БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ • BULGARIAN ACADEMY OF SCIENCES

ГЕОХИМИЯ, МИНЕРАЛОГИЯ И ПЕТРОЛОГИЯ • 34 • СОФИЯ • 1998
GEOCHEMISTRY, MINERALOGY AND PETROLOGY • 34 • SOFIA • 1998

Internal morphology of mineral crystals as clue to their growth histories. II. From kinematics to kinetics

Ilia Vesselinov

Abstract. A procedure is proposed for expressing the kinematic relations discussed in the first part of this study in valid kinetic terms to serve as a guideline in the analysis of crystal growth histories. It is based on the general relation that growth rate in solutions is proportional to the supersaturation and inversely proportional to the sum of the interface kinetics resistance and the diffusion transport resistance. A simple but adequate isotropic model has been selected from the literature to provide a theoretical background for analysis of absolute rates. It defines four major growth modes: kinetic mode which does not depend on transport processes, diffusion mode which does not depend on interfacial processes, and two other modes involving an interplay of interfacial and transport processes. In Part I they have been simulated by the constant-rate, decelerating, accelerating and oscillatory kinematic models, resp. Rate ratios in a crystal expressed in terms of these modes permit pinpointing the major factors responsible for the formation of kinematic patterns which is illustrated with the examples of straight, hyperbolic, parabolic and periodic edge trajectories described in Part I. The proposed procedure provides means for testing various mineral formation models both on small and large scales and prepare the basis for more thorough kinetic analyses by the modern theories of crystal growth.

Key words: crystal growth, mineral kinetics, sector zoning

Address: Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria, e-mail: ivess@geology.bas.bg

Веселинов, И. 1998. Вътрешната морфология на кристалите на минералите като индикатор на процесите на растежа им. II. От кинематика към кинетика. - *Геохим., минерал. и петрол.,* 34, 15-26

Предложен е начин за представяне на кинематичните зависимости, разгледани в първата част на работата, с кинетични величини, подходящи за анализ на най-важните характеристики на процесите на растеж. Той се основава на общовалидната зависимост, че в разтвори скоростта на кристален растеж е право пропорционална на пресищането и обратно пропорционална на сумата от съпротивленията на фазовата граница и на дифузионния пренос. За анализ на абсолютните скорости от теоретичната литература е подбран един прост, но достатъчно изчерпателен изотропен модел, който определя четири главни режима на растеж: кинетичен, в който процесите на пренос не играят роля, дифузионен, не зависещ от процесите на фазовата граница, и два режима, в които тези главни процеси са взаимно свързани. В първата част тези режими са моделирани съответно с постоянни, намаляващи, растящи и периодични кинематични функции. Отношенията на скоростите на стените на кристала в четирите режима позволяват да се определят главните фактори, довели до образуването на дадена вътрешно-морфоложка структура. Това е илюстрирано с примерите на праволинейни, хиперболични, параболични и периодични ръбни траектории, разгледани в първата част. Предложеният анализ позволява проверка на различни модели на минералообразувателния процес в голям и малък мащаб и създава основа за детайлни анализи на кинетиката посредством съвременните теории на кристалния растеж.

Ключови думи: кристален растеж, минерална кинетика, секторна зоналност
Адрес: Геологически институт, Българска академия на науките, 1113 София

Introduction

Measurement and analysis of internal morphological patterns, as proposed in the first part of the study (Vesselinov, 1998), result in a limited number of crystal growth models satisfying the kinematic relationships observed in a given specimen. In this second part, an attempt is made to trace back the kinematic constraints to the factors of crystallization responsible for the growth histories recorded by edge trajectory patterns. Gray (1971) was probably the first to approach this kind of problems by selecting growth mechanisms the kinetics of which would satisfy the measured rate ratios of faces. The voluminous literature on crystallization kinetics of minerals (e.g. Kirkpatrick, 1981; Sunagawa, 1987; Cashman, 1990; Holten et al., 1997; and their reference lists) concentrates on absolute rates and rarely offers studies on the implied effects on rate ratios although that is exactly what is needed to extend the analysis of measured patterns to kinetic constructions. In other words, a model describing the overall growth kinetics of a crystal should incorporate the kinetic relations of all growth pyramids of its faces, and they in turn should obey the kinematics recorded in the internal edge path patterns.

As pointed out by Sunagawa (1993), the overwhelming majority of minerals crystallize from multicomponent systems by the intricate mechanisms of solution growth. In trying to unravel their growth histories one is faced with the complexity of crystallization processes in nature requiring evaluation of many variable and often interrelated factors, the effects of which on morphology has been reviewed in detail by Sunagawa (1987). The direct approach of Gray (1971) to such problems may not be always feasible and/or exhaustive and this study proposes an analysis in more general terms combining the major crystal/environment interactions to serve as an intermediate step between kinematic and more thorough kinetic analyses. The procedure is based on the comprehensive treatise on crystallization processes by Chernov (1980, Chapters 14-17) which, among the other books on present-day theory and practice of crystallization, gives a clear view to the forces behind the relations between rate, size and shape, external and internal morphologies, in a form well suited for modelling kinematic patterns. It should be noted that a similar approach is used in designing crystal growth experiments (e.g. Givargizov, 1980), and there are also models for interpreting natural crystallization (e.g. Holten et al., 1997) and for computer programs of dendritic growth (Martyushev et al., 1997) using the same basic arguments.

