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Ternary-feldspar modeling and thermometry

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Abstract

A revised thermodynamic model for ternary feldspars—an extension of the approach of Ghiorso (1984)—was made possible by (a) inclusion of volume data for ternary feldspars and (b) adjustment of the compositions (within analytical error) of some of the experimental data points (Seck, 1971a). The excess free-energy expressions of Newton et al. (1980) are used for the plagioclase binary join and those of Haselton et al. (1983) for alkali feldspar. Excess terms for the An-Or join and for ternary interaction were obtained from Seck's experiments by the method of linear least squares. The new model is consistent with most occurrences of natural ternary feldspars and with experiments on strongly ternary feldspars. Most ternary feldspars have *negative* excess volumes—an important constraint on pressure corrections in geothermometry.

The activity expressions of this model permit yet another formulation of the two-feldspar geothermometer that fully takes ternary solution into account; it yields three temperatures, one each for Ab, Or, and An equilibria. Few published analyses of feldspar pairs give concordant temperatures, probably because small errors in composition strongly affect the calculated temperatures. However, if the compositions of coexisting feldspars are allowed to vary within expected analytical error, three concordant temperatures can be calculated for feldspar pairs that were close to being in equilibrium. The program presented will also indicate pairs that could not have been in equilibrium. This thermometer is more useful than previous two-feldspar thermometers because it (1) fully accounts for ternary solid solution, (2) indicates whether the two feldspars could have been in equilibrium, and (3) gives further information about how the feldspar compositions may have been changed by such postcrystallization processes as alkali exchange and subsolidus exsolution. Our thermometer yields temperatures similar to those obtained using the formulation of Haselton et al. (1983) for pairs of feldspars close to binary compositions, and much more reasonable temperatures for strongly ternary compositions than any previous thermometer.

Introduction and previous work

The ternary-feldspar system has been given much attention over the past few decades, mainly for purposes of geothermometry. In the ternary-feldspar system, $NaAlSi_3O_8$-$KAlSi_3O_8$-$CaAl_2Si_2O_8$ (for this paper, Ab, Or, and An components, respectively), there is complete solid solution at high temperatures on the Ab-Or and Ab-An binaries, but limited solid solution between An and Or and between plagioclase and alkali feldspars within the ternary. The compositions of the coexisting feldspars are strong functions of temperature; effects of pressure must also be taken into account. Most formulations of the feldspar thermometer concentrate on two feldspar binaries, Ab-An and Ab-Or, and do not fully account for ternary compositions (Barth, 1951; Stormer, 1975; Powell and Powell, 1977; Whitney and Stormer, 1977; Brown and Parsons, 1981; Haselton et al., 1983). Thermodynamically based thermometers should be designed to account for ternary solid solution in both the plagioclase and alkali feldspar phases (Brown and Parsons, 1985). These double-binary thermometers do not utilize the fact that two feldspars coexisting in equilibrium must have the activities of *all* their components equal, not just those of Ab. What is needed is a description of the system in ternary terms: ternary mixing parameters can be modeled from existing ternary experimental data and then used to predict temperatures of equilibrium of coexisting natural feldspars. A thermometer based on ternary expressions is not limited to compositions close to the feldspar binaries; it eliminates arbitrary projection of ternary compositions to the binaries; and, most important, it provides valuable tests for equilibrium between coexisting feldspars. It is incumbent on any petrologist, when applying any thermometer, to offer evidence that the phases involved were at some time in equilibrium; it may be necessary to reconstruct original compositions of exsolved phases, or to decide which portions of zoned feldspars may have been in equilibrium. A great advantage of a feldspar thermometer based on a ternary model is that it allows an additional test of equilibrium—provided, of course, that one believes the model to be correct—because the three si-

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TABLE 1. Excess terms for ternary feldspars (in joules)

	Ghiorso (1984)			Green and Usdansky (1986)			This study		
	W_H	W_S	W_V	W_H	W_S	W_V	W_H	W_S	W_V*
W_{AbOr}**	30978	21.4	0.361	18810	10.3	0.364	18810	10.3	0.394(0.017)
W_{OrAb}	17062		0.361	27320	10.3	0.364	27320	10.3	0.394(0.017)
W_{AbAn}†	28226			28230			28226		
W_{AnAb}	8471			8473			8471		
W_{AnOr}	**27983**	**−20.21**		**−65407**	**−114.104**	**2.1121**	**52468(497)**		−0.120(0.04)
W_{OrAn}	**67469**	**11.06**		**65305**	**12.537**		**47396(235)**		
W_{OrAbAn}	**−13869**	**−14.63**					**8700(897)**		−1.094(0.125)

Note: $W_G = W_H - TW_S + PW_V$. Absence of an entry means that the parameter was set or assumed to be zero. Boldface values are results of least-squares fits to the data of Seck (1971a, 1971b). Values in ( ) are uncertainties ($\pm 1\sigma$) in parameters.

* Excess volumes for this study were fitted to the data of Newton et al. (1980) and Kroll et al. (1986).

** *W* terms for Ab-Or taken from Thompson and Hovis (1979) [Ghiorso] and from Haselton et al. (1983) [Green and Usdansky, this study].

† *W* terms for An-Ab taken from Newton et al. (1980).

multaneous equilibria (among Ab, An, and Or components) provide redundant information on temperature.

Thus far, the only thermodynamic models that utilize both existing experimental data and explicit formulations for ternary mixing parameters are those of Ghiorso (1984) and of Green and Usdansky (1986). Both of these models, though successful for some feldspars, have certain drawbacks: (1) they are based on synthesis experiments, (2) they use a single equation of state for both monoclinic and triclinic feldspars, (3) they lack volume data for ternary feldspars, and (4) they predict unrealistic temperatures for many natural and synthetic ternary feldspars.

Because we needed to apply a solution model to strongly ternary natural and synthetic feldspars (Fuhrman, 1986; Fuhrman et al., unpub. ms.), we have devised yet another model—one that also includes volume data for ternary feldspars (Kroll et al., 1986). Our model shares the first two drawbacks of the earlier models—use of synthesis data and of a single equation of state. Because there must be a first-order thermodynamic difference between feldspars with the two different structures, at least two equations are required for a rigorous formulation. Although we recognize that feldspar models must ultimately use at least two separate equations, we believe that the data now available—both for phase equilibria and for volumes—do not justify such a level of sophistication. For example, it is not always clear which structure a given feldspar had when it was in equilibrium, yet such information would be absolutely essential if one were to try to fit a separate equation to each feldspar structure. Furthermore, separate equations would more than double the number of unknowns to be fitted to the data: additional Margules parameters would be required, and we would also need free-energy terms for the monoclinic-to-triclinic reactions for end-member Ab, An, and Or. Accordingly, we have retained the single-equation model despite its shortcomings, with the full realization that as well-reversed experimental data on ternary feldspars become available, two or more equations of state will be more appropriate.

Ternary solution model

A ternary solution model involves expressions for configurational entropy (ideal part of activity terms) and for excess free energy (activity coefficients). Ghiorso (1984) extended the Al-avoidance model for the entropy of plagioclase (Newton et al., 1980; Kerrick and Darken, 1975) to ternary feldspars; for pure ternary feldspars, his expressions are equivalent to the site-mixing terms (Price, 1985) that were adopted by Green and Usdansky (1986). Both of these models employ ternary Margules expressions for excess energy (Wohl, 1953; Andersen and Lindsley, 1981), which involve parameters for each of the three binaries, plus—in Ghiorso's model—a ternary excess term. Both models used published values for the Ab-An and the Ab-Or joins (Table 1). Because there are essentially no experimental data for the third binary (An-Or), they calculated asymmetric Margules parameters for it by modeling the experimental data of Seck (1971a, 1971b) for ternary pairs.

The results of these earlier calibrations are shown in Table 1. The conventions for labeling the parameters in Table 1 are those of Andersen and Lindsley (1981), Ghiorso (1984), and Green and Usdansky (1986); they are opposite to those used by Haselton et al. (1983). Ghiorso concluded that the ternary term is significant only at low *T*. His method yields a temperature dependence for each unknown, so his model uses six new parameters to describe the system: three excess enthalpies (W_H) and three excess entropies (W_S). Green and Usdansky likewise calculated six new parameters; however, they concluded that the ternary terms were unnecessary, and instead they extracted large *positive* excess volume terms for the An-Or binary on the basis of Seck's experiments at 1, 5, and 10 kbar (1971a, 1971b).

The approach adopted by Ghiorso and by Green and Usdansky provides a definite improvement on previous two-feldspar geothermometers by using explicit ternary mixing parameters to describe the feldspar system. However, both models have problems in predicting some feldspar relationships: they predict less miscibility in the ternary feldspars than is suggested by many natural feldspars. Among these are ternary mesoperthites from the Sybille Monzosyenite (Fuhrman, 1986) and from the Klokken Syenogabbro (Parsons and Brown, 1983). Independent thermometers suggest that these feldspars crystallized at 950–1020 °C, whereas Ghiorso's model would require temperatures above 1200 °C and the thermometer of Green and Usdansky gives strongly disparate temperatures for each of the three equilibria. It is likely that the determinations of Seck (1971a, 1971b) underestimate An in alkali feldspar, possibly as the result of analytical error or of incomplete equilibrium in Seck's experiments or both. Seck's analytical method, X-ray determinations combined with geometric constraints, has a probable uncertainly of up to 2 mol% (and even more for strongly ternary compositions) and allows considerable latitude in the choice of "best" values. He reported very low solubility of An in alkali feldspar and, more important, very little increase in that solubility with increasing temperature. By adopting Seck's values, the earlier modelers were forced to include a *negative* excess entropy term for one of the An-Or Margules parameters, a highly unusual property for silicates if real. As we show in a later section, very small increases (well within the analytical uncertainty) in the An content of alkali feldspar for Seck's higher-temperature experiments can eliminate the need for this negative excess entropy.

PRESENT STUDY

We have followed the approach of Ghiorso (1984) with the following exceptions: (1) we fitted the volume data of Kroll et al. (1986) and Newton et al. (1980) to obtain excess volumes for the An-Or join and for the ternary; (2) like Green and Usdansky (1986) we used the alkali feldspar model of Haselton et al. (1983) for the Ab-Or join; (3) we used Seck's data but (for reasons explained in a later section) omitted the 650 °C experiments; (4) we adjusted the compositions of some of Seck's experiments within his analytical uncertainty to give slightly more ternary solution at the higher temperatures.

