

The catalysis of mineral reactions by water and restrictions on the presence of aqueous fluid during metamorphism

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ABSTRACT. The problems of characterizing intergranular regions and of estimating rates of intergranular diffusion in metamorphic rocks are discussed. Intergranular regions can be anhydrous, hydrated but under-saturated with H₂O, or saturated with H₂O, but only in the latter case can a free aqueous fluid phase be present. Estimates of intergranular diffusion coefficients (D^{IGR}) at 550 °C, derived from a variety of published experimental work, vary from $\sim 10^{-8} \text{ m}^2 \text{ s}^{-1}$ for diffusion of species through an intergranular fluid film to $\leq 4 \times 10^{-24} \text{ m}^2 \text{ s}^{-1}$ for diffusion of SiO₂ or O in anhydrous grain boundaries in quartzite. Estimates of D^{IGR} for hydrated grain boundaries vary from $\sim 10^{-13} \text{ m}^2 \text{ s}^{-1}$ to $\sim 10^{-21} \text{ m}^2 \text{ s}^{-1}$; the concentration of H₂O in the grain boundaries and the identity of the diffusing species (generally unknown) may be important controlling factors, and there exists the possibility of a spectrum of values between these two extremes.

Using available kinetic data it is shown that a free aqueous fluid could never have been present in parts of the basement terrane of the Sesia Zone (Western Alps) during uplift from the eclogite facies, except possibly late in the cooling history. The breakdown of sodic pyroxene + quartz occurred in response to the localized infiltration of catalytic aqueous fluid, possibly over a time interval as short as 6-6000 a, and possibly under conditions remote from equilibrium. H₂O-present conditions during a dehydration reaction in metapelites of the Adula nappe (central Alps) could also have been of short duration. These examples are consistent with a model in which basement rocks at deep crustal levels are dry for long periods of time and in which the development of equilibrium mineral assemblages and microstructures generally occurs over relatively short periods of time under transitory fluid-present conditions (caused by devolatilization and/or infiltration).

KEYWORDS: metamorphism, diffusion, intergranular diffusion, aqueous fluid.

THE ubiquity of fluids during metamorphism of the Earth's crust is a subject of controversy. The classic view is that during metamorphism a free fluid phase is always present and that $P_{\text{fluid}} = P_{\text{load}}$ (Vernon, 1976, pp. 53, 57; Turner, 1981, pp. 2-3, 80). As an

example of this view, Etheridge *et al.* (1983, 1984) have presented arguments for a highly mobile and pervasive fluid with large-scale advective mass transport and crustal deformation, primarily by a solution-transfer mechanism (see also Ferry, 1984). However, in recent years, the ubiquity of a metamorphic fluid phase in time and space has been questioned using physical, petrological and geochemical arguments (Hoernes and Friedrichsen, 1978; Walther and Orville, 1982; Thompson, 1983; Yardley and Baltatzis, 1985; Heinrich, 1986). These arguments have led to the alternative view that a free fluid phase is only present for *limited* periods of time, i.e. while dehydration reactions are actually occurring and during fluid infiltration events. A further complication is that if the rate of removal of volatile species by diffusion equals the rate of production (by devolatilization), or if the rate of consumption equals the rate of supply (by infiltration), a free fluid phase may *never* be present during metamorphism (Thompson, 1955).

Hydrous fluid is an extremely effective catalyst in mineral reactions and mass transport (see below), and also has a pronounced effect on ductile rock deformation (e.g. Blacic and Christie, 1984). It is therefore important to resolve these issues in order to obtain a quantitative understanding of metamorphic processes. In addition, equilibria in metamorphic assemblages are most frequently interpreted assuming that $P_{\text{fluid}} = P_{\text{total}}$; when this assumption is not valid, pressure-temperature estimates derived from such studies may require reassessment.

This paper considers two related problems concerning aqueous fluids during metamorphism. First, the role of water as a catalyst in metamorphic reactions is discussed, emphasizing in particular that a whole spectrum of reaction rates is possible, with H₂O-concentration in intergranular regions, and grain boundary structure and width being important controlling factors. The necessity of

attempting to characterize these factors in rocks undergoing metamorphism is emphasized. Second, a preliminary attempt to address part of the problem is made by evaluating the duration of water-present conditions in some metamorphic terranes using available kinetic data and other arguments as constraints.

WATER AS A CATALYST IN MINERAL REACTIONS

Due to the large number of variables which affect the rates of mineral reactions, the quantitative evaluation of reaction kinetics during metamorphism has lagged far behind studies of phase equilibria (for reviews of the problems see Rubie and Thompson, 1985, 1986). In order to extrapolate experimental kinetic data to geological conditions, the effects of variables such as temperature, pressure, grain size, and the catalytic role of water must be understood. The effectiveness of water as a catalyst is qualitatively well known, and is so pronounced that the availability of water, rather than temperature, has been suggested, for example, as the most important factor controlling the rate of the gabbro to eclogite transformation during subduction (Ahrens and Schubert, 1975). However, apart from preliminary investigations of the quartz + periclase \rightarrow forsterite reaction (Fyfe *et al.*, 1958, pp. 84-5) and the aragonite \rightarrow calcite transformation (Brown *et al.*, 1962), there have been few experimental studies which enable the catalytic effect of water to be quantified for reactions of geological interest.

Before experimental data on the effect of H₂O on reaction rates is applied in studies of metamorphism, it is important to recognize that water can increase reaction rates in several different possible ways. These include (1) changing the reaction mechanism, pathway or rate-controlling step on a thin-section scale, and (2) changing the mechanism (of diffusion for example) on an atomistic scale without changing the overall rate-controlling step.

(1) The addition of water to reactants in a solid-solid reaction can change the transport mechanism from solid-state lattice or grain-boundary diffusion to diffusion through an aqueous fluid phase. Consequently, the rate-controlling step can change from diffusion to an interface process, and the activation energy and the rate equation describing the reaction also change. This change in mechanism must be favoured by a porous mineral aggregate and a large fluid-solid ratio. Many experimental kinetic studies of a variety of metamorphic reactions have been made under just such conditions, so that dissolution

or precipitation are probably rate-limiting (e.g. Matthews, 1980; see Wood and Walther, 1983). A possible example of water changing the transport mechanism and the rate-controlling step is shown by a study of the aragonite to calcite transformation under both wet and dry conditions at low pressure (Brown *et al.*, 1962). The activation energy with water present was about half the activation energy for dry conditions, and below 400 °C water enhanced the reaction rate by orders of magnitude (fig. 1). The data, however, suggest that above 500 °C the solid-state processes become faster than the solid-fluid processes, so that water is predicted to have no effect on the reaction rate at $T > 500$ °C.

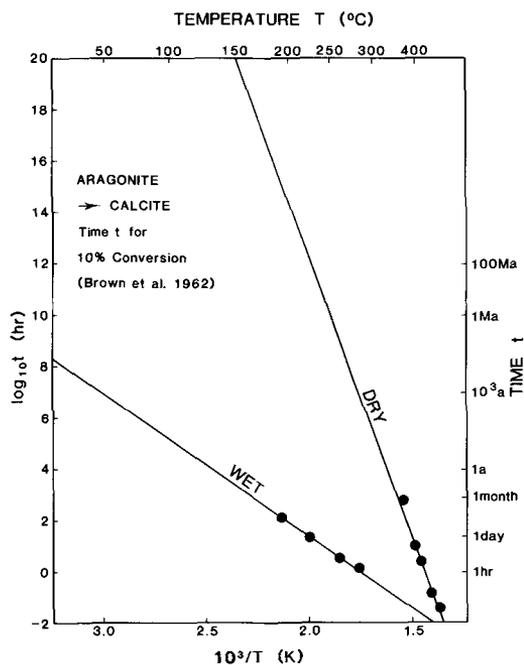


Fig. 1. A comparison of the rates of the aragonite \rightarrow calcite reaction under wet and dry conditions as a function of temperature (from Brown *et al.*, 1962). Experimental data points are plotted on an Arrhenius diagram in which $\log t$ is plotted against $1/T$, where t is the time for 10% conversion. Extrapolations of the data suggest that at 200 °C the reaction is slower by a factor of $\sim 10^{12}$ in the absence of water than in the presence of water, whereas at 500 °C the rates become similar.

Another example of the role of H₂O in changing the reaction mechanism is shown by data on the kinetics of the quartz + periclase \rightarrow forsterite reaction. Under dry conditions at 1100-1400 °C and 1 bar, Brindley and Hayami (1965) concluded that Mg was the main diffusing cation in the product

forsterite layer. However, with water present, at 650–700 °C and 1 kbar, Brady (1983) argued that the diffusive flux of Si through the product forsterite layer greatly exceeded that of Mg. The extrapolation of available data to $T \sim 600\text{--}700$ °C suggests that the reaction with H₂O present is faster by a factor of $10^8\text{--}10^{10}$ than under dry conditions (Fyfe *et al.*, 1958, pp. 84–5; Lenz *et al.*, 1977; Brady, 1983).

Kridelbaugh (1973) found that traces of H₂O changed the mechanism of the reaction quartz + calcite → wollastonite + CO₂. In the presence of pure CO₂, dissolution of calcite and nucleation of wollastonite on quartz grains occurred. With small traces of H₂O in the fluid (e.g. $X_{\text{CO}_2} = 0.95$) the mechanism changed to dissolution of quartz and nucleation of wollastonite on calcite grains (Kridelbaugh, 1973; Tanner *et al.*, 1985), presumably due to a greatly enhanced concentration of SiO₂ dissolved in the fluid.

