Toward a practical plagioclase-muscovite thermometer

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Abstract

The Na-K exchange reaction between plagioclase and muscovite has been formulated as a geothermometer utilizing a ternary-feldspar subregular solution model, a modified binary white mica solution model, and available thermochemical data that account for high and low structural states of feldspar. The plagioclase-muscovite geothermometer has been applied to pelitic metasedimentary rocks and peraluminous granitoids that have equilibrated at temperatures of 490–750°C and at pressures of 2–13 kbar. The equilibration temperatures of pelitic rocks, predicted from compositions of coexisting plagioclase and muscovite, are generally similar to those predicted by garnet-biotite geothermometry. The plagioclase-muscovite temperatures of peraluminous granitoids derived using the compositions of secondary muscovites are distinctly subsolidus, whereas temperatures estimated using primary muscovite compositions are near liquidus. Application of the plagioclase-muscovite thermometer extends the range of pelitic metasedimentary rocks and peraluminous granitoids for which equilibration temperatures may be estimated.

Introduction

Muscovite and feldspars are important constituents of pelitic metasedimentary rocks and peraluminous granitoids. The compositions of these coexisting minerals can be related by the Na-K exchange reaction:

$$KAlSi_3O_8 + NaAl_2Si_3AlO_{10}(OH)_2$$

K-feldspar paragonite

$$= NaAlSi_3O_8 + KAl_2Si_3AlO_{10}(OH)_2.$$
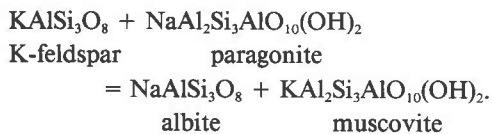
albite muscovite

Thompson (1974) and Chatterjee and Froese (1975) have provided extensive theoretical treatments of paragonite–muscovite–alkali feldspar relations in the system $NaAlO_2$-$KAlO_2$-Al_2O_3-SiO_2-H_2O. In particular, Thompson (1974) noted the temperature dependence of the exchange equilibrium and presented free-energy relations based on endmember thermodynamic data derived from both ion-exchange experiments (Iiyama, 1964) and from muscovite and paragonite dehydration experiments (Day, 1973; Chatterjee, 1973; Chatterjee and Johannes, 1974). However, when these relationships are applied to natural rock systems, predicted muscovite-alkali feldspar equilibration temperatures based on endmember thermodynamic data are generally less than 100°C, suggesting loss of albite component from K-feldspar during subsolidus re-equilibration (Labotka et al., 1981).

Kotov et al. (1969) proposed a geothermometer based on the distribution of Na between coexising muscovite and plagioclase. Talantsev (1971) presented a graphical

geothermometer based on the Na content of muscovite coexisting with sodic plagioclases (An_{0-25}). Tracy (1978) and Cheney and Guidotii (1979) demonstrated that the Ca, Na, and K distributions between muscovite and plagioclase exhibit regular variations with metamorphic grade. Cheney and Guidotti (1979) further showed that the compositions of coexisting muscovite and plagioclase could be used as a viable indicator of intensive parameter (T and/or f_{H_2O}) variation within a single, petrographically well-characterized terrane. They used the paragonite dehydration reaction involving albite, aluminosilicate, and quartz to estimate equilibration temperatures of lower sillimanite through sillimanite + K-feldspar zone metapelites from the Puzzle Mountain area, Maine. Because the paragonite dehydration equilibrium used by Cheney and Guidotti requires both an estimate of f_{H_2O} and the presence of an aluminosilicate polymorph, this geothermometer cannot be applied to rocks in which muscovite and plagioclase coexist in the absence of andalusite, sillimanite, or kyanite. In order to overcome difficulties involved with subsolidus re-equilibration of alkali feldspar during late-stage metamorphic and magmatic processes, or the absence of an aluminosilicate phase, the Na-K exchange relationship between muscovite and plagioclase has been investigated. This paper presents the formulation of a geothermometer based solely on the compositions of coexisting muscovite and plagioclase.

Thermodynamic background

Ternary-feldspar solution model and excess terms

The albite and orthoclase activities of plagioclase feldspars can be formulated in terms of a ternary model as follows (Wohl, 1953; Saxena, 1973):

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

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

where the interaction (Margules) parameters, W_G, which describe mixing relations within the Ab-Or, An-Ab, and An-Or binary systems, can be resolved into enthalpy, entropy, and volume terms; X_{Or}, X_{Ab}, and X_{An} are mole fraction of orthoclase, albite, and anorthite; and α terms represent the ideal contribution to the activity of albite component (Price, 1985),

$$\alpha_{Ab} = (X_{Ab})(2 - X_{Ab} - X_{Or})(X_{Ab} + X_{Or}),$$

and orthoclase component,

$$\alpha_{Or} = (X_{Or})(2 - X_{Ab} - X_{Or})(X_{Ab} + X_{Or}).$$

Green and Usdansky (1986) have shown that these activity-composition expressions, combined with the An-Ab Margules parameters of Newton et al. (1980), the Ab-Or Margules parameters of Haselton et al. (1983), and An-Or mixing parameters derived from Seck's (1971a, 1971b) experimental feldspar compositions, can be used to model ternary-feldspar equilibria.

