

Crystal Growth from the Melt: A Review

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Abstract

This paper reviews four aspects of crystal growth theory: the nature of the rate-controlling process, the mechanism controlling molecular attachment onto the growing crystal surface, the nature of the crystal-melt interface, and the stability of planar interfaces relative to cellular interfaces. The rate-controlling process may be diffusion in the melt, heat flow, or the reaction at the crystal-melt interface. Diffusion or heat-flow controlled growth generally leads to a cellular morphology. For most silicates, interface-controlled growth leads to a faceted morphology. If the rate-controlling process is the interface reaction, the mechanism at the interface may be either continuous, with molecular attachment occurring at all points on the crystal surface, or lateral, with attachment occurring only on steps of the surface. The mechanism actually occurring can be determined by the dependence upon undercooling of the growth rate corrected for the viscosity of the melt. The nature of the interface can be described in terms of the interface roughness, which may be considered to be the topographic relief on the surface. Materials with small latent heats of fusion, such as quartz, should have molecularly rough interfaces and grow with a nonfaceted morphology, while materials with large latent heats, such as most other silicates, should have smooth interfaces and grow with a faceted morphology. The stability of planar interfaces relative to cellular interfaces can be discussed in terms of diffusional, heat-flow, surface-energy, and kinetic effects. For a freely growing crystal, such as in a magma chamber, only the surface-energy and kinetic effects aid in stabilizing planar interfaces. An attempt has been made to illustrate each of the phenomena discussed with a silicate example, although in one case an organic example is necessary.

Introduction

A knowledge of how crystals grow from the melt and the effects of the various factors which may influence crystal growth is a potentially important tool in interpreting textural and chemical features and crystallization histories of igneous rocks. In recent years much work has been done on both the theoretical and experimental aspects of crystal growth phenomena. Most of it has been published in the materials science literature, and may not be readily available to many geologists. The purpose of this paper is to review this work and discuss some of the potential geologic applications. When possible, examples will be chosen from systems of some geologic interest.

Four aspects of crystal growth will be treated: the nature of the rate-controlling process, the mechanism controlling molecular attachment onto the growing crystal surface, the nature of the crystal-melt inter-

face, and the stability of planar interfaces relative to cellular interfaces.¹

The first detailed study of crystal-growth phenomena was by Tamman (1899), who measured the rate of crystal growth of augite (composition unspecified) from a melt. He found that the rate is zero at the liquidus, increases to a maximum, and then decreases with increasing undercooling (decreasing temperature). Volmer and Marder (1931) developed a simple theory to explain this relationship. Other early theoretical work includes that of Wilson (1900) and Frenkel (1932). In the geologic literature, crystal growth rates were measured for nepheline by Winkler (1947) and in the system CaO–MgO–Al₂O₃–SiO₂ by

¹ Cellular morphologies are those which exhibit periodic structures, usually considered to be due to diffusion of heat or matter. Good examples are skeletal crystals and dendrites. Spherulites may also be cellular structures, and will be considered so here. The matter, however, is presently of some debate. Crystal morphology will be discussed in detail in a later section.

Leonteva (1948). Unfortunately, these early experimental studies lacked the solid theoretical foundation necessary to design experiments and discuss results, this foundation developing later (Frank, 1949; Jackson, 1958a, 1958b; Hillig and Turnbull, 1956).

Much of the theory of crystal growth, especially interface stability theory, concerns problems related to constrained growth in which temperature gradients, or some other physical factor in the experiment, control crystal growth. In most magma bodies, however, the crystals are suspended in the melt, and growth is unconstrained. Since the objective here is to examine applications to geologic problems, only the theory of unconstrained growth will be discussed. References to problems of constrained growth are given in O'Hara *et al* (1968).

In discussing the theory of crystal growth, detailed derivations will not be given. These are generally available in the references given.

Rate-Controlling Processes for Crystal Growth

The rate at which a crystal grows can be controlled by any of three factors: diffusion in the melt (either long- or short-range), flow of latent heat away from the growing crystal surface, or reactions at the crystal-melt interface.

If controlled by long-range diffusion, the growth rate, Y , of a flat interface is given by Christian (1965, p. 441) as

$$Y = k(D/t)^{1/2} \quad (1)$$

where k is a constant involving concentration terms, D is the diffusion coefficient of the rate-controlling species in the melt, and t is time. Thus, plots of crystal size *versus* the square root of time are straight lines. If the observed crystal growth obeys this relationship, the rate-controlling process is probably long-range diffusion.

Composition gradients and associated diffusion near the crystal-melt interface (short-range diffusion) can also affect growth by causing the crystal to break up into a cellular morphology (Elbaum, 1959). In this case a steady-state relationship is established whereby the growth rate is independent of time (Christiansen, Cooper, and Rawal, 1973). These local effects will be discussed further in the section on experimental results in crystal growth kinetics.

If flow of latent heat away from the crystal-melt interface is the rate-controlling process, the interface generally has a cellular morphology. As with diffusion-induced instability, the rates are generally

independent of time. This effect, too, will be discussed in a later section.

The effect of heat flow on the growth of a planar interface controlled by the interface reaction has been examined by Hopper and Uhlmann (1973). In the small undercooling region (undercoolings less than that with the maximum growth rate), they have determined that if the rate of production of latent heat is faster than the rate of removal, buildup of latent heat at the interface will cause the temperature to rise until the growth rate slows down to the point where the latent heat can be removed at the same rate it is produced. Thus, the growth rate is ultimately controlled by the interface reaction, but the local temperature at the interface is higher than the bulk temperature. A detailed analysis of the interface temperature is essential when discussing the temperature dependence of experimentally determined growth rates.

If the reaction at the crystal-melt interface is the slowest step in the growth process, the growth rate is independent of position (for a homogeneous system) and therefore independent of time. Plots of crystal size *versus* time are straight lines. Straight-line plots, however, are not sufficient evidence to demonstrate interface control, since steady-state diffusion or heat flow can also give this relationship. It is necessary to examine the interface to determine that it is not cellular, and to determine that there are not significant composition gradients near the interface in the melt. If these criteria are met, the rate-controlling process is usually taken to be the interface reaction (see, for instance, Meiling and Uhlmann, 1967; Kirkpatrick, 1974a).

In general, it is expected that for most large magma bodies crystallizing at small undercoolings (Kirkpatrick, 1974b) the rate-controlling process will be the interface reaction. Indeed, for crystals to grow with stable planar interfaces, as crystals in large magma bodies apparently do, the rate-controlling process must be the interface reaction (Cahn, 1967). In other situations such as rapidly cooled lava flows or in devitrifying ash flow tuffs, where the ratio of growth rate to diffusion coefficient is much higher (Cahn, 1967), diffusion is expected to be important. The diffusion control results in the spherulitic or dendritic morphologies observed in these situations.

Theory of Interface-Controlled Growth

Study of interface-controlled growth yields more information about the details of the melt-crystal transformation than the study of any of the other rate-

controlling processes. A detailed discussion of interface-controlled growth will be given because (1) it is probably the rate-controlling process in the crystallization of most igneous rocks; (2) it is a major part of crystal-growth theory; and (3) it provides background for understanding the differences between the different mechanisms, especially at small undercoolings, when discussing the kinetics of crystallization of magma bodies (Kirkpatrick, 1974b). The body of theory concerning interface-controlled growth consists of a general rate equation, theories of idealized mechanisms occurring at the crystal-melt interface, and theories concerning the nature of the interface.

General Rate Equation

The general theory for the rate of interface-controlled growth was developed by Volmer and Marder (1931) and Turnbull and Cohen (1960). The treatment of Turnbull and Cohen considers the rates at which atoms or molecular groups attach to and detach from the crystal surface. According to reaction-rate theory, if an atom or molecular group moves from melt to crystal, it must leave its energy state in the melt, pass through an activated state, and then decay into the crystalline state. These states are illustrated in Figure 1. The free energy difference between the melt and the activated state is $\Delta G'$ and between the melt and the crystal ΔG_c .

The rate of molecular attachment, r_a , can be written

$$r_a = \nu \exp(-\Delta G'/RT) \quad (2)$$

where ν is an attempt frequency, R is the gas constant, and T is temperature in degrees Kelvin. The rate of detachment, r_d , can be written

$$r_d = \nu \exp[-(\Delta G_c + \Delta G')/RT] \quad (3)$$

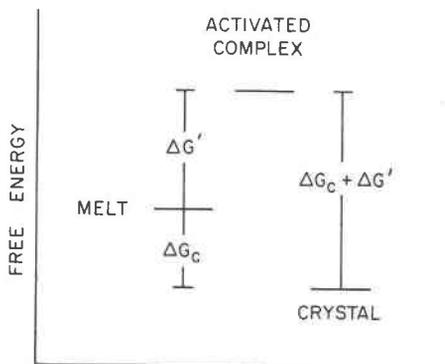


FIG. 1. Free energy relationships during the attachment process at the crystal-melt interface.

