The Nature and Significance of the Mechanism of Sillimanite Growth in the Connemara Schists, Ireland

Bruce W.D. Yardley*

Department of Geology, University of Manchester, Manchester M13 9PL, England

Abstract. During prograde metamorphism of the Connemara pelites, sillimanite first develops in biotite immediately adjacent to, or replacing, garnet. In some rocks, breakdown of garnet + muscovite and staurolite + muscovite + quartz leads to the development of fibrolite pseudomorphs after garnet. The textures indicate a constant volume replacement of garnet with movement of Al from staurolite and muscovite in the matrix towards the few, widely scattered, garnet sites. The complex ionic reaction patterns are the result of the strong preference of sillimanite to grow on biotite that is replacing garnet, and this pattern of preferred nucleations is taken to indicate that the equilibrium conditions for the reaction were only overstepped by the minimum required for initial sillimanite nucleation. Chemical movements were controlled by the heterogeneous nucleation pattern, not by intrinsic properties of the moving species. In order for extensive reaction to occur under near-equilibrium conditions, the rate at which the total thermal reaction proceeded must have been controlled by the supply of heat to the rocks rather than by diffusion or local reaction steps.

Introduction

In the Connemara region of Western Ireland there is an extensive inlier of Dalradian metasedimentary rocks that may be correlated quite closely with those of Donegal and the Scottish Highlands, (Kilburn et al., 1965). Over most of the area the metamorphism has reached at least amphibolite facies conditions, and the metamorphic grade increases southwards, approximately at right angles to the main structural
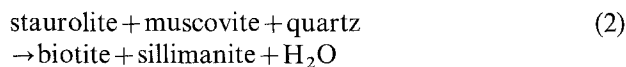
trends. In the district around Cur, south of the Maam Valley in north-east Connemara, there is a transition from staurolite zone to upper sillimanite zone assemblages in pelitic rocks (Yardley, 1976). This paper is concerned with the manner in which sillimanite develops in these rocks; all the samples discussed here come from a 4 km along-strike strip of a single, uniform, pelite horizon that trends at a small angle to the isograds (see Yardley (1976), Fig. 6).

Reactions

The diagnostic assemblage of the staurolite zone pellites is staurolite + muscovite + biotite + garnet + quartz, with plagioclase, ilmenite, and minor apatite, tourmaline, pyrite and chalcopyrite: minor graphite may be present but becomes rare or absent at higher grades. Sillimanite appears first as an additional phase in such rocks, and the resulting assemblage has 7 phases in the 6 component pelite subsystem $K_2O-MgO-FeO-Al_2O_3-SiO_2-H_2O$ (KMFASH of Thompson, 1976), (i.e. sillimanite, staurolite, biotite, muscovite, garnet, quartz, fluid). Sillimanite might therefore be expected to be the product of the univariant reaction:

$$\text{quartz} + \text{staurolite} + \text{muscovite} \qquad (1)$$
$$\rightarrow \text{biotite} + \text{garnet} + \text{sillimanite} + H_2O$$
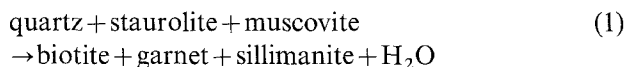
In fact however, garnet breaks down as sillimanite is produced, and the initial growth of sillimanite (fibrolite) may be considered to result from 2 separate continuous reactions operating simultaneously:

$$\text{staurolite} + \text{muscovite} + \text{quartz} \qquad (2)$$
$$\rightarrow \text{biotite} + \text{sillimanite} + H_2O$$

$$\text{garnet} + \text{muscovite} \rightarrow \text{biotite} + \text{sillimanite} + \text{quartz} \qquad (3)$$

In the Fe-end member system where these reactions become univariant, reaction 3 is only stable on

* *Present address:* School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, England

the high-temperature side of reaction 2 in the presence of H_2O (see Thompson (1976), Fig. 1D).

