

An Elle-based 2-D model for cation exchange reaction between garnet and biotite

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Abstract: We have developed a model for diffusion zoning development in garnet employing a numerical modeling system, Elle [Jessell et al. 2001]. The Elle system simulates textural development at thin section scale with an assumption that long term textural changes can be achieved by adding incremental processes. Many numerical models have been developed for the diffusion zoning pattern of garnet, but these models considered only lattice diffusion without allowing grain boundary diffusion. However, our model simulates the diffusion zoning in garnets by considering not only lattice diffusion but also grain boundary/lattice reaction and grain boundary diffusion.

Sub-processes for our garnet-biotite system include (1) lattice diffusion, (2) grain-boundary diffusion, and (3) grain boundary/lattice reaction. The finite difference explicit method was used for the numerical calculation of lattice and boundary diffusion. For diffusion calculation, chemical concentrations of individual nodal points are used to calculate the amount of transported cations with diffusion coefficients determined from experiments. For lattice/boundary reaction, the lowest energy compositions of garnet and biotite were calculated using the distribution coefficient. Experimental runs were performed to test the consistency and reproducibility of the results. The results demonstrate the consistency and reproducibility, but show somewhat different zoning from that of Spear (1991), due to reduced dimension (3D in nature vs 2D in our model) and the arbitrarily chosen reaction constant. In spite of these limitations, we feel that the model presented here is at least a good starting point for diffusive mass transfer in a material with grain boundary structure.

Table of Contents

Introduction	5
Assumptions, Data Structure and Algorithm	5
Results	9
Discussion	13
Concluding Remarks	14
Acknowledgements	14
References	14

Introduction

The garnet-biotite geothermometry is widely used by metamorphic petrologists to estimate the temperature condition of metamorphism [Spear 1993 and references therein]. The basic assumption for the geothermometry is temperature-dependent equilibrium distribution of Fe and Mg ions in biotite and garnet. During equilibration, diffusive mass transfer along the diffusion pathways (i.e. grain or phase boundaries) as well as volume diffusion within crystals of biotite and garnet occurs. The effect of temperature-dependent diffusion has been successfully demonstrated with finite difference calculations [e.g. Spear 1991; Ehlers et al. 1994; Powell & White 1995]. These models usually assume that the rate of grain boundary diffusion is much faster than the rate of volume diffusion in crystals. More specifically, these models assume that the rate-limiting step for equilibration is volume diffusion in garnet because the rate of diffusion in garnet is much slower than both diffusion in biotite [Hoffman & Giletti 1974; Cygan & Lasaga 1985] and diffusion along grain boundaries. Geologically meaningful results have been produced by these models and applied for the interpretation of zoning pattern in garnets [e.g. Spear 1991; O'Brien 1997].

Although the aforementioned models [e.g. Spear 1991; Ehlers et al. 1994] generated useful results, these models fail to produce thin-section scale textural features associated with the zoning patterns in garnet. For example, the effect of distribution geometry in phases participating in the reaction cannot be studied with the conventional model because of the simple assumption that volume diffusion in garnet is the rate-limiting step. Furthermore, these models cannot be used for multiple geologic processes, for example, deformation and metamorphism. In this paper, we present a two dimensional model where the ion exchange reaction occurs in a grain network created by digitally mapping a thin section. Since calculation of diffusion is enormously different for different dimensions (2D in our model vs 3D in nature), it is difficult to apply the model results for rocks. However, we believe that this type of approach can lead to further understanding of the ion exchange reaction since we can infer the effect of various textural parameters of rocks (e.g. phase distribution and grain size) on the development of zoning in garnet and we can also model the situation where textures change during metamorphism (e.g. grain growth and foliation development). We adopted the Elle scheme [Jessell et al. 2001] for the exchange reaction because the preexisting Elle code

allows us to model multiple processes by integrating incremental textural changes. We will present three examples of our model results; (1) zonation development at a constant temperature with different phase distribution of garnet and biotite, (2) zonation development at constant temperature with different textures of non-reacting matrix phases, and (3) zonation development during cooling.

Assumptions, Data Structure and Algorithm

Figure 1. Cation exchange reaction

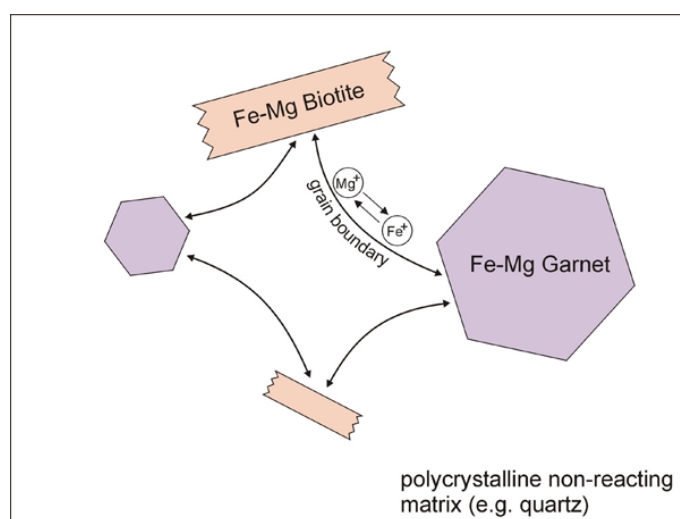
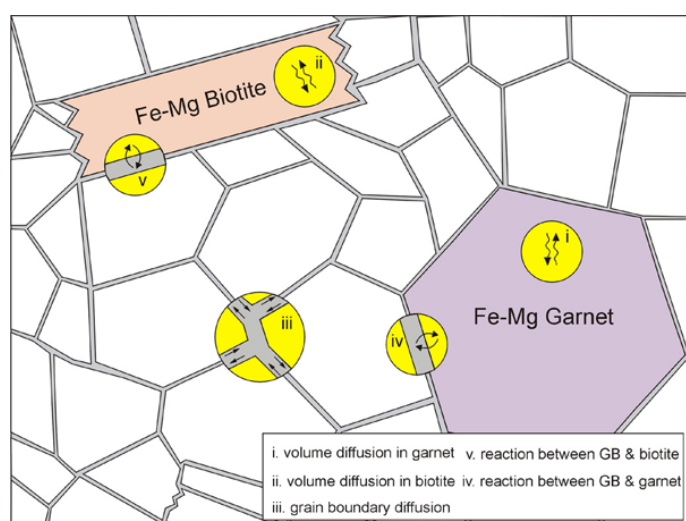


Diagram illustrating cation exchange reaction between garnet and biotite.