The growth rate, Y , is the difference of these two multiplied by the thickness per molecular layer, a_0 , and by f , the fraction of sites on the crystal surface available for attachment. This may be written

$$Y = fa_0 \nu \exp(-\Delta G'/RT)[1 - \exp(-\Delta G_c/RT)] \quad (4)$$

The chemical free energy difference is zero at the liquidus and increases with increasing undercooling. The growth rate, then, behaves as observed by Tamman (1899), and as shown, for example, in Figure 5. It is zero at the liquidus, increases to a maximum, and then decreases as the activation energy term begins to dominate.

At small undercoolings, Equation (4) may be expanded (Fine, 1964) to give

$$Y = fa_0 \nu \Delta G_c/RT \exp(-\Delta G'/RT) \quad (5)$$

At greater undercoolings ΔG_c becomes large relative to RT , and Equation (4) may be approximated by

$$Y = fa_0 \nu \exp(-\Delta G'/RT) \quad (6)$$

Neglecting pressure effects

$$\Delta G' = \Delta H' - T\Delta S' \quad (7)$$

where $\Delta H'$ is the activation enthalpy and $\Delta S'$ is the activation entropy. Substituting this into Equation (6) gives

$$Y = fa_0 \nu \exp(\Delta S'/R) [\exp(-\Delta H'/RT)] \quad (8)$$

Since the growth rate may be treated like a rate constant, a plot of $\ln Y$ versus $1/T$ has a slope of $-\Delta H'/R$ and an intercept at $1/T = 0$ of $\ln(fa_0 \nu) + \Delta S'/R$. $\Delta H'$ is thus easily determined, and $\Delta S'$ can be determined if f , a_0 , and ν are known or can be estimated. Since these three parameters are used only as the logarithm, the values need not be extremely accurate. The meaning of the activation entropy for crystal-growth processes, however, is not clear, and will not be discussed further.

This formalism appears to describe very well the rates of crystal growth in most systems. Because of the uncertainty in the values of f and the activation energy, however, it is not predictive. It can be made more predictive by approximating some of the parameters. Turnbull and Cohen (1960) defined a rate constant, D' , equivalent to a diffusion coefficient for transport across the melt-crystal interface, as

$$D' = a_0^2 \nu \exp(-\Delta G'/RT) \quad (9)$$

Substituting this into Equation (4) gives

$$Y = fD'/a_0[1 - \exp(-\Delta G_c/RT)] \quad (10)$$

Assuming that the Stokes-Einstein relationship,

$$D' = kT/3\pi a_0 \eta \quad (11)$$

holds where η is the viscosity, Equation (10) can be written

$$Y = fkT/3\pi a_0^2 \eta [1 - \exp(-\Delta G_c/RT)] \quad (12)$$

In general the free-energy difference between the melt and the crystal is not known. By assuming that the enthalpy and entropy differences are not sensitive functions of temperature, it may be approximated (Wagstaff, 1967) by

$$\Delta G_c = \Delta H_c \Delta T/T_L, \quad (13)$$

where ΔH_c is the latent heat of crystallization, and T_L is the liquidus temperature. Equation (13) then becomes

$$Y = fkT/3\pi a_0^2 \eta [1 - \exp(-\Delta H_c \Delta T/RT T_L)] \quad (14)$$

If the latent heat, fraction of sites, and viscosity are known or can be approximated, the growth rate can be calculated. In general, the fraction of available sites is the least well known, and this relationship can be applied easily only to materials where f can be taken as unity.

In studying crystal growth it is useful to rewrite Equation (14) and define the reduced growth rate, Y_r , as

$$Y_r = Y\eta/[1 - \exp(-\Delta H_c \Delta T/RT T_L)] \\ = kT/3\pi a_0^2 \cdot f \quad (15)$$

Y_r is, then, primarily a measure of the fraction of sites on the crystal surface available for molecular attachment, and can be used to calculate f if the temperature, growth rate, viscosity, latent heat, and a_0 are known.

This relationship is used to distinguish which mechanism controls the interface reaction, because f has a different temperature dependence for each mechanism.

At small undercoolings for many materials

$$\Delta H_c \Delta T/T_L \ll RT \quad (16)$$

Substituting this into Equation (14) (Jackson, 1967; Wagstaff, 1967) yields

$$Y \cong fk/3\pi a_0^2 \eta \Delta H_c \Delta T/RT_L \quad (17)$$

This relationship is also useful in determining the growth mechanism, especially if data at small undercoolings are available.

Mechanisms of Interface-Controlled Growth

The mechanism of growth may be defined as the manner in which atoms or molecular groups attach to the growing crystal surface. Two broad categories of mechanisms can be distinguished (Jackson, Uhlmann, and Hunt, 1967): lateral and continuous. The continuous mechanism operates when molecules can attach to the crystal surface at essentially any site, allowing the interface to advance uniformly. Lateral growth occurs by movement of one-molecule-high steps across the crystal surface. Molecules can attach only at the step; thus growth occurs at a particular place only when a step moves by. Two idealized types of lateral mechanisms can be distinguished: surface nucleation (Hillig, 1966; Calvert and Uhlmann, 1972) and screw dislocation (Hillig and Turnbull, 1956).

In silicate systems, the melt is too viscous to allow examination of the crystal surface as can be done with vapor growth crystals. Consequently, the only way to determine which of the various mechanisms operates in a given system is by the kinetics. This is generally done by determining the undercooling dependence of the reduced growth rate (Eq. 15).

Continuous Growth. For continuous growth (Wilson, 1900; Frenkel, 1932) f is generally assumed to be independent of temperature and equal to unity, but only the assumption that f is independent of temperature and large (Uhlmann, 1972) is really necessary. Because of this assumption, plots of Y_r or f versus ΔT should be straight lines with zero slope. In addition, Equation (17) may be written

$$Y\eta = K\Delta T \quad (18)$$

where K is a constant. Thus, at small undercoolings plots of $Y\eta$ versus ΔT should be straight lines with positive slopes.

Surface-Nucleation Mechanism. In the surface-nucleation mechanism (Hillig, 1966; Calvert and Uhlmann, 1972) it is assumed that molecules can attach only at the edges of one-molecule-thick layers on the crystal surface. Each layer is initiated by one or more one-molecule-thick nuclei, the formation of which obeys the classical laws of nucleation kinetics (Christian, 1965). Two cases can be distinguished (Calvert and Uhlmann, 1972): small crystal and large crystal. In the small-crystal case the growth rate is determined by the nucleation rate on the crystal surface. It is assumed that only one nucleus forms per layer and that this nucleus spreads completely over the surface before another forms. In the more generally useful large-crystal case, the growth rate de-

pends on both the nucleation rate and the rate of layer spreading. In either case the chemical free energy term in Equation (12) must now contain the line energy associated with the edge of the nucleus. Assuming a Boltzmann distribution of clusters (Uhlmann, 1972) the growth rate is given by

$$Y = K/\eta \exp(-B/T\Delta T) \quad (19)$$

where B is a constant containing the latent heat and line energy, η is the viscosity, and K is a constant.

Thus the reduced growth rate increases approximately exponentially with undercooling. In addition, plots of $\ln(Y\eta)$ versus $1/T\Delta T$ are straight lines with negative slopes.

Screw Dislocation Mechanism. The screw dislocation model (Hillig and Turnbull, 1956) assumes that screw dislocations emerge from the growing crystal face and cause a perpetual repeating step in the shape of an Archimedean spiral. As in the case of surface-nucleation-controlled growth, atoms or molecular groups can attach only at the layer edges. Because of the line energy associated with the step, the spacing between the coils of the spiral at the core is limited by the radius of the critical nucleus on the crystal surface.

The fraction of sites available for molecular attachment (Uhlmann, 1972) is given by

$$f \cong \Delta T/2\pi T_L \quad (20)$$

Thus, plots of f or Y , versus T should be straight lines with positive slopes. Incorporating Equation (20) into the small-undercooling approximation for the growth rate, Equation (18) yields

$$Y\eta = K\Delta T^2 \quad (21)$$

where K is a constant. Thus, near the liquidus, plots of $Y\eta$ versus ΔT^2 should be straight lines with positive slopes.

The Nature of the Crystal-Melt Interface

Two features of the crystal-melt interface have received theoretical treatment: interface diffuseness and interface roughness. The interface diffuseness may be defined as the distance over which molecules exist in a state transitional between the melt and the crystal. The interface roughness may be considered to be the topographic relief on the crystal surface. Consideration of the interface roughness has led to a predictive theory for the macroscopic form of the crystal surface.

