The influence of metastability on reaction kinetics involving zoisite formation from anorthite at elevated pressures and temperatures

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Abstract

The mechanisms and kinetics of the breakdown reactions of anorthite to zoisite, clinzoisite, and other products in unseeded runs have been studied at 400–700°C and 10–20 kbar, using X-ray diffractometry and scanning electron microscopy. Most of the runs were made at 10 kbar, and at this pressure, the equilibrium reactions in the anorthite-water portion of the CaO–Al₂O₃–SiO₂–H₂O system do not occur in the absence of stable reaction products, and are replaced by metastable reactions involving the formation of an aluminous mullite and zoisite and margarite:

At \( T > 675°C \):

\[ 12 \text{Anorthite} + 3 \text{H}_2\text{O} \rightleftharpoons 6 \text{zoisite} + \text{mullite} (\text{Al}_6\text{Si}_4\text{O}_{10}) + 5 \text{SiO}_2 (\text{aq}) \]  

(7a)

At \( T \leq 675°C \):

\[ 5 \text{Anorthite} + 2 \text{H}_2\text{O} \rightleftharpoons 2 \text{zoisite} + 1 \text{margarite} + 2 \text{quartz} \]  

(5)

At \( T \leq 500°C \) and at higher pressures, clinzoisite develops metastably at the expense of zoisite. The incoming of (5) at 675°C coincides with metastable projection of the \( P-T \) curve for the equilibrium reaction (5). All reactions involve solution-precipitation processes, with nucleation and growth of products appearing to initiate heterogeneously, but not epitaxially, on anorthite surfaces. Partially reacted anorthite grains show evidence of crystallographically controlled dissolution. The reaction rate increases from 400°C to 500°C, but decreases from 600°C to 700°C as the anorthite \( \rightleftharpoons \) zoisite boundary is approached. The experimental data favor the dissolution of anorthite as being the critical rate-determining process, and are consistent with the preservation of plagioclase in granulites.

Introduction

Experimental petrologists have long been familiar with the problems produced by metastable reactions in the investigation of phase-equilibrium boundaries. Even so, relatively little is known about the kinetics, mechanisms, and relation of the metastable reactions to the equilibrium reactions in the same system. The pioneering rate study of Greenwood (1963) on the dehydration of talc is a notable exception. The present study focuses on the metastable reactions accompanying breakdown of anorthite to zoisite, clinzoisite, and other phases at temperatures of 400–700°C and pressures of 10–20 kbar. Our aim is to determine the mechanisms and rate-determining factors of the reactions and the relationships that exist between the stable and metastable reactions in the system.

Figure 1 shows some of the experimentally determined phase relations in the system CaO–Al₂O₃–SiO₂–H₂O that are pertinent to the stability of anorthite and water at 400–800°C and 5–12 kbar. The three univariant boundaries emanating from the invariant point \( I_1 \) were determined experimentally by Goldsmith (1981), i.e.,

\[ \text{zoisite} + \text{kyanite} + \text{quartz} + \text{H}_2\text{O} \rightleftharpoons \text{liquid} \]  

(1)

\[ \text{anorthite} + \text{H}_2\text{O} \rightleftharpoons \text{liquid} \]  

(2)

\[ 4 \text{anorthite} + \text{H}_2\text{O} \rightleftharpoons 2 \text{zoisite} + \text{kyanite} + \text{quartz} \]  

(3)
The invariant point $I_2$ was determined from the intersection of (3) with the experimentally determined curve for the reaction (Nitsch et al., 1981):

$$\text{margarite} + \text{quartz} \rightleftharpoons \text{anorthite} + \text{kyanite} + \text{H}_2\text{O} \quad (4)$$

The two other curves emanating from $I_2$:

5 anorthite + 2 H$_2$O $\rightleftharpoons$ margarite  
+ 2 zoisite + 2 quartz \quad (5)

4 margarite + 3 quartz $\rightleftharpoons$ 5 kyanite  
+ 2 zoisite + 3 H$_2$O \quad (6),

have been calculated from a combination of the two experimental curves (3) and (4), with the entropy and volume data for margarite and zoisite from Perkins et al. (1980) and the remaining thermochemical values from Robie et al. (1978).

