of pure $CaAl_2SiO_6$ pyroxene has been shown by Hays (1966b). The $CaAl_2SiO_6$ pyroxene starting material was prepared from a mixture of pure chemical reagents at 20 kilobars and 1400°C. Natural anorthite from Kuttara Caldera, Hokkaido, Japan, contained less than 2 percent albite. Grossularite from Lake Jaco, Chihuahua, Mexico, and kyanite from Sultan Hamud, Kenya, East Africa, from the mineralogical collection of UCLA were used.

Reactants and products that had been mixed in approximately fifty-fifty proportions were placed in a platinum capsule of 1/16-inch diameter and 0.005 inch wall thickness.

The cell for the high-pressure chamber consisted of a pyrex glass cylinder containing a graphite tube heater. A schematic diagram of our furnace assembly is shown in figure 1. The sample holder materials were chosen for good pressure transmission properties and physical and chemical stability under the experimental conditions. Pyrex glass begins to soften at about 300°C, and it therefore becomes a good pressure transmitter and is a superior pressure transmitter to talc, boron nitride, or other solid materials.

All pressures reported in this paper have been corrected for friction. The friction corrections for all runs amounted to appoximately 10 percent of the observed pressure. Reported pressures are believed to be correct to within 1 kilobar.

Corrections were made for the effect of pressure on the electromotive force (emf) of the thermocouples, using the data obtained by Getting and Kennedy (personal communication). Typical values of this correction for platinum/platinum — 10 percent — rhodium thermocouples amounted to +5°C at 10 kilobars, +7.5°C at 20 kilobars, and +10°C at 30 kilobars. Unfortunately, temperature fluctuations were as much as

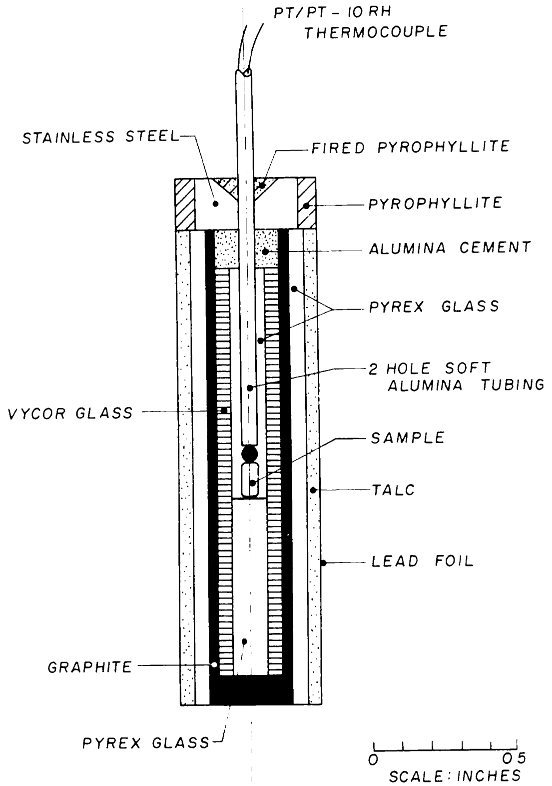

Fig. 1. Schematic diagram of furnace assembly.

$\pm$ 15°C for overnight runs. For shorter runs, the maximum fluctuation in temperature is $\pm$ 5°C.

Post-run phase identifications were made by X-ray diffraction and optical microscopy.

Anorthite is a very stable mineral, and the observed phase changes were very sluggish even at high temperature. Therefore, the few data below 1300°C given for this mineral are interpretations of slight changes in relative X-ray intensities of reactants and products.

EXPERIMENTAL RESULTS

The summarized results of all the runs are shown in tables 1, 2, and 3. The equilibrium boundaries of anorthite are plotted in figures 2 and 3.

