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ZONING IN IGNEOUS PLAGIOCLASE: NORMAL AND OSCILLATORY ZONING

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ABSTRACT. A sequence of oscillatory cores and thin, normally zoned, more sodic rims is characteristic of many igneous plagioclases, especially those of quartz diorites and granodiorites. The boundary between the core and rim may be euhedral or somewhat irregular and embayed; the core is commonly corroded, showing a patchy zoning formed by irregular inclusions of rim plagioclase composition.

The oscillatory zoning is believed to have formed in response to recurrent supersaturation of the melt in anorthite adjacent to the individual crystals. The abrupt change to normally zoned rims in the zoning sequence is thought to reflect late-stage saturation of the residual melt in volatiles. After saturation, agitation by the escaping volatiles maintains a uniform melt composition equalizing the rates of diffusion and crystallization. This prevents further supersaturation, permitting uninterrupted crystallization of the rims.

The occurrence of resorbed oscillatory cores in many plagioclases showing this zonal sequence supports the view that falling pressure accompanying rise of magma was a factor in bringing about saturation. As a result of the diminishing solubility of volatiles, further rise of these magmas led to rapid crystallization of the sodic rims and filling-in of the corroded cores. Formation of the oscillatory zoning through a mechanism of pressure changes due to recurrent release of volatiles cannot be reconciled with either the change in zoning or the timing of this change.

This zonal sequence is believed to show that loss of volatiles, even in plutonic rocks, occurs principally as a result of late-stage saturation rather than of leakage or diffusion without saturation. Late saturation in volatiles as recorded in the zonal sequence bears out the generally accepted low water content of granitic magmas.

INTRODUCTION

Most igneous plagioclase shows complex zonation. This zoning is unique in that the sequence from the center to the margin of a plagioclase crystal comprises a stratigraphic record whose variations mirror in detail the successive changes in magmatic environment. Because the interval of plagioclase crystallization in many igneous rocks covers a sizable fraction of the span of consolidation of the magma as a whole, an understanding of the processes responsible for these zonal features is a potentially invaluable key to the interpretation of magmatic history.

Much has been written, and many sharply conflicting opinions have been expressed as to the various factors that may influence plagioclase zoning. Unfortunately, many of these accounts suffer either in that they fail to relate the theory to accurate and detailed observations of specific zoned material or in that geologically or theoretically unrealistic conditions are invoked to explain the zoning. In the hope of avoiding these shortcomings, this study is restricted to those types of zoning which the literature and the writer's experience show to be extremely widespread in igneous plagioclase, and which can be related to the simplest and most fundamental of magmatic processes. Although many accidental factors may modify or complicate the zoning described here, the major zonal features are believed to reflect the interplay of only three basic magmatic events: (1) falling temperature, resulting from loss of heat to the environment; (2) falling pressure related to rise of the magma during emplacement; and (3) saturation of the melt in volatiles and resurgent boiling, as the result of either advanced crystallization or falling pressure. No new theoretical premises are involved here; the interpretations reached are all based on data stated or implied in the studies of earlier workers, notably Bowen (1913), Hills (1936), Carr (1954), and Yoder, Stewart, and Smith (1957).

The present paper is concerned largely with the effect of attainment of saturation in volatiles on plagioclase zoning. A subsequent paper will consider the effect of falling pressure on melt-crystal equilibrium and its influence on zoning. The principles developed here offer a new approach to evaluation of such fundamental problems as: the relative proportion of melt and crystals at the time of saturation of the magma in volatiles and at the time of emplacement; the timing of saturation with respect to emplacement, superheat, and the water content of magmas.

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THE ZONAL SEQUENCE

The plagioclase of many igneous granitic rocks in the compositional range quartz diorite-granodiorite-quartz monzonite shows a zonal sequence consisting of: (1) a core in which complex but regular oscillatory zoning is generally superimposed on a weak overall normal trend; followed by (2) a more sodic rim with strong normal zoning lacking oscillations (figs. 1 and 2). The oscillations commonly number in the dozens and in some crystals may approach as many as one hundred. The outer boundary of the core, though commonly euhedral (figs. 1, 2 A-B), is often somewhat irregular and embayed, suggesting resorption before deposition of the rim (fig. 2 C-D). Commonly the core is skeletal and shows a patchy zoning consisting of inclusions of more sodic plagioclase in continuity with and having the same composition as the rim (fig. 2 B-D). These corroded plagioclases show an abrupt break in composition between the cores and the rims. In plutonic rocks the sodic rim is subhedral or anhedral and varies considerably in thickness around individual grains. Its average thickness also varies among different granitic bodies and commonly in different parts of a single intrusion as well. The average thickness of the sodic rims, relative to the cores, commonly tends to vary as a function of the potash feldspar content of the rock, in general being widest in quartz monzonites and narrowest in quartz diorites. This zoning sequence was found to be characteristic of plagioclase in some eight Tertiary and Mesozoic granitic plutons in the Washington Cascades and was noted in thin sections of magmatic granites from many other areas. Not all magmatic quartz diorites and granodiorites show this zoning sequence, however. Some show oscillatory zoning throughout, and a few show only normal zoning, but in the writer's experience more show the zoning sequence than do not. This zoning is not restricted to granitic plagioclase but occurs in certain other plagioclase-rich igneous rocks, including some diabases, diorites, and gabbros, as well as some volcanic rocks. Entirely similar zoned plagioclase has often been described in the literature (Wenk, 1945; Larsen, 1948, Taubeneck, 1957, p. 199) or figured there without comment.

