

The main purpose of this paper is to demonstrate that the experimental data of Seck (1971a) can be cali-

brated to an asymmetric ternary regular solution approximation for the excess enthalpy and entropy of mixing of the ternary feldspars. When these excess functions are combined with an Al-avoidance model for the configurational entropy of the solution, the Gibbs free energy of mixing of the high-structural state solid phases in the system $\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8 - \text{KAlSi}_3\text{O}_8$ is described. Compositional derivatives of the Gibbs free energy of mixing then define the activities of each of the three end-member components as a function of composition, temperature and pressure. In this paper these modelled activities will be used to: 1) describe the compositions of coexisting ternary feldspars and the geometry of the extrapolated ternary feldspar solvus as a function of temperature and pressure, 2) define a new thermodynamically consistent analytical two-feldspar geothermometer, and 3) present estimates of the activity of the KAlSi_3O_8 component in plagioclase as a function of plagioclase composition, temperature and pressure.

Experimental database for calibrating the solution model

The most extensive experimental work on ternary feldspar solid solution is that of Seck (1971a, 1971b). He determined the compositions of over 100 coexisting feldspar pairs crystallized from ternary gels at 650°C and 1, 5 and 10 kbars, 750° and 825°C at 1 kbar and 900°C at 500 bars pressure. Brown and Parsons (1981) have recently reviewed the experimental method of Seck and have pointed out discrepancies between his results and that of other workers on the extent of the solvus in the ternary and the slope of the two-feldspar tie-lines. These discrepancies can be attributed to the sluggish kinetics which characterize the crystallization of phases in the ternary feldspar system (Johannes 1979). For example, when gels are used as starting materials, experience with the alkali-feldspar binary suggests that the position of the resulting "exchange solvus" (Parsons 1978) may be a function of bulk composition and time and generally lies displaced with respect to the binodal solvus in the system (one limb falling between the binode and the coherent spinode, the other between the binode and the anti-spinode). As Seck (1971a) utilized gels as starting materials these kinetic effects may be manifested in his results, although he performed several experiments to test the attainment of equilibrium and there is no indication that the ternary solvus he determined is a function of the bulk composition of the starting materials. Another source of uncertainty with regard to Seck's data is that he determined the Or-content of his feldspars using the $\bar{2}01$ X-ray method. In this manner Seck obtained ternary compositions by drawing a tie-line through the bulk composition fixed at its Or-rich end by an estimate of the Ab-content which was based on the limits of the two-feldspar field established in auxiliary experiments. Such a procedure may overestimate feldspar miscibility (Seck 1971a) which in turn will tend to alter the tie-line slopes and critically distort the geometry of the inferred "equilibrium" solvus.

Using similar arguments Johannes (1979) has criticized Seck's (1971a and 1971b) attempt at defining the

solvus of the ternary feldspars and claims to have determined the only "equilibrium" ternary feldspar data (one determination of the compositions of coexisting phases at 650°C and 1 kbar and two at 800°C and 1 kbar, see Figs. 2a and 2c). Johannes' criteria for establishing equilibrium are not unequivocal however (Brown and Parsons 1981), and after reviewing the available data one is left with the impression that none of the experimental studies in the ternary feldspar system is acceptable without reservation and that no two studies of "equilibria" in the system are mutually consistent. As 95% of the data were collected by Seck (1971a, 1971b) and as "the regularity of [Seck's] results is consistent with a good approach to equilibrium" (Brown and Parsons 1981) it is most compelling to utilize this database exclusively in calibrating a solution model for the ternary system. This is the approach to be taken here and it should be viewed as a interim solution in the progress toward thermodynamically modelling the activity/composition relations in the ternary feldspars. The Seck database will certainly demonstrate the correct general mathematical form for the excess free energy of the ternary system and will allow a three-component thermodynamic geothermometer to be formulated and tested against naturally occurring two-feldspar pairs. It should be apparent that by utilizing the Seck data exclusively the accuracy of the solution model can be questioned and therefore the problem of an independent means of verifying the results of the model will be brought up again below. In anticipation of the objection that the data does not warrant proceeding any further it will be shown in a subsequent section that independent estimates of the activity of KAlSi_3O_8 in plagioclase crystallizing from basalts indicate that Seck's (1971a, 1971b) data (particularly his high-temperature results along the plagioclase limb of the solvus) do not deviate grossly from equilibrium.

Solution model for the ternary feldspars

Excess terms

In constructing a solution model for the ternary feldspars it is important that correct parameterizations of the phase relations in the binaries be incorporated as limiting cases. This is particularly relevant as: 1) the Seck (1971a, 1971b) data may contain systematic experimental errors, 2) the binary phase relations are better known than those in the ternary, and 3) significant use of the model will be made in a compositional range outside the solvus, which is necessarily, in the case of the feldspars, close to the alkali-feldspar and plagioclase binaries. It seems appropriate, therefore, to first discuss solution models for the binary joins in the system $\text{NaAlSi}_3\text{O}_8 - \text{CaAl}_2\text{Si}_2\text{O}_8 - \text{KAlSi}_3\text{O}_8$. In the discussion that follows we will concentrate our attention on the thermodynamics of high-structural state feldspars as these most probably represent the structural states of the materials crystallized from gels by Seck (1971a, 1971b). The symbols An, Ab and Or will always refer to the phases whose formulas are $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 , respectively.

The excess entropy and enthalpy of mixing of structurally disordered alkali-feldspar solid solutions have

Table 1. Thermodynamic parameters

Thompson and Hovis (1979)		
$W_{Ab,Or}$	$7,404 - 5.12T$	(cals)
$W_{Or,Ab}$	4,078	(cals)
W_v	86.2	(cals/bar)
Newton et al. (1980)		
$W_{Ab,An}$	6,746.1	(cals)
$W_{An,Ab}$	2,024.7	(cals)

been recently discussed by Thompson and Hovis (1979), Brown and Parsons (1981) and Haselton et al. (1983). By combining a thorough analysis of the solution calorimetric measurements with a critical appraisal of the available phase equilibrium data Thompson and Hovis (1979) have concluded that the molar excess Gibbs free energy of mixing, \hat{G}^{ex} , can be expressed as an asymmetric binary regular solution which incorporates a symmetric excess volume of mixing:

$$\hat{G}_{Or,Ab}^{ex} = W_{Ab,Or} X_{Ab} X_{Or}^2 + W_{Or,Ab} X_{Ab}^2 X_{Or} + W_v P X_{Ab} X_{Or}, \quad (1)$$

where X_i denotes the mole fraction of component i . The parameters in Eq. (1) are tabulated in Table 1.

It should be noted that Thompson and Hovis' parameters incorporate strongly asymmetric values for the molar excess entropy of mixing (Table 1) which to some extent compensate for their strongly asymmetric excess enthalpy of mixing terms. This is to be expected as the entropy of mixing was calibrated from phase equilibrium data and the asymmetry of the alkali-feldspar solvus is opposite to that displayed by the calorimetrically measured enthalpy of mixing. Brown and Parsons (1981) have recognized the nature of these compensating terms and have attempted to extract enthalpy, entropy and volume of mixing expressions entirely from the solvus data (essentially the same data utilized by Thompson and Hovis 1979, and selected as best approximating the binodal solvus by Parsons, 1978). They obtain asymmetric volume, enthalpy and entropy of mixing expressions which well describe the binodal solvus. Haselton et al. (1983) have measured excess heat capacities of mixing in analbite-sanidine solid solutions and from these derived a symmetric excess entropy of mixing which is essentially temperature independent under geologic conditions. Using this entropy of mixing and experimental determinations of the position of the solvus they generate an asymmetric regular solution approximation for the excess enthalpy of mixing.

It is difficult to select, *a priori*, amongst these three parameterizations of the thermodynamic properties of disordered phases in the alkali-feldspar system; it being largely a matter of preference as to which type of experimental measurement should carry the most weight in the final formulation. In this paper the expressions and constants of Thompson and Hovis (1979) will be adopted because (as will be demonstrated below) their parameters generate an alkali-feldspar solvus, over the temperature range of interest, which is most consistent with the experimental data reported by Seck (1971a). Equation (1) has therefore been chosen to de-

scribe the solid solution properties along the alkali-feldspar join.

Newton et al. (1980) have published the only available measurements on the enthalpy of solution of high-structural state plagioclases from which they derive an asymmetric binary regular solution model for the molar excess enthalpy of mixing, \hat{H}^{ex} :

$$\hat{H}_{Ab,An}^{ex} = W_{Ab,An} X_{Ab} X_{An}^2 + W_{An,Ab} X_{Ab}^2 X_{An}. \quad (2)$$

The values of the interaction parameters in Eq. (2) are provided in Table 1. Carpenter and McConnell (1984) have pointed out that the small positive excess enthalpy of mixing of Newton et al. (1980) can be made to vanish by accounting for the $C\bar{1}=I\bar{1}$ structural transition at intermediate plagioclase compositions. Considering this Al/Si ordering transformation the enthalpy of solution data are interpreted as representing ideal mixing in a $C\bar{1}$ plagioclase extending from pure albite to a "fictive" $C\bar{1}$ anorthite over the range $An_0 - An_{55}$ with continuous transformation to the $I\bar{1}$ ordered state at more calcic compositions. As the effects of cation ordering are generally strongly temperature dependent, if the interpretation of Carpenter and McConnell (1984) is correct the mixing data of Newton et al. (1980) may apply strictly only up to 1,200°C. For the purpose of modelling the enthalpy of mixing along the An-Ab binary in this paper, Eq. (2) will be adopted and the order-disorder transformation will be dealt with in a highly generalized way, following Newton et al. (1980), by employing an Al-avoidance model for the entropy of mixing. It should be borne in mind that this approach effectively averages out the contributions of a true order-disorder transformation by producing a completely smooth transition between high albite and fully ordered anorthite. It has the advantage of being easily extended to ternary compositions and of limiting the number of thermodynamic components that are necessary to describe activity/composition relations in the system. In lieu of more extensive data Eq. (2) will be used to describe the excess free energy of mixing, rendering $\hat{G}_{Ab,An}^{ex}$ temperature and pressure independent along the plagioclase join.

