New developments in two-feldspar thermometry

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ABSTRACT

The thermodynamic model of the two-feldspar thermometer has been revised. From recent enthalpy and volume measurements in the (Na,Ca)- and (K,Ca)-feldspar binaries, new interaction parameters have been derived and previous ones have been updated. Entropy parameters have been fitted to the phase equilibrium data of Seck (1971) and Elkins and Grove (1990). The two data sets could be suitably combined into one. Ideal Ab, Or, and An activities have been expressed in terms of both the molecular mixing and Al-avoidance models.

Two-feldspar pairs from high-grade metamorphic rocks that cooled slowly under dry conditions suffer from a distinct type of retrograde resetting. Whereas the original An content in both the plagioclase and the alkali feldspar is preserved because the intercrystalline Ca + Al $\leftrightarrow$ (Na,K) + Si diffusion is sluggish, Na and K may be freely exchanged between phases. Mathematical reversal of the Na-K exchange at constant An yields the temperature at which the two feldspars originally coexisted. The shifts in Ab and Or contents obtained from the reversal reflect the relative plagioclase/alkali feldspar proportions observed in thin sections. Good agreement between calculated and measured ratios was found for feldspar pairs from Sri Lankan granulites. This observation represents a successful test of the reliability of the calculated Ab-Or shifts.

In contrast to dry metamorphic rocks, similar application of chemical constraints is not indicated in the case of volcanic rocks. Then the two-feldspar thermometer delivers three, usually incongruent temperatures: T(Ab), T(Or), and T(An). From the abundance of temperatures, Fuhrman and Lindsley (1988) suggested adjusting compositions within assumed chemical uncertainties (e.g., ±2 mol%) so that congruent temperatures could be obtained. However, the result is not unique. Depending on minute variations in the starting compositions, the temperatures may vary by several tens of degrees. In addition, temperatures vary to a similar extent depending on the type of search algorithm. Therefore, we advise users to completely abandon this practice. Instead, a statistical procedure is suggested: Two-feldspar compositions are randomly generated according to Gaussian distributions with their means at the observed compositions and standard errors chosen according to the quality of the chemical analysis. This procedure returns normally distributed temperatures [T(Ab), T(Or), T(An)] together with means and standard deviations. From the overlap of the three Gaussian curves the question of equilibrium or non-equilibrium crystallization of feldspar pairs may be addressed.

INTRODUCTION

To a good approximation, feldspars can be considered as ternary solid solutions composed of NaAlSi$_3$O$_8$, (Ab), KAlSi$_3$O$_8$, (Or), and CaAl$_2$Si$_2$O$_8$, (An). The compositions of two feldspars coexisting in a rock strongly depend on temperature, but less on pressure. Barth (1934, 1951) first suggested that the Ab component of plagioclase and alkali feldspar could be used as a geothermometer. Since then, thermodynamic models have been devised that in principle fully account for the ternary character of feldspars. However, the total number of enthalpic and entropic interaction parameters that appear in the models is larger than the number of parameters that are known from calorimetric measurements (e.g., Newton et al. 1980; Haselton et al. 1983; Carpenter et al. 1985; Hovis 1988). The missing parameters,

therefore, have been either fitted to existing compositional data obtained in phase-equilibrium experiments or have been simply ignored. For their fits, Fuhrman and Lindsley (1988) and Lindsley and Nekvasil (1989) used the experiments of Seck (1971), whereas Elkins and Grove (1990) performed new work to obtain an independent set of data on ternary compositions. One of the goals of the present paper is to improve and enlarge the set of interaction parameters that is based on calorimetric and volumetric measurements.

The paper is organized as follows. First, a brief account of the thermodynamic formulation of the two-feldspar thermometer is given. Second, previous interaction parameters are revised and new ones are introduced. Third, the evolution of non-equilibrium compositions during slow cooling is addressed and the correction of its effect on two-feldspar temperatures is reviewed. This is followed by a test of the reliability of the correction method that is independent of the chosen thermodynamic model. The impact of error propagation is considered. Finally, volcanic feldspar pairs

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are discussed, and a new method to deal with the question of their equilibrium or non-equilibrium crystallization is suggested.

THERMODYNAMIC FORMALISM FOR TWO-FELDSPAR THERMOMETRY

We will briefly summarize the formalism for the two-feldspar thermometer as far as it is useful below. Following previous treatments (e.g., Ghiorso 1984; Fuhrman and Lindsley 1988; Elkins and Grove 1990), we approximate ternary feldspars as continuous solid solutions devoid of phase transitions. Then, for two ternary feldspars, plagioclase Pl and alkali feldspar AF, coexisting in equilibrium, the activities a_i^j of their three components i are equal in each phase j:

$$a_{Ab}^{Pl} = a_{Ab}^{AF} \tag{1}$$
$$a_{Or}^{Pl} = a_{Or}^{AF} \tag{2}$$
$$a_{An}^{Pl} = a_{An}^{AF}, \tag{3}$$

where

$$a_{Ab} = \tilde{X}_{Ab}\tilde{\gamma}_{Ab} \text{ etc.} \tag{4}$$

$\tilde{X}_i$ is the ideal activity and $\tilde{\gamma}_i$ is the activity coefficient. $\tilde{X}_i$ is written as

$$\tilde{X}_i = X_i \cdot \delta_i^{config} \tag{5}$$

where X_i is the ith mole fraction and δ_i^{config} is a configurational entropy correction factor (Wen and Nekvasil 1994). When $\tilde{X}_i$ is expressed in terms of a molecular mixing model, the entropy correction factor is:

$$\delta_{Ab}^{config} = \delta_{Or}^{config} = \delta_{An}^{config} = 1. \tag{6}$$

Considering Al-avoidance, Price (1985) introduced entropy correction factors that can account for the presence of Sr and Ba-feldspar components, denoted as SrF and Cn, respectively, in ternary feldspars:

$$\delta_{Ab}^{config} = \delta_{Or}^{config} = 4\, X_{Al}^{\alpha} X_{Si}^{\alpha} (X_{Si}^{\beta})^2 \tag{7}$$
$$\delta_{An}^{config} = (X_{Al}^{\alpha})^2 (X_{Si}^{\beta})^2, \tag{8}$$

where X_{Al}^{α}, X_{Si}^{α} and X_{Al}^{β}, X_{Si}^{β} are the site occupancies of Al and Si mixing on two α and two β sites. In the case of strict Al-avoidance, Si fully occupies the two β sites, $X_{Si}^{\beta} = 1$. This is an approximate treatment of Al-avoidance. It agrees with results from Monte Carlo (Myers et al. 1998) and cluster variation methods (Vinograd and Putnis 1999, Fig. 13) in the limit of high An-contents. For practical purposes, it is preferable to rewrite Equations 7 and 8 in terms of mole fractions. For example, for a feldspar of composition $(Na, K)_{0.7}(Ca, Sr, Ba)_{0.3}Al_{1.3}Si_{2.7}O_8$, we have $X_{Al}^{\alpha} = \frac{1}{2} (1.3) = \frac{1}{2} (1 + X_{An} + X_{SrF} + X_{Cn})$, $X_{Si}^{\alpha} = \frac{1}{2} (0.7) = \frac{1}{2} (1 - X_{An} - X_{SrF} - X_{Cn})$, and $X_{Si}^{\beta} = 1$ so that Equations 7 and 8 become:

$$\delta_{Ab}^{config} = \delta_{Or}^{config} = (1 + X_{An} + X_{SrF} + X_{Cn})(1 - X_{An} - X_{SrF} - X_{Cn}) \tag{9}$$
$$\delta_{An}^{config} = \frac{1}{4} (1 + X_{An} + X_{SrF} + X_{Cn})^2. \tag{10}$$

