

Metasomatic zones in metamorphic rocks

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Abstract—Prediction of a unique sequence of metasomatic zones that would develop by intergranular diffusion with local equilibrium is possible only for relatively simple systems, unless extensive thermochemical and kinetic information is available. The complexity of the problem for a given example will depend on what portion of the set of chemical components required to describe the example are 'diffusing components', that is, components that move relative to 'inert markers'. Diffusing components are commonly K-components (THOMPSON, 1970) for the various local equilibria of a sequence of metasomatic zones, since diffusion tends to impose a monotonic variation of the chemical potentials of these components across the zones. The number of diffusing components may vary from zone to zone in a particular example, as may the number of diffusing components that are K-components. Calculation of the rate of growth of a specific sequence of zones is relatively straightforward only for cases where the zones are primarily due to the variation of the chemical potential of one independent diffusing component. Calculation of the material transfer involved in the growth of a sequence of zones, assuming a single sharp initial contact is meaningful only if 'inert markers' or a discontinuity in the otherwise-constant ratio of two components indicate the present location of the initial contact. Examination of some natural calc-silicate diffusion zones suggests that a diffusion-imposed gradient in the chemical potential of calcium is largely responsible for the observed zonation. Metasomatic zones developed at the boundaries of ultramafic bodies, however, are produced by diffusion-imposed chemical potential gradients of several components, notably silica and magnesia, the number varying from zone to zone.

INTRODUCTION AND ASSUMPTIONS

THE MODIFICATION of metamorphic rocks by metasomatic processes has been a popular and controversial topic in the petrologic literature for many years. Of the numerous natural occurrences for which metasomatism may be demonstrated, perhaps the most striking examples are those in which the metasomatism has produced distinct zones or bands of unusual mineralogy. The simple geometry of many metasomatically-produced mineral zones indicates that they contain a record of essentially one-dimensional metasomatism. The one-dimensional aspect of metasomatic zones along with a hopefully complete picture of various 'degrees' of metasomatism make such zones potentially quite useful in the understanding of metasomatic processes. While many important features of metasomatic zones have been discussed in the literature, some have been underemphasized or overlooked. In the following paragraphs I reconsider metasomatic zones with these features in mind and the hope of further clarifying some consequences of diffusion in metamorphic rocks.

As a guide to the discussion, I shall examine metasomatic zones in terms of the following questions. What information is contained in a sequence of metasomatic zones concerning the geochemical migration that produced them? Can the sequence of metasomatic zones produced for a given set of physical conditions be predicted? What information is needed for such a prediction? What are the qualitative effects of differing degrees of 'moveability' among diffusing

species? In order to answer these questions, some simple, hypothetical systems will be examined in detail. Predictions based on the simple systems are then compared with more complicated natural examples.

In order to discuss the development of metasomatic zones in metamorphic rocks, it is convenient to begin with some assumptions that will simplify the problem. Ultimate justification for the assumptions lies in a comparison of theoretical predictions with observations of natural examples.

(1) I shall assume that all mass transfer occurs by diffusion. As discussed by KORZHIINSKII (1970, p. 3), it is convenient to differentiate between two limiting material transfer mechanisms: diffusion metasomatism and infiltration metasomatism. Both may produce metasomatic zones, as may a combination of the two (FLETCHER and HOFMANN, 1974). Neglect of infiltration metasomatism is justified for low-porosity metamorphic rocks due to the probable absence of the flowing pore fluid required for infiltration.

(2) I shall assume that the problem may be adequately treated in terms of one-dimensional diffusion. This assumption requires that the rocks be homogeneous in any plane normal to the diffusion direction and, strictly speaking, excludes many common examples where spherical symmetry is appropriate (for example, FISHER, 1970; JOESTEN, 1974). However, restricting the model to one dimension allows most important features to be considered and takes full advantage of the simple geometry of many natural zones. Throughout the paper I shall refer to a diffusion column, which could be any cylinder of rock of

in the chemical potential of the component (see DENBIGH, 1951, p. 52). The motion of the component serves to reduce gradients in its chemical potential such that after a metamorphic event long enough to eliminate initial discontinuities, the chemical potential of the diffusing component will vary monotonically and continuously along the column. Thus, the value of the chemical potential of the single diffusing component, at any point in the column sufficiently affected by the diffusion, will depend on where that point is relative to the overall chemical potential gradient. In other words, the value of the chemical potential of the single diffusing component, for the local equilibria of planes in the diffusion column, depends on conditions *external* to those planes (that is, on the diffusion). By definition, therefore, the one diffusing component is a 'K'-component (THOMPSON, 1970) for the various local equilibria of the diffusion-produced metasomatic zones. To quote J. B. THOMPSON (1970, p. 543), "... we shall designate as K-components those components for which the chemical potentials are fixed by some medium that lies outside what we have selected as our thermodynamic system, or, in other words, components for which the chemical potential is *externally* controlled. We shall designate all other components as J-components." As a consequence, mineral assemblages that buffer the chemical potential of a diffusing component should be found only at isolated points (or planes) i. the diffusion column, and no zone of finite thickness should contain a buffering assemblage.

The fact that the single diffusing component, 3, is a K-component suggests that Fig. 1 is not the most convenient diagram for determining the sequence of metasomatic zones. More appropriate is Fig. 2 in which the chemical potential of component 3, μ_3 , is used as an independent variable, rather than its mole fraction. Figure 2 consists of 2-phase fields separated by horizontal 3-phase lines. This is in obvious contrast with the 3-phase fields and 2-phase lines of Fig. 1. Single phases are found along vertical lines in Fig. 2 and at points in Fig. 1. Figure 2 can be constructed entirely from the topology of Fig. 1 using the potential surfaces of GIBBS (1928, pp. 118-129). In some instances, however, it is not possible to determine the relative positions of certain 3-phase lines without additional thermodynamic data (for example, the 3-phase line F-A-D in Fig. 2). See KHORZHINSKII (1959, pp. 80-88) for a description of the method of construction.

Possible sequences of diffusion zones may be found directly from Fig. 2 by examining the two vertical lines that correspond in composition (in terms of components 1 and 2) with the initial assemblages X and Y. Since the weight or mole ratio of component 1 to component 2 cannot be changed by the diffusion process, the initial boundary will always be marked by a discontinuity in this ratio. Therefore, zones produced on one side of the initial boundary may be read moving down the vertical line labeled X (de-

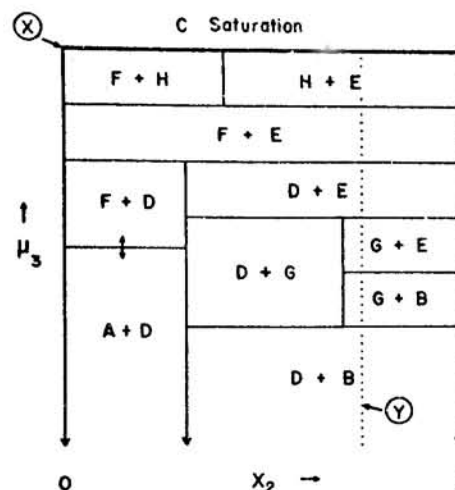
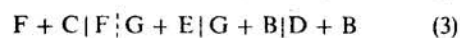
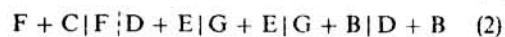


Fig. 2. A μ -X diagram for the hypothetical system of Fig. 1. The stable assemblages consistent with the topology of Fig. 1 are shown in terms of the chemical potential of component 3, μ_3 , and the bulk composition with respect to components 1 and 2, X_2 . Note that for most choices of the variables μ_3 and X_2 only two phases are stable. If component 3 is the only 'diffusing component', then diffusion may not change X_2 . Therefore, diffusional exchange between assemblages X and Y may only produce assemblages along the vertical lines corresponding to the compositions of X and Y.

creasing μ_3) and zones produced on the other side moving up the vertical line labeled Y (increasing μ_3), subject to the restriction that the chemical potential of component 3, μ_3 , be equal on either side of the final location of the initial boundary. Using a dashed line to indicate the relative position of the initial boundary, possible sequences of zones include:



All of these sequences are consistent with the initial assumptions and a monotonically increasing μ_3 across the zones.