Modeling of volumes

The molar volume of a ternary feldspar can be expressed as

$$V = X_{\mathrm{Or}}V_{\mathrm{Or}} + X_{\mathrm{Ab}}V_{\mathrm{Ab}} + X_{\mathrm{An}}V_{\mathrm{An}} + V^{\mathrm{xs}}, \tag{1}$$

where, from the expression for G^{xs} from Andersen and Lindsley (1981),

$$\begin{aligned} V^{\mathrm{xs}} = {} & W_{V,\mathrm{OrAb}}(X_{\mathrm{Or}}X_{\mathrm{Ab}})(X_{\mathrm{Ab}} + X_{\mathrm{An}}/2) \\ & + W_{V,\mathrm{AbOr}}(X_{\mathrm{Or}}X_{\mathrm{Ab}})(X_{\mathrm{Or}} + X_{\mathrm{An}}/2) \\ & + W_{V,\mathrm{OrAn}}(X_{\mathrm{Or}}X_{\mathrm{An}})(X_{\mathrm{An}} + X_{\mathrm{Ab}}/2) \\ & + W_{V,\mathrm{AnOr}}(X_{\mathrm{Or}}X_{\mathrm{An}})(X_{\mathrm{Or}} + X_{\mathrm{Ab}}/2) \\ & + W_{V,\mathrm{AbAn}}(X_{\mathrm{Ab}}X_{\mathrm{An}})(X_{\mathrm{An}} + X_{\mathrm{Or}}/2) \\ & + W_{V,\mathrm{AnAb}}(X_{\mathrm{Ab}}X_{\mathrm{An}})(X_{\mathrm{Ab}} + X_{\mathrm{Or}}/2) \\ & + W_{V,\mathrm{OrAbAn}}(X_{\mathrm{Or}}X_{\mathrm{Ab}}X_{\mathrm{An}}). \end{aligned} \tag{2}$$

Because excess volume parameters for the plagioclase binary join are not significant (Newton et al., 1980), they are set to zero. In addition, we treat excess volume for alkali feldspar as symmetric (Hovis, 1977; Kroll et al., 1986):

$$W_{V,\mathrm{OrAb}} = W_{V,\mathrm{AbOr}}. \tag{3}$$

Equation 1 therefore becomes

$$\begin{aligned} V = {} & X_{\mathrm{Or}}V_{\mathrm{Or}} + X_{\mathrm{Ab}}V_{\mathrm{Ab}} + X_{\mathrm{An}}V_{\mathrm{An}} + W_{V,\mathrm{OrAb}}(X_{\mathrm{Or}}X_{\mathrm{Ab}}) \\ & + W_{V,\mathrm{OrAn}}(X_{\mathrm{Or}}X_{\mathrm{An}})(X_{\mathrm{An}} + X_{\mathrm{Ab}}/2) \\ & + W_{V,\mathrm{AnOr}}(X_{\mathrm{Or}}X_{\mathrm{An}})(X_{\mathrm{Or}} + X_{\mathrm{An}}/2) \\ & + W_{V,\mathrm{OrAbAn}}(X_{\mathrm{Or}}X_{\mathrm{Ab}}X_{\mathrm{An}}). \end{aligned} \tag{4}$$

We used volume data from Kroll et al. (1986) and Newton et al. (1980) in a least-squares refinement of Equation 4 to yield values for $W_{V,\mathrm{OrAb}}$, $W_{V,\mathrm{OrAn}}$, $W_{V,\mathrm{AnOr}}$, and $W_{V,\mathrm{OrAbAn}}$ (Table 1). (Attempts to use other combinations of parameters—for example $W_{V,\mathrm{OrAn}}$ and $W_{V,\mathrm{AnOr}}$ without the ternary term—did not fit the data nearly so well; the refined value for $W_{V,\mathrm{OrAn}}$ was found to be zero within error and was therefore set to zero in the final fitting.) The value for $W_{V,\mathrm{OrAb}}$ is similar to such values found by Thompson and Hovis (1979) and Kroll et al. (1986), but is about 10% larger, a result of our fitting data for binary and ternary feldspar simultaneously. The data yield significant negative excess volumes for the ternary and for one of the An-Or binary terms, an important result because it implies that as feldspars become more strongly ternary, the effect of pressure on the miscibility gap becomes the opposite of that on the alkali feldspar binary: at constant temperature, the ternary-feldspar miscibility gap becomes narrower with increasing pressure. This effect is suggested independently by experiments on ternary feldspars, where at similar temperatures, higher pressures (5 kbar) produced more strongly ternary feldspars than did low pressures (1 atm) (Fuhrman, 1986). As in the case for the free energies, rigorous treatment of the volumes would require two equations, one each for triclinic and monoclinic feldspars. Nevertheless, the volume data clearly show that a single-phase ternary feldspar has a lower molar volume than do coexisting plagioclase and alkali feldspar (lying either on or close to the binary joins) of equivalent bulk composition. The small negative excess volume for the An-Or join derived from the volume data of Kroll et al. contrasts strongly with the large positive excess volume calculated by Green and Usdansky (1986) from Seck's tie line data. If Seck's polybaric experiments at 650 °C had been reversed and the compositions rigorously determined, we would accept the volumes extracted by Green and Usdansky; since neither is the case, we consider it preferable to use the measured volumes. That choice is being confirmed by continuing experiments on feldspar equilibria at 10 kbar (Hadjigeorgiou et al., 1987). The implications for the pressure effect on two-feldspar thermometers are profound.

We do not have a physical explanation for these negative volumes of mixing, which are unusual for silicates. If they were releated to the Al-Si substitution, the Ab-An join should be similarly affected, but it is not. We can only surmise they result from an unexpected interaction between K and Ca in the feldspar structure.

Activity expressions

The Al-avoidance model (Ghiorso, 1984) results in expressions for ideal activities of pure ternary feldspars identical to those given by the site-mixing model of Price (1985). Thus the site-mixing expressions used by Green and Usdansky (1986) are identical to Ghiorso's and our own for ternary compositions. Combination of the configurational terms with the expression for excess free energy of mixing yields

$$G^{\mathrm{mix}} = -TS^{\mathrm{conf}} + G^{\mathrm{xs}}. \tag{5}$$

$$\begin{aligned} G^{\mathrm{mix}} = {} & RT\{X_{\mathrm{Ab}}\ln[X_{\mathrm{Ab}}(1 - X_{\mathrm{An}}^2)] \\ & + X_{\mathrm{Or}}\ln[X_{\mathrm{Or}}(1 - X_{\mathrm{An}}^2)] \\ & + X_{\mathrm{An}}\ln[X_{\mathrm{An}}(1 - X_{\mathrm{An}})^2/4]\} \\ & + W_{\mathrm{OrAb}}(X_{\mathrm{Or}}X_{\mathrm{Ab}})(X_{\mathrm{Ab}} + X_{\mathrm{An}}/2) \\ & + W_{\mathrm{AbOr}}(X_{\mathrm{Or}}X_{\mathrm{Ab}})(X_{\mathrm{Or}} + X_{\mathrm{An}}/2) \\ & + W_{\mathrm{OrAn}}(X_{\mathrm{Or}}X_{\mathrm{An}})(X_{\mathrm{An}} + X_{\mathrm{Ab}}/2) \\ & + W_{\mathrm{AnOr}}(X_{\mathrm{Or}}X_{\mathrm{An}})(X_{\mathrm{Or}} + X_{\mathrm{Ab}}/2) \\ & + W_{\mathrm{AbAn}}(X_{\mathrm{Ab}}X_{\mathrm{An}})(X_{\mathrm{An}} + X_{\mathrm{Or}}/2) \\ & + W_{\mathrm{AnAb}}(X_{\mathrm{Ab}}X_{\mathrm{An}})(X_{\mathrm{Ab}} + X_{\mathrm{Or}}/2) \\ & + W_{\mathrm{OrAbAn}}(X_{\mathrm{Or}}X_{\mathrm{Ab}}X_{\mathrm{An}}). \end{aligned} \tag{6}$$

If we accept previously determined values for the Ab-An and Ab-Or joins, there are three unknown parameters in the expression above: W_{OrAn}, W_{AnOr}, and W_{OrAbAn}—or six if each of these W_G terms includes a temperature-dependent term (W_S).

At a given P and T, two coexisting feldspars must meet the equilibrium conditions:

$$a_{\mathrm{Ab}}^{\mathrm{alk}} = a_{\mathrm{Ab}}^{\mathrm{plag}} \tag{7}$$

$$a_{\mathrm{Or}}^{\mathrm{alk}} = a_{\mathrm{Or}}^{\mathrm{plag}} \tag{8}$$

$$a_{\mathrm{An}}^{\mathrm{alk}} = a_{\mathrm{An}}^{\mathrm{plag}}. \tag{9}$$

Equation 6 is combined with the relationship

$$RT \ln a_i = G^{\mathrm{mix}} + (1 - X_i)(\partial G/\partial X_i)_{T,P,X_j,X_k} \tag{10}$$

and, after differentiation and some simplification, we obtain the activities:

$$\begin{aligned} a_{\mathrm{Ab}} = {} & X_{\mathrm{Ab}}(1 - X_{\mathrm{An}}^2) \\ & \cdot\exp\{(W_{\mathrm{OrAb}}[2X_{\mathrm{Ab}}X_{\mathrm{Or}}(1 - X_{\mathrm{Ab}}) \\ & \qquad + X_{\mathrm{Or}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Ab}})] \\ & + W_{\mathrm{AbOr}}[X_{\mathrm{Or}}^2(1 - 2X_{\mathrm{Ab}}) + X_{\mathrm{Or}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Ab}})] \\ & + W_{\mathrm{OrAn}}[X_{\mathrm{Or}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Ab}} - 2X_{\mathrm{An}})] \\ & + W_{\mathrm{AnOr}}[X_{\mathrm{Or}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Ab}} - 2X_{\mathrm{Or}})] \\ & + W_{\mathrm{AbAn}}[X_{\mathrm{An}}^2(1 - 2X_{\mathrm{Ab}}) + X_{\mathrm{Or}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Ab}})] \\ & + W_{\mathrm{AnAb}}[2X_{\mathrm{Ab}}X_{\mathrm{An}}(1 - X_{\mathrm{Ab}}) \\ & \qquad + X_{\mathrm{Or}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Ab}})] \\ & + W_{\mathrm{OrAbAn}}[X_{\mathrm{Or}}X_{\mathrm{An}}(1 - 2X_{\mathrm{Ab}})])/RT\} \end{aligned} \tag{11}$$

