

Numerical Modeling of Growth Zoning at Nonstationary Crystallization of Solid Solutions: Metamorphic Garnets¹

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In this paper we consider crystallization of solid solutions and formation of growth zoning in minerals. To ascertain the role of various mechanisms producing zoning we have constructed kinetic models of nonsteady solid solution crystal growth. The equations obtained describe the temporal evolution of the solute and crystal composition. Since these equations are not solvable analytically we have solved them numerically by a fourth-order Runge–Kutta method. On the basis of this solution we can compute the zoning profiles for different crystallization modes and conditions. The constructed models have been used for study of mechanisms of zoning formation in metamorphic garnets. We conclude that the main mechanism of production of growth zoning is fractionation. The role of change of distribution coefficient in “equilibrium crystallization” is negligible. The modelling of zoning profiles reveals that simple arch-shaped profiles originate from crystallization in a closed system while complicated nonmonotonic profiles appear with crystallization in open systems under fluid flow. The duration of metamorphic garnet crystallization is estimated.

KEY WORDS: intracrystalline zoning; crystal growth; metamorphic crystallization; numerical modeling.

INTRODUCTION

Many natural and synthetic crystals are solid solutions. Microprobe studies show that most of them are zonal (Tracy, 1982). The intracrystal zoning can form during crystal growth (primary zoning) or during later transformations (secondary zoning). Though growth zoning is a fairly common phenomenon, its origin is insufficiently studied. Most investigators assume that zoning in natural crystals arises under control of thermodynamic conditions (temperature and pressure). The role of crystal growth kinetics in the origin of zoning is obscure. No theory exists for solid solution crystal growth. The effect of crystallization mechanisms on growth zoning patterns is unknown. Such disregard to growth zoning seems amazing.

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Most metamorphic garnets have chemical zoning manifested as a change of the divalent cation (Fe, Mg, Mn, and Ca) contents from crystal core to rim (Tracy, 1982). In normally zoned garnets Mn content decreases to the crystal edge, while Mg content rises. Fe content, as a rule, also rises. Garnets with normal zoning have usually arc- or bell-shaped concentration profiles. In reverse-zoned garnets Mn and Fe contents decrease while Mg content increases. The profile shape in these garnets is more complicated: the core is almost unzoned while composition in the rim changes abruptly. Both normal- and reverse-zoned garnets display antipathetic behavior of Mg and Mn. Other zoning types belong to complicated zoning including nonmonotonic change of element concentrations from the grain core to rim or sympathetic change of Mg and Mn contents. The content of calcium can change irregularly.

Interest in garnet zoning reflects the abundance of garnets and their importance to metamorphic thermobarometry. However, the origin of zoning is not obvious. In Azimov and Shtukenberg (2001) we showed that thermodynamic analysis is insufficient to reveal the main mechanism of formation of growth zoning. It compelled us to consider the kinetics of mixed crystal growth. The mathematical modelling of crystallization of solid solutions at disequilibrium and nonstationary conditions allows us to ascertain the effect of the crystallization mechanism on zoning character (trend and concentration profile shape). Since metamorphic minerals crystallize from aqueous fluid (Rubie, 1986), we have modelled solid solution crystal growth from aqueous solution. Note that similar calculations are useful not only for reconstruction of mineral genesis but also for prediction of zoning in industrial crystals.

THE PRINCIPAL MECHANISMS FORMING THE GROWTH ZONING

The component distribution between solid and aqueous solutions is described by the Henderson–Kracek equation (Henderson and Kracek, 1927):

$$\frac{c_i}{c_j} = K_{ij} \frac{x_i}{x_j} \quad (1)$$

where c_i is molality of the i th component in the aqueous solution, x_i is the mole fraction of the i th component in the solid solution, and K_{ij} is the distribution coefficient. This equation manifests that growth zoning forms with change of the solute composition or distribution coefficient. The solute composition can change because of fractionation in a closed system or mass influx in an open system. The distribution coefficient changes if temperature or pressure varies over crystallization. The intracrystalline diffusion must be negligible otherwise zoning pattern would be smoothed or obliterated.

Rayleigh fractionation was supposed by Hollister (1966) to explain the bell-shaped Mn concentration profiles. Hollister used the equation for fractionation of a

minor component. The fractionation behavior of major components in the aqueous solution can be described by the differential Doerner–Haskins equation [Doerner and Haskins, 1925]:

$$K_{ij}d \ln c_i = d \ln c_j. \quad (2)$$

This equation is suitable for equilibrium between the outer crystal layer and aqueous solution. Since the inner core retains its composition such crystallization was called quasiequilibrium. Integration of equation (2) at constant K_{ij} yields the relation

$$\left(\frac{c_i}{c_i^0}\right)^{K_{ij}} = \frac{c_j}{c_j^0}, \quad (3)$$

with index “0” indicating initial value of a parameter. Intensity of fractionation depends evidently on the value of the distribution coefficient. Equations (2) and (3) show the evolution of the composition of the aqueous solution with fractionation but do not describe the change of the crystal composition. The mass influx in open systems happens under advective mass transfer, for instance, in metasomatism. If fluid flow is nonstationary then intracrystalline zoning is determined by the evolution of the fluid composition (Drugova, Nikitin, and Terent’eva, 1970; Yardley and others, 1991).

Change of the intense parameters (temperature or pressure) during crystallization should modify the distribution coefficient. In turn, change of the distribution coefficient results in change of the composition of growing layer. So, in this case, zoning ensues not from steady partition but as a result of change of external conditions. In many authors’ opinion (e.g., Spear and Selverstone, 1983; Tracy, Robinson, and Thompson, 1976) just this mechanism is responsible for the primary zoning in metamorphic garnets. Some authors call it “equilibrium partition” or “equilibrium crystallization” though the last term means any crystallization with distribution coefficient independent from the crystal growth rate. Temperature is the main factor since the effect of pressure on the Fe/Mg distribution coefficient is negligible (Perchuk, 1977). Therefore we consider below only the temperature effect.

CONSTRUCTION OF MATHEMATICAL MODELS OF SOLID SOLUTION CRYSTAL GROWTH

Phase Relations in the System “Solid Solution – Aqueous Solution”

To describe the crystallization kinetics we should know the phase diagram of the system. We shall use the description of the phase relations in the system

“solid solution – aqueous solution” (SSAS) (Azimov and Shtukenberg, 2000). For simplicity let us consider the ideal solid solution especially because the mixing parameters in Fe–Mg–Mn garnets are low and close to zero. Solubility of an ideal solid solution is

$$\tilde{c} = \sqrt[\lambda]{\sum_i (x_i s_i^\lambda)} \quad (4)$$

where \tilde{c} is the bulk molality of the solute, s_i is the solubility of the pure i th end-member, x_i is the mole fraction of the i th component of the solid solution, and λ is an empirical parameter, approximately 2. Equation (4) describes the solidus of the SSAS system. Respectively, the solutus of this ideal solid solution may be described by equation

$$\tilde{c} = \sqrt[\lambda]{\frac{\sum_i c_i}{\sum_i \frac{c_i}{s_i^\lambda}}} = \sqrt[\lambda]{\sum_i \frac{y_i}{s_i^\lambda}} \quad (5)$$

in which y_i is the mole fraction of the i th component in the solute. The component distribution between solid and aqueous solutions obeys the Henderson–Kracek Eq. (1), and the distribution coefficient is

$$K_{ij} = \left(\frac{s_i}{s_j} \right)^\lambda. \quad (6)$$

This expression together with the Doerner–Haskins equation indicates that a less soluble component should be concentrated in the crystal while a more soluble component will be held in the aqueous solution. Therefore, the crystal core should be enriched with the less soluble component while the rim is richer in the more soluble component.

The Generalized Equation of Mixed Crystal Growth

Let us consider a growing crystal having a polyhedral form face. The volume W of the crystal can be expressed in general form as

$$W = \Phi r^3. \quad (7)$$

Taking into account the additivity of the volume of ideal solid solution we may write it also as

$$W = \Phi r_0^3 + \sum_i (w_i n_i). \quad (8)$$

Here, Φ is a shape factor (a numerical coefficient depending on the crystal shape), r is the crystal "radius" (the length of the normal to a crystal face), r_0 is the radius of the nucleus or seed, w_i and n_i are molar volume and mole amount of the i th component of the solid solution. The shape factor is eight for a cube, $4\sqrt{3}$ for an octahedron, $4\sqrt{2}$ for a dodecahedron, and $\frac{4}{3}\pi$ for a sphere.

