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"Mobile" Components in the Formation of Calc-Silicate Bands

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Abstract

The concept of 'mobile' component is examined in the context of specific and detailed studies of calc-silicate zoning. This zoning is produced by diffusion of volatile and non-volatile species down activity gradients controlled by a gradient in bulk composition. The zoning consists of a sequence of phase assemblages, each of which represents one local equilibrium environment. These local equilibrium assemblages may differ from each other in the number of phases, the identity of phases, and the identity of components whose chemical potentials are controlled internally ('inert' components) or externally ('mobile' components). The zonation complex usually changes with time. When this zoning occurs, the phase rule is most conveniently applied to each current local equilibrium assemblage. 'Mobile' components must be moveable so that external control of their chemical potentials can be established and maintained, but quite commonly they move less than some of the 'inert' components.

Introduction

Vidale (1968, 1969) and Hewitt (1970, 1973) have described and documented two types of calc-silicate zoning formed near the contacts of relatively thin carbonate-bearing layers in pelitic schists. Both types of zoning are caused by chemical potential gradients across the contacts; the first forms in response to a gradient in the activities of volatile components, such as CO_2 and H_2O, and the second in response to gradients in activities of non-volatile components, such as KCl, in the vapor phase. The question of whether the chemical potentials of the components are controlled inside or outside the local phase assemblage zones has played an essential part in the interpretation of the assemblages.

'Inert' and 'Mobile' Components

Two fundamental categories of chemical components have repeatedly proven useful in the description of rock systems: (1) components whose chemical potentials are controlled by the equilibrium phase assemblage being studied, and (2) components whose chemical potentials are controlled externally and imposed on that phase assemblage. Korzhinskii (1959) calls these components 'inert' and 'perfectly mobile' and defines 'inert' components as those ". . . whose masses or molar amounts (*i.e.*, extensive parameters) are equilibrium factors of the system," and 'perfectly mobile' components as ". . . those whose chemical potentials, activities, and concentrations in one of the phases or partial vapor pressures (*i.e.*, intensive parameters) are factors of equilibrium of the given system."

Zen (1963) suggests the terms, 'initial value components' and 'boundary value components,' ". . . because the values of their chemical potentials are determined either by the initial proportions or by the values of the potentials at the boundary of the system (mineral assemblage), respectively." This terminology is analogous to that used in other types of potential problems, such as heat flow.

Thompson (1970) designates 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." He designates all other components as 'J' components. Thompson's sense of the terms is slightly different from that of the others because he includes the possibility of segregating part of a coexisting assemblage from the system and considering it as external to the system.

In this paper, we shall designate each mineral assemblage zone as a system, and for simplicity, we shall use the relatively familiar terms 'inert' component and 'mobile' component for components whose chemical potentials are controlled inside and outside the system respectively.

The effect of the number of 'mobile' components on the maximum number of phases in a system is expressed by Korzhinskii's reformulation (Korzhinskii, 1936) of the Gibbs phase rule (Gibbs, 1928) from $f = c - p + 2$, to $f = c - p + 2 - m$, where f = variance, c = total number of independent components, p = number of coexisting phases, and m = number of components whose chemical potentials are externally controlled. Essentially, m new restrictions (fixed intensive variables) are introduced, decreasing the variance by that amount. Thus over a range of pressure, temperature and other intensive variables, $p \leq c - m$.

Types of Zoning

Two types of calc-silicate zoning will be discussed. The first will be referred to as zoning due to chemical potential gradients of volatile components, and the second as zoning due to chemical potential gradients of non-volatile components. Although all components exist in the vapor phase, we shall limit the term, volatile components, to those components that, when pure, occur as a fluid under the pressure and temperature conditions of the calc-silicate formation (for example, CO_2 and H_2O), and use the term, non-volatile components, for all others (for example, KCl and $CaCl_2$).

