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SOME OBSERVATIONS ON OSCILLATORY ZONING AND CRYSTALLIZATION OF MAGMATIC PLAGIOCLASE

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ABSTRACT

Measurements of concentration gradients in the boundary layers adjacent to plagioclase-volcanic glass interfaces indicate that plagioclase crystallization rate is diffusion controlled during certain stages of growth. A modified version of the theory of Harloff (1927) is offered as the most likely explanation of oscillatory zoning in plagioclase. Clouded plagioclase may result from the co-precipitation of plagioclase and iron and magnesium rich phases due to a build up of iron and magnesium in the boundary layer during plagioclase growth. The petrologic significance of plagioclase-magmatic liquid equilibrium pairs is considered.

INTRODUCTION

Compositional zoning of plagioclase crystals is common in many igneous rocks. Zoning patterns and their petrological significance have been described by Harloff (1927), Homma (1932), Hills (1936), Larsen *et al.* (1938), Leedal (1952), Vance (1962) and Pittman (1963). Small-scale periodic compositional variations or oscillations are often superposed on larger-scale, less regular changes in composition. These larger scale variations are ordinarily such that the anorthite mol % (An %) decreases outward from the center of the crystal. This is the general compositional trend observed during crystallization from a cooling magma and the combination has accordingly been termed oscillatory-normal zoning by Phemister (1934). Figure 1 is a schematic representation of oscillatory-normal zoning showing the range of values reported for the zone width and the amplitude of the compositional oscillations. Although changes in the amplitude of the oscillations and their width may be found in any crystal, the oscillations usually occur in groups within which both the width and the compositional variation pattern are quite consistent. For any such group of oscillations the average composition is constant to a good approximation. The oscillations detected in individual crystals may vary from fewer than ten to more than one hundred. Individual groups of oscillations may be separated by abrupt and noncyclic compositional changes. Figure 4 is a photomicrograph of a typical plagioclase crystal exhibiting oscillatory-normal zoning.

It is evident that compositional zoning in igneous plagioclase represents a potentially useful record of changes in the chemical and physical environment during crystallization. Unless the process giving rise to a particular type of zoning is well understood, however, this potential cannot be realized. There is at present little agreement among petrologists on the causes of oscillatory zoning although many theories have been advanced. Vance (1962) has recently reviewed the problem in an excellent summary and we will not treat the various theories in detail here. For our purposes it is sufficient to note that the proposed theories can be divided between those in which oscillatory zoning is caused by repeated changes in the plagioclase-liquid equilibrium variables of temperature, pressure, partial pressure of water, and liquid composition imposed either by conditions exterior to the magma system or as a result of relative movement of crystals and liquid in a large magma chamber, and the theory of Harloff (1927) which predicts oscillatory zoning as a result of a postulated interplay between diffusion and plagioclase growth rate. After a broad study of zoning in plagioclase, Emmons *et al.* (1953) concluded that

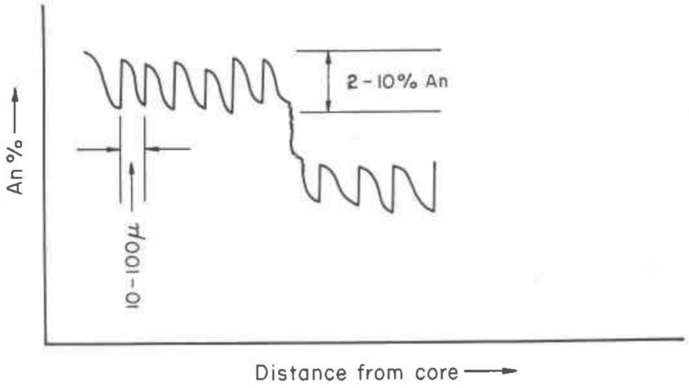

FIG. 1. Sketch of typical occurrence of oscillatory zoning in plagioclase phenocrysts.

> "Some simple explanation of the very thin oscillatory zones is needed. It should not be necessary to require growing crystals to move from liquid to liquid in their normal growth, and oscillatory zoning does characterize untwinned plagioclase crystals in lavas."

We agree with this view and would add that in our opinion the basis for the needed explanation has been with us since 1927.