The stability field of anorthite.—The reaction of anorthite to grossularite, kyanite, and quartz is very sluggish even at high pressure and high temperature. Runs of natural anorthite of 3 days duration at 29.5 kilobars and 1200°C show almost no change. Thus, the direct determination of anorthite breakdown under high pressures and at temperatures

TABLE 1

3 anorthite ⇄ grossularite + 2 kyanite + quartz

Number	Reactants	Pressure (Kb)	Temperature (°C)	Time (hours)	Products
58	An	29.5	1350	5	An
92	An + Gros + Ky + Q	31	1350	3.5	Gros, Ky grew
71	An	27	1300	21	An
91	An + Gros + Ky + Q	29	1300	5	An grew
59	An	28	1250	10	An
93	An + Gros + Ky + Q	29.5	1250	7.5	Gros, Ky grew
90	An + Gros + Ky + Q	27	1200	6.5	An diminished
95	An + Gros + Ky + Q	25.0	1150	10	Gros, Ky diminished
94	An + Gros + Ky + Q	26.5	1150	10	An diminished
98	An + Gros + Ky + Q	12.3	600	70.5	No apparent reaction
99	An + Gros + Ky + Q	20	950	33	An grew
100	An + Gros + Ky + Q	22	950	26.0	Gros, Q grew

An: anorthite; Gros: grossularite; Ky: kyanite; Q: quartz.
Starting material: natural minerals.

TABLE 2

3 anorthite ⇄ 3Ca-Tschermak's molecule + 3 quartz
⇄ grossularite + 2 kyanite + quartz

Number	Reactants	Pressure (Kb)	Temperature (°C)	Time (hours)	Products
85	An	29.5	1450	3	An
57	An	30	1400	8	An
104	Ca-Tsch + Q	30.5	1430	2.2	An
63	An	31.5	1400	3.8	Ca-Tsch + Q
72	An	31.5	1460	3.5	Ca-Tsch + Q
105	An	31.5	1490	2	Ca-Tsch + Q + small amount gl
64	An	33	1400	4.2	Gros + Ky + Q + Ca-Tsch
42	An	33.5	1470	3	Ca-Tsch + Q
106	Gros + Ky + Q	34	1445	3.5	Ca-Tsch grew + Q
43	An	35	1400	5	Gros + Ky + Q + small amount Ca-Tsch (unstable)
44	An	36	1510	1.5	Ca-Tsch + Q + small amount gl
56	An	36.5	1445	3	Gros + Ky + Q +small amount Ca-Tsch (unstable)
55	An	36.5	1475	3	Gros + Ky + Q + Ca-Tsch
45	An	37	1400	3.8	Gros + Ky + Q

An: anorthite; Ca-Tsch: Ca-Tschermak's molecule; gl: glass; Gros: grossularite; Ky: kyanite; Q: quartz.
Starting materials: both natural and synthetic minerals.

Table 3

Anorthite ⇄ melt
Anorthite ⇄ corundum + melt

Number	Reactants	Pressure (Kb)	Temperature (°C)	Time (hours)	Products
68	An	6.0	1575	0.8	gl
35	An	7.3	1570	0.8	gl + very little An
36	An	7.3	1600	0.95	gl
37	An	8.7	1580	0.95	gl
21	An	10	1560	1	An
22	An	10	1585	1	Cor + gl + little An
27	An	12.3	1590	1.4	Cor + gl
39	An	12.3	1620	0.8	small amount Cor + gl
25	An	12.3	1640	0.8	gl
20	An	14.5	1490	3	An
101	An	14.5	1550	1.5	An + small amount Cor
31	An	14.5	1575	0.9	Cor + gl
29	An	14.5	1590	1.5	Cor + gl
30	An	16	1590	1	Cor + gl
40	An	17	1560	1.5	Cor + gl
28	An	17	1590	0.8	Cor + gl
41	Cor + gl	17.3	1535	2.5	Cor + gl + An
24	An	19.3	1550	1.5	Cor + gl
26	An	19.3	1600	1	Cor + gl
14	An	21	1500	3	An + small amount Cor
11	An	21	1550	1.5	Cor + gl + small amount needle crystal
61	An	24.5	1540	1.5	Cor + gl + small amount needle crystal
62	Cor + gl	24.5	1510	3	Cor + gl + An An grew
63	An	27	1515	3	An + Cor + little gl
102	An	29.5	1490	2	An
34	An	29.5	1520	2	Cor + gl + small amount needle crystal
33	An	29.5	1550	0.8	Cor + gl
64	An	31.5	1500	1	Cor + gl + Ca-Tsch
65	An	34.2	1540	0.8	Cor + gl
103	An	36	1510	1.5	Ca-Tsch
66	An	36.5	1540	1	Cor + gl

An: anorthite; Cor: corundum; gl: glass; Ca-Tsch: Ca-Tschermak's molecule
Starting materials: both natural and synthetic minerals.