$$\begin{aligned} a_{\mathrm{Or}} = {} & X_{\mathrm{Or}}(1 - X_{\mathrm{An}}^2) \\ & \cdot\exp\{(W_{\mathrm{OrAb}}[X_{\mathrm{Ab}}^2(1 - 2X_{\mathrm{Or}}) + X_{\mathrm{Ab}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Or}})] \\ & + W_{\mathrm{AbOr}}[2X_{\mathrm{Ab}}X_{\mathrm{Or}}(1 - X_{\mathrm{Or}}) \\ & \qquad + X_{\mathrm{Ab}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Or}})] \\ & + W_{\mathrm{OrAn}}[X_{\mathrm{An}}^2(1 - 2X_{\mathrm{Or}}) \\ & \qquad + X_{\mathrm{Ab}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Or}})] \\ & + W_{\mathrm{AnOr}}[2X_{\mathrm{Or}}X_{\mathrm{An}}(1 - X_{\mathrm{Or}}) \\ & \qquad + X_{\mathrm{Ab}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Or}})] \\ & + W_{\mathrm{AbAn}}[X_{\mathrm{Ab}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Or}} - 2X_{\mathrm{An}})] \\ & + W_{\mathrm{AnAb}}[X_{\mathrm{Ab}}X_{\mathrm{An}}(1/2 - X_{\mathrm{Or}} - 2X_{\mathrm{Ab}})] \\ & + W_{\mathrm{OrAbAn}}[X_{\mathrm{Ab}}X_{\mathrm{An}}(1 - 2X_{\mathrm{Or}})])/RT\} \end{aligned} \tag{12}$$

$$\begin{aligned} a_{\mathrm{An}} = {} & [X_{\mathrm{An}}(1 + X_{\mathrm{An}})^2/4] \\ & \cdot\exp\{(W_{\mathrm{OrAb}}[X_{\mathrm{Ab}}X_{\mathrm{Or}}(1/2 - X_{\mathrm{An}} - 2X_{\mathrm{Ab}})] \\ & + W_{\mathrm{AbOr}}[X_{\mathrm{Ab}}X_{\mathrm{Or}}(1/2 - X_{\mathrm{An}} - 2X_{\mathrm{Or}})] \\ & + W_{\mathrm{OrAn}}[2X_{\mathrm{Or}}X_{\mathrm{An}}(1 - X_{\mathrm{An}}) \\ & \qquad + X_{\mathrm{Ab}}X_{\mathrm{Or}}(1/2 - X_{\mathrm{An}})] \\ & + W_{\mathrm{AnOr}}[X_{\mathrm{Or}}^2(1 - 2X_{\mathrm{An}}) \\ & \qquad + X_{\mathrm{Ab}}X_{\mathrm{Or}}(1/2 - X_{\mathrm{An}})] \\ & + W_{\mathrm{AbAn}}[2X_{\mathrm{Ab}}X_{\mathrm{An}}(1 - X_{\mathrm{An}}) \\ & \qquad + X_{\mathrm{Ab}}X_{\mathrm{Or}}(1/2 - X_{\mathrm{An}})] \\ & + W_{\mathrm{AnAb}}[X_{\mathrm{Ab}}^2(1 - 2X_{\mathrm{An}}) \\ & \qquad + X_{\mathrm{Ab}}X_{\mathrm{Or}}(1/2 - X_{\mathrm{An}})] \\ & + W_{\mathrm{OrAbAn}}[X_{\mathrm{Or}}X_{\mathrm{Ab}}(1 - 2X_{\mathrm{An}})])/RT\} \end{aligned} \tag{13}$$

These activity expressions are identical to those of Ghiorso (1984), except that we include excess volume terms in W_{ij} and we include the ternary terms that were accidentally omitted from his published equations.

By substituting Equations 11–13 into Equations 7–9 and gathering unknown parameters together, we obtain expressions with a constant term on one side (all known parameters) and the three unknown W_{ij} terms with their coefficients on the other. Like Ghiorso and Green and Usdansky, we then employ the method of least squares to solve for these unknown parameters using $3n$ equations derived from the n experimentally determined tie lines.

Experimental data base

Seck (1971a, 1971b) has presented the most extensive experimental data on coexisting ternary feldspars. There has been some question as to the attainment of equilibrium in these experiments (e.g., Johannes, 1979; Brown and Parsons, 1981) both because of the use of gels as starting materials and because of the general problem of slow reaction rates in feldspar experiments. Johannes (1979) determined two tie lines at 800 °C and one at 650 °C using crystalline starting materials; his experiments may have approached equilibrium more closely than did those of Seck. It is not clear a priori which data set is "better," but we have chosen to use Seck's data for our model because (1) Brown and Parsons (1981) noted that the regularity of Seck's results suggests an approach to equilibrium; (2) the number of Johannes's tie lines is too small to permit modeling whereas Seck's data base is more extensive; and (3) the previous workers had modeled the system using Seck's data, and we wanted to compare the resulting models.

The most important difference between our approach and those of Ghiorso and of Green and Usdansky lies in the use of the experimental data base. We omitted Seck's data at 650 °C because (a) they had the largest residuals in our initial least-squares refinement, (b) they are least likely to have approached equilibrium, and (c) it is not clear that high-temperature parameters would be appropriate for temperatures below 700 °C. Ghiorso used Seck's data as tabulated, an approach that would avoid bias if the errors in composition were randomly distributed. But it is clear from Seck's text and the smooth variation of composition in his figures that his analytical method—combined *d* spacings and geometric constraints—did not produce random errors! For each isotherm, one could draw slightly different tie lines and solvi that are equally compatible with the experiments. The X-ray data provide good determinations for Or but only poor constraints for An in alkali feldspars. Particularly striking are Seck's reported contents of An in alkali feldspars at 900 °C—values that seem suspiciously low when compared to many sanidines and that led to a *negative* W_S for one of the An-Or terms in the models both of Ghiorso and of Green and Usdansky. That negative W_S, in turn, is largely responsible for the unrealistic temperatures these models predict for many ternary feldspars, both natural and synthetic. Accordingly we attempted to improve the model by allowing small changes in Seck's published compositions subject to the following constraints: (1) no points were changed by more than 1.5 mol%; (2) new points remained consistent with Seck's auxiliary experiments that determine the extent of the two-feldspar field; (3) if one feldspar composition was changed by a large amount (≥ 1 mol%), the composition of the coexisting feldspar was always moved in a compensating fashion to maintain bulk composition; (4) data points were changed in directions that reduced the least-squares residual values and that were also compatible with the probable directions of analytical error. We emphasize that all compositions that we used as input to our least-squares refinement are compatible with Seck's experiments and thus are just as "valid" as his published values. The final data points used to calibrate the model, together with Seck's original data, are given in Fuhrman (1986). In general, the changes in Seck's published data involve small counterclockwise rotations for some tie lines and slightly more ternary solution for most of the 900 °C experiments; they also happen to make the revised tie lines more consistent with those of Johannes (1979) and with the calculated tie lines given by Ghiorso (1984).

Our method further departed from that of Ghiorso (1984) at this stage. We used a polythermal data base (750, 825, and 900 °C experiments of Seck) to solve our system of equations simultaneously for both W_H and W_S portions of each W_G. When we use the adjusted compositions as outlined above, there is no significant temperature dependence of the thermodynamic parameters; we obtained a good fit using only three W_H parameters (Table 1).

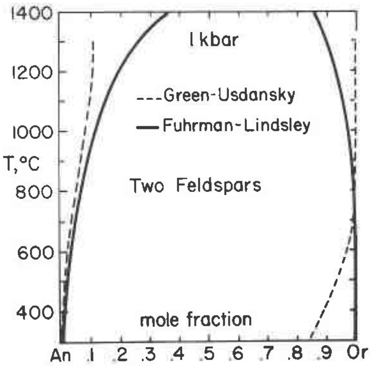

Fig. 1. Calculated solvi for the join An-Or based on the models of Green and Usdansky (1986) and this study. The solvi calculated by Ghiorso (written comm., 1987) are closely similar to ours. The apparent decreasing solubility of An in potassium feldspar with increasing temperature for the Green-Usdansky model reflects their negative values for W_H(AnOr) and for W_S(AnOr). Above approximately 1030 °C, the relations shown here are metastable with respect to assemblages containing leucite or liquid or both.

Green and Usdansky (1986) also fitted Seck's data polythermally, with the important difference that they also accepted his 650 °C experiments at 1, 5, and 10 kbar. Like Ghiorso, they used six adjustable parameters; however, they omitted ternary terms and instead calculated asymmetric Margules parameters for enthalpy, entropy, and volume on the An-Or join. We consider the direct volume measurements of Kroll et al. (1986, which presumably were not available to Green and Usdansky) to be strongly preferable to volumes extracted from the experimental tie lines—especially in view of our doubts as to whether Seck's 650 °C experiments reached equilibrium. Green and Usdansky clearly recognized the difficulties with Seck's compositions. They tried to avoid the problems of the uncertain An content of the alkali feldspars by using only the activity expressions for a_{Or} (our Eq. 8) to solve for the unknown Margules parameters. That approach is clever and indeed elegant, but as we will show below, it unfortunately results in some undesirable features of their model. We believe that our method of adjusting some of Seck's compositions, though less elegant, is preferable.

