

## Origin of K-feldspar megacrysts in granitic rocks: Implications of a partitioning model for barium

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### ABSTRACT

Conflicting theories for the origin of K-feldspar megacrysts in granitic rocks are principally (1) the megacrysts crystallized from a melt or (2) they grew by replacement from a water-rich fluid phase under subsolidus conditions. In order to help resolve this conflict, we previously showed that Ba-zoning profiles for megacrysts from two Precambrian granitic bodies from northern New Mexico could be correlated from crystal to crystal in the same hand specimen, provided crystal size is taken into account. The largest megacrysts from each body showed first an increase followed by a decrease in Ba from their centers outward. These reversals in the Ba concentration gradients are difficult to explain by a simple two-phase crystallization model if the partition coefficient for Ba between K-feldspar and silicate liquid or a water-rich fluid phase is  $> 1$  as indicated by experimental data. Analysis of the governing equations for partitioning of trace elements shows that such reversals could result from changes in the partition coefficient for Ba, changes in the concentration of Ba in the liquid, or changes in growth rate. Since quartz and plagioclase have partition coefficients for Ba that are  $< 1$ , an increasing concentration of Ba in a silicate liquid can be readily explained by crystallization of one or both of those phases simultaneously with the megacrysts. In order to test this hypothesis, we have devised a simple mathematical model that uses measured partition coefficients and experimentally determined crystallization sequences for granitic rocks to calculate zoning profiles that would have formed if K-feldspar crystals grew from a melt. The calculated profiles show that the reversed Ba zoning observed in the megacrysts is consistent with an igneous origin. Moreover, the presence or absence of reverse zoning is critically dependent on the temperature and relative timing of crystallization of K-feldspar, plagioclase, quartz, and mafic minerals, which in turn is sensitive to the water content of the magma. These results do not positively preclude subsolidus crystallization of megacrysts from an aqueous phase, but they do provide a mechanism for consistently producing the observed Ba-zoning profiles. No such mechanism is inherent in subsolidus crystallization or in more or less arbitrary changes in partition coefficients or growth rate. Alkali feldspar megacrysts exhibiting reversed zoning are thus best explained by crystallization from a melt.

### INTRODUCTION

Conflicting theories for the origin of K-feldspar megacrysts in granitic rocks are principally (1) the megacrysts are phenocrysts crystallized directly from a melt as a primary phase (Kerrick, 1969; Nemeč, 1975; Kuryvial, 1976) or (2) they are porphyroblasts that grew from a water-rich fluid phase under subsolidus conditions (Dickson and Sabine, 1967; Emmermann, 1968, 1969; Mehnert, 1969). In an earlier paper (Long and Luth, 1979), we discussed criteria previously suggested for distinguishing between these two possibilities and noted that interpretation of these criteria has been controversial. For example, the occurrence of megacrysts in the country rock adjacent to a granitic body has been taken as evidence that the mega-

crysts in the granite itself did not grow from a melt. Such arguments are commonly inconclusive in that other interpretations may be equally plausible. For example, the megacrysts in the country rock may have grown from a vapor phase that coexisted with the crystallizing magma now represented by the granitic body. Consequently, we determined Ba-zoning profiles from K-feldspar megacrysts in two Precambrian granitic bodies in northern New Mexico and used the occurrence of reversed zoning of Ba in conjunction with measured partition coefficients for Ba to infer an igneous origin for these megacrysts (Long and Luth, 1979).

In this paper we report the results of a simple crystallization and partitioning model for granitic magmas which

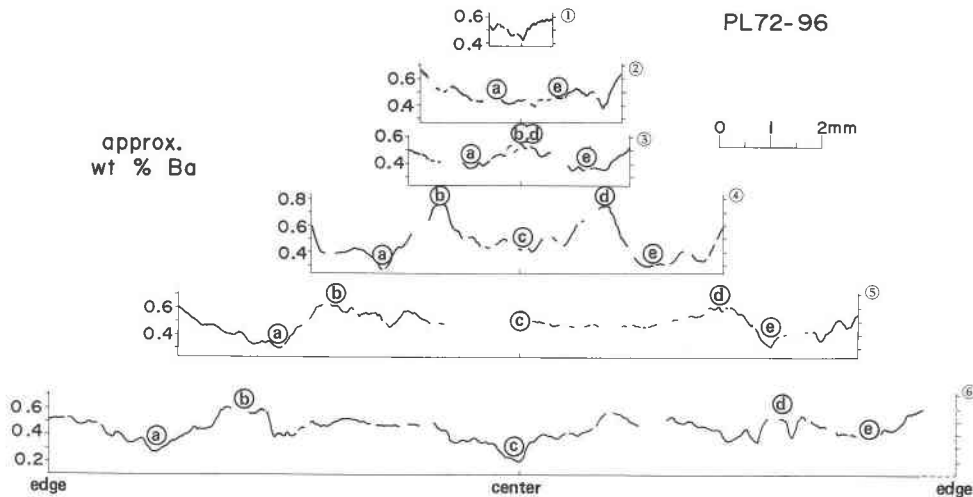


Fig. 1. Traverses for Ba from a series of megacrysts from a single hand specimen of Peñasco Quartz Monzonite. Correlation of points from one traverse to another are noted by lower-case letters (a through e). Smaller megacrysts apparently grew at later times than the larger megacrysts. Blank zones in the traverses are plagioclase inclusions, perthitic lamellae, small grains of a high-Ba phase, or epoxy. The smallest traverse (top of the figure) is a microcline crystal from the groundmass. Its zoning profile suggests that it grew last in the sequence of crystallization of the K-feldspar (from Long and Luth, 1979; reproduced by permission of the New Mexico Geological Society).