(2) Water can enhance reaction rates by changing the nature of the activated state, without changing the reaction mechanism on a thin-section scale. This effect is important, although poorly understood, in lattice diffusion. For example, the activation energy for Si–Al disordering in albite varies from 364 kJ mol⁻¹ for samples disordered in air to 280 kJ mol⁻¹ for samples disordered with $P_{\text{H}_2\text{O}} = 10$ kbar (Yund and Tullis, 1980). Water can also apparently create more sites for diffusion without changing the activation energy, thereby increasing the pre-exponential term in an Arrhenius equation. Burte and Nicholson (1972) reported this effect in a study of the reaction $2\text{CaO} + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4$ using cold-pressed reactants at 1000–1200 °C. The experiments were carried out in an atmosphere of N₂ at $P = 1$ bar both with and without a small partial pressure of H₂O. It was concluded that the effect of small traces of H₂O was to break Si–O–Si bonds in the Ca₂SiO₄ lattice and to form Si–OH groups, thereby creating new sites for the diffusion of Ca²⁺. The effect of H₂O was to increase the overall reaction rate by less than a factor of 2, which is small compared with the catalytic effects found at elevated pressures and for other reactions as noted above.

INTERGRANULAR MASS TRANSPORT

Mass transport in intergranular regions can occur by fluid flow transporting species in solution, by diffusion in a relatively static fluid phase or grain boundary film, or by grain boundary diffusion *sensu stricto*. Fluid flow occurs when grain boundary fluid films are relatively thick, i.e. when instantaneous fluid–rock ratios are high, whereas diffusion through a static grain boundary film requires a lower instantaneous fluid–rock ratio

(Walther and Wood, 1984, fig. 3). Grain boundary diffusion dominates in the absence of a continuous intergranular fluid film. It is generally thought that diffusion in static fluid films is dominant during metamorphism (e.g. Rutter, 1976; Brady, 1983; Walther and Wood, 1984).

Water in intergranular regions

Intergranular water is often envisaged as an adsorbed double monomolecular layer (e.g. Walther and Orville, 1982, p. 256). However if, as discussed below, grain boundaries are considered as regions of highly disordered lattice, rather than as discrete regions separating two surfaces, it may be more realistic to regard H₂O molecules as being structurally incorporated (i.e. dissolved) within grain boundaries.

Below a critical water–rock ratio it must be possible for all water to be structurally incorporated within the disordered lattice of grain boundaries (Vernon, 1976, pp. 54–5). In this case grain boundaries are undersaturated with respect to H₂O, there is no free fluid phase, and mass transport is by grain boundary diffusion (as discussed below). The chemical potential of H₂O as a component of the grain boundary can in principle be defined, but $P_{\text{H}_2\text{O}}$ in the physical sense cannot be defined (see Thompson, 1983, p. 539). Above the critical water–rock ratio at which grain boundaries are saturated with H₂O, a free aqueous fluid phase is present, and, provided this is continuous, mass transport can occur either by diffusion through a fluid film or by fluid flow.

The amount of water that can be dissolved in grain boundaries depends on three factors: (1) the concentration of sites which can accommodate H₂O-related species, which depends on the molecular structure and defect chemistry of grain boundaries; (2) the structural thickness (δ_s) of grain boundaries; and (3) the average grain diameter (\bar{d}). The last two parameters δ_s and \bar{d} determine the fraction of grain boundary per unit volume of rock. The structure and thickness of grain boundaries are both poorly known for silicates, as emphasized by the conflicting conclusions of the TEM studies of White and White (1981) and Ricoult and Kohlstedt (1983). White and White (1981) identified 10–30 nm wide zones of damage caused by exposure to the electron beam along grain boundaries in a quartz–mylonite and in a peridotite. Similar zones, between 10 nm and 100 nm in width have been identified by Bearley (1984) along quartz–plagioclase, quartz–biotite and other grain boundaries in rocks from the Ross of Mull contact metamorphic aureole in Scotland (fig. 2). There is a possibility that these are regions of disordered lattice and that the structural

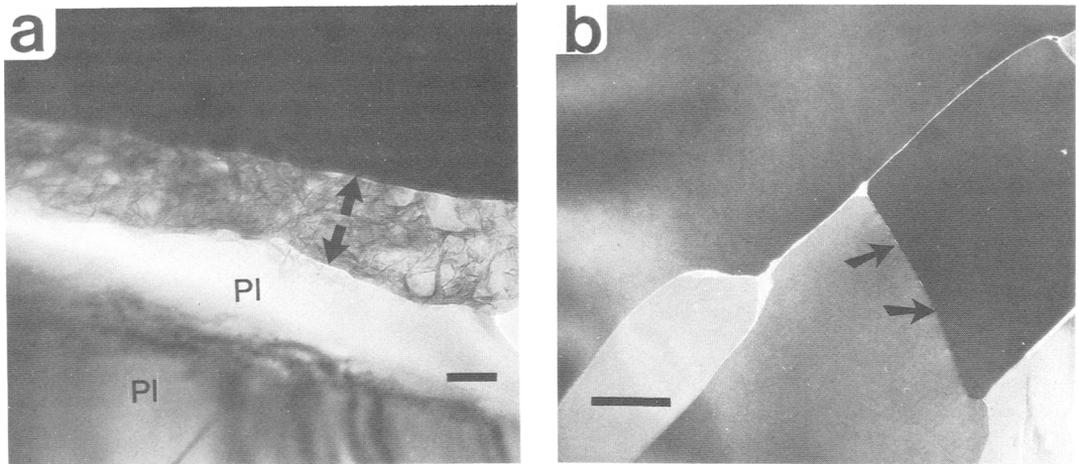


FIG. 2. 100 kV electron micrographs of grain boundaries, in rocks from the Ross of Mull contact aureole, Scotland, emphasizing some of the considerable uncertainties concerning the width and structure of grain boundaries in metamorphic rocks (from Brearley, 1984). (a) A zone of highly disordered material (arrowed) > 100 nm wide, situated along a grain boundary between quartz (top) and plagioclase (Pl). The disordered material contains unusually high concentrations of Ti and Mn which are thought to have been released into the grain boundary system during reactions involving the breakdown of biotite and garnet; therefore this structurally very wide grain boundary region may have been present under high-grade metamorphic conditions (Brearley, 1984). (Scale bar = 100 nm.) (b) Grain boundaries between fibrolite crystals which are oriented with their *c*-axes approximately parallel to the electron beam. Stepped voids ~ 1 nm wide are situated along these grain boundaries (arrowed) and could be an original *in situ* feature or could have developed during unloading. Wider voids, which are well-developed at triple points, are probably the result of either weathering or sample preparation. (Scale bar = 100 nm.)

width of grain boundaries in silicates can be substantially greater than in metals. However, Ricoult and Kohlstedt (1983) argued that the observed radiation damage occurs along zones of alteration caused by weathering or cooling and is not related to the width of primary grain boundaries. They estimated that the structural width of high angle ($\geq 15^\circ$) grain boundaries in olivine is ~ 0.5 nm. Considerable more work on the structure of grain boundaries in silicates is clearly required, and TEM observations on grain boundaries in synthetic aggregates, in which the weathering problem is absent, are likely to be particularly profitable.

In order to fully quantify the kinetics of metamorphic processes, two problems must be solved. First, diffusion coefficients for mass transport through fluid films, hydrated grain boundaries, and anhydrous grain boundaries must be determined. Crude estimates of these coefficients based on the sparse available data are reviewed below. Second, the mode of occurrence and concentration of H_2O in rocks undergoing metamorphism must be characterized as a function of time. A preliminary approach to this problem is made in a subsequent section.

Diffusion in fluid films

Diffusion coefficients for the transport of species in bulk aqueous solutions under metamorphic conditions are generally estimated to be $\sim 10^{-8} \text{ m}^2 \text{ s}^{-1}$ (Fletcher and Hofmann, 1974; Ildefonse and Gabis, 1976). Although it is often assumed that this value is applicable to diffusion of ions through thin aqueous films in intergranular regions (e.g. Ahrens and Schubert, 1975; Walther and Wood, 1984), Rutter (1976) has suggested that the diffusivity of ions in thin films is reduced by about five orders of magnitude relative to the diffusivity in a bulk fluid. The basis of this estimate is first the inverse relation between diffusivity and fluid viscosity, the Stokes-Einstein equation

$$D = kT/6\pi\eta r \quad (1)$$

where D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, η is the fluid viscosity, and r is the radius of the diffusing species, and secondly the observation, based on experimental work, that the apparent viscosity η_t of a thin film is enhanced relative to the viscosity η_b of a bulk fluid. It has been argued that the increased viscosity of fluids in capillaries and thin films is due

to the electroviscous effect (e.g. Smoluchowski, 1918; Elton, 1948; Davies and Rideal, 1963; McGregor, 1974), and theoretical analysis leads to the approximation

$$\eta_f \approx \eta_b + \frac{3\epsilon^2\zeta^2}{8\pi^2\delta_f^2\kappa} \quad (2)$$

(Elton, 1948) where ϵ = dielectric constant, ζ = electrokinetic potential (zeta potential), δ_f = thickness of the fluid film, and κ = specific conductivity. Using the values given by Elton (1948) η_f is predicted to be $10^5\eta_b$ for a film thickness of 2 nm, thus giving $D^f \approx 10^{-5}D^b$ from equation (1), where D^f and D^b are the diffusion coefficients for species in a fluid film and in a bulk fluid respectively (Rutter, 1976). This estimate must, however, be viewed with considerable doubt, mainly because the theoretical derivation of equation (2) uses approximations which restrict its validity to films with a thickness which exceeds the Debye double layer thickness λ by two orders of magnitude, i.e.

$$\frac{\delta_f}{\lambda} > 100 \quad (3)$$

(Rice and Whitehead, 1965, p. 4023). The Debye double layer thickness can be estimated from

$$\lambda = \left(\frac{\epsilon kT}{8\pi n e^2} \right)^{\frac{1}{2}} \quad (4)$$

(Elton, 1948) where n = ionic concentration and e = electronic charge, and Moore (1972, p. 512) lists calculated values in the range 0.5–50 nm. Thus equation (2) can only be applied to fluid films with a thickness exceeding 50 nm–5 μ m (depending on the exact value of λ). Using this range of limiting values, the *maximum* value of apparent viscosity which can be calculated from equation (2) is $\eta_f \approx 3\eta_b$ for typical metamorphic conditions [$\epsilon = 20$ (Helgeson and Kirkham, 1974), $\zeta = 15$ mV for a quartz–water interface (Lidström, 1968, p. 101), $\kappa = 10^{-6}$ ohm $^{-1}$ cm $^{-1}$, and $\eta_b = 10^{-3}$ Poise (Walther and Orville, 1982)].

