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The calculated individual effects of pressure and water content on phase equilibria in the granite system

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Abstract—The revised quasi-crystalline model has been used to calculate phase relations in the granite (An–Ab–Or–Qz–(H_2O)) system and bounding binary and ternary subsystems for pressures and water contents of relevance to felsic magma crystallization. The predicted phase relations have been compared with available H_2O–saturated experimental phase equilibrium data on the subsystems Ab–Or–H_2O, An–Ab–H_2O and An–Or–H_2O and indicate good agreement. Comparisons of experimental data against calculated phase relations for the bounding subsystems Ab–Or–Qz–H_2O, Ab–An–Qz–H_2O, Ab–Or–An–H_2O and An–Or–Qz–H_2O also indicate favorable agreement, particularly for the An–poor regions.

Use of the model in a predictive capacity to calculate H_2O–undersaturated phase relations for the granite system and relevant subsystems indicates that the effect of decreasing pressure or increasing H_2O content is the differential contraction of the Qz + L field and concommitant shift of the feldspar/quartz cotectics towards more Qz-rich melt compositions. Although H_2O–saturated phase relations also indicate a shift of the feldspar/quartz cotectics toward the Qz apex with decreasing pressure, the magnitude of this shift is less than for H_2O–undersaturated conditions. The shift in cotectic position under H_2O–saturated conditions is attributable to the combination of the opposing effects of changing both pressure and H_2O content.

INTRODUCTION

DEDUCTION of the crystallization and melting histories of igneous rocks purely from studies of natural rocks is complex because natural rocks are end products of numerous possible magmatic processes. In order to be able to evaluate the effects of natural magmatic processes on the crystallization behavior of magmas, the individual effects of pressure, volatile content and melt composition on phase equilibria must be understood. These variables can be isolated through experimentation under controlled laboratory conditions. Information obtained through experimental investigations on the effects of these variables on phase equilibria can be combined with data on natural rocks (*i.e.*, compositional, modal, and textural) to obtain more specific information regarding possible magmatic histories.

Experimental petrologic research has followed two main directions. Natural rock compositions have been melted under pressure and temperature conditions, and volatile contents which approximate those believed to exist within the earth's crust and mantle (*e.g.*, PIWINSKII and WYLLIE, 1968; 1970; EGGLER, 1972; CLEMENS and WALL, 1981). Such experimental investigations can effectively isolate variables such as pressure and volatile content; however, they do not effectively isolate compositional variables. It is, thus, difficult to generalize quantitatively the results of such experimental investigations and apply them to rocks much different in composition.

An alternate experimental approach was exemplified by the pioneering efforts of BOWEN (1913) and TUTTLE and BOWEN (1958) and more recently by workers such as BOETTCHER *et al.* (1984). This approach focuses on compositionally simple systems in order to evaluate systematically the effects of varying compositional variables in addition to the intensive variables pressure and temperature. Attempts to use information on the melting behavior of simple systems to explain the behavior of more complex systems, have led to the use of thermodynamic formalisms (*e.g.*, a Margules formalism). These formalisms have been applied to the interpretation of phase equilibrium data in order to model melt component mixing behavior (*e.g.*, BOTTINGA and RICHET, 1978; BERMAN and BROWN, 1984). Alternatively, direct calorimetric measurements of heats of mixing in simple systems have been conducted (*e.g.*, NAVROTSKY *et al.*, 1980; HERVIG and NAVROTSKY, 1984) which obviate the need for use of phase equilibrium data in the evaluation of melt component mixing behavior. Attempts have been made to use calorimetric results to calculate liquidus surfaces for systems in which insufficient calorimetric data are available (*e.g.*, WEILL *et al.*, 1980; NAVROTSKY *et al.*, 1980) with varying degrees of success. However, none of the above approaches have been able to predict phase equilibria in systems more complex than ternary using data from simple systems. GHIORSO *et al.* (1983) avoided the problems involved in extending the results of such approaches to complex natural compositions by using a Margules formalism to obtain mixing parameters from experimental data on natural multicomponent mafic compositions in a massive regression approach (see also GHIORSO and KELEMAN, 1987). Such an approach has intrinsic problems in terms of predictive capabilities for compositions lying outside the range used in the regression. Although the final goal of all modelling attempts on silicate melts is the accurate prediction of phase relations for natural compositions, insight into the chemical principles influencing melt behavior (*e.g.*, mixing behavior of melt components) can most readily be obtained through study of the behavior of compositionally simple systems as well as of the variations in phase relations induced by systematically increasing the number of compositional variables. Such an approach was adopted by BURNHAM (1981) in his development of the "quasi-crystalline" model.

The quasi-crystalline model of silicate melts has been extensively revised and refined in order to permit calculation of phase equilibria in the system Ab–Or–An–Qz–H_2O (granite system) for a variety of pressures and H_2O contents of relevance to felsic magma genesis (NEKVASIL, 1986). The modifications and refinements of the model as well as the sources of data used in the development of the revised model have been outlined in BURNHAM and NEKVASIL (1986). Calculated phase relations based on the revised model differ to the greatest extent from those based on the model of BURNHAM (1981) in the plagioclase-bearing subsystems of the granite system and differ only slightly in the haplogranite system. Through application of the revised model (BURNHAM and NEKVASIL, 1986), it was implied that use of experimental data for the fusion of the pure aluminosilicates as well as for the aluminosilicate-quartz (A + Qz) solidi in combination with the speciation model, permits calculation of phase equilibria throughout the granite system. In the following discussion, the model will be used to demonstrate the calculated individual effects of pressure and H_2O content on phase equilibria in the granite system. However, as a preliminary step to the utilization of the predictive capabilities of the model, such capabilities will be assessed by comparing calculated phase relations with those experimentally determined for subsystems of the granite system.

THE REVISED QUASI-CRYSTALLINE MODEL

The quasi-crystalline model (BURNHAM, 1981; BURNHAM and NEKVASIL, 1986) treats igneous rock melts as multicomponent solutions of chemically discrete and thermodynamically distinct neutral complexes or species that are correlated with thermodynamic components. It is considered in the model that these species mimic the stoichiometry of the solid phases that crystallize from the melts. Additionally, further species may be produced by homogeneous speciation reactions (*i.e.*, dissociation of a component or interaction between two or more components). The melt species (components) produced by speciation reactions have different stoichiometries and different thermodynamic properties relative to the components involved in the homogeneous reactions.