allows us to calculate the Ba-zoning profiles that would occur if K-feldspar megacrysts crystallized from a typical granitic melt. The purpose of the model is to determine quantitatively if crystallization from a melt could produce the reversals in Ba-zoning previously studied (Long and Luth, 1979). The model accounts for the temperature dependence of Ba partition coefficients and for experimentally determined crystallization sequences of plagioclase, quartz, and a mafic phase along with K-feldspar. Results from the model show that both reversed and normal zoning of the magnitude observed in megacrysts can be readily explained by crystallization from a melt. Furthermore, the model suggests that Ba zoning may provide significant insight into the crystallization history of granitic magmas.

#### PREVIOUS WORK

Numerous papers have been published on Ba zoning in K-feldspar megacrysts including Dickson and Sabine (1967), Emmermann (1968, 1969) Kerrick (1969), Nemeč (1975), Kuryvial (1976), and Brigham (1984). Our work on Ba zoning (Long and Luth, 1979) demonstrated that Ba-zoning profiles from megacrysts from the Puntigado Granite Prophyry and the Peñasco Quartz Monzonite, Precambrian rocks from northern New Mexico (Long, 1974, 1976), could be correlated from megacryst to megacryst provided that the size of the megacrysts was considered (Figs. 1, 2). We thus were able to conclude that smaller crystals nucleated at a time later than larger crystals in proportion to their size. The presence of reverse zoning, in conjunction with experimentally determined partition coefficients for Ba, was explained qualitatively by crystallization of quartz and plagioclase simultaneously with K-feldspar, *i.e.*, an igneous environment of crystallization for the megacrysts.

Data on compositions of natural K-feldspar suggest that

the partition coefficient for Ba ( $D_{Ba}^{af/liq} = C_{Ba}^{af}/C_{Ba}^{liq}$ , where *af* = K-feldspar, *liq* = silicate liquid, and *C* = concentration of Ba in superscripted phase) is generally  $> 1$ . Alkali feldspar consistently contains more Ba, when it is available in the system, than coexisting minerals (Wedepohl, 1969). This is true in igneous rocks regardless of the timing of K-feldspar crystallization. In basic to intermediate rocks, where K-feldspar is a common residual phase, Ba in K-feldspar is relatively high (e.g., Trzcieski and Kulick, 1972). The same is true for pegmatites if sufficient Ba is available, even though K-feldspar is commonly a primary phase (e.g., Afonina and Shmakin, 1970; Shmakin, 1971). The depletion of residual liquids in Ba by crystallizing K-feldspar means that there is limited Ba in pegmatite systems. McIntire (1963) noted that Ba tends to increase with differentiation in basic rocks but decreases in more felsic rocks, reflecting the respective timing of the crystallization of K-feldspar. Similarly, in hydrothermal systems, Ba is concentrated in K-feldspar if there is sufficient Ba in the system. Bethke and others (1976) have calculated the relative concentration of Ba in an aqueous phase of a hydrothermal system, thereby making it possible to estimate the partition coefficient if Ba concentration in K-feldspar is known. The results suggest that  $D_{Ba}^{aq/aqu} > 1$  (*aq* = aqueous phase).

Attempts to estimate  $D_{Ba}^{pl/liq}$  (*pl* = plagioclase) using groundmass and phenocryst Ba concentrations have been made by numerous investigators (Berlin and Henderson, 1969; Ewart and Taylor, 1969; Philpotts and Schnetzler, 1970; Nagasawa et al., 1971). Berlin and Henderson (1969) and Philpotts and Schnetzler (1970) published data for  $D_{Ba}^{af/liq}$ , which ranges from 1.17 to 8.95. These results confirm the inference made from the generally high Ba concentrations in K-feldspar.

Iiyama (1968, 1973) reported experimental measure-

ment of  $D_{Ba}^{af/liq}$  indicating a strong partitioning of Ba into sanidine ( $D_{Ba}^{af/liq} = 25$  at 600°C, 2 kbar). Iiyama (1972) also investigated the partitioning of Ba between a fluid phase and albite, between a fluid phase and anorthite, and among a fluid phase and two coexisting feldspars. The results of these studies indicate that Ba should be more or less equally distributed between a plagioclase of intermediate to albitic composition and a K-rich alkali feldspar that coexists with a vapor phase.

