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John B. Brady
Smith College, jbrady@smith.edu

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INTERGRANULAR DIFFUSION IN METAMORPHIC ROCKS

JOHN B. BRADY
Department of Geology, Smith College,
Northampton, Massachusetts 01063

ABSTRACT. Theoretical models of intergranular diffusion demonstrate that grain size and grain boundary width are the most important textural parameters influencing diffusion in metamorphic rocks. Taking diffusion in an aqueous solution as a limiting case for diffusion in the intergranular region of metamorphic rocks, it appears that the diffusivities of many species will be similar and relatively insensitive to variations in temperature and pressure over a wide range of metamorphic conditions. Observed variations in the mobility of chemical components during metamorphism may be related principally to variations in the ratio of the component density in the intergranular region to the component density in the minerals. Experimental studies of the growth of forsterite reaction zones around periclase crystals at 650° and 700°C and 1 kb water pressure provide an upper limit to the effective diffusivity of silica through polycrystalline forsterite: $D_{SiO_2} \leqslant 10^{-9}/a$ cm^2/s where a is the grain size in microns. This maximum diffusivity can be used to obtain minimum times for the growth of reaction zones in metamorphic rocks.

> *"Just as some metamorphic reactions must take place by motion of particles through the volume of minerals . . ., other petrogenetic processes require extensive motion of particles along mineral boundaries and in the interstices between mineral grains."* *Hans Ramberg (1952, p. 84)*

INTRODUCTION

Many geologists have suggested that the bulk of diffusive mass transfer in metamorphic rocks occurs along the boundaries between mineral grains (for example, Ramberg, 1952; Orville, 1962; Mueller, 1967; Carmichael, 1969; Fisher, 1970; Elliot, 1973; Ahrens and Schubert, 1975). This suggestion is founded in the belief that atoms may diffuse more rapidly along intergranular paths than along paths that require diffusion through crystals, particularly in the presence of a metamorphic fluid or of adsorbed volatile species such as H_2O. Support is provided by the common observation that chemical reactions lead to the growth of product minerals that completely surround reactant minerals indicating preferred access of diffusing species along grain boundaries (for example, Kennedy, 1959; Whitney and McLelland, 1973). In addition, grain boundary diffusion is known to be important for a variety of metallic and ceramic polycrystals on the basis of numerous experiments (for reviews, see Mehl, 1936; Turnbull, 1951; McLean, 1957; Gleiter and Chalmers, 1972; Kingery, 1974a,b).

In spite of the proposed significance of diffusion along intergranular paths, intergranular diffusion coefficients for rocks at metamorphic conditions are generally unknown. Because of the similarity between silicates and other oxides, one might expect the ceramic literature to be a source of useful data. Unfortunately, the extensive literature on diffusion in polycrystalline ceramics serves only to indicate qualitative features of grain boundary processes that may be true for rocks. Significant diffusion along grain boundaries has been found for some cations (for example, Sr and Ti in $SrTiO_3$, Rhodes and Kingery, 1966) and some anions (for example, O in corundum, Oishi and Kingery, 1960), and not for others (for example, Be in bromellite, Austerman and Wagner, 1966; Ni in bunsenite, Shim and Moore, 1957; and O in garnet, Paladino, Maguire, and Rubin, 1964). It is generally agreed, however, that temperatures well below the melting point and the presence of impurities along grain boundaries will enhance the importance of grain boundary diffusion relative to lattice diffusion (Wuench and Vasilos, 1966). Metamorphic rocks by their very nature contain many "impurities," some of which are likely to be concentrated at the contacts between minerals, perhaps as grain boundary phases or precipitates (Kingery, 1974b; Waff and Holdren, 1981). Volatiles, which must escape during metamorphism, are likely to be found in the intergranular region, possibly as an "intergranular film" or "dispersed phase" (Heier, 1965; Mueller, 1967). Ceramists have carefully dried the very pure samples used in diffusion experiments to avoid the major contribution even a small amount of water may have on grain boundary diffusion (Cabine, 1962; Tiernan, ms). In sum, grain boundary diffusion data for ceramics is simply not applicable to most metamorphic processes.

Similarly, the few data available on diffusion in rocks or pressed mineral powders are largely inappropriate for metamorphic processes owing to low temperatures and pressures (Garrels, Dreyer, and Howland, 1949; Wehrenberg and Silverman, 1965; Pandey, Tek, and Katz, 1974), dry, clean samples (Naughton and Fujikawa, 1959), excessive porosity (Vidale, 1969; Zaraiskii, Zharikov, and Stoyanovskaya, 1974; Li and Gregory, 1974; Ildefonse and Gabis, 1976), or the probable presence of microcracks (Kovalev, 1971). The use of actual metamorphic rocks for diffusion experiments is thwarted by the almost universal presence of microcracks (see Brace, 1972; Simmons and others, 1973; Sprunt and Brace, 1974). Because permeability is affected by microcracks, diffusion experiments on natural samples should also be strongly influenced by microcracks, which are not likely to persist during metamorphism (Brace and Orange, 1968; Nur and Simmons, 1970; Summers, Winkler, and Byerlee, 1978). Recent experiments, which appear to avoid the problems listed above, are available for diffusion of oxygen along perthite grain boundaries (Giletti and Nagy, 1981) and along dislocations in deformed albite (Yund, Smith, and Tullis, 1981), both in the presence of water. These data will be discussed below.

The purpose of this paper is two-fold: (1) to construct a theoretical framework within which the possible quantitative importance of intergranular diffusion for various metamorphic rocks may be evaluated, and (2) to present the results of a series of experiments designed to measure intergranular diffusion of silica. The first part was prompted by a concern over the consequences of geometrically complex, anastomosing grain boundary paths for diffusion in rocks. If diffusion measurements were obtained for one rock, how might these data be used to predict diffusion properties for other rocks with different textures and grain sizes? The experiments described in the second part were designed to avoid the problems, mentioned above, that have rendered many diffusion measurements inappropriate for metamorphic processes. The experiments involve monitoring the growth of polycrystalline forsterite reaction zones around periclase crystals in the presence of water.

EFFECTIVE DIFFUSIVITY FOR ROCK MODELS

In the following paragraphs the influence of rock texture (principally grain size and shape) on intergranular diffusion is explored. Simple rock models are examined for relationships among textural variables, intergranular diffusion rates, and the overall diffusive mass flux through a rock. To avoid confusion with the materials science literature in which the term "grain boundary" has specific connotations (compare Aaron and Weinberg, 1972), the term "intergranular region" (IGR) will be used to mean the interconnected, high-diffusivity paths in a rock including grain boundaries and any volatile phase or adsorbed layers that may be present. To this end it is assumed that the IGR may be characterized adequately by average or effective properties throughout any homogeneous metamorphic rock. The IGR is treated as a well-defined, locally homogeneous entity with definite boundaries separating it from adjacent crystals and occupying a small but finite volume of the rock. This approach is similar to ones used by Fisher (1951) and Guggenheim (1940) and ignores some of the observed complexities of grain boundary diffusion (see Yan and others, 1977).

If intergranular diffusion is to be important quantitatively, rates of diffusion along IGR paths must be several orders of magnitude larger than rates of diffusion along paths through the minerals present. This is a consequence of the small fraction of the volume of a metamorphic rock that is occupied by the IGR. Therefore, useful models for evaluating intergranular diffusion may be constructed that neglect differences between minerals and treat a rock as though it were a two-phase material. It is assumed that components have a very low diffusivity in one phase (the minerals) and a very high diffusivity in the other phase (the IGR). When expressed in this way, the diffusion problem is analogous to a great many others involving prediction of the average or effective physical properties of composite materials (for example, thermal conductivity, electrical conductivity, bulk modulus, magnetic permeability). This type of problem has been the subject of numerous papers (for reviews, see Hashin, 1970; Beran, 1971; Robertson and Peck, 1974; Watt, Davies, and O'Connell, 1976; Streider and Aris, 1973; Crank, 1975, chap. 12). These contributions form the basis for the following discussion.