It is convenient to approximate the natural system by one that is chemically simpler in order to compare the two types of zoning. The model system to be used here is K_2O–CaO–MgO–Al_2O_3–SiO_2–H_2O $\pm$ CO_2 $\pm$ KCl. This neglects the obviously important components, FeO–Fe_2O_3–Na_2O, but it still closely represents some simple carbonate-schist mixtures of natural systems. Only the phases quartz-calcite-dolomite-muscovite-potassium feldspar-anorthite-phlogopite-tremolite-diopside-wollastonite-vapor will be considered. Other phases such as zoisite, grossular, idocrase, and chlorite are common naturally, but are deleted here because they did not form under the conditions of Vidale's (1969) solution experiments. Although neglecting these phases prevents direct comparison with the natural assemblages, none of the principles governing the formation of the zoning are altered.

TABLE 1. ABBREVIATIONS

An	Anorthite	Ph	Phlogopite	P, P_T	Total Pressure
Cc	Calcite	Q	Quartz	P_F	Fluid Pressure
Do	Dolomite	Tr	Tremolite	X	Mole Fraction
Di	Diopside	V	Vapor	f	Fugacity
Ksp	K-feldspar	Wo	Wollastonite	a	Activity
Mu	Muscovite	T	Temperature		

Zoning Caused by Gradients in the Fugacities of Volatile Components

Zoning due to a gradient in fluid composition in natural limestones has been described for some of the thin-layered micaceous limestones in south-central Connecticut (Hewitt, 1973). Here zoning occurs in thin homogeneous layers of mica-bearing limestone surrounded by massive pelitic schists. In our model system, at constant temperature, constant fluid pressure equal to total pressure, and constant bulk solid composition, a gradient in fluid composition is present between a presumed infinite reservoir of water-rich fluid in the schist (composition A in Figure 1) and a more CO_2-rich fluid in the limestone. The isobarically univariant assemblage, Do–Q–Ph–An–Mu–Cc–V,[1] present in the center of the limestone buffers the fluid composition at value B in Figure 1.

Figure 1 shows the fluid composition gradient A − B superimposed on a partial set of $T - X_{CO_2}$ phase relations for the system. A combination of the observed natural phase relations, experimental phase relations, and the rules set forth by Schreinemakers (1916) were used in the construction of the diagram. At 6 kbar, the estimated temperatures and fluid compositions for the two isobaric invariant points (X) and (Y) are 580°C, $X_{CO_2} = 0.3$ and 520°C, $X_{CO_2} = 0.4$ respectively (Hewitt, 1973). The numbers 1 through 7 represent isobaric divariant regions, each of which contains a single stable assemblage for any particular bulk composition in the fluid composition gradient.

The complete sequence of assemblages that would occur for the bulk composition represented by the initial assemblage Do-Q-Ph-An-Mu-Cc-V, where quartz, vapor, and either calcite or wollastonite are always present in excess, is shown in Figure 2. For a homogeneous initial bulk composition the zones within the limestone are isochemical except for the

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[1] Abbreviations are listed in Table 1.