The abrupt transition from oscillatory core to normally zoned rim can, it is believed, be explained only in terms of magmatic processes. In order to show this, it is necessary to review briefly theories of the origin of zoning in igneous plagioclase.

ORIGIN OF THE OSCILLATORY ZONING

The origin of zoning in igneous plagioclase has been discussed in detail by several writers (Hills, 1936, Fuster, 1954, Ogniben, 1956; Scharbert, 1957), and only those points that bear on the present zonal features need be

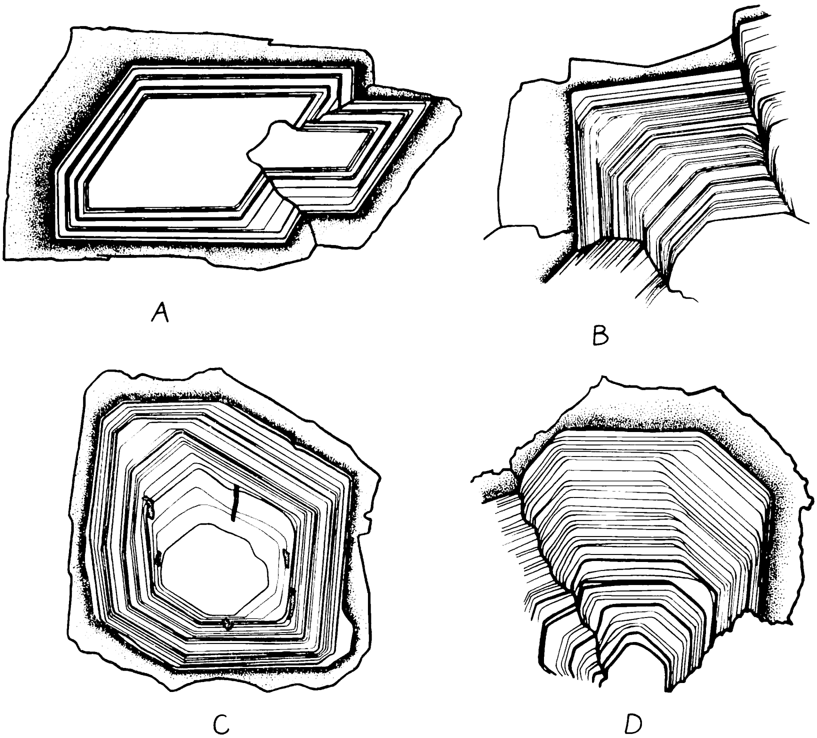

Fig. 1. Igneous plagioclase showing oscillatory zoned cores and normally zoned rims. Euhedral boundaries between core and rim. All sections are subparallel to (010); those not cut through to the center fail to show oscillatory zoning in the innermost core. C shows incipient patchy zoning consisting of small irregular inclusions of rim composition in the core.

A. Zonal sequence in calcic plagioclase (two coalescent grains in synneusis relationship), from basalt near Vantage, Washington. Width, 1.5 mm.

B. Zonal sequence in three coalescent oligoclase grains (An_{30}-An_{17}), Granodiorite from the Caulfeild pluton near Vancouver, B. C. Width, 1.5 mm.

C. Andesine (An_{52}-An_{40}). Quartz diorite from the Black Peak batholith near Rainy Pass, Washington. Width of crystal, 1.9 mm.

D. Zonal sequence in andesine-oligoclase (An_{30}-An_{18}). Quartz diorite, Beckler pluton, Skykomish, Washington. Width 1.4 mm.

considered here. It is generally agreed that normal zoning, the *leitmotiv* in igneous plagioclase, is to be explained largely in terms of nonreaction or incomplete reaction between melt and crystals in the formation of the mixed crystal series albite-anorthite (Bowen, 1913). This interpretation is followed here, though, as shown below, special conditions of crystallization appear to be essential to formation of simple normal zoning entirely lacking oscillations.

