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GRAIN BOUNDARY PROCESSES AND DEVELOPMENT OF METAMORPHIC PLAGIOCLASE

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GARY RAY BYERLY

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GRAIN BOUNDARY PROCESSES AND DEVELOPMENT OF METAMORPHIC PLAGIOCLASE

by

Gary Ray Byerly

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Grain boundary processes and development of metamorphic plagioclase

GARY R. BYERLY & THOMAS A. VOGEL

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Plagioclase from a progressively metamorphosed granodiorite changes as the metamorphic grade increases. Lower grade plagioclase are chemically inhomogeneous, with zoned rims containing distinct compositional levels of An_{0-3}, An_{17}, and An_{25}. As grade increases the plagioclase becomes more chemically homogeneous with An_{0-3} rims dominating. Microcline inclusions are controlled by internal defects at lower grades and grain boundaries at higher grades. Myrmekite rims are developed at the highest grade. Rims are dependent on surface energy factors and occur at triple points, high angle lattice misfits and other high energy surfaces. At low grades, rims form at plagioclase–plagioclase contacts and at higher grades, at plagioclase–microcline contacts. These changes are due to impurity segregation and grain boundary migration, and an increase of the latter process at higher grades.

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Most rocks have a considerable component of their genesis linked to solid state processes, and these processes control most of lithification, diagenesis, and metamorphism. In igneous rocks, especially plutonic rocks, there is the period of slow cooling in which many solid state phenomena must occur. Metamorphic rock textures are almost entirely controlled by solid state processes.

The most noticeable phenomena of the solid state are those associated with the grain boundaries of polycrystalline aggregates. An understanding of boundary or surface energy as well as some clarification of the exact nature of boundaries is of fundamental importance in the study of the solid state. From a petrologic point of view the most important solid state processes are grain boundary migration along with impurity segregation.

Plagioclase is most responsive to solid state processes. Because of its complexities, both with respect to composition and structure, it exhibits a wide range of characteristics during metamorphism. Features such as albite rimming, occurrence of discrete compositional zoning, development of antiperthite and myrmekite and presence of nonstochiometry are all common to plagioclase in the metamorphic environment. All of these characteristics have been an enigma in interpreting the petrogenesis of metamorphic rocks.

The purpose of this paper is to develop a model of grain boundary migration and impurity segregation and show how this model explains the characteristic features of plagioclase in metamorphic rocks.

Grain boundary processes

Grain boundary processes control the bulk properties of polycrystalline materials to such a degree that they have been studied quite extensively for application to industrial materials. This research has become a cornerstone of metallurgy, where the solid phases are simple metallic systems and empirical results fit the theories well. In contrast, ceramics, which consist of the more complex ionic and covalent compounds, has not developed as sophisticated a theory for the role of grain boundaries in solid state processes. Even so, grain boundaries are recognized as exerting a pronounced effect on the properties of the aggregate and greatly effect the kinetics of most solid state processes within the aggregate (Westbrook 1967). Natural silicate systems are the most complex of ceramic systems and little work has been done specifically towards understanding the role of grain boundary processes.

Model

A grain boundary may be defined as the zone separating two crystals that differ in crystallographic orientation, composition, or dimensions of the crystal lattice (McLean 1957). The physical gap is considered to be less than two or three atomic radii; however, the physical effects, most notably lattice strain, associated with a boundary may extend up to 50 μ into the crystal (Westbrook 1967). The strained lattices, which result from this boundary, add energy to the system which is generally called surface or grain boundary energy. This quantity is much smaller than the other sources of energy when considering the thermodynamics of reactions, however, it is widely accepted that in solid state reactions, surface energy plays a significant role.

Surface energy

Grain boundary migration and impurity segregation are directly controlled by surface energy. The surface energy associated with a given boundary is a function of the geometry of the boundary, orientation, specific type of phase to phase contact, distribution of impurities, and pressure and temperature. The geometrical component in the variation of surface energy is due to differences in grain boundary curvature. Areas of high curvature will have the highest associated surface energy. For this reason triple points will be areas of much higher energy. Grain size and shape thus contribute to the surface energy of an aggregate by regulating the amount of surface area and also the curvature of the boundaries.

To characterize the orientation of a specific boundary requires three parameters for each of the two opposing lattices, and two parameters for the boundary. The two opposing lattices may be coherent, random high angle, or in a 'twin' orientation (i.e. a specific low energy high angle orientation). Concurrently the boundary may be coherent with one of the lattices, random to both, or in some special low energy orientation intermediate to both lattices.

Energies will be lowest for coherent, 'twin', and special boundary orientations. The specific type of phase to phase contact certainly affects surface energy but the exact nature of this effect is not well understood. The meager experimental data on this indicate that unlike phase boundaries occur significantly more than expected from a random distribution of phases. This means that, at least in many cases, unlike phase boundaries are more stable than like phase boundaries (White 1968).

The effect of impurity additions to fired ceramics can drastically change their growth characteristics, controlling both grain sizes and phase distributions. Thermodynamically any impurity added to a boundary should lower the surface energy, however, some experimental evidence is in direct contradiction to this. White (1968) finds that while the addition of Cr_2O_3 to a fired ceramic decreases the apparent surface energy — a similar addition of Fe_2O_3 increases it. Experiments conducted by Gordon & Vandermeer (1966) on the coupled effects of orientation and impurities suggest that random high angle (high energy) boundaries segregate impurities to a much larger degree than the low energy type boundaries. The resulting effect is enough to make the random high angle boundaries significantly lower in surface energy than the coherent, 'twin', and special boundaries. Thus empirical evidence indicates that high energy boundaries can be stabilized by impurity segregation.