The reason for this reaction sequence appears to be the presence of significant Ca and Mn in the garnet. Reaction 3 is vapour-absent and very susceptible to variations in garnet composition; the extent to which the reaction has proceeded at any temperature therefore varies between different samples, and within a single outcrop at appropriate grade a complete range can be found between staurolite-sillimanite schists in which garnet is virtually uncorroded, and others in which the garnet is largely or wholly broken down.

The common assemblages of KMFASH phases found in the higher grade part of the staurolite-sillimanite transition zone are:

(a) staurolite + sillimanite + garnet
    + biotite + quartz   (*no* muscovite)
(b) staurolite + sillimanite + biotite
    + muscovite + quartz   (*no* garnet)
(c) sillimanite + garnet + biotite
    + muscovite + quartz   (*no* staurolite)

Garnets show textural evidence of breakdown in assemblages a and c, and the pseudomorph structures discussed below indicate that garnet was formerly present in rocks with assemblage b.

Some relevant analytical data from a range of rocks showing varying degrees of garnet breakdown (assemblages a and b) are given in Table 1. All the samples for which results are shown come from a small area of uniform grade. It is apparent that, as expected, garnet in more magnesian rocks tends to show the most extensive breakdown, however it may

Table 1. Analytical data from some isograde pelites. Samples 5 and 111: assemblage a, appreciable garnet remaining. 280: assemblage a, garnet very rare, occurs as small corroded relicts in some sillimanite-biotite pseudomorph textures. 281 and 186: assemblage b, sillimanite pseudomorphs after garnet are present. Rock analyses by X.R.F. from Yardley (1974). Mineral analyses by the A.R.L. EMX-SM microprobe, University of Washington, using natural mineral standards and Bence-Albee correction procedures

Sample	111	5	280	281	186
Rock Analyses					
Na/(Na+Ca)	0.69	0.74	0.78	0.78	0.75
Niggli mg	0.32	0.27	0.33	0.34	0.34
Mineral Analyses					
X_{Mg}^{bio}	0.42	0.32		0.37	
X_{Ab}^{plag}	0.72	0.86		0.83	
X_{gross}^{gt}	0.049	0.032		—	
X_{spess}^{gt}	0.058	0.081		—	
X_{pyr}^{gt}	0.120	0.079		—	

be stabilized by a high grossular content (sample 111), and there are also variations in spessartine content that might prove significant. As a result rocks with the same, superficially divariant, assemblage may show large variations in mineral X_{Mg} at constant grade.

The varying degrees of garnet breakdown observed at one grade due to compositional differences permits the reaction sequence to be studied in a compact suite of rocks of uniform thermal history, however there are no differences apparent from the changes observed in a range of samples studied over a range of metamorphic grades.

Reaction Textures

The textures that formed as sillimanite grew are illustrated in Figure 1. Where only small amounts of sillimanite are present, they occur as fibrolite mantling garnet grains and intergrown on biotite (Fig. 1A). This is also the mode in which sillimanite first appears at the sillimanite-in isograd. It is apparent from Figure 1 that the schistosity in the matrix is often bent around garnet grains, and fibrolite may be particularly abundant where biotite-rich foliae are tangential to the garnet surface. However some fibrolite is developed all around most garnets even at this stage (Fig. 1A), and since the deformation of the schistosity about the garnets predates formation of staurolite or sillimanite (Yardley, 1976), this preferential development of fibrolite where garnet impinges on the schistosity may be related to the occurrence of garnet and biotite in close proximity in these regions, rather than to any mechanical anisotropy.

As garnet becomes corroded it is replaced along cracks, in inclusions and around its margins by biotite, and this biotite is itself replaced by sillimanite. However the biotite growing within garnet is free of sillimanite; sillimanite only develops near the outer edge of the garnet (Fig. 1B). In practice it may be difficult to distinguish biotite that is incipiently replacing garnet along cracks (e.g. Fig. 1B) from earlier-formed biotite included in the garnet. However biotite is rarely found included in garnet at lower grades, and there is a gradation to large biotite plates within former garnet sites that are clearly not original inclusions (Fig. 1C). Sometimes such plates occur within garnet atolls.