In order to model Fe-Mg ion exchange reaction between garnet and biotite, we made several assumptions; (1) There is no migration of grain and phase boundaries. Therefore, only exchange reaction is considered in the model, without any net-transfer reaction involving phase boundary migration. (2) Only three phases exist in our model (Figure 1); (i) Fe-Mg garnet, (ii) Fe-Mg biotite, and (iii) a non-reacting phase (e.g. quartz). The volumetrically larger non-reacting phase forms a polycrystalline aggregate with a grain boundary network. The grain boundaries become pathways for Fe-Mg diffusion. (3) Five steps or subprocesses are considered for the ion exchange reaction (Figure 2); (i) volume diffusion in garnet, (ii) volume diffusion in biotite, (iii) grain boundary diffusion, (iv) reaction (or exchange) between garnet and grain boundary, and (v) reaction (or exchange) between biotite and grain boundary. An example illustrating how these subprocesses affect concentration along grain boundaries and at points in garnet and

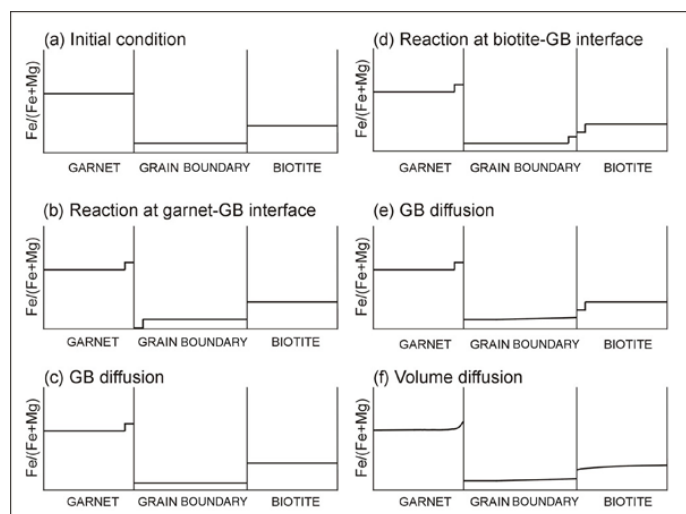
biotite is shown in Figure 3. (4) Equilibrium compositions for garnet and biotite are obtained using temperature-dependent distribution coefficient (K_D , [Ferry & Spear 1978]). The K_D value during program execution is calculated using the compositions at margins (or at the portion of crystal near phase boundaries). This calculated K_D is compared with the equilibrium K_D of Ferry & Spear (1978). Then the chemical composition at margins is allowed to change in the direction of approaching the equilibrium K_D .

Figure 2. Subprocesses for the ion exchange reaction



Subprocesses for the ion exchange reaction between garnet and biotite (GB: grain boundary).

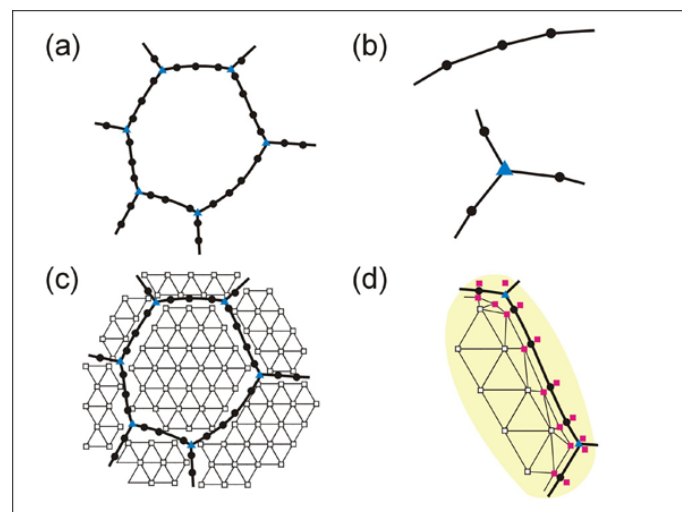
Figure 3. Concentraion profiles



Evolution of concentraion profiles after each subprocess (GB: grain boundary).

The data model is based on two kinds of node (Figure 4). The first data structure is the "bnode" (boundary node). Bnodes are linked by segments to define grains (Figure 4a). Bnodes can have properties such as their position, link type and concentration. A bnode can be type-2 or type-3 node depending on the link type (Figure 4b). A central bnode may be connected by segments to two neighbors (type-2 node). Type-3 nodes with three segments connecting three neighbors are used to define triple junctions. The second kind of data structure is "unode" (unconnected node, Figure 4c). The unode records the material property within a volume of crystal. For our type of model where diffusive mass flux is calculated, the unodes will carry concentration information, and they can have other information such as dislocation density for other types of models. In order to allow chemical exchange between a bnode (grain boundary) and a unode (grain), special unodes are inserted adjacent to the node Figure 4d.

Figure 4. Data-structure of the model



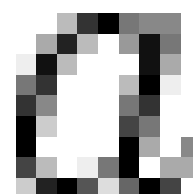
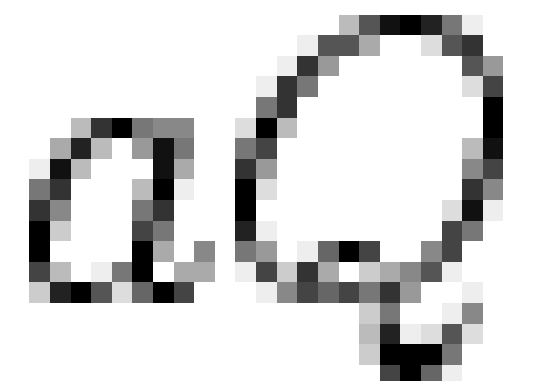
Data-structure of the model. (a) node structure for defining grains. (b) type-2node (top) and type-3 node (bottom). (c) unodes within grains. (d) special unodes at grain margins. (filled circle: type-2 node, filled triangle: type-3 node, open square: unode, filled square: special unode).