Direct experimental measurement of partition coefficients in synthetic and natural silicate melt systems doped with Ba and a variety of other trace elements has been made by Drake and Weill (1975). Their data are pertinent here insofar as their partition coefficients for Ba ( $D_{Ba}^{pl/liq}$ ) can be extrapolated to temperatures appropriate to granitic systems. They found that  $D_{Ba}^{pl/liq}$  for andesites and basalts is strongly dependent on temperature and remains <1 above 1060°C. Unfortunately, Drake and Weill did not separate the effect of temperature from the effect of bulk composition. The bulk compositions they used ranged from basalts to andesites in order to crystallize plagioclase over a temperature range of 1150–1400°C. The possible effects of bulk composition complicate the application of their data to granitic systems, but data from phenocryst-lava pairs for rhyolite strongly suggest that  $D_{Ba}^{pl/liq}$  remains <1 down to temperatures appropriate for the crystallization of more felsic rocks (Philpotts and Schnetzler, 1970; Ewart and Taylor, 1969; Berlin and Henderson, 1969).

Long (1978) and Long and Luth (1979) reported  $D_{Ba}^{af/liq}$  for a synthetic granite system based on experiments done at 2.5 and 8 kbar and over a range of temperatures and water contents. Long (1978) estimated the effect of bulk composition, water content, growth rate, and temperature on  $D_{Ba}^{af/liq}$ .

#### CRYSTAL GROWTH THEORY AND MODELING OF Ba ZONING

With the exception of the special case in which the partition coefficient equals 1, the trace element or solute is either rejected by the growing crystal and concentrated in the adjacent liquid or accepted by the crystal and depleted in the adjacent liquid. Depletion or concentration of solute adjacent to a growing crystal results in a diffusion boundary layer. The development of a diffusion boundary layer, in addition to solute depletion or concentration in the remaining liquid as a whole, will result in some type of zoning in a growing crystal. The importance of the diffusion boundary layer to producing zoning depends on the relative magnitudes of crystal growth rate and diffusivity of the solute in the liquid. The possible types of zoning that are theoretically possible have been discussed by Tiller and others (1953) and by Albarede and Bottinga (1972). The system of interest for the megacryst problem is a closed system in which diffusion in the solid phase limits solute redistribution (i.e., zoning persists) and in which development of a diffusion boundary layer is permitted if the growth rate of the crystal relative to the diffusivity of the solute in the liquid is large.

The assumptions specified by Albarede and Bottinga

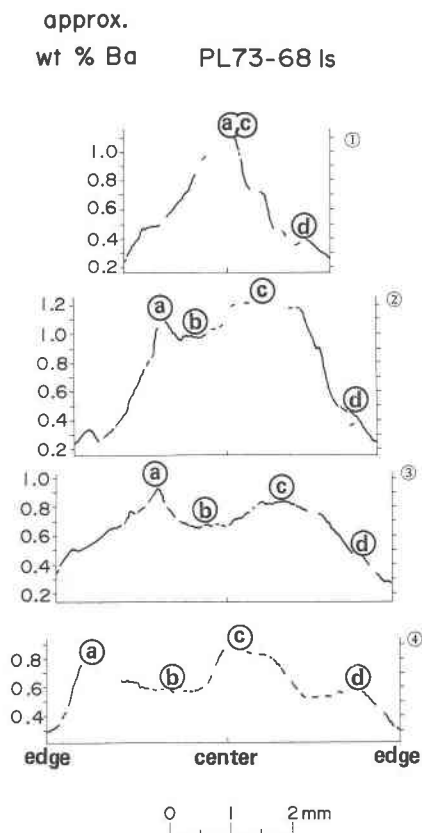


Fig. 2. Traverses for Ba from a series of megacrysts from a single hand specimen of Puntigudo Granite Porphyry. Correlation of points from one traverse to another are noted by lowercase letters. As in the previous figure, smaller megacrysts apparently grew later than the larger ones. In this sample, groundmass grains of microcline exhibit Ba concentrations that approximately equal the concentration of Ba at the edge of the megacrysts. The megacrysts from this sample also show a curious consistency in asymmetry of the profiles, i.e., the shape of the profiles near correlation point a versus that near point c (from Long and Luth, 1979).

(1972) for this system are (1) the crystal-liquid interface is planar; (2) some approach to equilibrium is maintained, at least right at the interface; (3)  $D_s^{i/liq} = a$  constant (where  $s$  is any solid phase and  $i$ , any component); (4) diffusivity of the solute equals a constant for a given phase; (5) the system comprises only two phases, a crystalline solid and a liquid; (6) the density of the solid phase and the density of the liquid phase are constant; and (7) the growth rate is constant. The mathematical expression of this case is the solution to the following differential equation (see App. 1 for an explanation of mathematical symbols):

$$d_i \frac{\partial^2 C_i^s}{\partial x^2} + v \frac{\partial C_i^s(x, t)}{\partial x} = \frac{\partial C_i^s(x, t)}{\partial t} \quad (1)$$