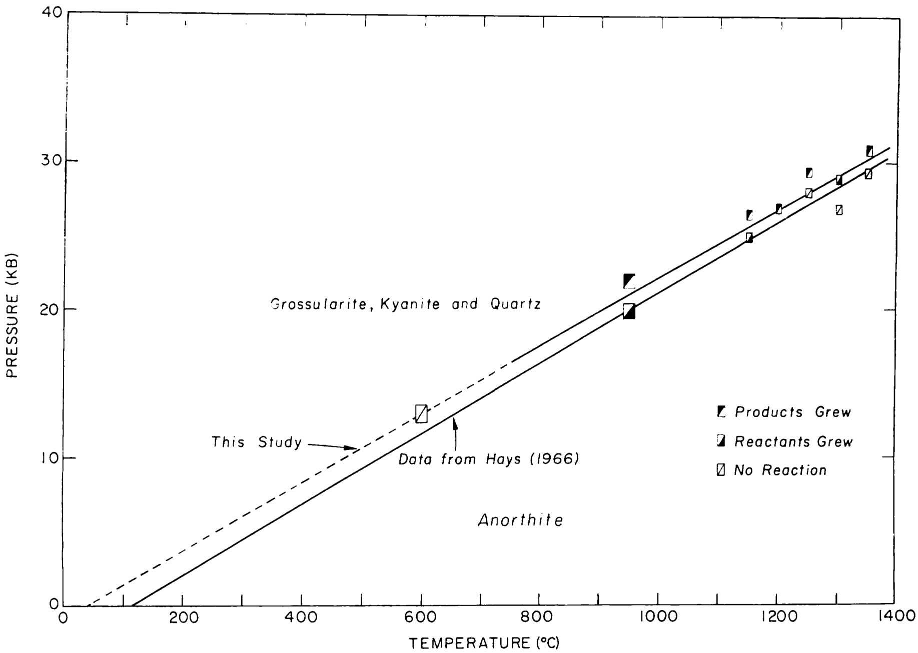

Fig. 2. The reaction of anorthite to grossularite plus kyanite plus quartz.

lower than 1300°C is experimentally difficult. The breakdown products were first determined by Boyd and England (1961) to be grossularite, kyanite, and quartz. We determined this reaction by growth relations beween reactants and products. The data above 1000°C are interpretations of slight changes in X-ray intensities. In runs below 1000°C, however, it was difficult to determine any significant change except for the growth of quartz.

The boundary curve for the reaction

$$3CaAl_2Si_2O_8 \text{ (anorthite)} \rightleftarrows Ca_3Al_2Si_3O_{12} \text{ (grossularite)} + 2\ Al_2SiO_5 \text{ (kyanite)} + SiO_2 \text{ (quartz)}$$

is shown in figures 2 and 3. We can expect that the anorthite will invert to a denser form or assemblage at high pressure, because this mineral is of low density, 2.762 grams per centimeter^3. The breakdown curve has a slope of 43°C per kilobar and is approximately represented by $T = 48 + 43\ P$, where T is in degrees centigrade and P is in kilobars. This boundary also agrees reasonably well with the curve calculated by Newton (1966b) and the experimental data by Hays (1966a). The volume change in this reaction is about 67.64 cubic centimeters per mole.

At 1200°C this curve lies about 3 kilobars lower in pressure than the albite breakdown curve and 8 to 10 kilobars higher in pressure than the transition curve for sillimanite to kyanite (fig. 4).