The presence of Sr and Ba raises the question of which mole fractions should be used in the expressions for the ideal activities (Eq. 5) and the activity coefficients (Eqs. 11–13 below). Should X_{SrF} and X_{Cn} be ignored or should they be considered somehow? It is usually observed that in two-feldspar pairs, Sr preferentially segregates into plagioclase, whereas Ba prefers the alkali feldspar. We thus decided from crystal-chemical reasons to redefine X_{An} as $X_{An}+X_{SrF}$ and X_{Or} as $X_{Or}+X_{Cn}$ and to use the redefined mole fractions in Equations 5 and 11–13, whereas the original ones were used in Equations 9 and 10 where they take care of the proper entropy correction factors. This treatment clearly lacks consistency, but we hope that, to some degree, it compensates for our lack of expressions for the contribution of Sr- and Ba-feldspar components to the activity expressions.

The activity coefficients in Equation 4 are usually formulated in terms of Margules interaction parameters, W^G. Applying the model of Wohl (1946, 1953) for ternary systems, the following expressions for the activities were obtained (Fuhrman and Lindsley 1988):

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

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

$$\begin{aligned} a_{An} = \tilde{X}_{An} \cdot \exp\{&(W_{OrAb}^G [X_{Ab} X_{Or} (\tfrac{1}{2} - X_{An} - 2\, X_{Ab})] \\ &+ W_{AbOr}^G [X_{Ab} X_{Or} (\tfrac{1}{2} - X_{An} - 2\, X_{Or})] \\ &+ W_{AbAn}^G [2\, X_{Ab} X_{An} (1 - X_{An}) + X_{Ab} X_{Or} (\tfrac{1}{2} - X_{An})] \\ &+ W_{AnAb}^G [X_{Ab}^2 (1 - 2\, X_{An}) + X_{Ab} X_{Or} (\tfrac{1}{2} - X_{An})] \\ &+ W_{OrAn}^G [2\, X_{Or} X_{An} (1 - X_{An}) + X_{Ab} X_{Or} (\tfrac{1}{2} - X_{An})] \\ &+ W_{AnOr}^G [X_{Or}^2 (1 - 2\, X_{An}) + X_{Ab} X_{Or} (\tfrac{1}{2} - X_{An})] \\ &+ W_{OrAbAn}^G [X_{Or} X_{Ab} (1 - 2\, X_{An})])/RT\}. \end{aligned} \tag{13}$$

The Margules parameters W^G are usually assumed to depend linearly on temperature, T, and pressure, P:
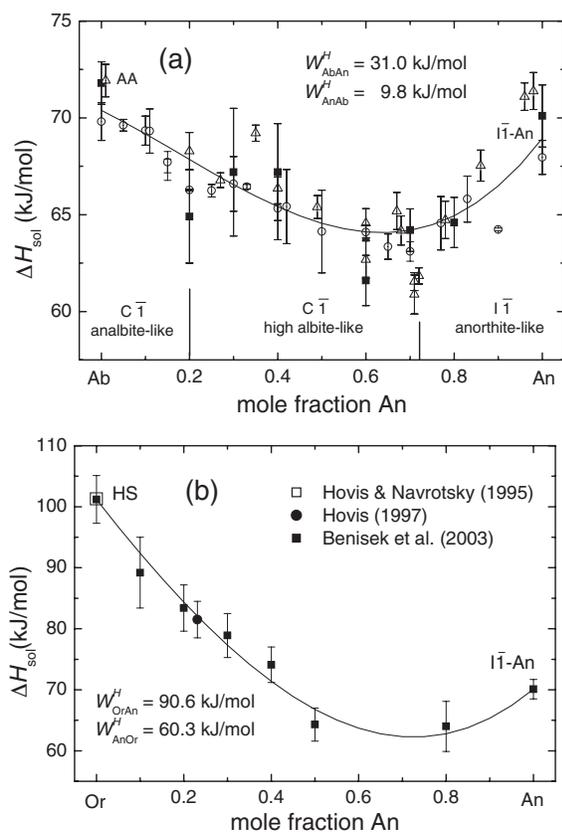
$$W^G = W^H - T\, W^S + P\, W^V \tag{14}$$

where W^H, W^S, and W^V are the enthalpic, entropic, and volumetric parameters, respectively. It is thus seen that a total of 21 parameters is necessary to fully describe ternary feldspars as a continuous solid solution. The approximative character of this model has been discussed by various authors (Brown and Parsons 1981, 1985; Kroll et al. 1993).

Equations 11–13 may be substituted into Equations 1–3 and each can be solved for T. Thus, from the chemical composition of a plagioclase-alkali feldspar pair, three temperatures of coexistence are obtained, $T(Ab)$, $T(Or)$, and $T(An)$, which ideally should agree.

REVISION OF INTERACTION PARAMETERS

Interaction parameters may be obtained directly from calorimetric and volumetric measurements or be obtained indirectly from a fit of Equations 1–3 to plagioclase-alkali feldspar pairs prepared at known *P-T* conditions (Seck 1971; Elkins and Grove 1990). First we introduce directly obtained parameters.

The enthalpic mixing properties of high structural-state plagioclase feldspars have been investigated by Newton et al. (1980), Carpenter et al. (1985), and Benisek et al. (2003) using high-temperature solution calorimetry. The enthalpies of solution, ΔH_{sol}, measured in these studies are plotted in Figure 1a. Although Benisek et al. (2003) provided a complex fit to these data, which took account of phase transitions at $X_{An} \approx 0.2$ and $X_{An} \approx 0.7$, the curve shown in Figure 1a assumes that solution enthalpies can be described by a simple mixing model. This provides a practical way of handling mixing properties for petrological purposes like geothermometry. The data were fitted

to a two-parameter Margules model:

$$\Delta H_{sol} = \Delta H_{sol}^{Ab} X_{Ab} + \Delta H_{sol}^{An} X_{An} - W_{AbAn}^H X_{Ab} (X_{An})^2 - W_{AnAb}^H (X_{Ab})^2 X_{An} \quad (15)$$

yielding interaction parameters $W_{AbAn}^H = 31 \pm 4$ and $W_{AnAb}^H = 10 \pm 4$ kJ/mol. We used unit weights in the calculation because standard errors were defined in different ways in the three data sets. Apparent "outliers" were downweighted. The interaction parameters are similar to those of Newton et al. (1980), who reported $W_{AbAn}^H = 28.2$ kJ/mol and $W_{AnAb}^H = 8.5$ kJ/mol. Giving higher weight to end-member enthalpies, Benisek et al. (2003) obtained larger W^H values: 40 kJ/mol and 14 kJ/mol, respectively. In the thermometer fit, these values resulted in a pronounced sensitivity of the temperature *T*(Ab*)* to slight compositional shifts. The smaller W^H values were therefore preferred.