At 10 kbar, the pressure at which most of our runs were made, the equilibrium reactions that are encountered with decreasing temperature are: (3) at $T = 715^\circ$C and (6) at $T = 550^\circ$C (Fig. 1). Metastable equilibrium reactions that could be encountered at 10 kbar are given by linear extrapolations of the equilibrium curves for reactions (5) and (4); $\approx 680^\circ$ and $\approx 630^\circ$C, respectively (Fig. 1). The calculated diagram in the CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O system by Perkins et al. (1980) also suggests lower temperature equilibria at 10 kbar involving diaspore, pyrophyllite and lawsonite. However, none of these phases were definitely identified in this study, and because the equilibria are not constrained by experimentally determined phase relations, they are omitted from Figure 1.

Our experimental procedure was to perform two or more runs of approximately 4 hours and of approximately 4 hours and of approximately

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxides wt. %</th>
<th>Ions per 8 oxygens</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>43.34</td>
<td>2.034</td>
</tr>
<tr>
<td>Al</td>
<td>35.11</td>
<td>1.952</td>
</tr>
<tr>
<td>Ca</td>
<td>19.57</td>
<td>0.982</td>
</tr>
<tr>
<td>Mg</td>
<td>0.51</td>
<td>0.047</td>
</tr>
<tr>
<td>Total</td>
<td>98.29</td>
<td>5.015</td>
</tr>
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1. Analyst D. Snaarnek. Fe was not analysed. An analysis of the Miyake anorthite given in Allen and Fawcett (1982) has FeO$_2$ = 0.59 wt%.
18 hours to define the main kinetic features of the reactions. The yields, nature of product phases, and textural relations between products and reactants were analyzed using X-ray diffraction (XRD) and with a scanning electron microscope (SEM) equipped for energy dispersive analyses (EDS). Scanning electron microscopy is becoming an increasingly important method in the analysis of experimental run products (e.g., Haas, 1972; Katz and Matthews, 1977; Matthews, 1980; Allen and Fawcett, 1982; Matthews et al., 1983). The detailed study of Allen and Fawcett (1982) on reaction textures accompanying equilibria among the phases zoisite-anorthite-calcite-H₂O-CO₂ has provided an excellent basis for interpreting reaction textures observed in our study. With but a few exceptions, for comparative purposes, the breakdown reactions of anorthite were not seeded with reaction products.

**Experimental methods**

The reactant was a natural anorthite from Miyakejima, Japan. An electron-microprobe analysis (Table 1) shows a small albite component, which, however, does not affect the position of reaction (3) (Goldsmith, 1982). The anorthite crystals, ejected as volcanic "bombs", were separated from included olivine and lava coating by hand picking, heavy liquid and magnetic separation. The anorthite product was >99% pure by grain count. The sample was ground and sieved to produce a 62-88 µm size fraction, convenient for the SEM examination.

All runs were carried out in piston cylinder apparatus using NaCl pressure media. Prior to heating the assembly was pumped to a predetermined pressure; on heating the thermal expansion of salt brought the run to the desired pressure. The run charges consisted of 20 mg anorthite + deionized water, sealed in platinum capsules. The ratio of water to anorthite was varied but consisted of 20 mg anorthite + deionized water, sealed in platinum capsules. The ratio of water to anorthite was varied but consisted of 20 mg anorthite + deionized water, sealed in platinum capsules.

Upon completion of a run the capsule was weighed as a check for leakage, and the water removed by heating the pierced capsule in an oven at 110°C. Eight mg of the dried solid product was ground for two minutes under acetone in a small mortar and a smear mount of constant size (1 × 1 cm) was prepared for X-ray diffraction analysis. After scanning in the 20 range 20-45° to identify the phases, each sample was scanned twice from 25-35° at 0.5°/min, the mount reversed 180°, and again scanned twice. The four measurements were averaged to give the peak height ratio:

\[ X_{Zo} = \frac{Zo (213,600,511)}{(Zo (213,600,511) + An (004))} \]

Independent calibration has shown that this ratio of peak heights (located at 28.04° for anorthite and 33.2° for zoisite) varies approximately linearly with the molar ratio Zo/(An+Zo) (Matthews, unpublished results), and thus can be used to quantify the degree of reaction. In the few runs in which clinozoisite was crystallized, the peak at 30.9° (113) was substituted for the 33.2° reaction Product was >99% pure by grain count. The sample was ground and sieved to produce a 62-88 µm size fraction, convenient for the SEM examination. The SEM studies were made with a Leitz microscope equipped for energy dispersive analyses (EDS). Scanning electron microscopy is becoming an increasingly important method in the analysis of experimental run products (e.g., Haas, 1972; Katz and Matthews, 1977; Matthews, 1980; Allen and Fawcett, 1982; Matthews et al., 1983). The detailed study of Allen and Fawcett (1982) on reaction textures accompanying equilibria among the phases zoisite-anorthite-calcite-H₂O-CO₂ has provided an excellent basis for interpreting reaction textures observed in our study. With but a few exceptions, for comparative purposes, the breakdown reactions of anorthite were not seeded with reaction products.