Note that the zones produced have at most two minerals. If the mole fraction of component 3 varied independently, then there would be several zones with *three* minerals. Note also that by not allowing components 1 and 2 to diffuse, zonal sequences may be produced with incompatible phases in contact at the initial boundary. However, assemblages at all boundaries are in partial equilibrium with respect to component 3 (cf. THOMPSON and WALDBAUM, 1968, p. 1968).

In order to predict which of the possible sequences will actually occur, or in other words, the relative value of μ_3 at the initial boundary, a considerable amount of additional information is necessary.

Specifically, the relative rates of widening of the possible zones on either side of the initial boundary need to be known (see below). Using this information, a material balance argument for the flux across the initial boundary, and the restriction that μ_3 vary monotonically and continuously, a unique sequence may be determined. Only for a binary system (where the lines X and Y in Fig. 2 would coincide) or for a system with very few stable minerals do the mineral compositions alone indicate a unique sequence of zones.

The growth of diffusion zones for the case where there is only one diffusing component is mathematically analogous to a variety of heat flow problems. For detailed discussions of these and related problems see BOOTH (1948), DANCKWERTS (1950), WEINER (1955), FRANTZ and MAO (1976), WEARE *et al.* (1976). From the listed papers it is clear that the relative rates of zone widening can be predicted if the following is known: the sequence of zones, the density of the diffusing component in the minerals of each zone, and the density of the diffusing component in the intergranular region at the zone boundaries. In addition, one must know or assume that the effective, steady-state intergranular diffusion coefficient (BRADY, 1975c) is the same for all zones. If the actual value of this diffusion coefficient is known, then absolute rates of zone widening may be calculated.

Thus, for the case of one diffusing component, possible sequences of zones may be delineated from the topology of the appropriate phase diagrams, if known. Although the example discussed above was for a 3-component system, additional components introduce difficulties only in terms of graphical representation. A probable sequence of zones may be selected from the possible sequences only if equilibrium densities of the diffusing component in the minerals and intergranular region are known.

ZONES PRODUCED BY TWO DIFFUSING COMPONENTS

The addition of a second diffusing component may considerably complicate an analysis of the growth of diffusion zones. To begin with, two diffusing components have the potential to interact while diffusing such that each may tend to diffuse in response to a gradient in the chemical potential of the other (see DENBIGH, 1951, p. 27). In addition, two diffusing components may react upon mixing so that the complexity of a mathematical description of zone growth is increased (HELFFERICH and KATCHALSKY, 1970; FRANTZ and MAO, 1974, 1976). Moreover, predicting the sequence of zones is complicated by the possibility that the two diffusing components may move at different rates or with different effective fluxes. The problem of interacting fluxes is a difficult one that becomes nearly intractable for multicomponent systems (see BRADY, 1975a, Section 4). Because of the complexity of the problem and complete lack of data

for systems and conditions of geologic interest, I shall assume here that there is no interaction among diffusive fluxes (all off-diagonal diffusion coefficients are zero). The effect of precipitation or dissolution upon mixing of two diffusing components was investigated for two-component systems by FRANTZ and MAO (1976). They found that zone sequences and growth rates are nearly the same with or without precipitation, so I will not consider the problem further here. On the other hand, complications in predicting the sequence of zones are worthy of some discussion, for qualitative behavior can be revealed that should help interpret natural examples.

Let us return to the example of the three-component system shown in Fig. 1. This time, however, let components 3 and 1 be diffusing components. Assuming the same initial configuration, what zone sequence should develop during a long anneal? Again, Fig. 1 is not the most convenient representation; Fig. 3A or 3B is more appropriate. In Figs. 3A and 3B, the chemical potentials of components 1 and 3 have been used as independent variables. As discussed above, this is appropriate for those portions of the diffusion column where both components are K-components. I have included two possible μ - μ diagrams to emphasize that Fig. 1 does not contain sufficient information to differentiate between the two geometries. For details of the construction of μ - μ diagrams, see KORZHINSKII (1959, Chapter IV).

If components 1 and 3 diffuse with equal facility, the probable sequence of zones may be read from a straight line drawn between the points X and Y

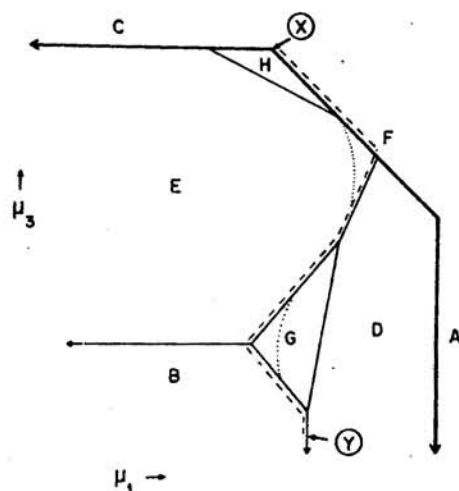


Fig. 3A. A μ - μ diagram for the hypothetical system of Fig. 1. The stable assemblages consistent with the topology of Fig. 1 are shown in terms of the chemical potentials of components 1 and 3. The dashed line indicates the assemblages of sequence (1), which assumes that component 3 is the only diffusing component. As indicated, the diffusion of component 3 may produce gradients in μ_1 . Some diffusion of component 1 could modify the sequence of assemblages as shown with the dotted line. The chemical potential of component 2 varies from point to point on this diagram.

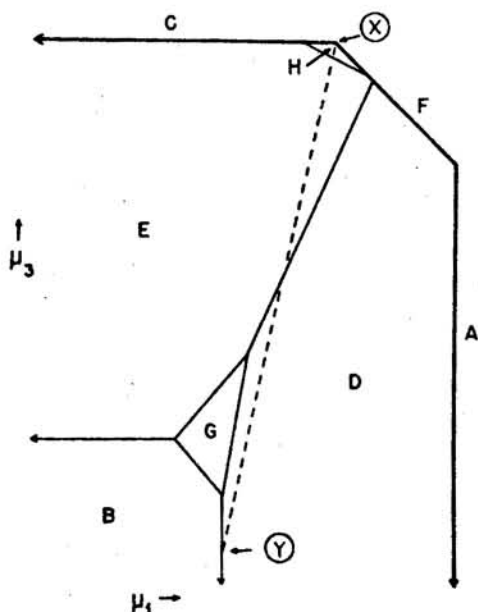


Fig. 3B. A μ - μ diagram for the hypothetical system of Fig. 1. Figure 3B is topologically identical to Fig. 3A, but geometrically distinct. The sequence of assemblages produced by diffusion of components 1 and 3 between assemblages X and Y is indicated by the dashed line. Note that this sequence is different from that which is suggested by Fig. 3A. Also note that the direction of motion of component 1 suggested by this geometry is opposite to that suggested by the geometry of Fig. 3A.