To describe the crystal growth rate we take the empirical power law equation:

$$\dot{r} = k\sigma^\kappa \quad (9)$$

where r is crystal growth rate, k is kinetic coefficient, σ is relative supersaturation, and κ is an exponent. At the dislocation crystal growth κ value is approximately 2. For the diffusion-controlled crystallization $\kappa = 1$ and $k = D/\delta$ where D is the diffusion coefficient and δ is the diffusion zone thickness [Chernov, 1984]. The relative supersaturation is defined by the ratio of solute concentrations in the supersaturated and saturated solutions:

$$\sigma = \frac{c}{\tilde{c}} - 1. \quad (10)$$

Further, we suppose that the component distribution does not depend on the crystal growth rate (such crystallization is called an equilibrium one). In this case, we can use equations (9) and (10) for the description of the crystallization kinetics in a system with isomorphous components [Soloviev and others, 1997]. Then, c in relation (10) is the total solute concentration, $c = \sum_i c_i$, and the equilibrium concentration \tilde{c} can be found from Eqs. (4) and (5). Substituting expression (4) into relation (10) and taking into account that $y_i = c_i / \sum_j c_j$ we derive an expression for supersaturation of aqueous solution with isomorphous components:

$$\sigma = \sqrt[\lambda]{\sum_i c_i \cdot \sum_i \frac{c_i}{s_i^\lambda}} - 1. \quad (11)$$

The general form of the mass balance equation for i th component in the system is

$$\dot{N}_i + \dot{n}_i - J_i = 0 \quad (12)$$

where N_i and n_i are mole amounts of the i th component in the aqueous solution and in the crystal and J_i is the total influx of the i th component into the system. In the closed system the last term is absent: $J_i = 0$.

If we denote the i th component amount in surface layer of the crystal as dn_i then its mole fraction x_i in the overgrowing layer is equal to $dn_i / \sum_j dn_j$. In equilibrium crystallization the composition of the crystal surface layer can be

expressed as

$$x_i = \frac{\frac{c_i}{s_i^*}}{\sum_j \frac{c_j}{s_j^*}}$$

Equation (11) for supersaturation contains the molalities of components c_i while mass balance equation (12) contains the mole amounts of components N_i in the solution. These quantities are connected to each other by relation, $N_i = mc_i$, where m is the solvent mass in the system. In a closed system, m is constant while in an open system it may change (for instance, with solvent evaporation or nonstationary solution flow through the system). Thus, the relation between change of the amount of the i th component in aqueous solution and their molality is controlled by the mode of crystallization.

The character of the kinetic coefficient dependence k on the solid solution composition is poorly studied. The linear form of the dependence $k = \sum_i x_i k_i$ seems to be unlikely since then the Arrhenius law would not be true for k even if it was valid for every k_i . Therefore, the form, $k = \prod_i k_i^{x_i}$, of compositional dependence seems to be preferable. Below, we use as parameter k implying a general form $k(x_i)$.

Equating relation (7) to (8), differentiating the resulting relation and inserting into the resulting relation (9), (11), and (12) with $n_i = 0$ at the initial moment we can write

$$\sum_i [w_i(\dot{N}_i - J_i)] = 3\Phi_k \left\{ r_0^3 + \frac{1}{\Phi} \sum_i \left[w_i \left(\Delta N_i + \int_0^t J_i dt \right) \right] \right\}^{2/3} \times \left(\sqrt[\lambda]{\sum_i c_i \cdot \sum_i \frac{c_i}{s_i^{\lambda}}} - 1 \right)^{\kappa} \quad (13)$$

with $\Delta N_i = N_i^0 - N_i$ being the change of the i th component amount in the aqueous solution during time t . Equation (13) describing crystallization in the SSAS system cannot be solved since we do not know the general interrelationship between N_i , J_i , and c_i . To find connections between these quantities we should consider various mechanisms of the crystallization.

Isothermal Desupersaturation

Isothermal desupersaturation is one of the basic crystallization mechanisms. Nonzero initial supersaturation $\sigma_0 > 0$ may be produced in various ways: solution cooling, solvent evaporation, and so on. The crystallization proceeds owing to

decrease of the supersaturation. Since the process is isothermal the solubilities s_i of components and their kinetic coefficients k_i do not change during the process. Desupersaturation happens in a closed system, hence $J_i = 0$ and $m = \text{const}$. Consideration of this transformation of equation set (13) yields a differential equation for the composition of the aqueous solution at desupersaturation:

$$\sum_i (w_i \dot{c}_i) = -\frac{3\Phi k}{m} \left\{ r_0^3 + \frac{m}{\Phi} \sum_i [w_i (c_i^0 - c_i)] \right\}^{2/3} \left\{ \sqrt[\lambda]{\sum_i c_i \cdot \sum_i \frac{c_i}{s_i^\lambda}} - 1 \right\}^\kappa. \quad (14)$$

With isothermal conditions, the distribution coefficients K_{ij} for each pair of components are constant. Therefore, the relation between two components of the aqueous solution obeys the integral form of the Doerner–Haskins Eq. (3). The solid solution consists of the z components, hence the crystallization can be described by the set consisting of Eq. (14) and $(z-1)$ equation (3). The initial condition is determined as relation $c_0 > \tilde{c}$. The only mechanism producing zoning under isothermal desupersaturation is fractionation.

The set can be reduced to a single equation. Let us introduce an auxiliary variable, α , such that $\alpha \equiv c_1/c_1^0$. Substituting α into (3), resigning K_{li} as K_i and transforming we get expressions for concentration and its time derivative: $c_i = c_i^0 \alpha^{K_i}$ and $\dot{c}_i = c_i^0 \alpha^{K_i-1} K_i \dot{\alpha}$. Substituting these relations into Eq. (14) we obtain the desired equation for crystallization in a system with isomorphous components and isothermal desupersaturation:

$$\dot{\alpha} = -\frac{3\Phi}{m} \cdot \frac{\alpha}{\sum_i (w_i K_i c_i^0 \alpha^{K_i})} k(\alpha) \left\{ r_0^3 + \frac{m}{\Phi} \sum_i [w_i x_i^0 (1 - \alpha^{K_i})] \right\}^{2/3} \times \left\{ \sqrt[\lambda]{\sum_i (c_i^0 \alpha^{K_i}) \sum_i \left(\frac{c_i^0}{s_i^\lambda} \alpha^{K_i} \right)} - 1 \right\}^\kappa. \quad (15)$$

The initial condition for this equation is $\alpha_0 = 1$. Equation (15), just like the set comprising Eq. (14) along with $(z-1)$ equation (3), has no analytical solution and should be solved numerically. Transforming the solution $\alpha = \alpha(t)$ we come to functions of the form $c_i = c_i(t)$ describing the evolution of solution composition. Then we can find solution supersaturation, crystal size, and composition.

Polythermal Crystallization in Closed System

Solubility reduction upon change of temperature produces supersaturation. Crystallization happens with cooling of the solution if the temperature coefficient is

positive (solubility rises with increasing temperature) and with heating if the temperature coefficient is negative. In the model under consideration crystallization is in a closed system ($J_i = 0$ and $m = \text{const}$) like desupersaturation. So polythermal (nonisothermal) crystallization can be described by the set of Eq. (14) and $(z-1)$ equation (2). The integral form of the Doerner–Haskins equation is inapplicable for nonisothermal process since the distribution coefficient K_{ij} depends in that case on temperature. The parameters k and s_i entering Eq. (14) depend on temperature also. The form of such dependence may vary. The kinetic coefficient shows usually the Arrhenius behavior:

$$k = k^* \exp\left(-\frac{E}{RT}\right) \quad (16)$$

In this expression, k^* is pre-exponential factor, E is activation energy, and R is universal gas constant (8.314472 J/mol · K).

