Reaction relations in the granite system: Implications for trachytic and syenitic magmas

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Abstract

In order to evaluate crystallization paths of feldspathic, silica-poor rocks such as trachytes and syenites characterized by high-temperature crystallization histories (as indicated by the paucity of hydrous minerals, the presence of ternary feldspar, and the occasional presence of high-temperature minerals such as pyroxene and olivine), a detailed theoretical investigation of the sodic region of the synthetic granite system, Ab-Or-An-Qz-(H₂O), was undertaken. Calculated phase relations in the feldspar system (i.e., the system Ab-Or-An- (H_2O)) and in the synthetic granite system were used to identify and investigate the regions of complete and incomplete resorption of plagioclase (and less importantly, alkali feldspar) as a function of pressure, activity of H₂O, and silica content. The regions of complete and incomplete resorption of feldspar contract markedly with increasing H₂O and with increasing silica; they shift to higher An contents with increasing pressure. At low H₂O contents, however, the resorptional regime can be entered even when the melt is silica-saturated. Trachytic and syenitic magmas are likely to enter a region of at least incomplete resorption of plagioclase at an early stage of their crystallization history. However, it is possible that these magmas could re-enter a coprecipitation region once the activity of water and of other melt components has increased sufficiently during crystallization. This type of crystallization history could also characterize magmas more siliceous than trachytes as long as the bulk An and Or contents were low and the albitic region could be reached while the H₂O content was still low.

INTRODUCTION

The crystallization histories of most felsic magmas, extrusive and intrusive, can be characterized by crystallization paths within the synthetic granite system, Na-AlSi₃O₈(Ab)-KAlSi₃O₈(Or)-CaAl₂Si₂O₈(An)-Si₄O₈ (Qz)- (H_2O) . Although this system presents an idealized view of the phase relations of natural felsic magmas in that it does not contain the components required to evaluate the stability of hydrous minerals, anhydrous ferromagnesian minerals, or oxides, such components generally constitute less than 20 mol% of the compositions of most felsic magmas. Felsic magmas giving rise to granitic and rhyolitic rocks are commonly silica- and H₂O-rich, and their crystallization paths within the synthetic granite system are characterized by coprecipitation of quartzo-feldspathic minerals. Once one or two feldspars begin to crystallize, with or without quartz, they will continue to do so until the solidus temperature is attained. Unless the magma is very poor in Or component (e.g., dioritic in composition) or is very potassic (e.g., hypersolvus alkali-feldspar granites), the assemblage at the solidus temperature will contain two feldspars. Calculated crystallization paths of such two-feldspar granitoids as a function of pressure. composition, and H₂O-content were discussed in detail by Nekvasil (1988a, 1988b).

Quartz-normative trachytes and syenites have bulk compositions similar to those of two-feldspar granitoids but commonly have lower normative-quartz contents and phase assemblages characterized by strongly ternary feldspar, general absence of quartz in the phenocrystic assemblage, and a crystallization history involving early precipitation of ternary andesine-oligoclase and anorthoclase-sodic sanidine, followed by precipitation of only the alkali feldspar (e.g., Rahman and MacKenzie, 1969; Ewart, 1981; Novak and Mahood, 1986). Figures 1a and 1b show projected compositions of selected trachytes (from Kane Springs Wash caldera, Nevada, Novak and Mahood, 1986; Sierra la Virulente, Mexico, Moll, 1981; Turritable Falls, Central Victoria, Ferguson, 1978; and southeast Queensland, Ewart, 1981) superimposed on the familiar frequency-of-occurrence diagrams for Ab-Or-An and Ab-Or-Qz (Tuttle and Bowen, 1958). Although the bulk compositions of trachytes such as these are not much different from those of average felsic rocks, with only slightly higher normative Ab and lower Qz contents, their textural and mineral characteristics imply a crystallization history considerably different from that of guartzsaturated, H₂O-rich felsic magmas. The trachytes plotted in Figures 1a and 1b have been reported as containing alkali feldspar that mantles resorbed cores of plagioclase.

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The phase relations discussed below will be used to explain such observations on the basis of peritectic-like behavior in the synthetic granite system that could yield equilibrium or fractional crystallization paths involving complete or incomplete resorption of one feldspar. Such paths differ considerably from the coprecipitational paths expected for most felsic rocks, and this difference has major implications for major- and trace-element evolution of relevant felsic magmas. This article will focus on the quantitative evaluation of phase relations in the synthetic granite system with reference to trachytic magmas and the effect that these phase relations have on the crystallization histories of such magmas. Fractional crystallization trends for sodic systems were discussed in detail by Abbott (1978); therefore, equilibrium crystallization paths will be emphasized in the following discussion in order to facilitate understanding of the natural processes that are likely to be intermediate between these two extremes. The following analysis is based on thermodynamic calculations, thereby departing from previous geometric approaches, and it presents a more quantitative approach to characterizing the nature of reaction relations.