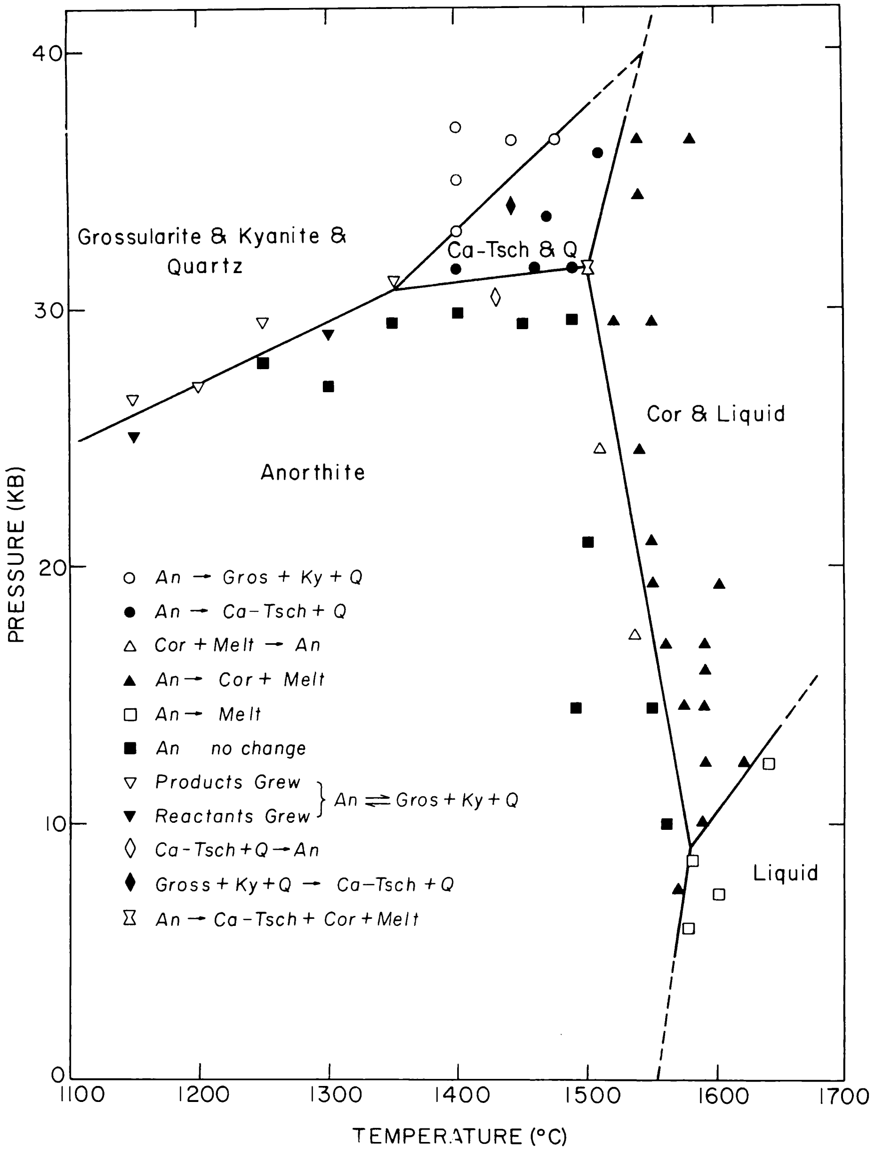

Fig. 3. The stability field of anorthite at high pressure and temperature.

Anorthite does not break down directly to grossularite, kyanite, and quartz at more than 30 kilobars and 1350°C. The breakdown of this mineral at above these pressures and temperatures is the following:

$$3CaAl_2Si_2O_8 \text{ (anorthite)} \rightleftarrows 3CaAl_2SiO_6 \text{ (pyroxene)} + 3SiO_2 \text{ (quartz)}$$
$$\rightleftarrows Ca_3Al_2Si_3O_{12} \text{ (grossularite)} + 2Al_2SiO_5 \text{ (kyanite)} + SiO_2 \text{ (quartz)}$$

