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Thermodynamic models of biotite pseudomorphs after staurolite

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Abstract

A local equilibrium, irreversible thermodynamic model was used to study biotite-rich pseudomorphs after staurolite in muscovite-bearing pelites near Rangeley, Maine. This type of pseudomorph is found in close proximity to sillimanite segregations which have grown during a staurolite breakdown reaction (Foster, 1977a). The local reactions and distribution of minerals expected to be produced by the growth of sillimanite near staurolite poikiloblasts in a matrix of muscovite, biotite, plagioclase, quartz and ilmenite were calculated using Gibbs-Duhem relations, conservation equations and relative thermodynamic diffusion coefficients in an SiO_2-fixed reference frame. Biotite-rich, plagioclase-rich, muscovite-free pseudomorphs are formed in the model when the muscovite-free mantle of a sillimanite segregation encloses a staurolite poikiloblast or grows over a muscovite-rich pseudomorph. The model produces biotite-rich, muscovite-free, plagioclase-free pseudomorphs when the muscovite-free, plagioclase-free mantle of a sillimanite segregation encloses a staurolite poikiloblast or grows over a muscovite-rich or plagioclase-rich pseudomorph. Biotite-rich pseudomorphs after staurolite in rocks from the lower sillimanite zone near Rangeley, Maine are similar to those calculated by the model. The proportion of muscovite-rich to biotite-rich pseudomorphs in the model is a function of the initial proportions of muscovite, plagioclase and staurolite, which govern the proportion of staurolite that is enclosed by sillimanite segregation mantles.

Introduction

Many staurolite breakdown reactions in pelitic schists are thought to proceed by cation exchange reaction mechanisms which form a variety of staurolite pseudomorph textures (*e.g.*, Bailes, 1980; Carmichael, 1969; Hietanen, 1968; Kwak, 1974). Muscovite-rich pseudomorphs after staurolite from the lower sillimanite zone near Rangeley, Maine (Guidotti, 1968, 1970, 1974) form when staurolite dissolves in one part of the rock providing components needed for the growth of sillimanite in other domains of the rock. These pseudomorphs are coarse-grained aggregates predominantly composed of muscovite with smaller amounts of biotite, plagioclase, ilmenite and quartz (Fig. 1). This texture is separated from the sillimanite segregations in the rock by a finer grained matrix containing the same mineral assemblage of biotite, muscovite, plagioclase, quartz, and ilmenite. The boundary between the pseudomorph and matrix is marked by a change in mica grain size and change in the mineral modes. Foster (1981) has presented an irreversible thermodynamic model, derived from the approach of Fisher (1973, 1975, 1977), which seems to explain muscovite-rich pseudomorphs after staurolite.

A second type of pseudomorph which is less common at Rangeley than the muscovite-rich pseudomorph is muscovite-free, biotite-rich, and plagioclase-rich with smaller amounts of quartz and ilmenite (Fig. 2). This texture is commonly enclosed by the muscovite-free mantle (Foster, 1977a) of a nearby sillimanite segregation. The muscovite-free mantle has the same mineral assemblage as the pseudomorph. The boundary between the pseudomorph and the mantle is marked by a change in mineral modes.

A third pseudomorph type, uncommon in the Rangeley area, is plagioclase-free, muscovite-free and rich in biotite with lesser amounts of quartz and ilmenite (Fig. 3). This texture is commonly enclosed by the muscovite-free, plagioclase-free mantle (Foster, 1981) of a nearby sillimanite segregation. The boundary between the pseudomorph and the mantle is marked by a change in mineral modes.

The purpose of this paper is to show that the model for muscovite-rich pseudomorphs (Foster, 1981) can also be used to explain biotite-rich pseudomorphs after staurolite. This provides a good test of the flexibility of the model because of the completely different mineral modes in the biotite-rich and muscovite-rich pseudomorphs.

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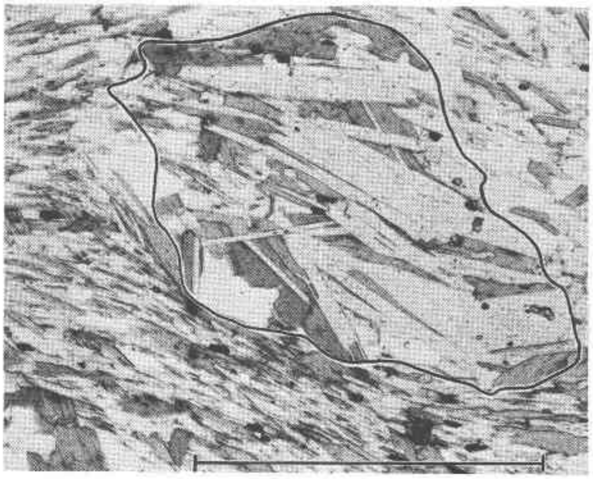

Fig. 1. Muscovite-rich pseudomorph after staurolite (51% muscovite, 26% biotite, 14% plagioclase, 8% quartz, 1% ilmenite). The boundary of the pseudomorph is shown by a solid line. The small, high relief blebs in muscovite in the pseudomorph are remnants of staurolite. The scale bar is 1 mm.

