# Plagioclase stability at elevated temperatures and water pressures

# JULIAN R. GOLDSMITH

Department of the Geophysical Sciences The University of Chicago Chicago, Illinois 60637

# Abstract

The breakdown of plagioclase to zoisite, kyanite, quartz, and a more sodic plagioclase in the system NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-H<sub>2</sub>O has been investigated with reversed reactions at 8, 9, and 10 kbar. At these pressures all plagioclase compositions from  $\sim$ An<sub>40</sub> to An<sub>100</sub> break down along *the same P-T curve as pure anorthite*, which can be described by the equation P = -4590 + 20.4T (P = bars,  $T = ^{\circ}$ C). The isobaric curves in the *T-X* section are thus represented by a horizontal line (constant temperature) between  $\sim$ An<sub>40</sub> and An<sub>100</sub>. At compositions more sodic than  $\sim$ An<sub>40</sub> the curves dip rather sharply to lower temperatures. In the regions beneath the curves, the composition of sodic plagioclase along the downdipping limb is in equilibrium with Zo + Ky + Qz. The remarkable behavior in the An<sub>40</sub>-An<sub>100</sub> region suggests that under the hydrothermal conditions of this study, regions of ordered anorthite develop in the plagioclase and subsequently react with water as would independent crystals of An. Partial melting of pure An in the presence of water begins at 10.2 kbar and 725° C. At 10.8 kbar a region of partial melt extends at nearly the same temperature from An<sub>30</sub> to An<sub>100</sub>.

The subsolidus experimental data compare favorably with observations on metamorphic rocks. Plagioclase compositions are significantly affected by  $P_{\rm H_2O}$  as well as temperature and it is probable that the configuration of the plagioclase breakdown curve at moderate to high pressures effectively cuts off the oligoclase limb of the peristerite gap. Except for very high grade or low pressure metamorphic conditions plagioclases in the range An<sub>40</sub> to An<sub>100</sub> are unstable with respect to zoisite or epidote.

# Introduction

Knowledge of the subsolidus relations in systems containing the feldspar components and water is essential to the understanding of crustal metamorphic rocks. Surprisingly little experimental work on breakdown of the intermediate plagioclase feldspars at elevated temperatures and pressures has been done, and most of our interpretations of the subsolidus behavior of plagioclase comes from observation of progressively metamorphosed rocks. Goldsmith (1982) has reviewed the literature on the role of mineralogical reactions as well as the effect of structural state in affecting the composition of the plagioclases. The current investigation was undertaken as a first step in the attempt to quantitatively evaluate the stability limits of plagioclase, particularly with respect to the breakdown of plagioclase to zoisite, kyanite, quartz, and a more sodic plagioclase. Before the day of readily available pistoncylinder and high-pressure gas-system devices little experimental work could be done. Reactions involving zoisite, for example, were not feasible in the older style rod bombs with a pressure ceiling of several kilobars. Plagioclase reactions involving diffusion exchange are almost impossibly sluggish (Goldsmith, 1952), and even those aided by the fluxing action of water tend to produce metastable products and cannot be readily equilibrated at low or moderate water pressures (Johannes, 1978). A significant increase in rate takes place in a number of different reactions at pressures well above 2 kbar (Goldsmith and Newton, 1974; Clayton *et al.*, 1975) but even so, in the current study at  $P_{\rm H_2O}$  of 8 kbar and greater, many of the runs were of two weeks' to a month's duration.

# Previous experimental data and calculated results on reactions of interest

Boettcher and Wyllie (1967, 1969) investigated the system albite-water; the join is effectively bina-



Fig. 1. Some of the *P*-*T* relations in the system anorthitewater (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-H<sub>2</sub>O). An = anorthite, Ky = kyanite, Qz = quartz, Zo = zoisite, L = liquid, V = vapor (phases intersected on the join An-H<sub>2</sub>O). Curve (1) is for the reaction  $4An + V \rightleftharpoons$ 2Zo + Ky + Qz + V. Curve (2) is for the reaction Zo + Ky + Qz + V  $\rightleftharpoons$  L. Curve (3) is for the reaction An + V  $\rightleftharpoons$  L. See Goldsmith (1981) for complete discussion.

ry up to 17 kbar, where the curve for the watersaturated melting of albite terminates at an invariant point as albite breaks down to jadeite and quartz. The join anorthite-water has been investigated by Newton and Kennedy (1963), Newton (1966), Boettcher (1970), and Goldsmith (1981); there is a subsolidus reaction involving zoisite, as well as an incongruent melting reaction that also produces zoisite. There has not, however, been any extensive investigation published on the subsolidus albiteanorthite-water (plagioclase- $H_2O$ ) relations.

The join CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-H<sub>2</sub>O is important to an understanding of the behavior of the more complex plagioclase-water system. Figure 1 is a diagram (from Goldsmith, 1981) illustrating some of the *P*-*T* relations in the join. Curve (1) is for the reaction 4 anorthite + H<sub>2</sub>O  $\rightleftharpoons$  2 zoisite + kyanite + quartz. Curve (2) is for the reaction zoisite + kyanite + quartz + vapor  $\rightleftharpoons$  liquid, and curve (3) for anorthite + vapor  $\rightleftharpoons$  liquid, the latter delimiting the fields of anorthite + vapor and zoisite + kyanite + liquid + vapor. Incongruent melting of anorthite and water begins at  $725^{\circ}$  C and 10.2 kbar, and is unusual in that the subsolidus assemblage anorthite + vapor lies on the high-temperature side of the boundary.

Storre and Nitsche (1974), noting reports of an increasing number of occurrences of margarite in metamorphic rocks, experimentally investigated the following reactions involving margarite:

margarite + quartz 
$$\rightleftharpoons$$
 anorthite  
+ kyanite/andalusite + H<sub>2</sub>O (1)

4 margarite + 3 quartz  $\rightleftharpoons$  2 zoisite + 5 kyanite + 3H<sub>2</sub>O (2)

Previously determined reactions involving phases of interest are:

margarite 
$$\rightleftharpoons$$
 anorthite + corundum + H<sub>2</sub>O (3)  
(Chatterjee, 1971; Velde, 1971)

2 zoisite + kyanite 
$$\rightleftharpoons$$
 4 anorthite  
+ corundum + H<sub>2</sub>O (4)  
(Newton, 1966)

2 zoisite + kyanite + quartz  

$$\approx 4 \text{ anorthite + H}_2\text{O}$$
 (5)  
(Newton, 1966)

From the five reactions Storre and Nitsche constructed a P-T diagram with several invariant points and a number of univariant reactions related to margarite stability. One of the invariant points placed at 650° C and 9 kbar is the upper P-T limit for the calculated reaction

 $\begin{array}{ll} 5CaAl_2Si_2O_8 + 2H_2O \rightleftharpoons 2Ca_2Al_3Si_3O_{12}(OH) \\ anorthite & zoisite \end{array}$ 

+ 
$$CaAl_4Si_2O_{10}(OH)_2$$
 +  $2SiO_2$   
margarite quartz

which would constrain the reaction

4 anorthite + 
$$H_2O \rightleftharpoons 2$$
 zoisite

+ kyanite + quartz (Fig. 1)

to a pressure range of stability of little more than 1 kbar. Chatterjee (1976) calculated equilibria involving margarite, and in the absence of other gases that would lower the activity of  $H_2O$ , located the invariant point where the Zo + Ky + Qz assemblage changes to Zo + Ma + Qz at 570° C and 7 kbar. Perkins *et al.* (1980), using new thermochemical data, also calculated reactions in the system CaO- $Al_2O_3$ -SiO<sub>2</sub>- $H_2O$ , and point out that the margarite and zoisite used by Storre and Nitsche contained significant amounts of impurities that may have affected their results. The univariant point calculated by Perkins *et al.* is at approximately  $610^{\circ}$  C and just over 8 kbar.

Although notice has been taken of the possible effect of Na as a margarite substituent by Perkins et al. (1980), little information exists on the effect of Na on mica-producing reactions. Franz and Althaus (1977) considered the stability relations of the assemblage paragonite-zoisite-quartz in the watersaturated system Na<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, and state that the addition of paragonite component to margarite, which ultimately forms a paragonite-rich solid solution produces a reaction of plagioclase to paragonite (solid solution) + zoisite + quartz that takes place at higher pressures than the reaction  $An_{100}$  +  $H_2O \rightleftharpoons Zo + Ky + Qz$ . Franz and Althaus also point out that Storre and Nitsche (1974) used a margarite containing "substantial amounts" of paragonite and ephesite component, and that the invariant point should be at a lower pressure, perhaps at the 7 kbar and 570° C value calculated by Chatterjee (1976).

Franz and Althaus determined experimentally that at 9 kbar or somewhat higher pressure, and temperatures below 500° C a synthetic plagioclase of composition  $An_{80}$  is completely decomposed to mica + zoisite + quartz. At 9 kbar and temperatures between 500 and 600° C,  $An_{80}$  is incompletely decomposed to mica, zoisite, and quartz, and that some feldspar of unknown composition remains. Details of their experiments are not given. The role of margarite in the present investigation will be briefly considered in a later section.

#### **Experimental methods**

All the experiments were carried out in piston-cylinder apparatus, using 0.75" diameter pressure chambers. Both NaCl and talc were used as pressure media: the design of the two assemblies was the same, and similar to that described by Newton in Johannes et al. (1971). No "frictional" correction was made for the NaCl assemblies (Johannes et al., 1971), and experience with comparative runs in this and other investigations (Goldsmith, 1981) indicate a 10 percent correction for talc relative to NaCl, with the following procedures. The NaCl assemblies were pumped to a predetermined pressure before heating 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. Talc expands very little on heating, and initial pumping was close to the desired final pressure. Significant initial overshooting in pressure was avoided in order to minimize any tendency to produce zoisite "on the way up", since this phase may persist metastably particularly in lowtemperature runs, as discussed below.

The starting materials (approximately 6 mg) were sealed in platinum capsules containing approximately 2 mg of water, and on completion of a run any capsule that did not ooze water when opened was discarded. Two side-by-side capsules were generally run in a single assembly, and a chromel-alumel thermocouple tipped with a thin layer of  $Al_2O_3$  was nested between them; temperatures were controlled to  $\pm 2^\circ$  C.

#### Starting materials

A variety of starting materials were used—several sets of synthetic plagioclase, several natural plagioclases, and several reversal mixtures of a synthetic plagioclase plus other phases. I. Synthetic plagioclases

(a) A series from  $An_{10}$  to  $An_{90}$  (wt.%) in 10 percent intervals, plus  $An_5$ , supplied approximately 30 years ago by J. F. Schairer, each crystallized from glasses with multiple heatings and crushings. The crystallization of the albitic compositions was a lengthy process ( $An_5$  was held at 1090–1100° C for a total of 170 days). (b) A number of synthetic plagioclase glasses supplied from the stock of the Geophysical Laboratory by H. S. Yoder, and crystallized hydrothermally at 700° C and 2 kbar H<sub>2</sub>O pressure. (c) A series of synthetic plagioclases crystallized by two different methods from glasses made in this laboratory, (1) hydrothermally at 700° C and 1–2 kbar water pressure, and (2) dry, at 1200° C and 20 kbar.

(d) Glasses supplied many years ago by N. L. Bowen, of  $Ab_8An_1$  and  $Ab_1An_5$  (molar proportions) also crystallized hydrothermally and dry, as in c), above, plus plagioclase of  $An_{25}$  composition crystallized by Bowen. These were used by Bowen in his 1913 determination of the Ab–An phase diagram.

(e) Anorthite  $(An_{100})$  prepared by reacting the oxides at approximately 1450° C with several cycles of heating and crushing.

II. Natural plagioclases, all large, rather clear crystals, low in K and Fe:

- (a) An<sub>15</sub>, Monteagle Township, Ontario, Canada
- (b) An<sub>20.5</sub>, Roan Mountain, North Carolina
- (c) An<sub>22.5</sub>, Bakerville, North Carolina
- (d) An<sub>30</sub>, Corundum Hill, North Carolina

III. Reversal mixes, in which the starting plagioclase compositions were  $An_{50}$ ,  $An_{40}$ , and  $An_{10}$ . The proportions and source of the phases in the three mixes are:

(a)  $4An_{50} + 2Zo + 1Ky + 1Qz$ . The bulk composition is  $An_{75}$ . The  $An_{50}$  was hydrothermally crystallized, the zoisite was from Buck Creek, North Carolina, kyanite from Litchfield, Connecticut, the quartz from Lisbon, Maryland.

(b)  $8An_{40} + 2Zo + 1Ky + 1Qz$ . Bulk composition is  $An_{60}$ . The  $An_{40}$  was crystallized at 1200° and 20 kbar, the zoisite was synthetic, reacted from the oxides and hydroxides at 750° and 15 kbar.

(c)  $8An_{10} + 2Zo + 1Ky + 1Qz$ . Bulk composition is  $An_{40}$ . The  $An_{10}$  was crystallized at 1200° C and 20 kbar, the zoisite was synthetic, as above. The kyanite and quartz in (b) and (c) were as in (a).

The plagioclase, zoisite, kyanite, and quartz were carefully blended under acetone in the proportions indicated, by mulling four times to dryness in an agate mortar and pestle. The mixes are designated in the run tables as  $An_{50R}$ ,  $An_{40R}$ , and  $An_{10R}$ . At least five X-ray diffraction scans were made of each to characterize the ranges of relative intensities of the major peaks and thus to establish what constitutes a significant difference in proportions of phases. The use of a different technique, not dependent on the proportion of phases alone was used in the reversal runs, and will be described below.

