

Ternary-feldspar mixing relations and thermobarometry

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ABSTRACT

The temperature and pressure dependencies of excess Gibbs free energy of mixing functions in the $\text{CaAl}_2\text{Si}_2\text{O}_8$ - KAlSi_3O_8 binary system have been estimated semiempirically using published Margules parameters for the $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$ and $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 binary systems and compositional data on coexisting experimental feldspars. The calculated anorthite-orthoclase interaction parameters permit simultaneous pressure-temperature solution of activity-composition relations based on anorthite, albite, and orthoclase exchange reactions between coexisting ternary feldspars. The proposed "ternary-feldspar thermobarometer" has been used to calculate equilibration conditions of feldspars in rhyolitic and trachytic rocks. Predicted temperatures of crystallization of feldspar phenocrysts from the Bishop Tuff agree closely with those predicted by Fe-Ti oxide thermometry; calculated pressures of feldspar equilibration are similar to estimates based on Fe-Ti oxide temperatures and the pressure dependence of the albite exchange reaction. The thermobarometer is sensitive to analytical uncertainties in the Or content of plagioclase and the An content of alkali feldspar, and to any systematic errors in the binary mixing parameters.

INTRODUCTION

It is known that stable equilibrium distribution of end-member components between coexisting plagioclase and alkali feldspars depends only on temperature and pressure. In particular, the distribution of albite component between coexisting, natural ternary feldspars has been used to estimate the equilibration temperature of the two phases at a given pressure. Most versions of this two-feldspar geothermometer have employed a "double binary" formulation based on thermodynamic properties of the limiting $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$ (An-Ab) and $\text{NaAlSi}_3\text{O}_8$ - KAlSi_3O_8 (Ab-Or) binary joins (Stormer, 1975; Whitney and Stormer, 1977; Powell and Powell, 1977; Brown and Parsons, 1981). With the possible exception of the Powell and Powell (1977) formulation, the effects of "minor" components—Or in plagioclase and An in alkali feldspar—have been largely ignored. The "minor" components probably cause significant perturbation of feldspar activity-composition relations, so that double-binary thermometers cannot account for the ternary nature of natural feldspar pairs (Brown and Parsons, 1985). Thus, activity-composition relations in plagioclase and alkali feldspars must be formulated in terms of a ternary solution model. Such a ternary model requires two excess free-energy (Margules) parameters to describe mixing relations along each binary join with the system An-Ab-Or.

The An-Ab and Ab-Or binary Margules parameters have been determined experimentally, but unfortunately, no experimental data on the An-Or solvus are available. The An-Or mixing parameters, however, have been deter-

mined empirically from experimental data on the compositions of coexisting ternary feldspars (Seck, 1971a, 1971b; Johannes, 1979). Green and Usdansky (1984) modeled the An-Or join in the ternary system as an asymmetric regular solution and reported interaction parameters W_G^{CaK} and W_G^{Ca} of 42.7 ± 3.0 and 62.6 ± 6.6 kJ/mol, respectively. They did not consider the influence of temperature or pressure on the mixing parameters. Ghiorso (1984) subsequently calibrated the temperature dependence of An-Or excess free-energy functions. His estimates were based only upon Seck's (1971a) experiments at 825 and 900°C at 1 kbar, and he adopted the Thompson and Hovis (1979) Ab-Or interaction parameters to generate the alkali-feldspar solvus. Ghiorso (1984, p. 288) noted that "the width of the calculated [alkali feldspar] solvus at lower anorthite contents is slightly greater than that inferred from Seck's (1971a) experimental results." Merkel and Blencoe (1982, and in prep.) pointed out that the excess free energy of mixing expressions of Thompson and Hovis (1979) yield a 2-kbar alkali feldspar solvus displaced toward the Or sideline and suggested a systematic inaccuracy in the Thompson and Hovis parameters. In addition, Ghiorso (1984) assumed negligible pressure dependence of mixing relations on the An-Or join. Seck (1971b) demonstrated a slight pressure dependence in the position of at least the plagioclase limb of the ternary-feldspar solvus near the $\text{CaAl}_2\text{Si}_2\text{O}_8$ endmember. Thus, both previous calibrations of mixing parameters along the An-Or join possess systematic inadequacies with regard to temperature and pressure variations. In the discussion that follows, mixing parameters for the plagioclase and alkali feldspar binaries are reviewed, the applicability of Seck's (1971a, 1971b) database is considered, and An-Or

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Margules parameters, based on orthoclase equilibria, are derived as functions of temperatures and pressure. The ternary activity-composition relations are then reformulated as a thermobarometer.

THERMODYNAMIC BACKGROUND

Ternary-feldspar solution model and excess terms

The three endmember activities of plagioclase and alkali feldspars can be written in terms of a ternary subregular solution model (Wohl, 1953; Saxena, 1973) as

$$\begin{aligned}
 RT \ln a_{Or} = RT \ln \alpha_{Or} & \\
 & + X_{Ab}^2 [W_G^{KNa} + 2X_{Or} (W_G^{NaK} - W_G^{KNa})] \\
 & + X_{An}^2 [W_G^{CaK} + 2X_{Or} (W_G^{CaK} - W_G^{CaK})] \\
 & + X_{An} X_{Ab} [0.5(W_G^{CaK} + W_G^{KCa} \\
 & \quad + W_G^{KNa} + W_G^{NaK} \\
 & \quad - W_G^{CaNa} - W_G^{NaCa}) \\
 & + X_{Or} (W_G^{CaK} - W_G^{KCa} \\
 & \quad + W_G^{NaK} - W_G^{KNa}) \\
 & + (X_{An} - X_{Ab}) (W_G^{CaNa} - W_G^{NaCa})],
 \end{aligned}$$

