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# A Thermodynamic Study of the Pseudobinary Join Muscovite-Paragonite in the System $KAlSi_3O_8$–$NaAlSi_3O_8$–$Al_2O_3$–$SiO_2$–$H_2O$

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## Abstract

With increasing temperature, muscovite–paragonite crystalline solution reacts with quartz to produce the assemblage alkali feldspar crystalline solution, an $Al_2SiO_5$ polymorph, and $H_2O$ fluid. Equilibria involving these phases in the system $KAlSi_3O_8$–$NaAlSi_3O_8$–$Al_2O_3$–$SiO_2$–$H_2O$ were calculated from thermodynamic data and are presented in isobaric $T$-$X$ sections and in a $P_{H_2O}$-$T$ projection.

The results find application in the interpretation of pertinent assemblages in medium- to high-grade, calcium-poor metamorphic rocks. The upper compatibility limit of the assemblage paragonite crystalline solution plus quartz, given by the univariant $P_{H_2O}$-$T$ curve of the reaction

$$\text{paragonite}_{ss} + \text{quartz} \leftrightharpoons \text{albite}_{ss} + \text{muscovite}_{ss} + Al_2SiO_5 + H_2O$$

lies within the stability fields of kyanite and andalusite, agreeing well with petrographic observations. The univariant $P_{H_2O}$-$T$ curve of the reaction.

$$\text{muscovite}_{ss} + \text{albite}_{ss} + \text{quartz} \leftrightharpoons \text{K feldspar}_{ss} + Al_2SiO_5 + H_2O$$

has been located within the stability fields of andalusite and sillimanite. A consideration of melting relations in the system $KAlSi_3O_8$–$NaAlSi_3O_8$–$Al_2O_3$–$SiO_2$–$H_2O$ leads to the conclusion that the assemblage K feldspar$_{ss}$ + sillimanite + quartz commonly observed in pelitic high-grade metamorphic rocks can be produced by a subsolidus reaction only if $P_{H_2O}$ is considerably less than $P_{total}$.

## Introduction

Dioctahedral micas are very common in diagenetically altered sediments and metamorphic rocks, but are less so in plutonic rocks. Several simple or coupled, single- or multi-site substitutions in the mica structure permit a wide range of composition. There is a limited K-Na substitution in the interlayer sites between the two end members muscovite $KAl_2[AlSi_3O_{10}(OH)_2]$ and paragonite $NaAl_2[AlSi_3O_{10}(OH)_2]$. Other substitutions include $Al \leftrightharpoons Fe^{3+}$ in the octahedral layer and coupled multi-site substitutions like $Na + Si \leftrightharpoons Ca + Al$, leading from paragonite to margarite end member, or $Al + Al \leftrightharpoons (Mg, Fe^{2+}) + Si$, leading from muscovite to phengitic K micas. And finally there is some $(OH) \leftrightharpoons F$ substitution in these minerals. At elevated temperatures, near the upper thermal stability of the assemblages paragonite + quartz and muscovite + quartz, the coupled multi-site substitutions become less prevalent. Consequently, the natural dioctahedral micas of medium- to high-grade metamorphic rocks may be regarded, to a first approximation, as binary crystalline solutions of muscovite and paragonite end members.

The thermal stabilities of the end members, muscovite and paragonite, are well known (Chatterjee and Johannes, 1974; Chatterjee, 1972). In the presence of quartz, they decompose to feldspar, aluminum silicate, and $H_2O$ fluid. The two end-member reactions may be represented by univariant curves in a diagram of $P_{H_2O} = P_{total}$ *vs* $T$ (Fig. 1).

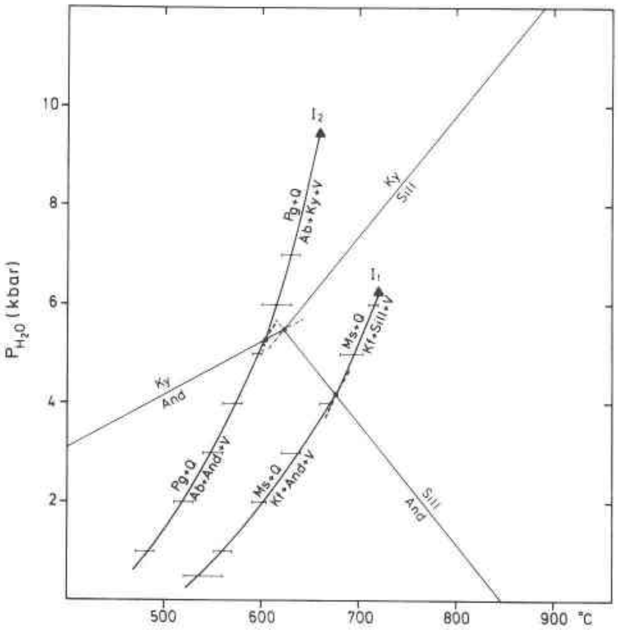

FIG. 1. The decomposition of muscovite and paragonite in the presence of quartz. Reactions terminate at invariant points $I_1$ and $I_2$ due to the formation of melt. Experimental data have been taken from Chatterjee (1972, 1974b) and Chatterjee and Johannes (1974). The $Al_2SiO_5$ transitions are shown according to Richardson *et al* (1969).

