
Crystal Growth Models in Metamorphic Tectonites

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Crystal growth models in metamorphic tectonites

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[Plate 11]

Recent models of crystal growth in metamorphic rocks have explained the lack of homogeneous equilibrium frequently found in porphyroblasts. The simple segregation model allows us to clearly distinguish between porphyroblasts which are often zoned and are in equilibrium with the matrix at the rim only, and the matrix minerals which show homogeneous equilibrium and recrystallize continuously. The assumptions of the simple model are instructive in that they focus our attention on some important problems of growth of minerals during deformation. The model enables us to define diffusion distances during porphyroblast growth and to distinguish more local diffusion distances which are superimposed on this porphyroblast diffusion and which are often related to deformation, e.g. shear zones and segregations. It emphasizes the ionic character of the reactions taking place during metamorphism and makes sense of some partition data between two minerals. The growth of minerals during deformation is considered and an attempt is made to connect the simple interface equilibrium model with deformation as shown by textures and microstructures in rocks. It is clear that the growth of minerals during metamorphism cannot be properly understood without a simultaneous appreciation of the chemical and mechanical processes occurring during metamorphism.

INTRODUCTION

Classical chemical equilibrium theory was applied with marked success up to about 1966 to explain actual mineral assemblages and reactions during the metamorphism of rocks. Homogeneous and heterogeneous equilibrium were considered normal; rocks were thought to have reached or closely approached equilibrium, and overstepping of reactions was considered unlikely (Fyfe, Turner & Verhoogen 1958; Turner 1968; Miyashiro 1973). Even if gradients in chemical potential existed because of diffusion kinetics, it was thought that recrystallization, possibly associated with deformation would eliminate them, at least over small distances. An accepted corollary to this theory was that rocks in chemical equilibrium usually show no evidence of events prior to the final major equilibration of the minerals. Thus assemblages and mineral compositions were thought to refer only to a single late peak of metamorphism. However, it was accepted, though not widely appreciated, that minerals in chemical equilibrium are not necessarily in textural equilibrium. Naturally, rocks in textural equilibrium were thought to be in chemical equilibrium (Zen 1963). Little account was taken of the role of deformation and geologists working on textures and microstructures in rocks were unable to reconcile the obvious history of mineral growth, breakdown, and deformation with a formal rather rigid non-historical equilibrium theory.

With the advent of the microprobe, work on metamorphic minerals, particularly garnet (Banno 1965; Atherton & Edmunds 1966; Hollister 1966; and others), it became clear that homogeneous equilibrium was rare and strong zoning was common in many porphyroblasts (figure 1). Simple zoning was interpreted in terms of a Rayleigh depletion model (Hollister

1966) or a segregation model (Atherton 1968*a*). These models implied that only the outer rim of the growing porphyroblast reacted with the matrix of the rock which changed composition with time and an interface equilibrium only obtained. Thus the interior of the porphyroblast was not usually in equilibrium with the matrix. Equilibrium reactions (interface intercrystalline and intracrystalline) clearly occurred in rocks but complete homogeneous equilibrium was rare and the history of the changing activities of the various components was considered to be sealed in the porphyroblasts. The new idea of interface equilibrium adds a more realistic dimen-

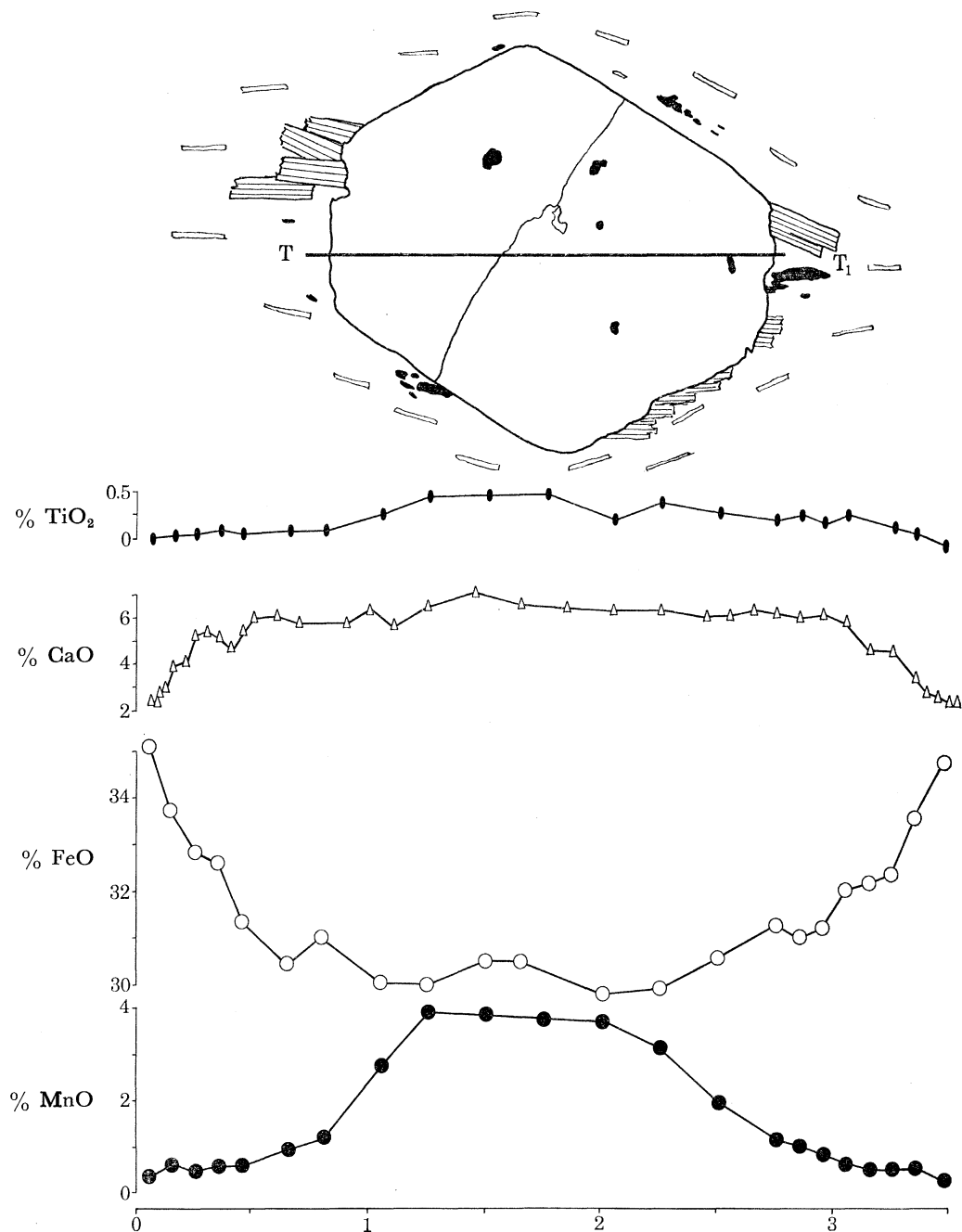


FIGURE 1. Electron microprobe traces of TiO_2 , MnO , Fe (total) and CaO across a garnet from the Scottish Dalradian; the traverse is indicated in the drawing of the garnet, T-T₁.

sion to the old approach and together they form a larger theory which allows us to combine the history of the chemical system with that of the textures. Now, chemical and mechanical equilibrium can be studied in a complimentary manner, having the same time base.

