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SOME CALC-SILICATE EQUILIBRIUM RELATIONS

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ABSTRACT. Pressure-temperature curves have been determined for the following univariant equilibria:

1. Zoisite + quartz = anorthite + grossularite + vapor
2. Grossularite + quartz = anorthite + wollastonite
3. Zoisite + sillimanite + quartz = anorthite + vapor

The runs were made in hydrothermal bombs and the solid-pressure piston-cylinder apparatus using natural minerals as starting material. Reaction (1) takes place at 500C° ± 15°C at 2000 bars water pressure. Reaction (2) takes place at 600° ± 10°C at 2000 bars. The third curve agrees with the findings of Newton and Kennedy (1963).

Several univariant equilibria can be calculated from the present work and published thermochemical data, including the stability curves of grossularite and anorthite. The breakdown curve of anorthite lies at a lower pressure than and rather close to that of albite, as determined by Birch and Le Conte (1960). The resulting fact that intermediate plagioclase breaks down nearly as a unit may have some geophysical application.

INTRODUCTION

The system CaO–SiO_2–Al_2O_3–H_2O is petrologically important because the ideal composition of many mineral species can be described with these components and because of the many simple chemical reactions among these minerals which have been deduced by thin-section study of metamorphic rocks. An example is the breakdown of zoisite in the presence of quartz to yield feldspar and garnet, according to the reaction:

$$\underset{\text{zoisite}}{4Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{quartz}}{SiO_2} = \underset{\text{anorthite}}{5CaAl_2Si_2O_8} + \underset{\text{grossularite}}{Ca_3Al_2Si_3O_{12}} + 2H_2O \quad (1)$$

The coexistence of zoisite and quartz is common in nature (Turner and Verhoogen, 1951, p. 462). The assemblage anorthite-grossularite is less common and is considered on petrologic grounds to represent rather high temperature metamorphism (Misch, 1964).

The reaction of grossularite and quartz to produce anorthite and wollastonite:

$$\underset{\text{grossularite}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{quartz}}{SiO_2} \rightleftharpoons \underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{wollastonite}}{2CaSiO_3} \quad (2)$$

is the classic dividing line between hornfelses and granulites on the low temperature side and their high temperature sanidinite equivalent (Fyfe, Turner, and Verhoogen, 1958, p. 212-213). The assemblage anorthite-wollastonite is rarely observed in regional metamorphic rocks (Misch, 1964). Its appearance may be considered to mark the highest temperatures encountered by rocks in solid-state regional metamorphism.

The reaction of anorthite with water to produce zoisite, aluminosilicate, and quartz limits the water pressures at which lime-rich plagioclase can survive. The balanced reaction is:

$$\underset{\text{anorthite}}{4CaAl_2Si_2O_8} + H_2O \rightleftharpoons \underset{\text{zoisite}}{2Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{sillimanite}}{Al_2SiO_5} + \underset{\text{quartz}}{SiO_2} \quad (3)$$

Although zoisite is more generally produced from anorthite by reaction with other minerals as well as with water (Newton and Kennedy, 1963), the P-T curve of the above reaction nevertheless can serve as a useful geobarometer.

Appearance of the ultra-high-temperature assemblages anorthite-gehlenite ($Ca_2Al_2SiO_7$) and anorthite-gehlenite-wollastonite in calc-silicate sanidinites to replace the assemblages grossularite-corundum and grossularite, respectively, occurs only in very high-temperature metamorphism of inclusions in basic igneous intrusive rocks (Tilley, 1948). This "pyrometamorphism" takes place at the highest temperatures that operate to reconstitute crustal rocks.

The dry breakdown of anorthite at high pressure would 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 break-down reaction was found by Boyd and England (personal communication) to be:

$$\underset{\text{anorthite}}{3CaAl_2Si_2O_8} \rightleftharpoons \underset{\text{grossularite}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{kyanite}}{2Al_2SiO_5} + \underset{\text{quartz}}{SiO_2} \qquad (4)$$

Calcic feldspar, which is characteristic of near surface basic rocks, would be replaced by garnet below the Mohorovičić discontinuity. The large negative volume change of reaction would account for the increase in seismic velocity at the crustal base. Knowledge of the P-T stability limits of dry anorthite can serve as an important test of the phase-change hypothesis.

Demonstration of chemical equilibrium is the essential requirement of experimental petrology at high temperatures and pressures if the results are to be meaningful in the direct interpretation of metamorphic rocks. Whereas the several reconnaisance studies which have been carried out in the system CaO–Al_2O_3–SiO_2–H_2O have yielded some useful information, failure to demonstrate equilibrium has limited the applicability of much of the work. Yoder (1950) deduced from experimental work that grossularite breaks down to anorthite, gehlenite, and wollastonite at 4000 bars pressure at some temperature below 1150°C. Roy and Roy (1957) reported that grossularite breaks down to anorthite, gehlenite, and wollastonite above 850°C at 1 kilobar. Pistorius and Kennedy (1960) worked out a preliminary P-T boundary for the grossularite-quartz reaction using the "simple squeezer" apparatus and oxide mixtures as starting material. They synthesized hydrogrossularite (with a variable deficiency of silica and excess of water relative to grossularite) below 750°C and found anhydrous grossularite to be stable in the presence of water only above that temperature. Roy and Roy (1957), on the other hand, concluded that anhydrous grossularite is stable in the presence of water at elevated pressure at temperatures as low as 500°C. Pistorius, Kennedy, and Sourirajan (1962) worked out tentative P-T boundaries for the

anorthite-water reaction (3) and the reaction of zoisite and sillimanite to form anorthite, corundum, and vapor. Glasses and natural scolecite ($CaAl_2Si_3O_{10} \cdot 3H_2O$) were used as starting material. The boundaries were not reversed. Winkler and Nitsch (1962) presented a P-T curve for zoisite-quartz reaction determined in the simple squeezer apparatus using synthetic crystalline anorthite and grossularite seeded with natural zoisite. They claimed a reversal of the equilibrium in cold-seal hydrothermal bombs at 2000 bars between the temperatures of 410 and 510°C. Merrin (ms) worked out a number of P-T curves for calc-silicate mineral reactions using cold-seal bombs and co-precipitated nitrate gels for most of his starting material. The zoisite-quartz reaction and the grossularite-quartz reaction (2) were two of the reactions studied. No unambiguous reversals were accomplished.