Absolute rates of crystal surfaces

Chernov's model of the major factors controlling the growth rate of a crystal surface, to be used in this study, is illustrated in Fig. 1. It considers a spherical crystal of density ρ g/cm^3 and radius r_x cm growing at a rate V cm/s from a supersaturated solution of concentration C g/cm^3 which drops to C_0 g/cm^3, its solubility value under the given environmental conditions, at the surface of isotropic kinetics β cm/s. The bulk phases are divided by a boundary layer of thickness δ cm across which the dissolved substance with a diffusion coefficient D cm^2/s (assumed constant) is transferred to the growing surface at a rate D/δ cm/s, and the surface takes it up at a rate β cm/s. Then $V = \Omega\beta_{\text{eff}}\Delta C$, where $\Omega = 1/\rho$, $\Delta C = (C - C_0)$, and $1/\beta_{\text{eff}} = (1/\beta + \delta/D)$. The general relation that in any process *the rate* $\propto$ *driving force / resistance,* is expressed

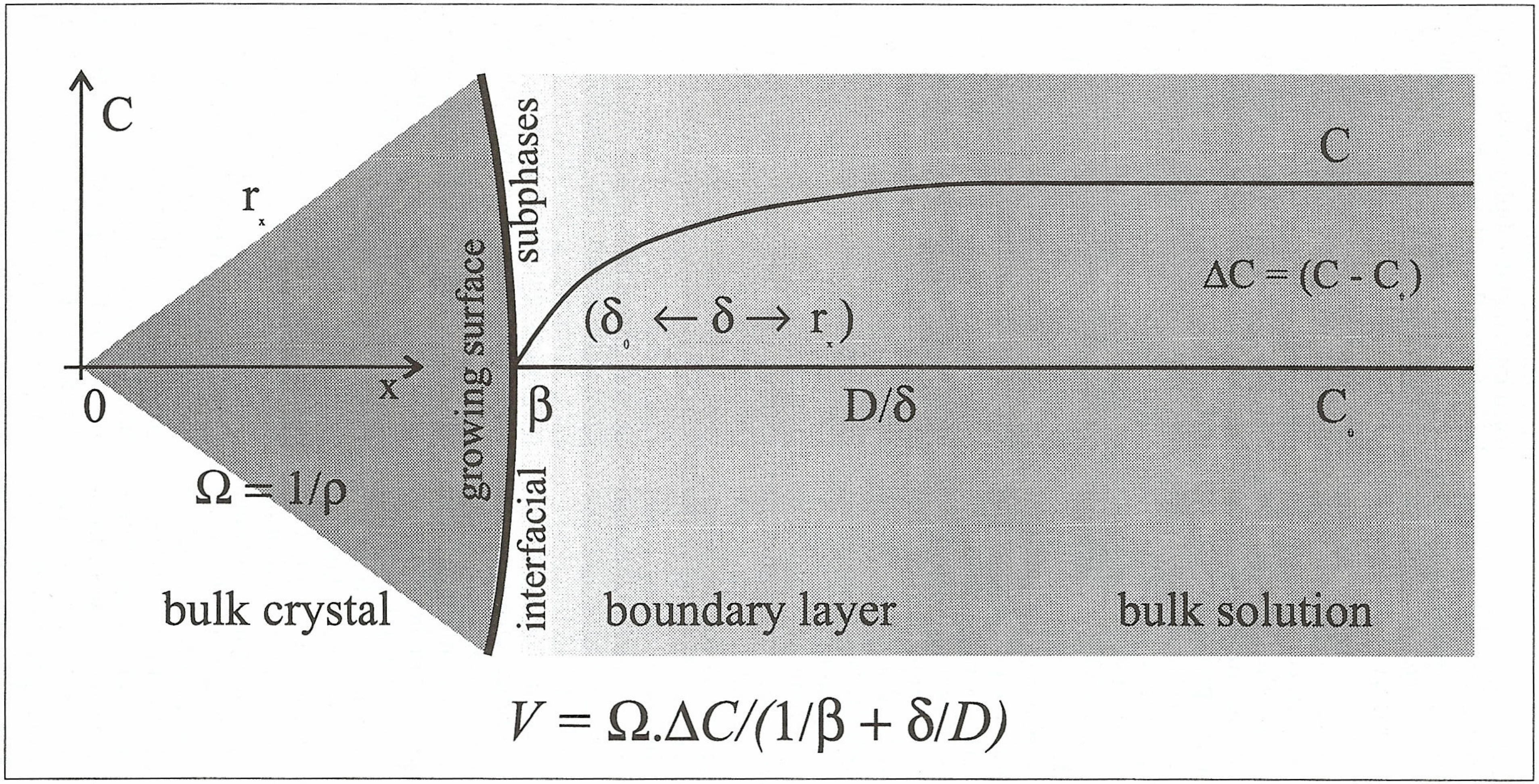


Fig. 1. The isotropic model of Chernov (1980) demonstrating the major factors controlling the absolute rates of a growing crystal surface
Фиг. 1. Изотропният модел на Chernov (1980), демонстриращ главните фактори, които определят абсолютните скорости на растящата кристална повърхност

here as

$$V = \Omega\Delta C/(1/\beta_{eff}),$$

which leads to the more special relation valid for solutions: *growth rate* $\propto$ *supersaturation / (interface kinetics resistance + diffusion transport resistance)*, expressed here as

$$V = \Omega\Delta C/(1/\beta + \delta/D)$$

For morphological purposes it can be expressed in still another form by considering that the slower the growth rate of a face the greater the probability of its occurrence on a crystal, i.e. its morphological importance (MI) is proportional to the inverse rate, or

$$MI \propto 1/V = (\rho/\Delta C)(1/\beta+\delta/D) = [(\rho/\Delta C)(1/\beta)] + [(\rho/\Delta C)(\delta/D)].$$

This latter form emphasizes the fact that the variety of crystal shapes, sizes and internal kinematic patterns is produced by the complex interplay of two major processes, those of interface reactions and diffusion transport, defined by the combinations of the driving force with the two resistances. We propose to use this generalized equation and Chernov's reasoning as a guide in the kinetics underlying the kinematics of recorded patterns (see also Sunagawa, 1987). To lay the groundwork for the subsequent discussion, the general features of the model are reviewed below, omitting many details and implications which, although important, are not relevant to the kinematics of the examples in Part I of this study.