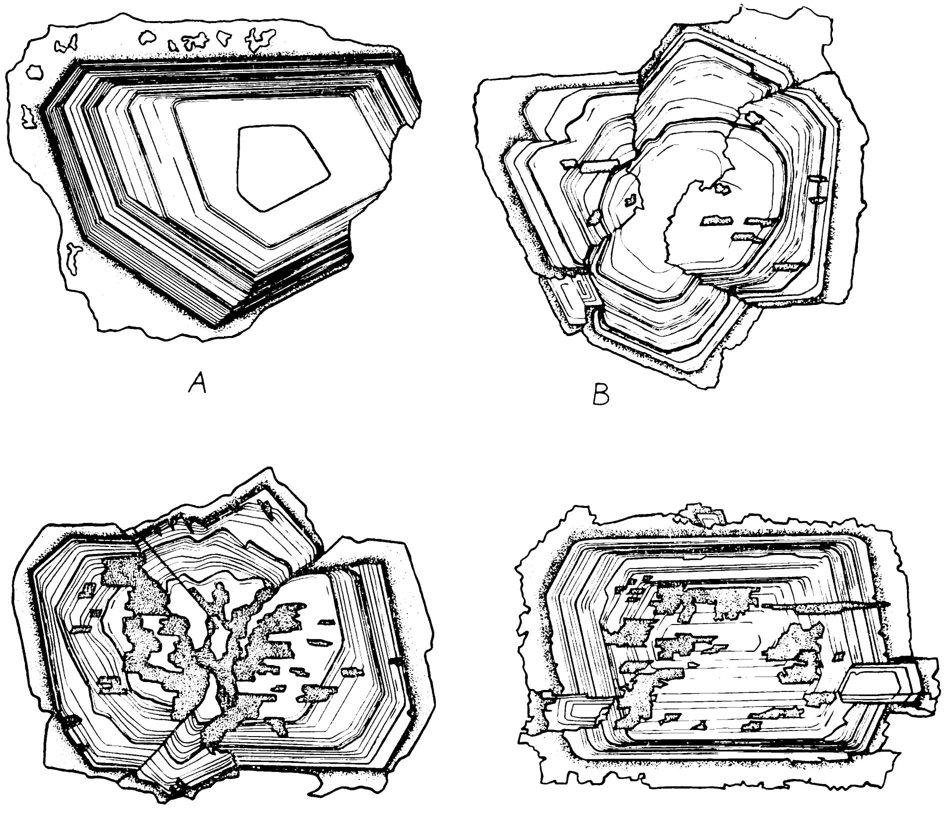

Fig. 2. Igneous plagioclase showing oscillatory zoned cores and normally zoned rims. All sections subparallel to (010). C and D show well developed patchy zoning consisting of inclusions of rim composition in the core and locally somewhat embayed and irregular boundaries between core and rim. B shows incipient patchy zoning.

A. Zonal sequence in andesine (An_{52}-An_{20}) from quartz diorite in the Squire Creek pluton, Darrington, Washington. The normally zoned sodic rim is intergrown with orthoclase. Width, 1.7 mm.

B. Zonal sequence in oligoclase (An_{32}-An_{15}) with Carlsbad (synneusis?) twinning. On lower left two small grains in synneusis relationship. Quartz diorite, Chilliwack batholith, Washington. Width, 2.6 mm.

C. Andesine (An_{52}-An_{18}) showing Carlsbad (synneusis?) twinning. Tertiary quartz diorite from the Grotto batholith near Monte Cristo, Washington. Width, 4.5 mm.

D. Zonal sequence in andesine (An_{54}-An_{22}). Three small grains in synneusis relationship and coalescent with the larger grain. Squire Creek quartz diorite, Darrington, Washington. Width, 3.1 mm.

There is no general agreement as to the origin of oscillatory zoning. Inasmuch as each of several factors may lead to reversals in zoning, and recurrent reversals, in turn, to oscillatory zoning, it is recognized at the outset that there are many types of oscillatory zoning and that these may be of quite different origins. One particular variety of oscillatory zoning is especially common, however. Inspection of the oscillatory zoning figured here and examination of some of the zoning curves of Wenk (1945, p. 157), Greenwood and McTaggart (1957), and Yeats (ms, p. 198) show that a striking feature of oscillatory zoning in many igneous plagioclases is the regularity in the compositional amplitude and width of adjacent delicate recurrences. A general feature of much of this regular zoning is that the recurrences, though mostly concordant, are often sharply demarked, suggesting a hiatus in crystallization. These regular oscillations are characteristic of the plagioclases described here, and it is the origin of this particular kind of oscillatory zoning with which this paper is chiefly concerned.

Beyond this regular oscillatory zoning, many of the plagioclases studied show additional complexities. Commonly the delicate oscillations occur at two or more compositional levels (sometimes separated by a corrosional interface). Clearly two distinct and different processes must have operated here; one recurring rhythmically and responsible for the regular oscillations, the other nonperiodic and irregular, related to the abrupt shift to a different composition.