### Run and reversal techniques

Reversed runs, as normally used to bracket an equilibrium boundary, are not easily done in systems where the reaction involves a change in the composition of a plagioclase feldspar. The hydrothermal breakdown reaction of the end-member anorthite (Goldsmith, 1981), 4 anorthite + vapor  $\rightleftharpoons$  2 zoisite + kyanite + quartz was reversed at temperatures of 550° C and above in runs of less than 3 weeks, for the reaction chiefly involves growth or dissolution of anorthite and zoisite, without change in the Al/Si ratio of either phase. The reaction in the system under consideration is one in which any shift in the plagioclase-zoisite equilibrium requires a change in the albiteanorthite ratio of the plagioclase. The extreme sluggishness of this process is well known (Goldsmith, 1952; Johannes, 1978). Locating the equilibrium boundaries in this investigation with runs all delineating full reversals of the equilibrium would be unrealistic, but an adequate number were made to validate the results of the numerous unseeded runs.

In order to establish the direction of a reaction involving the reversal mixes, it is necessary to determine the relative change in proportion of the phases involved, or to observe a change in composition of the plagioclase, or both. If the reaction progresses far enough, determination of the change in the ratio of phases may be relatively easy. If, however, rather little change takes place, even though it may be significant, determination with certainty based on relative intensities of X-ray diffraction peaks may be ambiguous. A number of factors, including orientation, grain size and crystallinity can influence intensities and introduce ambiguities, so that differences of at least 10–20% or more are required. On the other hand, determination of the composition of plagioclases from X-ray powder diagrams is fraught with difficulty, and differences of 10–20% in An content cannot be routinely detected.

Viswanathan (1971) has shown that K may be exchanged for Na in plagioclase at approximately 850° C in molten KCl. The exchanged product, unlike the original plagioclase, has a variation in volume and lattice constant *a* that varies significantly with composition, *i.e.*, with the Na/Ca ratio of the original plagioclase. The  $\overline{2}01$  spacing is particularly useful, and a number of synthetic plagioclases were exchanged and the  $\overline{2}01$  spacing calibrated against KBrO<sub>3</sub>, as a check on Viswanathan's determinative curves. Agreement was quite good, and the composition of exchanged runs in sample sizes of 5–10 mg was determinable to  $\pm 2$  percent An. There is a problem with X-ray determination of spacings of plagioclases more sodic than An<sub>10</sub>, possibly because of a non-linear change in lattice constants of silicate solid solutions near the end members as discussed by Newton and Wood (1980).

As Viswanathan points out, the more calcic plagioclases are more difficult to exchange completely, but no difficulty was experienced with calibration samples and run products in compositions up to  $An_{50}$ . The fine grained run products were held in molten KCl for three hours at 820–850° C. Significantly longer exchange times induced breakdown of the feldspar to leucite, kaliophilite, and possibly wollastonite. The K-exchange is an all or nothing process—one does not observe intermediate spacings produced by partial replacement of Na by K. Thus even if the exchange process is incomplete, the spacings of the exchanged and unexchanged portions are distinct, and if enough of the Kexchanged material is present, it is readily measurable. Bimodal or smeared reflections do appear in exchanged run products, but as a result of compositional gradation or variation produced by incomplete reaction during the high pressure experiment and not by partial exchange with KCl.

The reversal reactions may go either in the direction of forming zoisite (+ kyanite + quartz) and a lesser amount of a more sodic plagioclase from the starting plagioclase, or in the opposite direction by reacting zoisite (+ kyanite + quartz) with the original plagioclase to produce an increased amount of a more calcic feldspar. If the reaction were to go to completion, i.e., the equilibrium configuration, the plagioclase would represent the most calcic composition stable under the imposed P-T conditions, neglecting any metastability consequent upon unattained structural re-adjustments. Determination of the plagioclase composition in the reversal runs by K-exchange was much more sensitive and revealing than attempts to determine the direction of reaction by relative changes in X-ray diffraction peak intensities. The magnitude of the change as well as the direction was determinable in a single run. One other variant of the reversal reaction was tried-attempted rehomogenization of zoisite produced from plagioclase in a previous run.

Most of the runs were not reversal, but "half reversal" experiments, starting with the synthetic plagioclases, some with the natural crystals, in capsules sealed with approximately 25 wt.% water. All of the run products were examined under the petrographic microscope. Zoisite is readily detected in the presence of plagioclase even in very small traces or as very small crystals because of the large difference in relief. Optical examination in this case is a very sensitive method of detection; if one had to depend on the presence or absence of zoisite diffraction peaks in an X-ray pattern to establish a phase boundary a considerable error would result. Some of the runs produced rather large crystals of zoisite which were observable under a binocular microscope at very low magnification or even with the unaided eye. A number of run products were examined and the phases semi-quantitatively analyzed with a JEOL JSM-35 Scanning Electron Microscope (SEM), equipped with energy dispersive analysis (EDX).

Two capsules run together with plagioclases that compositionally bracketed the boundary curves, although unseeded with the reaction products, consistently produced zoisite in the more calcic of the two plagioclases, and none in the more sodic. The results were remarkably consistent and reproducible, and the identification of the curves as equilibrium rather than kinetically controlled or synthesis boundaries was validated by those reversal runs that were successfully carried out. The sensitivity of detection is illustrated by run PL144a (Table 5). The reversal mix did not show a detectable reaction, yet the companion run of An<sub>75</sub> alone (PL144b, Table 2) producd "abundant" zoisite in the unseeded runs.

The structural state of the synthetic plagioclases used as starting materials is presumed to be the high-temperature (largely disordered) modification, particularly in those samples crystallized at 20 kbar and 1200° C. The plagioclases that were crystallized dry (J. F. Schairer) produced very poorly resolved X-ray diffraction patterns (especially the more sodic compositions) in which only the strongest peaks were observable. However, even for these, at the completion of a run the X-ray pattern was crisp; "crystallinity" was greatly improved, even if significant recrys-



Fig. 2. Phase relations at  $P_{\rm H_2O} = 8$  kbar on the NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> join. Selected data from Table 1. Solid circles = plagioclase only present. Open circles = zoisite + plagioclase (kyanite and quartz not observed, see text). Half-filled circle = trace of zoisite observed. Arrow indicating 615° C is based on reversed reaction in pure An (see curve (1), Fig. 1). The region under the boundary curve is not on the Ab-An join (see text).

tallization was not apparent under the petrographic microscope. The structural state of the plagioclases in the run products remains to be determined.

#### **Identification of phases**

Almost all of the runs were made on compositions and at temperatures rather close to the boundary curve separating the field of plagioclase + vapor from that containing zoisite, in order to delineate it. Relatively little of any phases other than a rather small amount of zoisite and a plagioclase only very slightly more sodic than the starting composition could be expected. Rather few runs produced enough zoisite to be recorded in an X-ray diffraction pattern. In several at 650° C, 10.8 kbar, the pattern, although quite weak, appeared to be orthorhombic zoisite. Crystals produced from oxides and hydroxides or from glass of the composition 2CaO·3/2Al<sub>2</sub>O<sub>3</sub>·3SiO<sub>2</sub> at 15 kbar and 600–700° C are zoisite, which is clearly identifiable from its diffraction pattern. In several synthesis runs made by Matthews *et al.* (1981)



Fig. 3. Phase relations at  $P_{\rm H_2O} = 9$  kbar on the NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> join. Selected data from Table 2. Solid circles = plagioclase only present. Open circles = zoisite + plagioclase (kyanite and quartz not observed, see text). Arrow indicating 665° C is based on reversed reaction in pure An (see curve (1), Fig. 1). The crosses indicate no reaction, at 350° C. The region under the boundary curve is not on the Ab-An join (see text).



Fig. 4. Phase relations at  $P_{\rm H_2O} = 10$  kbar on the NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>3</sub>Si<sub>2</sub>O<sub>8</sub> join. Selected data from Table 3. Solid circles = plagioclase only present. Open circles = zoisite + plagioclase (kyanite and quartz not observed, see text). Half-filled circles = trace of Zo observed. Arrow indicating 715° C is based on reversed reaction in pure An (see curve (1), Fig. 1). The region under the boundary curve is not on the Ab-An join (see text).

at 15 kbar and 400° C, the product was almost certainly clinozoisite, although the diffraction pattern was not well resolved. A run at 15 kbar and 500° C produced what appeared to be a mixture of zoisite and clinozoisite. Zoisite- or clinozoisite-producing runs were carried out in the present study at 400° C at 8, 9, 10, and 10.8 kbar (Figs. 2–5), but the amounts present are inadequate to produce an X-ray pattern. At 400° C the crystals are very thin needles without observable birefringence, and their symmetry could not be determined on the basis of optical properties or morphology.

At temperatures  $> 600^{\circ}$  C, especially in runs where partial melting had taken place, the zoisite generally crystallized as



Fig. 5. Phase relations at  $P_{\rm H_2O} = 10.8$  kbar on the NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> join. Selected data from Table 4. Solid circles = plagioclase only present. Open circles = zoisite + plagioclase (kyanite and quartz not observed, see text). Open squares are in region of partial melt (zoisite + corundum + plagioclase + liquid). The solid arrows along the An<sub>100</sub> border at 730° and 770° C delimit the region of partial melt at 10.8 kbar on the join An-H<sub>2</sub>O (see Fig. 1). The question mark adjacent to the half-filled circle at 400° C indicates uncertainty about the presence or absence of zoisite. The curves delimiting the fields of partial melt are dashed because they were not closely determined.

Table 1. Data at 8 kbar

					the second se
	Sta	rting			
Run #	material		T00 1	Time.	Results
(PL-)	An	source	1.0	hrs.	(plus plagioclase)
90b	89.4	S	625	288	No Zo
92a	79.0	S	610	99	Small amount 70
152a	77	HT	625	100	No Zo
96	48.5	S	625	94	Very rare (tiny yls) 70
92b	48.5	S	610	99	Rare 70
					1410 20
152b	40	Н	625	100	No 7o
177a	33	HT	610	192	No Zo
188a	33	HT	570	220	Sparse 70
177b	30	HT	610	192	No 7o
185	30	HT	590	239	No Zo
			050	200	10 20
88b	30	HT	570	220	Sparse To
85b	28.8	S	610	165	No. 7o
14	25	HT	580	147	No Zo
26a	25	НТ	550	102	No 70
265	25		550	102	No Zo
	20		550	192	NO ZU
73a	25	HT	530	196	Very spanse To
20a	25	нт	500	335	Very sparse Zo
736	22 5	Ra	530	106	No contain 7a
206	20	HT	500	335	No Zo
99a	20	HT	450	333	Vory name Ze
554	20	113	400	337	very rare 20
91a	20	HT	400	743	Sparse Zo
10a	19 1	н	550	167	No 7o
07a	19 1	н	500	240	No Zo
105	15	ü	550	167	No Zot
075	15	54	500	240	NU ZU~
070		n i	500	240	mouerace 20°
99b	15	HT	450	337	No. 7o
916	15	HT	100	7/2	Bang (tiny yla) Za
14a	15	HT	400	672	Spance Za
146	11 1	HT	400	672	No 70
1 10			400	012	NO 20
00b <sup>∇</sup>	38 6	s	650	120	No. 70
	00.0	5	0.00	16.52	NU 7.U

All runs in NaCl assemblies.

8 = Schairer orystals H - Hydrothermal crystallization (700°, 1-2 kbar) HT = High temperature crystallization (1200°, 20 kbar)

Ba = Bakersville

An<sub>15</sub><sup>H</sup> gives spurious results (see text).

Run at 8.5 kbar

fairly thick, blocky prismatic crystals, with well-formed terminations. At lower temperatures a needle-like, or elongated habit was more common, although run duration may also affect the morphological axial ratio. In the larger crystals birefringence appeared normal, without anomalous color, but the crystals were usually not thick enough to demonstrate it. An occasional run, such as PL6a (An<sub>70</sub>, 9 kbar, 650° C, Table 2) produced acicular zoisite crystals up to 0.5 mm long, visible to the unaided eye. Occasionally clusters or rosettes were observed, but for the most part the zoisite crystals were isolated from each other and from the parent plagioclase. Zoisite was not observed growing in plagioclase, but crystallized by extraction of the appropriate elements from the feldspar with independent nucleation and growth of the zoisite. When abundant, the zoisite crystals are commonly an order of magnitude longer than the birefringent units (presumed crystal size) of the plagioclase. The extraction of CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> from the plagioclase to produce zoisite (+ kyanite + quartz?) and a more sodic plagioclase, at pressures of 8 kbar or more, results in a recrystallized plagioclase with a sharp and in some cases notably improved X-ray diffraction pattern.

No attempt was made to quantify the amount or proportion of zoisite in the run products; zoisite was generally too sparse for analysis by X-ray diffraction intensities, and optical estimates are biased by variations in size and shape of the crystals in different runs (e.g., a flood of very fine needles, or fewer blockier crystals). Tables 1-4 contain simple qualitative statements about the run products.

In runs with small amounts of reaction products a detailed SEM study is needed to seek out any phases such as quartz in a sea of plagioclase, or to distinguish kyanite or margarite from zoisite; neither identification can be readily made optically in the very fine-grained charges.

Quartz and margarite were identified as reaction products in two samples (PL221a and b, Table 3). The composition of the mica is unknown; identification was by (002) and (004) diffraction peaks at  $2\theta \sim 9.2^{\circ}$  and  $18.5^{\circ}$  respectively (CuK $\alpha$  radiation), and optical examination revealed the presence of a phase with higher birefringence than plagioclase, quartz, or zoisite.

Glass is not easily detected in small amounts, although it may appear as a brownish indistinct mass under the microscope. In somewhat larger quantities it was observed as isotropic material, occasionally coating or including plagioclase and zoisite. At this stage the runs were also somewhat crunchy when crushed. Globules, at times agglomerated into dumbbells or roe-like masses, occasionally surrounding small crystals, were generally present in the runs made at 700° C or more, whether melted or not. These represent quenched vapor, and are fairly distinctive.