CRYSTALLIZATION OF FELDSPARS IN THE SYNTHETIC GRANITE SYSTEM

Projected from H₂O, the liquidus relations for the synthetic granite system are characterized by three surfaces, one each for the locus of liquids (\pm vapor) coexisting with quartz and alkali feldspar, for alkali feldspar and plagioclase, and for quartz and plagioclase. As shown schematically in Figure 2, these surfaces intersect at a curve that represents the locus of liquids (\pm vapor) coexisting with plagioclase, alkali feldspar, and quartz. The synthetic granite tetrahedron shown (Fig. 2) represents the liquidus relations only at constant H₂O content or H₂O activity. The modifying effect of H₂O content as an independent compositional variable must be considered when assessing crystallization paths in the granite system, as most felsic magmas reach H₂O saturation only during the late stages of their crystallization history, if at all. Nekvasil (1988a) concluded that the major compositional effect of increasing H₂O content at constant pressure is the contraction of the primary liquidus volume for quartz. This result has been confirmed experimentally in part by the data of Holz et al. (1988) and of Nekvasil and Holloway (1989, and in preparation) through comparison of $H_2O_$ saturated phase relations and modifications induced by the presence of an H₂O-CO₂ fluid.

The liquidus relations in the synthetic granite system reflect the presence of the feldspar solvus. As recognized by Tuttle and Bowen (1958), Carmichael (1963), and others, felsic magmas that attain low temperatures because of the presence of considerable H_2O or other diluting components such as Qz evolve along crystallization paths that eventually reach the two-feldspar surface and remain either there or on the plagioclase + alkali feldspar + quartz + L curve to the solidus temperature. Therefore,



Fig. 1. Selected Qz-normative trachytes (in which partially resorbed cores of plagioclase mantled by alkali feldspar have been reported) projected into (a) the system Ab-An-Or and (b) the system Ab-Or-Qz. Frequency-of-occurrence contours from Tuttle and Bowen (1958) for rocks containing greater than 80% of the components Ab, An, Or, and Qz are shown for comparison. Symbols: solid circle, Turritable Falls, Victoria (Ferguson, 1978); solid square, southeast Queensland (Ewart, 1981); open square, Sierra la Virulente (Moll, 1981); solid triangle, Kane Springs Wash caldera, Nevada (Novak and Mahood, 1986).

two feldspars will remain part of the equilibrium assemblage to the solidus temperature (as shown schematically in Fig. 3a). Such paths are anticipated during equilibrium crystallization of bulk compositions lying within the T-X



Fig. 2. Schematic diagram of liquidus phase relations in the synthetic granite system at a constant water activity. The three liquidus surfaces $PI + Qz + L (\pm V)$, $PI + Af + L (\pm V)$ and $Af + Qz + L (\pm V)$ intersect to form a four- (or, if fluid saturated, five-) phase curve (indicated by the arrow).

volume of the ternary feldspar solvus at the solidus temperature or fractional crystallization paths if the entire synthetic granite system behaves in a eutectic-like fashion. Alternatively, if the magma were enriched in An or Or components, even if it were H_2O and quartz-saturated, the solvus might not be intersected at all during equilibrium or fractional crystallization. In such cases, as shown schematically for Qz-free compositions in Figure 3b, the plagioclase + alkali feldspar + liquid surface within the synthetic granite system would not be reached during crystallization, and two feldspars would never precipitate from the magma (e.g., An-rich diorites and many peralkaline rhyolites).

However, a third alternative may characterize the crystallization histories of specific high-temperature felsic magmas. During equilibrium crystallization of bulk compositions lying within the region between the T-X volume of the ternary feldspar solvus and the plagioclase + alkali feldspar + liquid (PAL) surface in the synthetic granite system, or PAL curve in the feldspar system, two feldspars will be stabilized eventually; yet, at a later stage, only one feldspar will be stable (Fig. 3c). The limits on the compositional range of bulk compositions that will undergo such complete resorption of a feldspar during crystallization hold only for equilibrium crystallization; any magma that reaches the PAL surface during fractional crystallization will undergo complete resorption of a feldspar and hence move off the surface as long as the surface is peritectic-like.