Newton and Kennedy (1963) determined the boundary for the anorthite-water reaction using sealed platinum capsules containing analyzed natural minerals and water in the solid-pressure (talc) piston-cylinder apparatus. Reversal of the equilibrium (that is, growth of one assemblage at the expense of its chemically equivalent assemblage) was accomplished at several different temperatures and pressures. Newton (1965) determined the dehydration boundary of zoisite in cold seal bombs and the piston-cylinder device using natural minerals. The equilibrium was reversed at several points along the curve.

Boyd and England (personal communication) located a point on the breakdown equilibrium of anorthite to grossularite, kyanite, and quartz using glass and crystalline anorthite as starting material. The runs were performed under dry conditions at 1350°C, where the kinetics are fast enough to secure reactions in 3 hours run time. Their point at 1350°C is 30.0 kilobars. A point of 1530°C, 30.0 kilobars was quoted in a recent review article (Boyd, 1964) due to a typographical error.

The present study includes experimental determinations of the equilibrium P-T curves for the reaction of zoisite and quartz, grossularite and quartz, and anorthite and water. In addition, several other equilibria and some thermodynamic data are calculated from the experimental data. Comparison of the present results with the earlier work will be presented.

EXPERIMENTAL METHODS

The experimental procedure used was identical to that of Newton (1965), with the exception that some of the runs were made in a 1-inch diameter pressure cavity, which required special pressure calibration, as none had been carried out previously. Starting materials were ground minerals. Drastic grinding was avoided so that structural degradation was unlikely. Zoisites from Shelburne Falls, Massachusetts, and from Buck Springs, North Carolina were used. The latter zoisite is described in New-

ton (1965). It contains 1.5 percent FeO + Fe_2O_3 as the major impurity. The Shelburne zoisite was used in the study of Newton and Kennedy (1963). It was analyzed by emission spectrograph and with the electron microprobe and found to contain 1.9 percent FeO + Fe_2O_3. The unit cell constants are $a_o = 16.182$ Å, $b_o = 5.558$, and $c_o = 10.030$.

The zoisite-quartz and anorthite-water reaction curves were determined using the Shelburne Falls zoisite. Sillimanite from Lisenz, Tyrol, grossularite from Asbestos, Quebec (FeO + Fe_2O_3 = 1.0 percent), anorthite from a Hawaiian olivine encrite (Na_2O = 0.24 percent), and wollastonite from Jefferson County, New York (0.10 percent MgO + FeO) were used. The garnet has a cubic cell constant of 11.846 Å. The other substances except for the wollastonite are described in Newton and Kennedy (1963) and Newton (1965).

The minerals were intimately mixed in reaction proportions by repeated stirrings under acetone until evaporation took place. About equal amounts of reactant and product assemblages were mixed together. The relative amounts of products and reactants before and after the runs were estimated by comparing X-ray diffractogram peak-heights. This method was entirely adequate to determine the direction of a reaction without any special care in X-ray preparation of the samples, as most of the reactions produced at high temperatures and pressures were nearly complete. The growth of the reactant assemblage at the expense of the product assemblage and vice versa at slightly different P-T conditions is the necessary and sufficient criterion for the demonstration of chemical equilibrium.

About 10 milligram amounts of sample were sealed with distilled water in welded platinum tubing. Those runs in which water oozed out when the capsule was cut open after the run were considered successful.

Temperatures during the run were measured with Chromel-P-Alumel thermocouples which were in contact with the platinum sample containers and controlled to ± 2°C automatically. Temperature differences across the 0.03-inch thickness of the flattened tubing must have been very small in spite of the high longitudinal gradients in the graphite-tube heater. At the completion of runs, the samples were quenched to 50°C in a few seconds.

The magnitude of the pressure inside the talc compression cell, which must be smaller than that calculated from ram thrust because of loss to internal friction, is known for the ½-inch-diameter chamber from cyclic measurement of piston-displacement versus ram pressure (Newton and Kennedy, 1963) and by determining the melting point of LiCl at elevated pressure (Newton, 1965). The apparent pressure loss due to friction in the ½-inch talc cell is 1500 ± 200 bars at 6000 bars nominal pressure and 1600 ± 200 bars at 10,000 bars nominal pressure, indepen-

TABLE 1

Runs in cold seal hydrothermal bombs. Starting materials natural minerals (see text)

No.	Pressure bars	Temperature °C	Time days	Results
	Reaction: 4 zoisite + quartz $\rightleftharpoons$ 5 anorthite + grossularite + 2 vapor			
1	1500	430	40	No apparent reaction
2	1500	470	40	No apparent reaction
3	2000	455	42	Growth of zoisite and quartz
4	2000	485	42	Growth of zoisite and quartz
5	2000	510	42	No apparent reaction
6	2000	535	42	Zoisite diminished
7	2000	560	42	Zoisite diminished greatly
	Reaction: Grossularite + quartz $\rightleftharpoons$ anorthite + 2 wollastonite			
8	1100	530	34	Grossularite grew
9	1100	650	34	Grossularite diminished greatly
10	1500	455	37	No apparent reaction
11	1500	490	37	No apparent reaction
12	1500	530	37	Grossularite grew
13	1500	570	37	No apparent reaction
14	1900	520	35	No apparent reaction
15	1900	555	35	Grossularite grew
16	2000	475	42	Grossularite grew
17	2000	540	39	Grossularite grew
18	2000	560	39	Grossularite grew
19	2000	590	39	Grossularite grew
20	2000	600	38	No apparent reaction
21	2000	610	45	Grossularite diminished
22	2000	630	38	Grossularite diminished greatly
23	2000	645	45	Grossularite and quartz disappeared
	Reaction: grossularite + corundum $\rightleftharpoons$ anorthite + gehlenite			
24	2000	800	3	Anorthite and gehlenite nearly disappeared

dent of sample temperatures below 850°C, the temperature at which the interior talc parts begin to "fire" at a finite rate.