Unfortunately, there is no experimental data on the An-Or solvus. However, the asymmetry of coexisting feldspar compositions close to the binary join reported by Seck (1971a) and the extent of ternary solid solution (possibly metastable?) exhibited in lunar lavas (Ryder et al. 1975) suggests that the excess free energy of mixing in this limiting binary might be strongly asymmetric. In addition, the experimental work of Seck (1971b) extrapolated to the An-Or join indicates a negligible pressure dependence. Based on these arguments the expression:

$$\hat{G}_{An,Or}^{ex} = W_{Or,An} X_{Or} X_{An}^2 + W_{An,Or} X_{Or}^2 X_{An} \quad (3)$$

will be adopted to describe the molar excess Gibbs free energy of mixing along the An-Or join. The interaction parameters which remain to be determined will be treated as functions only of temperature and not pressure.

Equations (1), (2) and (3) can be combined to generate an expression for the excess free energy of the solid solution within the ternary. Anderson and Lindsley

(1981) have discussed how this can be done in a manner which allows the incorporation of higher order ternary terms (e.g. three-way interactions: $W_{Ab,An,Or}$). Their arguments, which are based upon the observation that a Margules expansion of the ternary excess free energy leads to an interdependence of the asymmetric binary interaction parameters in a ternary solution, yields the following expression for \hat{G}^{ex} , recast in terms of the adopted feldspar components:

$$\begin{aligned}\hat{G}^{ex} = & W_{Ab,An} X_{Ab} X_{An} (X_{An} + \frac{1}{2} X_{Or}) \\ & + W_{An,Ab} X_{Ab} X_{An} (X_{Ab} + \frac{1}{2} X_{Or}) \\ & + W_{Ab,Or} X_{Ab} X_{Or} (X_{Or} + \frac{1}{2} X_{An}) \\ & + W_{Or,Ab} X_{Ab} X_{Or} (X_{Ab} + \frac{1}{2} X_{An}) \\ & + W_{Or,An} X_{Or} X_{An} (X_{An} + \frac{1}{2} X_{Ab}) \\ & + W_{An,Or} X_{Or} X_{An} (X_{Or} + \frac{1}{2} X_{Ab}) \\ & + W_{Ab,Or,An} X_{Ab} X_{Or} X_{An} + W_V P X_{Ab} X_{Or}.\end{aligned}\quad (4)$$

There are three undetermined parameters in Eq. (4) including a strictly ternary term whose necessity will be tested when fitting the solution model to the Seck (1971a) database (below). The symmetric pressure term has been retained for consistency with Eq. (1). The reader will note that Eqs. (1)–(3) (the binary models) can be recovered from Eq. (4) by successively setting each of the mole fractions to zero.

Configurational entropy

Newton et al. (1980) have pointed out that in order to rectify their determinations of the excess enthalpy of solution of the high-structural state plagioclases (which give rise to Eq. 2) with the cation exchange experiments of Orville (1972) an Al-avoidance configurational entropy model for the plagioclase feldspars (Kerrick and Darken 1975) must be adopted (see above). Therefore, in order to consistently model the configurational entropy of the three-component system we must extrapolate from the plagioclase binary into the feldspar ternary by reformulating the Al-avoidance entropy to account for the Or component. In doing so the procedure outlined in Kerrick and Darken (1975) will be followed.

Let n_{Al} and n_{Si} be the number of moles of aluminum and silicon in the feldspar, then:

$$n_{Al} = n_{Ab} + n_{Or} + 2n_{An}$$

$$n_{Si} = 3n_{Ab} + 3n_{Or} + 2n_{An}.$$

If there are α sites occupied by Al in pure anorthite, then:

$$n_{Si}^{\alpha} = n_{Ab} + n_{Or}$$

where n_{Si}^{α} is the number of moles of silicon atoms on α sites. Thus:

$$\begin{aligned}n_{Si}^{\alpha} + n_{Al} &= 2(n_{Ab} + n_{Or} + n_{An}) \\ &= 2(n_{Na} + n_K + n_{Ca})\end{aligned}$$

$$n_{Al} = n_{Na} + n_K + 2n_{Ca}.$$

Considering mixing of Na, K and Ca on the large cation site and Al and Si on the tetrahedral (α) site the

total number of accessible configurations, Ω , available to the ternary feldspar solution is

$$\Omega = \frac{(n_{Na} + n_K + n_{Ca})! [2(n_{Na} + n_K + n_{Ca})]!}{n_{Na}! n_K! n_{Ca}! (n_{Na} + n_K)! (n_{Na} + n_K + 2n_{Ca})!}.\quad (5)$$

The “configurational activity”, a_i^{conf} , of any of the three components in this solution is given by (Kerrick and Darken, 1975):

$$a_i^{conf} = k_i (\Omega / \Omega_i) \quad (6)$$

where Ω_i is the number of accessible configurations of the solution after the addition of one unit of component i , and k_i is a coefficient defined by the adopted standard state.^a From Eq. (5) we obtain:

$$\Omega_{Ab} = \frac{(n_{Na} + n_K + n_{Ca} + 1)! [2(n_{Na} + n_K + n_{Ca}) + 2]!}{(n_{Na} + 1)! n_K! n_{Ca}! (n_{Na} + n_K + 1)! (n_{Na} + n_K + 2n_{Ca} + 1)!} \quad (7)$$

$$\Omega_{Or} = \frac{(n_{Na} + n_K + n_{Ca} + 1)! [2(n_{Na} + n_K + n_{Ca}) + 2]!}{n_{Na}! (n_K + 1)! n_{Ca}! (n_{Na} + n_K + 1)! (n_{Na} + n_K + 2n_{Ca} + 1)!} \quad (8)$$

and

$$\Omega_{An} = \frac{(n_{Na} + n_K + n_{Ca} + 1)! [2(n_{Na} + n_K + n_{Ca}) + 2]!}{n_{Na}! n_K! (n_{Ca} + 1)! (n_{Na} + n_K)! (n_{Na} + n_K + 2n_{Ca} + 2)!} \quad (9)$$

Substituting Eqs. (7)–(9) and Eq. (5) successively into Eq. (6), expanding the factorials using Stirling's rule and evaluating the constants, k_i , from the definition of the standard state, we obtain:

$$a_{Ab}^{conf} = X_{Ab} (1 - X_{An}^2) \quad (10)$$

$$a_{Or}^{conf} = X_{Or} (1 - X_{An}^2) \quad (11)$$

and

$$a_{An}^{conf} = \frac{1}{4} X_{An} (1 + X_{An})^2. \quad (12)$$

Equations (10) and (12) reduce to the expressions given in Kerrick and Darken (1975) for the plagioclase binary and are thus consistent with those used by Newton et al. (1980). Equations (10) and (11) reduce to ideal one-site mixing expressions ($a_i^{conf} = X_i$) along the alkali-feldspar join ($X_{An} = 0$). This is consistent with Thompson and Hovis' (1979) formulation of the excess entropy of mixing within the binary (Table 1 and Eq. 1, above).

The Al-avoidance molar configurational entropy of the ternary feldspar solid solution is therefore given by:

$$\hat{S}^{conf} = -R \sum_i X_i \ln a_i^{conf}$$

or

$$\begin{aligned}\hat{S}^{conf} = & -R [X_{Ab} \ln [X_{Ab} (1 - X_{An}^2)] \\ & + X_{Or} \ln [X_{Or} (1 - X_{An}^2)] \\ & + X_{An} \ln [X_{An} (1 + X_{An})^2 / 4]].\end{aligned}\quad (13)$$

Combining Eqs. (4) and (13) the molar Gibbs free energy of mixing, \hat{G}^{mix} , can be written:

$$\hat{G}^{mix} = -T \hat{S}^{conf} + \hat{G}^{ex} \quad (14)$$

^a In this paper we define the standard state to be unit activity of the pure component at any T and P . Therefore, k_i is defined such that a_i is unity for the pure substance ($X_i = 1$).

