A simple model for sector zoning in slowly grown crystals: Implications for growth rate and lattice diffusion, with emphasis on accessory minerals in crustal rocks

E. Bruce Watson

Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180, U.S.A.

Yan Liang

Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, New York 12180, U.S.A.;
and Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.

Abstract

The occurrence of sector zoning in minerals of regional metamorphic or low-temperature intrusive origin implies that rapid growth is not required for the development of this particular form of homogeneous disequilibrium. It is shown here that sector zoning can be a natural consequence simply of slow lattice diffusion. Given anisotropic surface enrichment coupled with the low diffusivities typical of highly charged elements in refractory accessory minerals such as zircon and titanite, sector zoning can arise even in cases of growth rates as low as a few micrometers per million years. According to the proposed model, the development of sector zoning depends upon the competition between growth rate (V) and lattice diffusion (D_i) within the near-surface layer (l), such that above a critical value of Vl/D_i ($\sim$0.5–3), sector zoning is unavoidable in crystals that exhibit selective enrichment on some growth surfaces. Known diffusivities of rare earth elements in zircon and titanite lead to the expectation of sector zoning in these minerals with respect to REEs for reasonable geologic growth rates. Even in the case of clinopyroxene, diffusion of REEs and high field-strength elements may be slow enough to contribute to the development of sector zoning in laboratory-grown crystals.

Introduction

The phenomenon of sector zoning has been observed in a variety of minerals and synthetic crystals grown under a wide range of natural and laboratory conditions. The underlying cause, or at least a necessary condition for sector zoning, is generally understood to be preferential adsorption (incorporation) during growth of one or more components on a specific set of growth surfaces of an anisotropic crystal (e.g., Hollister, 1970; Nakamura, 1973; Dowty, 1976; Shimizu, 1981; Reeder and Paquette, 1989). Other, more specific models call upon differences in growth mechanism of the various faces of a crystal (e.g., Fouke and Reeder, 1992) or a diffusive boundary layer in the growth medium against the advancing crystal surface (e.g., Leung, 1974). Common to most models is the idea that the specific properties of the interfacial region between the crystal and its growth medium are responsible for the intersectoral differences in elemental abundances. Because of this inferred interface control, and perhaps also because sector zoning represents a blatant deviation from homogeneous equilibrium, the phenomenon is commonly described as "kinetically induced" (e.g., Paterson and Stephens, 1992). Despite the frequent use of this or similar terminology, it is unusual to find a case in which the equilibrium-limiting kinetic process is specifically identified.

A causal relationship with kinetics makes sector zoning an intuitively acceptable feature of crystals that have grown rapidly, such as phenocrysts in extrusive rocks or perhaps any crystals grown in a laboratory time frame, even if the specific kinetic mechanism cannot be identified. Other occurrences are more problematic in this respect. For example, Paterson and Stephens (1992) described sector zoning in titanite crystals from metaluminous granitoids, and numerous occurrences have been reported in zircon from intrusive igneous rocks (e.g., Fielding, 1970; Hoffman and Long, 1984; Paterson et al., 1989; Vavra, 1990; Hanchar and Miller, 1993; Benisek and Finger, 1993). Sector zoning in staurolite and other regional metamorphic minerals is also well documented (e.g., Hollister, 1970; Dowty, 1976). All these examples represent crystals that, by any reasonable calculation, could not have grown rapidly. In the case of zircon, for example, the low diffusivity of Zr in granitic melts, combined with the high demand for this dispersed element to form $ZrSiO_4$, leads to calculated growth rates of 10^{-19}–10^{-18} m/s for reasonable melt water contents and time-temperature histories (Watson et al., in preparation). This amounts to growth rates of only micrometers to tens of

micrometers in a million years. It seems unreasonable to assume that, at such low growth rates, one molecular monolayer on the surface of a growing crystal would not maintain partitioning equilibrium with a contacting hydrous melt at ~700 °C, or that a significant diffusive boundary layer would develop in the melt. Accordingly, it may be misleading in these cases to attribute the presence of sector zoning to interfacial disequilibrium. It is probable that the surfaces of these slow-growing crystals are continuously in equilibrium with the contacting growth medium. Unfortunately, the surface exchange-rate data needed to assess the extent of surface equilibration for a given growth rate are unavailable.

The purpose of this paper is to explore the circumstances under which sector zoning might develop even in cases of slow crystal growth. In the present usage, "slow" refers to growth that, in a given amount of time, leads to an advance of the crystal-melt interface by a distance many orders of magnitude smaller than the effective diffusive transport distance in the growth medium, i.e., conditions under which sector zoning is not attributable to a boundary-layer effect in the growth medium or a disequilibrium kinetic effect at the crystal-melt interface. A general model is developed in which the occurrence of sector zoning is indeed dependent upon the growth rate of the crystal but specifically in relation to the diffusivity of a surface-enriched element in the crystal lattice. The model represents a quantitative treatment of an idea originally suggested by Hollister (1970; his model III) and incorporating a more general formulation by Tiller and Ahn (1980); it is intended to extend, not supersede, existing ideas focusing upon interface enrichment alone and to offer an alternative to disequilibrium at the crystal-melt interface as a cause of sector zoning. Emphasis is placed on accessory phases in crustal rocks because the common occurrence of sector zoning in these minerals has been difficult to reconcile with their low inferred growth rates. The implications of the model for crystal-melt (fluid) partitioning and lattice diffusion of high field-strength elements are briefly explored.

The model

It is assumed in this paper that the ultimate cause of sector zoning is related to differences in atomic structure or growth mechanism among the various surfaces (forms) of a crystal. Here, as in previous models (e.g., Hollister, 1970; Hollister and Gancarz, 1971; Nakamura, 1973; Leung, 1974; Dowty, 1976), some surfaces are seen as more conductive than others to incorporation of impurity ions (usually incompatible elements) from the growth medium. Preferential surface adsorption is not regarded, however, as sufficient in itself to cause sector zoning because it does not explain how the structural and chemical characteristics of surfaces translate into compositional variation within a crystal, nor does it provide a clear connection between sector zoning and growth rate. The question addressed below concerns the circumstances under which enrichment of an element on certain growth

surfaces leads to observable sector zoning within the crystal volume.