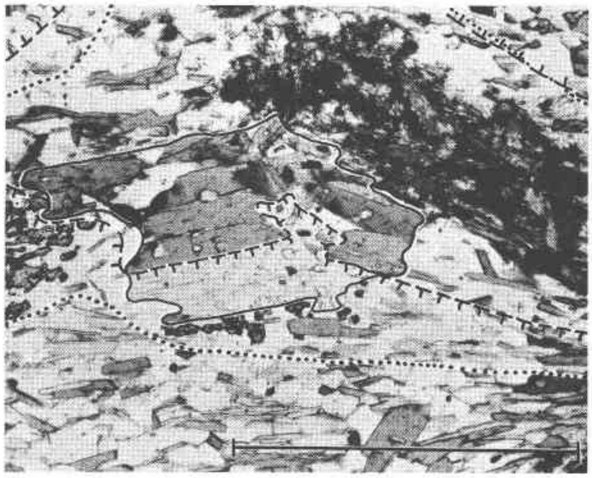

Fig. 3. Muscovite-rich, plagioclase-free pseudomorph (73% muscovite, 9% biotite, 17% quartz, 1% ilmenite) after staurolite being converted to a muscovite-free, plagioclase-free pseudomorph (86% biotite, 13% quartz, 1% ilmenite). The plagioclase-free mantle boundary is shown by the dotted line. The muscovite-free mantle boundary is shown by the dashed line. The tick marks are on the muscovite-bearing side. The scale bar is 1 mm.

Reaction models

Biotite-rich, muscovite-free pseudomorphs

The spatial relationship between muscovite-free mantles of sillimanite segregations and the muscovite-free, biotite-rich pseudomorphs after staurolite suggests that the local reactions which form the pseudomorphs are influenced by the nearby sillimanite segregation. Two possible mechanisms of pseudomorph formation suggested by the observed textural relations are shown in Figure 4: (a) the muscovite-free mantle of the sillimanite segregation grew around the staurolite poikiloblast before much staurolite had broken down so that most of the staurolite dissolved in a muscovite-free region or; (b) the muscovite-free mantle of the sillimanite segregation grew over a muscovite-rich pseudomorph, converting the muscovite in the pseudomorph to biotite and plagioclase.

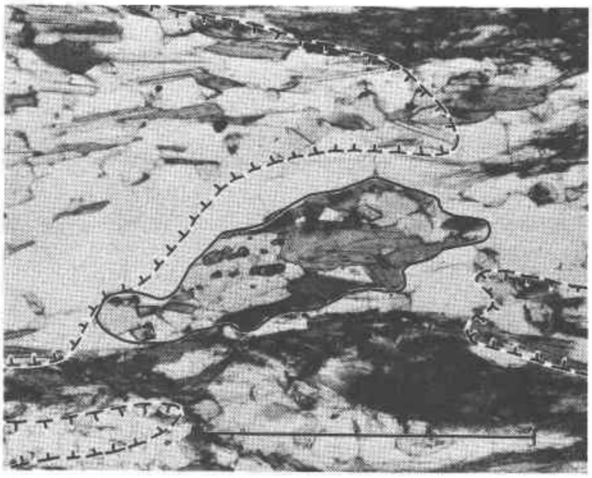

Fig. 2. Muscovite-free, biotite-rich, plagioclase-rich pseudomorph after staurolite (52% biotite, 38% plagioclase, 10% quartz). The pseudomorph boundary is shown by a solid line. Light gray grains are stained plagioclase. High relief grains within plagioclase in the pseudomorph are staurolite remnants. The matrix/muscovite-free mantle boundary is marked by the dashed line. The tick marks are on the matrix side of the line. The scale bar is 1 mm.

If the muscovite-free mantle of a sillimanite segregation grew around a staurolite poikiloblast, as shown in Figure 4a, the staurolite would be surrounded by a muscovite-free region which contains biotite, plagioclase, quartz, and ilmenite. The local reaction which takes place when a staurolite poikiloblast dissolves under local equilibrium, steady-state conditions while enclosed by biotite, plagioclase, quartz and ilmenite can be calculated by solving the system of equations shown in Figure 5 (see Foster, 1981, p. 261–264 for derivation). The first three rows of the square matrix represent the Gibbs–Duhem equations of the muscovite-free mantle phases biotite, plagioclase and ilmenite. These equations provide constraints on the chemical potential gradients in the mantle that govern diffusion to or from the segregations. The components SiO_2 and H_2O are not included in the Gibbs–Duhem equations because their chemical potential gradients are fixed at zero by the presence of quartz and a water-rich fluid phase in all domains of the rock. The next seven rows of the square matrix are conservation equations that relate the fluxes of FeO, $NaO_{0.5}$, MgO, $AlO_{1.5}$, $KO_{0.5}$, CaO, and TiO_2 in the mantle around the staurolite to the

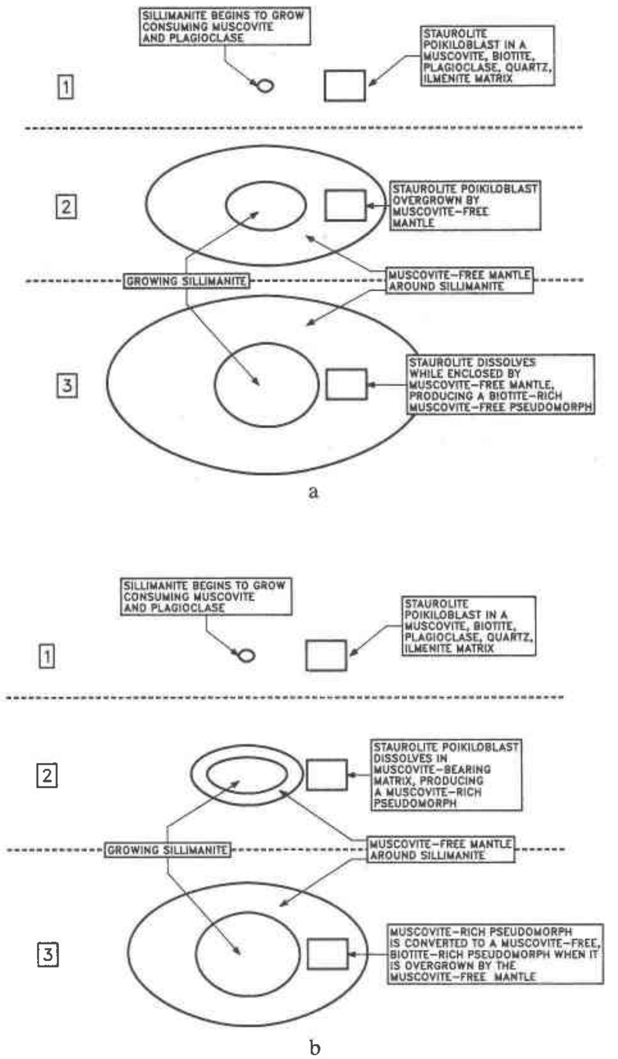

Fig. 4. Mechanisms for the development of muscovite-free, biotite-rich, plagioclase-rich pseudomorphs.