Generalizing from Bowen's (1913) study of plagioclase equilibrium melting we know that plagioclase crystallizing from a melt is enriched in Ca and Al and impoverished in Na and Si relative to the melt. Harloff hypothesized that the instantaneous growth rate of plagioclase during the first phase of the oscillatory cycle is rapid enough to reduce the Ca content of the near interface region of the melt so that subsequent crystallization results in progressively An poor plagioclase. However, the decreasing Ca content of the near-interface liquid also reduces the degree of supersaturation relative to the surface plagioclase and consequently the growth rate decreases. At this stage the diffusional flux of Ca toward the interface replenishes the near-interface melt *et l'histoire se répète*. This theory has perhaps not been looked into more thoroughly because no direct evidence has heretofore been presented for the diffusion-controlled growth stage which is a necessary (although not sufficient) postulate of Harloff's theory. During a study of plagioclase crystallization from magmas we have made certain observations indicating that diffusion-controlled crystallization does in fact occur under magmatic conditions.

DIFFUSION-CONTROLLED CRYSTALLIZATION

The rate determining step in plagioclase crystallization may be the diffusional flux of solute to the interface, the surface reactions by which dissolved plagioclase constituents are incorporated into the crystalline structure, or the dissipation of the heat of crystallization away from the interface. If Harloff's hypothesis is correct then magmatic plagioclase growth must be diffusion controlled. Theoretically it can be shown that conduction of the heat of crystallization away from the interface is unlikely to be rate determining in this case. Following Nielsen (1964), the growth of a spherical crystal where heat conduction is rate limiting is given by

$$\left[\frac{dr}{dt}\right]_h = \frac{\lambda RT^2V}{L^2r} \ln \frac{c}{s}$$

For diffusion controlled growth

$$\left[\frac{dr}{dt}\right]_d = \frac{VD(C-c)}{r}$$

In the above expressions dr/dt = crystal growth rate, R = gas constant, λ = thermal conductivity of magma, T = ° K., V = molar volume of plagioclase, L = heat of crystallization of plagioclase, r = crystal radius, D = diffusion coefficient of plagioclase in magma, c = mol-cm^{-3} of plagioclase in magma at interface, C = mol-cm^{-3} of plagioclase in the bulk magma, s = solubility of plagioclase in bulk magma in mol-cm^{-3}. As representative values we may take $\lambda \sim 4 \times 10^{-3}$ cal-sec^{-1}-cm^{-1}-°C^{-1} (soda lime-silica glass in Kingery, 1960), $T \sim 1300°$ K., $L \sim 2.9 \times 10^4$ cal-mol^{-1} (heat of fusion of anorthite, Bowen, 1928), $D \sim 7 \times 10^{-11}$ cm^2-sec^{-1} (diffusion coefficient of Si in molten silicate slag, Towers *et al.* 1957). The condition for heat conduction controlled growth becomes

$$\frac{(C-c)}{\ln c/s} > 2.3 \times 10^5 \text{ mol-cm}^{-3}$$

In a magma of density 2.7 gm-cm^{-3} containing 40 mol% of plagioclase component (An_{50}) the plagioclase concentration is approximately 4×10^{-3} mol-cm^{-3}. The concentration gradient, $(C-c)$, clearly cannot be greater than this and the above inequality would necessitate a supersaturation ratio such that

$$\ln c/s < 10^{-7}$$

which is hardly possible. The rate expressions used above incorporate various assumptions which make them only rather gross approximations for the case considered here. In using them specifically to rule out heat-controlled growth rate, however, the result is conclusive enough to warrant disregarding such considerations. Moreover, where crystal growth is heat conduction controlled we might anticipate a rounded habit with no well developed faces whereas the oscillatory zoning is invariably developed parallel to a few well-defined crystal faces of low index.

The low diffusion rates of silicon, aluminum and oxygen in silicate melts at magmatic temperatures (Doremus, 1962) indicate the possibility that some igneous plagioclase growth is diffusion controlled. If this is the case composition gradients should be developed in the magma near the interface between the magma and a growing crystal, and such gradients may be quenched in glassy igneous rocks under favorable circumstances. This can be shown to be the case for an oceanic basalt in which bytownite phenocrysts are enclosed by a fresh, homogeneous glassy matrix. The bulk analysis of this rock is given in Engel and Engel (1964). An electron-microprobe analysis in the vicinity of a glass-bytownite interface is shown in Figs. 2 and 3. Figure 2 shows photographs of oscilloscope images of line profiles of $K\alpha$ radiation across the interface superposed on scanning images of the interface area. Figure 3 represents quantitative analyses at selected points along a traverse to the interface. Although it would be more meaningful to present volume concentrations of the atoms it is impossible to recalculate the microprobe data in these terms due to uncertainties in the variation of the glass density. The profile is representative of those taken at various locations along the circumference of the phenocyrsts available in the section. For these analyses an accelerating potential of 15 kv and a beam focus of 1–2 μ were used in a modified ARL electron microprobe. Basaltic glass and bytownite were used as standards for the glass and plagioclase respectively, enabling corrections to be kept to a minimum. The phenocryst reveals faint oscillatory zoning under a polarizing microscope, and periodic variations of Ca and Na content measured on the microprobe correspond to oscillatory zoning with a compositional range of 84–88 An mol% and a zone width of 20–30 μ. Two microprobe analyses of the bytownite taken at 5 and 400 μ from the interface are given in Table 1.