Finite-difference approximation is used for the calculation of flux and changes in concentration. For diffusion calculations at triple junctions Figure 5a, fluxes (number of atoms per unit time through an area of grain boundary section) into a type-3 node, O, from three neighboring nodes (A, B, and C) are expressed with three equations

$$q_{0A} = -A \cdot D \cdot \delta \cdot \frac{C_0 - C_a}{X_a}$$

$$q_{0B} = -A \cdot D \cdot \delta \cdot \frac{C_0 - C_b}{X_b}$$

$$q_{0C} = -A \cdot D \cdot \delta \cdot \frac{C_0 - C_c}{X_c}$$



where q , A , D , C and X respectively represent flux, area of grain boundary section, diffusivity, concentration and length of a grain boundary segment (details for the quantities in the equations are shown in Figure 5a). Note that the area of grain boundary section (A) is equal to the quantity grain-boundary width (W_{GB}) multiplied by the thickness (t_{sample}) of the two dimensional Elle data structure, or

$$A = W_{gb} \cdot t_{sample}$$

divided by the volume occupied by the node O . The volume occupied by the node O can be approximated to be the half distance between node O and the considered node (A , B , or C). Thus, the volume becomes

The total flux (Q) becomes the sum of the quantities in the above three equations, or

$$\left[\frac{1}{2}(X_A \cdot W_A) + \frac{1}{2}(X_B \cdot W_B) + \frac{1}{2}(X_C \cdot W_C) \right]$$

$$Q = q_{0A} + q_{0B} + q_{0C} = -(W_{gb} \cdot t_{sample}) \cdot D \cdot \delta \cdot \left[\left(\frac{C_0 - C_A}{X_A} \right) + \left(\frac{C_0 - C_B}{X_B} \right) + \left(\frac{C_0 - C_C}{X_C} \right) \right]$$

Then, changes in concentration per time is expressed with the equation

Then, the total flux per unit time becomes

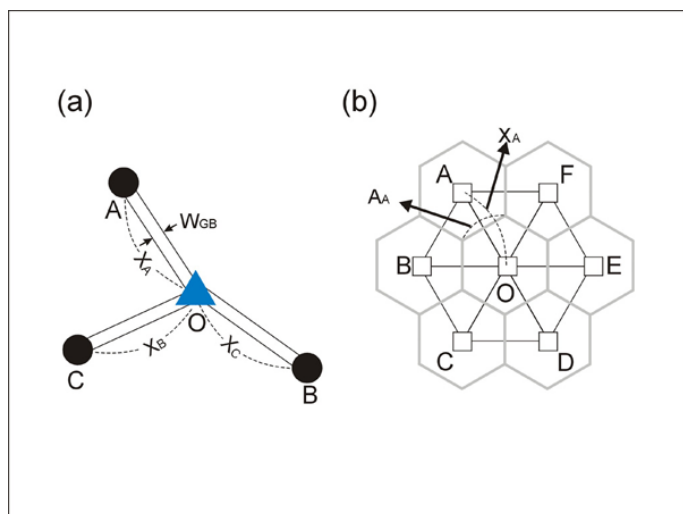
$$\frac{aC}{a} = \frac{aQ}{a} \cdot \left[\frac{1}{2}(X_A \cdot W_A) + \frac{1}{2}(X_B \cdot W_B) + \frac{1}{2}(X_C \cdot W_C) \right]^{-1}$$

$$\frac{aQ}{a} = -(W_{gb} \cdot t_{sample}) \cdot D \cdot \left[\left(\frac{C_0 - C_A}{X_A} \right) + \left(\frac{C_0 - C_B}{X_B} \right) + \left(\frac{C_0 - C_C}{X_C} \right) \right]$$

The change in concentration per unit time becomes

This relation can also be applied for diffusion calculations for type-2 nodes or grain boundary segments because a grain boundary segment can be constructed by omitting one link (e.g. node C in Figure 5a) from type-3 node.

Figure 5. Diffusion calculations



Diffusion calculations (a) at grain boundaries, (b) at grain interior part. See text for detail.

For the calculation of volume diffusion in crystals, unode data structures are used (Figure 5b). Most of unodes in a crystal are evenly distributed with a two dimensional hexagonal close-packed structure, but special unodes communicating with grain boundaries are placed next to grain-boundary nodes. The evenly distributed unodes and special unodes are triangulated for the finite-difference diffusion calculation (Figure 5b). The region represented by a unode (unode O in Figure 5b) is constructed by connecting the center of gravity points of neighboring triangles. The flux into O from the neighboring regions (A, B, C, D, E and F) can be expressed with the equation:

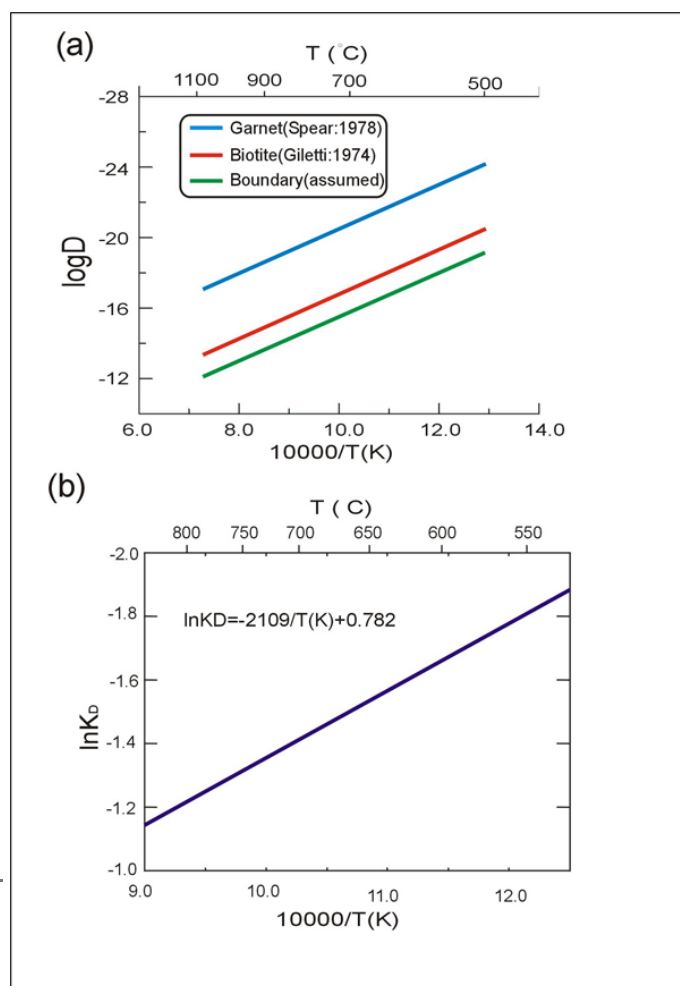
$$q_{OA} = -A_A \cdot D \cdot \delta \cdot \frac{C_0 - C_A}{X_A}$$

$$q_{OF} = -A_F \cdot D \cdot \delta \cdot \frac{C_0 - C_F}{X_F}$$

Where q, A, D, C and X respectively represent flux, area of flux section, diffusivity, concentration and distance between two nodes Figure 5b . In a similar manner explained above, q_C and a_C can be estimated using the flux from neighboring unodes. Then, a_C / a can be estimated by dividing q_C / a with the volume occupied by unode O.