The revised quasi-crystalline model (BURNHAM and NEKVASIL, 1986; NEKVASIL, 1986) retains the basic premises of the model as outlined by BURNHAM (1981). The refinements presented by the revised model are mainly constrained to the quantified aspects of the model. Refined internally-consistent expressions for the standard state free energies of fusion for the components *ab* (albite), *an* (anorthite), *or* (sanidine) and *qz* (Si_4O_8) were obtained. This was done by using phase equilibrium data for the systems Ab–An (BOWEN, 1913) at 1 atm, Or–H_2O (LAMBERT *et al.*, 1969), Qz–H_2O (KENNEDY *et al.*, 1962) and Qz (JACKSON, 1976), calorimetric heats of fusion, and available data on molar volumes, thermal expansions and compressibilities for the components. (See BURNHAM and NEKVASIL, 1986 for details on the data used and their sources.) The resulting expressions for the standard state free energies of fusion of the four components (listed in BURNHAM and NEKVASIL, 1986) were used to calculate the activities of the melt components *ab, an* and *or* along their experimentally-determined anhydrous solidi. The albite–H_2O model (BURNHAM, 1975) was used in addition, to evaluate the activities of these components along their H_2O-saturated solidi. In the selection of experimental solidi for this purpose, preference was given to the recent data of workers such as BOETTCHER *et al.* (1982, 1984).

As was predicted by BURNHAM (1981) and noted by BOETTCHER *et al.* (1982, 1984), with increasing pressure, the activities of the components *ab* and *an,* calculated using the revised model, decrease from 1.0 along their anhydrous and H_2O–saturated solidi. For the *or* component, however, the calculated activity along its dry and H_2O–saturated solidi decreases from 1.0 with *decreasing* pressure, reflecting the direction of increased proximity to the incongruent melting region (for details on the experimental data considered, see BURNHAM and NEKVASIL, 1986). The extent of lowering of the activities (relative to the experimental mol fractions) along the solidi has been interpreted as indicative of the extent of dissociation of the components in the melt through homogeneous reactions (BURNHAM, 1981; BOETTCHER *et al.,* 1984), and has been quantified as a function of pressure. In order to interpret the melt component behavior in the aluminosilicate-quartz binaries, the calculated lowering of the melt component activities (relative to their experimental mol fractions) at the eutectics was assumed to be attributable solely to interactions between the two relevant components. These interactions were considered describable by homogeneous stoichiometric reactions (NEKVASIL, 1986; BURNHAM and NEKVASIL, 1986). By using experimental pressure-temperature data on the aluminosilicate (A) + Qz solidi, the activity of each silicate component was calculated. A stoichiometric relation describing the lowering of the activities of each component from its experimental mole fraction entirely by interaction of the two components was formulated for each A–Qz binary. The stoichiometric relations permit calculation of the eutectic composition and its variation with pressure for each Qz–bearing binary system. Each stoichiometric relation then yielded the extent of interaction of *qz* (silica melt component) with the aluminosilicate component *a*. The extent of interaction of *a* with *qz* in each of the anhydrous and H_2O-saturated Qz–bearing "binaries" was quantified as a function of pressure using the calculated eutectic compositions. A detailed discussion is presented in NEKVASIL (1986) for each binary and the resulting equations have been summarized in BURNHAM and NEKVASIL (1986).

It was assumed that the lowering of the activity of *qz* and *a* in the region $X_a \leq X_a(E)$ (where $X_a(E)$ is the binary eutectic composition) is solely a result of interaction (and is not a combined result of dissociation of *a* as well as interaction of *a* with *qz*). This assumption was adopted due to the remarkable agreement of the predicted variation in eutectic composition with pressure with available compositional data in the A + Qz systems and the observation that the activity of *qz* along its pure solidus does not vary from 1.0 with pressure. The amount of lowering of the activities of the components from their experimental mole fractions in this region is obtained by weighting the value at the eutectics (from which the compositional dependence has been removed) by the product of the mol fractions of the two interacting components (in accordance with the mass action principle). In order to calculate H_2O–undersaturated phase relations it was also assumed that the extent of interaction is linearly proportional to the H_2O content from the anhydrous to the H_2O–saturated "binaries." These assumptions permit calculation of H_2O–saturated and H_2O-undersaturated relations within the granite system. The region $X_a > X_a(E)$ is of interest primarily in the calculation of complete binary A_1–A_2 (aluminosilicate–aluminosilicate) liquidus relations. Inasmuch as interaction was assumed to contribute solely to the lowering of the activity of the *a* component at the eutectics, yet at the pure aluminosilicate sidelines the lowering was attributed to dissociation, within this region, both dissociation and interaction are likely to be taking place. Due to the complexities involved in trying to assess the amounts of each type of speciation, the total deviation of the activity from the mol fractions has been quantified in this region.

A mixing model was adopted for the two ternary solid solutions, plagioclase and alkali feldspar, for use in the calculation of phase equilibria in the system Ab–Or–An–Qz(–H_2O). An excess free energy formalism was used which yields a Margules expansion of the ternary excess free energy. This formalism takes into account the resulting interdependence of the asymmetric binary interaction parameters in a ternary solid solution (based on the discussion of ANDERSON and LINDSLEY, 1981). For the binary Ab–Or interaction parameters, the asymmetric regular solution model of THOMPSON and HOVIS (1979) was used. For binary plagioclase, the results of the polynomial fit of BLENCOE (personal communication, 1981) to G^{ex} (excess free energy of mixing of crystalline An and Ab components) based on the ion exchange data of SEIL and BLENCOE (1979 and personal communication) were refit to yield asymmetric regular solution parameters which are linear with temperature. These interaction parameters in turn yield activity coefficients for binary plagioclase which remain greater than 1.0 and fall within the range given by CARPENTER and FERRY (1984) when extrapolated to the temperatures of the 1 bar melting loop. Use of these parameters obviates the need for use of Al-avoidance entropies (HENRY *et al.,* 1982). In order to obtain interaction parameters for the mixing behavior of the crystalline components An and Or consistent with the newly derived regular solution interaction parameters for binary plagioclase, the method of GHIORSO (1984) was adopted (albeit in a modified form). Expressions for the activities for the ternary asymmetric regular solution were combined with the ternary solid solution data of SECK (1971a,b) in order to obtain, through regression, interaction parameters for the An–Or binary solid solution. The interaction parameters of all three binary regular solutions were then adopted for use in the calculation of ternary feldspar/melt equilibria using modified versions of the activity-composition expressions of GHIORSO (1984). A summary of the asymmetric regular solution interaction parameters used in the calculations of phase relations in the granite system is presented in Table 1. The complete activity–composition relations for ternary feldspar solid solutions are not presented here but are discussed in NEKVASIL (1986).