$$\begin{aligned}
 RT \ln a_{Ab} = RT \ln \alpha_{Ab} & \\
 & + X_{Or}^2 [W_G^{NaK} + 2X_{Ab} (W_G^{KNa} - W_G^{NaK})] \\
 & + X_{An}^2 [W_G^{NaCa} + 2X_{Ab} (W_G^{CaNa} - W_G^{NaCa})] \\
 & + X_{Or} X_{An} [0.5(W_G^{NaK} + W_G^{KNa} \\
 & \quad + W_G^{CaNa} + W_G^{NaCa} \\
 & \quad - W_G^{CaK} - W_G^{KCa}) \\
 & + X_{Ab} (W_G^{KNa} - W_G^{NaK} \\
 & \quad + W_G^{CaNa} - W_G^{NaCa}) \\
 & + (X_{Or} - X_{An}) (W_G^{CaK} - W_G^{CaK})],
 \end{aligned}$$

and

$$\begin{aligned}
 RT \ln a_{An} = RT \ln \alpha_{An} & \\
 & + X_{Or}^2 [W_G^{CaK} + 2X_{An} (W_G^{CaK} - W_G^{CaK})] \\
 & + X_{Ab}^2 [W_G^{CaNa} + 2X_{An} (W_G^{NaCa} - W_G^{CaNa})] \\
 & + X_{Ab} X_{Or} [0.5(W_G^{CaK} + W_G^{KCa} \\
 & \quad + W_G^{CaNa} + W_G^{NaCa} \\
 & \quad - W_G^{KNa} - W_G^{NaK}) \\
 & + X_{An} (W_G^{KCa} - W_G^{CaK} \\
 & \quad + W_G^{NaCa} - W_G^{CaNa}) \\
 & + (X_{Ab} - X_{Or}) (W_G^{NaK} - W_G^{KNa})],
 \end{aligned}$$

where all ternary constants (C_{Or} , C_{Ab} , and C_{An} ; cf. Saxena, 1973) are assumed to equal zero; α_{Or} , α_{Ab} , and α_{An} are the ideal activities of Or, Ab, and An components in the feldspars; X_{Or} , X_{Ab} , and X_{An} are mole fractions of Or, Ab, and An in feldspar; and the interaction (Margules) parameters, W_G , describe excess free energy of mixing relations within the Ab-Or, An-Ab, and An-Or binary systems. The ternary activity expressions can be expanded to account

for variations of W_G parameters with temperature (T) and pressure (P) by substituting

$$W_G^{i-j}(P,T) = W_G^{i-j}(H(1,T)) - TW_S^{i-j}(1,T) + (P-1)W_V^{i-j},$$

where W_H^{i-j} , W_S^{i-j} , and W_V^{i-j} are excess enthalpy, entropy, and volume terms for each $i-j$ binary join. The ideal activity (α) of the feldspar endmembers may be expressed in terms of either an ideal entropy or an Al-avoidance configurational entropy of mixing model (cf. Kerrick and Darken, 1975).

Saxena and Ribbe (1972) estimated An-Ab excess free-energy parameters using an ideal entropy of mixing model and compositional data from Seck's (1971a) feldspar synthesis experiments at 650°C and 1 kbar and from Orville's (1972) Na-Ca plagioclase-chloride solution exchange experiments at 700°C and 2 kbar. Their two sets of calculated interaction parameters showed important differences, which were attributed partly to the fact that Seck's feldspars are ternary solutions. Newton et al. (1980) used calorimetrically measured enthalpies of solution to derive asymmetric W_H constants for a suite of synthetic Na-Ca plagioclases and also demonstrated negligible volume of mixing ($W_V \cong 0$) for these high-structural state feldspars. They concluded that their determination of heats of mixing could be reconciled with activities derived from Orville's (1972) experiments when ideal-activity (α) terms are expressed according to an Al-avoidance configuration entropy model (Kerrick and Darken, 1975) and no additional excess entropy of mixing (W_S) terms are considered. Carpenter and Ferry (1984), however, have argued that the Newton et al. high plagioclase mixing model exhibits inconsistencies with activity-composition relations for anorthite derived from experiments by Windom and Boettcher (1976), Goldsmith (1982), and Kotelnikov et al. (1981).

Thompson and Waldbaum (1968, 1969), Thompson and Hovis (1979), and Brown and Parsons (1981) have determined excess mixing functions for analbite-sanidine solid solutions; Bachinski and Muller (1971) estimated mixing parameters for low albite-microcline solid solution. Saxena and Ribbe (1972) noted that mixing parameters for the system Ab-Or calculated from Seck's ternary-feldspar data were similar to those determined by Thompson and Waldbaum (1969). Haselton et al. (1983) re-examined analbite-sanidine excess entropies of mixing and from solvus determinations calculated enthalpies of mixing that agreed with experimentally determined enthalpies of mixing (Hovis and Waldbaum, 1977). Their excess free energy of mixing expressions incorporated the symmetric volume of mixing terms of Hovis (1977). Haselton et al. (1983) also presented a two-feldspar "albite" geothermometer based on their revised analbite-sanidine mixing parameters, the Kerrick and Darken (1975) Al-avoidance configurational entropy model for plagioclase feldspar, and the Newton et al. (1980) An-Ab interaction parameters. Price (1985), however, pointed out that the Al-avoidance entropy model of Kerrick and Darkin (1975) applies strictly to binary systems and reformulated ideal-

activity (α) terms for ternary-feldspar endmembers based on configuration entropy and site-mixing considerations. He demonstrated that a geothermometer based upon such a revision of the Haselton et al. (1983) albite-exchange equilibria yielded temperatures that better fit the experimental temperatures of Seck (1971a) and Johannes (1979).