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Results and discussion

Nature of the reactions

A detailed microscopic investigation showed that kyanite was not present in any of the products of the anorthite + water reaction (Table 2). Reactions (3) and (6) do not occur in the absence of seeds of the equilibrium products.

The products from the anorthite + water reaction at 700°C and 675°C were zoisite and hexagonal plates of an aluminum silicate phase. The EDS spectrum of this phase was clearly distinguishable from that of the kyanite standard and quantitative analysis showed this phase to have an Al2O3:SiO2 ratio = 3:1. No other elements were identified in this phase except for very small traces of sodium. These crystals are believed to be mullite, known to deviate from the ideal formula 3Al2O3:2SiO2 (Agrell and Smith, 1960; Cameron, 1977; Deer et al., 1982). The mullite, zoisite and anorthite are intergrown (Fig. 2a,b,c) and suggest that the reaction can be represented by the model equation:

\[ 12 \text{anorthite} + 3 \text{H}_2\text{O} \rightarrow 6 \text{zoisite} + \text{mullite} + 5 \text{quartz} \]  
(7)

Quartz, however, was not identified in any product at 675°C and 700°C. Yields were low (XZo > 0.3) in runs at these temperatures, and the quartz 104 peak at 26.64° is partially masked by the 114 peak of anorthite at 26.5°. This, however, does not account for the failure to see quartz in the SEM examination, and the absence of quartz may be related to undersaturation with respect to aqueous silica; all quartz must be derived from the reaction. At 700°C and 10 kbar the solubility of quartz is 4.8 wt.%, Fournier and Potter (1982). A reactant system consisting of water and anorthite with a 15.5:1 molar ratio (Table 2), reacting according to equation (7), would require XZo to reach 0.38 for quartz saturation to be achieved. Moreover, this estimate represents a minimum value for quartz saturation since it ignores the complexing of silica in solution in the presence of feldspars (Allen, pers. comm.). The reaction processes at 675° and 700°C are more adequately described by equations involving incongruent solution, i.e.

\[ 12 \text{anorthite} + 3 \text{H}_2\text{O} \rightarrow 6 \text{zoisite} + \text{mullite} + 5 \text{quartz} \]  
(7a)

Incongruent solution of anorthite at high pressures within its stability field has been observed by Matthews et al. (1983).

A few scattered mullite plates are observed in products at 650°C (Table 2), but at and below 650°C margarite becomes a conspicuous phase, with a small amount also observed at 675°C. Margarite, zoisite and anorthite are intergrown (Fig. 3), suggesting that the reaction at \( T \leq 650°C \) and \( P_{H_2O} 10 \text{kbar} \) is

\[ 5 \text{anorthite} + 2 \text{H}_2\text{O} \rightarrow 2 \text{zoisite} + 2 \text{quartz} \]  
(5)

At temperatures \( \leq 650°C \) quartz is observed in the reaction products (Table 2 and Fig. 3d). At 600°C and 10 kbar the solubility of quartz is 1.9 wt.%, Fournier and Potter (1982), and in reaction (5) quartz saturation would be reached when XZo > 0.10.

The zoisite polymorph formed at 550° to 650°C, and 10 kbar is orthozoisite, but the reaction product at 450° and 500°C also contains clinozoisite, and clinozoisite is the dominant phase at 450°C. In the few runs made at higher pressures (450° and 15 kbar, 600° and 20 kbar) clinozoisite is also present (Table 2). In these higher pressure runs quartz is not observed. Solubility of quartz increases considerably at pressures above 10 kbar (Arndt and Kaiser, 1979), permitting reaction involving incongruent solution. An alternative possibility, suggested by a weak X-ray diffraction peak observed at 28.8° is that pyrophyllite may have formed by the reaction:

\[ 9 \text{anorthite} + 4 \text{H}_2\text{O} \rightarrow 4 \text{zoisite} + 2 \text{quartz} + \text{margarite} \]  
(8)

Pyrophyllite was not identified in the SEM analyses, but accurate identification was hampered by the extremely fine-grained nature of the products produced at higher pressures.