Muscovite activity relations

Binary solid solution between muscovite and paragonite is nonideal, and an asymmetric binary solution model generally has been used to express activity-composition relations of muscovite (Eugster et al., 1972; Thompson, 1974; Chatterjee and Froese, 1975; Cheney and Guidotti, 1979),

$$RT \ln a_{Ms} = RT \ln X_{Ms} + X_{Pa}^2[W_G^{Ms} + 2X_{Ms}(W_G^{Pa} - W_G^{Ms})],$$

and paragonite,

$$RT \ln a_{Pa} = RT \ln X_{Pa} + X_{Ms}^2[W_G^{Pa} + 2X_{Pa}(W_G^{Ms} - W_G^{Pa})],$$

where W_G^{Ms} and W_G^{Pa} are binary excess free energy of mixing parameters that can be expressed in enthalpy (W_H), en-

tropy (W_S), and volume (W_V) terms, and the mole fractions of muscovite and paragonite are given as

$$X_{Ms} = (X_K)(X_{Al}^{VI})^2$$
$$X_{Pa} = (X_{Na})(X_{Al}^{VI})^2$$

where

$$X_K = [K/(Na + K + Ca + Ba)],$$
$$X_{Na} = [Na/(Na + K + Ca + Ba)],$$

and

$$X_{Al}^{VI} = [Al^{VI}/(Fe + Mg + Mn + Ti + Al^{VI})]$$

defined on an atom per formula basis for the mica. Because muscovite and paragonite components of a white mica appear on opposite sides of the plagioclase-mica Na-K exchange equilibrium, the octahedral Al terms (i.e., X_{Al}^{VI}) of these mole-fraction expressions cancel. Thus, the exchange equilibrium would appear to be independent of Fe-Mg (celadonite) substitution in the octahedral sites of the white mica. Pigage and Greenwood (1982), however, have demonstrated that muscovite-paragonite activity relations are strongly affected by the ubiquitous presence of celadonite and/or phengite component. They considered a quaternary mixing model involving paragonite, muscovite, and two celadonite endmembers written in terms of pure K and pure Na, respectively, and excess W_G parameters that were assumed identical for the muscovite-paragonite and celadonite binary joins. On the other hand, several lines of evidence suggest only minor substitution of the Na endmember in white mica. Crystallographic studies indicate that because of the sizes of the cations involved, addition of Mg, Fe^{2+}, or Fe^{3+} to the octahedral sites would cause rotation and corrugation of the tetrahedral sheet, such that the interlayer site enlarges and becomes unfavorable for holding the small Na^+ in place (Bailey, 1984; Guidotti, 1984). Moreover, muscovite is always enriched in Fe and Mg relative to coexisting paragonite (Henley, 1970; Hock, 1974; Hoffer, 1978; Katagas and Baltatzis, 1980; Grambling, 1984; Guidotti, 1984). These relationships imply an antipathy between Fe-Mg substitution in the octahedral sites and Na occupancy of neighboring interlayer sites of white micas. It is therefore possible that most Na substitution in natural muscovites occurs as a paragonite component. This suggestion is supported by the generally low Na contents (0.02–0.04 atoms) of natural celadonites (Wise and Eugster, 1964; Boles and Coombs, 1975; Odom, 1984). Accordingly, the binary white mica solution model has been modified to reflect the possibility that Na enters the lattice of natural muscovites only as the paragonite endmember, whereas K would be present in both the muscovite and celadonite components. The muscovite mole-fraction terms (X_{Ms}) in the muscovite and paragonite activity expressions, given previously, have been modified by reducing X_{Ms} empirically as

$$X_{Ms} = [K/(Na + K + Ca + Ba)]$$
$$\cdot [(Al^{VI} - Na)/(Fe + Mg + Mn + Ti + Al^{VI})]$$

on an atoms per formula basis, where by virtue of the $(Al^{VI} - Na)$ term, only the K associated with the muscovite component is considered. The paragonite mole-fraction terms remain

$$X_{Pa} = [Na/(Na + K + Ca + Ba)],$$

where all Na is present as paragonite endmember. This asymmetric formulation of X_{Ms} and X_{Pa} is compatible with Grambling's (1984) suggestion that increased celadonite substitution shifts the position of the muscovite limb of the white mica solvus markedly toward higher K/(Na + K) ratios, but has limited effect on the compositions of coexisting paragonite (i.e., paragonite becomes only slightly less K-rich).

