

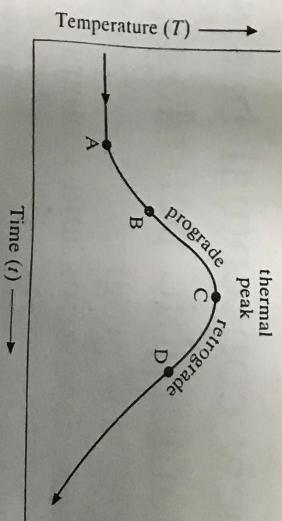
## 2 A new conceptual basis for metamorphic petrology: prograde and progressive metamorphism, isograds, isotherms and isobars

### 2.1 Temporal changes in $P-T$ conditions during metamorphism

#### 2.1.1 Prograde and retrograde stages

Although a metamorphic process generally involves temporal changes of both temperature and pressure, for simplicity we first consider the change of temperature only.

Figure 2.1 schematically illustrates a simple course of temperature change of a rock during regional metamorphism. The temperature of the rock first begins to increase at point A, and metamorphic crystallization begins at point B. Then, the temperature of the rock reaches a maximum value (C in Fig. 2.1). This is a **thermal peak** or **thermal maximum**. The period between B and C is called the **prograde stage** of metamorphism. Metamorphic crystallization in the prograde stage is simply called **prograde metamorphism**. It is followed by a gradual decrease of temperature, during which a small extent of metamorphic crystallization may occur, until point D is reached. If there is metamorphic crystallization at this stage, the period between C and D is called the **retrograde stage** of metamorphism. (Note that the prograde and retrograde stages have been defined here simply in relation to increasing and decreasing temperature, respectively, with no reference to variation in pressure.) The course and length of the temperature decrease depend mainly on the post-metamorphic history of uplift and consequent erosion of the region (e.g. England & Richardson



**Figure 2.1** Schematic diagram showing a possible course of change of temperature that a rock undergoes during regional metamorphism.

1977). If erosion is active, the rock approaches the surface accompanied by a relatively rapid decrease of temperature, until it is exposed on the surface.

If erosion is negligible, say, in an arid region, the rock may remain virtually at the same depth in the crust, and the temperature of the rock changes toward a certain value, corresponding to the steady-state geotherm for the area at that depth. If the heating that causes the metamorphism is brought about mainly by igneous intrusion, the temperature in the vicinity of the intrusive bodies will commonly become higher than the temperature corresponding to the steady-state geotherm. So, if there is no erosion, a thermal peak occurs and then the temperature decreases toward the value corresponding to the steady-state geotherm at the depth. However, if the temperature increase that causes the metamorphism is brought about by radioactive heating of an initially cold crust, and if there is no erosion, the temperature continues to increase toward the value corresponding to the steady-state geotherm at that depth. In this case, there is no thermal peak.

Thus, all metamorphic rocks now exposed on the surface have experienced one thermal peak or more, whereas metamorphic rocks that remain at depth may or may not have experienced a thermal peak. Erosion has an essential connection with the thermal history of metamorphic rocks.

### 2.1.2 Mineral changes in the prograde stage and thermal peak

Metamorphic crystallization at low temperatures produces hydrous minerals such as chlorite, muscovite and epidote in metapelites as well as in metabasites. In the prograde stage, these rocks undergo a series of **dehydration reactions**, e.g.  $B = D + H_2O$ , where  $B$  and  $D$  represent a mineral or minerals. If carbonate-rich sedimentary rocks are present, they undergo a series of **decar-**

**bonation reactions** such as  $B = D + CO_2$ . There are reactions that involve both  $H_2O$  and  $CO_2$ , such as  $B = D + H_2O + CO_2$ , and  $B + CO_2 = D + H_2O$  (Fig. 3.5). In some cases, a large amount of  $CO_2$  may be produced by the oxidation of graphite or of some graphitic material in pelitic rocks, which is caused by infiltrating fluid. The  $H_2O$  and  $CO_2$  produced by any method forms either an intergranular fluid phase or molecules adsorbed along boundaries between mineral grains. They probably move mainly upward to the surface of the Earth by mechanical flow through large or small channelways and/or by chemical diffusion through fluid and grain boundaries (Hanson 1992).