The transformation of the equation set to a single equation in this model is impossible. However, we can rewrite the set to make it more convenient for numerical solution:

$$\dot{c}_i = \frac{c_i}{s_i^\lambda} \cdot A, \quad (17)$$

where $i = 1, \dots, z$, and A is the factor common for all z equations:

$$A = -\frac{3\Phi k^* \exp\left(-\frac{E}{RT}\right)}{m \sum_j \frac{w_j c_j}{[s_j(T)]^\lambda}} \cdot \left\{ r_0^3 + \frac{m}{\Phi} \sum_j [w_j (c_j^0 - c_j)] \right\}^{2/3} \\ \times \left\{ \sqrt[\lambda]{\sum_j c_j \cdot \sum_j \frac{c_j}{[s_j(T)]^\lambda}} - 1 \right\}^\kappa.$$

As initial condition we accept zero supersaturation.

Crystallization in a closed system is accompanied by component fractionation. At the same time, the distribution coefficient depends on temperature. As a result, there are two different mechanisms producing the growth zoning.

Polythermal Crystallization From Aqueous Solution of Constant Composition

To estimate the effect of dependence of the distribution coefficient on temperature we shall examine the crystallization without the fractionation. It means that composition of the aqueous solution is constant during the whole crystallization.

Such crystallization is possible in an open system, with buffering of the solution composition or for the crystal being small in comparison with total amount of the solute in the system. Then, zoning is controlled only by the temperature dependence of the distribution coefficient. Therefore, such zoning can be called “temperature” zoning. Supersaturation of the solution in polythermal crystallization is produced with decreasing solubility. The total solute concentration, c , can be calculated from the system phase diagram:

$$c = (1 + \sigma_0) \left(\sum_i \frac{y_i}{(s_i^0)^\lambda} \right)^{-1/\lambda} = \text{const.}$$

σ_0 is the initial supersaturation and s_i^0 is solubility at the initial temperature T_0 . In this model, $y_i = \text{const.}$ Then, the crystal growth rate at temperature T is equal

$$\dot{r} = k^* \exp\left(-\frac{E}{RT}\right) \left\{ c^\lambda \sqrt[\lambda]{\sum_i \frac{y_i}{[s_i(T)]^\lambda}} - 1 \right\}^\kappa$$

and the crystal size can be found by time integration of the crystal growth rate:

$$r = \int_0^t \dot{r} dt$$

Isothermal Crystallization in the Open System: Model of the “Flow Reactor”

In the previous model, we have suggested that fractionation in the system is completely suppressed. It can be evoked, in particular, by very intense fluid flow. However, at lower fluid velocities, the fractionation takes place though less so than in a closed system. Open systems play an important role in metamorphic processes, therefore an investigation of the formation of intracrystalline zoning with fluid flow appears essential. The crystallization in an open system may be described by the “flow reactor” model which supposes steady flux of aqueous solution with constant velocity v and supersaturation σ through the system. In this case the influx of the i th component can be described with expression

$$J_i = Svd\Delta c_i \quad (18)$$

where S is fluid flow cross-section, d is fluid density ($m = Vd$ with V being the volume of the crystallization area) and $\Delta c_i = c_i^0 - c_i$ is difference between contents of the i th component in the inflowing fluid c_i^0 and in the fluid in the

crystallization area c_i . Substituting expression (18) into Eq. (13) and denoting $\omega = Sv/V$ we achieve the main equation for the crystallization in open system:

$$\sum_i (w_i \dot{c}_i) = \omega \sum_i (w_i \Delta c_i) - \frac{3\Phi k}{m} \left\{ r_0^3 + \frac{m}{\Phi} \sum_i \left[w_i \left(\Delta c_i + \omega \int_0^t \Delta c_i dt \right) \right] \right\}^{2/3} \times \left\{ \sqrt[\lambda]{\sum_i c_i \cdot \sum_i \frac{c_i}{s_i^\lambda} - 1} \right\}^k. \quad (19)$$

To describe the component relations in open system we can use the differential form of the Doerner–Haskins Eq. (2). To make the set of Eqs. (19) and (z-1) Eq. (2) more convenient for numerical solution, we transform it to a set of z equations of the form

$$\dot{c}_i = \frac{c_i}{s_i^\lambda} \mathbf{B} \quad (20)$$

where \mathbf{B} is the common factor:

$$\mathbf{B} = \frac{1}{\sum_j \frac{w_j c_j}{s_j^\lambda}} \left[\omega \sum_j (w_j \Delta c_j) - \frac{3\Phi k}{m} \left\{ r_0^3 + \frac{m}{\Phi} \sum_j \left[w_j \left(\Delta c_j + \omega \int_0^t \Delta c_j dt \right) \right] \right\}^{2/3} \times \left\{ \sqrt[\lambda]{\sum_j c_j \cdot \sum_j \frac{c_j}{s_j^\lambda} - 1} \right\}^k \right].$$

This equation set is similar to set (17), but it includes integro-differential equations which can be reduced by a change of variables to simple differential equations. For this, let us introduce auxiliary variables $\alpha_i = \int_0^t \Delta c_i dt$, then $c_i = c_0 - \alpha_i$ and $\dot{c}_i = -\dot{\alpha}_i$. By substituting these relations into set (20), we obtain the set consisting of z numerically solvable second-order differential equations:

$$\ddot{\alpha}_i = -\frac{c_i^0 - \alpha_i}{s_i^\lambda} \mathbf{C}$$

with common factor

$$C = \frac{1}{\sum_j \left(w_j \frac{c_j^0 - \dot{\alpha}_j}{s_j^\lambda} \right)} \left[\omega \left(\sum_j w_j \dot{\alpha}_j \right) - \frac{3\Phi k}{m} \left\{ r_0^3 + \frac{m}{\Phi} \sum_j [w_j (\dot{\alpha}_j + \omega \alpha_j)] \right\} \right]^{2/3} \\ \times \left\{ \sqrt[3]{\sum_j (c_j^0 - \dot{\alpha}_j) \cdot \sum_j \frac{c_j^0 - \dot{\alpha}_j}{s_j^\lambda} - 1} \right\}^\kappa.$$

The initial conditions for this set are defined by relation $\alpha_i^0 = 0$. It is evident that the system behavior depends on the value of the parameter ω . The physical meaning of it is the rate of solution replacement in the crystallization area. The ω value at constant V and S is determined by the flow velocity. At $v = 0$ the process is reduced to isothermal desupersaturation while at $v \rightarrow +\infty$ the solution concentration has no time to drop so $\dot{c}_i = 0$.

Numerical Parameters of Models

The parameter values selected are very important to the numerical calculations. Here, we report only their values. For detailed examination and discussion see Azimov (2000). We compute the zoning profiles for garnets in the isomorphous series “almandine $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – pyrope $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$.”

The solubilities of the garnet minerals, s_i , in unmineralized aqueous fluid were calculated for some T and P values using the thermodynamic data on garnets from Berman and Aranovich (1996) and on aqueous species from Tanger and Helgeson (1988) and Shock and Helgeson (1988), and the computer codes SUPCRT92 [Johnson, Oelkers, and Helgeson, 1992], GBFLOW [Grichuck, 1996], and FLUID [Skvirsky, 1995]. We interpolated the temperature dependence of solubility with expression $s = \exp(a_1 + a_2/T + a_3T)$ (mol/kg H_2O) where T is absolute temperature. At $P = 5$ kbar the coefficients are $a_1 = -5.894$, $a_2 = -9.873 \cdot 10^2$, and $a_3 = -4.629 \cdot 10^{-3}$ for almandine and $a_1 = -5.467$, $a_2 = -1.937 \cdot 10^2$, and $a_3 = -5.208 \cdot 10^{-3}$ for pyrope. The molar volumes of almandine and pyrope are equal to 115.24 and 113.11 cm^3/mol correspondingly [Berman and Aranovich, 1996]. The Fe : Mg ratio in the fluid is accepted to be 1. The garnet kinetic coefficient does not depend on the composition of mixed crystal and obeys the Arrhenius law (16) with parameters $k^* = 1.6 \cdot 10^{-5}$ cm/s and $E = 50$ kJ/mol estimated in Azimov (2000). For the exponent in Eq. (9), we use value $\kappa = 2$ corresponding to dislocation growth. The nucleus size $r_0 = 0.1$ μm .

