

Ideal site mixing in solid solutions, with an application to two-feldspar geothermometry¹

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Abstract

The activity of end member i , a_i , in a solid solution can be defined as $a_i = a_i^{\text{con}} \gamma_i$, where γ_i is an activity coefficient describing the departure from ideal solution and a_i^{con} is the ideal contribution to activity. Statistical thermodynamics yields an explicit expression for a_i^{con} in terms of configurational entropy and mixing on sites:

$$a_i^{\text{con}} = \prod_j \prod_A \left(\frac{n_j}{n_{Aj}} X_A^j \right)^{n_{Aj}}$$

where X_A^j is the mole fraction of component A, generally an ion or atom, on the j -site in the solid solution; n_j is the number of j -sites in one formula unit of any end member in the solid-solution series, and n_{Aj} is the number of A-components on the j -site in one formula unit of end member i . This general expression applies to binary, ternary, and complex, multicomponent solid solutions.

Application of this expression to feldspars yields an adjustment of the two-feldspar geothermometer. For natural feldspars containing Na, K, Rb, Ca, Ba, Sr, and Fe, the expression is

$$T_K = \frac{(X_{\text{Or}}^{\text{AF}})^2(18810 + 17030X_{\text{Ab}}^{\text{AF}} + 0.364P) - (X_{\text{An}}^{\text{Pl}})^2(28230 - 39520X_{\text{Ab}}^{\text{Pl}})}{10.3(X_{\text{Or}}^{\text{AF}})^2 + 8.3143 \ln \left\{ \frac{X_{\text{Na}}^{\text{O,Pl}} X_{\text{Al}}^{\text{Tl,Pl}} X_{\text{Si}}^{\text{Tl,Pl}} (X_{\text{Si}}^{\text{T2,Pl}})^2}{X_{\text{Na}}^{\text{O,AF}} X_{\text{Al}}^{\text{Tl,AF}} X_{\text{Si}}^{\text{Tl,AF}} (X_{\text{Si}}^{\text{T2,AF}})^2} \right\}}$$

Data in the system albite–orthoclase–anorthite–H₂O fit well enough to suggest that the proposed geothermometer is accurate to $\pm 50^\circ\text{C}$ in the range of 650 to 900°C for coexisting plagioclase and alkali feldspar for which $0.15 < X_{\text{Ab}}^{\text{AF}} < 0.50$.

List of Symbols

A = index on exchangeable components (usually ions, atoms, or vacancies) in the solid solution
 a_i = activity of end member i , the formula for which is expressed as $Z \prod_j \prod_A A(n_{Aj})$
 a_i^{con} = ideal contribution to activity of end member i (configurational activity)
 con = superscript for configurational entropy
 k = Boltzmann constant
 n_j = number of j -sites in one unit of any end member; one unit is defined as the combination of components that gives the formula of the end member
 n_{Aj} = number of A-components on j -sites in one unit of end member i in its standard state
 n_i = number of moles of end member i
 N = Avogadro's number

N_i = number of units of end member i in the solid solution
 N_A^j = number of A-components on j -sites
 $^\circ$ = superscript for standard state
 P = pressure in bars
 r = superscript for reference state
 R = gas constant
 S = entropy
 \bar{S}_i = partial molar entropy of i
 $\Delta\bar{S}_i^{\text{mix}}$ = change in \bar{S}_i in going from the standard state to the mixed (solid-solution) state
 $\Delta\bar{S}_i^{\text{id mix}}$ = contribution to $\Delta\bar{S}_i^{\text{mix}}$ that is attributable to ideal mixing
 T = temperature in kelvins
 W = number of possible configurations in the mixed state
 X_A^j = mole fraction of A on the j -site
 X_i = mole fraction of end member i
 Z = nonexchangeable components in the solid solution
 γ_i = activity coefficient of end member i

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μ = chemical potential
 Π = product
 ψ_i = probability of one configuration of components having the formula of i on one unit of the solid solution