From high-temperature plagioclase feldspars, Benisek et al. (2003) prepared a metastable Or-An series by K-exchange and determined their solution enthalpies. Because the Al,Si ordering state is not affected by the K-exchange, both series have similar enthalpy characteristics. However, in addition to ordering effects observed in the plagioclase binary, volume mismatch effects in the (K,Ca)-feldspars cause excess enthalpies to increase considerably. The calorimetric results are shown in Figure 1b together with data of Hovis and Navrotsky (1995) and Hovis (1997). By analogy to the plagioclases, a two-parameter Margules model has been chosen to describe the solution enthalpies yielding $W_{OrAn}^H = 91 \pm 14$ kJ/mol and $W_{AnOr}^H = 60 \pm 10$ kJ/mol.

W^V parameters of (Na,Ca)- and (K,Ca)-feldspars were calculated from the data of Kroll and Müller (1980) and Benisek et al. (2003). Using Equation 2 of Fuhrman and Lindsley (1988), the ternary W^V parameter was fitted to three disordered series of Kroll et al. (1986) and Hovis (1997). For the alkali feldspars, the enthalpic, entropic, and volumetric parameters were all taken from Hovis et al. (1991).

FIT OF INTERACTION PARAMETERS TO PHASE EQUILIBRIUM DATA

Following the preceding revisions, only six out of the original 21 parameters in Equations 11–13 are left to be determined from phase-equilibrium data: four entropic parameters of the Ab-An and Or-An binaries, plus the enthalpic and entropic parameters for ternary mixtures. The latter parameter was set to zero because W^H and W^S correlate when calculated simultaneously. The remaining five parameters were fitted to the ternary feldspar compositions of Seck (1971) and Elkins and Grove (1990), starting with the latter data. It appeared that the model so obtained also reproduced quite well the experiments of Seck (1971), notwithstanding the reservations that some authors expressed about Seck's data (e.g., Johannes 1979; Brown and Parsons 1981). We therefore decided to combine both data sets into one, weighting the data of Seck by a factor of 1/3 relative to the data of Elkins and Grove because his set is three times larger than theirs. The ideal activities $\tilde{X}_i$ were formulated both in terms of the molecular mixing and Al-avoidance models. It may be noted that we fitted the interaction parameters to the ternary feldspar compositions as they were originally published without allowing any shift. Fuhrman and Lindsley (1988) and Elkins and Grove (1990) adjusted the compositions to optimize their fits.

FIGURE 1. Enthalpies of solution for the (Na,Ca)- and (K,Ca)-feldspar binaries at 980 K in molten lead borate. The plagioclase data (**a**) are taken from Newton et al. (1980 = open dots), Carpenter et al. (1985 = triangles), and Benisek et al. (2003 = filled squares). The data for the (K,Ca)-feldspars (**b**) are taken from Hovis and Navrotsky (1995), Hovis (1997), and Benisek et al. (2003). The value of Hovis (1997) was converted from hydrofluoric acid calorimetry to lead borate calorimetry (Benisek et al. 2003). Error bars represent one standard deviation. The solution enthalpies were fitted to a two-parameter Margules model yielding (a)$W_{AbAn}^H = 31 \pm 4$ kJ/mol, $W_{AnAb}^H = 10 \pm 4$ kJ/mol, and (b) $W_{OrAn}^H = 91 \pm 14$ kJ/mol, $W_{AnOr}^H = 60 \pm 10$ kJ/mol (solid curves). AA = analbite, HS = high sanidine, I$\bar{1}$-An = anorthite with I$\bar{1}$ symmetry.

All interaction parameters are listed in Table 1 together with the results of Fuhrman and Lindsley (1988) and Elkins and Grove (1990). Comparing the molecular mixing with the Al-avoidance model, it is seen that in the molecular mixing model the W^S parameters of the (Na,Ca)- and (K,Ca)-feldspars are larger by 10–15 J/(mol·K). This result can be related to the entropy correction factor δ_i^{config}. In the molecular mixing model, it is set to 1 (Eq. 6). Therefore, the ideal activity is necessarily larger in this model than in the Al-avoidance model. On the other hand, the larger W^S parameters reduce the values of the activity coefficients so that the activities themselves have similar values in both models. The W^S values of the Al-avoidance model represent the excess vibrational entropy, whereas in the molecular mixing model they incorporate both the excess configurational and vibrational entropies.

The Al-avoidance model reproduces experimental tie-lines somewhat better than does the molecular mixing model. Therefore all calculations in the following are based on the Al-avoidance model. Figure 2 compares calculated with experimental temperatures demonstrating good agreement for both the data of Seck (1971) and Elkins and Grove (1990).

APPLICATION OF THE MODEL

Development of non-equilibrium compositions due to retrograde resetting

When the two-feldspar thermometer is applied to slowly cooled rocks, problems arise due to retrograde resetting effects. However, as shown by Kroll et al. (1993), these problems can be taken into account properly so that the thermometer will return reliable results.

Figure 3 shows the ternary feldspar diagram with isotherms calculated for 10 kbar using Margules interaction parameters given in Table 1 ("this work, Al-avoidance"). The open squares represent the composition of a feldspar pair in a granulite-facies metapelitic rock from the south-eastern part of the Highland Complex of Sri Lanka (sample "391a core", Raase 1998). The compositions of the coexisting plagioclase and alkali feldspar do not plot on a common isotherm. The Or content of the plagioclase is low relative to the An content of the alkali feldspar. This is most likely a consequence of retrograde resetting. Apart from

Al,Si ordering reactions after their growth, the plagioclase and alkali feldspar have to change their compositions to maintain internal equilibrium when following the ternary solvus down temperature. However, this process would involve exchange of Al and Si between crystals, which is an unlikely process. The diffusion coefficient at 800 °C for the coupled substitution (Na,K) + Si $\leftrightarrow$ Ca + Al is small relative to the interdiffusion coefficient for the exchange of only Na and K cations: $\bar{D} \approx 10^{-22}$ cm²/s for the coupled substitution compared to $\bar{D} \approx 10^{-12}$ cm²/s for the Na-K substitution (Yund 1983). Therefore, in the retrograde history of a rock, plagioclase and alkali feldspar will act as closed systems with regard to the intercrystalline transfer of Al and Si. However, exchange of K and Na cations will continue, albeit along a non-equilibrium path, driven by the decreasing solubility of K in plagioclase (with other phases possibly being involved). As the transfer of Ca from alkali feldspar to plagioclase is kinetically hindered due to the coupled substitution, intracrystalline decomposition into plagioclase and K-rich feldspar, i.e., perthitic exsolution, develops. Similarly, when no exchange partner like alkali feldspar is present, plagioclase typically shows antiperthitic unmixing which also involves intracrystalline (Na,K) + Si $\leftrightarrow$ Ca
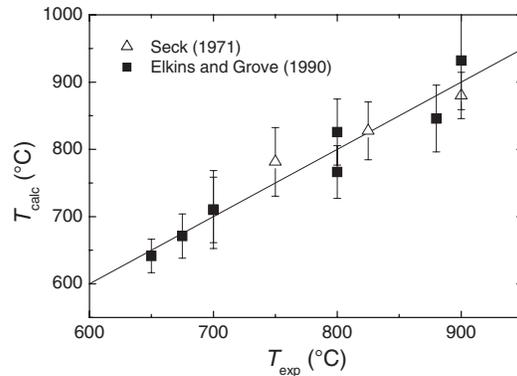
FIGURE 2. Temperatures calculated from the experimental two-feldspar compositions of Seck (1971) and Elkins and Grove (1990) plotted vs. experimental temperatures. The calculations employed the interaction parameters of "this work, Al-avoidance model" (Table 1). Error bars represent one standard deviation obtained from the variation of calculated temperatures $T(Ab)$, $T(Or)$, and $T(An)$ of each experiment.