Consider a planar, initially stationary interface between a crystal and the host medium with which it is in chemical equilibrium. In general, this medium would be a melt or fluid; here, the word "melt" is used as shorthand for any growth medium. Consider, also, that some incompatible element, i, is enriched in the surface layer (A_o) relative to its equilibrium concentration both within the crystal lattice and on other surfaces of the same crystal (see Fig. 1). As long as the crystal surface is stationary, this situation represents an equilibrium state, as implied by the schematic chemical potential vs. distance diagram in Figure 1a. The cause of the surface enrichment need not be specified but can be assumed to derive from a greater variety and flexibility of coordination opportunities for i on this particular surface (Nakamura, 1973; Dowty, 1976; Tiller, 1991).

The equilibrium state of Figure 1a is perturbed when the crystal begins to grow. For lack of a better representation, growth is depicted here as an instantaneous, stepwise addition of a thin layer to the crystal surface (see Fig. 1b). The former surface layer, A_0, is now within the volume of the crystal but retains, however briefly, its initial, surface-acquired concentration of i. This concentration exceeds that appropriate to equilibrium partitioning between the crystal volume and the growth medium. In thermodynamic terms, completion of former surface sites in A_0 by overplating of a new surface layer A_1 causes the activity of i (hence the chemical potential, μ_i) in layers A_0 and A_1 to increase (see Fig. 1b). The key feature of the present model is that, because both layers A_0 and A_1 are now part of the crystal volume, lattice diffusion of i is required to eliminate the resulting perturbation in μ_i. Consequently, any retention within the newly created crystal volume of the surface concentration of i depends upon the outcome of the race between advancement of the interface (which lengthens the distance over which diffusion of i must be effective to eliminate this excess) and lattice diffusion (which tends to eliminate excess i from the near-surface region of the crystal).

The outcome of the competition between diffusion and crystal growth can be assessed qualitatively by a simple calculation. If the half-width, l, of a growth layer (i.e., one silicate molecular monolayer) is assumed to be ~ 5 × 10^{-10} m (5 Å), then the average time required for addition of this layer to the crystal surface is given by $t = l/V$, where V is the growth rate in meters per second. Using the approximation for mean diffusive transport distance,

$$l \approx \sqrt{D_i t} \qquad (1)$$

where D_i is the lattice diffusivity of i (in square meters per second). Equating the diffusion time with the growth time by replacing t with l/V in Equation 1, we find that for the assumed value of l, the diffusion distance is comparable to the growth distance when $V/D_i \approx 2 \times 10^9$ m^{-1}. [The units of this ratio (inverse meters) and the use of a characteristic diffusion distance (l) suggest a dimension-

less quantity, Vl/D_i, that might be useful in a more rigorous and general treatment.] As a first approximation, we would expect a crystal to retain within its volume some memory of surface enrichment on selected growth faces if $V \geq 2 \times 10^9 D_i$. For the few instances of sector-zoned crystals in which both crystal growth rate and the diffusivity of a sectorally variable element can be estimated, this result agrees with observation. For example, the calculated geologic growth rates of zircon reported in the introduction (10^{-19}–10^{-18} m/s at 700 °C) would necessitate diffusivities at least as low as 10^{-28}–10^{-27} m²/s for sector zoning to develop. Cherniak et al. (1993) reported data for rare earth diffusion in zircon that extrapolate to diffusivities of $\sim 10^{-34}$ m²/s at 700 °C. According to our model, these values are by far low enough to lead to sector zoning of zircon with respect to rare earths (provided, of course, that selective adsorption of rare earths occurs on some growth surfaces).

The competition between growth rate and lattice diffusion in the development of sector zoning is modeled more rigorously as a case of surface-layer absorption and one-dimensional diffusion perpendicular to a moving boundary between two phases. Consider a crystal of initial half-length x_0 in chemical equilibrium with its surrounding melt. The chemical potential of some trace element i dissolved in this crystal has the usual definition

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i C_i) \qquad (2)$$

where μ_i^0 is the standard-state chemical potential of i, R is the gas constant, T is the absolute temperature, and γ_i is the activity coefficient of i. As shown in Figure 1a, the chemical potential μ_i is uniform everywhere in the crystal when the crystal and its surrounding melt are in the thermodynamic equilibrium. Hence, a necessary condition for the enrichment of i in the surface layer is that its activity coefficient γ_i in this layer be lower than that in the interior of the crystal. For a trace element, it is reasonable to assume that γ_i is a constant (γ_0) in the interior of the crystal and is a function of the spatial variable, x, in the surface layer [i.e., $\gamma_i = \gamma_0 g(x)$]. Hence, the chemical potential in Equation 2 is rewritten as

$$\mu_i = \mu_i^0 + RT \ln(\gamma_0 C_i) + RT \ln[g(x)] \qquad (3)$$

where the last term on the right side vanishes except in the surface layer. The origin of the crystal-growth axis is set at the initial crystal-melt interface (where $x = 0$), and the center of the crystal is located at $x = -x_0$. Equation 3 is essentially the same as that given by Tiller and Ahn (1980) for adsorption of a trace element on the surface of a crystal. Although the exact expression for $g(x)$ is not known for any silicate crystal, it is reasonable to assume that $RT \ln[g(x)]$ is at a minimum at the crystal-melt interface and increases sharply toward the interior of the crystal. For demonstration purposes, we follow Tiller and Ahn (1980) and assume that $RT \ln[g(x)]$ has the simple exponential form

