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THE ORIGIN OF OSCILLATORY ZONING IN PLAGIOCLASE: A DIFFUSION AND GROWTH CONTROLLED MODEL

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ABSTRACT. Zoning in plagioclase is due to two major mechanisms: (1) changes in general environmental variables such as temperature and pressure, and (2) constitutional supercooling. Constitutional supercooling is supersaturation that results from concentration gradients in the melt at the crystal-melt interface. Periodic zoning in plagioclase results from an interplay between the amount of supersaturation, growth and diffusion rates, and the nature of solid-liquid interface. The width and compositional range of the zones are a function of diffusion rates in the interface liquid. In zoned plagioclase, which results from constitutional supercooling, the maximum albite content of each zone will be relatively constant. This criteria can be used to identify zoning due to this mechanism.

INTRODUCTION

Zoning in plagioclase, because of its delicate variation and ubiquitous occurrence, has long been considered as having the potential of being a sensitive indicator of petrogenesis (for example: Bowen, 1928; Harloff, 1927; Wenk, 1945; Hills, 1936; Emmons, 1952; Vance, 1962; Bottinga, Kudo, and Weill, 1966; Pinwinski, 1968; Wiebe, 1968; and Lofgren, 1974a). Plagioclase zoning was thought to be most useful in making inferences about general environmental variables of the magma chamber (for example, changes in pressure, temperature, and water content). Weibe (1968) and Pavnov (1969) showed that much of the zoning of plagioclase could not be correlated between crystals in the rock bodies they studied, and therefore this zoning could not be accounted for by these variables. The purpose of this paper is to propose that most of the periodic, oscillatory zoning present in plagioclase is not due to general environmental variables (a temperature or pressure change) but results from changes in the growth rate of the crystal and diffusion rate of solute in the interface liquid in front of the crystal. A similar model has been developed to explain the distribution of solute during zone refining of metals and is referred to as constitutional supercooling (Rutter and Chalmers, 1953). We are using the term in a general sense to imply varying degrees of supersaturation due to concentration gradients in a melt as opposed to "supercooling" which implies supersaturation due to temperature variations. This usage of the term differs somewhat from the original definition but is useful, since it distinguishes compositionally induced changes in supercooling from thermally induced changes.

It is important to recognize zoning due to this mechanism for two reasons. First, if plagioclase zoning is to be used to make petrogenic inferences, then zoning due to constitutional supercooling must be separated from zoning due to general environmental variables. Second, the nature of the zoning produced by constitutional supercooling can

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itself be used to determine the nature of the liquid from which the zoned plagioclase crystallized, since it can occur only in systems in which the growth rate of a crystal exceeds the diffusion of solute in the melt.

ZONING MODELS

Crystallization from constitutionally supercooled liquids departs significantly from equilibrium crystallization (Rutter and Chalmers, 1953). Equilibrium between a solid and a bulk liquid requires that the whole of the solid is in equilibrium with the whole of the liquid at all times. To maintain equilibrium for the whole system requires that diffusion in both the liquid and solid is rapid enough to eliminate concentration gradients in both the liquid and solid, and this can occur only if the rate of advance of the crystal interface is slow with respect to diffusion rates. Concentration gradients will be present in the liquid if growth rate exceeds diffusion rate and will be present in the solid if its reaction rate with the liquid is slower than the growth rate.