Within the *P-T* field bounded by these two univariant curves, crystalline solutions of the mica end members as well as of the feldspar end members will be involved in these equilibria. The present paper deals with the calculation of phase relations involving the two crystalline solutions, in the presence of an $Al_2SiO_5$ polymorph, quartz, and $H_2O$ vapor. Similar calculations have been published by Thompson (1974). His presentation of theory, as well as the method of calculation, are different. Furthermore, we are using improved input data not available to him. Thus, although there is a general agreement between the calculated phase diagrams, we expect our results to be more precise.

## Theory

The coexistence of quartz, an $Al_2SiO_5$ polymorph, K-Na mica, and K-Na feldspar implies the following two equilibria:

$$KAl_2[AlSi_3O_{10}(OH)_2] + SiO_2 \leftrightharpoons KAlSi_3O_8 + Al_2SiO_5 + H_2O \qquad (1)$$

$$NaAl_2[AlSi_3O_{10}(OH)_2] + SiO_2 \leftrightharpoons NaAlSi_3O_8 + Al_2SiO_5 + H_2O \qquad (2)$$

The equilibrium constants may be expressed as

$$\ln K_{(1)} = \ln a^{fd}_{Kf} - \ln a^{mi}_{Ms} + \ln f_{H_2O}$$

$$\ln K_{(2)} = \ln a^{fd}_{Ab} - \ln a^{mi}_{Pg} + \ln f_{H_2O}$$

where $f_{H_2O}$ stands for the fugacity of $H_2O$ and $a^{fd}_{Kf}$ for the activity of $KAlSi_3O_8$ in the feldspar crystalline solution, $a^{mi}_{Ms}$ for the activity of $KAl_2[AlSi_3O_{10}(OH)_2]$ in the mica crystalline solution, *etc.* Defining the standard state of the solids as the pure solid at 1 bar and given *T*, and that of $H_2O$ vapor as the perfect $H_2O$ gas at 1 bar and given *T*, the following relationships hold at equilibrium at given *P* and *T* (in °K):

$$\Delta G_{(1)} = \Delta G^{\circ}_{(1)} + RT \ln K_{(1)} + \int_1^P \Delta V_{s(1)}\, dP \qquad (3)$$

$$\Delta G_{(2)} = \Delta G^{\circ}_{(2)} + RT \ln K_{(2)} + \int_1^P \Delta V_{s(2)}\, dP \qquad (4)$$

where $\Delta G$ is the Gibbs energy change of the reaction at any given pressure and temperature, $\Delta G^{\circ}$ is the standard Gibbs energy change (with reactants and products in their standard states) at the same temperature, and $\Delta V_s$ is the volume change of the reaction due to the solids. For many reactions, $\Delta V_s$ may be regarded as constant over a small range of pressure and temperature and practically equal to the standard volume change $\Delta V^{\circ}_s$ (*i.e.*, at one bar), at 25°C.

At equilibrium $\Delta G = 0$ and, therefore,

$$\Delta G^{\circ}_{(1)} = -RT(\ln a^{fd}_{Kf} - \ln a^{mi}_{Ms} + \ln f_{H_2O}) - \Delta V^{\circ}_{s(1)}(P - 1) \qquad (5)$$

$$\Delta G^{\circ}_{(2)} = -RT(\ln a^{fd}_{Ab} - \ln a^{mi}_{Pg} + \ln f_{H_2O}) - \Delta V^{\circ}_{s(2)}(P - 1) \qquad (6)$$

Introducing mole fractions ($X$) and activity coefficients ($\gamma$), and noting that for binary solutions $X^{fd}_{Ab} = (1 - X^{fd}_{Kf})$ and $X^{mi}_{Pg} = (1 - X^{mi}_{Ms})$, Equations (5) and (6) may be written

$$\Delta G^{\circ}_{(1)} = -RT\{\ln X^{fd}_{Kf} + \ln \gamma^{fd}_{Kf} - \ln X^{mi}_{Ms} - \ln \gamma^{mi}_{Ms}\} - RT \ln f_{H_2O} - \Delta V^{\circ}_{s(1)}(P - 1) \qquad (7)$$

$$\Delta G^{\circ}_{(2)} = -RT\{\ln (1 - X^{fd}_{Kf}) + \ln \gamma^{fd}_{Ab} - \ln (1 - X^{mi}_{Ms}) - \ln \gamma^{mi}_{Pg}\} - RT \ln f_{H_2O} - \Delta V^{\circ}_{s(2)}(P - 1) \qquad (8)$$

Following Carlson and Colburn (1942), the logarithm of the activity coefficients of a binary solution under isobaric-isothermal conditions may be expressed by a power series in $(1 - X)$. The coefficients consist of combinations of the logarithms of the activity coefficients at infinite dilution. By definition

$$W_G = RT \ln \gamma^{\infty}$$

where $\gamma^{\infty}$ is the activity coefficient at infinite dilution and $W_G$, commonly called a Margules mixing parameter, is the excess partial molar Gibbs energy at infinite dilution. Therefore, for the binary K-Na feldspar crystalline solution