CHEMICAL GROWTH MODELS

(a) *The simple segregation model*

The segregation model used (Atherton 1968*a*) to explain the bell shaped curves for MnO found in many garnet crystals relates specifically to the segregation of a trace or minor element during normal freezing, but it may also be used for solute distribution in a multiphase solid system. In rocks we may define the concentration of the minor element in the porphyroblast as:

$$C = kC_0(1-g)^{k-1}$$

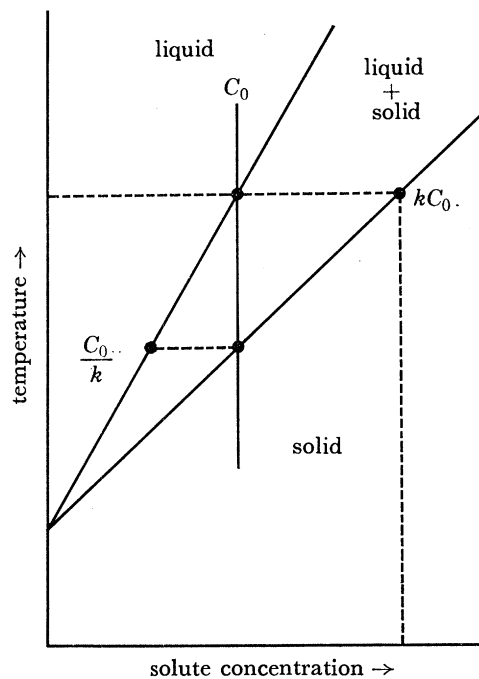


FIGURE 2. Part of a schematic phase diagram for a solute which increases the freezing point of the solvent (after Pfann 1952).

where k is the distribution coefficient or ratio of the concentration of the element in the porphyroblast to that in the matrix or given matrix mineral, C_0 is the initial concentration in the matrix or in a given matrix mineral, g is the fraction of the porphyroblast crystallized. This model is effective, but is based on three severely limiting assumptions, which are important in so far as they clearly limit the widespread application of the model. The assumptions are: (1) k is constant during the crystallization, (2) diffusion in the liquid or matrix is complete, and (3) diffusion in the porphyroblast is negligible. The severity of these assumptions has led to considerable fruitful inquiry about their nature when applied to rocks.

In the simple model, which relates specifically to freezing systems, k was considered to be independent of temperature (figure 2). In practice this is not true (Atherton 1968*a*; Kretz 1973)

although the problem only becomes acute in rocks if non-isothermal growth takes place, and even here it is possible to use a series of discrete values of k to determine the trend of solute concentration with changing temperature. To date in many systems containing garnet, growth appears to have been approximately isothermal. k will also be a function of the composition of the matrix and the porphyroblast at anything but low concentrations although distributions do appear to be unaffected even when, for example, the MnO is as high as about 6% in the garnet.

Assumption 2 is a very rigid requirement that is rarely true, for example even in the glassy matrix next to plagioclase crystals in basalts, compositional gradients can occur (Albarede & Bottinga 1972). For assumption 2 to be valid porphyroblast growth rate should be nearly zero. Crystal growth rates are as yet unknown in metamorphic rocks, but should be very slow if growth occurs over the span normally considered probable for a metamorphic event (up to about 10 Ma, Elliot 1973, p. 2059). Such a growth rate is to all intents and purposes nearly zero, and under such conditions matrix equilibrium, at least, should be reached. However, there is some considerable doubt as to the time taken for a porphyroblast to grow in relation to the total metamorphic event, both with regard to a possible incubation period and to the methods of measuring such events. Furthermore, metamorphic matrix minerals not infrequently show compositional gradients which suggests maximum temperatures were not maintained for the lengths of time envisaged above.

Assumption 3 is held to be valid by most workers, in spite of the fact that curves similar to the simple segregation curves found by Hollister (1966) and Atherton (1968*a*) have been calculated assuming late diffusion between porphyroblast and the matrix (Anderson & Buckley 1973). Other workers have considered late reaction of the matrix with the resorbed rim of the garnet to account for the curious rim reversals in MnO concentration (Grant & Weiblen 1971; Bethune & Laduron 1975), while still other workers have considered complete porphyroblast homogenization can occur at high temperatures (Blackburn 1969).

(b) *Complex zonations*

Apart from the simple bell-shaped traces, some garnets show more complex curves which may be related to more than one metamorphic event (Atherton & Edmunds 1966). In some cases, knowing the relation of the partition coefficient to grade from a simply metamorphosed area, it is possible to determine the partition coefficient for the earlier event from the core/rock composition, and also that of the later event, from the rim/matrix composition. Bethune *et al.* (1968) describe a garnet from the Alps with a central core, probably anti-alpine, which later suffered some resorption. A new discordant regrowth of garnet showing an 'ear' on the CaO profile characterizes the Alpine metamorphism. The edge of the garnet has an Mn-enriched zone which the authors interpreted in terms of late stage resorption. It should be possible to calculate the partition coefficients for both metamorphisms assuming there has been no internal diffusion in the porphyroblast, and an equilibrium interface distribution obtained.

The enrichment of MnO at the extreme periphery of some garnets has been interpreted in a variety of ways other than that above. For example, Edmunds & Atherton (1971) have suggested that a decrease in growth rate could produce an increase in the effective distribution coefficient, as shown by the sharp increase in the MnO profile. Such profiles have been computed for increasing but discrete values of k at the edge of a garnet, and are very similar to actual traces (unpublished data). Kretz (1973, p. 17) favoured an interpretation similar to this, except

that a restriction in diffusion in the matrix mineral (in this case chlorite) is the main factor. In garnets from aureole rocks of the Peruvian Coastal Batholith (Atherton & Brenchley 1972), complex andradite-grossularite zoning was explained in terms of the change of local reservoir composition during garnet growth as more resistant matrix phases entered the reaction during the very rapid heating and cooling cycle envisaged for these rocks. Such a situation is thought to be quite common.

Although some variation in interpretation is possible for the curious Mn variations found at the margins of some garnets, there is no doubt that the gross complex history shown in the probe traces has to be consistent with the textural and structural evidence. Such studies can only lead to a more complete knowledge of rock history.

In spite of the somewhat unrealistic nature of the assumptions which make the segregation model simplistic, it has been very useful in producing a framework for constructive thought on a series of subjects important to our understanding of the growth of minerals in rocks.