Model calculations of isothermal desupersaturation have been done for 500°C and 5 kbar. At this temperature, $s_{Alm} = 2.136 \cdot 10^{-5}$ mol/kg H_2O ,

$s_{\text{Prp}} = 5.812 \cdot 10^{-5}$ mol/kg H_2O , and $k = 0.21$ cm/year. The initial fluid supersaturation under isothermal desupersaturation is supposed to be 0.1–0.3. In polythermal crystallization, the initial fluid supersaturation is accepted to be zero. The temperature change obeys linear equation $T(t) = T_0 + qt$ with $q = 500\text{--}2000^\circ\text{C}/\text{Ma}$ and $T_0 = 773$ K (500°C). Such heating rate corresponds to a rock burial rate up to some centimeter per year.

Calculating crystallization in an open system, we consider the garnet crystal growth from unmineralized fluid (not containing dissolved salts, HCl and NaOH) at 500°C and 5 kbar and from alkaline fluid (1M NaOH) at 600°C and 5 kbar. In alkaline fluid $K_{\text{Fe-Mg}} > 1$ (the distribution coefficient is inverted) (Azimov and Shtukenberg, 2001). The solubilities of garnets in the alkaline fluid are equal to $7.403 \cdot 10^{-6}$ mol/kg H_2O for almandine and $2.429 \cdot 10^{-6}$ mol/kg H_2O for pyrope. The kinetic coefficient at 600°C is $k = 0.51$ cm/year. The fluid density at 500°C and 600°C ($P = 5$ kbar) is equal to 0.88 and 0.81 g/cm³. The flux velocities v used in the “flow reactor” model fluid lie in the range 0.005 to 500 cm/year.

DISCUSSION

Those of the models discussed above which describe crystallization in a closed system have analogous structures. Differential equation sets representing them describe the evolution of the aqueous solution during the growth of mixed crystals. We have solved these equation sets using a fourth-order Runge–Kutta method. To find the zoning profile for the crystallization at constant fluid composition any method of numerical integration may be used.

The solutions obtained have the form $c_i = c_i(t)$. Using them, we have calculated functions $x_i = x_i(t)$ and $r = r(t)$ and have found functional dependencies $x_i = x_i(r)$ describing intracrystalline zoning patterns (Figs. 1–7). We have calculated only zoning profiles for systems with two isomorphic components (Fe and Mg) but suggested models may analyze multicomponent solid solutions. Below, we consider separate models and obtained results in detail.

Isothermal Desupersaturation

In this model, growth zoning is produced by fractionation. Zoning contrast as it follows from Eq. (3) depends on the value of the distribution coefficient. The kinetic curves, $\sigma_i = \sigma_i(t)$, have sigmoidal shape (Fig. 1(a)). Supersaturation diminishes and asymptotically vanishes. The higher initial solution supersaturation the faster it diminishes and the earlier the system achieves equilibrium. Initial supersaturation in this case determines not only system disequilibrium but also crystallization nonstationarity. With desupersaturation, garnet crystals grow rather

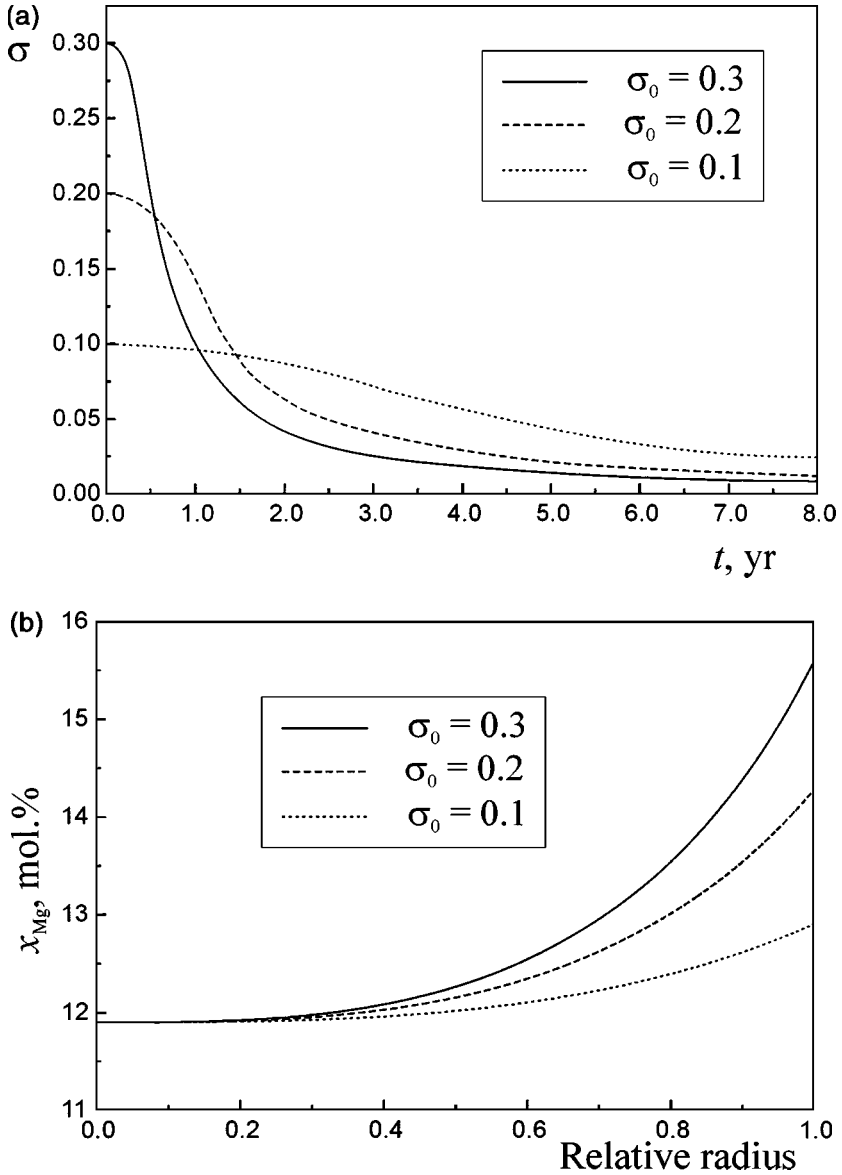


Figure 1. Crystallization of Fe-Mg garnet at the isothermal desupersaturation (500°C and 5 kbar). (a) evolution of the solution supersaturation; (b) zoning profiles. Values of the initial supersaturation σ_0 are given in the legend. For the explanations and parameters used see the text.