Calculated solubilities for the An-Or join. The Green-Usdansky model and our own predict similar solubilities between An and Or at 650–750 °C, but there are strong disagreements at higher and lower temperatures (Fig. 1). In particular, the strongly negative values for $W_{H,\mathrm{AnOr}}$ and $W_{S,\mathrm{AnOr}}$ in the Green-Usdansky model predict *decreasing* solubility of An in Or with increasing temperature—a most unlikely result. This feature carries over into the ternary system and seriously impairs temperatures calculated for any feldspar pairs that have more than minimal solution of An in alkali feldspar. The solubilities calculated by Ghiorso for his model (written comm., 1987) are similiar to those for our model up to approximately

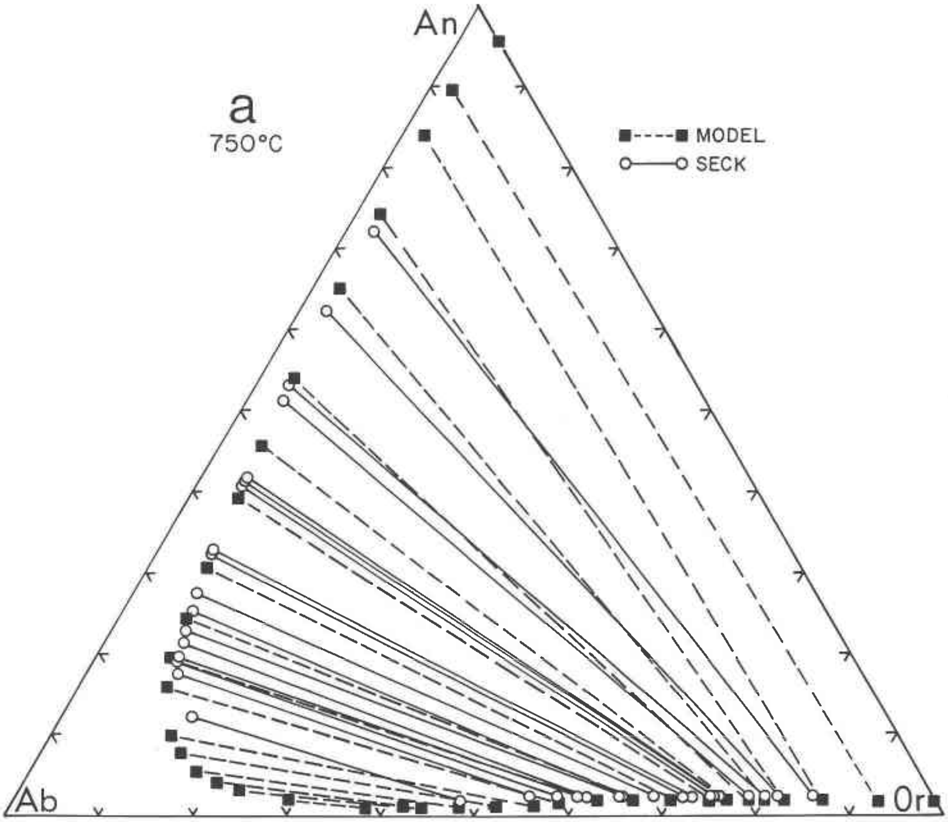

Fig. 2. Comparison of isotherms calculated from our model with the experimental data of Seck (1971a). (**a**) 750 °C, 1 kbar; (**b**) 825 °C, 1 kbar; (**c**) 900 °C, 0.5 kbar. In Fig. 2c, * marks the bulk composition of a mesoperthite homogenized by Morse (1969, p. 125).

1030 °C; above that temperature, An-Or relations become metastable with respect to assemblages involving leucite and liquid.

Comparison of isotherms

One way to test our model is to calculate isothermal sections of the ternary-feldspar miscibility gap and compare these with the data used to produce the model. Tie lines were calculated using a computer program that simultaneously matches activities of the three feldspar components. These tie lines and the isotherms they generate are compared with Seck's original data in Figures 2a–2c. In each figure, the dashed tie lines connect coexisting feldspars as predicted by our model; Seck's data are shown connected by solid lines. There is generally good agreement except at low An contents where our model predicts *less* miscibility at 750 °C and *more* miscibility at 900 °C than reported by Seck. Seck's compositional determinations for plagioclase should have the greatest error in this region, so the disagreement may be more apparent than real. Johannes's (1979) data at 800 °C also describe tie lines less steep than Seck's, but are subparallel to tie lines given by our model. Johannes's data suggest lower solubility of An in alkali feldspar than do Seck's data or our model.

Also shown in Figure 2c is the bulk composition of a mesoperthite that Morse (1969), on the basis of homogenization experiments and geometric constraints, considered to lie on the consolute curve for ternary feldspars at 0.5 kbar and 925 ± 5 °C. The agreement with our predicted consolute point for 0.5 kbar and 900 °C is remarkable, especially in view of the fact that Morse's experiments, which were of the dissolving type only, would permit a consolute point at a temperature somewhat lower than 925 °C.

We have also calculated isotherms for 1000 °C and 1100 °C at 1 kbar and 5 kbar (Fig. 3) in order to test the compatibility of the model with a number of natural ternary feldspars. These feldspars are estimated to have crystallized at temperatures of 950–1100 °C and pressures of 1–7 kbar. Our model is compatible with most of these estimates. The model of Ghiorso would require considerably higher temperatures for most of these feldspars [his 1200 °C isotherm (1984, Fig. 4) virtually coincides with our 1000 °C isotherm in much of the region Ab > 50], whereas the thermometer of Green and Usdansky

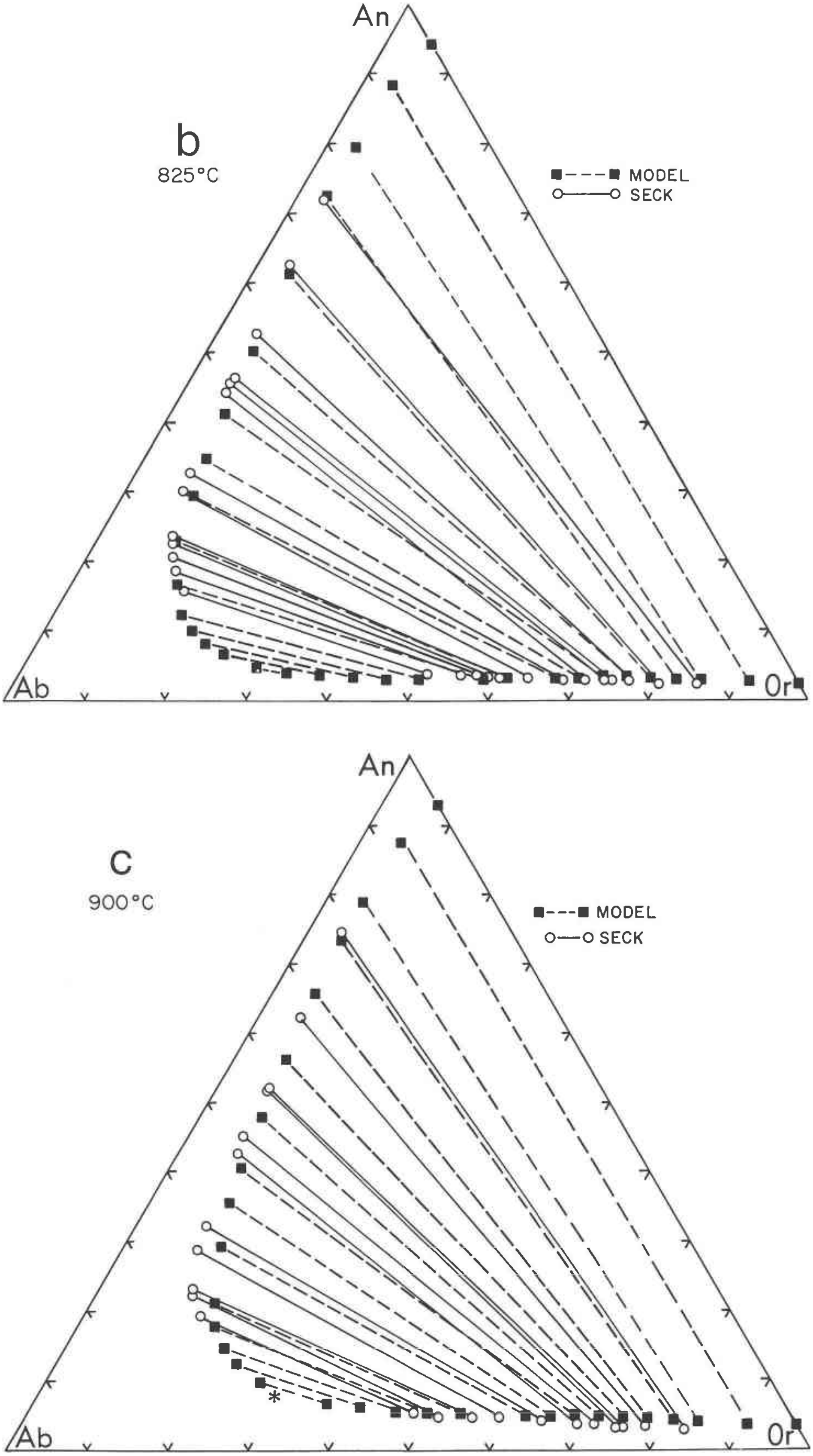

Fig. 2—*Continued.*

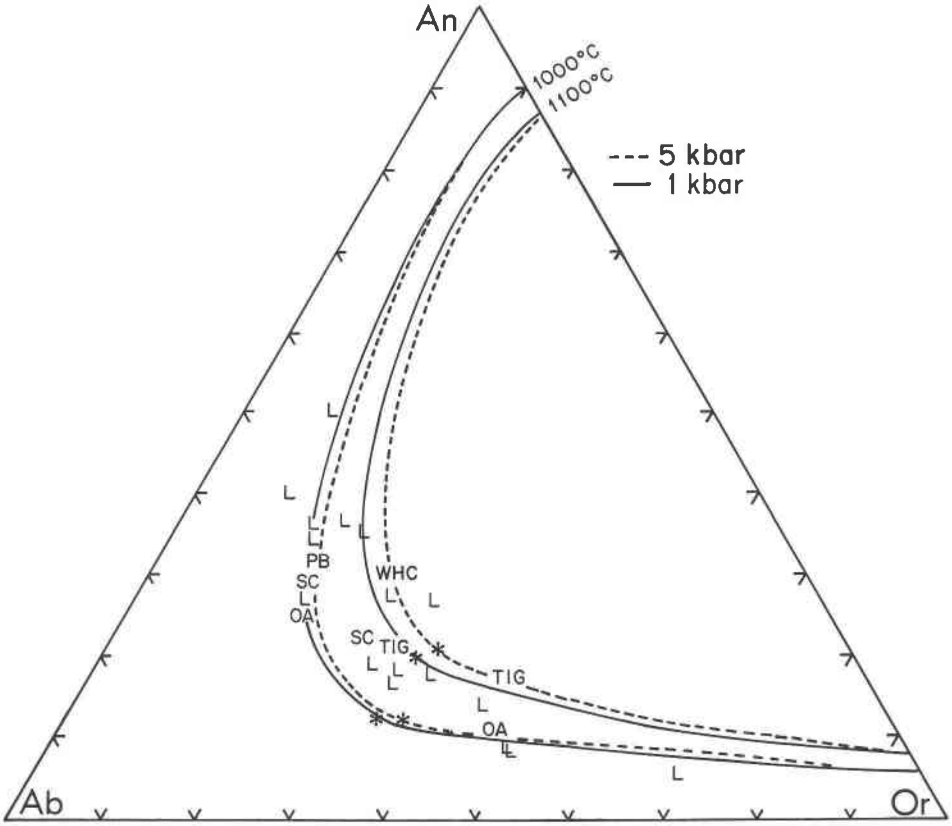

Fig. 3. Isotherms calculated by our model for 1000 °C and 1100 °C at 1 kbar and at 5 kbar; the corresponding consolute points are shown by *. Also plotted are compositions of strongly ternary natural feldspars: L = Sybille Monzosyenite, Fuhrman (1986); PB = Klokken Syenogabbro, Parsons and Brown (1983); OA = Oaxacan Complex, Mora and Valley (1985); SC = Scourie Complex, Rollinson (1982) and O'Hara and Yarwood (1978); TIG = Tigalak Intrusion, Wiebe and Wild (1983); WHC = Wyatt Harbor Complex, Huntington (1980).