It is difficult to determine, a priori, which of the proposed Margules parameters best describes the thermodynamic properties of the ternary-feldspar system. Nevertheless, based on previous discussion, the following excess mixing parameters and ideal activity-composition expressions have been adopted here to represent endmember activities along the An-Ab and Ab-Or joins: (1) the Newton et al. (1980) An-Ab excess enthalpy constants ($W_H^{\text{CaNa}} = 8473$ J/mol, $W_H^{\text{NaCa}} = 28\,226$ J/mol) with no excess entropy (W_S) or volume (W_V) of mixing terms; (2) the Haselton et al. (1983) Ab-Or excess enthalpy ($W_H^{\text{KNa}} = 27\,320$ J/mol, $W_H^{\text{NaK}} = 18\,810$ J/mol) and symmetric entropy ($W_S = 10.3$ J/mol·K) and volume ($W_V = 0.364$ J/bar) parameters; and (3) Price's (1985) ternary-feldspar ideal-activity terms:

$$\begin{aligned}\alpha_{\text{An}} &= (0.25)(X_{\text{An}})(1 + X_{\text{An}})^2, \\ \alpha_{\text{Ab}} &= (X_{\text{Ab}})(2 - X_{\text{Ab}} - X_{\text{Or}})(X_{\text{Ab}} + X_{\text{Or}}), \\ \alpha_{\text{Or}} &= (X_{\text{Or}})(2 - X_{\text{Ab}} - X_{\text{Or}})(X_{\text{Ab}} + X_{\text{Or}}).\end{aligned}$$

As described below, calibration of An-Or interaction parameters using alkali-feldspar Margules parameters presented by Thompson and Waldbaum (1969), Thompson and Hovis (1979), or Brown and Parsons (1981) produced consistently poorer mathematical solutions to the experimental ternary-feldspar data than those generated by the adopted parameters.

Evaluation of An-Or mixing parameters

Seck (1971a, 1971b) presented compositional data for 72 ternary-feldspar pairs from synthesis experiments at 650°C and 1, 5, and 10 kbar, 750 and 825°C at 1 kbar, and 900°C and 500 bars pressure. The standard-state chemical potentials for plagioclase and alkali feldspar solid solutions can be considered identical, so that the compositions of coexisting experimental feldspars are related through the anorthite, albite, and orthoclase exchange reactions. As a result, over 200 activity-composition relations can be written to represent equilibrium between Seck's experimental feldspars and solved simultaneously for the desired W_G^{CaK} and W_G^{KCa} parameters. Unfortunately, Seck's synthesis experiments were not reversed, and hence, there has been some question whether Seck's experimental ternary feldspars possess equilibrium compositions. Johannes (1979) has suggested that Seck's gel experiments crystallized coexisting feldspars of nonequilibrium composition: alkali feldspars too rich in Ab and plagioclases too rich in An. Brown and Parsons (1981) likewise questioned whether the experiments of Johannes (1979) represented complete equilibrium. They suggested that although the "very impressive regularity" of Seck's results could indicate an approach to equilibrium, none of the available ternary-feldspar experimental studies can be ac-

cepted without reservation. Brown and Parsons (1985) argued further that "meaningful mixing parameters" could not be extracted from existing ternary-phase synthesis data. Nevertheless, reasonable estimates of An-Or Margules parameters have been derived from Seck's (1971a, 1971b) database (Green and Usdansky, 1984; Ghiorso, 1984), and on this basis, the Seck database has been adopted to examine the temperature and pressure effects on An-Or mixing relations within the ternary-feldspar system.

Although inaccuracies may exist in orientation of Seck's experimentally determined tie lines, there is some agreement concerning the location of the ternary solvus in the studies of Seck and Johannes. This is significant because X_{An} and X_{Ab} exert a greater influence on the activity relations of Ab and An than that of Or, and any systematic errors in the compositions of the experimental feldspars might be minimized if only the orthoclase exchange equilibria were used to estimate the An-Or interaction parameters. Accordingly, two calibration procedures were undertaken: one employing only orthoclase equilibria (72 relations), the other involving all three endmember equilibria (216 relations). In each case, the ternary activity-composition relations based on Seck's (1971a, 1971b) complete database were arranged in matrix form, and standard multiple regression techniques were employed to estimate simultaneously the W_G^{CaK} and W_G^{KCa} parameters as functions of pressure and temperature. This procedure differs from the approach taken by Ghiorso (1984), who calculated separate W_G^{CaK} and W_G^{KCa} constants for each set of Seck's (1971a) experiments at a particular T and P , and determined a temperature dependence for these interaction parameters based on W_G values derived only from Seck's two highest-temperature (825 and 900°C) experiments at 1 kbar.

The standard errors of regression of calibrations based solely on orthoclase equilibria are relatively small (481–565 J). Larger standard errors characterize the calibrations that involve all three endmember equilibria (1276–1443 J). Although there is little difference in the standard error of calibrations based on alkali feldspar Margules parameters proposed by Thompson and Waldbaum (1969), Thompson and Hovis (1979), Brown and Parsons (1981), or Haselton et al. (1983), only regressions that used the parameters of Haselton et al. (1983) yielded constants that were all significant at better than the 90% confidence level.

The temperature and pressure dependencies of the interaction parameters predicted by the two calibration procedures are distinctly different. For example, those calibrations based on the Newton et al. (1980) and Haselton et al. (1983) parameters yielded the An-Or excess free-energy equations, expressed as enthalpy, entropy, and volume terms,

$$\begin{aligned}W_G^{\text{CaK}} &= -65\,407.0 + 114.1040T + 2.1121P \\ W_G^{\text{KCa}} &= 65\,305.4 - 12.5365T + 0.9699P\end{aligned}$$

when only the orthoclase equilibria were used, but,

$$\begin{aligned}W_G^{\text{CaK}} &= 20\,945.2 + 27.1739T - 0.4996P \\ W_G^{\text{KCa}} &= 30\,398.9 + 22.7831T + 1.6435P\end{aligned}$$

Table 1. Temperatures calculated from coexisting feldspar data of Seck (1971a, 1971b) and orthoclase, albite, and anorthite exchange reactions

<i>T</i> (°C)	<i>P</i> [*] (kbar)	Orthoclase		Albite		Anorthite	
		<i>T</i> (°C)**	S.D.†	<i>T</i> (°C)**	S.D.†	<i>T</i> (°C)**	S.D.†
Three endmember calibration							
650	1.0	636	19.8	664	24.9	875	3102.9
650	5.0	661	26.4	670	26.5	-353	3162.6
650	10.0	652	72.2	703	49.2	1005	1301.1
750	1.0	721	14.0	779	27.5	715	107.7
825	1.0	797	19.6	846	31.4	865	175.1
900	0.5	876	39.6	896	31.4	940	149.9
Orthoclase calibration							
650	1.0	638	18.1	665	21.1	638	63.7
650	5.0	682	23.9	663	24.7	531	46.2
650	10.0	672	42.1	684	36.4	380	31.0
750	1.0	736	17.4	760	25.6	670	21.8
825	1.0	826	27.7	811	22.3	651	16.9
900	0.5	917	22.8	885	28.8	695	18.0