$$\begin{aligned} \ln \gamma_{\mathrm{Kf}}^{\mathrm{fd}} &= \left(\frac{2W_{G,\mathrm{Ab}}^{\mathrm{fd}}}{RT} - \frac{W_{G,\mathrm{Kf}}^{\mathrm{fd}}}{RT}\right)(1 - X_{\mathrm{Kf}}^{\mathrm{fd}})^2 \\ &\quad + 2\left(\frac{W_{G,\mathrm{Kf}}^{\mathrm{fd}}}{RT} - \frac{W_{G,\mathrm{Ab}}^{\mathrm{fd}}}{RT}\right)(1 - X_{\mathrm{Kf}}^{\mathrm{fd}})^3 \\ \ln \gamma_{\mathrm{Ab}}^{\mathrm{fd}} &= \left(\frac{2W_{G,\mathrm{Kf}}^{\mathrm{fd}}}{RT} - \frac{W_{G,\mathrm{Ab}}^{\mathrm{fd}}}{RT}\right)(X_{\mathrm{Kf}}^{\mathrm{fd}})^2 \\ &\quad + 2\left(\frac{W_{G,\mathrm{Ab}}^{\mathrm{fd}}}{RT} - \frac{W_{G,\mathrm{Kf}}^{\mathrm{fd}}}{RT}\right)(X_{\mathrm{Kf}}^{\mathrm{fd}})^3 \end{aligned}$$

The activity coefficients of the mica crystalline solution may be similarly expressed.

Substituting the appropriate expressions for the activity coefficients into Equations (7) and (8), the following equations are obtained:

$$\begin{aligned} \Delta G^{\circ}_{(1)} &= -RT \ln X_{\mathrm{Kf}}^{\mathrm{fd}} - \{(2W_{G,\mathrm{Ab}}^{\mathrm{fd}} - W_{G,\mathrm{Kf}}^{\mathrm{fd}}) \\ &\quad \cdot (1 - X_{\mathrm{Kf}}^{\mathrm{fd}})^2 + 2(W_{G,\mathrm{Kf}}^{\mathrm{fd}} - W_{G,\mathrm{Ab}}^{\mathrm{fd}}) \\ &\quad \cdot (1 - X_{\mathrm{Kf}}^{\mathrm{fd}})^3\} + RT \ln X_{\mathrm{Ms}}^{\mathrm{mi}} \\ &\quad + \{(2W_{G,\mathrm{Pg}}^{\mathrm{mi}} - W_{G,\mathrm{Ms}}^{\mathrm{mi}})(1 - X_{\mathrm{Ms}}^{\mathrm{mi}})^2 \\ &\quad + 2(W_{G,\mathrm{Ms}}^{\mathrm{mi}} - W_{G,\mathrm{Pg}}^{\mathrm{mi}})(1 - X_{\mathrm{Ms}}^{\mathrm{mi}})^3\} \\ &\quad - RT \ln f_{\mathrm{H_2O}} - \Delta V^{\circ}_{s(1)}(P - 1) \qquad (9) \\ \Delta G^{\circ}_{(2)} &= -RT \ln (1 - X_{\mathrm{Kf}}^{\mathrm{fd}}) \\ &\quad - \{(2W_{G,\mathrm{Kf}}^{\mathrm{fd}} - W_{G,\mathrm{Ab}}^{\mathrm{fd}})(X_{\mathrm{Kf}}^{\mathrm{fd}})^2 \\ &\quad + 2(W_{G,\mathrm{Ab}}^{\mathrm{fd}} - W_{G,\mathrm{Kf}}^{\mathrm{fd}})(X_{\mathrm{Kf}}^{\mathrm{fd}})^3\} \\ &\quad + RT \ln (1 - X_{\mathrm{Ms}}^{\mathrm{mi}}) + \{(2W_{G,\mathrm{Ms}}^{\mathrm{mi}} - W_{G,\mathrm{Pg}}^{\mathrm{mi}}) \\ &\quad \cdot (X_{\mathrm{Ms}}^{\mathrm{mi}})^2 + 2(W_{G,\mathrm{Pg}}^{\mathrm{mi}} - W_{G,\mathrm{Ms}}^{\mathrm{mi}})(X_{\mathrm{Ms}}^{\mathrm{mi}})^3\} \\ &\quad - RT \ln f_{\mathrm{H_2O}} - \Delta V^{\circ}_{s(2)}(P - 1) \qquad (10) \end{aligned}$$

Equations (9) and (10) may be solved simultaneously by iteration at any given $P$ and $T$ for the two unknowns $X_{\mathrm{Kf}}^{\mathrm{fd}}$ and $X_{\mathrm{Ms}}^{\mathrm{mi}}$, if the following information is available:

(1) $\Delta V^{\circ}_{s(1)}$ and $\Delta V^{\circ}_{s(2)}$ at 25°C, *i.e.*, the molar volumes of all solids.

(2) The fugacity of $H_2O$ as a function of pressure and temperature.

(3) $\Delta G^{\circ}_{(1)}$ and $\Delta G^{\circ}_{(2)}$ as functions of temperature.

(4) The Margules mixing parameters as functions of pressure and temperature.

The molar volumes of the solid phases are well-known, those used in this paper being listed in Table 1. It will be assumed that the fluid phase is essentially pure $H_2O$. In such case, the fugacity may be obtained from Burnham, Holloway, and Davis (1969). The derivation of other information necessary for the calculations requires further discussion.