(1986) gives divergent temperatures for each of the equilibria.

Two-feldspar thermometry

Most of the two-feldspar geothermometers developed to date are based solely on the distribution of Ab component between plagioclase and alkali feldspars—the equilibrium $a_{\mathrm{Ab}}^{\mathrm{alk}} = a_{\mathrm{Ab}}^{\mathrm{plag}}$. However, as pointed out by Stormer (1975), Ghiorso (1984), and Green and Usdansky (1986), similar equations can be written for the Or and An components in two coexisting feldspaars. Substitution of the activity expressions (Eqs. 11–13) into Equations 7–9 permits calculation of three temperatures, each one expressing the equilibrium temperature based on the activity of that component. Ideally, for two feldspars in equilibrium, these temperatures will all be the same; in reality they rarely are, because of (1) analytical difficulties in determining exact feldspar compositions, (2) difficulties in estimating amounts of exsolution and re-equilibration that occurred after each feldspar crystallized or in identifying coexisting pairs when one or both feldspars are zoned, (3) uncertainties in the estimation of pressure (pressure coefficients of the three thermometers are different), and (4) errors associated with the model. The mole fractions of An in alkali feldspar and Or in plagioclase are particularly sensitive to the first two sources of error; this drastically affects the activity expressions for these two components. Ghiorso (1984) acknowledged these problems and developed a technique utilizing a least-squares method to find the one temperature that best satisfies all three activity equations. However, his method loses some important information, particularly a simple test for equilibrium: whether the three temperatures determined from the three equilibria (Ab, An, and Or components in the two feldspars) are close to each other or can be made close by modifying the feldspar compositions within their estimated analytical error.

Green and Usdansky (1986) used the different pressure coefficients for each equilibrium as a barometer by determining the pressure at which the differences among the temperatures are minimized. The approach is intriguing, but unfortunately errors of 0.5 mol% for Or in plagioclase or An in alkali feldspar can affect the calculated optimum pressure by 2 kbar or more. Thus we believe that it is more valid to use independent estimates of pressure and to use the redundant temperature information to evaluate the effects of analytical uncertainty on the thermometer.

The thermometer program

Our thermometer utilizes all the information given by the coexisting feldspars and provides insight into how and why different feldspar pairs give various kinds of results. It is based on three major assumptions: (1) the ternary-feldspar model presented above describes the system well; (2) feldspar can be analyzed with an overall accuracy of ±2 mol%; (3) the samples to which it is applied represent equilibrium compositions—or nearly so. Given these assumptions, an equilibrium two-feldspar pair should yield three congruent temperatures (here defined as being within ~40 °C of each other) if the compositions are allowed to vary up to 2 mol%. The program first calculates equilibrium temperatures based on the initial feldspar compositions and then systematically searches at successively larger increments around each feldspar composition for a pair of compositions that will minimize the *sum of differences* function

$$f(X_{\mathrm{Or}}, X_{\mathrm{Ab}}, X_{\mathrm{An}} \text{ in 2 feldspars}) = \big||T_{\mathrm{Ab}}| - |T_{\mathrm{Or}}|\big| + \big||T_{\mathrm{Or}}| - |T_{\mathrm{An}}|\big| + \big||T_{\mathrm{An}}| - |T_{\mathrm{Ab}}|\big|. \tag{14}$$

In other words, the program finds two compositions close to the original values that yield the smallest differences among the three temperatures given by the three activity equations. The details of this iteration and search method are given in Appendix 1. This concept of searching for an optimum tie line arbitrarily close to the analyzed compositions is similar but not identical to the procedure developed for pyroxene pairs by Davidson (Davidson and Lindsley, 1985, p. 402). The error in temperature, including analytical uncertainty of the compositions, is approximately ±40 °C.

Although our solution model was developed using the Al-avoidance model for configurational entropy (Ghiorso, 1984), we can substitute site-mixing expressions for the ideal portions of the activity terms because the site-mixing and Al-avoidance models are equivalent for pure Na-Ca-K feldspars (Price, 1985). It is especially useful to be able to include the effects of celsian component ($BaAl_2Si_2O_8$, Cn) for some volcanic feldspar pairs in which Cn equals or even exceeds An in the alkali feldspars. We have therefore included Cn in the configurational (ideal activity) terms even though we lack expressions for the contribution of Cn to the activity coefficients. Use of Cn in our program is optional; 0.01 to 0.02 mole fraction Cn in alkali feldspar raises the apparent temperature by 10–20 °C.

We have evaluated our two-feldspar thermometer by three kinds of tests: (1) its ability to yield correct temperatures for the experiments used to calibrate the model, (2) its ability to recover original compositions and temperatures for feldspar pairs that have been deliberately displaced from compositions that give three tightly clustered temperatures, and (3) comparison of temperatures for natural two-feldspar pairs with independent temperature estimates.

Comparing results of various feldspar thermometers

At present there are three different solution models for ternary feldspars and three quite different approaches for applying these in thermometry. Various combinations of the models and approaches could yield a total of nine "feldspar thermometers"! Possibly one of the six remaining combinations will be found to be the "best" thermometer, but we leave that project to others; in the discussion that follows, unless otherwise noted, we apply each thermometer in the way the original author(s) proposed.

Temperature recovery from experimental feldspar pairs

Table 2 shows the results of applying our feldspar geothermometer to the experiments of Seck (1971a) and Johannes (1979). Seck's 750 °C compositions yield temperatures that average about 30 °C high, the 825 °C samples yield temperatures very close to the experimental temperature, and the pairs from the 900 °C experiments generate temperatures 10 to 40 °C lower than the experimental temperatures. We compare these results with the temperature recovery from the preferred model of Green and Usdansky (1986; the "orthoclase calibration" of their Table 1). Their recovery of temperatures for the Ab and Or equilibria is in all cases as good as—in several cases better than—ours, but the An temperatures are a different story. For all but the data set at 650 °C and 1 kbar, their published An temperatures average 80 to 270 °C *below* the actual temperatures. In one sense, this comparison is unfair, for the Green-Usdansky temperatures are for Seck's compositions as originally reported, whereas ours reflect the best fits for compositions within the estimated analytical error, i.e., ±2 mol% of the original compositions. However, the intent here is to compare the approaches to thermometry as well as the models; we suggest that the improved overall fit for our model shows that our approach is the better one. The poor fit of the Green-Usdansky An temperatures is especially noteworthy because it is precisely the *negative* pressure coefficient for the An equilibrium that dominates the pressure calculation using their thermobarometer.

When our geothermometer is applied to the 800 °C pairs reported by Johannes (1979), it yields concordant temperatures that average 734 °C for one pair and 770 °C for the other (Table 2). The Green-Usdansky thermometer yields nearly concordant temperatures that average 801 °C for the first pair and somewhat discordant temperatures that average 836 °C for the other. Johannes's experiment at 650 °C yields temperatures that average 639 °C for our thermometer, but rather discordant temperatures by that of Green and Usdansky. For Seck's 650 °C experiments (which were omitted from our modeling) the *original* compositions used with our model yield T_{Ab} and T_{Or} very close to 650 °C, with T_{An} much higher—

TABLE 2. Temperature recovery from experiments on ternary feldspars

		P	This study			Green and Usdansky (1986)			(1)	(2)
	T (°C)	(kbar)	T_{Ab}	T_{An}	T_{Or}	T_{Ab}	T_{An}	T_{Or}	T_{Ab}	T_{Ab}
Seck (1971a)	650	1	699 ± 14	696 ± 11	691 ± 11	665 ± 21	638 ± 64	638 ± 18		
	750	1	780 ± 19	779 ± 18	779 ± 19	760 ± 26	670 ± 22	736 ± 17		
	825	1	825 ± 28	825 ± 23	824 ± 23	811 ± 22	651 ± 17	826 ± 28		
	900	0.5	863 ± 26	863 ± 27	861 ± 23	885 ± 29	695 ± 18	917 ± 23		
Johannes (1979)	800	1	733	730	740	770*	818*	813*	783*	805
	800	1	769	768	772	840*	865*	803*	862*	819
	650	1	621	641	656	586*	731*	674*	565*	

Note: (1) = Haselton et al. (1983); (2) = Ghiorso (1984).
* Calculated by us. Green and Usdansky temperatures for Seck's data are from their paper.

the last being just the opposite of the results from the Green-Usdansky thermometer. For these feldspar pairs, our thermometer eventually converged on congruent temperatures that average 30–40 °C too high. Possible explanations for the relatively poor recovery of the 650 °C temperatures by our thermometer include (1) our model is inaccurate in this region; or (2) Seck's 650 °C experiments did not reach equilibrium. On the basis of the discussion of volumes above, Seck's 650 °C experiments at 1, 5, and 10 kbar cannot *all* represent equilibrium; perhaps none of them do.

Overall, the ability of our thermometer to recover the experimental temperatures is good.