Developments in the theory of electrokinetic flow now enable the viscosity of fluid films with widths as low as the Debye double layer thickness to be predicted ($\delta_f/\lambda \geq 1$) (Rice and Whitehead, 1965; Levine *et al.*, 1975a, b; Olivares *et al.*, 1980). This theory shows that there is a maximum in the electroviscous effect for flow in capillary slits at a value of δ_f/λ which depends on ζ , and that at this maximum the viscosity enhancement is likely to be considerably less an order of magnitude ($\eta_f/\eta_b < 1.1$ –6.0) (Rice and Whitehead, 1965, fig. 8; Levine *et al.*, 1975a, figs. 4 and 5).

Experimental investigations of water and aqueous solutions in thin films and capillaries have

shown that the viscosity can be enhanced relative to that of the bulk fluid by an amount which significantly exceeds the predictions of the electrokinetic theory. For example, Churayev *et al.* (1970) found $\eta_f/\eta_b \approx 1.5$ for water in a capillary of radius 46 nm at room temperature. For the particular experimental conditions the electroviscous effect was predicted to raise the viscosity by < 2–3%, and Churayev (1970) concluded that 'the real cause of the observed viscosity changes is the modification of the structure of liquids under the influences of surface forces', and is not due to electrokinetic effects. In the experiments of Churayev *et al.* (1970) the enhanced viscosity of water in capillaries was found to become weaker with increasing temperature, and at 65 °C the viscosity became normal ($\eta_f/\eta_b = 1$).

In view of the uncertainties concerning thin fluid films under ambient conditions, it would certainly be premature to speculate on their properties under metamorphic conditions. However, at present there seems to be little reason to believe that viscosity and diffusion coefficients for thin aqueous films during metamorphism differ by more than an order of magnitude from the values for a bulk fluid. This conclusion is supported by the experimental data of Tanner *et al.* (1985, p. 600).

Grain boundary diffusion

When there is no free fluid phase present, mass transport occurs by grain boundary diffusion (and/or lattice diffusion). Water dissolved in grain boundaries must enhance rates of grain boundary diffusion, perhaps by replacing Si–O bonds by weaker hydrogen bonds and effectively reducing the energy of the activated state. This type of mechanism has been suggested by Beach (1982, p. 145) for diffusion of SiO₂ along mica grain boundaries. Diffusion coefficients for grain boundary diffusion (D^{gb}) are likely to be a function of the concentration of H₂O-related species in the grain boundaries, and there could be a whole spectrum of values ranging from D^{gb} for dry grain boundaries (no H₂O-related species) to D^{gb} for H₂O-saturated grain boundaries.

Pressure may have a significant effect on rates of diffusion along hydrated grain boundaries. For example, Tullis and Yund (1982) found that the rate of grain growth of wet quartz aggregates, presumed to be controlled by grain boundary diffusion, increased very significantly with pressure. Their explanation, that this effect was due to the increased solubility of SiO₂ in H₂O with increasing pressure, can only apply if a free fluid phase was present along the grain boundaries. An alternative possibility is that high pressure enhances diffusion

rates by increasing the concentration of some species, such as H_2O , OH^- , or H^+ , in grain boundaries, i.e. by a mechanism analogous to that suggested for lattice diffusion of oxygen in quartz (Giletti and Yund, 1984).

Data on rates of intergranular diffusion in a variety of materials have been discussed by Brady (1983) and Joesten (1983). Existing data which are applicable to silicates, together with three additional estimates, are summarized in Table I.

The estimate of D^{gb} for dry quartz is derived from a null-result grain growth experiment described by Tullis and Yund (1982, p. 303). They reported an absence of detectable grain growth in vacuum-dried novaculite, of grain size $4 \mu m$, when annealed at $1100^\circ C$ and 15 kbar for 72 hours. Isothermal grain growth in single phase aggregates is described by:

$$\bar{d}^2 - \bar{d}_0^2 = \frac{8\gamma\bar{V}D^{gb}t}{RT\delta_e} \quad (5)$$

(Joesten, 1983), where \bar{d}_0 and \bar{d} are the initial and final average grain sizes respectively, γ and \bar{V} are the surface free energy and molar volume of the phase respectively, D^{gb} is the coefficient of grain boundary diffusion for the rate-limiting species, t is time, R is the gas constant, and δ_e is an effective grain boundary width. Assuming that a grain size increase of $0.5 \mu m$ (12%) would have been detectable, at least by modifying the shape of the grains, the upper limiting value of D^{gb} given in Table I is obtained by letting $\bar{d}_0 = 4 \mu m$, $\bar{d} = 4.5 \mu m$, $t = 72$

hours, $T = 1100^\circ C$, $\gamma_{Qz} = 0.605 J m^{-2}$ (Brace and Walsh, 1962), and $\bar{V}_{Qz} = 2.269 \times 10^{-5} m^3$ (Robie *et al.*, 1978).

The estimate of D^{gb} for plagioclase is derived from the data for an orthothose of Boullier and Gueguen (1975). This rock consists of a mosaic of equant plagioclase grains, of grain size $\bar{d} = 50 \mu m$, which was naturally deformed at $600^\circ C$. The *maximum* amount of grain growth which could have occurred is $\bar{d} - \bar{d}_0 < 50 \mu m$. Assuming that the temperature of $600^\circ C$ was maintained for ≥ 10 Ma, the upper limiting value of D^{gb} given in Table I is obtained from equation (5), using $\bar{d} = 50 \mu m$ and $\bar{d}_0 = 1 \mu m$.

The final diffusion coefficient listed in Table I is for Mg_2GeO_4 spinel, which may be a good analogue for the corresponding silicate phase. The diffusion coefficient has been estimated by fitting the superplastic creep data for fine-grained ($\bar{d} = 3 \mu m$) spinel of Vaughan and Coe (1981) to the flow law

$$\dot{\epsilon} = \frac{82b^3 D^{gb} \delta_e \sigma}{\bar{d}^3 kT} \quad (6)$$

where $\dot{\epsilon}$ is the strain rate, b is the Burgers vector, and σ is the differential stress (Gifkins, 1976). An alternative flow law (Gifkins, 1976, equation 4a) gives an almost identical value for D^{gb} .

There are five main sources of uncertainty in the data of Table I.

(1) Some of the diffusion coefficients describe transport across (perpendicular to) grain boundaries

TABLE I. Estimates of grain boundary diffusion coefficients

| Mineral | Diffusing species | D^{gb} ($m^2 s^{-1}$) | D^{gb} ($m^2 s^{-1}$) | Q ($kJ mol^{-1}$) | Temperature range ($^\circ C$) | Comments | Source |
|--------------------|-------------------|-------------------------------|--------------------------------|---------------------|----------------------------------|---|-------------------------|
| Perthite | O^{18} | | $1.8 \times 10^{-11}/\delta_e$ | 155 | 500-700 | $P_{H_2O} = 1$ kbar. Diffusion along perthite lamellar boundaries. | Giletti and Nagy (1981) |
| Forsterite | O or SiO_2 | $<10^{-19}/\delta_e$ | | | 650-700 | $P_{H_2O} = 1$ kbar | Brady(1983) |
| Quartz | O or SiO_2 | | $0.8\delta_e$ | 210 ± 80 | 600-1000 | Hydrated grain boundaries inferred (see text) | Joesten (1983) |
| Quartz | O or SiO_2 | $<1.7 \times 10^{-9}\delta_e$ | | | 1100 | Dry. $P = 15$ kbar. Estimated from grain growth data of Tullis and Yund (1982). | See text |
| Plagioclase | ? | $<10^{-16}\delta_e$ | | | 600 | Dry (see text)? Estimated from data of Boullier and Gueguen (1975). | See text |
| Mg_2GeO_4 spinel | O or GeO_2 | | $7.6 \times 10^{-14}/\delta_e$ | 306 | 985-1250 | Dry. $P = 12-19$ kbar. Estimated from creep data of Vaughan and Coe (1981). | See text |

Note: The parameters in this table are related by the equation $D^{gb} = D_0^{gb} \exp(-Q/RT)$; δ_e is the effective grain boundary width (m) - see text.

(quartz and plagioclase), whereas the others describe transport along (parallel to) the grain boundaries. There is evidence to suggest that diffusion coefficients for these two processes are not identical (Peterson, 1983).