### Standard Gibbs Energy Changes

The following end member reactions have been experimentally investigated by Chatterjee (1972) and Chatterjee and Johannes (1974):

muscovite + quartz ⇆ sanidine + andalusite + $H_2O$

muscovite + quartz ⇆ sanidine + sillimanite + $H_2O$

paragonite + quartz ⇆ albite + andalusite + $H_2O$

paragonite + quartz ⇆ albite + kyanite + $H_2O$

The reactions involving andalusite have been investigated over a greater temperature range than those involving other $Al_2SiO_5$ polymorphs. Therefore, we have calculated the standard Gibbs energy changes for the two reactions involving andalusite according to Equations (5) and (6). In these cases, the activities of the solids are unity. The molar volumes listed in Table 1 and the fugacity of $H_2O$ given by Burnham *et al* (1969) were used. It was found that $\Delta G^{\circ}$ may be adequately expressed as a linear function of the absolute temperature, *i.e.* $\Delta S^{\circ}$

TABLE 1. Standard Molar Volumes of Solid Phases at 25°C

| Phase | Molar Volume cal bar -1 | Source of Data |
|---|---|---|
| Muscovite | 3.3654 ± 0.0007 | Chatterjee and Johannes, 1974 |
| Paragonite | 3.1545 ± 0.0012 | Chatterjee, 1974a |
| Sanidine | 2.6029 ± 0.0005 | Chatterjee and Johannes, 1974 |
| High albite | 2.3988 ± 0.0022 | Chatterjee, 1972 |
| Quartz | 0.54226 ± 0.00002 | Robie and Waldbaum, 1968 |
| Andalusite | 1.2302 ± 0.0004 | Chatterjee, 1972 |
| Kyanite | 1.0542 ± 0.0006 | Chatterjee, 1972 |
| Sillimanite | 1.1911 ± 0.0007 | Richardson et al., 1969 |

Uncertainties are two standard deviations.

TABLE 2. Standard Gibbs Energy Changes of Reactions Involving Micas, Feldspars, $Al_2SiO_5$ Polymorphs, Quartz, and $H_2O$ Fluid

| Reactions | $\Delta G^0$ cal | Remarks |
|---|---|---|
| Ms + Q = Kf + And + $H_2O$ | -37.789 T + 21091 | Derived from experimental data of Chatterjee and Johannes (1974) |
| Ms + Q = Kf + Sill + $H_2O$ | -38.739 T + 22156 | Calculated |
| Ms + Q = Kf + Ky + $H_2O$ | -35.906 T + 20371 | Calculated |
| Pg + Q = Ab + And + $H_2O$ | -39.876 T + 21226 | Derived from experimental data of Chatterjee (1972) |
| Pg + Q = Ab + Ky + $H_2O$ | -37.993 T + 20505 | Calculated |
| Pg + Q = Ab + Sill + $H_2O$ | -40.826 T + 22291 | Calculated |

Abbreviations:

Ms = muscovite; Pg = paragonite; Q = quartz; Kf = K feldspar; Ab = albite; And = andalusite; Ky = kyanite; Sill = sillimanite

is constant. In order to obtain $\Delta G^\circ$ of Reactions (1) and (2) involving other $Al_2SiO_5$ polymorphs, we combined the calculated $\Delta G^\circ$ with $\Delta G^\circ$ of the appropriate $Al_2SiO_5$ transition. For the $Al_2 SiO_5$ transitions, $\Delta G^\circ$ was calculated from the phase diagram of Richardson, Gilbert, and Bell (1969), using the molar volume data given in Table 1. Thus $\Delta G^\circ$ of all necessary end member reactions is obtained (Table 2).

## Margules Mixing Parameters

The feldspars coexisting with the micas in experimental phase equilibria studies were found to be disordered with respect to tetrahedral Al and Si (Chatterjee, 1972; Chatterjee and Johannes, 1974). Consequently, we have used the mixing parameters $W^{\mathrm{fd}}_{G,\mathrm{Kf}}$ and $W^{\mathrm{fd}}_{G,\mathrm{Ab}}$ for sanidine-high albite crystalline solutions (Waldbaum and Thompson, 1969, p. 1275).

The muscovite-paragonite solvus has been determined by Eugster *et al* (1972) and Blencoe and Luth (1973). The experiments of Eugster *et al* (1972) involved long runs and rate studies, and we consider them to be more reliable than those of Blencoe and Luth (1973). Therefore, we have used mixing parameters derived from the Eugster *et al* (1972) solvus at 2.07 kbar. However, we have modified the pressure dependence in the light of new volume data, because Eugster *et al* (1972, p. 176) had some reservations concerning the quality of the volume data available to them. In the absence of any convincing data on synthetic crystalline solutions, we have chosen to use the volume data of some well characterized natural micas in addition to those of the two synthetic end members. Although the natural micas do not belong strictly to the binary solution muscovite–paragonite, the deviation from the compositional join is small.

The data listed in Table 3 were used to obtain the following least-squares fit of the molar volume of the muscovite-paragonite crystalline solution

$$V_{\mathrm{soln}} = 3.15374 + 0.01351\,(X^{\mathrm{mi}}_{\mathrm{Ms}}) + 0.37709\,(X^{\mathrm{mi}}_{\mathrm{Ms}})^2 - 0.26804(X^{\mathrm{mi}}_{\mathrm{Ms}})^3 \qquad (11)$$

TABLE 3. Molar Volumes of Paragonite, Muscovite, and Muscovite–Paragonite Crystalline Solutions

| Molar Volume* cal $bar^{-1}$ | Composition** $X^{mi}_{Ms}$ | Source of Data | Remarks |
|---|---|---|---|
| 3.1545 ± 0.0006 | 0.0 | Chatterjee, 1974a | Synthetic pure $2M_1$ paragonite |
| 3.1577 | 0.047 | Zen et al., 1964 | Virtually on muscovite-paragonite join, with only 1.6 mole % Ca in the interlayer site |
| 3.1781 | 0.150 | Burnham and Radoslovich, 1964 | Composition from partial probe analysis; corroborated by structure refinement |
| 3.3058 | 0.650 | Burnham and Radoslovich, 1964 | Composition from partial probe analysis; structure refinement converged to $X^{mi}_{Ms}$ = 0.66 |
| 3.35605 ± 0.0006 | 0.896 | Güven, 1971 | Chemical analysis shows only insignificant phengitic component (Si = 3.02 per half cell) |
| 3.35948 | 0.905 | Rothbauer, 1971 | Chemical analysis shows Si = 3.08 per half cell |
| 3.3654 ± 0.0007 | 1.0 | Chatterjee and Johannes, 1974 | Synthetic pure $2M_1$ muscovite |

* Wherever quoted, uncertainties are two standard deviations.

