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TEXTURAL VARIATION OF SILLIMANITE SEGREGATIONS

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ABSTRACT

A local-equilibrium, irreversible-thermodynamics model was used to predict variations in sillimanite segregation textures as a function of matrix composition in pelitic schist. Relative coefficients of thermodynamic diffusion, that were derived from rocks in the lower sillimanite zone near Rangeley, Maine, are used with Gibbs–Duhem relations and conservation equations; they give the sequence of mantles, mineral modes in each mantle, relative chemical potential gradients and size ot segregation that is to be expected as sillimanite grows in a matrix of muscovite, biotite, plagioclase, quartz and ilmenite under conditions of constant $\mu(H_2O)$. Rocks with a muscovite-rich, biotite-rich, plagioclase-poor matrix containing more than one percent ilmenite should have plagioclase-free segregations. If the same matrix were rich in plagioclase, however, muscovite-free segregations would be predicted. In rocks with less than a few tenths of one percent ilmenite, the segregations should be ilmenite-free. Segregation textures observed in thin section show features similar to those predicted by the model. This suggests that material transport under local equilibrium conditions is an important process in rocks with such textures.

Keywords: material transport, metamorphic segregation, thermodynamic models, sillimanite.

SOMMAIRE

Un modèle thermodynamique irréversible à équilibre local prédit les variations texturales des ségrégations de sillimanite dans des schistes pélitiques en fonction de la composition de la matrice. Les coefficients thermodynamiques relatifs de diffusion sont dérivés des roches de la zone à sillimanite inférieure des environs de Rangeley (Maine). Avec ces coefficients, les relations Gibbs–Duhem et les équations de conservation donnent la séquence des gaines minérales, leur composition modale, les gradients relatifs du potentiel chimique et la taille prédite pour la ségrégation lors de la croissance de la sillimanite dans une matrice de muscovite + biotite + plagioclase + quartz + ilménite à $\mu(H_2O)$ constant. Les roches à matrice riche en muscovite et biotite et pauvre en plagioclase, et qui contiennent plus de 1% d'ilménite, devraient donner des ségrégations sans plagioclase. Si toutefois la même matrice était riche en plagioclase, les ségrégations seraient sans muscovite. Si la roche ne contient que quelques dixièmes pour cent d'ilménite, les ségrégations seraient dépourvues d'ilménite. Les textures de ségrégation observées en lame mince ressemblent à celles que prédit le modèle; on en conclut que le transport de la matière en équilibre local est un processus important des roches montrant de telles textures.

(Traduit par la Rédaction)

Mots-clés: transport de la matière, ségrégation métamorphique, modèles thermodynamiques, sillimanite.

INTRODUCTION

Irreversible thermodynamic models of mineral segregations have the potential to become powerful tools for interpreting the complex textures that result from material transport during metamorphism. The theoretical framework for this approach has been laid by a number of authors over the past decade (Fisher 1973, 1975, 1977, 1978, Fisher & Lasaga 1981, Frantz & Mao 1976, 1979, Loomis 1976, Weare *et al.* 1976), but the technique has been tested quantitatively with textures from metamorphic rocks in a few instances only (Fisher 1975, Joesten 1977, Loomis 1976, Foster 1981). The purpose of this paper is to show that the model presented by Foster (1981) for the growth of sillimanite segregations in pelitic schist successfully predicts previously unrecognized variations in mineral modes in sillimanite segregations from the lower sillimanite zone near Rangeley, Maine.

The development of the sillimanite segregations has been attributed to the cation-exchange mechanism of reaction shown in Figure 1 (Foster 1977a). The segregations form when sillimanite nucleates and grows in a matrix of biotite, muscovite, plagioclase, quartz and ilmenite at the expense of staurolite located in other domains of the rock. The sillimanite segregation depicted in Figure 1 is a common type in these rocks. It is distinguished by a sillimanite-rich core with small amounts of ilmenite plus quartz and a mantle composed of biotite, plagioclase, ilmenite and quartz. On the basis

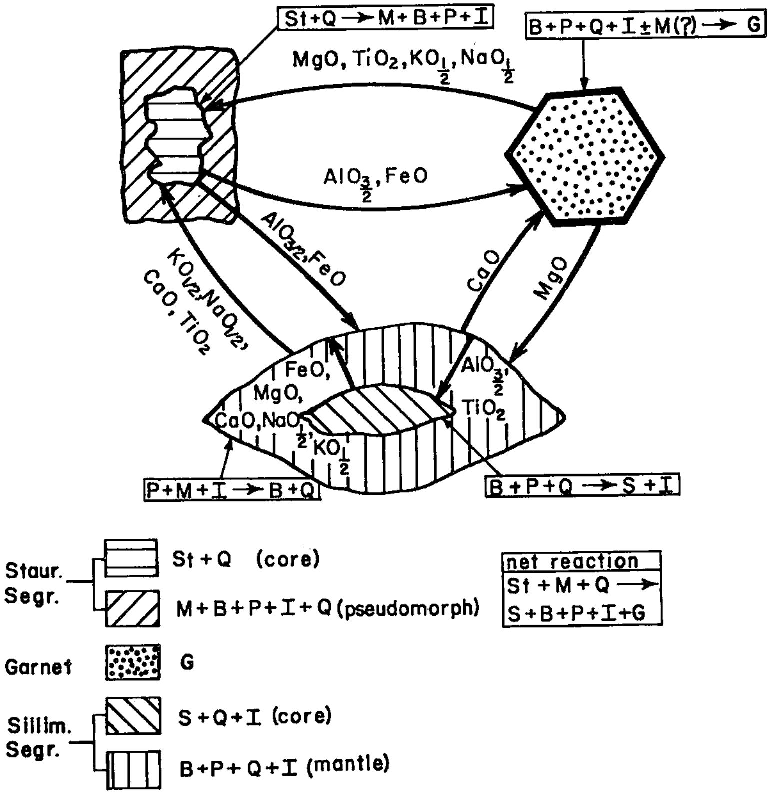


FIG. 1. Cation-exchange reaction mechanism for sillimanite-bearing rocks near Rangeley, Maine. Abbreviations: St staurolite, S sillimanite, G garnet, B biotite, M muscovite, P plagioclase, I ilmenite, Q quartz.

of an irreversible thermodynamic model of this texture, Foster (1976, 1981) suggested that other, less common types of segregations should be present, depending upon the proportions of matrix minerals. Examination of thin sections from the Rangeley region shows that the predicted variations are present.