THE SEGREGATION MODEL AND SOME PROBLEMS OF GROWTH OF METAMORPHIC MINERALS

(a) *Diffusion distances*

Diffusion distances are of some considerable importance and it may well be that 'the most important current problem is to determine the rock volume over which a particular system may be considered to be chemically closed' (Wood 1974, p. 389). Diffusion volumes determined from microprobe traces of MnO in zoned garnets (Atherton 1968*a*) varied with increasing grade and also with increasing porphyroblast size, as might be expected from the model. They increased from about 0.100 to 2.00 g (0.03 to 0.66 cm⁻³ or in radius from 0.2 to 0.49 cm). The determination of diffusion volumes assumes a spherical diffusion sphere and that the reactant minerals are homogeneous with respect to MnO. It also assumes there are no concentrations of minerals into bands etc. Matrix minerals do vary in MnO content, thus chlorite MnO > biotite MnO > phengite MnO > quartz or feldspar MnO. Furthermore, minerals with relatively high MnO contents do often show pronounced inhomogeneous distributions.

In deformed or deforming rocks therefore, spherically shaped diffusion reservoirs are unlikely, and diffusion volumes related to the deformation should be common. This is consistent with the evidence from the gneisses of the Grenville Series (Blackburn 1968), where the diffusion volumes determined from the garnet compositions are ellipsoidal with the long axis about 4 cm and are always parallel to the lineation and to the foliation. Evidence of reservoir size, from matrix data is consistent (Kwak 1970), for biotites show variations in composition over distances of a centimetre or less.

In contrast, in thermally metamorphosed rocks where recrystallization of the matrix has not occurred to such a great extent, and deformation is absent or very limited, diffusion volumes are spheres, somewhat smaller in size to those in deformed rocks (figure 3). Woodland (1963) in a study of some thermally metamorphosed pelitic rocks from northeastern Vermont found halo-like zones around staurolite and garnet demonstrating diffusion distances of 0.2–1.4 mm during porphyroblast growth. Notably in these rocks the diffusion spheres do not overlap, and within the spheres, the matrix minerals, except for quartz have disappeared. This is in marked contrast to deformed rocks, where haloes around porphyroblasts are generally absent. However, Rast (1965) has described garnets in a regionally metamorphosed rock, which grew

under static conditions in a quartz, biotite, feldspar matrix, and which show haloes of clear quartz some 3–4 mm in diameter. The biotite and feldspar have reacted out of the system. Nonetheless such spheres appear to be rare in deformed rocks and are much more common in thermally metamorphosed rocks.

The diffusion distances above are consistent with other data such as that of Phinney (1963) who found biotites of different composition in adjacent layers of a rock sample (see also Hagner, Leungs & Dennison 1965). But these distances only refer to diffusion of individual cations such as Mn and Fe and obviously not to H_2O which must move out of the rock during the dehydration reactions. To define diffusion distances we must consider individual elements in multi-component diffusion processes under varying conditions.

Superimposed on this pervasive porphyroblast diffusion are local zones where diffusion much exceeds the distances indicated above. Thus in quartz segregations in northwest Spain, kyanite is present as large, late, bladed crystals. In the adjacent rock, successive depletion of iron, calcium and potassium occurs up to the segregation, so that the rock next to the segregation is made up of kyanite + graphite only. Diffusion distances in this example are about half a metre. Much larger distances are suggested by Hagner, Collins & Clemency (1963) to account for a magnetite deposit associated with amphibolite and pegmatite in the eastern U.S.A. The iron–magnesium ratio in the ferromagnesian minerals decreases towards the ore body over a distance of some 37 m at least. The authors relate this to deformation as the ore body is parallel to the foliation, and lies in what are thought to be low pressure zones, formed during differential movement. Similar deformation induced local gradients are seen adjacent to shear zones (Beach 1974), and are thought by some workers to occur in hinges and limbs of folds.

This local ‘openness’ of the rock changes the diffusion regime so that the mobility of elements will vary in time and in space. The open nature of the rock is related to megascopic deformation processes. It is clear that diffusion must be clearly specified in terms of different chemical species as well as in terms of the different physical conditions, and to date there is little good information on diffusion on different scales.

(b) Contrasted matrix and porphyroblast behaviour

The segregation model emphasizes the difference between porphyroblast and matrix behaviour, which is clearly related to the distinction between matrix formers and porphyroblasts emphasized in textural studies (Rast 1965). The recrystallization of matrix formers has been widely studied by metallurgists and applied to rocks by many geologists. Textural equilibrium for minerals such as quartz and calcite is often approached, although preferred direction of growth particularly in the layered minerals is common. Grain boundary migration and increase in grain size during metamorphism is also common. In contrast porphyroblasts rarely show a preferred growth direction, and there is little evidence of grain boundary migration, or increase in size by coalescence during recrystallization. Indeed none of the recrystallization mechanisms taken from metallurgy apply to porphyroblasts. However, they do show in contrast to matrix minerals, multiphase growth, complex inclusion patterns related to growth, as well as overprinting of earlier structures. Variations in the velocity of growth and style of growth have also been suggested on strong textural evidence (Rast 1965). Matrix mineral and porphyroblast behaviour is clearly different in current chemical models of crystal growth, and related to this is the difference in behaviour during deformation.

