American Mineralogist, Volume 66, pages 1183–1188, 1981

The join $CaAl_2Si_2O_8$–H_2O (anorthite–water) at elevated pressures and temperatures

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Abstract

A portion of the join anorthite-water in the quaternary system $CaO–Al_2O_3–SiO_2–H_2O$ has been reinvestigated in the range 550°–990°C, from 7 to 16 kbar. The reaction 4 anorthite + $H_2O \rightleftarrows$ 2 zoisite + kyanite + quartz can be described by the equation $P = -4590 + 20.4T$, where P is in bars, T is in °C. The reaction is terminated at an invariant point at 725°C and 10.2 kbar, where melt first appears. The two reactions at higher temperatures and pressures are zoisite + kyanite + quartz + vapor $\rightleftarrows$ liquid, and anorthite + vapor $\rightleftarrows$ liquid, the latter delimiting the fields of anorthite + vapor and zoisite + kyanite + liquid + vapor. The incongruent melting of anorthite + water, beginning at 725°C, is significantly lower than earlier reported, and is unusual in that the solid assemblage anorthite + vapor lies on the high-temperature side of the boundary.

Introduction

In an investigation of the phase relations in the pseudo-ternary system $NaAlSi_3O_8–CaAl_2O_8–H_2O$ (plagioclase–water) it has been observed that from approximately An_{40} to An_{100} the plagioclases break down to a zoisite-bearing assemblage at 8–10 kbar at the same temperature as pure anorthite (Goldsmith, 1978), and at pressures higher than 10 kbar melting takes place over this same range of compositions. For these reasons, it became apparent that an accurate reexamination of the end-member breakdown and melting behavior in the presence of water was needed. The reaction

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

has been investigated by Newton and Kennedy (1963), Newton (1966), and Best and Graham (1978). Boettcher (1970), although not listing any experimental runs for this reaction, showed a univariant boundary based on his location of an invariant point in the system $CaO–Al_2O_3–SiO_2–H_2O$ which requires a slope significantly different from that determined by Newton. Perkins *et al.* (1977) calculated the slope of the reaction using an estimated entropy for zoisite derived from other reactions, fit the curve through Newton and Kennedy's (1963) and Newton's (1966) data, and extrapolated it to higher temperatures and pressures. Perkins *et al.* (1980) recalculated the slope, using newly measured thermodynamic data for zoisite, and obtained essentially the same result.

The onset of incongruent melting of anorthite in the presence of water takes place at a lower temperature than has previously been observed. Boettcher (1970) had correctly deduced the phase relations involving anorthite, and had investigated the melting behavior of the assemblage zoisite + kyanite + quartz + vapor, but his experiments indicated pressures significantly higher than those of the current investigation, probably because of the less plastic pressure media used at that time.

Experimental methods

All the experiments were carried out in piston-cylinder apparatus, using 0.75″ diameter pressure chambers. NaCl was used as the pressure medium for experimental runs that define the phase boundaries, in an assembly with a configuration similar to that described by Newton in W. Johannes *et al.* (1971). Before heating, the assembly was pumped to a predetermined pressure based on prior experience; the large thermal expansion of the salt during heating brought the run to the desired pressure, assuring a "piston-out" condition. A number of runs were carried out in talc assemblies with the

0003-004X/81/1112–1183$02.00

same geometry in order to obtain additional data on the effect of pressure media on sample pressure, generally referred to as "friction". No "frictional" correction was made for the NaCl assemblies (Johannes *et al.*, 1971). The reactants were sealed in platinum capsules containing excess water, and on completion of a run any capsules that did not ooze water when opened were discarded. Chromel-P-Alumel thermocouples tipped with a thin layer of Al_2O_3 were in contact with the Pt-capsules, and temperatures were controlled to ±2°C.

The starting materials were synthetic anorthite, synthetic zoisite, kyanite from Litchfield, Connecticut, and a pure vein quartz from near Lisbon, Maryland. The anorthite was made by reacting the oxides at approximately 1450°C with several cycles of heating and crushing. The zoisite was made from a mixture of reagent grade $Ca(OH)_2$, $Al(OH)_3$, and pure SiO_2 glass, reacted at 750°C and 15 kbar. No extraneous phases were observed in X-ray diffraction patterns or under the microscope in either synthetic phase. The major impurity in the kyanite is 0.93 percent Fe_2O_3.