Quantitative evaluation of crystallization paths involving resorptional behavior requires that the positional relations between the PAL surface and the solvus in P-T-Xspace be well known. Because of the difficulty of attaining equilibrium in experiments on dry albitic magmas, this information is generally lacking. Previous workers have resorted to geometric analysis in order to consider the possible phase relations and crystallization paths in the albitic region of the two-feldspar surface in the synthetic granite system based on limited experimental data.

Tuttle and Bowen (1958) recognized that the termination of the PAL curve (in the system Ab-Or-An) within the feldspar system and not at the Ab-Or base for low water pressures requires that this curve becomes a reaction curve somewhere along its length (i.e., the reaction $L \rightarrow Pl + Af$ is replaced by $Pl + L \rightarrow Af$ or $Af + L \rightarrow$ Pl). They further recognized that the resorption region would be most extensive at high temperatures because of the contraction of the solvus with temperature, and that in nature this region would be entered most readily during the crystallization of trachytic magmas characterized by low silica and H₂O contents. They were able to indicate schematically the region in which resorption could be expected but could not ascertain it in detail because of lack of data. Carmichael (1963) used natural feldspar data to obtain the general relations of the feldspar solvus and the two-feldspar curve in the feldspar system. He concluded that the most common reaction relation would be $L + Pl \rightarrow Af$. Later, in an attempt to further characterize resorption behavior in the synthetic granite system, Abbott (1978) used available experimental data to evaluate fractional crystallization paths in the resorptional regime and the effects of H₂O and excess silica content on these paths. He concluded that for quartz-saturated liquids, resorption of plagioclase is the only possible reaction relation regardless of the degree of H₂O-undersaturation along the PAL surface. For strongly quartz-undersaturated compositions, however, he further noted that it would be possible to resorb alkali feldspar, although resorption of plagioclase is most likely. Stewart and Roseboom (1962) and Henderson (1984) focused on defining the possible geometric configurations of the termination of the two-feldspar curve in the feldspar system. With the availability of thermodynamic models for the mixing of the anhydrous melt components in the synthetic granite system (Burnham and Nekvasil, 1986), the mixing properties of H₂O with these components, and the mixing properties of the feldspar components in ternary feldspar solid solutions, it is now possible to calculate the liquidus and solidus relations in the sodic region of the two-feldspar surface in the synthetic granite system. Such calculations provide internally consistent phase assemblages and compositions and can therefore be used to evaluate quantitative trends for equilibrium and fractional crystallization to complement earlier work.

The albitic region of the two-feldspar surface: Calculated phase relations

Phase relations in the albitic region of the two-feldspar surface in the synthetic granite system were calculated as described in Nekvasil (1988a). Activity-composition relations for the melt components albite, anorthite, or-

thoclase, and quartz were deduced from the revised quasicrystalline model (Burnham and Nekvasil, 1986). The effect of water in these melts was calculated from the albite-H₂O model of Burnham (1975). The thermodynamic mixing model used for ternary feldspars is modified from that of Lindsley and Nekvasil (1989). This model differs from that of Fuhrman and Lindsley (1988) in the incorporation of a molecular mixing model for the binary plagioclase solution and use of the Thompson and Hovis (1979) mixing model for the binary Ab-Or solid solutions. It differs from that of Nekvasil (1988a) in its use of a ternary interaction term, ternary volume terms and the adjustment of Seck's (1971) data (Fuhrman and Lindsley, 1988). This model for ternary feldspar predicts plagioclase compositions that are more Or-rich and alkali feldspar compositions that are more An-rich than those calculated by Nekvasil (1988a).

Calculated phase relations in the synthetic granite system agree favorably with experimentally obtained relations in the bounding subsystems (Nekvasil and Burnham, 1987) and within the compositional volume (Nekvasil, 1988a, 1988b). Although experimental data on the sodic region of the system are sparse, the results of comparisons throughout the system lend validity to the use of the model for predictive calculations within this region. Evaluation of the accuracy of the predicted placement of the geometric elements in T-X space must await new high-temperature experimental data. However, the geometric relations between the two-feldspar surface and the feldspar solvus and the crystallization trends arising from their relative positions are essentially independent

