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Review of the behavior of plagioclase under metamorphic conditions

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Abstract

The behavior of plagioclase feldspars under metamorphic conditions is reviewed. The literature on plagioclase composition as related to reactions involving zoisite (epidote) and other calcic phases, the peristerite gap, and the coexistence of intermediate plagioclases of various compositions is presented. The various ideas on the relative effects of structural states and of the role of chemical reactions on subsolidus relations are considered. Two views, not mutually exclusive, relative to plagioclase compositions, are apparent: a "homogeneous" view, emphasizing control by crystal-structural factors, and a "heterogeneous" view, dominated by sequential mineralogical reactions.

Mineralogy and petrology are supplementary and complimentary disciplines. Much of our understanding of the petrology and ultimately the geology of any portion of the earth is dependent on our knowledge of the properties and characteristics of minerals and of mineral interactions. The petrologist examines the minerals to help unravel the history of a rock; the mineralogist gains insight on mineral behavior from accumulated information on the rocks. Some minerals with limited compositional and structural variation have little to reveal. Others, such as the feldspars, may contain a great deal of information, but can be complex and stubborn in revealing their secrets. A voluminous literature on plagioclase has not yet clearly characterized the phase relations. The equilibrium picture is overlain by confusion compounded of and dominated by kinetic factors. Furthermore, heterogeneous mineralogical reactions can be affected by the varying energetics of different structural states. This review briefly covers and is restricted to the highlights of papers on plagioclase feldspars in metamorphic rocks, and is followed by a report on an experimental investigation that bears on plagioclase stability at elevated temperatures and water pressures.

Petrologists have long been aware of an increase in anorthite content in some metamorphic rocks accompanying an increase in metamorphic grade (Becke, 1913). Although earlier workers had considered a relationship between plagioclase and epidote or other Ca-rich minerals (see Christie, 1959), Ramberg (1943), largely on the basis of field evidence, attempted to explicitly define the nature of the relationship. Ramberg proposed an equilibrium between epidote and "anorthite-molecule" in the plagioclase:

$$\underset{\text{anorthite}}{2CaAl_2Si_2O_8} + 1/2H_2O \rightleftarrows \underset{\text{"epidote"}}{Ca_2Al_3O_{12}(OH)} + \underset{\text{kyanite}}{1/2Al_2SiO_5} + \underset{\text{quartz}}{1/2SiO_2}$$

He then wrote a reaction in which calcic plagioclase plus water breaks down to a more albitic plagioclase plus epidote, kyanite, and quartz and constructed a theoretical curve for the equilibrium in which, with decreasing temperature, an increasingly sodic plagioclase is stable with epidote. Ramberg was fully cognizant of the role of pressure and drew schematic diagrams of both isobaric and isothermal surfaces for the reaction. He considered this reaction relation to be a continuous one all the way from the greenschist to the granulite facies.

Ramberg (1949) extended his ideas on the plagioclase–epidote equilibrium to potassium-rich rocks with orthoclase and muscovite. A second continuous reaction occurs:

$$\underset{\text{anorthite}}{4CaAl_2Si_2O_8} + \underset{\text{orthoclase}}{KAlSi_3O_8} + H_2O \rightleftarrows \underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{epidote}}{2Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{quartz}}{2SiO_2}$$

Figure 1 is a reproduction of his (2-dimensional) diagram. The dashed curve, representing the equi-

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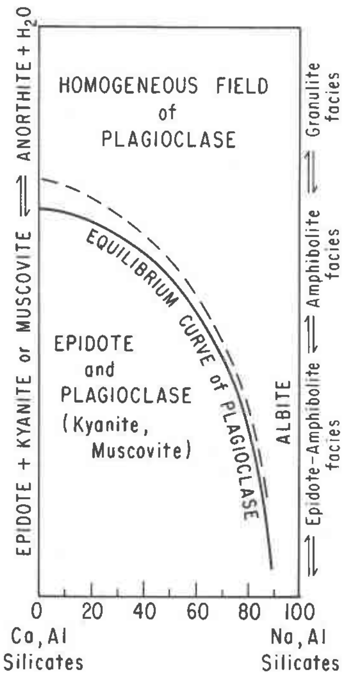

Fig. 1. Reproduction of Ramberg's (1949) subsolidus diagram of the plagioclase ⇄ epidote equilibrium, deduced in part from field observations.

librium of plagioclase and epidote in the presence of muscovite and potash feldspar is drawn somewhat above the K-free equilibrium because muscovite in association with K-feldspar and quartz has somewhat lower Al-activity than kyanite. Ramberg pointed out that increased H_2O pressure displaces the equilibrium toward epidote, as does increasing the Fe^{3+}/Al ratio because of the ability of epidote to incorporate Fe^{3+} in its structure. Ramberg considered the reactions of Figure 1 to span a temperature interval of approximately 500° C, and facies, representing temperature, are ploted on the vertical axis. He felt that the epidote–plagioclase equilibrium in most quartzo-feldspathic rocks cannot register *P–T* conditions higher than those that would develop An_{30-40} plus epidote, due to the low Ca/Na ratio in these rocks. Ramberg (1952) further extended the plagioclase–epidote relations to a more complex system containing $CaCO_3$ and indicated that rocks with the same plagioclase compositions may have formed at different temperatures, depending on the partial pressure of water.