defined by the initial assemblages. The actual μ - μ path described by the diffusion zones may not be exactly a straight line in Fig. 3A or 3B, since there is nothing to constrain μ_1 and μ_3 to vary exactly in unison. However, if both are equally 'effective' as diffusing components, that is, if each can diffuse

$$F + C \mid F \mid F + E \mid E \mid D + E$$

enough to ensure a monotonic and continuous variation in its chemical potential, the sequence of zones indicated by a straight line will be correct in most cases. For Fig. 3A this sequence would be

$$F + C \mid H \mid E \mid G \mid B \mid D + B, \quad (5)$$

and for Fig. 3B

$$F + C \mid H \mid E \mid D \mid D + B. \quad (6)$$

Again, the relative position of the initial boundary is indicated by a dashed line. It is possible to locate the initial boundary because component 2 does not

* The sequences (5) and (6) are not compatible with the conclusions of FRANTZ and MAO (1975) in terms of their predictions of the direction of zone boundary movements. The sequences

$$F + C \mid F \mid H \mid E \mid G \mid B \mid D + B \quad (5a)$$

and

$$F + C \mid C \mid H \mid E \mid D \mid D + B \quad (6a)$$

do fulfill their criteria and are also consistent with the present analysis.

diffuse (relative to 'inert' markers) and because there was no component 2 in the initial assemblage $F + C$. Thus, any assemblage containing component 2 must have been produced from the initial assemblage $D + B$. However, if both initial assemblages contained significant quantities of component 2, then the final location of the initial boundary could not be precisely specified without additional kinetic information because weight and mole ratios among all three components are variable. Other sequences consistent with a monotonic and continuous variation of both μ_1 and μ_3 are, of course, possible and may be derived by the reader.*

If the two diffusing components differ in their ease of transport, then a variety of additional zone sequences are possible. This situation might arise even if the two components have the same effective diffusion velocity, if they have markedly different densities in the intergranular region (see ILDEFONSE and GABIS, 1976, p. 299). Consider again the example represented by Figs. 1, 2, and 3A, and assume that component 3 is much more 'effective' as a diffusing component than component 1. In this case, a sequence of zones should develop very similar to those obtained above with component 3 as the only diffusing component. One of the possible sequences, (1), is indicated on Fig. 3A by dashed lines. Note that although there was initially little gradient in the chemical potential of component 1, the diffusion of component 3 will produce μ_1 gradients, including a maximum and a minimum. These gradients in μ_1 may be sufficient to cause enough diffusion of component 1 to alter the sequence of zones to those along the dotted path in Fig. 3A. Thus, a possible zone sequence with component 3 diffusing more readily than component 1 would be

$$F + C \mid F \mid G \mid G + B \mid D + B. \quad (7)$$

Zones E and G are the only zones for which component 1 is a K-component and would probably be narrow relative to the other zones. Similarly, if component 1 diffuses much more readily than component 3, a possible sequence would be

$$F + C \mid F \mid H \mid E \mid G \mid B \mid D + B. \quad (8)$$

Zones H, E, and G would be small compared to zones F and B, and are the only zones for which component 3 is a K-component. More possibilities exist, depending on the relative effectiveness of the two diffusing components.

The zone sequences predicted above are deceptively simple due to the number of components in the system examined. Somewhat greater generality may be obtained by considering a four-component system. For a four-component system with two diffusing components, the appropriate diagram for examining possible zone sequences would be 3-dimensional, with one composition axis and two chemical potential axes. Actually, only two μ - μ planes through such a μ - μ -X diagram need be considered: those corresponding to

the compositions of the two starting assemblages. These *planes* would be analogous to the *lines* X and Y in Fig. 2. Since two of the four components do not diffuse (relative to 'inert' markers), the initial boundary will always be marked by a discontinuity in the otherwise-constant weight or mole ratio of those components. The sequence of zones produced on one side of the initial boundary could be read from one of the $\mu-\mu$ planes and the sequence on the other side from the other $\mu-\mu$ plane. Unfortunately, the only guiding restriction relating these two sequences is that the chemical potentials of the two diffusing components be equal across the initial (=final) boundary—unless the effectiveness of the two as diffusing components differs, as in (7).

As mentioned above, the calculation of rates of zone growth is complicated by interacting fluxes and precipitation upon mixing. However, even if these effects are neglected, rates of zone widening may be difficult to determine when there is more than one diffusing component. The difficulty stems from the fact that if two or more diffusing components are K-components, the mineral assemblages of adjacent diffusion-produced zones generally will not buffer the chemical potentials of both the diffusing components at the common zone boundary; at least one of the chemical potentials is free to vary. This means that the boundary conditions commonly used for the mathematical solution of zone growth rates may not be obtained from equilibrium considerations. A method of solution has been suggested by FRANTZ and MAO (1975) for the case of stoichiometric minerals with known solubilities in the presence of an intergranular fluid phase and for which diffusion coefficients are known. WEARE *et al.* (1976) discuss solutions for zone growth rates where intergranular densities of diffusing components at the zone boundaries are assumed to be known.

DISCUSSION

Expanding the preceding discussion to cases of three or more diffusing components is not practical due to the limitations of graphical analysis. However, several characteristics of the simple systems considered probably also apply to multicomponent systems with many diffusing components.

(1) The mineral assemblage of a diffusion-produced zone may not buffer the chemical potential of any component that diffuses through that zone. This is a consequence of the principle of local equilibrium, the necessity of a continuously varying chemical potential to sustain diffusion, and the assumptions listed above. Thus, at least one of the components diffusing through a metasomatic mineral zone must be a K-component for the mineral assemblage of that zone.

(2) If some of the diffusing components are more effective in reducing their chemical potential gradients

than others, the number of diffusing components that are K-components may vary from zone to zone. Zones with the most K-components are likely to occur near the initial boundary, since the driving force for diffusion is likely to be greatest there. However, zones at other positions in the diffusion column may also have the full complement of K-components.

(3) If two or more components do not diffuse, weight ratios among these components in the diffusion-produced zones will not vary from those of the initial configuration. If available, such non-diffusing components which are stationary relative to 'inert' markers, may be used to locate an initial boundary and to calculate volume changes for the diffusion column. If there is only one non-diffusing component, an initial boundary can be located with certainty only if that component was absent or nearly absent from one of the initial assemblages or if additional textural information is available.

(4) Zone sequences may be easily predicted only for the simplest systems (only a few possible minerals or only two components) or for cases where there is only one diffusing component or only one J-component in each zone. Even if the number of diffusing components that are K-components is the same in each zone, there will commonly be a large number of acceptable possibilities, and a specific prediction is not possible without detailed thermochemical and kinetic data. If the number of diffusing components that are K-components varies from zone to zone, then zone sequence prediction may be even more difficult. In the latter case, the concept of a facies for diffusion-produced metasomatic zones (with facies diagrams such as Figs. 2 and 3) is not particularly useful (cf. BURT, 1971).

It would be convenient to be able to predict which components will be diffusing components for a particular example. Unfortunately, this will in general require detailed thermochemical and kinetic data, much of which is not presently available. However, for any component to be important as a diffusing component, certain minimum requirements must be met.