The special unodes placed adjacent to the grain boundary nodes can exchange atoms with the grain boundary nodes. The rate of exchange is assumed to be proportional to the concentration difference with a proportionality constant. The proportionality constant may have a meaning similar to the reaction constant. For the proportionality constant, we used an arbitrary value that allowed reaction sufficiently fast within a run time.

Figure 6. Parameters used for the exchange reaction

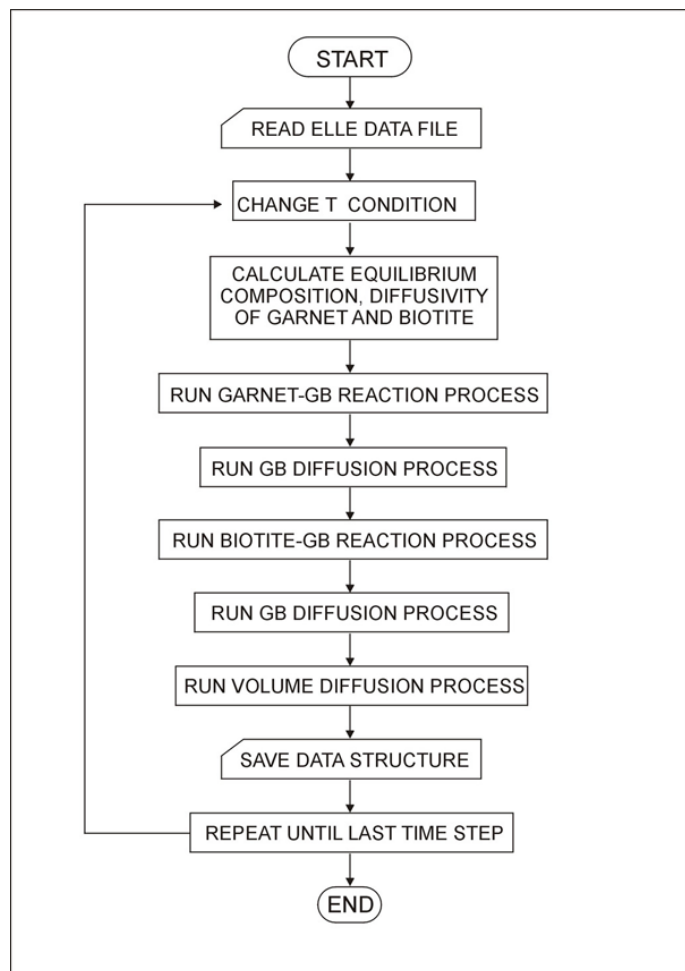


Parameters used for the exchange reaction in this study. (a) diffusivities. (b) distribution coefficient (K_D) between garnet and biotite.

Figure 6 shows the values of diffusivity (D) and distribution coefficient (K_D) used in this study. The temperature-dependent K_D determines the equilibrium composition of garnet and biotite, while the diffusivity (which is also temperature-dependent) determines the rate of equilibration. The diffusivity along the grain boundary is assumed to be about one order of magnitude faster than the

diffusivity within the biotite. This is based on general observations from metals [Askeland, 1994]. The overall flow chart of the model is shown in Figure 7.

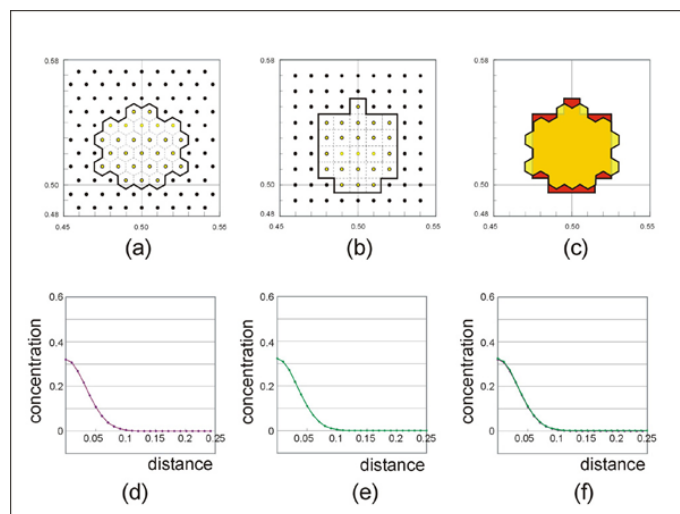
Figure 7. Flow chart for the model



Flow chart for the model.

Results

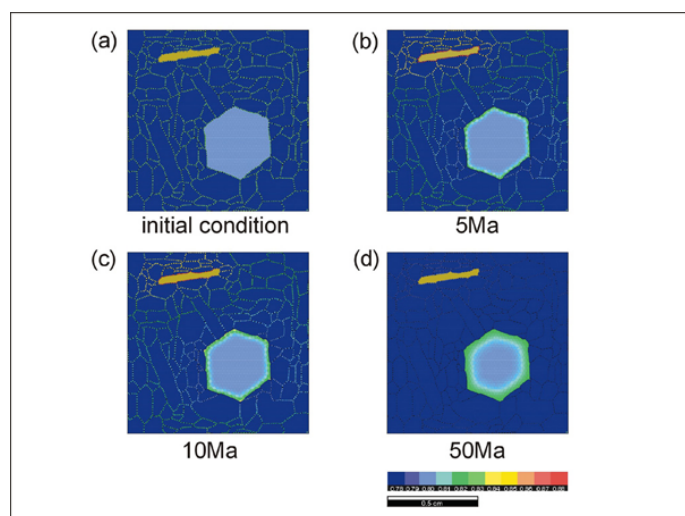
Figure 8. Comparison of the volume diffusion results



Comparison of the volume diffusion results between this model (a and d) and the conventional finite-difference grid model (b and e). Superposed diffusion source region (c) and concentration profile (f).