The percentage friction in the 1-inch-diameter chamber is known to be less than in the ½-inch-stage for advancing-piston pressure conditions. The melting point of LiCl and the calcite-aragonite transition at 400°C were used for calibration purposes. The former method yielded a correction of −1100 ± 100 bars at 10,000 bars nominal pressure. Hydrothermal quenching runs on calcite-aragonite mixtures at 400°C gave a friction correction at −1300 ± 150 bars at the same nominal pressure. The gas-apparatus data of Clark (1957) at 575°C and the hydrothermal bomb determination of Crawford and Fyfe (1964) at 100°C provided the calibration standard. Baker analyzed precipitated calcite and a natural aragonite from Herrungrund, Hungary, were used. The aragonite was analyzed with the microprobe and found to contain 0.32 perecent SrO as the major impurity. Crawford and Fyfe found their 100°C transition point to be independent of $SrCO_3$ content of the aragonite for as much

as 1.2 percent $SrCO_3$. If the same difficulty in quenching the aragonite phase exists at 400°C as was found by Bell (1964) above 600°C, the frictional loss determined in the way described above would be a maximal one. The calcite-aragonite curve determined by Simmons and Bell (1963) using the oscillating-piston squeezer would give a slight positive friction correction, that is, slight pressure magnification, which is not acceptable inasmuch as the calcite-aragonite runs were made with pressure conditions of piston-advance or "instroke cycle". All the runs of this study were made in this fashion.

The friction correction at 10 kilobars was taken as -1200 ± 200 bars, in accordance with the LiCl and calcite-aragonite data. Since the friction must go to zero with the nominal pressure, the correction in the range 0 to 10 kilobars was taken to be -0.12 times the nominal pressure.

EXPERIMENTAL RESULTS

The results of all the runs are listed in tables 1 to 3. The most pertinent runs serving to delimit the equilibrium boundaries are plotted in figure 1.

TABLE 2

Runs in ½-inch-diameter chamber. Starting material natural minerals (see text)

No.	Pressure bars	Temperature °C	Time hours	Results
	Reaction: 4 zoisite + quartz ⇌ 5 anorthite + grossularite + 2 vapor			
1	4600	610	67	Zoisite and quartz grew
2	4600	640	37	Zoisite diminished greatly
3	5200	650	38	Zoisite diminished greatly
4	6000	600	103	Zoisite grew greatly
5	6000	650	102	Zoisite grew greatly
6	6000	700	44	Zoisite and quartz disappeared
7	8000	750	10	Zoisite and quartz grew
8	8000	770	24	Zoisite diminished greatly
9	8000	790	8	Zoisite and quartz disappeared
	Reaction: Grossularite + quartz ⇌ anorthite + 2 wollastonite			
10	4700	680	96	Grossularite grew
11				
12	4700	700	144	Grossularite grew slightly
13	4700	710	15½	No apparent reaction
14	4700	720	60	Grossularite nearly disappeared
15	5500	750	72	Grossularite nearly disappeared
16	5700	695	12	Grossularite grew
17	5700	785	7	Grossularite + glass + minor anorthite
18	6000	750	29	Grossularite grew greatly
19	6700	700	9	Grossularite grew
20	6700	833	4	Grossularite and glass
21	7000	720	72	Anorthite and wollastonite disappeared
22	7000	780	9	Grossularite + glass
23	9700	745	7	Anorthite and wollastonite disappeared
24	9700	770	64	Anorthite and wollastonite disappeared
25	9700	790	5½	Grossularite + glass
26	9700	850	8½	Grossularite + glass

TABLE 3

Runs made in 1-inch-diameter chamber

No.	Pressure bars	Temperature °C	Time hours	Results
	Reaction: 4 zoisite + quartz $\rightleftharpoons$ 5 anorthite + grossularite + 2 vapor			
1	4700	600	38	Zoisite grew
2	5100	650	38	Zoisite diminished greatly
3	5600	650	23	Zoisite diminished greatly
4	5900	650	23	Zoisite grew
5	6300	650	22	Anorthite and grossularite disappeared
6	7000	720	8	Zoisite diminished
7	7300	720	6	Zoisite grew greatly
8	7800	720	11	Zoisite grew greatly
	Reaction: Grossularite + quartz $\rightleftharpoons$ anorthite + 2 wollastonite			
9	5500	750	72	Grossularite and quartz disappeared
10	5700	750	71	Grossularite and quartz diminished
	Reaction: 2 zoisite + sillimanite + quartz $\rightleftharpoons$ 4 anorthite + 2 vapor			
11	7100	550	38	Zoisite diminished
12	7300	550	44	Zoisite grew
13	7600	550	52	Zoisite grew greatly
14	8800	650	17	Zoisite diminished greatly
15	9000	650	26	Zoisite grew
16	9200	650	27	Zoisite grew greatly
17*	8700	650	30	Zoisite diminished

* Buck Creek zoisite used in place of Shelburne zoisite.