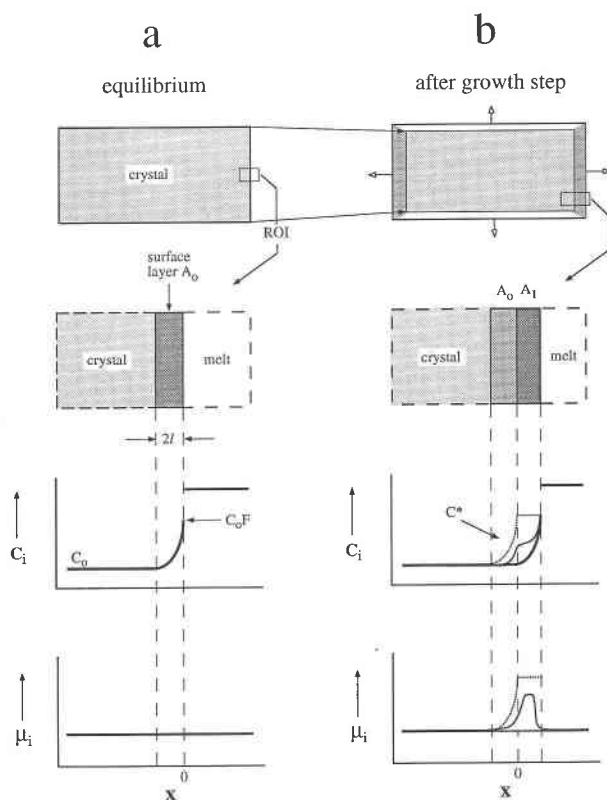$$RT \ln[g(x)] = -\ln(F)\exp(x/l), \qquad -x_0 \leq x \leq 0 \quad (4)$$

Fig. 1. Schematic profiles of concentration (C_i) and chemical potential (μ_i) for incompatible element i across the interfacial region of a crystal (**a**) in equilibrium with its growth medium and (**b**) immediately after an instantaneous growth step. At equilibrium, i is enriched in the surface layer because of the greater flexibility of available sites. After a growth step, the former surface layer A_0 becomes part of the crystal lattice, where i is less compatible than in the surface layer. The resulting perturbation in μ_i can be eliminated only by lattice diffusion. Fast lattice diffusion results in equilibrium growth (heavy solid lines in C_i and μ_i plots in **b**), whereas sluggish lattice diffusion leads to disequilibrium growth (thin solid line in **b**). In the limit of no lattice diffusion, the concentration in the newly grown sector approaches that of the surface concentration (dotted line in **b**). See text for discussion.

where l ($\ll x_0$) is the half-width of the surface layer, and F is the equilibrium surface-enrichment factor defined as the ratio of the crystal-surface concentration to its interior concentration when the crystal and its surrounding melt are in equilibrium (also given by Eq. 5 when $x = 0$). The equilibrium concentration distribution in the crystal, appropriate to the boundary layer potential (Eq. 4), has the form

$$C_i(x,0) = C_0 F^{\exp(x/l)}, \qquad -x_0 \leq x \leq 0 \qquad (5)$$

where C_0 is the concentration in the interior of the crystal. At time t, the crystal-melt interface advances to a new location, $xb = Vt$, assuming a constant growth velocity V. The half-length (X_0) of the growing crystal becomes
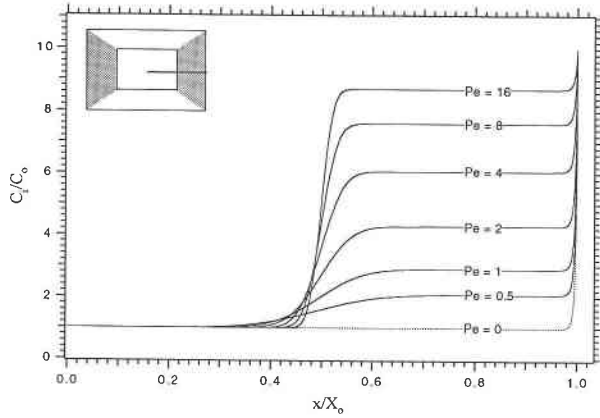
$$X_0 = x_0 + Vt. \qquad (6)$$

Fig. 2. Normalized concentration profiles of a surface-enriched element in a growing crystal for various values of growth Peclet number Pe ($F = 10$). The black bar in the inset shows the location of the profiles within a hypothetical sector-zoned crystal.

The diffusive flux $\mathbf{J}_i$ in the growing crystal, in a reference frame fixed to the original crystal-melt interface, is proportional to its chemical-potential gradient; that is

$$\mathbf{J}_i = -\frac{\mathrm{D}_i C_i}{\mathrm{R}T} \frac{\partial \mu_i}{\partial x}. \qquad (7)$$

Upon substitution of the chemical potential in Equations 3 and 4, we have the diffusive flux for component i, taking into account the effect of surface-layer enrichment,

$$\mathbf{J}_i = -\mathrm{D}_i \frac{\partial C_i}{\partial x} + \frac{\mathrm{D}_i \ln(F)}{l} C_i \exp[(x - Vt)/l]. \qquad (8)$$

In the absence of a source or sink, the requirement of mass conservation of i in the crystal leads to a diffusion equation for the trace element i in the growing crystal:

$$\frac{\partial C_i}{\partial t} = \mathrm{D}_i \frac{\partial^2 C_i}{\partial x^2} - \frac{\mathrm{D}_i \ln(F)}{l} \frac{\partial\{C_i \exp[(x - Vt)/l]\}}{\partial x}. \qquad (9)$$

Without surface enrichment (i.e., $F = 1$) Equations 8 and 9 recover Fick's first and second laws of diffusion. As pointed out by Tiller and Ahn (1980), the second term on the right side of Equation 8 or 9 represents a driving force for uphill diffusion when it is opposite in sign to the Fickian diffusion term (also see Tiller, 1991). It is this uphill diffusion that sustains the enrichment in the surface layer.