Cahn (1960) and Cahn, Hillig, and Sears (1964) have examined interface diffuseness, and have

postulated that crystal growth should occur by a lateral mechanism at small undercoolings but by a continuous mechanism at large undercoolings. Jackson *et al* (1967), however, have shown that the Cahn method is valid for second-order phase transitions, but not first-order transitions such as crystal growth.

Jackson (1958a, b) has treated interface roughness. In his model the interface is assumed to be initially flat, and molecules are allowed to attach randomly. He was able to calculate the free-energy change as a function of the fraction of sites filled and the parameter α , where

$$\alpha = \Delta H_c/RT_L \xi. \quad (22)$$

ξ is the fraction of the total binding energy per molecule binding the molecule to others in a plane parallel to the interface. It varies from 0 to 1, and is greater than 0.5 for the most closely packed crystallographic planes and less for less closely packed planes. The free-energy change as a function of the fraction of sites filled is plotted in Figure 2 for various values of α . For lattice planes with α -values less than 2, the minimum-free-energy configuration corresponds to one-half the sites filled, while for planes with

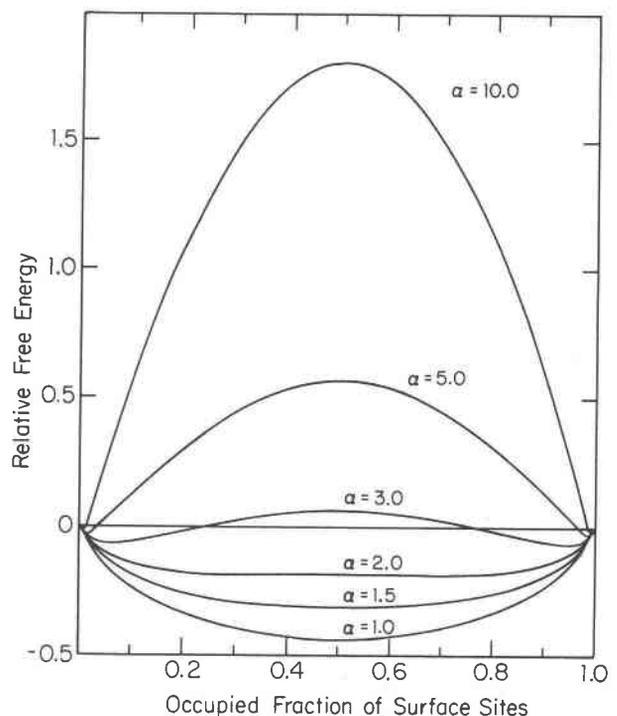


FIG. 2. Free energy of interfaces as a function of occupied fraction of surface sites for various values of α (after Jackson, 1958a, with permission).

α -values greater than 2 there are two minima corresponding to a few sites filled and a few sites empty. The half-filled configuration can be considered a rough interface, and the nearly-full or nearly-empty configuration a flat interface.

Thus, for materials with α less than 2 even the most close-packed planes should be rough, and new layers should form easily. The growth rate anisotropy should be small, and on a microscopic level the crystals should have a non-faceted morphology. For materials with α greater than 4 the close-packed planes should be smooth on an atomic scale, while the less close-packed planes should be rough. The growth rate should be highly anisotropic, and under the microscope the crystals should exhibit a faceted morphology.

Cahn *et al* (1964) have suggested that crystals that exhibit non-faceted morphologies—which Jackson (1958a, b) shows to have α values less than 2—should grow by a continuous mechanism, while crystals which are faceted (α greater than 2) should grow by a lateral mechanism. Jackson *et al* (1967) warn against making this correlation, since there is no theoretical justification for it. It appears, however, as will be discussed below, that in most experiments where both the morphology and the mechanism have been determined, this correlation can be made.

More recent work in this area has examined different attachment models (Leamy and Jackson, 1971), and attempts have been made to calculate growth rates (Jackson, 1968). The qualitative results concerning the interface morphology are similar to the earlier work. Much more work is necessary before this approach is capable of calculating growth rates for real crystals or examining in more detail the attachment process.

Crystal Growth Kinetics: Experimental Results

In recent years there have been a number of studies of the processes and mechanisms which control crystal growth. Unfortunately, few are directly applicable to growth from petrologically important melts. It seems worthwhile, however, to illustrate the various theoretical aspects of crystal growth which have been discussed. Most of the examples chosen are silicates, but in one case an organic example is necessary. Silica is one of the most thoroughly studied silicate materials and will be used to illustrate a number of phenomena.

In most cases the experimental procedure for measuring growth rates is to produce a homogeneous melt, quench it to a glass, reheat the glass to the

desired temperature in standard resistance furnaces, and measure the length of the crystals nucleated on the surface of the specimens as a function of time at constant temperature. In some cases, especially in systems which crystallize at low temperatures, the rates are measured using microscope heating-cooling stages by direct observation of the crystals as a function of time at constant temperature.

Diffusion-Controlled Growth

Diffusion-controlled growth has not been studied in as much detail as interface-controlled growth, probably because the existing theory does not allow as much detailed information to be obtained. There are, however, some interesting results in the silica system.

Figure 3 (Wagstaff, Brown, and Cutler, 1964) is a plot of crystal length *versus* the square root of time for cristobalite growing in O₂ and H₂O atmospheres from G.E. 204A fused quartz. The effect of water will be discussed below. This particular type of fused quartz is reduced, *i.e.*, oxygen deficient. The straight-line relationship (Eq. 1) indicates that the growth is diffusion controlled. Figure 4 is a plot of crystal size *versus* time for cristobalite growing from stoichio-

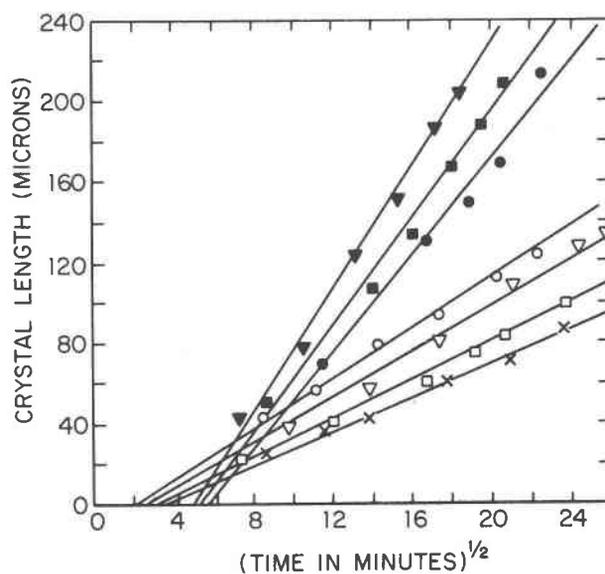


FIG. 3. Crystal length *vs* time^{1/2} for cristobalite growing from type 204A fused quartz at 1508°C in H₂O and O₂ atmospheres (after Wagstaff *et al*, 1964, with permission).

▼	567 mm H ₂ O	▽	485 mm O ₂
■	295 mm H ₂ O	□	323 mm O ₂
●	121 mm H ₂ O	X	161 mm O ₂
○	647 mm O ₂		

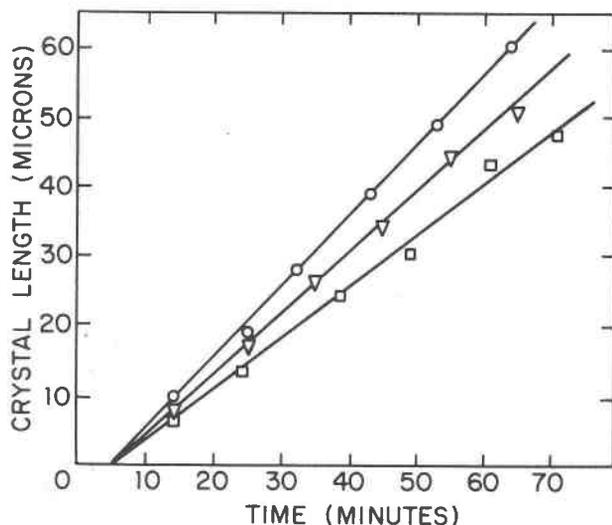


FIG. 4. Crystal length *vs* time for cristobalite growing from de-watered fused quartz at 1486°C in H₂O vapor atmospheres (after Wagstaff *et al*, 1964, with permission).

- 451 mm H₂O
- ▽ 129 mm H₂O
- 52 mm H₂O

metric fused quartz (Wagstaff *et al*, 1964). This straight-line relationship, along with morphologic evidence, indicates that growth from the stoichiometric material is controlled by the interface reaction.