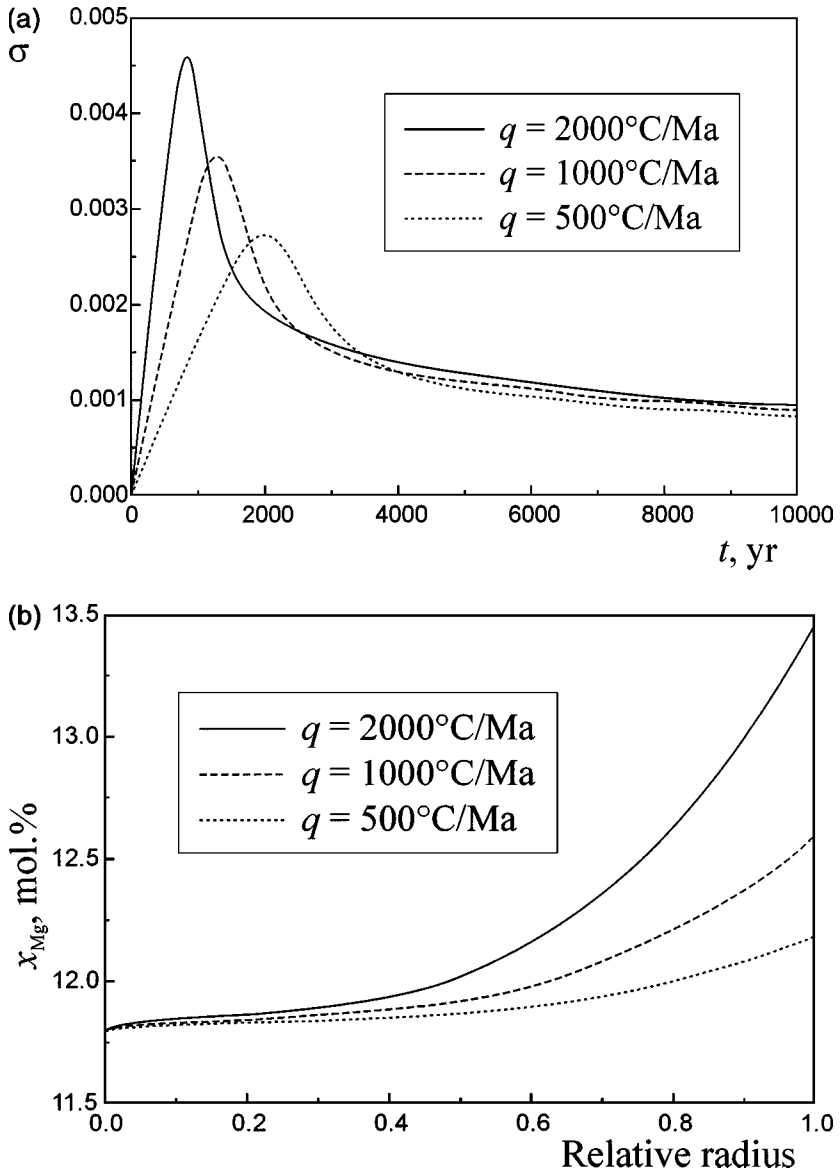


Figure 2. Polythermal crystallization of Fe–Mg garnet in the closed system at 5 kbar. (a) evolution of the solution supersaturation; (b) zoning profiles. Values of the heating rate q are given in the legend.

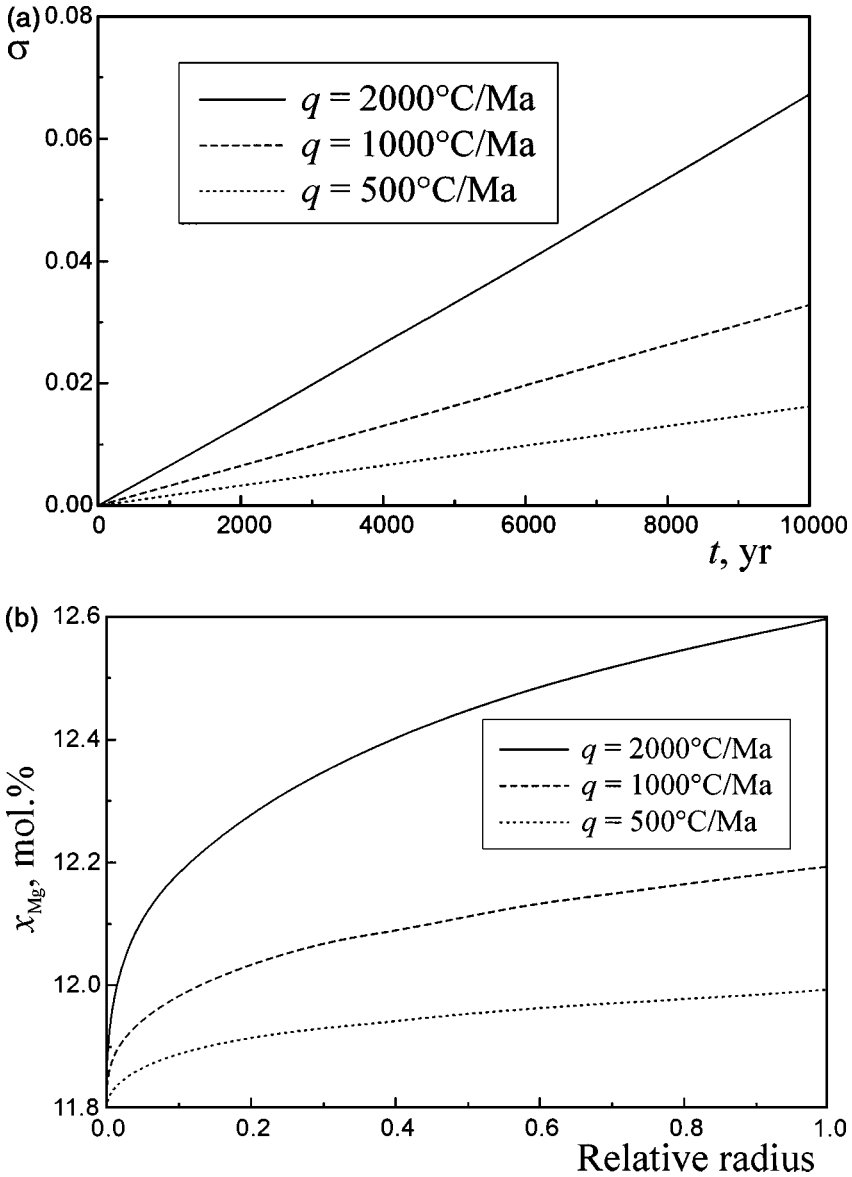


Figure 3. Polythermal crystallization of Fe–Mg garnet at 5 kbar and the constant fluid composition. (a) evolution of the solution supersaturation; (b) zoning profiles. Values of the heating rate q are given in the legend.

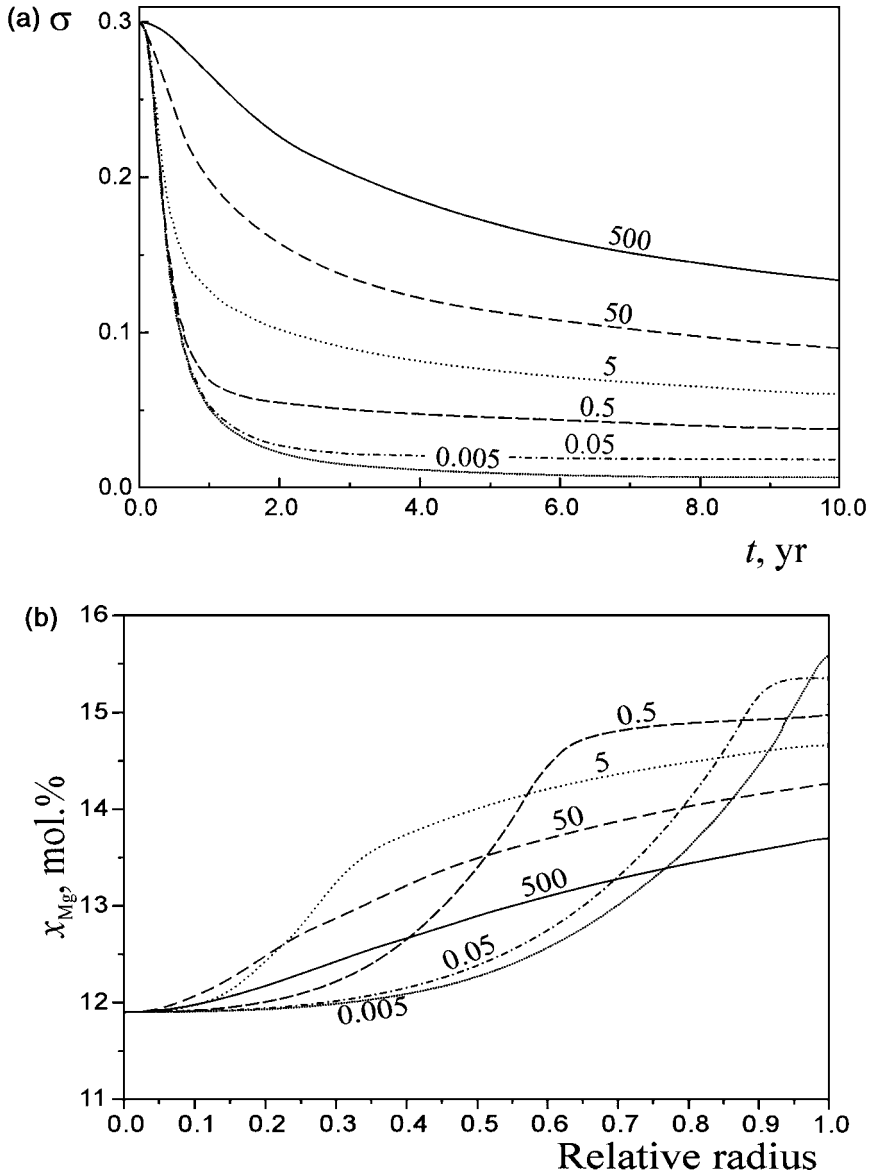


Figure 4. Crystallization of Fe–Mg garnet in the open system at 500°C, 5 kbar and various fluid flow rates ($\sigma_0 = 0.3$). (a) evolution of the solution supersaturation; (b) zoning profiles. The fluid flow velocities v (cm/year) are shown near curves.