A widely accepted model for zoning in plagioclase (Hyndmann, 1972; Turner and Veerhogen, 1960; Bowen, 1913) is based upon repeated changes of conditions exterior to the magma system causing changes in partial pressure of water, load pressure, and temperature and applying these changes in these variables in plagioclase-liquid equilibrium. In contrast, Harloff's (1927) diffusion-supersaturation model has not been widely accepted as a general model for zoning. It is surprising that constitutional supercooling has not been generally applied to natural silicate systems, since Harloff (1927) set the groundwork with his diffusion-supersaturation theory, and Rutter and Chalmers (1953) showed that concentration gradients in the melt at the crystal-melt interface must result in supercooling. Chalmers (1964) called this constitutional supercooling to contrast this with supercooling due to rapid cooling of a system. Harloff's diffusion-supersaturation theory has been eloquently restated and applied to plagioclase oscillatory zoning by Hills (1936) and Vance (1962). Bottinga, Kudo, and Weill's (1966) and Lofgren's (1974a,b) microprobe data clearly show that concentration gradients occur in silicate glass around plagioclase phenocrysts. Bottinga, Kudo, and Weill (1966) applied this data to develop further Harloff's (1927) diffusion-supersaturation theory. They proposed that the major shortcoming of Harloff's theory was that the system would approach a steady state, when the growth rate and diffusion rate are equal. Steady state systems may be produced artifically or in systems where the crystals grow according to the normal growth model. Neither of these conditions are applicable to plagioclase crystals. Bottinga, Kudo, and Weill suggested that oscillatory zoning in plagioclase crystals is the result of change from a planar to a diffuse interface (normal growth model) with changing degrees of supercooling (after Cahn, 1960). However, subsequent empirical data of growth mechanisms in feldspars (Klein and Uhlmann, 1974) have shown the normal growth model to be inapplicable to anorthite grown from its melt, which has been supercooled as much as 650°C. That is, the supercooling of anorthite crystallizing from its melt is not sufficient to provide the driving force necessary to cause the planar interface to become diffuse. The constitutional supercooling model presented below is similar to that proposed by Lofgren (1974a) for reverse zoning in plagioclases and is not dependent on the development of steady state conditions nor does it demand the presence of a diffuse interface.

THE MODEL

Constitutional supercooling will occur when the liquid in contact with an advancing solid-liquid interface has a composition different from the bulk composition of the liquid (Rutter and Chalmers, 1953; Tiller and others, 1953; Chalmers, 1964; Flemings, 1974). A concentration gradient in front of the interface will result in the liquidus temperature of the interface being lower than the liquidus temperature for the bulk liquid. It is important to realize that constitutional supercooling of the bulk liquid will occur even if the system is isothermal. That is, the equilibrium temperature will be that for the liquid immediately in front of the solid-liquid interface rather than that for the bulk liquid.

The concept of constitutional supercooling is most easily understood by starting with a simple equilibrium phase diagram and then considering deviations from equilibrium. We begin with a simple binary solid solution series between two components A and B (fig. 1). In order to initiate crystallization from a liquid of some composition, X, stable nuclei

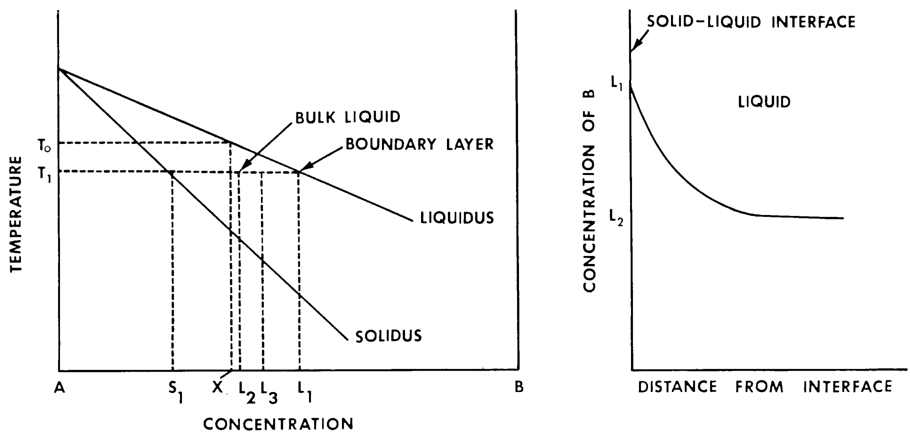

Fig. 1. A. Simple binary system illustrating constitutional supercooling. If a system is supercooled to T_1 and the growth rate of the solid exceeds the diffusion rate of solute in the liquid, the boundary layer adjacent to the crystal intersects the liquidus at L_1 while the bulk liquid is below the liquidus L_2. Diffusion of solute through the liquid will cause the boundary layer to migrate off the liquidus toward the bulk liquid. Growth rate will surpass diffusion rate, when the boundary layer reaches some intermediate composition L_3, and the boundary layer will again migrate toward the liquidus curve.