TABLE 1. Interaction parameters for ternary feldspars from Fuhrman and Lindsley (1988), F&L, Elkins and Grove (1990), E&G, and the present study; W^G(J/mol) = W^H(J/mol) – T(K) · W^S(J/mol K) + P(bar) · W^V(J/mol bar)

Model	W	AbOr	OrAb	AbAn	AnAb	OrAn	AnOr	OrAbAn
	W^H	18810	27320	28226	8471	52468	47396	8700
F&L	W^S	10.3	10.3	0	0	0	0	0
	W^V	0.394	0.394	0	0	0	–0.120	–1.094
	W^H	18810	27320	7924	0	40317	38974	12545
E&G	W^S	10.3	10.3	0	0	0	0	0
	W^V	0.3264	0.4602	0	0	0	–0.1037	–1.095
this study,	W^H	19550*	22820*	31000‡	9800‡	90600†	60300†	8000§
Al-avoidance	W^S	10.5*	6.3*	4.5§	–1.7§	29.5§	11.2§	0#
model	W^V	0.327*	0.461*	0.069‡	–0.049‡	–0.257‡	–0.210‡	–0.467‡
this study,	W^H	19550*	22820*	31000‡	9800‡	90600†	60300†	13000§
molecular	W^S	10.5*	6.3*	19.0§	7.5§	43.5§	22.0§	0#
mixing model	W^V	0.327*	0.461*	0.069‡	–0.049‡	–0.257‡	–0.210‡	–0.467‡

* Hovis et al. (1991).
† Benisek et al. (2003).
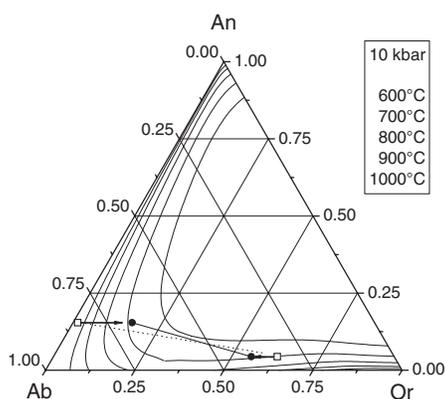‡ W^H and W^V parameters fitted to calorimetric and volumetric data.
§ W^H and W^S parameters fitted to experimental phase equilibrium data of Seck (1971) and Elkins and Grove (1990).
# W^S parameter set to zero.

+ Al exchange. In conclusion, as a consequence of the different ease of the K-Na and Al-Si exchange between coexisting feldspars, non-equilibrium pairs develop as we observe in natural rocks. In geothermometer calculations, this phenomenon causes the three temperatures T(Ab), T(Or) and T(An) to diverge. From the compositions of sample "391a core," we obtain T(Ab) = 664 °C, T(Or) = 476 °C, and T(An) = 1210 °C. Obviously, this is not a meaningful thermometer result.

Fuhrman and Lindsley (1988) addressed the problem of divergence and suggested that an analytical uncertainty of ± 2 mol% in each mol fraction should be allowed for. It is, however, not sensible to treat divergence in this way when the chemical shifts are systematic in nature, caused by resetting. Therefore, Kroll et al. (1993) suggested that the original compositions of the plagioclase and alkali feldspar crystals be restored by reversing the retrograde Na-K exchange at constant An. The reversal traces back the non-equilibrium path that the feldspar compositions followed during cooling, until the original equilibrium tie-line and the common isotherm on the calculated ternary solvus are recovered. Mathematically, the reversal is calculated by minimizing the variance of temperatures T(Ab), T(Or), T(An) by shifting the Na and K content of the two-feldspar compositions at constant An. In the calculation, it is not necessary to maintain constant bulk composition because phases other than plagioclase and alkali feldspar may have been involved in the exchange of Na and K during cooling of the parent rock (see below).

The filled circles in Figure 3 represent the equilibrium compositions of the feldspar pair obtained in the calculation. The compositional shifts, ΔX_{Or}^{Pl} and $-\Delta X_{Or}^{AF}$, are given in Table 2; they are much larger than ± 2 mol%. The temperature of the isotherm is T(Ab) = T(Or) = T(An) = 915 °C. This result agrees with Schenk et al. (1988) who concluded from two-pyroxene thermometry that the highest temperatures in the south-eastern part of the Highland Complex exceeded 900 °C. In ultra-high temperature metamorphic rocks (T_{max} > 1000 °C), it is expected that temperatures recovered from the resetting correction tend to

be higher than temperatures found from other cation-exchange thermometers. These may suffer from retrograde resetting which, in contrast to the two-feldspar thermometer, are difficult to account for.
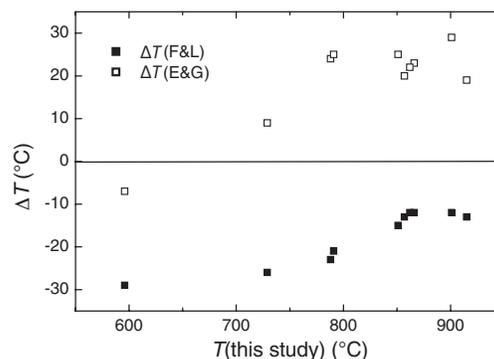
Comparison of temperatures

The resetting correction has been applied to several feldspar pairs from granulite-facies rocks of Sri Lanka. The temperatures obtained from the models of Fuhrman and Lindsley (1988), Elkins and Grove (1990), and this study are listed in Table 2 and shown in Figure 4. It could have been expected that our temperatures plot halfway between those of Fuhrman and Lindsley and Elkins and Grove because we have combined their data sets. However, at the high end our temperatures are closer to those of Fuhrman and Lindsley, whereas at the low end they are closer to those of Elkins and Grove. Possibly, the large number of fixed W^H values provides a framework that predetermines to some degree the shape of the calculated ternary solvus.

Temperatures obtained after Na-K reversal were also calculated from the model of Lindsley and Nekvasil (1989). Their temperatures are about 40 °C lower than ours. Raase (1998) concluded that compared with temperature estimates for Sri Lankan rocks obtained from garnet-orthopyroxene thermometry (Schumacher and Faulhaber 1994), the Elkins and Grove (1990) temperatures are systematically high, whereas the Lindsley and Nekvasil (1989) temperatures are low.