Introduction

Application of thermodynamics to natural systems requires knowledge of activity–composition relations for minerals that form solid solutions. Several approaches have been used to model activity–composition relations for ideal solutions. As examples, Kröger et al. (1959) used classical thermodynamics to consider mixing on structural sites, and Kerrick and Darken (1975) and Stoessell (1979) used statistical thermodynamics to come to the same general conclusions as the derivation in this paper. The results here differ from those of Kerrick and Darken (1975) and Stoessell (1979) principally in that mole fractions of components on sites (rather than mole fractions of end members) are used in the expression of the ideal contribution to activity. The expression derived by Powell (1977) is similar to that given here. However, because his expression does not involve a term for the standard state, it is not applicable generally. Price (1977) and Helgeson et al. (1978) presented formulations identical to those given here, but without rigorous derivations. This treatment explicitly illustrates the need for knowledge of the occupancy of sites in both the solid solution and end member in its standard state. This formulation also provides a simple equation for the ideal contribution to activity in terms of mole fractions on sites, which can be calculated, with some assumptions about site occupancy, from chemical analyses.

The advantage of the derivation in this paper over that in previous studies is that multicomponent solid solutions, which are typical in natural systems, can be treated with ease. The number of possible end members in the solid solution is not limited in this general approach.

Kerrick and Darken (1975) used plagioclase as an example for their expression of the ideal contribution to activity. Their formulation considers plagioclase as a binary solid solution of two end members, albite and anorthite. The following formulation allows one to more precisely consider natural plagioclases, which generally contain K and occasionally contain appreciable amounts of Sr and Ba. It will be shown that this approach yields a significant improvement in the applicability of the two-feldspar geothermometer proposed by Haselton et al. (1983).

Derivation of the expression for a_i^{con} , the ideal contribution to activity

The following four relations from statistical and classical thermodynamics (see, for example, Lewis and Randall, 1961) are the basis of this derivation:

$$\Delta S^{\text{con}} = k \ln W, \quad (1)$$

$$\bar{S}_i = \left(\frac{\partial S}{\partial n_i} \right)_{T,P,n_i \neq i}, \quad (2)$$

$$\mu_i = \mu_i^\circ + RT \ln a_i, \quad (3)$$

$$\left(\frac{\partial \mu_i}{\partial T} \right)_P = -\bar{S}_i \quad (4)$$

Let the activity of end member i in a solid solution, a_i , be defined in terms of an ideal contribution, a_i^{con} , and a non-ideal contribution, or activity coefficient, γ_i :

$$a_i = a_i^{\text{con}} \gamma_i. \quad (5)$$

For ideal solutions, $\gamma_i = 1$, (6)

and the partial molar entropy of mixing is entirely attributable to configurational entropy:

$$\Delta \bar{S}_{\text{mix}} = \bar{S}_i - \bar{S}_i^\circ = \Delta \bar{S}_i^{\text{d,mix}} = \bar{S}_i^{\text{con}} - \bar{S}_i^{\text{con},\circ}. \quad (7)$$

Because in equation (1), ΔS^{con} is the entropy difference between a mixed state and a reference state, for which there is only one possible configuration,

$$\Delta \bar{S}_i^{\text{con}} = \bar{S}_i^{\text{con}} - \bar{S}_i^{\text{con},r} \text{ and} \quad (8)$$

$$\Delta \bar{S}_i^{\text{con},\circ} = \bar{S}_i^{\text{con},\circ} - \bar{S}_i^{\text{con},r}. \quad (9)$$

Differentiation of equation (3) with respect to T and substitution of (4), (5), (6), (7), (8), and (9), yields:

$$\Delta \bar{S}_i^{\text{con}} - \Delta \bar{S}_i^{\text{con},\circ} = -R \ln a_i^{\text{con}}. \quad (10)$$

Noting that $n_i = N_i/N$ and $R = kN$, from equations (1) and (2) it is seen that

$$\Delta \bar{S}_i^{\text{con}} = \left(\frac{\partial \Delta S^{\text{con}}}{\partial n_i} \right)_{T,P,n_i \neq i} = R \left(\frac{\partial \ln W}{\partial N_i} \right)_{T,P,N_i \neq i}. \quad (11)$$

For end member i , where random mixing occurs on each j -site,

$$W = \prod_j \frac{(\sum_A N_A^j)!}{\prod_A (N_A^j)!}. \quad (12)$$

Sterling's approximation for large numbers yields

$$\ln W = - \sum_j \sum_A N_A^j \ln X_A^j, \quad (13)$$

where

$$X_A^j = \frac{N_A^j}{\sum_A N_A^j}, \quad (14)$$

the mole fraction of A on the j site. For a mixture of end members,

$$N_A^j = \sum_i n_{Aij} N_i. \quad (15)$$

Combination of equations (11), (13), (14), and (15) yields:

$$\Delta \bar{S}_i^{\text{con}} = -R \sum_j \sum_A n_{Aij} \ln X_A^j \quad (16)$$