* Experimental temperature and pressure.
** Average calculated temperature.
† Standard error of average calculated temperature (°C).

when all three endmember equilibria were considered (W_G in joules per mole, T in kelvins, and P in bars). The expressions yield different An-Or Margules parameters at any given pressure and temperature. For example, W_G^{CaK} and W_G^{CaCa} at 600°C and 2 kbar have predicted values of 39 347 and 56 294 J, respectively, based on the orthoclase calibration, but values of 43 672 and 53 579 J, respectively, based on the three endmember calibration. The differences between An-Or mixing parameters generated by the two calibration procedures reflect the effect of anorthite activity-composition relations on regressions involving all three endmember equilibria. In particular, it can be shown that many of the thermodynamic formulations of anorthite exchange reactions defined by Seck's coexisting feldspar compositions are dominated by exceptionally large ideal-activity terms (i.e., $RT \ln \alpha_{\text{An}}$) for the alkali feldspar and, hence, are extremely sensitive to the lack of fine compositional detail in the An content of alkali feldspar from some of Seck's experiments (cf. Ghiorso, 1984). This anomalous behavior of the anorthite equilibria is particularly evident when the calculations are reversed, and the estimated An-Or mixing parameters are used to calculate equilibration temperatures from the compositions of the experimental feldspar pairs. The calculations based on the orthoclase and albite equilibria produce relatively good fits between calculated temperatures and the experimental temperatures of Seck (1971a, 1971b) and Johannes (1979), but the anorthite equilibria generally yield erroneous results (Table 1). Although the validity of all estimated An-Or interaction parameters can be questioned in view of the different calibration results, the calculated temperatures suggest that systematic errors may be present in the calibrations involving the anorthite endmember exchange equilibria. Because of uncertainties concerning whether Seck's feldspar data represent complete structural and compositional equilibrium (Brown

and Parsons, 1985), recalculation of Seck's (1971a, 1971b) ternary-feldspar solvi using the estimated An-Or Margules parameters and compositions of experimental feldspar pairs (cf. Ghiorso, 1984) cannot be taken as a measure of the accuracy with which the derived activity-composition relations describe mixing relations in natural feldspars. Therefore, as an independent means of verifying the results and determining whether any of the calibrated An-Or mixing parameters are valid, the An, Ab, and Or activity-composition relations have been written as functions of pressure and temperature and used to calculate equilibration conditions of volcanic feldspar pairs.

EXAMINATION OF TERNARY-FELDSPAR THERMOBAROMETRY

Stormer (1975) pointed out that although the chemical-potential relationship $\mu_{\text{Ab}}^{\text{AF}} = \mu_{\text{Ab}}^{\text{PF}}$ is a necessary condition of equilibrium, the conditions $\mu_{\text{An}}^{\text{AF}} = \mu_{\text{An}}^{\text{PF}}$ and $\mu_{\text{Or}}^{\text{AF}} = \mu_{\text{Or}}^{\text{PF}}$ also must be satisfied simultaneously in order to establish equilibrium between coexisting plagioclase (PF) and alkali feldspars (AF). The ternary activity-composition relations for each of the exchange reactions, expressed in geothermometric form, are presented in Appendix 1. The P - T equilibrium curves defined by these three ternary activity-composition expressions should intersect at a unique pressure and temperature under equilibrium conditions. A single intersection of the three curves theoretically can be generated only by those compositions of (zoned) feldspar pairs that represent equilibrium-crystallization conditions. As illustrated in Figure 1, nonequilibrium feldspar compositions would be expected to yield multiple intersections, and the closure of these P - T intersections should reflect how closely the selected feldspar compositions approach equilibrium conditions. Application of these "ternary-feldspar" relations to natural rock systems, therefore can be expected to be further influenced by (1) a sensitivity

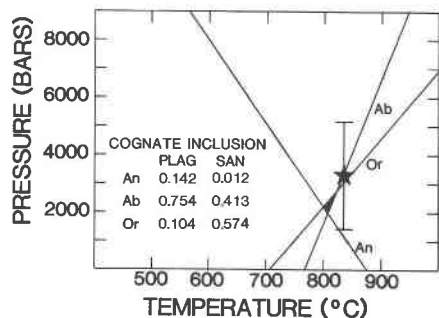


Fig. 1. Calculated ternary-feldspar equilibria for cognate inclusion 33P, Little Glass Mountain Rhyolite (Mertzman and Williams, 1981). The centroid of An, Ab, and Or univariant curve intersections (small black triangular area) indicates a temperature of 805°C, whereas the temperature predicted from compositions of Fe-Ti oxides is 836°C (star). Mertzman and Williams (1981) indicated that owing to the insensitivity of their pressure calculations, crystallization could have occurred at pressures between 1000 and 5200 bars (vertical line). The calculated pressure based on ternary-feldspar equilibria suggests that the inclusion minerals crystallized at about 2200 bars.

to analytical uncertainties for the An in alkali feldspar and the Or in plagioclase; (2) the feldspar compositions selected to represent the equilibrium pairs; and (3) any systematic errors in the estimated An-Or Margules parameters. A computer program, available from the authors, has been employed to calculate the P - T variation of the anorthite, albite, and orthoclase exchange reactions, determine the intersection point(s) of the univariant reaction curves, and if more than one intersection is found, compute the centroid of intersections in terms of temperature, pressure, and related standard deviations. This method of calculating conditions of feldspar equilibration was considered preferable to an iterative technique involving minimization of residual differences in activity equations for coexisting feldspars (Ghiorso, 1984). The explicit solution of the ternary activity-composition expressions used here does not require a pressure estimate, and the effects of analytical uncertainty and compositional variation of natural samples on estimated equilibration conditions can be more directly evaluated.