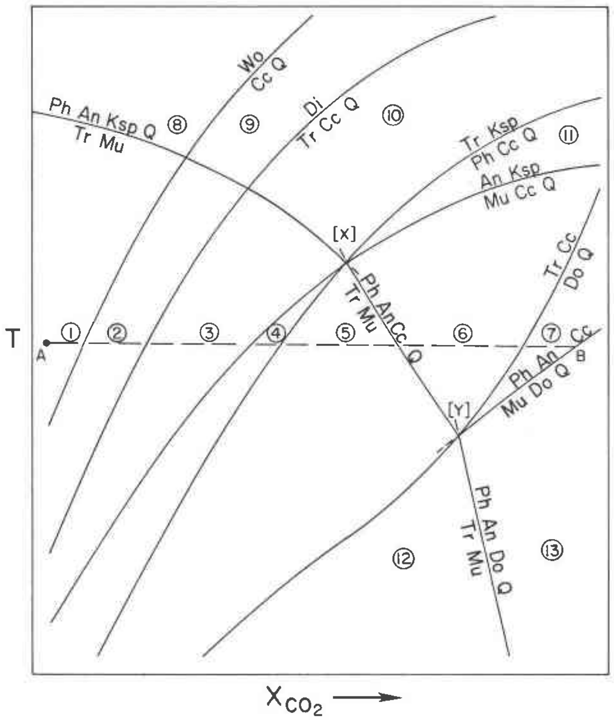

FIG. 1. One possible configuration of the H_2O-rich portion of the constant pressure T-X_{CO_2} phase diagram for the system K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2. The phases involved are Di-An-Ph-Ksp-Q-Tr-Mu-Wo-Cc-Do-V (see Table 1). The dashed line A-B represents a fluid composition gradient between a CO_2-rich fluid buffered at composition B by an isobarically univariant assemblage in a limestone, and an infinite reservoir of H_2O-rich fluid of composition A in an adjacent schist. Numbers (1) through (7) represent isobarically divariant regions along the fluid composition gradient A-B. Numbers (8) and (9) represent approximate regions where Vidale's (1969) experimental data were determined. The possible assemblages for the system and phases being considered are listed below for each isobarically divariant region.

(1) Tr-Ph-An-Mu-Q-V; Tr-Ph-Mu-Ksp-Q-V; Tr-Di-An-Ksp-Q-V; Tr-An-Mu-Ksp-Q-V; Di-Wo-An-Ksp-Q-V
(2) Tr-Ph-An-Mu-Q-V; Tr-Ph-Mu-Ksp-Q-V; Tr-Di-An-Ksp-Q-V; Tr-An-Mu-Ksp-Q-V; Di-Cc-An-Ksp-Q-V
(3) Tr-Ph-An-Mu-Q-V; Tr-Ph-Mu-Ksp-Q-V; Tr-Mu-An-Ksp-Q-V; Tr-Cc-An-Ksp-Q-V
(4) Tr-Ph-An-Mu-Q-V; Tr-Ph-Mu-Ksp-Q-V; Tr-Mu-Ksp-Cc-Q-V; Tr-Cc-Mu-An-Q-V
(5) Tr-Ph-An-Mu-Q-V; Ph-Cc-Mu-Ksp-Q-V; Tr-Mu-Ph-Cc-Q-V; Tr-Cc-An-Mu-Q-V
(6) Tr-Ph-An-Cc-Q-V; Ph-Cc-An-Mu-Q-V; Ph-Cc-Mu-Ksp-Q-V
(7) Ph-Cc-Mu-Ksp-Q-V; Ph-Cc-An-Mu-Q-V; Tr-Do-Ph-An-Q-V; Do-Ph-Cc-An-Q-V
(8) Ph-Mu-Ksp-An-Q-V; Tr-Ph-An-Ksp-Q-V; Tr-Di-An-Ksp-Q-V; Di-Wo-An-Ksp-Q-V
(9) Ph-Mu-Ksp-An-Q-V; Tr-Ph-An-Ksp-Q-V; Tr-Di-An-Ksp-Q-V; Di-Cc-An-Ksp-Q-V
(10) Ph-Mu-An-Ksp-Q-V; Tr-Ph-An-Ksp-Q-V; Tr-Cc-An-Ksp-Q-V
(11) Ph-Mu-An-Ksp-Q-V; Ph-Cc-An-Ksp-Q-V; Tr-Ph-Cc-An-Q-V
(12) Ph-Mu-Cc-Ksp-Q-V; Ph-Do-Cc-Mu-Q-V; Tr-Ph-Do-Mu-Q-V; Tr-Do-An-Mu-Q-V; Tr-Ph-An-Mu-Q-V; Do-Cc-An-Mu-Q-V
(13) Ph-Mu-Cc-Ksp-Q-V; Ph-Do-Cc-Mu-Q-V; Tr-Do-Ph-An-Q-V; Do-An-Ph-Mu-Q-V; Do-Cc-An-Mu-Q-V

freed volatiles CO_2 and H_2O. The widths of the zones are dependent on the range of X_{CO_2} over which the assemblage is stable (Fig. 1) as well as the precise shape of the fluid composition gradient. Boundaries between zones represent the isobarically univariant reaction curves. For this bulk composition and fluid gradient the general sequence of 'index minerals' from the center of the limestone outwards is phlogopite, tremolite, diopside, and wollastonite. This is similar to the sequence that would be obtained by increasing temperature at constant fluid composition. It might appear that the original layer was more calcic at the edges than in the center, but, as previously noted, all the zones are isochemical. The particular sequence of 'index minerals' produced in this zonation is the opposite of that which would be formed by a gradient in the activities of the non-volatile components at a schist-limestone contact in the divariant regions (8) and (9) of Figure 1.