Calibration of the model

A procedure for calibrating the three undetermined parameters in Eq. (4) from the data of Seck (1971a) will now be outlined. First we recognize that for any two coexisting feldspars on the solvus at a particular T and P the condition of heterogeneous equilibrium is:

$$a_{\text{Ab}}^{\text{plag}} = a_{\text{Ab}}^{\text{alk}}$$

$$a_{\text{Or}}^{\text{plag}} = a_{\text{Or}}^{\text{alk}}$$

and

$$a_{\text{An}}^{\text{plag}} = a_{\text{An}}^{\text{alk}}$$

or, equivalently:

$$RT \ln a_{\text{Ab}}^{\text{plag}} = RT \ln a_{\text{Ab}}^{\text{alk}} \quad (15a)$$

$$RT \ln a_{\text{Or}}^{\text{plag}} = RT \ln a_{\text{Or}}^{\text{alk}} \quad (15b)$$

$$RT \ln a_{\text{An}}^{\text{plag}} = RT \ln a_{\text{An}}^{\text{alk}} \quad (15c)$$

where the superscripts plag and alk denote plagioclase and alkali-feldspar. Applying the Darken equation

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

to Eq. (14) generates analytical expressions for these activities. After substitution of Eqs. (4) and (13) and some simplification, we obtain:

$$\begin{aligned} a_{\text{Ab}} = & X_{\text{Ab}}(1 - X_{\text{An}}^2) \\ & \cdot \exp[(W_{\text{Ab,Or}}[X_{\text{Or}}^2(1 - 2X_{\text{Ab}}) + X_{\text{Or}}X_{\text{An}}(\frac{1}{2} - X_{\text{Ab}})] \\ & + W_{\text{Or,Ab}}[2X_{\text{Ab}}X_{\text{Or}}(1 - X_{\text{Ab}}) + X_{\text{Or}}X_{\text{An}}(\frac{1}{2} - X_{\text{Ab}})] \\ & + W_{\text{Ab,An}}[X_{\text{An}}^2(1 - 2X_{\text{Ab}}) + X_{\text{Or}}X_{\text{An}}(\frac{1}{2} - X_{\text{Ab}})] \\ & + W_{\text{An,Ab}}[2X_{\text{Ab}}X_{\text{An}}(1 - X_{\text{Ab}}) + X_{\text{Or}}X_{\text{An}}(\frac{1}{2} - X_{\text{Ab}})] \\ & + W_{\text{Or,An}}[X_{\text{Or}}X_{\text{An}}(\frac{1}{2} - X_{\text{Ab}} - 2X_{\text{An}})] \\ & + W_{\text{An,Or}}[X_{\text{Or}}X_{\text{An}}(\frac{1}{2} - X_{\text{Ab}} - 2X_{\text{Or}})] \\ & + W_{\text{V}}P(1 - X_{\text{Ab}})X_{\text{Or}}]/RT] \end{aligned} \quad (16)$$

$$\begin{aligned} a_{\text{Or}} = & X_{\text{Or}}(1 - X_{\text{An}}^2) \\ & \cdot \exp[(W_{\text{Ab,Or}}[2X_{\text{Ab}}X_{\text{Or}}(1 - X_{\text{Or}}) + X_{\text{Ab}}X_{\text{An}}(\frac{1}{2} - X_{\text{Or}})] \\ & + W_{\text{Or,Ab}}[X_{\text{Ab}}^2(1 - 2X_{\text{Or}}) + X_{\text{Ab}}X_{\text{An}}(\frac{1}{2} - X_{\text{Or}})] \\ & + W_{\text{Ab,An}}[X_{\text{Ab}}X_{\text{An}}(\frac{1}{2} - X_{\text{Or}} - 2X_{\text{An}})] \\ & + W_{\text{An,Ab}}[X_{\text{Ab}}X_{\text{An}}(\frac{1}{2} - X_{\text{Or}} - 2X_{\text{Ab}})] \\ & + W_{\text{Or,An}}[X_{\text{An}}^2(1 - 2X_{\text{Or}}) + X_{\text{Ab}}X_{\text{An}}(\frac{1}{2} - X_{\text{Or}})] \\ & + W_{\text{An,Or}}[2X_{\text{Or}}X_{\text{An}}(1 - X_{\text{Or}}) + X_{\text{Ab}}X_{\text{An}}(\frac{1}{2} - X_{\text{Or}})] \\ & + W_{\text{V}}P X_{\text{Ab}}(1 - X_{\text{Or}})]/RT] \end{aligned} \quad (17)$$

$$\begin{aligned} a_{\text{An}} = & \frac{1}{4}X_{\text{An}}(1 + X_{\text{An}})^2 \\ & \cdot \exp[(W_{\text{Ab,Or}}[X_{\text{Ab}}X_{\text{Or}}(\frac{1}{2} - X_{\text{An}} - 2X_{\text{Or}})] \\ & + W_{\text{Or,Ab}}[X_{\text{Ab}}X_{\text{Or}}(\frac{1}{2} - X_{\text{An}} - 2X_{\text{Ab}})] \\ & + W_{\text{Ab,An}}[2X_{\text{Ab}}X_{\text{An}}(1 - X_{\text{An}}) + X_{\text{Ab}}X_{\text{Or}}(\frac{1}{2} - X_{\text{An}})] \\ & + W_{\text{An,Ab}}[X_{\text{Ab}}^2(1 - 2X_{\text{An}}) + X_{\text{Ab}}X_{\text{Or}}(\frac{1}{2} - X_{\text{An}})] \\ & + W_{\text{Or,An}}[2X_{\text{Or}}X_{\text{An}}(1 - X_{\text{An}}) + X_{\text{Ab}}X_{\text{Or}}(\frac{1}{2} - X_{\text{An}})] \\ & + W_{\text{An,Or}}[X_{\text{Or}}^2(1 - 2X_{\text{An}}) + X_{\text{Ab}}X_{\text{Or}}(\frac{1}{2} - X_{\text{An}})] \\ & - W_{\text{V}}P X_{\text{Ab}}X_{\text{Or}}]/RT]. \end{aligned} \quad (18)$$

Equations (16)–(18) may be substituted into Eqs. (15a)–(15c) and the terms representing the known quantities gathered on the left hand side of the equality. In doing so we obtain expressions of the form:

$$k_i = a_i W_{\text{Or,An}} + b_i W_{\text{An,Or}} + c_i W_{\text{Ab,Or,An}} \quad (19)$$

for each of the i components. The k_i , a_i , b_i and c_i are distinct functions of the compositions of the coexisting feldspars, the temperature and the pressure. The interaction parameters, W , in Eq. (19) are unknown. At any particular temperature these parameters can be approximated by least squares refinement of the $3n$ statements of Eq. (19) produced by Seck's (1971a) n determinations of the compositions of the coexisting feldspars on the solvus. The measurements are grouped in this fashion to allow the subsequent evaluation of the temperature dependence of the thermodynamic parameters.

The results of this calibration procedure are presented in Table 2 and Fig. 1. The number of coexisting feldspars used to calibrate the model at each temperature are reported. The standard error is the uncertainty (in calories) on predicting the value of k_i in Eq. (19). The residuals of k_i (actual minus predicted quantities) tend, at lower temperatures, to be negative for the equilibria involving the anorthite component and positive for the equilibria involving the albite component. Below each of the extracted interaction parameters in Table 2 is its associated standard error. The values indicated suggest that the asymmetric An–Or binary terms are significant at all four temperatures examined. The ternary term is not significant at the 95% confidence level at the higher temperatures and barely significant at lower T . Largely on the basis of these statistics higher order (asymmetric) ternary terms were not introduced into the formulation for the excess free energy (Eq. 4). It is also apparent from Table 2 that the model fits the data better at higher temperatures. It is conceivable that this is due to superior quality data (closer attainment of equilibrium compositions) in Seck's (1971a) higher temperature work.

As has been indicated above, alternative calibrations of the Seck database using the alkali-feldspar parameters proposed by Brown and Parsons (1981) and Haselton et al. (1983) resulted in much poorer fits. The overall standard error in residuals of the calibration of Seck's data using the alkali-feldspar parameters accepted here is 185 cal, while that which arises from Brown and Parsons (1981) parameters' is 452 cal and with those of Haselton et al. (1983), 479 cal. The temperature dependence of the standard errors in the alternative calibrations is not as pronounced as that given in Table 2. However, at no temperature do the standard errors of regression for the alternative fits become smaller in magnitude than those obtained using the parameters of Thompson and Hovis (1979). In all cases the distribution of residuals about the regression surface follows the pattern mentioned above. When plotted against temperature the parameters obtained from the alternative calibrations display the same relationships as those plotted in Fig. 1.

The temperature dependence of the model parameters is examined in Fig. 1 which clearly shows that the

Table 2. Results of the regression of the feldspar data of Seck (1971a)

	Interaction parameter with standard error (cals)				Proposed equation:
	650°C	750°C	825°C	900°C	
$W_{An,Or}$	11,315 271	11,062 137	11,993 137	12,355 105	$6,688.10$ $+4.83036T$
$W_{Or,An}$	15,226 886	12,064 322	13,222 281	13,024 187	$16,125.5$ $-2.64400T$
$W_{Ab,Or,An}$	-3,719 1,279	2,526 538	526 515	788 381	$-3,314.88$ $+3.49775T$
Data points	39	51	39	33	
Standard error ^a	289	167	135	93	
Multiple R^2	0.99644	0.99899	0.99938	0.99973	

^a Standard error of the residuals (cals) about the regression surface. See Eq. (19) of the text

points plotted at 750°C are inconsistent with those obtained at other T 's. A critical examination of Seck's 750°C data indicates that at this temperature the placement of the solvus is most poorly understood. He reports, for compositions of alkali-feldspar ranging from Or_{85} – Or_{55} (16 of the 17 data points at this T), a constant anorthite content of 2.5 mole% while the orthoclase content of the plagioclase varies from 3 to 9.6 mole%. This lack of detail concerning the shape of the alkali-feldspar leg of the solvus at 750°C probably leads to the inconsistency in the interaction parameters shown in Fig. 1. Though the problems apparent with Seck's data at 750°C appear less pronounced at 650°C they may be reflected in the larger uncertainties associated with the interaction parameters at this T (Table 2).

In light of these observations it appears prudent to accept the two high-temperature points to define the temperature dependence of each of the interaction parameters displayed in Fig. 1. This temperature dependence ignores the 750°C calibration but is substantially consistent with the determinations at 650°C. In the calculations that follow the strictly ternary interaction parameter was retained but it should be remembered that its contribution to the excess free energy of the solid may be statistically insignificant. Equations for the solid lines shown in Fig. 1 may be found in Table 2.