Recovery of original temperatures from randomly displaced compositions

We have tested the ability of our thermometer program to converge on consistent temperatures by taking pairs of compositions that yield closely similar temperatures (within 5 °C), randomly displacing one or both by 2 mol%, and allowing the program to search for the best answer. In almost all cases the program found the original compositions or pairs whose temperatures differ by only a few degrees from those indicated by the original ones. The one type of displacement for which the original compositions and temperatures (understandably!) could not be recovered is that which closely corresponds to an equilibrium pair for a lower or higher temperature. With that exception, the excellent recovery of the original temperatures shows the power of using the three thermometry equations simultaneously to search for equilibrium compositions.

Furthermore, the deviations between the original temperatures and those initially given by the displaced compositions provide insight into reasons why some natural pairs fail to yield concordant temperatures, because resetting of one or both compositions by geologic processes may also mimic our displacements of the compositions. For almost all random displacements from an equilibrium pair of compositions, T_{Ab} and T_{Or} change in the same direction while T_{An} changes, in many cases strongly, in the opposite direction. Thus suspiciously high or low anorthite temperatures commonly reflect overestimation or underestimation of An in alkali feldspar. Underestimation of Or in plagioclase (as for example when exsolved alkali feldspar is not included in the analysis) typically yields T_{Or} very much lower than the other two temperatures.

Results from natural feldspars

Feldspar pairs from volcanic rocks. Two-feldspar temperatures from volcanic rocks are an important test of a thermometer because it is probable that equilibrium compositions—if initially present—have been maintained. Analytical errors are more likely to be random, and thus adjustments to the compositions by our thermometer should be randomly distributed. Table 3 shows temperatures given by our thermometer and by those of Ghiorso (1984), Haselton et al. (1983), and Green and Usdansky (1986) for a number of volcanic feldspar pairs, along with independent estimates of temperature given by Fe-Ti oxide pairs where available. In most cases, the temperatures given by our thermometer compare favorably with those given by the other thermometers. Haselton et al. (1983) recommended against using their thermometer for feldspars that formed above 850 °C, where there may be a large ternary component in one or both of the feldspars. The results in Table 3 support their recommendation.

Feldspar pairs from the Fish Canyon Tuff are especially interesting because Stormer and Whitney (1985) have suggested a depth of origin corresponding to approximately 9 kbar, the pressure needed to produce agreement between two-oxide and two-feldspar temperatures (as based on thermometers available at that time) for these rocks. We do not take sides on this controversial issue, but we note that our thermometer makes smaller and more nearly random adjustments to the compositions for an assumed pressure of 3 kbar as compared to either 1 or 6 kbar. However, the 6-kbar to 8-kbar temperatures indicated by our thermometer still provide the closest match to revised oxide temperatures, so the general relationship noted by Stormer and Whitney still holds, whatever its cause. Inclusion of celsian components (which are available for these samples) raises the feldspar temperatures by about 20 °C—approximately equal to the effect of 1 kbar. If the Stormer and Whitney barometer

TABLE 3. Comparison of calculated temperatures for igneous ternary-feldspar pairs

	P	Plag.			Alk.			This study			Green-Usdansky			(1)	(2)
	(kbar)	Ab	Or	An	Ab	Or	An	T_{Ab}	T_{Or}	T_{An}	T_{Ab}	T_{Or}	T_{An}	T_{Ab}	T_{Ab}
					Volcanic pairs										
Carmichael (1965) Trachyte	1	0.654	0.073	0.273	0.379	0.603	0.018	849	821	832	933	799	890	857	993
Ewart (1965) Ignimbrite [750 °C]	1	0.632	0.041	0.326	0.319	0.653	0.028	807	756	776	810	631	708	689	871
Hildreth (1979)															
Bishop Tuff, early [720 °C]	1	0.798	0.061	0.141	0.362	0.630	0.008	676	676	671	698	603	817	622	708
late [780 °C]	1	0.702	0.076	0.222	0.337	0.650	0.013	770	772	779	789	730	817	761	812
Baldridge et al. (1981)															
Leucite basanite	0.001	0.253	0.029	0.718	0.168	0.791	0.041	909	892	902	774	779	588	856	1086
Phonolite-tephrite	0.001	0.477	0.072	0.451	0.293	0.675	0.033	905	868	903	1011	1343	676	910	1195
					Plutonic pairs										
W34-8-1 monzonite (LAC)	3	0.544	0.286	0.170	0.417	0.484	0.100	984	984	989	789	1146	444	>1200*	2010
SR-6A monzosyenite (LAC)	3	0.553	0.278	0.181	0.342	0.612	0.047	884	885	921	863	1755	562	>1200*	1298
Klokken Syenogabbro; Parsons and Brown (1983)	1	0.520	0.260	0.220	0.330	0.610	0.060	932	932	970	880	3163	608	>1200*	1356

Note: Temperatures from method of Green and Usdansky (1986) were calculated by us. (1) = Ghiorso (1984); (2) = Haselton et al. (1983). [ ] Fe-Ti oxide temperatures. Laramie (LAC) data from Fuhrman (1986).

* Temperature estimated from position of isotherms.

(1985) is used, it is clearly essential that the effects of Cn be taken into account.

Adjustments made by our thermometer to the compositions of volcanic feldspars are semirandom (Fuhrman, 1986, and unpub. data); in no case tested by us is the Or content of plagioclase, and only rarely is the An content of alkali feldspar, decreased. With these exceptions, other adjustments are about equally likely. It is entirely possible that our model slightly overestimates Or in plagioclase and An in alkali feldspar; conceivably those phases are able partially to purge themselves of those components even in quickly cooled rocks.

Feldspar pairs from plutonic igneous rocks. When our thermometer is applied to strongly ternary feldspar pairs (Table 3), it yields nearly concordant temperatures of 900–1000 °C. The pair from the Laramie monzonite gives a temperature of 985 ± 50 °C, which is consistent with two-pyroxene thermometry (980–1020 °C). These pairs consist of highly exsolved feldspars whose integrated compositions have large uncertainties (±4 mol%). The large uncertainty in composition is partially compensated for by the gentler slopes of the solvus for these compositions. The feldspar pair given by Parsons and Brown (1983) generates a temperature of ~940 °C, close to their estimate of 950–1000 °C for crystallization temperatures for the rocks in which the pair occurs.

The Green-Usdansky thermometer generally gives strongly divergent temperatures for these plutonic ternary feldspars, with Ab tempertures being closest to the independent estimates and An and Or temperatures typically several hundreds of degrees higher and lower, respectively.

Metamorphic feldspar pairs. Table 4 shows calculated temperatures using several thermometers for metamorphic feldspar pairs from Adirondack granulite-facies rocks. Very few metamorphic pairs give concordant tempera-

TABLE 4. Calculated temperatures for some feldspar pairs from granulite-facies metamorphic rocks

	Plag.			Alk.			This study			Green-Usdansky				
	Ab	Or	An	Ab	Or	An	T_{Ab}	T_{Or}	T_{An}	T_{Ab}	T_{Or}	T_{An}	(1)	(2)
				Bohlen and Essene (1977); calculated for 8 kbar										
BM-15	0.743	0.014	0.242	0.235	0.751	0.014	707	612	708	693	504	460	711	676
IN-11	0.785	0.017	0.193	0.348	0.639	0.006	764	604	750	791	510	707	804	750
MM-2	0.762	0.030	0.205	0.256	0.700	0.036	723	665	725	635	623	336	670	687
SR-31	0.713	0.010	0.273	0.314	0.638	0.031	763	598	766	730	464	438	797	776
SC-2	0.722	0.008	0.270	0.196	0.800	0.004	675	582	626	682	428	630	685	644
XY-9	0.796	0.014	0.183	0.355	0.605	0.037	770	583	704	678	461	331	741	747
XY-12	0.808	0.013	0.178	0.385	0.586	0.026	778	590	779	720	456	405	774	758
				Ehrhard (1986); calculated for 7.2 kbar										
HA-243	0.802	0.012	0.186	0.317	0.656	0.027	736	580	668	677	441	389	714	704
HA-260	0.697	0.008	0.295	0.192	0.798	0.010	648	586	655	668	425	532	678	642
HA-309	0.728	0.013	0.259	0.235	0.751	0.014	703	613	699	696	487	495	714	674
HA-349	0.735	0.009	0.256	0.223	0.760	0.017	695	585	681	667	428	460	685	658
HA-390	0.751	0.013	0.236	0.191	0.796	0.013	643	593	649	624	472	468	632	616

Note: T_{Ab}, T_{Or}, T_{An} from method of Green and Usdansky (1986) calculated by us using their thermometer. (1) = Haselton et al. (1983); (2) = Stormer (1975).

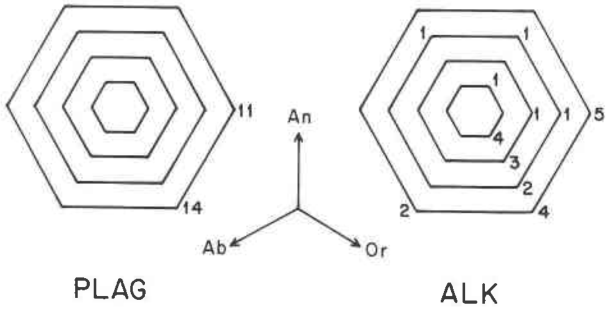

Fig. 4. Distribution of adjustments in compositions made by the thermometer program for feldspar pairs from Adirondacks granulite-facies metamorphic rocks. The innermost hexagon represents adjustments of 0.5 mol%; outward from this the hexagons represent adjustments of 1.0, 1.5, and 2.0 mol%. Adjustments are made while always holding one mole fraction constant. Numbers indicate frequency of samples adjusted.

tures with our thermometer; T_{Or} tends to be lower than the other temperatures, although T_{Ab} and T_{An} are generally similar. We assume that T_{Ab} reflects an equilibrium temperature but that T_{Or} may have been affected by loss of Or from plagioclase in these slowly cooled rocks. T_{Ab} is close to that given by Haselton et al. (1983), hardly surprising inasmuch as the two thermometers are based on the same binary parameters. Temperatures for these metamorphic rocks using the Green-Usdansky thermometer are less satisfactory: T_{Ab} is generally 20–40 °C lower than for the other thermometers (hence within uncertainty), but T_{An} and T_{Or} both tend to be much lower, by 100–200 °C.