By comparing chemical analyses of pelitic rocks metamorphosed at relatively low and high temperatures, Walther & Orville (1982) estimated that the average metapelite loses a total of 5.0 wt % of volatiles (2.6%  $H_2O$  + 2.4%  $CO_2$ ) during prograde metamorphism. If this amount of volatiles remained where it was produced, it would occupy 12 vol. % of the rock at 500 °C and 5 kbar. Actually nearly all the volatiles escape from the rock toward the Earth's surface.

The enthalpies of devolatilization reactions at 500 °C and 5 kbar are of the order of 84 kJ mol<sup>-1</sup> of released  $H_2O + CO_2$ . The heat required for devolatilization is about 170 kJ kg<sup>-1</sup> of average metapelite. If most devolatilization is assumed to occur in a temperature range of 400–600 °C, the heat required for heating from 400 ° to 600 °C is 210 kJ kg<sup>-1</sup> of the rock. Thus, a total of 380 kJ of heat energy is required for the metamorphism of each kilogram of average metapelite.

In addition, there are some prograde reactions that do not involve dehydration and decarbonation, such as phase transformations between polymorphs and Mg–Fe exchange reactions between coexisting ferromagnesian minerals. The thermal effects of such reactions are small compared with dehydration and decarbonation reactions.

When mafic igneous rocks with high-temperature mineral assemblages undergo low-temperature metamorphism, the reactions are exothermic. Because such rocks are present usually in small amounts compared with pelitic and calcareous rocks in regional metamorphic complexes, regional metamorphism as a whole is normally endothermic.

Rocks undergoing regional metamorphism are not isolated in space, but are underlain and overlain by other rocks which are also undergoing metamorphism. As discussed in §2.5, the thermal peaks of rocks in a metamorphic complex are not synchronous, but are reached at different times in different parts and at different depths, and the time differences could be up to tens of millions of years. The timing of the thermal peak may be earlier or later, with increasing depth, depending on the cause of metamorphism, the structure of metamorphic belt and other factors.

For example, in a case where a swarm of plutonic intrusions at a great depth

consists of four steps:  
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### NEW CONCEPTUAL BASIS OF METAMORPHIC PETROLOGY

is the main source of heat, in the crust above the level of the intrusions the metamorphic rocks probably reach their thermal peak at earlier times with increasing depth (Fig. 2.9).  $H_2O$  released by prograde reactions at greater depth rises into the higher crust where the temperature of metamorphism is lower. When the higher crust reaches its thermal peak, the deeper crust is already in a retrograde stage. So, most of the  $H_2O$  that rises from deeper crust could pass through rocks above in a relatively early part of their prograde stage. It is known in some regional metamorphic complexes that a large amount of externally derived  $H_2O$  infiltrates pervasively into pelitic rocks undergoing low-grade metamorphism (Ferry 1984). Such  $H_2O$  may come from pelitic rocks undergoing metamorphism at deeper levels as well as from associated plutonic intrusions.

Because metamorphic crystallization begins at point A in Figure 2.1, the earlier history of the rock is not recorded in mineral assemblages. In cases where the thermal-peak temperature is relatively high, most, or all, of the minerals that formed in the prograde stage are obliterated or compositionally adjusted, so that the resultant rock shows a mineral assemblage approximately equilibrated at the thermal-peak condition. In such a case, it is difficult to determine the history of mineralogical changes in the prograde stage.

#### 2.1.3 Mineral changes in the retrograde stage

In the retrograde stage, possible reactions that proceed with decreasing temperature are generally the reverse of prograde reactions, mostly producing minerals containing more  $H_2O$  and  $CO_2$ . For such reactions to take place, however,  $H_2O$  and  $CO_2$  must be present in the rock. If all the  $H_2O$  and  $CO_2$  evolved in the prograde stage have left the system before, and at, the thermal peak, such retrograde reactions cannot take place. In reality, usually only relatively small amounts of  $H_2O$  and  $CO_2$  appear to remain in the rock, causing only limited retrograde reaction. New hydrous minerals produced at this stage grow, for example, along margins and cleavages of thermal-peak minerals. Such retrograde minerals can be recognized from textural and compositional relations. Therefore, the mineral assemblages equilibrated at the thermal peak can usually be recognized and discussed.

It might be thought that during the retrograde stage the peak mineral assemblages will become increasingly unstable with decreasing temperature. This is not always true. For example, if a rock undergoes a univariant dehydration reaction  $A + B = C + H_2O$  in the late prograde stage, and if the released  $H_2O$  leaves the system, the mineral assemblage  $A + B + C$  (without  $H_2O$ ) forms. In the retrograde stage, this assemblage could continue to be stable at temperatures lower than the equilibrium temperature of the above reaction.