Impurity segregation

Impurity segregation can be considered to be any diffusional process which tends to segregate an impurity to some high energy area of the crystal, generally grain boundaries or internal defects. Westbrook (1967) has reviewed the subject so it will only be summarized here. The model which explains the observed thickness (up to 50 μ) of impurity segregated boundaries is one which calls on a diffusional coupling of vacancies and solute atoms. Westbrook represents the reaction thus:

$$\square + S_I \rightleftarrows S_S$$

where $\square$ is a vacancy, S_I an interstitial solute ion, and S_S a substitutional solute ion. Increasing temperature drives the reaction to the right by the thermal injection of vacancies. During the period of annealing solute ions are forced from their substitutional sites to interstitial sites coupled with a newly formed vacancy. This coupled vacancy–impurity will diffuse together through the lattice.

The grain boundary or internal defects act as sinks for vacancies and so a concentration gradient will form near these. As the vacancies are annihilated at the sinks a buildup of the impurity occurs. The large variation in diffusion rates between the variously sized and charged ions coupled to vacancies complicates this process. Westbrook further notes that impurity segregation often results in deviations from true stoichiometric proportions within a crystal.

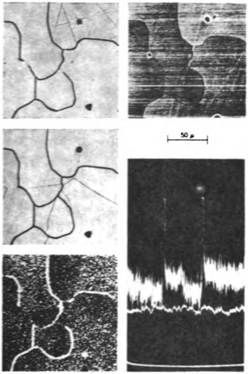

Fig. 1. Distribution of Fe in TaC + 1wt% Fe hot pressed 80 min at 2600 °C and 300 Kg/cm^2. *Upper left,* light micrograph; *middle left,* schematic diagram; *lower left,* FeK$_\alpha$ X-ray microprobe image; *upper right,* microprobe sample current; *lower right,* line scan for FeK$_\alpha$ (upper trace = FeK$_\alpha$, middle trace = background, lower trace = zero).

Note the impurity depleted zones, high impurity grain boundaries, and twin-like internal boundaries between the interior grain and the impurity swept outer zone. (From M. Klerk, in *The Electron Microprobe* edited by T. K. McKinley et al. Copyright © 1966, John Wiley & Sons, Inc.)

Grain boundary migration

Grain boundary migration is a movement of the boundary zone in response to a driving force, mechanical or chemical, resulting in a lowering of the free energy of the system. The velocity of migration is a function of the mobility of the boundary, essentially diffusion controlled, and the driving force, largely supplied by the reduction in surface energy as a result of the new boundary curvature, orientation, or phase to phase contacts.

The atomic movement in grain boundary migration may be quite simple. Diffusion over a distance of only a few atomic radii is all that is required for like phase boundaries. For unlike phase boundaries the diffusion must occur over much greater distances. Difficulties arise for complex compounds where diffusional rates for individual ionic species vary greatly. For pure materials geometry and orientation will control surface energy and thus grain boundary migration rates. For materials with impurities present, either as thin films, impurity segregated zones, or as a dispersed minor phase, grain boundary migration will be controlled by the distribution and amount of the impurity. The general effect of impurities is to lower surface energy and thus inhibit grain boundary migration. A nonuniform distribution of impurities will lead to nonuniform growth in an aggregate, or even in a single boundary.

The disappearance, by solution or breakdown, of a minor phase may cause 'unlocking' of boundaries and rapid readjustments in textures (Burke 1968).

This may be responsible for runaway grain growth, for example, the development of porphyroblasts in metamorphic rocks. For a particular boundary that is locked or slowed down by impurities, an increase in driving force, supplied by rising temperature or increased boundary curvature, causes the boundary to break away from the impurities it has been carrying. This results in low impurity areas separated by impurity rich areas parallel to the moving boundary. An interesting example of this is provided by work done by M. Klerk & E. Roeder (1966) using the microprobe to analyze the effect of impurities on grain boundary migration in ceramics (Fig. 1). Fig. 1 shows an impurity depleted zone and high impurity boundaries produced by grain boundary migration. Also to be noted are the internal boundaries between the normal impure grain and the impurity depleted zone. This may be some type of structural readjustment to the compositional boundary or could be a relict of the original boundary location. Klerk & Roeder found that these phenomena were quite dependent on the amount and type of impurity present in the ceramic, but more importantly on the cooling history of the material. This phenomena was only observed when a period of slow cooling followed the firing of the ceramic.

Evaluation of the model

The importance of this model lies in its ability to be tested in a number of ways and for a variety of materials — both synthetic and naturally occurring. DeVore (1955, 1959) and Voll (1960) both concluded that surface energy and the grain boundary phenomena controlled by it, were of major importance in petrologic systems. DeVore (1959) stated that nucleation sites, nucleation frequencies, extent of grain growth, and possibly modal composition could be controlled by surface energy. Sturt (1970) observed that intergranular plagioclase precipitated on select contacts only at a distance from a thermal contact whereas closer to the contact the intergranular plagioclase was ubiquitous. Sturt's (1970) data indicate that surface energy effects, while strong, are overcome by a large influx of thermal energy.