The boundary conditions are

$$d_i \frac{\partial C_i^s(0, t)}{\partial x} + (1 + D_i^s) v C_i^s(0, t) = 0 \quad (2)$$

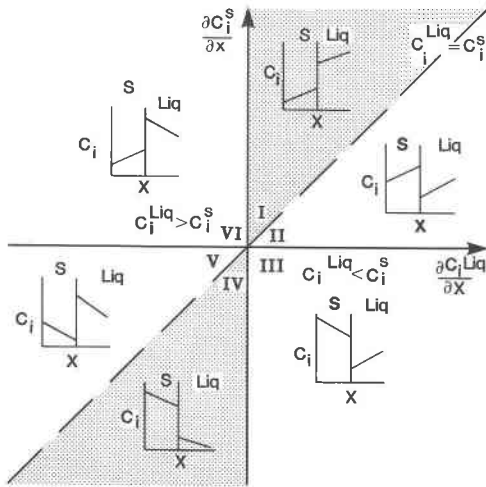


Fig. 3. Diagram representing possible combinations of gradients for a given component,  $i$ , in the solid (S) or the liquid (Liq) associated with a solid-liquid interface. Gradient in the solid is denoted as  $\partial C_i^S/\partial x$  and in the liquid as  $\partial C_i^{Liq}/\partial x$ . Lines of constant  $C_i^{Liq} - C_i^S$  are parallel to dashed line with slope  $d_i^{Liq}/d_i^S$  and intercept  $k(\partial X_i/\partial t)/d_i^S$  where  $k = C_i^{Liq} - C_i^S$ . Shaded regions (I and IV) are possible but unlikely in a closed, two-phase system because values of  $D_i^{Liq} > 1$  tend to deplete the adjacent liquid in the  $i$ th component and values of  $D_i^{Liq} < 1$  tend to enrich the adjacent liquid in the  $i$ th component. Reversals in the gradient of a component in zoning profiles require that conditions move from positive values of  $\partial C_i^S/\partial x$  to negative values or vice versa. Possible explanations for gradient reversals are a change in partition coefficient, a change in growth rate, or a change in liquid composition. Changes in liquid composition may simply result from crystallization of more than one phase in the system.

(mass balance and partitioning behavior) and

$$-d_i^S \frac{\partial C_i^S(x, t)}{\partial x} = 0 \quad (3)$$

(concentration gradients equal 0 at edge ( $\epsilon$ ) of system) and

$$C_i^0 = C_i^S(x, 0) = \frac{\text{mass of component } i}{\text{volume of system}} \quad (4)$$

(initial condition).

These boundary conditions mean that there is in fact no analytical solution, only numerical ones, to Equation 1. However, it is possible to rewrite the mass-balance equation into a form that is particularly useful in that it clearly relates the parameters of interest even though it does not allow a numerical solution for a diffusion profile as does Equation 1:

$$\frac{\partial X_i}{\partial t} (C_i^L - C_i^S) = d_i^S \left( \frac{\partial C_i^S}{\partial x} \right) - d_i^L \left( \frac{\partial C_i^L}{\partial x} \right). \quad (5)$$

It can be shown that for most cases where  $(C_i^L - C_i^S) < 0$  and as long as

$$d_i^L \left( \frac{\partial C_i^L}{\partial x} \right) > \left| \frac{\partial X_i}{\partial t} (C_i^L - C_i^S) \right|, \quad (6)$$

then  $C_i^S/x$  will be positive (see Long, 1976, App. VI, for derivation).

Thus, a crystal grown with  $D_i^{Liq} > 1$ , under the assumptions previously mentioned, should be normally zoned with respect to the  $i$ th component. Numerical solutions to Equation 1 (Albarede and Bottinga, 1972) corroborate this notion in that even when a steady state is reached and  $\partial C_i^S/\partial x$  becomes zero, no reversals in zoning are predicted. In order to rationalize the predicted absence of reversed zoning with the occurrence of reversed Ba zoning in megacrysts (Long and Luth, 1979), it is helpful to examine the circumstances under which reversals in Ba concentration gradients,  $\partial C_i^S/\partial x$ , can occur. A graphical representation of Equation 5 is shown in Figure 3, where the gradient in the solid phase is plotted against the gradient in the liquid at the solid-liquid interface. Figure 3 is divided into six regions based on possible combinations of gradients in the solid and liquid and the relative partition coefficients (here expressed as a difference,  $C_i^L - C_i^S$ ). Lines of constant  $C_i^L - C_i^S$  are parallel to the dashed line with slope  $d_i^L/d_i^S$  and intercept  $k(\partial X_i/\partial t)/d_i^S$ , where  $k = C_i^L - C_i^S$  and  $(\partial X_i/\partial t) =$  the crystal growth rate. Figure 3 illustrates that a reversal in  $\partial C_i^S/\partial x$ , requires that conditions change from region II or VI to region III of V (or vice versa). Stippled regions (I and IV) are regions where the gradients at the interface are inconsistent with the distribution coefficient.