Concentration gradients in the glass were detected for all the measured elements except calcium and sodium. Oxides of the elements plotted in Fig. 3 constitute 98–99 wt% of the glass. A calculated total analysis for

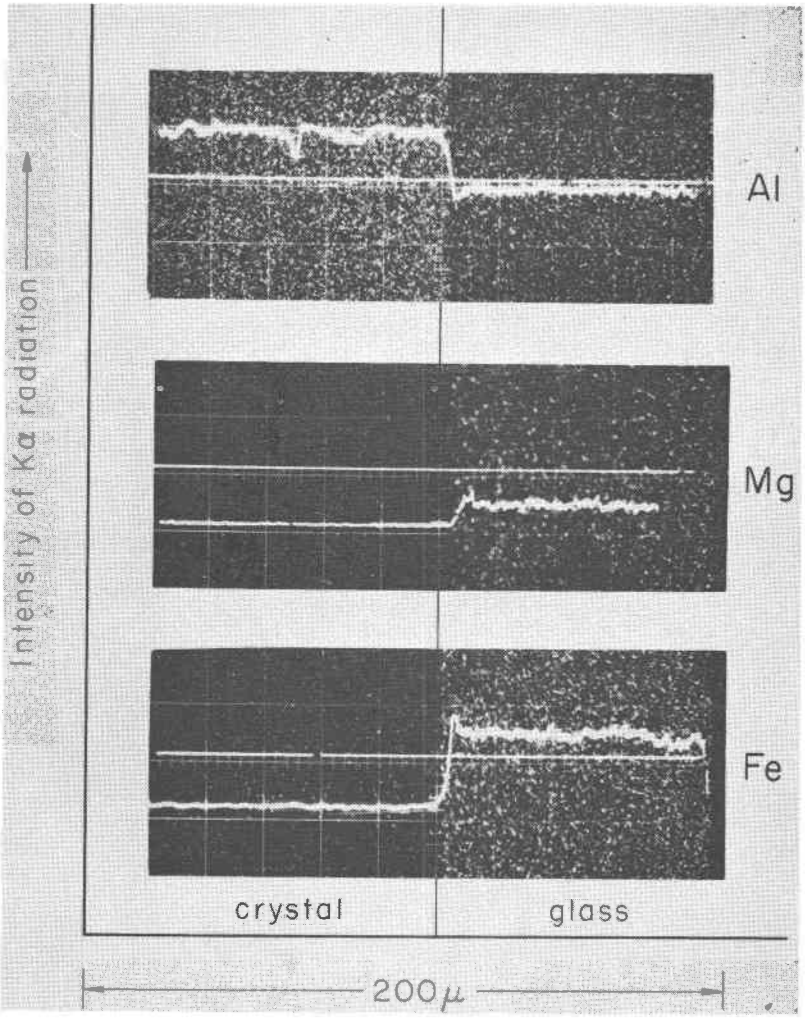

FIG. 2. Oscilloscope images of line profiles of Kα radiation for Al, Mg, and Fe across glass-crystal interface. The interface is approximately located by the sharp density change of the scanning image and the discontinuity in the superimposed line profile. The straight line locates the profile on the scanning image.

the bulk glass is given in Table 1 together with the analysis of the glass 3 μ from the interface. The sense and magnitude of the measured gradients leave little doubt that they are the result of plagioclase growth. Enrichment of the elements at 3 μ from the interface relative to the bulk glass is −12 mol% for Al, +28% for Mg, +31% for Fe and +3% for Si. For an interesting example of boundary layer gradients caused by dis-