In addition, muscovite and paragonite endmembers have been assumed to interact with all other components in the same manner as they interact with each other. In the absence of appropriate W_G parameters for celadonite or phengite components, the activity expressions have therefore been taken as

$$RT \ln a_{Ms} = RT \ln X_{Ms} + (1 - X_{Ms})^2$$
$$\cdot [W_G^{Ms} + 2X_{Ms}(W_G^{Pa} - W_G^{Ms})]$$

and

$$RT \ln a_{Pa} = RT \ln X_{Pa} + (1 - X_{Pa})^2$$
$$\cdot [W_G^{Pa} + 2X_{Pa}(W_G^{Ms} - W_G^{Pa})]$$

with $(X_{Ms} + X_{Pa}) \leq 1$.

Muscovite-paragonite Margules parameters have been determined experimentally by Eugster et al. (1972) and Blencoe and Luth (1973). Chatterjee and Froese (1975) adjusted the pressure dependence of the Eugster et al. Margules parameters based on a review of published data on the molar volumes of muscovite-paragonite solid solutions (in joules, kelvins, and bars):

$$W_G^{Ms} = 19\,456.0 + 1.6543T - 0.4561P$$
$$W_G^{Pa} = 12\,230.3 + 0.7104T + 0.6653P.$$

Pigage and Greenwood (1982) subsequently modified the Eugster et al. interaction parameters to take into account excess volumes of mixing determined experimentally by Blencoe (1977). Although the various W_V values lead to significantly different equilibrium solvus compositions of muscovite-paragonite solid solutions at high pressures (Blencoe, 1977), there is very little difference in calculated equilibrium curves using the various W_G^{Ms} and W_G^{Pa} parameters (Cheney and Guidotii, 1979; Pigage and Greenwood, 1982). The Margules parameters of Chatterjee and Froese (1975) have been adopted here, but the revised constants based on Blencoe's (1977) experimental data yield similar results when used to describe plagioclase-muscovite Na-K exchange equilibria.

PLAGIOCLASE-MUSCOVITE THERMOMETER

The ternary albite and orthoclase solution models, white mica activity relations, and high-temperature endmember thermodynamic data can be combined to formulate a plagioclase-muscovite thermometer. The Na-K exchange re-action, however, is complicated by differences in the struc-tural states of the low albite–microcline and high albite–sanidine solid solutions. The free-energy relationships of the reaction have therefore been calculated from the in-ternally consistent thermodynamic data of Helgeson et al. (1978), which take into account the structural state of plagioclase and alkali feldspars (Table 1). The variation of $RT \ln K_D$ with temperature is illustrated in Figure 1. The equilibrium condition that the Gibbs free-energy change (in joules per mole) is zero at a given temperature, T, and pressure, P, results in the following expression:

$$\Delta G^0 = -7.5805T - 2087.6587 - 0.0431P.$$

This free-energy relation, combined with the ternary-feld-spar and modified binary white mica activity models, leads to the following plagioclase-muscovite Na-K geother-mometric expression, with T in kelvins and P in bars:

$$T = (19\,456A + 12\,230B + 27\,320C + 18\,810D$$
$$+ 8473E + 28\,226F - 65\,407.0G$$
$$+ 65\,305.4H - 2087.6587)$$
$$+ P(-0.0431 - 0.456A + 0.6653B + 0.364C$$
$$+ 0.364D + 2.1121G + 0.9699H)/$$
$$(7.5805 - 8.3147 \ln K_D - 1.6544A$$
$$- 0.7104B + 10.3C + 10.3D$$
$$- 114.1040G + 12.5365H),$$

where

$$A = 1 - 4X_{Ms} + 5X_{Ms}^2 - 2X_{Ms}^3$$
$$- 2X_{Pa} + 4X_{Pa}^2 - 2X_{Pa}^3,$$

$$B = 2X_{Ms} - 4X_{Ms}^2 + 2X_{Ms}^3 + 4X_{Pa}$$
$$- 5X_{Pa}^2 + 2X_{Pa}^3 - 1,$$

$$C = 2X_{Ab}X_{Or}^2 + 0.5X_{Or}X_{An} - X_{Ab}^2 + 2X_{Or}X_{Ab}^2$$
$$- 0.5X_{An}X_{Ab} + 2X_{Or}X_{An}X_{Ab},$$