Possible causes of a reversal in the gradient in the solid are clear from Equation 5: (1) a change in the partition coefficient, (2) a change in the growth rate, or (3) a change in the liquid composition with respect to a particular component ( $C_i^L$ ) possibly resulting from crystallization of more than one phase in the system. Each of these possibilities violates, in some way, the assumptions previously stated; we therefore reconsider the original assumptions.

The first assumption of a planar crystal-liquid interface seems appropriate for megacrysts, particularly in view of the orientation of tabular plagioclase inclusions along ghost crystal faces (Long and Luth, 1979; Brigham, 1984). The second assumption of an approach to equilibrium at the growing interface is probably appropriate, considering the low growth rates for crystals in granitic melts and the experimental results that show little if any diffusion boundary layer, even at relatively high growth rates (Long, 1978). A constant  $D_i^{Liq}$ , required by assumption three, is demonstrably invalid; at the very least,  $D_i^{Liq}$  must be considered as a function of temperature. Assumption four is that the diffusivities are constant. In general, diffusivity will be a function of temperature and bulk composition of the solid or liquid phase. Still, the diffusivity of Ba in feldspar is sufficiently small that zoning persists in the megacrysts. It is also true that greater diffusivities at higher temperatures in early stages of growth may exert an effect on zoning. In any case, the diffusivity of Ba in the liquid certainly is much greater than in K-feldspar. The exper-

imental evidence suggests that the ratio of  $d_{\text{Ba}}^s$  to  $\partial X_i/\partial t$  is such that the diffusion boundary layer does not play an important role in zoning of the megacrysts. Thus, at low growth rates expected in slowly cooled granitic systems, changes in diffusivity may influence the exact form of zoning, but are unlikely to produce reversals in  $\partial C_i/\partial x$ .

The fifth assumption, that the system is limited to two phases, is inappropriate for the crystallization of most igneous rocks or for crystallization by replacement from a water-rich fluid phase. The possible effect of crystallization of phases other than the one in which the zoning occurs, must be considered. This is especially true if the phases differ markedly in concentration of the trace element of interest, which is the case for Ba in the major phases in granites.

The sixth assumption that density of the liquid equals density of the solid is unrealistic, particularly if any process of igneous differentiation is to take place by crystal settling or floating. Whereas the effect of making this assumption is probably small for silicate melt systems, it is possible to take account of density changes between phases by the proper choice of concentration parameters that allow the density of a given phase to be defined as

$$\rho = \sum_{i=1}^N C_i, \quad (7)$$

where  $N$  = the number of components.

The seventh assumption of constant growth velocity probably is not strictly valid, but as long as growth velocities are low relative to diffusivities, changes in velocity should have little effect on general zoning patterns; however, changes in growth rate may affect the details of a zoning pattern.

The assumption of a constant  $D_i^{\text{liq}}$  and of a two-phase system are particularly troublesome. Based on the experimental data in Long (1976, 1978) and Long and Luth (1979), a functional relationship for  $D_i^{\text{liq}}$  that describes its change with temperature can be substituted in Equation 5:

$$\begin{aligned} \frac{\partial X_i}{\partial t} (C_i)(1 - [(10^4/T)a + b]) \\ = d_i^s \frac{\partial C_i^s}{\partial x} - d_i^l \frac{\partial C_i^l}{\partial x}. \end{aligned} \quad (8)$$

This equation does not account for the crystallization of more than one phase.

Consideration of the experimental evidence directly is instructive. Long and Luth (1979) observed that despite an increase in  $D_{\text{Ba}}^{\text{liq}}$  with increasing temperature, experimentally grown alkali feldspar crystals still showed distinct normal zoning. Depletion of the liquid in Ba evidently was more significant, for the particular bulk composition of the system, than was the shift to larger values of  $D_{\text{Ba}}^{\text{liq}}$ . The zoning pattern for such a two-phase system will depend strongly on the amount of the crystalline phase and the exact values for the  $D_{\text{Ba}}^{\text{liq}}$  during the

crystallization interval. Nonetheless, the experimental data suggest that when alkali feldspar crystallizes from a granite melt with no other crystalline phases, the alkali feldspar tends to be normally zoned in Ba. Crystallization of significant amounts of plagioclase ( $D_{\text{Ba}}^{\text{liq}} < 1$ ) and/or quartz ( $D_{\text{Ba}}^{\text{liq}} = 0$ ) concomitantly with Or-rich alkali feldspar (e.g., the megacrysts) will tend to increase Ba in the residual liquid, compared to what it would have been without crystallization of plagioclase and quartz. This increase will be reflected by the Ba concentration in the alkali feldspar as it crystallizes. Thus, application of even a sophisticated version of the mass-balance equation (i.e., Eq. 8) for only two phases (solid and liquid) provides little information for interpreting zoning in the megacrysts. It is necessary to account for the changing liquid composition, with respect to any element of interest, as a variable dependent on the total crystallization sequence of the magma. Unfortunately, to trace the liquid composition during crystallization requires a knowledge of the proportions of crystalline phases and their compositions at each infinitesimal step of crystallization. Such knowledge is not generally available for quinary granite systems, nor can it ordinarily be inferred in detail from interpretation of rock textures. As a general case, however, subsolvus granites crystallize at least three phases simultaneously (quartz, plagioclase, and K-feldspar) during significant parts of their cooling histories. At a minimum, crystallization of quartz and plagioclase must be accounted for in any model of Ba zoning in K-feldspar.