The refinements summarized above have resulted in the formulation of new activity–composition relations for the melt components, the selection and development of solid solution mixing models for the binary and ternary feldspars and the derivation of pressure and temperature–dependent expressions for the free energy of fusion of the components constrained by available calorimetric data.

COMPARISON OF CALCULATED AND EXPERIMENTAL PHASE EQUILIBRIA

Complete aluminosilicate–aluminosilicate (A_1–A_2) binary liquidus relations have been computed using the equation of equilibrium (obtained by equating chemical potentials of *a* in solid and melt) shown below.

Table 1. Interaction parameters W_{A1-A2}, $W_{A2-A1} = a + bT$ for the feldspar components according to the asymmetric binary regular solution formulation

$$G^{ex}_{A1,A2} = W_{A1,A2}X_{A1}X^2_{A2} + W_{A2,A1}X^2_{A1}X_{A2}{}^*$$

Interacting component			Coefficients	
A1	A2	Parameter W(cal)	a	b
Ab	Or	A1, A2	7404	−5.120
		A2, A1	4078	—
Ab	An	A1, A2	3377	−1.476
		A2, A1	2683	−1.882
An	Or	A1, A2	5980	2.581
		A2, A1	17931	−5.494

* For Ab–Or interaction:

$$G^{ex}_{A1,A2} = G^{ex}_{A1,A2} + 0.086PX_{Ab}X_{Or}.^{\dagger}$$

† See text for sources.

$$\mathrm{Ln}\frac{a_i^{\mathrm{hm(am)}}}{a_i^{\mathrm{s}}} = -\frac{\Delta G^0_{\mathrm{m}i}(1,T) + \int_1^{\mathrm{P}} \Delta V_{\mathrm{m}i} dP}{RT}, \quad (1)$$

where $a_i^{\mathrm{hm(am)}}$ is the activity of component i (*ab, or, an,* or *qz*) in the hydrous or anhydrous melt evaluated from the quantified activity-composition relations for the pure components (*i.e.* functions of pressure and H_2O content), and a_i^{s} is the activity of component i in crystalline solution, evaluated using the ternary asymmetric solution model briefly summarized above. $\Delta G^0_{\mathrm{m}i}(1, T)$ and $\Delta V_{\mathrm{m}i}$ are the standard state free energy of fusion at 1 bar and T and the volume of fusion of the component i, respectively. The calculation of ternary feldspar/melt equilibria involves the linking of three of the above expressions (one for each feldspar component) in the following manner

$$\frac{a_{ab}^{\mathrm{hm(am)}}}{\gamma_{ab}^{\mathrm{Pl(Af)}}}\exp\left[\frac{\Delta G^0_{\mathrm{m}ab}(1,T) + \int_1^{\mathrm{P}} \Delta V_{\mathrm{m}ab}}{RT}\right] + \frac{a_{an}^{\mathrm{hm(am)}}}{\gamma_{an}^{\mathrm{Pl(Af)}}}\exp\left[\frac{\Delta G^0_{\mathrm{m}an}(1,T) + \int_1^{\mathrm{P}} \Delta V_{\mathrm{m}an}\cdot dP}{RT}\right] + \frac{a_{or}^{\mathrm{hm(am)}}}{\gamma_{or}^{\mathrm{Pl(Af)}}}\exp\left[\frac{\Delta G^0_{\mathrm{m}or}(1,T) + \int_1^{\mathrm{P}} \Delta V_{\mathrm{m}or}\cdot dP}{RT}\right] = 1, \quad (2)$$

where $\gamma_i^{\mathrm{Pl(Af)}}$ refers to the activity coefficient of component i in plagioclase or alkali feldspar. This expression includes the constraint that the sum of the mol fractions of the crystalline components Ab, An, and Or must be unity. The cryoscopic equations $((\Delta G^0_{\mathrm{m}i}(1, T) + \int_1^{\mathrm{P}} \Delta V_{\mathrm{m}i}\, dP)/RT)$ for the components *ab, or, an,* and *qz* are a function of temperature and pressure and are listed in BURNHAM and NEKVASIL (1986) as are the activity-composition relations for the melt and crystalline components. The calculation of complete binary A_1–A_2 liquidus relations thus involves solving the relevant equations for the saturation temperature.

Figures 1a–c show the calculated binary liquidus relations for plagioclase at 1 bar and 2 and 5 kbar under H_2O-saturated conditions. The 1 bar melting loop was included for reference. It, however, provides no test of the model in that it was used in the derivation of internally-consistent expressions for the standard state free energies of fusion of *ab* and *an* (NEKVASIL, 1986). For the 2 kbar melting loop, the calculated melting relations can be compared

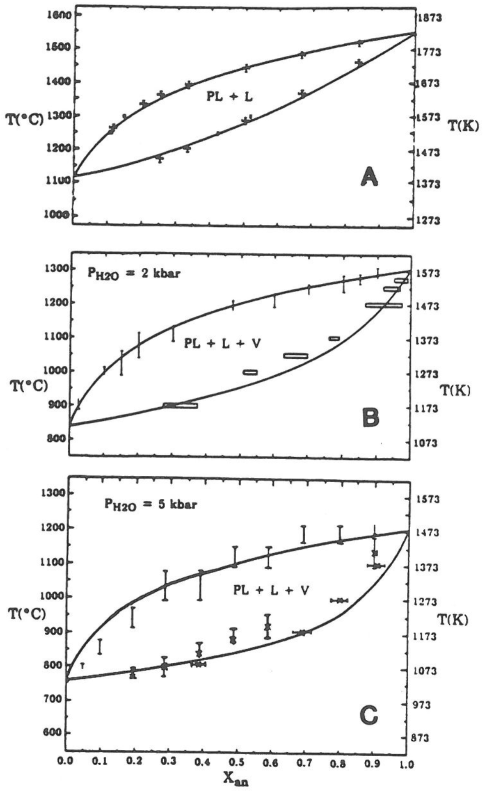

FIG. 1. Calculated plagioclase melting loop at (A) 1 bar, (B) P(H_2O) = 2 kbar and (C) P(H_2O) = 5 kbar. Experimental data, plotted for comparison, are from (A) BOWEN (1913); (B) ERIKSON (1979) (open rectangles indicate the compositional range obtained experimentally for each solidus datum) and (C) YODER *et al.* (1957) (vertical bars) and JOHANNES (1978) (horizontal bars). Error bars designated with a cross refer to solidus data.