Wagstaff *et al* (1964) believe that, taken together, these plots indicate that the diffusion of water to the interface to act as a mineralizer is not the rate-controlling process. Instead, the controlling diffusion is that of oxygen (as O²⁻ or H₂O) to the crystal surface to make a stoichiometric crystal. The linear $t^{1/2}$ relationship is observed for the non-stoichiometric material because as the crystals on the outside of the specimen get longer, the distance the oxygen must diffuse from the surrounding atmosphere to the crystal-melt interface increases.

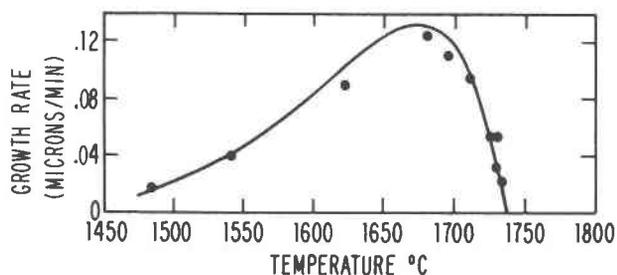


FIG. 5. Growth rates *vs* temperature for cristobalite growing from high purity fused quartz (after Wagstaff, 1969, with permission).

Continuous Mechanism

SiO₂ is one of the few silicate materials which is predicted to grow with a non-faceted morphology (α less than 2; Jackson *et al*, 1967). The growth rate of cristobalite from fused quartz has been measured under a number of different conditions by F. E. Wagstaff and his coworkers (Wagstaff *et al*, 1964; Wagstaff and Richards, 1966; Wagstaff, 1967, 1969). As illustrated in Figure 4, the rate of growth of cristobalite from stoichiometric fused quartz (Wagstaff *et al*, 1964) is time independent and is interpreted to be interface controlled. Figure 5 is a plot of growth rate *versus* undercooling for internally nucleated cristobalite growing from very pure fused quartz (Wagstaff, 1969).

Figure 6 is a plot of the reduced growth rate *versus* undercooling for the same experiments. The scatter near the melting point is unexplained. It can be seen that the reduced growth rate is independent of undercooling. Figure 7 is a plot of $Y\eta$ *versus* temperature for the same experiments. The data plot as a straight line. Both Figures 6 and 7 indicate a continuous growth mechanism.

In all cases the crystal morphology was non-faceted.

A similar set of results was obtained for GeO₂ (Vergano and Uhlmann, 1970a, b), which is also predicted to grow with a non-faceted morphology. In this case the reduced growth rate is again independent of undercooling, and the crystals are non-faceted.

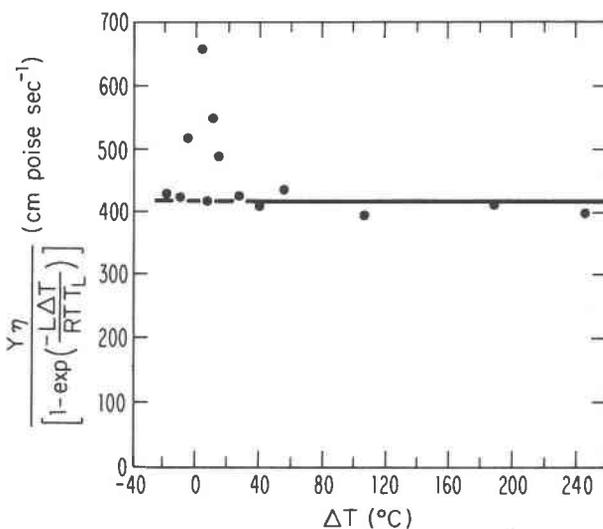


FIG. 6. Reduced melting and growth rates for cristobalite in fused quartz (after Uhlmann, 1972, from data of Wagstaff, 1969, with permission).

Materials which exhibit continuous growth can be used to determine the ability of Equation (14) to calculate the growth rates, since f is independent of temperature. Figure 8 is a plot of the calculated growth rates of cristobalite from fused quartz along with the observed rates (Wagstaff, 1967). The calculated rates are about an order of magnitude lower than the observed rates, but have the same temperature dependence. Vergano and Uhlmann (1970a, b) obtained similar results for GeO_2 . Wagstaff (1967) believes that this order of magnitude accuracy is quite good, considering the problems in estimating f , a_0 , and the rate constant. The main uncertainty is almost certainly in using the Stokes-Einstein approximation (Eq. 11) for the rate constant. The similarity of the temperature dependence for the observed and calculated rates is encouraging, and indicates that the substitution of the viscosity for the activation energy term, at least in this simple system, leads to acceptable results. Apparently the processes controlling viscous flow and crystal growth are very similar in this system.

Screw Dislocation Mechanism

The best example of screw-dislocation growth is sodium trisilicate ($\text{Na}_2\text{Si}_3\text{O}_7$) (Scherer, 1974). The growth rates were obtained using the standard resistance furnace technique.

At all temperatures the crystals exhibit a faceted morphology, and the growth rates are independent of time. The observed growth rate *versus* undercooling relationship is that expected from theory; zero at the liquidus, increasing to a maximum, and then decreasing.

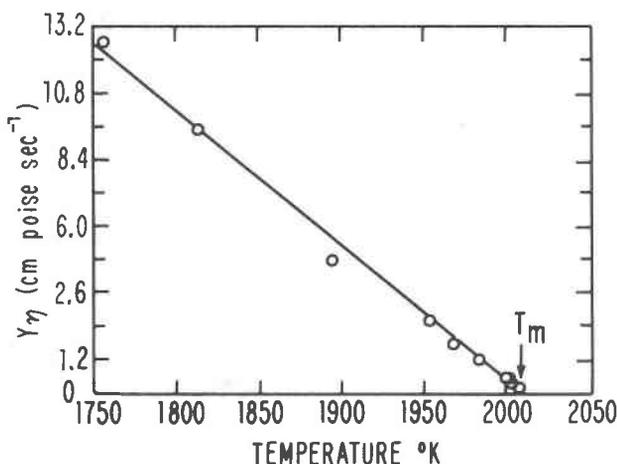


FIG. 7. Y_η vs temperature for cristobalite growing from high purity fused quartz (after Wagstaff, 1969, with permission).

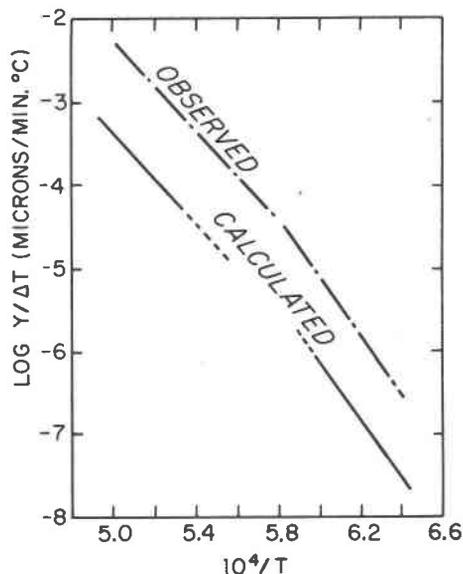


FIG. 8. Comparison of calculated and observed growth rates for cristobalite growing from high purity fused quartz (after Wagstaff, 1967, with permission).

Figure 9 is a plot of the reduced growth rate *versus* undercooling. The data fall on a straight line, verifying the screw dislocation mechanism.

A screw dislocation mechanism was also postulated, although with some reservations, for sodium disilicate (Meiling and Uhlmann, 1967a,b). All features of the growth process, including the plot of Y_η *versus* ΔT^2 , indicate a screw dislocation mechanism, except that the reduced growth rate *versus* undercooling plot is curved instead of straight.

Surface Nucleation Mechanism

The surface nucleation mechanism has been found to be operative in a number of systems including α -

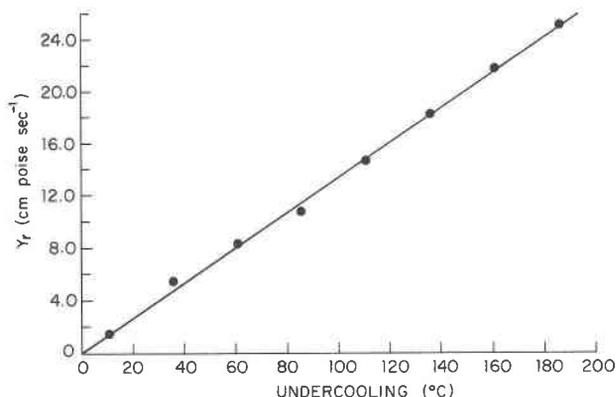


FIG. 9. Reduced growth rate vs undercooling from sodium trisilicate growing from its own melt (after Scherer, 1974).