#### MATHEMATICAL MODEL FOR SIMULATING Ba-ZONING PROFILES

In order to explicitly test the concept that Ba zoning in alkali feldspar reflects concomitant crystallization of plagioclase and quartz or other Ba-rejecting phases, we have constructed a mathematical model that calculates and plots the Ba-zoning profiles that would occur in alkali feldspar crystallizing from a granitic melt. In theory, by changing the relative timing of crystallization and the relative proportions of phases, it would be possible to produce almost any continuous zoning pattern desired. Experimental data are available, however, that constrain crystallization sequences in granitic magmas (e.g., Whitney, 1975). If a simplifying assumption is made about proportions of crystallizing phases, it is possible to use these experimental data to simulate Ba-zoning profiles in K-feldspar crystallizing from a given granitic melt composition.

The concentration of Ba in residual silicate melt and crystallizing phases is calculated by our model at infinitesimal temperature steps (0.1°C) from liquidus to solidus using simple mass-balance and solute-distribution equations. The output of the model is an estimate of the concentration of Ba as a function of position in an alkali feldspar crystallized over the entire interval from the temperature at which alkali feldspar first becomes stable to the solidus. The calculations were done on a Hewlett-Packard programmable calculator (HP-41C); the results

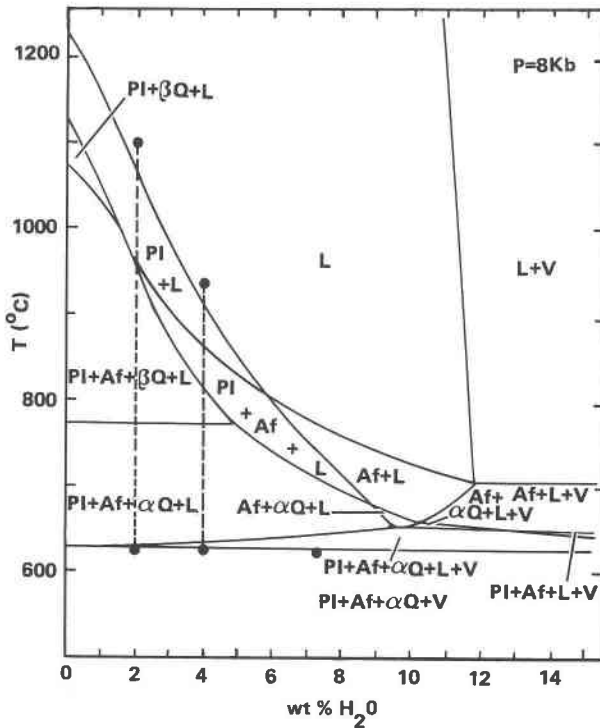


Fig. 4. Phase-assembly diagram (temperature versus wt percent H<sub>2</sub>O) for synthetic granodiorite (Whitney's, 1975, R1 composition) at 8 kbar. Vertical lines extending from liquidus to solidus are crystallization paths used for simulations 1 and 2 (Fig. 5). Phase boundaries from Whitney (1975).

were plotted on a Hewlett-Packard peripheral printer (HP-82143A).

Data for the model come from (1) experimentally determined values for  $D_{Ba}^{s/liq}$  reported in Drake and Weill (1975), Irving (1978), Long (1978), and Long and Luth, (1979) and (2) experimental data on phase relations in granitic systems reported by Whitney (1972, 1975) and Naney and Swanson (1980). The model deals with the problem of relative proportions of phases at a given stage of crystallization by assuming that phases begin to precipitate at the temperature at which they are first stable and continue to precipitate in linear proportion to temperature until they reach the solidus temperature, at which point they have a proportion equal to their modal abundance. Modal abundances for the calculations were taken from one of the samples studied previously (Peñasco Quartz Monzonite sample PL71-5; Long, 1976). The model further assumes that interface boundary layers discussed in the previous section are negligible and that chemical equilibrium is approached at each temperature step (i.e.,  $d_{Ba}^{liq}$  is large compared to growth rate; however, see Long, 1978, for a discussion of possible H<sub>2</sub>O buildup at growth interface). Moreover, solute redistribution is assumed not to occur once a given crystallization step is completed (i.e.,  $d_{Ba}^s = 0$ ). The model does, however, account for the effect of temperature on the partition coefficients for alkali feldspar and other crystallizing phases except for quartz,