A satisfactory test of the ternary mixing data has been considered to be the application of the activity-composition relations to feldspar pairs from volcanic rock suites for which independent temperature estimates are available, and for which, if possible, equilibrium relationships can be evaluated utilizing petrographic descriptions and chemical data for both minerals and rocks. The results of these thermometric calculations again indicate that the An-Or mixing parameters based on all three endmember exchange equilibria cannot reproduce reasonable equilibrium feldspar relationships (i.e., the equilibrium curves do not intersect, or intersect at geologically unrealistic pressures and/or temperatures). In contrast, thermobarometric calculations utilizing the An-Or Margules parameters based only on orthoclase distributions in Seck's

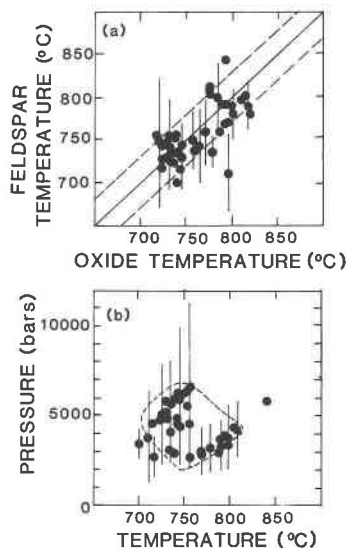


Fig. 2. Ternary-feldspar equilibration temperatures and pressures of the Bishop Tuff, California. (a) Ternary-feldspar equilibration temperatures, calculated using average phenocrystic plagioclase and sanidine compositions, are compared to corresponding Fe-Ti oxide temperatures (Hildreth, 1977). Dashed lines indicate the experimental uncertainty of the Fe-Ti oxide thermometer (Buddington and Lindsley, 1964). Vertical lines illustrate maximum (1 sigma) standard deviations associated with the predicted two-feldspar temperatures for individual samples throughout the crystallization interval of the Bishop Tuff. (b) P - T equilibration conditions of Bishop Tuff predicted by ternary-feldspar relations. Vertical lines represent the maximum uncertainties associated with the estimated crystallization pressures of individual samples (see text). Errors in ternary-feldspar equilibration conditions reflect both the systematic errors in the estimated An-Or mixing parameters, and how closely the average plagioclase and sanidine compositions represent equilibrium crystallization. The dashed circle indicates the range of Bishop Tuff crystallization temperatures and pressures estimated by Stormer and Whitney (1985).

(1971a, 1971b) experimental feldspars appear to yield reasonable P - T conditions. For example, the Bishop Tuff exhibits systematic variations in mineral chemistry and Fe-Ti oxide temperature and has been interpreted to represent continuous tapping of a thermally and chemically zoned magma chamber (Hildreth, 1977). Euhedral sanidine phenocrysts show signs of incipient resorption and only limited compositional zoning where sodic rims have developed as vapor-phase overgrowths, whereas coexisting oligoclase crystals are euhedral, rarely exhibit marginal resorption, and show a systematic compositional variation with eruption temperature although zoning of phenocrysts from individual samples seldom exceeds 3–4 mol% An component (Hildreth, 1979). Halliday et al. (1984) concluded that Nd, Sr, and O isotopic variations, as well as textural relations, suggested that the feldspar phenocrysts were precipitated in situ from an already chemically zoned magma. Hildreth (1979, p. 48) postu-

Table 2. Calculated equilibration temperatures and pressures of coexisting feldspars

Sample	X_{An}^{Fe}	X_{Ab}^{Fe}	X_{Or}^{Fe}	X_{An}^{Al}	X_{Ab}^{Al}	X_{Or}^{Al}	T (1) (°C)	T (2) (°C)	T (3) (°C)	T (4) (°C)	T (5) (°C)	P (bars)
Rhyolites, northern California (Carmichael, 1967)												
CAM 76	0.135	0.790	0.075	0.008	0.346	0.646	655	650	652	810	721 (33)	4 162 (1 814)
	0.161	0.775	0.065	0.007	0.329	0.663	653	650	651	n.a.	743 (34)	5 171 (1 790)
	0.111	0.812	0.077	0.009	0.365	0.626	653	645	629	n.a.	698 (47)	3 925 (2 877)
GM-402	0.144	0.783	0.073	0.008	0.373	0.619	680	670	670	800	772 (53)	5 490 (2 811)
CAM 81	0.173	0.735	0.092	0.020	0.400	0.580	746	745	767	850	772 (34)	1 193 (1 682)
CAM 86	0.196	0.717	0.087	0.019	0.403	0.578	768	760	796	920	824 (46)	1 939 (1 996)
Rhyolite, Taupo volcanic province (Ewart, 1965)												
P27834	0.326	0.632	0.041	0.028	0.319	0.653	758	800	689	750	785 (121)	3 417 (5 701)
Leucite trachytes, Roman province (Baldrige et al., 1981)												
90-05	0.376	0.545	0.084	0.044	0.431	0.526	1126	n.a.	1076	1016 ^a	1163 (185)	-986 (5 154)
89-21	0.435	0.518	0.047	0.056	0.442	0.502	1250	n.a.	794	1251 ^b	1167 (312)	4 469 (11 584)
										1214 ^c		
88-17	0.547	0.43	0.023	0.048	0.327	0.625	1087	n.a.	681	1000 ^c (100)	1012 (364)	7 354 (17 021)
Biotite trachyte, Tristan de Cunha (Ghiorso, 1984)												
442 ph	0.458	0.513	0.029	0.041	0.494	0.465	1594	n.a.	723	n.a.	2268 (1587)	33 279 (56 363)
442 ph	0.237	0.679	0.084	0.049	0.564	0.387	1123	910	1017	n.a.	1131 (127)	5 316 (4 464)
442 gdms	0.295	0.664	0.040	0.049	0.465	0.487	1069	910	638	n.a.	867 (174)	5 995 (9 017)
442 gdms	0.200	0.732	0.068	0.096	0.614	0.289	1069	n.a.	564	n.a.	708 (45)	4 389 (2 794)
Trachyte, Seibengebirge, Germany (Ghiorso, 1984)												
1909-261	0.243	0.683	0.074	0.020	0.414	0.566	823	823	840	n.a.	918 (89)	3 234 (3 473)

