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Modelling of the relations between reaction enthalpy and the buffering of reaction progress in metamorphism

JOHN RIDLEY

Institut für Mineralogie und Petrographie, ETH-Zentrum, CH-8092, Zürich, Switzerland*

ABSTRACT. A proportion of the heat added to a body of rock during prograde metamorphism will be absorbed in the chemical work of metamorphic recrystallization. When and where heat is so absorbed will affect the exact thermal histories of the rocks, and hence the metamorphic textures. This paper reports the results of modelling of the inter-relations between reaction progress and thermal histories in a rock column. The results suggest that volumes of rock undergoing reaction at any moment act as heat sinks and absorb heat from the surrounding rock, that reaction generally takes place close to the temperature at which nucleation took place, and that steady heating of a rock pile can give rise to a reaction history in which spurts of reaction are separated by 'quiet', non-reactive intervals.

KEYWORDS: prograde metamorphism, kinetics, heat flow, reaction enthalpy.

THE heat added to a body of rock during prograde metamorphism in part raises the temperature of the rock, and is in part used in the chemical work of metamorphic recrystallization. The reverse applies for retrograde metamorphism: heat is extracted from a rock by lowering its temperature and through energy released in retrograde reactions.

Recent studies have given calculations of how the heat added during metamorphism is partitioned between thermal and chemical work in a specific rock type at a specific temperature and pressure (Rice and Ferry, 1982; Ferry, 1983). The partitioning will not be constant throughout a metamorphic history, nor, in many circumstances, will the heat added to a large volume of rock become uniformly distributed through it. A portion of a rock body that is actually undergoing reaction may, therefore, absorb or produce a disproportionate amount of heat, i.e. it will act as heat sink or a heat source. This has the consequence that the rate of absorption of heat in a specific reaction need not necessarily be directly related to large-scale heat-flow patterns.

How the heat added becomes partitioned, and how this partitioning varies in time and space within a rock pile has implications for any study concerned with the determination of rate-controlling steps in metamorphism (Fisher, 1978), and hence for any study that uses reaction textures to make inferences about metamorphic histories.

This paper approaches the specific problem of determining the circumstances under which reaction-induced local heat sinks or heat sources will be significant during metamorphism, particularly regional prograde metamorphism. The approach involves simultaneous modelling of nucleation, growth, and temperature change in a rock column during idealized and simplified reaction histories.

Principles of modelling of reaction progress

Most studies to date of the controls and the magnitudes of reaction rates in metamorphism have considered only behaviour at constant temperature (Fisher, 1978; Walther and Wood, 1984). The principles of modelling of reaction progress in a system in which the rock temperature varies (and is controlled in part by the reaction progress itself) is outlined in the Appendix and in an earlier paper (Ridley, 1985). Reaction rate, at any instant, is taken to be a function not only of temperature, but also of the number and size of product grains (as in Fisher, 1978), this being a function of the nucleation history, and hence of the earlier thermal history of the rock.

The relations between reaction rate and heat flow within a rock column can be modelled by combining a reaction-rate calculation with the one-dimensional heat-flow equation. For details of this calculation see the appendix.

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* Present address: Department of Geology, University of Zimbabwe, PO Box MP 167, Mount Pleasant, Harare, Zimbabwe.

Environment of metamorphism. It is assumed in this paper—following the ideas of Oxburgh and Turcotte (1974), Bickle *et al.* (1975), and England and Richardson (1977)—that regional metamorphism is related to the burial and subsequent unroofing of rocks in orogenesis. These papers show how the metamorphic conditions at different levels in the crustal pile evolve during orogenesis.

In order to investigate reaction behaviour at a single metamorphic reaction, it is not necessary to consider the thermal evolution of the whole crust, but only that of a segment, this segment being thick enough so that heat absorption or production during reaction does not significantly affect the temperature at its base or its top.

Any segment within a crustal column will heat up, and therefore undergo prograde metamorphism, if the curvature of the instantaneous geotherm is such that the heat flow into the base of the segment is greater than the heat flow out through the top (fig. 1). Radiogenic heating, or shear heating may act as additional sources of heat. Fig. 1 illustrates a typical situation within a segment of a crustal column, as is predicted by the models of England and Richardson (1977), that will give rise to prograde metamorphism. This is the environment of metamorphism modelled in this paper. It is worth noting that the heat-flow regime illustrated will also be the case if metamorphism is the result of the emplacement of magmas at the base of the crust.

Discontinuous/continuous reaction. The modelling is for a strictly discontinuous reaction, i.e. a finite amount of reaction should take place at one temperature. Such a reaction will be an exception in metamorphism. The treatment of any reaction as discontinuous is, however, probably valid for at least the initial stages of reaction. Consider a divariant reaction (fig. 2). In an equilibrium history

