asymmetry of OH production with respect to the perihelion.

When a periodic comet approaches the sun the surface of its nucleus will still contain cubic (and perhaps hexagonal) ice. This will be favorable to heat conduction to deeper layers, even at large solar distances, and gas production will be decreased by this mechanism. The gas production rate of "old" comets is indeed lower than that of "young" ones (*15*).

The mechanism proposed here will have as a consequence that some orbits may be favorable to gas production and others favorable to conduction of heat into deeper layers of the nucleus. Phase transition with an increase of thermal conduction will prevail when the temperature of the nucleus at the perihelion is close to the transition temperature. When the temperature is much higher, a large amount of the newly formed crystalline ice crust will evaporate. We see that two comets of comparable age, with comparable mean radiation intensity received during their revolutions, may have very different gas production rates. For this reason it seems that, disregarding the differences in age of the comets, the orbit of Halley may be intrinsically more productive than that of Tempel 2, even if we take into account that the mean radiation intensity received is lower for Halley than for Tempel 2.

The mechanism proposed here is obviously not able to explain all differences in gas production rates in comets, but it may be one factor among others. A space mission could give further information on heat transmission in the nucleus.

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25 February 1980

Oscillatory Zoning in Plagioclase Feldspar

Abstract. *A kinetic mathematical model of crystal growth from the melt is used to describe quantitatively the phenomenon of oscillatory zoning in plagioclase feldspar. In this model, the functional dependence of crystal growth rate on both melt and crystal surface composition and the transport of material within the melt are explicitly considered. Oscillatory zoning is found to develop for a wide variety of such functional dependence and to be sensitive to the initial composition of the melt.*

Plagioclase feldspar, a common rock-forming mineral, consists of a solid solution between the end-members anorthite (An), $CaAl_2Si_2O_8$, and albite (Ab), $NaAlSi_3O_8$. Naturally occurring plagioclase frequently exhibits an oscillatory compositional zoning such that the mole fraction of the An end-member varies in a periodic fashion from the core to the rim of the plagioclase grain. The amplitude of this compositional oscillation is generally between 5 and 15 mole percent, and the wavelength is between 10 and 100 μm. Ten or more complete compositional oscillations may be observed in samples exhibiting this phenomenon (*1*).

Oscillatory zoning of plagioclase is commonplace in many geologically important and frequently occurring igneous rock types. An understanding of the cause of oscillatory zoning is essential for correct interpretation of the geologic history of such rock types as well as for the elucidation of the physicochemical processes of magma evolution. Numerous theories have been postulated to explain this phenomenon (*1, 2*), but none of them has led to a quantitative description of this patterning or the conditions leading to its development.

We present here a new crystal growth model based on the interaction of growth dynamics of a solid from a melt and diffusion of material within a melt (*3*). The chemical kinetic arguments that are introduced in this model account for the composition dependence of crystal growth rate and the formulation of the crystal growth process as a Stefan (moving boundary) problem. This model is the first to describe quantitatively oscillatory zoning and the range of control parameters over which it exists.

We consider the growth of plagioclase from a melt (magma) to be a kinetic process in which the layers at the crystal surface fill as a result of the construction of formula units of either the An or Ab end-member at a kink or other growth site. The melt from which plagioclase feldspars grow is a complex silicate liquid composed of various charged species (*4*). To simplify our considerations, we assume that the only relevant species for plagioclase growth are Na^+, Ca^{2+}, Al^{3+} (*5*), and SiO_4^{4-}; we ignore the possible participation of more complex Al- and Si-bearing species and polymers in the crystal growth process. This assumption leads to some loss of generality, but the results are essentially the same as for the case where other species such as AlO_4^{4-} are considered (*3*).

We postulate that the reaction sequences for the construction of formula units of An or Ab are based on (i) the tendency for charge neutrality and (ii) structural considerations; that is, we expect that it is easier to put the first ion at the base of the growth site rather than at the top and then to build up from the bottom. We assume a macroscopically planar crystal-melt interface and assume that plagioclase grows by a layer-filling mechanism (*6*), although the method can be applied to other interface structures and growth mechanisms (*3*). Making the assumption of rapid equilibration for most intermediate reactions for the formation of formula units, we obtain an incorporation rate G_{An} (in moles per square centimeter per second). Typical results are

$$G_{An} = \tilde{K}_{An}[Ca^{2+}][Al^{3+}]^2[SiO_4{}^{4-}]^2 \quad (1)$$

$$G_{Ab} = [Na^+][Al^{3+}]\{K_{Ab}{}^{(1)}[SiO_4{}^{4-}] + K_{Ab}{}^{(2)}[SiO_4{}^{4-}]^2\} \quad (2)$$

Other rate laws of similar structure are also possible (*3*), and the correct law will not be known until experimental data have been collected. However, our general conclusions do not require a precise rate law.