(1) Initially there must be a significant local gradient in the chemical potential of the component. Without such a driving force no diffusion will occur. For example, SiO_2 will not be a diffusing component in a rock that contains quartz throughout.

(2) The diffusion coefficient for the component must be large enough at the temperature of metamorphism to ensure a significant diffusion velocity along the available intergranular paths. Interestingly, the diffusion coefficients for most non-volatile components are probably very similar at the conditions of metamorphism, so that this may turn out not to be a crucial parameter (see WALTON, 1960; BRADY, 1975c).

(3) The density of the diffusing component in the intergranular region must be high enough to ensure a significant diffusive flux of the component relative to the time scale of metamorphism. Even with a large

chemical potential gradient and a high diffusion coefficient, there cannot be much diffusive flux without a high concentration (and therefore high concentration gradient) in the diffusion medium.

The components that are most 'effective' as diffusing components will be those that have a relatively low density in the zone minerals and a relatively high density in the intergranular region (cf. KORZHINSKII, 1970, p. 125). An obvious example of this is the case of volatile components whose density may be higher in the intergranular region than in the adjacent minerals. Indeed, the diffusion of volatile components such as H_2O and CO_2 may be so effective that gradients in their chemical potentials are eliminated on the scale of most diffusion zones. The constant chemical potentials of these components may be treated as boundary conditions in the application of the preceding analysis (THOMPSON, 1955, p. 80; KORZHINSKII, 1959, p. 16). Thus, the three-component system examined could be a four-component system, if one of the components is a K-component with a constant chemical potential throughout.

The reader should note that in a binary system there may be two diffusing components, in the sense that they both move relative to 'inert' markers, but only one may be a K-component. If the chemical potential of one component is specified by conditions external to a particular local equilibrium, the chemical potential of the other component is fixed by the single phase present through the Gibbs-Duhem relationship for that phase (at constant temperature and pressure). Similarly, for an n -component system at constant temperature and pressure, all n -components may be diffusing components, but a maximum of $n - 1$ may be K-components (see JOESTEN, 1974, p. 897).

Of the assumptions on which these generalizations are based, perhaps the one most obviously incorrect is the restriction that zone minerals be pure substances. Most natural zones involve some minerals with significant compositional variability. These minerals must continuously change their composition with that of the intergranular region as the zones develop, if their possible compositional variations may be expressed in terms of a linear combination of the diffusing components (KORZHINSKII, 1970, p. 115). Simple zone growth models that do not consider the necessary continuous reactions may be significantly in error. The qualitative results given above are otherwise unaffected by compositional variability.

The assumption of constant temperature and pressure throughout the period of metamorphism is also suspect for any natural example. Not only would a varying temperature cause varying growth rates, but it might also lead to the initial development of one sequence of zones, followed by modifications at conditions where other minerals are stable. The latter case could produce effects similar to those observed when the condition of a sharp initial boundary is violated. Either situation might be manifested in the final

product by a zone sequence that is not consistent with the monotonic variation of the chemical potential of at least one diffusing component that is a K-component.

NATURAL CALC-SILICATE ZONES

Perhaps the simplest example of calc-silicate zones described in the literature is that of JOESTEN (1974). He describes monomineralic zones that developed concentrically around chert nodules in a contact-metamorphosed limestone in Texas (see also TILLEY, 1948). Except for CO_2 , the minerals in Joesten's zones are in the binary system $CaO-SiO_2$. Thus, for a given temperature, pressure, and μ_{CO_2} , there is only one sequence of zones consistent with the assumptions of this paper.

Both CaO and SiO_2 are possible diffusing components, but only one may be a K-component (at constant μ_{CO_2}). The predicted sequence of zones is that consistent with a monotonic variation of μ_{SiO_2} (and μ_{CaO}). Joesten's observations at several locations in the thermal aureole (temperatures) confirm this prediction and lead him to similar conclusions. Because of its simplicity, it may be possible to use this example to obtain quantitative information on the timing of the metasomatic event, if appropriate intergranular diffusion data become available. Conversely, it may be possible to use a thermal model of the contact aureole to obtain diffusion data from the zones (George Fisher, personal communication, 1975).

Most natural calc-silicate zones are not as simple as those described by Joesten. More typical are calc-silicate zones like those described by THOMPSON (1975). Thompson's zones were found at a marble-pelitic schist contact in sillimanite grade metamorphic rocks from northern Vermont.

Thompson describes the zoning sequence

marble	garnet zone	coarse diopside zone	fine clinozoisite diopside zone	amphibolite zone	pelitic schist

Although chemically complex, it turns out that many important features of these zones may be represented on an ACF diagram with $A = Al_2O_3 + Fe_2O_3$, $C = CaO$, $F = FeO + MgO + MnO$. Quartz is present throughout, so a constant μ_{SiO_2} may be used as a boundary condition. Alkalies have been neglected, but they are abundant only in the pelitic schist. It should be recognized, however, that using the ACF diagram can only provide information on the relative movement of the components A, C, and F.

Minerals observed and compatibilities consistent with local equilibrium and THOMPSON's (1975) zones are shown in Fig. 4. To simplify the diagrams and discussion, I have assumed the minerals to be pure substances of ideal compositions. Compositions of the marble and pelitic schist are shown in Fig. 4 at the points labeled X and Y, respectively. If there is only

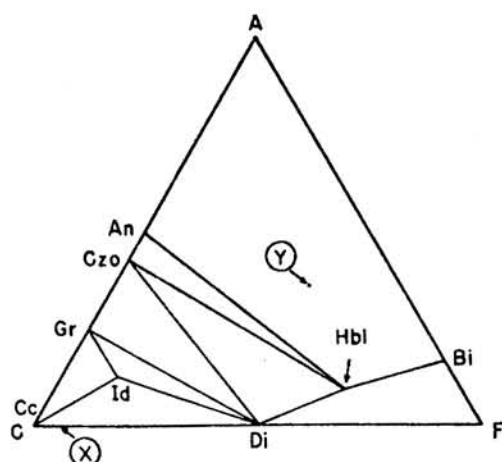


Fig. 4. An ACF diagram for some calc-silicate zones. Minerals and compatibilities consistent with the calc-silicate zones of THOMPSON (1975) are shown in terms of the components $A = \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, $C = \text{CaO}$, $F = \text{FeO} + \text{MgO} + \text{MnO}$. X and Y are the compositions of marble and pelite, respectively, adjacent to the diffusion zones. See Table 1 for mineral abbreviations.

one diffusing component, namely C ($=\text{CaO}$), then possible sequences of diffusion zones may be found along the vertical lines passing through the points X and Y in Fig. 5, which was constructed from the topology of Fig. 4. Possible sequences include (see Table 1 for mineral abbreviations):

Cc	Id	Gr	Di	Czo	An	pelitic	(9)
Di	Di	Di	Czo	Hbl	Hbl	schist	
Cc	Di	Id	Gr	Di	Czo	An	(10)
Di	Di	Di	Di	Czo	Hbl	Hbl	pelitic
Cc	Di	Gr	Di	Czo	An	pelitic	(11)
Di	Di	Di	Czo	Hbl	Hbl	schist	
Cc	Di	Di	Czo	An	pelitic	(12)	
Di	Czo	Hbl	Hbl	schist.			

In fact, sequence (9) is nearly identical to the detailed sequence described by Thompson. The only major difference is the absence of the zone $\text{Czo} + \text{Hbl}$ in Thompson's descriptions. However, on examination of Thompson's samples, small colorless amphiboles were found in his 'fine clinozoisite-diopside' zone, the proper location for a $\text{Czo} + \text{Hbl}$ zone.