Hexagonal-appearing platy crystals were also observed in a number of the runs associated with melt. These high-index crystals, isotropic when viewed normal to the hexagonal outline, were analyzed in runs PL36a and b, PL43a and b, and PL46a and b (Table 4) with the SEM, and proved to be corundum.

### **Experimental results**

Plagioclase-water reactions were carried out at 8. 9, 10 and 10.8 kbar. The data are contained in Tables 1-4; the reversal runs in Table 5. The largest number of runs were made at 9 and 10.8 kbar, most of them with talc pressure medium. The appropriate data are plotted in Figures 2-5.

Ramberg (1949) assumed a continuous change in plagioclase composition with temperature (Goldsmith, 1982, Fig. 1), and Noble (1962) suggested a flattening of a portion of the curve due to metastability, but Figures 2-4 indicate that within experimental error, plagioclase compositions from approximately An<sub>40</sub> to An<sub>100</sub> react with water to form a zoisite-bearing assemblage at the same temperature. Such a horizontal line in the subsolidus diagram at 8, 9, and 10 kbar would result if the activity of anorthite component in plagioclase were nearly constant over almost two-thirds of the compositional range-a most remarkable situation. A discussion of possible explanations and implications will follow, but it is apparent that all plagioclases more calcic than  $An_{40}$  break down to a more sodic plagioclase plus zoisite (and presumably kyanite and quartz) at the same pressures and temperatures as pure anorthite, along curve (1) in Figure 1. This curve can be described by the equation (Goldsmith, 1981) P = -4590 + 20.4T (P = bars, T = °C).

Plagioclases are stable relative to zoisite in the presence of water in the region above the bound-

Table 2. Data at 9 kbar

	Star	rting			D 1+-
Run #	mate	erial	T°C	lime,	(plus plagioclase)
(PL-)	An	source		11.2.	(plus plagioclase)
18a	89.4	S	680	47	No. 7o
19a	89 4	S	660	69	Rare Zo
18b	79	S	680	47	No Zo
89a	79	S	680	24	No Zo
23a	79	S	650	45	Sparse Zo (large xls)
1405	77	HT	650	216	Fairly abundant To
144h	75	HT	630	192	Abundant Zo
112	75	HT	550	22	Abundant Zo
17a	68.7	S	680	70	No Zo
19b	68.7	S	660	69	No Zo
225	c0 7		650	45	Sec
63	68.7	20	650	40	sparse Zo
6h <sup>7</sup>	58 6	2	650	72	Large Zo XIS (0.02 )
98b	58 6	5	650	71	Zo present
12a	52	Ĺ	600	46	Abundant Zo
1505	50	μт	600	262	No. Zo
176	3U 40 E	S S	690	203	NO ZO
7.2	40.0	5	650	/0	Pare Zo
7h	38 6	5	650	49	No Zo
84a	38.6	S	650	75	Sparse Zo ( $\sim 1/4$ kbar high)
70		c.	600	75	-
/9a	38.6	5	630	75	Zo present
94	38.0	3	650	75	Abundanic Zo (large XIS) Spance Zo (a 1/4 kban high)*
86a	33	н	650	67	70 present*
79b	33	Ĥ	630	75	Sparse Zo*
74.			600	70	
/4a	33	H	600	1/3	Zo present*
1428	30		600	142	Very sparse Zo
120	30	CH	600	40	No. Zo
865	28 8	S	650	67	No Zo
000	20.0	-			10 20
9b	28.8	S	600	73	No Zo
15a	20.0	5	600	99	NO ZO
70D	29.9	5	575	4/	NO ZO
10a	28.8	20	550	97	Zo present (large xis)
100	20.0		550	21	20 present (large kis)
11a	28.8	S	500	139	Zo present
142a	20	H	600	142	NO ZO
1092	25	B	575	1/2	Lo presentan
1272	25	HT	575	120	No Zo
1410			415	120	10 20

aries in Figures 2-4 up to temperatures at which melting begins. The field beneath the curves represents the region where plagioclase compositions more albitic than  $An_{40}$  along the down-dipping portion of the curve are in equilibrium with zoisite, kyanite (or margarite) and quartz. Figures 2–5 are not binary diagrams, but projections on the watersaturated NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>O<sub>8</sub> join in the 5-component system. Although the boundary curve itself is on the join, the phases in equilibrium with it (beneath the curve) are not, although the composition of zoisite is fairly close to that of anorthite (3An +  $Ca[OH]_2 = Zo).$ 

### Melting at 10.8 kbar

Figure 5, at 10.8 kbar shows partial melting from approximately An<sub>35</sub> to An<sub>100</sub>. At 10.8 kbar on the join  $CaAl_2Si_2O_8-H_2O$  the field of zoisite + kyanite + vapor + liquid is intersected from  $730^{\circ}$  to  $770^{\circ}$ (Fig. 1) so that a band of partial melt extends into Figure 5 from the anorthite end of the diagram, as

Table 2. (continued)

Run # (PL-)	Star mate An <sub>x</sub>	ting rial source	T°C	⊺ime, hrs.	Results (plus plagioclase)
184 <sup>∀</sup> 108b 106a 102a 14b	25 20.5 20.5 20.5 20.5 20.5	HT RM RM RM	560 575 550 500 450	286 143 168 210 197	Sparse Zo Sparse Zo Very sparse Zo Fairly abundant Zo Sparse Zo
127b	20	НТ	575	120	No Zo
106b	20	Н	550	168	No Zo
112b	20	НТ	550	22	No Zo
122a	20	НТ	530	168	No Zo
138a	20	НТ	530	166	No Zo
125a 130a 10b 11b 111	20 20 19.1 19.1 19.1	HT HT S H	500 450 550 500 500	335 430 91 139 311	Rare Zo Zo present No Zo No Zo Zo present
102b 14a 25a 16a 122b	19.1 19.1 19.1 19.1 19.1 15	H S S HT	500 450 400 350 530	210 197 336 366 168	Zo present Zo present Zo present No Zo (kinetics) No Zo
116a	15	H	500	332	Fairly abundant Zo*
125b	15	HT	500	335	No Zo
130h	15	HT	450	430	Sparse Zo
136a	15	KT	400	407	Sparse Zo
137a	15	KT	400	408	Sparse Zo
104b	15	HT	400	505	Zo present
116b	15	O	500	332	Sparse Zo
135b	10	HT	400	407	No Zo
137b	10	HT	400	408	No Zo
25b	9.5	S	400	336	No Zo
20a	100	see	680	46	Abundant Zo
20b	95		680	46	Abundant Zo
21a	100		700	68	Zo present
21b	95		700	68	Zo present
22a	100		720	43	Zo present
22b	95	text	720	43	Zo present
24a	100		740	96	Zo present
24b	95		740	96	Zo present
26a	100		760	44	Zo present
26b	95		760	44	Zo present
27a	100	see	780	42	Zo present
27b	95		780	42	Zo present
28a	100		780	0.5	Large Zo xls
28b	95		780	0.5	No Zo
29a	100		680	2	Zo Present***
29b	95	text	680	2	Zo present***
30a	100		720	18	Large Zo xls***
30b	95		720	18	Rare Zo***
31a	100		760	23.5	Large Zo xls, corroded***
31b	95		760	23.5	No Zo***
34	100		800	4	Zo, embayed fragments

Runs in talc assemblies, at nominal pressure of 10 kbar (10 percent "frictional" correction)

CH = An<sub>30</sub>, Corundum Hill, NC; RM = An<sub>20.5</sub>, Roan Mountain, NC;

 $O = An_{15}$ , Monteagle Twp., Ontario; L = Labradorite

∇ Runs in NaCl assemblies at 9 kbar

S = Schairer crystals
H = Hydrothermal crystallization (700°, 1-2 kbar)
HT = High temperature crystallization (1200°, 20 kbar)

B = Bowen crystals

Hydrothermal crystallization, spurious results (see text)

indicated by the dashed lines. The lower boundary of the field containing liquid is not well determined, but it is bracketed in the region near An35 at approximately 710-720° C, only 10-20° below that of the 730° C melting of pure anorthite. Thus, like

<sup>\*\*</sup> Off composition (see text)
\*\*\* Rapid heating, initial ? kbar

Table 3. Data at 10 kbar

D	Sta	rting			
(PL-)	An	source	T°C	lime,	Results (plus plagioglass)
78b 221a 148b 91a 151b	89.4 83 79 79 79 79	S HT S S S	710 500 730 725 705	69 623 48 49 71	Zo present Zo, Qz, Ma No Zo Very rare Zo Sparse Zo (small vis)
88a 221b 209a 147b 91b	79 77 50 50 48.5	S HT HT H S	700 500 700 690 725	73 623 48 169 49	Large Zo xls Zo, QZ, Ma Very sparse Zo Large Zo xls Very rare Zo
88b 202a 204a 206a 215	48.5 42 42 42 40	S НТ НТ НТ	700 700 675 675 720	73 24 72 47 47	Large Zo xls No Zo No Zo Largish Zo xls No Zo
202b 209b 204b 206b 195a	40 40 40 40 33	H HT H HT HT	700 700 675 675 620	24 48 72 47 92	Rare Zo Sparse Zo Zo present Largish Zo xls Zo present
210 208a 203a 195b 208b	30 30 30 30 25	нт нт нт нт нт	670 650 630 620 650	71 48 48 92 48	No Zo Zo present Zo present Zo present Very rare Zo (1 x1?)
205 200 207 212 200b	25 25 20 20 20	HT NT HT HT	630 575 630 600 575	48 96 72 96 96	Zo present Abundant Zo No Zo 1 tiny Zo x1 Very rare Zo
211a 211b 213a 216a 216b	20 15 15 15 15 11.1	нт нт нт нт нт	540 540 450 450 450	95 95 623 815 815	Sparse Zo No Zo Moderate amount Zo Moderate amount Zo Sparse Zo
218a 218b	11.1 5.0	HT HT	400 400	704 704	Moderate amount Zo No Zo

All runs in NaCl assemblies.

HE Tails of most decourses. S = Schairer crystals H = Hydrothermal crystallization (700°, 1–2 kbar) HT = High temperature crystallization (1200°, 20 kbar)

the plagioclase +  $H_2O$  breakdown reaction, the curve representing the beginning of hydrous melting of plagioclases is remarkably flat in the region An<sub>35</sub>-An<sub>100</sub>. At 10 kbar pure albite melts in the presence of water between 680° and 690° C (Boettcher and Wyllie, 1967, 1969), and only slightly lower at 10.8 kbar. A dashed line from the albite melting point is connected to the An<sub>35</sub> region, but there are no data involving melt in this region.

The boundary in Figure 5 representing the upper temperature limit of the field of partial melt emanating from anorthite is shown rising with temperature, as indicated by the limited data, although the phase relations in the 5-component system are unknown. Partial melting releases zoisite from the plagioclase, and blocky, well-formed crystals are observed at the onset of melting. Hexagonal plates of corundum are also observed in runs that display partial melting. Similar crystals were observed in the CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-H<sub>2</sub>O (Na-free) join (Goldsmith, 1981).

Stewart (1967) observed what he called " $\beta$ -Al<sub>2</sub>O<sub>3</sub>" of unknown composition, particularly in runs in anorthite-rich compositions at 10 kbar, decreasing in quantity to 5 kbar, and not observed below 5 kbar. Stewart stated that "The ' $\beta$ -Al<sub>2</sub>O<sub>3</sub>' arose from the incongruent solubility of anorthite in the gas, which was enriched in silica." Goldsmith (1980) observed the development of corundum from anorthite in the absence of water at pressures of 9 kbar and above, at temperatures well below melting. This "exsolution" of Al<sub>2</sub>O<sub>3</sub> to form a nonstoichiometric anorthite (Goldsmith, 1980) has not been specifically studied in the system CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-H<sub>2</sub>O, but several observations indicated the presence of corundum or "β-Al<sub>2</sub>O<sub>3</sub>" (Goldsmith, 1981); whether it is an "exsolution" product as in the case of the anhydrous system or a consequence of incongruent solubility enhanced by high pressures is not known.

#### **Reversal** experiments

The runs made with the reversal mixes are listed in Table 5, and illustrated in part in Figures 6-8. The arrows emanate from the composition of the starting plagioclase in the mix, and the heads of the arrows indicate the final compositions of the plagioclase, as determined on the K-exchanged feldspars. At 8 kbar (Fig. 6) the 650° C run of the An<sub>10</sub> starting mix had a very broad 201 peak, indicating a range of compositions, but the strongest portion represented a composition of An<sub>33</sub>, most of the way to the ultimate (bulk) composition of An<sub>40</sub>. The An<sub>50</sub> mix reacted very little, to approximately An53. At 580° C, the run on the  $An_{10}$  mix showed a bimodal 201 peak, representing compositions of  $\sim An_{10}$  and An<sub>28</sub>. It would appear that some of the starting mix remained unreacted, but that the plagioclase that did react went to a composition very close to the curve as drawn. The plagioclase of the run on the An<sub>50</sub> mix was unfortunately destroyed by holding it too long in the molten KCl, but an X-ray diffraction pattern has been made prior to the exchange process, and it clearly showed zoisite growth relative to plagioclase. An arrow of undetermined length ending in a question mark is therefore shown on Figure 6.