At more advanced stages of garnet breakdown, the garnet is replaced by biotite and fibrolite; original inclusion patterns are destroyed and atoll structures are sometimes developed. Even at advanced stages of garnet breakdown, relatively large amounts of biotite remain near the centre of the replacement texture, but the outer part of the replacement texture is very largely made up of matted fibrolite (Fig. 1C). The endproduct of garnet breakdown is a matted knot of fibrolite that may still accurately preserve the shape and size of the original garnet (Fig. 1D). Only minute vestiges of biotite remain in the sillimanite pseudomorphs where garnet has disappeared (compare Figs. 1C and 1D).

Ilmenite often recrystallizes into coarse clots during garnet breakdown, and such ilmenites in the replacement textures (e.g Fig. 1D) are typically more manganoan than those in the matrix (e.g. 4.56% MnO c.f. 3.37% MnO for matrix ilmenites; sample 5). Presumably this ilmenite contains Mn that was concentrated in garnet as it broke down, Ti and Fe may be derived from original ilmenite inclusions in garnet.

The most conspicuous feature of these rocks, apparent even in outcrop, is that almost all the sillimanite is concentrated around the sites of former or partially replaced garnets, or in thin felts
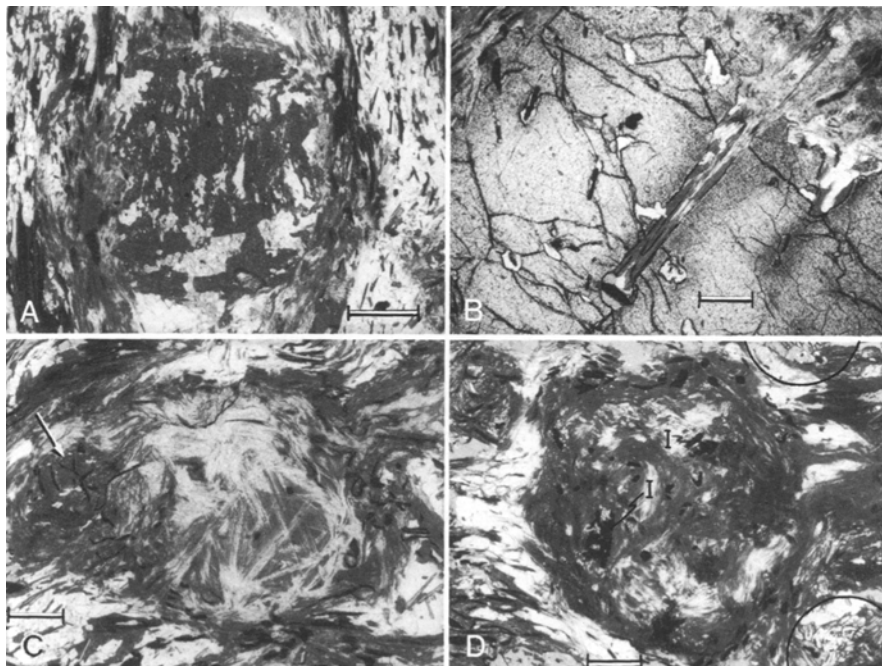
Fig. 1A–D. Progressive replacement of garnet by sillimanite. A sample 282; Comparatively complete, poikiloblastic garnet mantled by intergrown fibrolite and biotite; scale bar 1 mm. B sample 5; Detail of partially corroded garnet showing fibrolite-biotite intergrowths at margin; a biotite flake growing into the garnet along a crack contains very little fibrolite; scale bar 0.2 mm. C sample 117; Garnet largely replaced by fibrolite and biotite, a garnet remnant is arrowed. Note preferential directions of fibrolite growth on a large biotite plate within former garnet site. Fine, matted fibrolite completely enclosis the replacement texture; scale bar).5 mm. D sample 281; Complete fibrolite pseudomorph after garnet, preserving original shape. Note clots of recrystallized ilmenite in the pseudomorph (I) and small staurolite grains in the matrix (ringed) that are embayed by sillimanite-free biotite. All photographs in plane-polarized light