(2) The diffusion coefficients D^{sb} cannot be determined without knowing the value of the effective grain boundary width δ_e . The value of δ_e and its relation to the structural width of grain boundaries δ_s is poorly known for ceramics and silicates. δ_e is often estimated to lie between 10 and 100 nm (Brady, 1983; Joesten, 1983), but it could be as low as 0.5 nm (Peterson, 1983; Ricoult and Kohlstedt, 1983).

(3) The concentration and structural state of water in the grain boundaries is generally unknown. Although the values for perthite and forsterite were obtained from experiments with $P_{H_2O} = 1$ kbar, the diffusion coefficients are several orders of magnitude lower than the value of $10^{-8} \text{ m}^2 \text{ s}^{-1}$ for diffusion through a fluid. It is therefore presumed that, although the grain boundaries may have been saturated with H_2O , there was no continuous fluid film along the grain boundaries and these values are therefore representative of true grain boundary diffusion. The value for quartz estimated by Joesten (1983) was derived by combining data on the grain size of quartzite nodules in a thermal aureole with a modelled temperature-time history in order to evaluate the kinetics of grain growth. The only direct evidence available suggests that a CO_2 -rich fluid phase was present (Joesten, 1983, pp. 240-1). However, as the grain growth kinetics are consistent with those measured experimentally by Tullis and Yund (1982) on quartzite with 1-2 wt. % H_2O added (Joesten, 1983, p. 237, fig. 5), and as the diffusion coefficient is significantly larger than the estimated maximum value for dry quartz (Table I), it is inferred that the grain boundaries were at least partially hydrated (see also below). Also, there is no direct evidence to indicate whether D^{sb} for plagioclase applies to dry or hydrated grain boundaries. However, if the estimated diffusion coefficients for dry spinel and for dry quartz are extrapolated to 600 °C (using an activation energy of 300 kJ mol $^{-1}$ for quartz—a typical value for grain growth of dry oxides), the resulting values are almost identical to the plagioclase value. It is therefore suggested that the latter applies to dry grain boundaries.

(4) The nature of the diffusing species is generally unknown. On the basis of the compensation law, Joesten (1983, 1985) argued that oxygen diffusion is rate-limiting during grain growth in quartzite. If that is the case it is necessary to explain why the diffusion coefficient for oxygen diffusion in perthite lamellar boundaries is 7-9

orders of magnitude larger than D^{sb} for hydrated quartz at 600 °C (with δ in the range 10-100 nm). One possibility is that diffusion of SiO_2 is rate-controlling during grain growth of quartzite. Another possibility is that water had a significantly greater catalytic effect in the perthite diffusion experiments than in both the grain growth experiments of Tullis and Yund (1982) and the grain growth in the thermal aureole quartzite nodules described by Joesten (1983).

(5) There is some uncertainty about the validity of equation (5) for accurately describing the kinetics of grain growth (Martin and Doherty, 1976, pp. 228-34; Rubie and Thompson, 1985, p. 66). However, calculations based on a possibly more realistic rate equation (Martin and Doherty, 1976, equation 4.29) show that the effect of this uncertainty on calculated grain boundary diffusion coefficients is small compared with the effects of the other uncertainties discussed above.

Intergranular diffusion coefficients during metamorphism

Estimates of intergranular diffusion coefficients (D^{IGR}) at 550 °C, based on the preceding discussion and on extrapolations from the estimates of Table I, are listed in Table II. The estimate for dry quartz is based on an assumed activation energy of 300 kJ mol $^{-1}$, which, as noted above, is typical for dry oxides. The estimates suggest that diffusion through a free aqueous fluid phase is ~ 16 orders of magnitude faster than along dry grain boundaries at 550 °C. Diffusion coefficients for mass transport along hydrated grain boundaries can evidently vary from ~ 10^{-13} to ~ $10^{-21} \text{ m}^2 \text{ s}^{-1}$, with possible controlling factors being the concentration

TABLE II. Estimates of intergranular diffusion coefficients
 D^{IGR} ($\text{m}^2 \text{ s}^{-1}$) at 550 °C

| Aqueous fluid | 10^{-6} | |
|-----------------|----------------------------|-----------------------------|
| | $\delta_e = 10 \text{ nm}$ | $\delta_e = 100 \text{ nm}$ |
| Wet perthite | 3×10^{-13} | 3×10^{-14} |
| Wet quartz | 4×10^{-22} | 4×10^{-21} |
| Dry quartz | $\leq 4 \times 10^{-25}$ | $\leq 4 \times 10^{-24}$ |
| Dry Mg_2GeO_4 | 3×10^{-25} | 3×10^{-26} |

of H₂O in the grain boundaries, the nature of the diffusing species, and the grain boundary structure and width.

RESTRICTIONS ON THE PRESENCE OF AQUEOUS FLUID DURING METAMORPHISM

There are strong arguments to suggest that some lithologies have been affected by extensive fluid infiltration during regional metamorphism (e.g. Rumble *et al.*, 1982; Ferry, 1983; Graham *et al.*, 1983). Furthermore, Ferry (1984) has suggested that large-scale fluid infiltration of entire terranes may be an essential feature of metamorphism over the whole range of crustal conditions. In this section it is argued that parts of a terrane can remain 'dry' for extensive periods of time (e.g. tens of millions of years) and perhaps in some cases for an entire metamorphic cycle. It is shown that the duration of H₂O-present conditions during infiltration/dehydration events can be short, but it is emphasized that it is during these periods that metamorphic reactions, deformation, and microstructural evolution primarily occur.

It is important to note that some discussions of the evolution and migration of fluids during crustal metamorphism may have exaggerated the overall abundance of fluids, by specifically considering burial and prograde metamorphism of sediments which have an initially high volatile content (Norris and Henley, 1976; Walther and Orville, 1982; Walther and Wood, 1984). In some continental collision zones, a large proportion of the rocks undergoing metamorphism in a tectonically thickened crust are comparatively anhydrous basement rocks—schists and gneisses with a previous history of high-grade metamorphism, and calc-alkaline plutonic rocks. In the Western Alps, for example, lithologies which could have been initially rich in volatiles, such as Mesozoic sediments and ophiolites, constitute only 20% or less of the thickened crust of the Pennine and Sesia Zones (Laubscher and Bernoulli, 1980, fig. 2). The initial volatile content (H₂O + CO₂) of basement rocks is generally in the range 0.5–2.5 wt. % and is low compared with the value of 6.5–7.5 wt. % quoted by Walther and Orville (1982) for low-grade pelites.

It can be argued that sedimentary rocks, and especially pelitic varieties, will contain a free fluid phase continuously during prograde metamorphism as progressive compaction and dehydration occur (Norris and Henley, 1976; Fyfe *et al.*, 1978). However, such arguments cannot be applied to metamorphism of basement rocks, which are initially relatively anhydrous. Evidence for the origin, duration, and timing of fluid-present con-

ditions in two basement terranes of the Western and Central Alps, during specific parts of their tectonic history, is now considered.

The Sesia Zone

The Sesia Zone is the most southeastern tectonic unit of the Western Alps. It is a slice of continental crust which consisted, prior to the Alpine orogeny, of amphibolite- to granulite-facies metamorphic rocks, including ultrabasics, metabasites, metapelites, metacarbonates, and metasediments of quartzofeldspathic composition, intruded by granitic plutons of late Hercynian age (Compagnoni *et al.*, 1977). During an early-Alpine event (100–130 Ma) the Sesia Zone was tectonically emplaced to a depth of ≥ 50 km, and consequently a large part of the unit underwent a pervasive eclogite-facies metamorphism ($P > 15$ kbar, $T \approx 500$ – 560 °C), (Compagnoni, 1977; Compagnoni *et al.*, 1977; Koons, 1982; Lardeaux *et al.*, 1982; Rubie, 1984; Oberhaensli *et al.*, 1985). During its subsequent history the unit was uplifted back to the surface, and partially re-equilibrated first in the blueschist facies (~ 8 kbar, 470–490 °C, ~ 60 Ma BP) and subsequently in the greenschist facies (~ 4 – 5 kbar, ~ 400 °C, ~ 40 Ma BP) (see Rubie, 1984, fig. 3). To a first approximation, uplift was isothermal ($T = 500$ – 560 °C) for the initial 40 Ma, and occurred at an average rate of 0.5–0.75 mm/year.

Metastability of Na-pyroxene + quartz. Schists and gneisses containing the preserved assemblage quartz + jadeite or quartz + omphacite are common throughout the central Sesia Zone (Lombardo *et al.*, 1977; Koons, 1982). The sodic pyroxene in these rocks is often in direct contact with quartz and varies from being completely unaltered to partially or completely altered to a pseudomorphic albite-rich aggregate (fig. 3). The breakdown products include extremely fine-grained symplectites of albite + diopside or aegirine-augite, fine-grained albite ($\bar{d} \approx 10$ μm), and fine-grained aggregates of albite + phengite. Initially, alteration occurred along narrow veins which cut across crystals of sodic pyroxene (fig. 3b). With increased alteration irregular volumes of albite-rich material formed which eventually pseudomorphed entire crystals. When only partially reacted, pyroxenes often show no trace of reaction away from the localized regions of alteration, even when in direct contact with quartz (fig. 3c). The localized and often irregular geometry of altered regions suggests that localized infiltration of fluid occurred initially along fractures, and that this fluid acted as a catalyst for nucleation and growth of albite and other alteration products. Where fluid was absent along