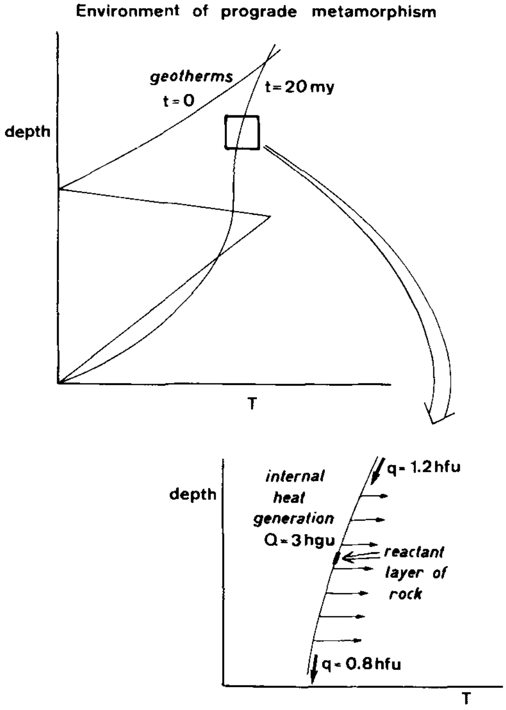

FIG. 1. Thermal environment of prograde metamorphism. After disturbance of the crustal geotherm as a result of thickening of the crust in orogenesis, the general effect is for rocks at depth in the crust to undergo a period of prograde metamorphism. The upper diagram shows schematic geotherms immediately after, and 20 m.y. after the crustal thickening event. The lower diagram illustrates the energy balance within a small segment of the crust 20 m.y. after thickening. The curvature of the instantaneous geotherm is such that there is a net influx of heat into the segment, hence giving rise to a steady rise in temperature. Reaction behaviour is studied in a layer of rock in the centre of this segment (see figs. 3–7).

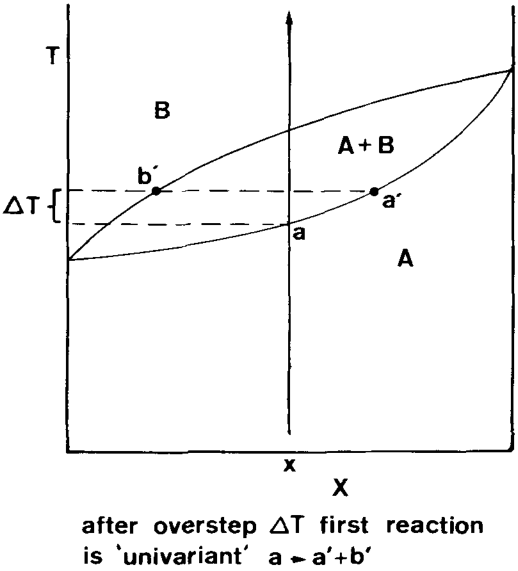

FIG. 2. Behaviour at a divariant reaction if a finite overstepping is required before nucleation of the product phase. After a finite overstepping, ΔT, of the equilibrium boundary, the most rapid return to equilibrium would be given through a reaction of the form $a \rightarrow a' + b'$, i.e. an effectively univariant reaction in which a finite amount of the product phase is produced at invariant temperatures.

the first appearance of the product phase should be to an infinitesimal volume. If, however, a finite overstepping of the equilibrium boundary is required before nucleation of the new phase or phases can take place, then, once nucleation has taken place, the equilibrium proportion of the products at that temperature is finite rather than infinitesimal.

Results of the modelling

Summary of the results of modelling of reaction progress in a situation in which lateral flow of heat is not taken into account. Fig. 3 shows, schematically, the prediction of how a typical prograde devolatilization reaction (i.e. a reaction with a large, negative ΔH_r) would run if there were a steady input of heat into the rock, and if there was no kinetic barrier to the nucleation of the new phase. Reaction starts after an infinitesimal overstepping of the equilibrium boundary. The reaction rate increases, and hence the amount of heat absorbed in reaction increases, with increasing overstepping. A point may be reached at which the heat absorption is equal to the external heat input. At this point, the reaction rate can be considered to be heat-flow controlled.

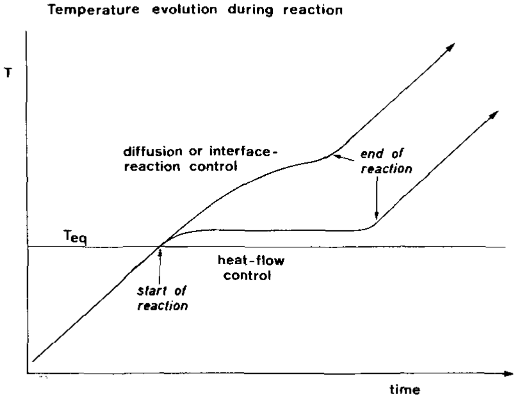

FIG. 3. Idealized temperature–time (T–t) histories during a prograde metamorphic reaction assuming that there is no kinetic barrier to the nucleation of the new phase. The two histories shown distinguish the cases where heat flow controls the reaction rate (the temperature is buffered by the reaction), and where reaction rate is controlled by diffusion of one species or by an interface process, e.g. dissolution or precipitation.

Fig. 4 illustrates, schematically, a T–t history under the same thermal conditions, but where a finite overstepping of the reaction boundary is required before nucleation of the products. This model is unrealistic as it ignores any effects of increased heat flow into the reacting body of rock whilst its temperature is held down during reaction. It is considered here in order to enable analysis of the more realistic models given below.

After the temperature increases above the equilibrium boundary no reaction takes place until nuclei form at a certain finite overstepping. The rate of nucleation increases rapidly with further increase in temperature until a time is reached when there are sufficient nuclei for the total reaction rate to be such that more heat is absorbed in reaction than is being supplied externally. The temperature then starts to decrease. The rate of formation of new nuclei is reduced. Growth on existing nuclei, however, continues as the temperature is reduced back towards the equilibrium temperature, though at a slower rate. A significant proportion of total growth is predicted to take place without the concurrent formation of new nuclei.