The products and the reactants were carefully blended in the molar proportions (4An + 2Zo + Ky + Qz) under acetone by mulling four times to dryness in an agate mortar and pestle. This starting material is called "reversal mix" in Table 1. Additional quartz was added to a number of runs to aid in the determination of the melting reaction; the presence or absence of quartz was more easily detected than the presence or absence of melt. Five 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. X-ray diffractometer patterns were made of all reaction products, and many were also examined in immersion oils wth a petrographic microscope. The anorthite and zoisite peaks dominate the diffractometer pattern of the reversal mix, and the relative intensities of these peaks were used to evaluate the direction of the subsolidus reaction. For this reason as well as for brevity, no mention is made of kyanite or quartz in this section of Table 1. Several selected runs were examined and the phases semi-quantitatively analyzed with a JEOL JSM-35 Scanning Electron Microscope (SEM), equipped with energy dispersive analysis (EDX) as a check on the characterization of assemblages on different sides of a reaction boundary.

Experimental results and discussion

Subsolidus breakdown of anorthite

The experimental data on the reaction

$$4 \text{ anorthite} + \text{vapor} \rightleftarrows 2 \text{ zoisite} + \text{kyanite} + \text{quartz} \tag{1}$$

are contained in Table 1. The runs made with talc as the pressure medium are listed at 90 percent of the nominal pressure; the 10 percent "frictional" correction is based on the data obtained in this and other (unpublished) investigations. Selected data from Table 1 are plotted in Figure 1, and the above

Table 1. Experimental reversals on the join $CaAl_2Si_2O_8$–H_2O

Run no.	T°	Kbar	Time (hrs.)	Results
PL172*	550	6.9	392	Strong Zo growth
PL166*	580	7	336	Fairly strong An growth
PL71	570	8	96	Complete reaction to Zo
PL73	590	8	71	No reaction
PL81	610	8	63	No reaction
PL85	610	8.1	164	No reaction
PL90	625	8	264	Strong reaction to An
PL100	650	8.5	120	Almost complete reaction to An
PL45T	640	9	69	Good Zo growth
PL42T	650	9	66	Slight reaction to Zo
PL98	650	9	71	Weak Zo growth
PL41	660	9	24	No reaction
PL138	675	9	144	Weak reaction to An
PL40T	680	9	66	Moderate reaction to An
PL154*	670	9.5	98	Complete conversion to Zo
PL157*	700	9.5	21	No reaction
PL48	680	10	119	Complete reaction to Zo
PL55	690	10	71	No reaction
PL156*	700	10	5	Complete reaction to Zo
PL78	710	10	68	Zo growth
PL165*	720	10	68	An growth
PL148	730	10	48	Strong An growth
PL82	735	10	39	An growth
PL158*	725	10.5	4.25	Almost complete reaction to Zo (+ Ky & Qz)
PL153a	730	10.5	47	Zo + Ky (Qz gone) Brownish "melt"
PL153b	730	10.5	47	Zo + Ky (Qz gone) Brownish "melt"
PL101a	750	10.5	70	Weak An growth
PL103	750	10.8	75	Zo growth, some melt
PL145T	775	10.8	7	Zo growth, some melt (see text)
PL160*	725	11	2	Almost complete conversion to Zo, Ky, Qz
PL164*	740	11	1	Zo + Ky + melt (no Qz)
PL159*	750	11	2	Zo + Ky + melt (no Qz)
PL167*	800	11	0.5	An + Zo + Ky (sintered) (no Qz) (see text)
PL169*	800	11	5.5	An + Zo + Ky (no Qz) (see text)
PL171*	800	11	2	Pumped to pressure (see text) Strong reaction to An (Qz present)
PL59	820	12	24	Zo + Ky + melt (An & Qz gone)
PL75a	850	12	5	Zo + Ky + melt
PL163	850	12	0.25	Zo + Ky + melt + residual An (no Qz)
PL80	870	12	5	Strong reaction to An (some Co or β-Al_2O_3)
PL161*	750	13	1	Essentially complete reaction to Zo, Ky, Qz
PL162*	775	13	0.75	Zo + Ky + melt + residual An (Qz gone)
PL179*	770	16	0.08	Complete reaction to Zo + Ky + Qz
PL178*	790	16	0.1	Zo + Ky + melt (An & Qz gone)