REACTION CALCULATIONS

The net reaction that takes place when sillimanite nucleates and begins to grow under local equilibrium, steady-state conditions in a matrix of muscovite, biotite, plagioclase, quartz and ilmenite can be calculated by solving the system of equations shown in Figure 2 (see Foster 1981, p. 261-264, for the derivation). The first four rows represent the Gibbs–Duhem equations of the matrix phases biotite, muscovite, plagioclase and ilmenite. These equations provide constraints on the chemical potential gradients in the matrix that allow material to diffuse 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 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 matrix to the amounts of those components produced or consumed by the sum of the reactions that take place in the segregation. The last two rows represent conservation equations for SiO_2 and H_2O, respectively. These two equations are used to calculate the amounts of quartz and water that take part in reactions. The relative phenomenological coefficients (thermodynamic diffusion coefficients) used in this study are those derived by Foster (1981) for a SiO_2-fixed frame of reference. 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. The mineral compositions used in this study are from specimen RA66N

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

FIG. 2. Matrix equation to solve for relative gradients in chemical potential in the matrix around a sillimanite segregation and for the net reaction within the segregation. *A* is the area of a sphere of radius *x* that encloses all or part of a segregation. L_{ij} is the thermodynamic diffusion coefficient that relates the flux of *i* to the chemical potential gradient of *j*. R_K is the stoichiometric coefficient of phase *K* for the net reaction within the volume of rock enclosed by surface *A*. $(\nabla\mu_i)_x$ is the chemical potential gradient of component *i* evaluated at a distance *x* from the centre of a segregation; ν_i^k and ν_{ik} are the stoichiometric coefficient of component *i* in mineral *k*. B, M, P, I, Q, W and S stand for biotite, muscovite, plagioclase, ilmenite, quartz, water and sillimanite, respectively. Components, 1, 2, 3, 4, 5, 6, 7, 8 and 9 are FeO, $NaO_{0.5}$, MgO, $AlO_{1.5}$, $KO_{0.5}$, CaO, TiO_2, SiO_2 and H_2O, respectively.

(Foster 1977a). I assume that the system is always in local equilibrium ($\Sigma\mu_i\nu_i = O$), in a steady state ($\partial c_i/\partial t = 0$), open to a water-rich fluid that fixes $\mu(H_2O)$, and that the mineral compositions and ratios of phenomenological coefficients are constant throughout the rock during the growth of segregations. The solution to the equations in Figure 2 is given in Table 1 under the column labeled "matrix".

The first seven terms in this column can be used to compare the relative values of the chemical potential gradients in the matrix of the rock. These gradients are the force that drives diffusion, which supplies or removes the components produced or consumed by the sum of the local reactions in the sillimanite segregation. The last six terms in the solution to the equations in Figure 2 give the net number of moles of biotite, muscovite, plagioclase, quartz, ilmenite and water produced (+) or consumed (−) during the growth of one mole of sillimanite in the segregation. The net reaction among the solid phases given by the calculation is:

$$0.28 \text{ muscovite} + 0.05 \text{ plagioclase} + 0.01 \text{ ilmenite} \rightarrow 1.0 \text{ sillimanite} + 0.06 \text{ biotite} + 0.52 \text{ quartz} \quad (1)$$

This reaction consumes three phases that are present in the matrix: muscovite, plagioclase and ilmenite. If the matrix is homogeneous and the grain size small relative to the segregation diameter, the reaction will entirely use up one of these phases to produce a mantle around the sillimanite that lacks one of the matrix phases. The composition of the matrix determines what type of mantle develops. If the ratio of one phase (A) to another phase (B) in the matrix is smaller than the ratio of A to B used in the reaction, then A near the growing sillimanite will be entirely consumed before B, producing a mantle around the sillimanite lacking in A. In the case of reaction (1), three types of mantle are possible. A muscovite-free mantle is produced if the ratio (moles of muscovite per unit volume of matrix)/(moles of plagioclase per unit volume of matrix) is less than 0.28/0.05 and the

TABLE 1. RELATIVE CHEMICAL POTENTIAL GRADIENTS AND NET REACTIONS WITHIN SEGREGATIONS

	Matrix	(P)	(M)	(PM)	(MB)	(PMB)	(I)	(IP)	(IM)	(IPM)	(IMB)	(IPMB)
$(\nabla\mu_{FeO})_x \cdot A/R_s$	0.05	0.05	-0.09	-0.11	0.00	0.00	0.05	0.05	-0.10	-0.13	0.00	0.00
$(\nabla\mu_{NaO_{0.5}})_x \cdot A/R_s$	-0.14	-0.10	-0.24	-0.01	-0.29	0.00	-0.14	-0.10	-0.24	-0.01	-0.29	0.00
$(\nabla\mu_{MgO})_x \cdot A/R_s$	0.05	0.05	-0.11	-0.14	0.00	0.00	0.04	0.05	-0.10	-0.12	0.00	0.00
$(\nabla\mu_{AlO_{1.5}})_x \cdot A/R_s$	0.10	0.10	0.22	0.26	0.27	0.34	0.10	0.10	0.22	0.27	0.27	0.34
$(\nabla\mu_{KO_{0.5}})_x \cdot A/R_s$	-0.33	-0.35	-0.18	-0.22	0.00	0.00	-0.34	-0.35	-0.17	-0.20	0.00	0.00
$(\nabla\mu_{CaO})_x \cdot A/R_s$	-0.07	0.00	-0.36	0.00	-0.46	0.00	-0.07	0.00	-0.37	0.00	-0.46	0.00
$(\nabla\mu_{TiO_2})_x \cdot A/R_s$	-0.05	-0.05	0.09	0.11	0.00	0.00	0.00	0.00	-0.06	-0.07	-0.00	0.00
R_B/R_S	0.06	0.07	-0.11	-0.13	----	----	0.06	0.06	-0.10	-0.12	----	----
R_M/R_S	-0.28	-0.29	----	----	----	----	-0.27	-0.29	----	----	----	----
R_P/R_S	-0.05	----	-0.28	----	-0.35	----	-0.06	----	-0.29	----	-0.35	----
R_I/R_S	-0.01	-0.01	0.03	0.04	0.00	0.00	----	----	----	----	----	----
R_Q/R_S	0.52	0.43	0.38	-0.27	-0.01	-1.00	0.53	0.44	0.34	-0.34	-0.01	-1.00
R_W/R_S	0.43	0.45	0.22	0.27	0.00	0.00	0.43	0.45	0.20	0.25	0.00	0.00

ratio (moles of muscovite per unit volume of matrix)/(moles of ilmenite per unit volume of matrix) is less than 0.28/0.01. A plagioclase-free mantle is produced if the ratio (moles plagioclase per unit volume of matrix)/(moles muscovite per unit volume of matrix) is less than 0.05/0.28 and the ratio (moles plagioclase per unit volume of matrix)/(moles ilmenite per unit volume) is less than 0.05/0.01. An ilmenite-free mantle is formed if the ratio (moles ilmenite per unit volume of matrix)/(moles muscovite per unit volume of matrix) is less than 0.01/0.28 and the ratio (moles ilmenite per unit volume of matrix)/(mole plagioclase per unit volume of matrix) is less than 0.01/0.05.