Such a schematic history as illustrated in fig. 4 is predicted for any devolatilization (high negative ΔS_r) reaction (Ridley, 1985). The qualitative behaviour is independent of the actual values of the various parameters in the nucleation-rate and growth-rate equations, or whether growth is controlled by diffusion or by the interface reaction.

Modelling of linked reaction and thermal histories in a vertical column of rock. If one ignores the possible effects of reaction enthalpy, it can be seen from the models of regional metamorphism of England and Richardson (1977), that most prograde metamorphic reactions will take place whilst there is an effectively constant input of heat into the rock, i.e. $\partial T/\partial t$ is constant. This condition is taken as the normal thermal regime of prograde metamorphism.

Figs. 5 and 6 show two contrasting model temperature–time histories for rocks undergoing reaction in a rock column under such a thermal regime. The major differences between the two model histories are the geothermal gradient through the column and the percentage volume of the rock assumed to be partaking in the reaction. The amount of heat absorbed per volume of rock reacting, and the growth-rate equations are the same in the two cases.

In both cases reaction is assumed to take place within a layer 100–140 m thick sandwiched between rocks in which no reaction is taking place at the temperatures concerned. There is a temperature gradient across the reacting layer of rock, the base being hottest, and reaction, therefore, starts earliest here.

The two example histories shown illustrate the two broad categories of reaction and temperature history predicted. These are, respectively, *unstable*,

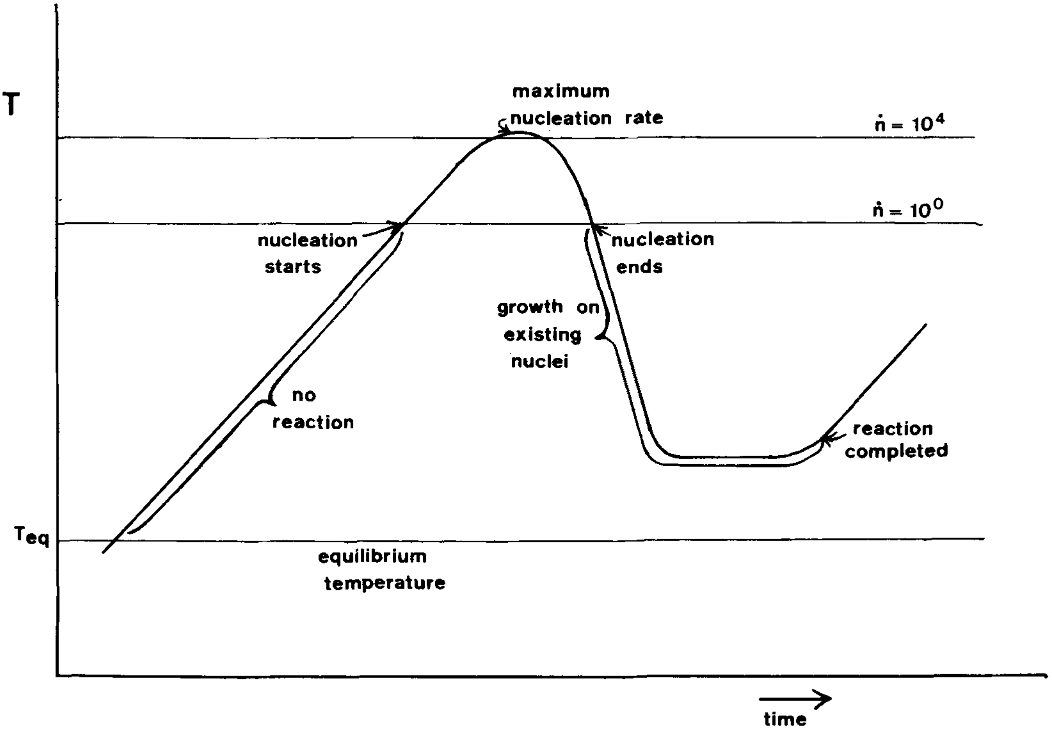

FIG. 4. Schematic thermal and reaction history under the same conditions as those of fig. 3, but where a finite overstepping of the reaction boundary is required before nucleation of the products can take place (after Ridley, 1985). $\dot{n}$ is the nucleation rate.

in which reaction can be considered as taking place in spurts separated by periods in which the rock is heating up, and *stable*, in which reaction more or less steadily progresses up through the reactant layer.

Whether the reaction history is 'stable' or 'unstable', there are certain constant characteristics of all model histories. In both these cases the overstep required for nucleation is 8 °C, and reaction takes place within 2 °C of the temperature of nucleation without large changes in temperature. In all models reaction takes place essentially at the temperature of nucleation. In addition, in all model histories, the band of rock undergoing reaction at any point in time acts as a heat sink. The flow of heat into this band of rock is several times greater than the flow of heat into a band of the same thickness elsewhere in the column.