Evaluation of the driving force requires knowledge of the solubility curve of the given substance and analysis of the origin of supersaturation and the potential causes of its variation (an example can be found in Vesselinov, Kerestedjian, 1995). Combined with the diffusion resistance, it defines the flux of matter to the adsorption layer of small thickness δ_0 on the surface, and generally reflects the environmental conditions. Combined with the interface kinetics resistance, it defines the flux from dissolved to solid state via interfacial processes which depend on the state of the interface (degree of thermodynamic or kinetic roughening, presence of defects such as screw dislocations acting as step sources, etc.), its crystallochemical characteristics, presence of foreign species, incl. solvent, which may or may not interact with the interface and may form interfacial subphases in the adsorption layer (recently, a theory has been developed by Liu, Bennema, 1995, to account for their effects on growth kinetics and morphology). Crystal and environment interact through the medium of the boundary layer, the thickness of which may vary from the minimum δ_0 (e.g. in stirred solutions) virtually to infinity, closely approximated by a distance comparable to the crystal size r_x, in unstirred solutions under certain conditions. Chernov's analysis gives criteria for distinguishing between growth-controlling processes. Thus, in stagnant solutions under the condition $V \ll D/r_x$, diffusion is stationary across r_x and the rate equation becomes

$$V = \Omega\beta\Delta C/(1 + \beta r_x/D)$$

where the dimensionless ratio $\beta r_x/D$ is Chernov's criterion for the rate-limiting process during growth. Two extreme cases are distinguished.

Kinetic mode. If $\beta r_x/D \ll 1$, the diffusion resistance can be neglected (because $\delta \sim \delta_0$), the rate $V = \Omega\beta\Delta C$ does not depend on crystal size which increases as $r_x = \Omega\beta\Delta Ct$. In Part I of this study, the kinetic mode at constant β and ΔC is simulated by the CM model (see also Fig. 2a).

The kinetic coefficient β depends on the supersaturation, i.e. it reflects the reaction of the growing surface to the deviations from equilibrium. The specific response, in turn, depends primarily on the interface roughness and defect structure of the surface which define its growth mechanism: layered (by screw dislocations or two-dimensional nucleation) or continuous (normal, according to Chernov). Sunagawa (1987) gives an instructive diagram of the rate variation with supersaturation outlining the ranges in which a growth mechanism is active. At the lowest supersaturations, growth takes place by the screw dislocation mechanism, β is proportional to ΔC (see also Chernov, 1980) so that $V \propto \Delta C^2$. In the range of medium supersaturations, layered growth still predominates although it proceeds by two-dimensional nucleation, and $V \propto \Delta C$. At the highest supersaturations, the surface is no longer smooth and growth is continuous at $V \propto \Delta C$ again. In terms of kinetic resistances, $1/\beta$ is lowest on perfectly rough interfaces, and is lower on defect surfaces providing screw dislocation step sources than on perfectly flat interfaces requiring 2D nucleation for their growth. The types of interfaces, which may vary even on one and the same crystal, are described and illustrated in Sunagawa (1987).

It may be seen that both crystal size and its form constrain the ranges of absolute rates, by means of D/r_x, and supersaturations, via the growth mechanism producing flat or curved surfaces which are observed as concentric zoning in internal morphological patterns. It should be noted that the lower the kinetic resistance $1/\beta$ the greater the chances for the condition $\beta r_x/D \ll 1$ to be violated and for the crystal to leave the kinetic growth mode.

Diffusion mode. If $\beta r_x/D \gg 1$, the rate-limiting step is diffusion transfer across $\delta \sim r_x$, the kinetic resistance is small and can be neglected, the size increases as $r_x = (2\Omega\Delta CD)^{1/2}t^{1/2}$ and the rate decelerates as $V = \Omega\Delta CD/r_x$. Steady state is never reached in this mode. At constant D and ΔC we obtain the DM model in Part I of this study (see also Fig. 2b).