Zoisite-quartz reation.—Reaction (1) was readily reversible in runs of a few hours duration at water pressures above 4000 bars and temperatures above 650°C. The region of uncertainty is very small, indicating that the impurity content of the starting minerals has negligible effect on the position of the equilibrium. At 2 kilobars and about 500°C the reaction ran much more slowly. The 2 kilobar reaction temperature is 500 ± 15°C. The slope is 23.0 ± 2 bars/°C. The determination of Winkler and Nitsch (1962) gave 450°C with a slope of 9.3 bars/°C and that of Merrin (ms) for epidote of 3 to 16 percent Fe_2O_3 extrapolates to about 370°C at 2 kilobars with a slope of 13.7 bars/°C. The low temperatures and flat slopes of the earlier determinations are probably explainable on a kinetics basis at lower temperatures, with reactions slow enough that "over pressing" was required to produce zoisite at a finite rate. In Merrin's case, fast nucleation and persistence of the high-entropy anhydrous assemblage in the stability field of zoisite and quartz probably took place until such temperatures were reached that the equilibrium tendency prevailed.

Zoisite and garnet overgrowths from runs at 550, 650, and 750° (no. 18, table 2; nos. 2, 13, table 3) were scanned slowly with X-rays using a corundum internal standard. The zoisite overgrowths had a unit cell very slightly smaller than that of the starting material. The cell constants of zoisite overgrowths are $a_0 = 16.170$ Å, $b_0 = 5.552$,, and $c_0 = 10.035$. The

difference is presumably because the overgrowths were necessarily very low in Fe_2O_3, having at most 0.3 percent. The fact that zoisite of 0.3 percent Fe_2O_3 content formed at the expense of anorthite and garnet at a given pressure only a few degrees lower than the temperature at which zoisite of 1.9 percent Fe_2O_3 reacted with quartz to form anorthite and garnet demonstrates that small Fe_2O_3 content has no measurable effect on the stability of the zoisite. The unit cells of garnet overgrowths were very slightly larger than the cell of the starting garnet, with $a_0 = 11.855$ Å. The value found by Skinner (1956) for pure synthetic anhydrous grossularite was 11.851. It is not certain, therefore, whether the larger cell size of overgrowths is due to the necessarily high purity compared with the starting material (at most 0.1 percent MgO + Fe_2O_3 in runs on reaction (2) compared to 1.0 percent Fe_2O_3) or whether the garnet overgrowths were very slightly hydrous. In either case the small region of experimental uncertainty of the equilibria guarantees that the small amounts of H_2O and Fe_2O_3 in the garnet do not appreciably change the positions of reactions (1) and (2).

Grossularite-quartz reaction.—This reaction was much more sluggish than the zoisite-quartz reaction even though the boundary is located

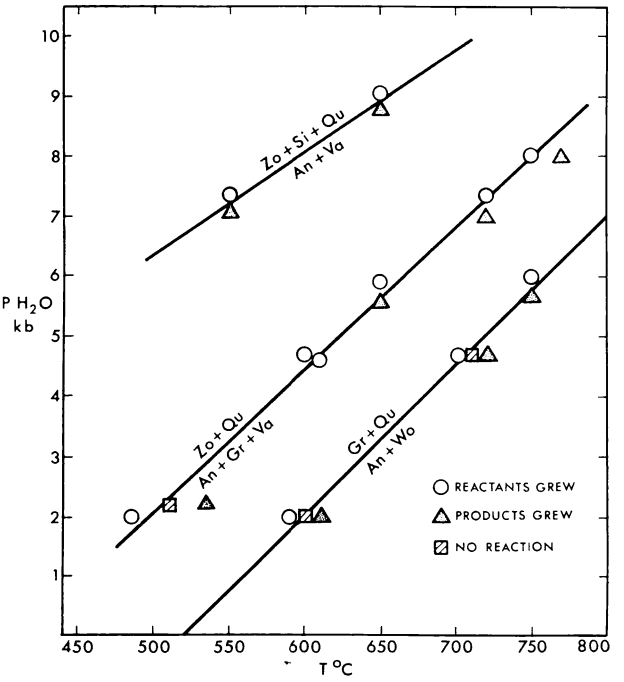

Fig. 1. Experimentally determined equilibria. Points plotted are the most definitive runs from tables 1, 2, and 3 which determine the location of the curves. Zo =zoisite; Qu = quartz; An = anorthite; Gr = grossularite; Si = sillimanite; Wo = wollastonite; Va = vapor.

60 to 90°C higher in temperature. Runs of 3 days duration are not sufficient to produce an indication of equilibrium below 680°C and 4.5 kilobars water pressure. The reaction is clearly reversible in 2-day runs at 750°C and 5.5 kilobars and fast enough to give an indication of equilibrium in 40 days at 600°C and 2 kilobars. Runs above 800°C and 8 kilobars produced melting, as indicated in the quench product by a strong X-ray pattern of grossularite, with quartz, anorthite, and wollastonite absent, hard sintering of the charge, and presence of glass of index about 1.54 detectable microscopically. In all probability a field of grossularite and melt was entered. No attempt was made to pursue the melting relations. The reaction temperature at 1 atmosphere is 250 ± 15°C. The slope is 25.0 ± 2 bars/°C.

The present curve for the grossularite-quartz reaction differs grossly from the curves of Pistorius and Kennedy (1960) and Merrin (ms). The former authors reported a minimum pressure of 13 kilobars at 600° necessary to stabilize grossularite and quartz relative to anorthite and wollastonite. Their slope is 5.0 bars/°C. The discrepancy is undoubtedly explainable on the basis of drastic over-pressing in the simple squeezer necessary to create the dense assemblage instead of the faster-nucleating high-entropy assemblage from oxide starting mixes. The determination of Merrin indicated that the reaction boundary was located at 530°C independently of pressure, with the assemblage grossularite-quartz on the high-temperature side of the boundary. These results are probably due to the swift metastable nucleation of the high-entropy assemblage anorthite and wollastonite from the nitrate gels at low temperatures, with approach to the growth of equilibrium phases only at temperatures above 530°C.