amounts of those components produced or consumed by the sum of the reactions which take place in the pseudomorph. The last two rows represent conservation equations for SiO_2 and H_2O, respectively. These two equations are used to calculate the amount of quartz and water that take part in the reaction. The mineral compositions used in this study are given in Table 1. They are from specimen RA66N (Foster, 1977a). Manganese and zinc were ignored because they are only important in incongruent reactions involving garnet and staurolite (Foster, 1977a).

The relative thermodynamic diffusion coefficients (phenomenological coefficients) used in this study are those derived by Foster (1981) for a SiO_2-fixed reference frame. They are $AlO_{1.5} = 5.9$, $FeO = 2.6$, $MgO = 1.8$, $KO_{0.5} = 1.0$, $NaO_{0.5} = 0.9$, $TiO_2 = 0.4$ and $CaO = 0.2$. These values were calculated from the observed modes, volumes, and mineral compositions in sillimanite segregations and muscovite-rich pseudomorphs after staurolite using a weighted least squares procedure (Foster, 1981, p. 265–267). This method gives the set of coefficients that best fit the observed data in both types of segregations. To illustrate the sensitivity of the pseudomorph models to the diffusion coefficients, test calculations were made using values for the aluminum coefficient from 0.1 to 15. The other coefficients were held constant at the optimum values given above. The configuration chosen for the test was a staurolite poikiloblast (71% staurolite, 29% quartz by volume) dissolving in a matrix of biotite, muscovite, plagioclase, quartz and ilmenite. The results are shown in Figure 6. It gives the molar stoichiometric coefficients (R_K) for the net reaction in the staurolite pseudomorph when one mole of staurolite is dissolved ($R_S = -1.0$). The minerals most sensitive to changes in the aluminum coefficient are quartz and muscovite. Biotite, plagioclase and ilmenite are more sensitive to the iron, sodium and titanium coefficients, respectively. The heavy portion of the quartz and muscovite curves show the range of stoichiometric coefficients that would produce a ratio of quartz to muscovite which lies within one standard deviation of the mean value in specimen RA66N. The mean and standard deviation were determined by point counting 27 muscovite-rich pseudomorphs. Note that the values for the aluminum coefficient that produce acceptable results lie within the standard deviation about the mean given by Foster (1981). Generally, variation of the diffusion coefficient for any component within the standard deviations given in Figure 4 of Foster (1981) does not cause drastic changes in the modeled textures.

An SiO_2-fixed reference frame was chosen for the study because quartz is present throughout the rock, fixing the chemical potential gradient of SiO_2 at zero for constant temperature and pressure. Therefore, an SiO_2-fixed reference frame should be equivalent to an inert marker reference frame if cross terms involving SiO_2 in the inert marker diffusion coefficients are negligible. The equivalence of the SiO_2-fixed and inert marker reference frames in the vicinity of muscovite-rich pseudomorphs has been demonstrated by Foster (1981, Fig. 3, p. 265)[1].

For the model, I assume that the system is always in local equilibrium ($\Sigma \nu_i \nabla \mu_i = 0$), open to a water-rich fluid which fixes μ_{H_2O}, and that the mineral compositions and thermodynamic diffusion coefficient ratios are constant throughout the rock during the growth of the segregations. In addition, sinks or sources due to compositional changes in the fluid along grain boundaries are assumed to be negligible so that the system approximates a steady state ($\partial c_i/\partial t \cong 0$ in Equation (7), Foster, 1981, p. 262). The values of four of the terms in the solution to the equations in Figure 5 are given in the first row of Table 2. They give

[1] Note: the label of the vertical axis of Fig. 3 in Foster (1981) should read ($-V_i/V_{KO\ 0.5}$) rather than ($V_i/V_{KO\ 0.5}$).

$$
\begin{pmatrix}
\nu_1^B & \nu_2^B & \nu_3^B & \nu_4^B & \nu_5^B & \nu_6^B & \nu_7^B & 0 & 0 & 0 & 0 & 0 \\
\nu_1^P & \nu_2^P & \nu_3^P & \nu_4^P & \nu_5^P & \nu_6^P & \nu_7^P & 0 & 0 & 0 & 0 & 0 \\
\nu_1^I & \nu_2^I & \nu_3^I & \nu_4^I & \nu_5^I & \nu_6^I & \nu_7^I & 0 & 0 & 0 & 0 & 0 \\
L_{11} & 0 & 0 & 0 & 0 & 0 & 0 & \nu_{1B} & \nu_{1P} & \nu_{1I} & 0 & 0 \\
0 & L_{22} & 0 & 0 & 0 & 0 & 0 & \nu_{2B} & \nu_{2P} & \nu_{2I} & 0 & 0 \\
0 & 0 & L_{33} & 0 & 0 & 0 & 0 & \nu_{3B} & \nu_{3P} & \nu_{3I} & 0 & 0 \\
0 & 0 & 0 & L_{44} & 0 & 0 & 0 & \nu_{4B} & \nu_{4P} & \nu_{4I} & 0 & 0 \\
0 & 0 & 0 & 0 & L_{55} & 0 & 0 & \nu_{5B} & \nu_{5P} & \nu_{5I} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & L_{66} & 0 & \nu_{6B} & \nu_{6P} & \nu_{6I} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & L_{77} & \nu_{7B} & \nu_{7P} & \nu_{7I} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \nu_{8B} & \nu_{8P} & \nu_{8I} & \nu_{8Q} & \nu_{8W} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \nu_{9B} & \nu_{9P} & \nu_{9I} & \nu_{9Q} & \nu_{9W}
\end{pmatrix}
\cdot
\begin{pmatrix}
(\nabla\mu_1)_x \cdot A/R_S \\
(\nabla\mu_2)_x \cdot A/R_S \\
(\nabla\mu_3)_x \cdot A/R_S \\
(\nabla\mu_4)_x \cdot A/R_S \\
(\nabla\mu_5)_x \cdot A/R_S \\
(\nabla\mu_6)_x \cdot A/R_S \\
(\nabla\mu_7)_x \cdot A/R_S \\
R_B/R_S \\
R_P/R_S \\
R_I/R_S \\
R_Q/R_S \\
R_W/R_S
\end{pmatrix}
=
\begin{pmatrix}
0 \\ 0 \\ 0 \\ -\nu_{1S} \\ -\nu_{2S} \\ -\nu_{3S} \\ -\nu_{4S} \\ -\nu_{5S} \\ -\nu_{6S} \\ -\nu_{7S} \\ -\nu_{8S} \\ -\nu_{9S}
\end{pmatrix}
$$