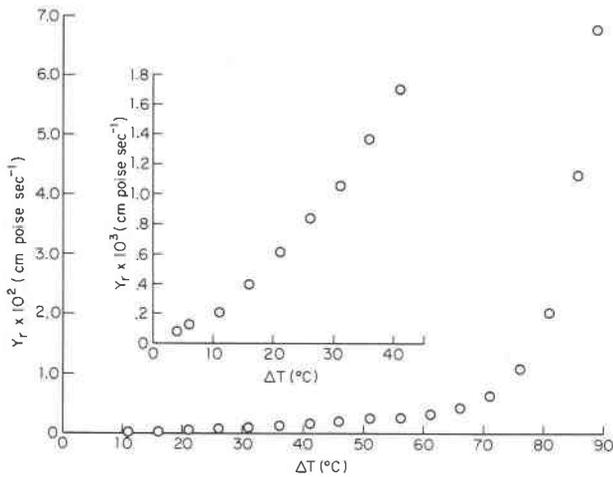


FIG. 10. Reduced growth rate *vs* undercooling for α -phenyl o-cresol growing from its own melt (after Scherer and Uhlmann, 1972, with permission).

phenyl o-cresol (Scherer and Uhlmann, 1972) and $\text{CaMgSi}_2\text{O}_6$ pyroxenoid growing from a melt of the same composition (Kirkpatrick, 1974a). The growth rates of α -phenyl o-cresol were determined using a microscope heating-cooling stage, while those of the pyroxenoid were obtained using standard resistance furnace techniques. α -phenyl o-cresol exhibits the expected relationship between growth rate and undercooling. The small undercooling region could not be reached for $\text{CaMgSi}_2\text{O}_6$ because of errors due to rapid crystal growth when passing through the growth rate maximum. At all temperatures the crystals for both materials are faceted.

Figure 10 is a plot of the reduced growth rate *versus* undercooling for α -phenyl o-cresol. Figure 11

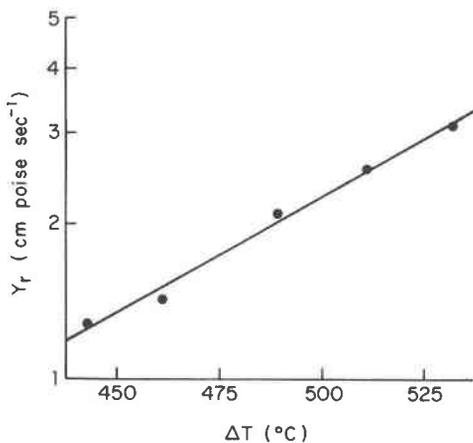


FIG. 11. Reduced growth rate *vs* undercooling for $\text{CaMgSi}_2\text{O}_6$ pyroxenoid growing from its own melt (after Kirkpatrick, 1974a, with permission).

is a similar plot for the pyroxenoid (vertical scale is logarithmic). In both cases the relationship is approximately exponential in ΔT , as predicted by the surface nucleation theory. Figures 12 and 13 are $Y\eta$ *versus* $1/T\Delta T$ plots for α -phenyl o-cresol and the pyroxenoid respectively. Both plots have negative slopes, in agreement with the theory. The curves, at least for α -phenyl o-cresol, are not straight lines as predicted. This seems to be a general phenomenon, and has been observed in several systems including tri- α naphthyl benzene and o-terphenyl (Scherer and Uhlmann, 1972) and lead tetraborate (DeLuca, Eagan, and Bergeron, 1969). Recent data (D. R. Uhlmann, personal communication) indicate that anorthite growing from its own melt also behaves in this manner. This relationship can be accounted for (Scherer and Uhlmann, 1972) by a changing *line energy*, which is the energy associated with the edge of the nucleus on the crystal surface.

Computer simulations of crystal growth (Gilmer and Bennema, 1972) have indicated that the growth of crystals with high latent heats may be describable by a surface-nucleation model at small undercoolings, but with line energies smaller than expected. Recent extensions of these calculations (see, for instance, Scherer *et al*, 1975) have shown that at large undercoolings the growth can be described by surface-nucleation models with normal line energies. Combining these gives rise to the curved $Y\eta$ *versus* $1/T\Delta T$ plots observed.

Interface Morphology

Jackson's theory (1958a,b) of interface morphology is perhaps the most spectacular success of all of crystal growth theory. To the author's knowledge, the crystal morphology of all materials so

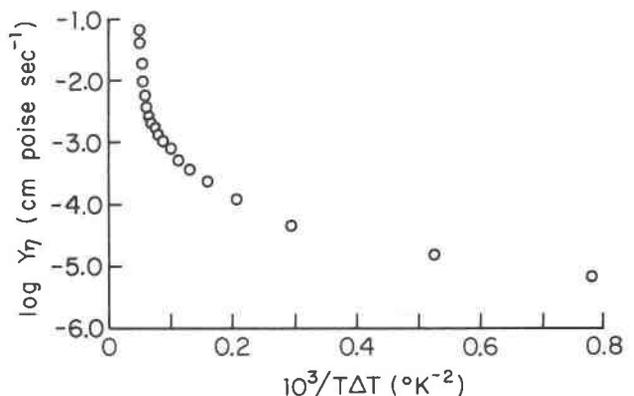


FIG. 12. $\log(Y\eta)$ *vs* $1/T\Delta T$ for α -phenyl o-cresol growing from its own melt (after Scherer and Uhlmann, 1972, with permission).

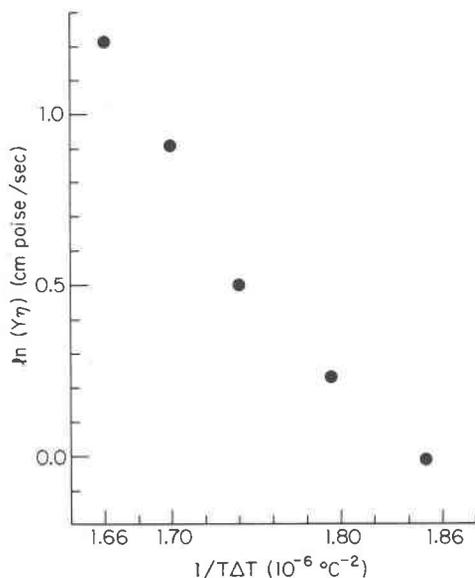


FIG. 13. $\ln(Y\eta)$ vs $1/T\Delta T$ for $\text{CaMgSi}_2\text{O}_6$ pyroxenoid growing from its own melt (after Kirkpatrick, 1974a, with permission).

far investigated is that predicted by the theory. Materials with small heats of fusion have a non-faceted (anhedral) morphology, and materials with large heats of fusion have faceted (euhedral) morphologies.

In addition, the correlation between lateral mechanisms (sodium trisilicate, α -phenyl o-cresol, $\text{CaMgSi}_2\text{O}_6$) and faceted morphologies, and between non-faceted morphologies and continuous mechanisms (SiO_2 , GeO_2 , seem to be verified in the systems so far studied. This growing body of experimental evidence will have to be taken into consideration in further theoretical work on growth mechanisms.

Activation Energies for Crystal Growth

In theory, time-independent growth rates can be treated like other rate constants, and activation energies can be calculated from them. According to classical rate theory, the activation energy measures the enthalpy difference between the rate-controlling group in the melt near the crystal surface and in the activated state. It is a measure, then, of the ease of molecular rearrangement that must take place during the growth process. This rearrangement is difficult to picture in detail, but may include rotation and breaking or stretching of bonds.

The interpretation of activation energies for growth processes must at all times be very tenuous. Many factors, in addition to the one being examined

in a particular set of experiments, can influence the results. These factors include small amounts of impurity, including water, and small degrees of non-stoichiometry.

Three systematic studies of activation energies of crystal growth processes will be discussed here: SiO_2 - H_2O (Wagstaff and Richards, 1966), $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ (Kirkpatrick, 1974a) and CaO - MgO - Al_2O_3 - SiO_2 - FeO (Williamson, Tipple and Rogers, 1968).