The strong dependence of surface energy on the geometrical properties of an aggregate has led to investigations by several in the field of petrology. Kretz (1966) observed that triple points in metamorphic rocks were in positions for theoretical minimum surface energy. Ehrlich et al. (1972) found a strong response of surface area and grain shape to a metamorphic gradient. Exact phase to phase relationships have been tested by several petrologists. Flinn (1969) has shown that in metamorphic rocks unlike contacts are statistically favored over like contacts at a high level of significance. This observation agrees with White's (1968) data on phase distributions in ceramics. From theoretical reasoning unlike phases should be higher energy because of the greater mismatch of lattices. The only explanations for Flinn's and White's observations can be: (1) the increased effect of impurities on lower-

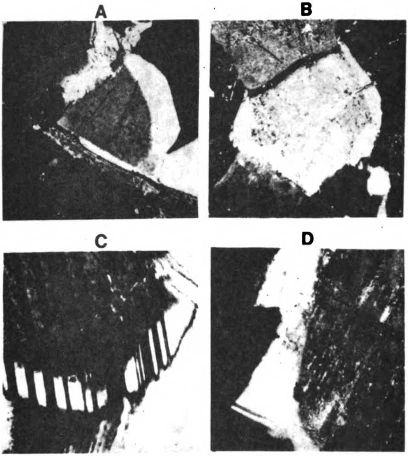

Fig. 2. (A) Central grain is plagioclase with large rim at contact with the microcline grain at right and much smaller rim at contact with biotite grain at bottom (about 300 ×).
(B) Central plagioclase grain has developed rims at contacts with plagioclase grains to right and left of it. Upper plagioclase grain has developed a rim in contact with the central grain (about 300 ×).
(C) Basal termination of plagioclase with microcline contact resulting in large distinct rim (about 300 ×).
(D) Plagioclase (right) with blocky rim developed at microcline contact. Boundary is distinctly controlled by lattice of plagioclase as noted from twinning and cleavage (about 400 ×).

ing the surface energy for the unlike boundaries (similar to the effect noted by Gordon & Vandermeer (1966) on random high angle boundaries above), (2) higher activation energy for unlike boundaries due to differences in crystal structure and chemical composition whereas like boundaries have low activation energies with the source material for diffusion being available in the immediate vicinity of the boundary. In other words, the low-energy like boundaries are more mobile than the high-energy unlike boundaries due to differences in activation energies.

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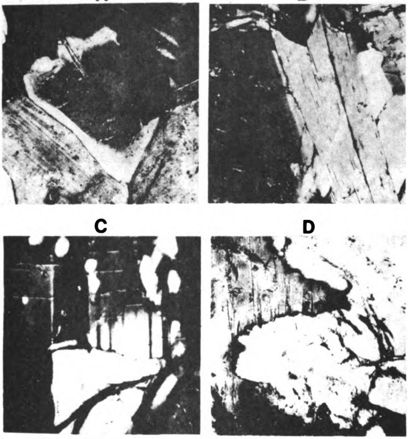


Fig. 3. (A) Plagioclase (central) developing rims at contacts with microcline (lower left, lower right, upper left). No rim at biotite (right) contact. Note increase in size of rim near the higher energy area of the triple point (about 150×).
(B) Plagioclase (left) contact with biotite (right). Note the twin-like laminae which make up the rim at this contact. Each of these lamina are compositionally distinct units, the outer lamina at An_{0-3}, the middle lamina at An_{17}, and the interior of the grain is An_{25} (about 300×).
(C) Plagioclase (upper) in contact with microcline. Rim has developed along portion of contact. Also note development of large quartz blebs in the plagioclase (about 300×).
(D) Plagioclase (right) in contact with microcline. Pluglike growth into the microcline is also characterized by the development of fine myrmekite quartz near the boundary (about 300×).

Grain boundary response to a metamorphic gradient: Plagioclase in the Cross Lake Gneiss

The relationships discussed in this paper are part of a study of the effects of metamorphism on the Cross Lake Gneiss in the Grenville Provence of south-eastern Ontario (Chapman 1968, Ehrlich et al. 1972). This gneiss is a lenticular granodioritic pluton that has intruded and cooled before

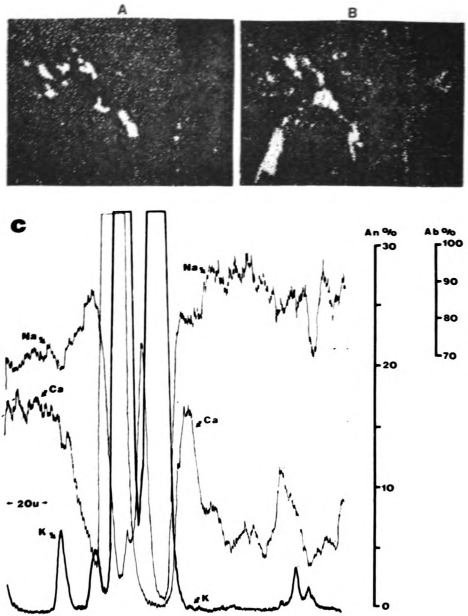


Fig. 4. From upper greenschist facies. Electron microprobe, scale 20μ per division, quartz grain in uppermost right corner, plagioclase–plagioclase boundary running from upper right corner to middle bottom. (All microprobe analyses were made with an ARL EMX microprobe with a beam diameter of about 0.5 micron.)

(A) Ca-K_α X-ray microprobe image. Note calcite blebs occurring within plagioclase.

(B) K-K_α X-ray microprobe image. Note large microcline blebs occurring with calcite within the plagioclase grain.