Fig. 3. Schematic representation of the variation in equilibrium crystallization histories of magmas undergoing crystallization of feldspar at constant H_2O -activity (a_w). The relative positions of the liquidus (in this case either the two-feldspar curve for quartz-free compositions or the four-phase curve for quartz-saturated compositions) and corresponding polythermal solvus section are shown by the solid curves. (a) The bulk composition (shown by the star) lies within the solvus T-X volume at the solidus temperature. The three-phase triangles (dashed lines) indicate the evolution of the three-phase equilibria. The heavy curves with arrows indicate the variation in feldspar composition and melt during crystallization; the arrowheads indicate the direction of decreasing temperature. Although two feldspars remain part of the equilibrium assemblage to the solidus temperature, they may either precipitate simultaneously, or one feldspar may undergo incomplete resorption as the temperature decreases. (b) The bulk composition lies in a region outside the T-X volume of the feldspar solvus and away from the two-feldspar + L curve (or four-phase curve, if Qz-saturated). In this case only one feldspar crystallizes to the solidus temperature. (c) The bulk composition lies outside of the T-X volume of the solvus but between the solvus volume and the liquidus curve. At some stage of the crystallization history two feldspars are stabilized, but eventually only one feldspar remains stable. Once complete resorption of one feldspar has taken place, the melt will move off the two-feldspar curve.

of the thermodynamic models used. Calculations using other thermodynamic solution models for the feldspars (e.g., Nekvasil, 1988a; Lindsley and Nekvasil, 1989; Hovis, personal communication) and melt (e.g., ideal mixing) yield the same trends and conclusions as discussed below.

Figures 4a and 4b show the calculated PAL curve and corresponding polythermal solvus section (which indicates the compositions of feldspars in equilibrium with melt along the PAL curve) with selected three-phase triangles at 2 kbar for $a_w = 1.0$ (~5.8 wt%) and $a_w = 0.1$ (~1.2 wt%) respectively, in the Qz-free system Ab-Or-An-(H₂O) projected from H₂O as a simplified model for the synthetic granite system. The PAL curve near the Or-An-(H₂O) sideline is metastable with respect to leucite





Fig. 4. Calculated phase relations in the system Ab-Or-An-(H,O) at 2 kbar for (a) $a_w = 1.0$, and (b) $a_w = 0.1$ showing the plagioclase + alkali feldspar + L (PAL) curve and the corresponding polythermal solvus section (which indicates the compositions of feldspars in equilibrium with melt along the PAL curve). The calculated composition of feldspar at the consolute point on the polythermal solvus section is given by the letter k. The trachytes of Fig. 1 are plotted for reference. The arrowheads on the Ab-Or base indicate the position of the An-free thermal minimum. Selected three-phase triangles have been included for reference. (a) The composition represented by the star is from southeast Queensland (with projected composition An_{4.7}Ab_{58.3}-Or₃₇₀); the evolution of its melt and crystalline phases during equilibrium crystallization are shown by the dash-dot curves with arrows. The dashed field boundaries are as in (b) below; the field labels (A–D in [b]) have been omitted for clarity. (b) $a_w = 0.1$.

Symbols are as in (a). The composition represented by the star is from Sierra la Virulente (with projected composition An_{8.4}Ab_{53.5}Or_{38.1}); the evolution of its melt and crystalline phases during equilibrium crystallization are shown by the dash-dot curves with arrows. The regions labeled A, B, C, and D indicate ranges of bulk compositions for which complete resorption of plagioclase (A), complete resorption of alkali feldspar (B), incomplete resorption of plagioclase (C), or incomplete resorption of alkali feldspar (D), is expected at some stage during the equilibrium crystallization history. Compositions a-g are plotted for reference to Fig. 5. Point n is the neutral point of Abbott and indicates the melt composition for which the back tangent to the change in liquid composition intersects the alkali feldspar composition. It marks the point at which a melt undergoing fractional crystallization along the PAL curve will leave the curve upon further crystallization.

and a silica-enriched liquid (Goranson, 1938; Boettcher et al., 1984). The H₂O-saturated PAL curve lies at lower An contents than that for $a_w = 0.1$ and extends closer to the Ab-Or base. The contraction of the Af + L (+ V) field indicates that at high H₂O contents it is likely that plagioclase will be the feldspar that forms first and that the melt must become considerably depleted in An content before alkali feldspar will be stabilized. As anticipated by Tuttle and Bowen (1958), Stewart and Roseboom (1962), Carmichael (1963), and others, the twofeldspar region of the solidus contracts at the higher temperatures induced by lower water activity, resulting in two feldspars with distinctly more ternary character than those crystallizing under H_2O -saturated conditions. The