Bowen (1928, p. 275), Homma (1932), and others have explained oscillatory zoning in terms of various mechanisms of repeated differential movement between plagioclase crystals and a compositionally or thermally heterogeneous melt. While such movement could be expected to produce zoning, the various mechanisms proposed lack periodicity and reversibility. Clearly they cannot account for the compositionally regular and delicate rhythmic zoning considered here.

Hills (1936, p. 54) and Carr (1954) have discussed the effect of variation in confining pressure on plagioclase crystallization, and Carr has interpreted oscillatory zoning in plagioclase from the Skaergaard intrusion in terms of cyclic pressure changes accompanying convective overturn. His explanation, although in agreement with the relations at Skaergaard, requires such special conditions that it cannot be applied to oscillatory plagioclase in general. Furthermore, as convective rise by this mechanism leads to lowered confining pressure, resorption is commonly to be expected, and should result in irregular corroded boundaries among individual oscillations. This is not in accord with the sharp, concordant boundaries that are usually present in the oscillatory zoning considered here.

Many investigators have invoked recurrent release of volatiles to account for oscillatory zoning. This hypothesis, however, clearly cannot explain the remarkable periodicity of regular oscillatory zoning, for a magma body possesses no built-in control permitting rhythmic discharge of uniform amounts of volatiles dozens of times in succession. Moreover, repeated loss of volatiles is likely to be significant only in a near-surface, subvolcanic environment. Regular oscillatory zoning, however, is very widespread in plutonic rocks.

Karl (1959, p. 143) and Boone (1959, p. 1572) independently have presented a more elaborate version of the release of volatiles hypothesis. They believe oscillatory zoning to be caused by fluctuations in pressure attendant upon recurrent release of volatiles. Although this currently fashionable mechanism appears to be workable, it is again unlikely that it could produce the regular oscillations considered here or that it could operate in any but a near-surface environment. Additional evidence that loss of volatiles cannot be responsible for the oscillations in the present zonal sequence is presented below.

Several recent workers have proposed that oscillatory zoning may be formed by secondary processes involving diffusion in the solid state. Fuster and Ibarrola (1956) have attributed certain types of relatively coarse irregular oscillatory zoning to diffusive magmatic reaction in which the pattern of replacement is largely controlled by primary zonal features. These coarse oscillations, however, are quite unlike the present delicate and regular zoning. Turner and Verhoogen (1958, p. 102) suggest that some types of zoning may be the result of unmixing. To the present writer such secondary mechanisms of zoning seem incompatible not only with the stability of the plagioclase lattice (Goldsmith, 1952, p. 289) but with the obvious primary magmatic textural features of the zoning considered here (e.g. Vance, 1961a, p. 1099, 1115). In any case, exsolution could no more produce rhythmic concentric zoning in plagioclase than it does in perthitic intergrowths in alkali feldspar, for which relatively coarse unmixing actually can be demonstrated.

The most satisfactory general explanation for delicate and regular oscillatory zoning in igneous plagioclase is the ingenious hypothesis of Harloff (1927), as later clarified by Hills (1936) in his diffusion-supersaturation theory. This hypothesis accounts for regular oscillations in terms of non-equilibrium crystallization related to variation in the rates of crystallization and diffusion leading to recurrent supersaturation of the melt in its anorthitic constituents. The mechanism operates as follows: (1) diffusion of anorthitic material brings about supersaturation of the melt immediately adjacent to the crystal; (2) when a certain value of supersaturation is reached, crystallization of a small normal zone takes place, impoverishing the adjacent melt in its anorthitic component; (3) diffusion of new anorthitic material to the crystal fails to keep pace with crystallization, which consequently slows and then ceases; (4) the sequence is repeated. The overall normal zone progression of the oscillations reflects progressive cooling of the melt according to the scheme of Bowen (1913).

It is remarkable that the diffusion-supersaturation theory has not gained wider acceptance. Entirely similar rhythmic crystallization due to recurrent supersaturation is so well established for salts in aqueous solution that it is surprising to find it questioned for viscous magmas. As noted by Harloff (1927), formation of exceedingly regular and delicate oscillatory zoning in ordinary table salt is readily observed under the microscope by permitting a drop of water saturated in salt to evaporate. The diffusion-supersaturation mechanism has the unique advantage that it is a built-in, internal process operating in response to normal crystallization and it is not dependent on accidental external factors. It avoids the drastic, yet regularly and uniformly repeated reversals of temperature, pressure, or bulk chemical composition required by most of the other hypotheses of oscillatory zoning.

ORIGIN OF THE NORMALLY ZONED RIMS

Possible causes of the abrupt change from oscillatory cores to normally zoned rims must now be examined. The onset of crystallization of the normally zoned rims is a sharply marked episode reflecting a sudden change in magmatic environment to new conditions, which persisted throughout the remainder of plagioclase crystallization. And, as judged by the frequency with which the zonal sequence is found, this change is characteristic of a great many granitic magmas. The zonal change is typically late, occurring at a relatively advanced stage in crystallization, as indicated by the large volume of the plagioclase cores compared to the rim. This timing is of critical significance, for it suggests that the zonal change may be genetically linked to separation of the volatile phase from the melt, likewise an event that generally occupies only the later stages of magmatic consolidation.