$$D = X_{Or}^2 - 2X_{Ab}X_{Or}^2 + 0.5X_{Or}X_{An} - 2X_{Or}X_{Ab}^2$$
$$- 0.5X_{An}X_{Ab} - 2X_{Or}X_{An}X_{Ab},$$

$$E = 2X_{Ab}X_{An}^2 + 0.5X_{Or}X_{An} + X_{Or}X_{An}X_{Ab}$$
$$+ 0.5X_{An}X_{Ab} - X_{An}X_{Ab}(X_{An} - X_{Ab}),$$

$$F = X_{An}^2 - 2X_{Ab}X_{An}^2 + 0.5X_{Or}X_{An} - X_{An}X_{Ab}X_{Or}$$
$$+ 0.5X_{An}X_{Ab} + X_{An}X_{Ab}(X_{An} - X_{Ab}),$$

$$G = -0.5X_{Or}X_{An} - X_{An}X_{Or}(X_{Or} - X_{An})$$
$$- 2X_{Or}X_{An}^2 - 0.5X_{An}X_{Ab} - X_{Or}X_{An}X_{Ab},$$

$$H = -0.5X_{Or}X_{An} + X_{An}X_{Or}(X_{Or} - X_{An})$$
$$- X_{An}^2 + 2X_{Or}X_{An}^2 - 0.5X_{An}X_{Ab}$$
$$+ X_{Or}X_{An}X_{Ab},$$

$$\ln K_D = \ln X_{Ms} + \ln[X_{Ab}(2 - X_{Ab} - X_{Or})$$
$$\cdot (X_{Ab} + X_{Or})]$$
$$- \ln X_{Pa} - \ln[X_{Or}(2 - X_{Ab} - X_{Or})$$
$$\cdot (X_{Ab} + X_{Or})],$$

Table 1.   Thermodynamic data (Helgeson et al., 1978)

| | $H^0_{(298,1)}$ | $S^0_{(298,1)}$ | C_P | | | V^0 (cm³/ |
	(kJ/mol)	(J/mol·K)	a	b × 10³	c × 10⁻⁵	mol)
Muscovite	−5972.275	287.859	408.191	110.374	−106.440[a]	140.71
Albite	−3931.621	207.150	258.153	58.158	−62.802[b]	100.25
			342.586	14.870	−209.844[c]	
Paragonite	−5928.573	277.818	407.647	102.508	−110.625[a]	132.53
Alkali feldspar	−3971.403	213.928	320.566	18.037	−125.290[c]	108.87

Note: Upper temperature limits for the heat-capacity power-function coefficients are (a) 1000° K, (b) 479° K, and (c) 1400° K.

X_{Or}, X_{Ab}, and X_{An} are mole fractions of orthoclase, albite, and anorthite in plagioclase, and X_{Ms} and X_{Pa} are mole fractions of muscovite and paragonite in white mica. The application of this equation requires an independent estimate or a geobarometric determination of P, because the pressure dependence of the calculated temperature varies from 11 to 21° per kilobar depending upon the compositions of the coexising minerals.

TESTING OF GEOTHERMOMETER

There are various ways in which the plagioclase-muscovite geothermometer could give spurious results. Systematic errors might easily result from erroneous assumptions concerning the mixing relations in feldspar and mica solid solutions. Moreover, it is likely that the geothermometer results will be extremely sensitive to analytical uncertainties in the Or composition of plagioclase feldspars. In view of these potential difficulties, it is important to show that temperatures calculated with the geothermometer are geologically reasonable. As the logical way of testing the plagioclase-muscovite geothermometer, temperatures have been calculated utilizing compositions of coexisting feldspar-mica pairs from pelitic metasedimentary rocks and peraluminous granitoids, for which independent temperature determinations and complete mineral analyses are available.

Pelitic metasedimentary rocks

Plagioclase and muscovite commonly coexist with garnet and biotite in these pelitic assemblages; thus, the plagioclase-muscovite temperatures may be compared directly to those calculated with garnet-biotite thermometry. Results of application of the plagioclase-muscovite thermometer to five metapelite suites are presented in Table 2. Unfortunately, several modifications of the experimentally calibrated garnet-biotite thermometer of Ferry and Spear (1978) have been proposed to model nonideal mixing of garnet solid solutions (Holdaway and Lee, 1977; Hodges and Spear, 1982; Pigage and Greenwood, 1982; Ganguly and Saxena, 1984). In some rocks, the different garnet-biotite calibrations yield somewhat varied temperatures, so that it is difficult to determine, a priori, which calibration is appropriate. As a result, temperatures predicted by all these calibrations are presented in Table 2 for comparison.