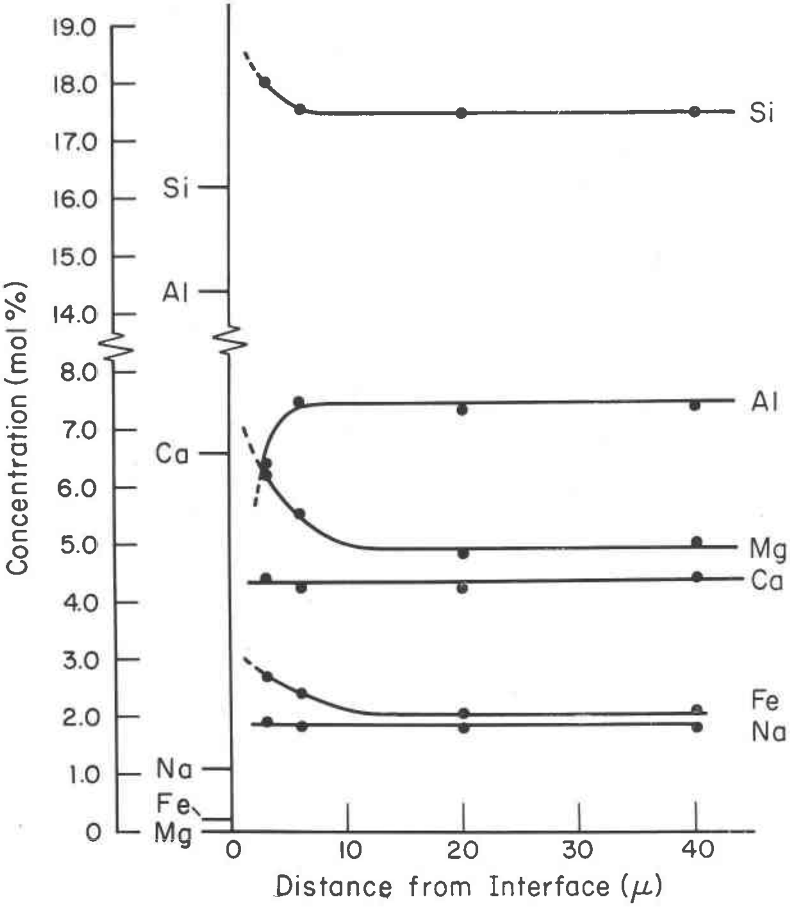

FIG. 3. Concentration gradients in basaltic glass near bytownite phenocryst. Microprobe analysis recalculated to mol % assuming sum of oxides equal to 100%.

solution in silicate liquids the reader is referred to Oishi *et al.* (1965). Slight but inevitable displacement of the sample relative to the electron beam focus which occurs between analyses for the different elements renders it impossible to obtain more accurate profiles of the gradients over the restricted distances involved. The absence of a Na and Ca gradient is probably due to their greater mobility compared with Si and Al, and to their much less extreme fractionation between liquid and plagioclase compared to Fe and Mg. It is worth noting that once the diffusion constant of the element controlling plagioclase crystallization is known, the measured gradient of this element in the boundary layer would make it possible to calculate the instantaneous growth rate of the

TABLE 1. ANALYSES AND NIGGLI MOLECULAR NORMS OF BASALT GLASS AND ANALYSES OF BYTOWNITE PHENOCRYST

Method of analysis as follows: (1) cation measured on microprobe (2) calculated from bulk rock analysis and mode (Engel and Engel, 1964) and plagioclase analysis (3) total Fe measured on microprobe, Fe^{2+}/Fe^{3+} from bulk rock analysis (4) all Fe in plagioclase assumed to be Fe^{3+}.

	Glass		Bytownite	
	Bulk	3 μ from interface	5 μ from interface	400 μ from interface
SiO_2	49.8^1	49.4^1	44.9^1	44.7^1
TiO_2	1.2^2	nd	nd	nd
Al_2O_3	17.7^1	14.9^1	34.0^1	34.6^1
Fe_2O_3	0.4^3	0.6^3	0.9^1	0.7^1
FeO	6.7^3	8.4^3	0.0^4	0.0^4
MnO	0.3^2	nd	nd	nd
MgO	9.3^1	11.4^1	nd	nd
CaO	11.3^1	11.3^1	17.0^1	17.6^1
Na_2O	2.7^1	2.7^1	1.5^1	1.3^1
K_2O	0.1^2	nd	nd	nd
H_2O+	0.6^2	nd	nd	nd
P_2O_5	0.1^2	nd	nd	nd
Total	100.2	98.7	98.3	98.9
n_D	1.594 ± .001		number of ions based on 32 oxygens	
D	2.80		Si 8.42	8.33
			Al 7.51 } 16.05	7.59 } 16.02
Ap	0.3	—	Fe 0.12	0.10
Il	1.6	—	Ca 3.42	3.51
Or	0.5	—	Na 0.56 } 3.98	0.46 } 3.97
Ab	24.5	25.0		
An	35.3	27.8		
Mt	0.5	0.6		
Hy	9.2	0.0		
Di	15.2	22.0		
Ol	12.9	24.6		
Fe/Mg in px and ol	0.33	0.39		
An/(An+Ab) mol %	59	53	86	88

crystal. Unfortunately the data presently available on diffusion in a restricted compositional range of silicate melts is insufficient since diffusion rates are strongly dependent on composition, especially water content.