Check of the reliability of the resetting correction

Figure 3 shows that mathematically reversing the retrograde resetting lets the plagioclase "391a core" gain more Or than the alkali feldspar lose Or. If no phases other than the two feldspars are involved in the Na-K exchange, the different shifts are directly related to the proportions of plagioclase and alkali feldspar in the rock. In our case, we expect that the amount of alkali feldspar is about twice the amount of plagioclase because the Or shift of the alkali feldspar is only about half that of the plagioclase. The comparison of calculated chemical shifts with observed proportions of plagioclase and alkali feldspar opens up a new possibility to check whether the resetting correction performed with a chosen thermodynamic model returns reasonable answers. We expect that:

FIGURE 3. Ternary feldspar diagram calculated for P = 10 kbar using interaction parameters of "this work, Al avoidance model." Open squares represent observed compositions of coexisting plagioclase and alkali feldspar in a granulite-facies metapelite from Sri Lanka (sample "391a core" of Raase 1998). The compositions represent non-equilibrium conditions (broken line). Filled circles represent compositions obtained from the resetting correction. They define an equilibrium tie-line on a common isotherm (915 °C).

FIGURE 4. Deviation of two-feldspar temperatures obtained from the models of Fuhrman and Lindsley (1988), F&L, and Elkins and Grove (1990), E&G, from temperatures obtained in this study (Table 2).

TABLE 2. Two-feldspar geothermometry following the resetting correction method of Kroll et al. (1993)

|	Raase (1998)				Kroll et al. (1993)					
Sample	391a core	397 core	398 core	44	VSL 522	VSL 516	VSL 51	VSL 464	BSL 43-1	VSL523 mesoperthite
Paragenesis	Qtz,AF,Pl,Grt (Bt,Sil)	Qtz,AF,Pl (Grt,Sil)	Qtz,AF,Pl (Grt,Sil)	Qtz,AF,Pl Grt (Bt, Ms,Cal,Sil)	Qtz,AF,Pl	Qtz,AF,Pl	AF,Grt, Bt,Ms (Pl,Cpx)	Qtz,AF,Pl Amph, Bt,Ms	Qtz,AF,Pl, Grt, Cpx,Opx	AF + Pl lamellae
P (kbar)	10	10	10	7	8	8	8	8	11.5	5.5
					Composition					
X_{Ab}^{Pl}	0.833	0.781	0.777	0.741	0.799	0.800	0.793	0.697	0.735	0.840
X_{Or}^{Pl}	0.013	0.014	0.018	0.020	0.018	0.020	0.017	0.017	0.009	0.009
X_{An}^{Pl}	0.154	0.204	0.205	0.238	0.182	0.180	0.190	0.286	0.256	0.151
X_{Cn}^{Pl}	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
X_{Ab}^{AF}	0.328	0.313	0.267	0.193	0.233	0.342	0.385	0.277	0.267	0.167
X_{Or}^{AF}	0.625	0.638	0.700	0.785	0.729	0.623	0.576	0.693	0.708	0.830
X_{An}^{AF}	0.044	0.043	0.030	0.013	0.031	0.034	0.033	0.022	0.021	0.003
X_{Cn}^{AF}	0.003	0.006	0.003	0.009	0.007	0.001	0.006	0.008	0.004	0.000
					Na-K reversal					
ΔX_{Or}^{Pl}(F&L)	0.171	0.137	0.101	0.039	0.116	0.119	0.115	0.056	0.070	0.027
$-\Delta X_{Or}^{AF}$	0.060	0.014	0.025	0.021	0.101	0.004	−0.052	−0.059	−0.061	0.010
ΔX_{Or}^{Pl} (E&G)	0.170	0.137	0.104	0.043	0.118	0.122	0.117	0.060	0.075	0.030
$-\Delta X_{Or}^{AF}$	0.093	0.054	0.064	0.058	0.136	0.040	−0.015	−0.017	−0.018	0.035
ΔX_{Or}^{Pl}(this work)	0.153	0.119	0.086	0.033	0.103	0.105	0.103	0.046	0.057	0.029
$-\Delta X_{Or}^{AF}$	0.073	0.029	0.042	0.047	0.117	0.020	−0.036	−0.034	−0.039	0.039
					Temperature (°C)					
F&L (1988)	902	889	836	703	844	854	850	765	770	567
E&G (1990)	934	930	876	738	877	889	884	812	816	589
this work	915	901	851	729	857	866	862	788	791	596
					Molar ratio					
AF/Pl^{calc} (F&L)	2.8	10.0	4.1	1.8	1.1	28.8	−2.2	−1.0	−1.2	2.6
AF/Pl^{calc} (E&G)	1.8	2.6	1.6	0.7	0.9	3.0	−7.6	−3.4	−4.1	0.9
AF/Pl^{calc} (this work)	2.1	4.0	2.0	0.7	0.9	5.6	−2.8	−1.3	−1.5	0.7
AF/Pl^{obs}	1.5	3.1	1.7	0.6	0.6	4.4	not measured			0.7

Notes: The calculations were performed using the mixing parameters of Fuhrman and Lindsley (1988), F&L, Elkins and Grove (1990), E&G, and this study. Observed molar ratios of alkali feldspar and plagioclase, AF/Pl^{obs}, are compared with calculated ratios, AF/Pl^{calc}. The calculated ratios follow from the chemical shifts of alkali feldspar, ΔX_{Or}^{AF}, and plagioclase, ΔX_{Or}^{Pl}, obtained when reversing the Na-K exchange: $-\Delta X_{Or}^{Pl}/\Delta X_{Or}^{AF}$ = AF/Pl^{calc}. Note that the ratios are positive when plagioclase and alkali feldspar are virtually the only Na,K-bearing phases in the rock, but are negative when other Na,K-bearing phases are present. Parentheses enclose phases that occur in minor amounts (less than 5 vol%). See text for further comments.

$$-\Delta X_{Or}^{Pl} /\Delta X_{Or}^{AF} \approx (AF/Pl)^{obs} \qquad (16)$$

where $(AF/Pl)^{obs}$ is the observed molar ratio and ΔX_{Or} is the calculated chemical shift. We determined volumetric ratios by point counting under the petrographic microscope and converted them into molar ratios with the help of Equation 2 of Fuhrman and Lindsley (1988) (Table 2). Seven samples (391a, 397, 398, 44, VSL522, VSL516, VSL523) contain no or almost no Na,K-bearing phases other than the two feldspars. In three samples (VSL51, VSL464, BSL43-1), muscovite, biotite, amphibole, and clinopyroxene are present that may have influenced the Na,K content of the feldspars by exchange or mineral reactions.

The observed and calculated molar ratios are listed in Table 2 and plotted in Figure 5. Ignoring samples VSL51, VSL464, and BSL43-1, it is seen that the calculated ratios based on the Fuhrman-Lindsley interaction parameters are larger than the observed ratios, whereas good agreement is found for the models of Elkins and Grove (1990) and the present study. Molar ratios calculated from the Lindsley and Nekvasil (1989) model are about as high as the ratios obtained from the Fuhrman and Lindsley (1988) model.