The simplest results to interpret are those in the system SiO_2 - H_2O . Wagstaff and Richards (1966) found the activation energy for growth of cristobalite from stoichiometric, very pure fused quartz to be 134 kcal/mole, if dry, but 77 kcal/mole in a hydrous atmosphere. This decrease is similar to that for the activation energy for viscous flow of fused quartz with increasing H_2O content (Hetherington and Jack, 1962). The rates of growth also increase greatly with water present (Figs. 3 and 14). These results can be interpreted in the classical manner. Water enters the melt structure by breaking strong (Si-O-Si) bonds

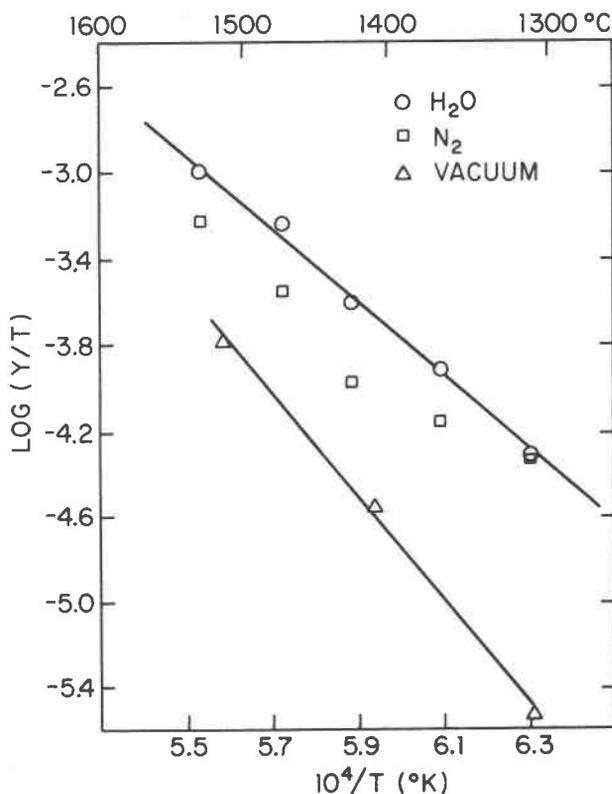


FIG. 14. Comparison of growth rates of cristobalite growing from stoichiometric fused quartz in H_2O , N_2 , and vacuum (after Wagstaff and Richards, 1966, with permission).

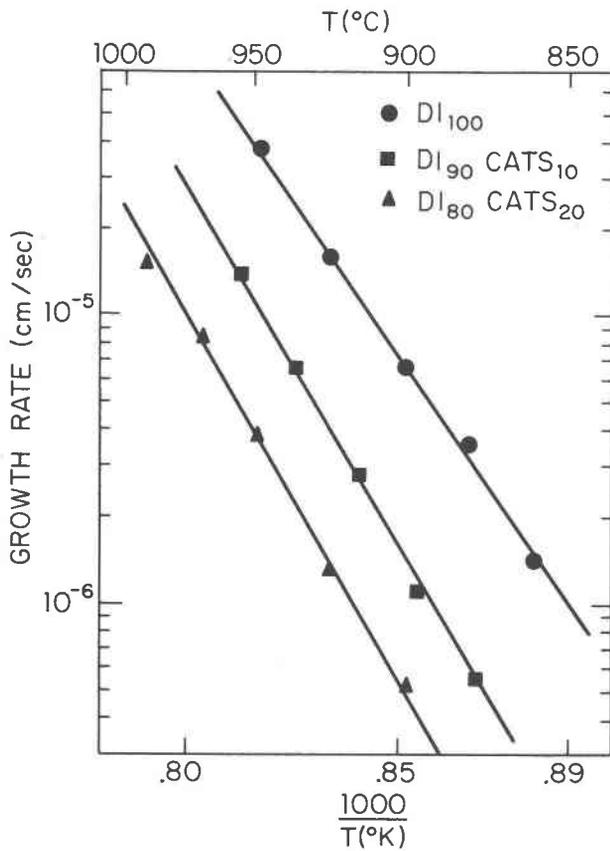


FIG. 15. Arrhenius plots of the growth rates of pyroxenoids in the system $\text{CaMgSi}_2\text{O}_6$ (Di)- $\text{CaAl}_2\text{SiO}_6$ (Cats), mole percent (after Kirkpatrick, 1974a, with permission).

and creating much weaker (Si-OH-HO-Si) bonds. It is much easier, then, for a silica tetrahedron or group of tetrahedra in the melt to break or stretch its bonds with the melt and move into the activated state.

Arrhenius plots ($\ln Y$ versus $1/T$) for the growth rates of pyroxenoids with the composition of the melt in the system $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ are shown in Figure 15 (Kirkpatrick, 1974a). The activation energies increase with increasing aluminum content. These results can be interpreted by noting that while Al-O bonds in tetrahedral coordination (substituting for silicon) are weaker than Si-O bonds, Al-O bonds in six-fold coordination (modifier sites in the melt) are stronger than Ca-O or Mg-O bonds. Assuming that some aluminum enters both sites in the melt, as it does in the crystal, the activation energy increase must be due to the aluminum in the modifier sites. Thus, the rate-controlling process can be pictured as a silica tetrahedron or group of tetrahedra breaking or stretching its bonds with the modifier cations, and

not as the breaking of Si (Al)-O bonds within the tetrahedral groups, as might first be expected. These conclusions, like all those made from activation energies, must be considered very tentative and subject to modification when additional data become available.

Williamson *et al* (1968) have examined the effect of iron content and oxidation state on the activation energy of spherulitic growth of anorthite and wollastonite from a melt of the composition SiO_2 , 53; Al_2O_3 , 15; CaO , 30; MgO , 2 wt percent. Five grams equivalent FeO was added per 100 grams base glass with this composition, and the heat treatment controlled to give $\text{Fe}^{2+}/\Sigma\text{Fe}$ values of from 26 to 70 percent. Figure 16, a plot of $\text{Fe}^{2+}/\Sigma\text{Fe}$ versus activation energy, shows a trend that follows the trend of increasing activation energy for viscous flow with increasing ferrous iron. The authors give no detailed explanation of this change, but note that the values for melts rich in ferric iron are consistent with activation energies for cation diffusion, while those for melts rich in ferrous iron are consistent with activation energies for viscous flow.

Interface Stability

For a crystal growing freely in a melt, as most crystals in a magma body probably do, there is always a tendency for the crystal-melt interface to break up into cells of one form or another (dendrites or skeletal crystals, for instance). In fact, the classical theory of constitutional supercooling (Tiller *et al*,

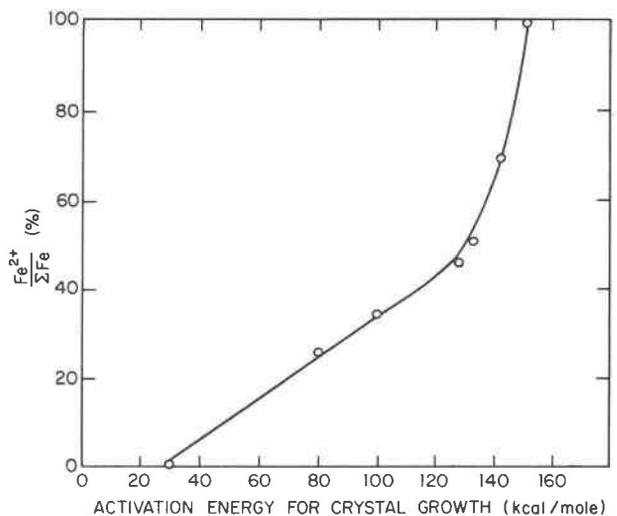


FIG. 16. Activation energy for crystal growth from CaO - MgO - SiO_2 - Al_2O_3 - FeO glasses as a function of percent total iron as iron +2 (after Williamson *et al*, 1968, with permission).

1953; Rutter and Chalmers, 1953) predicts that a freely growing crystal always should. The observation that large faceted crystals, such as phenocrysts in volcanic rocks, can be grown has led to a large literature examining this problem of interface stability. An understanding of these ideas is important in any attempt to interpret the origin of textural features of igneous, especially volcanic, rocks. This section will discuss constitutional supercooling and the later work on interface stability. The next section will illustrate these ideas with examples from experimental and natural systems.

Constitutional Supercooling

If a crystal is growing freely in a melt of the same composition, the latent heat generated must flow away from the interface, causing the temperature to decrease away from the crystal. Thus, in the temperature range above the maximum growth rate, any small protuberance which may form on the surface will be at a lower temperature than the rest of the interface, and will, therefore, grow faster and extend even further from the general plane of the surface, causing the interface to take on a cellular morphology. This may be called thermal instability, and there is a tendency for it to occur for every freely growing crystal.

If the crystal does not have the same composition as the melt there will be, in addition to the thermal effect, a compositional effect, called constitutional supercooling, due to material more soluble in the melt than in the crystal being rejected by the crystal. This phenomenon has been described in detail by Rutter and Chalmers (1953) and Elbaum (1959). For systems in which the melt is richer in impurity than the crystal, the amount of impurity in the melt will decrease away from the growing crystal. Thus, the liquidus temperature will increase away from the interface, as will the undercooling (Fig. 17). Thus, in the small undercooling region a protuberance will grow progressively faster the farther it gets from the general crystal surface. It appears, as evidenced by the growth of spherulites (Lofgren, 1971; Kirkpatrick, 1974a), that even at temperatures below the maximum growth rate this constitutional effect can cause instability and override the effect of decreasing growth rate with falling temperature.