### TEMPORAL CHANGES IN P-T CONDITIONS

Some metamorphic reactions do not involve participation of volatiles such as  $H_2O$  and  $CO_2$ , e.g. polymorphic transformations, exsolution, and Mg-Fe exchange reactions. Such reactions would continue in the retrograde stage until they are halted by decreased temperature. Hence, geothermometers based on exsolution and Mg-Fe exchange reactions may record the temperature at different time points during the course of metamorphism from the mineral assemblages produced by dehydration reactions, and thus will give different values of temperature.

The amount of retrograde minerals in ordinary metamorphic rocks is usually very small, whereas very high-temperature metamorphic rocks (the granulite-facies rocks described in Ch. 11) are characteristically apt to show relatively intensive retrograde changes. This is probably partly because the early part of the retrograde stage in the latter case is still at relatively high temperatures, with a high rate of chemical reaction, and partly because  $H_2O$  is more plentifully supplied than in lower-temperature metamorphism, owing to the onset of partial melting at such high temperatures. Where partial melting occurs, a considerable part of the  $H_2O$  evolved by prograde reactions may remain in the rock, dissolved in the interstitial melt. During the course of temperature decrease, this melt is crystallized, and the  $H_2O$  dissolved in it is released, contributing to the progress of hydration reactions in the surroundings.

For example, in crust thickened by thrusting of a large sheet of crustal rocks over pre-existing crust, thermal peak is reached at later times with increasing depth (e.g. A. B. Thompson & England 1984; Fig. 5a). In such a case, the  $H_2O$  liberated by prograde reactions at great depths rises to higher crustal levels, where rocks may already be in a retrograde stage. If the rising  $H_2O$  passes pervasively through minute fractures whose spacing is of the order of the grain size, or through grain boundaries, it will come into contact with all the rock materials above the site of dehydration, causing intensive retrograde reactions. On the other hand, if the rising  $H_2O$  passes through widely spaced major channelways, it will come into contact only with the walls of the channelways, to which retrograde reactions will be confined; usually the latter appears to be the case.

Walther & Orville (1982) considered that real regional metamorphism is usually close to the latter case. The fluid produced by devolatilization is probably saturated or close to saturation in  $SiO_2$  with respect to quartz. Because the solubility of quartz in  $H_2O$  decreases with decreasing temperature and pressure (Fig. 4.1), the aqueous fluid will precipitate quartz as it moves toward the Earth's surface. Quartz veins, which are a common feature of regional metamorphic complexes, could have been major channelways for the passage of volatiles (cf. Connolly & Thompson 1989).

In the crustal levels above the igneous intrusions that are the main cause of

heating, the thermal peak of rocks is reached at a later time with decreasing depth (Fig. 2.9). In this case, the  $H_2O$  liberated by prograde reactions rises to higher crustal levels, where rocks are in prograde stages. So, the  $H_2O$  may not have a great effect on mineral equilibria, although the upward movement of such  $H_2O$  may have a marked influence on the temperature distribution and chemical migration within the crust.

#### 2.1.4 P-T-t paths and T-X-t paths of regional metamorphic rocks

**2.1.4.1 P-T-t (pressure-temperature-time) path of metamorphic rock.** It is not only temperature but also pressure that appears generally to change during the course of regional metamorphism. Increasing pressure is caused by increasing thickness of the overlying crust, probably due either to mechanical deformation such as thrusting and folding or to magmatic intrusion into higher horizons in the crust. Decreasing pressure is caused either, by crustal deformation, or by erosion. The change over time of  $P$ - $T$  conditions that a rock experiences during metamorphism is called the  **$P$ - $T$ - $t$  path** of the rock. The  $P$ - $T$ - $t$  paths of metamorphic rocks appear to be very diverse, depending on the details of the mechanical and thermal history of the region. They vary with the position and depth in which the rock in question lies within a metamorphic complex (e.g. Harte & Dempster 1987, Ghent & Stout 1988).

Figure 2.2 illustrates four of the possible types of  $P$ - $T$ - $t$  paths in relation to equilibrium curves of dehydration and solid-solid reactions shown on a  $P$ - $T$  diagram. If the effects of deformation and erosion are negligibly small, and if heating is caused by intrusions into deeper levels, the heating and cooling of a rock takes place under a virtually constant pressure, as illustrated by the  $P$ - $T$ - $t$  path of case (a).