Only one example of the possible zonation sequences that can be formed by an activity gradient of volatile components has been described above. Different sequences may be produced by varying bulk composition, temperature, pressure, or the range, shape, or direction of the fluid composition gradient. While the sequence formed by an activity gradient in the non-volatile components can be opposite to those formed by a gradient in the volatile components, this would not be true in general. Moreover, this mechanism of zone formation applies not only to the limestones but to the surrounding pelites as well. In fact, any composition material may be zoned as long as (1) an activity gradient is maintained in the fluid and (2) reactions dependent on volatile activities can occur.

Zoning Caused by Gradients in Activities of Non-volatile Components

We are again dealing with a relatively thin calcareous layer in a predominantly pelitic metamorphic rock. Steep activity gradients exist for non-volatile components between mineral assemblages of the Ca-rich layer and the Ca-poor schist. The effect of diffusion down these gradients will be examined at constant temperature and constant total pressure

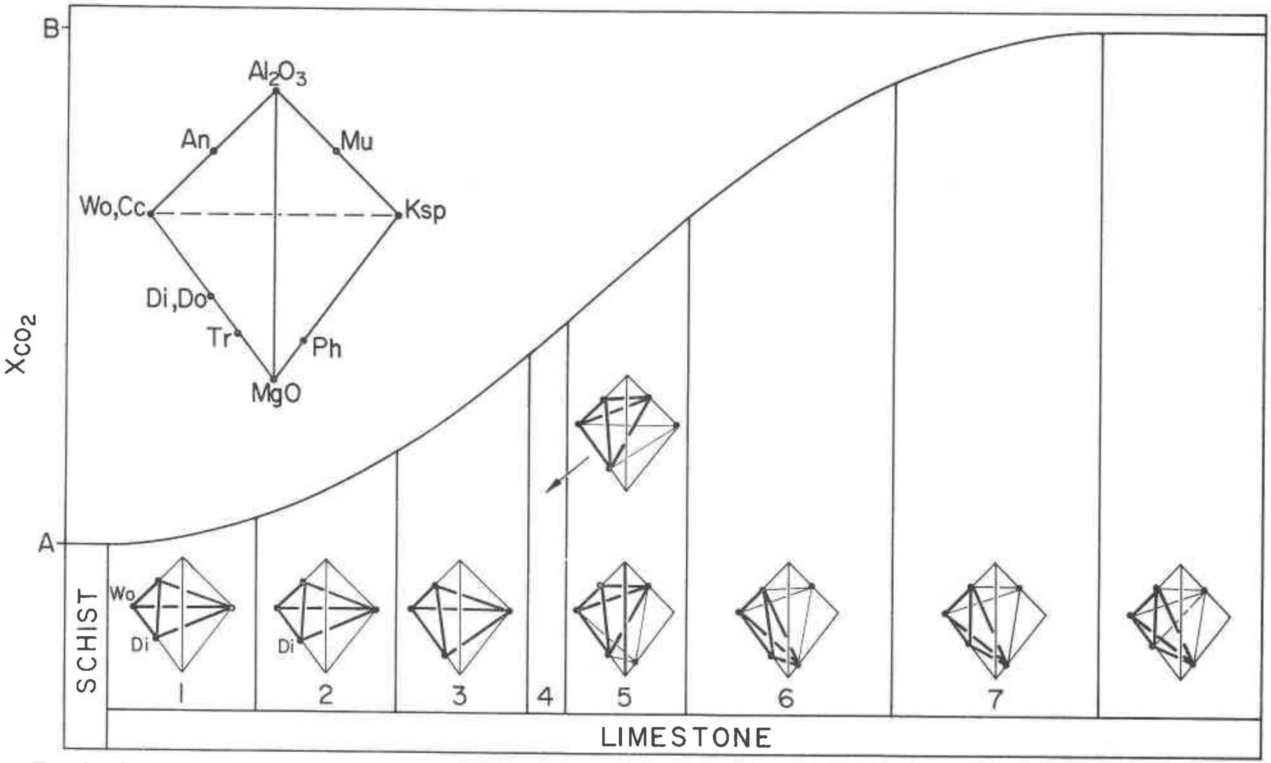

FIG. 2. The possible sequence of assemblages for the initial isobarically univariant assemblage Ph-An-Cc-Mu-Do-Q-V due to a gradient in the activities of the volatile components along the isothermal isobaric fluid composition gradient A-B. The numbered assemblages correspond to regions (1) through (7) in Figure 1. Quartz, vapor and either calcite or wollastonite are always present in excess. The widths of the zones are determined by the shape of the fluid composition gradient and the temperature at which the gradient occurs.

equal to fluid pressure. The model presented is based on a combination of field and experimental studies (Vidale, 1968, 1969). Experimental work was done in the system K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-KCl ± CO_2 at 600°C and 2 kbar $P_F = P_T$. The CO_2-free experimental system will be discussed because no a_{CO_2}/a_{H_2O} gradient was present in the experiments to cause formation of the kind of calc-silicate zones discussed in the last section.