Lyons (1955) plotted plagioclase compositions against metamorphic grade in the Hanover quadrangle (New Hampshire–Vermont) as a check against Ramberg's (1943) diagram. He observed that in a general way the separation of the plagioclase–epidote and plagioclase fields followed Ramberg's curve, and the data clearly indicated a gradual increase in the anorthite content of the plagioclases with increasing grade of metamorphism. He noted significant deviations, however, and indicated that there are problems, as recognized by Ramberg, in its use as an index of intensity of metamorphism. In addition, Lyons noted, "... a great paucity of metamorphic plagioclase in the range of An_{10}–An_{20}."

Ramberg's (1943, 1949, 1952) deduced curves were continuous in nature, implying an equilibrium that varies continuously with temperature (or metamorphic grade). A number of field studies in regionally metamorphosed terranes had given some indication of a rapid conversion of albite to oligoclase or sodic andesine over a short distance, but it is likely that the first clear-cut evidence for a discontinuous increase in plagioclase composition with increasing grade was described from greywackes of the Missi series, Manitoba (Ambrose, 1936; see Brown, 1962). Ambrose commented on abundant epidote, and assumed that original intermediate plagioclase of volcanic rocks has reacted, "... according to the familiar equation: plagioclase + water + iron = albite + epidote + alumina + silica." He noted that water-clear albite persists with little change through the biotite zone, but with the appearance of garnet, the anorthite content of the plagioclase rises abruptly from An_{6-8} to An_{28-32} and that epidote is greatly diminished in amount above the garnet isograd, concomitant with the appearance of oligoclase.

Since the earlier years of the 20th century, when the nature of the isomorphous replacement of Na and Si for Ca and Al in the plagioclase feldspars became known, petrologists had long considered the plagioclases to be an ideal solid solution series. The dogma of one rock, one plagioclase (excluding zoning, or other non-equilibrium phenomena) prevailed. Chao and Taylor (1940) were the first to observe superstructure reflections in X-ray diffraction patterns of intermediate plagioclases, indicating structural complexities. Chao and Taylor considered this as evidence against a complete solid solution series, although a strong hint had earlier appeared when Taylor *et al.* (1934) found the *c*-axis of anorthite to be twice that of albite. Köhler (1942a, b) and Larsson (1941) were the first to explicitly describe optical differences between plagioclases of plutonic and volcanic rocks, and thus to differentiate high-temperature from low-temperature plagioclases. Cole *et al.* (1951) showed that low-temperature plagioclase from An_{30} to An_{72} had complex superstructures. Laves (1951, 1954) reported that there are plagioclases in the compositional range of approximately An_5–An_{17}, among them peristerites, that show two phases in "single-crystal" X-ray photographs. Laves estimated the compositions of the exsolved phases to be approximately An_0 and An_{30}. Gay and Smith (1955) confirmed this observation, and refined the estimation of composition of the two phases as $An_{3\pm2}$ and $An_{23\pm2}$. This region of composition was termed the "peristerite gap". Additional crystallographic work and refinement was done by Ribbe (1960, 1962), Brown (1960), and Fleet and Ribbe (1965).

Christie (1959) pointed out the significance of the peristerite gap in low-temperature plagioclases, and that as a consequence Ramberg's smooth unbroken curve needed modification. He also assumed an immiscibility gap in the intermediate region delineated by Cole *et al.* (1951) in the low-temperature plagioclases. On the basis of the discontinuity produced by the peristerite phenomenon, Christie stated that the plagioclase epidote thermometer was useless.

At this same time de Waard (1959) published on basic and pelitic schists of the Usu massif in Timor and noted changes in the An content of the plagioclases over relatively short distances, reflecting a succession of narrow zones of metamorphism. He found the frequency of occurrence of plagioclase between An_5 and An_{20} to be remarkably low, particularly in the basic schists. He was almost certainly unaware of the evidence of a peristerite gap, and suggested that the abrupt change is coupled to the formation of garnet in pelites and hornblende in basic rocks. The papers by Christie (1959) and de Waard (1959) set off a small flurry of activity in the early 1960's on the niceties of the plagioclase compositional problem from two points of view: (a) facies boundaries, and (b) crystal-chemical aspects.

From this point until the present there have been numerous field observations, a number of interpretive papers, rather few experimental studies, and many crystallographic investigations, all related to the plagioclases, and directly or indirectly, to their behavior in metamorphic and low-temperature environments. Some of the earlier interpretive papers are by Rutland (1961, 1962), Christie (1962), Noble (1962), Sen (1963) and Kretz (1963). Noble (1962) summarized the previous field and theoretical work relative to the peristerite gap and presented a further refinement of the Ramberg–Christie diagrams. He also considered the effect of intermediate metastable plagioclases, suggesting that the increased free energy raises and flattens the plagioclase–epidote equilibrium curve in the An_{35}–An_{50} range, reducing the temperature interval in which calcic andesine is stable.