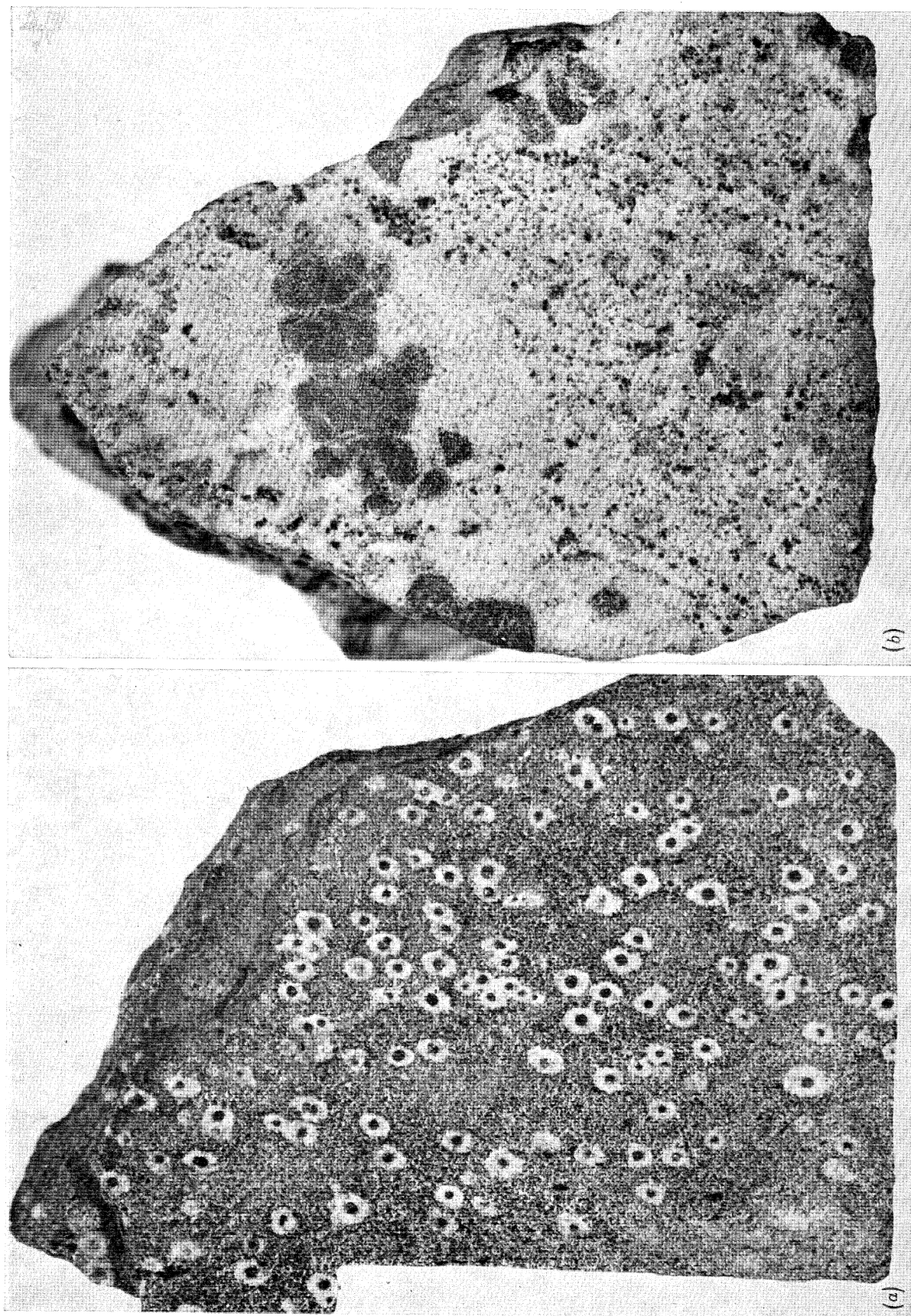


FIGURE 3. (a) Diffusion spheres around magnetite, in quartz-biotite-feldspar rock from the Runconada inlier, Coastal Batholith, Peru; (magn. $\times 1.4$). (b) Diffusion zone around garnet in a quartz, biotite, feldspar, muscovite aureole rock; (magn. $\times 2$).

(Facing p. 260)

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In the matrix, diffusion processes will level potential gradients, the process according to Mueller (1967) being assisted by differential stresses which produce recrystallization creep. There is diffusion on two scales, firstly, lattice diffusion of various types (Elliot 1973), which is important in the recrystallization kinetics of matrix minerals. The fact that most individual matrix minerals are unzoned points to the efficiency of this diffusion under metamorphic conditions. Secondly, large scale diffusion between crystals over greater distances than an average crystal length. This is accomplished by ionic diffusion along grain boundaries or through pores. Diffusion to equilibrate the matrix will be enhanced if dehydration reactions producing H_2O and a decrease in volume are occurring at the same time. This diffusion will also be enhanced by recrystallization creep when matrix minerals nucleate, increase in size and are deformed. As we have seen porphyroblasts do not recrystallize, hence according to Mueller (1967) remain zoned. He considers the garnet to be a strong competent crystal in a less competent matrix of layered minerals and quartz etc, and the growth environment of the garnet to be nearly hydrostatic while deformation in the matrix would be plastic or fluid in form. The garnet is not stressed enough to produce diffusive flow.

However, the grain growth seen in some inclusions in garnets (Harris & Rast 1960) may not be the result of recrystallization creep, but growth under 'static conditions', and the final 'general matrix coarsening' a late annealing process which is partly a response of a strain energy developed during an earlier deformation (Harte & Johnson 1969). It is also possible that in some cases there is no grain growth during porphyroblast growth (Harte & Johnson 1969). But in spite of the problems still apparent in understanding matrix behaviour during porphyroblast growth it is indisputable that recrystallization and growth are common in the matrix and not in the porphyroblast, although the precise role of deformation in relation to chemical homogenization is still not clear.

(c) Ionic reactions

Mineral reactions between porphyroblast and matrix must be ionic in type, for if we consider MnO in garnet, the fractionation factor between the matrix and the porphyroblast is very large. Abstraction of MnO from the matrix minerals must be rapid and hence very likely through a fluid phase, where manganese must be present as an ion. The analogy between a solid-liquid equilibrium is obvious.

Grain boundary migration is clearly enhanced by water and has been considered to be the main process in diffusion creep which permits the deformation (Elliot 1973), at least at low temperatures. However, I think intracrystalline diffusion in the matrix minerals, which may be the rate controlling step, must be efficient if the concentration curves are due to simple segregation. Generally the experimental diffusion data used refers to self-diffusion of oxygen etc in single crystals. This may be misleading as layered mineral recrystallization involves multi-component diffusion, dissolving and nucleation of minerals of different composition as well as dehydration and steady state creep as metamorphism progresses. Diffusion in natural systems may well proceed much more rapidly than we might suspect from data on self-diffusion of atoms such as oxygen, which is probably the slowest moving component.

(d) Partition and segregation

Basic partition theory relates to the distribution of elements between minerals where homogeneous and heterogeneous equilibrium have been reached. Under conditions of segregation

we may define a logarithmic partition coefficient (McIntyre 1963, p. 1237) which will differ from the equilibrium, partition coefficient. There will also be a change in the partition coefficient which will depend on the crystallization rate. It is evident that meaningful partition data may be difficult to extract from natural systems showing marked segregation.

The segregation model makes sense of some partition data (see table 1), for example matrix minerals very often show simple linear or curvilinear relations for the partition of most elements between the two phases, while porphyroblast-matrix mineral partition curves are irregular or complex except for MnO, which we have already seen has a distribution explicable using an interface equilibrium model. Some of these irregularities must be due to composition effects, but some is almost certainly due to poor sampling of the zoned minerals, and/or polyphase metamorphism which will give distributions in the porphyroblast related to all the *PT* conditions passed through, while the matrix minerals will show a distribution related only to the last phase of metamorphism (Kwak 1970).

Similar mixed distribution coefficients can occur if the garnet grew during a non-isothermal phase or re-equilibration of the periphery took place during a later event.

TABLE 1. DISTRIBUTION GRAPHS FOR SOME MINERAL PAIRS

	V ₂ O ₃	MnO	Ti	Mg	Fe	Cr	Zr
garnet-biotite	×	○	×	×	×	?	×
garnet-hornblende	×	○	×	×	×	⊖	×
biotite-hornblende	○	○	○	○	○	○	×

(×), no simple curve form; (○), linear or curve form; (⊖), poor curve form.

Garnet is the refractory porphyroblast phase; zirconium distributions are poor, probably because of contamination from zircon.