MANTLE DEVELOPMENT

Plagioclase-free segregations

If plagioclase is the first mineral to be consumed by reaction (1), the reaction that takes place in the portion of the sillimanite segregation surrounded by the plagioclase-free (P) mantle is constrained by the Gibbs–Duhem relations of the phases in the (P) mantle and the conservation equations written among the remaining matrix phases and growing sillimanite. The net reaction in the portion of the segregation enclosed by the (P) mantle can be calculated by solving the system of equations created by deleting the Gibbs–Duhem equation for plagioclase (row three of the square matrix and right-hand-side column matrix), the plagioclase terms in the conservation equations (column ten of the square matrix) and the plagioclase reaction coefficient (R_p/R_s in the left-hand-side column matrix) in Figure 2. The solution is given under the column labeled (P) in Table 1. The reaction taking place in the portion of the segregation surrounded by the (P) mantle is given by the R_j/R_s terms in Table 1, column (P). The relative gradients in chemical potentials in the (P) mantle can be compared using the first seven terms in Table 1, column (P). The reaction that takes place among the solid phases in the part of the segregation enclosed by the (P) mantle is:

0.29 muscovite + 0.01 ilmenite → 1.0 sillimanite + 0.07 biotite + 0.43 quartz (2)

Because reactions (1) and (2) are not the same, there must be a reaction at the matrix/(P) mantle boundary that accounts for the difference. This reaction can be calculated by subtracting reaction (2) from reaction (1). It is:

0.05 plagioclase → 0.01 muscovite + 0.09 quartz .... (3)

The amount of each phase present in the (P) mantle can be calculated by computing the number of moles of each phase in the amount of matrix needed to supply 0.05 moles of plagioclase, and then subtracting the number of moles of reactants and adding the number of moles of products in reaction (3). The modes of the phases in the (P) mantle can be calculated by using molar volumes to convert from mole fraction to volume %.

A mantle lacking plagioclase and muscovite or a mantle lacking plagioclase and ilmenite will form when reaction (2) consumes one of the phases in the plagioclase-free mantle. If the muscovite/ilmenite molar ratio in the plagioclase-free mantle is less than 0.29/0.01, then a plagioclase–muscovite-free (PM) mantle will form. If the muscovite/ilmenite ratio is greater than 0.29/0.01, then an ilmenite–plagioclase-free (IP) mantle will form. The reaction that occurs in the portion of the segregation inside of the (PM) or (IP) mantle can be computed by removing the terms in the matrix equation in Figure 2 that represent the consumed phases, and then solving the equation for the chemical-potential-gradient terms in the new mantle and the coefficients for the net reaction in the portion of the segregation enclosed by the mantle lacking two matrix phases. The results of this calculation are given in Table 1 under the columns labeled (IP) and (PM). The reaction at the boundary between the (P) mantle and the (IP) or (PM) mantle can be calculated by subtracting the reaction coefficients in column (IP) or (PM) of Table 1 from the reaction coefficients in column (P) of Table 1. In the case of an (IP) mantle, the reaction at the (P) mantle/(IP) mantle boundary is:

0.01 ilmenite + 0.01 quartz → 0.01 biotite (4)

whereas in the case of a (PM) mantle the reaction at the (P) mantle/(PM) mantle boundary is:

0.29 muscovite + 0.05 ilmenite → 0.20 biotite + 0.70 quartz .... (5)

Reaction (4) or (5) can be used to calculate the mineral modes in the (IP) or (PM) mantle by subtracting or adding the reaction coefficients to the amount of (P) mantle that contains 0.29 moles of muscovite or 0.01 mole of ilmenite, and then converting from mole fraction to volume %. The volume of the (P) mantle can be calculated by subtracting the volume of (P) mantle consumed by reaction (4) or (5) from the volume of (P) mantle produced by reaction (3). The volume of (P) mantle produced by reaction (3) is determined by calculating the number of moles of each phase present in the volume of matrix containing 0.05 moles of plagioclase, subtracting or adding the number of moles of each phase consumed or produced during the conversion of matrix to (P) mantle by reaction (3), multiplying the number of moles of each phase by the approriate molar volume, and then summing the volumes of the phases in the region produced by the conversion of matrix to (P) mantle. The volume of (P) mantle consumed by reaction (4) or (5) is the volume of plagioclase-free mantle containing 0.01 moles of ilmenite or 0.29 moles of muscovite. The reaction in column (IP) or (PM) of Table 1 can be used to determine the type of mantle that forms when a third matrix phase has been consumed. In the case of the (IP) mantle, muscovite is the next phase to disappear, because it is the only phase consumed by the net reaction occurring in the part of the segregation surrounded by the (IP) mantle. The reaction at the (IP) mantle/(IPM) mantle boundary is:

0.29 muscovite → 0.18 biotite + 0.77 quartz .... (6)

It was calculated by subtracting the reaction in column (IPM) of Table 1 from the reaction given in column (IP).