Stability Theories

The fact is, however, that large faceted (euhedral) crystals can grow. The problem of why this is true has been treated by many workers (Mullins and Sekerka,

1964; Cahn, 1967; O'Hara *et al.*, 1968). Much theoretical work still needs to be done, but it appears that interface attachment kinetics can significantly stabilize planar interfaces against thermal and compositional destabilizing effects.

The fundamental work of Mullins and Sekerka (1964) paved the way in this problem. They did not take interface attachment kinetics into account, however, and were not able to predict stabilization of planar interfaces to crystal sizes more than an order of magnitude larger than the critical size for nucleation (Cahn, 1967). Mullins and Sekerka allowed the interface to be perturbed, did a Fourier analysis of the perturbations, and, by solving Laplace's equation for diffusion of both heat and matter near the perturbations, determined which wavelength perturbations grow and which decay. Examples would be the distance between dendrite arms or between holes in a skeletal crystal. If any wavelength perturbation grows, the interface is considered to be unstable. Their equation contains three terms involving surface energy, thermal gradients, and composition gradients respectively. In the case of a freely growing crystal only the surface energy term contributes to stabilization.

The next step was to introduce diffusion parallel to the interface (Coriell and Parker, 1966). Indeed, by leveling out the composition gradients parallel to the interface such diffusion can lead to increased stability of spheres and cylinders. The effect of interface diffusion on planar interfaces has not been investigated.

The final step, so far, is to introduce interface attachment kinetics into the solution. Coriell and Parker (1967) have examined the effect of attachment kinetics on the stability of growing spheres, and Kolter and Tiller (1967) have examined the same problem for cylinders. In both cases, they found that slow rates of molecular attachment can stabilize the interface. In both cases, however, as the radius of cur-

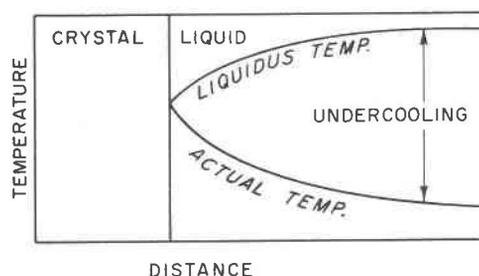


FIG. 17. Generalized undercooling distribution in the melt in the vicinity of a freely growing crystal which is rejecting impurity.

vature increases to infinity (*i.e.*, to a flat interface) the stabilizing effect becomes less and less, until the models always predict breakdown of a planar interface (O'Hara *et al.*, 1968).

O'Hara *et al.* (1968) and Cahn (1967) have examined the effect of attachment kinetics on the stability of planar interfaces and polygonal crystals (apparently freely growing crystals) respectively. Like the other workers cited above, they followed the Mullins and Sekerka form of analysis. In both cases they found that taking the kinetics into account, *i.e.*, not allowing equilibrium to be established at the interface, greatly increased the stability. Cahn found that for a faceted crystal the critical crystal radius for the onset of instability is of the order of D/Y_i , where D is the diffusion coefficient of the rate-controlling component in the melt and Y_i is the initial growth rate of the crystal. For crystals with a radius smaller than this critical value, the morphology is stable, while for larger crystals, it is unstable. This radius also corresponds to the onset of diffusion-controlled growth. Cahn also feels that if a crystal has an anisotropic surface energy, as most silicates do, the shape of the instabilities once they form should reflect the anisotropy of the surface energy. O'Hara *et al.* (1968) believe that for crystals with anisotropic growth rates, like most silicates, the most stable faces

will still be present on the instabilities. In either case, we should expect to find faceted instabilities on most geologic materials.

When a crystal face becomes unstable, then protuberances develop and grow. Heat and uncrystallizable components flow away from the growing protuberances, not only perpendicular to the general trend of the interface, but parallel to it. Thus, additional protuberances will be inhibited from developing in the vicinity of one already formed because of the locally increased temperature and impurity content. A regular distribution of protuberances will develop with a periodicity depending upon the ratio of the growth rate and the diffusion coefficient in the melt (Keith and Padden, 1963).

Morphologies of Crystals in Geologic Systems

As discussed above, the rate of crystal growth increases with increasing undercooling for a large temperature range. Diffusion coefficients in a melt, on the other hand, decrease with increasing undercooling. Thus, following Cahn (1967), we could expect increasing instability of planar interfaces with increasing undercooling. In addition, following Keith and Padden (1963) and Lofgren (1974), we can expect the wavelength (spacing) of the instabilities, whatever the form, to decrease with increasing undercooling,

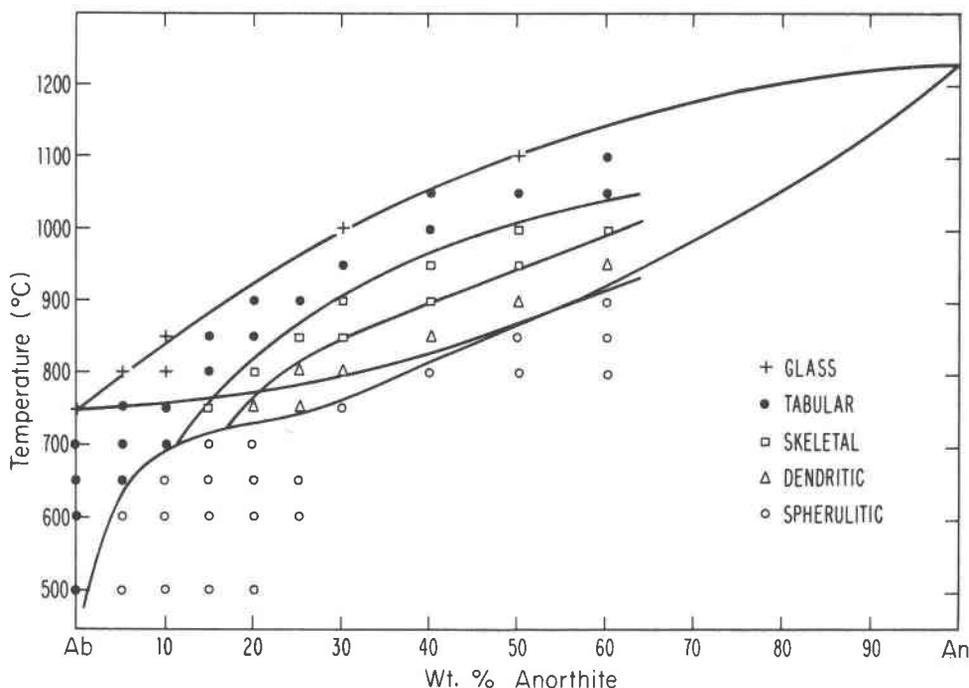


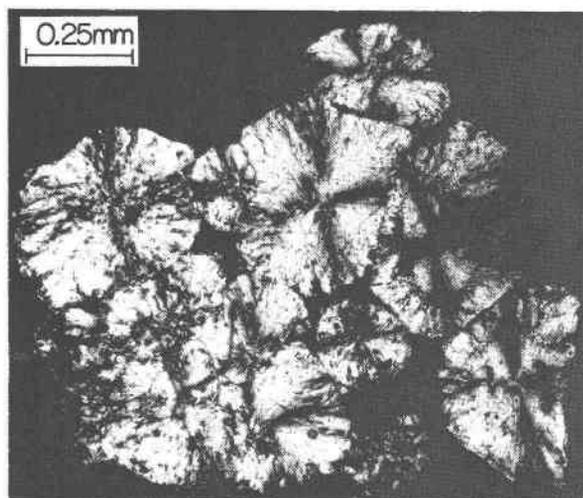
FIG. 18. Morphologies of plagioclase crystals grown in water-saturated plagioclase melts at 5 kbar (after Lofgren, 1974, with permission).

because D/Y decreases with increasing undercooling. This is in fact what we observe in both experimental and natural situations.

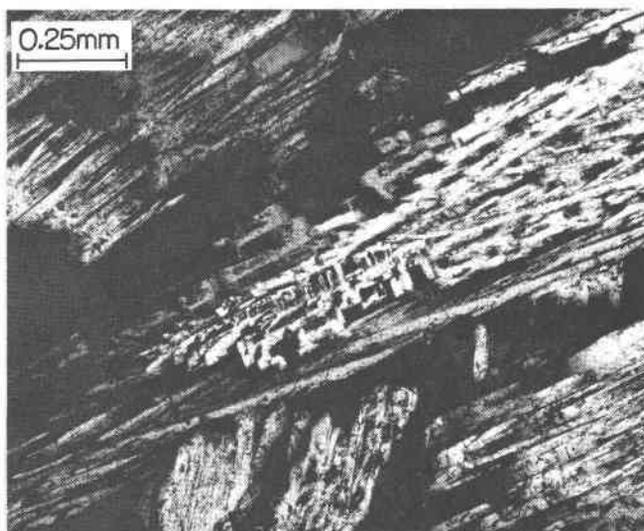
Lofgren (1974) has studied the morphology of plagioclase crystals growing at 5 kbar in water-saturated plagioclase melts as a function of composition and temperature. His results are plotted in Figure 18. Photomicrographs illustrating his results are shown in Plate 1. At small undercoolings, less than about 100°C , he found tabular crystals (Plate

1d). Then, in the intermediate plagioclase range, he found skeletal crystals (Plate 1c), dendrites (Plate 1b), and finally spherulites (Plate 1a), at progressively larger undercoolings. Near albite he found that the undercooling range of tabular crystals increases drastically and that the skeletal and dendritic forms are not present.