Notes: (1) Stormer (1975); (2) Brown and Parsons (1981; Fig. 2); (3) Ghiorso (1984); (4) Fe-Ti oxide temperature except (a) Sr plagioclase-liquid, (b) Ba plagioclase-liquid, and (c) biotite/apatite F-OH geothermometers; (5) this paper. Numbers in parentheses are 1-sigma deviations of P - T intersections (see text). Temperatures 1-3 calculated at $P = 1$ kbar.

lated that "the Fe-Ti oxide temperatures which reflect equilibrium at the moment when titanomagnetite-ilmenite-liquid communication was interrupted by eruption, also represent equilibration temperatures for the entire phase assemblages." Such an interpretation is supported by calculated "ternary-feldspar" equilibration temperatures that closely approach those predicted by Fe-Ti oxide thermometry (Fig. 2a). Estimated P - T relations are similar to those that Stormer and Whitney (1985) calculated using Fe-Ti oxide thermometry and the pressure dependence of the albite exchange reaction (Fig. 2b). The fit between estimated feldspar and oxide equilibration conditions is remarkable considering that average plagioclase and sanidine and not specific zone compositions were used in the calculations. In addition to uncertainties associated with the derived thermodynamic equations and precision of individual feldspar analyses, therefore, the standard deviations of predicted P - T intersections of the An, Ab, and Or equilibrium curves (17-81 degrees and 0.7-4.1 kbar) probably reflect how closely Hildreth's average feldspar compositions represent equilibrium conditions for the individual samples.

Equilibration temperatures and pressures estimated for other volcanic rocks are given in Table 2, together with 1-kbar temperatures predicted by the Stormer (1975), Brown and Parsons (1981), and Ghiorso (1984) two-feldspar geothermometers. In general, the "ternary-feldspar thermobarometer" predicts reasonable crystallization temperatures for two-feldspar pairs in both trachytes and

rhyolites. However, coexisting feldspars in trachytic lavas tend to yield P - T estimates with large uncertainties (e.g., Roman lavas, Table 2). These uncertainties may originate because the average compositions of plagioclase and sanidine phenocrysts in trachytes have steep tie-line slopes that are not parallel to those defined by two-feldspar pairs from either rhyolites or Seck's (1971a, 1971b) experiments. Such tie-line orientations have been interpreted to reflect a temperature or a liquid bulk-composition effect that distorts the shape of the ternary solvus in the trachytic liquid during feldspar crystallization (Carmichael, 1963; Rahman and Mackenzie, 1969; Baldrige et al., 1981). In many cases, however, the distinctive tie-line orientations, derived from averaged feldspar compositions, may not represent equilibrium feldspar pairs. As illustrated by plagioclase and sanidine in a Tristan de Cunha biotite trachyte (no. 442, Table 2), the calculated "ternary-feldspar" equilibration conditions and magnitude of associated uncertainties depend primarily on which feldspar compositions (and consequently which tie-line orientations) are selected to represent equilibrium. The groundmass feldspars of the trachyte, which yield P - T estimates with the smallest standard deviations, define tie-line orientations subparallel to those of Seck's (1971a, 1971b) experimental feldspars. This result suggests that the slopes of tie-lines defined by coexisting equilibrium feldspars in trachytes and rhyolite are not different. Instead, plagioclase may be joined by sanidine at a later stage of crystallization in trachytic lavas than in less calcic rhyolites (Carmichael,

1963), so that only the more sodic plagioclases have co-precipitated with sanidine in trachytes. Thus, the average composition of plagioclase in trachytes may always be richer in An than that of any plagioclase that was in stable equilibrium with sanidine. In the same fashion, the large uncertainties in estimated conditions of "ternary-feldspar" equilibration of the Roman lavas probably indicate the nonequilibrium nature of the average feldspar compositions used in the P - T calculations (Table 2).

It should be remembered that calculated temperatures and pressures based on feldspars that are unlikely to have been in equilibrium can be grossly misleading because the results may look reasonable (Powell, 1985). Because the ternary-feldspar thermobarometer appears extremely sensitive to compositional variations in coexisting feldspars, a detailed understanding of mineral and textural relations in each rock is a necessary prerequisite to its application and to predicted temperatures and pressures having any geologic credibility. It can be shown that although the two-feldspar geothermometers based solely on the albite-exchange reaction are capable of yielding reasonable temperature estimates at an assumed pressure, the exchange equilibria involving An and Or may not approach equilibrium under the same P - T conditions. The prediction of nonequivalent equilibration conditions supports Brown and Parsons (1981, 1985) contention that "double-binary" thermometers cannot account satisfactorily for the ternary nature of natural feldspars.

SUMMARY AND CONCLUSIONS

Excess free energy of mixing expressions for the system An-Or have been calibrated as functions of pressure and temperature using the distribution of Or in the experimental feldspar pairs of Seck (1971a, 1971b) and the solution properties of the An-Ab and Ab-Or binaries proposed by Newton et al. (1980) and Haselton et al. (1983), respectively. The binary Margules parameters, combined with a ternary subregular solution model and an ideal site-mixing model for the configurational entropy of solution, have been used to solve simultaneously An, Ab, and Or activity-composition relations. Unlike previous formulations of the two-feldspar geothermometer (Stormer, 1975; Whitney and Stormer, 1977; Powell and Powell, 1977; Brown and Parsons, 1981; Haselton et al., 1983; Ghiorso, 1984; Price, 1985), such an explicit solution of the An, Ab, and Or activity-composition expressions does not require a pressure estimate before an equilibration temperature can be calculated. Instead, the proposed thermodynamically based model permits estimation of both P and T of equilibration based solely on the composition of coexisting feldspars. This "ternary-feldspar" thermobarometer, however, appears to be extremely sensitive to analytical precision and to definition of equilibrium feldspar composition. Its use may also be limited by questions about whether Seck's experimental feldspars, on which the estimated An-Or mixing parameters are based, possess equilibrium compositions. Nevertheless, the formulation of the thermobarometer, presented here, is thermodynamically correct and emphasizes the potential of ternary-

feldspar equilibria and the urgent need for further experimental work on either the An-Or binary or the ternary-feldspar system.

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APPENDIX 1.