B. Distribution of solute away from the solid-liquid interface in a constitutionally supercooled liquid.

must be formed, and this will occur only after some degree of supercooling ($To-T_1$) has occurred. The solid will crystallize such that, at equilibrium, the composition of the solid will be S_1 when the composition of the liquid in contact with the solid is L_1. If either diffusion rate of B away from the solid-liquid interface or diffusion of A to the solid-liquid interface is less than the growth rate, a concentration gradient will develop in the melt away from the crystal. A possible distribution of B in the liquid is shown in figure 1B. A distribution of this general form will occur in any system in which the diffusion of solute through the liquid is less than the growth rate of the crystal. The zone of increased B concentration is referred to as the boundary layer (Rutter and Chalmers, 1953). If the boundary layer composition is at L_1 (fig. 1A, B) the bulk liquid (L_2) has a composition somewhere between the initial composition (X) and that of the boundary layer. Because the bulk liquid composition (L_2) departs from the actual liquidus composition (L_1), it is constitutionally supercooled as defined by Chalmers (1964) (note that constitutional supercooling is due to diffusion gradients only).

Constitutional supercooling and plagioclase zoning.—Nonperiodic zones in plagioclase may be best explained by variations in temperature, load pressure, and vapor pressure. However, to call upon regular, periodic changes in these variables to account for oscillatory zoning in plagioclase is not reasonable. A model for crystal growth that can account for periodic variations in a crystal without changes in external conditions is needed. One mechanism is to crystallize plagioclase under variable growth rates.

The major factor that can vary the growth rate of a crystal is the degree of supercooling. At large degrees of constitutional supercooling (for example, fig. 1A, L_3 at T_1) crystallization will be rapid while at equilibrium (fig. 1A, L_1 and T_1) the growth ceases. This simple fact, along with the planar nature of the plagioclase solid/liquid interface, provides the explanation of the driving force for oscillatory zoning.

Klein and Uhlmann (1974) in their crystallization studies of anorthite from its melt over the temperature ranges between 1173° and 1273° K and between 1523° and 1773° K demonstrated that growth of plagioclase crystals proceeds by nucleation and lateral migration of steps. This implies the existence of significant barriers to crystallization. That is, a certain amount of supercooling is necessary to nucleate the steps on the interface. As the degree of supercooling decreases, the chance of successful nucleation of steps becomes exceedingly small, and the diffusion rates of specie in the melt ("molecules of B", used as an analogy) exceeds the growth rate of the interface. Hence, the growth mode of the plagioclase interface presents a kinetic barrier to crystallization.

Consider the following model for the development of zoning in plagioclase with reference to the albite-anorthite phase diagram (fig. 2). An initial supersaturation is necessary to form stable nuclei and results from a change in temperature and/or pressure conditions in the magma and not from constitutional supercooling. If a system of composition X

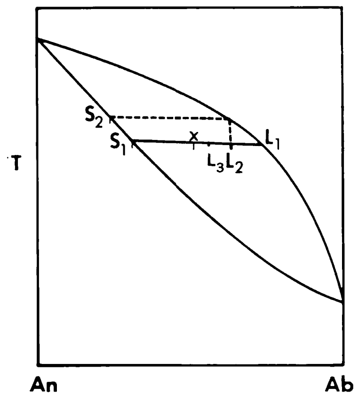

Fig. 2. Anorthite–albite binary showing the compositional variation of the boundary layer liquid between L_1 anl L_2 along the tie line L_1-S_1. Corresponding variation in solid composition is represented by the range in solid compositions S_1 and S_2. The bulk liquid composition represented by X becomes L_3 after a period of initial crystal growth.

is supercooled to the S_1-L_1 tie line, the solid and liquid composition will migrate toward L_1 and S_1. During the initial growth, the diffusion rates in the melt will be less than the growth rate of the crystal causing the formation of a boundary layer. Therefore, it is the boundary layer and not the bulk liquid that will be of composition L_1, when the crystal composition is S_1. After the period of initial crystallization, the bulk liquid will be of some intermediate composition (L_3). With a boundary layer composition of L_1, the flux of specie (solute) is a maximum because of the large compositional difference between L_1 and L_3. Therefore, with diffusion of solute into the liquid, the boundary layer composition will migrate off the liquidus curve becoming more calcic. If plagioclase grew with a diffuse interface, growth rates would respond immediately to the changing composition with supercooling in the liquid, and a steady-state system would be established. However, because the plagioclase crystals grow with a faceted, smooth interface, diffusion of solute through the melt may cause the liquid to migrate a considerable distance off the liquidus before the crystal starts to grow again. Once the liquid migrates off the liquidus to some composition L_2 (the supercooling necessary to nucleate new steps), a new growth cycle will begin. The exact composition of the new zone cannot be predicted, but it would fall somewhere to the left of S_1 and is shown as S_2 in figure 2. The solid and liquid compositions then migrate back toward S_1 and L_1. The growth rate will exceed the diffusion rate until the solid and boundary layer compositions are at L_1 and S_1. Systems in which growth rates are slower than diffusion rates will not form a boundary layer, and, therefore, the crystals will not show oscillatory zoning due to constitutional supercooling. At S_1 and L_1, the diffusion rates again exceed growth rates, and the cycle will begin to repeat itself. For each cycle, the maximum anorthite content of a zone is determined by the position of L_2 which is a measure of constitutional supercooling necessary to initiate growth on a planar interface. The maximum albite composition is determined by the positions of L_1 and S_1 on the binary phase diagram.