Comparisons and extrapolations

A detailed comparison between isothermal sections of the ternary solvus measured by Seck (1971a, 1971b) and those calculated using Eq. (14) and the parameters of Tables 1 and 2 can be seen in Figs. 2a–2d and Figs. 3a–3b. These diagrams also depict the slopes of two-feldspar tie-lines which have been constructed using an activity matching algorithm for solvus construction described by Barron (1976, 1983). In each figure Seck's compositional data on coexisting feldspars are shown connected by dotted lines. Agreement at 650°C and 1 kbar is poor at low anorthite contents

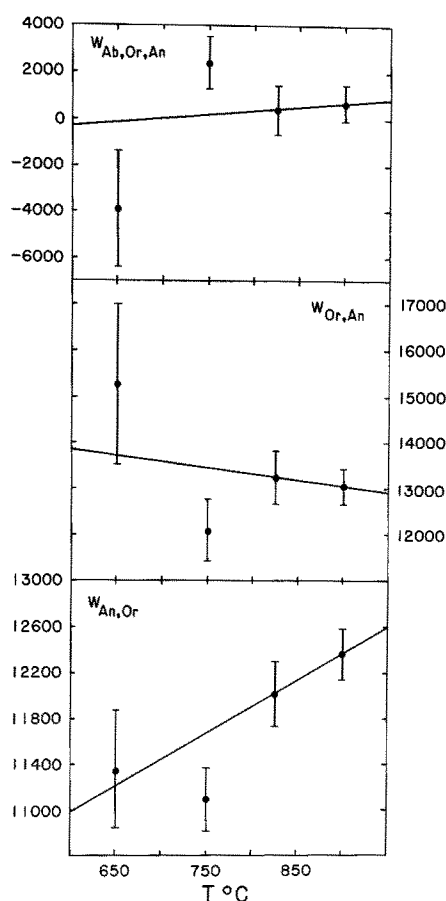


Fig. 1. Interaction parameters extracted from the experimental data of Seck (1971a) plotted as a function of temperature. The energy parameters are reported in calories and the brackets about these values indicate plus or minus two standard errors. The solid lines (equations reported in Table 2) pass through the two high-temperature points for each parameter

Table 3. Temperature recovery from the coexisting feldspar data of Seck (1971a)

T (°C)	P (kbars)	Average calculated T (°C)	Standard error of the average calculated T (°C)
650	1	661.12	29.84
750	1	774.41	34.61
825	1	833.19	25.26
900	0.5	905.54	23.93
		+14.84	28.91

The most significant deviations (positive) occur at the highest mole fractions of albite

and this is primarily due to the adopted solution model for the Ab–Or join. Seck's projected binary solvus appears to be much more asymmetric than that accepted by more recent workers (Parsons 1978; Thompson and Hovis 1979). The "equilibrium" data of Johannes shown in Fig. 2a describe much shallower tie-lines than those indicated by Seck (1971a). The data at 750°C (Fig. 2b) demonstrate better agreement, particularly as

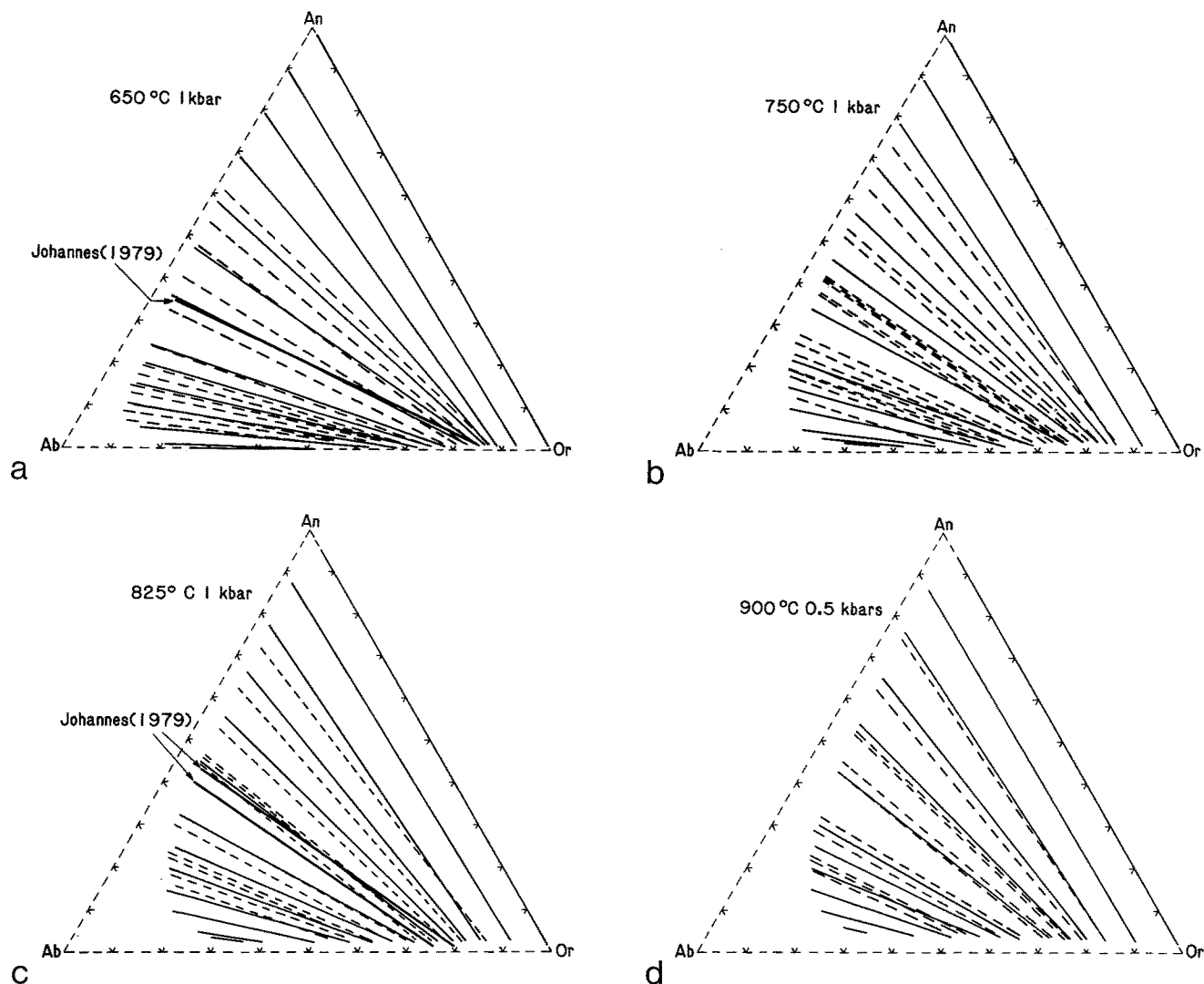


Fig. 2a-d. Calculated compositions of coexisting feldspars computed using the activity matching algorithm of Barron (1976, 1983) and Eqs. (16-18). These compositions are joined by the solid tie-lines and define the extent of the solvus. The dotted lines connect the experimentally determined compositions of Seck (1971a). **a** Solvus at 650°C and 1 kbar. The heavy solid line connects the compositions of coexisting feldspars determined at this temperature and pressure by Johannes (1979). **b** Solvus at 750°C and 1 kbar. **c** Solvus at 825°C and 1 kbar. The heavy solid lines connect the compositions of coexisting feldspars determined at 800°C and this pressure by Johannes (1979). **d** Solvus at 900°C and 500 bars

concerns the extent of the solvus at low anorthite contents. Considering the observed fit, the decision to dismiss the 750°C calibration parameters in favor of the equations of Table 2 appears justified. At 825°C and 900°C (Figs. 2c, 2d) the agreement (shape of the isothermal solvus section and slopes of tie-lines) is quite good. In both cases the width of the calculated solvus at lower anorthite contents is slightly greater than that inferred from Seck's (1971a) experimental results. The equilibrium tie-lines proposed by Johannes (1979) are shown in Fig. 2c for comparison.

In Figs. 3a and 3b the pressure dependence of the ternary solvus is examined. The coexisting feldspar compositions of Seck (1971b) are plotted and compared against descriptions of the solvus generated by the model equation. The pressure dependence in the proposed ternary solution model arises from that of the Ab-Or binary (Table 1). The agreement at 650°C and 5 kbars (Fig. 3a) is remarkable, but once again suggests

a more substantial asymmetry in the projected binary solvus of Seck (1971b). Though the calculated solvus of Fig. 3b broadly conforms to Seck's (1971b) measurements, the agreement is less than satisfactory. Given the fact, however, that the pressure dependence and shape of the Ab-Or solvus has been anchored on the parameters of Thompson and Hovis (1979) it does not appear that the discrepancies seen in Figs. 3a or 3b can be rectified by pressure dependent ternary ($W_{Ab,Or,An}$) or binary ($W_{Or,An}$, $W_{An,Or}$) terms.^b Consequently, additional pressure dependent terms have not been included in the

^b Brown and Parsons' (1981) asymmetric volume of mixing expression would tend to shift the calculated solvus more towards the albite apex at elevated P . However, Hovis (1977) determined the excess volume of mixing on those alkali-feldspar specimens upon which Thompson and Hovis' (1979) parameters of Table 1 are based, and his measurements indicate *no* asymmetry along the Ab-Or join.