The geometric relations between the solvus and the two-feldspar curve determine the compositional space in which a bulk composition must lie if complete resorption of one of the feldspars will take place during equilibrium crystallization. Area A in Figure 4b, which is bounded by the envelope enclosing L + Pl tie lines of the three phase triangles that fall outside of the solvus, the line connecting the composition of the melt at the termination of the PAL curve to the composition of the feldspar at the consolute point on the polythermal solvus section, and the portion of the polythermal solvus section between the intersections of these curves, is the region in which a bulk composition must lie if alkali feldspar will be completely resorbed during equilibrium crystallization. Similarly, area B, which is bounded by the line connecting the termination of the two-feldspar curve to the consolute point on the polythermal solvus section, the PAL curve, and the polythermal solvus section between the intersections of these curves, is the region in which a bulk composition must lie for plagioclase to be completely resorbed during crystallization. Inasmuch as the termination of the twofeldspar curve lies at a composition less potassic than the composition of the consolute point for high H₂O contents and yet lies at a higher Or content than the consolute point for low H₂O contents, the region of complete resorption of alkali feldspar changes its configuration and becomes a smaller percentage of the complete resorptional region with decreasing H₂O content. Additionally, the entire region of complete resorption (areas A and B) shifts to higher An contents with decreasing H₂O contents, requiring bulk compositions with higher An or lower Or contents for complete resorption of either feldspar to occur. The very small region of complete resorption of alkali feldspar at low H₂O contents indicates that for hightemperature feldspathic melts (e.g., trachytes), plagioclase is much more likely than alkali feldspar to undergo resorption.

For bulk compositions lying within the solvus T-X volume at the solidus temperature, precipitation of feldspar can take place in either coprecipitational or resorptional mode, but complete resorption of a feldspar cannot occur during equilibrium crystallization. Simple mass balance constraints for the three components and three phases were used to determine the bulk compositional region (areas C and D in Fig. 4b) in which incomplete resorption will commence at some stage before the last 0.5% of the system crystallizes. Figure 5 shows calculated variations in plagioclase proportions during equilibrium crystallization along the PAL curve for the series of bulk compositions a-g indicated in Figure 4b. At high bulk An contents, once the PAL curve is reached, two feldspars will coprecipitate to the solidus temperature (as indicated by the positive slope of curve a in Fig. 5). As the bulk An content is decreased, however, bulk compositions are obtained for which coprecipitation changes to resorption



of a feldspar (e.g., plagioclase, for the compositions d-gin Fig. 5). The arrows (in Fig. 5) indicate the onset of resorption of plagioclase. As the bulk An content is decreased further, the onset of resorptional behavior commences at an earlier stage of the equilibrium crystallization history. Such calculations for several bulk compositional series (as in Fig. 5) indicate a locus of points describing a curved boundary of a region (region C in Fig. 4b) in which the high proportion of alkali feldspar in the system and the more An-rich nature of this feldspar relative to the melt requires the resorption of some plagioclase to release An. Compositions more An-rich than this boundary have a small enough proportion of alkali feldspar at the solidus temperature that the melt can provide the An requirements for both feldspars during crystallization. Similar calculations outline the region of bulk compositions for which alkali feldspar will undergo partial resorption (region D of Fig. 4b).

As seen in Figures 4a and 4b, the consolute point (k) on each solvus section separates the very minor region of incomplete resorption of alkali feldspar from the major field of incomplete resorption of plagioclase. The region of incomplete resorption of plagioclase shrinks markedly under H_2O -saturated conditions (cf. Figs. 4a and 4b). The trachytes plotted for reference (in Figs. 4a and 4b) indicate that at low H_2O contents, even for equilibrium crystallization, a crystallization path involving resorption will generally be required. If the H_2O content is sufficiently low, complete resorption of plagioclase could take place

30 Plagioclase proportion (mol%) 25 b 20 C 15 d e শ 10 ♠ 5 0 0.39 0.41 0.33 0.35 0.37 0.29 0.31 Position along PAL curve (Xab)

40

35

P=2kbar; a(w)=0.1



Fig. 6. (a) Variation in phase proportions (in mol%) during equilibrium crystallization under H_2O -saturated conditions along the two-feldspar curve for the projected southeast Queensland bulk composition of Fig. 4a. Symbols: Pl, plagioclase; Af, alkali feldspar; M, hydrous melt. Numbers in parenthesis refer to temperature in °C. (b) Variation in phase proportions (in mol%) during equilibrium crystallization under H_2O -undersaturated conditions along the PAL curve for the projected Sierra la Virulente bulk composition of Fig. 4b. Symbols are as in (a).

during equilibrium crystallization; at higher H_2O contents incomplete resorption would be more likely.