* *Contain extra quartz*
T *Talc pressure medium. All other runs in NaCl.*
Talc runs recorded at 10% below nominal pressure.
An = anorthite, Co = corundum, Ky = kyanite, Qz = quartz, Zo = zoisite

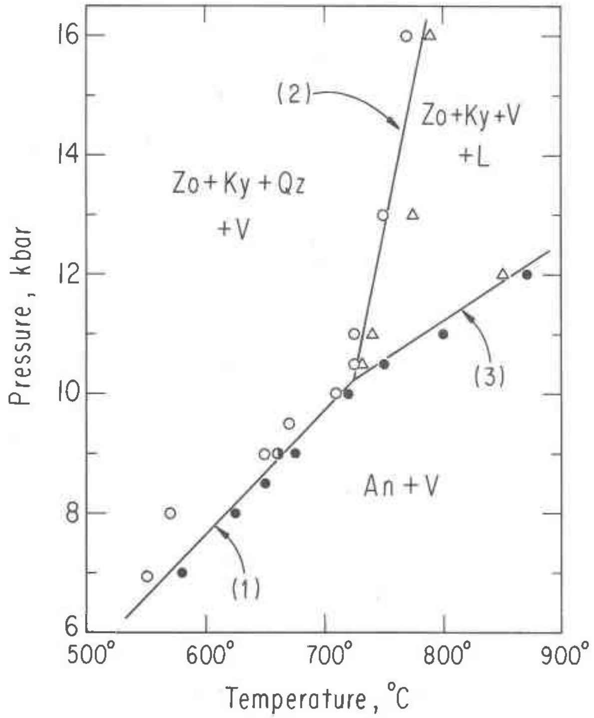

Fig. 1. Some of the P–T relations in the system anorthite-water ($CaAl_2Si_2O_8$–H_2O). An = anorthite, Ky = kyanite, Qz = quartz, Zo = zoisite, L = liquid, V = vapor (phases intersected on the join An–H_2O).

Solid circles represent growth of An, open circles growth of Zo + Ky + Qz, half-filled circle is no reaction, open triangles development of L and disappearance of Qz.

Curve (1) is for the reaction 4An + V $\rightleftarrows$ 2Zo + Ky + Qz + V. Curve (2) is the the reaction Zo + Ky + Qz + V $\rightleftarrows$ L. Curve (3) is for the reaction An + V $\rightleftarrows$ L. The compositions of the liquid and vapor in the field bounded by curves (2) and (3) varies with P and T, as do the relative ratios of L and of V to Ky and to Zo (assuming vapor-saturated compositions).

subsolidus reaction is represented by the boundary at pressures below the invariant point. An "eye-ball" best fit gives an equation for the curve $P = -4590 + 20.4T$ (P = bars, T = °C). The maximum variation in slope permitted within the experimental points as they are plotted is ±2.3 bars/°C. The slope calculated by Perkins *et al.* (1980) is 19.3 bars/°C based on the entropy of anorthite from Robie *et al.* (1978). Using a "corrected" value assuming partial disorder in anorthite (0.7 cal $K^{-1}mol^{-1}$) they obtained a slope of 20.6 bars/°C, essentially identical with this determination. Based on brackets at but two pressures, 6 kbar and 10 kbar, Best and Graham (1978) show a slope of approximately 35 bars/°C. The deviation of Best and Graham's curve from the present and earlier experimental work and the disagreement of their slope with thermochemical calculations might indicate errors in the location of their 6 kbar bracket, for the 10 kbar bracket shows tighter reversal limits and is closer to the curve presented here and by Newton and Kennedy (1963). Garwin and Graham (personal communication) have redetermined the reaction at 6 kbar, with results that are in much closer agreement with the present work, and which cast doubt on the Best and Graham (1978) 6 kbar datum.

Partial melting of anorthite + H_2O

At approximately 10.2 kbar and 725°C an invariant point marks the onset of partial melting with the development of a field of zoisite + kyanite + liquid + vapor. The steep high pressure boundary in Figure 1 represents the general reaction

$$\text{zoisite} + \text{kyanite} + \text{quartz} + \text{vapor} \rightleftarrows \text{liquid} \qquad (2)$$

and the boundary with a slope but slightly less than the subsolidus reaction is for the reaction

$$\text{anorthite} + \text{vapor} \rightleftarrows \text{liquid}. \qquad (3)$$

Boettcher (1970) determined the limits of the anorthite + H_2O field to higher temperatures through a series of reactions where the products become successively zoisite + corundum + liquid, corundum + liquid, and ultimately liquid only. Boettcher showed a maximum pressure of approximately 14 kbar and 885°C at an invariant point between the fields of anorthite + vapor, zoisite + kyanite + liquid, and zoisite + corundum + liquid. The curve of reaction 3 in Figure 1 extrapolates to slightly over 12 kbar at 885°C.