A = The area of a sphere of radius x which encloses all or part of a segregation.

L_{ij} = The thermodynamic diffusion coefficient which relates the flux of i to the chemical potential gradient of j.

R_K = The stoichiometric coefficient of phase K for the net reaction within the volume of rock enclosed by surface A.

$(\nabla\mu_i)_x$ = The chemical potential gradient of component i evaluated at a distance x from the center of a segregation.

$\nu_i^k = \nu_{ik}$ = The stoichiometric coefficient of component i in mineral k.

Fig. 5. Matrix equation to solve for the chemical potential gradients and stoichiometric coefficients around staurolite (S) dissolving in a biotite (B), plagioclase (P), ilmenite (I), quartz (Q) mantle saturated with a water-rich phase (W). Components 1, 2, 3, 4, 5, 6, 7, 8, 9, are FeO, $NaO_{0.5}$, MgO, $AlO_{1.5}$, $KO_{0.5}$, CaO, TiO_2, SiO_2, and H_2O, respectively.

the net amounts of biotite, plagioclase, ilmenite, and quartz produced (−) or consumed (+) when 1 mole of staurolite dissolves ($R_S = -1$). The net reaction (in moles) among the solid phases given by the calculation is:

$$1.0 \text{ staurolite} + 5.66 \text{ quartz} + 0.11 \text{ ilmenite} \rightarrow 1.33 \text{ biotite} + 2.23 \text{ plagioclase} \quad (1)$$

This reaction consumes staurolite and quartz in a volume ratio of 4.4 to 1. Because the volume percent of quartz in staurolite poikiloblasts ranges from 25–30% in the rocks under consideration, the staurolite is entirely consumed by the reaction before the quartz is used up. The reaction consumes staurolite and ilmenite in a volume ratio of 63 to 1; a few ilmenite grains in a poikiloblast will allow ilmenite to persist when the staurolite is consumed. The resulting pseudomorph consists of the biotite and plagioclase produced by Reaction (1) plus the few percent poikiloblastic quartz and small amount of ilmenite not used by Reaction (1). If ilmenite is entirely consumed by Reaction (1) an ilmenite-free mantle will develop around the staurolite. The modes, morphology, and local reaction calculated by the model for the texture formed when

Table 1. Molecular formulas of minerals used in this study

	Fe*	Na	Mg	Al	Si	K	Ca	Ti	H_2O
Staurolite	3.204	0.000	0.412	17.577	7.731	0.000	0.000	0.104	2
Biotite	2.766	0.058	1.834	3.514	5.403	1.657	0.000	0.221	2
Muscovite	0.115	0.323	0.085	5.630	6.146	1.572	0.000	0.050	2
Plagioclase	0.000	0.769	0.000	1.221	2.779	0.002	0.219	0.000	0
Ilmenite	1.960	0.000	0.000	0.000	0.000	0.000	0.000	2.018	0
Quartz	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0
Sillimanite	0.000	0.000	0.000	2.000	1.000	0.000	0.000	0.000	0

*All iron reported as FeO

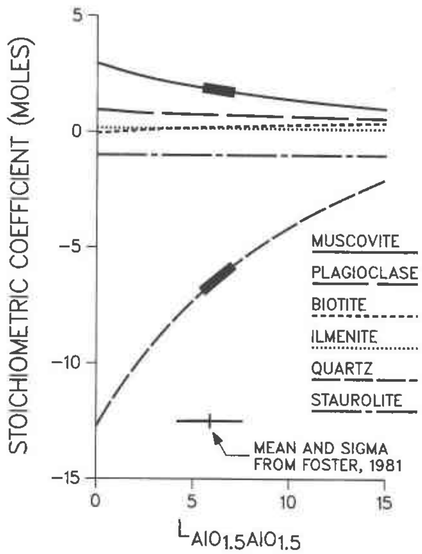

Fig. 6. Stoichiometric coefficients (R_K) calculated by the model for staurolite dissolving in a matrix of muscovite, biotite, plagioclase, quartz and ilmenite as a function of the aluminum diffusion coefficient. The heavy portion of the muscovite and the quartz curves show where the quartz to muscovite ratio in the model is within one standard deviation of the observed ratio. The mean and standard deviation of the aluminum diffusion coefficient calculated by Foster (1981) is also shown.