against the experimental data of ERIKSON (1979). The calculated liquidus agrees well with the experimental data. The solidus also agrees in the regions close to the endmembers but indicates some discrepancies at intermediate compositions. Within this region, however, lie the greatest differences between equilibrium crystal and melt compositions and therefore, the intermediate compositions mark the compositional region in which the probability is greatest that the co-existing phases did not equilibrate in the run durations of the experiments. The greatest discrepancy occurs at 1000°C, a temperature at which ERIKSON (1979) noted direct evidence for disequilibrium in that he obtained inconsistent crystal compositions. Figure 1c shows the calculated melting loop at 5 kbar pressure and under H_2O-saturated conditions and, for comparison, the data of YODER *et al.* (1957) supplemented by solidus data of JOHANNES (1978). The liquidus data and sparse solidus data of YODER *et al.* (1957) indicate a narrower melting loop than that determined at P(H_2O) = 2 kbar by ERIKSON (1979), which would imply the unlikely condition of a positive temperature dependence of the solid solution interaction parameters for plagioclase. The solidus data of JOHANNES (1978), on the other hand, does indeed indicate a wider melting loop. Once again, the major discrepancies appear to occur in the region of intermediate plagioclase compositions. JOHANNES (1978) noted the difficulty in attaining equilibrium at temperatures below 900°C, therefore, the calculated melting loop may more realistically represent the true melting relations of plagioclase at this pressure.

Figures 2a–c show the calculated melting loops for the subsystem Ab–Or(–H_2O) at 1 bar, and 2 and 5 kbar pressure for H_2O-saturated conditions. As was the case for the calculation of the plagioclase melting relations, only the melting behavior of the pure components and the cryoscopic equations for

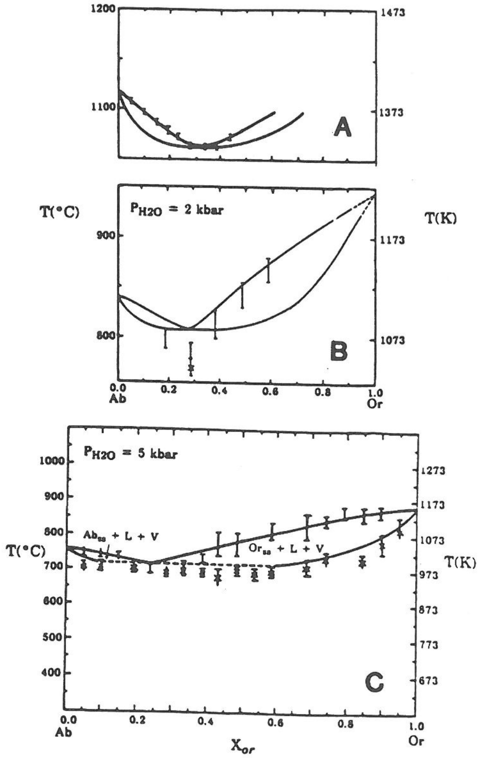

FIG. 2. Calculated Ab–Or melting relations at (A) 1 bar; (B) P(H_2O) = 2 kbar and (C) P(H_2O) = 5 kbar. Experimental data, plotted for comparison, are from (A) SCHAIRER (1950); (B) BOWEN and TUTTLE (1950) and (C) YODER *et al.* (1957). Solidus data are indicated by crosses.

ab and *or* were used in combination with a mixing model for binary alkali feldspar (*i.e.*, the asymmetric regular solution model of THOMPSON and HOVIS, 1979) in the calculations. The calculated 1 bar azeotropic relations of the system Ab–Or are shown in Figure 2a and the experimental data of SCHAIRER (1950) have been plotted for comparison. As evidenced by this figure, the agreement is very good. Figures 2b and 2c show the calculated melting loop and eutectic relations at 2 and 5 kbar (H_2O-saturated), respectively. Plotted for comparison in Figures 2b,c are the 2 kbar data of BOWEN and TUTTLE (1950) and the 5 kbar data of YODER *et al.* (1957), respectively. The calculated liquidus relations at each pressure agree with the experimental data. The calculated solidus temperature at both 2 and 5 kbar, however, is approximately 20 degrees higher than that experimentally determined.

The calculated phase relations for the H_2O–saturated system Or–An at 5 kbar are shown in Figure 3 along with the experimental data of YODER *et al.* (1957). Once again, the agreement is good. The slight discrepancy at high An contents is attributable to use of an H_2O–saturated melting curve based on the data of YODER (1965) and ERIKSON (1979) in the development of the revised model. [This curve lies at lower temperatures than the data of YODER *et al.* (1957).]. The calculated solidus once again appears to lie at a temperature about 20 degrees higher than that suggested by the experimental data.

Liquidus relations for the A–Qz(–H_2O) bounding binaries have been calculated. These calculations use the cryoscopic equation for each component and the activity-composition relations obtained from available pressure-temperature data on the A + Qz solidi (see BURNHAM and NEKVASIL, 1986 for details). Few experimental data are available for the liquidus limbs in these binary subsystems. Therefore, evaluation of the predicted liquidus limbs can not be readily undertaken. Consistency can be assessed, however, by comparison of the calculated and experimentally based phase relations of the ternary subsystems.

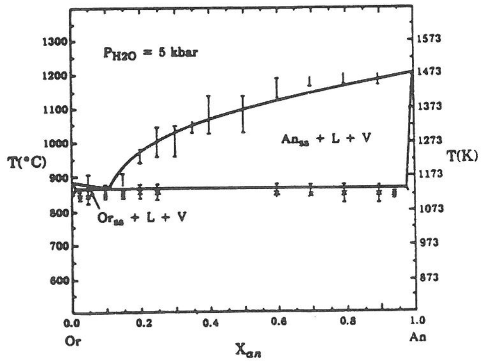

FIG. 3. Calculated An–Or melting relations at $P(H_2O)$ = 5 kbar. Experimental data, plotted for comparison are from YODER *et al.* (1957). Solidus data are indicated by crosses.