Curve (b) represents a clockwise  $P$ - $T$ - $t$  path, where the pressure of a rock located initially at a relatively shallow depth increases rapidly by thickening of the overlying crust, and this is accompanied by a slow temperature increase. While temperature is still increasing, the crust is uplifted to restore isostatic equilibrium, and so active erosion on the surface begins to result in a decrease of pressure. After the thermal peak, the rock may take one of several courses, such as  $B_1$  and  $B_2$ , depending upon the relative magnitude of the effects of cooling and erosion. In path (b), the pressure at the thermal peak is considerably lower than the maximum pressure that the rock experiences, and a considerable decrease of pressure takes place over a small range of temperature around the thermal peak (A. B. Thompson & Ridley 1987).

Some  $P$ - $T$ - $t$  paths make the determination of thermal-peak mineral assemblages difficult. For example, if the  $P$ - $T$ - $t$  path of a rock in the vicinity of the

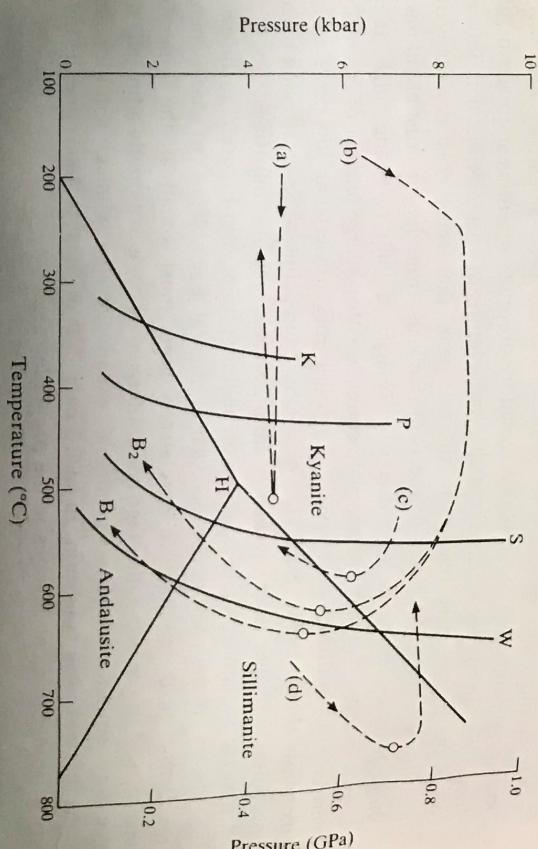


Figure 2.2 Univariant equilibrium curves for some metamorphic reactions (solid lines). Lines K, P, S and W represent equilibrium curves for four different dehydration reactions in the presence of pure  $H_2O$  fluid. The reactions are as follows: (K) kaolinite + 2 quartz = pyrophyllite +  $H_2O$ ; (P) pyrophyllite = kyanite (or andalusite) + 3 quartz +  $H_2O$ ; (S) staurolite + muscovite + quartz = sillimanite (or kyanite or andalusite) + garnet + biotite +  $H_2O$ ; (W) hypothetical. The three straight lines meeting at point H are the boundaries between the stability fields of three polymorphs of  $Al_2SiO_5$  (andalusite, kyanite, and sillimanite). Four of the possible  $P$ - $T$ - $t$  paths (a), (b), (c) and (d) of a metamorphic rock are shown by dashed lines. An open circle represents a thermal peak in each path.

thermal peak is like curve (c), kyanite might be transformed into sillimanite with decreasing temperature, and this sillimanite might be mistaken for a product of increasing temperature or the thermal peak. In an analogous way, some  $P$ - $T$ - $t$  paths might cause a dehydration reaction to occur with decreasing temperature.

Curve (d) shows a type of anti-clockwise  $P$ - $T$ - $t$  path commonly observed in high-temperature gneiss regions (Bohlen 1991). Such a path may be followed where basaltic magma is intruded from the mantle into the lower and middle crust, causing an increase of temperature in the crust. A rock in the lower crust experiences an increase in temperature and pressure as shown in the path. After the thermal peak, the cooling process is nearly isobaric, because the relatively high density of basaltic magmas does not cause isostatic uplift and erosion.

#### NEW CONCEPTUAL BASIS OF METAMORPHIC PETROLOGY

The minerals produced in the prograde stage usually decompose partly or completely at and before the thermal peak, whereas those produced in the retrograde stage are commonly preserved. Hence, the  $P-T-t$  path in the retrograde stage is easier to decipher than that in the prograde stage. In many cases, K-Ar dating of a number of minerals with different closure temperatures gives a quantitative history of post-peak cooling.