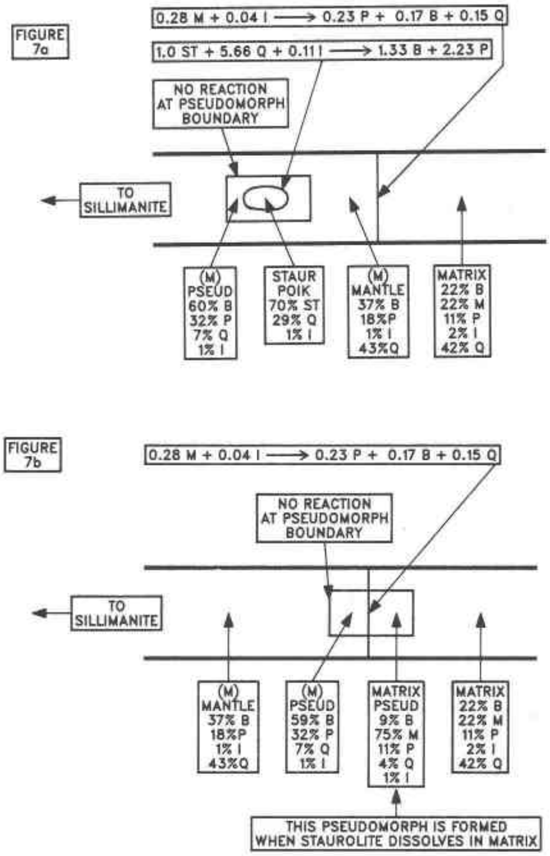

Fig. 7. Local reactions and mineral modes calculated by the model for the formation of muscovite-free, biotite-rich, plagioclase-rich pseudomorphs after staurolite. (M) stands for muscovite-free. M=muscovite, B=biotite, P=plagioclase, I=ilmenite, Q=quartz, St=staurolite

a staurolite poikiloblast containing 70% staurolite, 29% quartz and 1% ilmenite has been partially replaced are given in Figure 7a. Note that the mineral modes for the pseudomorph predicted by the model are similar to those of the muscovite-free, biotite-rich, plagioclase-rich pseudomorph shown in Figure 2.

The $(\nabla\mu_i)_x \cdot A/R_S$ terms in the solution to the equations in Figure 5 are tabulated in the first row of Table 3. If these terms are multiplied by their respective diffusion coefficients they give the net amount of each component required to diffuse to or from the dissolving staurolite to balance Reaction (1). A negative value in Table 3 means the component is removed from the reaction site by mass transfer through the region around the staurolite. A positive value means the component is supplied to the reaction by transport through the region around the staurolite.

If the muscovite-free mantle of a sillimanite segregation grew over a pre-existing muscovite-rich staurolite pseudomorph, as shown in Figure 4b, the muscovite-rich pseudomorph contains the same phases as the muscovite-bearing matrix. Therefore, the local reaction at the muscovite-free mantle/muscovite-rich pseudomorph boundary can be calculated by the same method Foster (1981, p.

Table 2. Stoichiometric coefficient ratios (R_K/R_S) for staurolite reactions in four types of sillimanite segregation mantles

	R_B/R_S	R_P/R_S	R_I/R_S	R_M/R_S	R_Q/R_S	reaction number
(M) mantle	-1.33	-2.23	0.11	——	5.66	(1)
(MP) mantle	-1.53	——	0.16	——	0.53	(3)
(MPI) mantle	-1.47	——	——	——	0.23	(4)
(P) mantle	-0.14	——	-0.15	-2.02	5.39	(6)

Table 3. Chemical potential gradient terms ($(\nabla \mu_i)_x \cdot A/R_S$) for reactions in Table 2

component	FeO	$NaO_{0.5}$	MgO	$AlO_{1.5}$	$KO_{0.5}$	CaO	TiO_2	reaction number
(M) mantle	0.10	1.92	1.12	-1.73	2.21	2.87	-0.10	(1)
(MP) mantle	0.27	0.10	1.31	-2.08	2.53	0.00	-0.26	(3)
(MPI) mantle	0.33	0.09	1.26	-2.11	2.44	0.00	0.58	(4)
(P) mantle	-0.88	0.71	0.01	-0.98	3.39	0.00	0.85	(6)

Table 3.

267–269) used for the muscovite-free mantle/matrix boundary of a sillimanite segregation. The reaction is:

$$0.28 \text{ muscovite} + 0.04 \text{ ilmenite} \rightarrow 0.17 \text{ biotite} + 0.23 \text{ plagioclase} + 0.15 \text{ quartz} \quad (2)$$

The major differences between the muscovite-rich pseudomorph and muscovite bearing matrix that will affect the model are the mineral modes. When Reaction (2) consumes matrix of the composition shown in Figure 7, it creates a muscovite-free mantle with a composition of 37% biotite, 18% plagioclase, 43% quartz and 1% ilmenite (see Foster, 1981, p. 269 for calculation method). If Reaction (2) consumes a muscovite-rich pseudomorph of the composition shown in Figure 7b, it creates a muscovite-free pseudomorph with a composition of 59% biotite, 32% plagioclase, 7% quartz and less than 1% ilmenite. If Reaction (2) uses up all of the ilmenite in the pseudomorph an ilmenite-free pseudomorph will form. The texture is still distinct after it is overgrown by the muscovite-free mantle because the proportions of biotite, quartz, plagioclase and ilmenite are different in the portions of the mantle formed from the muscovite-bearing matrix. The modes, morphology, and local reactions calculated by the model for the texture produced when a muscovite-rich pseudomorph has been overgrown by the muscovite-free mantle of a sillimanite segregation are shown in Figure 7b. The material transport through the mantle and matrix can be calculated from the chemical potential gradient terms given in Table 2 of Foster (1981).

Note that the modes of the minerals in the muscovite-free pseudomorph in Figure 7b are nearly identical to those of the muscovite-free pseudomorph in Figure 7a. If muscovite and staurolite are entirely consumed, it would not be possible to distinguish the two cases on the basis of the mineral modes from the resulting pseudomorph.