This result suggests that Thompson's zones may be largely a consequence of the motion of one diffusing component, namely C, relative to A and F. Further evidence is contained in Fig. 6, in which the chemical analyses calculated by Thompson for various locations in his zones are shown on an ACF diagram. Although there is a good deal of scatter in the analyses, the dominant trend indicated in Fig. 6 radiates from the C corner of the triangle. The ideal trends that would be observed if C was the only diffusing component are indicated by the lines labeled X and Y in Fig. 6. The scatter observed about the line Y is expected for several reasons. Thompson's

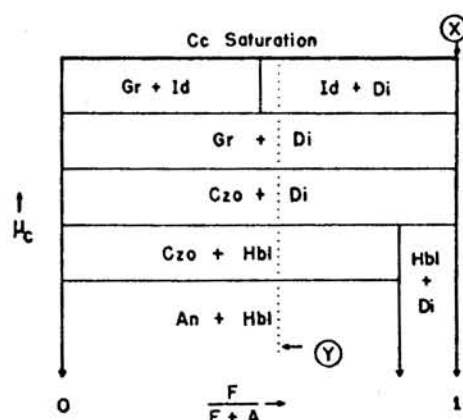


Fig. 5. A μ -X diagram for the system of Fig. 4. Stable assemblages consistent with the topology of Fig. 4 are shown in terms of the chemical potential of component C and the bulk composition with respect to components F and A. X and Y indicate the marble and pelite, respectively. The dotted line shows the possible assemblages that may be produced from the pelite with the addition of component C by diffusion.

analyses were calculated from modes determined from 'linear point counts'. Assuming that the original pelitic schist was like the remaining pelite, then inhomogeneities in its A:F ratio were present on a scale larger than that averaged by a linear point count parallel to those inhomogeneities. An examination of

Thompson's samples indicated that if modes for entire zones are used, the chemical analyses calculated more nearly fit the line Y.

The most significant deviation from the line Y in Fig. 6 is that of the points near the composition of diopside. Although these points might also be attributed to an initial inhomogeneity, there is another possible explanation: component A or F may have locally been a diffusing component. In Fig. 7, the chemical potentials of both C and A are used as independent variables. The dashed line path in Fig. 7 between the points labeled X and Y corresponds with sequence (9), which was obtained from Fig. 5 assuming that only C is a diffusing component. A modification of the dashed path that is consistent with Thompson's zones is indicated by the dotted path that crosses the diopside field. Thus, allowing A to diffuse enough locally to assure an independent variation of its chemical potential would tend to produce a diopside zone in the proper location. Allowing F

Table 1. Mineral abbreviations

Act = actinolite	Gr = grossularite
Alm = almandine	Hbl = hornblende
An = plagioclase (anorthite)	Id = idocrase
Bi = biotite	Mag = magnesite
Cc = calcite	Mus = muscovite
Chl = chlorite	Qz = quartz
Czo = clinozoisite	Serp = serpentine
Di = diopside	Tc = talc
Gar = garnet	Tr = tremolite

to diffuse locally would tend to produce clinozoisite and eliminate diopside at the same location, as may be deduced from Fig. 8. Therefore, if the local increase in the modal percentage of diopside observed by Thompson was produced by the local independent diffusion of A or F, rather than an initial inhomogeneity, it was probably A that was the diffusing component.

Another point in favor of A diffusing, rather than F, is the observation that the diopside and amphibole in several zones show a textural similarity, in terms of their distribution, to the biotite of the adjacent pelitic schist. This suggests that the F component of the biotite may be less able to diffuse than the A component. Whatever the case, it is clear that neither the A component nor the F component had a significant diffusion flux over more than a few millimeters, relative to inert markers, while a large quantity of the C component moved several centimeters. It follows that an inert marker present at the original marble-pelitic schist boundary would now be located between Thompson's marble and garnet zone. Interestingly, VIDALE (1969) found that the C component had a much greater concentration than either the A or F component in the fluids equilibrated with her experimentally-produced calc-silicate zones. This is consistent with the importance of C diffusion suggested here.

Of course, C was not the only component that moved relative to inert markers. Some H_2O and CO_2

must have left the region of the zones altogether, if the assumptions listed above are correct. CO_2 must have been released upon the decomposition of calcite to produce the calcium that was added to the pelitic schist. Similarly, partial dehydration would occur as the pelite reacted with the added calcium to form calc-silicates. As discussed by THOMPSON (1975), the escape of these volatile components entails a considerable volume loss at constant pressure. Alkalis have also left the calc-silicate zones, in favor of the pelitic schist. This occurs when alkalis lose their associated aluminum to stabilized calcium aluminum silicates, as the chemical potential of calcium rises. The important point is that these components, H_2O , CO_2 , K_2O , and Na_2O have been able to virtually eliminate gradients in their chemical potentials on the scale of the diffusion zones. Therefore, it is the diffusion-imposed gradient in the chemical potential of CaO (and possibly Al_2O_3 locally) that is responsible for the observed mineralogic zoning. Ideally, this means that the rate of growth of these zones could be calculated, if the appropriate diffusion data and intergranular densities for CaO were available. However, what the 'appropriate' diffusion data are remains uncertain (BRADY, 1975c). This is emphasized by the presence of similarly proportioned zones at Thompson's Vermont locality that range in overall width by an order of magnitude.

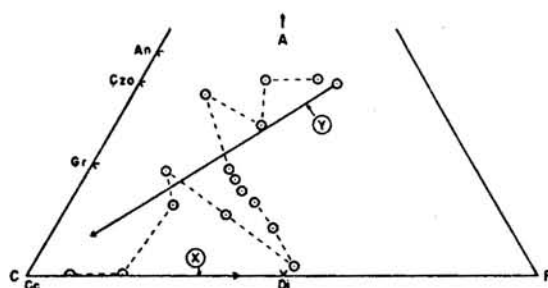


Fig. 6. Bulk compositions of the calc-silicate zones of THOMPSON (1975). The calculated chemical compositions given by Thompson for a sequence of calc-silicate diffusion zones are shown on an ACF diagram. The lines labeled X and Y are the trends that would be expected if C was the only diffusing component, on the basis of the assumptions of this paper. Note that the compositions fall on the two-phase tie lines of Fig. 5.

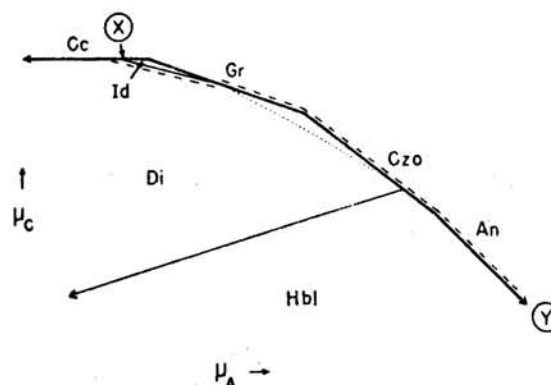
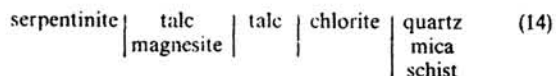


Fig. 7. A μ_C - μ_A diagram for the system of Fig. 4. The dashed line indicates the sequence of assemblages (9) that would be produced between a marble X and a pelite Y if component C is the only diffusing component. A modification that might be produced by the local diffusion of A is shown by the dotted line.