It is believed that this change within the zonal sequence can be understood only by accepting Hills' theory for the origin of the oscillatory zoning of the cores and by postulating late-stage saturation of the residual melt in volatiles. If Hills' theory is correct, initiation of normal zoning in the sodic rims records a sudden environmental change in the melt such that diffusion is no longer able to bring about recurrent supersaturation, and essentially continuous plagioclase crystallization ensues. This change is believed to reflect boiling-off of the volatile phase after saturation. Migration of the newly generated volatiles tends to agitate the melt and keep it compositionally homogeneous. This counteracts the tendency for diffusion to supersaturate the melt adjacent to the plagioclase crysals and favors uninterrupted crystallization. Once saturation is attained, separation of volatiles continues through to the final crystallization of the melt, producing regular normally zoned rims which are continuous to the margins of the crystals. Such continuous normal zoning indicates that the recurrent supersaturation mechanism has been completely supressed. In a few of the rocks studied, however, plagioclase rims that otherwise have only the usual normal zoning show faint, barely discernible regular oscillations of extremely small compositional amplitude. It thus appears that agitation by the volatile phase is not always sufficiently vigorous to offset the recurrent supersaturation effect fully. The development of these exceedingly faint oscillations in the rims may possibly be correlated with slow crystallization and attainment of saturation in situ which would entail relatively quieter evolution of volatiles than saturation during rise of magma, a process that involves rapid separation of the volatile phase.

Saturation of a melt in volatiles leading to separation of the volatile phase may occur by either of two mechanisms. The first is based on the experience that crystallization of the anhydrous phases brings about gradual enrichment of the residual liquid in its volatile constituents. Thus, as the concentration of volatiles rises with progressive crystallization, saturation may be attained and, with further crystallization, lead in turn to the separation of excess volatiles from the melt. This well known process is termed second boiling or resurgent boiling. Once the boiling has started, the released volatiles may migrate within or from the magma according to local pressure and concentration gradients. After saturation, plagioclase crystallization will continue in situ with further loss of heat to the environment. Such crystallization will most commonly be essentially isobaric (at least in larger magmatic bodies in which downward migration of volatiles is possible) and will lead to formation of uninterrupted normal zoning lacking oscillations.

Because the solubility of volatiles in granitic melts varies directly with the confining pressure (Goranson, 1938; Tuttle and Bowen, 1958, p. 54), saturation and resurgent boiling may also occur due, not to advanced crystallization alone, but to rise of magma to higher levels of lesser pressure. Yoder, Stewart, and Smith (1957, p. 207) have presented a phase equilibrium diagram for the plagioclase series in a water-saturated system at high pressure. Comparison of this diagram with that of the dry system at atmospheric pressure (Bowen, 1913) shows that a sudden isothermal decrease in pressure, as would occur with rapid upward movement of a water-saturated magma, is such as to shift the equilibrium abruptly but continuously from a melt with higher water content at high pressure to a still saturated but drier melt at lower pressure. Such a displacement of equilibrium involves continuous separation of volatiles and rapid precipitation of progressively more sodic plagioclase and will result in the formation of normally zoned plagioclase showing a large range in compositional variation.

That decreasing pressure is often a major factor in bringing about saturation in volatiles is supported by the detailed zonal features in many of these plagioclases. These crystals show irregularly resorbed oscillatory cores filled in crystallographic continuity with a more sodic plagioclase having the same composition as the rims. These complex and irregular intergrowths may be termed *patchy zoning*. As will be discussed at length in a subsequent paper, this patchy zoning has formed in direct response to rise of magma in the crust. Formation of this zoning involves an initial phase of intense plagioclase resorption, followed by renewed crystallization in which the corroded core is filled and surrounded by more sodic material. This sequence of development is clear in terms of Carr's thermodynamic data (1954, p. 372), which indicate that for water-deficient plagioclase systems: (1) the liquidus is lowered with falling pressure; and (2) a more sodic plagioclase will crystallize from a given melt at lower pressure than at higher pressure. The corrosion is attributed to essentially isothermal fall in pressure related to rise of a water-deficient melt. Resorption proceeds until pressure decrease is sufficient to permit the dissolved volatiles to saturate the melt (now augmented by the volume of the resorbed material). Once saturation is attained, further rise of the magma leads to resurgent boiling and crystallization at lower pressure of more sodic plagioclase to form the patchy zoning and normally zoned rims. The degree of corrosion and the width of the compositional gap between the core and the rim vary sympathetically and as a direct function of the decrease in confining pressure during resorption.