Most of the reversals were carried out at 9 kbar and are shown in Figure 7. Several reversal runs were made before the K-exchange technique was used, and although effectively repeated using Kexchange, the results in terms of growth or depletion of phases are described here. The An<sub>50</sub> mix was

Table 4. Data at 10.8 kbar

Tab.	le 4.	(continued	)
------	-------	------------	---

Run #	Starting material		70.0	Time.	Results"
(PL-)	An s	ource	1°C	hrs.	(plus plagioclase)
49a 49b 38a 145b 36a	89.4 79 79 79 79 79	S S S S	800 800 780 775 750	23 23 21 7 66	Melt + xls" Melt + xls Melt + xls Melt + xls Melt + xls
103 <sup>V</sup> 1415 1435 385 365	79 75 75 68.7 68.7	S H H S S	750 750 750 780 750	75 54 48 21 66	Melt + xls Melt + xls Melt + xls Melt + xls Melt + xls
5a 131a 43a 5b 57	68.7 60 58.6 58.6 48.5	S HT S S S	650 600 750 650 775	46 238 46 46 21	Zo present Much Zo Melt + xls Zo present Melt + xls
43b 47a 46a 4a 56	48.5 48.5 48.5 48.5 38.6	S S S S S S S	750 750 730 650 775	46 44 67 68 24	Melt + xls Melt + xls Melt + xls Zo present Melt + xls
183a 47b 46b 32a 4b	38.6 38.6 38.6 38.6 38.6 38.6	S S S S S S	760 750 730 700 650	40 44 67 43 68	Melt + xls Melt + xls Melt + xls Sparse Zo (large xls) Zo present
183b 77a 180a 72a <sub>⊽</sub> 192a <sup>⊽</sup>	33 33 33 33 33 33	н н нт н нт	760 740 730 710 700	40 76 49 75 23	Melt + xls Melt + xls Melt + xls Moderate Zo* No Zo
201a <sup>∇</sup> 77b 180b 87b 192b <sup>∇</sup>	33 30 30 30 30	НТ СН НТ СН НТ	700 740 730 700 700	24 76 49 73 23	Sparse Zo Melt + xls Melt + xls Sparse Zo No Zo
72b 32b 8a 2015⊽ 109a	28.8 28.8 28.8 25 25	S S HT H	710 700 650 700 690	75 43 68 24 73	No Zo No Zo Zo present (large xls) Rare Zo (trace melt?) No Zo

run at 675° C (PL138a), 10° C above the curve, and at 650° C (PL140a), 15° C below the curve. Slight plagioclase growth relative to zoisite was observed in the former, slight zoisite growth relative to plagioclase in the latter. No certain reaction was observed in a run at 630° C (PL144a). At 690° C (PL150a) the An<sub>50</sub> mix showed good growth of plagioclase, which when K-exchanged, gave a value of An<sub>65</sub>. This mix was also run at 690° C (PL147a) and 10 kbar (the only 10 kbar reversal-mix run that was made) and showed zoisite growth relative to plagioclase. This run is not plotted, but reference to Figure 4 indicates that 690° C is 25° below the curve, as opposed to the 25° above the curve at 9 kbar; thus a clear-cut reversal is indicated.

At 625° C (PL168a) the An<sub>50</sub> mix showed increased zoisite; the  $\overline{2}01$  peak was bimodal, with the principal peak shifted to An<sub>43</sub>. The An<sub>10</sub> mix at 625° C (PL168b) also showed a bimodal peak, with compositions of An<sub>10</sub> (unreacted) and An<sub>32</sub>. Another reversal run at 625° C (PL175a) with An40 mix

Run #	mater	ial	T°C	Time	Results <sup>®</sup>
(PL-)	An s	ource		hrs.	(plus plagioclase)
65b	25	B	690	22	Sparse Zo**
61b	25	B	675	19	Sparse Zo**
115a	25	H	675	48	No Zo
117a	25	H	650	117	Very rare Zo
128a	25	HT	650	77	Rare Zo
197a⊽ 194a 115b 117b 128b	25 25 22.5 22.5 22.5 22.5	HT HT Ba Ba Ba	650 600 675 650 650	99 100 48 117 77	No Zo Moderate Zo No Zo Very rare Zo Sparse Zo
109b 119b 44b 97a 95a	20.5 20.5 20.5 20.5 20.5	RM RM RM RM	690 630 600 575 550	73 72 118 96 168	No Zo No Zo Very sparse Zo Very rare Zo Very rare Zo
13b	20.5	RM	550	69	Abundant Zo
94a	20.5	RM	525	166	- Small amount Zo
123b	20	HT	650	47	No Zo
119a	20	HT	630	72	Zo present
121a	20	HT	600	70	Small amount Zo
194b <sup>∇</sup>	20	HT	600	100	Small amount Zo
8b	19.1	S	650	68	No Zo
44c	19.1	S	600	118	No Zo
13a	19.1	S	550	69	Abundant Zo
50a	19.1	S	500	166	Abundant Zo
93a	19.1	S	500	242	Zo present
113b	15	H	610	70	Sparse Zo*
105a	15	H	580	168	Moderate Zo*
118b	15	H	575	120	Abundant Zo* (see 118a)
101b	15	H	565	143	Sparse Zo*
99b	15	H	550	171	Very sparse Zo*
121b	15	HT	600	70	No Zo
198a⊽	15	HT	600	146	No Zo
118a	15	HT	575	120	No Zo (see 118b)
124a	15	HT	550	168	No Zo (very very rare?)
133a 129a 105b 97b 101a	15 15 15 15 15	HT HT O O	530 500 580 575 565	144 360 168 96 143	Moderate Zo Moderate Zo No Zo Very rare Zo No Zo
95b 99a 124b 94b 93b	15 15 15 15 15	0 0 0 0	550 550 550 525 500	168 171 168 166 242	Very rare Zo Very rare Zo Very sparse Zo Very sparse Zo Moderate Zo
133b	11.1	НТ	530	144	No Zo
129b	11.1	НЈ	500	360	Sparse Zo
134a	11.1	НТ	480	168	Sparse Zo
198b	10	НТ	600	146	No Zo
134b	10	НТ	480	168	No Zo
50b 35b 63a 63b	9.5 9.5 9.5 5	s s s	500 400 400 400	166 331 336 336	No Zo Sparse Zo Sparse Zo No Zo (very very rare Zo?)

Runs in tale assemblies, at nominal pressure of 12 kbar (10% "frictional" correction)

The contrast correction V Runs in NaCl assemblies, at 10.8 kbar  $CH = An_{30}$ , Corundum Hill, NC;  $Ba = An_{22.5}$ , Bakersville, NC;

RM = An<sub>20.5</sub>, Roan Mountain, NC; 0 = An<sub>15</sub>, Monteagle Twp., Ontario

S = Schairer crystals

H = Hydrothermal crystallization (700°, 1-2 kbar) HT = High temperature crystallization (1200°, 20 kbar)

B = Bowen crystals

Hydrothermal crystallization, spurious results (see text)

\*\* Off composition (see text)

Zoisite and corundum present in runs partially melted

showed zoisite growth and a sharp  $\overline{2}01$  peak representing An<sub>36</sub>. The companion run (PL175b) of An<sub>10</sub> mix showed zoisite to be depleted, and the  $\overline{2}01$  peak

#### GOLDSMITH: PLAGIOCLASE STABILITY

Run # (PL-)	Starting material An_R	T°C	P, kbar	Time, hrs.	Results and mol percent An of products
174a 174b	50 R (+Qz) 10 R	650	8	359	Little change (An <sub>50-53</sub> ) 201 smeared. ~An <sub>33</sub>
155a 155b	50 R 10 R	580	8	363	Some Zo growth (Sample lost in KCl) Bimodal 201. An <sub>10</sub> +An <sub>28</sub>
150a	50 R	690	9	263	Good Plag growth (An <sub>65</sub> )
138a	50 R	675	9	144	Slight Plag growth
183a 183b	40 R 10 R	675	9	360	An <sub>47</sub> An <sub>39</sub> (Bulk comp. = An <sub>40</sub> )
140a	50 R	650	9	216	Slight Zo growth
182a 182b	50 R 40 R	640	9	385	An <sub>46</sub> No reaction
144a	50 R	630	9	192	No certain reaction
168a 168b	50 R (+Qz) 10 R	625	9	330	$\frac{201}{201}$ bimodal. An <sub>43</sub> . Zo growth 201 bimodal. An <sub>10</sub> +An <sub>32</sub>
175a 175b	40 R 10 R	625	9	473	Z01 sharp. An <sub>36</sub> . Zo growth Z01 bimodal. An <sub>10</sub> +An <sub>30</sub> . Zo depleted
176a 176b	40 R 10 R	657	9.5	359	No certain reaction 201 sharp. An <sub>35</sub> . Plag growth
147a	50 R	690	10	169	Zo growth
189a 189b	40 R 10 R	700	10.3- 10.8	221	An <sub>37</sub> (see text) <sup>An</sup> 35
190a 190b	100 + 42 42 + 15	700	9	719	No reaction (see text) Significant homogenization
 217a 217b	PL14a (P1ag+Zo) P135b (P1ag+Zo)	550	8	336	No apparent resorption Completely resorbed (see text)
A A A	$m_{50}R = 4An_{50} + 2Z$ $m_{40}R = 8An_{40} + 2Z$ $m_{10}R = 8An_{10} + 2Z$	0 + Ky 0 + Ky 0 + Ky	+ Qz (1 + Qz (1 + Qz (1	Bulk con Bulk con Bulk con	mposition = $An_{75}$ ) mposition = $An_{60}$ ) mposition = $An_{40}$ )

Table 5. Reversal runs

was a doublet indicating compositions of  $An_{10}$  (unreacted) and  $An_{30}$ , a rather good bracketing of the curve. At 640° C the  $An_{50}$  mix (PL182a) moved to  $An_{46}$  and the  $An_{40}$  mix (PL182b) showed no reaction. The  $An_{40}$  composition at 640° C is rather close to the equilibrium boundary, and there is little driving force for the reaction.

At 675° C, above the boundary, the  $An_{40}$  mix (PL183a) reacted to  $An_{47}$ , and the  $An_{10}$  mix (PL183b) all the way to  $An_{39}$  (bulk composition is  $An_{40}$ ). Another run previously made at 675° C had been overpressed and ran very close to 0.5 kbar high, or 9.5 kbar. The  $An_{40}$  mix (PL176a) showed no reaction; at this pressure, the equilibrium boundary is very close to 675° C. The  $An_{10}$  mix (PL176b)

showed plagioclase growth, with a sharp 201 peak at  $An_{35}$ . At 9.5 kbar,  $An_{35}$  is very close to the boundary curve.

Figure 8 shows a single pair of reversal runs at 10.8 kbar. The pressure during this run fluctuated, and ran somewhat low for most of the time. It is listed at 10.3–10.8 kbar. An<sub>40</sub> mix (PL189a) had a sharp  $\overline{2}01$  peak, shifted to An<sub>37</sub>. The An<sub>10</sub> mix (PL189b) ended up at An<sub>35</sub>. The bracketing is quite close, and what appears as an overshooting of the equilibrium by the An<sub>10</sub> mix may well be the appropriate reaction at the somewhat lower pressure of the run.

In two of the runs (PL168a and PL174a) additional quartz was added to the  $An_{50}$  reversal mix as a



Fig. 6. Boundary curve at  $P_{\rm H_{2}O} = 8$  kbar (see Fig. 2) with arrows indicating reversed reactions (see text). Tail of arrow represents initial composition of plagioclase in reversal mix, arrow head is final composition. Question mark denotes uncertain final composition.

check as to whether or not any melting was taking place under the conditions of the reversal runs. The validity of the reversals might be questioned if partial melting is involved. Quartz is the solid phase that is eliminated when hydrous melting occurs in anorthite at > 10 kbar (Goldsmith, 1981). If quartz remains after reaction there can have been no melting and the additional quartz makes the observation more certain. No melting was apparent in these runs.

The direction of reaction of the runs made with the reversal mixes is clear and unambiguous. All of the mixes run in the field of plagioclase + vapor grew plagioclase relative to zoisite (plus kyanite + quartz), and the plagioclase became more calcic. All of the mixes in the field of plagioclase + zoisite + kyanite + quartz grew zoisite relative to plagioclase, and the plagioclase became more sodic. Several runs close to the boundary showed little or no reaction. Several of the reversal runs that approached the downward-dipping portion of the



Fig. 7. Boundary curve at  $P_{\rm H_2O} = 9$  kbar (see Fig. 3) with arrows indicating reversed reactions (see text). Tail of arrow represents initial composition of plagioclase, tip of arrow head is final composition. Data in Table 5.



Fig. 8. Boundary curve at  $P_{\rm H_2O} = 10.8$  kbar, with dashed solidus (see Fig. 5). Arrows indicate reversed reactions (see text). Tail of arrow represents initial composition of plagioclase, tip of arrow head is final composition. Data in Table 5.

boundary curve bracketed the curve, in agreement with its position as determined by the zoisite crystallizations from the unseeded plagioclases.

The arrow-lengths in Figures 6-8 indicate that the reactions involving compositional change in the plagioclases run more readily in the direction of an increased anorthite content. This may at least in part be due to greater reactivity of the more sodic compositions, but it may also be controlled by mechanisms associated with the Na-Ca and Al-Si exchange process. This result runs counter to the intuitive feeling that it might be easier for zoisite to be crystallized from plagioclase than to be resorbed in it. On the other hand, the reaction involving the change from Al<sup>VI</sup> in zoisite to Al<sup>IV</sup> in plagioclase may be faster than the converse; Al<sup>IV</sup> is the higher entropy state. Orville (1972) noted that at 700° C and 2 kbar the reaction  $2NaAlSi_3O_8 + CaCl_2 \rightleftharpoons$  $CaAl_2Si_2O_8 + 2NaCl + 4SiO_2$  proceeded much more rapidly in the right-hand, quartz-producing direction, and closely approached equilibrium within one day. The reaction proceeded much more slowly in the left-hand, quartz-consuming direction, and equilibrium was not approached within 30 days. Johannes (1978), in discussing the extraordinary slowness of reaction rates in the system Ab-An- $H_2O$  at 5 kbar says, "It also appears that reaction rates are even slower for experimental conditions where an An-rich plagioclase should react to an Abricher plagioclase than vice versa."