TERNARY-FELDSPAR ACTIVITY-COMPOSITION RELATIONS

Utilizing the An-Ab Margules parameters of Newton et al. (1980), the Ab-Or Margules parameters of Haselton et al. (1983), and the An-Or mixing parameters estimated from orthoclase equilibria (Appendix Table 1), the appropriate ternary equilibrium-temperature relationships (in kelvins; assuming identical standard states for An, Ab, and Or components in both feldspars) are given by the following expressions.

Orthoclase component

$$T_{\text{Or}} = \{ [W_H^{\text{Ca}}A + W_H^{\text{CaK}}B + W_H^{\text{Na}}C + W_H^{\text{NaK}}D + W_H^{\text{CaNa}}E + W_H^{\text{CaCa}}F] + [W_H^{\text{Ca}}A + W_H^{\text{CaK}}B + W_H^{\text{Na}}C + W_H^{\text{NaK}}D]P \} / \{ -8.3147 [\ln[X_{\text{Or}}^{\text{PF}}(2 - X_{\text{Ab}}^{\text{PF}} - X_{\text{Or}}^{\text{PF}})(X_{\text{Ab}}^{\text{PF}} + X_{\text{Or}}^{\text{PF}})] - \ln[X_{\text{Or}}^{\text{AF}}(2 - X_{\text{Ab}}^{\text{AF}} - X_{\text{Or}}^{\text{AF}}) \cdot (X_{\text{Ab}}^{\text{AF}} + X_{\text{Or}}^{\text{AF}})] \} + [W_S^{\text{Ca}}A + W_S^{\text{CaK}}B + W_S^{\text{Na}}C + W_S^{\text{NaK}}D],$$

where

$$A = (X_{\text{An}}^{\text{PF}})^2(1 - 2X_{\text{Or}}^{\text{PF}}) + 0.5X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}} - X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}}X_{\text{Or}}^{\text{PF}} - [(X_{\text{An}}^{\text{AF}})^2(1 - 2X_{\text{Or}}^{\text{AF}}) + 0.5X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}} - X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}}X_{\text{Or}}^{\text{AF}}],$$

$$B = 2X_{\text{Or}}^{\text{PF}}(X_{\text{An}}^{\text{PF}})^2 + 0.5X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}} + X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}}X_{\text{Or}}^{\text{PF}} - [2X_{\text{Or}}^{\text{AF}}(X_{\text{An}}^{\text{AF}})^2 + 0.5X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}} + X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}}X_{\text{Or}}^{\text{AF}}],$$

$$C = (X_{\text{Ab}}^{\text{PF}})^2(1 - 2X_{\text{Or}}^{\text{PF}}) + 0.5X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}} - X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}}X_{\text{Or}}^{\text{PF}} - [(X_{\text{Ab}}^{\text{AF}})^2(1 - 2X_{\text{Or}}^{\text{AF}}) + 0.5X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}} - X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}}X_{\text{Or}}^{\text{AF}}],$$

$$D = 2X_{\text{Or}}^{\text{PF}}(X_{\text{Ab}}^{\text{PF}})^2 + 0.5X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}} + X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}}X_{\text{Or}}^{\text{PF}} - [2X_{\text{Or}}^{\text{AF}}(X_{\text{Ab}}^{\text{AF}})^2 + 0.5X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}} + X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}}X_{\text{Or}}^{\text{AF}}],$$

$$E = -0.5X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}} + X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}}(X_{\text{An}}^{\text{PF}} - X_{\text{Ab}}^{\text{PF}}) - [-0.5X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}} + X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}}(X_{\text{An}}^{\text{AF}} - X_{\text{Ab}}^{\text{AF}})],$$

and

$$F = -0.5X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}} - X_{\text{An}}^{\text{PF}}X_{\text{Ab}}^{\text{PF}}(X_{\text{An}}^{\text{PF}} - X_{\text{Ab}}^{\text{PF}}) - [-0.5X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}} - X_{\text{An}}^{\text{AF}}X_{\text{Ab}}^{\text{AF}}(X_{\text{An}}^{\text{AF}} - X_{\text{Ab}}^{\text{AF}})],$$

Albite component

$$T_{\text{Ab}} = \{ [W_H^{\text{Ca}}G + W_H^{\text{CaK}}H + W_H^{\text{Na}}I + W_H^{\text{NaK}}J + W_H^{\text{CaNa}}K + W_H^{\text{CaCa}}L] + [W_H^{\text{Ca}}G + W_H^{\text{CaK}}H + W_H^{\text{Na}}I + W_H^{\text{NaK}}J]P \} / \{ -8.3147 [\ln[X_{\text{Ab}}^{\text{PF}}(2 - X_{\text{An}}^{\text{PF}} - X_{\text{Or}}^{\text{PF}})(X_{\text{An}}^{\text{PF}} + X_{\text{Or}}^{\text{PF}})] - \ln[X_{\text{Ab}}^{\text{AF}}(2 - X_{\text{An}}^{\text{AF}} - X_{\text{Or}}^{\text{AF}}) \cdot (X_{\text{An}}^{\text{AF}} + X_{\text{Or}}^{\text{AF}})] \} + [W_S^{\text{Ca}}G + W_S^{\text{CaK}}H + W_S^{\text{Na}}I + W_S^{\text{NaK}}J],$$

Appendix Table 1. Adopted thermodynamic parameters

Interaction	W_r (J/mol)	W_g (J/mol·K)	W_v (J/bar)	Source
Ca-Na	8 473	0	0	Newton et al. (1980)
Na-Ca	28 230	0	0	Newton et al. (1980)
K-Na	27 320	10.3	0.364	Haselton et al. (1983)
Na-K	18 810	10.3	0.364	Haselton et al. (1983)
Ca-K	-65 407	-114.104	2.1121	This study
K-Ca	65 305.4	12.5365	0.9699	This study

where

$$G = -0.5X_{Or}^{PF}X_{An}^{PF} + X_{Or}^{PF}X_{An}^{PF}(X_{Or}^{PF} - X_{An}^{PF}) \\ - [-0.5X_{Or}^{AF}X_{An}^{AF} + X_{Or}^{AF}X_{An}^{AF}(X_{Or}^{AF} - X_{An}^{AF})],$$