In the example of fig. 5—the 'unstable' reaction history—reaction in the lowest 60 m of the reactant layer takes place effectively simultaneously. The amount and rate of reaction is sufficient to reduce the temperature of the whole rock column to a level at which nucleation in the partially, or totally unreacted rock above is stopped. Reaction in the 60 m of rock above this takes place after a delay of about 0.05 m.y., after the whole column has been reheated up to a temperature at which nucleation could again take place. Reaction in this part of the reactant layer likewise takes place effectively simultaneously, and there is a further hiatus before reaction higher in the pile.

In contrast, in the example shown in fig. 6, the reaction rate at any instant in time (i.e. the volume of rock transformed in the whole rock column per unit length of time) is close to constant. In addition, reaction at any time is taking place in a band within the rock column of close to constant thickness, in this case 15–20 m. This band moves progressively and steadily up through the pile. The rate of reaction is never such as to reduce the rock temperature. A steady state is reached in which the rate of reaction is balanced by conductive heat transfer into the reacting band of rock.

This latter history is similar to that predicted if there is no kinetic barrier to nucleation, the

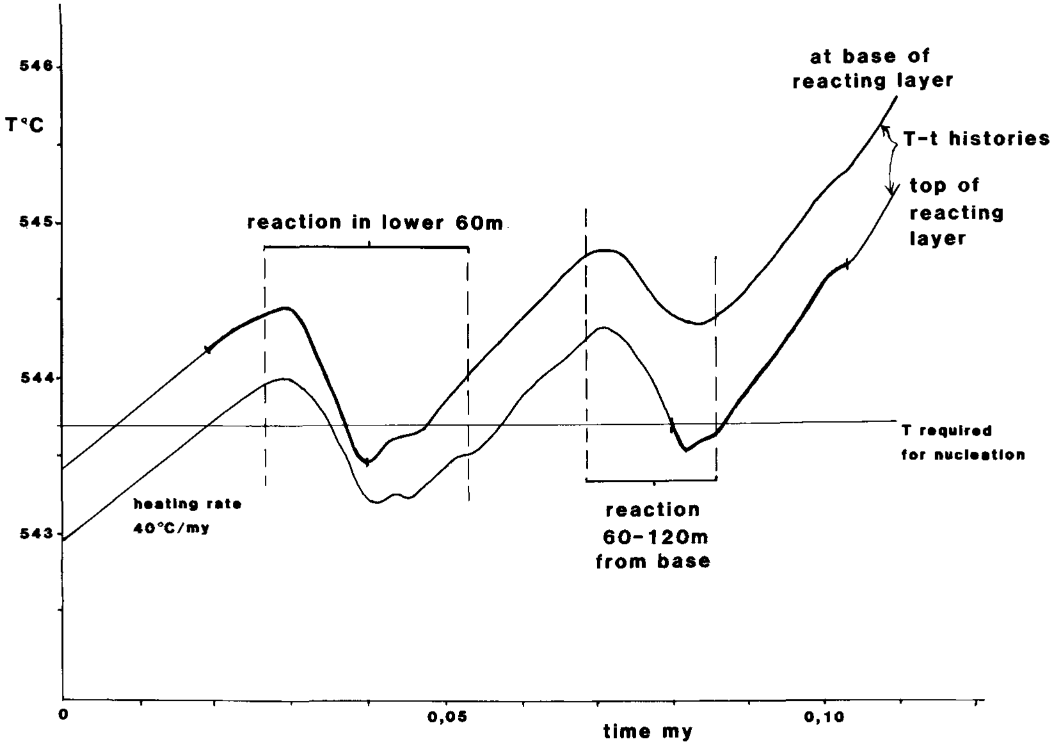

FIG. 5. Reaction and thermal history during a prograde reaction in a 160 m layer of reactant rock sandwiched between layers of rock that do not undergo reaction at the temperatures of interest. T–t histories are shown for rocks at the top and the base of the reactant layer. The thickened portions of these paths indicate the periods over which the bulk of the reaction at these levels takes place. There is a general increase in temperature down through the pile. Model parameters: equilibrium temperature, 535 °C; interfacial free energy (γ'), $0.02\ \mathrm{J\ m^{-2}}$; reaction rate controlled by intergranular diffusion with $D = 1.7 \times 10^{-12}\ \mathrm{m^2\ s^{-1}}$.

difference being that reaction takes place at the temperature of nucleation rather than at the equilibrium temperature.

The exact values of any of the parameters in the growth-rate and nucleation-rate equations—intergranular diffusion rates, the interfacial free energy, the exact volume of rock reacting, etc.—have only a relatively minor effect on the form of the predicted reaction and temperature histories. This can be understood by considering the effects of a change in one of these parameters. If chemical diffusion is slower, then the growth rate of any grain will be slower. The rate of absorption of heat by reaction will be slower, and hence the rock temperature will rise to a level at which more nuclei are formed—counteracting the effects of reduced diffusion rates on the total reaction rate.

When and where 'stable' as opposed to 'unstable' reaction behaviour occurs will be a function of heating rates, the overstep required for nucleation, growth rates, and the volumetric amount of rock reacting. The difference may, under certain circumstances, be an indicator of differing heating rates.

Fig. 7 shows temperature–time histories for rocks 1 km away from a layer undergoing reaction under the same conditions as in fig. 6. The 'disturbance' in the T–t history due to the reaction is a smoothed and slightly delayed equivalent of the T–t history of the reacting layer. Fig. 7 also shows the T–t history for reaction under the same conditions, but where the amount of rock reacting per unit volume is twice as great (10%, compared to 5%). There is a steeper temperature gradient towards the reacting body of rock in the second case and the length of time required for reaction is not significantly longer. The heat flow into this layer is greater. The reaction controls the heat flow as much as the heat flow controls the rate of reaction.