Brown (1962) presented an excellent review and clarification of the subject of peristerite unmixing in the plagioclases and related metamorphic and facies series. His summary of the field observations indicated that the rate of increase in the composition of the most basic plagioclase with increasing metamorphic grade is continuous or nearly so in rocks of the andalusite–sillimanite type and perhaps in the low-pressure intermediate type. A jump occurs between about An_7 and about An_{20} in the kyanite–sillimanite type and the high-pressure intermediate type, and in the jadeite–glaucophane type only albite seems to exist. He mentioned that the relation between garnet and the discontinuity in plagioclase composition is not clear; there is an implication that reactions involving garnet and other Ca-rich phases may or may not be important in this connection. Sen (1963) pointed out that not all plagioclases unmix, thus breaks in composition are not always present, and at any rate are of no avail in delineating metamorphic facies. Demarcation must be made on empirical grounds based on petrographic observations, and checked against other independent evidence of facies transitions, such as reactions involved in the metamorphic process.

Kretz (1963) restated Ramberg's (1943, 1949, 1952) emphasis on the fact that by the nature of their compositions plagioclase–epidote reactions must involve one or more additional phases, and that knowledge of the reactions is essential to an understanding of plagioclase thermometry. Through the use of some simplifying assumptions, Kretz derived equations to interrelate the composition of plagioclase, temperature, pressure, chemical potential of H_2O and the composition of the other solid solutions that take place in six univariant universal reactions, three of which were considered by Ramberg:

$$\text{epidote} + \text{muscovite} + \text{quartz} \rightleftarrows \text{anorthite} + \text{potash feldspar} + H_2O \quad (1)$$

$$\text{epidote} + \text{kyanite} + \text{quartz} \rightleftarrows \text{anorthite} + H_2O \quad (2)$$

$$\text{epidote} + CO_2 \rightleftarrows \text{anorthite} + \text{calcite} + H_2O \quad (3)$$

$$\text{epidote} + \text{chlorite} + \text{quartz} \rightleftarrows \text{actinolite} + \text{anorthite} + H_2O \quad (4)$$

$$\text{epidote} + \text{actinolite} + \text{quartz} \rightleftarrows \text{anorthite} + \text{calcic pyroxene} + H_2O \quad (5)$$

epidote + quartz

$$\rightleftarrows \text{anorthite} + \text{grossularite} + H_2O \qquad (6)$$

He then modified the equilibria by imposing feldspar ordering, or non-ideal behavior in the reactions, and thus for the first time attempted to treat two of the factors that are involved in the behavior of plagioclase under metamorphic conditions.

Rambaldi (1973) found a general increase in the anorthite content of plagioclase and a decrease in the Al content of epidote with increasing metamorphic grade in metasediments and metavolcanics near Bancroft, Ontario. Plagioclase crystals are commonly zoned, becoming richer in anorthite toward the rims, and epidote crystals may also be zoned, enriched in iron toward the rims. The plagioclases associated with epidote are mostly oligoclases and andesines, with a maximum of An_{40}. The plagioclase in rocks without epidote is generally albitic. Misch (1968) also observed that plagioclase more calcic than An_{37-40} is rare in the epidote-bearing subfacies of the amphibolite facies Skagit Gneiss of Washington State. Rambaldi attributes the increasing An content to the breakdown of epidote, and considered fifteen possible mineralogical reactions that may be involved in the various compositional changes. More complex reactions than those discussed by Kretz (1963) are recognized, and generally involve sphene and Fe–Ti oxides. Höy (1976) also observed "positive zoning" of metamorphic plagioclases (increase of An content toward the rim) associated with prograde metamorphism, and "negative zoning" with retrograde reactions in the Riondel area of British Columbia. These phenomena are associated with the model reaction clinozoisite + tremolite + quartz $\rightleftarrows$ diopside + plagioclase + H_2O. The distribution of isograds and the variation in plagioclase composition in the above assemblage is modeled using T–X_{CO_2} diagrams calculated at 5 kbar pressure, indicating that An content increases with increasing T and X_{CO_2}; Höy indicated that in the assemblage epidote – actinolite – quartz – diopside – plagioclase, plagioclase compositions $> An_{60}$ are reached at temperatures above 600° C and at X_{CO_2} values of 0.5–0.6. Ghent and DeVries (1972) had also considered the role of X_{CO_2} in plagioclase compositions. Bird and Helgeson (1981), in an extensive review and treatment of the system Na_2O–K_2O–CaO–FeO–Fe_2O_3–Al_2O_3–$_2O$–HCl–$_2$ at temperatures to 5 kbar and 600° C, conclude that the complex zoning commonly exhibited by both plagioclase and epidote solid solutions in geologic systems can be attributed to minor isothermal/isobaric changes in the composition of coexisting aqueous solutions.

It is apparent that there have been two different views on mechanisms controlling plagioclase compositions, particularly in metamorphic rocks. One might be called an internal, or homogeneous mechanism, controlled by structural discontinuities, order–disorder, or other crystallographic features in the feldspar. The other is the result of external, or heterogeneous factors, such as progressive or retrogressive sequences of mineral reactions induced by changing P–T conditions, producing discontinuities in plagioclases as a consequence of "abrupt" changes in mineral assemblages. Either is feasible and both might be operative: discussion of the homogeneous view began with Chao and Taylor (1940), and evidence for compositional discontinuities in natural plagioclases presumably produced by structural control is given, for example, by Doman *et al.* (1965), and DeVore (1956). The concept of heterogeneous control is implicit in the writings of Ramberg (1943, 1949, 1952) and espoused by others since that time.