Reaction textures

The textural relationships illustrated in Figures 2 to 4 are typical of solution-precipitation reactions. Mullite-forming runs at 700°C are illustrated in Figure 2. The anorthite is seen in early and more advanced states of dissolution in Figures 2a, b, and 2d, respectively. Edges and other high surface energy facets have been rounded by the solution process (Figs. 2b, d) with cavities or pits developing in the anorthite out of which single or clusters of elongate zoisite crystals have grown (Figs. 2a,b,d). The zoisite crystals typically are elongated parallel to the b-axis. Allen and Fawcett (1982) note that this elongation is in agreement with a statement of the Bravais law which states that crystal growth occurs most rapidly in the direction with the smallest crystallographic spacing. Zoisite crystals commonly radiate in clusters which appear to be located either heterogeneously on anorthite surfaces or perhaps from nuclei on other zoisite crystals (Figs. 2b,d). Thus, zoisite growth appears to undergo heterogeneous nucleation on the reactant grains, followed by secondary nucleation on early growing zoisite crystals. The mullite plates are independently intergrown with anorthite and zoisite and exhibit a well-defined hexagonal morphology (Fig. 2b,c).

Reaction textures of margarite-forming reactions are shown in Figure 3. Margarite is occasionally observed as...
isolated sheets, but most commonly consists of densely packed clusters of thin flakes associated with the reactant (Fig. 3a,b,c, 4c). Intergrowth of margarite with zoisite is also observed (e.g., Fig. 3c, 4c). The zoisite crystals show the previously noted tendency to grow in clusters from a growth center or to grow out of solution-etched pits in the anorthite (Fig. 3c,d), but they also appear to be smaller and more numerous than those grown at 700°C. Quartz appears as small crystals (Fig. 3d) and undoubtably also occurs as quench crystals. Anorthite surfaces show more prominent etch features than observed in 700°C runs, with some evidence for parallel arrangements of etch pits (Fig.
3b,d, 4b). More advanced states of anorthite dissolution are illustrated in Figures 4a, b. Figure 4a shows an anorthite crystal rounded and scalloped by solution, leaving essentially isolated grains. In Figure 4b the anorthite surface is corrugated by deep parallel pits. Allen and Fawcett (1982) observed identical behavior (their plate 3E); the etch pits aligned with 001, with their short axes coplanar and their long axes parallel to the c-axis. Berner (1980) identifies such etch features as the product of a dissolution process the rate of which is controlled by surface reaction kinetics; the rounding or scalloping is presumably the result of the more rapid solution of high surface free-energy artifacts, mainly edges.

The zoisite crystals formed in runs at 500°C tend to be...
Fig. 4. SEM micrographs illustrating the anorthite solution texture and clinozoisite and zoisite crystal textures at $T \leq 500\,^\circ\mathrm{C}$.
(a) Highly corroded anorthite grain showing rounded surfaces with some etch pit development (AnZ-10); (b) strongly etched anorthite surface with flat zoisite crystals (AnZ-28); (c) flat zoisite crystals, margarite and possibly clinozoisite growing on an anorthite surface at 500°C (AnZ-28); (d) bundles of clinozoisite needles from a reaction at 450°C (AnZ-39).

more tabular than those observed at higher temperatures (Figs. 4b,c), and unequivocal identification of clinozoisite proved difficult because of the very fine grain size of the products in clinozoisite-forming reactions. Clinozoisite appears as bundles of very fine needle-like crystals (Fig. 4d), a texture suggestive of very rapid nucleation and growth. The ubiquity of zoisite crystals, and their spontaneous heterogeneous nucleation characteristics, suggest that nucleation kinetics are not significant to the overall reaction kinetics. The apparent random development of the zoisite crystals also suggests that epitaxis is not influencing nucleation and growth.

Rates of reaction

The $X_{zo}$ data given in Table 2 do not take into account the stoichiometries of the reactions. For example, an $X_{zo}$
value of 0.25 for a run reacted according to (5) (5 moles An → 2 moles Zo) corresponds to a value of 0.45 for the fraction of the original anorthite which has reacted. Therefore values of reaction progress expressed as $1 - X_{An}$, where $X_{An}$ is the fraction of unreacted anorthite, are also given in Table 2, according to the stoichiometries of reactions (7a) for 700°C and 675°C runs and reaction (5) for all runs at lower temperatures.