In a segregation with a (PM) mantle, biotite will be used up to form a (PMB) mantle if the molar ratio of biotite/quartz in the (PM) mantle is less than 0.13/0.27, whereas quartz will be entirely consumed if the ratio is greater than 0.13/0.27, to form a (PMQ) mantle. The reaction at the (PM) mantle/(PMB) boundary is calculated by subtracting the reaction in column (PMB) from column(PM) in Table 1. It is:

0.13 biotite → 0.04 ilmenite + 0.73 quartz (7)

Because the relative coefficient of thermodynamic diffusion is unknown for SiO_2, a solution cannot be obtained for the net reaction inside a (PMQ) mantle. However, test calculations indicate that the reaction is relatively insensitive to the value of the SiO_2 coefficient: the relative value of the SiO_2 diffusion coefficient was varied from 0.1 to 10, and the reaction inside the (PMQ) mantle always consumed biotite and produced sillimanite and ilmenite. The modes of the (IPM) or (PMB) mantles may be calculated from the modes of the (IP) or (PM) mantles and reaction (6) or (7) in the same way they were calculated for the (P), (IP) and (PM) mantles. The volumes of the (IP) or (PM) mantle can be calculated from the mode of the (P) mantle and reactions (4) and (6) or (5) and (7).

The net reaction that takes place in the portion of a segregation surrounded by an (IPM) mantle consumes both quartz and biotite; a biotite-free mantle (IPMB) will form if the molar biotite/quartz ratio is less than 0.12/0.34, whereas a quartz-free (IPMQ) mantle will form if the ratio is larger than 0.12/0.34. The reaction at the (IPM) mantle/(IPMB) mantle boundary is computed from the columns (IPM) and (IPMB) in Table 1.

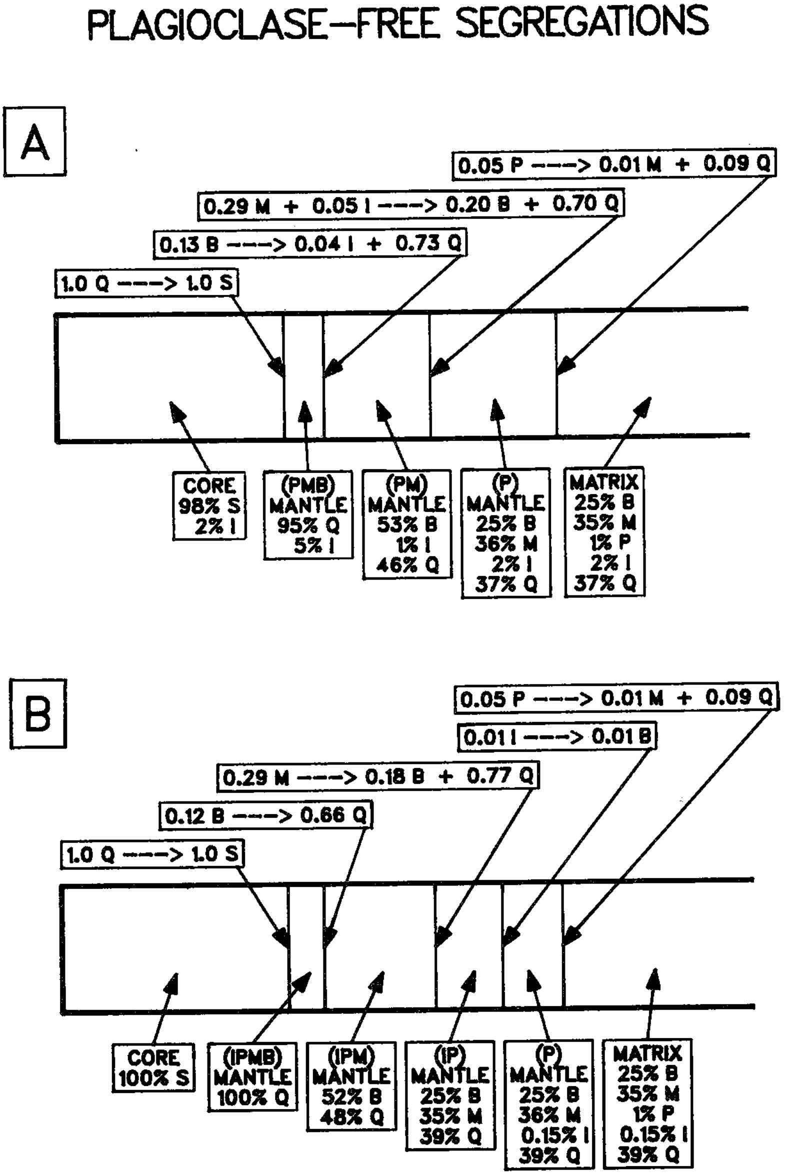


FIG. 3. Core-to-matrix sections through spherical plagioclase-free segregations calculated by the model for two different compositions of matrix. Reactions at mantle boundaries are given in horizontal boxes above each section. Modes of matrix, mantles and core are given in vertical boxes below each section. Mineral abbreviations as in Fig. 1.

It is:

0.12 biotite → 0.66 quartz .... (8)

The quartz in the (IPMB) mantle is converted to sillimanite at the sillimanite core/(IPMB) mantle boundary by the reaction:

1.0 quartz → 1.0 sillimanite ....(9)

Similarly, the quartz in the (PMB) mantle of an ilmenite-bearing segregation is converted to sillimanite at the sillimanite core/(PMB) mantle boundary by reaction (9). As discussed by Foster (1981, p. 269-270), the ilmenite present in a (PMB) mantle does not take part in the