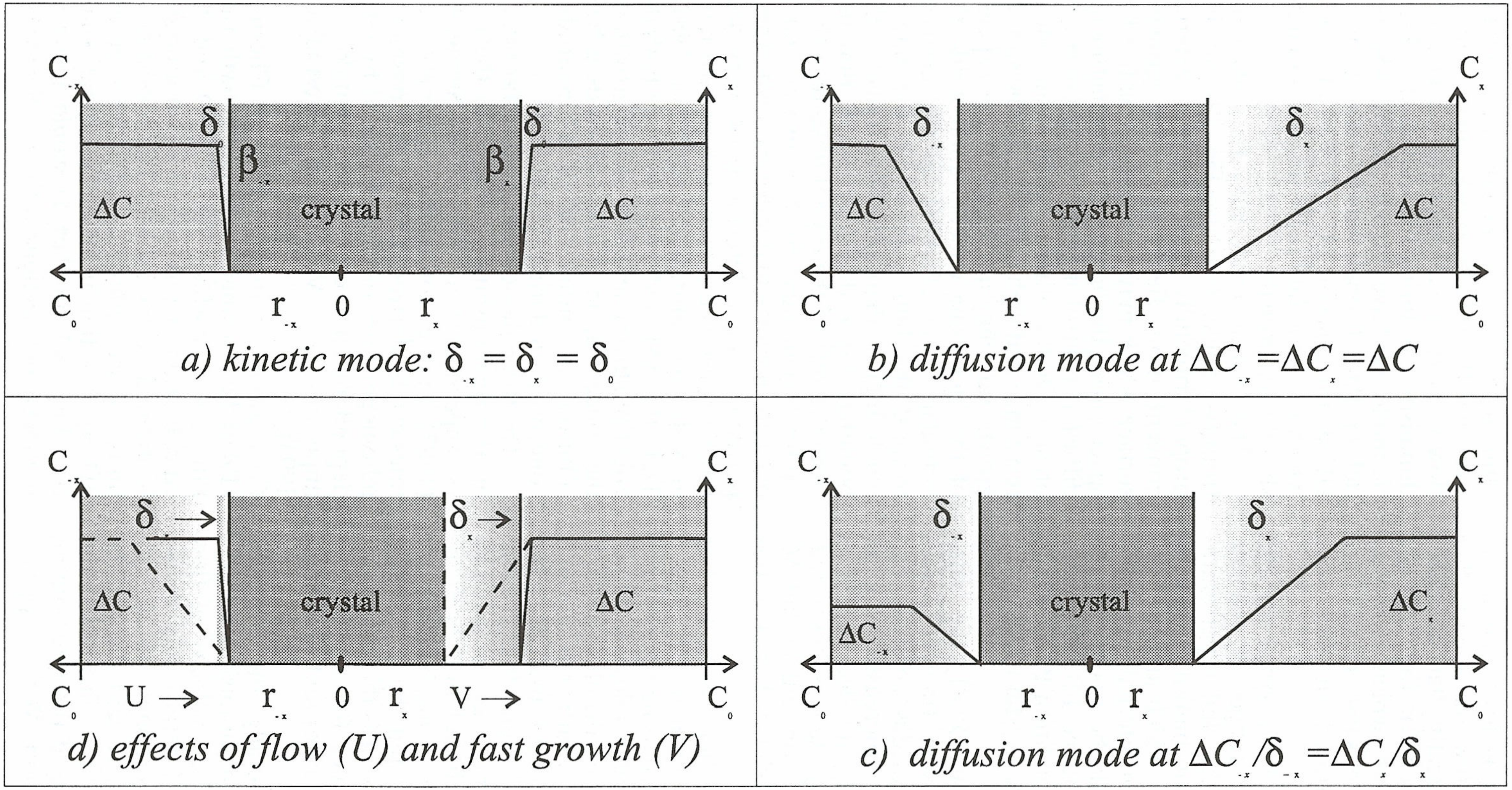
The main feature here is that, after exceeding a certain critical size which diminishes with the increasing supersaturation, the crystal loses morphological stability and the starving surface disintegrates into separate sinks for the insufficient nutrient. Morphologically, the event is marked by the onset of hopper and dendritic growth. Expressions for the critical size are given by Chernov (1980), and the relations with supersaturation and growth mechanisms are discussed and illustrated by Sunagawa (1987). The relevant point is that again size and shape provide clues for constraining the ranges of absolute rates and supersaturations.

Stirred solutions. Generally, the effect of stirring is described as δ diminishing from r_x to δ_0 with the increasing velocity of flow towards the surface. Chernov has shown that δ diminishes proportionally to the square root of flow velocity and the surface growth rate increases parabolically with the increasing flow velocity if the rate-limiting step is material transport. With δ approaching δ_0 the interface kinetics control takes over and the rate becomes independent of flow velocity. To account for the effect of diminishing δ during the transition to kinetic mode, we have introduced the AM model in Part I obtained by writing $V = \Omega U\Delta C$ for constant ΔC and a rate $U \propto t$ at which the boundary layer thickness diminishes during growth.

The stirring mode may be considered from two angles (see also Fig. 2d). Stirring proper forcefully closes in the external concentration field onto the growing surface which may be regarded as fixed in space during the process. By eliminating the diffusion control it removes the constraint on size. On the other hand, at a low kinetic resistance and high driving force the surface growth rate may accelerate at the expense of the increasing concentration inside the boundary layer climbing up the gradient towards the bulk solution. If the rate is much higher than diffusion transfer, the boundary layer thickness would diminish from the side of the crystal towards a fixed external boundary. Such a process takes place for instance in dendritic growth where perfectly rough interfaces of very low kinetic resistance permit high growth rates at high supersaturation (Sunagawa, 1987). Thus, the AM model may simulate both the effect of stirring and that of fast growth up the concentration gradient towards a bulk solution of more or less invariable concentration during the process.

The three modes discussed so far follow up the relationships illustrated in the rate vs. supersaturation diagram of Sunagawa (1987). Further constraints on the absolute rates can be derived from the compositional inhomogeneities of crystals caused by rate-dependent non-equilibrium uptake of impurities (e.g. Vesselinov, Kerestedjian, 1995).