Up until this point there had been no recognition of the existence of two optically distinguishable plagioclase phases in any rock other than presumed disequilibrium associations (see for example, Sen, 1963). Evans (1964), in a combined microprobe and universal stage study (microscopy by F. J. Turner), was the first to report clear-cut duality in plagioclase composition from schists of the almandine and oligoclase zones in New Zealand. The albites are very pure, the bulk of the grains below $An_{1.0}$. Epidote is present in all of the rocks. The coexisting oligoclase ranges from $An_{18.3}$ to $An_{25.6}$, averaging $An_{21-24.5}$, and the two plagioclases occur side by side as distinct grains. There is some tendency for oligoclase to occur as thin irregular strips along albite grain boundaries.

Observations of two plagioclase rocks became relatively common after Evans' (1964) note, perhaps because the ice was broken, but also because of the availability of the electron microprobe. Tsuji (1966) studied the Higo metamorphics in Kyusyu, Japan, where two plagioclases, one with albite and the other with oligoclase or andesine composition, occur side by side in the same thin section. Intermediate compositions do not occur. Although the compositional gap seems to decrease with rising temperature and minimum and maximum An contents converge to An_{14} in the central part of the highest temperature (garnet) zone, Tsuji cautioned against the use of a presumed peristerite gap as the sole explanation, pointing out the possibility of a reaction at the boundary between the epidote amphibolite and the amphibolite facies where albite, chlorite, and actinolite react to form a component of amphibole that enriches the plagioclase in Ca.

Crawford (1966) studied two suites of regionally metamorphosed semi-pelitic schists from Vermont and New Zealand in order to investigate the paragenesis of low-temperature plagioclase. On the basis of coexisting albite and oligoclase, and taking into consideration reactions to produce different associated Ca-rich phases, Crawford outlined a peristerite solvus with a vertical albite limb and a sloping oligoclase limb, at pressures on the order of 5–7 kbar. The solvus maximum occurs at about 450–500° C (corresponding to the almandine–staurolite isograds in the Vermont area) and spans the plagioclase compositions An_1 to An_{24} at lower temperatures.

Cooper (1972) followed progressive mineralogical changes in metabasic rocks of a Barrovian-type series, from greenschist to amphibolite facies in the southern Alps of New Zealand. This area is the same as that studied by Evans (1964) and Crawford (1966). As did Crawford, Cooper used coexisting compositions of albite and oligoclase through the garnet zone to outline the form of the peristerite solvus. At the oligoclase isograde the compositions are An_{0-1} and An_{23-25}. In Vermont the calcium mineral participating in the development of oligoclase is a carbonate, in New Zealand, epidote. Cooper noted that oligoclase first appears as thin discontinuous rims around an albite nucleus at the garnet–oligoclase–hornblende isograd, and although oligoclase is soon in evidence as individual grains, zoned grain relationships persist throughout the garnet zone. With increasing metamorphic grade through the garnet zone oligoclase increases in amount, becoming more sodic in composition, while albite decreases, becoming more calcic. Cooper stated that true amphibolite facies status is attained by the final disappearance of albite at the second oligoclase isograd, either by the complete replacement of albite cores by oligoclase, or (probably simultaneously) by the rise of sodic plagioclase above An_{10}, presumably due to closure of the peristerite solvus.

Morteani and Raase (1974) found abrupt changes in plagioclase compositions, seen especially as reverse zoning, even three-fold zoning, in epidote-bearing, amphibole-free rocks of the eastern Alps. The plagioclase cores are commonly 0–6% An, with 14–19% An in the rims. Compositions between An_5 and An_{15} are rare, presumably representing the peristerite gap. Plagioclases more calcic than An_{35} are also rare. Only calcite-free or low-calcite rocks were studied, as the An-content of the plagioclase is significantly increased in rocks with greater than 20% carbonate. They noted that the presence of margarite may also influence the Ca-content of the plagioclase, as indicated by Ackermand and Morteani (1973). In epidote-containing rocks, they call upon the peristerite gap plus an ill-defined two-stage metamorphic process with increasing temperatures to account for the feldspar compositions.

Frey and Orville (1974) studied a margarite-bearing black shale from the central Swiss Alps with the following unusual features:

1) The first plagioclase to appear in the lower-grade greenschist facies is not albite, but oligoclase–andesine ($\sim An_{30}$).
2) The An-content commonly remains constant with increasing metamorphic grade.
3) Some rocks at the transition from the greenschist to the amphibolite facies show unusually high An-contents (up to An_{70}). Graphical analysis of the system $CaO–Na_2O–Al_2O_3–SiO_2–H_2O–CO_2$ (with SiO_2, H_2O, and CO_2 in excess) with the phases pyrophillite, paragonite, margarite, zoisite, calcite, and plagioclase satisfactorily explains the variable compositional nature of the plagioclase and additionally points to the importance of certain specific reactions under varying conditions of *P–T–X* in controlling the composition of the feldspar.

The importance of the Fe content of epidote and the oxidation potential on the composition of the associated plagioclase was discussed by Hörmann and Raith (1973), who investigated the Fe^{3+} content of epidotes in a metamorphic series from Tyrol, Austria. Fe^{3+} in epidote as well as the oxidation ratio ($Fe^{3+} \times 100/Fe^{3+} + Fe^{2+}$) decreases from greenschist to almandine–amphibolite facies. Redox reactions were suggested that account for observed mineral assemblages and that may explain the increase of An-content of coexisting plagioclase with increasing metamorphic grade. The importance of oxidation and of the value of P_{CO_2}/P_{H_2O} was also considered by Rambaldi (1973).