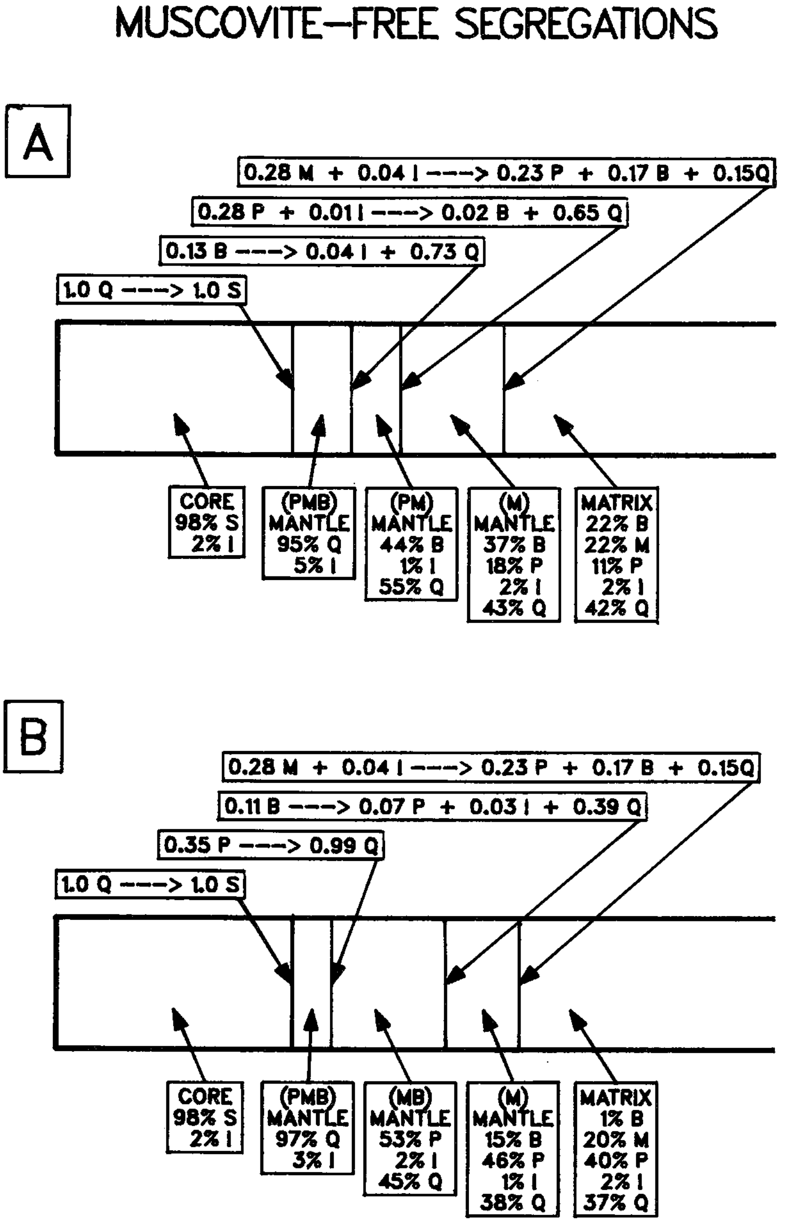


FIG. 4. Core-to-matrix sections through spherical muscovite-free segregations calculated by the model for two different compositions of matrix. Reactions, modes and abbreviations as in Fig. 3.

reaction and is passed into the sillimanite core. The mode of the sillimanite core region is calculated by using reaction (9) and the mode of the (PMB) mantle to calculate the amount of ilmenite transferred to the core during the growth of one mole of sillimanite.

The two possible morphologies calculated for quartz-bearing sillimanite segregations with plagioclase-free outer mantles are shown in Figure 3. The two types of segregations were produced by changing the amount of ilmenite in the matrix. Each drawing represents a cross-section

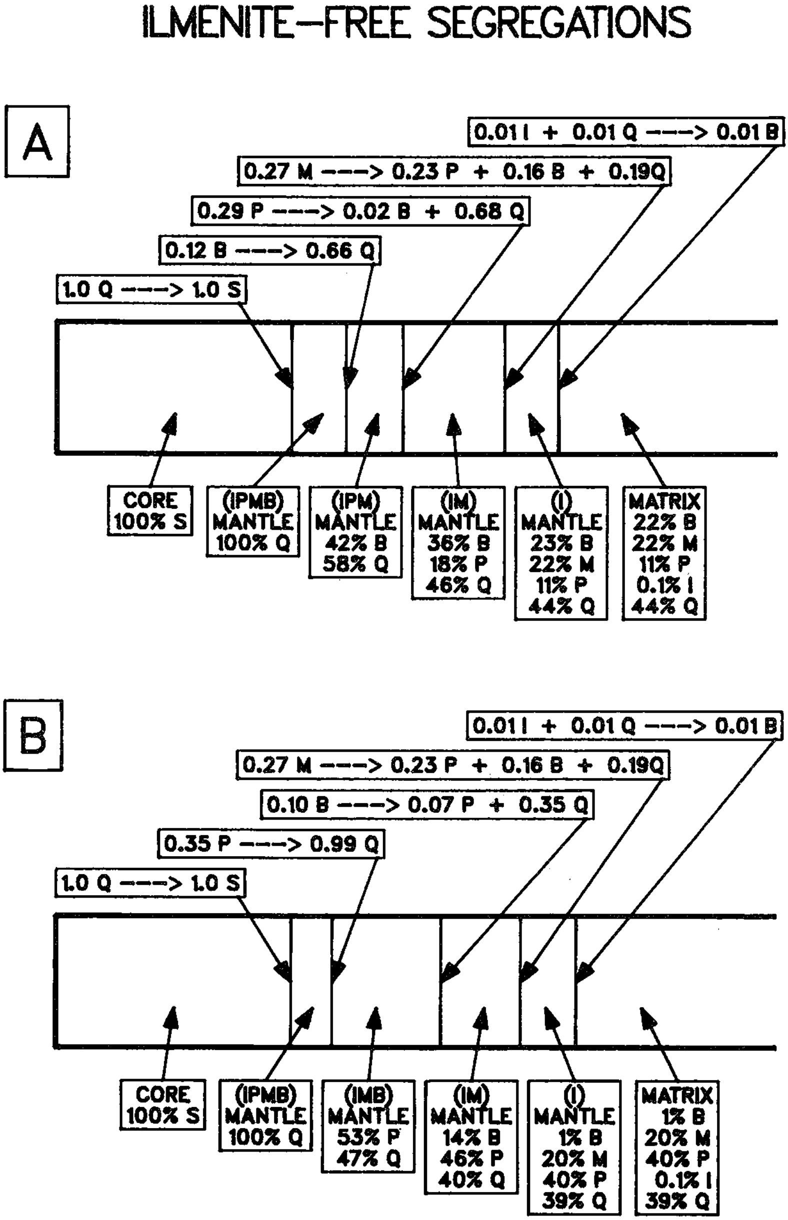
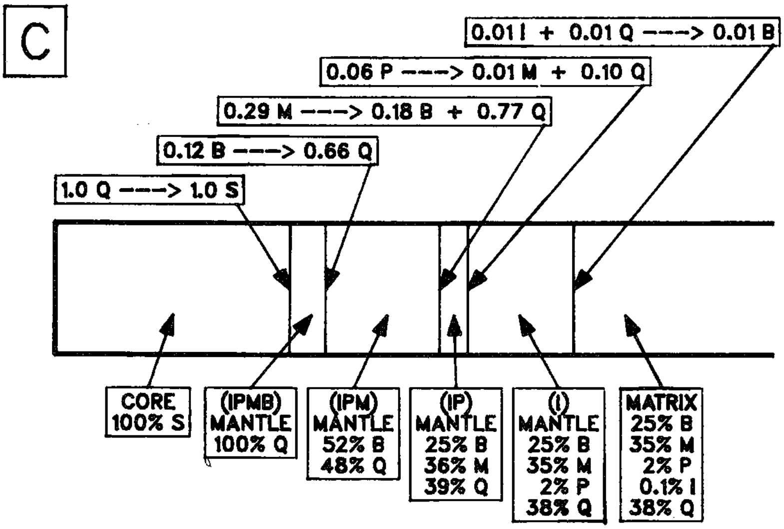