MAFIC MINERALS IN CLOUDED PLAGIOCLASE

Clouding due to the inclusion of minute particles is characteristic of some plagioclase occurrences. Often the inclusions occur in zones parallel to what may be inferred to have been the crystal-liquid interface during some stage of growth, *e.g.*, parallel to the outlines of partially resorbed crystals. The latter type of occurrence has been described in detail by Bentor (1951). The included particles are typically crystallites of hematite, magnetite, ilmenite, biotite, pyroxene and olivine. A partially resorbed core of plagioclase is surrounded by more calcic plagioclase. Incorporated in this more calcic plagioclase, immediately adjacent to the core, is the cloudy zone containing the mafic cyrstallites. Bentor (1951) has reasoned that the partial resorption of the core occurred when these crystals were brought into contact with undersaturated liquid of a portion of the magma which earlier had crystallized the core crystals but which in this portion has reached a less advanced stage of crystallization. The term autoresorption is used for this process, and the reader is referred to Bentor's paper for the details of the interpretation up to this point. The dissolution of the plagioclase core may cause a large supersaturation with respect to more calcic plagioclase in the liquid immediately surrounding the core which results in rapid crystallization of the calcic plagioclase around the core. It is then believed that some liquid is incorporated within the rapidly growing crystal, and that these liquid inclusions later crystallize the mafic inclusions.

The considerable enrichment in iron and magnesium in the boundary layer adjacent to a rapidly growing crystal which we have demonstrated may have some bearing upon this stage of the interpretation. The composition of the boundary layer in certain cases is possibly sufficient to cause nucleation of iron and magnesium rich minerals while the plagioclase grows. The resulting co-precipitation of plagioclase and mafic microlites would not necessarily involve the trapping of liquid, the presence of which often cannot be demonstrated in the clouded plagioclase. The possible significance of an enriched boundary layer in the general problem of the interpretation of crystalline and liquid inclusions should not be overlooked.

Oscillatory Zoning

The preceding discussion has shown that magmatic plagioclase growth is diffusion controlled at some stage of the crystallization process as postulated in Harloff's theory of the origin of oscillatory zoning. Some additional, more obscure aspects of this theory and its implications will now be discussed.

We assume that a finite supersaturation is necessary to initiate precipitation of a zone. The first stage of zone growth is diffusion controlled. The crystal is at all times enriched in aluminum and impoverished in silicon relative to the melt. Furthermore, the solid solution plagioclase can change composition and grow at a rate such that the net rate of uptake of aluminum at the surface is greater than the diffusional flux of aluminum across the boundary layer. It is useful to somewhat oversimplify this relationship by saying that crystal growth is faster than diffusion. The result is a zone of steadily decreasing An%. But the disparity between diffusion and growth rate must eventually decrease. The net rate at which material is incorporated into the lattice depends, other things being equal, upon the degree of supersaturation of the boundary layer, a supersaturation which has been steadily decreasing during this growth stage. Moreover, the flux of material to the interface is increasing with the increase of the chemical gradient resulting from crystal growth. The continuous decrease of An% in the plagioclase becomes less pronounced and after an initial transient period a steady-state may be approached with corresponds to the low An% tail of the cycle often observed.

It is at this point that a missing link occurs in the theory. The most commonly observed zoning pattern shows a rather abrupt rise of An% back to or nearly back to its original value at the start of the succeeding cycle indicating either a termination of growth or at least a marked decrease in growth rate. During this stage it is clear that the roles are reversed, and that diffusion must be more rapid than growth. Harloff's original explanation was that the crystal continued to grow slowly until it encountered a wave of diffusing calcium at which point the cycle repeated itself with the growth of An rich material. According to Hills (1936) growth ceased altogether until diffusion built up the supersaturation to its original level. It is not obvious why growth should either slow down or cease in order to allow the supersaturation to build up to its original value. It might appear more likely that a steady-state regime would be reached when growth and diffusion rates were equalized. The transition from the end of one cycle to the beginning of the next must be explained and to simply state that the sequence is repeated ignores the problem.