(C) Mid-north-south microprobe line traverse across the middle of the field for Ca, Na, and K. Note the dominance of the An_{17} and An_{0-3} levels, and the changes in plagioclase composition near the blebs.

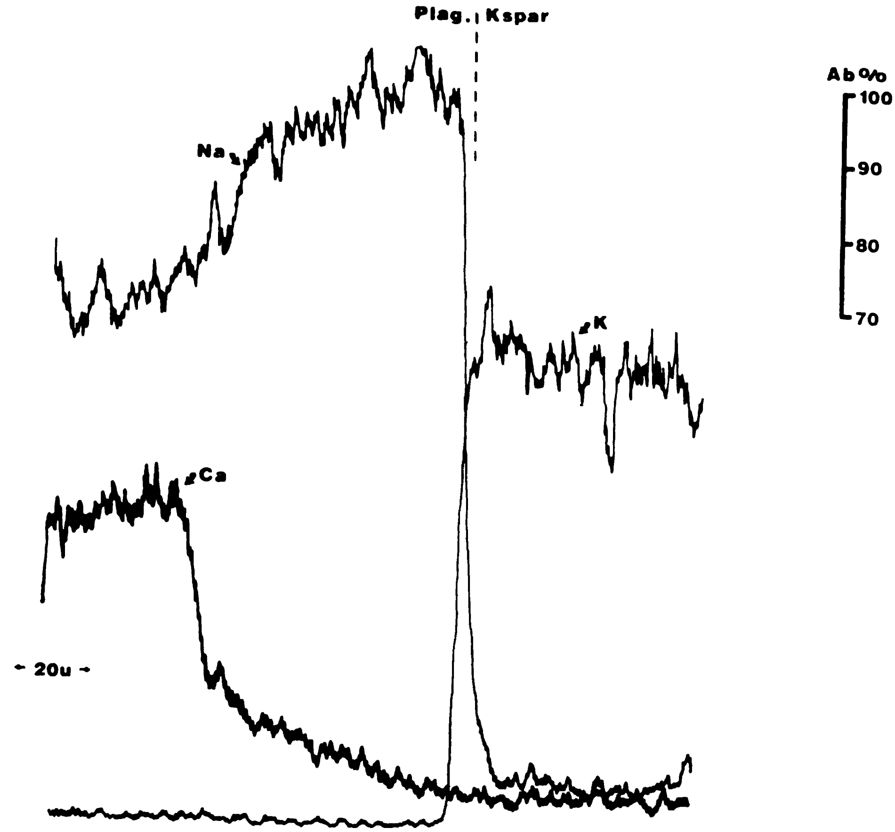


Fig. 5. From lower amphibolite facies. Microprobe line traverse across plagioclase–microcline boundary for Ca, Na, and K. Note sharp discontinuity between An_{25} core and An_{0-3} rim.

being subjected to a metamorphic gradient ranging from upper greenschist to middle amphibolite facies (Chapman 1968). These conditions are ideal for a study of phase boundary reactions in response to a regional metamorphic gradient.

The earlier studies indicate a very good response of textural variables to the gradient. Ehrlich et al. (1972) find that both shape and surface area of plagioclase grains are more effective in defining the gradient than are standard compositional variables. Rimmed plagioclases occur over the complete range of metamorphic conditions. Several observations are common to all samples.

1. The rims are crystallographically coherent to a plagioclase host.
2. The development of plagioclase rims is dependent on the neighboring phase at the boundary (Fig. 2A). There is an observed order of preference in the phase to phase boundaries at which the plagioclase rims develop and extent to which they develop. The order for a given sample is dependent on position in the gradient.

3. Development of the rims is related to the relative lattice orientations of the two phases determining the boundary. High angle lattice misfits have the best developed rims (Fig. 2B). Any contacts involving the basal terminations of plagioclase grains are highly favored as sites (Fig. 2C).
4. The plagioclase rim is not of uniform thickness over any specific contact. This results from a tendency of the interphase boundary to minimize the angle of misfit with one or both of the lattices involved in the contact. The adjustment of boundary curvature and triple-point relationships add to this effect (Figs. 2D and 3A).

Upper greenschist facies

Grain boundary relationships of plagioclase from the upper greenschist facies are the most variable and contain rims which are relatively large in comparison to their grain diameter (e.g. up to $\frac{1}{4}$ of their grain diameter). The microprobe study shows that plagioclase rims from this metamorphic grade vary in composition with two distinct compositions near An_{0-3} and An_{17} (Fig. 4C). The cores are generally near An_{25}. All three compositional levels may be observed in a single grain. The type of grain boundary influences the width or in many cases the very presence of a rim. For example, plagioclase–plagioclase boundaries have the largest and most widespread development of rims, with minor rims at plagioclase–microcline and plagioclase–biotite boundaries.

Calcite and microcline inclusions occur within the plagioclase cores and the rims of An_{17} composition, but they rarely occur with the albitic rims (Fig. 4). These inclusions form along interior structural defects and boundaries, and often have haloes of a more sodic or calcic composition than the plagioclase host.

Compositionally inhomogeneous and nonstoichiometric plagioclase grains are characteristic of this metamorphic grade (Fig. 4). The inhomogeneities appear to be due to annealing or sintering of several grains together, leaving relict boundaries in the interior.