FIG. 5. Core-to-matrix sections through spherical ilmenite-free segregations calculated by the model for three different compositions of matrix. Reactions, modes and abbreviations as in Fig. 3.



from the centre of a spherical segregation into the matrix. The right-hand side of the section has been left open to emphasize that components are entering and leaving the system by diffusion through the matrix. The distance from the centre of the segregation to each mantle boundary is the radius of a sphere having a volume equal to that of the mantles inside of the boundary. The absolute size of the segregation depends upon the amount of sillimanite growth in the core of the segregation. However, the sequence of mantles, the mineral modes and the relative thickness of the mantles are independent of the amount of sillimanite growth once the radius of the segregation has reached several grain diameters in size.

Muscovite-free segregations

If muscovite is the first mineral to be consumed by reaction (1), the net reaction that takes place in the portion of the segregation enclosed by the muscovite-free (M) mantle can be calculated by solving the system of equations in Figure 2, after deleting the Gibbs–Duhem equation for muscovite, the muscovite terms in the conservation equations and the R_m/R_s term. The solution is given in Table 1 under column (M). The net reaction that takes place among the solid phases in the portion of the segregation surrounded by the (M) mantle is given by the R_j/R_s terms in column (M) of Table 1. It is:

$$0.28 \text{ plagioclase} + 0.11 \text{ biotite} \rightarrow 1.0 \text{ sillimanite} + 0.03 \text{ ilmenite} + 0.38 \text{ quartz} \quad \ldots\ldots (10)$$

The reaction at the matrix/(M) mantle boundary, shown in Figure 4, can be calculated by subtracting reaction (10) from reaction (1). The modes of the phases in the (M) mantle are calculated from the matrix/(M) mantle reaction and matrix mode, in the same way the modes were calculated for the (P) mantle in the previous section.

Because reaction (10) consumes plagioclase and biotite, either a (PM) mantle or a (MB) mantle will form inside of the (M) mantle. If the molar ratio of biotite/plagioclase in the (M) mantle is greater than 0.11/0.28, plagioclase will be consumed first and a (PM) mantle will form. If the ratio is less than 0.11/0.28, biotite will be used first and a (MB) mantle will form. The reactions taking place in the portions of the segregation inside of the (PM) or (MB) mantle are given by the R_j/R_s terms in Table 1 under the columns (PM) or (MB). The reaction at the boundary between the (M) mantle and the (MB) or (PM) mantle, shown in Figure 4, is calculated by subtracting the reaction in column (PM) or (MB) from reaction (10). The modes of the phases in the (PM) or (MB) mantle and the volume of the (M) mantle are calculated using the procedure discussed for the plagioclase-free segregation in the previous section.

If the segregation develops a (PM) mantle, the portion of the segregation inside this mantle will develop a (PMB) mantle or a (PMQ) mantle in the same manner as the plagioclase-free segregations with a (PM) mantle. The reaction at the (PM) mantle/(PMB) mantle boundary in a muscovite-free segregation is reaction (7), whereas the reaction inside of the (PMQ) mantle cannot be calculated because the relative diffusion coefficient for SiO_2 is not known.

If a (MB) mantle develops in the muscovite-free segregation, either plagioclase or quartz in the (MB) mantle will be used up to form a (PMB) mantle or a (MBQ) mantle. The reaction at the boundary between the (MB) mantle/(PMB) boundary, which is shown in Figure 4, is calculated by subtracting the R_j/R_s terms in column (PMB) from column (MB) in Table 1. The quartz at the (PMB) mantle/sillimanite core boundary is converted to sillimanite by reaction (9), whereas the ilmenite in the (PMB) mantle is passed to the core without reacting. The reaction inside of the (MBQ) mantle cannot be calculated because of the lack of a relative diffusion coefficient for SiO_2.

Cross-sections showing the calculated morphologies for different types of quartz-bearing, muscovite-free sillimanite segregations are shown in Figure 4. The mineral modes, mantle volumes and mantle–boundary positions were calculated by the methods used for the plagioclase-free segregations, as discussed previously.

Ilmenite-free segregations

If ilmenite is the first mineral in the matrix consumed by reaction (1), the net reaction that takes place in the portion of the segregation enclosed by the ilmenite-free (I) mantle can be calculated by removing the ilmenite terms in the equations given in Figure 2. The reaction among the solid phases is given by the R_j/R_s terms in column (I) of Table 1. It is:

0.27 muscovite + 0.06 plagioclase → 0.06
biotite + 0.53 quartz + 1.0 sillimanite (11)

Note that the stoichiometric coefficients of this reaction are very similar to those of reaction (1) because the reaction at the matrix/(I) mantle boundary that consumes ilmenite involves only small amounts of the other phases. Because reaction (11) is so similar to reaction (1), the distribution of plagioclase, muscovite, biotite and quartz in the segregation that develops from a given matrix composition will be very similar to the segregations containing ilmenite that were discussed in the previous two sections. The possible configurations of quartz-bearing segregations that do not contain ilmenite are given in Figure 5. The solution to the equations in Figure 2 for reactions in the portion of the segregation surrounded by different types of ilmenite-free mantles are given in Table 1. Comparison of the chemical potential terms and reaction coefficients in the ilmenite-free segregation with those of ilmenite-bearing segregations shows that the presence of ilmenite has very little effect on the reaction coefficients of the other phases; the only chemical potential gradient that changes significantly is that of TiO_2. Consequently, the segregations shown in Figure 5 are essentially the same as those in Figures 3 and 4, except for the distribution of small amounts of ilmenite.