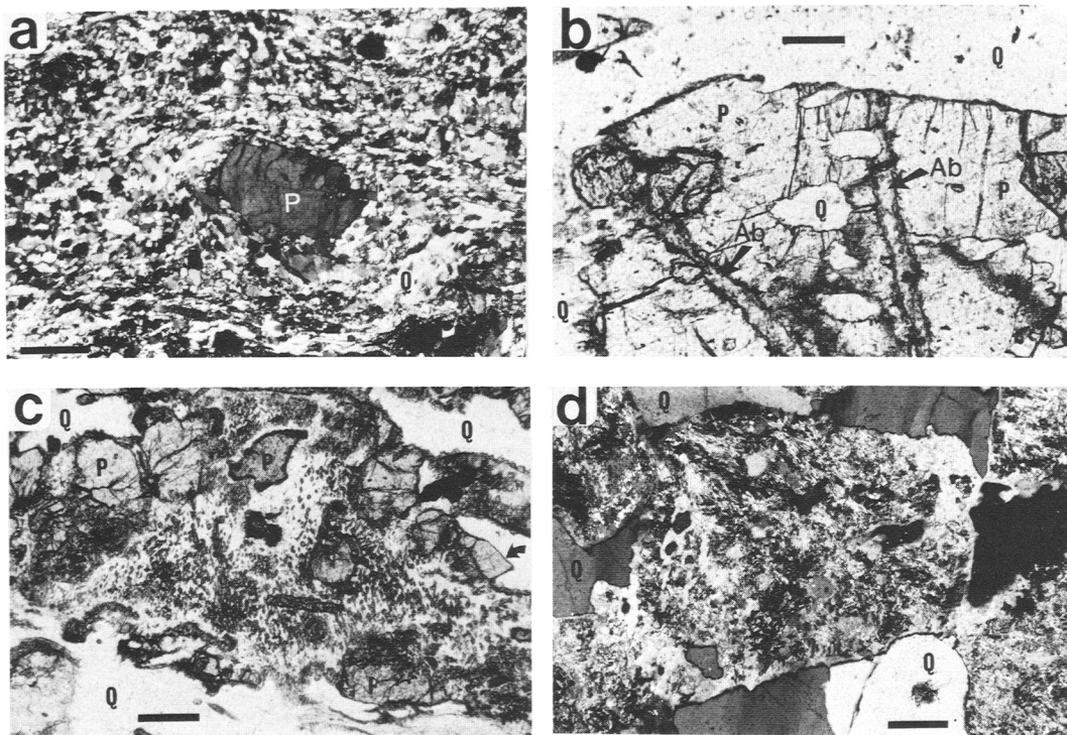


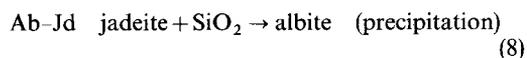
FIG. 3. Photomicrographs of sodic pyroxene (P) showing various degrees of reaction to fine-grained albite and other alteration products. The pyroxene is surrounded by quartz (Q) in all cases. These examples, from rocks of the central Sesia Zone, must all have followed approximately the same *PTt* path during uplift, and the extent of reaction depended on the availability of fluid which acted as a catalyst. (a) A jadeite crystal (centre), contained in a matrix of fine-grained ($\bar{d} = 45 \mu\text{m}$) dynamically recrystallized quartz, shows no trace of alteration to albite. (Quartz mylonite from a shear zone, Val d'Aosta; crossed polars; scale bar = 400 μm .) (b) Part of a large jadeite crystal in contact with quartz. The jadeite is altered to fine-grained albite along two veins $\sim 60 \mu\text{m}$ wide (Ab), but only shows a very narrow reaction rim (1–10 μm wide) along quartz–jadeite grain boundaries. (Schist, Valchiusella; plane polarized light; scale bar = 200 μm .) (c) A large omphacite crystal showing irregular and extensive alteration to a fine-grained symplectite of albite + diopside. Irregular relics of omphacite remain, and locally omphacite–quartz grain boundaries show no trace of reaction (arrowed). (Schist, Valchiusella; plane polarized light; scale bar = 400 μm .) (d) Sodic pyroxene crystals totally replaced by a fine-grained aggregate of albite + phengite. (Schist, Valchiusella; crossed polars; scale bar = 200 μm .)

pyroxene–quartz grain boundaries, the reaction failed to occur for kinetic reasons.

Fine-grained phengite (+albite) is a common reaction product when the extent of alteration is large or complete (fig. 3d). There is no evidence to suggest that phengite inclusions were present within sodic pyroxenes prior to the breakdown reaction, and it must therefore be assumed that infiltrating hydrous fluid not only acted as a catalyst but also participated as a reactant. In addition, alkali-exchange reactions between the solid phases and the fluid must have occurred, with the abundance of phengite suggesting that fluid–rock ratios were large.

Kinetics of jadeite + quartz \rightarrow albite. The kinetics of the jadeite + quartz \rightarrow albite reaction have been

modelled in order to test the hypothesis that the reaction only occurred when catalysed by infiltrating aqueous fluid, and also to attempt to constrain the duration of fluid-present conditions. In the model reaction a growing layer of albite, of thickness x and average grain size \bar{d} , forms between single crystals of quartz and jadeite. It is assumed that SiO_2 is the only mobile component, which is consistent with the observation that albite replaces jadeite but not quartz. Reactions occur at the quartz–albite (Qz–Ab) and albite–jadeite (Ab–Jd) interfaces as follows



and SiO_2 diffuses through the intergranular region in the albite aggregate. The model can equally well represent growth of an albite layer between a jadeite crystal and a fluid-filled planar fracture which acts as a supply of aqueous silica (cf. fig. 3b). The overall reaction involves the sequential steps of dissolution, transport, and precipitation, and the slowest of these is rate-controlling. As the enthalpy of reaction is fairly low, the possibility that heat-flow could be rate-controlling is not considered. The rate of dissolution and precipitation (reactions 7 and 8) in the presence of aqueous fluid can be estimated from the rate equation evaluated by Wood and Walther (1983) for a variety of interface-controlled reactions, at conditions fairly close to equilibrium ($-\Delta G_r < 0.4 RT$)

$$\frac{dm}{dt} = -K_r \frac{\Delta G_r}{RT} \quad (9a)$$

where dm/dt is the rate of mass transfer per unit surface area and ΔG_r is the free energy of reaction. The rate constant K_r is given by

$$\log K_r = -\frac{2900}{T} - 2.85$$

gram atoms of oxygen $\text{m}^{-2} \text{s}^{-1}$. (9b)

In the experiments of Schramke *et al.* (in press) involving muscovite, quartz, K-feldspar, andalusite, and H_2O , andalusite precipitation was found to be rate-controlling and was slower by a factor of ~ 10 than rates predicted by equation (9b). Although equation (9b) should be valid if dissolution of quartz is rate-controlling, it may overestimate the reaction rate if albite precipitation is the rate-controlling step. The effect of this uncertainty on the results of the modelling is considered below.

The rate of reactions (7) and (8) in the absence of aqueous fluid must be considerably slower than that predicted by equation (9b). Loomis (1979) has estimated a rate of sillimanite dissolution as 10^{-7} – 10^{-8} cm/year in high-grade metamorphic rocks from the aureole of the Ronda peridotite, Spain, which are inferred to have been 'fairly dry'. This value is slower by a factor of $\sim 10^4$ than the rate calculated from equation (9) for the jadeite + quartz \rightarrow albite reaction. Although the uncertainty in the rates of reactions (7) and (8) in the absence of aqueous fluid is large, a wide range of values (10^{-3} – 10^{-9} cm/year) can be used in the modelling without affecting any of the conclusions listed below.

If lattice diffusion and fluid flow are both negligible, the flux of SiO_2 through the albite layer can be estimated from

$$J_{\text{SiO}_2} = -\frac{D_{\text{SiO}_2}^{\text{IGR}} C_{\text{SiO}_2} \varphi \tau}{RT} \frac{d\mu_{\text{SiO}_2}}{dx} \quad (10)$$

(Walther and Wood, 1984), where $D_{\text{SiO}_2}^{\text{IGR}}$ is the intergranular diffusion coefficient for SiO_2 , C_{SiO_2} is the concentration of SiO_2 in the grain boundary or fluid film, φ is the volume fraction occupied by the grain boundary or fluid film, τ is tortuosity, and $d\mu_{\text{SiO}_2}/dx$ is the chemical potential gradient of SiO_2 . φ can be approximated by $2\delta/\bar{d}$ where $\delta = \delta_f$ when a fluid film is present and $\delta = \delta_e$ for fluid-absent conditions. When the reaction is diffusion-controlled, under steady-state conditions $d\mu_{\text{SiO}_2}/dx = \Delta G_r/x$. Substituting these relationships into equation 10 gives

$$J_{\text{SiO}_2} = -\frac{2D_{\text{SiO}_2}^{\text{IGR}} C_{\text{SiO}_2} \delta \tau \Delta G_r}{RT\bar{d}x} \quad (11)$$

J_{SiO_2} has been calculated using $\tau = 0.7$ (Walther and Wood, 1984), and $\bar{d} = 10 \mu\text{m}$ (see fig. 3). The reaction has been modelled with diffusion through an aqueous fluid film, along hydrated grain boundaries, and along dry grain boundaries using diffusion coefficients listed in Table II, and values of 10 nm and 100 nm have been used for both the fluid film thickness and the effective grain boundary width. The concentration of SiO_2 in the intergranular region (C_{SiO_2}) has been taken as 10^2 mol. m^{-3} in a fluid and 3×10^4 mol. m^{-3} in grain boundaries (see Walther and Wood, 1984). Data of Holland and Powell (in press) were used to calculate ΔG_r .