Predictions of textures formed during reaction. Certain qualitative or semi-quantitative features of reaction textures can be predicted by considering

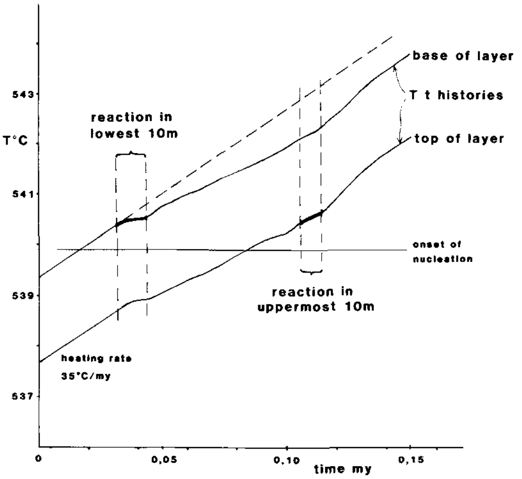

FIG. 6. Reaction and thermal history during a prograde reaction in a 100 m thick reactant layer. *T–t* histories are shown for the top and bottom of this layer. The thickened lines indicate the periods over which reaction takes place at these levels. Model parameters: equilibrium temperature, 531 °C; interfacial free energy (γ'), 0.02 J m^{-2}, reaction rate controlled by intergranular diffusion with $D = 1.7 \times 10^{-12}$ m^2 s^{-1}. The most significant differences between the conditions of this model and those of fig. 5 are a steeper geothermal gradient—hence reducing the thickness of rock over which reaction takes place at any point in time, and a smaller proportion of rock reacting (5% as opposed to 10%).

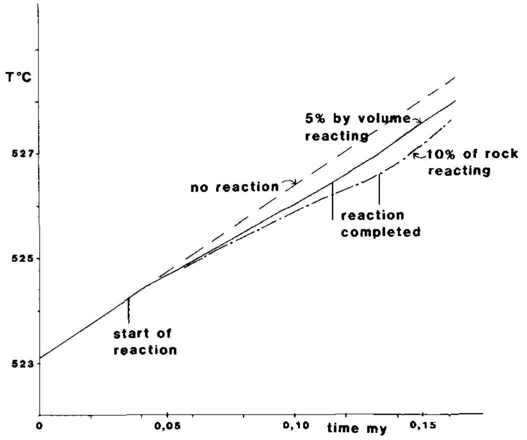

FIG. 7. *T–t* histories for rocks 1 km above a layer undergoing reaction. The solid line shows the history during reaction under the same conditions as for fig. 6. The line with alternate dots and dashes shows the effect of reaction under the same conditions, but where reaction involves 10% rather than 5% of the reactant layer. The dashed line shows the thermal history if no reaction takes place.

these model reaction histories. Absolute grain sizes, relative grain sizes at different points in a reacting column of rock, and grain-size distributions are all predicted in the models.

For a metamorphic temperature between 500 and 550 °C, with the range of physical properties such as interfacial free energy and intergranular diffusion chosen (see Appendix), grain sizes between 0.05 and 30 mm are predicted. The exact grain sizes are strongly dependent on the exact values of the various physical parameters assumed.

In an 'unstable' reaction history of the type illustrated in fig. 5, significantly different grain sizes are predicted for different levels in the column. The base of the column was heated to the highest temperature before reaction enthalpy had an effect on the rock temperature. The number of nuclei is therefore predicted to be greatest here, and hence the final average grain size smallest. The average grain size will increase further up the pile until a level is reached at which nucleation took place during both temperature peaks. Here, new nuclei would have formed in a rock with a small number of already existing large grains. The result will be a bimodal grain-size distribution. The earlier, large grains will become progressively rarer at higher levels in the pile.

Grain sizes in a metamorphic rock may obviously be influenced by factors other than the temperature-time history. Small differences in rock composition or differences in the grain size of the earlier assemblage may affect relative grain sizes and the patterns of grain-size distributions. The interpretation given above is an example of the complexity of patterns that may result from an 'unstable' reaction history.

Reaction histories at a mappable isograd. The heat-flow regime for the isograd reaction at an isograd must be different to that during a 'normal' prograde reaction. In the latter case, the rock continues to heat up after the reaction has gone to completion. In contrast, the isograd reaction at an isograd marks the metamorphic peak (T_{max}), i.e. the rocks were heated up to the temperature required for reaction, and no further.