In order to test the algorithm for volume diffusion within crystals, the result from the diffusion algorithm (discussed above) is compared with the result from the well-known finite difference scheme [e.g. Crank 1975; p. 141]. This type of test was carried out because of some complexities in the unode-involved diffusion algorithm (e.g. calculation of flux area and estimation of the concentration field represented by a single unode). We compared the concentration profiles with the point-source initial condition (Figure 8). Since the geometry of nodal distribution is different between the two methods, the area represented by a node is different and this resulted in different concentration profiles. To avoid this, a source region instead of a point source was constructed with multiple points. When geometrically similar regions are used (Figure 8a, b, and c) it is found that the concentration profiles are almost identical (Figure 8d, e, and f). Thus, we believe that the diffusion algorithm using unodes produces numerically correct results.

Figure 9. Results of garnet-biotite exchange reaction run #1

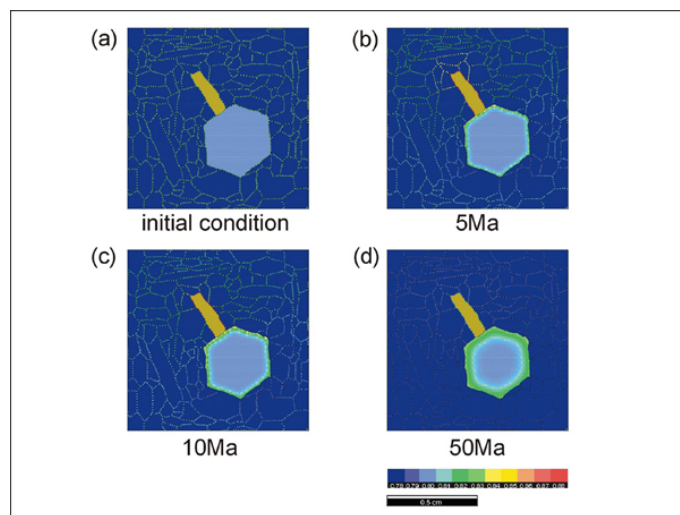


Results of garnet-biotite exchange reaction run #1 (dot: grain-boundary nodes, yellowish brown: biotite, blue: quartz, hexagonal crystal: garnet). The colors in garnet represent the mole fraction of Fe. Compare the result with Figures 2 and 3 to see how distribution geometry of garnet and biotite affects the reaction rate.

We have carried out three types of experiments; (1) at a constant temperature with different distribution of phases participating in the exchange reaction (run #1 to 3), (2) at a constant temperature with varying matrix textures where the matrix does not participate in the reaction (run #4 to 8), and (3) during cooling (run #9). The experiments (run #1 to 3) at a constant temperature are intended to investigate how the pattern of garnet zonation is affected by the distribution and amount of biotite. The initial compositions for garnet and biotite are 0.8 and 0.6 (in Fe mole fraction), respectively. Since these compositions are disequilibrium compositions at the experimental temperature condition of 600°C, the garnet and biotite start to exchange ions to approach the equilibrium K_D value. Simulation 1 shows the results of run #1 where a single biotite and a single garnet are present with quartz matrix. Since the differences in the garnet composition are small, we have optimized CLUT (color look up table) for the garnet composition. Therefore, the biotite composition as well as the grain boundary chemistry is not expressed correctly under the selected CLUT. Concentric zonation pattern is developed in garnet. Since the biotite grain is located in the upper left, we can expect some differences in biotite-facing sides of garnet, but such differences are not observed. This could be because of the boundary geometry in this model; the Elle texture assumes

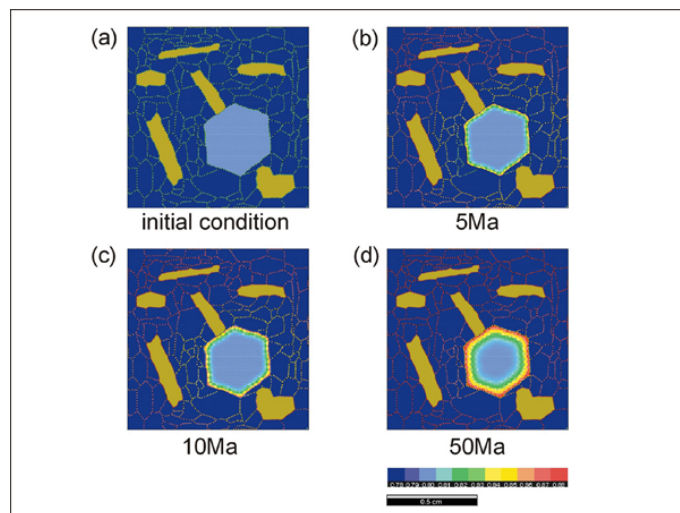
ring boundary (i.e. the upper boundary is attached to the lower boundary and this is also true for the left and right boundaries).

Figure 10. Results of garnet-biotite exchange reaction run #2



Results of garnet-biotite exchange reaction run #2.

Figure 11. Results of garnet-biotite exchange reaction run #3

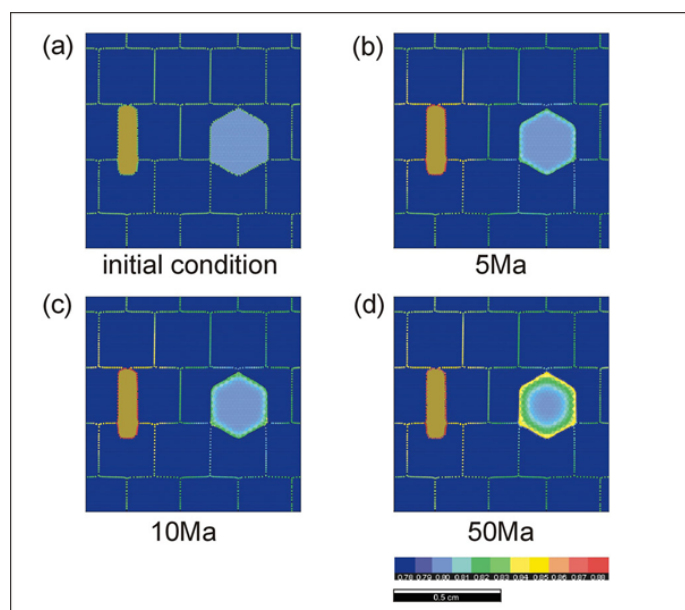


Results of garnet-biotite exchange reaction run #3.