The second postulate of our model is that the rate constants in Eqs. 1 and 2 depend on the surface composition of the growing crystal. There are several types of growth sites on the surface of a crystal, differing in the number of nearest An or Ab formula units already attached (*7*).

The rate constants for reactions leading to the attachment of melt species at the several types of growth sites will differ depending on the relative number of nearest An or Ab formula units for a growth site of a given geometry (a kink, for example). The rate constants in Eqs. 1 and 2 are, therefore, functions of the solid surface mole fraction of An formula units. Because of symmetry and compatibility considerations, we thus postulate that new An formula units most favorably add to growth sites where the majority of nearest already added units were An and likewise Ab would be favorably added to those sites with a majority of Ab nearest neighbors. Thus the rate constants in Eqs. 1 and 2 have a positive feedback dependence such that An growth is favored by An-rich surfaces and Ab growth by Ab-rich ones.

Let us now formulate the growth of plagioclase crystals as a Stefan (moving boundary) problem (*8*). We take the evolution of the relevant melt species to be determined by Fick's law,

$$\partial c_i/\partial t = D_i \partial^2 c_i/\partial x^2$$

for species i at concentration c_i (in moles per cubic centimeter) where x and t are position and time variables, respectively, and D_i is the diffusion coefficient of species i. We assume that the crystal is infinite and planar and located in $x < R(t)$, where the crystal rim is at $R(t)$. At $R(t)$ we have the boundary condition relating the incorporation rate g_i of species i to the influx from diffusion, $D_i \partial c_i/\partial x$, and to the amount of material swept out, $(dR/dt)c_i$; that is,

$$g_i = D_i \partial c_i/\partial x + (dR/dt)c_i$$

Experimental data (*9*) suggest, however, that for melts with bulk compositions in the range of interest for this study, the (D_i) values of the relevant species are ordered as follows: $D_{\mathrm{Na}^+} \gg D_{\mathrm{Ca}^{2+}} > D_{\mathrm{Al}^{3+}} > D_{\mathrm{SiO}_4{}^{4-}}$. Because Na^+ and Ca^{2+} diffuse relatively quickly, we assume that $[\mathrm{Na}^+]$ and $[\mathrm{Ca}^{2+}]$ are constant, held at their values far from $R(t)$. Thus we can incorporate these factors into the respective rate constants and rewrite Eqs. 1 and 2 as

$$G_{\mathrm{An}} = N(f)A^2S^2$$

and

$$G_{\mathrm{Ab}} = B(f)AS^2 + C(f)AS$$

Here A and S are the concentrations of Al and Si in general and at the rim in G_{An}, G_{Ab}; $N(f)$, $B(f)$, and $C(f)$ are the rate constants written to emphasize the functional dependence on f, the crystal surface mole fraction of An. Let ρ (in moles per cubic centimeter) be the molar density of formula units of An or Ab in the solid (An and Ab have essentially the same molar density). Then the rim advancement is given by

$$\frac{dR}{dt} = \frac{G_{\mathrm{An}} + G_{\mathrm{Ab}}}{\rho}$$

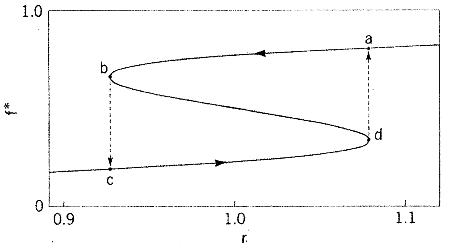

Fig. 1. Surface mole fraction f^* of An determined from Eq. 3 showing a zoning cycle $a \rightarrow b \rightarrow c \rightarrow d \rightarrow a$. Values of parameters chosen were $N(1) = 5.83 \times 10^{-2}$ cm^{10} mole^{-3} sec^{-1}, $B(0) = 5.10 \times 10^{-4}$ cm^7 mole^{-2} sec^{-1}, and $\nu = \beta = 0.15$. We chose values for $N(1)$ and $B(0)$, using data consistent with whole rock analysis data of periodically zoned samples, $[\mathrm{Na}^+] = 0.37\rho$, $[\mathrm{Ca}^{2+}] = 0.24\rho$, $\rho = 1.0 \times 10^{-2}$ mole cm^{-3}, and taking the remaining rate coefficients $\bar{K}_{\mathrm{An}}$ and $\bar{K}_{\mathrm{Ab}}$ to be of an order of magnitude consistent with crystal growth experiments on An or An-Ab mixtures.