The standard state for end member i is defined such that

$$X_A^j = \frac{n_{Aij}}{n_j}, \quad (17)$$

where

$$n_j = \sum_A n_{Aij}, \quad (18)$$

the number of j -sites in the solid solution. Therefore the standard state has a configuration entropy term itself:

$$\Delta \bar{S}_i^{\text{con}, \circ} = -R \sum_j \sum_A n_{Aij} \ln \left(\frac{n_{Aij}}{n_j} \right) \quad (19)$$

Combinations of equations (10), (16), and (19) yields the explicit expression of the ideal contribution to activity in terms of mixing on sites:

$$a_i^{\text{con}} = \prod_j \prod_A \left(\frac{n_j}{n_{Aij}} X_A^j \right)^{n_{Aij}}. \quad (20)$$

As examples, ideal contributions to the activities of feldspars are listed in Table 1.

The ideal contribution to activity can be viewed as a probability function. Because the probability of finding an A-component on any j -site is equal to the mole fraction of A on the j -site, the probability of one combination of components having the formula of end member i on one unit of the solid solution, Ψ_i , is given by the product:

$$\Psi_i = \prod_j \prod_A (X_A^j)^{n_{Aij}}. \quad (21)$$

Similarly,

$$\Psi_i^{\circ} = \prod_j \prod_A \left(\frac{n_{Aij}}{n_j} \right)^{n_{Aij}}. \quad (22)$$

Note that $1/\Psi_i^{\circ}$ is the constant, k_i , in the derivation of Kerrick and Darken (1975). Combining (20), (21), and (22),

$$a_i^{\text{con}} = \Psi_i / \Psi_i^{\circ}; \quad (23)$$

the ideal contribution to the activity of end member i is equal to the probability of finding in the solid solution one

configuration with the formula of end member i divided by the probability of finding that configuration in the standard state.

Equation (20) has broad application in thermodynamic studies of geological systems. Many minerals occur in solid solutions that can be characterized by multiple end members. Examples of mineral groups for which equation (20) can be easily applied include feldspars, pyroxenes, olivines, amphiboles, biotites, garnets, epidotes, illites, chlorites, smectites, carbonates, iron-titanium oxides, and copper-iron sulfides. By making assumptions about which elements mix on which crystallographic sites, one can recast accurate chemical analyses of naturally occurring minerals in terms of mole fractions on sites. Equation (20) then provides an expression of the ideal contribution to the activity of any end member within the solid solution. Equation (23) provides a simple means for handling ideal contributions to activity in solid solutions for which random mixing on sites does not apply. For example, short-range order in spinels (Stormer, 1983) can be approached as a conditional probability. Equations (20) and (23) demonstrate that one must know the site distributions in the mineral as well as in the end member in its standard state. If data on site distributions are lacking, ambiguity in assumptions about site occupancy and short-range order can be incorporated in error analysis.

Application to two-feldspar geothermometry

Improvement of the two-feldspar geothermometer proposed by Haselton et al. (1983) is an example of the applicability of the above formulation for the ideal contribution to activity. These authors used their experimental data plus those of Orville (1963), Luth and Tuttle (1966), Seck (1972), Goldsmith and Newton (1974), Smith and Parsons (1974), Lagache and Weisbrod (1977), Hovis and Waldbaum (1977), and Hovis (1977, 1982) to derive activity-