In run #2 where biotite is placed adjacent to garnet (Simulation 2), the diffusion effect is more pronounced for the biotite-facing side compared with the opposite side of the garnet. Therefore, we can expect that the distribution geometry of phases participating in reactions can influence the exchange reaction. In run #3 (Simulation 3), we have increased the volume fraction of biotite to see how the

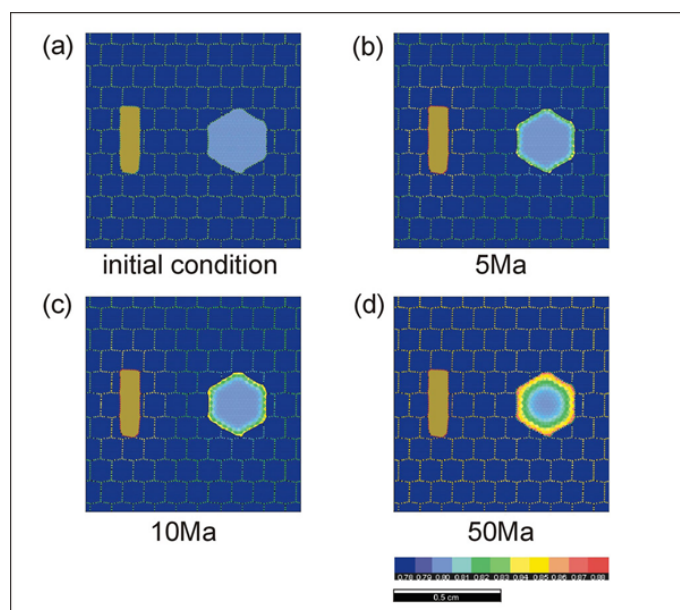
amount of biotite can affect the exchange reaction. The amount of biotite seems to be an important factor during exchange reaction. An increased amount of biotite enhances the rate of reaction by providing more ions and possibly by larger surface area for ionic exchange between biotite and grain boundary. Experiments (run #4 to 8) were carried out to see the effects of matrix texture on the rate of exchange reaction. The initial conditions for these runs are identical to those used in experimental runs #1 to 3.

Figure 12. Results of garnet-biotite exchange reaction run #4



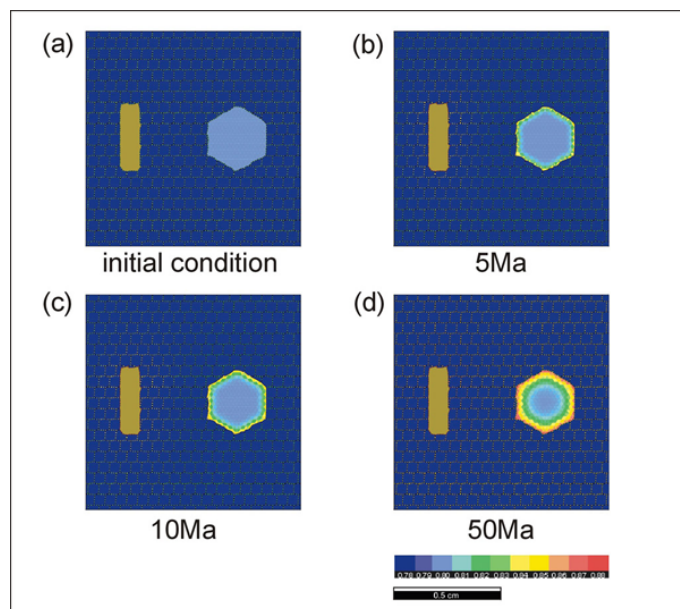
Results of garnet-biotite exchange reaction run #4. Compare the result with simulations 2 and 3 to see how the matrix grain size affects the reaction rate.

Figure 13. Results of garnet-biotite exchange reaction run #5



Results of garnet-biotite exchange reaction run #5.

Figure 14. Results of garnet-biotite exchange reaction run #6

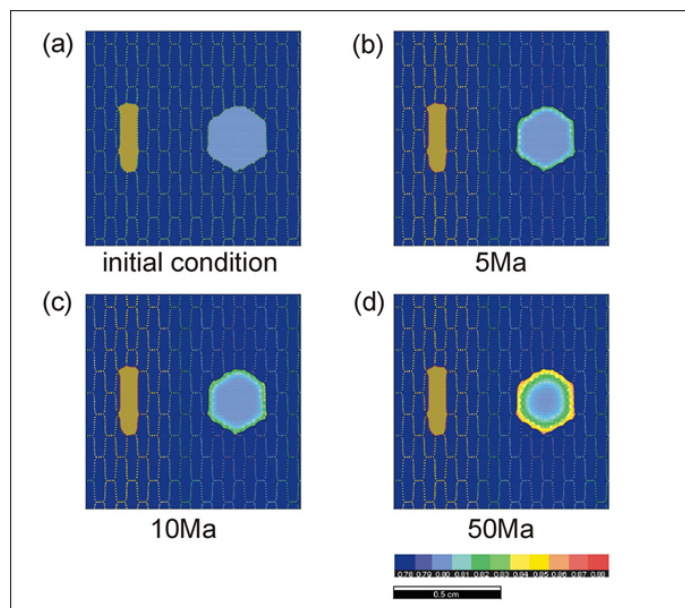


Results of garnet-biotite exchange reaction run #6.

Simulations 4 - 6 (run #4 to 6) show the effect of grain size in the matrix that does not participate in the exchange reaction. The rate of the ion exchange reaction is enhanced as the grain size in the matrix phase decreases. This result

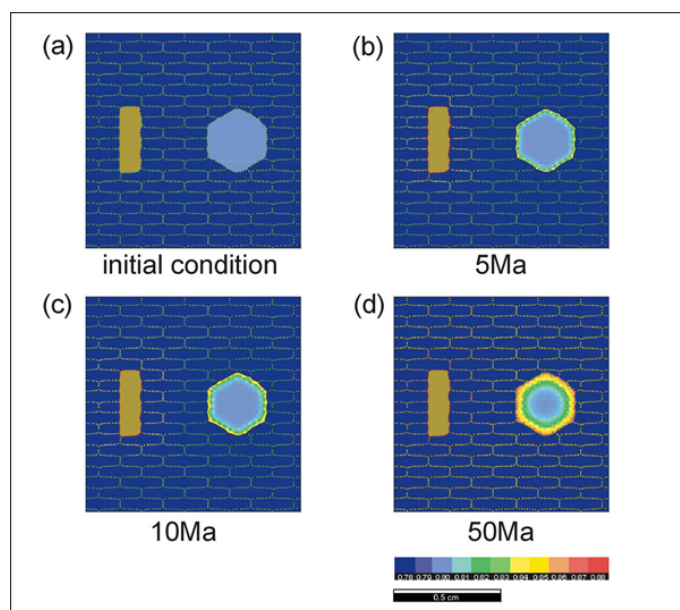
is expected since the amount of ion transportation will increase as the density of grain boundary area per unit volume (i.e. flux area) increases. The effect of grain-shape foliation in the matrix as well as the geometry of diffusion pathways is also investigated.