The stability field of pyroxene (Ca-Tschermak's molecule) + quartz is

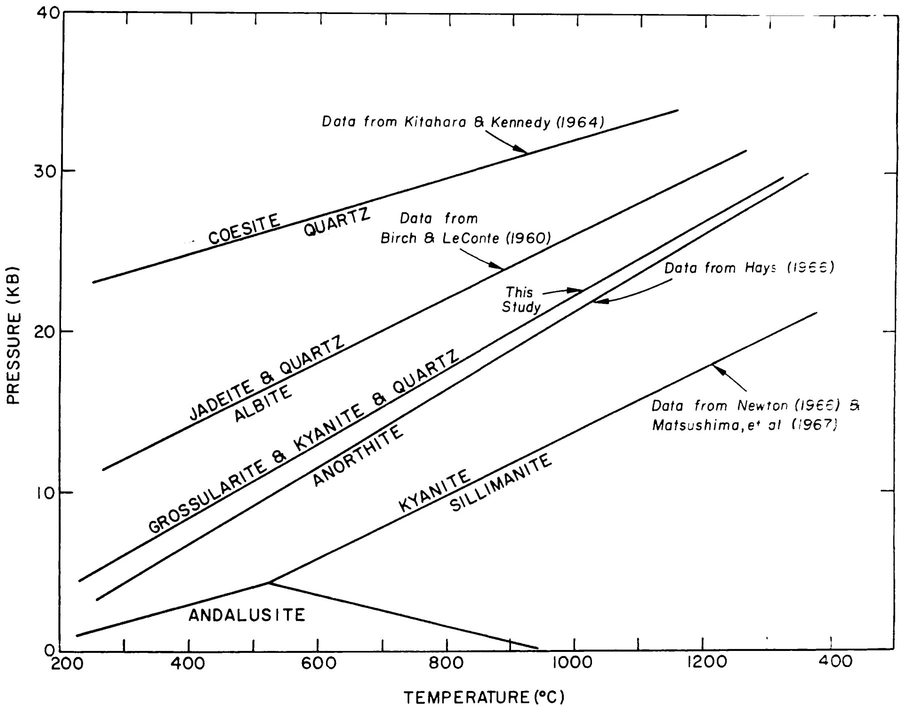

Fig. 4. Some pertinent high pressure equilibrium boundaries.

relatively narrow even at high pressure and high temperature. These mineral assemblages melt incongruently at about 1510°C to corundum + liquid. The experimental equilibrium line between anorthite and Ca-Tschermak's molecule + quartz is drawn with a slope of 6.5 bars per degree or 165°C per kilobar. At pressures above 31 kilobars, Ca-Tschermak's molecule + quartz also breaks down into grossularite + kyanite + quartz. The boundary for this reaction has a slope of 47.0 bars per degree. A triple point between anorthite, Ca-Tschermak's molecule + quartz, and grossularite + 2 kyanite + quartz is about 1350 ± 10°C, 30.7 ± 0.5 kilobar.

Garnet grows rapidly on the higher-pressure side of the equilibrium curve. Runs in the field of grossularite, kyanite, and quartz on the low temperature side of the equilibrium curve often produced metastable Ca-Tschermak's molecule.

The calculated volume change for anorthite to Ca-Tschermak's molecule + quartz is about 43.80 cubic centimeters per mole, and the change for Ca-Tschermak's molecule + quartz breakdown to grossularite, kyanite, and quartz is 23.84 cubic centimeters per mole.

Using the thermochemical data of table 4, calculated slopes for these two curves are 10.8 bars per degree and 47.9 bars per degree, respectively.

TABLE 4
Thermochemical properties of crystalline phases at 298.15°K, 1 atm

	Molar volume (cm^3)	grams per $centimeter^3$	Molar entropy Cal/degree
Anorthite ($CaAl_2Si_2O_8$)	100.73	2.762	48.5
Corundum (Al_2O_3)	25.5	3.988	12.17
Grossularite ($Ca_3Al_2Si_3O_{12}$)	125.35	3.595	57.73
Kyanite (Al_2SiO_5)	43.3	3.674	20.02
Quartz (SiO_2)	22.6	2.648	9.88
Cs-Tschermak's molecule ($CaAl_2SiO_6$)	63.53	3.438	34.63

The melting of anorthite.—Boyd and England (1961) recognized that anorthite melts incongruently to corundum + liquid at about 10 kilobars and that the slope of the melting curve is negative. The incongruent melting products were also determined by Hays (1966a) to be corundum and liquid. He located points in the incongruent melt field at 28 and 34 kilobars at a temperature of 1450°C.