(e) *Progressive and non-progressive metamorphism*

Commonly in garnet porphyroblasts we can see features which enable us to synthesize a deformation history, but we very rarely see these features in the matrix minerals due to continuous crystallization of these minerals during growth and perhaps a final annealing recrystallization. The matrix minerals may show new geometric arrangements in space, i.e. along a second cleavage. Rarely are early matrix minerals preserved, except as relics inside porphyroblasts. Commonly, however, porphyroblasts are persistent and may often be present in the rock as metastable relics. We may say that matrix minerals show true *progressive* metamorphism while porphyroblasts usually do not. Logically the fact that they do not re-equilibrate constantly with the matrix, indicates growth is non-progressive. The changing composition of the matrix with time is beautifully demonstrated by the variation in composition and size of biotites inside and outside garnet; while the inertness of the porphyroblast is emphasized by the lack of homogenization of garnet even during later migmatization and a general lack of unzoned crystals (Atherton & Edmunds 1966). The *non-progressive* character of porphyroblast growth also follows from the evidence of Atherton (1968*a*) that the *k* value determined from the core composition, decreases with increasing grade and each garnet appears to have grown nearly isothermally. That is, the centres of the higher temperature garnets are not made up of lower temperature garnets, so that the garnets cannot have grown with increasing temperature. In rocks from the upper garnet zone the reactions producing garnet at lower grade were overstepped, so that garnets grew only at the maximum temperature reached in each rock. Some

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authors (Carmichael 1969) would disagree with this and maintain that reactions in metamorphic rocks were truly progressive and earlier porphyroblast stages had been completely eliminated. I think textural and probe analysis does not sustain this model, except for the matrix minerals from which most, if not all, of the porphyroblast phases are produced.

This does not mean that porphyroblasts never break down, but I would suggest reactions involving porphyroblasts are frequently confined to late deformation periods and/or associated hydration producing chlorite, kaolinite, muscovite and sericite, etc. In which case higher or lower temperature porphyroblasts may grow from the pseudomorph of matrix minerals during a later metamorphic event.

(f) The relation of textures and chemical zonation in crystals

Probe traces across garnets are frequently only explicable in terms of textural and petrological evidence, thus reversals in MnO content at the rims of garnets have been related to observed resorption (Evans & Guidotti 1966). Homogeneous atoll garnets may be interpreted in terms of rapid crystallization with an effective distribution coefficient which is dependant on the crystallization rate (Edmunds & Atherton 1971). Polyphase metamorphic textures have been used to explain complex element traces. In all these instances, and many more, a coherent picture of the history of the growth of the crystal has been obtained only when the textural and chemical patterns have been studied together. In these cases the chemical interface 'equilibrium' model has been clearly connected to the textural and deformational history of the rock.

(g) Variance

Many reactions producing garnet (and other porphyroblasts) would appear to have occurred at constant grade and without any degree of compositional freedom. The phases should therefore be invariant in composition. Unzoned garnets are rare, except at high grade, hence the variance of the rocks must be greater than generally recognized, or growth must have occurred over a temperature range (see Brown 1969). In general, simple symmetrically zoned garnets show isothermal growth, or if anything growth during slightly decreasing temperatures (Atherton & Edmunds 1966; Atherton 1968*a*). If garnets are produced at constant grade and zoning occurs, clearly the variance must be greater than that implied in normal graphical analysis, e.g. AFM diagrams also (see Rumble 1974).

DIFFUSION IN PORPHYROBLASTS

So far crystal growth models have been discussed on the assumption that no diffusion occurred in the porphyroblast during growth or later. This has been queried; thus Blackburn (1968), thought equilibration readily occurred during polyphase metamorphism in the high grade Grenville gneisses. General evidence from garnets in granulite facies rocks (see Himmelberg & Phinney 1967) also suggests that zoning may be slight or lacking. But although zoning may be slight there is much evidence to suggest that if it was initially present it was not homogenized later. For example rocks which are migmatized or thermally metamorphosed contain earlier garnet which is still zoned (Atherton & Edmunds 1966; Edmunds & Atherton 1971) while garnets from andesites (Brousse & Bizouard 1972) and from some eclogites (Bryhni & Griffin 1971) are zoned. This is not of course to imply that these zonations are necessarily due entirely to simple segregation.

Slight zoning may well result from the low partition coefficient for MnO expected at high temperatures. The data of Atherton (1968*a*) show that the partition coefficient MnO garnet:MnO rock decreases markedly even up to the middle grades of metamorphism and will clearly approach 1 at higher temperatures.

Nonetheless, Anderson & Buckley (1973) have put forward interesting semi-quantitative diffusion models to explain the zoning in garnets. Their model assumes that originally the garnet was unzoned, later redistribution between the matrix and the porphyroblast results in the present distribution, which is similar in form to the segregation curve. The assumptions of the models are severe, especially with respect to the initial state of the rock system and the static nature of the interface. The production of the initial homogeneous garnet/matrix system seems to pose some problems with regard to material balance in a fixed reservoir system. However, their models do extend our ideas beyond the existing models for porphyroblast-matrix behaviour. Firstly, their two-reservoir model offers an alternative explanation of the normal segregation type curve and the reverse MnO trend at the rim of the crystal. Secondly, the models explain the occurrence of different forms of zoning found in adjacent grains in the same rock (Hollister 1969, Fig. 7).

However, it is interesting to note that Anderson & Buckley (1973) thought that diffusion of Ti^{4+} should be negligible at metamorphic temperatures, so that any non-homogeneous distribution should be due to growth. They quote probe data on garnets which show no zonation in Si, Al and Ti, implying that garnets may not have grown according to the segregation model. But Ti zonation does occur (figure 1) and accordingly the associated element distributions are almost certainly due to segregation.

In the preceding paper Anderson considers multi-component diffusion in garnet. This is a valuable approach and I think his views are not necessarily at variance with those expressed here in so far as the diffusion processes he envisages would probably occur at higher temperatures than were ambient in most of the examples discussed here. It must be said, however, that the concentration curves found in zoned crystals are of a simple form and not uniquely explained by the segregation model.

MATRIX BEHAVIOUR

(a) *Diffusion controlled models*

The simple segregation model described above accounts for many traces found in garnets, and has found general acceptance (Kretz 1973), however, it suffers from strong limitations particularly with regard to matrix behaviour. It does not take into account the kinetics of diffusion in the matrix, particularly when crystal growth is rapid. Negative depletion in the matrix has been observed (see earlier) and may be quite common. So far this negative depletion has been observed in the ferromagnesian layered minerals only, principally in biotites. It should be made clear that this depletion phenomena is seen in the matrix as a whole, not in individual crystals which are very frequently unzoned. Thus biotites may be progressively depleted in iron as garnet porphyroblasts are approached, included biotites having the lowest Fe/Mg ratio (Kwak 1970; Grant & Weiblen 1968; Evans & Guidotti 1966).

The difference in composition between biotites inside garnet and in the matrix as shown by Evans & Guidotti (1966) is an armouring effect and demonstrates the changing composition of the matrix with garnet porphyroblast growth. It does not necessarily show that diffusion was slow in the matrix. However, the data of Kwak (1970) and Grant & Weiblen (1968) do

show a variation in the Fe/Mg ratios in biotites away from garnet, clearly demonstrating diffusion rates were not sufficiently rapid to homogenize the matrix, although *when* these gradients were set up is difficult to say.