Zonal sequences in which there is well developed patchy zoning (i.e. intense corrosion and a sharp break in composition between the core and the rim) characteristically indicate that saturation was related to falling pressure and rise of magma in the crust. Attainment of saturation in situ, chiefly as the result of progressive crystallization, leads to a zonal sequence lacking patchy zoning and in which the compositional change from core to rim is gradual.

The sensitivity of both melt-crystal equilibria and the solubility of volatiles to confining pressure underscores the necessity for wider appreciation of the powerful influence of falling pressure on magmatic evolution. This need is all the more urgent in light of the fact that most magmas were generated at depths far below the site of their final emplacement. Two aspects of the role of falling confining pressure require special emphasis. First, rapidly decreasing pressure will in general cause resorption of earlier crystals in a melt unsaturated in volatiles. Once saturation has been attained, however, further fall in pressure will lead to crystallization. Thus, in melts containing dissolved volatiles, continuous decrease in confining pressure may lead to abrupt and discontinuous change in phase equilibrium relations. Second, in water-saturated melts pressure decrease may bring about isothermal crystallization or even crystallization with rising temperature (Karamata, 1956, p. 79; Tuttle and Bowen, 1958, p. 69).

The timing of the change from oscillatory to normal zoning is believed to be incompatible with origin of the oscillatory zoning in these plagioclases by any mechanism of recurrent release of volatiles. Discharge of volatiles, whether following saturation or by leakage (see below), must tend to occur late, after crystallization has led to concentration of volatiles in the residual melt. But the oscillations are invariably early in the zonal sequence and cannot, therefore, be explained by loss of volatiles. If we postulate a melt sufficiently rich in volatiles to permit their release from the earliest stages of plagioclase crystallization, then the normally zoned portion of the zoning sequence remains unexplained, for discharge of volatiles, once begun, cannot be halted indefinitely but must continue through the final stages of consolidation. The wide occurrence of this zonal sequence shows that, in the plutonic environment at least, separation and loss of volatiles after saturation is commonly gradual and continuous, rather than episodic, and often, if not generally, causes normal zoning rather than oscillatory zoning.

By the present interpretation, plagioclases with only the regular oscillatory zoning indicate that any saturation of the melt in volatiles took place after the plagioclase had completed its crystallization. The much less common situation of plagioclases with only normal zoning generally appears to indicate saturation prior to the beginning of plagioclase crystallization. It is possible, however, that simple normal zoning in some rocks reflects crystallization of a magma stirred by turbulent flow, vigorous convection, or some mechanism other than resurgent boiling.

A final point may be noted with regard to the zonal sequence in granitic rocks. There is a distinct general tendency for more potassic granites to have a higher *rim/core ratio* (the volume of the normally zoned rims relative to the oscillatory cores) than quartz dioritic and granodioritic rocks. This is believed to result from earlier crystallization of potassium-feldspar, and of quartz in the more silicic rocks, which accelerates saturation of the melt relative to the interval of plagioclase crystallization. A higher average water content in these more potassic magmas (e.g. as a result of differentiation) is a possible modifying factor that would have the same general effect. In any event, the tendency toward regular variation in the rim/core ratio with composition is obscure unless the zoning is interpreted in terms of saturation. Variation in the rim/core ratio within individual plutons provides a possible means of tracing the migration of volatiles during consolidation. Taubeneck (1957, p. 197) has noted that in the Bald Mountain batholith, Oregon, the plagioclase of the interior granodiorites show a higher rim/core ratio than those of the marginal quartz diorites. This supports the interpretation that the compositional variation of the batholith is related to differentiation involving downward migration and concentration of volatiles (Vance, 1961b).

Many hypabyssal and volcanic porphyries show zoning sequences that are analogous to those of plutonic plagioclase and may be related to attainment of saturation in volatile constituents by the melt (fig. 1 A). Hills (1936, p. 52) notes that some porphyries show oscillatory zoned phenocrysts and nonoscillatory, normally zoned groundmass plagioclase. He explains this in terms of the diffusion-supersaturation theory, stating that supersaturation leading to oscillatory zoning is more likely between widely spaced phenocrysts than between closely spaced groundmass crystals. This interpretation is not entirely satisfactory, because the groundmass plagioclase of many porphyries, especially those rich in glassy or cryptocrystalline groundmass, does show oscillatory zoning, at least in the cores of the crystals. This latter group of rocks appears to represent a less advanced stage of crystallization in which volatiles were insufficiently concentrated to saturate the residual melt at the time the groundmass plagioclase began to crystallize. Thus, separation of volatiles failed to occur, permitting continued development of oscillatory zoning by the diffusion-supersaturation mechanism. On the other hand, those porphyries with only normally zoned nonoscillatory groundmass plagioclase tend to be more nearly holocrystalline and thus more likely to have attained saturation. The normally zoned groundmass plagioclase in these rocks is commonly much more sodic than the oscillatory phyric plagioclase and often correlates with narrow normally zoned sodic rims of the latter. These data are in agreement with the the interpretation that saturation, loss of volatiles, and initial crystallization of the normally zoned plagioclase occurred during rise of the magma to higher crustal levels.