Variations in phase proportions along the two-feldspar curve have been calculated for a southeast Queensland trachyte and a Sierra la Virulente trachyte assuming they crystallized under equilibrium conditions with a constant (externally buffered) H_2O content of the magmas; the results are in Figures 6a and 6b. Plagioclase is the liquidus phase for both compositions. The projected southeast

Oueensland trachyte composition used in the calculations for H₂O-saturated conditions lies directly on the solvus curve, thereby requiring that all of the plagioclase must have just undergone complete resorption by reaction with the melt when the solidus temperature is reached. As is seen by the reversal in slope of the Pl curve in Figure 6a, early precipitation of plagioclase (+ Af) is followed by complete resorption of plagioclase. Once resorption commences, the variation in abundance of plagioclase is highly nonlinear, with the majority of resorption occurring within a very small temperature interval close to the solidus temperature. The projected composition of the Sierra la Virulente trachyte, on the other hand, lies within the field of complete resorption of plagioclase. In this case, once the PAL curve is reached and alkali feldspar begins to crystallize, plagioclase immediately begins reacting with the melt (Fig. 6b), and this reaction goes to completion once the bulk composition lies on the tie line between alkali feldspar and melt. At this stage further crystallization (of alkali feldspar only) will result in movement of the melt off the two-feldspar curve and into the Af + L field.

The equilibrium crystallization paths described above differ significantly from those of fractional crystallization. Once the PAL curve is reached during fractional crystallization, the melt composition will change in one of the following two ways. If the back tangent to the PAL curve at any melt composition intersects the corresponding twofeldspar tie line, then the melt will continue to evolve along the PAL curve. If however no intersection occurs, then continued fractional crystallization will drive the melt off the PAL curve into the Af + L field. For every condition of pressure and H₂O activity (at which the PAL curve does not intersect the Ab-Or sideline), there is a unique melt composition along the PAL curve at which the back tangent to the PAL curve intersects the corresponding two-feldspar tie line at the alkali-feldspar composition. This composition marks the "neutral" point of Abbott (1978). For fractional crystallization, this point also indicates where the PAL curve changes from even to odd (that is, from eutectic-like to peritectic-like). Any melt that reaches the PAL curve on the Or-side of the neutral point during fractional crystallization will evolve along this curve until the neutral point is reached. At this point the melt composition will move off the PAL curve. Initial compositions for which fractional crystallization drives the melt onto the PAL curve on the sodic side of the neutral point will experience no evolution along the PAL curve but will instead leave the curve immediately.

If the neutral point also marks the composition where the PAL curve changes from eutectic-like to peritecticlike for equilibrium crystallization, then melts that reach the PAL curve on the sodic side of the neutral point during equilibrium crystallization should begin resorbing plagioclase just as the PAL curve is reached. As discussed below, however, this is generally not the case. The calculated composition of the neutral point at 2 kbar and a_w = 0.1, for example, is 31 mol% Ab. Calculated changes



Fig. 7. Calculated phase relations in the system Ab-Or-An -(H₂O) at 5 kbar for (a) $a_w = 1.0$ and (b) $a_w = 0.1$. Fields and symbols are as in Fig. 4a. The composition represented by the star in (b) is from the Kane Springs Wash caldera (with projected composition An_{11.6}Ab_{53.4}Or_{35.0}); the evolution of the composition of its melt and crystalline phases during equilibrium crystallization are shown by the dash-dot arrowed curves. The fields are as in Fig. 4b. There is no region of resorption in (a).

in the proportion of plagioclase crystallizing along the PAL curve under equilibrium conditions for a series of bulk compositions indicate the composition along the PAL curve at which coprecipitation of plagioclase and alkali feldspar is replaced by resorption of plagioclase for each bulk composition. As indicated in Figure 5 (for the bulk compositions a-g of Fig. 4b), the position along the PAL curve where resorption commences depends upon bulk composition; coprecipitation can continue well past the neutral point along the PAL curve. However, bulk compositions reaching the solidus temperature before the melt has evolved to the neutral point will not undergo any resorptional behavior; therefore, the two-feldspar tie line indicating the solid compositions at the neutral point represents a limit for the extent of the field of incomplete resorption of plagioclase (area C in Fig. 4b). Calculations such as those conducted for Figure 5 readily indicate that reaching the neutral point during evolution of a melt along the PAL curve is a necessary, but insufficient, condition

for the involvement of a resorptional stage during equilibrium crystallization. This conclusion regarding the significance of the neutral point for equilibrium crystallization was also reached by Boettcher (1980) in his analysis of the system Ab-Or- H_2O .