Extent of reaction has been modelled for the initial 40 Ma of a pressure-temperature-time path along which the Sesia Zone is presumed to have uplifted to the surface. It is assumed that, after crossing the jadeite + quartz = albite equilibrium boundary, uplift to the surface occurred at a constant rate over a period of 100 Ma, and that for the initial 40 Ma uplift was isothermal ($T = 550^\circ\text{C}$). As actual temperatures may have been slightly lower than 550°C (Rubie, 1984, fig. 3), the modelling may exaggerate the extent of reaction. It is assumed that the reaction starts by nucleation of a 1 nm thick albite layer when the pressure reaches a value of 100 bars below the equilibrium value.

The diffusive flux and the rate of precipitation/dissolution have been calculated from equations (11) and (9) respectively at successive times, and growth of the albite layer has been calculated as a function of time from the rate equation for the slower process. When interface-controlled, the growth rate is constant over periods $\leq 10^4$ a because ΔG_r is almost constant on this time scale, and, from equation (9a), at time t

$$x = -\frac{\bar{V}_{\text{ab}} K_r \Delta G_r t}{2RT} \quad (12)$$

where \bar{V}_{ab} is the molar volume of albite. When

the reaction is diffusion-controlled, from equation (11)

$$\frac{dx}{dt} = \bar{V}_{ab} J_{\text{SiO}_2} = -\frac{2\bar{V}_{ab} D_{\text{SiO}_2}^{\text{IGR}} C_{\text{SiO}_2} \delta \tau \Delta G_r}{RT \bar{d} x}$$

and

$$\int_{x_1}^{x_2} x dx = -\frac{2\bar{V}_{ab} D_{\text{SiO}_2}^{\text{IGR}} C_{\text{SiO}_2} \delta \tau}{RT \bar{d}} \int_{t_1}^{t_2} \Delta G_r dt. \quad (13)$$

As the uplift rate is taken as constant, ΔG_r can be written as a linear function of time and equation (13) can be easily solved for $x(t)$.

Results of the modelling, shown as a set of $x(t)$

curves in fig. 4, suggest that the reaction rate is slower by a factor of $\sim 10^8$ under completely dry conditions than under water-present conditions. At some stage the reaction changes from being interface-controlled to diffusion-controlled (see also Fisher, 1978, fig. 7). The time at which this change occurs depends on D^{IGR} and on the rate of dissolution/precipitation; using equation (9a) for the rate of this latter process, the time varies from < 1 day ($D^{\text{IGR}} = 10^{-17} \text{ m}^2 \text{ s}^{-1}$) to 10^3 – 10^4 a ($D^{\text{IGR}} = 10^{-8} \text{ m}^2 \text{ s}^{-1}$). For dry conditions the reaction is predicted to be diffusion-controlled throughout unless the rate of dissolution/precipitation is $< 10^{-8} \text{ cm/year}$.

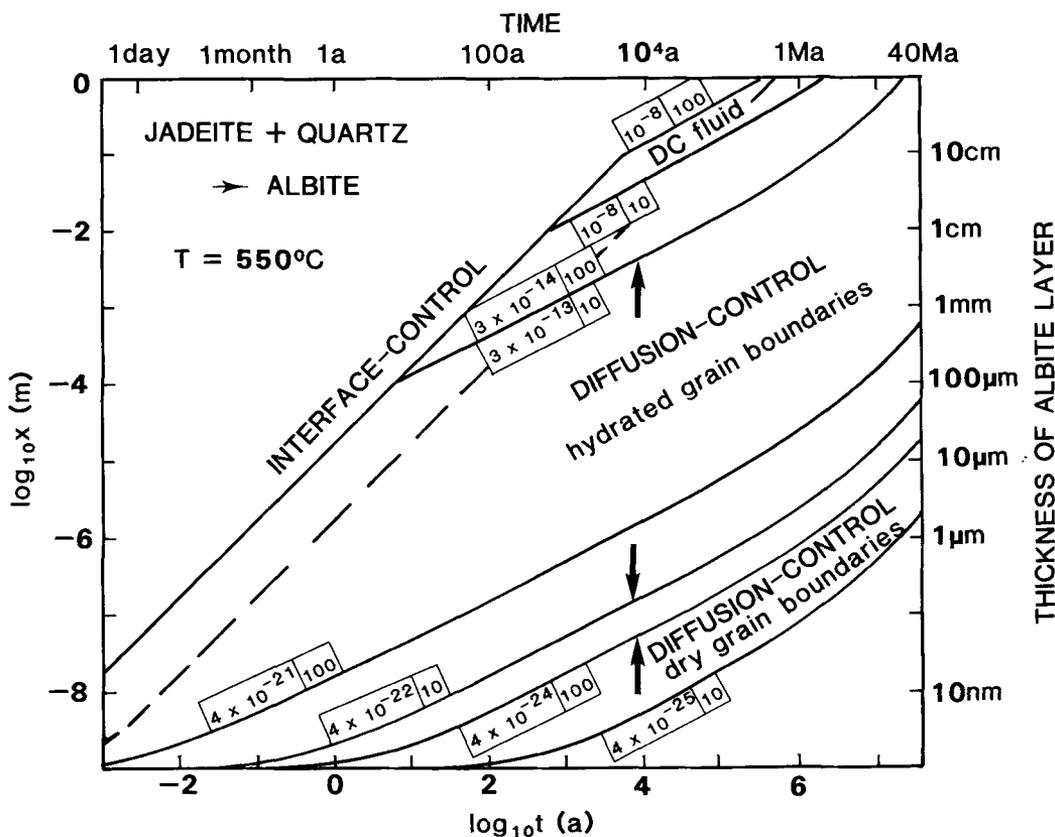


FIG. 4. A selection of possible reaction curves showing the thickness of an albite layer (x) as a function of time for the model reaction jadeite + quartz \rightarrow albite under conditions of 550°C and decreasing pressure (see text). The reaction can be either interface-controlled or diffusion-controlled and with relatively large diffusion coefficients there is a change from interface-control to diffusion-control at some stage during the reaction. The curve for interface-controlled reaction in the presence of aqueous fluid has been calculated from equation (9a); the broken line represents a possible limit of uncertainty in equation (9a). Curves for diffusion-controlled reaction have been calculated from equation (13) using the intergranular diffusion coefficients estimated for aqueous fluid, hydrated grain boundaries and dry grain boundaries (Table II), and limiting curves for the latter two sets of conditions are arrowed. Curves are labelled with values of the diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$) and δ_e or δ_f (nm). (DC = diffusion-control.) For simplicity, curves for interface-controlled reaction, in the absence of aqueous fluid, as discussed in the text, have been omitted.

Several conclusions can be made concerning H₂O in rocks of the Sesia Zone during uplift through the albite-stability field.

(1) In cases where there has been no reaction between jadeite and quartz (fig. 3a), the possibility of a free aqueous fluid phase occurring along the quartz-jadeite grain boundaries at any time during uplift can be excluded. Experiments of Matthews (1980) and Rubie (unpublished data) show that nucleation of albite on jadeite surfaces is extremely rapid in the presence of aqueous fluid over a wide range of conditions ($T = 400\text{--}600\text{ }^{\circ}\text{C}$, $P = 1\text{--}10$ kbar), and fig. 4 shows that, once nucleated, the albite layer would grow to a readily observable thickness ($\geq 10\text{ }\mu\text{m}$) in less than 1–10 a at 550 °C.

With $D^{\text{IGR}} = 4 \times 10^{-22}\text{ m}^2\text{ s}^{-1}$ (the lowest value for hydrated grain boundaries listed in Table II) and $\delta = 10\text{ nm}$, the predicted thickness of the albite layer after 40 Ma is $\sim 60\text{ }\mu\text{m}$. Therefore, unless nucleation was a problem, the possibility of grain boundaries remaining in a permanently hydrated state during uplift can also be excluded in cases where reaction has failed to occur. However, grain boundaries could have remained in a hydrated state for a limited period of time (e.g. $< 10^5$ a) without the growth of a readily observable albite layer ($x < 1\text{ }\mu\text{m}$).

With the D^{IGR} values for dry grain boundaries given in Table II, fig. 4 predicts the growth of a 1–10 μm thick albite layer after 40 Ma at 550 °C. Where reaction is absent, either albite could have failed to nucleate in the absence of H₂O, or the actual grain boundary diffusion coefficient could have been smaller than the values used in the modelling.

(2) In cases where sodic pyroxene is partially or completely pseudomorphed by albite and other reaction products, the extent of reaction is highly variable with the dimensions of albite-rich aggregates varying from $< 100\text{ }\mu\text{m}$ to 1 cm. If the reaction was catalysed by infiltrating aqueous fluid, fig. 4 suggests that the time required to produce such alteration varies from < 6 a to ~ 600 a. If the rate of dissolution/precipitation is reduced by a factor of 10 to allow for uncertainties in equation (9), the time required is $< 60\text{--}6000$ a. Alternatively, if the reaction was catalysed by H₂O structurally incorporated in hydrated grain boundaries, in the absence of a free aqueous fluid phase (i.e. by the localized introduction of H₂O by grain boundary diffusion), the time required is poorly constrained and could lie between ~ 10 a and ~ 40 Ma (fig. 4)!

The fact that reaction products are often highly localized can be used to argue against the possibility of the reaction occurring slowly over a period as long as 40 Ma because on such a timescale H₂O is expected to diffuse and to become uniformly

distributed in the grain boundary system. The localization of reaction products supports the case for localized fluid infiltration, with the fluid phase persisting for relatively short time periods ($< 6\text{--}6000$ a). The duration of fluid-present conditions could be the main factor controlling the extent of reaction. The common occurrence of veins of albite and symplectite in jadeite and omphacite (fig. 3b) suggests that transport of SiO₂ occurred either by diffusion through a vein fluid or by fluid flow, and therefore also supports infiltration of a discrete fluid phase. Hydration reactions which produced phengite as an abundant reaction product (fig. 3) were probably important in limiting the duration of fluid-present conditions.