E. Wenk (1962) observed that the An content of plagioclase associated with calcite is almost uniform in a given region and tends to be high, although it varies from area to area dependent on the grade of metamorphism. Wenk and Keller (1969) examined 700 amphibolites from the central Alps, and distinguished zones of albite amphibolites, oligoclase amphibolites, andesine amphibolites, and labradorite amphibolites, apparently as discontinuous sequences of plagioclase composition. Although heterogeneous control was not specifically discussed, the observations (with calcite present in particular) and the zonal relationship implied a mechanism controlled by mineralogical reactions. This view became strongly modified in later papers by H.-R. Wenk and coworkers when transmission electron microscopy and single-crystal X-ray work were used in association with the earlier microscopic and field petrographic techniques. Wenk *et al.* (1975) described intergrowths of andesine (An_{34}) and labradorite (An_{66}) with textures indicating simultaneous equilibrium growth. Although mineral associations (chiefly zoisite and/or scapolite) in direct contact with the plagioclases are considered, emphasis is placed on structure. Wenk *et al.* clearly stated that the microscopic intergrowths represent end members of the intermediate plagioclase miscibility gap. They noted DeVore's (1956) thesis that An_{33} and An_{66} are crystallographically "stable" compositions and Wenk *et al.* felt that in an intergrowth both phases have similar crystal structure but with a reverse Ca–Na and Al–Si arrangement, symmetrical to An_{50}. Transmission electron microscope observations display anti-phase boundaries (APB's) that record structural transformations, and are indicative of pre-existing but now unstable single-phase structures. Wenk *et al.* noted that the superstructure produced by ordering is maintained regardless of chemical composition, and that the boundary between labradorite and andesine is therefore a kind of chemical APB superposed in the intermediate plagioclase superstructure with periodic APB's on a smaller scale which extend through both structures. They also pointed out that the orientation of the feldspars makes this intergrowth difficult to see in ordinary thin sections and that it might go undetected in many rocks.

Even more complex relations were described by Wenk and Wenk (1977) from a single outcrop from Val Carecchio in the central Alps. In addition to stepwise change in An-content from An_{18-25} in leucocratic gneiss to $An_{90\pm3}$ in marble bands, they described microscopic intergrowths of andesine $An_{33\pm6}$ with labradorite $An_{67\pm5}$ (as in Wenk *et al.*, 1975) and of labradorite An_{62-70} with bytownite/anorthite An_{88-92}. In one sample three plagioclases are intergrown.

Phillips *et al.* (1977) found intergrowths of An_{61} and $An_{69.5}$ in plagioclase from a plagioclase–quartz–biotite gneiss from Broken Hill, New South Wales. This intergrowth spans the range between Bøggild (An_{47} and An_{58}) and Huttenlocher (An_{67} and An_{90}) intergrowths, in a region generally considered "homogeneous". Grove (1977) studied plagioclases in volcanic, shallow plutonic, deep-seated plutonic, and metamorphic environments, and calculated approximate cooling rates. All plagioclases were in the range An_{65}–An_{85}. In the most rapidly cooled plagioclases there was no evidence of exsolution. With progressively slower cooling the composition range of two-phase intergrowths increases. In all of the plagioclases there is evidence of local disequilibrium, and there may be second generation lamellae with variation of composition on a submicroscopic scale. Grove feels that "Huttenlocher plagioclases" are useful as indicators of cooling history.

Garrison (1978) found eight discrete domains within the compositional range of the Bøggild and Huttenlocher intervals in metamorphosed igneous plagioclases in metabasalts from the Llano Uplift, central Texas. It is estimated that the (shallow) amphibolite-grade metamorphism took place near 3.5 kbar and 650° C (~1200 m.y. ago), and the compositions of the eight domains are An_{38}, An_{42-64}, An_{55-58}, An_{60}, An_{65}, An_{70}, An_{80}, and An_{88-91}. He suggested that (1) both Bøggild and Huttenlocher intergrowths could be present in the same zoned grain, (2) the immiscibility region may be extremely complex, allowing more than the four metastable end-member compositions to exist, or (3) a disequilibrium situation exists within the unmixing intervals due to unfavorable metamorphic conditions. Garrison feels the second to be the most probable.

One of the tenets of petrology is that equilibrium is closely approached in metamorphic rocks. Observations suggestive of disequilibrium, as above, are occasionally reported. Hunahashi *et al.* (1968) found a "surprisingly wide" difference in the An-content of coexisting plagioclases in some plutonic and metamorphic rocks in Japan, even in one thin section. They later indicated that the compositions An_{22}, An_{27}, An_{33}, An_{43}, An_{50}, An_{55}, An_{62}, An_{67}, and An_{78} crystallize more readily than others, and they correlated these compositions with presumed structurally-favored regions of composition, although the concept of local or "mosaic" equilibrium on the scale of a single thin section was also espoused. Byerly and Vogel (1973) studied grain-boundary effects accompanying changes in the composition of plagioclase in the progressively metamorphosed Cross Lake gneiss in southern Ontario. The lower-grade plagioclases of the granodiorite are chemically inhomogeneous with zoned rims containing distinct compositional levels of An_{0-3}, An_{17}, and An_{25}. As the grade increases, the plagioclase becomes more homogeneous, with An_{0-3} rims dominating. Braun and Müller (1975) found very large compositional variations over distances of 10–20 μm in lower-grade metamorphosed "basaltoid" and "granitoid" rocks. They stated that only at temperatures greater than 600° C (upper amphibolite facies) is homogenization of the plagioclase (and garnets) initiated, so that at lower temperatures thermometry dependent upon An-contents in the plagioclases or Mn/Fe relations in the garnets is not possible.