** The compositions of the mica crystalline solutions in terms of $X^{mi}_{Ms}$ were obtained by projecting onto the ideal muscovite-paragonite join from any other atom (Ca, Ba, etc.) present in the interlayer site.

with volume expressed in cal/bar. Following Waldbaum and Thompson (1968, p. 2001–2002), the excess partial molar volume at infinite dilution $W_V$ may be obtained from the molar volume equation:

$W^{\mathrm{mi}}_{V,\mathrm{Ms}} = -0.1090$ cal/bar and
$W^{\mathrm{mi}}_{V,\mathrm{Pg}} = 0.1590$ cal/bar.

The calculated molar volume has been plotted in Figure 2 as well as the data points used in obtaining Equation (11). Accepting the mixing parameters at 2.07 kbar derived from the solvus of Eugster *et al* (1972) and incorporating the above values of $W_V$, we obtain the following expressions:

$$W^{\mathrm{mi}}_{G,\mathrm{Pg}} = 2923.1 + 0.1590P + 0.1698T \qquad \text{(12a)}$$

$$W^{\mathrm{mi}}_{G,\mathrm{Ms}} = 4650.1 - 0.1090P + 0.3954T \qquad \text{(12b)}$$

with $W_G$ in cal, $P$ in bars, and $T$ in °K.

## Results

Using input data discussed in previous sections, Equations (9) and (10) were solved by iteration at any given $P$ and $T$ for the two unknowns $X^{\mathrm{mi}}_{\mathrm{Ms}}$ and $X^{\mathrm{fd}}_{\mathrm{Kf}}$. A computer program in Fortran IV calculated solutions with a convergence of ±0.0001 $X$ of the compositions of coexisting feldspar and mica crystalline solutions. At a given isobar, solutions were obtained at a number of different temperatures. Two isobaric sections will be discussed in some detail.

Isobaric phase relations in the system $KAlSi_3O_8$–$NaAlSi_3O_8$–$Al_2O_3$–$SiO_2$–$H_2O$ may be projected from $H_2O$, $Al_2SiO_5$, and $SiO_2$ onto the $T$-$X$ plane, where $X$ refers to the atomic fraction K/(K + Na) in the crystalline solutions. Such an isobaric section conveniently displays the following features of the phase equilibria: (a) the feldspar and mica solvi; (b) the divariant mica-feldspar transition loop; and (c) polymorphic transitions of $Al_2SiO_5$.

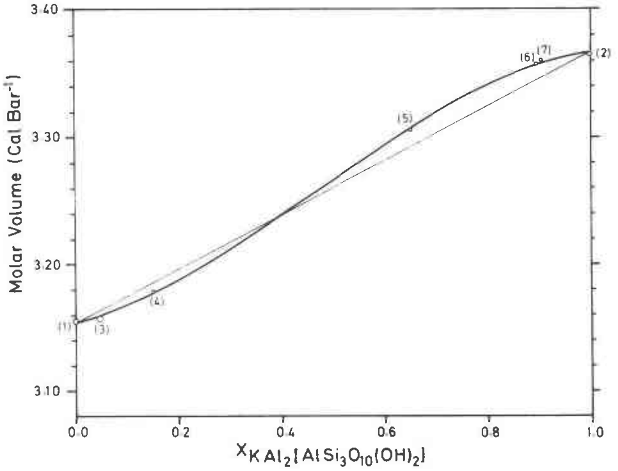

FIG. 2. Molar volume of the muscovite-paragonite crystalline solution. Numbers 1 and 2 refer to synthetic $2M_1$ paragonite and muscovite respectively; the remaining numbers correspond to various natural crystalline solutions listed in Table 3. The size of the data points indicate the estimated uncertainties.

TABLE 4. Compositions of Coexisting Feldspars and Micas in the 4 kbar $T$-$X_K$ Section

| P kbar | T°C | $X^{fd}_{Kf}$* | $X^{mi}_{Ms}$* | Stable $Al_2SiO_5$ polymorph |
|---|---|---|---|---|
| 4 | 575 | 0.0129 | 0.0468 | andalusite |
| 4 | 580 | 0.0259 | 0.8132 | andalusite |
| 4 | 590 | 0.0328 | 0.8496 | andalusite |
| 4 | 600 | 0.0416 | 0.8738 | andalusite |
| 4 | 610 | 0.0535 | 0.8918 | andalusite |
| 4 | 620 | 0.0702 | 0.9060 | andalusite |
| 4 | 630 | 0.0972 | 0.9179 | andalusite |
| 4 | 635 | 0.1197 | 0.9232 | andalusite |
| 4 | 640 | 0.6611 | 0.9326 | andalusite |
| 4 | 645 | 0.7527 | 0.9480 | andalusite |
| 4 | 650 | 0.8242 | 0.9630 | andalusite |
| 4 | 660 | 0.9466 | 0.9896 | andalusite |

*In every case, the input data converged to a tolerance of 0.0001 $X_K$.