Figure 4 shows the phase relations in the haplogranite system at $P(H_2O) = 2$ kbar as determined by TUTTLE and BOWEN (1958). In general, the calculated liquidus relations (Figure 4b) agree with the experimental data in the bounding binaries as well as within the ternary. It is interesting to note that the 800°C isotherm appears to be drawn inconsistently, relative to the other isotherms in Figure 4a, a direct result of attempts by TUTTLE and BOWEN (1958) to incorporate their binary Ab–Or data. The calculated 800°C isotherm on the other hand, is consistent with the other calculated isotherms and the higher calculated binary minimum temperature (see above discussion of binary relations). The discrepancies between the positions of the calculated and experimentally based isotherms on the very steep quartz liquidus surface could be corrected by a small compositional change of 1–2 mol percent Qz. Such a correction of TUTTLE and BOWEN's (1958) compositions in this region is not unreasonable because they used an open-capsule technique in many of these experiments and may have preferentially lost silica to the fluid (BURNHAM, personal communication, 1983). The calculated 2 kbar minimum composition of $Qz_{34}Ab_{42}Or_{25}$ agrees well with that of TUTTLE and BOWEN (1958) ($Qz_{35}Ab_{40}Or_{25}$). TUTTLE and BOWEN (1958) also determined the compositions of feldspars coexisting with quartz and melt for two melt compositions (along the cotectic). Figure 4a shows a comparison of the data versus the calculated melt composition with which Or_6 and Or_{56} (determined by 690°C by TUTTLE and BOWEN (1958) and calculated at 712°C) and quartz are in equilibrium. The compositional agreement is within 2 mol percent. The calculated minimum temperature of 709°C, however, is higher than the <700°C approximated from TUTTLE and BOWEN (1958).

Figures 4c,d show the experimentally based phase relations for the haplogranite system as determined by LUTH *et al.* (1964) at 5 kbar under H_2O-saturated conditions and the calculated phase relations for comparison. As determined experimentally, the model predicts that above about 3.5 kbar, the feldspar solvus will be intersected by the liquidus surface and an additional cotectic will appear separating two feldspar + L fields. At $P(H_2O)$'s only slightly above that of the initial intersection of the ternary solvus, the binary solvus will not necessarily have been intersected because the binary Ab–Or mini-

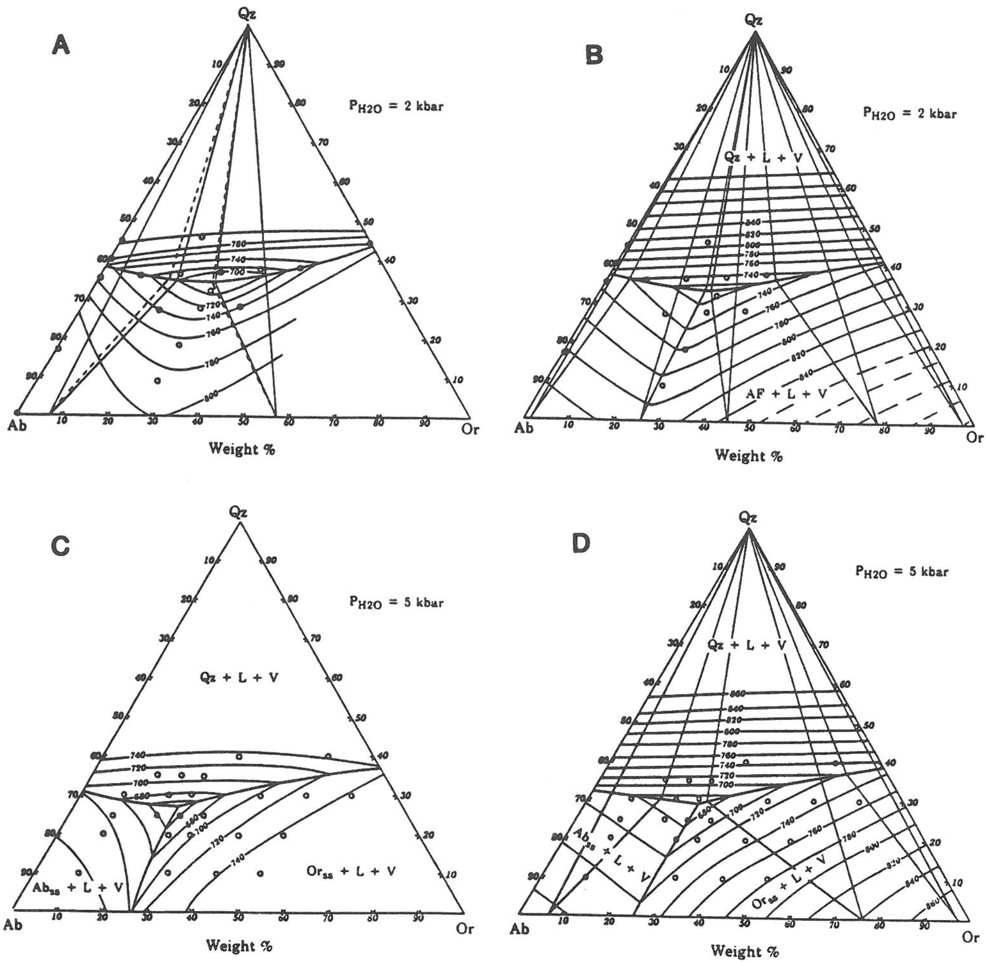

FIG. 4. Experimental data and calculated phase relations in the haplogranite system at P(H_2O) = 2 and 5 kbar. (A) Isotherms and experimental data (open circles) at P(H_2O) = 2 kbars from TUTTLE and BOWEN (1958). The solid three-phase triangles are based on the data of TUTTLE and BOWEN (1958); the dashed three-phase triangles are calculated and shown for comparison. (Note that the 700°C isotherm on the quartz liquidus surface as drawn by TUTTLE and BOWEN (1958) is thermodynamically implausible in curvature.) (B) Calculated phase relations at P(H_2O) = 2 kbar. Experimental data of TUTTLE and BOWEN (1958) (open circles) are plotted to facilitate comparison with (A). (C) Isotherms and experimental data of LUTH *et al.* (1964) (open circles) at P(H_2O) = 5 kbar. (D) Calculated phase relations at P(H_2O) = 5 kbar. Experimental data of LUTH *et al.* (1964) have been plotted to facilitate comparison with (C).

mum lies at higher temperatures than the ternary minimum. Therefore, at such pressures the feldspar cotectic will not extend fully to the Ab–Or sideline from the ternary eutectic. At P(H_2O) = 5 kbar, however, both the calculated and experimentally based phase relations indicate that the solvus has also been intersected in the binary. There is good agreement (within the stated experimental error of ±10°C) between most of the experimental points and the calculated relations. The calculated ternary eutectic composition of $Qz_{29}Ab_{46}Or_{25}$ compares well with the value of $Qz_{27}Ab_{50}Or_{23}$ of LUTH *et al.* (1964) as does the calculated eutectic temperature of 662°C with the experimentally determined ternary eutectic temperature of 650° ± 10°C. It is interesting to note that the 700°C isotherm as drawn by LUTH *et al.* (1964) (700°C) is inconsistent in curvature with respect to that of their other isotherms. This may have been induced by forcing agreement of their ternary data with their earlier determined binary Ab–Or eutectic temperature. If this isotherm were redrawn to be consistent with the others the binary eutectic temperature would be closer to the 725°C calculated. Calculated three-phase triangles are shown in Figure 4d and indicate the changes in alkali feldspar composition along the cotectic.