Compositional inhomogeneities. Chernov (1980) has distinguished four growth rate ranges within which 3D, 2D, 1D and 0D equilibration of foreign species in a crystal is attained during growth. The lowest rates under quasiequilibrium conditions permit 3D equilibration in the bulk crystal which (see Fig. 1a,b in Part I) would result in homogeneous sections with non-observable



a) kinetic mode: $\delta_{-x} = \delta_x = \delta_0$

b) diffusion mode at $\Delta C_{-x} = \Delta C_x = \Delta C$

c) diffusion mode at $\Delta C_{-x}/\delta_{-x} = \Delta C_x/\delta_x$

d) effects of flow (U) and fast growth (V)

Fig. 2. Relative role of interface kinetics and diffusion transport resistances. *a*) transport resistance is negligible and the growth rates are defined by the interface kinetics coefficients of faces at the given supersaturation; *b*) interface resistances are negligible and the growth rates are defined by the boundary layer thicknesses; *c*) same as *b*) but at equal concentration gradients defining equal growth rates of faces; *d*) solution flow towards the interface and fast growth of the interface towards the supersaturated solution have one and the same effect of diminishing the boundary layer thickness and promoting growth

Фиг. 2. Относителна роля на съпротивленията на фазовата граница и на дифузионния пренос. *а*) съпротивлението на преноса е пренебрежимо малко и скоростите на растеж се определят от кинетичните коефициенти на стените при даденото пресищане; *b*) кинетичните съпротивления са пренебрежимо малки и скоростите на растеж се определят от ширината на съответния граничен слой; *c*) като *b*), но при еднакви градиенти на концентрацията, определящи еднакви скорости на растеж на стените; *d*) потокът на разтвора към повърхността и бързият растеж на повърхността към преситения разтвор имат един и същ ефект на намаляване на ширината на граничния слой и ускоряване на растежа edge trajectories, and the foreign species concentration in the respective zones will be proportional to that in the environment by the partitioning coefficient K<or>1 at equilibrium. At greater deviations from equilibrium and correspondingly higher growth rates the process may become too fast to allow bulk equilibration and the surface will trap the species in non-equilibrium concentrations proportional to those in the environment (unstirred solution) by a factor $K_{eff} = KC_{i(0)}/C_{i(\infty)} = K/[K + (1 - K)\exp(-V\delta_i/D_i)]$ where $C_{i(0)}$, $C_{i(\infty)}$ are the foreign species concentrations at the crystal surface and in the bulk solution resp., and $D_i/\delta_i = V_i$ is the rate of impurity species transport from solution to crystal. These higher rates may, however, permit 2D equilibration in the surface layer, and if the crystal develops crystallographically non-equivalent faces it may show sectors (Fig. 1c in Part I) due to differences of the 2D equilibrium partitioning coefficients in the respective face layers. Further increase of absolute rates may result in 1D equilibration along growth steps only and then inhomogeneities will occur inside a sector due to non-equilibrium partitioning along crystallographically non-equivalent orientations (Paquette, Reeder, 1990, have described such intrasectoral zoning in calcite). Finally, at the highest rates, 0D equilibration will be possible at interfacial kink sites only and the crystal composition will repeat that of the environment.

Impurities of various kinds affect primarily the kinetic resistance $1/\beta$ increasing or decreasing it (Chernov, 1980; Sunagawa, 1987). The interplay between interface kinetics and diffusion transport may also lead to oscillatory zoning patterns as shown by many workers, in addition to those which may be imposed by compositional variations in the bulk solution (e.g. Holten et al., 1997). To account for such situations, we have introduced the OM model in Part I in which oscillations are imposed on a given rate V_x. By rearranging the above-given equation of Chernov we get

$$V_i/V_x = 1/\{\ln[(1/K)-1] - \ln[(1/K_{eff})-1]\} = 1/\{\ln[(1/K)-1]-\ln[(C_{i(\infty)}/KC_{i(0)})-1]\}$$

in which K_{eff} may vary from K at $\delta_i \to 0$ (or δ_0) to unity at $\delta_i \to \infty$ (or r_x), and in turn V_i/V_x may vary from very large to very small values. The OM model simulates such variations by $V = V_x(1 + V_i/V_x)$ in which V_i is replaced by a simple cosine function.

Finally, a note should be made about the negative feedback indicated by Chernov's rate equation in stagnant solutions. Indeed, if for instance the kinetic resistance $1/\beta$ increases for some reason, V decreases and the concentration field closes in upon the growing crystal diminishing the diffusion resistance δ/D and opposing the rate change. Thus, rates may be rather stable against fluctuations under certain conditions.

Rate ratios

In order to use Chernov's isotropic model for analysis of kinematic patterns we have introduced anisotropy by writing subscripts to the quantities in the rate equation relating to surfaces x,y in a crystal to obtain

$$V_y/V_x=\{[(\rho/\Delta C_x)(1/\beta_x)] + [(\rho/\Delta C_x)(\delta_x/D)]\} / \{[(\rho/\Delta C_y)(1/\beta_y)] + [(\rho/\Delta C_y)(\delta_y/D)]\}$$

In other words, kinetic ratios based on Chernov's model are required to satisfy Laemmlein's kinematic ratios derived from measurements (Part I). In the above expression, ΔC's are also given subscripts to account for possible anisotropy of growth mechanisms $[\Delta C/(1/\beta)]$ and of concentration gradients $[\Delta C/\delta]$ around the crystal. If ΔC is equal in the environment, the expression is reduced to

$$V_y/V_x = (1/\beta_x + \delta_x/D)/(1/\beta_y + \delta_y/D)$$

reflecting environmental anisotropy of the boundary layer only. A note should be made here on the fact that supersaturation vanishes in the rate ratio expressions (and in the kinematic functions) although it is implicitly present in the resistance terms. This seemingly lost information is recoverable through analysis of absolute rates by Chernov's model. Some effects of the growth modes, discussed in the previous section, on relative rates are readily seen, as follows.