extending out into the schistosity from the margins of the pseudomorphs (Fig. 1C). This is despite the fact that in the parent rocks garnet is usually sparse (<5% of the mode) and occurs as only a few large porphyroblasts, whereas biotite is abundant throughout these rocks. The amount of sillimanite produced by reaction 3 is sufficient to replace about 75% of the original garnet; however garnets may be completely replaced by sillimanate, and even where some garnet and biotite remain, most of the sillimanite in the rock occurs either as a replacement of part of the garnet or in felts immediately adjacent to the garnet. Some of this sillimanite must therefore be produced by reaction 2, and staurolite grains show partial resorbtion and replacement by plagioclase, quartz and biotite. However sillimanite never grows in immediate contact with staurolite in these rocks, *and is virtually absent from biotites that replace staurolite* (Fig. 1D).

Interpretation

(a) The Relationship Between Sillimanite and Biotite

Chinner (1961) has suggested that the intimate association of fibrolite and biotite (especially where the sillimanite develops preferentially in particular orientations, as in Fig. 1C) results from the biotites' providing favourable sites for sillimanite nucleation. However, many recent authors have favoured the suggestion by Carmichael (1969) that fibrolite-biotite intergrowths result from the simultaneous growth of both phases.

In the suite of rocks studied here, the biotite that initially replaces garnet along cracks and inclusion boundaries does not contain any fibrolite except where it passes to the outer margin of the garnet. At the more advanced stage of replacement represented by Figure 1C, a significant amount of biotite remains in the replacement texture, but this contains sillimanite throughout. After complete garnet breakdown the pseudomorphs are nearly pure sillimanite and have only a very little biotite remaining as minute, isolated vestiges betwee fibrolite bundles. Thus it appears that the sillimanite-free biotite that initially replaces garnet is itself subsequently replaced by sillimanite, i.e. the observations support Chinner's model of selective nucleation of sillimanite on biotite.
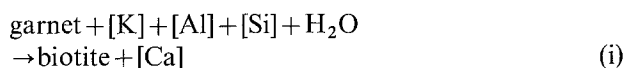
(b) The Ionic Reaction Cycle

The redistribution of material in a rock, accompanying isochemical breakdown of certain phases and growth of others, can be described by a series of local, ionic reactions that when taken together sum to give the thermal reaction (Carmichael, 1969). However the ionic reaction written to describe any particular process depends on the reference frame assumed (Gresens, 1965). Since little or no distortion of ear-
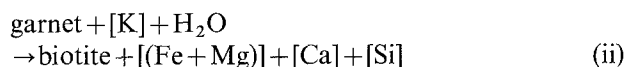
lier-formed tectonic fabrics has accompanied the development of sillimanite, it appears that growth or dissolution of phases involved in the reactions takes place by constant volume replacement, in part involving matrix minerals. Ionic reactions do not appear to perform mechanical work on the rock matrix. Nevertheless a constant volume frame is not strictly accurate for some transformations. For example many garnets may initially contain numerous quartz inclusions and these are expelled during replacement. Thus the final volume of sillimanite pseudomorph occupies the volume formerly occupied by garnet + quartz inclusions, sillimanite may also spread out into the schistosity.