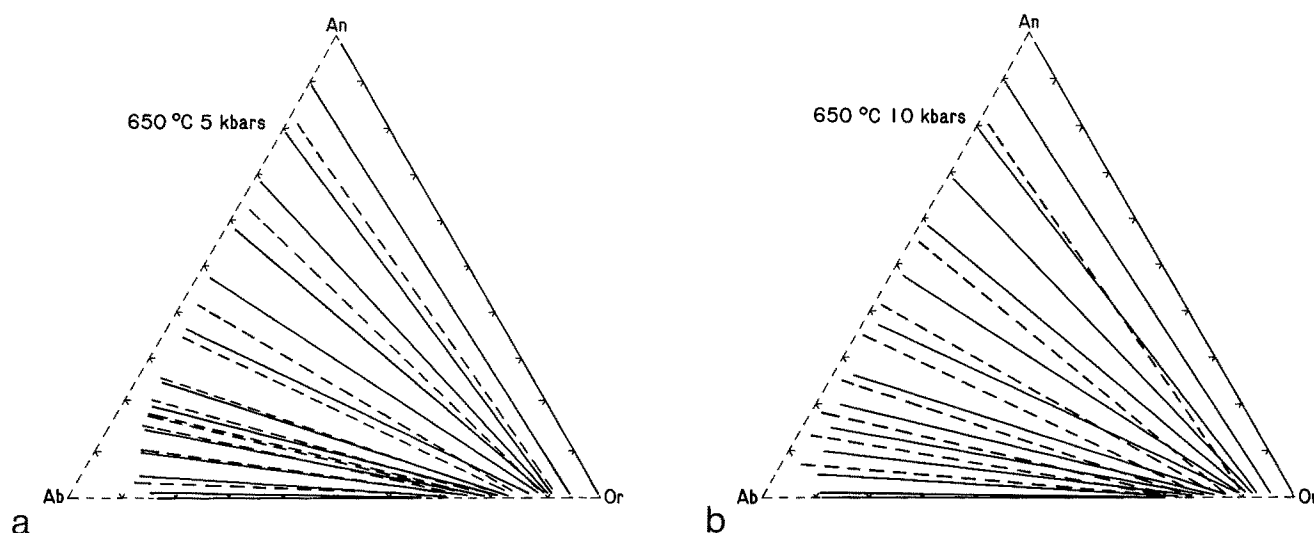


Fig. 3a and b. Calculated compositions of coexisting feldspars computed using the activity matching algorithm of Barron (1976, 1983) and Eqs. (16–18). These compositions are joined by solid tie-lines and define the extent of the solvus. The dotted lines connect the experimentally determined compositions of Seck (1971 b). **a** Solvus at 650 °C and 5 kbars. **b** Solvus at 650 °C and 10 kbars

Table 4. Coexisting feldspars examined by Brown and Parsons (1981)

	<i>T</i> (°C)	<i>P</i> (kbars)	mole fraction						<i>T</i> (°C)				
			Ab	Or	An	Ab	Or	An	(1)	(2)	(3)	(4)	(5)
Johannes (1979)	800	1	0.20	0.79	0.01	0.51	0.06	0.43	700	691	681	783	805
	800	1	0.24	0.75	0.01	0.54	0.06	0.40	780	730	720	862	819
Seck (1971 a)	825	1	0.39	0.57	0.04	0.69	0.10	0.21	(825)	784	722	878	837
Carmichael (1965) Trachyte		1	0.60	0.33	0.07	0.66	0.07	0.27	~750	1,374	1,206	3,137	917
Carmichael et al. (1974) Rhyolite		1	0.34	0.65	0.01	0.78	0.08	0.14	650	658	644	704	666
Stormer and Whitney (1977) ^a Granulite	750–800	7	0.247	0.720	0.033	0.679	0.003	0.318	760	716	675	748	1,043
O'Hara and Yarwood (1978) ^b Gneiss	1,150 ± 100	15	0.37	0.48	0.15	0.69	0.08	0.23	~1,050	970	673	768	1,073

(1) Brown and Parsons (1981) graphical (Fig. 2), 18° C/kbar for $P > 1$ kbar; (2) Stormer (1975); (3) Powell and Powell (1977); (4) Haselton et al. (1983); (5) this paper

^a Corrected (quoted as weight fractions by Brown and Parsons, 1981). Average composition of SA-118 with average calculated temperature. Stormer and Whitney (1977) also report other granulite data which is summarized here: sample 378 (737° C (2), 2,278° C (5)), S-107 (632° C (2), 633° C (5)), Ped-7 (460° C (2), 547° C (5))

^b Composition quoted in Brown and Parsons (1981) is $\text{Na}_{0.54}\text{K}_{0.19}\text{Ca}_{0.27}$ coexisting with $\text{Na}_{0.69}\text{K}_{0.07}\text{Ca}_{0.24}$ and is erroneously inferred by O'Hara and Yarwood (1978) to be a high-temperature pair. This cannot be so as both feldspars lie on the same side of the consolute curve (Fig. 4). The compositions given here represent an assemblage reportedly stable at lower temperatures

model and the reader is warned against applying it much above a pressure of 5 kbars.

In Fig. 4 the extent of ternary feldspar immiscibility is indicated as a function of temperature. The points shown were calculated using the same method as for Figs. 2 and 3 and tie-lines may be constructed by connecting the plotted feldspar pairs. The computed consolute (critical solution curve) is indicated on Fig. 4 and should be compared to that suggested by Parsons and Brown (1983). Their consolute swings about 5 mol% closer to the Ab–An join before encountering the curve shown in Fig. 4 at about the 1,400° C solvus

isotherm. Parsons and Brown's (1983) consolute bracket, derived from a detailed analysis of a two-perthite alkali gabbro, would plot about 2 mol% to the left, at $\sim \text{An}_{18}$, of the calculated critical curve. The consolute path of Fig. 4 is located at considerably more *potassic* compositions than that indicated by Carmichael et al. (1974, p. 224) who deduce its position from a study of groundmass feldspars in shoshonitic and nepheline-bearing trachytic lavas. However, it is located at substantially more *sodic* compositions than that suggested by Henderson and Gibb (1983) who infer a consolute bracket from a study of feldspar crystallization trends

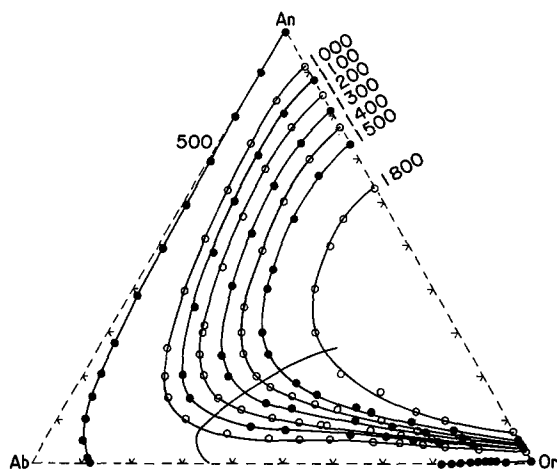


Fig. 4. Calculated compositions of coexisting feldspars computed using the activity matching algorithm of Barron (1976, 1983) and Eqs. (16–18). These compositions define the extent of the 1 bar solvus. Compositional sections through the solvus are indicated as a function of temperature ($^{\circ}\text{C}$) and the consolute (critical solution curve) has been plotted for convenience. For clarity, tie-lines between coexisting feldspars are not drawn. These calculations represent considerable extrapolations in temperature from the database of Seck (1971a)

in a wide variety of differentiating alkaline basic magmas (theralites, crinanites, essexites, techenites and nepheline dolerites). It is therefore difficult to judge the general validity of the consolute computed from the solution model proposed here.

The extent of ternary feldspar miscibility displayed in Fig. 4 is considerably less than that suggested by Parsons and Brown (1983). Their proposed 950°C – $1,000^{\circ}\text{C}$ solvus isotherm roughly coincides, at high Ab-contents, with the $1,300^{\circ}\text{C}$ isotherm shown in Fig. 4. This presents an unresolvable dilemma, as $1,300^{\circ}\text{C}$ is clearly too high a temperature to account for the formation of Parsons and Brown's (1983) mesoperthite-cryptoperthite pair, while at the same time their $\sim 1,000^{\circ}\text{C}$ isotherm admits far too much miscibility to account for coexisting feldspar pairs in trachytes and leucite-bearing two-feldspar lavas (see Table 5 and below). The ternary solvus suggested by Parsons and Brown (1983) is dome shaped and flattens abruptly above 900°C , remaining symmetric at higher temperatures. This solvus geometry would imply a temperature dependence of the Gibbs free energy of mixing in the ternary which cannot be inferred from an examination of Seck's (1971a, 1971b) data. The solvus displayed in Fig. 4 does not flatten at higher temperatures and is highly asymmetrical. It should be noted that hypothetical solvus isotherms have been metastably projected into the ordered feldspar region (500°C) and above the ternary liquidus in Fig. 4 to demonstrate this geometry. The notable asymmetry for Ab-poor compositions may be reflected in the extensive "metastable?" orthoclase contents of many lunar plagioclases (Ryder et al. 1975).

Geothermometry

Previous attempts at two-feldspar geothermometry (e.g. most recently Brown and Parsons 1981) have utilized a diagram of the mole fraction of Ab in the plagioclase

plotted as a function of temperature against the Ab mole fraction in the alkali-feldspar. Corresponding plots for the Or and An mole fractions may also be used as geothermometers but require rather more accurate compositional data on the An-content of the alkali-feldspar and the Or-content of the plagioclase. It should be emphasized, however, that *all three* mole fraction pairs should yield the same equilibration temperature when coexisting feldspars are used as a geothermometer. This is invariably not the case owing to difficulties in determining precise enough compositions of the feldspars, approximating the smooth curves from the original experiments, and the potential inapplicability of the original experimental work to natural two-feldspar equilibria. For these reasons an alternate means of feldspar geothermometry has been devised which utilizes all three components in each feldspar by iteratively finding the temperature which allows the activity of each component in the plagioclase to best approximate the corresponding activity in the alkali-feldspar. This two-feldspar geothermometer employs activity/composition relations derived from the solution model proposed here. The details of its construction and use are given in the Appendix.

In Table 3 the results of applying the new feldspar geothermometer to the database of Seck (1971a) are tabulated. These calculations provide an alternative measure of the deviation in temperature equivalent to the caloric uncertainties generated in fitting this database (see Table 2). It is apparent that the calculated temperatures are systematically a bit high and this, as is the major source of the standard deviation at each T , is due primarily to high positive deviations of the model temperatures at low An-contents. The reason for this concerns the departure of the Seck (1971a) solvus from that proposed by Thompson and Hovis (1979) and Parsons (1978).