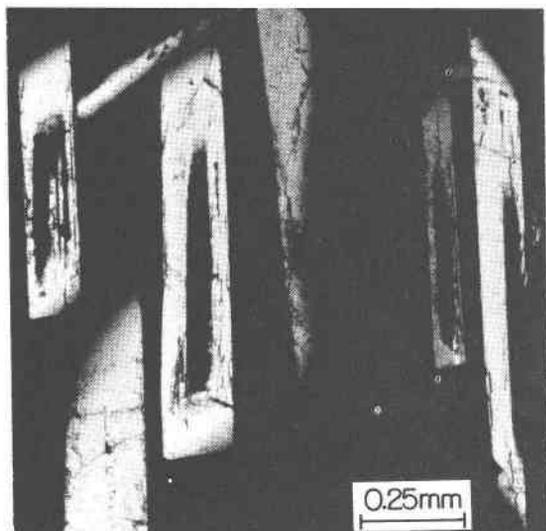
These results are consistent with the qualitative predictions of interface stability theory. Since uncrystallizable components are present in all the runs,



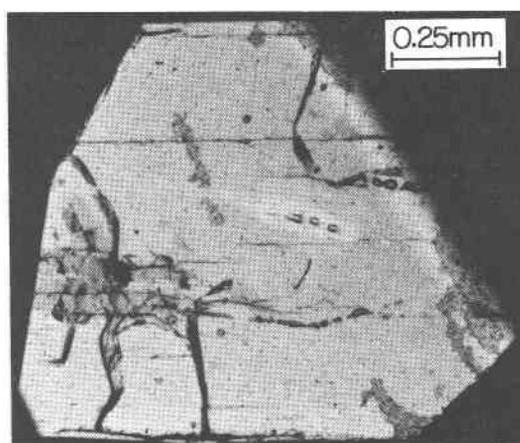
(a)



(b)



(c)

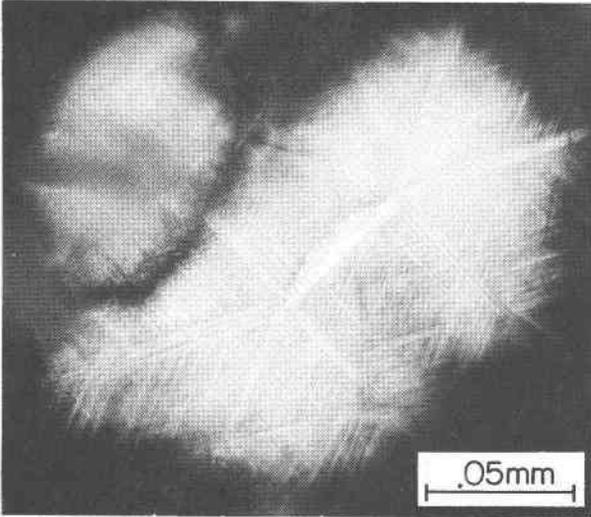


(d)

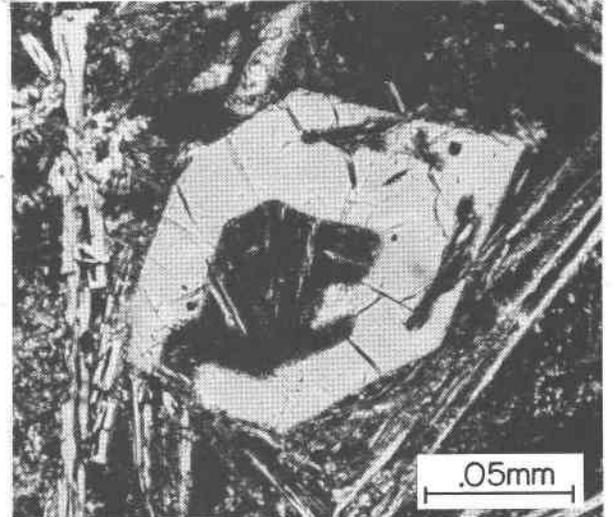
PLATE 1. Photomicrographs of plagioclase crystals grown at 5 kbar from water-saturated plagioclase melts (from Lofgren, 1974, with permission). (a) fine spherulites, $\Delta T = 430^{\circ}\text{C}$. (b) dendritic crystals, $\Delta T = 200^{\circ}\text{C}$. (c) skeletal crystals, $\Delta T = 100^{\circ}\text{C}$. (d) tabular crystals, $\Delta T = 50^{\circ}\text{C}$.

the theory would predict interface instability at some point. In the smallest undercooling range—where D is large and Y small and D/Y , therefore, large—planar interfaces are stable and the crystals are euhedral. At increasing undercoolings D/Y decreases and eventually reaches the critical value, and planar interfaces are not stable. The first instabilities to appear have long wavelengths, resulting in skeletal

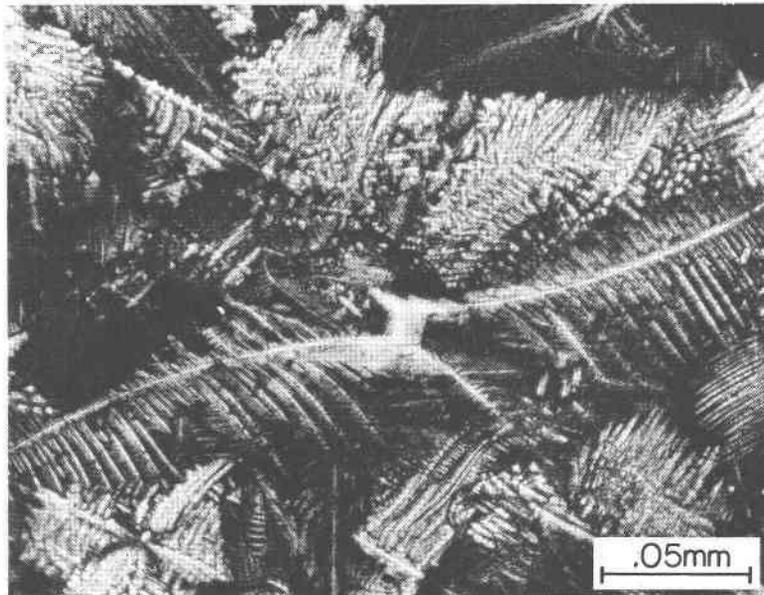
crystals. With progressively larger undercooling the wavelengths of the instabilities decrease as D/Y decreases. At temperatures below the maximum in the growth rate curve, where Y decreases with falling temperature, D/Y will still retain a small value, since D is also decreasing rapidly. It is interesting to note (and unexplained by the theory) that the instabilities are crystallographic (either skeletal or dendritic) until



(a)



(b)



(c)

PLATE 2. Olivine crystals from pillow basalts (from Bryan, 1972, with permission). (a) fine dendrites from the pillow margin. (b) skeletal crystals from the pillow center. (c) open dendrites from the pillow interior.

very large undercoolings, where the morphology is spherulitic, with the crystallites exhibiting non-crystallographic branching.

At all undercoolings where the morphology can be observed in detail, the interfaces on the instabilities exhibit facets, even though the overall morphology is cellular. This is in agreement with both Cahn's (1967) and O'Hara *et al.*'s (1968) predictions that highly anisotropic crystals would show faceted instabilities.

The ideas of interface stability theory are also well illustrated by the subsea basalts studied by Bryan (1972). His photomicrographs of olivine crystals growing in various parts of a pillow are shown in Plate 2. Near the outside, where the cooling was fastest and the crystallization occurred at the lowest temperature, the olivines (Plate 2a) have a very fine dendritic morphology. Further in (Plate 2c) the olivine is in the form of feathery dendrites and the spacing between the instabilities is larger. In the center of the pillow, where the cooling was slowest and the crystallization occurred at the smallest undercooling (Plate 2b), the olivine, while showing some crystal faces, is cellular, but the size of the instabilities is of the order of the size of the crystals. Throughout the pillow the cooling rate must have been fast enough so that most of the crystallization occurred below the temperature range where the interfaces are stable, but above that necessary for spherulitic growth. The temperature range where most of the crystallization occurred increases from the outside of the pillow to the inside.

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