Fig. 8 shows a heat-flow regime for a segment of a rock column that will give rise to a temperature–time history of a form required to produce an isograd. The heat flow at the top and base of the rock column must vary with time. Such variations in heat flow are predicted in thermal models of the whole crust (e.g. England and Richardson, 1977). Increasing heat flow through the top of a segment of the crust, for instance, may be the result of

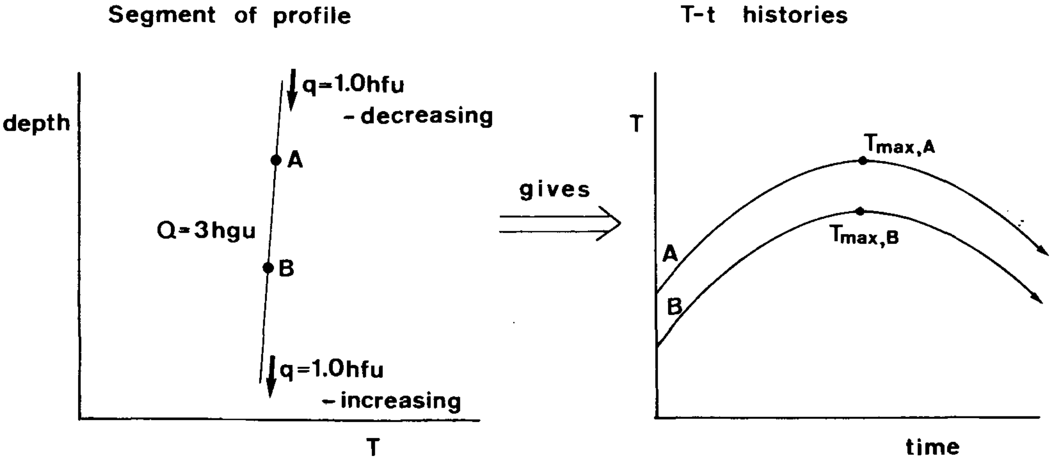

FIG. 8. Energy balance in a segment of the crust, and resulting T-t histories at a metamorphic 'peak'. This will be the thermal regime at a mappable isograd if rock 'B' never reaches a temperature high enough for reaction to take place, whilst rock 'A' does. ($T_{\mathrm{max.B}} < T_{\mathrm{isograd}} < T_{\mathrm{max.A}}$).

erosion and increasing proximity of the earth's surface.

Fig. 9 shows an example T-t history for an isograd reaction, and fig. 10 shows some predictions of textures at different points across the resulting isograd. In this history, reaction went to completion in the lowest 60 m of the reactant layer. Between 60 and 100 m from the base the reaction was incomplete when the rock was cooled back through the equilibrium temperature. Higher in the pile there was no significant reaction (fig. 10). The major difference between this thermal history and that shown in fig. 5 is that, in this case, after the initial reaction-induced fall in temperature, the temperature does not again rise to a level at which further nucleation can take place. One consequence of this is that reaction, within at least some of the pile, takes place at temperatures significantly lower than the temperature of nucleation, i.e. at lower degrees of overstepping than is the case in a 'normal' prograde reaction.

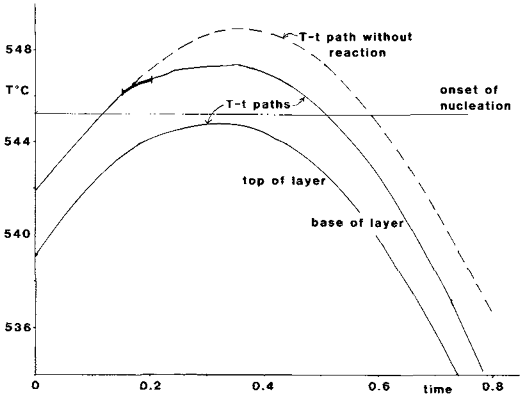

FIG. 9. T-t histories for rocks on either side of a mappable isograd in a 140 m thick layer of reactant rock. The thermal regime is such that heat is first added to the rock column, and later extracted from it. Model parameters: equilibrium temperature, 522 °C; interfacial free energy (γ'), 0.04 J m^{-2}; reaction rate controlled by diffusion with $D = 1.7 \times 10^{-12}$ m^2 s^{-1}. Heat absorbed in reaction in the lower 60 m of the layer prevents the upper parts of the layer reaching the temperature required for nucleation to take place.

Certain predictions of textures to be seen at isograds can be made from the results of these models. The zone of persistence (Carmichael, 1979, i.e. the zone over which both the reactant and product assemblages of a nominally univariant reaction exist together), is predicted to be a few tens of metres thick. This zone exists because of limited rates of reaction.

Fig. 10 shows the variations in average grain size predicted at different levels across an isograd. The largest grains are expected within the zone of persistence, especially at the higher-grade end of this zone. These grains would have grown at lower degrees of overstepping than grains on the high-grade side of the isograd. Where the reaction takes place at lower degrees of overstepping, reaction rate is more likely to be controlled by the interface reaction than by diffusion (Kirkpatrick *et al.*, 1979; Walther and Wood, 1984). A lower degree of overstepping in addition reduces the likelihood of a

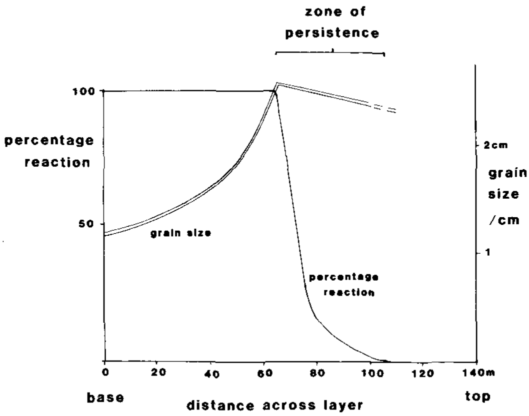

FIG. 10. Reaction progress and largest grain size of the product phase plotted against depth in reactant band, for the reaction and thermal history shown in fig. 9. The data plotted are for the moment in time when the rock cools down through the equilibrium temperature. The zone of persistence is that in which both the reactant and product assemblages of a nominally univariant reaction exist together (Carmichael, 1979).

disequilibrium composition or structure of the product phase (Carpenter and Putnis, 1985).