Brown and Parsons (1981) expressed some concern that previous thermodynamically based feldspar geothermometers may be no more justified than their graphical counterparts. If the thermodynamic geothermometer is correctly formulated, however, there is a distinct advantage in using it to obtain a temperature when faced with the task of performing a two-variable non-linear graphical interpolation (Brown and Parsons 1981, Fig. 2). This is particularly the case if extrapolating above the published isotherms. In Table 4 a comparison is provided between the "thermodynamic geothermometer" proposed here and the feldspar geothermometers of Stormer (1975), Powell and Powell (1977), Brown and Parsons (1981) and Haselton et al. (1983). Stormer (1975), Powell and Powell (1977) and Haselton et al. (1983) used a pseudo-thermodynamic formulation for their geothermometers but neglected to completely describe the feldspars as a ternary system, calibrating upon Seck's (1971a) data projected to the plagioclase and alkali-feldspar joins. The feldspar compositions reported in Table 4 were used by Brown and Parsons (1981) to compare geothermometric approaches. Examining Table 4 it is evident that the proposed geothermometer, by and large, is a better estimator of temperature than any of the pseudo-thermodynamic analytical geothermometers. The calculated temperatures given for the trachyte reflect the fact that

Table 5. Comparison of calculated temperatures for coexisting feldspars

	P (kbars)	mole fraction (normalized to 1.000)						T (°C)				
		Ab	Or	An	Ab	Or	An	(1)	(2)	(3)	(4)	(5)
Carmichael (1963)	1	0.330	0.648	0.022	0.777	0.074	0.148	675	652	622	676	684
Pitchstones and Rhyolites	1	0.362	0.607	0.031	0.540	0.107	0.354	~1,100	956	916	1,374	1,077
	1	0.358	0.615	0.027	0.851	0.063	0.087	600	623	584	607	685
	1	0.368	0.620	0.012	0.786	0.071	0.143	675	674	656	723	652
	1	0.389	0.590	0.021	0.821	0.074	0.105	650	661	629	675	635
Carmichael (1965)	1	0.396	0.600	0.004	0.640	0.073	0.287	915	857	851	1,115	1,122
Trachytes	1	0.379	0.603	0.018	0.654	0.073	0.273	890	814	787	993	857
	1	0.594	0.335	0.071	0.656	0.072	0.272	~1,100	1,363	1,195	3,063	927
	1	0.456	0.491	0.054	0.546	0.140	0.314	HT	1,219	1,143	2,559	1,477
	1	0.489	0.488	0.023	0.573	0.065	0.363	HT	1,252	1,218	2,499	none
Ewart (1965) ^a	1	0.319	0.653	0.028	0.632	0.041	0.326	750	758	722	871	689
Ignimbrite, Taupo, N.Z.												
Rahman and MacKenzie (1969)	1	0.4761	0.4833	0.0406	0.4956	0.0529	0.4514	HT	1,571	1,548	15,170	1,068
Trachytes	1	0.4229	0.5210	0.0561	0.4945	0.0652	0.4403	HT	1,269	1,205	3,060	958
	1	0.3980	0.5473	0.0547	0.4506	0.0537	0.4957	HT	1,325	1,277	4,340	909
	1	0.4256	0.5168	0.0576	0.4797	0.0581	0.4622	~1,100	1,342	1,285	4,254	922
	1	0.4103	0.5313	0.0584	0.4668	0.0466	0.4866	~1,100	1,319	1,263	3,954	842
	1	0.4149	0.5299	0.0551	0.4587	0.0463	0.4950	~1,100	1,378	1,333	5,526	852
	1	0.4136	0.5190	0.0675	0.5056	0.0509	0.4435	~1,050	1,192	1,105	2,300	834
Latite	1	0.4179	0.5263	0.0558	0.3793	0.0460	0.5747	HT	1,939	2,024	-1,729	902
Hildreth (1979) ^b												
Bishop Tuff early	1	0.362	0.630	0.008	0.798	0.061	0.141	650	661	649	708	622
late	1	0.337	0.650	0.013	0.702	0.076	0.222	745	715	697	812	761
Baldrige et al. (1981) ^c												
Leucite basanite	0.001	0.168	0.791	0.041	0.253	0.029	0.718	900	949	922	1,086	856
Leucite trachytes	0.001	0.340	0.613	0.047	0.444	0.023	0.533	HT	1,087	1,039	1,787	681
	0.001	0.457	0.488	0.055	0.533	0.045	0.422	HT	1,250	1,177	2,725	794
Leucite phonolite	0.001	0.372	0.577	0.051	0.583	0.054	0.364	~1,100	886	814	1,105	788
Häuyne-leucite phonolite	0.001	0.431	0.526	0.044	0.540	0.084	0.376	HT	1,126	1,067	2,006	1,076
Leucite-rich-phonolitic-tephrite	0.001	0.285	0.674	0.041	0.445	0.100	0.455	~1,000	925	882	1,333	1,015
Phonolitic-tephrite	0.001	0.293	0.675	0.033	0.477	0.072	0.451	~1,000	890	855	1,195	910
Beddoe-Stephens et al. (1983) ^d												
Ignimbrite	1	0.276	0.712	0.012	0.586	0.042	0.372	800	743	729	876	728
	1	0.249	0.742	0.009	0.579	0.038	0.383	750	710	700	821	705
Carmichael (written communication)												
Rhyolite	1	0.346	0.646	0.008	0.790	0.075	0.135	650	655	644	702	652
(Cam 73, Mono Craters) ^e	1	0.329	0.663	0.007	0.775	0.065	0.161	650	653	642	703	651
	1	0.365	0.626	0.009	0.812	0.077	0.111	640	653	640	689	629
Obsidian		0.373	0.619	0.008	0.783	0.073	0.144	670	680	668	740	670
(406, Glass Mtn) ^f	1											
Rhyolite		0.400	0.580	0.020	0.735	0.092	0.173	745	746	714	834	767
(Cam 81, Inyo Craters) ^g	1											
Rhyolite		0.403	0.578	0.019	0.717	0.087	0.196	755	768	738	881	796
(Cam 86, Inyo Craters) ^h	1											

Number of significant digits as reported by the authors. Temperatures are rounded to the nearest degree.

(1) Brown and Parsons (1981), Fig. 2; (2) Stormer (1975); (3) Powell and Powell (1977); (4) Haselton et al. (1983); (5) this paper

^a Fe—Ti oxide temperature 750°C (Ewart et al., 1971)

^b Early, ~720°C; late ~780°C (Fe—Ti oxide temperatures)

^c Temperatures for Brown and Parsons were graphically interpolated assuming a pressure of 1 kbar

^d Feldspar analyses assumed to be reported in mol %

^e Fe—Ti oxide temperature 810°C (Carmichael 1967)

^f Temperature estimate, 800–850°C

^g Temperature estimate, 850°C

^h Fe—Ti oxide temperatures, 920°C, 960°C (Carmichael 1967)

Table 5 (continued)

	P (kbars)	mole fraction (normalized to 1,000)						T (°C)				
		Ab	Or	An	Ab	Or	An	(1)	(2)	(3)	(4)	(5)
Biotite Trachyte	1	0.494	0.465	0.041	0.513	0.029	0.458	HT	1,594	1,569	14,537	723
(442, Tristan da Cunha)	1	0.564	0.387	0.049	0.679	0.084	0.237	825	1,123	1,005	1,667	1,017
(grdms)	1	0.465	0.487	0.049	0.664	0.040	0.295	910	931	841	1,145	638
(grdms)	1	0.614	0.289	0.096	0.732	0.068	0.200	none	1,069	755	1,197	564
Trachyte	1	0.414	0.566	0.020	0.683	0.074	0.243	825	823	790	992	840
(1909–261, Siebengebirge, Germany)												

its coexisting feldspars probably represent a dis-equilibrium pair (see below) though the geothermometer proposed here does give the most geologically reasonable temperature. In addition, the calculated temperatures for the rhyolite, despite their uniformity, average about 150°C below the estimated temperature of eruption. These observations on the rhyolite and trachyte suggest the need for a more complete analysis.

In Table 5 a detailed comparison is provided for volcanic rocks having two feldspars present as phenocrysts or as groundmass phases. All the two feldspar pairs in Table 5 have tie-lines that are more or less sub-parallel to those of Seck (1971a, 1971b) with the exception of the last three phenocryst pairs from the trachytes of Carmichael (1965), all the two-feldspar pairs reported by Rahman and McKenzie (1969), those from the leucite-trachytes and hauyne-leucite-phonolite of Baldridge et al. (1981) and those from the biotite-trachyte of Carmichael (written communication). It appears that the distinctly different orientations of tie-line slopes displayed by coexisting feldspars in trachytes in contrast to the consistent slopes exhibited by the less alkalic lava types has never been adequately appreciated. Indeed, Carmichael (1965), Rahman and McKenzie (1969) and Carmichael et al. (1974) have suggested that the disparity in tie-line slopes between rhyolites and some trachytes is due to a temperature or a liquid bulk composition effect which would tend to distort the shape of the ternary solvus under the conditions at which these feldspars formed. If the effect were due to temperature the solvus would have to drastically change shape between 900° and ~1,000°C, an event which is possible but on the basis of Seck's data, highly unlikely. Affecting the solvus geometry by crystallizing feldspar pairs from liquids of different bulk composition would imply that the solid solution of relatively minor amounts of components other than $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 has a profound effect on the free energy of mixing in the ternary.