The development of sillimanite pseudomorphs after garnet can be broken down into 2 stages, an initial replacement of garnet by biotite and the subsequent replacement of this biotite by sillimanite. The replacement of garnet by biotite can be written in different ways by assuming different reference frames, for example:
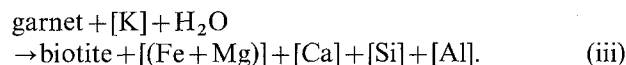
at constant (Fe + Mg):

$$\text{garnet} + [K] + [Al] + [Si] + H_2O$$
$$\rightarrow \text{biotite} + [Ca] \tag{i}$$

at constant Al:

$$\text{garnet} + [K] + H_2O$$
$$\rightarrow \text{biotite} + [(Fe + Mg)] + [Ca] + [Si] \tag{ii}$$

at constant volume:

$$\text{garnet} + [K] + H_2O$$
$$\rightarrow \text{biotite} + [(Fe + Mg)] + [Ca] + [Si] + [Al]. \tag{iii}$$

Square brackets denote components added or removed in solution, Mn and details of Fe−Mg cation exchange reactions are neglected. The development of biotite in cracks and inclusions means that locally the constant volume reference frame is not appropriate. Probably the ionic reaction may vary between (i), (ii) and (iii) around individual garnets in response to very local constraints.
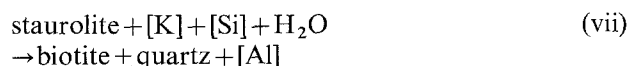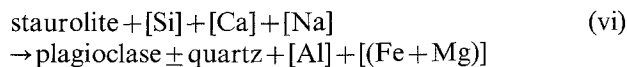
The replacement of biotite by sillimanite cannot conserve (Fe + Mg) and does not conserve Al, instead complete replacement takes place at approximately constant volume:

$$\text{biotite} + [Al] + [Si] \tag{iv}$$
$$\rightarrow \text{sillimanite} + [K] + [(Fe + Mg)] + H_2O.$$

The Al required for the sillimanite pseudomorphs must come in part from breakdown of muscovite and in part from breakdown of staurolite. Muscovite breaks down in the matrix without any specific textures being readily associated with the process. Notionally it may be considered to be replaced by quartz:

$$\text{muscovite} + [Si] \rightarrow [K] + [Na] + [Al] + H_2O + \text{quartz.} \tag{v}$$
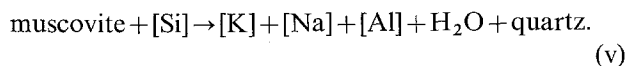
The principle ionic reactions at staurolite margins are of the type:

$$\text{staurolite} + [Si] + [Ca] + [Na] \tag{vi}$$
$$\rightarrow \text{plagioclase} \pm \text{quartz} + [Al] + [(Fe + Mg)]$$

$$\text{staurolite} + [K] + [Si] + H_2O \tag{vii}$$
$$\rightarrow \text{biotite} \pm \text{quartz} + [Al]$$

where both are written for constant volume replacement.

The reactions necessary to close the cycle involve muscovite and biotite. Biotite components 'displaced' by reaction (iv) may form new biotite grains in the matrix, or enlarge existing grains. Notionally this growth may be considered as replacing quartz:

$$\text{quartz} + [K] + [(Fe + Mg)] + [Al] + H_2O \tag{viii}$$
$$\rightarrow \text{biotite} + [Si].$$
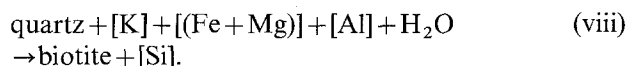
Finally some muscovite may be converted to biotite, notionally by a direct replacement:

$$\text{muscovite} + [(Fe + Mg)] \rightarrow \text{biotite} + [Al] + [Si]. \tag{ix}$$
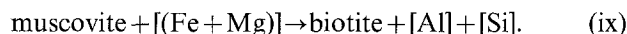
The essential features of this ionic reaction cycle are summarized in Figure 2.