The Penfold Creek occurrence represents complexly folded garnet, kyanite-staurolite, and sillimanite zone rocks that outcrop within the Omineca geanticline and at the northern extremity of the Shuswap metamorphic complex, British Columbia (Fletcher and Greenwood, 1979). The pelites are characterized by some variation in composition between plagioclase grains within individual specimens, both primary and secondary muscovite, and two generations of garnet that may represent two pulses of the same metamorphism. The various garnet-biotite thermometers yield temperatures that range from 383 to 712°C at an estimated pressure of 7000 bars; some samples are characterized by a bimodal distribution of calculated temperatures, 399 to 538°C and 599 to 695°C. The plagioclase-muscovite thermometer indicates equilibration temperatures between 466 and 674°C. The temperatures of Penfold Creek rocks are in general agreement with those predicted using the Hodges-Spear, Holdaway-Lee, and Ganguly-Saxena formulations of the garnet-biotite thermometers, but there is no apparent correlation between the plagioclase-muscovite temperatures and those derived from any specific garnet-biotite thermometer (Table 2).

Pigage (1982) described metamorphic mineral assemblages in the Azure Lake area of the Shuswap metamorphic complex, British Columbia, that are characteristic of the kyanite, kyanite-sillimanite, and sillimanite zones of the Barrovian series. Pigage and Greenwood (1982) concluded that observed mineral assemblages represent a close approach to equilibrium and used the intersection of several mineral equilibria with the kyanite-sillimanite reaction curve to estimate metamorphic pressures of 5133 to 6731 bars. Their revised Ferry and Spear (1978) garnet-biotite geothermometer yields temperatures up to 100 degrees higher than those calculated with the other calibrations (579–603°C). The calculated plagioclase-muscovite temperatures of the Azure Lake rocks range between 500 and 601°C and, typically, are generally intermediate between those predicted by the Holdaway-Lee and Pigage-Greenwood garnet-biotite thermometers.

Hodges and Spear (1982) used pelitic schists of the Mt. Moosilauke region, New Hampshire, to evaluate the internal consistency of a variety of published geothermometers and geobarometers with the Al_2SiO_5 invariant point of Holdaway (1971). The rocks studied by Hodges

and Spear contain andalusite and/or sillimanite, but do not contain kyanite. Sillimanite occurs either as subhedral prismatic grains or as fibrolite intergrown with muscovite; where present, andalusite occurs as subhedral to anhedral porphyroblasts. The described textures suggest that all samples equilibrated at temperatures above the aluminosilicate triple point (501°C) and that the two samples containing both andalusite and fibrolite (146B, 146D) may have equilibrated near the intersection of the muscovite breakdown and andalusite-sillimanite reaction curves (545–590°C). In this case, only the calibration of the garnet-biotite thermometer by Pigage and Greenwood (1982) produces comparable temperatures (561 and 621°C); all other calibrations generally yield temperatures of the aluminosilicate triple point or lower. Application of the plagioclase-garnet-Al_2SiO_5 geobarometer (Ghent, 1976; Ghent and Stout, 1981) produced preferred pressure estimates that range from 2677 to 2918 bars. Two Mt. Moosilauke rocks have plagioclase-muscovite temperatures (422 and 441°C) that suggest subsolidus re-equilibration, but four samples yield temperatures above the triple point (514–588°C) that are consistent with the observed aluminosilicate minerals. The compositions of plagioclase and muscovite in Mt. Moosilauke specimen 90A define a temperature of 801°C, which reflects the anomalously high Or content of plagioclase porphyroblasts in this rock.

Zen (1981) described mineral assemblages from slightly calcic, chloritoid, garnet, and kyanite-staurolite zone pelitic rocks from the Taconic Range in southwestern Massachusetts and adjacent areas of Connecticut and New York. Comparison of the mineral assemblages with hydrothermal phase-equilibrium data suggests that the approximate range of metamorphic conditions was 400–600°C at pressures probably about 4 kbar. Garnet-biotite thermometry yields a similar range of temperatures (416–607°C). Plagioclase-muscovite thermometry yields temperatures of 438–567°C, which are in general agreement with garnet-biotite temperatures.

Hodges and Royden (1984) described kyanite-grade pelitic schists from the Efjord area, northern Norway, that exhibit abundant textural evidence of retrograde re-equilibration under nonuniform pressure-temperature conditions. The presence of second-stage kyanite in all retrograde samples indicates that the P-T path of tectonic uplift occurred entirely within the kyanite stability field. The plagioclase-garnet-Al_2SiO_5 geobarometer (Ghent, 1976; Ghent and Stout, 1981), coupled with garnet-biotite thermometry, yields estimated pressures that range from 3 to 14 kbar at temperatures of 471 to 853°C. Plagioclase-muscovite temperatures (423–873°C) exhibit the same variation with pressure as that shown by the garnet-biotite temperatures (Hodges and Royden, 1984; Fig. 8).