The diffusion problem for a two-phase composite may be stated more specifically as follows: given a two-phase rock, AB, consisting of a volume fraction V_A of phase A (the minerals) and a volume fraction V_B of phase B (the IGR) such that $V_A + V_B = 1$, what will be the value of the effective diffusion coefficient for component *i*, D_i^{AB}, in the rock AB? An "effective" diffusion coefficient is the diffusion coefficient that would be determined in an experiment with a composite material on a scale that does not resolve the inhomogeneities of that material. Assume that component *i* is the only diffusing component, that the diffusivities of component *i* are D_i^A and D_i^B in phases A and B, respectively, and that the equilibrium density of component *i* is the same in the two phases. Without further information on the geometry of the distribution of A and B in the composite, the only results available are numerical limits within which the actual value of D_i^{AB} must lie.

Bounds for D_i^{AB} based on the geometrically limiting parallel and series composite configurations (fig. 1) are given in table 1. Also included are the more restrictive bounds derived by Hashin and Shtrikman (1962) and independently by Prager (1963) for statistically homogeneous and isotropic materials (see also Strieder and Aris, 1973, chap. 2). Unfortunately, when the diffusivities are very different in the two materials, the upper and lower bounds are far apart. To get a more precise estimate of the effective diffusion coefficient D_i^{AB}, it is necessary to examine some specific rock models with idealized geometries. A selection of appropriate models from the literature is given in table 1. Only models that allow the IGR to be continuous are considered. The terms that scale D_i^{AB} in several of the models of table 1 are related to the "effective directional porosity" of Garrels, Dreyer, and Howland (1949) and to the "formation resistivity factor" of Archie (1942). See Berner (1980, chap. 3) for a recent discussion of these concepts concerning diffusion in sediments.

Upper and lower bounds to D_i^{AB} along with the models of table 1 are shown in figure 2 assuming for illustrative purposes that $D_i^A = (10^{-6}) \times (D_i^B)$. The striking feature of figure 2 is that except for the plate geometry, the models cluster near the geometric upper bound defined by the parallel geometry. This means that except for diffusion normal to the schistosity

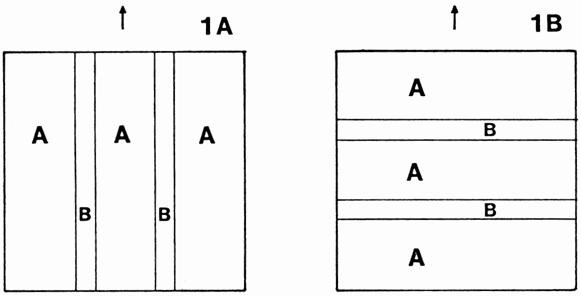


Fig. 1. Limiting geometries for two-phase rock models. The effective diffusion coefficient, D_i^{AB}, for a hypothetical two-phase rock will be maximized for diffusion in the direction indicated if the phases are arranged in parallel (A) and will be minimized if the phases are arranged in series (B). Compare Hill (1963).

TABLE 1
Effective diffusivities for some rock models

D_i^{AB}/D_i^B	Geometry	Restrictions	Reference
$V_B + (1 - V_B)\frac{D_i^A}{D_i^B}$	Parallel (fig. 1A) upper bound	none	Hill (1963) Crank (1975, p. 273)
$\frac{D_i^A}{V_B D_i^A + (1 - V_B) D_i^B}$	Series (fig. 1B) lower bound	none	Hill (1963) Crank (1975, p. 273)
$\frac{2V_B}{3 - V_B}$	Statistically homogeneous Hashin-Shtrikman upper bound	$D_i^B >> D_i^A$ $V_A > V_B$	Hashin and Shtrikman (1962, eq 4.7)
$\frac{(1 + 2V_B)}{(1 - V_B)}\frac{D_i^A}{D_i^B}$	Statistically homogeneous Hashin-Shtrikman lower bound	$D_i^B >> D_i^A$ $V_A > V_B$	Hashin and Shtrikman (1962, eq 4.8)
$\frac{2V_B}{3 - V_B}$	Concentrically mantled spheres Random distribution All sizes	$D_i^B >> D_i^A$	Maxwell (1892, p. 440) Hashin and Shtrikman (1962, eq 4.6)
$\frac{(V_A + V_B \ln V_B)V_B}{2(V_A + V_B \ln V_B) - (1/2)V_B(\ln V_B)^2}$	Statistical model Probability assumptions	$D_i^A = 0$	Prager (1960, eq 63)
$(2/3)V_B$	Mantled cubes Primitive cubic lattice One size	$D_i^B >> D_i^A$ $V_A >> V_B$	Waff (1974)
$(8/27)V_B$	Mantled cubes Tetragonal body-centered lattice Diffusion parallel to 4-fold axis	$D_i^B >> D_i^A$ $V_A >> V_B$	Brady (ms, p. 63)
$(1/216)V_B$	Mantled tetragonal plates (length: width – 10:1) Tetragonal body-centered lattice Diffusion parallel to 4-fold axis	$D_i^B >> D_i^A$ $V_A >> V_B$	Brady (ms, p. 63)
$(0.86)V_B$	Mantled tetragonal rods (length: width = 10:1) Tetragonal body-centered lattice Diffusion parallel to 4-fold axis	$D_i^B >> D_i^A$ $V_A >> V_B$	Brady (ms, p. 63)

of rocks that contain an abundance of micas, effective diffusion coefficients will be relatively insensitive to crystal shape or rock fabric (within a factor of two or three). In other words, the tortuosity of IGR diffusion paths does not vary as much from rock to rock as other parameters. This result is in part due to the fact that only models that allow the IGR to be continuous were considered. While this restriction may need further discussion, the result is nevertheless interesting. On the other hand, *crystal size* is of critical importance, as indicated in figure 2 by the strong variation of D_i^{AB} with V_B. Fine-grained rocks will have more grain boundary area per unit volume (and hence a larger V_B) than coarse-grained rocks. The significance of crystal size has been emphasized in studies of deformation by grain-boundary diffusion mechanisms (Coble creep) (for example, Stocker and Ashby, 1973; Elliot, 1973; and Kerrich, Beckinsale, and Durham, 1977).

Although the specific models of table 1 are drastically oversimplified, the qualitative results are reasonable. Using rectangular minerals leads to overestimates of the effects of tortuosity and grain geometry. Actual rocks may have effective diffusion coefficients closer to the parallel limit than the rectangular estimates. In the following sections, the parallel geometry

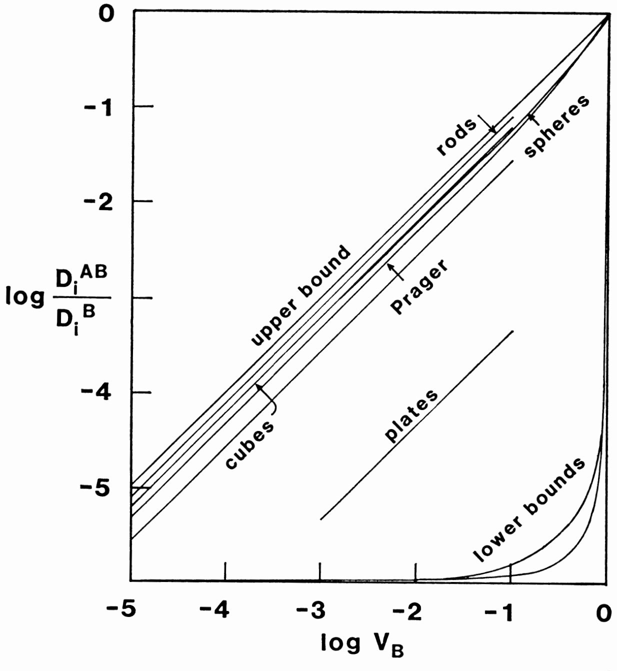


Fig. 2. A comparison of the effective diffusivities of various rock models. The logarithm of the ratio of the effective diffusion coefficient D_i^{AB} to the intergranular diffusion coefficient D_i^{B} is shown as a function of the logarithm of the volume fraction of the IGR, V_B. It is assumed that the intergranular diffusion coefficient is six orders of magnitude greater than the intercrystalline diffusion coefficient D_i^{A}. Note that most models are close to the upper bound.

will be used. Results obtained will maximize the effect of intergranular diffusion but should be nearly correct for rocks with a wide variety of grain shapes.