Additional information concerning this section:

i) paragonite + quartz ⇌ albite + andalusite + $H_2O$
570 ± 10°C at 4 kbar (Chatterjee, 1972)
ii) muscovite + quartz ⇌ K feldspar + andalusite + $H_2O$
665 ± 5°C at 4 kbar (Chatterjee and Johannes, 1974)
iii) andalusite ⇌ sillimanite
683°C at 4 kbar (Richardson et al., 1969)

Calculated compositions in the 4 kbar section are listed in Table 4. Unique solutions were obtained in each case. These compositions are plotted in Figure 3 as well as the stable portions of the feldspar and mica solvi and the andalusite-sillimanite transition. The feldspar solvus was obtained from Waldbaum and Thompson (1969, Table 1 and Eq. 3a). The mica solvus was calculated according to Equation (12) by Scatchard's method recently described by Luth and Fenn (1973).

The mica-feldspar transition loop shows two discontinuities. At about 578°C (bracketed between 575-580°C) the mica composition reaches the solvus. Also, there is a sharp change in the slope of the feldspar limb of the loop. These features reflect the reaction

$$\text{paragonite}_{ss} + \text{quartz}$$
$$\rightleftharpoons \text{albite}_{ss} + \text{muscovite}_{ss} + \text{andalusite} + H_2O \qquad (13)$$

The second discontinuity in the transition loop is observed near 638°C (bracketed between 635–640°C), where the feldspar composition reaches

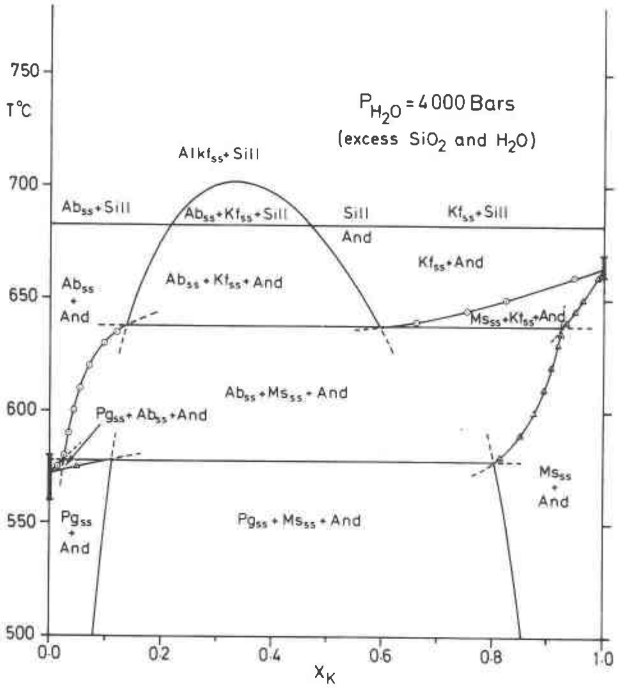

FIG. 3. Calculated phase relations of the pseudobinary join muscovite–paragonite at 4 kbar $P_{H_2O}$. Compositions of mica (triangles) and feldspar (circles) crystalline solutions are plotted as mole fractions $X_K$ (*cf* Table 4). Melting relations have been ignored.

the solvus. Again, there is a corresponding break in the slope of the mica limb of the transition loop. In this case, the reaction is

$$\text{muscovite}_{ss} + \text{albite}_{ss} + \text{quartz} \rightleftharpoons \text{K feldspar}_{ss} + \text{andalusite} + H_2O \qquad (14)$$

Calculated compositions in the 7 kbar isobaric section are listed in Table 5 and plotted in Figure 4. The details of this section are similar except that the mica-feldspar loop crosses the kyanite-sillimanite transition. Accordingly, one observes at this temperature an additional break in the slopes of the mica and feldspar limbs of the transition loop. It is interesting to note that the 705°C isotherm yielded two solutions. The second pair of compositions (see Table 5) would plot on the metastable extensions of the mica-feldspar transition loop, *i.e.*, within the stability field of the assemblage $Ab_{ss}$ + $Ms_{ss}$ + Sill (Fig. 4). This implies that in reality Reaction (14) takes place just above 705°C. In fact, wherever double solutions are obtained, the temperature bracket may be considered to be good to ±1°C.

In all, seven isobaric sections from 1 to 7 kbar were calculated. These data, listed in Table 6, may be used to construct a projection of the phase relations onto the $P_{H_2O} = P_{total}$ *vs* $T$ surface (Fig. 5). The univariant curves involving the mica end members are identical to those given in Figure 1. At elevated temperatures and pressures, some of the subsolidus equilibria of Figure 5 will be metastable with respect to hydrous silicate melts. In the two limiting systems, the invariant points $I_1$ and $I_2$ (Fig. 1) involving quartz, mica, feldspar, $Al_2SiO_5$, melt, and $H_2O$ are fairly well established (Chatterjee and Johannes, 1974; Chatterjee, 1974b). These invariant points lie on the minimum melting curves in the systems $SiO_2$–$KAlSi_3O_8$–$Al_2O_3$–$H_2O$ and $SiO_2$–$NaAlSi_3O_8$–$Al_2O_3$–$H_2O$, respectively, which are about 5–10°C lower than the minimum melting curves in the corresponding systems without $Al_2O_3$. On this basis, it is estimated that the minimum melting curve in the quinary system $SiO_2$–$KAlSi_3O_8$–$NaAlSi_3O_8$–$Al_2O_3$–$H_2O$ is also 5–10°C lower than in the system without $Al_2O_3$ given by Merrill, Robertson, and Wyllie (1970). Reaction (13) will terminate at a pressure somewhat below invariant point $I_2$ and Reaction (14)