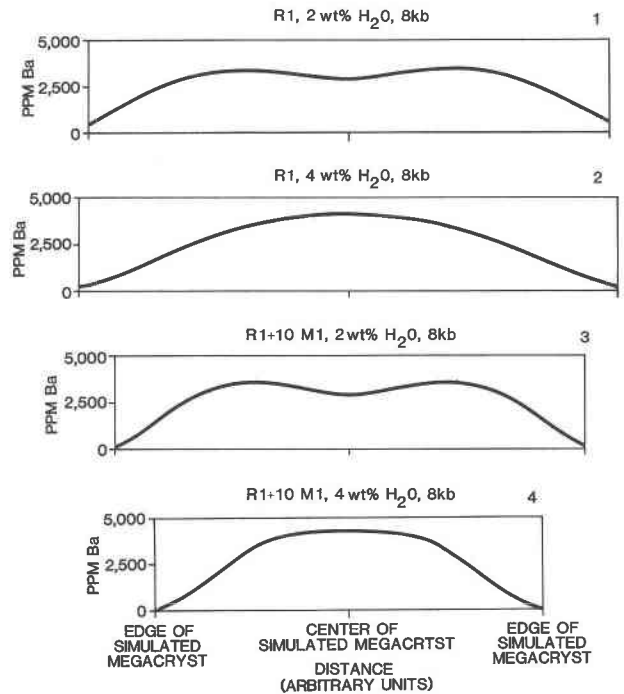


Fig. 5. Calculated Ba-zoning profiles for alkali feldspar at 2 and 4 wt% water for both mafic-bearing and mafic-free compositions. The profiles represent zoning that would have formed if the megacrysts had grown over the entire temperature range of stability of alkali feldspar for the particular bulk composition simulated. Composition R1 (simulations 1 and 2) is from Whitney (1975), R1 + 10 M1 (simulations 3 and 4) is from Naney and Swanson (1980). Water content differences of only 2 wt% can apparently influence the presence or absence of reverse Ba zoning in megacrysts that grow from a melt. See text for description of model for calculating the profiles.

which is considered to incorporate no Ba into its structure. The model does not explicitly consider the effect of changing the liquid bulk composition on  $D_{Ba}^{s/liq}$  because (1) compositional effects are partly included in the temperature dependence observed by Long (1976, 1978) and (2) insufficient data are available to permit reasonable modeling (see Long, 1978, for further discussion).

Typical crystallization sequences for the model are illustrated in Figure 4. Figure 4 also shows that water content has a dramatic effect on both the order of appearance of phases and the temperature intervals over which they appear. Consequently, calculations were performed at water contents ranging from 2 to 10 wt% water for two synthetic compositions, one with mafic components and one without.

Calculated Ba-zoning profiles (Fig. 5) for each composition at 2 and 4 wt% water show that the reverse zoning (Figs. 1, 2) of the type described by Long and Luth (1979) can be readily explained by crystallization of phases that reject Ba simultaneously with the alkali feldspar.

The calculated profiles demonstrate that the timing and temperature of crystallization of these phases relative to

alkali feldspar is critical to the resulting Ba-zoning profiles. A difference of 2 wt% water (2 vs. 4 wt%) changes the relative timing of phases sufficiently to make the difference between the presence or absence of reverse zoning.

At 2 wt% water, during the early phase of alkali feldspar crystallization, plagioclase is able to compete effectively with the tendency of alkali feldspar to reduce Ba in the residual melt and thus to create reverse zoning. At 4 wt% water, plagioclase crystallizes later relative to alkali feldspar and at lower temperatures where  $D_{Ba}^{pl/qz}$  is greater than at higher temperatures; as a result, plagioclase is not able to create reverse zoning. Similarly, addition of hornblende as a mafic phase at 2 wt% water (simulation 3, Fig. 5) enhances the reversed zoning slightly because it increases Ba in the residual liquid early in the crystallization of alkali feldspar.

Quartz appears to be relatively ineffective in creating reverse zoning in the calculated profiles because of its relatively late crystallization. However, if sufficient quantities of quartz crystallized late, reverse zoning at the edge of a crystal could be developed. Notice that the concentration gradient is beginning to flatten at the edge of simulation 2 (Fig. 5). Crystallization of additional quartz in the system would have created reverse zoning similar to that at the edge of the Peñasco Quartz Monzonite megacrysts in Figure 1.

#### DISCUSSION

Because of the simplifying assumptions—particularly the assumption that phases crystallize in linear proportion to temperature and the fact that the effects of changes in bulk composition of the residual liquid are ignored—the model can only explain general zoning trends. However, the model does not result in Ba concentration gradients as steep as found in several profiles shown in Figures 1 and 2. This result could be explained by variations in the relative rates and proportions of crystallization of plagioclase, quartz, or a mafic phase caused by equilibrium phase relations not predicted by the model, by compositional changes in residual liquid or alkali feldspar, or by changes in intensive parameters imposed by physical conditions of emplacement and cooling (e.g., pressure changes upon ascent of the magma). Interface kinetics (diffusion boundary layers) may also be important, but the experimental evidence suggests that such effects, if present, are more likely to provide an explanation for minor variations in the actual zoning profiles.