Figures 7a and 7b show the calculated phase relations at 5 kbar in the feldspar system for $a_w = 1.0$ (~8.5 wt% H₂O) and $a_w = 0.1$ (~1.5 wt% H₂O). Under H₂O-saturated conditions, the PAL curve extends completely to the Ab-Or-H₂O sideline, implying that, in the system Ab-Or-H₂O, the solvus has been intersected before the solidus temperature is reached (Yoder et al., 1957). The higher water solubility in H₂O-saturated 5-kbar melts results in decreased liquidus temperatures, a concomitant expansion of the feldspar solvus section relative to that at 2 kbar, and a loss of the region of resorption. All of the trachytes plotted have bulk compositions lying within the solvus region at this pressure and H₂O content. For these magmas at 5 kbar, two feldspars will precipitate eventu-



Fig. 8. Variation in phase proportions (in mol%) during equilibrium crystallization under H_2O -undersaturated conditions along the PAL curve for the projected Kane Springs Wash bulk composition in Fig. 7b. Symbols are as in Fig. 6a.

ally, and both will remain present to the solidus temperature, should the H₂O content build up to saturation during crystallization. At low H₂O activities, the effect of increasing pressure is to increase temperatures along the two-feldspar surface (Nekvasil, 1988b). There is a slight shift of the two-feldspar curve to higher An contents but a stronger contraction of the solvus section. This results in a net expansion of the compositional region of complete resorption. The variations in phase proportions along the PAL curve for a Kane Springs Wash composition at low $a_{\rm w}$ are shown in Figure 8. Within a temperature range of 7 °C, the melt moves from a coprecipitational regime to one of resorption. Unlike the southeast Queensland composition (Fig. 6b), the solidus temperature has not been reached when plagioclase is completely resorbed; instead, the system is only 60% crystalline. The change in mode is not reflected in the variation of the fraction of liquid but in the dramatic increase in proportions of alkali feldspar.

Comparison of Figures 4a, 4b, 7a, and 7b indicates that temperature has the greatest effect on the extent of the resorptional regime. Therefore, resorption of plagioclase is most likely for trachytic and syenitic magmas during the early stages of their crystallization history, while the H_2O content is low. It can be concluded that the requirements for a felsic magma to enter the resorptional field during crystallization are that the bulk composition be sodic and at relatively high temperature (i.e., dry). The decrease in H_2O -solubility with decreasing pressure indicates that at low pressures it may even be possible to enter the resorptional regime under H_2O -saturated conditions; however, the bulk composition must be much lower in An content relative to that required at higher pressures.

The calculated phase relations (Figs. 4 and 7) involve only the Qz-free system Ab-Or-An-(H₂O). Although the trachytes plotted in Figure 1b are not Qz-saturated, they do contain significant proportions of normative Qz component. Therefore, the effect of excess silica on the extent of the resorptional regime must be evaluated quantitatively. The calculated effect of normative Qz component in the system is shown in Figures 9a and 9b at 2 kbar in projections of the four- (or five-) phase curve from the Oz apex in the synthetic granite system into the feldspar system at $a_{\rm w} = 1.0$ and $a_{\rm w} = 0.1$, respectively. As predicted by Carmichael (1963) and Abbott (1978), the addition of diluting components such as quartz results in temperature depression and concomitant expansion of the solvus section. At low a_w and 2 kbar confining pressure, the resorptional region is still sizeable at Qz-saturation and could be entered by many of the trachytes plotted. This indicates that quartz saturation alone does not preclude resorptional behavior of the feldspars; rocks such as quartz syenites may show evidence of having gone through a resorptional regime at one stage of their crystallizational history. There is a shift, however, of the complete resorption region towards more albitic and less anorthitic compositions with increasing normative Qz components. Under H₂O- and Qz-saturated conditions at 2 kbar, the resorptional region has been almost completely swamped by the expansion of the solvus section (Fig. 9a) indicating that H₂O-rich siliceous rocks would not be able to enter the resorptional region during the late stages of their crystallization history.

Figure 10 indicates the variation of phase proportions along the four-phase curve in the synthetic granite system $(a_w = 0.1)$ for the Sierra la Virulente composition of Figure 4b. This curve is reached from the two-feldspar surface as the melt attains saturation with quartz. Just as the curve is reached from the two-feldspar surface, the system consists of 30 mol% plagioclase, 21 mol% alkali feldspar, and 49 mol% melt. The solidus temperature is reached within 2 °C as the plagioclase drops to 8%, and alkali feldspar and quartz climb to 51 and 41% respectively. Plagioclase begins resorbing on the two-feldspar surface before the four-phase curve is reached. This behavior continues once the melt has reached the four-phase curve, although quartz begins to precipitate. For this composition, the solidus temperature is reached before complete resorption of plagioclase takes place, thereby differing from the behavior of the Qz-free equivalent composition (Fig. 6c).