Discussion

How well do the predictions of the models compare with real examples? The validity of the approach to modelling metamorphic reactions described here, and the applicability of the growth- and nucleation-rate laws chosen, can be tested by comparing the predictions with observable textures and other features of metamorphic rocks.

The grain sizes predicted by the models are of the same order as observed in metamorphic rocks (0.05–30 mm at 500–550 °C). If the rates of diffusion and rates of interface reactions estimated are reasonable, this correspondence implies that the amount of overstepping before nucleation that has been inferred here (5–50 °C) is also reasonable.

The vertical thickness of 'zones of persistence' at univariant reactions are predicted to be of the order of a few tens of metres. Few studies of metamorphic terrains report data with which comparison can be made. Over this zone both products and reactants should be in contact with the grain-boundary system. Relicts of a low-grade phase may be preserved much longer if they become mantled by a new phase, and hence the dissolution rate becomes controlled by intragranular diffusion rates (e.g. Hollister, 1977). In the case studied by Guidotti (1974), despite uncertainties over the dip of the isograds, it appears that the width of the transition zone between staurolite and sillimanite grade rocks is between 50 and 100 m.

Few studies have been likewise reported of differences in grain sizes, grain size distributions, and textures of a specific phase from different grades of metamorphism in a single area (see Atherton, 1968). The modelling suggests that rocks within a few tens of metres of an isograd may show distinctive textures. The high-grade phase is predicted to be coarser at the isograd than more than 100 m upgrade of it, and this phase should show evidence of slower growth at lower degrees of overstepping.

Garnet textures at the garnet isograd of the Scottish Highlands have been described by Atherton (1964, 1968). The textures differ from point to point along the length of the isograd. In places, the garnet is seen as rare, small, and euhedral grains, and elsewhere as poikiloblasts restrictively grown within quartz lenses. It is not clear whether these differences are the result of differing thermal histories, or of differences in nucleation and growth patterns.

One possible example of the type of behaviour predicted in the modelling is seen in albite growth after phengite in partially overprinted blueschist-facies metapelites from the island of Syros, Greece (Ridley, unpubl. thesis, Edinburgh University).

Where the lower pressure overprint is effectively complete, albite is seen as interlocking, xenomorphic grains with scattered small opaque inclusions (fig. 11*a*). Where the overprinting is at most partial, albite is seen as extremely skeletal grains, replacing only the earlier white mica and with, generally, many fewer nuclei (fig. 11*b*).

Possible indicators of tectonic processes. In this paper it is assumed that metamorphism is the 'passive' response of rocks to changing pressure and temperature. These changes may be either the result of orogenesis, or the intrusion of magma. The predictions of features to be seen associated with prograde reaction are dependent on the choice of this as the thermal regime of metamorphism. The modelling ignores, for instance, the possibilities that a metamorphic reaction may be prompted or catalysed by an influx of fluid or by deformation, or that a rapid influx of fluid may be the direct thermodynamic impetus for reaction. The influence of these factors may swamp the effects of small differences in temperature. Different thermal histories are to be expected at an isograd if the increasing temperature is in part the result of shear heating. Shear heating will produce a local thermal anomaly that will decay rapidly once deformation ceases.

The example illustrated in fig. 11 of different textures of a product phase where a reaction

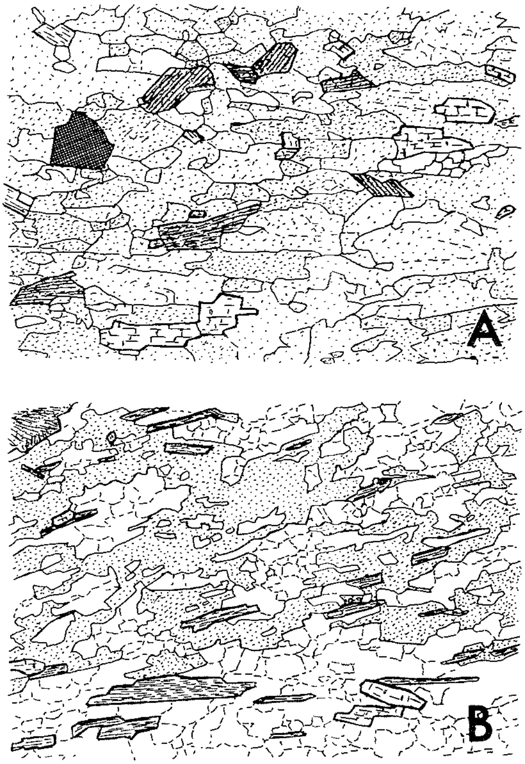

FIG. 11. Micrographs showing an example, within a single suite of rocks, of contrasting textures where a certain reaction has gone to completion, and where it has remained incomplete. The reaction is the down-pressure overprinting of phengitic mica by albite from a suite of blueschist-facies metapelites from the island of Syros, Greece. The mineralogy is quartz (unornamented), albite (light stipple), phengite (ornamented to show cleavage), chlorite (cleavage plus stipple), epidote (high relief), and hematite (cross-hatched). The sample 'a' showing complete reaction, shows interlocking equigranular and weakly elongate albite grains. The sample 'b' showing incomplete reaction, shows a single large poikiloblastic grain of albite which has grown mimicking the earlier mica fabric. Both micrographs are on the same scale—long dimension 0.8 mm.

has gone to completion and where it has remained incomplete is a good example of static, entirely post-tectonic metamorphic recrystallization. Regional fluid influx may have influenced the reaction (Matthews and Schliestedt, 1984), but one can rule out any possible effects of shear heating, or a catalytic effect of deformation on reaction. Is such 'passive' recrystallization the exception or the rule in regional metamorphism?