Figure 3 shows the composition tetrahedron for region (8) of Figure 1 and represents mineral assemblages observed in the experimental studies. The starting bulk composition gradient used ranges from 'pelitic schist' on the right through the tetrahedron (arrow) to Ca-rich wollastonite rock on the left, and crosses the series of isothermal isobaric invariant assemblages: Mu–Ph–An–Q–Ksp–V, Ph–Tr–An–Q–Ksp–V, Tr–Di–An–Q–Ksp–V, and Di–Wo–An–Q–Ksp–V.

Figure 4 shows log activty of K^+ plotted against log activty of Ca^{2+} for the bulk chemical gradient ranging from pelitic schist on the left (A) to wollastonite rock on the right (B). The four six-phase 'invariant' assemblages are seen as quadruple points on this diagram. Experimentally determined values for K^+ and Ca^{2+} concentrations in the vapor phase have been used directly (without activity coefficients) for numerical values of activities for the two 'invariant' points on the left. The slope so defined corresponds closely to the theoretical slope of 1/2 for reaction (1). Experimental data for the two "invariant" points on the right was less reproducible because of quench difficulties (Vidale, 1968) and numerical values for the activities have been approximated by combining experimental data with the theoretical slope.

The slopes of reaction curves (2), (3), (6), and (7) in the log a_{K^+} − log $a_{Ca^{2+}}$ plane are somewhat arbitrary because additional information on stoichiometry is required to specify reactions whenever "exchange" of more than two cations is involved. Experimental transport shows that the set of reactions being considered must account for movement of K^+, Ca^{2+}, Mg^{2+}, and Al^{3+}. Actual solution species at 600°C

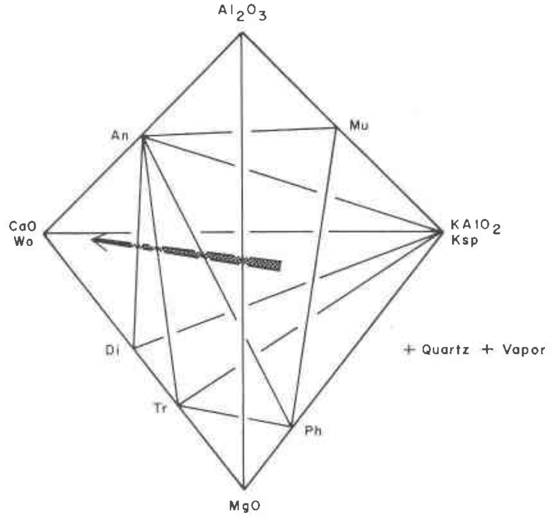

FIG. 3. Coexisting phases at 600°C, 2 kbar, and $P_{H_2O} = P_T$ in the system K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O (Vidale, 1968).