MAXIMUM EFFECTIVE DIFFUSION COEFFICIENTS

To evaluate the possible quantitative significance of intergranular diffusion, it is convenient to determine maximum values for the effective diffusivities of important diffusing species. Using the parallel geometry discussed above, it is possible to estimate D_i^{AB} (max) for component *i* if upper limits can be obtained for (1) the effective IGR diffusivity (D_i^B) and (2) the effective IGR volume fraction (V_B). While neither of these quantities is generally available, careful estimates of their values should provide the desired upper bounds.

A plausible maximum for the IGR diffusion coefficient D_i^B would be the diffusion coefficient for component *i* in a dilute aqueous solution at the conditions of interest. Water is likely to be the most abundant volatile in the IGR of most metamorphic rocks. If present merely as an adsorbed film a few nanometers or less in thickness, intergranular water would have physical properties that differ from those of a bulk solution, due to the influence of adjacent crystals (Henniker, 1949; Fyfe, Turner, and Verhoogen, 1958, p. 40; Adamson, 1976, chap. VI). The structured nature of adsorbed water as well as "viscous drag" due to diffusion in small passages (Beck and Schultz, 1970) should work to lower diffusion rates relative to values for a bulk solution. Therefore, diffusion coefficients for a bulk aqueous solution should provide the desired maximum value for D_i^B.

Unfortunately, diffusion data for aqueous solutions at metamorphic temperatures and pressures are almost nonexistent. The only relevant data known to this author are the ingenious measurements by Ildefonse and Gabis (1976) of the diffusivity of silica in a dilute aqueous solution. Ildefonse and Gabis found that $D_{SiO_2}^{H_2O} = 2.4\ (\pm\ 0.8) \times 10^{-4}$ cm^2/s at 550°C and 1 kb water pressure. While this number could be used for D_i^B, it is instructive to look further. Diffusion coefficients in aqueous solutions have been predicted with some success from viscosity data using the Stokes-Einstein equation (Jost, 1952, p. 432; Erdey-Gruz, 1974, chap. 3) and for charged species from limiting equivalent conductances (Robinson and Stokes, 1959, chap. 11; Nigrini, 1970). To use either method for geologic problems requires some extrapolation of viscosity or conductance data to geologically important temperatures and pressures.

Walton (1960) examined the available viscosity data for water and found that over a surprisingly wide range of conditions important for metamorphism the viscosity of supercritical water is relatively insensitive to variations of temperature and pressure (see also Ahrens and Schubert, 1975, p. 393). Available data show that water viscosity varies almost linearly with water density, which is comparatively uniform for metamorphic conditions. Using the Stokes-Einstein relation, Walton showed that for metamorphic conditions the product $D_i^{H_2O} \cdot r$, where r is the radius of the diffusing particle, is very nearly equal to 10^{-11} cm^3/s (within a factor of 2). Walton's results suggest that for diffusing species with radii of 0.1 nm or greater $D_i^{H_2O} < 10^{-3}$ cm²/s. Interestingly, Walton's (1960, fig. 2) estimate of the diffusivity of silica is within a factor of two of that determined by Ildefonse and Gabis (1976).

Most electrolytes are significantly associated under the conditions of metamorphism. Therefore, the effective radii of the diffusing species for many elements will be very similar. This means that to the extent that the Stokes-Einstein model is correct, many elements should have very similar diffusion coefficients over a wide range of temperature and pressure. In other words, the activation energy term is small in an Arrhenius expression for diffusion. This conclusion is supported by the recent conductance measurements of Frantz and Marshall (1980), who showed that the limiting equivalent conductances for 2:1 salts are within 5 percent of the values for 1:1 salts. Limiting equivalent conductances vary by less than a factor of two over a wide range of metamorphic conditions (Marshall, 1968), again suggesting that diffusion coefficients will not be very sensitive to variations in temperature and pressure. On the basis of conductance data Fletcher and Hofmann (1974) concluded that a diffusivity of 10^{-4} cm²/s is reasonable for components in aqueous solutions at metamorphic conditions. For all these reasons, a value of 10^{-3} cm²/s will be used as an upper limit to the IGR diffusivity.

With a maximum value for D_i^B in hand, the parallel geometry may be used to obtain a maximum effective diffusion coefficient D_i^{AB} if V_B can be determined. One approach would be to use measured porosities of metamorphic rocks as an estimate of V_B. However, the observed porosities of 0.1 to 2.4 percent (Wenk and Wenk, 1969) are probably influenced by the post-metamorphic introduction of microcracks. In addition, some of the porosity may be due to isolated pores (see Norton and Knapp, 1977). An alternative approach is to assume that the IGR volume is uniformly distributed along grain surfaces. V_B may then be represented in terms of the average grain diameter (a) and an average IGR width (δ). This division is desirable, because grain size is easily measured and may vary significantly from rock to rock. The effective IGR width δ may be similar from rock to rock, but it is generally unknown. On the scanning electron microscope photos of Brace and others (1972) and Sprunt and Brace (1974), it appears that uncracked grain boundaries are less than 10 nm wide. Whether the IGR width exceeds this value under high fluid pressures is not known. There is evidence that the high velocity diffusion region for ceramics in some cases may be greater than 1 μm in width (Wuensch and Vasilos, 1964; Mimkes and Wutig, 1970; Mistler and Coble, 1974), but most of that width would have to be in the adjacent crystals (see Elliot, 1973; Joesten, 1983). In the absence of further data, 10 nm will be used as a maximum average IGR width.

For rocks with an average grain diameter (a) greater than or equal to 0.1 mm, the parallel model yields

$$D_i^{AB} = D_i^B \cdot \delta/(a + \delta) \cong D_i^B \cdot \delta/a < 10^{-7}\ (\mathrm{cm}^2/\mathrm{s}) \qquad (1)$$

This estimate is probably a good upper limit for the effective diffusion coefficient for a variety of elements in many metamorphic rocks over a wide range of conditions (400°-800°C, 2-8 kb). The estimate is not particularly sensitive to temperature and pressure because, as noted above, the viscosity of water (and therefore D_i^B) does not appear to vary significantly within this range of conditions. Except for the possibility of an average grain size less than 0.1 mm or an average IGR width greater than 10 nm, variations in all obvious parameters, such as the radius of the diffusing particles, tortuosity of the diffusion paths, surface effects of adjacent solids, or the absence of an intergranular fluid, should reduce the magnitude of the actual effective diffusion coefficient.

Giletti and Nagy (1981) have measured the diffusion of ^{18}O along the boundaries separating the Na and K phases in a perthite in hydrothermal runs at 1 kb and 500° to 700°C. Assuming a grain boundary width (δ) of 10 nm, they obtained a $D_{^{18}O}^B$ of 1×10^{-10} (cm^2/s) at 600°C. Yund, Smith, and Tullis (1981) studied the enhanced rate of uptake of ^{18}O from an aqueous solution by an albite with a high dislocation density. From their data and assuming a dislocation pipe radius of 0.4 nm, they obtained a $D_{^{18}O}^B$ of 4×10^{-9} cm^2/s at 600°C and 2 kb. If the same δ were used, the two numbers would be almost identical. These numbers are 6 to 7 orders of magnitude smaller than the maximum D_i^B used above, implying that the calculated maximum effective diffusion coefficient (1) may be unreasonably high. The discrepancy may stem from the assumption that the IGR is uniform and continuous. Joesten (1983) evaluated D_i^B for oxygen in polycrystalline quartz from coarsening data on chert nodules in a contact metamorphic aureole. His value of D_O^B at 600°C is 0.2 to 5.2×10^{-15} cm^2/s, assuming a δ of 100 nm. An absence of water in the contact aureole may explain why his numbers are so much smaller than the measured ^{18}O diffusivity for feldspar grain boundaries.