Table 1. Ideal contributions to the activities of feldspars

Case	n_j -values	n_{Aij} -values	a_{Ab}^{con}	a_{An}^{con}
1. Random mixing of Na, K, Ca, Sr, and Ba on one o-site and of Al, Si, and Fe ³⁺ on four T-sites	$n_o = 1$ $n_T = 4$	$n_{Na,Ab,o} = 1$ $n_{Al,Ab,T} = 1$ $n_{Si,Ab,T} = 3$ $n_{Ca,An,o} = 1$ $n_{Al,An,T} = 2$ $n_{Si,An,T} = 2$	$\frac{256}{27} X_{Na}^o X_{Al}^T (X_{Si}^T)^3$	$16 X_{Ca}^o (X_{Al}^T)^2 (X_{Si}^T)^2$
2. Random mixing of Na, K, Ca, Sr, and Ba on one o-site; Al-avoidance restricts Al, Si, and Fe ³⁺ mixing to two T1-sites; no substitution for Si on two T2-sites in standard state	$n_o = 1$ $n_{T1} = 2$ $n_{T2} = 2$	$n_{Na,Ab,o} = 1$ $n_{Al,Ab,T1} = 1$ $n_{Si,Ab,T1} = 1$ $n_{Si,Ab,T2} = 2$ $n_{Ca,An,o} = 1$ $n_{Al,An,T1} = 2$ $n_{Si,An,T2} = 2$	$4 X_{Na}^o X_{Al}^{T1} X_{Si}^{T1} (X_{Si}^{T2})^2$ $(X_{Si}^{T2} = 1 \text{ if Al-avoidance is strictly obeyed})$	$X_{Ca}^o (X_{Al}^{T1})^2 (X_{Si}^{T2})^2$
3. Random mixing of units of NaAlSi ₃ O ₈ , KAlSi ₃ O ₈ , and CaAlSi ₃ O ₈	$n = 1$	$n_{Ab} = 1$ $n_{An} = 1$	X_{Ab}	X_{An}

composition relations for albite in alkali feldspar. Haselton et al. (1983) followed the revision suggested by Powell and Powell (1977) for the geothermometer of Stormer (1975). The subregular solution model for activity coefficients used by Powell and Powell (1977) is a reasonable approach and reduces to a simple expression independent of Ca-content, because the Ca-content of alkali feldspar is low relative to the Na-content. Similarly, any activity-coefficient terms related to small amounts of Sr, Ba, or Fe³⁺ mixing would be expected to be negligible for most natural feldspars.

Haselton et al. (1983) argued for Al-avoidance in albite-anorthite solid solutions. Because the same standard state for albite must be used in equating the activity of albite in alkali feldspar with the activity of albite in plagioclase, Al-avoidance should also be considered in determining the ideal contribution to activity of albite in alkali feldspar (see Table 1, case 2). The preferred expression for the activity of albite in alkali feldspar, a_{Ab}^{AF} , which uses equation (20) for the ideal contribution to the activity, is

$$a_{Ab}^{AF} = 4X_{Na}^{o,AF} X_{Al}^{T1,AF} X_{Si}^{T1,AF} (X_{Si}^{T2,AF})^2 \cdot \exp \left\{ \frac{(X_{Or}^{AF})^2 (18810 + 17030 X_{Ab}^{AF} - 10.3T + 0.364P)}{8.3143T} \right\} \quad (24)$$

Note that for almost all alkali feldspars for which Al-avoidance is strictly obeyed,

$$4X_{Na}^{o,AF} X_{Al}^{T1,AF} X_{Si}^{T1,AF} (X_{Si}^{T2,AF})^2 \simeq X_{Ab}^{AF} \quad (25)$$

and equation (24) reduces to equation (3) of Haselton et al. (1983).

Kerrick and Darken (1975) showed that the correct expression for the ideal contribution to activity of feldspar end members is dependent not only on the Ca, Na, and K contents but also on the Al-Si ordering (see Table 1). Because Al-Si ordering in plagioclase and alkali feldspars is complex (Ribbe, 1983), the simple model used in the two-feldspar geothermometer, which assumes random mixing on the T1 sites, may not be entirely correct. The activity-coefficient terms incorporate departures from the assumed model. Equations (20) and (23) indicate that a theoretically correct two-feldspar geothermometer requires knowledge of site distributions in albite in its standard state and in the coexisting plagioclase and alkali feldspar at the equilibrium temperature and pressure. More experimental work is needed to determine site distributions as well as compositions of coexisting feldspars.