Three specimens (VSL51, VSL464, and BSL43-1) behave differently from the rest. Both ΔX_{Or}^{Pl} and ΔX_{Or}^{AF} have positive signs, i.e., the Or contents of plagioclase and alkali feldspar increase by the resetting correction. This may happen when other Na,K-bearing phases are present that affect the Na,K content of the feldspars by exchange processes and/or mineral reactions. Such phases are in fact present in the three specimens, whereas the other samples effectively contain only plagioclase and alkali
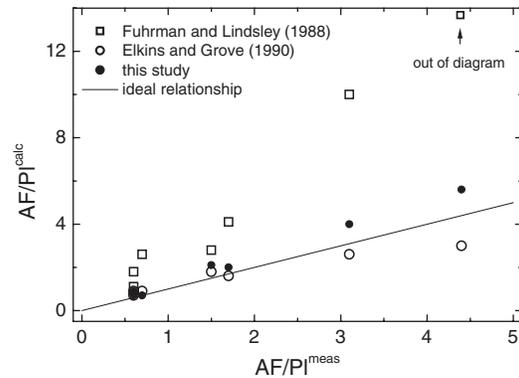
FIGURE 5. Calculated vs. observed alkali feldspar-plagioclase molar ratios. The observed ratios were obtained by point counting under the petrographic microscope; the calculated ratios derive from the chemical shifts obtained from the resetting correction method (Table 2).

feldspar as Na,K-bearing phases (Table 2).

It should be emphasized that the validity of the resetting correction is not called into question by the sign of the Or shifts. Under the premise of constant An, the correction procedure searches for the original tie-line and the common isotherm, whatever directions in the ternary diagram the feldspar compositions followed during cooling, opposite or parallel.

Application of the thermometer to low temperatures

The interaction parameters listed in Table 1 relate to high structural state feldspars. It may thus be asked, down to what

temperatures can the thermometer be applied with confidence? To provide an answer, we have investigated a mesoperthite that is the only Na,K-bearing phase in a granulite-facies rock (Kroll et al. 1993, sample VSL523). The bulk composition corresponds to a minimum temperature on the ternary solvus of 915 °C. During cooling, a regular mesoperthitic texture developed by exchanging all three components Ab, Or, and An between the lamellae. At some temperature, $T_{closure}$, the intracrystalline exchange Ca + Al $\leftrightarrow$ (Na,K) + Si between the lamellae must have ceased while the Na-K exchange continued. The resetting correction yields $T_{closure} = 596$ °C at $P = 5.5$ kbar (Table 2). The observed molar ratio (AF/Pl)^{obs} for the lamellae is 0.7. This value is also obtained from the calculated chemical shifts. We therefore assume that the thermometer may be applied down to temperatures of about 600 °C. Note that at this temperature, the two feldspar phases are still in their "high" structural states. The alkali feldspar is in the sanidine state, which is stable down to about 500 °C, and the plagioclase is in a high albite-like state, as seen from Carpenter (1981, Fig. 2d).

Uncertainty of calculated temperatures

One of the sources of uncertainty in calculated temperatures is the pressure estimate. Table 1 shows that the volume mixing parameters for the Or-An binary are negative, contrasting with the positive parameters for the Ab-Or binary (see Kroll et al. 1995 for a discussion of negative excess volumes). Therefore, although the Or-An solvus becomes narrower with increasing pressure, the addition of Ab component counteracts this effect into the ternary field. As a result, the pressure effect on the ternary solvus is only moderate so that a wrong estimate of pressure has only a small impact on calculated two-feldspar temperatures. The effect of the pressure uncertainty may be obtained as follows. Raase (1998) indicated for specimen "391a core" a pressure of $P = 10$ kbar. The error in the estimate of P, assumed to be $\sigma = \pm 2$ kbar, propagates into the estimate of the two-feldspar temperature. From a random number generator, we produced 10 000 P values according to a Gaussian distribution with $<P> = 10$ kbar and $\sigma = \pm 2$ kbar. For each pressure the concordant two-feldspar temperature was calculated. This procedure yielded a virtually normal distribution of temperatures from which the mean and standard deviation of 915 ± 11 °C were obtained.

Another source of uncertainty is the chemical analysis. Again, we chose "391a core" as an example and assumed that relative compositional standard errors amount to 3% for X_{Ab}^{Pl}, X_{An}^{Pl}, X_{Ab}^{AF}, X_{Or}^{AF}, 10% for X_{Or}^{Pl}, and 15% for X_{An}^{AF}, X_{Cn}^{Pl} and X_{Cn}^{AF}. By analogy to the treatment of the uncertainty in the pressure estimate, 10 000 mole fractions were generated around each of the eight measured mole fractions according to Gaussian distributions with standard deviations as assumed. The 10 000 feldspar pairs mostly yielded concordant temperatures that were again normally distributed with mean and standard deviations of 915 ± 19 °C. The ambiguity associated with correct integration of exsolution textures would contribute to this uncertainty. Another uncertainty results from the determination of interaction parameters, but this is difficult to fix. When only the effects of the uncertainties in pressure and composition are considered, our calculation yields $T = 915 \pm 22$ °C.

Volcanic rocks

In contrast to metamorphic rocks, no intercrystalline exchange is expected in rapidly cooled volcanic rocks so that temperatures may be derived from the chemical compositions of feldspar pairs as measured. As noted above, Fuhrman and Lindsley (1988) suggested that compositions be adjusted within an overall uncertainty of ±2 mol% until a tie-line is found so that $T(Ab) = T(Or) = T(An)$. This procedure has been built into two-feldspar thermometer programs like MTHERM3 (Fuhrman and Lindsley 1988) and SOLVCALC1,2 (Wen and Nekvasil 1994) and has been widely followed. However, the problem with this procedure is that the obtained tie-line is not unique. When one tie-line exists within the two-percent uncertainty range, then within the same range a manifold of other tie-lines located on the manifold of isotherms that cut the circular 2% area must necessarily exist. All these tie-lines are equally valid solutions to a search algorithm because, unlike the usual optimization situation, no global but only local minima exist. The search algorithm just hits one of the minima, for all of which $T(Ab) = T(Or) = T(An)$ is fulfilled. Which of the minima is found depends on the particular minimization algorithm and on the starting composition.

This problem may be shown by way of an example. Hildreth (1979) investigated the temperature zonation in the magma chamber of the Bishop Tuff (eastern California) using oxide and two-feldspar thermometry. For a feldspar pair from the late ash flow, the SOLVCALC2 code calculates $T(Ab) = T(Or) = T(An) = 727$ °C as the concordant temperature (using the mixing model of this study, Al-avoidance, Table 1). In contrast, a search algorithm written for EXCEL (Microsoft Corp.) finds a different tie-line for which 767 °C is the concordant temperature. Furthermore, when starting from compositions that are slightly different from the original composition (all within the ±2 mol% uncertainty), it is easy to find other tie-lines for which $T(Ab) = T(Or) = T(An)$. A few are selected in Table 3 to demonstration for demonstration. From 727 to 788 °C they cover a temperature range of about 60 °C. In the end, the non-uniqueness of the calculated tie-line, its dependence on the search algorithm and the vast range of calculated temperatures lead us to conclude that the widely followed practice of adjusting compositions should be abandoned.