COMPARISON WITH OBSERVED TEXTURES

Segregations collected from the lower sillimanite zone (Guidotti 1970, 1974) near Rangeley, Maine, illustrate some of the variations modeled in the previous section (Fig. 6). Generally, the muscovite-free and plagioclase-free mantles are well defined and fit the model closely because 1) micas and plagioclase are evenly distributed and 2) the mantles are at least several grain diameters in width. The interior parts of the segregations such as (PBM) and (PMQ) mantles are not well defined and are commonly intergrown with fibrolite from the core of the segregation. These inner mantles are commonly very thin relative to the diameters of minerals involved in the reactions, so that the assumptions of homogeneous matrix and relatively thin reaction zones between thick mantles begin to break down. Even so, regions corresponding to the inner mantles can usually be identified. They show up as thin, dark fringes around the cores of the segregations in Figure 6.

The assumption of a homogeneous matrix also does not hold when a segregation has grown large enough to encompass regions of matrix with different compositions, such as in a rock with sedimentary laminations. In that case, the segregation can have several mantle sequences, depending upon the local composition of the original matrix. An example of this type of variation is shown in the lower part of Figure 6a, where the plagioclase-free mantle crosses the muscovite-free mantle.

Because the presence or absence of ilmenite makes only a small difference in the models, I have not shown photomicrographs of all the possible permutations of ilmenite-free mantles that are in Figures 3, 4 and 5. Note however, that ilmenite grains in the core of the segregations in Figures 6a and 6d are larger than matrix ilmenite, suggesting they have grown when biotite breaks down in the interior of the segregation as predicted by the model.

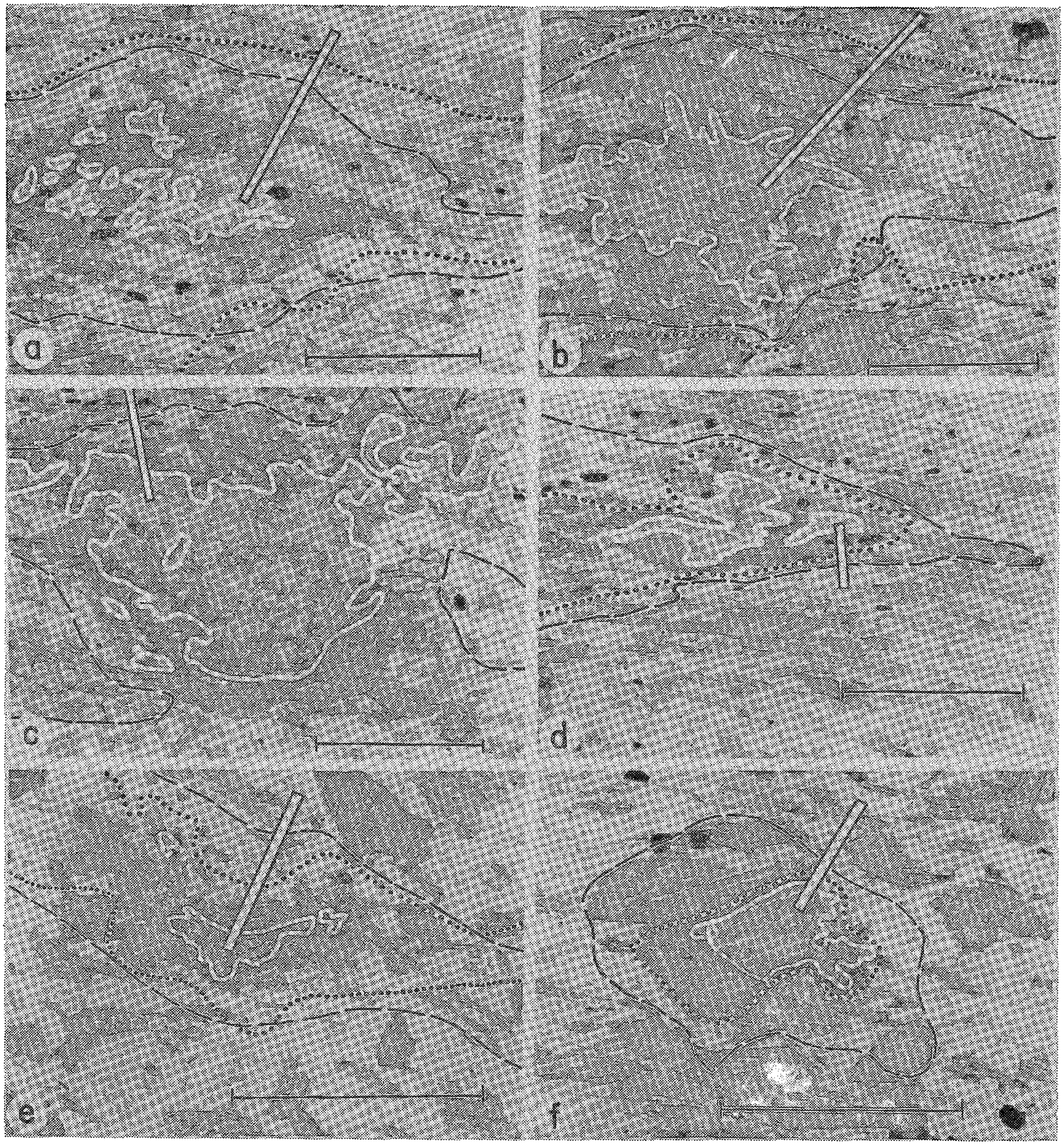


FIG. 6. Sillimanite segregations from the lower sillimanite zone near Rangeley, Maine. A solid line encloses the sillimanite-rich core. A dotted line marks the position of plagioclase closest to the core. A dashed line marks the position of muscovite closest to core. Bar scale is 1 mm. a) White bar gives location of mantle sequence (P): (PM): (PMB) similar to Fig. 3a. Dark region adjacent to the sillimanite core is a sillimanite–quartz intergrowth that represents the (PMB) mantle. b) White bar gives location of mantle sequence (P): (IP): (IPM): (IPMB) similar to Fig. 3b. Dark region adjacent to the sillimanite is a sillimanite–quartz intergrowth that represents the (IPMB) mantle; c) White bar gives location of mantle sequence (M): (MB): (PMB) similar to Fig 4b. Plagioclase persists into the dark region adjacent to the sillimanite core. The (PMB) mantle is thin or absent. High-relief grains on the right side of the figure are garnet. d) White bar gives location of mantle sequence (M): (PM): (PMB) similar to Fig. 4a. Dark region adjacent to the sillimanite core is a sillimanite–quartz intergrowth that represents the (PMB) mantle. e) White bar gives location of mantle sequence (I): (IM): (IPM): (IPMB) similar to Fig. 5a. Matrix with ilmenite lies outside field of view. f) White bar gives location of mantle sequence (I): (IM): (IMB): (IPMB) similar to Fig. 5b. Dark area adjacent to the sillimanite core is a sillimanite–quartz intergrowth representing the (IPMB) mantle.