$$H = -0.5X_{Or}^{PF}X_{An}^{PF} - X_{Or}^{PF}X_{An}^{PF}(X_{Or}^{PF} - X_{An}^{PF}) \\ - [-0.5X_{Or}^{AF}X_{An}^{AF} - X_{Or}^{AF}X_{An}^{AF}(X_{Or}^{AF} - X_{An}^{AF})],$$

$$I = 2X_{Ab}^{PF}(X_{Or}^{PF})^2 + 0.5X_{Or}^{PF}X_{An}^{PF} + X_{An}^{PF}X_{Ab}^{PF}X_{Or}^{PF} \\ - [2X_{Ab}^{AF}(X_{Or}^{AF})^2 + 0.5X_{Or}^{AF}X_{An}^{AF} + X_{An}^{AF}X_{Ab}^{AF}X_{Or}^{AF}],$$

$$J = (X_{Or}^{PF})^2 - 2X_{Ab}^{PF}(X_{Or}^{PF})^2 + 0.5X_{Or}^{PF}X_{An}^{PF} - X_{An}^{PF}X_{Ab}^{PF}X_{Or}^{PF} \\ - [(X_{Or}^{AF})^2 - 2X_{Ab}^{AF}(X_{Or}^{AF})^2 + 0.5X_{Or}^{AF}X_{An}^{AF} - X_{An}^{AF}X_{Ab}^{AF}X_{Or}^{AF}],$$

$$K = 2X_{Ab}^{PF}(X_{An}^{PF})^2 + 0.5X_{Or}^{PF}X_{An}^{PF} + X_{An}^{PF}X_{Ab}^{PF}X_{Or}^{PF} \\ - [2X_{Ab}^{AF}(X_{An}^{AF})^2 + 0.5X_{Or}^{AF}X_{An}^{AF} + X_{An}^{AF}X_{Ab}^{AF}X_{Or}^{AF}],$$

and

$$L = (X_{An}^{PF})^2 - 2X_{Ab}^{PF}(X_{An}^{PF})^2 + 0.5X_{Or}^{PF}X_{An}^{PF} - X_{An}^{PF}X_{Ab}^{PF}X_{Or}^{PF} \\ - [(X_{An}^{AF})^2 - 2X_{Ab}^{AF}(X_{An}^{AF})^2 + 0.5X_{Or}^{AF}X_{An}^{AF} - X_{An}^{AF}X_{Ab}^{AF}X_{Or}^{AF}],$$

Anorthite component

$$T_{An} = \{ [W_H^{KCa}M + W_H^{CaK}N + W_H^{KNa}O + W_H^{NaK}Q \\ + W_H^{CaNa}R + W_H^{NaCa}S] \\ + [W_V^{KCa}M + W_V^{CaK}N + W_V^{KNa}O + W_V^{NaK}Q]P \} / \\ \{ -8.3147 \langle \ln[0.25X_{An}^{PF}(1 + X_{An}^{PF})^2] \\ - \ln[0.25X_{An}^{AF}(1 + X_{An}^{AF})^2] \rangle \\ + [W_S^{KCa}M + W_S^{CaK}N + W_S^{KNa}O + W_S^{NaK}Q] \},$$

where

$$M = 2X_{An}^{PF}(X_{Or}^{PF})^2 + 0.5X_{Ab}^{PF}X_{Or}^{PF} + X_{An}^{PF}X_{Ab}^{PF}X_{Or}^{PF} \\ - [2X_{An}^{AF}(X_{Or}^{AF})^2 + 0.5X_{Ab}^{AF}X_{Or}^{AF} + X_{An}^{AF}X_{Ab}^{AF}X_{Or}^{AF}],$$

$$N = (X_{Or}^{PF})^2(1 - 2X_{An}^{PF}) + 0.5X_{Ab}^{PF}X_{Or}^{PF} - X_{An}^{PF}X_{Ab}^{PF}X_{Or}^{PF} \\ - [(X_{Or}^{AF})^2(1 - 2X_{An}^{AF}) + 0.5X_{Ab}^{AF}X_{Or}^{AF} - X_{An}^{AF}X_{Ab}^{AF}X_{Or}^{AF}],$$

$$O = -0.5X_{Ab}^{PF}X_{Or}^{PF} - X_{Ab}^{PF}X_{Or}^{PF}(X_{Ab}^{PF} - X_{Or}^{PF}) \\ - [-0.5X_{Ab}^{AF}X_{Or}^{AF} - X_{Ab}^{AF}X_{Or}^{AF}(X_{Ab}^{AF} - X_{Or}^{AF})],$$

$$Q = -0.5X_{Ab}^{PF}X_{Or}^{PF} + X_{Ab}^{PF}X_{Or}^{PF}(X_{Ab}^{PF} - X_{Or}^{PF}) \\ - [-0.5X_{Ab}^{AF}X_{Or}^{AF} + X_{Ab}^{AF}X_{Or}^{AF}(X_{Ab}^{AF} - X_{Or}^{AF})],$$

$$R = (X_{Ab}^{PF})^2(1 - 2X_{An}^{PF}) + 0.5X_{Ab}^{PF}X_{Or}^{PF} - X_{An}^{PF}X_{Ab}^{PF}X_{Or}^{PF} \\ - [(X_{Ab}^{AF})^2(1 - 2X_{An}^{AF}) + 0.5X_{Ab}^{AF}X_{Or}^{AF} - X_{An}^{AF}X_{Ab}^{AF}X_{Or}^{AF}],$$

$$S = 2X_{An}^{PF}(X_{Ab}^{PF})^2 + 0.5X_{Ab}^{PF}X_{Or}^{PF} + X_{An}^{PF}X_{Ab}^{PF}X_{Or}^{PF} \\ - [2X_{An}^{AF}(X_{Ab}^{AF})^2 + 0.5X_{Ab}^{AF}X_{Or}^{AF} + X_{An}^{AF}X_{Ab}^{AF}X_{Or}^{AF}],$$

and X_{Or} , X_{Ab} , and X_{An} are mole fractions of orthoclase, albite, and anorthite in plagioclase (PF) and alkali feldspar (AF).