TABLE 5. Compositions of Coexisting Feldspars and Micas in the 7 kbar $T$-$X_K$ Section

| P kbar | T°C | $X^{fd*}_{Kf}$ | $X^{mi*}_{Ms}$ | Stable $Al_2SiO_5$ polymorph |
|---|---|---|---|---|
| 7 | 635 | 0.0107 | 0.0447 | kyanite |
| 7 | 640 | 0.0253 | 0.1296 | kyanite |
| 7 | 645 | 0.0334 | 0.8134 | kyanite |
| 7 | 650 | 0.0369 | 0.8338 | kyanite |
| 7 | 660 | 0.0453 | 0.8618 | kyanite |
| 7 | 670 | 0.0561 | 0.8815 | kyanite |
| 7 | 675 | 0.0627 | 0.8895 | kyanite |
| 7 | 680 | 0.0705 | 0.8966 | kyanite |
| 7 | 685 | 0.0771 | 0.9001 | sillimanite |
| 7 | 690 | 0.0893 | 0.9072 | sillimanite |
| 7 | 695 | 0.1054 | 0.9138 | sillimanite |
| 7 | 700 | 0.1287 | 0.9197 | sillimanite |
| 7 | 705 | 0.1742 | 0.9254 | sillimanite |
| 7 | 705 | 0.5029 | 0.9249** | sillimanite |
| 7 | 710 | 0.6491 | 0.9374 | sillimanite |
| 7 | 715 | 0.7293 | 0.9504 | sillimanite |
| 7 | 720 | 0.7940 | 0.9627 | sillimanite |
| 7 | 730 | 0.9049 | 0.9841 | sillimanite |
| 7 | 735 | 0.9565 | 0.9932 | sillimanite |

*In each case, the input converged to a tolerance of 0.0001 $X_K$.

**This pair of compositions represents metastable equilibrium with respect to the former pair at 705°C and 7 kbar. See discussion in text.

Additional information concerning this section:

i) paragonite + quartz ⇌ albite + kyanite + $H_2O$
630 ± 10°C at 7 kbar (Chatterjee, 1972)

ii) muscovite + quartz ⇌ K feldspar + sillimanite + $H_2O$
This reaction is metastable at 7 kbar due to melting at 6.3 kbar (Chatterjee and Johannes, 1974). Extrapolation to 7 kbar gives a temperature of about 740°C.

iii) Kyanite ⇌ sillimanite
684°C at 7 kbar (Richardson et al., 1969)

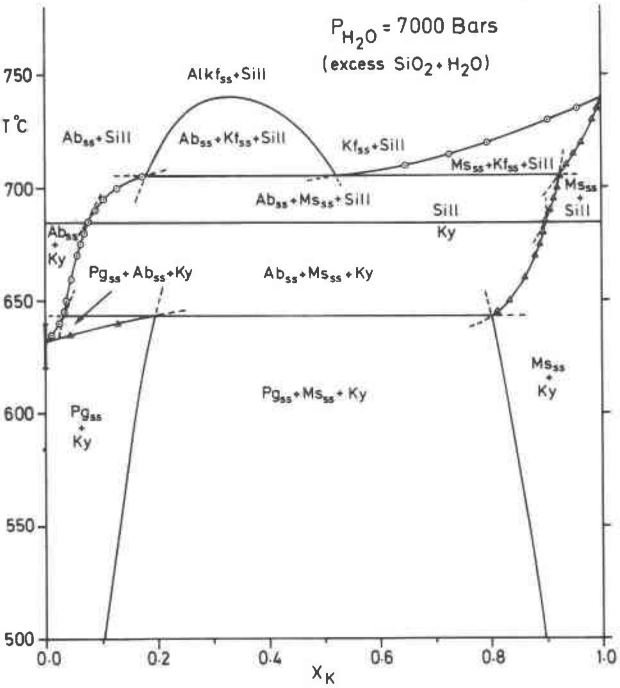

FIG. 4. Calculated phase relations of the pseudobinary join muscovite–paragonite at 7 kbar $P_{H_2O}$. Compositions of mica (triangles) and feldspar (circles) crystalline solutions are plotted as mole fractions $X_K$ (*cf* Table 5). Melting relations have been ignored.

will terminate at its intersection with the minimum melting curve in the quinary system, at approximately 635°C and 4 kbar $P_{H_2O}$.

## Geological Applications

There are two main applications of the phase relations shown in Figure 5.

1. The univariant reactions (13) and (14) may be used as boundaries of $P_{H_2O}$-$T$ conditions for suitable mineral assemblages.
2. The compositions of coexisting mica and feldspar crystalline solutions may be used as an indicator of $P_{H_2O}$-$T$ conditions.

Geological applications are, of course, dependent upon the degree of approximation of natural assemblages by the model system. Thus in many high-grade pelitic rocks, oligoclase is present rather than an alkali feldspar and the dioctahedral micas may show several different substitutions, as previously discussed. Bearing these restrictions in mind, a few natural occurrences will be considered.