CHEMICAL POTENTIAL GRADIENTS AND MASS TRANSFER

The chemical potential terms given for each type of mantle in Table 1 can be used to examine the forces that drive material transport in the segregation. The relative gradients in chemical potential for each component in a segregation within a single mantle of a segregation or the matrix can be compared by using the ratio of the $(\nabla\mu_i)_x \bullet A/R_s$ terms in a single column from Table 1 because the A/R_s terms will cancel. Chemical potential profiles across the segregation can be constructed by integrating the chemical potential terms from the centre of the segregation to the matrix using equation (24) of Foster (1981). The total amount of a component transported through a mantle during the growth of one mole of sillimanite can be calculated by multiplying the chemical potential terms in Table 1 by the relative coefficient of thermodynamic diffusion for the component. The chemical potential terms can also be used to evaluate important sources and sinks of a component in a segregation. The amount of a component produced or consumed by a local reaction can be calculated by examining the amount of the component transported through mantles on either side of the reaction interface. Examination of the sinks and sources for the seven components transported in the models reveals that, as might be expected, the supply of most components is governed by the phases that are rich in that particular component.

Iron and magnesium

The main sink for FeO and MgO in the segregation is the reaction that converts muscovite to biotite at a matrix/(M) mantle boundary or a (P) mantle/(PM) mantle boundary. Approximately two-thirds of the iron and magnesium used in this reaction is produced by a biotite-breakdown reaction in the interior of the segregation at a (M) mantle/(MB) mantle boundary or a (PM) mantle/(PMB) mantle boundary. The remaining third is supplied from outside the segregation by diffusion through the matrix surrounding the segregation.

Sodium

In segregations with a (P) mantle, two-thirds of the $NaO_{0.5}$ that leaves the segregation by diffusion through the matrix is produced by the breakdown of muscovite at the (P) mantle/(PM) mantle boundary; one-third is produced by the breakdown of plagioclase at the matrix/(P) mantle boundary. In a segregation with a (M) mantle, however, the process is more complicated. The breakdown of plagioclase at the (M) mantle/(PM) mantle boundary or the (MB) mantle/(PMB) mantle boundary produces almost twice as much sodium as leaves the segregation through the matrix. In this case, the sodium produced by the plagioclase breakdown is transported through the outer mantles to the matrix/(M) mantle boundary, where half of the sodium is consumed by a reaction that converts muscovite to plagioclase and biotite. The sodium that is not consumed by this reaction leaves the segregation by diffusion down the chemical potential gradients in the matrix.

Aluminum

The main sink for $AlO_{1.5}$ is the sillimanite-forming reaction at the sillimanite core/(PMB) mantle boundary. Approximately one-third of the aluminum used to form sillimanite in the segregation is supplied from outside the segregation by diffusion through the matrix; one-third is supplied by the breakdown of muscovite at the matrix/(M) mantle boundary, or the (P) mantle/(PM) mantle boundary; one-sixth is supplied by the breakdown of plagioclase at the (M) mantle/(PM) mantle boundary, and one-sixth is supplied by the breadown of biotite at the (PM) mantle/(PMB) mantle boundary or the (M) mantle/(MB) mantle boundary.

Potassium

The main sources of potassium in the rock are reactions that breakdown micas. About two-thirds of the $KO_{0.5}$ that leaves the segregation by diffusion through the matrix is produced by the breakdown of biotite at the (PM) mantle/(PMB) mantle boundary or the (M) mantle/(MB) mantle boundary. The potassium produced by this reaction diffuses across the biotite-bearing outer mantles to the matrix/(M) mantle boundary or the (P) mantle/(PM) mantle boundary, where the remaining third of the $KO_{0.5}$ is produced by the breakdown of muscovite.

Calcium

The calcium that leaves the segregation by diffusion through the matrix is entirely produced by the plagioclase-breakdown reaction at the matrix/(P) mantle boundary, the (M) mantle/(PM) mantle boundary or the (MB) mantle/(MBP) mantle boundary.

Titanium

In segregations containing ilmenite, the main source of TiO_2 is the reaction at the matrix/(M) mantle or (P) mantle/(PM) mantle boundary, where ilmenite and muscovite are consumed. One-third of the titanium produced by this reaction leaves the segregation by diffusion through the matrix; the remaining two-thirds is transported by diffusion to the interior of the segregation, where it is used by the biotite-breakdown reaction to make ilmenite at the (M) mantle/(MB) mantle boundary or the (PM) mantle/(PMB) mantle boundary. In segregations that are ilmenite-free there are two sources of titanium. One is the biotite-breakdown reaction at the (IPM) mantle/(IPMB) mantle boundary or the (IM) mantle/(IMB) mantle boundary. All of the titanium produced by this reaction diffuses to the outer part of the segregation, where it is consumed by the reaction converting muscovite to biotite at the (I) mantle/(IM) mantle boundary or the (IP) mantle/(IPM) boundary. The second source is the breakdown of ilmenite at the matrix/(I) mantle boundary. All of the TiO_2 produced by this reaction leaves the segregation by diffusion down chemical potential gradients in the matrix.

CONCLUSIONS

In this study, I have shown that a local equilibrium, irreversible thermodynamic model correctly predicts previously unrecognized textural variations in sillimanite segregations from the lower sillimanite zone near Rangeley, Maine. Work in progress on other types of segregations (Foster 1977b, 1978, 1980 and unpublished data) suggests that this type of model is valid in many rocks over a wide range of metamorphic grade. Once these models have been thoroughly tested and once relative coefficients of thermodynamic diffusion are available for a wide range of metamorphic conditions, it should be possible to reconstruct the mineral assemblages of each metamorphic event in a polymetamorphic terrane from the textures preserved in the rock. If the relative coefficients of diffusion change significantly as a function of temperature or pressure, it may even be possible to use subtle differences in segregation mantle thickness and modes as a geothermometer–geobarometer for each event. A great deal of work remains to be done before irreversible thermodynamic models are routinely applied to metamorphic textures, but the method has the potential to add an exciting dimension to the study of metamorphic rocks.

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