AN INTERGRANULAR DIFFUSION EXPERIMENT

If actual intergranular diffusion coefficients are near the maximum given in (1), then their measurement should be possible on a laboratory time scale. However, as discussed in the introduction, obtaining geologically applicable numbers may be difficult. To avoid the problem of microcracks, a rock should be used that has not suffered the stresses of cooling and decompression. An experiment that avoids cooling stresses involves the growth of an "armoring" reaction zone around a single crystal packed in the powder of an incompatible mineral along with an aqueous solution. Once a reaction zone has formed, diffusion across the zone is required for its further growth. The rate of growth of the reaction zone should thus be a measure of the effective diffusivity within the reaction zone.

The actual experimental setup is shown in figure 3. One or more cleaved crystals of synthetic periclase (1-2 mm rectangular solids) were sealed in 3 mm gold tubing along with natural quartz powder and water or a sodium chloride solution. In some instances the periclase crystals were wrapped with platinum wire, which served as an inert marker. The charge was then placed in a cold-seal pressure vessel and maintained at a pressure of 1 or 2 (± 0.05) kb and a temperature of 600° to 750°C (± 10°) for a period of from 3 hr to 8 weeks. Following a compressed air quench, the gold capsule was carefully peeled from around the charge. The sample was mounted in epoxy, cross-sectioned by grinding, and examined in reflected light.

Reaction rims formed around the periclase crystal in every run. Forsterite was invariably one of the product minerals. Brucite and talc were produced in a few runs. No chain silicate was positively identified in any run. On the basis of exploratory runs, the majority of experiments were conducted at 1 kb and 650° or 700°C using pure water. For these conditions, a single monomineralic forsterite reaction zone was produced. A photomicrograph of a typical sample is shown in plate 1. The forsterite rims are polycrystalline with sufficient density and coherence to take a high polish locally. The grain size of the forsterite, observed with a scanning electron microscope, is 1 μm or less. In many instances the forsterite rim is separated from the periclase crystal by a small gap; however, congruency of the rim and the periclase crystal suggests that separation occurred either during the quench or during the mounting procedure. Scanning electron micrographs of polished reaction rims show an amount of porosity that is surprising in light of the results discussed below (pl. 2). In each rim examined, however, some portion appears to have a very low porosity, typically as a layer along the outside face. Because the polycrystalline forsterite is considerably less competent than the adjacent periclase, the porosity may be apparent and due to plucking during polishing. The fact that the forsterite invariably surrounds the periclase (inside the platinum wires) rather than the quartz and the probable high concentration of silicon relative to magnesium in these solutions (Frantz, Popp, and Boctor, 1981) prove that the main diffusive flux across the forsterite zone was of silicon, rather than magnesium.

Results of the diffusion experiments expressed in terms of the thickness of the forsterite reaction rims as a function of run duration are shown in figure 4. Evidently the forsterite rim could grow rapidly to a width of about 25 μm during the first few minutes of the experiment. Forsterite

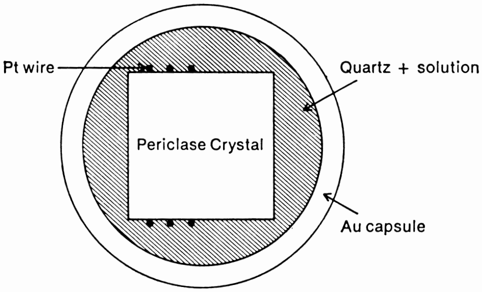
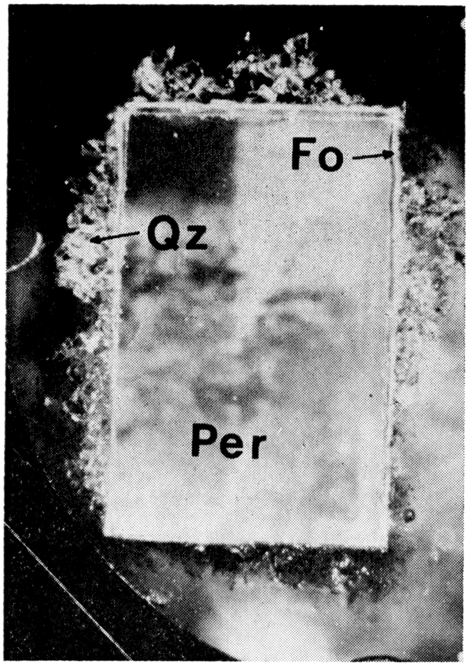


Fig. 3. Starting configuration for the diffusion experiment.

PLATE 1



A photomicrograph of a polished cross section of a diffusion run of 2 weeks at 700°C and 1 kb. The central periclase crystal (1.7 × 2.6 mm) is surrounded successively by a uniform rim (20 μm thick) of polycrystalline forsterite and clusters of quartz crystals. The whole assemblage is set in epoxy in a circular holder. Shadows mottle the periclase crystal.

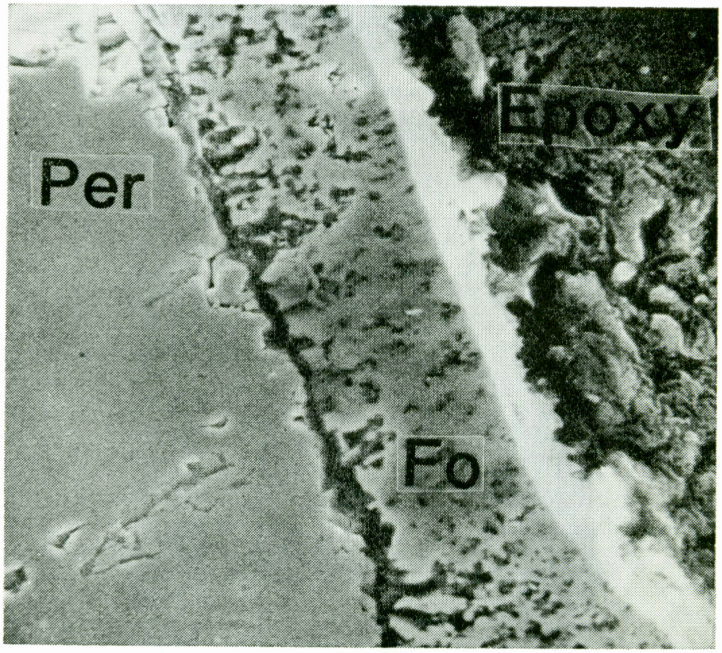
rims from runs as long as 8 weeks, however, were not consistently thicker than rims from runs an hour in duration. It may be concluded from these data that a change in the rate of reaction rim growth occurred early in the experiments. An end to measurable rim growth must record a change in kinetics. All the reactants were still present and had demonstrated the capacity for reaction. A plausible interpretation is that the connected porosity of the forsterite rim was "plugged" as the rim grew, creating the desired "tight" grain contacts, and reducing the effective diffusivity of silica below that required for measurable growth. An upper bound on the effective diffusivity of silica can be calculated from these results.

If the diffusive flux of silicon was much greater than the flux of magnesium such that the forsterite-producing reaction occurred at the periclase–forsterite interface, then eq (3) of Booth (1948) may be used to describe the growth of the forsterite rim as follows:

$$L^2 = 2 \cdot D_{SiO_2}{}^{RIM} \cdot t \cdot \Delta\rho_{SiO_2}{}^{IGR}/\rho_{SiO_2}{}^{Fo} \tag{2}$$

See also Crank (1975, p. 298). L (cm) is the thickness of the reaction rim, $D_{SiO_2}{}^{RIM}$ (cm^2/s) is the effective diffusion coefficient of silica, t (s) is the duration of the anneal, $\Delta\rho_{SiO_2}{}^{IGR}$ is the change in density of SiO_2 in

PLATE 2



A scanning electron micrograph of an 8 week run at 700°C and 1 kb in water. The polycrystalline forsterite rim is about 20 μm wide. Visible porosity in the forsterite rim may be due to plucking during polishing.