Kinetic mode. In the extreme case, the diffusion resistances can be neglected and the ratio reduces to $V_y/V_x = \beta_y/\beta_x$ (Fig. 2a). It would also require low absolute rates

$V_{x,y} \ll D/r_{x,y}$ which generally imply low supersaturation, relatively small crystals, layered growth by screw dislocations and internal homogeneity. If the kinetic coefficients are constants, this mode will produce stationary forms with straight edge trajectories independently of the magnitude of supersaturation and its variation in the environment (Part I, the middle column in Fig. 2), and the measured kinematic ratio will be equal to that of the kinetic coefficients. Crystal shapes will depend on structural anisotropy, symmetry related faces will show equal development and distorted forms are not to be expected. Deviations from point group symmetry should be ascribed to interface kinetics factors such as different defect structures of the faces of a form (Sunagawa, 1987) or surface-active adsorbents covering only part of the faces of a form. On the other hand, changes in the environment during growth introducing adsorbents acting selectively on the kinetic coefficients of different forms will change their rate ratio which will be marked by a change in the direction of edge paths. Generally, this mode may be expected to produce (sequences of) straight edge trajectories.

Diffusion mode. In the extreme case, the kinetic resistances can be neglected and the ratio will reflect the anisotropy of environment only, being reduced to $V_y/V_x = (\Delta C_y/\delta_y)/(\Delta C_x/\delta_x)$, and even to $V_y/V_x = \delta_x/\delta_y \approx (1/r_y)/(1/r_x)$ if ΔC is equal around the crystal (Fig. 2b,c). Compared to the kinetic mode, it may be expected to occur at higher absolute rates and in larger crystals, implying higher supersaturations, wider range of growth mechanisms, as well as probable compositional heterogeneity. Since kinetic resistance does not play a role in this mode, it is close to the isotropic model of Chernov and may be expected to produce less anisometric shapes in which the interface kinetics differences of faces will be smoothed out. The differences in the nutrient environment however will stand out and will be reflected for instance in unequal development of symmetry related faces. Since the growth process never reaches steady state in this mode, constant rate ratios will not be characteristic of it, and curvilinear edge trajectories would be generally expected.

Intermediate modes. The countless situations between the above extreme modes have to be described by the complete rate ratio expression above. Generally, they may be expected to result in complicated ratio functions yet it seems that in many cases the terms in the right-hand sums may be approximated by simple functions judging by the edge trajectory patterns. That reminds us of the kinetics/transport negative feedback capable of damping down rate variations in a changing environment. Simple functions can be envisaged for instance in the distorted growth of symmetry related faces in stagnant environment with constant and equal kinetic resistances but constant and different diffusion resistances. Motion of such crystals in the environment will reduce or eliminate the differences by the effect of stirring and will restore symmetry. Fig. 2d illustrates that an external flow of the solution towards the growing surface may have the same effect on the thickness of the boundary layer as fast growth of the surface towards a slowly reacting environment. It seems that rate changes induced by compositional variations produce the most complex ratio patterns. As indicated by Chernov's relations of absolute rates they may reflect changes in the bulk solution, or the interface response to the redistribution of chemical species in the boundary layer during growth, or both. The variety of possible situations however makes pointless any further discussion of generalities and emphasizes the importance of studies of specific crystallization histories.

Edge path patterns: from kinematics to kinetics

Although few, the examples of growth kinematics discussed in Part I of this study provide opportunities for inquiring into the kinetics of natural crystallization in less general terms.

Straight trajectories. Edge paths represented by sequences of straight lines have been exemplified in Part I with Vavra's work on accessory zircon (1993). In order to use Chernov's model, the condition $V \ll D/r$ should be satisfied. Rates in magmatic systems has been evaluated as low as $10^{-10} \div 10^{-11}$ cm/s (Cashman, 1990; Sunagawa, 1993). Then, up to sizes of $r = 10^{-1}$ cm, the diffusion coefficients of rock-forming components in magma should be $D \gg 10^{-11} \div 10^{-12}$ cm^2/s, a condition leaving ample space for applying Chernov's equation since estimations give values of D up to 10^{-7}-10^{-6} cm^2/s. If we assume further that after the initial act of nucleation growth proceeds in concentration field of equal ΔC around a crystal (supersaturation variations are not excluded), then face rate ratios will be expressed as $V_y/V_x = (\beta_y/\beta_x)(1 + \beta_x r_x/D)/(1 + \beta_y r_y/D)$ where $\beta r/D$ is the criterion for distinguishing between kinetic and diffusion modes. For reasonable values of about 10^{-4} -10^{-5} cm/s (Chernov, 1980), up to sizes of about 10^{-2} cm, i.e. in the cores of zircon crystals, growth will be kinetics controlled and $V_y/V_x = (\beta_y/\beta_x)$ (similar situations are discussed in Cashman, 1990). With the gradual transition to diffusion mode in larger crystals these simple relations will be complicated by the diffusion resistance terms and the differences in the interface kinetics resistances of faces will become less dominant which may result in richer zircon morphologies. This general trend implies the following. The simplest and best expressed morphological relations to environment are to be sought in zircon cores. The early developed crystal forms and their rate ratios are directly defined by the specific temperature/composition conditions in magmas as given in the widely known diagram of zircon morphology. Their later history is increasingly influenced by transport processes and, as shown by Vavra (1993), passes through many events recorded by sharp changes of rate ratios of early forms and appearance of new forms. Vavra's analysis has also shown that conclusions based on final shapes can be misleading, and the reason is that the forms produced by the process are not stationary. This does not invalidate the significance of zircon morphology for genetic constructions, it only calls for further work using the kinetic interpretation of kinematic patterns as a guideline.