Peraluminous granitoids

Plagioclase and muscovite are also important constituents of these granitic rocks, but only locally coexist with mineral pairs that have compositions applicable to geothermometry. As a result, most available temperature es-
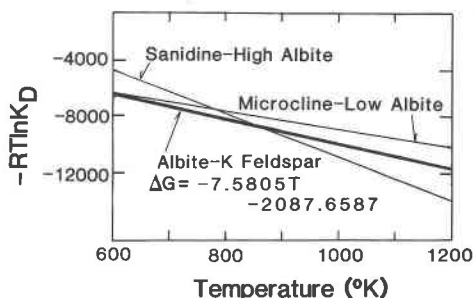

Fig. 1. Variation of $RT \ln K_D$ with temperature for the Na-K exchange reaction between plagioclase (all structural states) and muscovite (heavy line) based on thermodynamic data of Helgeson et al. (1978). Reaction curves for the exchange reaction calculated using thermodynamic data of sanidine–high albite and microcline–low albite solid solutions are also shown.

timates are based upon phase-equilibrium considerations, such as biotite–iron oxide stability relations. Five peraluminous granitoid suites, chosen to test the thermometer, are discussed below, and estimated equilibration temperatures are presented in Table 3.

Green and Usdansky (1984) described the petrology, mineralogy, and crystallization conditions of two-mica epidote-bearing granitoids of the Alabama tin belt. Garnet-biotite and apatite-biotite F-OH geothermometry suggested temperatures of 630 to 740°C, whereas ilmenite and biotite stability relations suggested temperatures up to 770°C. Calculated plagioclase-muscovite temperatures range from distinctly subsolidus (414°C) to near liquidus (740°C).

Kistler et al. (1981) described two-mica granites in the Ruby Mountains, Nevada, and reported garnet-biotite equilibration temperatures between 365 and 505°C based on the Goldman and Albee (1977) calibration. Other calibrations of the garnet-biotite thermometer, however, give temperatures of 527–725°C. The calculated plagioclase-muscovite temperatures are higher than those predicted by all but the Pigage-Greenwood garnet-biotite thermometer (Table 3) and reflect the coexistence of K-rich muscovite with K-rich plagioclase in these granites.

Czamanske et al. (1981) detailed the chemistry of rock-forming minerals of the Cretaceous-Paleocene batholith in southwestern Japan. They noted significant differences in the chemistry of primary and secondary muscovites, in agreement with the characteristics outlined by Miller et al. (1981). Temperatures based on two-feldspar geothermometry indicated that none of the suites faithfully retains solidus feldspar relations; perthitic alkali feldspar in all samples has lost Ab. Ilmenite and biotite stability relations in f_{O_2}-T space, however, suggest equilibration temperatures of 680–810°C. Plagioclase-muscovite temperatures calculated using primary and secondary mica compositions are given in Table 3.

Bradfish (1979) investigated conditions of muscovite crystallization in the Teacup Granodiorite, Arizona, and concluded that the mica in all facies of the intrusion was