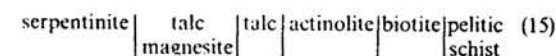
ZONING ASSOCIATED WITH ULTRAMAFIC BODIES

Metasomatic zones are commonly found along the contacts of ultramafic bodies in regional metamorphic terrains. Due in part to the economic value of associated talc deposits, many examples of these 'blackwall' zones have been described in the literature (for example, GILLSON, 1927; HESS, 1933; READ, 1934; PHILLIPS and HESS, 1936; BROWNLOW, 1961; CHIDESTER, 1962, 1968; CURTIS and BROWN, 1969, 1971; CARSWELL *et al.*, 1974). Certain features are common to many zoned ultramafics, and from these an idealized sequence of zones may be constructed. The ideal sequences may be used to reveal some major factors controlling zone formation.

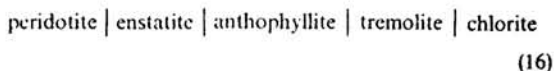
PHILLIPS and HESS (1936) describe two main types of blackwall zoning sequences, one apparently forming at higher temperatures than the other. The lower temperature type occurs with the ideal sequence



and the higher temperature type with the ideal sequence



Chlorite is present in many samples of the higher temperature type, primarily occurring between the biotite zone and actinolite zone. Phillips and Hess suggest that this chlorite is a retrograde alteration of the higher temperature sequence (15). READ (1934), however, includes chlorite in his ideal sequence for a Shetland Islands locality that is otherwise identical to (15). An even higher temperature sequence is described by CARSWELL *et al.* (1974). They describe symmetrically zoned veins in a peridotite with chlorite in the center and the ideal sequence



Contacts between the peridotite and country rock also show sequence (16), but with biotite between the chlorite zone and the siliceous country rock.

Because of the number of components involved in these sequences, it is useful to consider the status of the volatile components H_2O and CO_2 before attempting a graphical analysis. H_2O has been added to the original peridotite in all sequences; CO_2 has been added in the two lower temperature sequences. The general absence of assemblages buffering μ_{H_2O} , the general abundance of hydrous minerals, and the typical behavior of many metamorphic rocks are consistent with H_2O being a diffusing component that has established a constant value of its chemical potential in all zones (except in those cases where unserpentinized peridotite remains). CO_2 is less abundant and μ_{CO_2} is buffered by the ideal assemblage antigorite + talc + magnesite, at constant μ_{H_2O} . This suggests

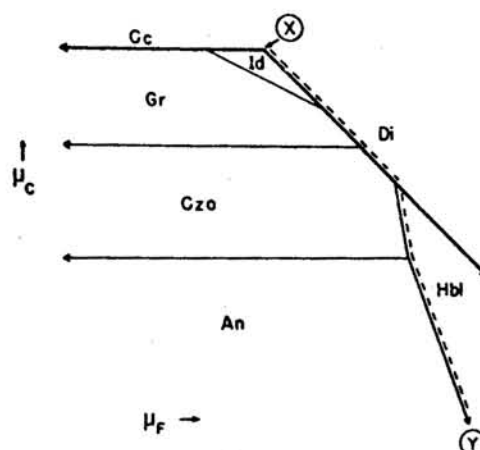


Fig. 8. A μ_C - μ_F diagram for the system of Fig. 4. The dashed line indicates sequence (9), which might be produced between marble X and pelite Y if component C is the only diffusing component. Note that local diffusion of component F would most likely produce a zone of Czo.

that although CO_2 is probably a diffusing component and a K-component in all zones (except possibly the serpentinite), it has not eliminated all gradients in its chemical potential. Fortunately, it does not appear to be important to evaluate variations in μ_{CO_2} , except for the talc + magnesite zone. Therefore, I shall consider both μ_{H_2O} and μ_{CO_2} to be constant throughout the zones and neglect the talc + magnesite zone, which is primarily the result of a diffusion-imposed gradient of μ_{CO_2} (see GREENWOOD, 1967).

At constant temperature, pressure, μ_{H_2O} and μ_{CO_2} , the minerals present in the lower temperature sequence (14) may be adequately represented on an AMS composition diagram, with $A = Al_2O_3 + Fe_2O_3$, $M = MgO + FeO + MnO$, $S = SiO_2$ (see Fig. 9). The initial compositions of the serpentinite and quartz-mica schist are approximated by the points X and Y, respectively. Using the procedures discussed above, possible sequences of zones may be

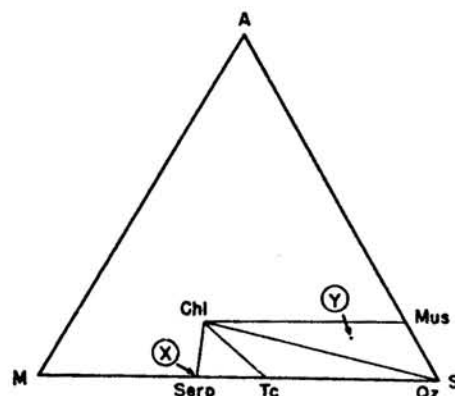
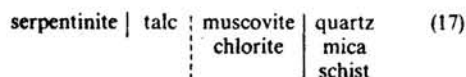
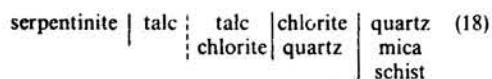


Fig. 9. An AMS diagram for ideal, lower temperature 'blackwall' zones. Mineral compatibilities consistent with the lower temperature sequence of diffusion zones of PHILLIPS and HESS (1936) are shown on an AMS diagram with $A = Al_2O_3 + Fe_2O_3$, $M = MgO + FeO + MnO$, $S = SiO_2$. X and Y indicate the bulk compositions of serpentinite and pelite adjacent to the 'blackwall' zones.

easily determined from the topology of Fig. 9 for the case of one diffusing component. If S is the only diffusing component a possible sequence would be



where the dashed line indicates the initial contact. Similarly, if M is the only diffusing component, a possible sequence would be



Both of these sequences are indicated on Fig. 10 along with the observed sequence. It is clear from Fig. 10 that for the chlorite zone, both S and M must be diffusing components that are K-components. S and M are probably also both diffusing components for the talc zone, but only one may be a K-component in the presence of talc. Note that by including muscovite in Fig. 10, and in the rocks, I have tacitly assumed that variations in μ_{K_2O} are not important. Since K_2O appears to have moved from the blackwall region into the adjacent pelitic schist, there is probably a gradient in μ_{K_2O} decreasing toward the schist. Neglecting this gradient does not appear to yield contradictory results.

As the reader can verify, the higher temperature sequence (15) is graphically quite similar to the lower temperature sequence (14), with biotite playing the same topologic role as chlorite. The only major difference is the presence of actinolite, which implies that CaO had become an effective diffusing component with the increase in temperature. Indeed, CaO must diffuse through the actinolite zone and biotite zone

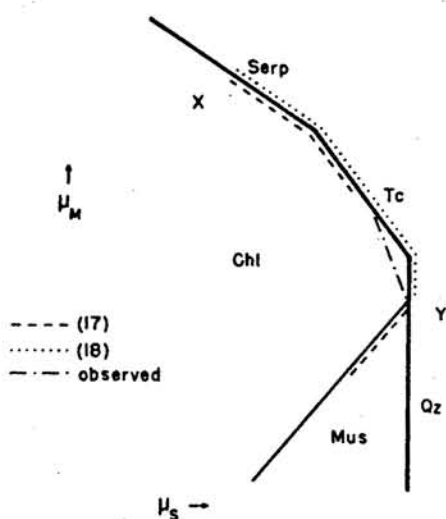


Fig. 10. A μ_M - μ_S diagram for the system of Fig. 9. Sequences (17) and (18) are shown on this diagram along with the observed sequence of diffusion zones. Neither (17), for which S is the only diffusing component, nor (18), for which M is the only diffusing component, duplicate the observed sequence. It appears that both M and S must be diffusing components, at least in the chlorite zone.