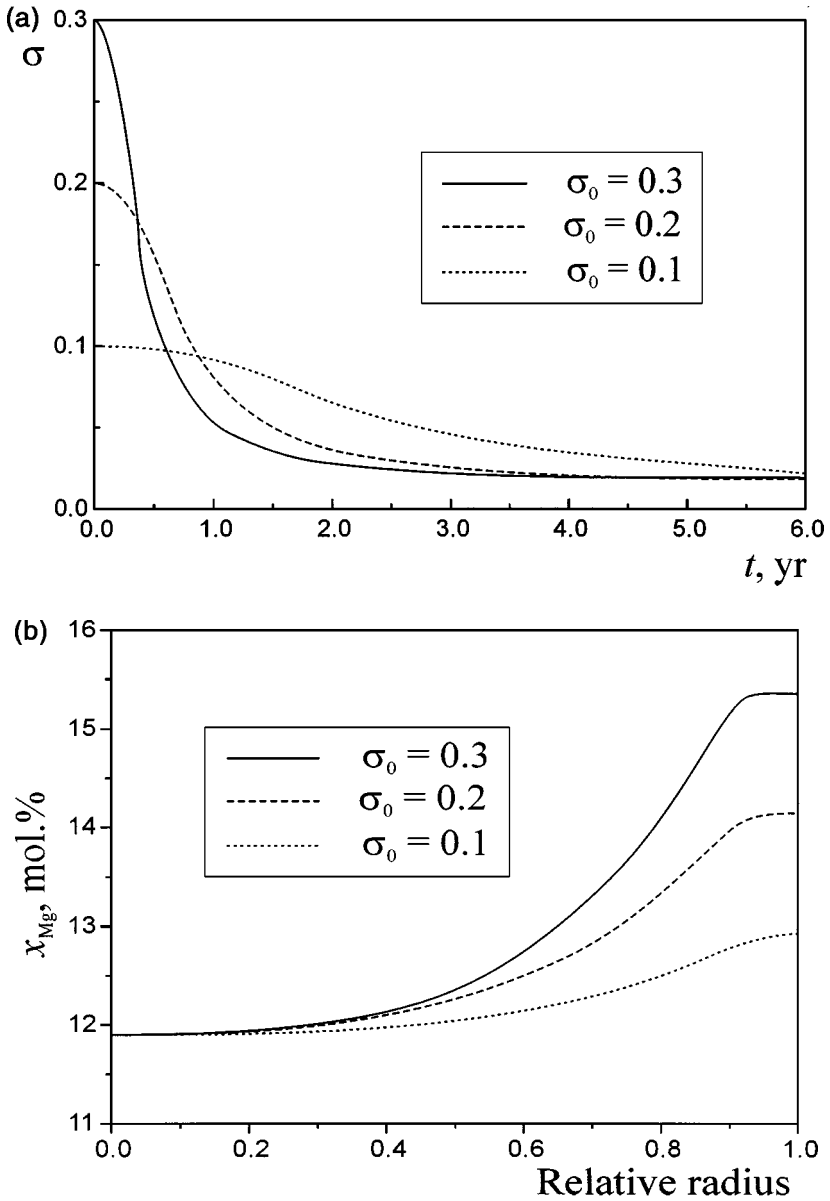


Figure 5. Crystallization of Fe–Mg garnet in the open system at 500°C, 5 kbar and various initial fluid supersaturations. (a) evolution of the solution supersaturation; (b) zoning profiles (the velocity of the fluid flow $v = 0.05$ cm/year); (c) evolution of the solution supersaturation; (d) zoning profiles (the fluid flow velocity $v = 50$ cm/year). Values of the initial supersaturation σ_0 are given in the legend.

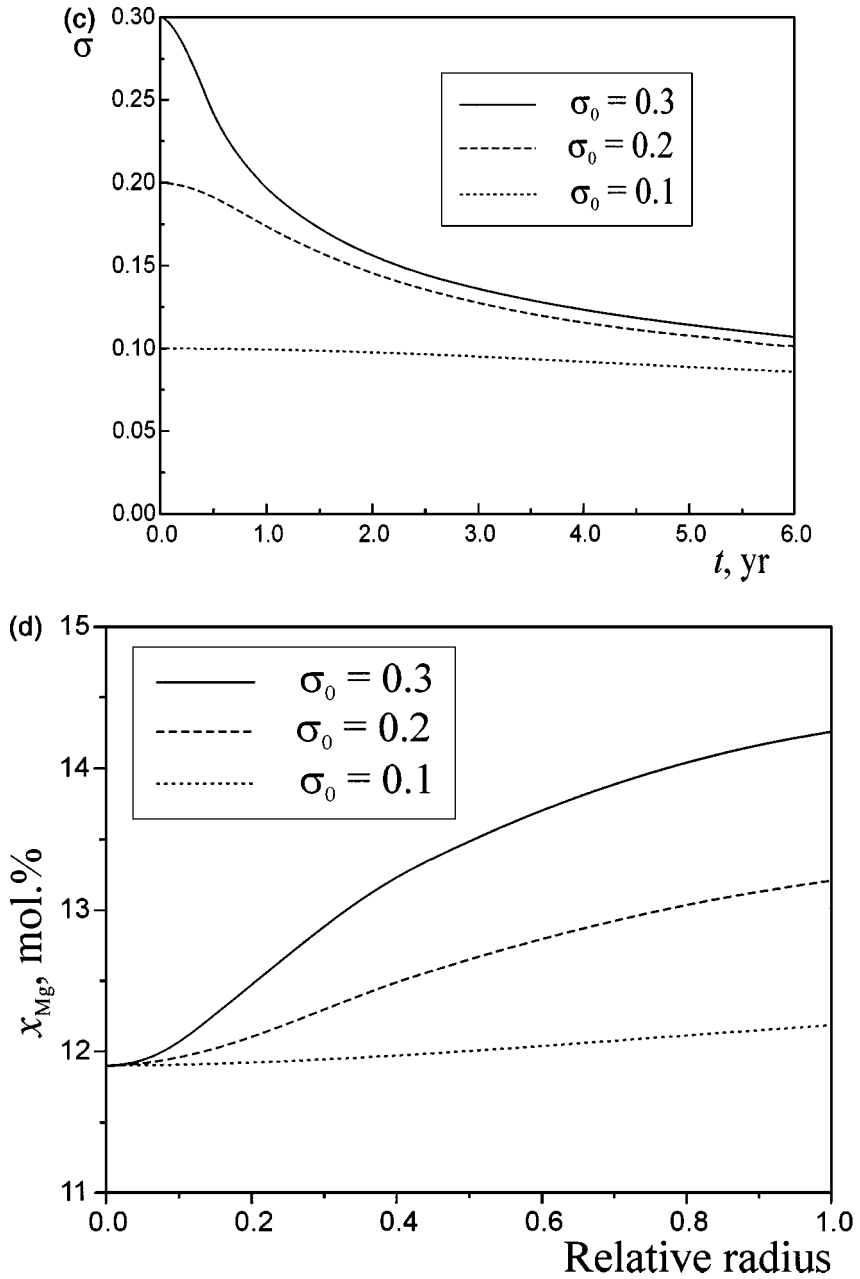


Figure 5. Continued.