Biotite-rich, muscovite-free, plagioclase-free pseudomorphs

The association of muscovite-free, plagioclase-free pseudomorphs with muscovite-free, plagioclase-free mantles of sillimanite segregations suggests that formation of these pseudomorphs is also related to the growth of sillimanite. Four possible mechanisms for the formation of this texture are suggested by the observed relations: (1) the plagioclase-free and muscovite-free mantles of a sillimanite segregation grew around a staurolite poikiloblast before much staurolite had broken down so that the staurolite dissolved in a muscovite-free and plagioclase-free mantle; (b) the muscovite-free, plagioclase-free mantle of a sillimanite segregation grew over a muscovite-free, biotite-rich pseudomorph produced by one of the mechanisms shown in Figure 4; (c) the plagioclase-free mantle of a sillimanite segregation grew around a staurolite poikiloblast which then dissolved, producing a plagioclase-free, muscovite-rich psedomorph which was overgrown by a muscovite-free, plagioclase-free mantle; (d) a plagioclase-free mantle of a sillimanite segregation grew over a plagioclase-bearing, muscovite-rich pseudomorph converting it to a plagioclase-free, muscovite-rich pseudomorph which in turn was consumed by a plagioclase-free, muscovite-free mantle of a sillimanite segregation. The type of pseudomorph formed by mechanism (a) can be modeled by calculating the local reaction if staurolite is allowed to dissolve in a biotite, quartz, ilmenite mantle. This can be accomplished by deleting the plagioclase terms in the matrix equation shown in Figure 5 and solving for the remaining unknowns. The stoichiometric coefficient ratios for this reaction (3) are given in row two of Table 2. The chemical potential gradient terms, which can be used to calculate the net mass transfer produced by Reaction (3), are given in row 2 of Table 3. If there is little or no ilmenite in the staurolite poikiloblast, Reaction (3) should form an ilmenite-free mantle by consuming ilmenite in the region surrounding the poikiloblast. The local reaction involving staurolite inside of this mantle can be calculated by removing the ilmenite and plagioclase terms from the matrices in Figure 5. The stoichiometric coefficient ratios and chemical potential gradient terms for this reaction (4) are given in row three of Table 2 and Table 3. The morphology, local reactions, and mineral modes in the pseudomorph calculated by the model for mechanism (a) are shown in Figure 8a and 8b. Figure 8a shows the configuration if the sillimanite segregation has a muscovite free mantle. Figure 8b shows the configuration if the sillimanite segregation has a plagioclase-free mantle (Foster, 1982).

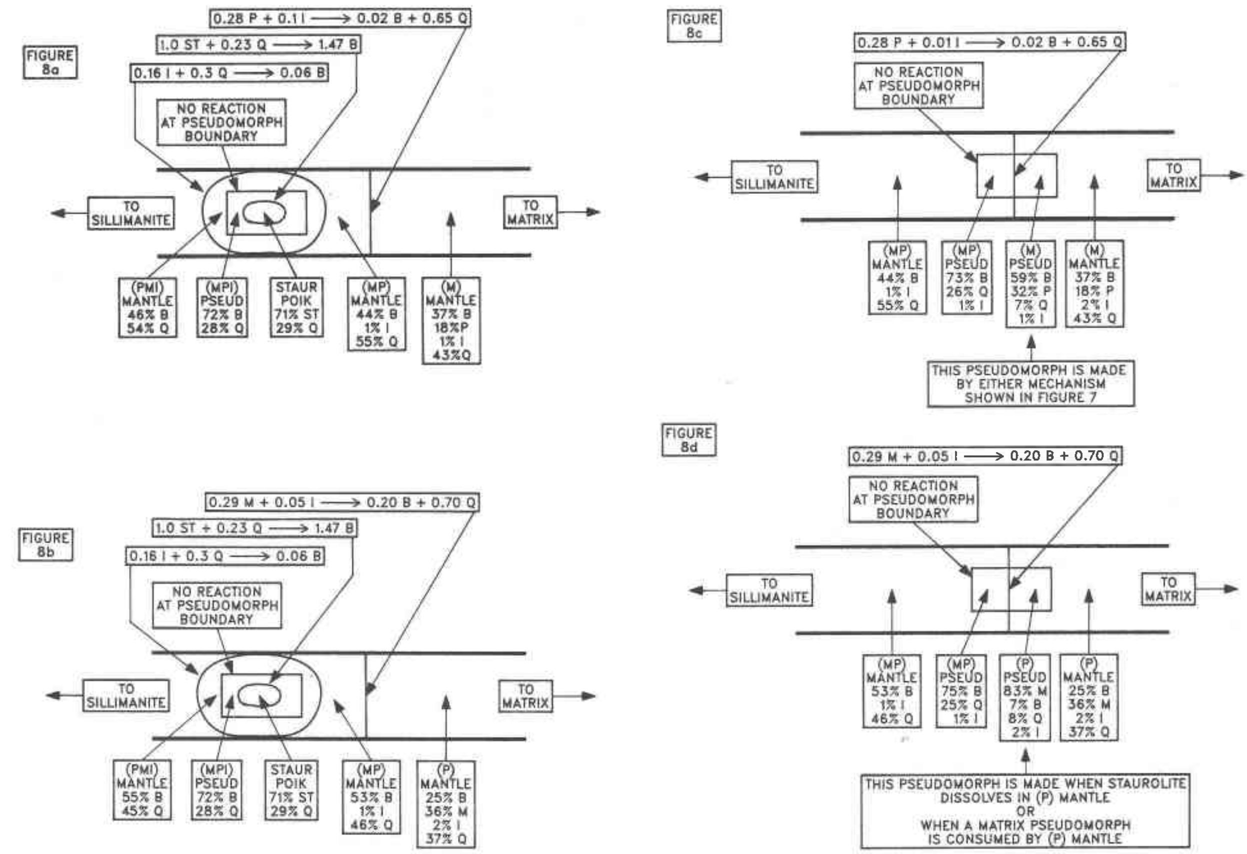

Fig. 8. Local reactions and mineral modes calculated by the model for the formation of muscovite-free, plagioclase-free, biotite-rich pseudomorphs after staurolite. Mineral abbreviations same as in Fig. 7. Minerals not present are shown in parentheses.