Solutions to Equation 9 are obtained when the initial and boundary conditions are specified. For simplicity, we assume that the growth process is started from a seed or core in equilibrium with its medium (Eq. 5; see also the inset of Fig. 2). The usual no-flux condition is required at the center of the crystal, that is

$$\left[\frac{\partial C_i}{\partial x}\right]_{x=-x_0} = 0, \qquad x = -x_0. \qquad (10)$$

This is a good approximation as long as $x_0 \gg l$. For the

examples given below, we assume that the surrounding melt is well stirred and has a constant composition throughout the crystal-growth period. Because the crystal and its surrounding melt are always in chemical equilibrium at the crystal-melt interface when the growth rate is small, the boundary condition at the surface of the crystal is written as

$$C_i(x\mathrm{b},t) = C_0 F, \qquad x = x\mathrm{b}. \qquad (11)$$

A constant melt concentration in Equation 11 is justified when the rate of growth is much slower than the rate of diffusion of the trace element i in the melt (see our definition of slow growth in the introduction). The one-dimensional diffusion equation (Eq. 9) along with its initial conditions (Eqs. 5 and 6) and boundary conditions (Eqs. 10 and 11) constitute a moving boundary problem. It has one unknown, C_i, and four physical parameters, D_i, F, l, and V. To make the problem more tractable and for reasons that will be apparent below, Equation 9 along with its initial and boundary conditions are nondimensionalized by choosing the proper length (l), time (l^2/D_i), and concentration (C_0) scales, as follows: $x = lx'$, $t = l^2/D_i t'$, $C_i = C_0 C_i'$ where the primed variables are nondimensional. The resulting equations are

$$\frac{\partial C_i'}{\partial t'} = \frac{\partial^2 C_i'}{\partial x'^2} - \ln(F) \frac{\partial[C_i' \exp(x' - Pe \cdot t')]}{\partial x'},$$
$$-x_0' < x' \leq x\mathrm{b}' \qquad (12)$$

$$C_i'(x', 0) = F^{\exp(x')}, \qquad -x_0' < x' \leq 0 \qquad (13)$$

$$\left[\frac{\partial C_i'}{\partial x'}\right]_{x'=-x_0'} = 0, \qquad x' = -x_0' \qquad (14)$$

$$C_i'(x\mathrm{b}', t') = F, \qquad x' = x\mathrm{b}' \qquad (15)$$

$$X_0' = x_0' + x_\mathrm{b}'$$
$$= x_0' + Pe \cdot t' \qquad (16)$$

where $Pe \equiv Vl/D_i$ is the ratio between diffusive time scale (l^2/D_i) and growth time scale (l/V) and is called the growth Peclet number for the surface layer. Equations 12–16 have one unknown, C_i', and two dimensionless parameters, F and Pe. Tiller and Ahn (1980), in a reference frame fixed to the moving crystal-melt interface, obtained exact steady-state solutions to a more general form of Equation 9. Although the concentration distribution in the surface layer was fully captured, the steady-state solutions were unable to estimate the concentration in the interior of the crystal (Tiller and Ahn, 1980). The concentration behind the surface layer is determined by solving the time-dependent Equation 9 or 12. In the next section, we present some numerical solutions to the above time-dependent moving boundary problem using a finite difference method.

RESULTS

Equations 12–16 were integrated numerically in a fixed grid using an explicit finite difference scheme (e.g., Crank,
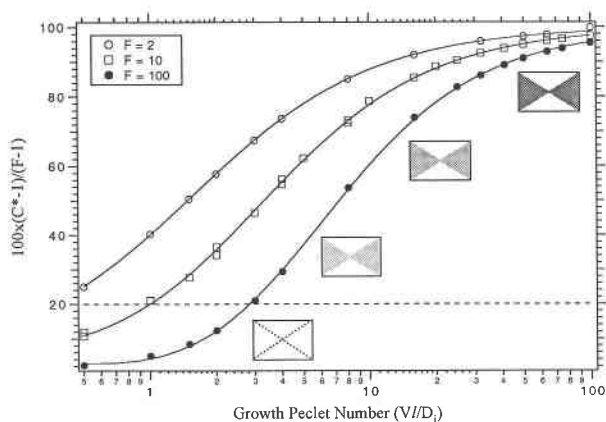
Fig. 3. Percent of enrichment in the growing sector as a function of the growth Peclet number for three choices of F (2, 10, and 100). The three sets of data points (open circle, open square, and solid circle) were obtained from numerical simulations. The solid lines are best fits to each data set. For reasons of practicality (see text), a crystal is considered to be sector zoned if enrichment amounting to >20% of the equilibrium surface concentration develops in the modeled growth sector. By this definition, for Pe < 0.5, sector zoning cannot develop by the mechanism described in this paper. Values greater than ~0.5–3 (depending on F), on the other hand, lead inevitably to sectoral enrichment of any element that is preferentially adsorbed onto the growth surface. For Pe > 100, the concentration in the growth sector closely approaches the surface concentration (C_0F). Concentration contrast in growth sectors is illustrated by the light-dark contrast in the schematic crystal insets.