Kinetics of grain growth. A further constraint on the presence of H₂O in some rock types is provided by data on the kinetics of grain growth. The mylonite shown in fig. 3a, from a shear zone in the central Sesia Zone (Val d'Aosta), consists of jadeite crystals in a matrix of fine-grained dynamically recrystallized quartz with an average grain size $\bar{d} = 45 \pm 5\text{ }\mu\text{m}$. As there is no trace of reaction between jadeite and quartz, the deformation which produced the shear zone and the quartz fabric is presumed to have occurred in the jadeite + quartz stability field. As shown below, the magnitude of the grain size of the quartz, together with data on the kinetics of grain growth of single phase quartz aggregates, can be used to show that this rock must have been completely dry during all or most of its uplift history. The uncertainty in the validity of equation (5), mentioned above, is not likely to affect this conclusion.

The kinetics of non-isothermal grain growth of single phase aggregates have been described by a general form of equation (5)

$$\bar{d}^2 - \bar{d}_0^2 = \frac{8\gamma\bar{V}}{R} \frac{D_0^{\text{gb}}}{\delta_e} \int_{t_0}^{t_1} \frac{1}{T(t)} \exp\left(\frac{-Q}{RT(t)}\right) dt \quad (14)$$

and from Joesten's (1983) evaluation of D_0^{gb}/δ_e and Q (Table I)

$$\bar{d}^2 - \bar{d}_0^2 = 10.66 \times 10^{-6} \times \int_{t_0}^{t_1} \frac{1}{T(t)} \exp\left(\frac{-210\text{ kJ mol}^{-1}}{RT(t)}\right) dt \text{ m}^2. \quad (15)$$

As discussed above, equation (15) is consistent with experimentally-determined grain growth kinetics of quartz aggregates in the presence of H₂O, when the experimental data are extrapolated to low pressure (500 bars) (Joesten, 1983, pp. 244–5). The kinetics of grain growth of dry quartz aggregates can be estimated from the null result experiment

of Tullis and Yund (1982) discussed above, and assuming an activation energy of 300 kJ mol^{-1} :

$$\bar{d}^2 - \bar{d}_0^2 \leq 5.84 \times 10^{-3} \times \int_{t_0}^{t_1} \frac{1}{T(t)} \exp\left(\frac{-300 \text{ kJ mol}^{-1}}{RT(t)}\right) dt \text{ m}^2. \quad (16)$$

Equations (15) and (16) have been integrated numerically along two possible temperature-time paths estimated for the Sesia Zone. These paths, shown in fig. 5, begin at 500 and 560 °C respectively, and bound the range of T - t estimates based on petrological data and radiometric dating (Rubie, 1984, fig. 3). In the calculations of grain growth in the presence of H_2O (equation 15), an initial grain size (\bar{d}_0) of 20 μm has been used; the value of \bar{d}_0 ,

however, is not critical, and the calculated $\bar{d}(t)$ curves are insensitive to \bar{d}_0 in the range 1–50 μm . In calculations of grain growth in the absence of H_2O (equation 16) an initial grain size of 40 μm has been used.

The results of the grain growth calculations based on equation (15) show that, had the grain boundaries of the mylonite been hydrated throughout the uplift history, the grain size of the quartz aggregate would have increased to 350–800 μm depending on the exact thermal history (fig. 5). Furthermore, as the experiments of Tullis and Yund (1982) show that grain growth in the presence of H_2O is faster at 15 kbar than at 2 kbar by a factor of $\sim 10^2$, these results are likely to be underestimates. There is a significant uncertainty in the values of the pre-exponential term and the activation energy term of equation (15) (Joesten, 1983).

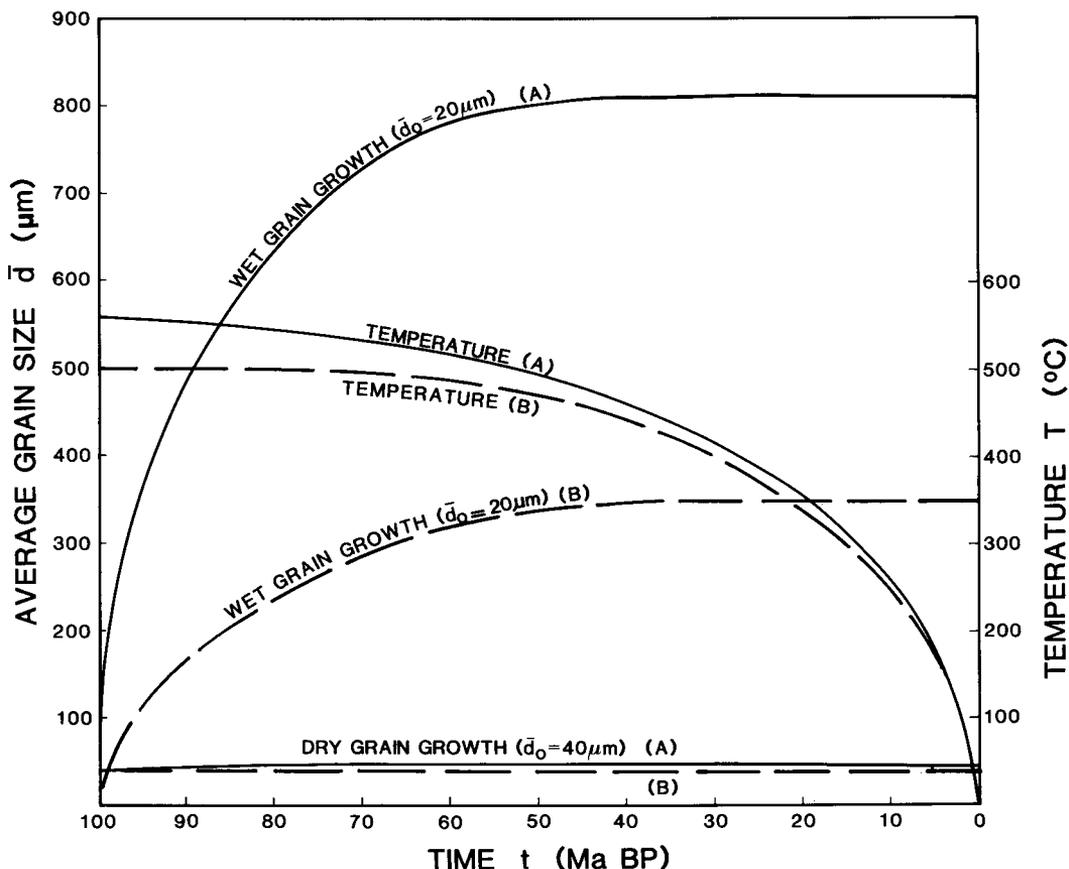


FIG. 5. Grain size-time curves showing nonisothermal grain growth of quartz aggregates under both dry and H_2O -present conditions. The curves have been obtained by integrating equations (15) and (16) along the two alternative temperature-time paths (A) (solid lines) and (B) (broken lines) which have been estimated for the Sesia Zone during uplift.

Using extreme values at the limit of this uncertainty which predict the slowest possible rate of grain growth, and integrating equation (15) along the lower temperature $T-t$ path with $\bar{d}_0 = 5 \mu\text{m}$, the final grain size is estimated as $74 \mu\text{m}$, which is almost double the actual grain size.

For uplift under dry conditions and starting from an initial grain size of $40 \mu\text{m}$, equation (16) predicts little or no grain growth with a final grain size of $40\text{--}47 \mu\text{m}$ (fig. 5).

The equilibrium microstructure which typically develops during grain growth (Tullis and Yund, 1982, fig. 1) is absent in the quartz aggregate of the mylonite (fig. 3a), thus suggesting that significant grain growth failed to occur during uplift. This observation, together with the grain growth calculations (fig. 5), preclude the possibility of hydrated grain boundaries persisting throughout the entire uplift history and show that the mylonite could have remained completely dry during uplift. However, the possibility of grain boundaries existing in a hydrated state for a limited period of time cannot be excluded. Fig. 6 shows grain size as a function of time under isothermal conditions for both dry and hydrated grain boundaries. With $\bar{d}_0 = 45 \mu\text{m}$, negligible grain growth is to be expected under H_2O -present conditions for periods of $< 10^4$ a at 560°C or $< 10^5$ a at 500°C . This is consistent with the conclusions of an earlier section on the lack of reaction between jadeite and quartz.

Water-absent conditions at high pressure. Meta-quartz diorite is a lithology in the Sesia Zone which is likely to have remained at least fairly dry throughout the complete 100–130 Ma tectonic cycle of underthrusting and subsequent uplift back to the surface; it has been described by Koons and Rubie (1983) and Koons *et al.* (in press). Orthogneiss of quartz diorite to granodiorite composition outcrops over a large area ($> 100 \text{ km}^2$) in the central Sesia Zone, and contains rare lenses, ~ 100 m across, of undeformed meta-quartz diorite with well-preserved igneous textures and with plagioclase pseudomorphically replaced by jadeite + quartz + zoisite (Compagnoni and Maffeo, 1973; Rubie, 1983). Corona textures, variable mineral chemistries and zoning patterns indicate that the meta-quartz diorite was in a state of disequilibrium on a thin-section scale during high-pressure metamorphism as a result of slow intergranular diffusion rates (Koons and Rubie, 1983; Koons *et al.*, in press). As discussed above, slow rates of diffusion are likely to be a consequence of dry or near-dry grain boundaries (see also Tracy and McLellan, 1985), and it is possible that the reactions which produced zoisite in the plagioclase pseudomorphs consumed any H_2O which might otherwise have been present (Koons *et al.*, in press).