Our discussion thus far has assumed that the crystallization of a group of oscillatory zones occurs rapidly relative to the cooling of the magma and may be considered essentially as an isothermal process. That this is approximately so is indicated by the fact that the average composition of neighboring zones is relatively constant. When a change of average composition does occur it is such that outer zones have less An% which follows from the definition of oscillatory-normal zoning. Any temperature change to be considered will then be a slight decrease in temperature which tends to keep the melt boundary layer continually supersaturated and will not explain why growth ceases or slows down appreciably at the end of a cycle. It is possible that at the end of a cycle the crystal is slightly displaced so that it is once more brought into contact with liquid of the bulk composition. The number of zones and the regularity of the zoning pattern necessitate that repeated movements take place always at the end of the cycle. This may not be as improbable as it first appears to be if we consider that the growth rate is slower near the end of the cycle and consequently this stage occupies a correspondingly longer period. Perhaps a more valid objection to such a mechanism is that in a relatively viscous magma the boundary layer in which the gradients occur will remain associated with the crystal during relative motion of crystal and liquid.

Cahn (1960) has considered the effect of the structure of the interface on the relationship between driving force for crystal growth and growth mechanism. Such considerations applied to the growth of an oscillatory zone lead to a possible qualitative explanation of the phenomenon. At the start of a zone we assume a very smooth face which offers no energetically favorable sites for growth until the driving force (*i.e.*, supersaturation) exceeds the minimum necessary for two dimensional nucleation. At this point growth commences by lateral movement of a step across the face, but since two dimensional nucleation on an incomplete surface is not much more difficult than on the originally smooth complete surface, the interface may soon extend through a large number of atomic layers. The interface becomes diffuse and now offers abundant steps, kinks and traps. The problem of maintaining a sufficient driving force for continued growth while at the same time continually decreasing the An% of the near-interface liquid is now alleviated by considering that the necessary driving force itself decreases as the interface becomes diffuse. During this stage there is a high surface density of energetically favorable sites and growth is uniform (Cahn, 1960), *i.e.*, the interface is propagated normal to itself rather than by repeated lateral extension of sharp steps across the face. This is a period of relatively rapid growth during which the boundary layer becomes depleted in aluminum. Toward the end of the cycle the driving force decreases to a point where further growth is increasingly limited to only the most favorable sites and the rough face begins to repair itself. Eventually the interface once more becomes sharp and further appreciable growth is precluded until diffusion again builds up the supersaturation necessary to repeate the cycle. The net effect is periodic growth of plagioclase in layers of variable composition (*i.e.*, zones). It was Harloff who indicated a possible analogy with the growth by layers of NaCl from aqueous solution visible under the microscope.

What has been stated is an elaboration of Harloff's original ideas. On the basis of the concentration gradients found in the boundary layer and of the high contrast in Al content between crystal and liquid it is probable that in this instance the flux of Al to the interface regulates the compositional pattern of the zoning rather than the relative diffusion rates of the Ca-Na pair which Harloff postulated. One consequence of this theory which has not been considered is that since zoning is the result of a relatively delicate balance between the net rate of crystallization and diffusion rates, we might expect the zoning pattern to change for different crystallographic planes. The postulated cycle will be completed more rapidly in the direction of fastest growth and consequently the number of zones should be greater in this direction. We have examined with the