DISCUSSION

If repeated changes of general environmental variables (for example, temperature, pressure) are responsible for periodic zoning in plagioclase, then the stratigraphy of the plagioclase zones within individual plagioclase crystals should record these events. In contrast, if periodic zoning is due to constitutional supercooling, then there should be no correlation of zoning between crystals, since the zoning is controlled by the diffusion gradient in the liquid at the individual crystals. Wiebe (1968) has shown that in plagioclase from a granite stock, only the major abrupt discontinuities in plagioclase compositions can be correlated and that oscillatory zones cannot be related. Wiebe stated that the compositions of the inner cores were commonly as variable in an individual thin section as in the entire pluton. The coarse oscillatory zones of the inner cores could not be correlated in composition or number between phenocrysts. Wiebe's data strongly support the constitutional supercooling model for the origin of the oscillatory zoning.

Figure 3 is a microprobe trace showing a typical example of periodic zoning in plagioclase. The plagioclase comes from an andesite flow of Arenal Volcano, Costa Rica. The microprobe data were obtained from the nine spectrometer ARL-SEM microprobe at the Smithsonian Institution. Data points were taken every two microns from the edge of the crystal to the center. The curve was constructed by using only those points that exhibited mutual variation with respect to CaO, Na_2O, Al_2O_3, and SiO_2. Data was taken in this manner, because, at this scale, microprobe data would be extremely sensitive to impurities and crystal imperfections. By using only those points that show mutual variation in all the major elements, we are confident that the variation measured is reflecting variation in plagioclase composition rather than impurities. The disadvantage of taking data every two microns is that the crests and troughs of the compositional zones are not located exactly. However, the ability to record simultaneously all the major elements far outweighs this disadvantage.

The general trend of plagioclase compositions across the crystal is an inner, calcic core and an outer sodic zone. The inner zone (figure 3A) has oscillatory zoning with the wavelength (width) of the zones being 8 to 10 microns and composition amplitude (variation) between approximately 8 and 2.0 percent albite. In the outer zone (fig. 3B) the wavelengths of the periodic zones are generally 12 to 20 microns with amplitude varying between 2.2 and 10.5 percent albite. Within the inner zone (fig. 3A) there are three anomalously high albite zones: (A) is in the center of the crystal and most likely associated with nucleation of the crystal, (B) and (C) are interpreted as due to variation in external factors. The transition from the inner zone to the outer zone (D) is clearly due to external factors. The fine oscillatory zoning in the inner zone and the coarse ones in the outer zone can all be explained by constitutional supercooling.

The interface liquid during the formation of the inner, more calcic core, must have been less siliceous and at a higher temperature, and thus the diffusion in the liquid was more rapid, resulting in less compositional difference between the boundary layer and the bulk liquid for a given amount of constitutional supercooling. In other words, the diffusion rates in the liquid control the variation in composition and width of the zoning. The results are that the periodic zones within the inner part of the crystal are narrower and have a smaller compositional range. The outer zones have greater wavelength and amplitude than the inner zones due to the decrease in diffusion rates in the more siliceous magma.