The results of the model indicate that the phase equilibria of granitic rocks may constrain possible zoning patterns for Ba in K-feldspar phenocrysts. Specifically, we predict that three types of zoning patterns will predominate: (1) normal zoning (Fig. 2, traverse 1; Fig. 5, simulations 2 and 4); (2) reversed cores with normal rims (Fig. 2, traverses 2, 3, and 4; Fig. 5, simulations 1 and 3); and (3) normal and/or reversed cores with late reversed rims (Fig. 1, traverse 4). The model does not attempt to address the occurrence of oscillatory zoning (Dickson and Sabine, 1967; Brigham, 1984) presumably oscillatory zoning could

be superimposed on any of the general patterns. Whereas other profiles are possible, they are less probable than the three types noted above. Certain patterns, such as continuously reversed zoning in large megacrysts, are not expected.

A subsolidus origin for megacrysts would require a relatively consistent change of Ba concentration in a fluid phase during megacryst growth, and there is no obvious mechanism for such behavior. We suggest instead that K-feldspar porphyroblasts will exhibit little or no zoning. As noted in Long and Luth (1979), the Puntigudo Granite Porphyry has undergone epidote alteration, and in most of these altered rocks the megacrysts retain their characteristic zoning pattern (Long, 1976). However, in the most severely altered rocks, the relict megacrysts have a constant, relatively high Ba content that apparently reflects homogenization of Ba in the megacrysts during alteration. We infer that the presence of a fluid phase accompanying epidote alteration acts as a catalyst for diffusion of Ba and hence would homogenize Ba in porphyroblasts during their growth. An extension of the model presented here that incorporates diffusion coefficients for Ba appropriate for low-temperature hydrothermal-alteration conditions could be used to determine if this inference is correct.

#### CONCLUSIONS

Results of a mathematical model of alkali feldspar, plagioclase, quartz, and a mafic phase crystallizing from a granitic melt demonstrate that reverse Ba zoning, similar to that observed in megacrysts, can be readily produced in a magmatic system. This result confirms our previous conclusion (Long and Luth, 1979) that the megacrysts from the Puntigudo Granite Porphyry and the Peñasco Quartz Monzonite are indeed phenocrysts and that the mechanism of Ba rejection by plagioclase, quartz, and a mafic phase produced the reversals in Ba concentration consistently observed in these megacrysts. Growth of the megacrysts by replacement mediated by a water-rich fluid phase does not appear to provide such a mechanism.

The modeling results further suggest that three general types of Ba zoning will predominate in K-feldspar phenocrysts: (1) normal zoning, (2) reverse-zoned cores with normal-zoned rims, and (3) reversed and/or normal cores with reverse rims. Other patterns are possible, but certain patterns, such as continuously reversed zoning in large megacrysts, are not expected. Differences among these three types of zoning may reflect slight to large differences in intensive variables for granitic systems. More sophisticated modeling studies may further quantify these differences.

Additional field, geochemical and experimental studies are needed. For example, we need to know the functional dependence of trace-element partition coefficients on temperature, pressure, melt- and solid-phase composition, and growth kinetics. It does not necessarily follow from this study that all K-feldspar megacrysts in granites are of strictly igneous origin, and it would be useful to examine Ba zoning in megacrysts, as well as K-feldspar phenocrysts

from volcanic rocks, from a wide range of environments in order to test our prediction about the types of zoning that are most predominant. Additional modeling studies could then allow interpretation of zoning patterns in terms of crystallization history and ultimately provide greater insight into the conditions of emplacement of granitic rocks.

#### ACKNOWLEDGMENTS

We are indebted to R. H. Jahns for suggesting the study of the granitic rocks of the Dixon-Peñasco area that ultimately led to the work we report here. His encouragement and critical comment on our earlier work on Ba zoning are deeply appreciated. R. C. Ewing and R. H. Vernon made review comments that significantly improved the manuscript.

Financial support for one of us (WCL) was provided by National Science Foundation Grant GA-1684 to W. C. Luth and R. H. Jahns. Part of the work reported here was conducted while one of us (PEL) held a National Science Foundation Graduate Fellowship at Stanford University.

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### APPENDIX 1. EXPLANATION OF MATHEMATICAL SYMBOLS

$C_i^s, C_i^l$  = solute concentration of the  $i$ th component in the solid and liquid phase, respectively.

$D_i^{s/l}$  = interface ( $x = 0$ ) partition coefficient defined as  $C_i^s(0,t)/C_i^l(0,t)$ .

$d_i^s, d_i^l$  = diffusivity of the  $i$ th component in the solid and liquid phase, respectively.

$\partial X_i/\partial t$  = velocity of the crystal-liquid interface (I); i.e., crystal growth rate.

$(x,t)$  = position and time within the coordinate system ( $x = 0$  denotes position of crystal-liquid interface).

$T$  = absolute temperature, degrees kelvin.

$a, b$  = linear coefficients describing the temperature dependence of  $D_i^{s/l}$ .

liq, aqu = substituted for  $l$  above; refer to silicate liquid and a water-rich fluid phase, respectively.

af, pl, qtz = substituted for  $s$  above; refer to alkali feldspar, plagioclase, and quartz, respectively.