Despite some variability in the $1 - X_{An}$ results (e.g., runs AnZ-20,25) the experimental data show clearly defined trends with respect to temperature (Table 2). Figure 5 is an isochronal plot of temperature versus $1 - X_{An}$ for runs made with an initial water/mineral ratio of ~15.5:1. Between 400–500°C the rate of reaction increases with temperature, whereas at 600–700°C there is a marked decrease in rate with increasing temperature. This decrease in rate with increase in temperature is also indicated by runs made at 600–700°C with an initial water/mineral ratio of ~4.3:1 (Table 2) and also appears independent of which metastable reaction (5 or 7a) is occurring (Fig. 5). The decreasing rate is related to proximity to the stable anorthite-zoisite boundary curve (i.e., reaction 3), at which temperature the reaction rate involving these two phases reaches zero, under equilibrium conditions.

In addition to the well defined effects of temperature, the amount of water in the system also has a significant effect on the reaction rate. As we have noted, variation in amount of water in the system is expressed in Table 2 in terms of the initial water-anorthite molar ratio, ($H_2O$/An). Increasing this ratio also increases the rate of reaction. This is evident in Table 2 from a comparison of runs made at 700°, 650° and 600°C with $H_2O$ ratios of 4.3 and 15.5, respectively, and from comparison of the runs made for 17 hours at 600°C in which the $H_2O$/An ratios were increased from 4.2 to 15.7. Martin and Fyfe (1970) also noticed an increase in the hydration rate of enstatite and forsterite as a function of the water/mineral ratio. They attributed this to an enhancement in the rate of incongruent solution reactions, which in this study would correspond to an acceleration of reactions such as (7a) by allowing silica to pass more rapidly into solution. If this hypothesis is correct, then the rate of reaction should increase from 600°C to 700°C because the activity of silica in solution increases (Fournier and Potter, 1982). However, any such effect is masked by the approach to the anorthite–zoisite boundary (reaction 3). It is notable that in the runs made closest to this boundary (700°C) the reaction with $H_2O$/An = 15.5 appears to come to a stop at $X_{Zo} = 0.25$. This is well below the calculated maximum of 0.38 for attaining silica saturation with respect to quartz, and is indicative of the strong influence of the anorthite–zoisite boundary on reaction rate.

Although only a few runs were made at pressures greater than 10 kbar, the effect of increasing pressure is to enhance the reaction rates, as would be expected for “hydration” reactions.

The influences of the anorthite–zoisite boundary are clear, but it is also important to know whether other phase boundaries might be affecting the reactions. Reaction (6) does not occur and the development of margarite + quartz corresponds to reaction (5). The metastable extension of the equilibrium boundary for reaction (5) projected up from the invariant point 12 in Figure 1 intersects the 10 kbar abscissa at approximately 680°C. Although derived from a calculated slope, this temperature is in remarkably good agreement with the experimentally observed formation of margarite (+ quartz) at $T \leq 675°C$. The formation of clinzoisite at $T \leq 500°C$ at 10 kbar presents a problem because the location the Fe-free clinzoisite–zoisite boundary remains uncertain. Jenkins et al. (1983), reversed reaction (3) at 550°C for both zoisite polymorphs, and showed that Fe-free clinzoisite is metastable with respect to zoisite. They also suggested an equilibrium inversion temperature of ~200°C, on the basis of compositional data on naturally coexisting zoisite and clinzoisite and empirical temperature estimates.

Experimental runs made at this laboratory using mixtures...
of zoisite and clinozoisite show that growth of zoisite at $P_{H_2O} = 15$ kbar occurs at temperatures as low as 350°C. Thus it must be concluded that clinozoisite was crystalized metastably in this study, and its presence or absence is not related to any equilibrium boundary.