1. The assemblage paragonite–sillimanite–quartz has not been recorded in nature (Chatterjee, 1972). Experimental work is in accord with this observation. The substitution of K increases the thermal stability of the assemblage quartz-paragonite$_{ss}$ by only a few degrees; the univariant curve of Reaction (13) does not cross the stability field of sillimanite. Thus, quartz-sillimanite-paragonite$_{ss}$ are not compatible under any condition (even less so if $P_{H_2O} < P_{total}$). Coupled substitutions like Ca + Al $\leftrightharpoons$ Na + Si or (Mg, $Fe^{2+}$) + Si $\leftrightharpoons$ Al + Al in the mica structure would further reduce the thermal stability of paragonite. Two substitutions which conceivably might raise the thermal stability of paragonite are Al $\leftrightharpoons$ $Fe^{3+}$ and (OH) $\leftrightharpoons$ F; however, no experimental data are yet available on their effects. On the other hand, paragonite$_{ss}$ has been observed to react with quartz to yield kyanite plus albite$_{ss}$ (Purtscheller, Hoernes, and Brown, 1972; Hoernes, 1973, p. 98).
2. High-grade pelitic metamorphic rocks are characterized by the stabilization of the assemblage K feldspar + sillimanite at the so-called "second" sillimanite isograd due to Reaction (14). In relatively K-rich rocks, muscovite$_{ss}$ remains stable for approximately another 30°C before the muscovite end member decomposes according to Reaction (2). Thus the assemblage quartz-muscovite$_{ss}$–K feldspar$_{ss}$–sillimanite (or andalusite) is stable over a temperature range of approximately 30°C, causing the "smearing out" of the second sillimanite isograd reported in some areas (Evans and Guidotti, 1966; Guidotti, 1970). Both muscovite$_{ss}$ and K feldspar$_{ss}$ become progressively enriched in K with

TABLE 6. Calculated Temperature Brackets of Reactions (13) and (14)

| P kbar | Reaction (13) with andalusite | Reaction (14) with andalusite |
|---|---|---|
| 1 | 490 - 495 °C | 550 - 555 °C |
| 2 | 520 - 525 °C | 580 - 585 °C |
| 3 | 550 - 555 °C | 610 ± 1* °C |
| 4 | 575 - 580 °C | 635 - 640 °C |
| 5 | 600 - 605 °C | metastable |
| | Reaction (13) with kyanite | Reaction (14) with sillimanite |
| 5 | metastable | 660 - 665 °C |
| 6 | 620 - 625 °C | 680 - 685 °C |
| 7 | 640 - 645 °C | 705 ± 1* °C |

*In these cases, two solutions were obtained, the implication of which is discussed in the text.

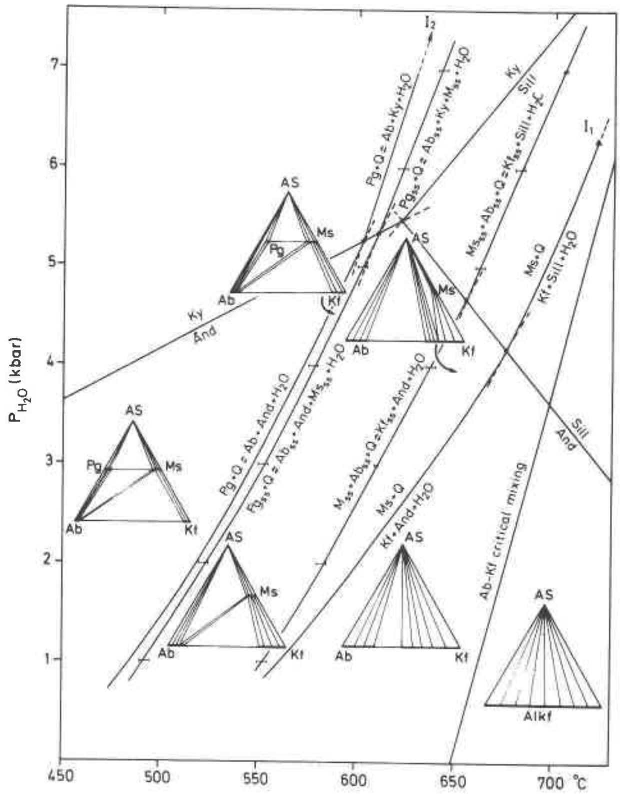

FIG. 5. Various equilibria in the system $KAlSi_3O_8$–$NaAlSi_3O_8$–$Al_2O_3$–$SiO_2$–$H_2O$, in part reproduced from Figure 1. In addition, two calculated reactions are shown, as well as the high albite–sanidine critical curve from Waldbaum and Thompson (1969).

The compatibility triangles illustrate phase relations as projections from $H_2O$ and $SiO_2$. Melting relations have been ignored. Invaniant point $I_2$ shown in Figure 1 is off scale in Figure 5.

increasing temperature. Phase equilibria in the model system are consistent with these field observations.

3. If $P_{H_2O} = P_{total}$, Reaction (14) will terminate within the andalusite field in an invariant point involving melt as an additional phase. Therefore, the assemblage K feldspar–sillimanite–quartz common in high-grade pelitic metamorphic rocks can form under subsolidus conditions only if $P_{H_2O}$ is less then $P_{total}$. This is in agreement with other phase equilibria. For example, Froese (1973) concluded that the assemblage quartz–K feldspar–sillimanite–biotite–garnet also reflects conditions of $P_{H_2O} < P_{total}$.

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