Anorthite-water reaction.—The pressure calibration of the ½-inch-talc pressure cell with 0.006-inch-wall stainless steel heater used by Newton and Kennedy (1963) was quite uncertain. For this reason the curve for the breakdown of anorthite at higher water pressures was redetermined using the 1-inch-diameter chamber. The two starting mixes used (with different zoisites and one mix having an excess of quartz) gave compatible results. The 650° pressure of the reaction is 8.9 ± 0.3 kilobars, with a slope of 17.0 ± 1.5 bars/°C. The value determined by Newton and Kennedy at 650°C was 9.0 ± 0.5 kilobars with a slope of 15.0 ± 2.0 bars/°C.

According to several published experimental determinations of the kyanite-sillimanite equilibrium (Clark, Robertson, and Birch, 1957; Clark, 1961; Kennedy, 1961; Bell, 1963) the line for the anorthite-water reaction should lie well within the sillimanite field of stability. The value at 650°C given by Clark (1961) is 12.7 kilobars. This value, however, involves a great extrapolation from high temperatures—the equilibrium was reversed by Clark only above 1300°. Moreover, the Kennedy and Bell determinations, though carried out at much lower temperatures, were made with Bridgman anvil devices in which conditions of considerable

pressure uncertainty and high shear stress prevailed. Thus the several published results on kyanite-sillimanite equilibrium, although they are essentially in agreement, cannot be considered definitive. Very recently the present author has carried out a hydrothermal determination of the equilibrium kyanite-sillimanite reaction pressure at 750°C by the methods used in the present study. The experiments were done in the 1-inch-diameter cavity on natural minerals with good temperature and pressure measurement and control. The pressure thus determined at 750°C was 8.1 ± 0.3 kilobars, in contrast to the figure of 14.1 kilobars given by Clark (1961). A pressure of 6.0 kilobars at 650°C would result if the slope is calculated from available thermodynamic data.

Thus there is reason to suspect that the zoisite–quartz–sillimanite equilibrium determined by the present experiments is a metastable equilibrium in this pressure and temperature range, zoisite–quartz–kyanite being the equilibrium products of the reaction of anorthite and water. The recent experiments referred to indicated also that sillimanite could not revert to kyanite at 650° in the absence of kyanite seeds in runs of a few hours or days duration. The metastability of sillimanite would therefore not affect the univariant nature of the anorthite-water equilibrium of the present work.

DISCUSSION OF RESULTS

Many petrologically useful thermochemical quantities can be determined from the experimental data. Some of the most important calculated quantities follow.

1. *Entropy of grossularite and zoisite.*—The high-temperature entropy of grossularite has not yet been measured calorimetrically. A value at 650°C can be computed from the slope of the grossularite and quartz field boundary, using the measured high temperature entropy values of anorthite, wollastonite, and quartz (Kelley, 1960; Kelley and King, 1961). The value at this temperature is 172.7 entropy units (eu). It may be compared with the value of 177.5 determined by adding the entropies of the oxides and making a correction for the high density of grossularite of $\frac{\Delta S}{\Delta V} = 0.5 \frac{\text{eu}}{\text{cc}}$ as suggested by Fyfe, Turner, and Verhoogen (1958). The values of Fyfe, Turner, and Verhoogen are perhaps to be preferred because of the great dependence of the calculated entropy of grossularite on the slope of reaction (2), which is subject to some uncertainty. The close agreement of the entropy values derived in two different ways does, however, demonstrate that the curve for reaction (2) is thermodynamically consistent with published entropy data.

The entropy of zoisite at 650°C can be estimated from the slopes of reaction (1) and (3) using the estimated entropy for grossularite. Curve (1) yields $192.1 \frac{\text{cal}}{\text{o-mole}}$, curve (3) yields 196.2, and the zoisite breakdown curve of Newton (1965) yields 194.0. The method of Fyfe, Turner, and Verhoogen (1958) using CaO, Al_2O_3, $Al(OH)_3$ (boehmite), and quartz

with a density correction of $\Delta S/\Delta V = 0.5 \frac{eu}{cc}$ gives 191.3; Ca $(OH)_2$, CaO, Al_2O_3, and SiO_2 give 193.6. The entropy of zoisite at 650° may thus be taken as 193 ± 2 eu. The agreement of the values obtained shows that the experimental curves are in good thermodynamic consistency with published entropy data. The method of Fyfe, Turner, and Verhoogen (1958) probably gives entropy values for zoisite that are correct to within 2 percent in the temperature range 400° to 800°C.

2. *Stability of grossularite.*—The equilibrium 2 grossularite $\rightleftharpoons$ anorthite + 3 wollastonite + gehlenite may be located in the P-T plane if a standard entropy value for gehlenite is estimated. A standard entropy of $45.5 \frac{cal}{o\text{-}mole}$ is given by the method of Fyfe, Turner, and Verhoogen (1958). That this value is likely to be within 0.5 cal/o-mole of the correct one may be seen by comparing the S^0_{298} values for anorthite and wollastonite estimated in the same way with the measured values. Using the heat capacity coefficients for anorthite, wollastonite, and quartz given by Kelley (1960) with the experimental data for reaction (2) and the published heats of formation of anorthite and wollastonite (Robie, 1962) and gehlenite (Neuvonen, 1952) the 1-atmosphere thermal decomposition point for grossularite is found to be 798 ± 15°C. The initial slope of the reaction is 25.4 bars/°C. The grossularite field boundary is plotted in figure 2. It is consistent with the observation of Roy and Roy (1957) that grossularite is unstable at 1 kilobar above 850°C and with the observation of Yoder (1950) that the grossularite breakdown point lies below 1177°C at 4200 bars.