Theoretical models for liquid-crystal systems have been developed, from the segregation model, which takes into account diffusion in the liquid. Where diffusion alone is not rapid enough to maintain a homogeneous liquid the solute concentration will be depleted around the growing crystal (for $k > 1$). The setting up of this depleted region (transient stage), is followed by a steady state stage (Tiller *et al.* 1953). In the garnet-matrix analogy the garnet would grow with an initial concentration of kC_0 and fall to a steady state value of C_0 (see Tiller *et al.* 1953; Atherton 1968*a*, Fig. 5). This transient region is unlikely to be seen in natural crystals for the value x from the start of crystallization to that when the concentration in the solid drops to within 67% of C_0 (approximate onset of the steady state) is about 0.6 μm in a porphyroblast of about 2 cm diameter [$x \approx D/kR$, where D is the diffusion rate, k the partition coefficient and R , the linear growth rate (Tiller *et al.* 1953)]. A diffusion rate of 10^{-16} cm^2/s (see Anderson & Buckley 1973, p. 94) and a growth time of 1 Ma was used. Anderson & Buckley's value for the diffusion coefficient may be too small, but it would have to increase by 10^4 to be significant. Unfortunately we have no real data on D or on R to make the above remarks anything more than a suggestion. The change in composition of the solid (porphyroblast) during the transient stage, for small values of k , is given by:

$$C_s = C_0\{(1-k) [1 - \exp(-k(R/D)x)] + k\},$$

where x is the distance from the beginning of crystallization and the other symbols are listed earlier (Tiller *et al.* 1953, see also Albarede & Bottinga 1972). In the steady state the solid composition must be the same as the original liquid or matrix. I have no knowledge of garnet MnO compositions near to the matrix values over a considerable proportion of the crystal; they are usually well above the C_0 value, and even at the rims of the crystals the value rarely drops to the matrix value although it may approach it. This might suggest that transient and steady state growth as defined above do not occur. But it may well be that our data for diffusion and crystallization rates is not good enough to allow us to distinguish steady state and transient conditions properly.

Albarede & Bottinga (1972) distinguish a further model (B-3) to that of Tiller *et al.* (1953), where the reservoir is finite. The segregation model is a limiting case of this model where α is large ($\alpha = D/RL$ where L is the dimension of the reservoir). The minor element concentration in the porphyroblast in this model would not drop to C_0 according to Albarede & Bottinga (1972, Fig. 5, p. 149), and the steady state would be quickly realized for small values of α . However, there is some problem with their analysis because clearly the Tiller model is the other limiting case as α becomes very small, i.e. the reservoir size becomes very large for a given D/R value. Under these conditions C_s must approach C_0 . In practice it would be very difficult in natural systems, to distinguish this model from the other two without precise information on D , R and L .

Theoretical treatments of impurities in melts and crystals consider a further model between the so called 'perfectly stirred' melt model where equilibrium is complete in the liquid, and the diffusion limited distributions discussed immediately above. This relates to 'partially stirred' melts and is done by introducing an effective distribution coefficients (figure 4). The distribution of trace metals is diffusion-controlled in a layer next to the crystal, elsewhere it is homogeneous

due to stirring. Burton *et al.* (1953) evaluated this layer and showed that the effective distribution coefficient varied from 1 to k^* (equilibrium value) with decreasing crystal growth rate. This idea was used by Edmunds & Atherton (1971) to explain rapid increases in MnO in very small aureole garnets from Fanad where supersaturated conditions and therefore rapid initial crystallization was indicated by the textures. In metamorphic rocks we may equate stirring to deformation, recrystallization and reaction processes going on in the matrix, which must assist in matrix homogenization.

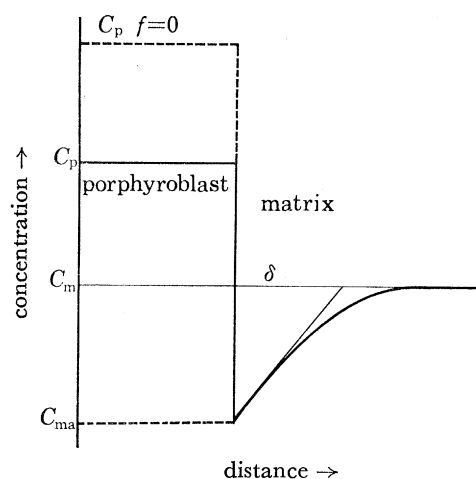


FIGURE 4. Solute distribution adjacent to a growing interface in a partially stirred melt (after Brice 1965). Distribution coefficients: k_0 , equilibrium; k^* , interface; k_{eff} , effective;

$$k_0 = C_p/C_m, \quad f = 0$$

$$k_{\text{eff}} = C_p/C_m, \quad f = f$$

$$k^* = C_p/C_{ma}, \quad f = f$$

where C_p and C_m are the concentrations of trace or minor element in the porphyroblast and matrix respectively and C_{ma} is the concentration in the matrix at $t = 0$; f is the linear growth rate, cm s^{-1} .

A further model may be considered where diffusion is restricted in the matrix but there is non steady-state conditions (Kretz 1973). Diffusion is restricted in both the matrix and the porphyroblast. This model has been used to explain the reverse zoning seen in some garnets.

Finally, the matrix mineral composition may be modified by a late local event causing a reworking of the edges of the garnet and the very immediate local biotites and chlorites, which are often homogenous. In an example quoted by Hess (1971) the Mn concentration in the garnet is constant and it is the Fe and Mg concentrations which change antipathetically at the rim. This example contrasts sharply with that of Bethune & Laduron (1975), in which Mn is concentrated in the rim of the garnet and the Fe and Mg show a decrease. They conclude with strong textural supporting evidence that Mn is resorbed into the garnet rim, but no textural data is supplied by Hess (1971) to help elucidate the mechanism of his proposed exchange process.

In general, I think many of the variations in composition seen in the matrix minerals may well be due to reactions late in the metamorphism, but these need not necessarily be separate from the main phase. If recrystallization and porphyroblast growth took place isothermally and

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later with decreasing temperature (Atherton 1968*b*), the bulk of the recrystallization of the matrix may well have occurred under widespread heterogeneous equilibrium conditions, but as growth slowed and the temperature dropped more local gradients would be set up and only the final gradients would be frozen in the matrix compositions. The absence of post porphyroblast matrix coarsening would help to preserve such gradients in the matrix.

(b) Diffusion haloes in the matrix

The diffusion haloes mentioned earlier are important in that they clearly demonstrate how reactions take place in the matrix during porphyroblast growth, and their general restriction to thermally metamorphosed rocks emphasizes the difference in matrix behaviour during deforming and non-deforming conditions.

Other characteristics of thermal growth, particularly in the porphyroblasts are:

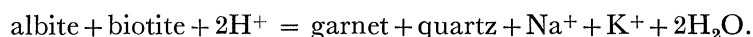
(a) nucleation is often confined to compositionally distinct parts of the rock (Edmunds & Atherton 1971),

(b) growth often appears to have taken place in supersaturated conditions, and terminates before completion of the reaction, and there is a gross lack of even layerite equilibrium (Atherton & Brenchley 1972),

(c) nucleation is 'instantaneous'.