1975). Growth simulations were conducted for various combinations of F and Pe to characterize the competition between lattice diffusion through the surface layer and growth of the crystal. These results are summarized in Figures 2–4. Figure 2 presents normalized concentration profiles in a growing crystal at selected values of growth Peclet number when $F = 10$. For the purpose of presentation, the spatial variable (x) is normalized to the final crystal length (X_0). As shown in Figure 2, at a selected Peclet number, the crystal has two broad regions of nearly uniform but distinct compositions, one in the interior of the original seed crystal and the other in the newly grown sector of the crystal. This results from the competition between growth rate and lattice diffusion within the surface layer (see Figs. 1 and 2). When the rate of diffusion is much faster than the rate of growth ($Pe \rightarrow 0$), the interior of the crystal has ample time to exchange with its surrounding melt through the surface layer. The effect of uphill diffusion, due to the second term in Equation 9 or 12, eliminates any concentration buildup in the interior of the crystal. Equilibrium distribution prevails (dotted line in Fig. 2). As the rate of growth increases, uphill diffusion through the surface layer becomes progressively less efficient. Under these circumstances, some fraction of excess i in the surface layer is trapped in the interior of the newly grown crystal, creating a sector of concentration enrichment behind the surface layer (Fig. 2). The
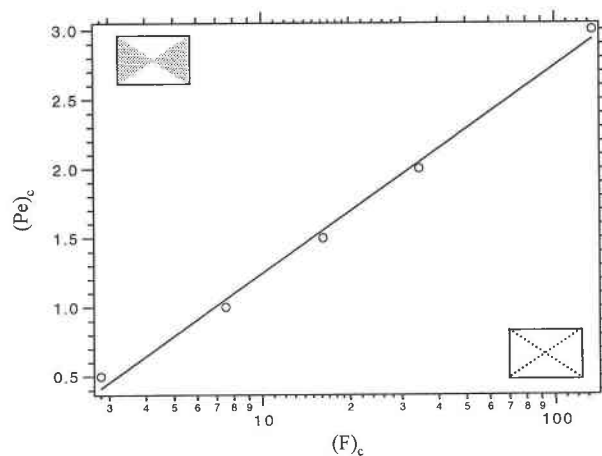

Fig. 4. Plot showing the dependence of the critical Peclet number Pe_c upon the critical surface-enrichment factor F_c. The value of Pe_c or F_c is considered to be that which causes relative enrichment in the newly grown sector of 20% (see text and Fig. 3). Observable sectoral zoning is present when $Pe > Pe_c$ at a given F.

enrichment in this sector is sustained because of the slow rate of lattice diffusion in the interior of the crystal. As the rate of crystal growth further increases, lattice diffusion becomes negligible compared with the growth rate, and the concentration in the growing sector approaches that in the enriched surface. In general, sector zoning develops whenever the extent of crystal growth in a given time interval is larger than the length scale of lattice diffusion. The concentration in the enriched sector (C^*) behind the surface layer is independent of the final length of the crystal (Fig. 2).

Figure 3 displays the percent of enrichment in the growing sector as a function of the growth Peclet number for three choices of the equilibrium surface-enrichment factor F (2, 10, and 100). The dependence of C^* on F is small, although a nearly linear relation exists between $\ln C^*$ and $\ln F$ for a given Pe. This diagram also reveals that the critical Vl/D_i value estimated previously is a very good approximation of the maximum permissible value for any enrichment whatsoever to occur in the growth sector. For reasons of practicality, the critical value is redefined at this point to specify the value needed to cause enrichment amounting to 20% of the surface concentration at a given F; this value is designated Pe_c (Fig. 4). This redefinition is considered prudent because of the limitations imposed by in situ analytical methods for trace elements; accordingly, a critical value leading to plausibly detectable enrichment is specified. As shown in Figure 4, the variation of Pe_c is rather small (~0.5–3) for the range of F considered (~2–100).

It is important to underscore the point that the behavior of a surface-enriched element in this model does not depend upon the absolute values of D_i, V, or l. The growth Peclet number Vl/D_i alone is important in controlling enrichment within a growth sector when the equilibrium

surface-layer enrichment factor F is specified. For a given amount of total growth, irrespective of the time required for this growth to occur, the concentration profiles shown in Figure 2 are identical for identical values of Vl/D_i.

DISCUSSION AND IMPLICATIONS

Limitations of the model

One type of limitation of the proposed model is related to the simplifying assumptions made for the sake of computational tractability. The most important of these is the assumption that the concentration of element i is constant in the growth reservoir at the crystal-melt interface. This is a reasonable assumption as long as the length scale of crystal growth is much shorter than the length scale of chemical diffusion in the melt. For simplicity, constant growth rate V and diffusivity D_i were used in the simulations. Allowing growth rate or melt concentration to increase with time would increase concentration from core to rim in the sector of interest, but it would not affect the fundamental conclusion concerning the presence or absence of sectoral enrichment. It is also possible that lattice diffusion in the near-surface region of a crystal is characterized by a diffusivity somewhat higher than that of the true crystal interior. This, again, has little affect on our conclusions because lattice diffusion behind the surface layer is always sluggish when $Pe > Pe_c$. Variations in the behavior of the system brought about by an enhanced near-surface diffusivity would not be distinguishable from variations caused by a reduction in the thickness (l) of the surface layer because Vl/D_i is the critical parameter. The assumption of the simple exponential relation of the excess chemical potential for the surface-layer enrichment in Equation 4 was made for demonstration purposes. Preliminary calculations using other choices of excess chemical potential for the surface layer (e.g., linear-step function, error function, and other forms of integral functions) results in concentration profiles similar to those shown in Figure 2. Furthermore, the enrichments in the growing sector, C^*, are within 15% of that obtained using the exponential function (Eq. 4) when the surface-layer thickness (δ), defined as

$$\delta = \frac{1}{\ln[g(0)]} \int_{-\infty}^{0} \ln[g(x)] \, dx \qquad (17)$$

for a given $RT \ln[g(x)]$, is the same as that for the exponential function, that is $\delta = 2l$. All these are viewed as secondary characteristics of the behavior of the system and are omitted from the simulations. The presence of core $\rightarrow$ rim concentration variations in natural sector-zoned crystals does not invalidate the present model.