Data available for the other bounding ternary subsystems of the granite system are sparse. Figure 5 shows the cotectic and isotherms as determined by YODER (1968) at 5 kbar pressure under H_2O-saturated conditions for the system Ab–An–Qz–H_2O. For comparison, the calculated cotectic is also indicated. The calculated cotectic differs only slightly compositionally from that of YODER (1968) indicating a maximum compositional difference of 6 weight percent. The temperatures calculated along the cotectic agree with the experimentally based isotherms. However, there are significant differences in the calculated cotectic temperature for a given X_{ab}/X_{an} ratio of the melt. JOHANNES (1978) noted that the experiments of YODER (1968) were unreversed and he was unable to reproduce the cotectic temperatures obtained by YODER (1968).

Phase relations in the system Ab–Or–An–H_2O at $P(H_2O)$ = 5 kbar were determined by YODER *et al.* (1957); their results are shown in Figure 6a. Figure 6b shows the calculated liquidus relations under the same conditions of pressure and H_2O content. At high An contents agreement between the positions of the calculated isotherms and those drawn of YODER *et al.* (1957) is good. The greatest divergence occurs in the region of the cotectic. According to YODER *et al.* (1957), the liquidus surface has a fairly constant slope until very close to the sideline. This is in large part a result of their acceptance of their binary melting loop (see Figure 4c). The calculated liquidus relations on the other hand, indicate more curvature in the sloping surface. The isotherms in the alkali feldspar field agree in the binary (Ab–Or) with those calculated, however, the strong temperature depression and marked change in curvature of the eutectic portrayed by YODER *et al.* (1957) within the ternary (Figure 6a) were not detected during calculation. However, this is a compositionally complex region with high Ab contents and low temperatures where the possibility of disequilibrium in the experiments is great.

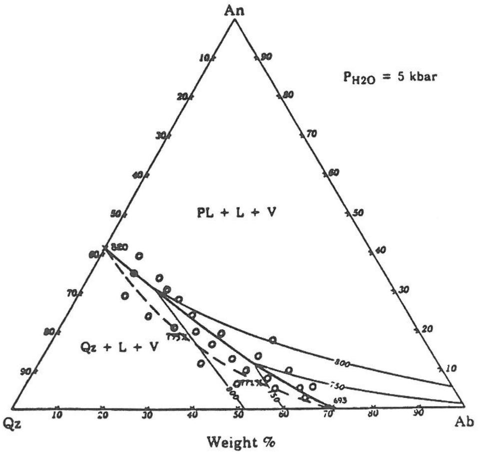

FIG. 5. Experimental data (open circles), isotherms and the plagioclase/quartz cotectic in the system Ab–An–Qz–H_2O at $P(H_2O)$ = 5 kbar as determined by YODER (1968). The calculated cotectic is shown by the dashed curve. Several calculated cotectic temperatures have been shown for ease of comparison with the experimentally-based isotherms of YODER (1968).

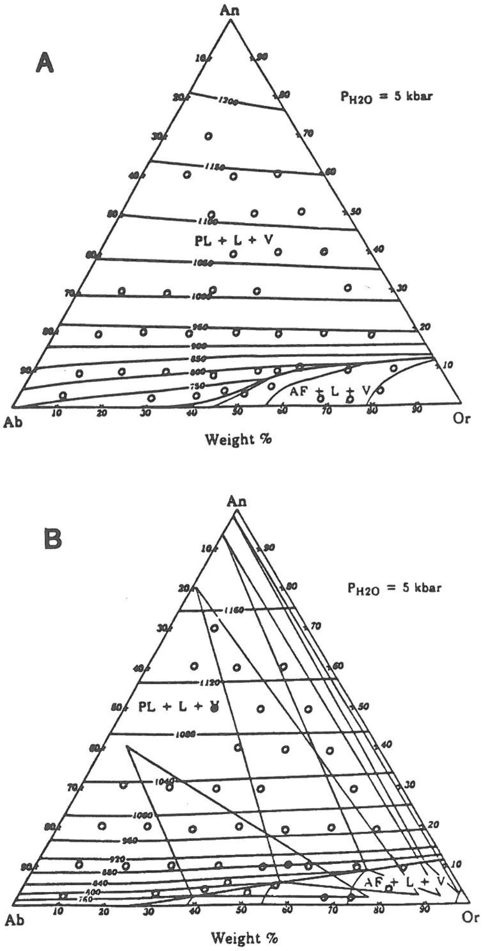

FIG. 6. Calculated and experimentally based phase relations and isotherms in the system Ab–Or–An–H_2O at $P(H_2O)$ = 5 kbar. Experimental data (open circles) are from YODER *et al.* (1957) in (A); calculated relations are shown in (B). The symbols PL and AF refer to plagioclase and alkali feldspar respectively.

The position of the ternary eutectic in the system An–Or–Qz–H_2O for H_2O-saturated conditions has been determined by WINKLER and LINDEMANN

(1972) and Winkler and Ghose (1973). The eutectic temperatures that they obtained have been verified by Johannes (1984) as lying at 738°C and 700°C at 2 and 5 kbar, respectively. The calculated eutectic temperatures are 752°C and 720°C, respectively. The calculated and experimentally determined eutectic compositions, however, differ markedly in An content from the 14 weight percent An determined by Winkler at 5 kbar to the 5 weight percent calculated. This great discrepancy may arise from imprecise quantification of the interaction behavior of *qz* and *an* which is based on sparse experimental data (although the differences may also be due to experimental problems as noted by Johannes, 1978).