Some insight in the process of compositional change was given by an experiment in which homogenization of plagioclases was attempted. Mechanical mixtures of equal weights of powdered synthetic crystalline  $An_{42}$  and  $An_{15}$  and of  $An_{100}$  and  $An_{42}$  (PL190a and b, Table 5) were sealed in capsules with water and run at 700° C and 9 kbar for

719 hours. K-exchange of the initial mixtures produced well-resolved and readily measured 201 reflections of the two plagioclases (0.37°20 separation). The run product of the  $An_{15} + An_{42}$  mixture after K-exchange showed a broadened 201 peak with two distinct maxima at compositions of An<sub>22</sub> and An<sub>33</sub> (approximately 0.13°20 separation). Thus the reaction went more than half-way to complete homogenization, and apparently by a mechanism of diffusive interchange, rather than by one involving dissolution and reprecipitation of the equilibrium composition. This homogenization differs, however, from the reversals, for two feldspars rather than a feldspar and zoisite are involved. There was no observable reaction in the  $An_{42} + An_{100}$  mixture. This may be related to the ultimate stability of plagioclase solid solutions in this composition range at this temperature as discussed in a following section.

Considering the sluggishness of the reactions involving compositional change in plagioclases, the results of the reversal experiments are rather gratifying, and the location and the interpretation of the curves as equilibrium boundaries seems reasonable. The relatively high pressures used in this study are probably responsible for the approach to equilibrium, and the kinetic advantage of high water pressures is illustrated by Goldsmith and Newton (1974) and Clayton et al. (1975). It is unlikely that satisfactory data could have been obtained at much lower pressures. Johannes (1978) stresses the observation that experiments in the systems Ab-An-H<sub>2</sub>O and Qz-Ab-An-H<sub>2</sub>O demonstrate that reaction rates and attainment of equilibrium compositions are extremely dependent on temperature. Time studies in the Ab-An-H<sub>2</sub>O system at 5 kbar show that at 1000° C a constant (and presumably equilibrium) composition of plagioclase is reached within one hour, whereas at around 700° C (an extrapolated) 10,000 years are needed to reach equilibrium. Johannes found that at 5 kbar and 900° C run times of approximately 200 hours were necessary to approach compositional equilibrium in the plagioclases, and at 800° C the reaction is too slow to attain constant compositions within reasonable times. It remains to be determined whether the difference in the rate of reactions observed at 8 kbar and above in the system Ab-An-H<sub>2</sub>O at approximately 700° C in this study and the failure of reaction (Johannes, 1978) at 800° C and 5 kbar is solely attributable to the 3 kbar (and greater) difference in pressure, or to this plus other differences in experimental methods and type of reaction.

A pair of runs were also made to determine whether or not the re-solution of zoisite in plagioclase could be used as a variant of the reversal technique. An optical observation of the absence or diminution of zoisite in plagioclase in a re-run sample previously held in the zoisite-containing field, if feasible, would be simpler than the Kexchange method. Run numbers PL14a (An<sub>20</sub>, 450° C, 9 kbar), and PL35b (An<sub>10</sub>, 400° C, 10.8 kbar) were re-run with H<sub>2</sub>O as PL217a and b (Table 5), at 500° C and 8 kbar for 336 hours. Both PL14a and PL35b had needles and small prismatic zoisite crystals of approximately the same size and about the same quantity. The An<sub>20</sub> composition at 550° C is 50° C above the curve (solid triangle, Fig. 6), and the An<sub>10</sub> composition is approximately 200° C above it (open triangle, Fig. 6). The  $An_{10}$  composition showed complete resorption of the zoisite, whereas the  $An_{20}$  appeared essentially the same under the microscope as the originally run sample; no certain re-solution was apparent. Whether this difference is due to a difference in reactivity because of the difference in plagioclase compositions, or because of the relative locations with reference to the equilibrium boundary was not determined. It appears that reversals based on re-homogenization of plagioclase-zoisite (plus kyanite and quartz) assemblages may require too large a degree of superheating to provide adequately sensitive results.

# Effect of starting materials

Differences in behavior in several starting materials were observed as the investigation proceeded. Synthetic plagioclases crystallized (dry) at temperatures of from 1090° to over 1300° C by J. F. Schairer were used in the initial experiments. Additional runs were made on plagioclases crystallized hydrothermally from glasses at 1-2 kbar and 700° C, and on several natural plagioclases. A sample of  $An_{25}$ crystallized from a glass (conditions unknown) by N. L. Bowen in 1912-1913 was also used. Inconsistent results began to be observed in several of the preparations; hydrothermally crystallized An<sub>15</sub> and An<sub>33</sub> (JRG) and N. L. Bowen's An<sub>25</sub> in particular produced zoisite at temperatures well above the boundary determined with other preparations, acting as if they were more calcic than the presumed (synthesized) composition. For example, in an experiment to check the aberrant behavior, An<sub>15</sub> crystallized hydrothermally and crystallized from the same glass dry at 1200° C and 20 kbar were run together (PL118a and b, 10.8 kbar, 575° C, Table 4). The high-temperature plagioclase remained all feld-

spar, whereas the hydrothermal plagioclase produced rather abundant zoisite. Some of the hydrothermally crystallized samples seemed to give reasonable and consistent results, however, whereas a few were suspect. Hydrothermal crystallization of plagioclases at 1-2 kbar takes place fairly rapidly at about 700° C, and there is no compelling reason to assume that the first crystals to form would represent the bulk composition of the feldspar. Although 700° C is far enough below the solidus that one might assume that the equilibrium-type relation that produces a more calcic feldspar than the bulk composition at super solidus temperatures would not hold, it is not unlikely that such Ca-enriched plagioclases could be formed metastably. Parsons (1969) observes just this behavior in the alkalifeldspars; when gels and glasses are crystallized hydrothermally below their solidus the crystals present when crystallization is incomplete do not have the same Na:K ratio as the starting material but bear a relation to the starting material analogous to that between crystals and liquids coexisting at the liquidus. A similar effect could be produced by hydrothermal leaching of soda and silica-rich material from the plagioclase glass immediately prior to crystallization. At 700° C re-equilibration of plagioclases to a homogeneous composition will not easily take place, and compositional variation is not readily detectable in ordinary X-ray powder diffraction patterns. What appears to be a well-resolved sharp pattern could represent somewhat inhomogeneous plagioclase. It is likely that at least some plagioclases could have crystallized enough material more calcic than the bulk (presumed) composition that observable zoisite would be produced at temperatures higher than those expected.

Analysis of the An<sub>25</sub> composition crystallized at high temperature by N. L. Bowen with the electron microprobe revealed significant Na-deficiency; the material was no longer a stoichiometric feldspar, although it is close to An<sub>28</sub> in composition. Inconsistent experimental results were also obtained from the natural plagioclases, again possibly the result of slight compositional inhomogeneities, although the effect of structural state cannot be discounted. The An<sub>15</sub> sample from Ontario was observed to be a low-temperature form (Wenk, 1969). Because of uncertainties as to the effect of structural state of natural plagioclases, the run data are not plotted in Figures 2-5, although the data are listed in the tables. The most consistent and trustworthy starting material was the same as that used by Newton et al. (1980), plagioclase crystallized at

1200° C and 20 kbar for periods of approximately 3 hours.

### The nature of the zoisite-producing reaction

The anorthite +  $H_2O$  breakdown reaction (curve 1, Fig. 1) to zoisite, kyanite, and quartz is terminated at 10.2 kbar by partial melting, and is also constrained at lower temperatures and pressures by the reaction involving margarite in place of kyanite:

$$5An + 2H_2O \rightleftharpoons 2Zo + Ma + 2Qz$$

The current investigation does not define the exact nature of the unseeded hydrothermal breakdown reaction of plagioclase. Zoisite is always evident as a product, and although the originally blended kyanite and quartz are evident in the reversal runs, and with the exception of quartz in PL221a, b, to be described shortly, neither kyanite nor quartz have been observed in the products of the unseeded plagioclase runs. This is not to say that they are absent, but that if present, they are not readily detectable. Kyanite might not be expected to spontaneously nucleate and grow in an unseeded run under the P-T conditions used. Newton (1969) showed that the Al<sub>2</sub>SiO<sub>5</sub> triple point was at a significantly lower P and T than determined by Althaus (1967) in part because of the extreme grinding of the kyanite used by Althaus that effectively destroyed the kyanite seeds. Newton was unable to crystallize kyanite in its stability field at pressures below approximately 11 kbar at 750° C in a kyanite-sillimanite mix when kyanite seeds had been highly degraded by grinding.

Goldsmith (1981) reversed the reaction  $4An + H_2O \rightleftharpoons 2Zo + Ky + Qz$  at 7 kbar, but the criteria used for determination of reaction direction depended upon relative amounts of anorthite and zoisite, not upon growth or diminution of kyanite and quartz. It is possible that the reaction could produce margarite, even in the presence of kyanite seeds, and its presence may be missed. If so, the presumption of kyanite-producing reaction would be erroneous. A reversal run at 6.9 kbar and 550° C (plotted in Fig. 1) was carefully examined under the petrographic microscope, with no sign of a mica. Zoisite, plagioclase, kyanite, and quartz, all originally present, were evident.

All of the runs that define the curves of Figures 2– 5 were examined optically, and in none of them was there any indication of a highly birefringent, micaceous phase. This does not prove that the equilibrium reaction does not involve margarite or paragonite solid solutions, particularly at the lower pressures and temperatures, for the nucleation of brittle mica in the absence of seeds may be just as difficult as the nucleation of kyanite. The effect of feldspar stoichiometry and the effect of vapor composition on the amounts and nature of the product phases are unknown. The vapor tends to be silica-rich, which may help to diminish the quartz, especially in the case of the small amount of reaction that takes place near the boundary curves, and the precise compositions of the other principal phases are unknown but also might influence the nature of the product phases when in minor amounts. Anorthite has been shown to be alumina-deficient at pressures of at least 9 kbar and above (Goldsmith, 1980, 1981), but no information is available on plagioclase solutions.

There is thus no indication in the current study in runs close to the boundary curves for any reaction other than An + H<sub>2</sub>O  $\rightleftharpoons$  Zo + Ky + Oz. There are no obvious breaks or discontinuities in the boundary curves. In the present work, only one experiment was carried out at conditions similar to those described in a previous section by Franz and Althaus (1977), well below the plagioclase-zoisite boundary curve. An<sub>83</sub> and An<sub>77</sub> were run at 500° and 10 kbar for 623 hours (Runs PL221a and b, Table 3). Both produced zoisite + plagioclase + margarite + quartz, all detectable in the X-ray diffraction patterns. The proportions appeared to be appropriate for the equilibrium ratios; the run with An<sub>77</sub> contained more of the (sodic) plagioclase than did  $An_{83}$ , as would be expected. These are the only runs in which either margarite or a margarite-paragonite solid solution and quartz were observed. It is obvious from runs PL221a and b and the work of others that brittle mica replaces kyanite at moderate to low temperatures, and it is likely that at least the lower temperature portions of the curves for sodic compositions represent metastable equilibria. The P-Tconditions for the transition from the kyanite to the margarite reaction even in the Na-free system are uncertain, and the relations in the Na-containing system are completely unknown. The determination of the reactions involving plagioclase and the margarite-paragonite phase or phases is guite important for a full understanding of metamorphic relations, but is outside the scope of this study. An experimental study at the low temperatures of the equilibria, although needed, will be tedious and time-consuming. None of these considerations, however, affect the flat breakdown boundaries of Figures 2-4 that mark the region of instability of plagioclases from approximately  $An_{40}$  to  $An_{100}$  in the *P*-*T* range studied.

#### The crystallization behavior of zoisite

Early attempts to synthesize zoisite at pressures up to 2 kbar invariably failed (Ehlers, 1953), and pressures above 2 kbar were not generally attainable until the early 1960's. Below approximately 4 kbar zoisite does not nucleate, and even in seeded runs at 3-5 kbar it is very sluggish in reacting and crystallizing (Fyfe, 1960; Merrin, 1962; Liou, 1973). In this study at 8 kbar and above, zoisite grew in its stability field from unseeded plagioclases with such consistency that these synthesis runs were successfully used to define the field in which plagioclase and zoisite coexist. There seemed to be no exception to this observation in runs of adequate length at temperatures above 400° C. Runs of 366 hours at 9 kbar and 350° C on An<sub>19,1</sub> and An<sub>9,5</sub> (PL16a and b, Table 2), failed to crystallize zoisite. Both runs are plotted in Figure 3 and although the An<sub>9.5</sub> composition is essentially on the curve,  $An_{19,1}$  is well in the field of zoisite stability. No further attempts were made to crystallize zoisite from sodic plagioclases at temperatures below 400° C.