The departure that this paper takes from Haselton et al. (1983) is in the activity expression for albite in plagioclase. Haselton et al. (1983) used the subregular solution model for activity coefficients developed for the binary albite-anorthite by Newton et al. (1980), who, in turn, used the formulation of Kerrick and Darken (1975) for the ideal contribution to activity. The Kerrick and Darken (1975) formulation is correct only for the binary. For plagioclases with K-substitution, activity of albite in plagioclase, a_{Ab}^{PI} , is more correctly formulated with the use of equation (20) as:

$$a_{Ab}^{PI} = 4X_{Na}^{o,PI} X_{Al}^{T1,PI} X_{Si}^{T1,PI} (X_{Si}^{T2,PI})^2 \cdot \exp \left\{ (X_{An}^{PI})^2 \frac{(28230 - 39520 X_{Ab}^{PI})}{8.3143T} \right\} \quad (26)$$

Note that activity coefficient terms for limited K-, Sr-, and Ba-substitution in plagioclase are assumed to be negligible. This substitution, however, is accounted for implicitly in the ideal contribution to the activity through the expressions for mole fractions on sites.

The ideal contribution to the activity of albite in high-temperature plagioclase with K-substitution is higher than the corresponding value calculated by the formula of Kerrick and Darken (1975). For example, plagioclase with composition $Ab_{5.4}An_{4.0}Or_6$ (Johannes, 1979) has $a_{Ab}^{con,PI} = 0.454$, whereas $(X_{Ab}^{PI})^2 (2 - X_{Ab}^{PI}) = 0.426$. This difference is enough to cause an overestimation of equilibrium temperature using the geothermometer of Haselton et al. (1983). The preferred expression for temperature is

$$T_K = \frac{(X_{Or}^{AF})^2 (18810 + 17030 X_{Ab}^{AF} + 0.364P) - (X_{An}^{PI})^2 (28230 - 39520 X_{Ab}^{PI})}{10.3(X_{Or}^{AF})^2 + 8.3143 \ln \left\{ \frac{X_{Na}^{o,PI} X_{Al}^{T1,PI} X_{Si}^{T1,PI} (X_{Si}^{T2,PI})^2}{X_{Na}^{o,AF} X_{Al}^{T1,AF} X_{Si}^{T1,AF} (X_{Si}^{T2,AF})^2} \right\}} \quad (27)$$

Note that if Al-avoidance is strictly obeyed, $X_{Si}^{T2} = 1$. If Fe³⁺ substitution is minimal, and if only Na, K, Ca, Ba, and Sr end members are considered, the ideal contributions to the activities can be expressed in terms of mole fractions of end members and

$$T_K = \frac{(X_{Or}^{AF})^2 (18810 + 17030 X_{Ab}^{AF} + 0.364P) - (X_{An}^{PI})^2 (28230 - 39520 X_{Ab}^{PI})}{10.3(X_{Or}^{AF})^2 + 8.3143 \ln \left\{ \frac{X_{Ab}^{PI} (2 - X_{Ab}^{PI}) - X_{Or}^{PI} (X_{Ab}^{PI} + X_{Or}^{PI})}{X_{Ab}^{AF} (2 - X_{Ab}^{AF}) - X_{Or}^{AF} (X_{Ab}^{AF} + X_{Or}^{AF})} \right\}} \quad (28)$$

Note that for natural feldspars containing Sr and Ba, $X_{Ab} + X_{An} + X_{Or}$ should not be normalized to 1 when using equation (27) or (28).

This two-feldspar geothermometer is compared in Figure 1 with the geothermometer from which it was derived (Haselton et al., 1983). At 800°C the two data points of Johannes (1979) agree about as well with either geothermometer (734° and 808° with this approach versus 783° and 862° with that of Haselton et al., 1983). The fit with experimental studies of Seck (1971), however, is much better with this approach than with that of Haselton et al. (1983). Whereas this approach reproduces most of Seck's (1971) data within ±50°C between 650 and 900°C, the geothermometer of Haselton et al. (1983) tends to considerably overestimate temperatures.

Discussion

Johannes (1979) and Haselton et al. (1983) noted that the ternary feldspar experiments of Seck (1971) may not represent equilibrium. The relatively good fit between calculated and experimental temperatures (Fig. 1) suggests, however, that equilibrium may have been approached. The fit is, nonetheless, not perfect. Four data points of Seck (1971),

those for which $X_{Ab}^{AF} < 0.15$, and one point for which $X_{Ab}^{AF} > 0.5$ were excluded from the calculation of means because the calculated temperatures fell well beyond the range of values otherwise calculated at the same experimental temperature. In addition, what may be either systematic model or experimental errors are suggested by slight underestimation of temperature at relatively low values of X_{Ab}^{AF} and overestimation at relatively high values of X_{Ab}^{AF} . More equilibrium experiments in the ternary feldspar system clearly are needed.