The type of pseudomorph expected to be formed by mechanism (b) can be modeled by using Reaction (D) of Foster (1981):

$$0.28 \text{ plagioclase} + 0.01 \text{ ilmenite} \rightarrow 0.02 \text{ biotite} + 0.65 \text{ quartz} \quad (5)$$

This is the reaction calculated by the model for the boundary between the muscovite-free mantle and the muscovite-free, plagioclase-free mantle of a sillimanite segregation. If it consumes a plagioclase-rich, biotite-rich, muscovite-free pseudomorph, the plagioclase will be eliminated and replaced by biotite giving a texture with 73% biotite, 26% quartz and 1% ilmenite. The morphology, modes, and local reactions calculated by the model for this type of pseudomorph are given in Figure 8c. The mass transfer through the mantles produced by Reaction (5) can be calculated from the chemical potential gradient terms given in Table 2 of Foster (1981).

The type of pseudomorph produced when a staurolite poikiloblast dissolves within a plagioclase-free mantle (mechanism c) can be calculated by replacing the plagioclase terms with muscovite terms in the matrices shown in Figure 5. The solution to these equations gives the stoichiometric coefficient ratios and chemical potential gradient terms for Reaction (6). They are tabulated in row 4 of Table 2 and Table 3. Reaction (6) will produce a pseudomorph containing 83% muscovite, 7% biotite, 8% quartz and 2% ilmenite from a poikiloblast which contains 71% staurolite, 29% quartz. This pseudomorph can be converted to a biotite-rich pseudomorph if it is overgrown by the muscovite-free, plagioclase-free mantle of a sillimanite segregation. The reaction calculated by Foster (1982) at the interface between the plagioclase-free mantle/muscovite-free, plagioclase-free mantle of a sillimante segregation is:

$$0.29 \text{ muscovite} + 0.05 \text{ ilmenite} \rightarrow 0.20 \text{ biotite} + 0.70 \text{ quartz} \quad (7)$$

This reaction converts the muscovite-rich pseudomorph produced by Reaction (6) to one with biotite, quartz, and a small amount of ilmenite as shown in Figure 8d. A photomicrograph of this type of pseudomorph is shown in Figure 3.

The type of pseudomorph produced when a preexisting muscovite-rich, plagioclase-bearing pseudomorph is overgrown by a plagioclase-free mantle of a sillimanite segregation (mechanism d) can be modeled by using the matrix/plagioclase-free mantle reaction calculated by Foster (1982):

$$0.004 \text{ biotite} + 0.055 \text{ plagioclase} \rightarrow 0.013 \text{ muscovite} + 0.01 \text{ ilmenite} + 0.94 \text{ quartz} \quad (8)$$

This reaction would convert a pseudomorph containing 75% muscovite, 9% biotite, 11% plagioclase, 4% quartz and 1% ilmenite to one with 83% muscovite, 7% biotite, 8% quartz and 2% ilmenite. This texture is essentially the same as the one produced by Reaction (6). If it is overgrown by a muscovite-free, plagioclase-free mantle, Reaction (7) will convert it to the biotite-rich, muscovite-free, plagioclase-free pseudomorph shown in Figure 8d. The mass transfer through the mantles required by Reactions (7) and (8) can be calculated from the chemical potential gradients given in Table 1 of Foster (1982).

Note that the calculated modes for the biotite-rich pseudomorphs shown in Figure 8a, b, c and d are nearly identical. It is not possible to distinguish between the various mechanisms on the basis of mineral modes.

Discussion

The main factors that determine the most common pseudomorph are the proportions of staurolite, muscovite, and plagioclase in the rock when sillimanite begins to grow. If the ratio of muscovite to staurolite and the ratio of plagioclase to staurolite is relatively high, the mantles that develop around growing sillimanite will not be very thick, permitting most of the staurolite in the rock to dissolve in a matrix of muscovite, biotite, plagioclase and quartz (±ilmenite). This process will produce muscovite-rich pseudomorphs which contain several percent plagioclase, biotite, and quartz (±ilmenite) such as the one shown in Figure 1. Only staurolites which lie next to sillimanite nucleation sites will form biotite-rich pseudomorphs via one of the reaction mechanisms discussed in the previous section.

In rocks where the muscovite to staurolite ratio is low and the plagioclase to staurolite ratio is high, thick muscovite-free mantles around sillimanite should develop after a relatively small amount of sillimanite growth. These mantles would enclose most staurolite poikiloblasts early in the breakdown reaction, permitting the staurolite to dissolve in a muscovite-free mantle as shown in Figures 4a and 7a. The portion of staurolite pseudomorphs that had formed in the matrix would initially be muscovite-rich. These would be converted to muscovite-free pseudomorphs if they were consumed by a muscovite-free mantle as shown in Figures 4b and 7b. The dominant pseudomorph in these rocks would be biotite-rich and plagioclase-rich, similar to the one shown in Figure 2. A few muscovite-rich pseudomorphs could be located in regions of the rock which had not been overgrown by muscovite-free mantles.

Rocks with low muscovite to staurolite ratios and low plagioclase to staurolite ratios would develop thick muscovite-free, plagioclase-free mantles before much staurolite had broken down to sillimanite. Much of the staurolite in the rock would then dissolve in a muscovite-free, plagioclase-free environment, producing biotite-rich and quartz-rich (±ilmenite) pseudomorphs as shown in Figures 8a and 8b. Muscovite-rich or plagioclase-rich pseudomorphs which formed prior to being enclosed by a muscovite-free, plagioclase-free mantle would be converted to biotite plus quartz pseudomorphs (±ilmenite) by one of the mechanisms shown in Figures 8c and 8d. The predominant pseudomorph in these rocks would be biotite-rich and quartz-rich. A few pseudomorphs with plagioclase and/or muscovite might exist in regions that were not consumed by the plagioclase-free, muscovite-free mantles.