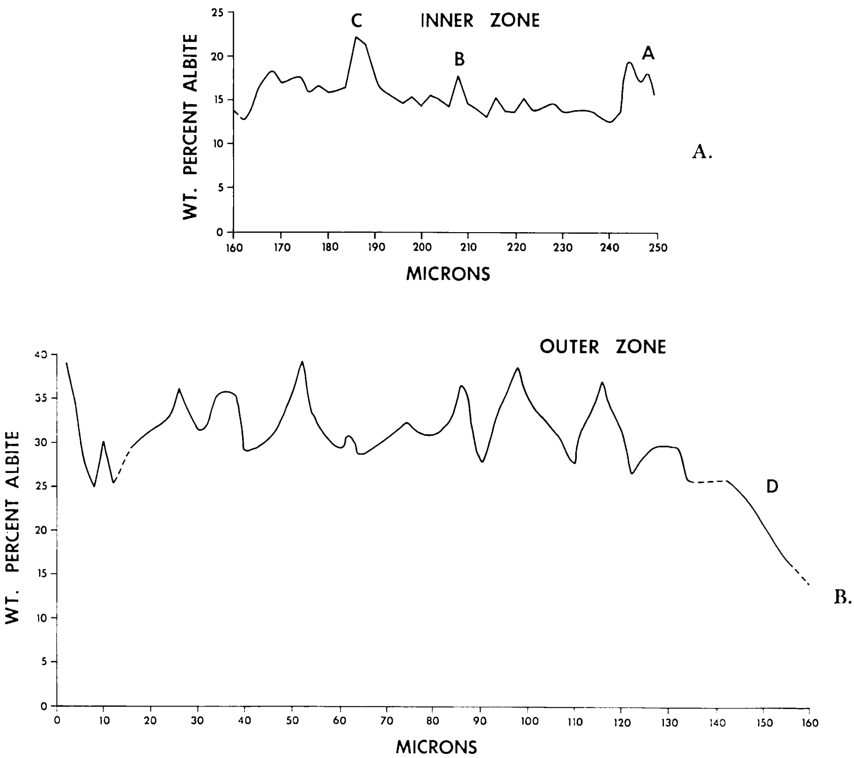

Fig. 3. A. Plot of compositional variation in wt percent albite across the inner zone of phenocryst.

B. Compositional variation plotted across outer zone of phenocryst. Major discontinuities are probably the result of changes in external factors, while the fine, oscillatory zoning can be explained by constitutional supercooling.

In terms of the proposed model, the maximum albite content in each zone would represent crystallization from the equilibrium composition, L_1, whereas the minimum albite composition in each zone represents crystallization from a constitutionally supercooled liquid L_2. The composition of the interface liquid at equilibrium should be relatively constant. Therefore, in zoning due to constitutional supercooling, the maximum albite content in each zone should be constant or vary in a continuous manner (for example, continuously becoming more albitic). However, if the zoning is due to change in external factors (temperature or pressure change), there would be an abrupt increase in the maximum albite content with drop in temperature or pressure, and there would be no reason for the maximum albite content of the zones to be systematically related. One criteria to use in determining if zoning is due to external variables or constitutional supercooling is that in zoning that results from a constitutionally supercooled liquid the maximum albite content in each should be nearly constant; zoning due to external factors will vary considerably (see fig. 4).

CONCLUSIONS

We propose that constitutional supercooling is a viable model for oscillatory zoning in plagioclase. The wavelength and amplitudes of individual zones are directly related to the properties of the liquid. That is, zoning that results from a liquid with relatively high diffusion rates should have a short wavelength and small amplitude. In contrast, long wavelength/large amplitude zoning would indicate low diffusion rates in the melt. Spectral analysis of zoning patterns in naturally occurring plagioclases should, therefore, yield important information on the nature and evolution of the melt from which the crystals grew. Some of the

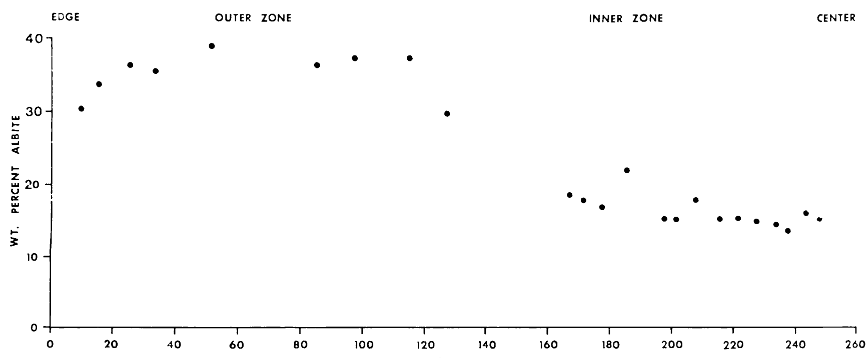

Fig. 4. Plot of the maximum albite content of zones across a zoned plagioclase phenocryst from the center to the edge of the crystal. Regions of the crystal where the maximum albite content of the zones are constant or slightly increasing indicate zoning attributable to constitutional supercooling.

factors that would affect the nature of a zoning spectrum are temperature, silica content, and water content, because these variables affect the viscosity of the melt and diffusion rates in the melt.