Figure 15. Results of garnet-biotite exchange reaction run #7



Results of garnet-biotite exchange reaction run #7. Compare the result with Figure 16 to see how the direction of grain-shape foliations and the geometry of diffusion pathways affect the reaction rate.

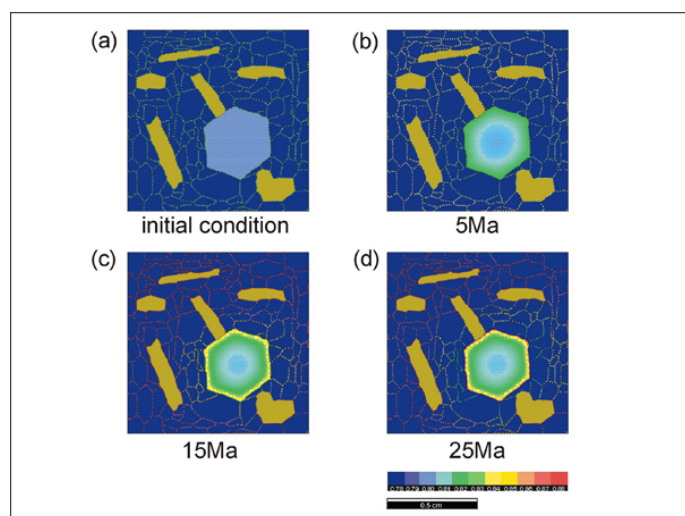
Figure 16. Results of garnet-biotite exchange reaction run #8



Results of garnet-biotite exchange reaction run #8.

Simulations 7 and 8 show the experimental results with a north-south and east-west oriented foliation, respectively. When the foliation direction is east-west (Simulation 8), the rate of reaction is faster because the geometry of the diffusion pathways is simpler. In run #9 (Simulation 9), we have performed a cooling experiment from 750°C to 450°C with a cooling rate of 10°C per Ma. The biotite distribution geometry is the same as in run #3. Equilibrium compositions are used for the starting composition (garnet Fe mole fraction = 0.8 and biotite Fe mole fraction = 0.54). Since the rate of diffusion becomes slower during cooling, sluggish changes in zonation pattern occur during the late stages of cooling.

Figure 17. Results of garnet-biotite exchange reaction run #9

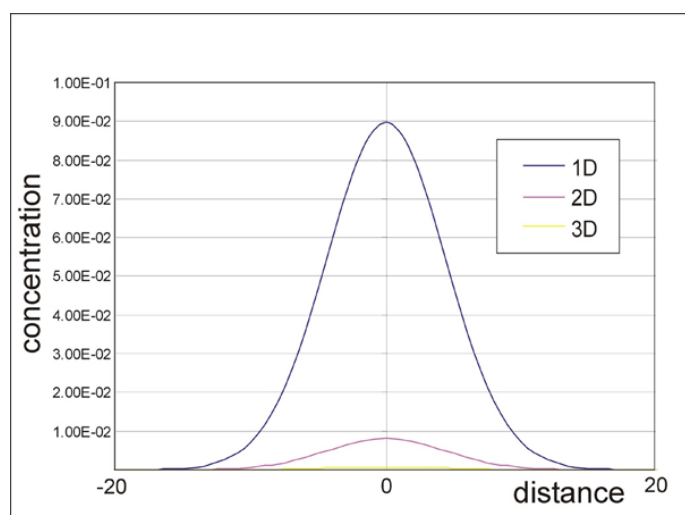


Results of garnet-biotite exchange reaction run #9.

Discussion

Although the current model for Fe-Mg exchange reaction produced the predicted results, the model has several limitations and uncertainties in algorithm. These will be briefly discussed here.

Figure 18. Results of volume diffusion from a point source in one, two, and three dimensions



Results of volume diffusion from a point source in one, two, and three dimensions. The calculations were made using finite-difference methods described in Crank (1975).

The major limitation of the model is dimension-related problem. Since diffusive mass transfer in rocks occurs in

three dimensions, our two-dimensional model has a fundamental limitation when we apply the model to the interpretation of the natural zoning. Figure 18 shows the comparison of concentration profiles in point-source diffusing systems of one, two, and three dimensions. Not surprisingly, the two-dimensional model (like in our Elle based model) shows much slower diffusion than the three-dimensional result. Therefore, it is impossible to model natural diffusive process with the current model. Expansion of data structure is necessary to allow three-dimensional diffusive mass process (Figure 19).