3. *Grossularite-corundum reaction.*—At some temperature below the decomposition point of grossularite the assemblage grossularite-corundum must be replaced by anorthite and gehlenite. Using the data of reaction (2) the 1-atmosphere grossularite and corundum reaction point at 1 atmosphere is found to be 710 ± 15°C (fig. 2). The slope is 22.7 bars/°C so that the value at 2000 bars is 809°C. A hydrothermal run at 2000 bars on crystalline material (run no. 24, table 1) also gave results indicating that the curve lies above 800°C at that pressure.

4. *Heat of formation of sillimanite.*—The difference in Gibbs energy, ΔG, for the reaction of quartz and corundum to form sillimanite at 650°C and 3400 bars may be found by using the curves for reactions (1) and (3) in conjunction with the zoisite breakdown curve of Newton (1965). At 650°C and 8900 bars ΔG for reaction (3) is zero. At 650°C and 5600 bars the ΔG is 6330 calories, neglecting the differential compressibility of the solid phases over the pressure interval. The effect of pressure on the Gibbs energy of water over the range 8900 to 5600 bars was evaluated from the tables of Sharp (1962). At 650° and 5600 bars, ΔG for reaction (1) is zero. If zoisite is eliminated between the two reactions, the net reaction is:

$$3 \text{ anorthite} = \text{grossularite} + 2 \text{ sillimanite} + \text{quartz} \qquad (A)$$

with a ΔG of 12660 calories. At 650°C and 3400 bars ΔG for reaction (1) is −5870 cal and ΔG for the reaction:

6 zoisite = 6 anorthite + 2 grossularite + corundum + 3 H_2O

is zero (Newton, 1965). If zoisite is eliminated between this reaction and reaction (1) the net reaction is:

3 anorthite = grossularite + 3 quartz + 2 corundum (B)

with a ΔG of 17610 calories. Combining this reaction and reaction (A), grossularite may be eliminated to give:

quartz + corundum = sillimanite (C)

with a ΔG of −1145 calories at 1 atmosphere. The heat of formation of sillimanite from the oxides at 25°C is found to be −173 cal/mole using the known heat capacities of the three minerals (Pankratz and Kelley, 1964). This value is in excellent agreement with the value of −356 which

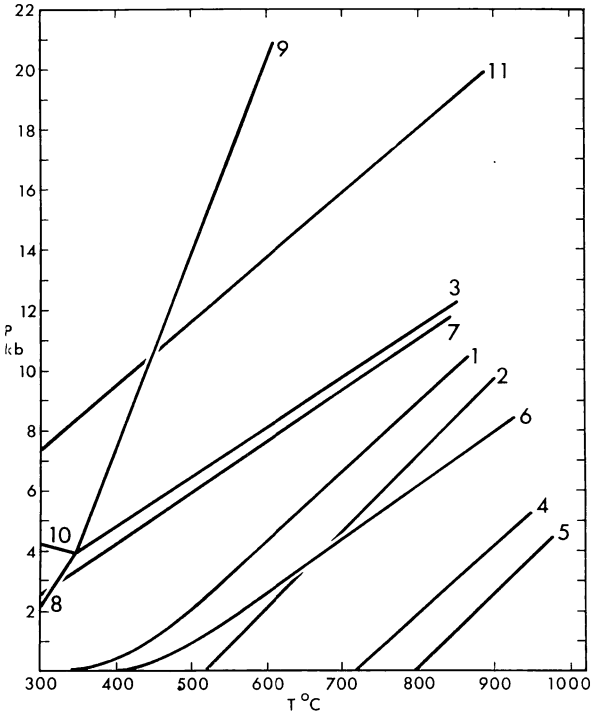

Fig. 2. Collection of calc-silicate univariant reaction curves. 1. Zo + Qu = An + Gr + Va (present results); 2. Gr + Qu = An + Wo (present results); 3. Zo + Si + Qu = An + Va (present results); 4. Gr + Co = An + Ge (present results); 5. Gr = An + Wo + Ge (present results); 6. Zo = An + Gr + Co + Va (Newton, 1965); 7. Zo + Si = An + Co + Va (present results); 8. Law = An + Va (Crawford and Fyfe, 1965); 9. Law = Zo + Si + Qu + Va (Newton and Kennedy, 1963); 10. Law + An = Zo + Si + Qu (Newton, ms.); 11. Gr + Ky + Qu = An (present results).

Low temperature assemblages are on the left hand sides of the equations.

Abbreviations are listed in legend for figure 1 except for the following: Co = corundum; Ge = gehlenite; Law = lawsonite; Ky = kyanite.

was deduced from published P-T stability diagrams of aluminosilicates by Waldbaum (1965) and amply confirms the very small aluminosilicate heats of formation.

5. *Zoisite-sillimanite reaction.*—The P-T curve for the reaction:

2 zoisite + sillimanite $\rightleftharpoons$ 4 anorthite + corundum + vapor

can be calculated from the present data. At 650°C and 8900 bars ΔG for the anorthite-water reaction is zero and ΔG for the reaction of quartz and corundum to form sillimanite is −789 calories. If the latter reaction is subtracted from the former, the net reaction is the zoisite-sillimanite reaction with a ΔG of 789 calories. ΔG for this reaction will vanish if the pressure is changed by −400 bars. The calculated curve is shown in figure 2. A preliminary curve for this reaction found by Pistorius, Kennedy, and Sourirajan (1962) using oxide starting materials in the simple squeezer apparatus indicates a minimum pressure of 14 kilobars at 550°C necessary to stabilize zoisite and sillimanite and a negative P-T slope for the reaction. The discrepancy is undoubtedly explained by the large amount of overpressing necessary at lower temperatures to create zoisite at a finite rate in preference to the faster-nucleating anhydrous high-entropy assemblage anorthite-corundum. This condition is ameliorated at higher temperatures, so that the simple-squeezer synthesis boundary changes slope and becomes tangent to the equilibrium boundary at temperatures above 800°.