These characteristics are a product of the speed and short duration of the thermal event.

The diffusion haloes in figure 3 and other examples, characteristically do not overlap and are notable for the absence of matrix minerals such as biotite and feldspar. There is no direct evidence that diffusion to produce the new porphyroblast extended beyond the halo. If this is so we have a rock made up of two components: the original matrix and a new depleted matrix in halo-form with a new porphyroblast at the centre. Such a feature might well form by an ionic reaction as postulated by Carmichael (1969):



The crystalline phases dissolve incongruently, some ions go into solution, the remainder combine with other ions from solution to form the new phases. The reaction above is simplified in that the biotite Mg/Fe ratio is greatly in excess of that in the garnet so the reaction will also produce Mg ions. It is conceivable that there is an exchange reaction with the rest of the rock, such that some modification of the matrix composition is likely, but we have no direct evidence of this occurring.

In contrast, in regionally metamorphosed rocks nucleation of garnet has been shown to be random (Kretz 1973), growth often appears to have gone to completion and nucleation is often continuous. More interestingly to the discussion diffusion haloes are usually absent. In contrast then diffusion must not be dominantly confined to a small shell around the new porphyroblast and therefore the reactant phases changed composition throughout the rock. As Hess (1971, p. 186) points out his garnets from a cordierite gneiss could not have grown from a strictly local environment, i.e. where only grains in contact were in equilibrium, because 'Fe-Mg free haloes would be expected around garnet grains if the chemical source was local'. He thought diffusion reservoirs were about 6 times the size of the garnet, that is several cubic centimetres in volume, and also that reservoirs should overlap (see also Atherton 1968*a*).

Accepting that diffusion haloes are usually confined to thermally metamorphosed rocks and that nucleation and growth of the matrix minerals is driven by energy from both chemical and

strain sources (see next section), it would seem that the absence of haloes in deformed rocks is due to the complex interplay of the following:

(a) Profound intracrystalline deformation in the matrix minerals which allows rapid lattice diffusion, so that gradients in chemical potential are quickly levelled by exchange reactions, and reactant ions are readily supplied to the new porphyroblast. Intercrystalline diffusion distances will also be enhanced by the differential stresses and movement.

(b) Continuous nucleation would produce new matrix crystals randomly throughout the rock, so inhibiting the production of Mg-Fe poor haloes. This continuous nucleation will be a function of a long heating-cooling cycle, chemical instability and deformation, all of which should combine to produce completion of reaction and overlapping of diffusion reservoirs, as well as new nucleation sites.

In contrast in thermally metamorphosed rocks, intracrystalline deformation is absent, or very limited, diffusion within grains will be slow and chemical gradients within grains common (Atherton & Brenchley 1972). *In situ* local incongruent dissolving of the matrix minerals near the new porphyroblasts, would occur from the grain boundary inwards. The rapid heating-cooling cycle, the consequent supersaturation and lack of deformation should result in instantaneous nucleation, incomplete reaction and restriction of diffusion reservoirs.

(c) *Chemical and deformational controlled recrystallization*

The continuously changing equilibrium composition of the matrix minerals during porphyroblast growth may well be important in the recrystallization process. Thus Etheridge & Hobbs (1974) in a study of the deformational and chemical controls on recrystallization of mica (this includes nucleation and growth) found that only a few of the new grain orientations in their experiments could be explained by recognized strain induced mechanisms. They concluded that stored plastic strain energy was generally not sufficient to overcome barriers to nucleation in the layer silicates.

The energy equation for nucleation is:

$$\Delta G = (g_{\beta} - g_{\alpha} + g_s) + \xi A - \sigma \nu$$

where ΔG is the overall free energy difference between the host phase α and the new phase β , g_{β} and g_{α} are the chemical energies of β and α respectively, g_s is the elastic strain energy increase when α changes to β and σ and ξ are the stored plastic strain energy and the surface energy respectively, ν and A are the volume and area of the new nucleus β . Following Etheridge & Hobbs (1974) if a phase becomes unstable, the chemical driving forces for nucleation of the new phase add significantly to those due to stored strain energy. This chemical instability could well be that due to depletion of the matrix by the growing porphyroblast.

Etheridge & Hobbs (1974) found small but significant differences in Fe, Ti, Al and Mg in biotite single crystals between the new and the old phases and concluded that nucleation and growth, in deformed matrix micas, of a new mica with a different composition than the host, is promoted by free energy differences resulting from differences in chemical composition and stored strain energy. The new equilibrium chemical composition may be due to the matrix system changing in composition as a result of porphyroblast growth rather than slight chemical fluctuations during the nucleation stage as suggested by Etheridge & Hobbs (1974). Cahn (1961) suggests this latter process of small rearrangements over large areas in the host phase, requires more work than the more traditional nucleation process, but is favoured kinetically

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because it involves easier diffusion paths. However, the experiments of Etheridge & Hobbs (1974) did not involve matrix and porphyroblast minerals (as defined here), so these particular differences in composition cannot at first sight be explained by using the segregation model. Nevertheless a similar small difference in composition between porphyroblastic prekinematic biotite and small synkinematic biotite again in Mg, Fe, Al and Ti is described by Kaminen & Carrara (1973), which the authors envisaged was due to a depletion process similar to that described in this paper. They considered that not only did some elements have large fractionation coefficients relative to other elements, but some elements move earlier than others, i.e. are released earlier from the reactant phases. What the authors are saying, I think, is that ionic reactions involve multicomponent diffusion and the new phase may be a different composition due to kinetic factors. Such an explanation seems very likely for the experimental studies as run times are short, and possibly this is also true in some rocks. The idea is close to that of Kretz (1973) for a non-equilibrium matrix model and that of Atherton & Brenchley (1972) which explained a variation in activity of certain elements with time as a function of breakdown of the reactant phases.

In conclusion it is very clear that we need to know a lot more about the interaction of chemical and strain energy controlled processes in rocks, for as Etheridge & Hobbs (1974) suggest, recrystallization is controlled by local strains and stress and defects in the structure as well as by chemical processes producing equilibrium mineral assemblages at given temperatures, pressures and activities.