The other kind of limitation (or uncertainty) of the model concerns its range of applicability in terms of crystal growth rate. As noted earlier, sector zoning in rapidly grown crystals is commonly attributed to sluggish interface kinetics (e.g., Kouchi et al., 1983), which means, presumably, that growth is too fast to allow establishment of partitioning equilibrium between the surface and the

growth medium. It is not possible at present to identify the maximum growth rate at which this equilibrium can be maintained, and so there is no clear demarcation between the realm in which the present model is the only plausible one (i.e., where surface partitioning equilibrium is maintained) and the realm in which interface disequilibrium can play a role. It is important to note that the explanation of sector zoning proposed here, i.e., lattice diffusion that is slow in relation to growth rate, can still operate even if partitioning equilibrium is not maintained at the surface.

Test cases from nature and the laboratory

Having quantified the outcome of the hypothesized competition between V and D_i in the development of sector zoning, and recognizing the possible limitations listed above, we can examine previously reported cases to see if our explanation is consistent with observation. Unfortunately, there are few instances in which constraints exist on both V and D_i (see Table 1). Because the main focus of this paper is upon slowly grown minerals, emphasis is placed on natural zircon and titanite crystals, but test calculations are also performed for some synthetic clinopyroxenes. In the absence of any real constraints on the value of l, we use 5 Å for reasons given previously.

The sector-zoned titanite crystals from Scottish Caledonian granitoids described by Paterson and Stephens (1992) were a principal stimulus for the work leading to this paper. These crystals are predominantly euhedral, range in size from ~0.2 to ~1 mm, and display pronounced sector zoning of the rare earths and other elements involved in charge compensation when REEs replace Ca (e.g., Fe^{3+}, Al, and Ti). Growth rates of these crystals cannot be estimated accurately because neither the cooling rates of the host plutons nor the crystallization intervals of titanite are well constrained. For computing V values, growth of 100 μm was considered to occur over time intervals ranging from 10^4 to 10^6 yr, which is probably a reasonable range for intrusive rocks. Known diffusivities for REE in titanite range from 5×10^{-28} m^2/s (700 °C) to 1×10^{-25} m^2/s (800 °C) (Cherniak, 1995), yielding Pe values of ~0.02 to ~300 (Table 1), which easily span the critical range. The calculation at least permits the development of sector zoning by the proposed mechanism.

Because of the large margin for error, the ballpark computation described earlier (based on $l^2 \approx D_i t$) for REE zonation in zircon clearly demonstrates the plausibility of the critical Vl/D_i concept in the case of zircon. For the sake of completeness, results based on the more rigorous numerical model are shown in Table 1. Because REE diffusion in zircon is so sluggish (Cherniak et al., 1993), growth rates four or five orders of magnitude slower than our calculated values (Watson et al., in preparation) would still produce sector zoning by the proposed mechanism ($Pe = 5 \times 10^5$–5×10^6). Our preliminary data on diffusion of U and Hf in zircon reveal diffusivities even lower

TABLE 1. Summary of input data, sources, and results of the model test calculations described in the text

Sector-zoned mineral	Reference	Element	V (m/s)	Known D_i (m²/s)	D_i reference	$Pe \, (= Vl/D_i)$*
Nat. titanite	Paterson and Stephens, 1992	REE	10^{-18}–10^{-16}	5×10^{-26} (700 °C) 1×10^{-25} (800 °C)	Cherniak, 1995	1.6–317 0.02–3.2
Nat. zircon	e.g., Fielding, 1970	REE	10^{-19}–10^{-18}	1×10^{-34} (700 °C)	Cherniak et al., 1993	5×10^{5}–5×10^{6}
Syn. cpx	Kouchi et al., 1983	Al (Ti)	10^{-8}	3×10^{-17}	Grove and Wagner, 1993	0.17
Syn. cpx	Skulski et al., 1994; Hart and Dunn, 1993	REE	10^{-9}	1×10^{-18}	Sneeringer et al., 1984	0.50

* For a surface-layer half-thickness (l) of 5 Å, the minimum Peclet number (Pe_c) required for sector zoning is 0.5–3.0, depending on the value of the surface-enrichment factor, F (see text, Figs. 3 and 4).

than those for REEs. Consequently, enrichment in either of these elements on selected growth surfaces could easily result in sectoral variations in U or Hf abundance.

Because crystals cannot grow zircon at a rate as low as several micrometers per 10^{10} yr, the foregoing calculations raise an obvious question: Why don't all zircon crystals exhibit sector zoning? It is possible that near-surface lattice diffusion really is faster than true lattice diffusion (see limitations discussed above), and so the diffusivities of Cherniak et al. (1993) may not be relevant to the problem. However, it is also possible that sector zoning in zircon is in fact ubiquitous and we simply fail to detect it.

The mineral exhibiting what igneous petrologists might consider the classic example of sector zoning is clinopyroxene, which commonly shows sectoral variation of highly charged elements (e.g., Ti, Al, Cr, and REEs). Numerous examples have been reported, both in natural rocks (e.g., Strong, 1969; Hollister and Gancarz, 1971; Wass, 1973; Nakamura, 1973; Downes, 1974; Leung, 1974; Shimizu, 1981) and in experimental products (e.g., Kouchi et al., 1983; Hart and Dunn, 1993; Skulski et al., 1994). In contrast to titanite and zircon, clinopyroxene crystals cannot always be regarded as slowly grown. In fact, the synthetic examples noted above are known to have grown at rates that are rapid (10^{-9}–10^{-6} m/s) compared with diffusive transport in the melt. For such cases, satisfactory explanations for the occurrence of sector zoning already exist. It is instructive, nevertheless, to see whether the V vs. D_i competition we describe could be a contributing factor to this classic case of sector zoning.