Conclusions

The results of this study show that the model of Foster (1981), originally proposed for muscovite-rich pseudomorphs after staurolite, can be used to quantitatively model biotite-rich pseudomorphs as well. The model suggests: (1) muscovite-rich pseudomorphs containing small amounts of biotite, plagioclase and quartz form if a staurolite poikiloblast dissolves in a matrix where muscovite, biotite, plagioclase, and quartz are present (Foster, 1981); (2) muscovite-rich, plagioclase-free pseudomorphs containing small amounts of biotite and quartz form when the plagioclase-free mantle of a sillimanite segregation consumes a matrix pseudomorph or when a staurolite poikiloblast dissolves while surrounded by the plagioclase-free mantle of a sillimanite segregation; (3) biotite-rich, plagioclase-rich, muscovite-free pseudomorphs containing quartz form when a matrix pseudomorph is consumed by the muscovite-free mantle of a sillimanite segregation or when a staurolite poikiloblast dissolves while surrounded by the muscovite-free mantle of a sillimanite segregation; (4) biotite-rich, plagioclase-free, muscovite-free pseudomorphs containing quartz form when a pseudomorph is consumed by the muscovite-free, plagioclase-free mantle of a sillimanite segregation or when a staurolite poikiloblast dissolves in the muscovite-free, plagioclase-free mantle of a sillimanite segregation. According to the model, all four types of pseudomorphs may be present in one rock. The predominant pseudomorph type should depend upon the proportions of muscovite, plagioclase and staurolite at the initiation of staurolite breakdown. In rocks with abundant muscovite and plagioclase, muscovite-rich, plagioclase-bearing pseudomorphs should predominate because most of the pseudomorphs will be in the matrix of the rock. Rocks which are rich in muscovite and poor in plagioclase should primarily have muscovite-rich, plagiclase-free pseudomorphs because most pseudomorphs will be enclosed by the thick plagioclase-free mantles of sillimanite segregations. In rocks poor in muscovite but rich in plagioclase the predominant pseudomorph type should be biotite-rich, plagioclase-rich, muscovite-free because most pseudomorphs will be enclosed by the thick muscovite-free mantle around sillimanite segregations. Rocks poor in both muscovite and plagioclase should have pseudomorphs which are predominantly biotite-rich and quartz-rich because most pseudomorphs will be enclosed by the thick muscovite-free, plagioclase-free mantles around sillimanite segregations.

Comparison of the modeled textures with those found in specimens from the lower sillimanite zone near Rangeley, Maine shows that all four types of pseudomorph textures are present. Pseudomorphs which are muscovite-free or plagioclase-free are uncommon in the Rangeley rocks because the mantles around the sillimanite segregations are thin, rarely enclosing staurolite pseudomorphs. Preliminary studies (Foster, 1977b, and unpublished data) suggest that models of this type may also be used to interpret other types of prograde and retrograde pseudomorphs such as those described by Kwak (1974) and Bailes (1980). This indicates that irreversible thermodynamic models have the potential to become valuable tools for the petrologist trying to interpret complex reaction textures and the processes which form them.

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References

Bailes, A. H. (1980) Geology of the File Lake Area. Manitoba Department of Energy and Mines Geological Report 78-1.

Carmichael, D. M. (1969) On the mechanism of prograde metamorphic reactions in quartz-bearing pelitic rocks. Contributions to Mineralogy and Petrology, 20, 244–267.

Fisher, G. W. (1973) Non-equilibrium thermodynamics as a model for diffusion-controlled metamorphic processes. American Journal of Science, 273, 897–924.

Fisher, G. W. (1975) The thermodynamics of diffusion-controlled metamorphic processes. In A. R. Cooper and A. H. Heuer, Eds., Mass Transport Phenomena in Ceramics, p. 111–122. Plenum, New York.

Fisher, G. W. (1977) Nonequilibrium thermodynamics in metamorphism. In D. G. Fraser, Ed., Thermodynamics in Geology, p. 381–403. Riedel, Boston.

Foster, C. T., Jr. (1977a) Mass transfer in sillimanite-bearing pelitic schists near Rangeley, Maine. American Mineralogist, 62, 727–746.

Foster, C. T., Jr. (1977b) Staurolite pseudomorph textures (abstr.) Geological Society of America, Abstracts with Programs, 9, 979.

Foster, C. T., Jr. (1981) A thermodynamic model of mineral segregations in the lower sillimanite zone near Rangeley, Maine. American Mineralogist, 66, 260–277.

Foster, C. T., Jr. (1982) Textural variation of sillimanite segregations. Canadian Mineralogist, 20, 379–392.

Guidotti, C. V. (1968) Prograde muscovite pseudomorphs after staurolite in the Rangeley–Oquossoc area, Maine. American Mineralogist, 53, 1368–1376.

Guidotti, C. V. (1970) The mineralogy and petrology of the transition from the lower to upper sillimanite zone in the Oquossoc area, Maine. Journal of Petrology, 11, 277–336.

Guidotti, C. V. (1974) Transition from staurolite to sillimanite zone, Rangeley Quadrangle, Maine. Geological Society of America Bulletin, 85, 475–490.

Hietanen, A. (1968) Belt Series in the region around Snow Peak and Mallard Peak, Idaho. U. S. Geological Survey Professional Paper 344-E.

Kwak, T. A. P. (1974) Natural staurolite breakdown reactions at moderate to high pressures. Contributions to Mineralogy and Petrology, 44, 57–80.

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