The invariant point in Figure 1 is the I_2 point shown in the schematic Figure 5 of Boettcher (1970). Curves of several other univariant reactions in the system CaO–Al_2O_3–SiO_2–H_2O are associated with this point, and depending upon the starting composition, the phase assemblage in the field Zo + Ky + L + V can vary. In addition to the above four phases, it is possible to have the assemblages Zo + Qz + L + V, and Ky + Qz + L + V. The relative amounts of the four phases Zo, Ky, melt and vapor vary with P and T, thus the composition of the liquid (melt) and vapor phases vary with position in this field. The assemblage shown in Figure 1 is valid for at least one vapor saturated composition on the $CaAl_2Si_2O_8$–H_2O join in the quaternary system

$CaO–Al_2O_3–SiO_2–H_2O$; the phases encountered are those intersected on the join.

The break in slope between the curves for reaction 1 and reaction 3 is rather small, as is the amount of liquid formed, and the onset of melting can easily be missed. The melt is not strikingly obvious in an ordinary microscopic examination, and the amount of quartz involved in the reaction is small enough that the intensities of the principal diffraction peaks for quartz (and kyanite which overlaps it) in the X-ray patterns of reactants and products are much weaker than the strongest anorthite and zoisite peaks. In order to detect the onset of melting with assurance, additional quartz, in amounts several times that of the "reversal mix" was added to those runs made to bracket reactions 2 and 3, as noted in Table 1. The only effect of the additional quartz on the reaction is to produce an additional amount of liquid, and its disappearance in an X-ray pattern when partial melting occurs is obvious and definitive. The curves for reactions 2 and 3 were not reversed; the onset of melting destroys all of the quartz and thus the presence of "seeds" essential to the concept of product and reactant "reversal". At the completion of a run in the melt field, the products could have been blended with additional reversal mix and re-run, but in light of the very crisp reactions at temperatures above 700°, especially those involving a liquid phase, attempted reversals were deemed unnecessary.

In fitting their calculated slope for reaction 1 through Newton and Kennedy's (1963) and Newton's (1966) data, Perkins *et al.* (1980) found that the calculated and observed slopes agreed quite well, although the Newton and Kennedy (1963) brackets at 12 kbar and at 13–14 kbar fall below the curve. It is now apparent that this is largely due to the break in slope between reactions 1 and 3 produced by the onset of melting at just above 10 kbar, a break small enough that it went unnoticed by Newton and Kennedy who fit a single straight line through the data. Perkins *et al.* (1980) extended the reaction of temperatures well into the field of partial melt. Newton (1966) defined the curve with brackets at but two temperatures, 550° and 650°C, well below that at which melting begins.

Earlier workers had underestimated the potency of water as a flux in inducing melting in anorthite. Yoder (1965) worked at 5 and 10 kbar with $CaAl_2–Si_2O_8–H_2O$ in a 10 kbar "gas apparatus" and did not observe any melting until the high-temperature reaction to liquid (±corundum) took place. The 10 kbar limitation kept him just below the field of partial melting.

A problem developed with locating the curve of reaction 3, using the "piston-out" technique and the NaCl pressure medium. The *P–T* path produced by the heating of the initially underpressurized assembly passed through the field of zoisite + kyanite + melt + vapor. Thus a point that is just below the curve of reaction 3, in the field of anorthite + vapor, showed evidence of having melted. For example, the runs made at 800° and 11 kbar (see run #'s PL-167, 169, 145, Table 1) under normal circumstances were initially pressurized to 7.5 kbar at room temperature, and thermal expansion carries them to the desired 11 kbar at 800°C. This path intersects the steep reaction boundary 2 at approximately 10.5 kbar, where melting begins, and cuts across the lower portion of the field of partial melting. Thus the lower-temperature portion of reaction boundary 3 had to be determined by a piston-in technique, where the assembly was initially pressurized to a lower value, so that the *P–T* path resulting from the heating and expansion of the assembly crossed reaction boundary 1 at pressures below that of the invariant point, and the final pressurization was done at the temperature of the run. At somewhat higher temperatures this procedure was unnecessary. In the run at 12 kbar and 870°C, using the normal piston-out technique, the run product showed strong anorthite growth, and no sign of melt. At a temperature this high, it appears that re-equilibration takes place readily after partial melting. This phenomenon emphasizes the rather unusual configuration of the diagram, where crystallization is induced by raising the temperature of the partially molten assemblage, or conversely, partial melting takes place on cooling anorthite + vapor. This behavior is observed in a few other systems such as the "retrograde" melting of muscovite in the system $K_2O–Al_2O_3–SiO_2–H_2O$ (Huang and Wyllie, 1974).