The fraction of solid An being deposited at any instant is $f^* = G_{\mathrm{An}}/(G_{\mathrm{An}} + G_{\mathrm{Ab}})$. In general, $f \neq f^*$. However it takes only a very short time to fill one crystal layer, and hence f rapidly approaches f^*. Thus we have $f \approx f^*$, where

$$f^* = \frac{N(f^*)AS}{N(f^*)AS + B(f^*)S + C(f^*)} \qquad (3)$$

This yields an equation for $f^* = f^*(A, S)$.

To complete the mathematical formulation of the model, we need phenomenological functions for $N(f)$, $B(f)$, and $C(f)$ occurring in G_{An}, G_{Ab}. We have found several forms of functional dependence that lead to oscillatory zoning (*3*). In this report we will discuss only the case where the equations have the form

$$N(f) = N(1)\,[\nu + (1 - \nu)f^2]$$

$$B(f) = B(0)\,[\beta + (1 - \beta)\,(1 - f)^2]$$

$$C(f) = C(0)\,[\gamma + (1 - \gamma)\,(1 - f)^2]$$

where $N(1)$, $B(0)$, and $C(0)$ are the rate constants for An and Ab growth from pure melts of their respective composition and ν, β, and γ are constants $(0 < \nu, \beta, \gamma < 1)$ that control the intensity of the surface compositional feedback effect.

To understand how oscillatory zoning works in this model, let us take the expressions for $N(f)$ and $B(f)$ as above but set $C(f) = 0$ for simplicity. Combining these expressions with Eq. 3, we obtain

$$[r(1 - \nu) - \beta + 1]f^{*3} - [2(1 - \beta) + r(1 - \nu)]f^{*2} + [r\nu + 1]f^* - r\nu = 0 \quad (4)$$

where $r = N(1)A/B(0)$. In Fig. 1 we show the solution $f^*(r)$ to Eq. 3 for data in the caption. Note that there is a domain of multiple valuedness. A schematic limit cycle is also shown wherein one might expect to see a jumping of f^* from branch to branch if the concentrations in the melt far from the crystal rim (A^∞ and S^∞) were chosen properly.

The resulting periodic zoning phenomenon can be qualitatively explained in terms of Fig. 1. Suppose we start at point *a*. Then An is being predominantly de-

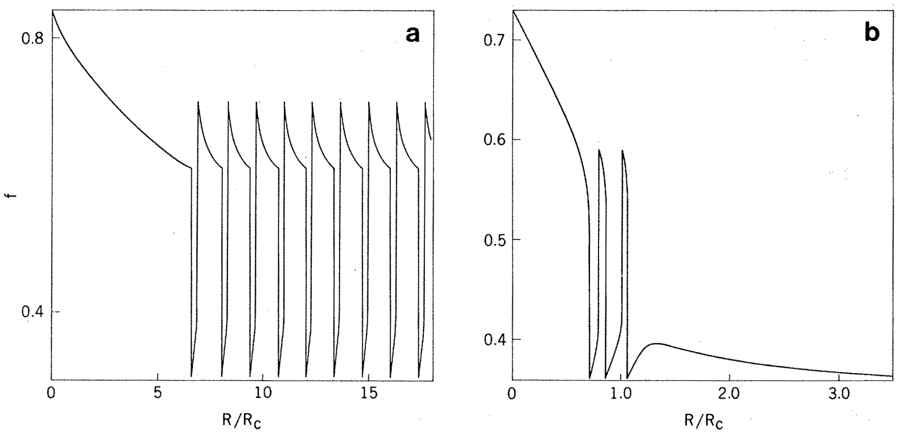

Fig. 2. (a) Numerical simulation of oscillatory zoning showing the mole fraction f of An as a function of the distance R from the center of the crystal ($D_{\mathrm{A}} = 3D_{\mathrm{S}}$). Data are as in the caption of Fig. 1 with $A^\infty = 1.2\rho$, $S^\infty = 2.5\rho$, and $D_S = 1.0 \times 10^{-9}$ cm^2 sec^{-1}. The characteristic length unit R_{C} is defined by $D_{\mathrm{S}}/(dR/dt)^\infty$, where ∞ denotes evaluation at (A^∞, S^∞). For these parameters $R_{\mathrm{C}} = 2.09 \times 10^{-3}$ cm. (b) Transient oscillatory zoning on an overall normal trend with parameters from (a) except that $C(0) = 1.0 \times 10^{-7}$ cm^4 mole^{-1} sec^{-1}, $\gamma = 0.15$, and $\beta = 0.25$; with these values, $R_{\mathrm{C}} = 2.31 \times 10^{-3}$ cm.

posited and hence Al at the rim is being used up. Thus r [which is proportional to the melt Al at $R(t)$] drops. This proceeds until point b is reached. Then Al decreases further at $R(t)$, causing a jump down to point c. Now a growth more rich in Ab occurs, and hence the amount of Al can increase since less Al is being used up; but the crystal is still advancing, pushing the excess Al ahead of it. This continues until point d is reached, at which time a jump to point a occurs, completing the cycle.