Saturation in volatiles appears to be the one event that correlates with all the details of the change in zoning in terms of both physical chemistry and the available experimental evidence. Other processes capable of the abrupt change required (such as: vertical movement of magma leading to rapid variation in confining pressure without saturation; changes in magma composition or temperature due to sudden introduction of new magma; or, sudden initiation of stirring by vigorous convection, turbulent flow, or some mechanism other than resurgent boiling), are inadequate to explain either the specific character of the change in zoning or the timing of this change. This zonal sequence is so widespread that it clearly requires a process generally operative in magmas, not an accidental one. In hydrous magmas only saturation appears to satisfy this condition. The decisive point, of course, is the consistently late timing of the zonal change. This is in agreement with the widely accepted low water content of most magmas which would permit saturation only in the later stages of crystallization.

WENK'S HYPOTHESIS

Wenk (1945, p. 161) has proposed a different origin for the contrasted oscillatory cores and normally zoned rims. His explanation of the oscillatory zoning is essentially a revival of Phemister's (1934) diffusion-reaction theory and involves recurrence of the following sequence of events: (1) crystallization of calcic plagioclase tending to make the melt immediately adjacent to the crystals more albitic; (2) reaction between crystals and albitic melt with development of a sodic zone; (3) a gradual increase in An-concentration around the crystals by diffusion leading to renewed deposition of more calcic plagioclase. As pointed out by Hills (1936), however, there is no conceivable reason for reaction to occur between crystals and melt in equilibrium, and the calcic plagioclase, having just crystallized, is obviously in equilibrium with the adjacent melt. Hornblende crystallization, apparently because it involves removal of anorthitic material from the melt, is considered by Wenk to be necessary for development of oscillatory zoning; and, after completion of hornblende formation, only normal zoning is supposed to develop in the plagioclase. Why this should be so is never made entirely clear. Wenk's evidence for the connection between plagioclase zoning and hornblende crystallization appears to rest partly on the correlation of the crystallization of oscillatory plagioclase and hornblende as interpreted from textures in thin section, and partly on the observation that oscillatory plagioclase is restricted to hornblende-bearing rocks. Contemporaneity of hornblende crystallization with that of the oscillatory plagioclase cores may possibly be correct. Even so, without supporting evidence this scarcely seems to establish a causal relation. Wenk's contention that oscillatory zoning is found only in hornblende-bearing rocks is incorrect, however. The writer has observed spectacular oscillatory zoned cores succeeded by normally zoned plagioclase rims in such diverse hornblende-free rocks as biotite quartz monzonite and tholeiitic basalt. Oscillatory zoning alone (i.e. without sodic rims) is so widespread in hornblende-free magmatic rocks as to require no comment. Apart from the obvious point that early crystallization of hydrous minerals will tend to postpone the second boiling effect, it is unlikely that hornblende crystallization plays any essential role in the development of regular oscillatory zoning in plagioclase. (As noted by many investigators, initiation and cessation of crystallization of Ca- and Al-bearing silicates such as augite and hornblende should influence plagioclase-melt equilibria; these changes are a possible cause of the irregular shifts in composition sometimes superimposed on the regular oscillatory zoning.)

LOSS OF VOLATILES BY DIFFUSION

As pointed out by Goranson (1937), and emphasized by Verhoogen (1949, p. 125) and Barth (1952, p. 139), it is conceivable that a melt may be subjected to higher pressures than the volatile phase, for instance, where the country rock is permeable to the volatiles but not to the melt. Under such conditions the volatile phase may diffuse or leak upward out of the magma without saturation's even being attained.

Although this mechanism is widely cited in the literature, it is difficult to visualize conditions under which such a process could be long maintained, nor apparently has it ever been demonstrated by independent geologic evidence. It is certainly clear that loss of volatiles by such leakage and diffusion without saturation cannot be related to the zonal sequence described here and that this process must be dismissed for rocks which show such zoning. Leakage by the differential pressure mechanism would have no consistent time of initiation with reference to plagioclase crystallization, but would occur whenever the pressure on the volatiles in the magma becomes less than the pressure on the melt. This might occur at any time either before or during crystallization of the magma. Furthermore, leakage could not only be initiated at any time but would terminate anytime that the avenues for escape of volatiles are sealed up. Thus, if the zonal sequence had in some way been controlled by leakage rather than saturation, regular oscillatory zoning should, in some rocks, reinstate itself and succeed the normal zoning. This was not observed in any of the zoned plagioclases studied. Finally, if we can accept Bowen's (1928, p. 295) estimate as to the excessively slow rate of diffusion of volatiles in silicate melts, it is altogether unlikely that leakage is a sufficiently vigorous process to stir the melt and terminate development of oscillatory zoning by the diffusion-supersaturation mechanism. These points indicate that saturation in volatiles, not leakage and diffusion, is responsible for the change to normal zoning. Larsen's skepticism (1948, p. 166) as to the attainment of saturation by plutonic magmas appears to be unjustified.