6. *Breakdown of anorthite under pressure.*—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. The breakdown products were determined by Boyd and England (personal communication) to be grossularite, kyanite, and quartz. They located a point on the breakdown curve at 1350°C and 30 kilobars with runs on glass and crystalline anorthite. Runs below 1200°C on anorthite glass performed in the dry way yield metastable anorthite to 40 kilobars (Boyd, personal communication). Runs on anorthite glass at higher temperatures often crystallize to an alumina-deficient anorthite structure plus corundum. Hydrothermal runs at lower temperatures yield zoisite at much lower pressures. Thus, direct determination of the anorthite breakdown under pressure is fraught with experimental difficulties.

A calculation of the anorthite breakdown can be made using reactions (1) and (3). At 650°C and 8900 bars water pressure, ΔG for reaction (3) is zero and ΔG for reaction (1) is 8350 calories. If reaction (1) is subtracted from reaction (3) the net reaction is:

3 anorthite $\rightleftharpoons$ grossularite + 2 sillimanite + quartz

with a ΔG of 8350 calories. The volume change for the reaction is 54.60 cubic centimeters, neglecting a 10-kilobar compression effect. At 650°C and 12.7 kilobars, which is the sillimanite-kyanite inversion point deduced by Clark (1961), ΔG is 3280 calories. If the Clark point is assumed to be correct, ΔV becomes 66.22 cubic centimeters at 12.7 kilobars. The

increase of pressure necessary to eliminate the remaining ΔG is 2050 bars. Thus the breakdown pressure of anorthite at 650°C by this calculation is 14770 bars. The 1-atmosphere compressibilities of the minerals are of the order of 10^{-6}/bar. Since reactants and products are roughly of the same compressibility and since compressibility decreases with pressure, a 16-kilobar compression is unlikely to affect ΔV of the reaction by more than 5 percent, so that the ΔV of the reaction at 650°C and 16 kilobars can be taken as 63.0 ± 3.0 cubic centimeters. The effect of a 16-kilobar compression on the entropies of the minerals is thus apt to be less than

$$\delta V \left(\frac{\delta S}{\delta V} \right) \sim 3 \text{ cc} \times \frac{0.5 \text{ eu}}{\text{cc}} = 1.5 \text{ eu},$$

which may also be neglected. Using the calculated entropy of grossularite at 650°C of 172.7 cal/o-mole and the measured 1-atmosphere densities and entropies of the minerals, a slope of 21.8 bars/°C is obtained. The breakdown is plotted in figure 2. At 1350°C the breakdown pressure is 30.1 kilobars if a straight line is assumed.

If, on the other hand, the recently determined provisional point of 6.0 kilobars at 650°C for the sillimanite-kyanite inversion is accepted, the calculated anorthite breakdown at 650°C comes out to be 1.1 kilobars lower in pressure than if the Clark value of 12.7 kilobars is assumed. The curves resulting from the two assumptions are shown in figure 3. The agreement with the Boyd and England point at 1350°C is good.

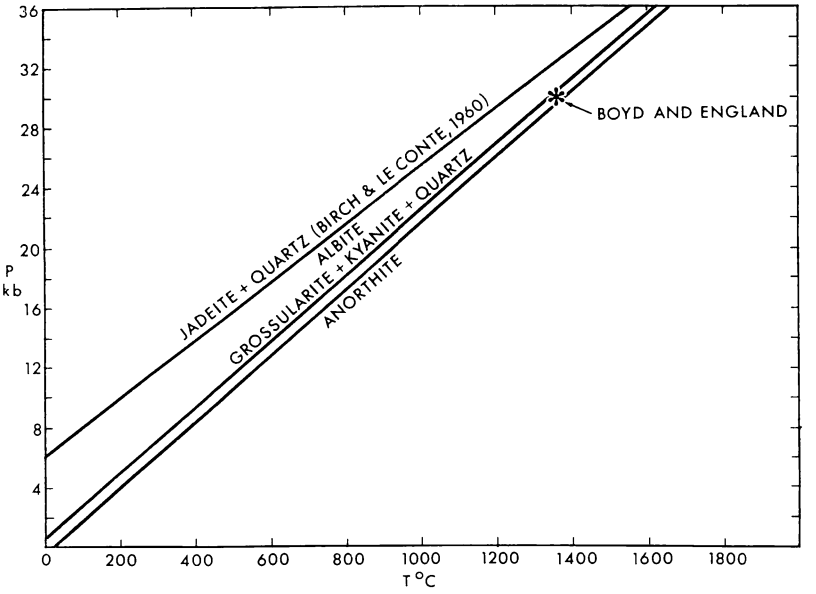

Fig. 3. Feldspar breakdown curves. The higher-pressure anorthite breakdown curve assumes the kyanite-sillimanite data of Clark (1961). The lower-pressure curve assumes the author's provisional kyanite-sillimanite data (see text).

PETROLOGIC APPLICATION

Several applications of the experimental and calculated curves may be made to the interpretation of the conditions of crystallization of metamorphic rocks which bear certain characteristic pairs of minerals. A necessary assumption that must be made in connection with the equilibria involving water is that water pressure was essentially equal to total pressure at the time of mineral formation. Since lime silicates often developed from the metamorphism of impure limestone, CO_2 may have been present in many instances in amounts capable of supporting a considerable portion of the total pressure. This possibility must be kept in mind when applying the present results.

Another assumption that may be made is that small amounts of other components such as Fe_2O_3 in zoisite and garnet will make only small shifts in the positions of the curves. This is consistent with the findings of Merrin (ms) and Newton (1965). Many natural examples of calc-silicate assemblages may then be found which show close enough approach to 4-component chemistry to be reasonably interpreted with the aid of the present data.