Figure 19. Possible data structure for three dimensional diffusive mass transfer

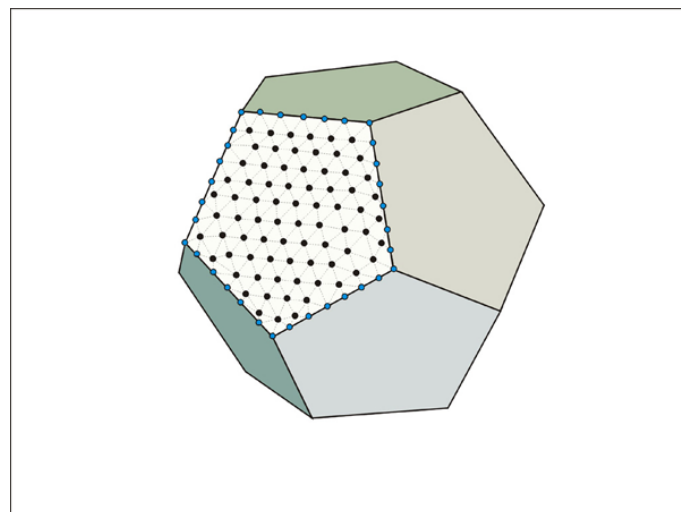


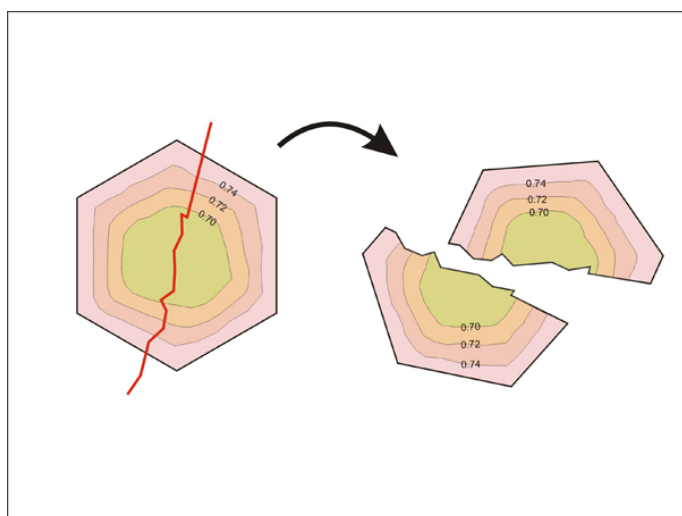
Illustration of a possible data structure for three dimensional diffusive mass transfer.

The exchange process of grain chemistry with the grain boundary chemistry was made using the special unodes (Figure 4b). The proportionality constant was introduced to calculate the rate of exchange, and the constant may have a meaning similar to the reaction constant. For the results presented here, we used an arbitrary value that produced sufficiently fast reaction during each run. However, the proportionality constant can have a fundamental effect on the bulk rate of ion exchange reaction. For example, when the constant approaches to the value of zero, the reaction ceases in the model. In spite of the fundamental importance, it is not clear which value should be chosen for natural rocks.

When the model calculates the equilibrium composition for garnet and biotite, the distribution coefficient (K_D) is used (described in assumption (4)). The program finds the

unodes adjacent to the grain boundaries. Then the average concentrations for garnet and biotite are calculated for these unodes. The concentration values are used to calculate the distribution coefficient within the system. The calculated value of the distribution coefficient is compared with the predicted equilibrium value of the distribution coefficient by Ferry & Spear (1978). Then the exchange reaction proceeds in the direction of approaching the equilibrium value of the distribution coefficient. This type of calculation sometimes can produce incorrect results. Figure 20 illustrates a situation where incorrect results can be produced where heterogeneous garnets (e.g. fractured garnet) are present in the system. When the volumes of interfacial garnets have different composition (like in Figure 15), a complicated situation may arise. For example, some garnet interfaces should lose Fe to reach chemical equilibrium while other interfaces should gain Fe. However, this type of complicated processes may not be possible in our model since we simply average the compositions of interfacial garnet in order to compare the average value with the equilibrium value. We feel that this simplification sometimes may produce incorrect results while approaching the state of equilibrium. A more robust way of dealing with heterogeneous garnet composition will be to calculate the local Gibbs free energy for the volumes occupied by interfacial unodes. Then, the direction of exchange reaction (i.e. Fe gain or loss) can be determined in the direction of lowering local Gibbs free energy.

Figure 20. Heterogeneous compositions



Heterogeneous compositions of garnet at grain margins by fracturing (Numbers and dashed curves represent Fe)

mole fraction and isochemical contours, respectively). See text for details of this effect on exchange reaction.

As stated earlier, we feel that the current model has many problems in simulating natural garnet-biotite exchange reactions. However, we also think that this type of approach will eventually lead to the development of more realistic model since it is difficult to solve this problem analytically because many parameters are changing during metamorphism. For example, textural changes in matrix such as grain growth and development of foliation commonly occur during metamorphism. Since the framework of the model is Elle [Jessell et al. 2001] which allows simultaneous operation of many subprocesses (e.g. grain growth, recrystallization, and deformation), we believe that the algorithm presented here may be used to build a more complete model for thin-section scale textural development.

Concluding Remarks

We have shown that the Fe-Mg exchange reaction between garnet and biotite can be modelled using the Elle data structure. Hybrid types of nodes (nodes and unodes) are used for the calculation of diffusive mass transfer along grain boundaries and within the volume of garnet and biotite. However, there are major limitations due to reduced dimensions in the model and unknown reaction constant at the interface. There are also uncertainties in algorithm when calculating the local equilibrium. In spite of these limitations and uncertainties, we feel that the model presented here can be at least a good starting point to model diffusive mass transfer in a material with grain boundary structure.

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References

- Askeland, D.R., 1994. The science and engineering of materials, 3rd ed: PWS Publishing Company, Boston, p.812.
- Crank, J., 1975. The Mathematics of diffusion, 2nd ed.: Oxford University Press, Oxford, p. 414.
- Cygan R. T. & Lasaga, A.C., 1985. Self-diffusion of magnesium in garnet at 750° to 950°C. *Am. J. Sci.* 285, 328-350.
- Ehlers, K., Powell, R. & Stuwe, K., 1994. Cooling rate histories from garnet+biotite equilibrium. *Am. Miner.* 79, 737-744.
- Ferry, J. M. & Spear, F.S., 1978. Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. *Contrib. Mineral. Petrol.* 66, 113-117.
- Florence, F.P. & Spear, F.S. (1991) Effects of diffusional modification of garnet growth zoning on P-T path calculations. *Contrib. Mineral. Petrol.* 107, 487-500.
- Hoffman, A.W. & Giletti, B.J., 1974, Iron microprobe analysis of a potassium self-diffusion experiment in biotite, *Earth Planet. Sci. Lett.* 24, 48-52.
- Jessell, M. W., Bons P. D., Evans L., Barr T. D. & Stuewe K. 2001. Elle : the numerical simulation of metamorphic and deformation microstructures. *Computers and Geosciences* 27, 17-30.
- O'Brien, P. J., 1997. Garnet zoning and reaction textures in overprinted eclogites, Bohemian Masif, European Variscides: A record of their thermal history during exhumation. *Lithos* 41, 119-133.
- Powell, R. & White, L., 1995. Diffusive equilibrium between minerals during cooling: an analytical extension to Dodson's equation for closure in one dimension. *Geol. J.* 30, 295-305
- Spear, F. S., 1991. On the interpretation of peak metamorphic temperatures in light of garnet diffusion during cooling. *J. Metamorph. Geol.* 9, 379-388.
- Spear, F. S., 1993. Metamorphic phase equilibria and pressure-temperature-time paths: Mineralogical Society of America, Washington, D.C., p.799.