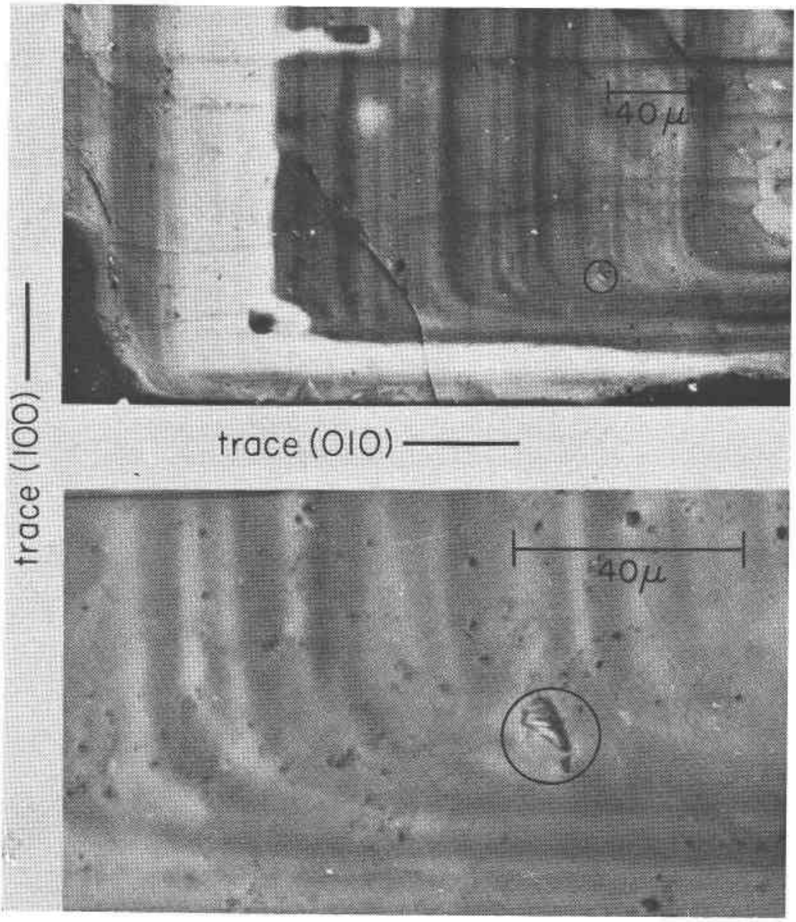

FIG. 4. Oscillatory zoning in oligoclase crystal. Some zones developed along (100) are absent along (010).

microprobe the calcium content of a number of phenocrysts in which oscillatory zoning is well developed. For elongate crystals the number of oscillations detected in the long dimension is systematically greater than that in the short dimension. The zones examined were 10–30 μ wide in the long dimension of the crystal and appear to be only slightly narrower in the short dimension. The elongation factor of the crystals is approximately two, and since the analyses were made at 3 μ intervals it is considered unlikely that zones in the short dimension were overlooked. This feature can be observed in the photomicrograph of Fig. 4, and is difficult to explain by any of the other theories proposed for the origin of oscillatory zoning.

Plagioclase-magma Equilibrium

It is often difficult to determine whether or not plagioclase phenocrysts have grown from a magma represented by the rock in which they are now enclosed. Textural criteria such as evidence for crystal settling are often absent or ambiguous. The role of plagioclase crystallization during magmatic differentiation is of primary importance, and it is surprising that there have not been more attempts to gather detailed information on this problem such as in the work of Larsen *et al.* (1938) and Carmichael (1960). The results of the microprobe analysis set forth here suggest one possible line of attack. Detection of concentration gradients in the near-interface glass leave little doubt that the phenocryst was actively growing in the liquid at the time of quenching. It is not unreasonable to assume that the plagioclase rim is nearly in equilibrium with the liquid. Some uncertainty exists with respect to the supersaturation necessary to maintain growth. In this connection it should also be remembered that zoned plagioclase results in an inhomogeneous lattice in which some strain exists relative to a homogeneous lattice of the same composition. Harloff (1927) found possible evidence for this by noting that the orientation of the optical indicatrix in zoned plagioclase did not correspond exactly to that in homogeneous plagioclase. It is not known to what extent this factor may shift the ideal equilibrium between liquid and homogeneous plagioclase. We assume that the effect is small relative to the usual uncertainties involved in determining equilibrium factors. The liquid 3 μ from the interface and the plagioclase rim may be treated as an equilibrium pair for purposes of petrologic analysis, and such pairs usefully complement the experimental work being undertaken on systems approaching actual magmatic compositions.

At present no reliable quantitative model exists for treating equilibrium crystallization of plagioclase from magmas. Bowen's (1913) work on melting in the anorthite-albite system has proved to be an extremely valuable guide for interpreting crystallization trends in igneous rocks.

The enrichment of Ca/Na and Al/Si in the plagioclase relative to the liquid and the decrease in An% of the plagioclase with falling temperature which are characteristic of crystallization in the An-Ab system have also been well documented in magmatic systems. It has, however, become standard practice to compare magmatic crystallization of plagioclase to the two-component system in a more direct manner. Normative plagioclase content of magmas have been applied directly to the liquidus curve of the An-Ab melting diagram in attempts to determine plagioclase-liquid equilibrium pairs during magmatic crystallization (*e.g.*, Larsen *et al.*, 1938; Carmichael, 1960). Such an approach implicitly assumes that normative An/(An+Ab) of a magma is a meaningful parameter in discussing plagioclase-liquid equilibrium and furthermore that the equilibrium fractionation of An/Ab between liquid and plagioclase is similar in the magma and the An-Ab system. We believe that there are valid reasons for abandoning this approach.