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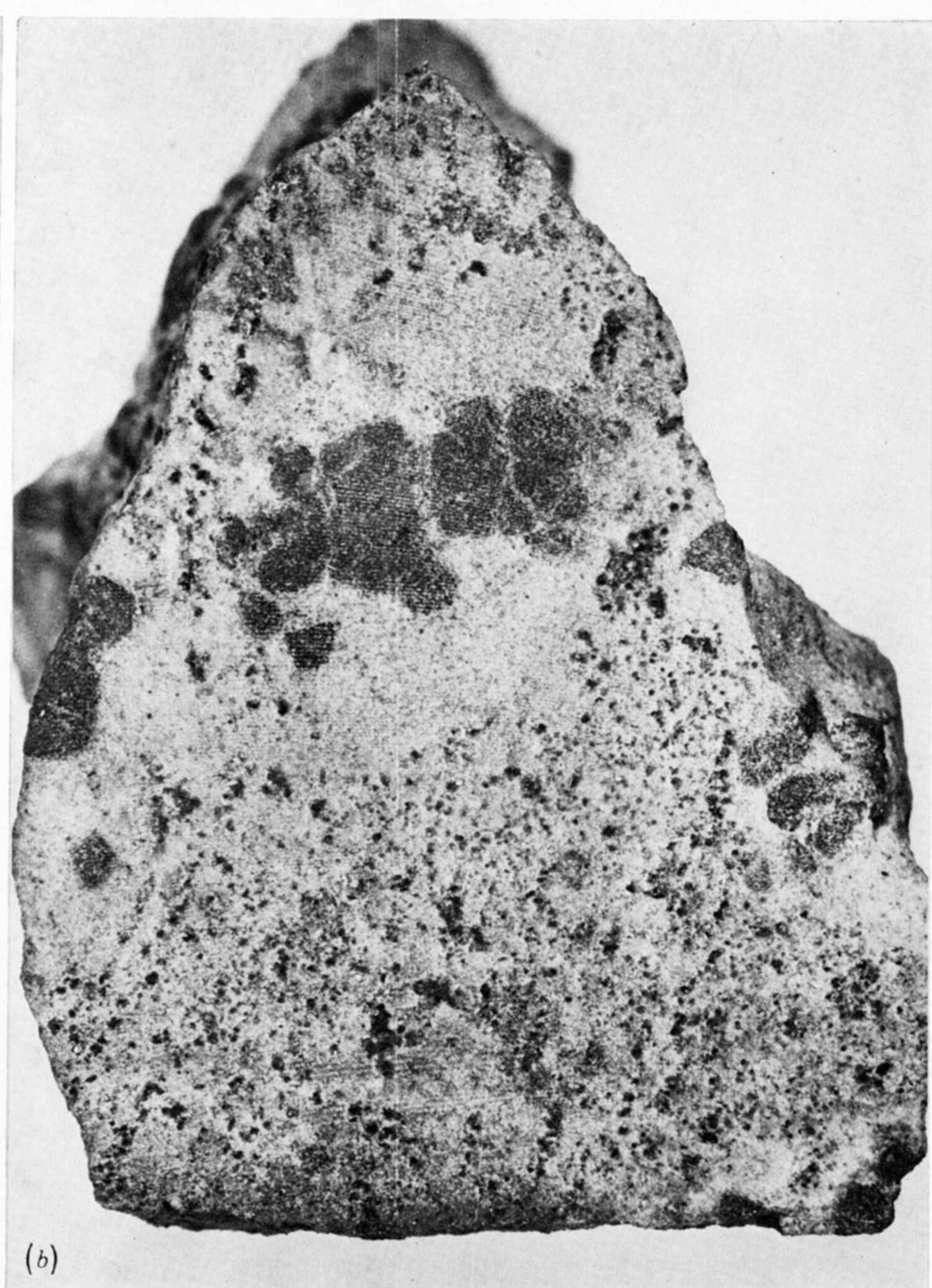
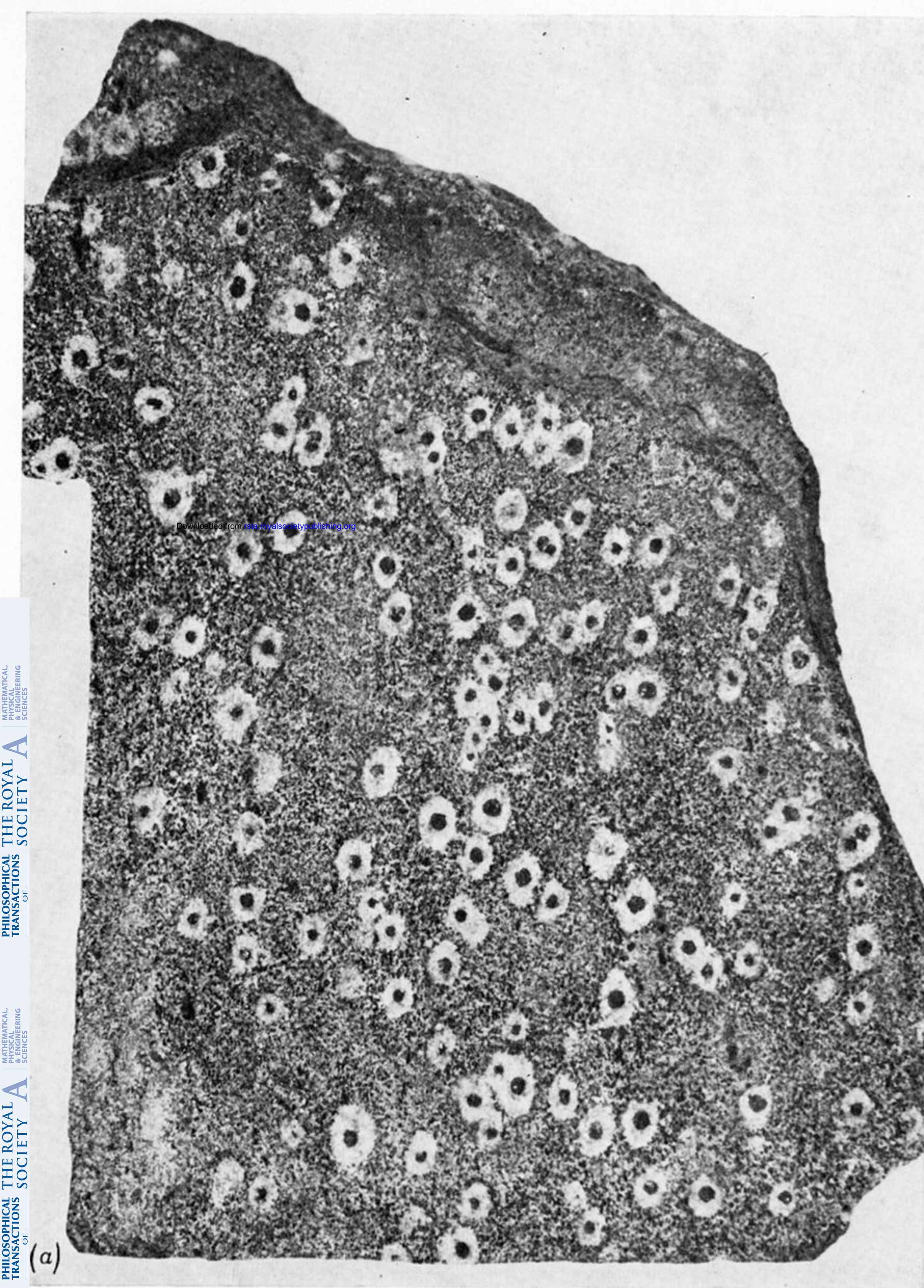


FIGURE 3. (a) Diffusion spheres around magnetite, in quartz-biotite-feldspar rock from the Runconada inlier, Coastal Batholith, Peru; (magn. $\times 1.4$). (b) Diffusion zone around garnet in a quartz, biotite, feldspar, muscovite aureole rock; (magn. $\times 2$).