An observation on textures and a corundum complication

Runs PL-146 and PL-159 were examined with the Scanning Electron Microscope (SEM,). These runs, at 725° and 750°C and 11 kbar, bracket the curve of reaction 2. They have altogether different textures from each other. At 725°C the products were very fine grained, with a crystalline size of approximately 1 μm. Crystals of zoisite, kyanite, and quartz were all clearly resolvable, however, and readily identifiable with the energy dispersive analysis. Grain overlaps produced compositional effects due to the small grain size and the fact that a carbon substrate was not used. In addition, there were very small crystals of either corundum, or β-Al_2O_3. A small amount of Ca that appeared in the Al_2O_3 analyses may have been due to overlap with adjacent zoisite or may have been real if the phase is β-Al_2O_3.

In the run at 750°C the crystals were an order of magnitude larger, and zoisite and kyanite were readily identified and analyzed. There were also sizeable spheres that were SiO_2-rich with lesser amounts of Al and Ca. There is little doubt that they were quenched melt. In addition, there were small "spheres" showing only Al_2O_3 (no Ca) in the analysis, undoubtedly corundum. The "spheres" of corundum suggest that the small crystals of the run without melt are also corundum rather than β-Al_2O_3.

Goldsmith (1980) has shown that in the anhydrous melting of anorthite corundum appears with the melt at pressures of 9 kbar and above. 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. Corundum was not detectable with certainty in the X-ray diffraction patterns of the run-products in this investigation. "Hexagonal" plates of high refractive index were observed under the petrographic microscope in several of the runs at 10 kbar and above, but optical identification of corundum (or β-Al_2O_3) in the fine-grain mélange of the reversal mix whch contains several high-index phases is quite difficult. No statement can be made about the presence or absence of corundum as a function of P and T conditions, but it is likely that it is present, at least in the quartz-absent fields of anorthite + vapor and zoisite + kyanite + vapor + liquid at pressures of 10 kbar and greater.

It is difficult to account for the corundum in the two runs examined with the SEM by an exsolution mechanism from anorthite as discussed by Goldsmith (1980), as in both cases the assemblages contain zoisite and kyanite, not anorthite. It is possible, but unlikely, that the corundum formed before the anorthite reacted and persisted metastably during the run, particularly in the field of zoisite + kyanite + quartz. It is also not impossible that it is residual from the original syntheses. Although it should not be ignored, it is not present in an amount adequate to have any significant effect on the phase relations.

Additional comments

In the absence of other phases, anorthite breaks down in the presence of H_2O to zoisite, kyanite, and quartz at approximately 4 kbar below the anhydrous anorthite breakdown to grossular, kyanite, and quartz. The onset of melting in anorthite is at a temperature low enough that partial melting in rocks containing basic plagioclase can be achieved at lower temperatures than had formerly been thought, at least at pressures near the base of the crust. There is very little difference in the temperature at which partial melting begins in the presence of water in pure anorthite and the intermediate plagioclases at H_2O pressures of approximately 10 kbar; the solidus is quite flat from An_{35} to An_{100} (Goldsmith, unpublished data), so that anatexis in rocks of bulk compositions much more basic than granites or granodiorites is quite feasible. Melting temperatures can of course be further lowered by the addition of other components.

Acknowledgments

This research was supported by NSF grant EAR 78-13675 (Geochemistry Program). I am indebted to Robert C. Newton for discussion and advice, to Wiliam Moloznik, who keeps this laboratory operational, and to Dexter Perkins III and Mark Barton, who critically read the manuscript. Alan and Mira Matthews were of great help with the SEM analyses.

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Manuscript received, April 23, 1981;
accepted for publication, June 15, 1981.