We emphasize that it is essential to reintegrate the compositions of *plagioclases* as well as those of the alkali feldspars in order to obtain consistent temperatures for these and other deep-seated rocks. For many such pairs, it is likely that there has been some re-equilibration or other modification of compositions after peak temperatures were reached. Possible changes in composition could be due to internal and/or granule exsolution or perhaps to alkali exchange with a fluid phase. Such changes should be reflected in the directions that the compositions tend to be adjusted using our thermometer. For alkali feldspars, the major process is the exsolution of Ab-rich plagioclase. It is now an accepted practice to reintegrate exsolved perthites in order to estimate original compositions (Bohlen and Essene, 1977). However, some workers appear to ignore exsolved K-rich feldspar in plagioclase even in cases where it can still be recognized. Quite clearly such obviously exsolved plagioclases should be reintegrated, but users of our thermometer (or any thermometer based on a ternary model) should also look for evidence of *external* granule exsolution of alkali feldspar from plagioclase and take that into account as well. Figure 4 shows the directions and amounts that compositions have been adjusted by our thermometer for 25 metamorphic pairs from the Adirondacks (Bohlen and Essene, 1977; Ehrhard, 1986; the original data are summarized in Fuhrman, 1986). The perthites of these pairs have been integrated, and there is a fairly regular distribution of adjustments around the original composition for alkali feldspars. For plagioclase, however, all the compositions "require" increased Or component, implying that some regular process or processes may have affected their compositions.

APPLICATION, DISCUSSION, AND COMPARISON OF THERMOMETERS

Choosing a two-feldspar thermometer

Potential users of two-feldspar thermometry are faced with a number of possible thermometers calibrated in recent years: Haselton et al. (1983); Ghiorso (1984); Green and Usdansky (1986); and the one presented here. The thermometers based on ternary formulations should be inherently preferable to the double-binary formulation of Haselton et al. for feldspars that have more than trivial amounts of the third component. For several reasons, we believe that our ternary formulation is superior to those of Ghiorso and of Green and Usdansky. By accepting the experimental data of Seck as tabulated (Seck, 1971a, 1971b), those workers were forced to employ a negative term for excess entropy on the An-Or join. That negative term greatly restricts the amount of ternary solution calculated for temperatures at and above 1000 °C, where both natural and synthetic systems show extensive solution. Our model incorporates the extensive volume data of Kroll et al. (1986), which show distinct negative volumes of mixing for both the An-Or join and ternary feldspars. The large *positive* volumes calculated for the An-Or join from Seck's polybaric experiments (Green and Usdansky, 1986) are clearly inappropriate and should not be used. The poor recovery of anorthite temperatures by the Green-Usdansky model ($T_{\mathrm{An}} = 531$ °C at 5 kbar, 380 °C at 10 kbar) for the 650 °C experiments used to calibrate their model (Green and Usdansky, 1986; their Table 1) probably reflects the deleterious effect of these volume terms.

Thermobarometry using two feldspars?

Although each of the three equilibria for coexisting feldspars has a different pressure coefficient, we strongly caution against using two feldspars for simultaneous thermometry and barometry (Green and Usdansky, 1986), because small errors in composition have a very large effect in the apparent pressure. Furthermore, most of the potential barometric information in the Green-Usdansky thermobarometer lies in the negative pressure coefficient of T_{An}. As outlined above, however, the ability of their model to recover T_{An} values for the 5-kbar and 10-kbar experiments *used to calibrate the model* is distinctly poor. Thus, apparent pressures calculated for the calibrating experiments themselves would be seriously in error.

The examples of thermobarometry presented by Green and Usdansky (1986) are very striking. Their example from Little Glass Mountain Rhyolite (their Fig. 1) shows the three feldspar temperatures converging at about 2.2 kbar to a temperature very close to that indicated by Fe-Ti oxides. At first glance, this result provides support for the idea of using their model for thermobarometry, because independent estimates of pressure are around 3.2 kbar (Mertzman and Williams, 1981). However, the feldspar compositions used by Green and Usdansky to produce their Figure 1 are evidently the representative analyses of Mertzman and Williams (1981; sample 33P, Table 3). The plagioclase composition appears to be that of a rim, but the sanidine plots well within a cluster of points (Fig. 4 of Mertzman and Williams) and is most unlikely to have been in equilibrium with the plagioclase. Use of the probable rim composition (the most Ab-rich sanidine) in the Green-Usdansky thermobarometer yields a poor convergence at approximately 725 °C and -1 kbar, much less satisfactory than those workers obtained using the apparently nonequilibrium pair (1986; their Fig. 1). In contrast, it is interesting to note that when the compositions used by Green and Usdansky are allowed to vary (that is, using their model but our approach to thermometry), the sanidine composition moves toward the inferred rim composition, and the resultant temperature (calculated for 3.2 kbar) is in excellent agreement with the temperature independently estimated by Mertzman and Williams (1981). Clearly the Green-Usdansky model is a better thermometer than barometer for this example!

The agreement between temperatures inferred for the Bishop Tuff using two-oxide thermometry by Green and Usdansky using only their two-feldspar thermobarometer (1986, Fig. 2a) and those from two-oxide thermometry (Hildreth, 1977) is impressive. However, their inferred range of pressure (2.5 to 6.5 kbar; their Fig. 2b) is less well constrained and is marginally higher than the pressure range estimated by Hildreth (1.5 to 5 kbar). It is true that Stormer and Whitney (1985) inferred pressures of 4 to 6 kbar for the Bishop Tuff using their two-oxide, two-feldspar barometer, but those pressures are controversial. Furthermore, application of the Stormer-Whitney technique using our feldspar thermometer, together with an improved oxide thermometer, yields pressures of 2 to 3 kbar (Grunder et al., 1987), much closer to Hildreth's original estimates.

Use of our two-feldspar thermometer

We emphasize that the thermometer presented here (or any ternary-feldspar thermometer) should not be used without an understanding of the method and the implications of the results. The thermometer yields three general classes of results, designated by the relationship inferred for the original feldspars: (1) equilibrium pair, $T_{\mathrm{Ab}} \simeq T_{\mathrm{An}} \simeq T_{\mathrm{Or}}$; (2) close-to-equilibrium pair, $T_i \simeq T_j \neq T_k$; and (3) nonequilibrium pair, $T_{\mathrm{Ab}} \neq T_{\mathrm{An}} \neq T_{\mathrm{Or}}$. In the discussion that follows, the reader should bear in mind that T_{Ab} is controlled mainly by the orientation (rotation) of the tie line, whereas T_{An} and T_{Or} are dominated by the width and position of the two-feldspar field.

Equilibrium pair = concordant temperatures. If, within the ±2 mol% analytical error, the geothermometer program finds two feldspar compositions that yield temperatures whose sum of differences [$f(X_i)$ of Eq. 14] is less than 80,—that is, the highest and lowest temperatures are within ~40 °C of each other, well within the estimated uncertainties of the thermometer and model—it is reasonable to conclude that the feldspar compositions represent equilibrium. In this case, the temperature accepted for the rock should be the mean of the three temperatures, with an error of 30–50 °C that will include all three temperatures.

Close-to-equilibrium pair: two concordant temperatures, one different by ~100 °C. In many cases, two of the activity equations yield concordant temperatures, while the third yields a temperature about 100 °C higher or lower. As mentioned above, T_{An} is quite sensitive to An content of alkali feldspar and T_{Or} to Or content in plagioclase. Usually it is one of these temperatures that is discordant, indicating a probable error in the determination of the "minor" ternary component in either plagioclase or alkali feldspar. A common example from plutonic rocks is the case of perthite (whose composition has been carefully reintegrated) that is said to coexist with plagioclase having a small reported Or content (1–2 mol%). Such pairs invariably give either two concordant temperatures (if the plagioclase is not too far from its equilibrium composition) or three discordant temperatures (if even the 2 mol% variation allowed does not yield an equilibrium composition for the plagioclase). For the case where two temperatures are approximately equal and the third is ~100 °C off, the temperature taken for the rock should be the mean of the two concordant temperatures, but the feldspar pair should be re-examined carefully in an attempt to explain the discordance of the third. Another possible cause of discordant temperatures is a serious error in estimating pressure, but the error would have to be larger than several kilobars to have much effect.

Nonequilibrium pair = discordant temperatures. There are three general cases where the three temperatures are all significantly different. The first is where T_{Ab} lies between T_{An} and T_{Or} and the difference between the latter two is less than 500 °C. In this case, the orientation of the tie line (which dominates T_{Ab}) may be close to equilibrium; however, the more sensitive T_{An} and T_{Or} are thrown off by relatively small errors in composition. Here the temperature T_{Ab} can be taken as that of the rock, but the user should try to understand why the other two temperatures are off and, for plutonic feldspars, should probably try estimating possible granule exsolution or alkali exchange and input new compositions reflecting these estimates to see if they give more reasonable and concordant temperatures.

In the second case, the range between the highest and lowest temperatures is also less than 500 °C, but T_{Ab} does not lie between T_{An} and T_{Or}. In many such cases, T_{Ab} is the highest and probably reflects a close-to-equilibrium orientation of the tie line; but as described above, T_{Or}

and T_{An} are low because compositions may not quite be on the solvus at T_{Ab}. When T_{Ab} is the lowest temperature, it is probable that the orientation of the tie line has been strongly affected by some postcrystallization process and T_{Ab} does not reflect an equilibrium temperature. In these cases, the thermometer should not be used without an attempt to determine why or how the tie line has been rotated and which temperature is closest to representing the equilibrium value.

The third case of three discordant temperatures is where the difference between the highest and lowest temperatures is greater than 500 °C. Such a feldspar pair is nowhere near being in equilibrium—most likely the orientation of the tie lines, which dominates T_{Ab}, is inconsistent with the model at geologically reasonable temperatures. Wildly discordant temperatures will also be generated by feldspar pairs that plot on the same side of the consolute curve, as is the case for some pairs given by Mora and Valley (1985) where plagioclase having very little Or co-occurs with ternary feldspars. These pairs are strongly incompatible with the model and therefore give unlikely and discordant temperatures. For pairs that give very discordant temperatures, the user should compare them with the isotherms to verify that they lie on opposite sides of the consolute curve. If they do, but still give very discordant temperatures, one should consider the possibility of magma mixing or incorporation of xenoliths in igneous rocks and should look for evidence of disequilibrium such as resorbed rims or overgrowths.