Some zoning in plagioclase results from changes in general environmental variables and not from constitutional supercooling. These zones will be represented by abrupt changes in the zoning spectrum and yield important petrogenic information when recognized as being formed by changes in the conditions of the melt.

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REFERENCES

Bowen, N. L., 1913, The melting phenomena of the plagioclase feldspars: Am. Jour. Sci., 4th ser., v. 35, p. 577-599.

——— 1928, The Evolution of Igneous Rocks: Princeton, N.J., Princeton Univ. Press, 332 p.

Bottinga, Y., Kudo, A., and Weill, D., 1966, Some observations on oscillatory zoning and crystallization of magmatic plagioclase: Am. Mineralogist, v. 51, p. 792-806.

Cahn, J. W., 1960, Theory of crystal growth and interface motion in crystalline material: Acta Metallurgica, v. 8, p. 554-562.

Chalmers, Bruce, 1964, Principles of Solidification: New York, John Wiley & Sons, 319 p.

Emmons, R. C., ed., 1953, Selected petrogenic relationships of plagioclase: Geol. Soc. America Mem. 52, 142 p.

Flemings, M. C., 1974, Solidification Processing: New York, McGraw Hill Book Co., 364 p.

Harloff, C., 1927, Zonal structure in plagioclase: Leidsche Geol. Mededeel., v. 2, p. 99-114.

Hills, E. S., 1936, Reverse and oscillatory zoning in plagioclase feldspar: Geol. Mag., v. 73, p. 49-56.

Hyndmann, D. W., 1972, Petrology of Igneous and Metamorphic Rocks: New York, McGraw Hill Book Co., 533 p.

Klein, L., and Uhlmann, D. R., 1974, Crystallization behavior of anorthite: Jour. Geophys. Research, v. 79, p. 4869-4874.

Lofgren, Gary, 1971, Speculitic textures in glassy and crystalline rocks: Jour. Geophys. Research, v. 76, p. 5635-5648.

——— 1974a, Temperature induced zoning in synthetic plagioclase feldspar, *in* Mackenzie, W. S., and Zussman, J., eds., The Feldspars: Manchester, England, Manchester Univ. Press, p. 362-376.

——— 1974b, An experimental study of plagioclase morphology: Am. Jour. Sci., v. 274, p. 243-273.

Panov, Ye. N., 1969, Composition and zoning of plagioclase in granitoids of northeast Transbaykal: Geochem. Internat., v. 6, p. 824-835.

Pinwinski, A. J., 1968, Studies of batholitic feldspar: Sierre Nevada, California: Contr. Mineralogy Petrology, v. 17, p. 204-223.

Rutter, J. W., and Chalmers, B., 1953, A prismatic substructure formed during the solidification of metal: Canadian Jour. Physics, v. 31, p. 15-39.

Turner, F. J., and Verhoogen, John, 1960, Igneous and Metamorphic Petrology: New York, McGraw Hill Book Co., 694 p.

Tiller, W. A., Jackson, K. A., Rutter, J. W., and Chalmers, B., 1953, The redistribution of solute atoms during the solidification of metals: Acta Metallurgica, v. 1, p 331-357.

Vance, J. A., 1962, Zoning in igneous plagioclase: normal and oscillatory zoning: Am. Jour. Sci., v. 260, p. 746-760.

Wenk, Edward, 1945, Die Koexistenzbed in gungen zwischen Hornblende, Biotic und Feldspaten und die Bedeutung der oszillierenden Zonarstruktur: Schweizer. min. pet. Mitt, v. 25, p. 141-164.

Wiebe, R. A., 1968, Plagioclase stratigraphy: A record of magmatic conditions and events in a granite stock: Am. Jour. Sci., v. 266, p. 690-703.