From the above examples, it can be concluded that the model is able to predict the general topology of the liquidus surfaces of the subsystems of the granite system. Additionally, it is reasonable to conclude that although the calculated phase diagrams may not be correct in every quantitative detail, the model can certainly be used in a predictive capacity to obtain information regarding general quantitative trends.

Quantification of the activity–composition relationships was also undertaken for the anhydrous subsystems using the same approach as taken in the H_2O–saturated systems (Nekvasil, 1986; Burnham and Nekvasil, 1986). Evaluation of the model's predictive capabilities in the anhydrous granite sytem, however, is more problematic due to the paucity of experimental data arising from the difficulty of overcoming kinetic problems in the very viscous melts that characterize the anhydrous region of this system. However, the phase assemblage data of Whitney (1972) can be used for comparison of calculated anhydrous phase relations for compositions within the granite system (Nekvasil-Coraor and Burnham, 1983; 1984). If the activity–composition relations obtained from the anhydrous and H_2O–saturated unary solidi and A + Qz solidi are assumed linear with H_2O content from these two limiting conditions, very good agreement can be obtained between Whitney's (1972) experimental data in the H_2O–undersaturated region and calculated saturation curves. On the basis of this agreement (Nekvasil, 1986; Nekvasil-Coraor and Burnham, 1983), it is concluded that the model can provide at least a first order quantitative assessment of the phase relations in the H_2O–undersaturated regions. This capability is of great importance in that it permits the calculation of the individual effects of pressure and H_2O content on phase equilibria in the granite system. It is through the isolation of the effects of these variables that more insight can be gained into the crystallization and melting histories of silicic magmas.

THE EFFECTS OF PRESSURE AND H_2O CONTENT

The effects of pressure and H_2O content on the positions of the cotectic surfaces within the granite tetrahedron have direct bearing on the crystallization path of a silicic magma. The pioneering efforts of Tuttle and Bowen (1958) and Luth *et al.* (1964) on the determination of the haplogranite liquidus relations at several pressures (under H_2O–saturated conditions) clearly elucidated the effects of increasing $P(H_2O)$ on the haplogranite cotectic, that is, on the intersection of the quartz/alkali feldspar cotectic surface with the Ab–Or–Qz ternary subsystem. Inasmuch as the solubility of H_2O in silicic melts increases with pressure, two variables were being changed simultaneously in these experiments and the resulting data represented the effect of both variables. Natural felsic melts are generally H_2O–undersaturated until the late stages of crystallization; therefore, the results of these experiments do not simulate common natural magmatic conditions and it is very important that the individual effects of each variable be evaluated.

The following discussion will focus on the predicted effects of pressure and X_w^m (the mol fraction of water in the melt) on the cotectic surfaces within the granite system. As can be seen in Figure 7, the granite system contains three cotectic surfaces. The quartz/plagioclase cotectic surface separates the ex-

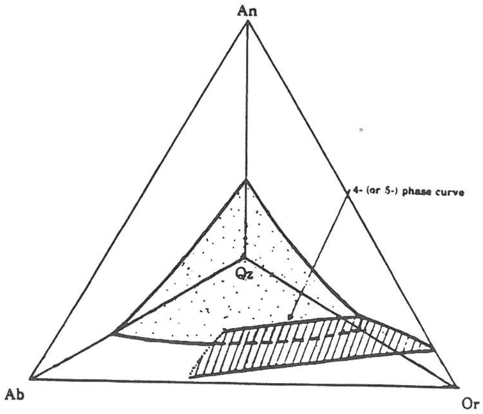

FIG. 7. General phase relations in the granite tetrahedron. The stippled surface denotes the plagioclase + quartz + L cotectic surface whereas the ruled region denotes the alkali feldspar + plagioclase cotectic surface. The intersection of the three cotectic surfaces defines the 4- (or 5-) phase curve. At high $P(H_2O)$, the alkali feldspar/plagioclase cotectic surface intersects the haplogranite base.

tensive Pl (plagioclase) + L field from the less extensive Qz + L field. The plagioclase/alkali feldspar cotectic surface is much flatter and separates the Pl + L field from the AF (alkali feldspar) + L field. Only at high P(H_2O) does this surface intersect the haplogranite subsystem. The intersection of the two cotectic surfaces marks the emanation curve of a third minor cotectic surface separating the Qz + L field from the AF + L field. The emanation or intersection curve of these three surfaces, is the 4-phase curve (or 5-phase curve if fluid is present). This curve is of great importance in that it indicates the compositions of melts formed in equilibrium with quartz and two feldspars in the source region.

Figure 8 shows the calculated cotectics in the granite system for 2, 3 and 5 kbar at $X_w^m = 0.20$ (1.9 weight percent H_2O) as a demonstration of the effects of pressure. It is apparent that the effect of increasing pressure is to expand preferentially the Qz + L field at the expense of the Pl(AF) + L fields. The feldspar cotectics, on the other hand, show only very slight differential pressure effects. The pressure sensitivity of Qz + L field can be readily attributed to the larger ΔV of fusion for Si_4O_8 relative to that for the aluminosilicates (NEKVASIL, 1986).

The calculated effects of increasing X_w^m isobarically are shown in Figure 9. Increasing H_2O content results in a contraction of the Qz + L field and thus induces an effect opposite to that resulting from increasing pressure at constant H_2O content. Once again this differential effect is much stronger for the Qz + L field than for the Pl(AF) + L fields. The smaller ΔH of fusion of Si_4O_8 relative to that of the feldspars indicates that an equal the change in the activity of the *qz*and *a* melt components such as upon the addition of H_2O will result in a greater change in the quartz/melt equilibrium temperature than in the feldspar/melt equilibrium temperature.

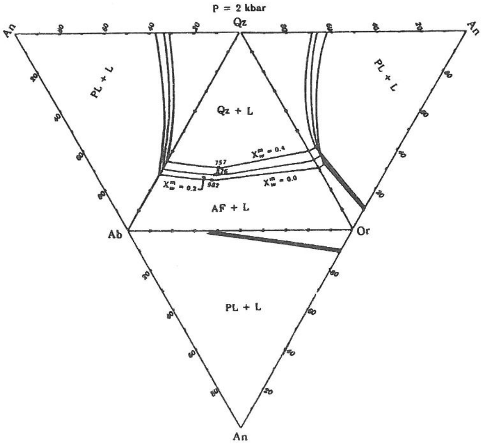

FIG. 8. Calculated cotectic relations in the granite tetrahedron at $X_w^m = 0.20$ (1.9 weight percent) and 2, 3 and 5 kbar pressure, demonstrating the effects of pressure variation on the cotectic surfaces. The granite tetrahedron has been unfolded to facilitate visualization of the intersections of all cotectic surfaces with the bounding ternary subsystems (*i.e.*, faces of the tetrahedron).