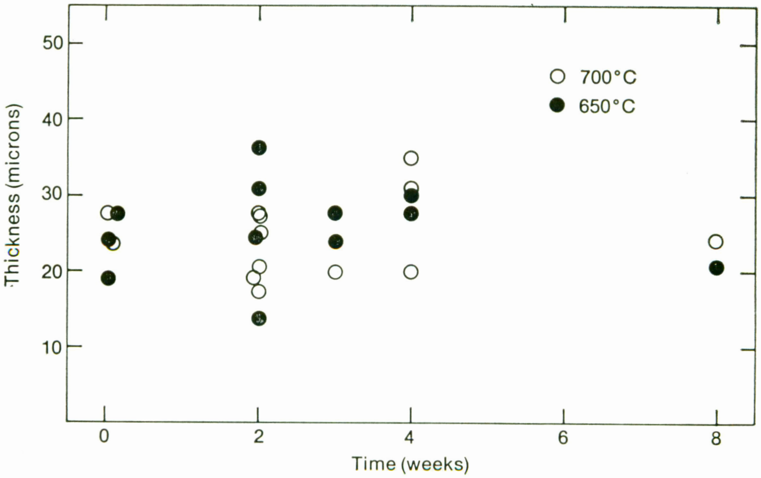


Fig. 4. Results of the diffusion runs expressed in terms of the thickness of the forsterite reaction rims as a function of the run duration. The uncertainty of each point in terms of observed variations in rim thickness is ± 5 μm.

the IGR across the forsterite rim, and $\rho_{SiO_2}{}^{Fo}$ is the density of SiO_2 in forsterite. The term $D_{SiO_2}{}^{RIM}$ includes any contributing effects of IGR porosity and tortuosity and would change if either of those variables changed. If it is assumed that 25 μm thick rims formed during the first few minutes of the experiment and that a doubling of rim thickness (from 25 to 50 μm) would be detected, no observed growth in 8 weeks leads to a maximum effective diffusivity of silica through the 1 μm sized polycrystalline forsterite of 2×10^{-9} cm²/s using $\rho_{SiO_2}{}^{Fo}$ of 2.28×10^{-2} mole/cm³ (Robie, Hemingway, and Fisher, 1978) and $\Delta\rho_{SiO_2}{}^{IGR}$ of 2.25×10^{-5} mole/cm³ (Walther and Helgeson, 1977; Burnham, Holloway, and Davis, 1969; Helgeson and others, 1978). If the apparent porosity of the forsterite rim (pl. 2) is included, as well as the possibility that only a small part of the rim was actually "plugged," then the maximum would be even smaller. The fact that the observed maximum is considerably lower than that estimated above is evidence that diffusion along IGR paths is not as fast as in a bulk aqueous solution. Recalling eq (1), $D_{SiO_2}{}^{RIM} = D_{SiO_2}{}^{IGR} \cdot \delta/a$. If δ and $D_{SiO_2}{}^{IGR}$ do not vary from rock to rock, then $D_{SiO_2}{}^{ROCK} < 10^{-9}/a$ cm²/s where a is the grain size in μm. For $\delta = 10$ nm, $D_{SiO_2}{}^{IGR} < 10^{-7}$ cm²/s, which is three orders of magnitude larger than the value given for ^{18}O diffusion by Giletti and Nagy (1981) and three orders of magnitude smaller than the value determined by Idlefonse and Gabis (1976) for diffusion in an aqueous solution, all for similar conditions.

MINIMUM TIMES FOR METAMORPHIC EVENTS

It was argued above that the diffusivities of many species should be similar in aqueous solutions over the midrange of crustal metamorphic conditions. To the extent that this is true, the maximum effective diffusivity of silica determined above may be used as a maximum value for the diffusivities of other components during metamorphism. A *maximum* diffusivity may be combined with measurement of reaction textures to yield *minimum* times required to form those textures by diffusion.

It has been clearly demonstrated by the work of Frantz and Mao (1976, 1979), Weare, Stephens, and Eugster (1976), Joesten (1977), and others that a rigorous analysis of the growth of reaction textures in metamorphic rocks is rather complicated, requiring more data than are generally available. A simpler approach can be used to obtain minimum times if the simplifying assumptions serve only to minimize further the calculated times. A common reaction texture that requires diffusion for its development is the mineral-assemblage zoning that occurs adjacent to veins or between layers of contrasting composition. If it is assumed that the growth of such metasomatic zones is in response principally to the diffusion of one component (compare Brady, 1977), then a modified version of solution (2) used to evaluate the forsterite reaction rims above is appropriate.

Using a maximum $D_i{}^{ROCK}$ of 10^{-9} cm²/s for a rock with a 1 μm grain size, the desired expression is

$$t_{min} = L^2 \cdot a \cdot S \cdot 10^{+9} \cdot \Delta\rho_i{}^{IGR}/\rho_i{}^{ROCK} \qquad (3)$$

where t_{min} is the minimum time (s), and L is the thickness of the reaction zone(s) (cm). The parameter a is the average grain size (diameter) in units of μm. This parameter is needed because the effective diffusivity is directly related to the number of grain boundaries (fig. 2). a is given in units of μm, because this was the grain size for which the maximum D_i^{ROCK} was determined. The parameter S is a scale factor equal to one half for the boundary conditions of a tarnishing reaction as originally considered by Booth (1948) and as used in (2) above (see also Sippel and Foster, 1963). For the case of bimetasomatism considered by Korzhinskii (1970, p. 134) and Frantz and Mao (1976, 1979), S is equal to one quarter. That S should be one quarter for the bimetasomatic geometry follows by analogy from the solutions for diffusion in "a pair of semi-infinite solids" and "an infinite system — surface composition constant" as given in Shewmon (1963, p. 11-14) and elsewhere. Although this is a crude approximation, the minimum time can be assured by a proper choice of the density terms $\Delta\rho_i^{IGR}$ and ρ_i^{ROCK}. $\Delta\rho_i^{IGR}$ should be given a maximum value: set $\Delta\rho_i^{IGR} = \rho_i^{IGR}$ for equilibrium with the original mineral assemblage rich in i, assuming $\rho_i^{IGR} = 0$ in the assemblage poor in i. Because no solubility data are available for IGR fluids, data for aqueous solutions at the appropriate pressure and temperature must be used (for example, Frantz, Popp, and Boctor, 1981). Similarly, the overall density of the diffusing component i in the reaction zones, ρ_i^{ROCK}, should be assigned a minimum value. This would be the difference in density of i between the "leading" reaction zone and the original rock being replaced. In the case of bimetasomatism, there are two "leading" zones, and the lower value should be chosen.

Minimum times from eq (3) may be read from figure 5. The ordinate in figure 5 is the logarithm of thickness L (cm) of the metasomatic zones. The abscissa is the logarithm of the product of the effective diffusion coefficient (cm²/s) and the time (s). For convenience, the abscissa is also labelled in units of t_{min}/a for the case of $D_i^{ROCK} = 10^{-9}$ cm²/s as in (3). Figure 5 is contoured in units of $\Delta\rho_i^{IGR}/\rho_i^{ROCK}$ with the solid lines for the bimetasomatic geometry (S = 1/4) and the dashed lines for the tarnishing geometry (S = 1/2). To determine a minimum time for a specific case of reaction zoning, find the horizontal line corresponding to the zone thickness. Read the value of t_{min}/a for the point of intersection of the selected horizontal line and the contour appropriate to the density ratio and geometry of the zones. Multiply the value of t_{min}/a so determined by the average grain size in microns (a) to obtain the minimum time in years for the formation of the reaction zones.