Table 2. Plagioclase-muscovite temperatures of pelitic metamorphic rocks

Sample	X_{An}	X_{Ab}	X_{Or}	X_{Pa}	X_{Ms}	F-S	P-G	H-S	H-L	G-S	T	P (bars)
					Penfold Creek (Fletcher and Greenwood, 1979)							
5	0.359	0.635	0.005	0.146	0.786	596	560	668	617	599	674	7 000
6	0.292	0.705	0.003	0.238	0.700	534	596	553	549	523	565	7 000
7	0.302	0.694	0.003	0.167	0.766	648	676	663	626	577	561	7 000
8	0.260	0.738	0.002	0.238	0.695	572	628	600	576	545	488	7 000
9	0.290	0.708	0.002	0.241	0.693	521	577	538	536	510	505	7 000
10	0.310	0.685	0.003	0.202	0.721	529	594	551	546	514	574	7 000
11	0.290	0.706	0.003	0.186	0.742	539	599	573	553	525	558	7 000
12	0.202	0.794	0.003	0.222	0.714	602	630	617	596	568	508	7 000
13	0.206	0.789	0.005	0.236	0.704	625	677	640	613	582	585	7 000
14	0.282	0.712	0.005	0.163	0.762	631	700	659	617	619	625	7 000
15	0.129	0.868	0.003	0.202	0.726	640	674	650	621	623	466	7 000
					Azure Lake (Pigage, 1982)							
373	0.277	0.718	0.004	0.170	0.763	545	602	573	557	545	565	5 678
121	0.314	0.681	0.004	0.160	0.772	535	651	603	578	535	581	5 546
367	0.394	0.602	0.003	0.140	0.791	533	608	571	548	535	580	5 783
82	0.278	0.716	0.004	0.160	0.772	525	626	549	542	524	552	5 133
398	0.207	0.788	0.005	0.209	0.734	541	652	557	553	544	562	5 528
492	0.227	0.766	0.003	0.209	0.734	543	618	579	569	534	505	5 979
223	0.337	0.658	0.004	0.150	0.782	533	621	570	556	529	601	6 035
2-376	0.277	0.716	0.005	0.150	0.782	555	641	585	564	547	592	5 828
2-13	0.309	0.685	0.005	0.140	0.791	523	656	552	542	535	600	5 396
74	0.358	0.638	0.003	0.120	0.792	581	658	612	582	578	569	6 731
59	0.256	0.738	0.005	0.150	0.782	557	682	581	565	549	579	5 828
40	0.240	0.758	0.003	0.179	0.754	540	580	558	553	530	500	5 264
					Mt. Moosilauke (Hodges and Spear, 1982)							
78B	0.116	0.876	0.006	0.245	0.713	468	533	477	499	488	514	3 918
80D	0.280	0.714	0.006	0.172	0.776	489	565	512	518	513	588	3 444
90A	0.141	0.831	0.026	0.237	0.721	486	568	497	513	504	801	3 801
92D	0.108	0.888	0.003	0.252	0.701	491	557	501	518	508	422	3 493
145E	0.089	0.905	0.004	0.231	0.727	498	567	507	524	524	441	3 167
146B	0.241	0.753	0.005	0.190	0.767	519	621	538	540	527	531	2 722
146D	0.243	0.750	0.005	0.190	0.762	464	561	480	498	486	532	2 677
					Taconic Range (Zen, 1981)							
463-1	0.190	0.804	0.005	0.280	0.687	509	568	524	530	544	538	4 000
339-1	0.266	0.729	0.004	0.237	0.721	416	500	447	461	458	547	4 000
356	0.138	0.853	0.008	0.225	0.727	469	508	492	501	479	567	4 000
103-1	0.120	0.875	0.005	0.187	0.733	460	515	475	495	517	484	4 000
103-2	0.300	0.694	0.004	0.170	0.761	510	607	545	531	561	548	4 000
234-1	0.368	0.630	0.002	0.133	0.815	452	495	473	489	479	472	4 000
14-1	0.247	0.750	0.002	0.200	0.763	443	474	460	482	469	438	4 000
1052-2	0.059	0.930	0.010	0.187	0.780	505	548	520	527	516	535	4 000
					Efjord (Hodges and Royden, 1984)							
8B	0.541	0.454	0.004	0.120	0.785	712	853	775	673	653	873	13 000
8C	0.143	0.853	0.003	0.152	0.737	491	527	507	516	466	423	3 600
12E	0.207	0.788	0.004	0.101	0.776	485	528	503	512	475	451	3 300
18A	0.295	0.699	0.004	0.101	0.751	476	573	523	507	492	546	6 000
21A	0.302	0.694	0.003	0.166	0.703	471	634	499	503	489	524	4 900
21C	0.312	0.680	0.008	0.075	0.780	554	640	597	565	533	675	8 000
21F	0.252	0.744	0.004	0.111	0.781	557	615	584	565	526	546	7 000

Notes: Garnet-biotite thermometer calibrations as follows: F-S, Ferry and Spear (1978); P-G, Pigage and Greenwood (1982); H-S, Hodges and Spear (1982); H-L, Holdaway and Lee (1977); and G-S, Ganguly and Saxena (1984). T = plagioclase-muscovite geothermometer.

probably secondary and resulted from subsolidus reactions involving a coexisting aqueous phase. Predicted plagioclase-muscovite temperatures (478 and 530°C) are compatible with such an interpretation and with temperatures predicted by some but not all garnet-biotite thermometers (Table 3).

Ferry (1978, 1979) discussed the origin of hydrothermally altered feldspars and mica in samples of granitic rock from south-central Maine. He reported alteration assemblages consisting of muscovite, calcite, quartz, epidote, plagioclase, and alkali feldspar that record temperatures of 415 to 435°C at 3500 bars. The measured fractionation of Ab component between coexisting plagioclase and microcline yields temperatures of 415 to 454°C at the same pressure, although Ferry (1978, 1979) did not present data that would permit evaluation of the other two feldspar endmember equilibria in order to determine whether stable equilibrium has been achieved between all