Lower amphibolite facies

In contrast to the upper greenschist facies, plagioclase in the lower amphibolite facies have rims that are optically more distinct, having sharp boundaries with the host plagioclase (Fig. 5). Also, in contrast to the lower grade rocks, the most favorable site for rim development is plagioclase–microcline, with minor plagioclase–plagioclase, plagioclase–biotite, and rare plagioclase–quartz rims. In general the plagioclase at this grade are more stoichiometric and more compositionally homogeneous than the lower grade.

The three compositional levels (An_{0-3}, An_{17}, An_{25-30}) (Fig. 6) are present but the An_{0-3} level occurs more frequently here than at the lower levels.

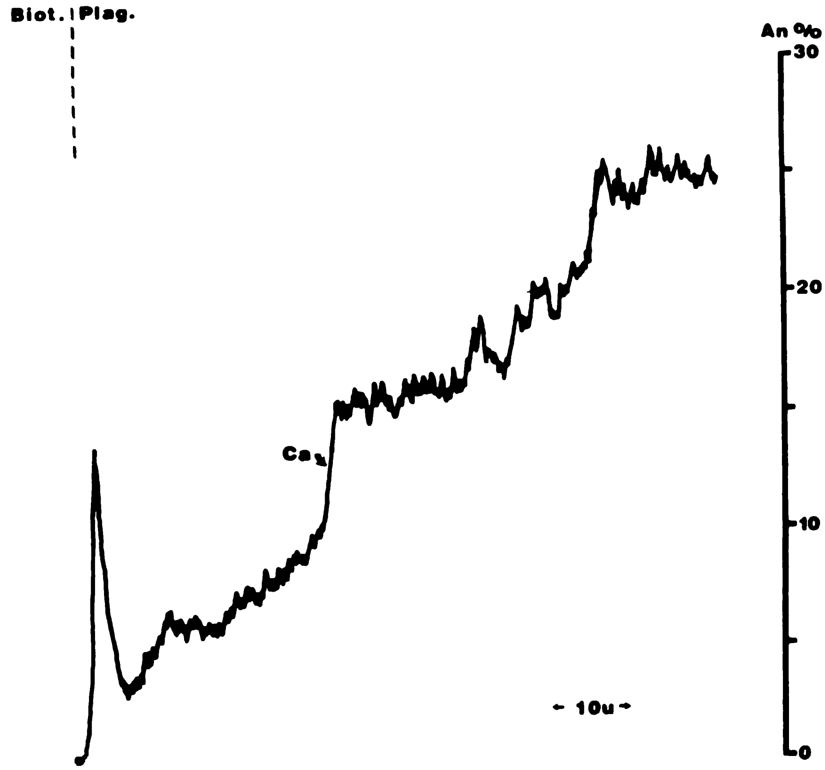


Fig. 6. From lower amphibolite facies. Microprobe line traverse across biotite–plagioclase boundary for Ca. Note distinct composition zones near boundary; also high calcium boundary.

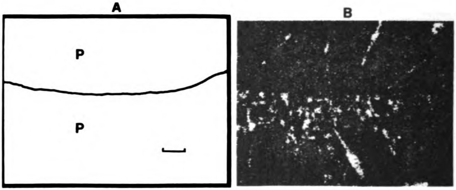
Occasionally an increase in An content is observed at the outermost rim but this is much better developed at higher grades.

Compositionally distinct twin-like, laminae are developed, most noticeably at biotite–plagioclase boundaries (Fig. 3B). The composition of the lamina at the boundary is An_{0-3}, with the adjacent lamina being An_{17} and the interior part of the plagioclase An_{25} (Fig. 6).

In contrast to the lower grade plagioclase, the microcline inclusions of this middle grade are controlled more by the external grain boundaries, whereas in the lower grades these are more controlled by internal defects (Fig. 7). In both grades the albite rims are free of microcline impurities. Small quartz blebs also occur as impurities at this grade, but these are much better developed in the higher grade rocks.

Middle amphibolite facies

The plagioclase from the middle amphibolite facies, when compared to the upper greenschist and lower amphibolite grades, are chemically more homogeneous and, except for rare occasions, contain rims only at plagioclase–



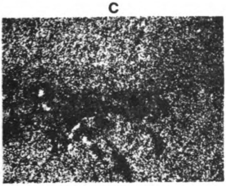
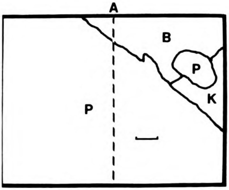
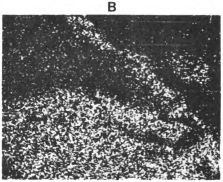


Fig. 7. From lower amphibolite facies.
(A) Sketch from electron microprobe sample current photograph of plagioclase–plagioclase boundary. Bar equals 20 microns (P = plagioclase).
(B) K-K_α X-ray microprobe image. Note large amounts of microcline blebs near boundary.
(C) Ca-K_α X-ray microprobe image. Note calcium deficiency near microcline blebs (An_{0-3}) and near boundary.

microcline boundaries. These rims are more distinct and relatively small, when compared to the much larger grain sizes at this grade, the rims are generally An_{0-3} and the interior An_{25-30}. Microcline inclusions show the same general relationships as the lower amphibolite grades, being controlled by the external grain boundary rather than interior defects as in the lowest grade samples (Figs. 8 and 9). Calcic outer rims (An_{10-20}), a feature which was only rarely observed in the lower amphibolite facies, is a common occurrence in these rocks (Fig. 8). These calcic rims often contain quartz impurities as a myrmekitic intergrowth and often show a plug-like growth into the adjacent microcline grains (Figs. 10 and 3D).