Hyperbolic trajectories. In kinetic terms, the hourglass structure of authigenic albite (Kastner, Waldbaum, 1968, and Part I) indicates that growth started at high supersaturation and the high absolute rates resulted in inclusion entrapment by all growth pyramids. Supersaturation diminished with time because the {010} rates reached the range permitting inclusion-free growth, and the fact that this new mode resulted in higher ratios relative to the inclusion-rich {100} and {001} pyramids indicates that inclusions retarded the {010} absolute rates, i.e. that their β's were lower before the onset of inclusion-free growth. The DM model in Part I, found to best represent the pattern, has used constant supersaturation for simplicity but it is easily seen that introducing diminishing ΔC will only emphasize the features marked by the simpler model. They are characterized by rates inversely proportional to the increasing r's which leads us directly to the diffusion mode of growth of all faces as described in previous sections. This is at variance with the analysis of Gray (1971) of the same pattern who obtained hyperbolic edge paths from ratios of two faces growing by 2D surface nucleation mechanism, i.e. by considering only the effect of growth mechanisms $[\Delta C/(1/\beta)]$ and omitting that of concentration gradients $[\Delta C/\delta]$. As pointed out already that would be true if growth was dominated by the kinetic mode. The features of albite occurrence, as described by Kastner, Waldbaum (1968), are strongly suggestive of transport control in support of the alternative model proposed above. It is interesting that Kirkpatrick (1981) in his discussion of the kinetics of magmatic crystallization has emphasized the rarity of the diffusion mode in igneous environments. It may well be that in authigenic crystallization taking place under completely different conditions this mode, characterized by hyperbolic patterns producing nonstationary morphologies, is the dominant growth kinetics.

Parabolic trajectories. In the titanaugite pattern of Gray (1971; see also Part I), the kinematic relations of the two {010} faces have given $V_{-x}/V_x = 1.5$. Their symmetry equivalence excludes β differences. The simplest assumption of equal ΔC's in front of the faces gives $1.5 = (1 + \beta\delta_x/D)/(1 + \beta\delta_{-x}/D)$ from which $(\delta_x - 1.5\delta_{-x}) = D/2\beta$ meaning that a constant $\Delta\delta$, responsible for the unequal development of faces, has been maintained during growth. For the face (001) we have obtained in accordance with the AM model $V_y \propto t$, which leads us to the „stirring“ mode with δ diminishing during growth. Since solution flow directed only to (001) can be safely excluded, there remains the alternative of interface motion towards the bulk solution as discussed in a previous section (Fig. 2d). The low kinetic resistance along the growth direction required for that case is readily explained by the structure of chain silicates. This picture of the process is again at variance with that of Gray (1971) who inferred diffusion-controlled growth of {010} and kinetics-controlled one of (001). In an unstirred solution, however, that would imply slower rate of the latter form in disagreement for instance with the structural properties of titanaugite. This and the previous example show the advantages of an analysis in more general terms for pinpointing the major factors responsible for specific effects in complex situations.

Oscillatory patterns. As illustrated in Part I by the OM model, if certain special conditions are not satisfied to give rise to straight (or curved) edge paths, any repeated variation of the rates of adjacent faces will produce an undulated (periodic) trajectory. Chernov's expression for rate-dependent uptake of impurities clearly distinguishes the possible causes of variations: either external, imposed on the interface kinetics $[\Delta C/(1/\beta)]$ from the environment outside the boundary layer, or interfacial, involving an interplay between $[\Delta C/(1/\beta)]$ and $[\Delta C_i/(D_i/\delta_i)]$ inside the boundary layer, or a superposition of the two. Thus, it provides a useful tool for kinetic analysis of patterns subject of much recent study and debate as to the relative role of the above processes (e.g. Holten et al., 1997). Generally, purely external processes would produce variations of lower frequency that may or may not affect the crystal depending on the total time of growth which may be as short as a few days (e.g. the estimates of Shimizu, 1990, for augite phenocrysts). There is no constraint of this sort in interfacial processes as follows for instance from the reaction-transport autocatalytic mechanism proposed by Ortoleva (1990) for solid solutions. High-frequency oscillations imposed on a sector boundary are shown in Fig. 4c of Part I, and Gray (1971) have described the already discussed parabola in titanaugite as marked by concentric oscillatory zoning. The additional fact that these short-wave oscillations are coupled with such a local phenomenon as distorted shape makes a hypothesis for external control extremely unrealistic in that example. Another illustration of the feedback mechanism of Ortoleva (1990) is the pattern in arsenopyrite (Vesselinov, Kerestedjian, 1995) some features of which have been illustrated in Fig. 4f of Part I. The kinematic reconstruction has also shown that continuous rate oscillations may produce seemingly discontinuous compositional changes implying that the simpler, continuous model of Ortoleva (1990) may turn out to be applicable in cases for which sharp compositional variations have been ascribed to sharp rate changes without actually testing the kinematics. Edge trajectories provide the means for such tests as well as measurable quantities such as wavelengths and amplitudes which, combined with compositional characteristics, are of key importance for detailed modelling of oscillatory patterns in the framework of Ortoleva's theory.