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APPENDIX: METHODS OF MODELLING

Nucleation-rate law. The nucleation rate at any point in the rock, assuming that reaction has not gone to completion, is taken to be given by:

$$\dot{n} = A_n \exp\left(\frac{-16\pi\gamma^3}{3\Delta G_r^2\, kT}\right) \tag{1}$$

(McLean, 1965), where A_n is a constant given by:

$$A_n = \exp(-\Delta G^*/kT) N_0\, \nu \tag{2}$$

(see Christian, 1975, p. 441). (ΔG^* = free energy of activation, N_0 = Avogadro's number, ν = atomic vibration frequency, γ = interfacial free energy (0.06–0.6 J m^{-2}), T = absolute temperature, k = Boltzmann's constant, ΔG_r = the free energy released per unit volume of rock transformed).

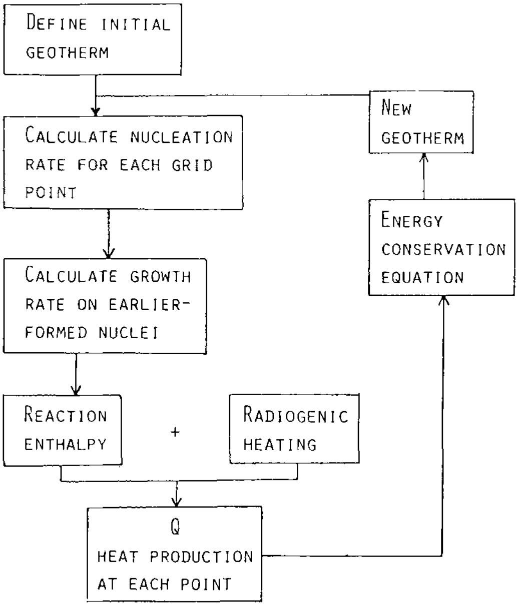

FIG. 12. Simplified flow diagram for the program to calculate linked reaction and thermal histories in a rock column.

Nucleation is assumed to take place at grain edges or grain corners (Cahn, 1956). For such a case, the value of γ in the equation above is reduced to γ', where $\gamma' \simeq \gamma/6$, in order to take into account the energy released in the destruction of old grain boundaries.

Growth-rate laws. If the growth rate of an individual grain is controlled by the interface reaction, this growth rate is given by

$$\dot{g} = A_g \exp(-\Delta G^*/kT)[1-\exp(-\Delta G_r/RT)] \qquad (3)$$

(Christian, 1975, p. 479), where A_g is a constant given approximately by $\delta_\beta \nu$ (δ_β is the thickness of a layer of ions). ΔG_r is here the free energy released per mole of reactant.

If growth is controlled by the rate of diffusion of one species to the growing interface, the rate of growth is given by

$$\dot{g} = \sqrt{\left(\frac{c^m - c^\alpha}{c^\beta - c^\alpha}\right)\left(\frac{D}{2t}\right)} \qquad (4)$$

(Christian, 1975, p. 487) where: c^m is the matrix concentration of the diffusing species, c^β is the concentration in the matrix at the growing surface, c^α is the concentration in the growing grain, and D is the diffusion coefficient (10^{-11}–10^{-16} m^2 s^{-1}).

Reaction rate. It can be seen from equations 3 and 4, that the volumetric amount of reaction at any grain is a function of the time since the grain nucleated. The reaction rate within a volume of rock must be calculated from the integral

$$\dot{r}_{t^*} = \int_{t=0}^{t=t^*} \dot{V}(t)\dot{n}(t)\,\partial t \qquad (5)$$

$\dot{V}(t)$ = the volumetric growth rate for grains nucleated at time t, $\dot{n}(t)$ = the nucleation rate at time t, t^* = the actual time.

Linked reaction and thermal histories within a rock column. Fig. 12 shows a simplified flow diagram for the computer program used in the calculation of linked reaction and thermal histories within a rock column. The rock column is represented by a grid with points 10 m apart within the reactant layer, and 100 m apart elsewhere. In most cases the total column height was between 8 and 10 km. The initial geotherm is taken so as to give a steady and uniform increase in temperature throughout the pile (see figs. 1 and 8).

After the heat production 'Q' has been calculated for each grid point, the energy conservation, or heat-flow equation is solved using the Crank-Nicolson finite-difference numerical method for a time interval δt—hence giving a new geotherm to be used for calculating new rates of nucleation and growth. The time increment (δt) is taken as small enough so that a doubling of this increment will not lead to a cumulative difference in the calculated temperature of more than 1 °C, i.e. the oscillations in temperature shown in figs. 5 and 7 are not the result of computational instabilities.

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