(c) The Mobility of Al

It is commonly assumed, following Carmichael, that Al may be considered immobile during metamorphism, but this does not appear to be the case in these rocks. The development of sillimanite pseudomorphs after garnet at constant Al would involve a reduction in volume of more than 50%, whereas the evidence from partially replaced garnets is that the process conserves volume. A decrease in volume due to replacement at constant Al would lead to a bowing-in of the schistosity towards the pseudomorph and this is never observed. Nearby upper sillimanite zone rocks have relict inclusions of staurolite in plagioclase, and if Al did not move this would require a comparable large volume increase for which there is no textural evidence.

Additional evidence for movement of Al comes from the textures of andalusite porphyroblasts that develop in the same pelite horizon by similar reactions in adjacent areas (Yardley, 1976). Andalusite forms large porphyroblasts sometimes of the order of 1 cm across and up to an order of magnitude larger than grains of other minerals in the rock. These porphyroblasts commonly include, and may have nucleated on, grains of staurolite (in contrast to the antipathetic relationship between sillimanite and staurolite). They
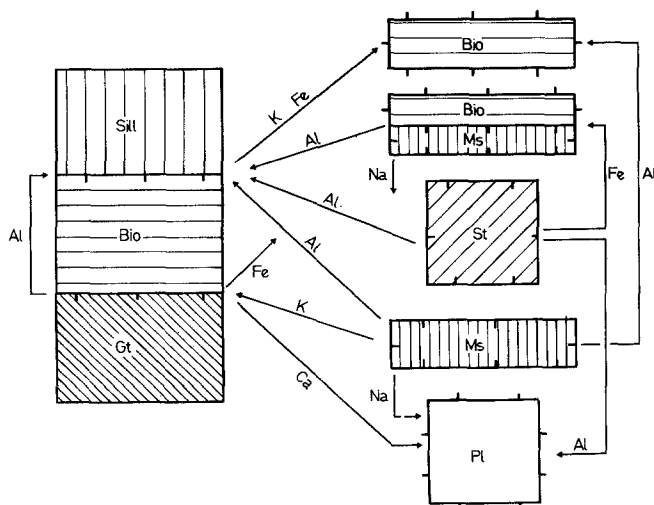
Fig. 2. Schematic representation of ionic reaction cycle. Ticks denote direction of movement of grain boundaries. *Sill* sillimanite; *Bio* biotite; *Ms* muscovite; *St* staurolite; *Gt* garnet; *Pl* plagioclase

also include biotite and ilmenite and thereby preserve a schistosity (see Yardley, 1976, Fig. 7A); however matrix quartz and plagioclase are completely replaced. The schistosity preserved in andalusite passes out into the matrix with little or no distortion, thus growth of these porphyroblasts was by constant volume replacement and considerable movement of Al was required.

It is noted that Foster (1975) has recently found that sillimanite zone textures from Maine cannot be satisfactorily explained in a constant-Al reference frame.

Significance of the Pattern of Ionic Reactions

The ionic reaction pattern illustrated in Figure 2 is dominated by the selective growth of sillimanite in biotite that replaces garnet, rather than in pre-existing biotite or biotite after staurolite. For reasons discussed above, this pattern is believed not to represent simultaneous growth. However no consistent compositional differences have been found between biotites that replace garnet and those that occur in the adjacent matrix, which might have explained the nucleation pattern of sillimanite. It is possible that, in view of the strong partitioning of Fe and Mn into garnet, steady state chemical potential gradients might have maintained an Fe and Mn enriched biotite in the immediate vicinity of garnet for the duration of continuous garnet breakdown, but this cannot be proven.

Whatever the reason however, it is this pattern of nucleation and growth of sillimanite that controls

the pattern of local metasomatic migrations. Rather different patterns are found where andalusite grew by similar thermal reactions, e.g. since andalusite appears to nucleate on staurolite there is a net flux of Al towards some staurolite grains instead of away from them all.