Compositions close to anorthite nucleate and crystallize zoisite so readily that An<sub>100</sub> and An<sub>95</sub> could not be used to define the boundary curve between the field of plagioclase + H<sub>2</sub>O and that of plagioclase + zoisite + kyanite + quartz. These compositions produced large zoisite crystals during the heating process, even when the run was brought from room temperature to approximately 700° C in 15-20 seconds. This is illustrated in Table 2 by runs PL20a and b, 21a and b, 22a and b, 26a and b, 30a and b, 31a and b and PL34. Run PL28a was brought up quickly, and held for 30 minutes. Large zoisite crystals persisted, although at 780° C it is 115° above the boundary curve. Runs PL30a and b, brought up to 720° C rapidly and initially pumped only to 7 kbar, well into the anorthite + vapor field, also showed large zoisite crystals. Run PL31a, held at 760° C for 23<sup>1</sup>/<sub>2</sub> hours, showed corroded zoisite seemingly dissolving or converting to anorthite. PL34, at 800° C, superheated by 135° C, showed fragments and embayed zoisite crystals, surely converting to anorthite. An<sub>95</sub> was somewhat slower in producing zoisite, but the synthesis technique for locating the curve could only be used with plagioclases of An<sub>90</sub> and more sodic compositions which always nucleated, but did so slowly enough that the run could be brought to temperature before the



Fig. 9. Solid line is boundary curve for  $P_{\rm H_2O} = 10$  kbar, from Figure 4. Dotted and dashed curves are calculated (R. C. Newton, unpublished) from thermochemical data (Newton *et al.*, 1980). Dotted curve calculated from an ideal solution model. Dashed curve based on Margules reduction of the calorimetric data plus entropies of mixing predicted by the Al-avoidance model (Kerrick and Darken, 1975). The area above the curves is region of plagioclase stability relative to zoisite, the region beneath the curves of plagioclase + zoisite + kyanite + quartz.

zoisite crystallized. The location of the pure anorthite terminus of the curve was necessarily done with reversal mixes (Goldsmith, 1981, and see Fig. 1). Goldsmith (1976, 1980) also discusses the problem of not being able to suppress the development of zoisite at high pressures if even a trace of moisture is present.

# The configuration of the isobaric curves-Discussion

The flat portions of the curves at 8, 9, and 10 kbar are, within experimental uncertainty and in the limited pressure range studied, sections of a planar surface in P-T-X space. This behavior is remarkable, and not readily explainable on the basis of known thermodynamic data. As drawn, Figures 2-4 are compatible with unit activity of anorthite in plagioclase from approximately An<sub>40</sub> to An<sub>100</sub>. This cannot be reconciled with the activity data obtained by Orville (1972) from ion-exchange experiments at 700° C and 2 kbar, which show nearly ideal An activity in plagioclase in this composition range.

Figure 9 contains the 10 kbar curve (solid line from Fig. 4), along with two curves calculated by R. C. Newton (unpublished) with data derived from high-temperature solution calorimetry on high-temperature synthetic plagioclases (Newton *et al.*, 1980). The dashed curve is based on the Margules reduction of the calorimetric data plus the entropies of mixing predicted by the Al-avoidance model of Kerrick and Darken (1975). The Gibbs energy of mixing at 970 K using this model agrees quite well with Orville's (1972) mixing function derived from his cation exchange experiments at 700° C. The dotted curve is calculated from an ideal solution model. A similar configuration with a concave upward portion in the Ca-rich region, with an inflection and downward dipping region in the Narich portion, is obtained by plotting activity of anorthite in plagioclase at an arbitrary constant temperature against mol fraction.

What would be the effect of Al–Si (and Na–Ca) ordering on plagioclase reaction behavior? Figure 2 of Newton *et al.* (1980) shows a maximum excess enthalpy of mixing in high-state plagioclase of approximately 1.5 kcal. The enthalpy of Al/Si disorder in albite, on the other hand, is about 3 kcal, significantly greater than the enthalpy of mixing. Although there are no data on enthalpy of disorder of plagioclases other than albite (and no measurements of the entropy of intermediate plagioclases exist), it is likely that order-disorder relations in the plagioclases would overpower the effect of enthalpy of mixing, and thus have a large effect on the curves of Figures 2–4.

Newton *et al.* (1980) were unable to use hydrothermally crystallized plagioclases in their calorimetric determinations of enthalpies of solution. Hydrothermal crystallization at 700–750° C and 1000 bars for 3–5 days gave feldspars with good Xray patterns but which resulted in very scattered calorimetric data, presumably because of uncontrollable variations in structural state and the presence of vapor-solution products in the charges. The scatter was always in the direction of increased enthalpy of solution (Newton, personal communication), as would be expected of partially ordered feldspars.

Eberhard (1967) hydrothermally annealed synthetic plagioclase at temperatures from 500-800° C at one kbar, and in the range An<sub>0</sub>-An<sub>60</sub> observed a range of intermediate degrees of order based on the  $2\theta(131)-2\theta(1\overline{3}1)$  indicator of structural state (see, for example, Ribbe, 1975). MacKenzie (1957) had earlier reported partial ordering of pure albite and Martin (1969), crystallization of highly ordered albite. Orville (1972) reports structural state changes for Ab100 and Ab70 at 700° C and 2 kbar for 1000 hours much like those observed by Eberhard and by MacKenzie for albite, and states that this structural state, as measured by  $\Delta 2\theta(131-131)$ , is less than a quarter of the way from high albite toward the low albite structure, and values of  $\Delta 2\theta (131-131)$  for experiments of 6 days have nearly reached the constant limiting value characteristic of the equilibrium structural state at 700° C. Wenk (1978) heated a volcanic plagioclase (An<sub>66</sub>) with diffuse e-reflections at 870° C and 2 kbar for 50 days, and observed ordering of the intermediate superstructure and sharpening of the satellite reflections. All these indications of increased order, even by treatment at 1-2 kbar indicate the likelihood of a significant effect on the breakdown reaction as compared to high structural state plagioclases.

The effect of introducing partial order in the plagioclases in a model calculation seems fruitless without prior knowledge of the ordering scheme, its degree and its variation with composition. Although the entropy difference could be more than adequate in a quantitative sense to account for the disagreement between the observed and calculated curves, it could well go in the wrong direction, for increasing the degree of order in the plagioclase of the calculated curve would tend to stabilize plagioclase relative to zoisite, and thus drop it further in temperature, assuming the ordered plagioclase is more stable at this temperature than the disordered plagioclase. Under any circumstances, enthalpy of solution data on plagioclases treated at the pressures and temperatures of the experimental curves are needed, and such a program is planned as a continuation of the present work. The observation of enhanced reaction rates at H<sub>2</sub>O pressures of 8-10 kbar as compared to 2 kbar makes it appear likely that Al-Si ordering may also be enhanced, and this has been observed in KAlSi<sub>3</sub>O<sub>8</sub> (Goldsmith, unpublished data). Data on enthalpy of solution of variously treated plagioclase will supply more quantitative information than empirical evidence provided by lattice constants or indicators such as  $\Delta 2\theta(131 -$ 131).

In the absence of any information on the structural state of the feldspars of this investigation, or of the effect of structural state on the zoisite-producing reaction I would like to speculate on a possible explanation for the flat region of the plagioclase breakdown curves. Simply stated it could be the result of segregation of anorthite in the structure of the plagioclases at a scale such that  $H_2O$  at elevated pressures and temperatures could react with the anorthite component as if it were in a separated phase. Such behavior would require a substantial amount of organization and ordering in the synthetic plagioclases *during the course of the experiments*.

A number of models have been proposed to explain the structural complexities of the intermediate plagioclases and a combination of X-ray diffraction and electron microscopy have recently made inroads and given insights into the variegated nature of plagioclases. The simplest scheme by which a plagioclase can be "ordered" is to have interleaved regions of pure anorthite and pure ordered albite; only the "walls" or connecting regions would not have complete Al-Si order. This concept in a sense goes back to the early days of feldspar structural work by Taylor (Chao and Taylor, 1940), and has been rethought and refined by many feldspar specialists over the years (see discussion and review by Smith and Ribbe, 1969; Smith, 1974). More recently transmission electron microscopy (TEM), including direct lattice imaging in intermediate plagioclases has revealed antiphase boundaries (APB's) delineating anorthite or anorthite-like bands, and in labradorites alternation of albite-like and anorthitelike bands (see for example Kitamura and Morimoto, 1977; Nakajima et al., 1977).

If plagioclases order or segregate Al and Si and Na and Ca into detectable compositional and structural units of anorthite and albite, they obviously display chemical heterogeneity, even if on a rather fine scale. Segregation into discrete (incoherent or "unmixed") phases is not essential to define the anorthite portion of the structure. The zoisite-forming behavior in the range An<sub>40</sub>-An<sub>100</sub> is as if the plagioclase were a mechanical mixture of those two end-members. This is intuitively in accord with the structure of intermediate plagioclases as revealed by TEM observations in which segregated units occur. Although the APB's seen with TEM indicate coherency of the structure, the protons or hydroxide ions that become intimate with the plagioclase at elevated temperatures and pressures can hardly be expected to have been educated in the niceties of coherency versus incoherency. Runs PL190a and 190b (Table 5), previously considered, may provide additional evidence for the view that solid solutions between  $An_{40}$  and  $An_{100}$  are not stable in the neighborhood of 700° C, irrespective of their stability relative to zoisite. The mixture of  $An_{15}$  and  $An_{42}$ reacted at 700° C and 9 kbar in 719 hours more than half of the way to a homogeneous plagioclase. There was no observable reaction in the mixture of  $An_{42}$  and  $An_{100}$ . Failure to react proves nothing, but the difference in behavior is suggestive of possible instability.

If the interpretation of separate domains is correct, the phase relations could be as drawn in Figure 10. The simple schematic solvus of Figure 10a



Fig. 10. (a) Simple schematic solvus in plagioclase feldspars indicating inherent instability of solid solutions; unmixing not realized because of kinetic barriers. (b) Solvus transected by zoisite-producing reaction in the presence of water at an appropriate pressure. The upper (dashed) portions of the solvus, as in (a), generally not observed to develop separate phases for kinetic reasons. This schematic portion of the diagram is shown as a more complex region by Smith (1972, 1974). The dotted lines are metastable extensions of the solvus cut-off by the zoisite-forming reaction, which is shown quantitatively in Figs. 2–4.

would be transected by the zoisite-producing reaction in the presence of water at an appropriate pressure, as in Figure 10b, with an upper dashed solvus region that, for kinetic reasons, is not observed to develop separate phases. An attempt to resolve this problem in the region above the horizontal curves of Figures 2–4 is currently underway. The initial depression of the curve at the An side of the diagram, required by Raoult's Law, appears to be too small to have been detected.

The data of Tables 1–4 and Figures 2–5 can be used to illustrate the P-T behavior of the plagioclases in terms of breakdown to zoisite + kyanite + quartz. Figure 11 is a projection on the P-T plane of the breakdown curves of An<sub>100</sub> and An<sub>30</sub>, An<sub>20</sub> and An<sub>10</sub>, the compositions selected from the curves of Figures 2–5. The An<sub>100</sub> curve and its associated boundary curves delimiting the field of partial melt on the An-H<sub>2</sub>O join are taken from Figure 1.

Plagioclases from approximately  $An_{40}$  to  $An_{100}$ under the conditions of this investigation all react with water to produce zoisite + kyanite + quartz along the  $An_{100} P-T$  curve. The space between the  $An_{30}$  and  $An_{100}$  curves thus represents the region in which plagioclases betwen  $An_{30}$  and  $An_{40}$  become unstable. The greater stability of the more sodic plagioclases is illustrated in Figure 11. Although the lower temperature reaction or reactions are unknown, if margarite were to replace kyanite the appropriate CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> isopleths of plagioclase would be deflected to higher temperatures, decreasing the stability of plagioclase relative to zoisite.

### Plagioclase stability and metamorphic rocks

The relative importance of reactions involving plagioclase in a heterogeneous (chemical) sense in metamorphism as opposed to reactions controlled chiefly by internal or structural ("homogeneous") properties of the plagioclases has been reviewed from field and laboratory viewpoints by Goldsmith (1982). Certainly the presence or absence of a feldspar, or the range of compositions present, can be related to the bulk composition (including volatiles) as well as P and T in the system. On the other hand, the structural state of a particular plagioclase may also influence its stability and therefore its persistence. These factors apply to pre-existing igneous or earlier metamorphic plagioclases and perhaps to a lesser extent to metamorphic plagioclase produced by reaction, dependent upon whether the plagioclase crystallized metastably in a hightemperature state or in equilibrium with the environment (Christie, 1962; Rutland, 1962).

Wenk and Wenk (1977) presented a tentative diagram showing variation of plagioclase composition as a function of metamorphic grade and rock composition based on examination of plagioclase from a number of localities. A slightly modified version presented by Wenk (1979a) is reproduced as Figure 12. The temperature scale (metamorphic grade) is based on Wenk's estimates from the Tertiary metamorphic region in the Central Alps.



Fig. 11. CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> isopleths of plagioclase stability as function of  $P_{H_{2O}}$  and T. The curve labeled An<sub>100</sub> is taken from Fig. 1, and represents the reaction  $4An + V \rightleftharpoons 2ZO + Ky + Qz +$ V. The region labeled Zo + Ky + V + L is the field of partial melt for the composition An<sub>100</sub>. The solid circles are points arbitrarily taken at An<sub>10</sub>, An<sub>20</sub>, and An<sub>30</sub> from the isobaric boundary curves of Figs. 2–5 at 8, 9, 10, and 10.8 kbar. The region to the right of the isopleths represents conditions of stability of plagioclase more calcic than that of the appropriate isopleth; the region to the left, of breakdown of that composition to zoisite + kyanite + quartz.



Fig. 12. Diagram from Wenk (1979) indicating structural complexities of plagioclases from a variety of metamorphic localities, as revealed by single-crystal X-ray diffraction analysis, plotted as a hypothetical temperature–composition diagram. Isolines show the variation of wave length of the intermediate plagioclase superstructure, as observed from e-satellite reflections. The ordinate represents metamorphic grade, or temperature. Wenk's analysis from field data indicates a temperature range of 400–600° C for region C, 600–800° C for region B, and 700–800° C for A. The region of interest for this investigation is labeled "no metamorphic plagioclase", being analogous to the area under the curves of Figs. 2–4.