Nord *et al.* (1978) also reported on compositionally-zoned plagioclase microporphyroblasts in phyllites from southwestern Massachusetts. Rocks from the lowest metamorphic grade yield unzoned albite. At slightly higher grade albite cores and thin outer rims have an intervening narrow zone of An_{13-17}. At higher grades, plagioclase is complexly zoned in one of two ways: either the composition drops stepwise from an oligoclase to an albite rim, or the composition of the core gradually increases outward from An_{19} to An_{24}, then abruptly drops to an albite rim. All of these phenomena are in rocks at grades below the appearance of chloritoid and garnet. Above the garnet isograd the zoning is simple, with a core of An_{13} and a gradual outward increase to a maximum of An_{25}. It is estimated that the rocks were metamorphosed at no more than 350° C, and a few kilometers overburden, well below the peak of the peristerite solvus as estimated by Crawford (1966) and others. Metastable crystallization is indicated, although there are no data to distinguish whether a single or double stage of metamorphism was involved.

Spear (1977, 1980) observed two-plagioclase assemblages in hornblende–plagioclase calc-silicates and amphibolites (Mt. Cube Quadrangle, New Hampshire and Vermont) that provide evidence for a miscibility gap in the range $An_{39\pm3}$–$An_{88\pm3}$ at an estimated temperature of 530° C. There is a systematic partitioning of Na and Ca between plagioclase and the M4 site of coexisting hornblende with Na enriched in the feldspar. The two-feldspar assemblages are associated with low-Na hornblende, Na $= 0.07\pm0.04$ in the M4 site. At another locality the association albite and oligoclase is manifested by an absence of tie-lines from hornblende to plagioclase in the range An_2–An_{14}; the estimated temperature is 490° C.

Wenk (1979a) further estimated the influence of metamorphic grade on the nature of the intermediate plagioclase superstructure (An_{30}–An_{70}), chiefly by 0*kl* precession X-ray photography, determining the wavelength of the superstructure in metamorphic plagioclases from the central Alps. Wenk observed wavelength variation with temperature (metamorphic grade) of a periodic APB structure in the plagioclases, and considers this to be the result of a continuous ordering process. The wavelength changes from 20 to 70Å over the temperature range 500–800° C, and Wenk suggested that this may be a useful indicator of metamorphic grade. Wenk (1979b) also reported on the assemblage albite (An_0)–anorthite (An_{95}), plus actinolite and pargasite, and clinozoisite. This ultimate plagioclase assemblage is in low-grade poikiloblastic amphibolite schists from an ophiolite series near the Tertiary Bergell granite of the central Alps. Using TEM, Wenk's conclusion from the APB evidence is that albite and anorthite are formed from decomposition of intermediate plagioclase in the amphibolite with pargasitic hornblende coexisting with actinolite, and that the anorthite is not a relic. Wenk is unable to explain the assemblage, but feels that anorthite must be stable under some metamorphic conditions.[1]

Finally, and to return to the heterogeneous view, Lindh (1978) attempted a thermodynamic treatment of the complex system involving plagioclase and pointed out the complexities of plagioclase–zoisite thermometry, stressing the need to know what decomposition products are in equilibrium with anorthite. As did many previous writers, he assumed a strong stabilizing influence of Na in the

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[1] Dexter Perkins III (personal communication) has observed associations of albite and An_{65} in amphibolites from Quebec, also in the presence of hornblende and a sodic or pargasitic hornblende. The calcic plagioclase is in blebs at or near the contact of the original hornblende and the sodic (and Fe-rich) hornblende derived from it. The presumption is that the albite is the stable feldspar, and the calcic plagioclase was formed in association with the secondary sodic amphibole.

plagioclase structure, and suggested that the stepwise increase in anorthite content reported by many is in part caused by a changing mineral paragenesis and not necessarily only by discontinuities in the plagioclase crystal structure.

In addition to being structurally complex, the plagioclase feldspars in any process involving structural or compositional change must undergo diffusive reorganization that requires breaking the very strong Si–O and Al–O bonds (Goldsmith, 1952). The refractory behavior of plagioclases, coupled with multiple levels or even a continuum of metastable states and a variety of paths available toward various lower-energy ordered configurations, breeds complexity and variability. Newton *et al.* (1980), in investigating the thermochemistry of high structural state plagioclases, observed "fine structure" in the enthalpy data, particularly in hydrothermally crystallized specimens. It was stated that the variations may be real, inasmuch as plagioclase is a very complex substance and could well show various small thermodynamic "events" at various compositions, such as local ordering. Recent and current observations on plagioclases are rapidly enlarging our descriptive bank, even if understanding lags somewhat behind. Omitted from this review are all the theoretical and structural papers, as well as a host of recent transmission electron microscope (TEM) and associated electron diffraction (and X-ray diffraction) studies (going back to McLaren, 1974; McConnell, 1974a, b; Nissen, 1974; Nord *et al.*, 1974), even though they may relate to the subject of plagioclase stability.