Conclusion

Sunagawa (1993), in addition to his note that the emphasis in modern mineralogy has shifted from studies of equilibrium states to mineral kinetics, wrote also that „We have at present no method to evaluate quantitatively the growth rates or the time required to complete the growth based on the characterization of single crystals“. It has been argued here that the analysis of internal morphological patterns can help to fill in this gap using the following procedure. Prepare oriented crystal sections (Vesselinov, 1997) and expose the edge trajectories of crystal forms during growth. Measure the edge paths and express them in terms of Laemmlein's rate ratio functions, then use model rates to „grow" crystals by the computer which satisfy the measured kinematic relations (Part I, Vesselinov, 1998). Finally, use Chernov's model as a guideline in an analysis of the kinetics underlying the observed kinematics as proposed in this study. In this way the quantitative kinematic information, implicitly present in single-crystal edge trajectories and derivable with great accuracy, can be related to the evidence already available from observations in nature and laboratory experiments. Thus, the proposed procedure provides means for testing various mineral formation models both on small and large scales and prepare the basis for more thorough kinetic analyses by the modern theories of crystal growth.

Acknowledgements. The study was financially supported by the National Science Fund, Grant H3-434.

References

Cashman, K. V. 1990. Textural constraints on the kinetics of crystallization of igneous rocks. - In: Nicholls, J., J. K. Russel (Eds) *Modern Methods of Igneous Petrology: Understanding Magmatic Processes*. Reviews in Mineralogy, Miner. Soc. Amer. Series, **24**, 259-314.

Chernov, A. A. 1980. Processes of crystallization. - In: Chernov, A. A. (Ed.) *Modern Crystallography. III. Crystal Growth*. (Russian Edition) M., Nauka, 7-232. English translation. 1984. Springer Series of Solid-State Sciences, **36**. Berlin-Heidelberg-New York, Springer.

Givargizov, E. I. 1980. Crystallization from the vapour (gas) phase. - In: Chernov, A. A. (Ed.) *Modern Crystallography. III. Crystal Growth*. (Russian Edition) M., Nauka, 233-278. English translation. 1984. Springer Series of Solid-State Sciences, **36**. Berlin-Heidelberg-New York, Springer.

Gray, N. H. 1971. A parabolic hourglass structure in titanaugite. - *Amer. Mineral.*, **56**, 952-958.

Holten, T., B. Jamtveit, P. Meakin, M. Cortini, J. Blundy, H. Austrheim. 1997. Statistical characteristics and origin of oscillatory zoning in crystals. - *Amer. Mineral.*, **82**, 596-606.

Kastner, M., D. R. Waldbaum. 1968. Authigenic albite from Rhodes. - *Amer. Mineral.*, **53**, 1579-1602.

Kirkpatrick, R. J. 1981. Kinetics of crystallization of igneous rocks. - In: Lasaga, A. C., R. J. Kirkpatrick (Eds) *Kinetics of Geochemical Processes*. Reviews in Mineralogy, Miner. Soc. Amer. Series, **8**, 321-398.

Laemmlein, G. G. 1948. Sector structure of crystals. - In: Laemmlein, G. G. 1973. *Morphology and Genesis of Crystals*. M., Nauka, 107-132 (in Russian).

Liu, X. Y., P. Bennema. 1995. Models for the interface between crystal and mother phase. Calculation of actual bond energies at the interface. Implications for growth kinetics and morphology. - *Current Topics in Crystal Growth Research*, Univ. of Nijmegen, The Netherlands, 1-71.

Martyushev, L. M., V. D. Seleznev, S. A. Skopinov. 1997. Computer modelling of morphological instability and dendritic growth by the method of diffusion fluxes. - *Kristallografiya*, **42**, No 5, 802-808 (in Russian).

Ortoleva, P. J. 1990. Role of attachment kinetic feedback in the oscillatory zoning of crystals grown from melts. - *Earth-Sci. Rev.*, **29**, 3-8.

Paquette, J., R. J. Reeder. 1990. New type of compositional zoning in calcite: insights into crystal growth mechanisms. - *Geology*, **18**, 1244-1247.

Shimizu, N. 1990. The oscillatory trace element zoning of augite phenocrysts. - *Earth-Sci. Rev.*, **29**, 27-37.

Sunagawa, I. 1993. Crystal growth in the Mineral Kingdom. - *J. Cr. Growth*, **128**, 397-402.

Sunagawa, I. 1987. Morphology of minerals. - In: Sunagawa, I. (Ed.) *Morphology of Crystals, Part B*. Tokyo, Terrapub, 509-587.

Vavra, G. 1993. A guide to quantitative morphology of accessory zircon. - *Chem. Geol.*, **110**, 15-28.

Vesselinov, I. 1997. Preparing oriented single-crystal sections for measurements of internal morphology. - *Geochem., Mineral. and*

Petrol. (Sofia), **32**, 117-123.

Vesselinov, I. 1998. Internal morphologies of mineral crystals as clues to their growth histories. I. Growth kinematics. - *Geochem., Mineral. and Petrol.* (Sofia), **34**, 3-14 .

Vesselinov, I., T. Kerestedjian. 1995. Kinetic aspects of sector zoning in arsenopyrite: A case study. - *Mineral. Petrol.*, **52**, 85-106.

Accepted April 30, 1998
Приета на 30.04. 1998 г.