Wenk notes that for each composition, except pure albite, there is a minimum temperature below which no metamorphic plagioclase has been found. The configuration of the area with no metamorphic plagioclase in Figure 12, particularly the almost flat region from approximately An<sub>35</sub> to An<sub>100</sub>, is very much like that outlined by the plagioclase breakdown curves. Figure 2 at 8 kbar would match the upper temperature limit shown in Figure 12, and reasonably lower metamorphic pressures would produce a good temperature match. The association of An<sub>37-42</sub> with An<sub>87-92</sub> observed by Spear (1977, 1980), where the systematic partitioning of Na and Ca between hornblende and plagioclase is evidence for an equilibrium association, is compatible with the results of this investigation and with the immiscibility gap illustrated by Smith (1974, p. 6).

The complexity of the intermediate plagioclases as illustrated by Figure 12 covers most of the compositional range. In this and other representations (Smith, 1974, p. 6; McConnell, 1974a) a variety of phenomena are described; Huttenlocher and Bøggild intergrowths and other reported two-plagioclase or multiphase assemblages producing clusters of solvus-like inverted festoons, complex X-ray diffraction pattterns including e-satellite reflections associated with superstructures of various wavelengths, complex TEM patterns showing APB's, all these things with confusing differences as reported by various investigators. Nothing approaching a generally agreed-upon (equilibrium) phase diagram is at hand. Compositional and structural equilibration seems essentially impossible even on a geological time scale in the absence of a flux such as H<sub>2</sub>O that aids in breaking strong Al-O and Si-O bonds and fosters diffusion and structural rearrangement. It is generally appreciated that the complexity and confusion is due to metastability (Smith and Ribbe, 1969). There are no clearly defined solvi in the plagioclases, and no well-developed unmixed textures akin to the perthites. The alkali feldspars show relatively clear-cut exsolution for two reasons: (a) Al-Si rearrangement in the network is unnecessary, and (b) both end member feldspars are stable in the presence of water at "metamorphic" temperatures and pressures. The Al-Si diffusional barrier in plagioclase is significant, and anorthite is not stable in the presence of water at the more elevated P and T ranges where unmixing would be kinetically favored.

Smith and Ribbe (1969), Smith (1972, 1974, 1975), and McConnell (1974a, 1978) have suggested that the variously ordered intermediate plagioclase states are metastable with respect to ordered albite and anorthite which are not observed at low temperatures only because of kinetic barriers. Kinetic barriers, important as they are, are not the whole story. The equilibrium unmixing and/or ordering states in plagioclase are not observed in metamorphic rocks beause the processes are too slow in the absence of water, and in the presence of water zoisite is formed in the place of calcic plagioclase.

Figures 2–5 and Figure 11 indicate that, even neglecting a peristerite gap, extrapolation of the curves representing the breakdown reaction (to zoisite + kyanite + quartz) produces rather sodic plagioclases, although the Ca-content would be increased at lower water pressures. No specific experimental attempt was made to observe the phenomena in the presumed region of the peristerite gap, but it is not at all unlikely that the lowertemperature portions of the curves of Figures 2–5 are metastable extensions into the region of the gap. At 10.8 kbar the plagioclase in equilibrium with zoisite at 400° C is approximately  $An_6$ ; at 8 kbar it is



Fig. 13. A hypothetical representation of plagioclase stability relations, at 6 kbar, with respect to the peristerite gap. The boundary curve separating the field of plagioclases from plagioclase + zoisite (with horizontal portion at 520° C) is extrapolated from Figs. 2-4. The representation of the peristerite gap is arbitrary, partially based on the work of Crawford (1966), and may extend to somewhat higher temperatures. The region above the 6 kbar boundary curve is a presumed region of mixedlayer plagioclases where ordered layers or domains of anorthite are interposed with domains of disordered, sodic plagioclase. The region just below the boundary represents one of equilibrium of plagioclases from ~An24 to An40 with zoisite (+ kyanite and quartz). At the intersection of the boundary curve with the calcic limb of the peristerite gap the boundary curve is cut-off, and a region of ordered albite (with but little Ca) in equilibrium with zoisite is produced. A second (or higher) order phase transition from ordered (low) to disordered (high) albite is presumed. The inset diagram represents the peristerite gap as the result of a first-order phase change in albite. This diagram indicates how the gap is encroached upon with increasing pressure. It may be even less evident than shown here at 6 kbar.

approximately  $An_{14}$ . In the New Zealand rocks studied by Crawford (1966) the first appearance of two plagioclases was at the almandine isograd, whereas the first appearance of two plagioclases in the Vermont rocks is below this isograd. Crawford (1966) located the crest of the peristerite solvus between the almandine and staurolite isograds in the Vermont rocks, and suggested a temperature of 450–500° C. Wenk and Wenk (1977) suggested that the peristerite gap closes in the staurolite zone, possibly 50–100° C higher than the crest suggested by Crawford. At 8–10 kbar the sodic portion of the plagioclase breakdown curves clearly transgresses a large portion of the presumed peristerite region.

Figure 13 is a representation of plagioclase– $H_2O$  relations at 6 kbar, in part based on extrapolation of the plagioclase +  $H_2O \rightleftharpoons Zo + Ky + Qz$  breakdown relations, and in part a representation of the peristerite gap as a solvus modeled largely after Crawford (1966). Also indicated is a possible representation of the gap as a "binary loop" produced by first-order phase relations between high and low albite. If Crawford's estimate of the solvus crest at 450–500° is correct, and the generally accepted limit of the oligoclase limb at  $\sim An_{24}$  is accepted, there is a limited range of temperature in which 2 phases can be in equilibrium: it is 50° C or less at 6 kbar. If the right hand limb is steeper than indicated, the temperature interval in the gap is increased, but the composition of the oligoclase in the limb cannot reach An<sub>24</sub>. At 8 kbar the breakdown curve is at approximately 540° C at An<sub>24</sub>, and if the gap is as indicated in Figure 13, the temperature range is reduced essentially to zero. If the oligoclase limb is steepened so that say, at 400° or lower it reaches An<sub>24</sub>,  $P_{H,O}$  would have to be significantly less than 6 kbar to avoid cutting off the limb by the breakdown curve. Crawford's text and diagrams clearly express the effect of  $P_{\rm H,O}$  on the intersection of the oligoclase limb of the solvus with a presumed calcium mineral-plagioclase equilibrium curve, and Orville (1974) also mentioned the likelihood of this phenomenon.

It is thus possible that the plagioclase breakdown relations effectively "smother" or engulf the peristerite gap at 8 kbar and above. If a binary loop is involved, the somewhat higher temperature of the albite order-disorder relations would permit a larger temperature range of coexistence of two plagioclases. The relative rarity of peristerites may well be related to this effect. At lower pressures where the gap might be more in evidence, the kinetics of phase separation, already hampered by low temperatures, would not have the pressure-enhanced reaction advantage. At higher pressure the gap may be effectively obliterated. The effect of  $P_{\text{total}}$  on the configuration of the gap itself, whether a solvus or an inversion loop, should be very small, and can be neglected for the purposes of this discussion. Extrapolation of the present data would indicate that peristerites or oligoclase in association with albite might not be found in metamorphic rocks crystallized at pressures above 6–7 kbar. If the crest of the solvus is less than 500° C, and if a spinodal that is significantly narrower than the presumed gap is necessary for the process to take place, plagioclase breakdown will effectively limit phase separation at even lower pressures.

An indication of the effect of pressure on the discontinuous jump from albite to oligoclase is shown in the work of Laird (1980, 1981), who found that in mafic schists containing epidote from Vermont the discontinuity takes place in the biotite zone (or even lower grades) in low-pressure sam-

ples, while it occurs in the garnet zone in mediumpressure schists. In high-pressure mafic schists (Laird and Albee, 1981) containing sodic amphibole and omphacite, the *P* and *T* estimates are  $9\pm 2$  kbar and  $450^{\circ}\pm 100^{\circ}$  C, and the plagioclase is albite,  $An_{0.2}$ to  $An_{1.}$ 

It is generally assumed in the literature that the peristerite gap represents an equilibrium feature. Viswanathan (1973) doubts that peristerites are two phases, and considers them modulated structures, not unlike intermediate plagioclases. The development of two resolvable plagioclases in the range  $An_0-An_{25}$  in some rocks is a prograde and not an unmixing phenomenon, and could represent a metastable association. The field relations of rocks containing peristerite are not well defined, and the phase relations related to peristerite phenomena remain highly speculative (Carpenter, 1981).

Not all natural plagioclases of the appropriate composition unmix (Sen, 1963). In the absence of phase separation for whatever reason, the breakdown curves, which dip more steeply with decreasing temperature in the sodic compositional range have a configuration and location in reasonably good agreement with petrologic observation. Miyashiro (1973, p. 249) notes that the reaction of sodic plagioclase with epidote should be influenced by T,  $P_{\rm s}$ ,  $P_{\rm H,O}$ ,  $P_{\rm O_2}$  and by the minerals occurring in association with the albite and epidote, and that the rate of compositional variation of plagioclase with rising temperature should differ in different metamorphic terranes. He claims that petrographic experience, however, has shown that the rate of compositional variation is usually gentle up to 30 percent An, above which it becomes very fast. For this reason (Ramberg, 1952), a plagioclase composition of 30 percent An in equilibrium with epidote was taken as the boundary between the epidoteamphibolite and amphibolite facies.

In addition to the composition-temperature behavior, Figure 11 indicates that plagioclase composition is quite sensitive to  $P_{\rm H_2O}$ . Again aside from peristerite complications metamorphic pressure must be evaluated if temperature estimates are to have any meaning. Miyashiro (1973) notes that at the change of calcic amphiboles in metabasites from actinolite to hornblende, the composition of metabasite plagioclase is about 5 percent An in the high pressure terrane of the Sanbagawa belt and the Barrovian region of the Scottish Highlands, but is 20–30 percent An in the low-pressure regional meta-

morphic terranes in Japan. Under low-pressure contact metamorphic conditions, Miyashiro indicates that labradorite may be present. Miyashiro recognizes that his amphibole reference point does not represent a definite temperature, but that the relations described suggest the possibility that the formation of a more calcic plagioclase is promoted by lower rock pressure. At 10 kbar and 400° C Figure 4 indicates a plagioclase composition of  $\sim An_7$ . At the extrapolated value for 6 kbar (Fig. 13), it is  $\sim An_{20}$ . At pressures not much below 6 kbar a value of  $An_{25-30}$  is not unreasonable.

Carmichael (1978) considers a number of diagnostic mineral assemblages in pelitic schists that define a series of "bathograds" that are temperature independent. Five invariant points within the system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO-MgO-Na<sub>2</sub>O-K<sub>2</sub>O-H<sub>2</sub>O permit the ordering of relative pressures in metamorphic terranes. Plagioclase is not used in the reactions, but Carmichael notes that CaO, as the most important "impurity" component could change the equilibrium pressures of two of the invariant points. He suggests that the composition of plagioclase in rocks be routinely determined so as to be able to evaluate the effect of CaO on the bathograd determination. I would suggest that the composition might provide an additional index or check on the bathograd determination considering the pressurecomposition behavior of the plagioclase if in equilibrium with epidote or zoisite.

No consideration has been given to the effect of ferric iron on the plagioclase-zoisite relations. Ramberg (1949) noted that increasing the Fe<sup>3+</sup>/Al ratio will displace the equilibrium toward epidote inasmuch as epidote incorporates Fe<sup>3+</sup> in its structure. Strens (1963), Holdaway (1966, 1972) and Liou (1973) report experimental work and Miyashiro and Seki (1958) a field study indicating that increasing  $Fe^{3+}$  stabilizes epidote with respect to zoisite and clinozoisite. A thermodynamic analysis by Bird and Helgeson (1981) shows a dramatic increase of epidote relative to plagioclase and an aqueous phase with increasing Fe<sup>3+</sup> substitution. Experimental work on the system Ab-An-H<sub>2</sub>O with Fe<sup>3+</sup> as an added component becomes more complicated and an additional mineral containing ferric iron is necessary as a buffer. In nature at least several minerals can and probably do play this role; an amphibole for example can contain several possible buffering species, such as Fe, Al, and Ca. The use of an amphibole in experimental systems makes for difficulties with reaction and equilibrium, however, and something as simple as magnetite may be necessary.

It is likely that substitution of  $Fe^{3+}$  in epidote enlarges its field of stability relative to the essentially Fe-free plagioclase. This is tantamount to raising the isobaric curves of Figures 2–4 and Figure 13. Doing so would produce more sodic feldspars in equilibrium with epidote in the absence of a peristerite gap, and would also further encroach on the region of the gap, acting in the same way as does an increase in H<sub>2</sub>O pressure. Examination of field data in the light of the observed effect of  $P_{H_2O}$  and ferric iron content on plagioclase compositions and phenomena related to "peristeritic reactions" might be fruitful.

Although investigation of melting phenomena has been restricted to a limited portion of the solidus at 10.8 kbar, it is apparent that the zoisite-forming reaction can produce a relatively sodic melt from rather calcic plagioclases at temperatures far below those of the plagioclase melting loop. In the region above the dashed solidus of Figure 5, melts more sodic than  $An_{30}$  are formed at little over 700° C.

# Acknowledgments

This research was supported by NSF grant EAR 7813675 (Geochemistry Program). I am indebted to many friends and colleagues for aid and encouragement over a long period of time. Discussions with Hans Ramberg, beginning in 1947, acted as the impetus for hydrothermal experiments with plagioclase in the late 1940's and early 1950's, none of which produced zoisite. N. L. Bowen and J. F. Schairer kindly supplied me with synthetic plagioclases and some glasses, later supplemented by several samples donated by H. S. Yoder from the Geophysical Laboratory supply. Robert C. Newton provided advice and stimulation, and some of the plagioclases he crystallized for thermochemical work were used in this study. I am also indebted to Mark D. Barton, Dexter Perkins III, and J. V. Smith for thoughtful discussions, to H. R. Wenk and Ian Steele for natural plagioclases. Ian Steele supplied electron microprobe data on these and a number of synthetic crystals and glasses, and Ian D. Hutcheon kindly examined several run products with the TEM. I am continuously indebted to William Moloznik, toolmaker, who keeps the high-pressure laboratory operational, and to Cassandra Spooner, whose translation of my miserable script into typescript requires extraordinary skill and patience.