The results of runs made using the anorthite–zoisite/kyanite/quartz reversal mixtures (Table 3) shed further light on the above observations. At 700°C, 10 kbar and 17 hours reaction, the reversal mixture gives the same yield within experimental error (after subtracting out the proportion of zoisite seeds) as given by the equivalent unseeded run (Table 2). At 500°C, 10 kbar and 450°C, 15 kbar, 17 hour runs show extensive reaction, and the same is observed in equivalent unseeded runs. However, the products in the seeded runs contain only zoisite, and no clinozoisite. It is apparent that seeds aid the formation of the stable phase, but do not affect the overall kinetics of reaction. The formation of mullite, a phase with a disordered structure (Agrell and Smith 1960, Deer et al, 1982) is probably induced by the favoring of structures with higher entropy configurations during nucleation and growth; the higher entropy, more readily nucleated, metastable phase commonly is observed to crystallize more rapidly than the stable phases. However, entropy considerations do not provide an adequate explanation for the crystallization of clinozoisite, because Jenkins et al. (1983) suggest that the entropy of clinozoisite is 10 J mol$^{-1}$K$^{-1}$ less than that of zoisite. It is conceivable that a disordered form of clinozoisite is crystallizing, but an alternative possibility, suggested by the unusual morphology of the clinozoisite crystals (Fig. 4d) and the higher molar volume of clinozoisite (Jenkins et al. 1983) is that surface energy factors are influential in nucleation and growth (cf. Fyfe et al. 1958, p. 259; Matthews 1976).

**Summary and Conclusions**

Several metastable reactions between anorthite and water, in the absence of seeds, take place at various temperatures and pressures. The equilibrium reaction (3) in particular is not observed, and the reactions appear to be represented by equations (7a) and (5). Mullite, clinozoisite, and margarite are all produced in a $P$–$T$ region where kyanite and zoisite are stable, and the margarite growth appears related to the metastable extension of the boundary curve of reaction (5).

All the reactions take place by a solution-precipitation mechanism, with free growth of reaction products and no evidence for arming or "in situ" replacement of one phase by another. Partially dissolved anorthite grains show evidence of crystallographically controlled etching. The nucleation of product phases may initiate heterogeneously on anorthite surfaces, but when observed to do so the tendency for growth to take place in randomly orientated clusters suggests that epitaxis is not strongly influencing nucleation and growth (cf. Haas, 1972).

The following phenomena all suggest that the anorthite dissolution process is the critical rate controlling mechanism in the crystallization of zoisite from anorthite:

(1) The absence of any obvious influence of product seeds on reaction rate.

(2) The rate appears independent of the zoisite polymorph that crystallizes.

(3) The rate decreases as the anorthite–zoisite boundary curve is approached.

(4) The rate increases with an increase in the relative amount of water.

(5) The rate increases with increasing $P_{H_2O}$, and the metastable growth of clinozoisite is enhanced.

(6) The lower limit of reaction at 400°C appears governed by a correspondingly low rate of dissolution.

The decrease in rate of reaction between 600° and 700°C is related to proximity to the anorthite–zoisite boundary. Rate-depressing influences of equilibrium boundaries have also been noted by Schramke and Kerwick (1982) for the reaction: muscovite + quartz = sanidine + andalusite + water, and, by inference, for the reactions of enstatite and forsterite with water by Martin and Fyfe (1970). To explain the phenomenon, Martin and Fyfe (1970) proposed a simple “activated complex” model, in which the reverse reactions (which in this case would be the reactions of anorthite with other product phases) make an increasingly important contribution to the overall reaction kinetics as the equilibrium boundary is approached. It can also be noted that modern physical theories of renormalization (e.g., Ma, 1976) also predict rate-depression in the region of critical phenomena.

Our observations emphasize the potential of scanning electron microscopy in experimental petrology and reiterate the importance of using reversal mixtures in phase equilibrium studies. These data are not presumed to have specific application to petrological problems. However, it has been shown that at elevated temperatures and water pressures plagioclases in the range from An$_{100}$ to An$_{70}$ all react to form zoisite along the anorthite–zoisite boundary curve (Goldsmith, 1982). If it is assumed that the kinetic behavior observed with anorthite can be applied to calcic plagioclases, some limited conclusions can be drawn on the behavior of plagioclase-bearing assemblages in medium to high-grade metamorphic rocks. In the presence of sufficient amounts of water, the plagioclase breakdown reactions will proceed rapidly, even if at temperatures somewhat displaced from equilibrium. Only at low metamorphic temperatures, significantly below 400°C, could reaction kinetics influence the occurrence of a reaction. Nucleation of product phases would not present a problem; it has been shown that metastable phases develop as ready alternatives to the stable phases. The key factor in governing the survival of plagioclase is the activity and relative quantity of water. High water activities and contents would favor the rapid occurrence of the breakdown reactions to a zoisite- (or epidote-) bearing assemblage, and low water activities would favor the preservation of plagioclase. Two contrasting environments of
metamorphism reflect this generalization: hydrothermal
metamorphism at ocean ridges and granulite facies meta-
orphism in the roots of precambrian shield terranes.

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