and 2 kbar are probably predominantly hydrated molecular chlorides for the acidic cations (Franck, 1956a, 1956b, 1961) and hydrated molecular hydroxides for the basic cations (Fuoss, personal communication). Reactions have been formulated for Figure 4 assuming decreasing ease of transport and exchange in the order H^+, K^+, Ca^{2+}, Mg^{2+}, and Al^{3+}. Excess quartz is assumed to provide Si^{4+}.

Starting from the four "invariant" assemblages comprising the continuous bulk chemical gradient shown in the tetrahedron, components tend to diffuse through the pore solution down their own activity gradients, thus effecting a redistribution of chemical elements and a lessening of the activity gradients. The horizontal dashed line, A-C, shows the sequence of zones of assemblages remaining after K^+ has moved down its activity gradient until no gradient remains. These "invariant" and "univariant" zones, starting from the "schist" are: Mu–Ph–An–Q–Ksp–V, Ph–Tr–An–Q–V, Tr–Di–An–Q–V, and Di–Wo–An–Q–V. The activity of K^+ is now held at a constant value across the schist-wollastonite rock sequence by the "infinite" schist buffer. All assemblages except the schist now contain one less phase and have K^+ as a mobile component.

With Ca^{2+}-bearing species also moving down their activity gradients, four-phase assemblages appear and broaden between the five-phase ones. The zonation sequence now includes Mu–Ph–An–Q–Ksp–V ("schist"), Ph–An–Q–V, Ph–Tr–An–Q–V, Tr–An–Q–V, Tr–Di–An–Q–V, Di–An–Q–V, and Di–Wo–An–Q–V. This sequence is produced experimentally in four weeks at 600°C, 2 kbar, and 2*N* chloride solution, starting from the four "invariant" assemblages. Closely analogous sequences are commonly observed in sillimanite-grade rocks.

Transport of additional components such as Mg^{2+} and Al^{3+} also takes place, both experimentally and in nature, and a two-dimensional log-activity diagram becomes inadequate. Metasomatic transport undoubtedly begins in nature before these high-grade assemblages have formed and may continue during subsequent retrograde metamorphism. The model presented here is thus greatly simplified; however, the general concepts that it demonstrates are valid.

Relative Effect of Volatile and Non-volatile Activity Gradients on Zonation Sequences

Calc-silicate zoning in natural systems may be affected by variables other than the ones already discussed. For example, gradients in fluid pressure or

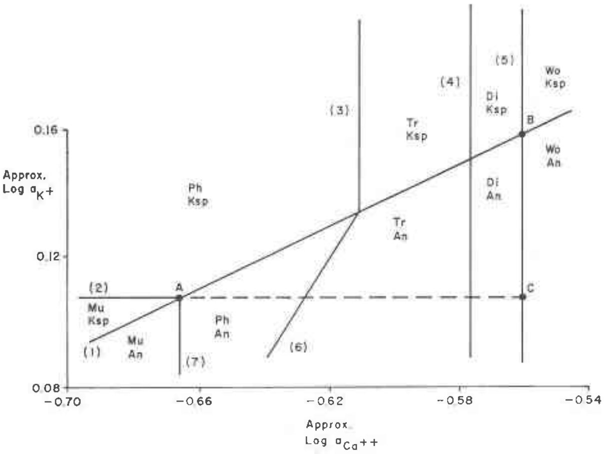

FIG. 4. Possible reaction curves in the log a_{K^+} − log $a_{Ca^{++}}$ plane for the system K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-KCl at 600°C, $P_T = P_F = 2$ kbar, and 2 normal chloride solution. Quartz and vapor are also present in all assemblages. (Activity values approximated by experimentally determined concentrations, Vidale, 1968)