IMPLICATIONS FOR TRACHYTES AND SYENITES

When compared with common granites and rhyolites, trachytes and their plutonic equivalents, syenites, tend to be lower in An and Or content (and hence are more albitic) as well as lower in Qz and other diluting components. Additionally, they commonly lack hydrous minerals and often contain evidence (e.g., ternary feldspars) for high temperatures. If the compositions of the trachytes plotted in Figure 1 can be considered as typical,



Fig. 9. Calculated Pl + Af + Q + L (+ V) (PAQL) curve at 2 kbar for (a) $a_w = 1.0$ and (b) $a_w = 0.1$ projected from the Qz apex of the synthetic granite system onto the system Ab-Or-An-(H₂O) and the corresponding polythermal solvus sections. Fields and symbols are as in Fig. 4b. The composition represented by the star in (b) is the Sierra la Virulente composition of Fig. 4b (An_{7.1}Ab_{45.2}Or_{32.3}Qz_{15.4} or, in projection from Qz, An_{8.4}Ab_{53.5}Or_{38.1}); the evolution of its melt and crystalline phases during equilibrium crystallization are shown by the dash-dot curves with arrows. The regions of resorption in (a) are very small and are not shown.

then the melt-evolution paths of trachytes under nearequilibrium crystallization conditions are likely to intersect regions in which a reaction relation between plagioclase and melt to produce alkali feldspar replaces coprecipitation of two feldspars, thereby resulting in at least incomplete resorption of plagioclase. This becomes increasingly likely at high pressures and low H₂O contents. although low pressures do not preclude resorption as long as the H₂O content is also low. As both H₂O and Qz have the same qualitative effect of reducing the temperatures at which two feldspars and melt coexist, resorption is essentially precluded for compositions that are both H₂Oand quartz-saturated, unless the pressure is very low. The degree to which any resorption will take place during equilibrium crystallization is highly dependent upon bulk composition, H₂O content, and the presence of diluting components such as quartz. This is very different from

the case of fractional crystallization, where there is a unique point, independent of bulk composition, along the PAL curve for every pressure and a_w at which coprecipitational behavior is replaced by resorptional behavior (Abbott, 1978).

The phase relations discussed above are for fixed H_2O and Qz activities and indicate the dramatic effect of H_2O and Qz on the resorptional regime in the synthetic granite system. However, natural compositions are not likely to be buffered in either H_2O or Qz contents through the presence of hydrous minerals or a fluid phase (in the case of H_2O) or through the precipitation of quartz (in the case of Qz) until the late stages of their crystallization history. During the unbuffered stages of their crystallization path, the melts will pass through a continuum of conditions intermediate to those shown at water activities of 0.1 to 1.0. This implies that as H_2O and Qz activities increase



Fig. 10. Variation in phase proportions (in mol%) during equilibrium crystallization under H_2O -undersaturated conditions along the PAQL curve for the projected Sierra la Virulente composition of Figs. 4a and 9b. Symbols: Qz, quartz (SiO₂); others are as in Fig. 6a.

during crystallization, the resorptional regions continuously contract. Unlike in the case of buffered crystallization, during which once a resorptional regime is entered, resorption will continue to the solidus temperature, in the unbuffered case it may be possible to re-enter the coprecipitational regime because of the increase of H₂O and non-feldspathic components in the melt during equilibrium crystallization. Such magmas may have a complex crystallization history characterized by precipitation of first one and then two feldspars, followed by partial or complete resorption of one feldspar (most likely plagioclase) and then reprecipitation of two feldspars. Entrance into the resorptional regime would be most likely to occur during the early stages of the crystallization history while the melt is still hot and low in diluting components. A record of crystallization histories involving complete resorption of plagioclases appears to be preserved by accidental inclusions of partially resorbed andesine-oligoclase grains within anorthoclase-sodic sanidine crystals. This phenomenon has been reported widely (e.g., Rahman and MacKenzie, 1969; Ewart, 1981).

During the resorption of plagioclase there is a considerable increase in the proportion of alkali feldspar. If this occurs while a significant amount of melt is still present, grain-boundary interference will be avoided, and large crystals of alkali-feldspar crystals could grow during the resorptional phase. Furthermore, if quenching to produce a trachyte did not occur, but rather the magma were able to continue to crystallize, concentrating H_2O and silica in the process, it may be possible to grow a late-stage second generation of two feldspars. This possibility was also postulated by Abbott (1978) as a result of fractional crystallization along the PAL curve and the four-phase curve in

the synthetic granite system (i.e., the PAQL curve). Detailed calculations of unbuffered crystallization paths and comparisons with natural syenitic and trachytic rocks are needed to evaluate the likelihood of such paths and will be the subject of a future article.

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