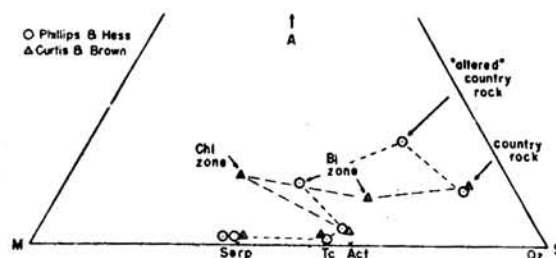


Fig. 11. Bulk compositions of some ultramafic 'blackwall' zones. Chemical compositions of 'blackwall' zones given by PHILLIPS and HESS (1936) and CURTIS and BROWN (1969) are shown on an AMS diagram. Note the change in A content between the chlorite zone and the actinolite zone.

for the former to grow by diffusion. As noted above, the status of chlorite in the higher temperature sequence is uncertain. However, it is reasonable to believe that both chlorite and biotite may be stable at least for conditions intermediate between those that produced sequences (14) and (15). This case is more difficult to treat graphically, but that biotite should appear in the sequence nearest the country rock is consistent with the overall trends in μ_{SiO_2} and μ_{MgO} . The major features of the zones in all suggested sequences, however, are primarily due to the diffusion of both S and M.

Chemical analyses of a higher temperature sequence (15) from Chester, Vermont (PHILLIPS and HESS, 1936) are shown in Fig. 11 along with chemical analyses of the Shetland Islands zones of READ (1934) [analyses from CURTIS and BROWN (1969)]. The analyses match very closely the ideal mineral compositions, suggesting that the ideal sequence (15) is a good approximation to the natural examples. The discontinuity between the actinolite zone and biotite (or chlorite) zone in relative A content would suggest that this is the location of the initial contact. Such a conclusion, however, is only valid if it is certain that A was not a diffusing component and did not move relative to inert markers (if present). Definite evidence for an initial boundary in the absence of verified inert markers is only given by a discontinuity in the otherwise-constant weight ratio of two components. This information is available for the Shetland Islands example in the analyses of CURTIS and BROWN (1969, 1971). The Al/Cr ratio and, less perfectly, the Al/Ni ratio both show a sharp discontinuity at the actinolite-chlorite boundary. Of course, the initial boundary might be slightly into the actinolite zone or into the chlorite zone, since the chemical analyses used are an average for each zone. More closely spaced analyses are necessary to determine a precise location. With the initial boundary located, quantitative evaluation of material transport is possible, using procedures such as those outlined by GRESENS (1957) and BABCOCK (1973). The material transfer calculations presented by CURTIS and BROWN (1969) based on a different initial boundary (chosen to maintain constant volume) cannot be correct. Similarly, material

	Peridotite	Serp	Tc + Mag	Tc	Act	Chl	Bi	Country Rock
H ₂ O								
CO ₂								
SiO ₂								
MgO (+FeO+MnO)								
CaO								
K ₂ O (+Na ₂ O)								

Fig. 12. The K-components of individual 'blackwall' zones. Probable K-components for each zone of an ideal sequence of ultramafic 'blackwall' zones are indicated by horizontal lines. This selection of K-components is consistent with the diffusion models discussed in the text.

transfer calculations by CHIDESTER (1962), who also uses what is basically a constant volume assumption for several lower temperature sequences from northern Vermont, are probably not correct. However, Chidester's numbers should be very nearly correct, since the initial boundary he chooses is close to the chlorite-talc boundary, which is the initial boundary indicated by his chemical analyses and the criteria discussed above.

Some of the preceding discussion may be clarified by Fig. 12, in which the probable K-components for each zone of the higher temperature sequence (15) are identified. Although Fig. 12 is based on idealized sequences, the general picture is probably correct. Except for μ_{H_2O} , which may be nearly constant throughout, the chemical potentials of the listed K-components should show a monotonic variation across the zones indicated.

The highest temperature sequence (16) is very much like the other two, except that a gradient in μ_{H_2O} is more likely in this case. The mineral names are changed, but the topology of the AMS diagram remains the same. I would, however, like to suggest a possible alternative origin to that proposed by CARSWELL *et al.* (1974). The sequence (16) is found as a symmetrical 'vein' in a peridotite body in southern Norway. Carswell *et al.* postulate a fluid-filled fracture in the ultramafic body along which the peridotite could exchange material with the country rock (a migmatite terrain), either by fluid flow or diffusion. If this were the case, one might expect a sequence of zones to form that match those on the ultramafic side of the initial contact. If the lower temperature sequences may be used as a guide, then the observed sequence should stop with the actinolite zone rather than the chlorite zone. Perhaps a more reasonable explanation is to postulate a granitic dike, such as those common to migmatite terrains, as producing the original compositional discontinuity. If the dike was not too thick, then its material could be exhausted by diffusion, resulting in sequence (16). This

would require loss of potassium, probably along the dike to the country rock. However, this loss of potassium, which is relatively easy to move, is not difficult when compared with the material transfer of other components, some of which may be hard to move, suggested by the model of Carswell *et al.*

CONCLUDING REMARKS

In general terms, the natural examples of metasomatic zones examined above are consistent with the theoretical models outlined near the beginning of this paper. Details and complexities of specific examples that are not consistent with the simple models are expected, due to probable violations of the simplifying assumptions. The encouraging point is that observed zones do have much in common with the simple models.

Metasomatic zones do contain information about what components have moved by diffusion during metamorphism. This information is most easily obtained by comparing observed zone sequences with those predicted by simple models. In principle, the zones can indicate which components have moved and with what relative ease of transport. The most effective diffusing components, or the components that can establish independent variations of their chemical potentials, are likely to be those with the highest density in the intergranular region of a rock (BRADY, 1975c). Thus, metasomatic zones may contain information about the nature of the intergranular region of metamorphic rocks.

The results of this paper are entirely qualitative. Quantitative information on the duration of metamorphic events might be obtained from metasomatic zones if a considerable quantity of experimental information becomes available. In particular, effective diffusion coefficients (BRADY, 1975c) for several components and the parameters that control them must be determined. Due to the variable thickness of metasomatic zones, even at a single locality, a minimum time for zone growth is probably the best possible result.

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REFERENCES

- BABCOCK R. S. (1973) Computational models of metasomatic processes. *Lithos* **6**, 279–290.
- BOOTH F. (1948) A note on the theory of surface diffusion reactions. *Trans. Faraday Soc.* **44**, 796–801.
- BRADY J. B. (1975a) Reference frames and diffusion coefficients. *Amer. J. Sci.* **275**, 954–983.
- BRADY J. B. (1975b) Chemical components and diffusion. *Amer. J. Sci.* **275**, 1073–1088.