Zoisite and quartz are a pair characteristic of greenschists, some amphibolites (Turner and Verhoogen, 1951), and some granulites (Kennedy, W. Q., 1949), but not hornfelses or sanidinites (Eskola, personal communication). Some pegmatites also contain epidote and quartz (Lapham, 1957). The saussuritization of plagioclase gives rise to zoisite and quartz, as well as calcite, hydromica, hydrogarnet, and other minerals. The present experimental results indicate that the coexistence of zoisite and quartz indicates equilibration temperatures of less than 600°C, except for rocks formed at very high pressures, deep in the crust. If the curve for the beginning of melting of a typical pegmatite (Jahns and Burnham, 1958) is superposed on figure 2, it may be seen that pegmatites containing zoisite and quartz are likely to have formed at depths greater than 10 kilometers and temperatures less than 600°C. The chemically equivalent anhydrous assemblage, anorthite-grossularite is characteristic of calc-silicate hornfelses and cordierite-anthophyllite amphibolites (Fyfe, Turner, and Verhoogen, 1958). Anorthite-grossularite is a key assemblage in the metamorphic rocks of the Nanga Parbat region, indicating higher temperatures than the zoisite-quartz assemblage but lower than the assemblage anorthite-wollastonite (Misch, 1964). This temperature is probably 650 to 700°C if reasonable depths are assumed. The feldspar and garnet from Nanga Parbat are nearly end-member minerals, and water was available, to judge from the presence of migmatites.

Grossularite and quartz are a characteristic hornfels pair. The chemically-equivalent pair anorthite-wollastonite occur mostly in very high temperature contact zones around basic intrusions. They indicate temperatures higher than the pair grossularite and quartz and lower than anorthite-gehlenite (Yoder, 1950, p. 249). This temperature is probably higher than 650°C. Coexisting anorthite and wollastonite are rare in

regionally metamorphosed rocks. The pair was found by Misch (1964) in the Nanga Parbat suite. The minerals closely approach ideal composition. Grain contacts of the two minerals show incipient back-reaction to grossularite and quartz. Temperatures in excess of 700°C are indicated for these rocks if they represent (as Misch believes) a rather deep-seated zone of origin. This temperature lies at the upper limit of temperatures encountered by geosynclinal rocks in deep mountain-root regional metamorphism.

The assemblage zoisite-sillimanite-quartz is rare indeed, one possible reason being that free aluminosilicate is not likely to occur in lime-rich rocks. Another possible reason is that kyanite may be the stable aluminosilicate at the anorthite-water reaction boundary. A few eclogites containing zoisite-kyanite-quartz are known (Newton and Kennedy, 1963). Reaction (3) does put an upper limit on the P-T conditions under which anorthite will survive in the presence of water. The P-T history of intrusive rocks having very calcic plagioclase must conform with the curve for reaction (3). The extrapolation of the curve to near surface pressures suggests that the incipient formation of zoisite from plagioclase found in many gabbroic rocks may have taken place at temperatures below 150°C.

Zoisite-sillimanite reaction.—Zoisite is rarely found with sillimanite or kyanite. The pair is listed in Turner and Verhoogen (1951) as a possible amphibolite assemblage. Maximum temperatures for the survival of this assemblage would appear to be 450 to 500°C for rocks formed at levels in the crust other than the deepest zones.

Anorthite breakdown at high pressure.—The most important mineralogical effect in the transition of basalt to eclogite at high pressure and the inversion of lighter-colored crustal rocks to denser chemical equivalents is the disappearance of plagioclase feldspars, their place being taken by garnet and jadeitic pyroxene. A typical basalt would have nearly the density of eclogite if its plagioclase were converted to jadeite, grossularite, kyanite, and quartz. Of course the 6 to 8 percent MgO and similar amount of iron oxides present in basalt would enter the breakdown reaction and would presumably have the effect of bringing the pressure requirement down, inasmuch as MgO-bearing pyroxene is stable at lower pressures than soda pyroxene. That the breakdown of plagioclase alone may take place over a rather small pressure interval is suggested by the proximity of the breakdown curves of albite and anorthite shown in figure 3. A large negative ΔG of mixing of the plagioclase components would raise the breakdown pressure somewhat, but at temperatures well below the 1-atmosphere plagioclase liquidus the ΔG of mixing for intermediate plagioclase is much smaller than the ideal solution value and may be slightly positive for some compositions as shown by the phenomenon of peristeritic unmixing (Ribbe, 1960). Breakdown pressure requirements for the plagioclase mix-crystals greatly in excess of those of the end-members are therefore not to be expected. It may be con-

cluded tentatively that intermediate plagioclase breaks down nearly as a unit under high pressure.

The pressure stability limit of plagioclase has a bearing on the nature of the lower crustal boundary, or Mohorovičić discontinuity, according to the hypothesis that it marks the transition from basalt to eclogite (Lovering, 1958; Kennedy, 1959). It is suggestive that the present breakdown curve for anorthite passes through the point 11.8 kilobars and 600°C, which conditions are currently regarded as most probable for the base of the normal continental crust (Birch, 1963). The breakdown of calcic plagioclase at 600°C may not lie far above this pressure.

On the other hand, the experimental basalt-eclogite determination of Ringwood and Green (1964) at 1100°C from basaltic glass indicated a very broad transition interval for the inversion. Plagioclase and garnet coexisted over a range of nearly 8 kilobars, according to their experiments. Their eclogite facies lower pressure boundary lies very close to the present anorthite breakdown curve. They concluded that the basalt-eclogite transition could not give a sharp seismic discontinuity and that no conceivable geothermal P-T curve could cross from the basalt region to the eclogite region in such a way as to explain the seismic phenomena. Their interpretation must be accepted with appropriate hesitation, however, when the fact of metastable persistence of plagioclase to very high pressures is remembered. It must also be kept in mind that several recent detailed seismic investigations of crustal structure have revealed much more gradational crust-mantle transitions than were formerly thought to exist (Pakiser, 1963). Finally, if the bulk composition of continents is somewhat more siliceous than basaltic composition, the pressure requirements for garnet-pyroxene mineralogy would be correspondingly raised.

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