In other words, *the relative mobilities and movement patterns of different chemical constituents in these rocks are dominantly controlled by the nucleation patterns of product phases rather than by any intrinsic properties of the moving species.* Mobilities of species may still be important however in determining metamorphic textures: given a particular pattern of nucleation many minerals may grow either as inclusion-free porphyroblasts or as inclusion-riddled poikiloblasts, and the amount of chemical migration required may be very different for the extreme cases. There is a potential relationship between metamorphic textures and mineral growth rates.

The selective nucleation pattern of sillimanite also has implications for the nature of the rate limiting step in metamorphic reactions. It is implicit in the assumption that a particular component, e.g. Al, remains immobile during metamorphism, that diffusion provides the rate limiting step for metamorphic reactions. However if a homogeneous rock is heated in a closed system above the temperature for a reaction to proceed, and the product minerals are first nucleated at the few very favourable sites, the rate of further reaction may be constrained by either: (i) the rate of diffusion of material to the growing grains through a pore fluid or along grain boundaries. (ii) The rate of dissolution or precipitation reactions at interfaces between reactant or product grains and the pore fluid. (iii) The rate of supply of heat to the rock.

If steps i or ii control the rate of the total thermal reaction, then the heat supplied will continue to raise the temperature of the rock in addition to driving reaction. The resultant increase in overstepping will however tend to increase the rates of steps (i) and (ii) by increasing ΔG_r. For prograde reactions this increase in driving force will not be offset by kinetic constraints. Furthermore nucleation of product phases at a greater range of sites is likely as ΔG_r increases, so that the distances over which diffusion need take place will be reduced. Thus irrespective of the initial rate limiting step after nuclei first form, prograde reaction rates will tend to speed up until their rate is controlled by the supply of heat.

Conclusions

In the rocks described here, sillimanite appears to nucleate only at the most favourable type of site and

even distinguishes amongst different types of biotite. It is concluded that the amount of overstepping of the equilibrium conditions during continuous reaction was minimal. As a result extensive diffusion took place over distances controlled in these samples by the distribution of preferred sites for sillimanite nucleation. The relative mobilities of different components was controlled by the reaction stoichiometry and nucleation pattern, not by intrinsic properties of moving species. It is therefore deduced that the rate at which the total thermal reaction proceeded was controlled by the rate of supply of heat to the rock at temperatures very close to the equilibrium condition.

Complex ionic reaction cycles of this type leading to redistribution within a small closed system, have been found to be quite common since they were first described in detail by Carmichael (1969). This study suggests that they result from reaction taking place at conditions close to equilibrium so that product nucleation sites are strictly limited, and it is therefore implicit that the regional heat flow is the rate limiting step for such reactions.

References

Carmichael, D.M.: On the mechanism of prograde metamorphic reactions in quartz-bearing pelitic rocks. Contrib. Mineral. Petrol. **20**, 244–267 (1969)

Chinner, G.A.: The origin of sillimanite in Glen Clova, Angus. J. Petrol. **2**, 312–323 (1961)

Foster, C.T.: Diffusion controlled growth of metamorphic segregations in sillimanite grade pelitic rocks near Rangeley, Maine, U.S.A. Ph.D. Thesis, The Johns Hopkins University (1975)

Gresens, R.L.: Composition-volume relations of metasomatism. Chem. Geol. **2**, 47–65 (1967)

Kilburn, C., Pitcher, W.S., Shackleton, R.M.: The stratigraphy and origin of the Portaskaig Boulder Bed series (Dalradian). Geol. J. **4**, 343–360 (1965)

Thompson, A.B.: Mineral reactions in pelitic rocks: I. Prediction of P−T−X (Fe−Mg) phase relations. Am. J. Sci. **276**, 401–424 (1976)

Yardley, B.W.D.: The deformation, metamorphism and metasomatism of the rocks of the cur area, Connemara, Eire. Ph.D. Thesis, Bristol University (1974)

Yardley, B.W.D.: Deformation and metamorphism of Dalradian rocks and the evolution of the Connemara cordillera. J. Geol. Soc. Lond. **132**, 521–542 (1976)