On thermodynamic grounds that argument is not very plausible despite the experimental evidence to the contrary along the Ab–Or join (Luth and Tuttle 1966; Luth and Fenn 1973; Luth et al. 1976). Such evidence has been questioned (Smith and Parsons 1974) on the basis that crystallization of feldspars from non-stoichiometric gels of widely different bulk composition is kinetically controlled and hence path dependent. The crux of this argument being that all the experimental determinations of alkali-feldspar solvi are consistent with *approaches* to equilibrium from *different* initial metastable feldspar crystallites. As the influence of bulk composition on the solvus geometry of the binary is equivocal, there seems little justification for invoking it as a major effect in the ternary.

A much more plausible explanation for the contrasting tie-lines is suggested by the petrographic observation that the plagioclase phenocrysts of most trachytes, prior to eruption, were either in the act of being resorbed or had already been jacketed by an envelope of sanidine and hence were chemically fractionated from the liquid. Mechanisms to account for the resorption of plagioclase by trachytic liquids have been discussed by Carmichael (1963, 1965) and Rahman and McKenzie (1969). The most logical explanation of the trachytic tie-lines is to assume that the plagioclase and sanidine phenocrysts represent a dis-equilibrium pair and that during resorption or mantling of the plagioclase the sanidine became significantly more *sodic* in composition. This explanation is consistent with the fact that two-feldspar pairs (Table 5) from the German trachytes (first two analyses of Carmichael, 1965, and the last of Carmichael, written communication) show no petrographic evidence for resorption and have two-feldspar tie-lines sub-parallel to those of Seck (1971a). As a practical concern, and by way of condensing the above discussion, it should be realized before applying any existing two-feldspar geothermometer that “equilib-

^c Perry (1968) has studied chemical variation in the feldspars and has shown that some degree of non-stoichiometry is statistically significant. However, examination of the volcanic feldspars of Table 5 using his methodology reveals no systematics in non-stoichiometry with regard to rock type. Bruno and Facchinelli (1974) have determined that up to 15 wt % SiO_2 can dissolve in anorthite at high temperature. Extensive silica solid solution is consistent with chemical analyses of lunar plagioclases but has not been observed in terrestrial igneous plagioclase (Beaty and Albee 1980). This

lunar phenomena may be due to rapid, metastable crystallization. The suggestion of Carman and Tuttle (1967) that excess silica exists in solid solution in sanidine from rhyolites (i.e. lavas where the silica activity is defined by quartz phenocrysts) is dubious as it is based on the production of quartz and two-feldspars during the recrystallization of sanidine phenocrysts at 500°C and 10 kbars in gold capsules containing 10% water. The production of quartz by Carman and Tuttle (1967) may only reflect the incongruent dissolution of sanidine with attendant preferential partitioning of the metals into the aqueous phase

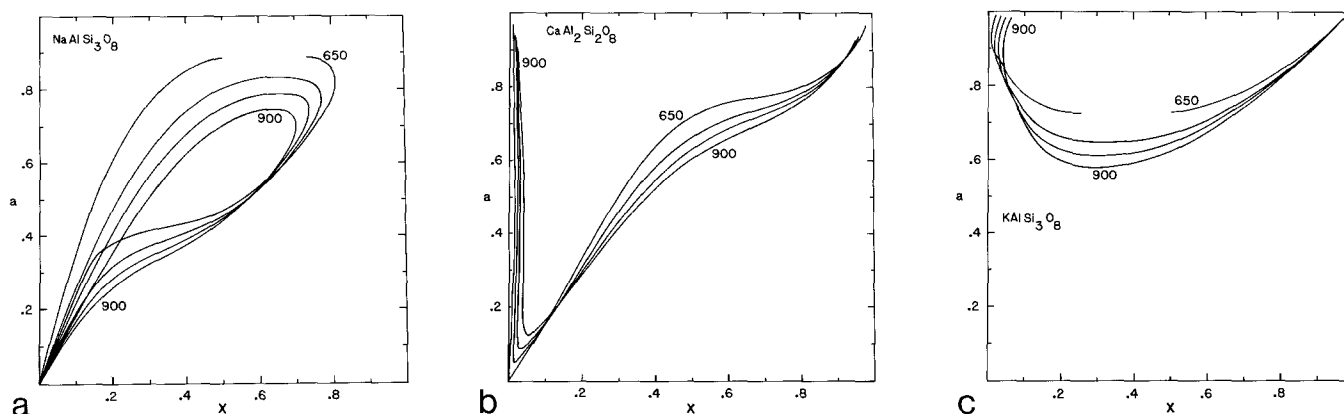


Fig. 5a-c. The activity of $\text{NaAlSi}_3\text{O}_8$ **a**, $\text{CaAl}_2\text{Si}_2\text{O}_8$ **b** and KAlSi_3O_8 **c** in feldspars coexisting along the ternary solvus at 650°C, 750°C, 825°C and 1 kbar and 900°C and 500 bars. Horizontal lines of constant activity describe the mole fractions of $\text{NaAlSi}_3\text{O}_8$ **a**, $\text{CaAl}_2\text{Si}_2\text{O}_8$ **b** and KAlSi_3O_8 **c**, respectively, in coexisting feldspars

rium" feldspar pairs are defined to be those consistent with the data of Seck (1971a, 1971b). Feldspar temperatures reported for most of the trachytes in Table 5 are therefore meaningless even if they agree with geologic "intuition".

An examination of the quartz-bearing lavas of Table 5 indicates that the calculated temperatures are slightly to significantly below the expected ones. One possible explanation might be that Seck (1971a, 1971b) overestimated the extent of feldspar miscibility (see above) which would have the effect of producing apparently lower temperatures for coexisting natural two-feldspar pairs. It seems in general best to regard two-feldspar temperature estimates as a minimum bound on the temperature of phenocryst formation in rhyolites.

With regard to the leucite-bearing lavas of Baldrige et al. (1981) some positive statement can be made for the thermodynamic two-feldspar geothermometer proposed here. In these lavas the calculated temperatures (column 5) are varied but generally fall below 1,000°C. The phenocryst assemblage of the leucite trachytes has been estimated, from F-exchange equilibria between apatite and biotite, to have formed at about 1,000 \pm 100°C. As the two feldspars in the Roman lavas are in the groundmass, temperatures inferred from these phases should be lower. The extent of solid solution in groundmass nepheline suggests a temperature of 900°C for the leucite phonolite. For all these lavas the mole per cent sanidine dissolved in leucite indicates temperature on the order of 800°C and the distribution coefficients of Ca/Sr and Ba/Ca between groundmass plagioclase and sanidine suggest temperatures between 610° and 750°C, though Baldrige et al. (1981) admits that these latter estimates must certainly be too low. Those temperatures for the leucite-bearing lavas in Table 5, calculated using the geothermometer proposed here, fall within the suggested range.

The problems associated with two-feldspar geothermometry are a consequence of the extraordinarily difficult task of achieving equilibrium solvi in the laboratory and the equally difficult task of verifying an equilibrium tie-line in natural samples. These difficulties are not modified by the manner in which the geothermometer is constructed. There are no overall advantages of a thermodynamically consistent analyti-

cal geothermometer (like the one proposed here) over an equivalent graphical representation (Brown and Parsons 1981) except that the analytical form will allow a consistent and rigorous extrapolation in temperature and pressure while the graphical projection is far less versatile. Because of its extrapolative ability the thermodynamic geothermometer is inherently preferable, but it should always be remembered that it cannot be better than the data upon which it is calibrated and cannot generate correct temperatures in the absence of equilibrium.

Activity/composition relations and the activity of KAlSi_3O_8 in plagioclase

Activity versus composition diagrams are provided in Fig. 5 for all three components of the ternary feldspars. The curves shown apply to activities along the ternary solvus at the indicated temperature calculated using Eqs. (16)–(18) and the parameters of Table 1 and 2. Figure 5c emphasizes the high values for the activity of KAlSi_3O_8 , despite its small mole fraction, in plagioclase feldspars.

As the activity/composition relations of KAlSi_3O_8 in plagioclase are of some petrologic interest, Table 6 has been prepared (using Eq. 17 and the parameters of Tables 1 and 2) to demonstrate these relations in some detail. If a "conventional activity coefficient" is defined for KAlSi_3O_8 , i.e.

$$\gamma_{\text{KAlSi}_3\text{O}_8} = a_{\text{KAlSi}_3\text{O}_8} / X_{\text{KAlSi}_3\text{O}_8},$$

then the tabulated calculations show that in the indicated composition range (Table 6) it varies from 93.18 to 3.032. If we consider a "typical" plagioclase crystallizing from a tholeiite at 1,200°C with a composition between $\text{An}_{78}\text{Or}_2$ and $\text{An}_{78}\text{Or}_1$, $\gamma_{\text{KAlSi}_3\text{O}_8}$ may be interpolated from Table 6 to be between 8.83 and 9.10. Ghiorso and Carmichael (1980) were able to estimate a Henry's law coefficient for KAlSi_3O_8 in plagioclase using liquid-solid equilibria involving plagioclase coexisting with essentially tholeiitic melts. They obtain $\gamma_{\text{KAlSi}_3\text{O}_8}$ equal to 9.47 (\pm 2.44) in good agreement with the values predicted using the proposed solution

Table 6. Activity of KAlSi_3O_8 in feldspar as a function of the mole fractions of $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 and temperature