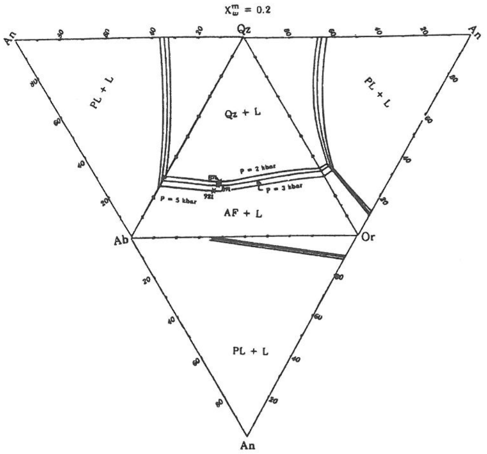

FIG. 9. Calculated cotectic relations within the granite tetrahedron at 2 kbars pressure for $X_w^m = 0.0, 0.20$ (1.9 weight percent H_2O) and 0.40 (3.7 weight percent H_2O), demonstrating the effect of variable H_2O content on the cotectic surfaces. The tetrahedron has been unfolded as described in Figure 8.

The individual effects of pressure (Figure 8) and H_2O content (Figure 9) can be compared with Figure 10 which shows the effects of changing both pressure and H_2O content (*i.e.*, changing P(H_2O)

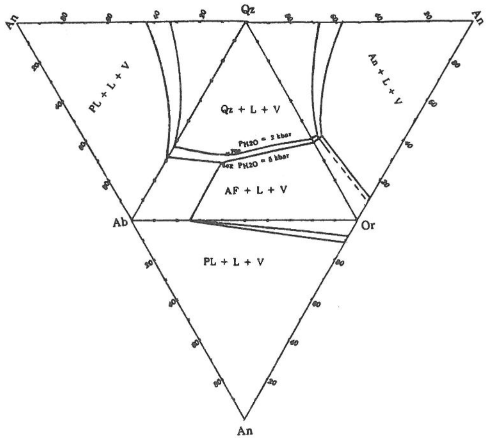

FIG. 10. Calculated cotectic relations within the granite tetrahedron at P(H_2O) = 2 and 5 kbar (H_2O–saturated), demonstrating the combined effects of varying pressure and H_2O content. The tetrahedron has been unfolded as described in Figure 8.

under H_2O-saturated conditions). In this case, the effects of increasing H_2O content (due to increased H_2O solubility with pressure) are offset by the effects of increased pressure. The net effect is a slight expansion of the Qz + L field with increased $P(H_2O)$. This illustrates the importance of understanding the individual effects of pressure and H_2O content on phase equilibria in the granite system and the inadequacy of sole use of H_2O-saturated phase relations for the interpretation of magmatic history.

DISCUSSION

The results of phase equilibria calculations in the granite system using the revised quasi-crystalline model indicate that decreasing pressure and increasing H_2O content result in a contraction of the Qz + L field at the expense of the Pl(AF) + L fields. On a compositional basis, the feldspar fields adjacent to each other are only slightly affected by changes in these two variables. The effects of these variables on the liquidus temperatures, however, are considerable.

A given Qz-poor, Or-rich hydrous (but H_2O–undersaturated) magma in which one feldspar is forming will begin crystallizing a second feldspar (at the two feldspar cotectic surface) when the remaining melt has attained a specific composition. For such a magma, the composition at which the second feldspar begins to appear is approximately constant, that is, it is relatively independent of initial H_2O content of the magma. Differences in H_2O content, however, will strongly affect the crystallization history after this surface has been reached. With higher H_2O contents, the Qz + L field contracts, shifting the 4-phase curve (*i.e.*, the intersection curve of the cotectic surfaces within the tetrahedron) toward the Qz apex and away from the An and Or apices. Therefore, higher H_2O contents for a given bulk composition will required that more plagioclase and alkali feldspar components be removed from the melt in order to enrich it in silica before the 4-phase curve is intersected. This, in turn, implies that the percentage of these crystals will be higher (and the fraction of silicate melt remaining lower) at the onset of crystallization of quartz than would be expected for lower bulk H_2O contents. It is important to note that the 4-phase curve continuously shifts during crystallization in response to the increase in H_2O content in the melt upon the crystallization of anhydrous phases. Because of this shift, crystallization paths for these melts follow an infinite succession of tetrahedra and the system must be considered truly quinary.

For tonalitic compositions (*i.e.*, poor in Or), the differences in crystallization path of a melt at different H_2O contents will be more pronounced at an earlier stage of crystallization, because of the sensitivity of the position of the quartz/plagioclase cotectic surface to the H_2O content of the melt. Melts with higher H_2O contents must crystallize more plagioclase to enrich the remaining melt in silica before quartz will appear (in reflection of the shift of the cotectic surface toward the Qz apex). Therefore, the H_2O content strongly affects the composition of the melt at the intersection of the melt composition path with the cotectic surface and the onset of crystallization of quartz. As was mentioned above, the position of the 4-phase curve also shifts towards the Qz apex with increasing H_2O content. The contraction of the plagioclase/quartz cotectic surface resulting from higher H_2O contents implies that the 4-phase curve will be intersected 'earlier' at higher H_2O contents, that is, alkali feldspar will appear after less quartz has crystallized than would be the case for the same bulk composition but lower initial H_2O content.

The strong, but opposing, effect of pressure indicates that crystallization at high pressures will result in a strongly increased likelihood of quartz appearing as the liquidus phase for compositions low in An. It also indicates that decompression, such as during ascent of the magma, will preferentially affect earlier crystallized quartz relative to any early crystallized feldspar. Such quartz will be resorbed to various extents in attempt to reestablish an equilibrium assemblage with a more silica-rich melt.

It is apparent from the strong differential effect of pressure and H_2O content on the Qz + L field that for bulk compositions lying close to the cotectic surfaces, the pressure and H_2O content of the system will determine the identity of the liquidus phase. Therefore, for such magmatic compositions, if the liquidus phase can be identified texturally, the model can be used to place constraints on the depth of initial emplacement as well as on the H_2O content of the magma. (For an example of such application, see LONG *et al.*, 1986.) It is hoped that such calculations will prove invaluable to the interpretation of the crystallization and melting histories of natural felsic rocks.

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