In the study of synthetic clinopyroxenes ($CaMgSi_2O_6$-$CaTiAl_2O_6$) by Kouchi et al. (1983), crystals were grown at several levels of supercooling, which led to growth rates ranging from 10^{-9} to 3×10^{-6} m/s for the various crystal faces. Sectoral variations in both major (Si, Ca, and Mg) and minor components (Al and Ti) were noted, the latter being most pronounced at a supercooling of 25 °C, at which the average growth rate for the various crystal faces was 10^{-8} m/s. At this V value, the minimum diffusivity required for sector zoning to develop by the proposed mechanism is 2×10^{-18} m²/s. Directly relevant diffusion data do not exist, but the values reported by Grove and Wagner (1993) for [6]Al[4]Al = [6]Mg[4]Si interdiffusion may represent a reasonable order-of-magnitude estimate. As shown in Table 1, the Grove and Wagner diffusivity is several times too high to allow our mechanism to contribute to sector zoning ($Pe = 0.17$). However, diffusion of Ti^{4+} may well be characterized by a somewhat lower diffusivity than that for [6]Al[4]Al = [6]Mg[4]Si interdiffusion, and so the possibility remains that the competition between lattice diffusion and growth rate played some part in the minor element sectoral heterogeneity reported by Kouchi et al. (1983).

Augite grown in crystal-liquid partitioning studies by Skulski et al. (1994) and Hart and Dunn (1993) displays sector zoning of several trace cations, all of which have a charge of +3 or greater and thus are likely to be slow diffusing. The intersectoral chemical variation includes the rare earth elements, which are the one group of elements for which some diffusion data are available for clinopyroxene (Sneeringer et al., 1984). The diffusivity for Sm in diopside leads to $Pe = 0.5$, which is at the low end of the critical range. Again, given the inherent uncertainty not only in diffusion data but also in applying D_i values measured for one mineral to another mineral of slightly different structure and composition, it is possible that Pe is well within the critical range in this example of sector zoning. Note, also, that use of a surface-layer thickness >5 Å would assure $Pe > Pe_c$ even with the data used.

Some of the best examples of sector zoning are found in carbonate minerals. Sector-zoned calcite crystals exist both in nature, where growth is slow (e.g., calcite cements), and in the laboratory, where growth is relatively fast (Reeder and Paquette, 1989). To our knowledge, no data are available for diffusion of sectorally variable ions in carbonates, but it seems conceivable that the sector-zoning mechanism proposed here could play a role in diagenetic and related processes simply because diffusion is generally so slow at the relevant temperatures. Reeder (1991) made the intriguing suggestion that sector zoning might include (or cause) intracrystalline differences in the stable isotopic composition of calcite. Given some isotopic fractionation among growth surfaces, and low diffusivities for the isotopes of interest, the present model certainly allows this possibility.

Implications for element partitioning and diffusion

Assuming for the moment that the mechanism proposed here is responsible for the development of sector zoning in accessory minerals, we call attention to some

potentially useful implications of knowing the critical growth Peclet number Vl/D_i. One possible use is to place constraints on diffusivities: for example, a case of sector zoning in which the growth rate is constrained would provide the opportunity to calculate a maximum lattice diffusivity for the sectorally variable element(s). Conversely, a case of sector zoning in which knowledge of diffusion parameters were available would allow a minimum growth rate to be estimated. In a crude way, such an estimate can be attempted for the case of titanite discussed previously: assuming, arbitrarily, that the crystals described by Paterson and Stephens (1992) grew at an average temperature of 700 °C, then $D_{REE} = 5 \times 10^{-28}$ m²/s (Cherniak, unpublished data). For a critical V/D_i of 5×10^9 m (5 Å surface thickness), the growth rate must have been at least 2.5×10^{-18} m/s (7.9×10^{-5} μm/yr) for sector zoning to develop.

Another possible application is the calculation and use of surface-enrichment factors. For the case of zircon discussed previously, where Pe is much higher than the critical value, it is reasonable to assume that the concentration of a REE in any sector is equivalent to C_0F. Accordingly, knowledge of the equilibrium concentration in the crystal, C_0, would allow direct calculation of the surface-enrichment factor, F. Even if knowledge of C_0 is unattainable, it is possible that intersectoral partitioning is temperature sensitive and could be calibrated as a thermometer.

Another implication of the model presented here derives from the demonstrated linkage between sector zoning and lattice diffusion: sectoral variations in element concentration could, under special circumstances, be caused solely by direction-dependent diffusion. Suppose, for example, that some degree of surface enrichment in a particular element occurs on all growth surfaces of a given mineral. If the growth rate is more or less the same for all surfaces, and of the right magnitude to yield an average Vl/D_i close to the critical value, then significant anisotropy in D_i could lead to sector zoning. Well-documented cases exist of anisotropic diffusion, even in nonmicaceous minerals. For example, fivefold to tenfold variations in D_i with crystallographic direction have been observed for Sr diffusion in feldspars (e.g., Cherniak and Watson, 1992) and pyroxenes (Sneeringer et al., 1984). Much larger degrees of diffusive anisotropy have been reported occasionally for other minerals and diffusants (e.g., for Cl-F exchange in apatite; Brenan, 1993).

A final point concerning the results of our model is that the combination of slow lattice diffusion and any kind of surface enrichment of trace elements, even if the enrichment is uniform on all surfaces, can lead to apparent bulk-crystal partition coefficients that depart from equilibrium. The presence of chemically distinct sectors in a phenocryst provides a convenient and clear indicator of disequilibrium partitioning. However, if surface enrichment were nonselective, disequilibrium partitioning could result from high Vl/D_i and be essentially undetectable.

Drawing meaningful conclusions from the model im-plications discussed above necessitates the use of caution, especially in situations in which very slow growth is not a foregone conclusion. What is badly needed in the application of the model to igneous and metamorphic rocks, is knowledge of the high-temperature kinetics of element partitioning between the surface layer and the host medium of a growing mineral. Inferences based on use of Pe concerning growth rate and diffusion in sector-zoned minerals would be on much firmer ground if surface equilibrium could be generally assumed for all but the most rapidly grown crystals.