Consider for example, the bimetasomatic reaction zones between pelitic and calcareous units described by Vidale (1969, #RMV-9-65). Reaction zones 3 to 5 of Vidale (table 5) can be ascribed principally to the diffusion of Ca (Brady, 1977). These zones are approx 5.5 cm in total thickness. Grain size is variable, but 0.5 mm is a conservative average. A value for ρ_{Ca}^{ROCK} can be calculated from the chemical analyses listed in Vidale (1969, table 8). Using the difference in CaO between zones 5 and 6 along with an approximate density of 2.7 yields $\rho_{Ca}{}^{ROCK}$ of 1.16×10^{-3} moles of Ca per cm^3 of rock. The assemblage quartz–diopside–tremolite at the boundary between zones 5 and 6 constrains the molality of $CaCl_2$ in an aqueous solution of known total chloride. Solubility data are not available for the probable conditions of the formation of these zones (550°-650°C, 5-7 kb). Data are available at 600°C and 2 kb (Frantz, Popp, and Boctor, 1981) and will be used for a first approximation (for a 1 molal total chloride $m_{CaCl_2} = 0.49$). Using a solution density of 0.846 (Burnham, Holloway, and Davis, 1969; 600°, 6 kb), $\rho_{Ca}{}^{IGD} = 4.1 \times 10^{-4}$ moles of Ca per cm^3 of solution. The density ratio for figure 4 is thus about 0.35, which leads to a t_{min} of 3.4×10^5 yrs. The calculated t_{min} depends critically on the estimate of $\rho_{Ca}{}^{IGD}$. For example, if total chloride were taken as 0.1 molal, the resulting t_{min} would be 3.4×10^6 yrs. Of course the calculated time also depends on the maximum $D_i{}^{ROCK}$ used. If the grain boundary diffusivities of oxygen reported by Giletti and Nagy (1981) are used for the 1 molal chloride case, a calculated time (no longer minimum) would be 3.4×10^8 yrs. This unreasonable result suggests that their numbers are too low for this application.

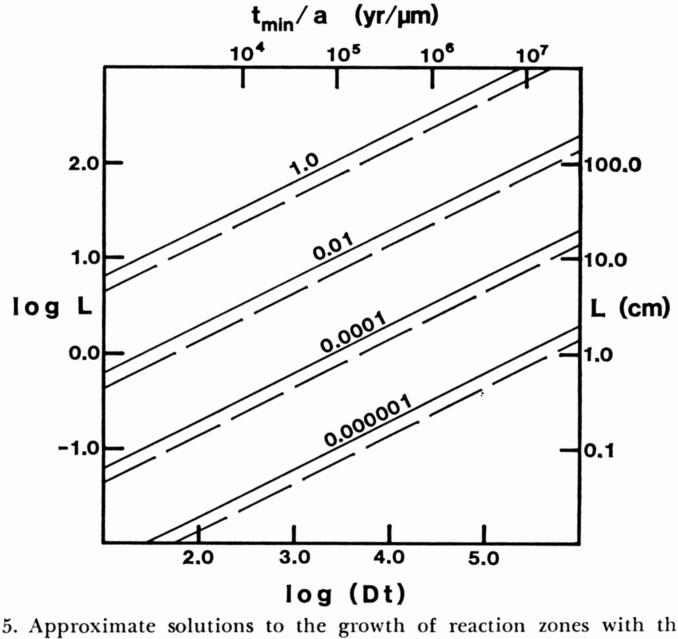


Fig. 5. Approximate solutions to the growth of reaction zones with the bimetasomatic (solid lines) and tarnishing (dashed lines) zone geometries are shown in terms of the logarithm of the thickness of the reaction zone(s) and the logarithm of the product of the effective diffusion coefficient (cm^2/s) and the time (s). The contours are for various values of the density ratio $\Delta\rho_i{}^{IGR}/\rho_i{}^{ROCK}$. Minimum times (yrs) are shown for the maximum $D_i{}^{ROCK}$ of 10^{-9} (cm^2/s) but must be corrected for grain size as described in the text.

DISCUSSION

Few petrologists will be surprised by the conclusion that it took *at least* a few hundred thousand years to form the reaction zones described by Vidale (1969). However, a minimum time constraint has not been generally available and could prove useful for many applications. Note that the minimum time calculated is not for the whole orogeny but rather the minimum time that the sample was at physical conditions within the stability field of the reaction zone minerals. Considering that the maximum time for the total orogeny might be as little as 10 m.y. (Naylor, 1971), the minimum time calculated may be a fairly tight constraint.

Several important features of intergranular diffusion in metamorphic rocks are apparent in the preceding discussion and calculation. (1) The presence of an IGR fluid, notably H_2O, in some form can greatly enhance intergranular diffusion. This is true because of both enhanced diffusivities and enhanced solubilities in the IGR. The influence of other volatiles such as CO_2 can probably be evaluated by examining their effect on solubilities and viscosity, where data are available. (2) The grain size of a rock is the most important visible textural parameter influencing intergranular diffusion in metamorphic rocks: smaller crystals mean more intergranular paths per unit cross section. The width δ of the IGR is also of critical importance but remains an unknown quantity. This width, and therefore IGR diffusivities, may increase significantly as P_{fluid} approaches P_{total} during devolatilization reactions (Walther and Orville, 1982; Brace, 1972). In rocks with significant porosity, the porosity-permeability product is probably more important than grain size (Pandey, Tek, and Katz, 1974). (3) Differences among the apparent mobilities of elements in metamorphic rocks (Blackburn, 1968; Carmichael, 1969) are principally due to differences in solubilities in the IGR, rather than contrasting diffusivities. Based on the arguments given above, IGR diffusivities of most elements should be very similar (within a factor of 2 or 3). Element concentrations in the IGR, on the other hand, range over several orders of magnitude, if bulk solution measurements can be used as a guide. The equal importance of concentration and diffusivity has been formalized by Frantz and Mao (1976) in their "diffusion potential" and has been noted by others (for example, Vidale and Hewitt, 1973). If the diffusing species interacts with the rock, then the density ratio $\Delta\rho_i^{\mathrm{IGR}}/\rho_i^{\mathrm{ROCK}}$, rather than the IGR concentration, will be the controlling parameter. Fletcher and Hofmann (1974) demonstrated the importance of this ratio (their "fluid-solid isotherm") for infiltration as well as diffusion.

The kinetics of many metamorphic processes depend on the kinetics of intergranular diffusion (Fisher, 1978). Intergranular diffusion is governed by the physical properties of the IGR. Because the IGR may vary from rock to rock and even from time to time during metamorphism, a complete characterization of the physical properties of the IGR is not likely to be forthcoming, except possibly for some special cases. Therefore, kinetic descriptions may have to be framed in terms of inequalities, rather than exact solutions.

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REFERENCES

Aaron, H. B., and Weinberg, F., 1972, Preferential diffusion along interphase boundaries: Acta Metall., v. 20, p. 339-344.

Adamson, A. W., 1976, Physical Chemistry of Surfaces: New York, John Wiley & Sons, 698 p.

Ahrens, T. J., and Schubert, G., 1975, Gabbro-eclogite reaction rate and its geophysical significance: Rev. Geophysics, v. 13, p. 383-400.

Archie, G. E., 1942, The electrical resistivity log as an aid in determining some reservoir characteristics: Am. Inst. Mining Metall. Engineers Trans., v. 146, p. 54-62.

Austerman, S. B., and Wagner, J. W., 1966, Cation diffusion in single-crystal and polycrystalline BeO: Am. Ceramic Soc. Jour., v. 49, p. 94-99.

Beck, R. E., and Schultz, J. S., 1970, Hindered diffusion in microporous membranes with known pore geometry: Science, v. 170, p. 1302-1305.

Beran, M., 1971, Application of statistical theories to heterogeneous materials: Physica Status Solidi, v. 6, sec. A, p. 365-384.

Berner, R. A., 1980, Early Diagenesis: Princeton, N.J., Princeton Univ. Press, 241 p.

Blackburn, W. H., 1968, The spacial extent of chemical equilibrium in some high-grade metamorphic rocks from the Grenville of Southeastern Ontario: Contr. Mineralogy Petrology, v. 19, p. 72-92.

Booth, F., 1948, A note on the theory of surface diffusion reactions: Faraday Soc. Trans., v. 44, p. 796-801.

Brace, W. F., 1972, Pore pressure in geophysics, *in* Heard, H. C., Borg, I. Y., Carter, N. L., and Raleigh, C. B., eds., Geophysical Monograph Series Vol. 16, Flow and Fracture of Rocks: Washington, D.C., Am. Geophys. Union, p. 265-273.