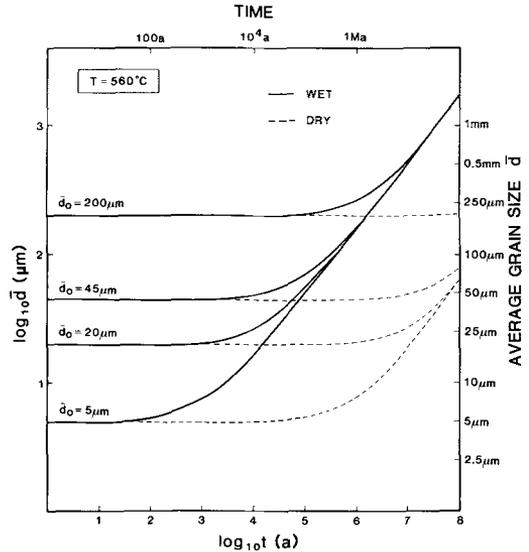


FIG. 6. Grain size–time curves showing isothermal grain growth of quartz aggregates under both dry and H_2O -present conditions at 560°C , for initial grain sizes (\bar{d}_0) in the range $5\text{--}200 \mu\text{m}$. The curves have been calculated using equations (15) and (16).

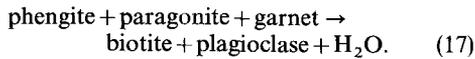
The absence of any subsequent reaction of jadeite + quartz to albite in the meta-quartz diorite is indicative that dry conditions persisted in this lithology during uplift back to the surface (as discussed above).

There is microstructural evidence, discussed by Koons *et al.* (in press), that the orthogneiss, which is volumetrically much more abundant than the meta-quartz diorite, was derived by high-strain deformation of this latter lithology. During deformation, reaction rates increased and a state of equilibrium (on the scale of a thin section) was approached as a result of enhanced intergranular diffusion rates. In the deformed rocks, a depletion in ^{18}O , an increase in water content as indicated by whole-rock chemical data and the partial replacement of jadeite by phengite indicate infiltration by at least small quantities of hydrous fluid during or after the deformation (Frueh-Green, 1985; Oberhaensli *et al.*, 1985; Koons *et al.*, in press). It is possible, therefore, that it was the catalytic effect of this fluid which was primarily responsible for the enhanced diffusion rates and an approach towards equilibrium.

Adula nappe

Basement rocks of the Adula nappe (central Alps), including metapelites, metabasites and ortho-

gneisses, underwent an eclogite- to amphibolite-facies transition during the Tertiary (Leptontine) metamorphism (Heinrich, 1982, 1986). Heinrich (1982) has shown that, as a result of this transition, a dehydration reaction occurred in the metapelites of the form



This reaction is estimated by Heinrich (1982) to have released a small amount of water (~ 0.16 mol. of H_2O per kg of schist, which is less than one tenth of the total H_2O loss during prograde metamorphism of an average pelite, as estimated by Walther and Orville, 1982).

Reaction (17) had a very pronounced effect on the mechanical properties of the metapelite, and catalysed a high-strain deformation event which produced isoclinal folds and an axial planar schistosity, and obliterated evidence of earlier (eclogite-facies) structures. There is evidence that this enhanced deformability resulted from the formation of transiently fine-grained reaction products (plagioclase + biotite) combined with the release of H_2O into the grain boundary network (Rubie, 1985; Rubie and Heinrich, in prep.).

Lenses of mafic eclogite contained within the metapelites hydrated in the amphibolite-facies by reactions which changed the assemblage garnet + omphacite + kyanite to hornblende + plagioclase. This alteration developed on the margins of the eclogite lenses and produced an outer concentric zone of amphibolite and an inner zone (surrounding relict eclogite) in which a plagioclase–diopside symplectite replaced omphacite (Heinrich, 1982, fig. 3). These zones were evidently produced by the infiltration of hydrous fluid into the mafic lenses from the surrounding pelites, and Heinrich (1982) has suggested that this fluid was supplied by the pelite dehydration reaction.

The survival of unaltered eclogite indicates that water-absent conditions persisted locally in the cores of mafic lenses for tens of millions of years. The theory discussed by Rutter and Brodie (1985) for the propagation of a hydration interface into anhydrous rock can be applied to these lenses. If the thickness and permeability of the hydrated margins of the lenses are known, the time required for their development, by the permeation of aqueous fluid, can be estimated. This time would be a measure of the duration of H_2O -present conditions (with $P_{\text{H}_2\text{O}} = P_{\text{load}}$) in the pelites during the dehydration reaction. The thickness of the hydrated margins can be estimated as ~ 1 – 3 m; this value is not well constrained, however, because there is evidence that the hydrated margins were affected significantly by the amphibolite-facies deformation (see Heinrich,

1982, fig. 3). The permeability of eclogite when affected by hydration reactions must be very low because volume increases will tend to seal up pores and cracks. Rutter and Brodie (1985) estimate that a permeability $\sim 10^{-26}$ m^2 is likely under such conditions, which is three orders of magnitude lower than the lowest measurable value. Using a permeability of 10^{-26} m^2 , Rutter and Brodie's (1985, fig. 1) calculations show that permeation of water over a distance of 1–3 m would occur in a time of 10^5 – 10^6 a. With the much larger permeability of 10^{-18} m^2 , a value considered by Etheridge *et al.* (1984) to be common during metamorphism, the predicted time is only ~ 9 hours. These figures can be interpreted as indicating that the aqueous fluid phase produced by the dehydration reaction was present in the metapelites for a very limited time period (< 1 Ma). At present, however, this interpretation is subject to large uncertainties. (1) The permeability of hydrated eclogite is not known to within an order of magnitude. (2) On the basis of fluid inclusion studies, Yardley (1983) has suggested that dehydrating pelites lose water in spurts rather than continuously, and that each time fluid loss occurs the fluid pressure temporarily drops below the load pressure. If this were the case, the above time estimate might only represent a small part of the total duration of the reaction. (3) A further complication is indicated by the presence of H_2O -poor fluid inclusions in the metapelites (Yardley, pers. comm.), the significance of which is currently unknown. A possible explanation is that infiltration by H_2O -poor fluids occurred during the dehydration reaction, due to permeability-enhancement, thus diluting the water released by reaction (17). In that case, with $P_{\text{H}_2\text{O}} < P_{\text{fluid}}$, the above calculation would underestimate the duration of fluid-present conditions. However, modest fluid–rock ratios and/or short residence time for the fluid in the metapelites is suggested by a lack of homogeneous isotopic re-equilibration in these rocks (Frueh-Green and Thompson, 1985).

It can be argued that high-strain deformation of the metapelites, and coarsening of biotite + plagioclase aggregates (reaction products) from $\bar{d}_0 < 50$ μm to $\bar{d} \approx 250$ μm both occurred under fluid-present conditions (Rubie and Heinrich, in prep.). If fluid-present conditions did persist for a relatively short time period, the duration of the dehydration reaction, the high-strain deformation event, and grain coarsening of the metapelites could also have been short. If the kinetics of grain coarsening of two phase aggregates could be quantified, such data could further constrain the duration of fluid-present conditions by a method analogous to that used above for the quartz mylonite of the Sesia Zone.

Conclusions

Available data support the hypothesis that basement rocks are dry for long periods of time under metamorphic conditions. Water-present conditions result from fluid infiltration, but in the examples examined the duration of these events is evidently short compared with an orogenic time scale, and the distribution of fluid is often localized. Metamorphic reactions, including solid–solid reactions, can occur as a result of fluid infiltration into previously dry rocks due to the catalytic effects of water, and can therefore occur at conditions which deviate significantly from equilibrium (Yardley and Baltatzis, 1985; Koons *et al.*, in press). The jadeite + quartz → albite reaction discussed above could, for example, have occurred under greenschist-facies conditions at a pressure much lower than the equilibrium pressure. In cases where only partial reaction has occurred, the extent of reaction may have been largely controlled by the duration of fluid-present conditions.

The applicability of experimental kinetic data to evaluating the pressure–temperature–time (*PTt*) paths of metamorphic rocks is limited to examples in which the fluid content is well-characterized as a function of time. The simplest such case is for rocks which are known to have been continuously dry during part of their metamorphic history. For example, Carlson and Rosenfeld (1981) were able to constrain the *PTt* path of the Franciscan terrain during uplift using their experimental kinetic data for the aragonite → calcite reaction under dry conditions. Franciscan rocks which contain relict aragonite must have been completely dry throughout their uplift history because the reaction is so fast in the presence of water at ~ 200 °C (fig. 1) that no aragonite could otherwise have survived.

If the *PTt* path of metamorphic rocks can be independently estimated, suitable kinetic data can be used to evaluate the presence of fluid as a function of time, as has been attempted in this paper. However, to make any significant progress in evaluating the rates of metamorphic reactions and processes, we need to understand when water occurs as a free fluid phase and when it occurs as structurally incorporated grain-boundary species. The effect of water in enhancing intergranular diffusion in both of these cases needs to be carefully investigated and quantified by a variety of experimental techniques. These might include grain growth experiments (Tullis and Yund, 1982; Joesten, 1983), diffusion experiments (Giletti and Nagy, 1981), and electrical conductivity experiments. Related problems, which are also poorly understood, are the structure of grain boundaries in silicates, the effect of water on nucleation kinetics,

and the effect of fluid composition (e.g. H₂O–CO₂ mixtures) on the rates of metamorphic reactions.

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