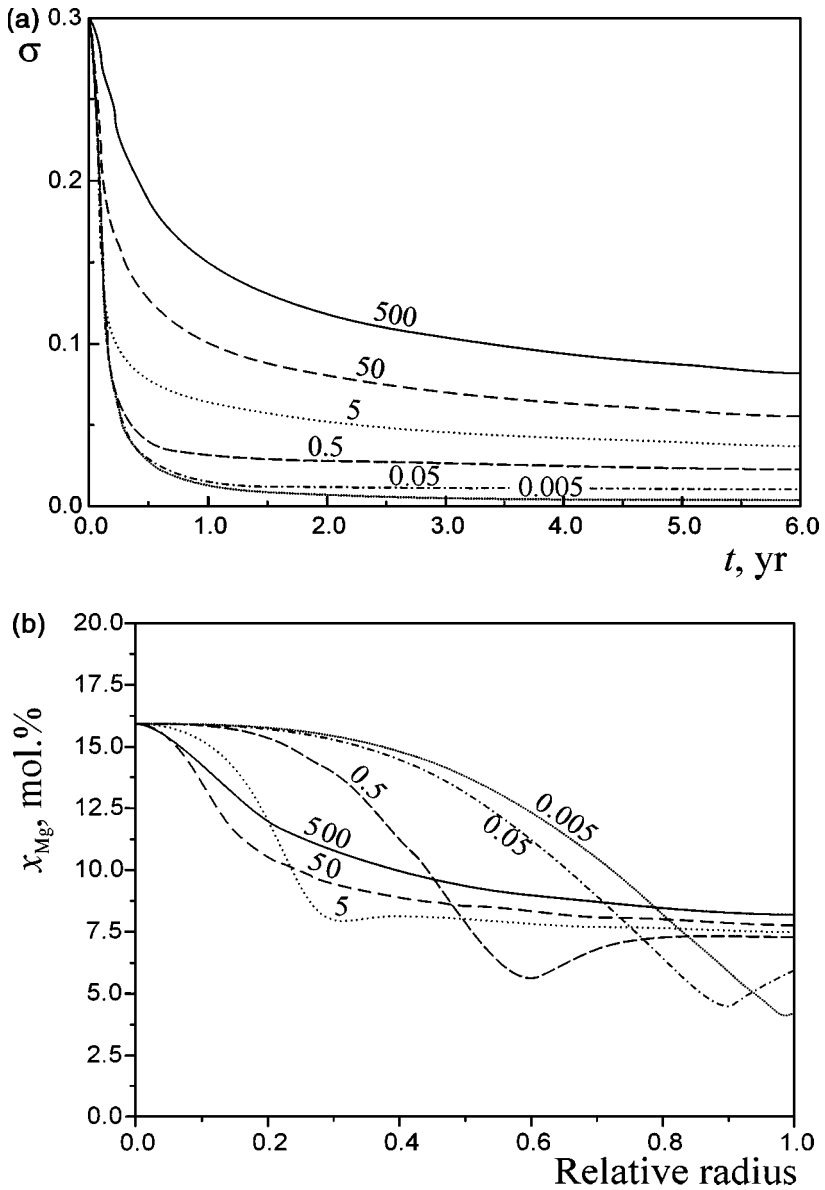


Figure 6. Crystallization of Fe–Mg garnet in the open system from 1 M NaOH solution at 600°C, 5 kbar and various fluid flow rates ($\sigma_0 = 0.3$). (a) evolution of the solution supersaturation; (b) zoning profiles. The fluid flow velocities v (cm/year) are shown near curves.

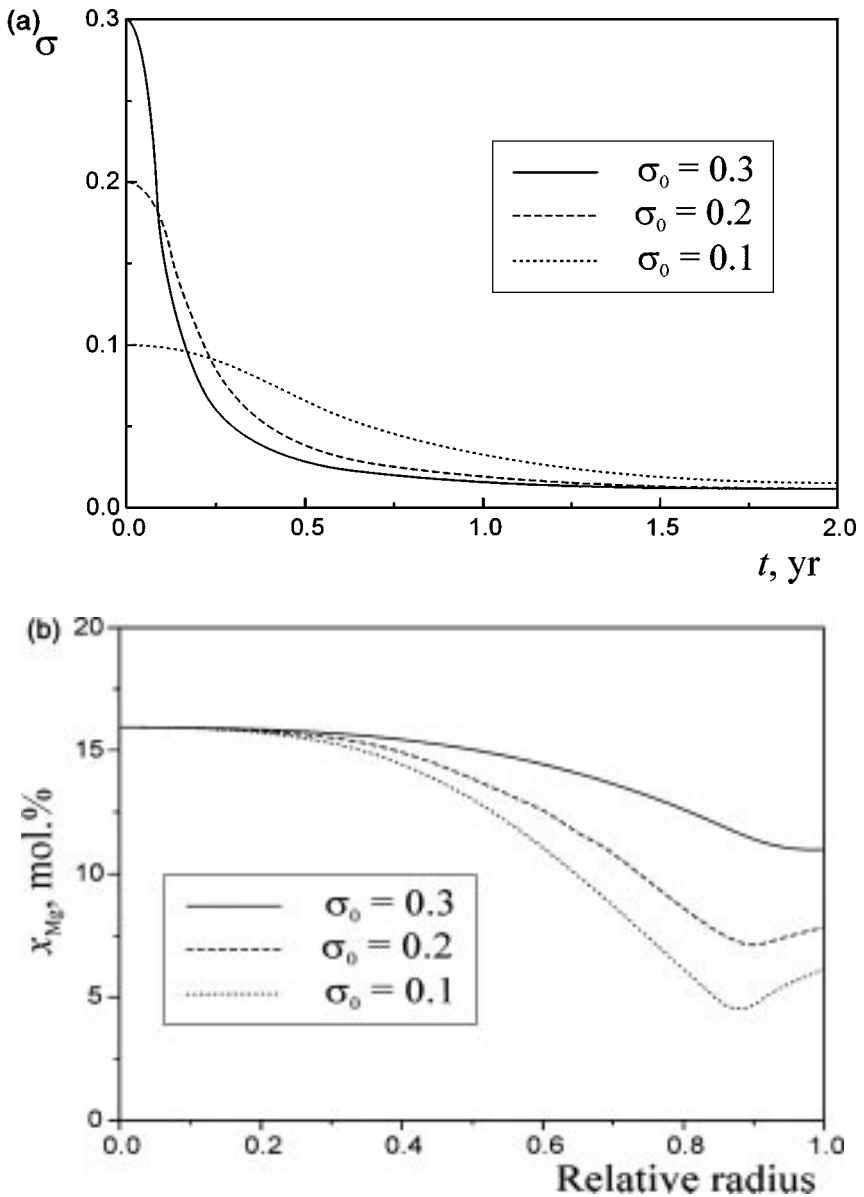


Figure 7. Crystallization of Fe–Mg garnet in the open system from 1 M NaOH solution at 600°C, 5 kbar and various initial fluid supersaturations. (a) evolution of the solution supersaturation; (b) zoning profiles (the velocity of the fluid flow $v = 0.05$ cm/year); (c) evolution of the solution supersaturation; (d) zoning profiles (the fluid flow velocity $v = 50$ cm/year). Values of the initial supersaturation σ_0 are given in the legend.

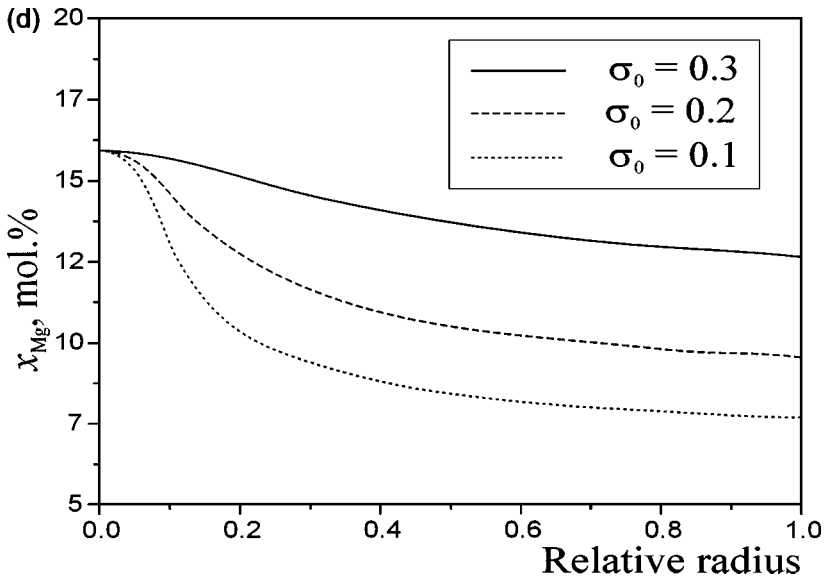
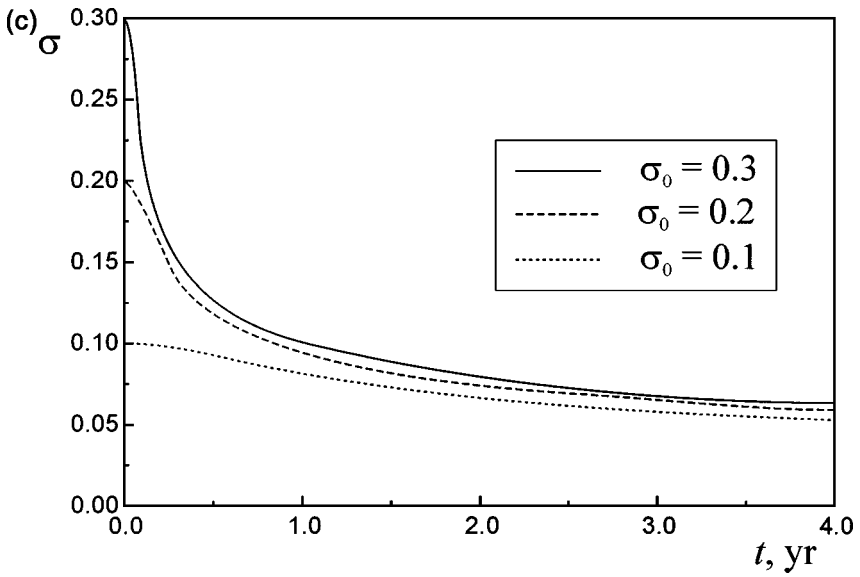