It is the chemical potentials of $CaAl_2Si_2O_8$ and $NaAlSi_3O_8$ which are fundamental to the liquid-plagioclase equilibrium. A normative calculation of an analysis redistributes the constituents into mineral molecules according to certain well known equilibrium trends of magmatic crystallization. The essential constituents of plagioclase (Ca, Na, Al and Si) may be distributed among many molecules other than An and Ab in the norm, and none of the normative molecules are representative of actual species in the liquid. It would be surprising therefore if normative An and Ab gave reliable estimates of the chemical potentials of these two components.

Bowen (1928) showed that the An-Ab melting equilibrium could be satisfactorily calculated by assuming ideal mixing of An and Ab molecules in both liquid and solid solution. Consequently equilibrium fractionation in the An-Ab system should be of the form

$$\ln\left[\left(\frac{\mathrm{An}}{\mathrm{Ab}}\right)_{\mathrm{p}}\Big/\left(\frac{\mathrm{An}}{\mathrm{Ab}}\right)_{\mathrm{l}}\right]=\frac{\mathrm{A}}{\mathrm{T}}-\mathrm{B}$$

where An and Ab are the mol % of these two components, p = plagioclase, l = liquid, T = ° K., and A and B are constants. Experimental data are also available for plagioclase-liquid equilibrium in three-component systems. If the practice of treating normative plagioclase of chemically complex magmas as a two-component system directly comparable to the An-Ab system has any theoretical or empirical merit, it should certainly be applicable to the three-component systems. Figure 5 is a plot of equilibrium fractionation *vs.* reciprocal temperature for the two-component plagioclase system and for representative equilibrium pairs in the three-component systems albite-anorthite-sphene and albite-anorthite-diopside. The equilibrium fractionation is clearly different in all three, and

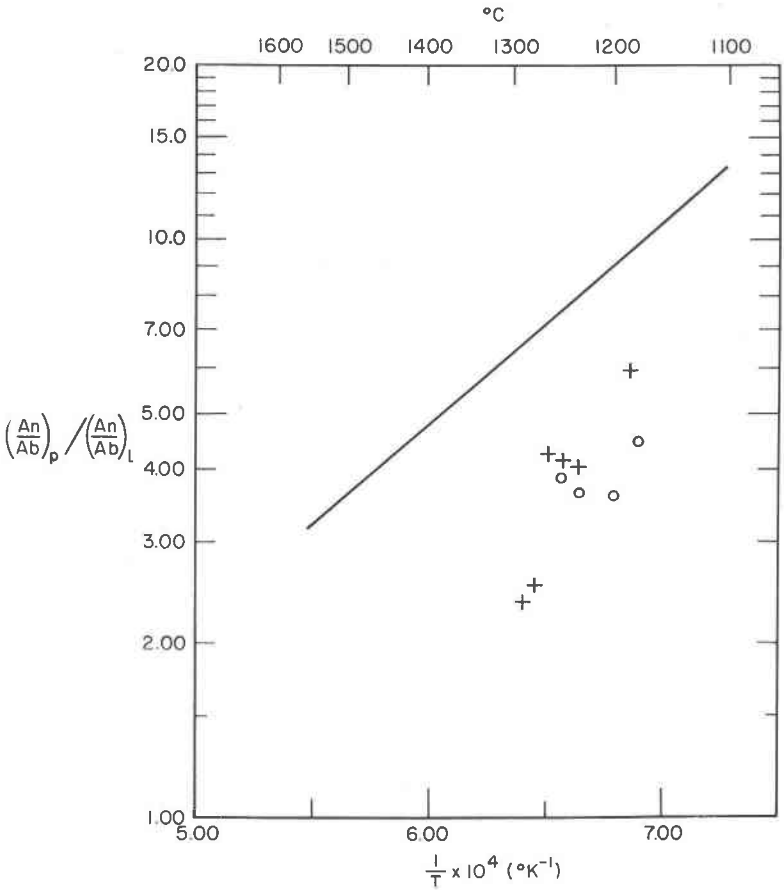

FIG. 5. Plagioclase-liquid equlibrium. Straight line = $CaAl_2Si_2O_8$-$NaAlSi_3O_8$ system (Bowen, 1913), ○ = $CaAl_2Si_2O_8$-$NaAlSi_3O_8$-$CaMgSi_2O_6$ system (Bowen, 1916), + = $CaAl_2Si_2O_8$-$NaAlSi_3O_8$-$CaTiSiO_5$ system (Prince, 1943).

there is no reason to suppose that the fractionation in magmatic systems will be similar to the two-component system.

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