The melting point of anorthite at 1 atmosphere is 1553°C, and at atmospheric pressure the melting is congruent. According to our experimental results, anorthite melts congruently up to about 9 kilobars, and this melting curve is positive. The melting curve has a slope of 2.7°C per kilobar and can be approximately represented by $T = 1553 + 2.7 P$, where T is in degrees centigrade and P is in kilobars. This slope also agrees reasonably well with the curve calculatd by Smith (1963). The pertinent data for anorthite are melting point at atmospheric pressure: 1823°K, Δ V 0.0087 $centimeters^3$ per gram, Δ H 105 calories per gram, dT/dP: 0.151°C per calorie per $centimeter^3$, 0.00365°C per atm, 0.17°C per kilometer.

Above 9 kilobars anorthite melts incongruently with a negative slope to pressures of 31.6 kilobars. Runs at 12.3 kilobars and about 1620°C have very small amounts of corundum, and no corundum is seen above 1640°C at the same pressure. A boundary between anorthite and corundum + liquid region is defined quite sharply. However, small amounts of needle crystals (kyanite?) are still left in the corundum + liquid region of the highest pressures. Runs on synthetic anorthite below the temperature of the incongruent melting curve often crystallize to an alumina-deficient anorthite plus small amounts of corundum.

The incongruent melting curve has a slope of −3.5°C per kilobar. The liquidus has a slope of 14.8°C per kilobar above 9 kilobars. Ca-Tschermak's molecule + quartz also breaks down to corundum + liquid; however, this slope is positive. This curve has a slope of approximately 5.5°C per kilobar.

DISCUSSION OF RESULTS

Many minerals under low pressure have crystal structures of low density with relatively open frameworks of atoms. The most common of these are quartz and feldspars, which are the most abundant minerals in the Earth's crust in continental areas. The alumino silicates generally have the aluminum ion in fourfold coordination with oxygen. In high-pressure phases, aluminum tends to be in sixfold coordination, as in the more closely packed structures such as garnets, pyroxenes, and kyanite.

The volume relations in the anorthite breakdown reaction are as follows:

3 anorthite	⇄	grossularite	+ 2 kyanite	+ quartz
3 $CaAl_2Si_2O_8$		$Ca_3Al_2Si_3O_{12}$	2 Al_2SiO_5	SiO_2
(100.73 x 3)		125.35	(43.3 x 2)	22.6
		234.55		

$\Delta V = 67.64$

3 anorthite	⇄	3 Ca-Tschermak's molecule	+ 3 quartz
3 $CaAl_2Si_2O_8$		3 $CaAl_2SiO_6$	3 SiO_2
(100.73 x 3)		(65.53 x 3)	(22.6 x 3)
		258.39	

$\Delta V = 43.80$

The breakdown products of anorthite under high pressure somewhat resemble the mineral assemblage of the kyanite eclogite from the quarry at Silberback, Munchberg Massif, Germany. This kyanite eclogite is of special interest because of its high alumina content. The stability limit of plagioclase has a bearing on the nature of the lower crustal boundary, or Mohorovicic discontinuity, if this discontinuity is the transition from basalt to eclogite (Lovering, 1958; Kennedy, 1959).

Two noteworthy features of the phase diagram for anorthite under high pressure are: (1) the negative slope of the corundum + liquid boundary which shows a triple point involving anorthite, corundum + liquid, and liquid at 9 ± 0.5 kilobars, 1580 ± 10°C; and (2) presence of Ca-Tschermak's molecule among the anorthite breakdown products. The negative value of dT/dP for the anorthite ⇄ corundum + liquid reaction indicates that the ratio $\Delta V / \Delta S$ for this reaction must also be negative.