In the preceding section, we offered a statistically valid procedure that accounts for chemical uncertainties. It relies on Gaussian distributions of plagioclase and alkali feldspar compositions produced by a random number generator. The width of the Gaussian distributions can be chosen in accordance with the reliability of the chemical analysis. The calculation of temperatures results in near-normal distributions of $T(Ab)$, $T(Or)$, and $T(An)$ from which the means and standard deviations can be obtained. From the overlap of the Gaussian curves one may discuss whether or not the feldspars crystallized at equilibrium.

We have applied the method of random compositions to two examples, the first of which is the Bishop Tuff (late) feldspar pair, already noted above. Because compositional errors were not reported, we have assumed the same values as for sample "391a core." We also had to assume that the feldspars are homogeneous. The results of the statistical calculation are shown in Figure 6a

and Table 4. The three temperatures range between 669 °C and 779 °C. T(An) does not overlap with T(Or) and T(Ab) within mutual 1σ deviations. The feldspar pair may thus be suspected not to have crystallized at equilibrium. This finding may be compared with the results of the SOLVCALC2 and EXCEL codes, both of which provided concordant temperatures appearing to be equilibrium conditions. When the observed compositions of the feldspar pair are plotted on a ternary diagram and isotherms are drawn through the plagioclase and alkali feldspar data points, temperatures of 766 °C and 719 °C are obtained for the plagioclase and alkali feldspar crystallization, respectively.

The second example is taken from Bachmann et al. (2002), who gave a detailed analysis and genetic interpretation of the chemical zoning in a feldspar pair from the Fish Canyon Tuff, San Juan volcanic field (Table 4). A pair of zones termed T1 was considered by them to represent equilibrium crystallization. Assuming the same chemical uncertainty as above, we calculated the distribution of temperatures given in Figure 6b. The three temperatures are identical within 1σ limits and may thus indeed indicate equilibrium crystallization.

In conclusion, the widely accepted method of adjusting compositions has no merits for neither metamorphic nor volcanic rocks. The method of randomly generating two-feldspar pairs, however, provides a firm statistical basis for investigating the coexistence of plagioclase and alkali feldspar. In volcanic rocks, this method permits the distinction between equilibrium and non-equilibrium pairs. In the case of non-equilibrium, two isotherms each for the plagioclase and the alkali feldspar composition, representing the minimum temperatures of crystallization, may be calculated.

CAVEATS

During slow cooling under essentially dry conditions, characteristic of granulite-facies rocks, regular exsolution textures develop in alkali feldspars. String perthites and regular lamellar mesoperthites are typical. If, however, a hydrothermal event occurs, regular textures are replaced by irregular textures like patch or vein-perthite, inter alia (e.g., Voll et al. 1994). The solution/redeposition process that is responsible for textural restructuring and changes in the state of Al,Si order not only may affect the textures, but may also change the bulk composition (Brown and Parsons 1981). Therefore, care must be taken when the two-feldspar thermometer is applied to rocks that experienced hydrothermal events [like re-metamorphosed granulites (Büsch and Mehnert 1991), granites (Majewski 1988), pegmatites, etc.]. Whenever the bulk composition has been altered after previous equilibration, the thermometer results have to be treated with caution. Then, the resetting correction will not return the original compositions and equilibration temperatures.
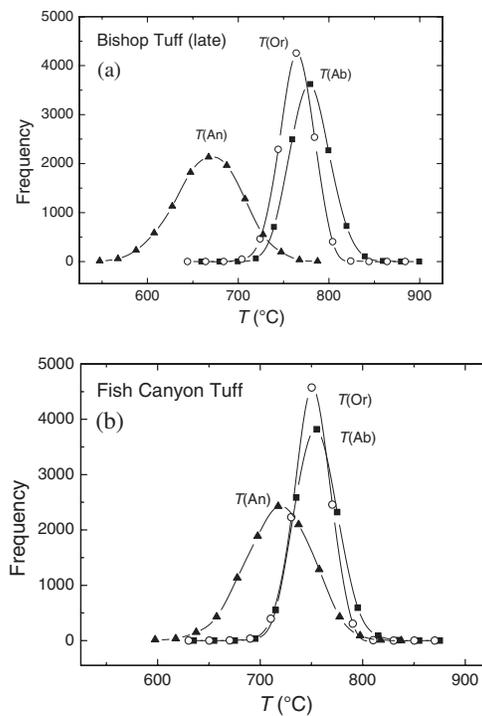
FIGURE 6. Normal distributions of temperatures T(Ab), T(Or) and T(An) found for the feldspar pairs from **(a)** the "Bishop Tuff (late)" (Hildreth 1979) and **(b)** the Fish Canyon Tuff (Bachmann et al. 2002). The temperatures were calculated from a randomly generated distribution of feldspar pair compositions centred at the observed compositions with suitably chosen standard errors (see text).

TABLE 3. Selected concordant temperatures T(conc) = T(Ab) = T(Or) = T(An) and respective compositions for the "Bishop Tuff (late)" feldspar pair (Hildreth 1979)

| T_{conc}(°C)	X_{Ab}^{Pl}	X_{Or}^{Pl}	X_{An}^{Pl}	X_{Ab}^{AF}	X_{Or}^{AF}	X_{An}^{AF}
	0.702	0.076	0.222	0.337	0.650	0.013
727	0.7148	0.0628	0.2224	0.3163	0.6692	0.0144
736	0.7099	0.0652	0.2249	0.3210	0.6634	0.0157
747	0.7066	0.0685	0.2249	0.3276	0.6553	0.0171
757	0.7031	0.0720	0.2249	0.3342	0.6472	0.0186
767	0.6933	0.0730	0.2337	0.3342	0.6455	0.0203
778	0.6952	0.0799	0.2349	0.3476	0.6303	0.0221
788	0.6856	0.0804	0.2340	0.3462	0.6300	0.0238

Notes: Compositions were adjusted within ±2 mol% of the original values given in the second line of the table. The mixing model of the present study (Al-avoidance) and a pressure of 1 kbar were used for the calculation.

TABLE 4. Average temperatures T(Ab), T(Or), T(An) and their standard errors for two examples of feldspar pairs from volcanic rocks

Sample	P	Composition: Pl then AF				T		Comment
	(kbar)	Ab	Or	An	Cn		(°C)	
Bishop Tuff (late)	1	0.702	0.076	0.222	–	T(Ab)	779±22	non-equilibrium
Hildreth (1979)		0.337	0.650	0.013	–	T(Or)	764±18	T(Pl) ≈ 766°C
						T(An)	669±36	T(AF) ≈ 719°C
Fish Canyon (T1)	2	0.6296	0.0473	0.3221	0.0010	T(Ab)	755±20	equilibrium
Bachmann et al. (2002)		0.2598	0.6964	0.0145	0.0293	T(Or)	750±17	T(Pl) ≈ T(AF)
						T(An)	717±33	≈ 748°C

Notes: Each triplet of temperatures derives from 10000 AF- and Pl-pair compositions randomly distributed about the observed compositions. The following relative standard errors of mole fractions have been assumed in generating a normal distribution of compositions: 3% for X_{Ab}^{Pl}, X_{An}^{Pl}, X_{Ab}^{AF}, X_{Or}^{AF}, 10% for X_{Or}^{Pl} and 15% for X_{An}^{AF}, X_{Cn}^{Pl} and X_{Cn}^{AF}. The overlap of the Gaussian curves for T(Ab), T(Or) and T(An) indicates whether the feldspar pairs may be at equilibrium or at non-equilibrium. In the case of non-equilibrium, minimum temperatures were calculated each for the plagioclase and the alkali feldspar.