$X_{\text{NaAlSi}_3\text{O}_8}^{\text{feldspar}}$	T (°C)	$X_{\text{KAlSi}_3\text{O}_8}^{\text{feldspar}}$								
		0.005	0.01	0.015	0.02	0.03	0.04	0.05	0.075	0.10
0.2	650	0.4642	0.8824	1.258	1.594	2.161	2.604	2.944	3.445	3.603
	750	0.2535	0.4868	0.7008	0.8968	1.239	1.521	1.751	2.140	2.332
	850	0.1542	0.2985	0.4333	0.5589	0.7844	0.9780	1.143	1.448	1.631
	1,050	0.07149	0.1402	0.2060	0.2690	0.3868	0.4939	0.5906	0.7906	0.9380
	1,250	0.04056	0.08025	0.1190	0.1569	0.2297	0.2984	0.3630	0.5062	0.6239
0.4	650	0.2471	0.4693	0.6687	0.8473	1.149	1.387	1.572	1.858	1.971
	750	0.1583	0.3027	0.4344	0.5542	0.7618	0.9318	1.070	1.304	1.422
	850	0.1097	0.2111	0.3047	0.3910	0.5434	0.6719	0.7796	0.9740	1.088
	1,050	0.06228	0.1209	0.1761	0.2279	0.3223	0.4052	0.4779	0.6206	0.7185
	1,250	0.04102	0.08017	0.1175	0.1531	0.2193	0.2791	0.3331	0.4452	0.5292
0.6	650	0.1461	0.2783	0.3976	0.5053	0.6892	0.8368	0.9539	1.144	1.231
	750	0.1036	0.1983	0.2847	0.3635	0.5003	0.6128	0.7047	0.8624	0.9454
	850	0.07812	0.1501	0.2163	0.2773	0.3845	0.4744	0.5494	0.6837	0.7611
	1,050	0.05047	0.09757	0.1415	0.1824	0.2559	0.3193	0.3738	0.4774	0.5442
	1,250	0.03657	0.07102	0.1034	0.1339	0.1895	0.2385	0.2814	0.3663	0.4249
0.8	650	0.08786	0.1674	0.2394	0.3044	0.4157	0.5052	0.5764	0.6923	0.7450
	750	0.06674	0.1276	0.1830	0.2334	0.3205	0.3918	0.4495	0.5468	0.5955
	850	0.05324	0.1020	0.1467	0.1876	0.2589	0.3179	0.3664	0.4505	0.4954
	1,050	0.03754	0.07223	0.1043	0.1338	0.1860	0.2301	0.2670	0.3338	0.3727
	1,250	0.02901	0.05598	0.08104	0.1043	0.1458	0.1813	0.2115	0.2676	0.3022

model. As another independent appraisal of the results tabulated in Table 6, activity coefficients for KAlSi_3O_8 in 123 plagioclases crystallizing from liquids ranging in composition from basalt to leucite basanite (discussed in Ghiorso et al. 1983) were calculated using Eq. 17 and the parameters of Tables 1 and 2. These plagioclases range in composition from An_{88} to An_{50} and Or_1 to Or_8 . A value of $\gamma_{\text{KAlSi}_3\text{O}_8}$ equal to 9.47 (± 0.87) is obtained, in uncanny agreement with Ghiorso and Carmichael (1980). Ghiorso et al. (1983), considering just the most Or-rich plagioclases crystallizing from the more alkalic rocks and using the same procedure as Ghiorso and Carmichael (1980) obtain a value of 4.87 (± 1.28) for $\gamma_{\text{KAlSi}_3\text{O}_8}$. This number, however, is not based upon the established enthalpy of fusion of sanidine and as such is probably not as secure as that value reported in Ghiorso and Carmichael (1980) and suggested by the present calculations.

Summary and conclusions

A solution model has been described which provides activity/composition relations for high-structural state ternary feldspars in the system $\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$ – KAlSi_3O_8 . Though calibrated upon the coexisting two-feldspar data of Seck (1971a) the model is forced to be consistent with the established and more secure solution properties of the constituent binaries. This emphasizes a problem with Seck's (1971a) experimentally determined tie-lines close to the alkali-feldspar solvus, which are interpreted as metastable and are inconsistent with the established solvus for the binary (Thompson and Hovis, 1979; Parsons 1978). Nevertheless, the data for the bulk of the ternary can be approximated within the error of measurement using 1) a simple Al-avoidance model for the configurational entropy, 2) established equations for the excess free

energy of the plagioclase and alkali-feldspar binaries, and 3) only three parameters for describing the excess properties of the An–Or binary (2) and the ternary (1).

A geothermometer based upon the proposed solution model has been constructed and compared to existing two-feldspar geothermometers (Stormer 1975; Powell and Powell 1977; Brown and Parsons 1981; Haselton et al. 1983). Application of these to a wide variety of volcanic rock types demonstrates some of the major problems associated with two-feldspar geothermometry and indicates some small degree of preference for the thermodynamically consistent geothermometer proposed here.

The proposed activity/composition relations, and indirectly the data of Seck (1971a) along the plagioclase limb of the solvus at low An-contents, have been independently assessed by computing the activity of KAlSi_3O_8 in plagioclase feldspars crystallizing from basaltic liquids and comparing it to that obtained from examining plagioclase-liquid equilibria (Ghiorso and Carmichael 1980). The agreement is excellent and lends some support to extrapolating the proposed ternary feldspar model up in temperature to the liquidus of basic lavas. At these temperatures the activity/composition relations can be used in conjunction with the silicate liquid solution model of Ghiorso et al. (1983) to calculate the compositions of ternary feldspars precipitating from magmatic liquids as a function of temperature and pressure.

Appendix: Computation of temperature from the composition of coexisting feldspars

Let a_i^{plag} denote the activity of the i th component (either $\text{NaAlSi}_3\text{O}_8$, $\text{CaAl}_2\text{Si}_2\text{O}_8$ or KAlSi_3O_8) in plagioclase and a_i^{alk} the activity of the i th component in alkali-feldspar. It can be

seen from Eqs. (16)–(18) that a_i^{plag} and a_i^{alk} are functions of temperature, pressure and the mole fractions of each component ($X_i^{\text{plag}}, X_i^{\text{alk}}$). If two feldspars coexist, at equilibrium, then

$$a_i^{\text{plag}} = a_i^{\text{alk}} \quad (\text{A-1})$$

for all components i . In principle, from the compositions of the coexisting feldspars and an estimate of the pressure, Eq. (A-1) can be solved for T using any feldspar component. This is most easily accomplished using some numerical procedure such as Newton's method for the root of a non-linear equation. However, if a solution to Eq. (A-1) is obtained for the $\text{NaAlSi}_3\text{O}_8$ component it does not necessarily mean that the equivalent expressions for the $\text{CaAl}_2\text{Si}_2\text{O}_8$ and KAlSi_3O_8 components will be satisfied exactly. This would be the case only if the feldspars were in stable equilibrium, if there were no errors associated with the compositional data on the two phases, if the solution model from which the activities are calculated represents the experimental data exactly, and if the experimental data provides an accurate description of the feldspar solvus. Therefore, in general, the function:

$$f_i(T) = a_i^{\text{plag}} - a_i^{\text{alk}} \quad (\text{A-2})$$

will be non-zero for at least two of the three components. As no one particular component should be made to satisfy Eq. (A-1) in preference to the other two, the object is to find a T such that the three equations

$$a_{\text{NaAlSi}_3\text{O}_8}^{\text{plag}} - a_{\text{NaAlSi}_3\text{O}_8}^{\text{alk}} = 0 \quad (\text{A-3a})$$

$$a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plag}} - a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{alk}} = 0 \quad (\text{A-3b})$$

$$a_{\text{KAlSi}_3\text{O}_8}^{\text{plag}} - a_{\text{KAlSi}_3\text{O}_8}^{\text{alk}} = 0 \quad (\text{A-3c})$$

are satisfied in a least squares sense.^a This amounts to minimizing the sum of squares of the residuals to Eqs. (A-3a) to (A-3c) as a function of T . This minimization can be conveniently written as the mathematical problem:

$$\min [f_{\text{NaAlSi}_3\text{O}_8}^2(T) + f_{\text{CaAl}_2\text{Si}_2\text{O}_8}^2(T) + f_{\text{KAlSi}_3\text{O}_8}^2(T)] \quad (\text{A-4})$$

The problem posed by Eq. (A-4), minimizing a non-linear sum of squares, can be solved using any of the uni-directional non-linear minimization algorithms described in most textbooks on numerical analysis (e.g. Nash 1979). A computer program is available from the author which extracts an equilibrium temperature, given a pressure estimate and the compositions of coexisting feldspars, by solving the problem posed by Eq. (A-4) using the activity/composition relations provided in the text. The minimization algorithm (No: 17 Success-failure linear search with parabolic inverse interpolation) is taken from Nash (1979). This program was used for all the geothermometric calculations presented in the text.

Acknowledgements. Discussions with B. Evans and particularly I.S.E. Carmichael were very useful in many aspects of this study. Thorough reviews by J.C. Stormer and I. Parsons were greatly appreciated. Though neither of these reviewers may agree with the approach or conclusions reached in this paper, I am certain that their stimulating points of contention have served to greatly clarify the arguments and substantially im-

prove the content. I would like to thank L. Criscenti for helping to resolve certain difficult relationships amongst resorbing feldspars and F. Bardsley for patiently drafting the figures. Computer time was generously provided by the College of Arts and Sciences at the University of Washington.

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^a It can be argued (J.C. Stormer, oral communication) that as the $\text{CaAl}_2\text{Si}_2\text{O}_8$ component in the alkali-feldspar is extremely sensitive to analytical uncertainty, Eq. (A-3b) should not be used as a restriction on the equilibrium temperature. The same argument could also be made, though somewhat less convincingly, for the KAlSi_3O_8 component of the plagioclase feldspars. In the calculations reported in Tables 4 and 5 all three equilibria (Eqs. A-3a–A-3c) were utilized so as to be consistent with the calibration of Seck's (1971a) database

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Received January 23, 1984; Accepted June 6, 1984