Plagioclase under high pressure reacts to form pyroxenes such as jadeite and Ca-Tschermak's molecule with quartz. However, the stability field for jadeite + quartz and Ca-Tschermak's molecule + quartz is quite different. The former is stability over the wide range of temperature and pressure, but the field of Ca-Tschermak's molecule + quartz is very narrow even at high pressure and high temperature, and it reacts at higher pressures to form grossularite, kyanite, and quartz. Thus, the apparent absence of pure Ca-Tschermak's molecule as a natural mineral is not surprising although natural pyroxenes contain rather small amounts of Ca-Tschermak's molecule. Recent work by Boyd and England (1960b) has shown that orthopyroxenes under high pressure may take a large amount of Al_2O_3 into solid solution. Clinopyroxene from eclogites and olivine bombs frequently also contain substantial amounts of this component.

ACKNOWLEDGMENTS

Our special thanks are due Mr. Terrence Thomas, who has kept our high pressure apparatus in good working condition. Also many thanks are due our colleagues, Dr. W. G. Ernst, J. Grace, and I. Getting, who have reviewed this manuscript and made many helpful suggestions for laboratory work.

Partial financial assistance from the Office of Naval Research, contract N00-14-67A-0111-001 is gratefully acknowledged.

REFERENCES

Birch, Francis, and LeConte, Paul, 1960, Temperature-pressure plane for albite composition: Am. Jour. Sci., v. 258, p. 209-217.

Boyd, F. R., Jr., and England, J. L., 1960a, Apparatus for phase equilibrium measurements: Jour. Geophys. Research, v. 65, p. 741-748.

__________ 1960b, Minerals of the mantle: Carnegie Inst. Washington Year Book 59, p. 47-52.

__________ 1961, Melting of silicates at high pressure: Carnegie Inst. Washington Year Book 60, p. 113-125.

Clark, S. P., Jr., 1961, A redetermination of equilibrium relations between kyanite and sillimanite: Am. Jour. Sci., v. 259, p. 641-650.

Clark, S. P., Jr., Schairer, J. F., and deNeufville J., 1962, Phase relations in the system $CaMgSi_2O_6$-$CaAl_2SiO_6$-SiO_2 at low and high pressure: Carnegie Inst. Washington Year Book 61, p. 59-68.

Hays, J. F., 1966a, Lime-alumina-silica: Carnegie Inst. Washington Yearbook 65, p. 234-239.

__________ 1966b, Stability and properties of the synthetic pyroxene $CaAl_2SiO_6$: Am. Minerologist, v. 51, p. 1524-1529.

Jayarman, A., Klement, W., Jr., Newton, R. C., and Kennedy, G. C., 1963, Fusion curves and polymorphic transitions of the group III elements at high pressure: Physics and Chemistry of Solids, v. 24, p. 7-18.

Kennedy, G. C., 1959, The origin of continents, mountain ranges, and ocean basins: Am. Scientist, v. 47, p. 491-504.

Kennedy, G. C., and La Mori, P. N., 1962, The pressures of some solid-solid transitions: Jour. Geophys. Research, v. 67, p. 851-856.

Kennedy, G. C., and Newton, R. C., 1962, Solid-liquid and solid-solid transitions in some pure elements at high pressures, *in* Warschauer, D. M., and Paul, William, eds., Solids under pressure: New York, McGraw-Hill Book Co., p. 163-178.

Kitahara, S., and Kennedy, G. C., 1964, The quartz-coesite transition: Jour. Geophys. Research, v. 69, p. 5395-5400.

Lovering, J. F., 1958, The nature of the Mohorovicic discontinuity: Am. Geophys. Union Trans., v. 39, p. 947-955.

Matsushima, Shogo, Kennedy, G. C., Akella, Jagannadham, and Haygarth, John, 1967, A study of equilibrium relations in the system Al_2O_3-SiO_2H_2O and Al_2O_3-H_2O: Am. Jour. Sci., v. 265, p. 28-44.

Newton, R. C., 1966a, The kyanite-sillimanite equilibrium at 750°C: Science, v. 151, p. 1222-1225.

__________ 1966b, Some calc-silicate equilibrium relations: Am. Jour. Sci., v. 264, p. 204-222.

Smith, F. G., 1963, Physical geochemistry: Reading, Mass., Addison-Wesley Publishing Co., Inc., 624 p.

Tschermak, G., 1914, Über die chemische Zusammensetzung tonerdehaltiger Augite: Tschermaks Mineralog. Petrog. Mitt., v. 32, p. 520-534.