AVAILABILITY OF THERMOMETER CODES

The two-feldspar thermometer can be used with files based on the programs "MATHEMATICA" (Wolfram Research, Inc.) and "EXCEL" (Microsoft Corp.), which can be obtained from the authors. The "MATHEMATICA" file is self-explanatory. With the "EXCEL" file, the solver has to be installed so that the variance of the temperatures T(Ab), T(Or), and T(An) can be minimized when correcting for resetting effects (the solver works only when the country code is set to "Great Britain"). The program "SOLVCALC" by Wen and Nekvasil (1994) may also be used. A recent version may be downloaded from the internet. The program calculates isotherms and tie-lines. It cannot account for a Sr or Ba-feldspar component. Also, when fixing An as required by the resetting correction the optimization algorithm returns erroneous results, in contrast to the MATHEMATICA and EXCEL algorithms. When dealing with volcanic rocks, only the MATHEMATICA file can generate Gaussian distributions of temperatures via a random number generator.

REFERENCES CITED

Bachmann, O., Dungan, M.A., and Lipman, P.W. (2002) The Fish Canyon magma body, San Juan Volcanic Field, Colorado: Rejuvenation and eruption of an upper-crustal batholith. Journal of Petrology, 43, 1469–1503.

Barth, T.F.W. (1934) Temperatures in lavas and magmas and a new geologic thermometer. Naturen, 6, 187–192.

——— (1951) The feldspar geologic thermometers. Neues Jahrbuch Mineralogie Abhandlungen, 82, 143–154.

Benisek, A., Kroll, H., Cemič, L., Kohl, V., Breit, U., and Heying, B. (2003) Enthalpies in (Na,Ca)- and (K,Ca)-feldspar binaries: a high temperature solution calorimetric study. Contributions to Mineralogy and Petrology, 145, 119–129.

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.

Büsch, W. and Mehnert, K.R. (1991) Antiperthites in granulites and similar structures in migmatites of the Black Forest. Neues Jahrbuch Mineralogie Abhandlungen, 162, 117–133.

Carpenter, M.A. (1981) A "conditional spinodal" within the peristerite miscibility gap of plagioclase feldspars. American Mineralogist, 66, 553–560.

Carpenter, M.A., McConnell, J.D.C., and Navrotsky, A, (1985) Enthalpies of ordering in the plagioclase feldspar solid solution. Geochimica et Cosmochimica Acta, 49, 947–966,

Elkins, L.T. and Grove, T.L. (1990) Ternary feldspar experiments and thermodynamic models. American Mineralogist, 75, 544–559.

Fuhrman, M.L. and Lindsley, D.H. (1988) Ternary-feldspar modeling and thermometry. American Mineralogist, 73, 201–215.

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

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. (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. (1988) Enthalpies and volumes related to K-Na mixing and Al-Si order/disorder in alkali feldspars. Journal of Petrology, 29, 731–763.

——— (1997) Hydrofluoric acid solution calorimetric investigation of the effects of anorthite component on enthalpies of K-Na mixing in feldspars. American Mineralogist, 82, 149–157.

Hovis, G.L. and Navrotsky, A. (1995) Enthalpies of mixing for disordered alkali feldspars at high temperature: A test of regular solution thermodynamic models and a comparison of hydrofluoric acid and lead borate solution calorimetric techniques. American Mineralogist, 80, 280–284.

Hovis, G.L., Delbove, F., and Roll Bose, M. (1991) Gibbs energies and entropies of K-Na mixing for alkali feldspars from phase equilibrium data: Implications for feldspar solvi and short-range order. American Mineralogist, 76, 913–927.

Johannes, W. (1979) Ternary feldspars: Kinetics and posssible equilibria at 800°C. Contibutions 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. and Müller, W. (1980) X-ray and electron-optical investigation of synthetic high-temperature plagioclases. Physics and Chemistry of Minerals, 5, 255–277.

Kroll, H., Evangelakakis, Ch., and Voll, G. (1993) Two-feldspar geothermometry: a review and revision for slowly cooled rocks. Contributions to Mineralogy and Petrology, 114, 510–518.

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

Kroll, H., Kotelnikov, A.R., Göttlicher, J., and Valyashko, E.V. (1995) (K, Sr)-feldspar solid solutions: the volume behaviour of heterovalent feldspars. European Journal of Mineralogy, 7, 489–499.

Lindsley, D.H., and Nekvasil, H. (1989) A ternary feldspar model. EOS, 70, 506.

Majewsky, P. (1988) Die chemische Zusammensetzung koexistierender Alkalifeldspaete und Plagioklase—Ursache und Bedeutung. Dissertation, Universitaet Hannover, 1–134

Myers, E., Heine, V., and Dove, M.T. (1998) Some consequences of Al/Al avoidance in the ordering of Al/Si tetrahedral framework structures. Physics and Chemistry of Minerals, 25, 457–464

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

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

Raase, P. (1998) Feldspar thermometry: A valuable tool for deciphering the thermal history of granulite-facies rocks, as illustrated with metapelites from Sri Lanka. The Canadian Mineralogist, 36, 67–86.

Schenk, V., Raase, P., and Schumacher, R. (1988) Very high temperatures and isobaric cooling before tectonic uplift in the Highland series of Sri Lanka. Terra Cognita, 8, 265

Schumacher, R. and Faulhaber, S. (1994) Evaluation of P-T estimates on garnet-pyroxene-plagioclase-quartz-bearing granulite-facies rocks from Sri Lanka. Precambrian Research, 66, 295–308.

Seck, H.A. (1971) Koexistierende Alkalifeldспäte und Plagioklase im System NaAlSi₃O₈-KAlSi₃O₈-CaAl₂Si₂O₈-H₂O bei Temperaturen von 650 °C bis 900 °C. Neues Jahrbuch Mineralogie Abhandlungen, 115, 315–345.

Vinograd, V. and Putnis, A. (1999) The description of Al, Si ordering in aluminosilicates using the cluster variation method. American Mineralogist, 84, 311–324

Voll, G., Evangelakakis, C., and Kroll, H. (1994) Revised two-feldspar geothermometry applied to Sri Lankan feldspars. Precambrian Research, 66, 351–377.

Wen, S. and Nekvasil, H. (1994) SOLVCALC; an interactive graphics program package for calculating the ternary feldspar solvus and for two-feldspar geothermometry. Computers and Geosciences, 20, 1025–1040.

Wohl, K. (1946) Thermodynamic evaluation of binary and ternary liquid systems. Transactions of the American Institute of Chemical Engineers, 42, 215–249.

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

Yund, R.A. (1983) Diffusion in feldspars. In P.H. Ribbe, Ed., Feldspar Mineralogy, Vol. 2, 2nd ed., 203–220. Reviews in Mineralogy, American Mineralogical Society, Washington, D.C.