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References

Ackermand, D. and Morteani, G. (1973) Occurrence and breakdown of paragonite and margarite in the Greiner Schiefer Series (Zillerthaler Alps, Tyrol). Contributions to Mineralogy and Petrology, 40, 293–304.

Ambrose, J. W. (1936) Progressive kinetic metamorphism in the Missi series near Flinflon, Manitoba. American Journal of Science, 32, 257–286.

Becke, F. (1913) Über Mineralbestand und Struktur der Kristallinischen Schiefer. Akademie der Wissenschaften, Vienna. Mathematisch-Naturwissenschaftliche Klasse. Denkschiften, 75, 1–51.

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.

Braun, E. and Müller, G. (1975) Zur chemischen Variabilität regionalmetamorph gebildeter Plagioklase, Epidote und Granate. Contributions to Mineralogy and Petrology, 52, 193–211.

Brown, W. L. (1960) The crystallographic and petrological significance of peristerite unmixing in the acid plagioclases. Zeitschrift für Kristallographie, 113, 330–344.

Brown, W. L. (1962) Peristerite unmixing in the plagioclases and metamorphic facies series. Norsk Geologisk Tidsskrift, 42 (Feldspar volume), 354–382.

Byerly, G. R. and Vogel, T. A. (1973) Grain boundary processes and development of metamorphic plagioclase. Lithos, 6, 183–202.

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.

Christie, O. H. J. (1959) Note on the equilibrium between plagioclase and epidote. Norsk Geologisk Tidsskrift, 39, 268–271.

Christie, O. H. J. (1962) Feldspar structure and the equilibrium between plagioclase and epidote (discussion). American Journal of Science, 260, 149–153.

Cole, W. F., Sörum, H. and Taylor, W. H. (1951) The structure of the plagioclase felspars, I. Acta Crystallographica, 4, 20–29.

Cooper, A. F. (1972) Progressive metamorphism of metabasic rocks from the Haast Schist group of southern New Zealand. Journal of Petrology, 13, 457–492.

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.

DeVore, G. W. (1956) Al–Si positions in ordered plagioclase feldspars. Zeitschrift für Kristallographie, 107, 247–264.

Doman, R. C., Cinnamon, C. G. and Bailey, S. W. (1965) Structural discontinuities in the plagioclase feldspar series. American Mineralogist, 50, 724–740.

Evans, B. W. (1964) Coexisting albite and oligoclase in some schists from New Zealand. American Mineralogist, 49, 173–179.

Fleet, S. G. and Ribbe, P. H. (1965) An electron-microscope study of peristerite plagioclases. Mineralogical Magazine, 35, 165–176.

Frey, M. and Orville, P. M. (1974) Plagioclase in margarite-bearing rocks. American Journal of Science, 274, 31–47.

Garrison, J. R., Jr. (1978) Plagioclase compositions from metabasalts, southeastern Llano uplift: plagioclase unmixing during amphibolite-grade metamorphism. American Mineralogist, 63, 143–149.

Gay, P. and Smith, J. V. (1955) Phase relations in the plagioclase felspars: composition range An_0 to An_{70}. Acta Crystallographica, 8, 64.

Ghent, E. D. and De Vries, C. D. S. (1972) Plagioclase-garnet-epidote equilibria in hornblende-plagioclase bearing rocks from the Esplanade Range, British Columbia. Canadian Journal of Earth Sciences, 9, 618–635.

Goldsmith, J. R. (1952) Diffusion in plagioclase feldspars. Journal of Geology, 60, 288–291.

Grove, T. L. (1977) Structural characterization of labradorite-bytownite plagioclase from volcanic, plutonic and metamorphic environments. Contributions to Mineralogy and Petrology, 64, 273–302.

Hörmann, P.-K. and Raith, M. (1973) Bildungsbedingungen von Al–Fe (III)–Epidoten. Contributions to Mineralogy and Petrology, 38, 307–320.

Höy, T. (1976) Calc-silicate isograds in the Riondel area, southeastern British Columbia. Canadian Journal of Earth Sciences, 13, 1093–1104.

Hunahashi, M., Kim, C. W., Ohta, Y. and Tsuchiya, T. (1968) Co-existence of plagioclases of different compositions in some plutonic and metamorphic rocks. Lithos, 1, 356–373.

Köhler, A. (1942a) Die Abhängigkeit der Plagioklasoptik vom vorangeagangen Wärmeverhalten. Tschermaks Mineralogische und Petrographische Mitteilungen, 53, 24–49.

Köhler, A. (1942b) Drehtischmessungen an Plagioklaszwilling von Tief-und Hochtemperaturoptik. Tschermaks Mineralogische und Petrographische Mitteilungen, 53, 159–179.

Kretz, R. (1963) Note on some equilibria in which plagioclase and epidote participate. American Journal of Science, 261, 973–982.

Larsson, W. (1941) Petrology of interglacial volcanics from the Andes of northern Patagonia. Bulletin of the Geological Institution of the University of Upsala, 28, 191–405.