Attempts have been made to decipher the  $P-T-t$  paths of rocks in the prograde stage by investigating zoned crystals and inclusions in them (e.g. Atherton 1968, A. B. Thompson et al. 1977, Spear & Selverstone 1983).

In recent years it has been found in some metamorphic areas that the thermal peak is followed by a great decrease of pressure under nearly isothermal conditions. Such a stage of pressure decrease (decompression stage) should be distinguished from the retrograde stage outlined above, which is characterized by a decrease of temperature with, or without, variation in pressure.

#### 2.1.4.2 $T-X-t$ (temperature-composition-time) path of intergranular fluid

Most reactions in prograde metamorphism are dehydration and decarbonation reactions, whose equilibria are controlled not only by pressure and temperature but also by the chemical potentials of  $H_2O$  and  $CO_2$  in the rock. At a given pressure and temperature, the chemical potentials of  $H_2O$  and  $CO_2$  are functions of the composition of the intergranular fluid, if present, in the rock.

The composition of an intergranular fluid may change because of addition of  $H_2O$  and/or  $CO_2$ , liberated by, respectively, the dehydration and/or decarbonation reactions that occur in the rock. Moreover, fluids coming from other sources may mix with the intergranular fluid, and may drive reactions in the rock. Fluid thus formed may leave the rock and rise toward the Earth's surface, and thereafter a new intergranular fluid may form. Thus, intergranular fluid has a history of change of composition during the course of metamorphism.

The chemical reactions that take place are controlled by equilibria between fluid and rock, which vary with pressure and temperature, particularly the latter. So the history of compositional change of intergranular fluid during the course of metamorphism is usually represented in a  **$T-X$  diagram**, which shows temperature as the ordinate and the mole fraction of a component in fluid as the abscissa. Commonly intergranular fluids are regarded, approximately as binary solutions composed of  $H_2O$  and  $CO_2$ . In this case,  $X$  usually denotes the mole fraction of  $CO_2$ , as for example in Figures 6.1 and 6.9.

#### 2.1.5 Complex $P-T-t$ paths and plurifacial metamorphism

In Figures 2.1 and 2.2, it is assumed that metamorphic rocks experience only

#### PROGRESSIVE METAMORPHISM

one thermal peak and only one pressure maximum. In some cases, however, metamorphic rocks experience two or more thermal peaks and/or pressure maxima in the course of a single complex tectonic event. In these cases, minerals formed at an earlier time may survive a later phase of crystallization as metastable relics. Such rocks contain two or more distinct groups of minerals, which formed at different times under different  $P-T$  conditions. Metamorphic rock of this type was named **plurifacial rock** by W. P. de Roever & Nijhuis (1963). The term **plurifacial metamorphism** is used to denote the sequence of metamorphic crystallization that has produced a plurifacial rock. Some plurifacial metamorphic rocks show mineral assemblages formed in a series of genetically related crystallization stages in the course of a single orogeny, while others are the results of two or more unrelated distinct orogenies (or thermal events) that affected the same rock. The latter case is so-called **polymetamorphism**.

**Retrogressive metamorphism** is a special case of plurifacial metamorphism. The term retrogressive metamorphism was used in the past with the two different meanings: (a) retrograde metamorphism as defined above, that is, metamorphic crystallization with decreasing temperature immediately after the thermal peak; and (b) a younger independent metamorphic event that is lower in temperature than the older one in a polymetamorphic complex. The term provides considerable convenience for actual descriptive work, because in many cases we cannot determine with certainty to which of the above two cases the retrogressive metamorphism under investigation belongs.

## 2.2 Progressive metamorphism, isograds, thermal-peak isotherms and isobars, and field $P-T$ curves

#### 2.2.1 Spatially progressive metamorphism

It is common that different parts within a metamorphic region show different thermal-peak  $P-T$  conditions, and that the spatial variation of thermal-peak  $P-T$  conditions is continuous and is of a great enough magnitude to cause mineralogical changes clearly recognizable under the microscope. Within a metamorphic region, variations in temperature usually produce much greater mineralogical changes than do pressure variations. Therefore, we usually ascribe mineralogical changes across a metamorphic region mainly to a laterally (i.e. spatially) progressive increase of thermal-peak temperature. The metamorphism of such a metamorphic region is called **progressive metamorphism**. The classic pro-