- BRADY J. B. (1975c) Intergranular diffusion in metamorphic rocks. Ph.D. thesis, Harvard University.
- BRADY J. B. (1976) Models for intergranular diffusion in metamorphic rocks (abstr.). *EOS* **57**, 338.
- BROWNLOW A. H. (1961) Variation in composition of biotite and actinolite from monomineralic contact bands near Westfield, Massachusetts. *Amer. J. Sci.* **259**, 353-370.
- BURT D. M. (1971) The facies of some Ca-Fe-Si skarns in Japan. *Carnegie Inst. Wash. Yearb.* **70**, 185-188.
- CARSWELL D. A., CURTIS C. D. and KANARIS-SOTIRIOU R. (1974) Vein metasomatism in peridotite at Kalskaret near Tafjord, South Norway. *J. Petrol.* **15**, 383-402.
- CHIDESTER A. H. (1962) Petrology and geochemistry of selected talcbearing ultramafic rocks and adjacent country rocks in north-central Vermont. *U.S. Geol. Surv. Prof. Paper* **345**, 207 pp.
- CHIDESTER A. H. (1968) Evolution of the ultramafic complexes of northwestern New England. In *Studies of Appalachian Geology, Northern and Maritime*, (editors E. Zen, W. S. White, J. B. Hadley and J. B. Thompson, Jr.), pp. 343-354. Interscience.
- CURTIS C. D. and BROWN P. E. (1969) The metasomatic development of zoned ultrabasic bodies in Unst, Shetland. *Contrib. Mineral. Petrol.* **24**, 275-292.
- CURTIS C. D. and BROWN P. E. (1971) Trace element behavior in the zoned metasomatic bodies of Unst, Shetland. *Contrib. Mineral. Petrol.* **31**, 87-93.
- DANCKWERTS P. V. (1950) Unsteady-state diffusion or heat-conduction with moving boundary. *Trans. Faraday Soc.* **46**, 701-712.
- DARKEN L. S. (1948) Diffusion, mobility and their interrelation through free energy in binary metallic systems. *Amer. Inst. Mining Met. Engrs Trans.* **175**, 184-201.
- DENBIGH K. G. (1951) *The Thermodynamics of the Steady State*, 103 pp. Methuen.
- FISHER G. W. (1970) The application of ionic equilibria to metamorphic differentiation: an example. *Contrib. Mineral. Petrol.* **29**, 91-103.
- FISHER G. W. and ELLIOTT D. (1974) Criteria for quasi-steady diffusion and local equilibrium in metamorphism. In *Geochemical Transport and Kinetics*, (editors A. W. Hofmann, B. J. Giletti, H. S. Yoder, Jr. and R. A. Yund), pp. 231-241. Carnegie Inst. Washington.
- FLETCHER R. C. and HOFMANN A. W. (1974) Simple models of diffusion and combined diffusion-infiltration metasomatism. In *Geochemical Transport and Kinetics*, (editors A. W. Hofmann, B. J. Giletti, H. S. Yoder, Jr. and R. A. Yund), pp. 243-259. Carnegie Inst. Washington.
- FRANTZ J. D. and MAO H. K. (1974) Metasomatic zoning resulting from intergranular diffusion: a theoretical model. *Carnegie Inst. Wash. Yearb.* **73**, 384-392.
- FRANTZ J. D. and MAO H. K. (1975) Bimetasomatism resulting from intergranular diffusion: multimineralic zone sequences. *Carnegie Inst. Wash. Yearb.* **74**, 417-424.
- FRANTZ J. D. and MAO H. K. (1976) Bimetasomatism resulting from intergranular diffusion: I. A theoretical model for monomineralic reaction zone columns. *Amer. J. Sci.* **276**, 817-840.
- GIBBS J. W. (1928) *The Collected Works of J. Willard Gibbs*, Vol. 1, 434 pp. Yale University Press.
- GILLSON J. L. (1927) Origin of Vermont talc deposits. *Econ. Geol.* **22**, 246-285.
- GREENWOOD H. J. (1967) Mineral equilibria in the system $MgO-SiO_2-H_2O-CO_2$. In *Researches in Geochemistry*, (editor P. H. Abelson), pp. 542-567. John Wiley.
- GRESENS R. L. (1967) Composition-volume relationships of metasomatism. *Chem. Geol.* **2**, 47-65.
- DE GROOT S. R. and MAZUR P. (1962) *Nonequilibrium Thermodynamics*. 510 pp. North Holland.
- HELFFERICH F. and KATCHALSKY A. (1970) A simple model of interdiffusion with precipitation. *J. Phys. Chem.* **74**, 308-314.
- HESS H. H. (1933) The problem of serpentization, etc. *Econ. Geol.* **28**, 636-657.
- ILDEFONSE J.-P. and GABIS V. (1976) Experimental study of silica diffusion during metasomatic reactions in the presence of water at 550°C and 1000 bars. *Geochim. Cosmochim. Acta* **40**, 297-303.
- JOESTON R. (1974) Local equilibrium and metasomatic growth of zoned calc-silicate nodules from a contact aureole, Christmas Mountains, Big Bend region, Texas. *Amer. J. Sci.* **274**, 876-901.
- KORZHINSKII D. S. (1959) *Physicochemical Basis of the Analysis of the Paragenesis of Minerals*, 142 pp. Consultants Bureau, Inc.
- KORZHINSKII D. S. (1970) *Theory of Metasomatic Zoning*, (trans. by Jean Agrell), 162 pp. Oxford University Press.
- PHILLIPS A. H. and HESS H. H. (1936) Metamorphic differentiation at contacts between serpentinite and siliceous country rocks. *Amer. Mineral.* **21**, 333-362.
- READ H. H. (1934) On zoned associations of antigorite, talc, actinolite, chlorite, and biotite in Unst, Shetland Islands. *Mineral. Mag.* **23**, 519-540.
- THOMPSON A. B. (1975) Calc-silicate diffusion zones between marble and pelitic schist. *J. Petrol.* **16**, 314-346.
- THOMPSON J. B., JR. (1955) The thermodynamic basis for the mineral facies concept. *Amer. J. Sci.* **253**, 65-103.
- THOMPSON J. B., JR. (1959) Local equilibrium in metasomatic processes. In *Researches in Geochemistry*, (editor P. H. Abelson), pp. 427-457. John Wiley.
- THOMPSON J. B., JR. (1970) Geochemical reaction and open systems. *Geochim. Cosmochim. Acta* **34**, 529-551.
- THOMPSON J. B., JR. and WALDBAUM D. R. (1968) Mixing properties of sanidine crystalline solutions: I. Calculations based on ion-exchange data. *Amer. Mineral.* **53**, 1965-1999.
- TILLEY C. E. (1948) Earlier stages in the metamorphism of siliceous dolomites. *Mineral. Mag.* **28**, 272-276.
- VIDALE R. J. (1969) Metasomatism in a chemical gradient and the formation of calc-silicate bands. *Amer. J. Sci.* **267**, 857-874.
- WALTON M. (1960) Molecular diffusion rates in supercritical water vapor estimated from viscosity data. *Amer. J. Sci.* **258**, 385-401.
- WEARE J. H., STEPHENS J. R. and EUGSTER H. P. (1976) Diffusion metasomatism and mineral reaction zones: general principles and application to feldspar reaction zones. *Amer. J. Sci.* **276**, 767-816.
- WEINER J. H. (1955) Transient heat conduction in multiphase media. *Brit. J. Appl. Phys.* **6**, 361-363.