Table 3. Plagioclase-muscovite temperatures of peraluminous granitoids

Sample	X_{An}	X_{Ab}	X_{Or}	X_{Pa}	X_{Ms}	F-S	P-G	H-S	H-L	G-S	T^*	T	P (bars)
Alabama tin belt (Green and Usdansky, 1984)
ATB-67	0.337	0.644	0.008	0.070	0.753	635	863	689	618	740	n.a.	698	8000
ATB-58	0.354	0.635	0.010	0.070	0.753	n.a.	n.a.	n.a.	n.a.	n.a.	760[a]	740	8000
RF-20s	0.017	0.969	0.006	0.060	0.780	n.a.	n.a.	n.a.	n.a.	n.a.	463[b]	414	6000
RF-3s	0.224	0.754	0.008	0.060	0.785	n.a.	n.a.	n.a.	n.a.	n.a.	584[b]	536	6000
Ruby Mountains (Kistler et al., 1981)
11-66A	0.008	0.866	0.125	0.068	0.828	538	725	548	550	630	n.a.	718	5000
31-66D	0.010	0.905	0.085	0.064	0.836	514	607	527	533	609	n.a.	671	5000
Tea Cup Granodiorite (Bradfish, 1979)
LN-1	0.126	0.863	0.012	0.065	0.776	501	774	512	525	615	n.a.	530	5000
SN-19	0.146	0.844	0.008	0.055	0.770	590	916	607	586	720	n.a.	478	5000
Japanese batholiths (Czamanske et al., 1981)
6510s	0.245	0.739	0.014	0.020	0.769	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	485	5000
T25s	0.017	0.969	0.006	0.060	0.780	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	556	5000
T173bc	0.224	0.754	0.008	0.060	0.785	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	669	5000
T173Br	0.354	0.635	0.010	0.070	0.753	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	651	5000
T76	0.017	0.969	0.006	0.060	0.780	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	669	5000
T133r	0.224	0.754	0.008	0.060	0.785	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	678	5000
	0.354	0.635	0.010	0.070	0.753	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	616	5000
Augusta, Maine (Ferry, 1978, 1979)
694s	0.122	0.871	0.005	0.040	0.842	n.a.	n.a.	n.a.	n.a.	n.a.	403[c]	376	3500
698s	0.137	0.858	0.004	0.040	0.816	n.a.	n.a.	n.a.	n.a.	n.a.	447[c]	364	3500
821s	0.170	0.817	0.012	0.040	0.791	n.a.	n.a.	n.a.	n.a.	n.a.	415[d]	474	3500
838s	0.173	0.816	0.009	0.040	0.816	n.a.	n.a.	n.a.	n.a.	n.a.	423[d]	446	3500
276s	0.213	0.780	0.006	0.030	0.798	n.a.	n.a.	n.a.	n.a.	n.a.	435[d]	401	3500
787s	0.096	0.900	0.003	0.030	0.798	n.a.	n.a.	n.a.	n.a.	n.a.	442[c]	315	3500

Notes: Garnet-biotite thermometer calibrations as follows: F-S, Ferry and Spear (1978); P-G, Pigage and Greenwood (1982); H-S, Hodges and Spear (1982); H-L, Holdaway and Lee (1977); and G-S, Ganguly and Saxena (1984). Other temperature estimates (T^*) based on (a) biotite-apatite F-OH exchange equilibria, (b) biotite-ilmenite stability relations, (c) two-feldspar albite geothermometer, and (d) muscovite–calcite–epidote–plagioclase–alkali feldspar equilibria; n.a., not applicable. Where indicated, analyses represent (c) core or (r) rim of primary (p) muscovite, or secondary (s) muscovite. T, plagioclase-muscovite geothermometer.

feldspar endmembers. The calculated plagioclase-muscovite temperatures are compatible with those predicted by other geothermometric techniques (Table 3).

SUMMARY AND CONCLUSIONS

Available thermochemical data have been used to calibrate the Na-K exchange reaction between plagioclase and muscovite as a geothermometer. The formulation of the plagioclase-muscovite geothermometer accounts for high and low structural states of feldspar and utilizes plagioclase activity-composition relations expressed in terms of a ternary subregular solution model. Binary mica solution models have been modified to account for increased $K/(K + Na)$ in the muscovite component associated with increased celadonite and/or phengite substitution. The geothermometer has been applied to pelitic metasedimentary rocks and peraluminous granitoids that crystallized at temperatures of 415–725°C and pressures of 2.5–13.0 kbar. The predicted equilibration temperatures using plagioclase-muscovite pairs generally fall within the range of equilibration temperatures estimated using other geothermometric techniques (e.g., garnet-biotite thermometry). Observed discrepancies between calculated temperatures appear to be related to re-equilibration of muscovite and/or plagioclase. Application of the plagioclase-mus-

covite geothermometer extends the range of pelitic and peraluminous rocks for which equilibration temperatures may be estimated.

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