This qualitative description was verified (see Fig. 2a) by means of a numerical simulation of the Stefan problem with the phenomenological laws given above. The numerical simulation was carried out by discretizing Fick's law and the equation of motion for the rim. The values of $A^{\cdot}$ and $S^{\cdot}$ ($x \gg R(t)$) were chosen consistent with data from whole rock samples wherein zoning of plagioclase was observed. The discontinuities in the solid composition profile correspond to the jumps $b \rightarrow c$ and $d \rightarrow a$ of Fig. 1. Before the oscillations set in, there is—as in naturally occurring plagioclase samples—a "normal trend" wherein f decreases monotonically.

For a second example we take the expression for $N(f)$, $B(f)$, and $C(f)$ as above but choose $C(f)$ via the parameters given in the legend to Fig. 2b. A transient oscillatory zoning situation is produced (Fig. 2b), as is commonly observed.

With our model for crystal growth from the melt it is possible to quantitatively simulate the oscillatory zoning which occurs naturally in plagioclase feldspars. Oscillation is found to result from the interplay of the following factors: (i) the dependence of the growth law on melt and solid surface composition, (ii) the stoichiometry of the solidification reactions, (iii) the diffusion of melt species, and (iv) the motion of the growing crystal rim. The particular dependencies of the growth law on solid surface and melt composition were based on a number of reasonable conjectures. However, this facet of the approach can only be put on a more solid foundation when more complete experimental growth data are available. Our goal here was to show that the phenomenon can indeed be explained in a growth kinetic-diffusion model. Furthermore, the detailed form of the growth rate law is, from the above qualitative description based on Fig. 1, not expected to be crucial for our theory (although it can clearly affect the wave form).

Oscillatory zoning in plagioclase feldspar is an excellent example of a structure that is far from equilibrium (*10*) resulting from an interplay between nonlinearity and nonequilibrium conditions. Such phenomena have been recently found in many biological, chemical, and physical systems.

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Agrarian Potential, Population, and the Tarascan State

Abstract. *Estimates based on potential maize crops and maize consumption patterns of the 15th-century Mesoamerican protohistoric Tarascan population living within its geopolitical core (Lake Pátzcuaro Basin) indicate that this population had not maintained itself through agricultural- and lacustrine-carrying capacity alone. It was through having to obtain basic resources such as maize from outside the basin that the Tarascans developed mechanisms that formed the particular character of their state.*

In A.D. 1519, the year of the European entry into the central highlands of Mexico, much of western Mexico was dominated by an independent entity named by the Spaniards the Tarascan kingdom. Tarascan society, contemporary with the Aztec, has been compared with it in generalizations made about the evolution of the state in Mesoamerica. It has been concluded that the Tarascan political system represents a simpler form than the Aztec political organization (*1*). Such a conceptual construct has presumed a comparability in Tarascan human ecology. However, as far as we know, until now no investigators have attempted to evaluate the role played by environmental variables in the development of the Tarascan political system. We designed a project to model the protohistoric cultural ecology of the geopolitical core of the Tarascan state, the Lake Pátzcuaro Basin (*2, 3*). One part of this study has as its goal the estimation of the actual maximum population that could have been supported primarily by the local resources during the florescent Tarascan state in the last century before European contact. These figures, based on potential maize crops and maize consumption patterns (*4, 5*), indicate that the population of the Tarascan core was well above the local carrying capacity of the Lake Pátzcuaro Basin. The Tarascans of the basin obtained basic resources from outside the basin through both economic and political mechanisms that contributed significantly to the particular character of the Tarascan state.

The paleoecological reconstruction for the protohistoric period shows a slightly wetter, perhaps warmer, climate associated with a lake level about 15 m higher than the present (*3, 6*). When the climatic data are combined with data on water resources, it has been possible to determine broad classes of agricultural land (Table 1). As the modern agricultural land classes are based on studies of land subject to simple hoe and plow cultiva-