CONCLUDING REMARKS

This paper provides a quantitative discussion of a mechanism by which differences in the composition of specific growth surfaces can be retained in the interior of a crystal as sector zoning. We show that there exists a critical ratio of growth rate to lattice diffusivity, Vl/D_i, above which the development of sector zoning is inevitable given surface-specific enrichment in component i. The proposed model explains the occurrence of sectoral chemical heterogeneity in minerals from both metamorphic and slowly cooled intrusive rocks. Under appropriate circumstances, and with due caution, the model can be used to draw conclusions about growth rate and diffusion in minerals exhibiting sector zoning.

ACKNOWLEDGMENTS

REFERENCES CITED

Benisek, A., and Finger, F. (1993) Factors controlling the development of prism faces in granite zircons: A microprobe study. Contributions to Mineralogy and Petrology, 114, 441–451.

Brenan, J.M. (1993) Kinetics of fluorine, chlorine and hydroxyl exchange in fluorapatite. Chemical Geology, 110, 195–210.

Cherniak, D.J. (1995) Sr and Nd diffusion in titanite. Chemical Geology, in press.

Cherniak, D.J., and Watson, E.B. (1992) A study of strontium diffusion in K-feldspar, Na-K feldspar and anorthite using Rutherford backscattering spectroscopy. Earth and Planetary Science Letters, 113, 411–425.

Cherniak, D.J., Hanchar, J.M., and Watson, E.B. (1993) Rare earth diffusion in zircon. Eos, 74, 651.

Crank, J. (1975) The mathematics of diffusion (2nd edition), 414 p. Oxford University Press, London.

Downes, M.J. (1974) Sector and oscillatory zoning in calcic augites from Mt. Etna, Sicily. Contributions to Mineralogy and Petrology, 47, 187–196.

Dowty, E. (1976) Crystal structure and crystal growth: II. Sector zoning in minerals. American Mineralogist, 61, 460–469.

Fielding, P.E. (1970) The distribution of uranium, rare earths, and color centers in a crystal of natural zircon. American Mineralogist, 55, 428–440.

Fouke, B.W., and Reeder, R.J. (1992) Surface structural controls on dolomite composition: Evidence from sectoral zoning. Geochimica et Cosmochimica Acta, 56, 4015–4024.

Grove, T.L., and Wagner, T.P. (1993) Is adiabatic melting of oceanic mantle a disequilibrium process? Constraints from element diffusion rates in high-Ca pyroxene. Eos, 74, 284.

Hanchar, J.M., and Miller, C.F. (1993) Zircon zonation patterns as revealed by cathodoluminescence and backscattered electron images: Implications for interpretations of complex crustal histories. Chemical Geology, 110, 1–13.

Hart, S.R., and Dunn, T. (1993) Experimental cpx/melt partitioning of 24 elements. Contributions to Mineralogy and Petrology, 113, 1–8.

Hoffman, J.F., and Long, J.V.P. (1984) Unusual sector zoning in Lewisian zircons. Mineralogical Magazine, 48, 513–517.

Hollister, L.S. (1970) Origin, mechanism, and consequences of compositional sector-zoning in staurolite. American Mineralogist, 55, 742–766.

Hollister, L.S., and Gancarz, A.J. (1971) Compositional sector-zoning in clinopyroxene from the Narce area, Italy. American Mineralogist, 56, 959–979.

Kouchi, A., Sugawara, Y., Kashima, K., and Sunagawa, I. (1983) Laboratory growth of sector zoned clinopyroxenes in the system $CaMgSi_2O_6$-$CaTiAl_2O_6$. Contributions to Mineralogy and Petrology, 83, 177–184.

Leung, I.S. (1974) Sector-zoned titanaugites: Morphology, crystal chemistry, and growth. American Mineralogist, 59, 127–138.

Nakamura, Y. (1973) Origin of sector-zoning of igneous clinopyroxenes. American Mineralogist 58, 986–990.

Paterson, B.A., and Stephens, W.E. (1992) Kinetically-induced compositional zoning in titanite: Implications for accessory-phase/melt partitioning of trace elements. Contributions to Mineralogy and Petrology, 109, 373–385.

Paterson, B.A., Stephens, W.E., and Herd, D.A. (1989) Zoning in granitoid accessory minerals as revealed by backscattered electron imagery. Mineralogical Magazine, 53, 55–62.

Reeder, R.J. (1991) Surfaces make a difference. Nature, 353, 797–798.

Reeder, R.J., and Paquette, J. (1989) Sector zoning in natural and synthetic calcites. Sedimentary Geology, 65, 239–247.

Shimizu, N. (1981) Trace element incorporation into a growing augite phenocryst. Nature, 289, 575–577.

Skulski, T., Minarik, W.G., and Watson, E.B. (1994) High-pressure experimental trace element partitioning between clinopyroxene and basaltic melts. Chemical Geology, 117, 127–147.

Sneeringer, M.A., Hart, S.R., and Shimizu, N. (1984) Strontium and samarium diffusion in diopside. Geochimica et Cosmochimica Acta, 48, 1589–1608.

Strong, D.F. (1969) Formation of hour-glass structure in augite. Mineralogical Magazine, 37, 472–479.

Tiller, W.A. (1991) The science of crystallization: Microscopic interfacial phenomena, 391 p. Cambridge University Press, Cambridge, U.K.

Tiller, W.A., and Ahn, K.-S. (1980) Interface field effects on solute redistribution during crystallization. Journal of Crystal Growth, 49, 483–501.

Vavra, G. (1990) On the kinematics of zircon growth and its petrogenetic significance: A cathodoluminescence study. Contributions to Mineralogy and Petrology, 106, 90–99.

Wass, S.Y. (1973) The origin and petrogenetic significance of hour-glass zoning in titaniferous clinopyroxenes. Mineralogical Magazine, 39, 133–144.