Brace, W. F., and Orange, A. S., 1968, Further studies of the effects of pressure on electrical resistivity of rocks: Jour. Geophys. Research, v. 73, p. 5407-5420.

Brace, W. F., Silver, E., Hadley, K., and Goetze, C., 1972, Cracks and pores: a closer look: Science, v. 178, p. 162-163.

Brady, J. B., ms, 1975, Intergranular diffusion in metamorphic rocks: Ph.D. thesis, Harvard Univ., 165 p.

——— 1977, Metasomatic zones in metamorphic rocks: Geochim. et Cosmochim. Acta, v. 41, p. 113-125.

Burnham, C. W., Holloway, J. R., and Davis, N. F., 1969, Thermodynamic Properties of Water to 1,000°C and 10,000 Bars: Geol. Soc. America Spec. Paper 132, 96 p.

Cabine, J., 1962, La diffusion intergranulaire et la structure des joints intergranulaires dans les halogenures alcalins: Jour. Chim. Physics Physiochim. Biol., v. 59, p. 1123-1141.

Carmichael, D. M., 1969, On the mechanism of prograde metamorphic reactions in quartz-bearing pelitic rocks: Contr. Mineralogy Petrology, v. 20, p. 244-267.

Crank, J., 1975, The Mathematics of Diffusion: Oxford, Clarendon Press, 414 p.

Elliot, D., 1973, Diffusion flow laws in metamorphic rocks: Geol. Soc. America Bull., v. 84, p. 2645-2664.

Erdey-Gruz, T., 1974, Transport Phenomena in Aqueous Solutions: New York, John Wiley & Sons, 512 p.

Fisher, G. W., 1970, The application of ionic equilibria to metamorphic differentiation: an example: Contr. Mineralogy Petrology, v. 29, p. 91-103.

——— 1978, Rate laws in metamorphism: Geochim. et Cosmochim. Acta, v. 42, p. 1035-1050.

Fisher, J. C., 1951, Calculation of diffusion penetration curves for surface and grain boundary diffusion: Jour. Appl. Physics, v. 22, p. 74-77.

Fletcher, R. C., and Hofmann, A. W., 1974, Simple models of diffusion and combined diffusion-infiltration metasomatism, *in* Hofmann, A. W., Giletti, B. J., Yoder, H. S., Jr., and Yund, R. A., eds., Geochemical Transport and Kinetics: Washington, D.C., Carnegie Inst. Washington, p. 243-259.

Frantz, J. D., and Mao, H. K., 1976, Bimetasomatism resulting from intergranular diffusion: I. A theoretical model for monomineralic reaction zone sequences: Am. Jour. Sci., v. 276, p. 817-840.

——— 1979, Bimetasomatism resulting from intergranular diffusion: II. Prediction of multimineralic zone sequences: Am. Jour. Sci., v. 279, p. 302-323.

Frantz, J., and Marshall, W., 1980, Electrical conductances of aqueous calcium chloride and magnesium chloride solutions from 25° to 600°C at pressures to 4000 bars, *in* Straub, J., and Scheffler, K., eds., Water and Steam; Their Properties and Current Industrial Applications: Oxford, Pergamon Press, 704 p.

Frantz, J. D., Popp, R. K., and Boctor, N. Z., 1981, Mineral-solution equilibria — V. Solubilities of rock-forming minerals in supercritical fluids: Geochim. et Cosmochim. Acta, v. 45, p. 69-77.

Fyfe, W. S., Turner, F. J., and Verhoogen, J., 1958, Metamorphic Reactions and Metamorphic Facies: Geol. Soc. America Mem. 73, 259 p.

Garrels, R. M., Dreyer, R. M., and Howland, A. L., 1949, Diffusion of ions through intergranular space in water-saturated rocks: Geol. Soc. America Bull., v. 60, p. 1809-1828.

Giletti, B. J., and Nagy, K. L., 1981, Grain boundary diffusion of oxygen along lamellar boundaries in perthitic feldspars: EOS (Am. Geophys. Union Trans.), v. 62, p. 428.

Gleiter, H., and Chalmers, B., 1972, High Angle Grain Boundaries, Progress, *in* Chalmers, B., Christian, J. W., and Massalski, T. B., eds., Materials Science, v. 16: Oxford, Pergamon Press, 272 p.

Guggenheim, E. A., 1940, The thermodynamics of interfaces of systems of several components: Faraday Soc. Trans., v. 36, p. 397-412.

Hashin, Z., 1970, Theory of composite materials, *in* Wendt, F. W., Liebowitz, H., and Perrone, N., eds., Mechanics of Composite Materials: Oxford, Pergamon Press, p. 201-242.

Hashin, Z., and Shtrikman, S., 1962, A variational approach to the theory of the effective magnetic permeability of multiphase materials: Jour. Appl. Physics, v. 33, p. 3125-3131.

Heier, K. S., 1965, Metamorphism and the chemical differentiation of the crust: Geol. Foren. Stockholm Forh., v. 87, p. 249-256.

Helgeson, H. C., Delany, J. M., Nesbitt, H. W., and Bird, D. K., 1978, Summary and critique of the thermodynamic properties of rock-forming minerals: Am. Jour. Sci., v. 278-A, 229 p.

Henniker, J. C., 1949, The depth of the surface zone of a liquid: Rev. Modern Physics, v. 21, p. 322-341.

Hill, R., 1963, Elastic properties of reinforced solids, some theoretical principles: Jour. Mech. Phys. Solids, v. 11, p. 357-372.

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. et Cosmochim. Acta, v. 40, p. 297-303.

Joesten, R., 1977, Evolution of mineral assemblage zoning in diffusion metasomatism: Geochim. et Cosmochim. Acta, v. 41, p. 649-670.

——— 1983, Grain growth and grain-boundary diffusion in quartz from the Christmas Mountains (Texas) contact aureole: Am. Jour. Sci., v. 283-A (Orville v.), p. 233-254.

Jost, W., 1952, Diffusion in Solids, Liquids, Gasses: New York, Academic Press, 558 p.

Kennedy, W. Q., 1959, The formation of diffusion reaction skarn by pure thermal metamorphism: Mineralog. Mag., v. 32, p. 26-31.

Kerrich, R., Beckinsale, R. D., and Durham, J. J., 1977, The transition between deformation regimes dominated by intercrystalline diffusion and intracrystalline creep evaluated by oxygen isotope thermometry: Tectonophysics, v. 38, p. 241-257.

Kingery, W. D., 1974a, Plausible concepts necessary and sufficient for interpretation of grain boundary phenomena: I, grain-boundary characteristics, structure, and electrostatic potential: Am. Ceramic Soc. Jour., v. 57, p. 1-8.

——— 1974b, Plausible concepts necessary and sufficient for interpretation of grain boundary phenomena: II, solute segregation, grain-boundary diffusion, and general discussion: Am. Ceramic Soc. Jour., v. 57, p. 74-83.

Korzhinskii, D. S., 1970, The Theory of Metasomatic Zoning: London, Oxford Univ. Press, 162 p.

Kovalev, G. N., 1971, Diffusion along grain boundaries in rock in the presence of water: Acad. Nauk SSSR Doklady, v. 197, p. 176-178.

Li, Y.-H., and Gregory, S., 1974, Diffusion of ions in sea water and in deep-sea sediments: Geochim. et Cosmochim. Acta, v. 38, p. 703-714.

Marshall, W. L., 1968, Conductances and equilibria of aqueous electrolytes over extreme ranges of temperature and pressure: Rev. Pure Appl. Chemistry, v. 18, p. 167-186.

Maxwell, J. C., 1892, A Treatise on Electricity and Magnetism: Oxford, Clarendon Press.

McLean, D., 1957, Grain Boundaries in Metals: Oxford, Oxford Univ. Press, 346 p.

Mehl, R. F., 1936, Diffusion in solid metals: Am. Inst. Mining Metallurgical Engineers Trans., v. 122, p. 11-56.