(1) $An + 4Q + 2KCl = 2Ksp + CaCl_2$
(2) $Mu + 6Q + 4H_2O + 2KCl + 3MgCl_2 = Ph + 2Ksp + 8HCl$
(3) $Ph + 8Q + 4H_2O + 2CaCl_2 + 2MgCl_2 = Tr + Ksp + 8HCl$
(4) $Tr + 2Q + 2H_2O + 3CaCl_2 = 5Di + 6HCl$
(5) $Di + CaCl_2 = 2Wo + MgCl_2$
(6) $Tr + An + 2HCl + 2KCl + MgCl_2 = 2Ph + Q + 3CaCl_2$
(7) $Ph + An + 8HCl = Ksp + 2Q + 4H_2O + 3MgCl_2 + CaCl_2$

in the activities of components such as oxygen, methane, fluorine, or chlorine may cause two assemblages of different compositions to react near their contact and form a sequence of assemblage zones. The specific variables discussed here have been emphasized because they were documented by the authors as the main causes of calc-silicate zoning in a large number of natural samples.

Zoning caused by a volatile component gradient requires an original limestone composition where different assemblages are stable as a result of variable fluid composition. A "dirty" mixture of carbonate and silicates can normally be zoned by this process whereas a pure calcite layer normally can not. Non-volatile component zoning can form as long as the gradient in bulk chemical composition requires more than one equilibrium assemblage to be present. Normally, the larger the compositional contrast, the larger the chemical potential gradient will be.

Volatile zoning depends on the maintenance of an a_{CO_2}/a_{H_2O} gradient between the central buffering assemblage of the calc-silicate band and the low-CO_2 pore fluid reservoir of the schist. Extensive transport of the volatile components will exhaust the buffering assemblage in the calc-silicate and flatten the gradient. Non-volatile zoning also depends on the maintenance of activity gradients. However, because the concentration and activity gradients of the non-volatile components in the pore solution tend to be small, conditions strongly favoring transport are required to establish the zoning. These conditions may include: high chemical potential gradients, high proportion of pore fluid, high permeability, high concentration of salt in the pore fluid, and, especially, high temperature (Vidale, 1969).

Both types of zoning occur to some degree in all natural samples studied in detail (Vidale, 1968; Hewitt, 1970), but usually one or the other dominates. Zoning caused by a volatile component gradient appears most important at low metamorphic grade where diffusion is at a minimum, but where the activity gradient for volatile components can form and exist for relatively long periods. Higher temperatures favor diffusion transport and the volatile component gradient is rapidly destroyed as the reactants buffering the fluid composition in the center of the limestone layers are exhausted. At the same time, movement of non-volatile components through the vapor phase increases, and the zones formed by their transport grow at the expense of the zones formed by the volatile component gradient. The second type of zoning is usually observed to dominate by the middle-to-upper amphibolite facies.

Summary and Conclusions

The concepts of 'mobile' component and local equilibrium are particularly well illustrated for diffusion metasomatism by the calc-silicate examples described.

The volatile-gradient model involves control of a_{CO_2}/a_{H_2O} by an infinite reservoir of H_2O-rich pore fluid at the edge of the calc-silicate band and by an isobaric univariant buffering assemblage at the center of the band. CO_2-rich fluid from the central buffering zone mixes with the H_2O-rich fluid in the schist reservoir at a slow rate, establishing and then maintaining a steady-state gradient. As CO_2 or H_2O becomes 'mobile' for the intermediate zones, these are observed to contain one less phase.

The non-volatile-gradient model involves progressive change of a zonation sequence by diffusion of cation-bearing species in the chemical potential gradients between the Ca-rich layer and the Ca-poor schist. Cation activities are internally buffered by some zones and externally imposed on others, and, where an activity is externally imposed, one less phase is observed. Zone boundaries and the number of phases within zones change through time, the number of phases decreasing as activities become externally controlled.

These examples demonstrate the convenience of treating each mineral assemblage zone as a local equilibrium system (Thompson, 1959) and show the effect of 'mobile' components in decreasing the number of phases. They also show it is essential for a 'mobile' component to be moveable, in order to establish and maintain external control of activity, but, at a given time, a 'mobile' component is not necessarily moving as much as another component that is 'inert.'

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