In summary, the nature of the plagioclase grain boundaries change as the metamorphic grade increases. In the lower grades, the plagioclase are chemically inhomogeneous, showing continuous zoning on the rims as well as distinct compositional levels of An_{0-3}, An_{17} and An_{25-30} with some non-stoichiometry present. Rimming is most commonly developed on plagioclase–plagioclase grain boundaries. As the metamorphic grade increases, the plagioclase become chemically more homogeneous with An_{0-3} rims dominating and the most strongly developed rims on plagioclase–microcline boundaries. Concurrently the microcline inclusions vary from being associated with internal defects in the grains to being associated with the boundaries, near, but rarely in, the albite rims. At the highest grades calcic myr-





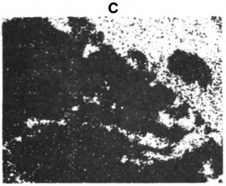
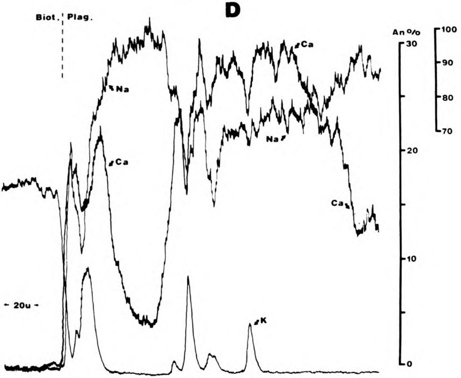


Fig. 8. From middle amphibolite facies.
(A) Sketch of electron microprobe sample current photograph. Bar equals 20 microns (P = plagioclase, B = biotite, K = microcline).
(B) Ca-K$_\alpha$ X-ray microprobe image. Note calcium deficiency in upper left (An_{0-3}) with higher calcium in outermost rim.
(C) K-K$_\alpha$ X-ray microprobe image. Defines biotite grain. Note large microcline grains parallel to sub-boundary between An_{25} and An_{0-3}.
(D) Mid-north-south microprobe line traverse for Ca, Na, and K.



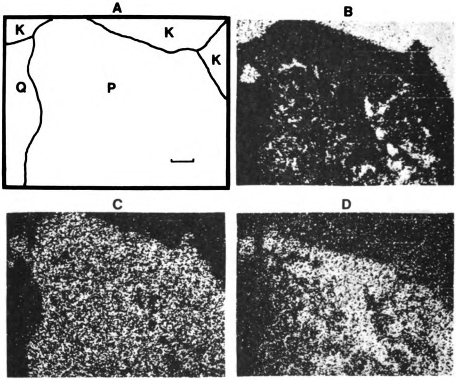
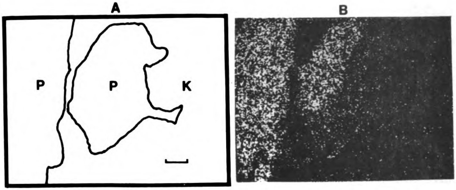


Fig. 9. From middle amphibolite facies.
(A) Sketch of electron microprobe sample current photograph (Q = quartz, others as above).
(B) K-K_α X-ray microprobe image. Note distribution within plagioclase, especially the heavy concentration parallel to the left plagioclase–microcline boundary; also the lack of microcline blebs in the An_{0-3} rim along the lower plagioclase–microcline boundary.
(C) Na-K_α X-ray microprobe image.
(D) Ca-K_α X-ray microprobe image. Note calcium deficiency near microcline blebs and low plagioclase–microcline boundary (An_{0-3}), and at plagioclase–quartz boundary (An_{17}).

mekitic rims are commonly present. Grain boundaries effect textural as well as compositional changes. The development of plagioclase rims is dependent on surface energy factors as can be seen by triple points, high angle lattice misfits, and lattice terminations all having the best development of rims. Surface energy effects are also shown to be important from the type of phase to phase boundary controlling the nature of the rim, although this in part may be a kinetic factor. It is found that these surface energy effects are present from upper greenschist to granulite facies conditions, a wide range of petrogenetic environments (this study and Ramberg 1962).

Discussion

Similar phenomena have been observed and discussed by a number of petrologists through the years. Ramberg (1962) notes albite rims forming at plagioclase–microcline and microcline–microcline contacts in amphibolite



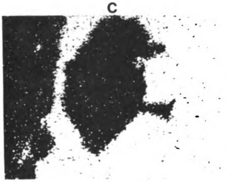


Fig. 10. From middle amphibolite facies.
(A) Sketch of electron microprobe sample current photograph. Note pluglike growth of plagioclase into microcline (legend as above).
(B) Ca-K_α X-ray microprobe image. Note deficiency of calcium in outer rim of plug (An_{0-3}).
(C) K-K_α X-ray microprobe image.

and granulite facies rocks. He suggests that they result from an oriented overgrowth of albite on microcline or plagioclase. Growth is always into an incoherent microcline and surface energy must control this process to some degree. He concludes that rims are a result of exsolving sodium from microcline, during metamorphism or slow cooling of a high temperature rock. Further evidence of a microcline source, he states, is the lack of rims at plagioclase–plagioclase or plagioclase–quartz boundaries. Hubbard's (1967) study of myrmekitic rims is based on a similar exsolution model. Vacancy controlled diffusion of sodium and calcium out of the microcline structure produces overgrowths at the plagioclase–microcline boundaries. Subsequent breakdown of the vacancy stabilized Schwanke's molecule $Ca(AlSi_3O_8)_2$ forms vermicular quartz within the overgrowth. A microprobe study of myrmekites by Widenfalk (1969) has shown concentration gradients of sodium and calcium within microcline grains — the edges being most depleted.