The manuscript was significantly improved after critical reading by R. C. Newton, Dexter Perkins III, Mark Barton, and David M. Jenkins.

#### References

 Althaus, E. (1967) The triple point andalusite-sillimanite-kyanite. Contributions to Mineralogy and Petrology, 16, 29-44.
 Bird, D. K. and Helgeson, H. C. (1981) Chemical interaction of aqueous solutions with epidote-feldspar mineral assemblages in geologic systems. II. Equilibrium constraints in metamorphic/geothermal processes. American Journal of Science, 281, 576–614.

- Boettcher, A. L. (1970) The system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O at high pressures and temperatures. Journal of Petrology, 11, 337-379.
- Boettcher, A. L. and Wyllie, P. J. (1967) Hydrothermal melting curves in silicate-water systems at pressures greater than 10 kilobars. Nature, 216, 572-573.
- Boettcher, A. L. and Wyllie, P. J. (1969) Phase relationships in the system  $NaAlSiO_4$ -SiO<sub>2</sub>-H<sub>2</sub>O to 35 kilobars pressure. American Journal of Science, 267, 875-909.
- Carmichael, D. M. (1978) Metamorphic bathozones and bathograds: a measure of the depth of post-metamorphic uplift and erosion on the regional scale. American Journal of Science, 278, 769–797.
- Carpenter, M. A. (1981) A "conditional spinodal" within the peristerite miscibility gap of plagioclase feldspars. American Mineralogist, 66, 553-560.
- Chao, S. H. and Taylor, W. H. (1940) Isomorphous replacement and superlattice structures in the plagioclase felspars. Royal Society (London) Proceedings, series A, 175, 76–87.
- Chatterjee, N. D. (1971) Preliminary results on the synthesis and upper stability limit of margarite. Naturwissenschaften, 58, 147.
- Chatterjee, N. D. (1976) Margarite stability and compatibility relations in the system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O as a pressuretemperature indicator. American Mineralogist, 61, 699–709.
- Christie, O. H. J. Feldspar structure and the equilibrium between plagioclase and epidote (discussion). American Journal of Science, 260, 149–153.
- Clayton, R. N., Goldsmith, J. R., Karel, K. J., Mayeda, T. K. and Newton, R. C. (1975) Limits on the effect of pressure on isotopic fractionation. Geochimica et Cosmochimica Acta, 39, 1197–1201.
- Crawford, M. L. (1966) Composition of plagioclase and associated minerals in some schists from Vermont, U.S.A., and South Westland, New Zealand, with inferences about the peristerite solvus. Contributions to Mineralogy and Petrology, 13, 269– 294.
- Eberhard, E. (1967) Zur Synthese der Plagioklase. Schweizerische Mineralogische und Petrographische Mitteilungen, 47, 385-398.
- Ehlers, E. G. (1953) An investigation of the stability relations of the Al-Fe members of the epidote group. Journal of Geology, 61, 231-251.
- Franz, G. and Althaus, E. (1977) The stability relations of the paragenesis paragonite-zoisite-quartz. Neues Jahrbuch Mineralogie Abhandlungen, 130, 159-167.
- Fyfe, W. S. (1960) Stability of epidote minerals. Nature, 187, 497-498.
- Goldsmith, J. R. (1952) Diffusion in plagioclase feldspars. Journal of Geology, 60, 288–291.
- Goldsmith, J. R. (1976) Scapolites, granulites, and volatiles in the lower crust. Bulletin of the Geological Society of America, 87, 161–168.
- Goldsmith, J. R. (1980) The melting and breakdown reactions of anorthite at high pressures and temperatures. American Mineralogist, 65, 272–284.
- Goldsmith, J. R. (1981) The join CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-H<sub>2</sub>O (anorthite-

water) at elevated pressures and temperatures. American Mineralogist 66, 1183-1188.

- Goldsmith, J. R. (1982) Review of the behavior of plagioclase under metamorphic conditions. American Mineralogist, 67, 643-652.
- Goldsmith, J. R. and Newton, R. C. (1974) An experimental determination of the alkali feldspar solvus. In W. W. MacKenzie and J. Zussman, Eds., The Feldspars, p. 337–359. Manchester University Press, Manchester
- Holdaway, M. J. (1966) Hydrothermal stability of clinozoisite plus quartz. American Journal of Science, 264, 643–667.
- Holdaway, M. J. (1972) Thermal stability of Al–Fe epidote as a function of  $f_{O_2}$  and Fe content. Contributions to Mineralogy and Petrology, 37, 307–340.
- Johannes, W. (1978) Melting of plagioclase in the system Ab-An-H<sub>2</sub>O and Qz-Ab-An-H<sub>2</sub>O at  $P_{H_2O} = 5$  Kbars, an equilibrium problem. Contributions to Mineralogy and Petrology, 66, 295-303.
- Johannes, W., Bell, P. M., Mao, H. K., Boettcher, A. L., Chipman, D. W., Hays, J. F., Newton, R. C. and Seifert, F. (1971) An interlaboratory comparison of piston-cylinder pressure calibration using the albite-breakdown reaction. Contributions to Mineralogy and Petrology, 32, 4–38.
- Kerrick, D. M. and Darken, L. S. (1975) Statistical thermodynamic models for ideal oxide and silicate solid solutions with application to plagioclase. Geochimica et Cosmochimica Acta, 39, 1431–1442.
- Kitamura, M. and Morimoto, N. (1977) The superstructure of plagioclase feldspars. A modulated coherent structure of the eplagioclase. Physics and Chemistry of Minerals, 1, 199–212.
- Laird, J. (1980) Phase equilibria in mafic schist from Vermont. Journal of Petrology, 21, 1–37.
- Laird, J. (1981) Pressure, temperature, and time indicators in mafic schist: their application to reconstructing the polymetamorphic history of Vermont. American Journal of Science, 281, 127–175.
- Laird, J. and Albee, A. L. (1981) High-pressure metamorphism in mafic schist from northern Vermont. American Journal of Science, 281, 97–126.
- Liou, J. G. (1973) Synthesis and stability relations of epidote, Ca<sub>2</sub>Al<sub>2</sub>FeSi<sub>3</sub>O<sub>12</sub>(OH). Journal of Petrology, 14, 381–413.
- MacKenzie, W. S. (1957) The crystalline modifications of NaAlSi<sub>3</sub>O<sub>8</sub>. American Journal of Science, 255, 481–516.
- Martin, R. F. (1969) The hydrothermal synthesis of low albite. Contributions to Mineralogy and Petrology, 23, 323-339.
- Matthews, A., Goldsmith, J. R. and Clayton, R. N. (1981) Oxygen isotope fractionation between zoisite and water. Abstract, European Colloquium on Geochronology, Cosmochronology, and Isotope Geology VII, Jerusalem.
- McConnell, J. D. C. (1974) Analysis of the time-temperaturetransformation behavior of the plagioclase feldspars. In W. S. MacKenzie and J. Zussman, Eds., The Feldspars, p. 460-477. Manchester University Press, Manchester, England.
- McConnell, J. D. C. (1978) The intermediate plagioclase feldspars: an example of a structural resonance. Zeitschrist für Kristallographie, 147, 45–62.
- Merrin, S. (1962) Experimental investigation of epidote paragenesis. Ph.D. Thesis, Pennsylvania State University.
- Miyashiro, A. (1973) Metamorphism and Metamorphic Belts. John Wiley and Sons, New York.

Miyashiro, A. and Seki, Y. (1958) Enlargement of the composi-

tion field of epidote and piemontite with rising temperature. American Journal of Science, 256, 423–430.

- Nakajima, Y., Morimoto, N. and Kitamura, M. (1977) The superstructure of plagioclase feldspars. Electron microscopic study of anorthite and labradorite. Physics and Chemistry of Minerals, 1, 213–225.
- Newton, R. C. (1966) Some calc-silicate equilibrium reactions. American Journal of Science, 264, 204–222.
- Newton, R. C. (1969) Some high-pressure hydrothermal experiments on severely ground kyanite and sillimanite. American Journal of Science, 267, 278–284.
- Newton, R. C., Charlu, T. V. and Kleppa, O. J. (1980) Thermochemistry of the high structural state plagioclases. Geochimica et Cosmochimica Acta, 44, 933–941.
- Newton, R. C. and Kennedy, G. C. (1963) Some equilibrium reactions in the join CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-H<sub>2</sub>O. Journal of Geophysical Research, 68, 2967–2983.
- Newton, R. C. and Wood, B. J. (1980) Volume behavior of silicate solid solutions. American Mineralogist, 6, 733-745.
- Noble, D. C. (1962) Plagioclase unmixing and the lower boundary of the amphibolite facies. Journal of Geology, 70, 234–240.
- Nord, G. L., Jr., Hammarstrom, J. and Zen, E-an (1978) Zoned plagioclase and peristerite formation in phyllites from southwestern Massachusetts. American Mineralogist, 63, 947–955.
- Orville, P. M. (1972) Plagioclase cation exchange equilibria with aqueous chloride solution: results at 700° C and 2000 bars in the presence of quartz. American Journal of Science, 272, 234–272.
- Orville, P. M. (1974) The "peristerite gap" as an equilibrium between ordered albite and disordered plagioclase solid solution. Bulletin de la Société francaise de Minéralogie et de Cristallographie, 97, 386–392.
- Parsons, I. (1969) Subsolidus crystallization behaviour in the system KAlSi<sub>3</sub>O<sub>8</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O. Mineralogical Magazine, 37, 173-180.
- Perkins, D. III, Westrum, E. F. and Essene, E. J. (1980) The thermodynamic properties and phase relations of some minerals in the system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Geochimica et Cosmochimica Acta, 44, 61-84.
- Ramberg, H. (1949) The facies classification of rocks: a clue to the origin of quartzo-feldspathic massifs and veins. Journal of Geology, 57, 18–54.
- Ramberg, H. (1952) The Origin of Metamorphic and Metasomatic Rocks. University of Chicago Press, Chicago, Illinois.
- Ribbe, P. H. (1975) Optical properties and lattice parameters of plagioclase feldspars. In P. H. Ribbe, Ed., Feldspar Mineralogy, Mineralogical Society of America Short Course Notes, R-53-72.
- Rutland, R. W. R. (1962) Feldspar structure and the equilibrium between plagioclase and epidote: a reply. American Journal of Science, 260, 153–157.
- Sen, S. K. (1963) Some consequences of ordering and unmixing in sodic plagioclases on epidote-plagioclase equilibrium in regionally metamorphosed rocks. American Journal of Science, 261, 786-789.
- Smith, J. V. (1972) Critical review of synthesis and occurrence of plagioclase feldspars and a possible phase diagram. Journal of Geology, 80, 505–525.
- Smith, J. V. (1974) Feldspar Minerals, Volume I. Crystal Structure and Physical Properties. Springer-Verlag, New York.
- Smith, J. V. (1975) Phase equilibria of plagioclase. In P. H.

Ribbe, Ed., Feldspar Mineralogy, Mineralogical Society of America Short Course Notes, Chapter 7.

- Smith, J. V. and Ribbe, P. H. (1969) Atomic movements in plagioclase feldspars: kinetic interpretation. Contributions to Mineralogy and Petrology, 21, 157–202.
- Spear, F. S. (1977) Evidence for a miscibility gap in plagioclase feldspar in the composition range An<sub>39</sub>–An<sub>88</sub>. Carnegie Institution of Washington Yearbook, 76, 619–621.
- Spear, F. S. (1980) NaSi *⇒* CaAl exchange equilibrium between plagioclase and amphibole. Contributions to Mineralogy and Petrology, 72, 33–41.
- Stewart, D. B. (1967) Four-phase curve in the system  $CaAl_2Si_2O_8$ -SiO<sub>2</sub>-H<sub>2</sub>O between 1 and 10 kilobars. Schweizerische Mineralogische und Petrographische Mitteilungen, 47, 35-59.
- Storre, B. and Nitsch, K.-H. (1974) Zur Stabilität von Margarit im System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Contributions to Mineralogy and Petrology, 43, 1-24.
- Strens, R. G. J. (1965) Stability and relations of the Al-Fe epidotes. Mineralogical Magazine, 35, 464-475.
- Velde, B. (1971) The stability and natural occurrence of margarite. Mineralogical Magazine, 38, 317–323.

- Viswanathan, K. (1971) A new X-ray method to determine the anorthite content and structural state of plagioclase. Contributions to Mineralogy and Petrology, 30, 332–335.
- Viswanathan, K. (1973) Kationenaustausch von Peristeriten mit Beobachtungen an Pulver-und Einkristallaufnahmen. Contributions to Mineralogy and Petrology, 41, 145–150.
- Wenk, E. and Wenk, H.-R. (1977) An-variation and intergrowths of plagioclases in banded metamorphic rocks from Val Carecchio (Central Alps). Schweizerische Mineralogische und Petrographische Mitteilungen, 57, 41–57.
- Wenk, H.-R. (1969) Annealing of oligoclase at high pressure. American Mineralogist, 54, 95-100.
- Wenk, H.-R. (1978) Ordering of the intermediate plagioclase structure during heating. American Mineralogist, 63, 132–135.
- Wenk, H.-R. (1979) Superstructure variation in metamorphic plagioclase. American Mineralogist, 64, 71–76.

Manuscript received, September 16, 1981; accepted for publication, March 9, 1982.