CONCLUSIONS

The model presented here represents an improvement over existing solution models for ternary feldspars. When used for two-feldspar thermometry, it gives consistent and reasonable temperatures both for feldspar pairs with nearly binary compositions and for feldspars with substantial ternary component. Perhaps one of the most practical uses of this model and thermometer is as a test for equilibrium between co-occurring feldspars. The relative success of this model is permissive evidence that the 750–900 °C experiments of Seck (1971a) closely approached equilibrium. Our model should also be useful in modeling the crystallization of ternary feldspars from hot, dry melts; it is much more successful for such feldspars than are the models of Ghiorso (1984) and of Green and Usdansky (1986). The thermometer of Green and Usdansky generally gives good temperatures in its range of calibration (650–900 °C) and at relatively low pressures. It is not appropriate for strongly ternary feldspars, and—because it uses volume terms now known to be in conflict with measured volumes—it should not be used as a barometer.

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REFERENCES CITED

Andersen, D.J., and Lindsley, D.H. (1981) A valid Margules formulation for an asymmetric ternary solution: Revision of the olivine-ilmenite thermometer, with applications. Geochimica et Cosmochimica Acta, 45, 847–853.

Baldridge, W.S., Carmichael, I.S.E., and Albee, A.L. (1981) Crystallization paths of leucite-bearing lavas: Examples from Italy. Contributions to Mineralogy and Petrology, 76, 321–335.

Barth, T.F.W. (1951) The feldspar geologic thermometers. Neues Jahrbuch für Mineralogie Abhandlungen, 82, 143–154.

Bohlen, S.R., and Essene, E.J. (1977) Feldspar and oxide thermometry of granulites in the Adirondack Highlands. Contributions to Mineralogy and Petrology, 62, 153–169.

Brown, W.L., and Parsons, I. (1981) Towards a more practical two-feldspar geothermometer. Contributions to Mineralogy and Petrology, 76, 369–377.

——— (1985) Calorimetric and phase-diagram approaches to two-feldspar geothermometry: A critique. American Mineralogist, 70, 356–361.

Carmichael, I.S.E. (1965) Trachytes and their feldspar phenocrysts. Mineralogical Magazine, 34, 107–125.

Davidson, P.M., and Lindsley, D.H. (1985) Thermodynamic analysis of quadrilateral pyroxenes. Part II: Model calibration from experiments and applications to geothermometry. Contributions to Mineralogy and Petrology, 91, 390–404.

Ehrhard, L.E. (1986) Low activities of H_2O at the amphibolite-granulite transition, northwest Adirondacks: Evidence for pre-Grenville melting and dehydration. M.S. thesis, State University of New York at Stony Brook, ix + 64 p.

Ewart, A. (1965) Mineralogy and petrogenesis of the Whakamaru ignimbrite in the Maraetai area of the Taupo volcanic zone, New Zealand. New Zealand Journal of Geology and Geophysics, 8, 611–677.

Fuhrman, M. (1986) The petrology and mineral chemistry of the Sybille Monzosyenite and the role of ternary feldspars. Ph.D. dissertation, State University of New York at Stony Brook, x + 214 p.

Ghiorso, M.S. (1984) Activity/composition relations in the ternary feldspars. Contributions to Mineralogy and Petrology, 87, 282–296.

Green, N.L., and Usdansky, S.I. (1986) Ternary-feldspar mixing relations and thermobarometry. American Mineralogist, 71, 1100–1108.

Grunder, A.L., Hadjigeorgiou, C.H., Lindsley, D.H., and Andersen, D.J. (1987) Two-oxide, two-feldspar barometry revisited: I. Effect of revised calibrations. Geological Society of America Abstracts with Programs, 19, 686.

Hadjigeorgiou, C.H., Grunder, A.L., and Lindsley, D.H. (1987) Two-oxide, two-feldspar barometry revisited: II. Direct experimental calibration. Geological Society of America Abstracts with Programs, 19, 689.

Haselton, H.T., Jr., Hovis, G.L., Hemingway, B.S., and Robie, R.A. (1983) Calorimetric investigation of the excess entropy of mixing in analbite-sanidine solid solutions: Lack of evidence for Na,K short-range order and implications for two-feldspar thermometry. American Mineralogist, 68, 398–413.

Hildreth, W. (1977) The magma chamber of the Bishop Tuff: Gradients in pressure, temperature, and composition. Ph.D. dissertation, University of California, Berkeley, 328 p.

——— (1979) The Bishop Tuff: Evidence for the origin of compositional zonation in silicic magma chambers. Geological Society of America Special Paper 180, 45–75.

Hovis, G.L. (1977) Unit-cell dimensions and molar volumes for a sanidine-analbite exchange series. American Mineralogist, 62, 680–686.

Huntington, H.D. (1980) Anorthositic and related rocks from Nukasorsuktokh Island, Labrador. Ph.D. dissertation, University of Massachussetts, Amherst, xii + 134 p.

Johannes, W. (1979) Ternary feldspars: Kinetics and possible equilibria at 800 °C. Contributions to Mineralogy and Petrology, 68, 221–230.

Kerrick, D.M., and Darken, L.S. (1975) Statistical thermodynamic models for ideal oxide and silicate solid solutions, with application to plagioclase. Geochimica et Cosmochimica Acta, 39, 1431–1442.

Kroll, H., Schmiemann, I., and von Cölln, G. (1986) Feldspar solid solutions. American Mineralogist, 71, 1–16.

Mertzman, S.A., and Williams, R.J. (1981) Genesis of Recent silicic magmatism in the Medicine Lake Highland, California: Evidence from cognate inclusions found at Little Glass Mountain. Geochimica et Cosmochimica Acta, 45, 1463–1478.

Mora, C.I., and Valley, J.W. (1985) Ternary feldspar thermometry in granulites from the Oaxacan Complex, Mexico. Contributions to Mineralogy and Petrology, 89, 215–225.

Morse, S.A. (1969) Feldspars. Carnegie Institution of Washington Year Book 67, 120–130.

Newton, R.C., Charlu, T.V., and Kleppa, O.J. (1980) Thermochemistry of high structural state plagioclases. Geochimica et Cosmochimica Acta, 44, 933–941.

O'Hara, M.J., and Yarwood, G. (1978) High pressure-temperature point on an Archean geotherm, implied magma genesis by crustal anatexis, and consequences for garnet-pyroxene thermometry and barometry. Philosophical Transactions of the Royal Society of London A, 288, 441–456.

Parsons, I., and Brown, W.L. (1983) A TEM and microprobe study of a two-perthite alkali gabbro: Implications for the ternary feldspar system. Contributions to Mineralogy and Petrology, 82, 1–12.

Powell, M., and Powell, R. (1977) Plagioclase-alkali feldspar geothermometry revisited. Mineralogical Magazine, 41, 253–256.

Price, J.G. (1985) Ideal site-mixing in solid solutions, with applications to two-feldspar geothermometry. American Mineralogist, 70, 696–701.

Rollinson, H.R. (1982) Evidence from feldspar compositions of high temperatures in granite sheets in the Scourian complex, NW Scotland. Mineralogical Magazine, 46, 73–76.

Seck, H.A. (1971a) Koexistierende Alkalifeldspäte und Plagioklase im System $NaAlSi_3O_8$-$KAlSi_3O_8$-$CaAl_2Si_2O_8$-H_2O bei Temperaturen von 650 °C bis 900 °C. Neues Jahrbuch für Mineralogie Abhundlungen, 115, 315–345.

——— (1971b) Der Einfluss des Drucks auf die Zusammensetzung koexistierender Alkalifeldspäte und Plagioklase. Contributions to Mineralogy and Petrology, 31, 67–86.

Stormer, J.C., Jr. (1975) A practical two-feldspar geothermometer. American Mineralogist, 60, 667–674.

Stormer, J.C., and Whitney, J.A. (1985) Two-feldspar and iron-titanium oxide equilibria in silicic magmas and the depth of origin of large volume ash-flow tuffs. American Mineralogist, 70, 52–64.

Thompson, J.B., Jr., and Hovis, G.L. (1979) Entropy of mixing in sanidine. American Mineralogist, 64, 57–65.

Whitney, J.A., and Stormer, J.C., Jr. (1977) The distribution of $NaAlSi_3O_8$ between coexisting microcline and plagioclase and its effect on geothermometric calculations. American Mineralogist, 62, 687–691.

Wiebe, R.A., and Wild, T. (1983) Fractional crystallization and magma mixing in the Tigalak layered intrusion, the Nain anorthosite complex, Labrador. Contributions to Mineralogy and Petrology, 84, 327–344.

Wohl, K. (1953) Thermodynamic evaluation of binary and ternary liquid systems. Chemical Engineering Progress, 49, 218–219.

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APPENDIX 1. DESCRIPTION OF THERMOMETRY PROGRAM MTHERM3

The thermometer program calculates three temperatures, one for each activity equation (Eqs. 7–9) for any given two co-occurring feldspars. The program searches in hexagons of increasing radius around the original compositions until either the sum of differences (see Eq. 14) is smaller than that requested, or until the limits of analytical uncertainty have been reached (2 mol%). The hexagons are made by holding one component constant while the other two components are changed (see program lines 250 to 310 and 700 to 800). The program flags the compositions that give temperatures with the smallest sum of differences and updates these compositions as smaller sums are encountered. The order of search is as follows: plagioclase composition is changed by 0.5 mol%, then by 1.0 mol%, then by 1.5 mol%, and finally by 2.0 mol%, while alkali feldspar is first unchanged and then successively varied in steps of 0.5, 1.0, 1.5, and 2.0 mol%. This process continues until every combination of plagioclase and alkali feldspar compositions from the original ones to 2 mol% away from the original compositions has been searched through or until the lower limit of sum of differences requested is reached. When the search is completed, the program prints out the most concordant temperatures, and the compositions used to calculate these temperatures.

Where celsian contents of the feldspars are known, that information should be used in the thermometer; our program has an option for including Cn. Although our model has no information on the effect of Cn on the activity coefficients of the other components, we have used the site-mixing approach of Price (1985) to express the contribution of Cn to the ideal activities of those components. Cn is excepted from the permutations of composition described above.

We will provide listings of BASIC program MTHERM3. Those who would like copies of the program (for IBM-PC and compatible computers) should send a formatted 5.25-in. diskette. The compiled program is approximately 9 kilobytes long; it requires approximately the same amount of memory to run. All requests should be addressed to Lindsley.