Though Ramberg and Hubbard suggest exsolution and grain boundary migration for their albite and myrmekitic rims, a simple grain boundary migration model will not explain the observations of the present study. Impurity segregation occurring simultaneously with grain boundary migration and diffusion from an external source for some of the material involved in the reactions must be incorporated into the model.

The phase to phase contacts at which plagioclase rims develop give some indication of the nature of the process involved. A model for microcline–microcline and microcline–plagioclase rims is grain boundary migration with material exchange across the boundary. This would require a simple oriented overgrowth of exsolving sodium and calcium, and a reorienting of the $AlSi_3O_8$ framework at the boundary. As noted by Ramberg (1962) this process should not lead to rim formation contacts other than those involving microcline.

The formation of rims at plagioclase–plagioclase, plagioclase–quartz, and plagioclase–biotite boundaries does not fit a simple grain boundary migration model. With respect to plagioclase–plagioclase boundaries, compositionally distinct rims on one or both sides of the boundary (as observed in the present study) cannot be the product of simple grain boundary migration. Because no readily available source exists for the albite, plagioclase–quartz and plagioclase–biotite, these rimmed boundaries cannot be produced by a simple grain boundary migration model with exchange of material across the interface as postulated for the microcline–plagioclase and microcline–microcline boundaries. Plagioclase–biotite boundaries are not ragged or embayed and show no evidence of being replaced. Thus grain boundary migration can only produce these rims if the biotite is being pushed in front of the migrating boundary. Material would need to be supplied from a source external to the migrating boundary.

The multi-process model

Six general observations concerning the composition of the rims need be explained by any model proposed for grain boundary phenomena in plagioclase.

1. There are three distinctly favored plagioclase compositions An_{25} in the host, with An_{17} and An_{0-3} in the rims. An_{17} is favored in the low grade rims and An_{0-3} in the high grade rims.
2. Rims and host are often nonstoichiometric and compositionally heterogeneous at the low grade, but are stoichiometric and homogeneous at the high grade.
3. In the albitic rims of the high grade samples there is often a calcium enriched outer rim.
4. The rims are continuous with the host at low grades but generally have a distinct sub-boundary with the host at higher grades.
5. There is an order of preference in the specific phase to phase contacts at which rims form. Plagioclase–plagioclase is favored at low grades, plagioclase–microcline at high grades.
6. The shape and continuity of the rim varies from low grade to high grade, being continuous along any one boundary at low grades and discontinuous with small plug shaped areas at the high grades. (It should be noted that the plug shaped rims are only at plagioclase–microcline boundaries.)

A model for the observed formation and variation of the rims that occur on plagioclase–plagioclase, plagioclase–quartz, and plagioclase–biotite boundaries involves grain boundary annealing which is a combination of impurity segregation, concurrent with grain boundary migration. That progressive metamorphism results in annealing is apparent from the continuous trend of highly heterogeneous plagioclase at low grades to very homogeneous plagioclase at high grades. Using the impurity segregation model, as described earlier in the paper, impurity ions are linked with vacancy sites in the crystal lattice and together they diffuse towards high energy areas of the crystal. The high energy areas are most notably the external grain boundary, but also include internal sub-boundaries, twin planes, and larger scale lattice defects.

In applying the impurity segregation model to these plagioclase rims, the question immediately becomes: which of the major elements can be considered an impurity within the plagioclase lattice? Potassium is an impurity and will be dealt with in detail below. Sodium and calcium can also be considered as impurities if An_{0-3}, An_{17} and An_{25} are optimum (i.e. low energy) structures for plagioclase compositions (Doman et al. 1965). Deviations from these compositions result in a higher total energy of the system, thus excesses of sodium and calcium above or below these compositions can be considered impurities in the model proposed above. Near grain boundaries or other high energy areas of the crystal, expulsion of the excess calcium or sodium readjusts the plagioclase to more stable compositions of An_{17} or An_{0-3}. In addition, from the observations presented above, the albitic rims (An_{0-3}) are more effective at lowering the boundary energy than the oligoclase (An_{17}) rims. The albitic rims, however, require more energy to form by the above mechanism since they require a much more drastic change in the aluminum–silicon ratio. This leads to the observed preference of An_{17} at the low grade and An_{0-3} at the high grade. The inability of the aluminum–silicon framework to readjust to low energy conditions may be the reason for the areas of nonstoichiometry within the plagioclase crystals at the low grades of metamorphism. At the higher grades there is an expulsion of the calcium to the boundaries, but under these high energy conditions the stoichiometry is maintained by a concomitant adjustment in the aluminum–silicon ratio resulting in the expulsion of silicon to form myrmekitic quartz intergrowths at the boundaries.

The development, with increasing metamorphic grade, of twin-like laminae consisting of an albite outer lamina, an An_{17} inner lamina, and an An_{25} host produces a pair of sub-boundaries at the An_{0-3}–An_{17} and An_{17}–An_{25} interfaces. These sub-boundaries must represent a structural readjustment to decrease the surface energy between these compositional zones within the crystal.