PETROGENIC IMPLICATIONS

Several petrogenetic implications follow from the interpretation of the zoning given above. The theory strongly supports the validity of Hills' explanation of regular oscillatory zoning. Moreover, the zonal sequence of oscillatory core and normally zoned rim develops in response to a physiochemically and geologically acceptable model of magmatic behavior, tying in with progressive crystallization and gradual concentration of volatiles, and, usually in the later stages of consolidation (sometimes in conjunction with rise of magma in the crust), with final saturation and release of volatiles. As it is unlikely that this zonal sequence could be duplicated by metamorphic processes, the zoning is taken to be evidence of direct magmatic crystallization.

The zonal sequence is also believed to indicate that saturation in volatiles and discharge of a separate volatile phase (resurgent boiling) is a normal event in the crystallization of many magmas and is probably much more significant than their loss from the melt through a hypothetical process of leakage or diffusion.

Because saturation in volatiles is recorded as a sharply marked episode, it provides a fixed reference point in the sequence of magmatic consolidation. It is therefore proposed that the time of saturation, as established in terms of plagioclase crystallization, be selected as the beginning of the *late magmatic* *stage of crystallization.* In this way not only do the terms early and late magmatic acquire the precise physiochemical meaning they have lacked in the past but, in many rocks, these stages can be recognized in terms of textural features in thin section. This line of demarcation between the early and late magmatic stages is especially advantageous because of the sharply contrasted physiochemical behavior of magmas before and after saturation in volatiles (see above), and because certain other processes, such as the formation of exsolution perthites, uralitization of pyroxene, biotization of hornblende, and other secondary features can sometimes be related to the activity of a separate volatile phase in the late magmatic stage. It may be objected that by this definition those magmas that were saturated in water at the outset of crystallization omit the early magmatic stage, whereas magmas that have lost their volatiles through leakage or have used them up entirely in the formation of hydrous minerals omit the late magmatic stage. This criticism, however, seems to be outweighed by the advantage of having a workable definition with clearly marked boundaries which, nevertheless, preserves the early-late time sequence demanded by the vague previous usage.

If correctly interpreted, the present zoning sequence bears a direct relation to the water content of the magma at the time of saturation. The full implications of this will not be discussed here, but a few points of special interest may be briefly considered. First, the modal volume of the oscillatory cores, the *core index*, fixes a lower limit to the volume of crystals in the melt at the time of saturation. Values close to 50 are common in many quartz diorites and granodiorites and indicate that a minimum of 50 percent of the melt had crystallized by the time of saturation. This is in agreement with the low values now generally accepted for the water content of granitic magmas (Ingerson, 1950; Tuttle and Bowen, 1958, p. 78), which would admit of saturation in volatiles only in the later stages of crystallization. Goranson (1938) found that the maximum water content of an albitic (or granitic) melt does not much exceed 10 percent even at very high confining pressures. Thus, the magma giving rise to a rock with a core index of 50 cannot have contained more than about half this amount, that is, 5 percent water in the melt phase at the time of saturation. Certainly it contained appreciably less, because minerals other than plagioclase had probably begun to crystallize before saturation occurred and because saturation in most cases will have taken place at levels much higher than those associated with maximum effective confining pressure.

Where the depth at which saturation took place can be determined, this approach may permit close approximation to an absolute upper limit to the water content of the initial magma. In such an analysis the maximum water content will be the combined amount determined from the core index plus that now bound in the primary hydrous minerals. (This treatment of the water content of the hydrous minerals probably does not introduce much error on the positive side, for the common occurrence of biotite and hornblende phenocrysts in porphyries in which the plagioclase shows only regular oscillatory zoning indicates that their water is generally drawn from the melt, not from the excess volatile phase.) However, in view of the possibility of migration and concentration of volatiles in the magma (Kennedy, 1955, p. 490; Vance, 1961b), caution must be exercised in applying the results of these calculations to the magmatic body as a whole. Values determined from the early crystallized marginal portions of an intrusion (for which there has been less opportunity for enrichment in volatiles by differentiation) should provide the most accurate estimates of the initial water content.

The modal volume of the normally zoned rims, the *rim index*, fixes a lower limit to the volume of the melt remaining at the time of saturation. Thus, a rock with a core index of 50 and a rim index of 5 consisted of somewhere between 50 and 95 percent crystals and 5 and 50 percent liquid when saturation occurred. These values not only make it possible to set an upper limit on the water content of the magma at the time of saturation but also provide a rough picture of the physical state of the magma at a fixed, physiochemically defined stage in its crystallization.

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