Figure 7. Continued.

rapidly (about 10 years at 500°C and initial supersaturation 0.1 and about 500 years at the same temperature and initial supersaturation 0.01). The zoning profiles are monotonic and cup- or arc-shaped (Fig. 1(b)). They are like common profiles in garnets with normal zoning. Zoning contrast for the same values of the cocrystallization (distribution) coefficient is controlled by initial supersaturation of the parent solution. High initial supersaturation leads to high contrast zoning.

Polythermal Crystallization in Closed System

The kinetic curves $\sigma_i = \sigma_i(t)$ of the polythermal crystallization in the closed system obtained by solving equation set (17) are shown in Fig. 2(a). The supersaturation changes nonmonotonically in this process since it is a superposition of two competing processes: increase due to the solubility decrease with system heating and decrease due to crystallization. The zoning profiles for polythermal crystallization are similar to simple cup- or arc-shaped (Fig. 2(b)). Increase of heating rate leads to higher supersaturation and steeper slope of the function $\sigma(t)$, that is, higher nonstationarity. Correspondingly, increase of nonstationarity results in more zoning contrast. Probably, heating rates used for calculations are overestimated in comparison with real values, but they allow emphasis of the contribution of thermal nonstationarity to zoning contrast.

Polythermal Crystallization From the Aqueous Solution with Constant Composition

Which of two mechanisms producing zoning in closed system (fractionation or “equilibrium crystallization” with change of thermodynamic conditions) are prevalent? Zoning trends in both cases should be the same (Azimov and Shtukenberg, 2001). To reveal the contribution of “equilibrium crystallization” we have considered crystallization without fractionation. Supersaturation evoked by heating (Fig. 3(a)) increases monotonically. The higher the heating rate, the higher the contrast of zoning profiles (Fig. 3(b)). However, concentration gradients of components in the crystal drop as this crystal grows. Such a profile shape is unusual for natural garnets. Comparison of Figs. 2(b) and 3(b) demonstrates that crystals growing at constant fluid compositions display less contrast zoning profiles than crystals growing at polythermal crystallization in closed system. Even with a heating rate of thousands of degrees per million years zoning formed under polythermal crystallization from a fluid with constant composition is extremely slight. This means that fractionation is the prevalent mechanism producing zoning in both polythermal and isothermal crystallization. The role of “equilibrium crystallization” with change of temperature is negligible.

Isothermal Crystallization in Open System

Many researchers have noted the great significance of fluid flow in metamorphism. However the influence of moving fluid on garnet growth zoning has been hardly studied. Only limited features of growth zoning under fluid flow are discussed by Whitney and Ghent (1993), and Whitney and others (1996a,b). These studies show that fluid flow affected the shape of zoning profiles in metamorphic garnets. A model of the crystallization in an open system allows us to study the effect of the fluid flow on zoning. Most interesting are the not too high fluid flow rates at which the influx of the components does not suppress the fractionation entirely. Since we suggested that volume of the crystallization area V and flow cross-section S in the model under consideration are fixed then fluid flow velocity v is unambiguously related to the parameter ω (whose physical meaning is the rate of solution renovation in the crystallization area). Therefore we consider just v as parameter of the crystallization process.

In a system with steady fluid flow, the supersaturation decreases monotonically (Figs. 4(a) and 6(a)) as with desupersaturation in a closed system. With time, supersaturation achieves a steady level. Figures. 4(b) and 6(b) demonstrate that at the same initial supersaturation the shape of profiles is determined by v . At low v zoning patterns are simple arc-shaped and similar to ones formed under isothermal desupersaturation. Augmentation of the fluid stream velocity leads to inflexion of profile near crystal rim. At relatively low fluid velocity the zoning trend remains but at high v values it becomes opposite at the inflection point. The partition trend stays unmodified. Further intensification of fluid flow leads to disappearance of inflexion and flattening of zoning patterns. Profiles become hat-shaped. At even higher flow velocities the growing crystal is unzoned. Thus, zoning in crystals growing under fluid flow can be nonmonotonic despite fractionation being the only mechanism producing zoning with isothermal crystallization.

Dependence of zoning on process disequilibrium (at constant v) is demonstrated in Figs. 5 and 7. It is evident that diminution of initial supersaturation results in profile flattening. Thus, here, as in a closed system, zoning contrast depends on initial supersaturation. In the low-supersaturated system the zoning is less pronounced. One can also see (Figs. 5 and 7) that the effect of fluid velocity on the shape of zoning profiles depends on the value of the solution supersaturation. Garnets crystallized from both unmineralized and alkaline solutions have profiles with analogous shape though with opposite zonal trends.

According to our calculations, garnets growing from unmineralized fluid at low stream velocities have normal zoning trend in the core and reverse zoning trend in the rim. Profiles in Figs. 4 and 5 are similar to profiles in garnets from greenschist and epidote-amphibolite metamorphic facies rocks. "Hat-shaped" profiles are known also in normal-zoned garnets. Earlier they were explained by diffusional smoothing (Woodsworth, 1977). However, experimental data on solid-state

diffusion (Chakraborty and Ganguly, 1991) show that diffusion rate at 550–650°C is too low for significant relaxation of zoning. At last, zoning profiles calculated using the model of crystallization from alkaline solution in open system (Figs. 6 and 7) resemble zoning profiles in garnets having classic reverse zoning.

CONCLUSION

The above modelling displays that, in a closed system, fractionation is the main mechanism forming zoning with the different modes of crystallization. Contribution of “equilibrium crystallization” with change of thermodynamic conditions is negligible. This is indeed not surprising. As shown in Figs. 1 and 2, the duration of growth of a single garnet crystal amounts from a few years to tens of thousands of years. Such estimation is close to that of Walther and Wood (1984). During this time, temperature rises by less than 10 degrees. The crystal growth rate at metamorphism is evidently higher than the heating rate. Therefore, metamorphic crystallization is near isothermal. In the open system, fractionation is also the basic factor. However, the role of fractionation depends on the degree of system openness. High rate of mass influx results in weakening of zoning patterns.

Zoning contrast is determined by both thermodynamic and kinetic factors. The main thermodynamic factor is the value of the distribution coefficient determined by ratio of the component solubilities in the aqueous solution. The larger the distribution coefficient the more contrast zoning is found. The leading kinetic factors are disequilibrium, nonstationarity, and intensity of mass fluxes. The effect of the kinetics is apparent from the difference between profile shapes for various crystallization modes. Indeed, in three of the four models zoning forms due to the fractionation. Nevertheless one can see clear distinctions between profiles.

As modelling shows, complicated (nonmonotonic) zoning can arise during crystal growth under steady fluid flow. This means that nonmonotonic zoning profiles do not point inevitably to polymetamorphic garnet history. In particular, reverse zoning can appear in crystallization from alkaline aqueous fluid. In that case, formation of inverted rims in garnets points to quite high rate of fluid infiltration.

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