The change in order of preference of the specific phase to phase contacts with grade of metamorphism is due to a change in the dominant process forming the rims. Plagioclase–plagioclase boundaries first respond only to

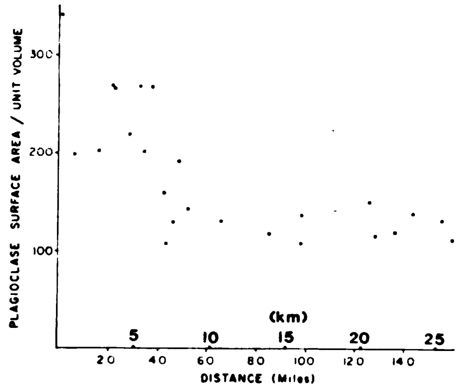


Fig. 11. Response of plagioclase surface area per unit volume to the metamorphic gradient. Ordinate is calibrated in square centimeters per cubic centimeter.

impurity segregation. A slight increase in grade causes a rapid readjustment of the plagioclase–plagioclase boundary network by grain boundary migration, eliminating the more mobile boundaries and resulting in a larger mean grain size for the plagioclase (Fig. 11). This rapid textural adjustment coincides with the upper limits of the greenschist facies. The remaining plagioclase–plagioclase boundaries respond very little above the greenschist facies. Conversely, below amphibolite facies, plagioclase boundaries with other phases are not mobile. The response of plagioclase-other boundaries is marked by impurity segregation and first occurs near the greenschist–amphibolite facies transition. The middle amphibolite grain boundary phenomena are largely controlled by grain boundary migration which is characterized by rapid plug-like growth into microcline of albitic and myrmekitic plagioclase. This change in the morphology of the rims from continuous at low grades (Fig. 2C), to blockly (Fig. 2D), to plug-like at the highest grades (Fig. 3D), is further evidence for the change in relative intensities of the two processes, grain boundary migration and impurity segregation.

The occurrence and distribution of microcline and quartz inclusions within the plagioclase can be explained by impurity segregation and grain boundary migration. The following observations are consistent with and support this model.

1. Potassium concentrations and microcline blebs in the plagioclase occur over the entire range of metamorphic conditions studied. They are often enclosed by potassium-free albitic or calcic haloes.
2. They occur within the host, or the An_{17} rim, but rarely within the An_{0-3} rim.
3. They generally form in groups parallel to the rim-host sub-boundary or the external boundary of the plagioclase.
4. In the low grade samples they occur with calcite.

Two general observations are made on the distribution of free quartz within plagioclase.

5. Free quartz first appears with annealed plagioclases — that is, only in homogeneous, stoichiometric plagioclases of the higher grades.
6. There are two types of free quartz: (1) large internal blebs and (2) small vermicular blebs associated with the outermost calcic rims in the high grade samples.

The potassium was present in the plagioclase, before metamorphism, as a homogeneously distributed impurity at concentrations of 2–4 mole percent orthoclase. During progressive metamorphism the potassium diffuses to high energy sites to form microcline. At internal boundaries and defects antiperthitic blebs form while at the grain boundary, new microcline grains are nucleated or additional growth of preexisting microcline occurs. Quartz blebs in the plagioclase are due to the breakdown of the vacancy stabilized Schwanke's molecule. These form as the vacancies diffuse to internal defects. This would be compatible with the association of quartz and annealed stoichiometric plagioclase. The vermicular quartz in the myrmekitic rims is formed in a like manner as the vacancy linked calcium is expelled from the albite rims to the boundary forming the more calcic and myrmekitic outer rim as vacancies are neutralized at the boundary.

The association of calcite and microcline interstitial to plagioclase probably results from migration of calcium to the same high energy areas that are segregating potassium. The occurrence of calcium as a carbonate indicates the ubiquitous presence of $CO_3^=$ in the vapor phase.

Summary

This paper has attempted to present a model for the response of plagioclase to a metamorphic gradient. This response is, to a large degree, controlled by grain boundaries and results in albite rimming, discrete composition zoning, formation of antiperthite and myrmekite, and the development of nonstoichiometry. All of these features have been observed by metamorphic petrologists, but to date their origin has not been satisfactorily explained. Surface energy is a major factor in controlling the processes involved and is itself a function of the geometrical properties, the distribution of phases, and the distribution of impurities within the rock aggregate. Two related processes, which occur with annealing of any crystalline aggregate, can explain a major part of the variation of the plagioclase found in metamorphic rocks. These are grain boundary migration and impurity segregation.

Grain boundary migration is the movement of the boundary zone between two grains in an attempt to lower the free energy of the system. Impurity segregation is the diffusional process which tends to segregate impurities to high energy areas within a crystal, generally grain boundary regions or large scale lattice defects.

The observed variation of grain boundary phenomena in the Cross Lake Gneiss can be explained by this model. The development of three levels of

plagioclase composition near grain boundaries is an impurity segregation response to lower the energy of the system. Concentrations of potassium near grain boundaries and internal defects are likewise explained. The presence of nonstoichiometric areas within the plagioclase at low grades is due to the inability of the aluminum and silicon to respond as readily to impurity segregation as do the potassium, sodium and calcium. The appearance of quartz blebs and myrmekitic quartz at grain boundaries is a result of changing silicon–aluminum ratios at higher grades of metamorphism in response to changes in the potassium, sodium, and calcium noted above. The change in phase-to-phase contacts at which grain boundary phenomena are found is due to the increased occurrence of grain boundary migration with increasing grade of metamorphism.

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