Laves, F. (1951) Relationship between exsolved plagioclase and its host. American Crystallographic Association, (abstr.) Washington Meeting, 33.

Laves, F. (1954) The coexistence of two plagioclases in the oligoclase compositional range. Journal of Geology, 62, 409–411.

Lindh, A. (1978) Aspects on plagioclase–epidote thermometry. Neues Jahrbuch für Mineralogie Abhandlungen, 133, 113–131.

Lyons, J. B. (1955) Geology of the Hanover quadrangle, New Hampshire–Vermont. Geological Society of America Bulletin, 66, 105–146.

McConnell, J. D. C. (1974a) Analysis of the time-temperature-transformation 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. (1974b) Electron-optical study of the fine structure of a schiller labradorite. In W. S. MacKenzie and J. Zussman, Eds., The Feldspars, p. 478–490. Manchester University Press, Manchester, England.

McLaren, A. C. (1974) Transmission electron microscopy of the feldspars. In W. S. MacKenzie and J. Zussman, Eds., The Feldspars, p. 378–423. Manchester University Press, Manchester, England.

Misch, P. (1968) Plagioclase compositions and non-anatectic origin of migmatitic gneisses in northern Cascade Mountains of Washington State. Contributions to Mineralogy and Petrology, 17, 1–70.

Morteani, G. and Raase, P. (1974) Metamorphic plagioclase crystallization and zones of equal anorthite content in epidote-bearing, amphibole-free rocks of the western Tauernfenster, eastern Alps. Lithos, 7, 101–111.

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.

Nissen, H.-U. (1974) Exsolution phenomena in bytownite plagioclases. In W. S. MacKenzie and J. Zussman, Eds., The Feldspars, p. 491–521. Manchester University Press, Manchester, England.

Noble, D. C. (1962) Plagioclase unmixing and the lower boundary of the amphibolite facies. Journal of Geology, 70, 234–240.

Nord, G. L., Jr., Heuer, A. H. and Lally, J. S. (1974) Transmission electron microscopy of substructures in Stillwater bytownites. In W. S. MacKenzie and J. Zussman, Eds., The Feldspars, p. 522–535. Manchester University Press, Manchester, England.

Phillips, E. R., Chenhall, B. E., Stone, I. J. and Pemberton, J. W. (1977) An intergrowth of calcic labradorite in a plagioclase–quartz–biotite gneiss from Broken Hill, New South Wales. Mineralogical Magazine, 41, 469–471.

Rambaldi, E. R. (1973) Variation in the composition of plagioclase and epidote in some metamorphic rocks near Bancroft, Ontario. Canadian Journal of Earth Sciences, 10, 852–868.

Ramberg, H. (1943) En undersøkelse av Vestrandens regionalmetamorfe bergarter. Norsk Geologisk Tidssdrift, 23, 1–174.

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. (1960) An X-ray and optical investigation of the peristerite plagioclases. American Mineralogist, 45, 626–644.

Ribbe, P. H. (1962) Observations on the nature of unmixing in peristerite plagioclases. Norsk Geologisk Tidssdrift, 42 (Feldspar volume), 138–151.

Rutland, R. W. R. (1961) The control of anorthite content of plagioclase in metamorphic crystallization. American Journal of Science, 259, 76–79.

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.

Spear, F. S. (1977) Evidence for a miscibility gap in plagioclase feldspar in the composition range An_{39}–An_{88}. Carnegie Institution of Washington Yearbook, 76, 619–621.

Spear, F. S. (1980) NaSi $\rightleftarrows$ CaAl exchange equilibrium between plagioclase and amphibole. Contributions to Mineralogy and Petrology, 72, 33–41.

Taylor, W. J., Darbyshire, J. A. and Strunz, H. (1934) An X-ray examination of the feldspars. Zeitschrift für Kristallographie, 87, 464–498.

Tsuji, S. (1966) Possible effects of peristerite solvus in plagioclase of the Higo metamorphics, Kyushyu, Japan. Journal of the Geological Society of Japan, 72, 63–68.

Waard, D. de (1959) Anorthite content of plagioclase in basic and pelitic crystalline schists as related to metamorphic zoning in the Usu massif, Timor. American Journal of Science, 257, 553–562.

Wenk, E. (1962) Plagioklas als Indexmineral in den Zentralalpen Die Paragenese Calcit-Plagioklas. Schweizerische Mineralogische und Petrographische Mitteilungen, 42, 139–152.

Wenk, E. and Keller, F. (1969) Isograde in Amphiboliterserien der Zentralalpen. Schweizerische Mineralogische unde Petrographische Mitteilungen, 49, 157–198.

Wenk, E. and Wenk, H.-R. (1977) An-variation and intergrowths of plagioclases in banded metamorphic rocks from Val Carrechio (Central Alps). Schweizerische Mineralogische und Petrographische Mitteilungen, 57, 41–57.

Wenk, E., Wenk, H.-R., Glauser, A. and Schwander, H. (1975) Intergrowth of andesine and labradorite in marbles of the central Alps. Contributions to Mineralogy and Petrology, 53, 311–326.

Wenk, H.-R. (1979a) Superstructure variation in metamorphic plagioclase. American Mineralogist, 64, 71–76.

Wenk, H.-R. (1979b) An albite-anorthite assemblage in low-grade amphibolite facies rocks. American Mineralogist, 64, 1294–1299.

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