Green and Usdansky (1984) used the experimental work of Seck (1971) to estimate Margules parameters for the anorthite-orthoclase binary. Their values are not large enough relative to albite-anorthite and albite-orthoclase terms to have an appreciable effect on the two-feldspar geothermometer. Because most natural plagioclases contain only small amounts of K and because most natural alkali feldspars contain only small amounts of Ca, the additional terms that would be introduced into the geothermometer (see Powell and Powell, 1977) are insignificant.

Ghiorso (1984) also used the data of Seck (1971) to derive activity coefficients that account for K-Ca as well as K-Na and Na-Ca mixing. Ghiorso's formulation of the two-feldspar geothermometer involves equating activities of not only albite in coexisting plagioclase and alkali feldspar but also anorthite and orthoclase. Ghiorso's fit of Seck's data is somewhat improved over the fit shown in Figure 1. Average calculated temperatures are approximately equal, but Ghiorso was able to fit all Seck's data with estimated standard deviations of approximately 30°C. Ghiorso noted that activities of orthoclase calculated from plagioclase compositions in basaltic rocks are in agreement with values independently calculated using liquid-solid equilibria.

The fact that the average calculated temperatures of Ghiorso (1984) are essentially the same as those calculated with equation (28) indicates that the two-albite geothermometer is more sensitive to values of the ideal contribution to activity than to the choice of non-ideal terms for K-Ca mixing. The ideal terms used by Ghiorso (1984) are correct only for ternary feldspars. For natural feldspars containing appreciable amounts of Fe, Ba, Sr, or Rb, equation (20) and the expressions given for case 2 in Table 1 should be used when applying Ghiorso's method.

The proposed geothermometer, equation (27) or (28), appears to yield temperatures accurate to within 50°C in the range of 650 to 900°C for feldspar pairs in which $0.15 < X_{Ab}^{AF} < 0.50$. Application of this geothermometer or the perhaps more broadly applicable geothermometer of Ghiorso (1984) requires, of course, equilibrium between coexisting feldspars. Brown and Parsons (1981) suggested useful tests for equilibrium. If, because of slow kinetics (Johannes, 1979), previously crystallized plagioclase does not equilibrate with the magma from which alkali feldspar crystallizes, calculated temperatures will tend to be too high.

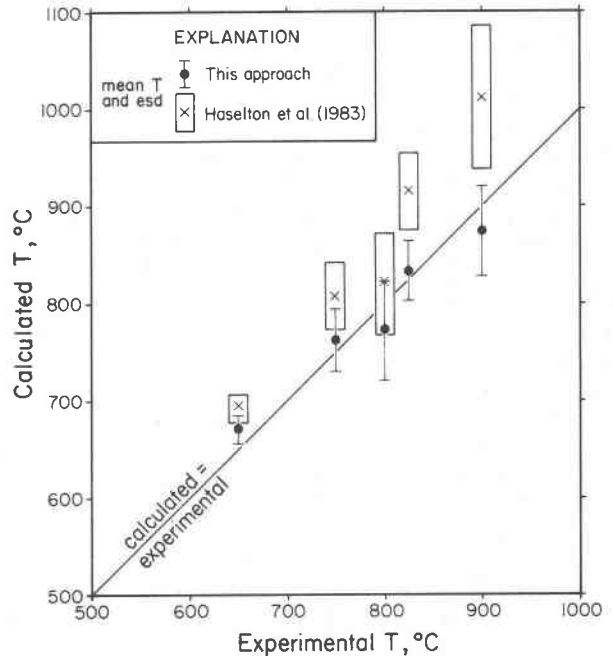


Fig. 1. Comparison of the proposed two-feldspar geothermometer with that of Haselton et al. (1983). Data are from Johannes (1979) at 800°C and 1000 bar ($n = 2$) and from Seck (1971) at 650°C and 1000 bar ($n = 12$), 750°C and 1000 bar ($n = 15$), 825°C and 1000 bar ($n = 12$), and 900°C and 500 bar ($n = 10$) on feldspar pairs for which $0.15 < X_{Ab}^{AF} < 0.50$.

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