Mimkes, J., and Wuttig, M., 1970, Diffusion in wide grain boundaries: Jour. Appl. Physics, v. 41, p. 3205-3209.

Mistler, R. E., and Coble, R. L., 1974, Grain-boundary diffusion and boundary widths in metals and ceramics: Jour. Appl. Physics, v. 45, p. 1507-1509.

Mueller, R. F., 1967, Mobility of the elements in metamorphism: Jour. Geology, v. 75, p. 565-582.

Naughton, J. J., and Fujikawa, U., 1959, Measurement of intergranular diffusion in a silicate system: iron in forsterite: Nature, v. 184, p. 54-56.

Naylor, R. S., 1971, Acadian orogeny: an abrupt and brief event: Science, v. 172, p. 565-582.

Nigrini, A., 1970, Diffusion in rock alteration systems: I. prediction of limiting equivalent ionic conductances at elevated temperatures: Am. Jour. Sci., v. 269, p. 65-91.

Norton, D., and Knapp, R., 1977, Transport phenomena in hydrothermal systems: the nature of porosity: Am. Jour. Sci., v. 277, p. 913-936.

Nur, A., and Simmons, G., 1970, The origin of small cracks in igneous rocks: Internat. Jour. Rock Mech. Min. Sci., v. 7, p. 307-314.

Oishi, Y., and Kingery, W. D., 1960, Self-diffusion of oxygen in single crystal and polycrystalline aluminum oxide: Jour. Chem. Physics, v. 33, p. 480-486.

Orville, P. M., 1962, Alkali metasomatism and feldspars: Norsk Geol. Tidsskr., v. 42, p. 283-315.

Paladino, A. E., Maguire, E. A., and Rubin, L. G., 1964, Oxygen ion diffusion in single-crystal and polycrystalline yttrium iron garnet: Am. Ceramic Soc. Jour., v. 47, p. 280-282.

Pandey, G. N., Tek, M. R., and Katz, D. L., 1974, Diffusion of fluids through porous media with implications in petroleum geology: Am. Assoc. Petroleum Geologists Bull., v. 58, p. 291-303.

Prager, S., 1960, Diffusion in inhomogeneous media: Jour. Chem. Physics, v. 33, p. 122-127.

——— 1963, Diffusion and viscous flow in concentrated suspensions: Physica, v. 29, p. 129-139.

Ramberg, H., 1952, The Origin of Metamorphic and Metasomatic Rocks: Chicago, Chicago Univ. Press, 317 p.

Rhodes, W. H., and Kingery, W. D., 1966, Dislocation dependence of cationic diffusion in $SrTiO_3$: Am. Ceramic Soc. Jour., v. 49, p. 521-526.

Robertson, E. C., and Peck, D. L., 1974, Thermal conductivity of vesicular basalt from Hawaii: Jour. Geophys. Research, v. 79, p. 4875-4888.

Robie, R. A., Hemingway, B. S., and Fisher, J. R., 1978, Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures: U.S. Geol. Survey Bull. 1452, 456 p.

Robinson, R. A., and Stokes, R. H., 1959, Electrolyte Solutions: London, Butterworths, 571 p.

Shewmon, P. G., 1963, Diffusion in Solids: New York, McGraw-Hill, 203 p.

Shim, M. T., and Moore, W. J., 1957, Diffusion of nickel in nickel oxide: Jour. Chem. Physics, v. 26, p. 802-804.

Simmons, G., Richter, D., Todd, T., and Wang, H., 1973, Microcracks: their potential for obtaining P-T history of rocks [abs.]: Geol. Soc. America Abs. with Programs, v. 5, p. 810-811.

Sippel, R. F., and Foster, M. R., 1963, Grain boundary diffusion and metasomatism: Jour. Geology, v. 71, p. 251-255.

Sprunt, E. S., and Brace, W. F., 1974, Direct observation of microcavities in crystalline rocks: Internat. Jour. Rock Mechanics Min. Sci. Geomech. Abs., v. 11, p. 139-150.

Stocker, R. L., and Ashby, M. F., 1973, On the rheology of the upper mantle: Rev. Geophysics Space Physics, v. 11, p. 391-426.

Streider, W., and Aris, R., 1973, Variational Methods Applied to Problems of Diffusion and Reaction: New York, Springer-Verlag, 109 p.

Summers, R., Winkler, K., and Byerlee, J., 1978, Permeability changes during the flow of water through Westerly granite at temperature of 100°-400°C: Jour. Geophys. Research, v. 83, p. 339-344.

Tiernan, R. J., ms, 1969, Diffusion of thallium chloride into single crystals and bicrystals of potassium chloride: Ph.D. thesis, Mass. Inst. Technology, 151 p.

Turnbull, D., 1951, Grain boundary and surface diffusion, *in* Atom Movements: Cleveland, Am. Soc. Metals, p. 129-152.

Vidale, R. J., 1969, Metasomatism in a chemical gradient and the formation of calc-silicate bands: Am. Jour. Sci., v. 267, p. 857-874.

Vidale, R. J., and Hewitt, D. A., 1973, 'Mobile' components in the formation of calc-silicate bands: Am. Mineralogist, v. 58, p. 991-997.

Waff, H. S., 1974, Theoretical considerations of electrical conductivity in a partially molten mantle and implications for geothermometry: Jour. Geophys. Research, v. 79, p. 4003-4010.

Waff, H. S., and Holdren, G. R., Jr., 1981, The nature of grain boundaries in dunite and lherzolite xenoliths: implications for magma transport in refractory upper mantle material: Jour. Geophys. Research, v. 86, p. 3677-3683.

Walther, J. V., and Helgeson, H. C., 1977, Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures: Am. Jour. Sci., v. 277, p. 1315-1351.

Walther, J. V., and Orville, P. M., 1982, Volatile production and transport in regional metamorphism: Contr. Mineralogy Petrology, v. 79, p. 252-257.

Walton, M., 1960, Molecular diffusion rates in supercritical water vapor estimated from viscosity data: Am. Jour. Sci., v. 258, p. 385-401.

Watt, J. P., Davies, G. F., and O'Connell, R. J., 1976, The elastic properties of composite materials: Rev. Geophysics, v. 14, p. 541-563.

Weare, J. H., Stephens, J. R., and Eugster, H. P., 1976, Diffusion metasomatism in mineral reaction zones: general principles and application to feldspar alteration: Am. Jour. Sci., v. 276, p. 767-816.

Wehrenberg, J. P., and Silverman, A., 1965, Studies of base metal diffusion in experimental and natural systems: Econ. Geology, v. 60, p. 317-350.

Wenk, H.-R., and Wenk, E., 1969, Physical constants of Alpine rocks (density, porosity, specific heat, thermal diffusivity and conductivity): Schweizer min. pet. Mitt., v. 49, p. 343-357.

Whitney, P. R., and McLelland, J. M., 1973, Origin of coronas in metagabbros of the Adirondack Mtns., N.Y.: Contr. Mineralogy Petrology, v. 39, p. 81-98.

Wuench, B. J., and Vasilos, T., 1964, Grain-boundary diffusion in MgO: Am. Ceramic Soc. Jour., v. 47, p. 63-68.

——— 1966, Origin of grain-boundary diffusion in MgO: Am. Ceramic Soc. Jour., v. 49, p. 433-436.

Yan, M. F., Cannon, R. M., Bowen, H. K., and Coble, R. L., 1977, Space-charge contribution to grain-boundary diffusion: Am. Ceramic Soc. Jour., v. 60, p. 120-127.

Yund, R. A., Smith, B. M., and Tullis, J., 1981, Dislocation-assisted diffusion of oxygen in albite: Phys. Chem. Minerals, v. 7, p. 185-189.

Zaraiskii, G. P., Zharikov, V. A., and Stoyanovskaya, F. M., 1974, Experimental study of bimetasomatic skarn formation, *in* Zharikov, V. A., and Zyryanov, V. N., eds., Contributions to Physical-Chemical Petrology, Volume IV: Moscow, Acad. Sci. USSR, p. 29-71.