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Synthetic muscovite solid solutions in the system K_2O-Al_2O_3-SiO_2-H_2O

Philip E. Rosenberg
Department of Geology, Washington State University, Pullman, Washington 99164-2812, U.S.A.

Abstract

Muscovite solid solutions coexisting with sanidine or mullite, quartz, and fluid have been synthesized in the system K_2O-Al_2O_3-SiO_2-H_2O between 500 and 700°C at 2 kbar from gels of muscovite composition + water and from pyrophyllite or kaolinite and quartz + KOH solutions of varying concentration. Characterization of muscovite is based on X-ray diffractometry and analytical electron microscopy. Structural formulas have been calculated, assuming 12 oxygens per unit cell, by assigning sufficient H^+ so that Al^{3+} would complete the tetrahedrally coordinated sites and fill ⅔ of the octahedrally coordinated ones.

Gel muscovites (1M) are slightly alumina rich and K deficient with respect to end-member muscovite, apparently because of the crystallization of small amounts of metastable sanidine; they have the largest basal spacings observed (d_{005} = 2.010–2.012 Å). Muscovites (1M) coexisting with sanidine and quartz are silica rich and K deficient and have smaller basal spacings (d_{005} = 2.005–2.007 Å). Silica-rich, K-deficient $2M_1$ muscovites synthesized with mullite and quartz have the smallest basal spacings (d_{0010} = 2.002–2.005 Å) and nearly constant chemical composition. Basal spacing varies with $[Si/(Si + {}^{IV}Al)]$ and to a lesser extent with particle size.

Compositional variations can be accounted for by the substitution $Si^{4+} = Al^{3+} + X^+$, where X^+ is K^+ or H^+; small excesses of H^+ have been inferred in a few samples. Silica-rich, K-deficient muscovites, $[K_{1-x}Al_2(Si_{3+x}Al_{1-x})O_{10}(OH)_2]$, represent solid solution toward pyrophyllite, whereas the reverse substitution characterizes gel muscovites. Experiments with compositions higher and lower in K suggest a stable range of muscovite-pyrophyllite solid solutions terminating with the composition $K_{0.8}Al_2(Si_{3.2}Al_{0.8})O_{10}(OH)_2$. These solid solutions occur in nature as discrete micaceous phases and as components of mixed-layer (mixed-phase) illites.

Introduction

Muscovite solid solutions in the system K_2O-Al_2O_3-SiO_2-H_2O have long been suspected, based on studies published a decade or more ago by Munoz (1968), Eugster et al. (1972), Velde (1973), and Rosenberg (1973). Analysis of submicroscopic synthetic crystals was not possible in these studies and, therefore, muscovite compositions were inferred from basal spacing and data derived from bulk chemical analyses.

Munoz (1968) reported that stoichiometric muscovite compositions prepared as oxide mixtures, kaolinite + KOH solutions, and gels yielded small amounts of sanidine in addition to muscovite and cautioned that withdrawal of sanidine from muscovite bulk compositions may result in the crystallization of nonstoichiometric muscovite. Since few quantitative data were given by Munoz (1968), an experimental investigation of muscovite solid solutions in the system was initiated (Rosenberg, 1973) in an effort to determine the nature and extent of these solid solutions. The substitution $Si^{4+} = Al^{3+} + X^+$, where X^+ is H^+ or K^+, was proposed, but a detailed account was not published at that time because inferred compositional variations could not be verified.

In a study of synthetic muscovite-paragonite solid solutions, Eugster et al. (1972) inferred compositions mainly from basal spacing measurements, but special electron-microprobe techniques were used to analyze isolated mica particles much smaller than the diameter of the electron beam. An apparent K deficiency accompanied by a large scatter in basal spacings was observed in muscovites crystallized from Na-free compositions. However, the disaggregation of run products may not have been complete, and there was no way to be sure that a particle represented a single crystal rather than a crystal aggregate that might contain a second phase (Eugster et al., 1972).

Micaceous phases synthesized in the system K_2O-Al_2O_3-SiO_2-H_2O at 2 kbar by Velde (1973) in the temperature range 225–420°C and, in a more recent study, by Velde and Weir (1979) at approximately 320°C, were thought to be K deficient and richer in silica and water than end-member muscovite. In the latter study, solid solution was inferred to extend along the muscovite-pyrophyllite join

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from Ms$_{100}$ to Ms$_{80}$Py$_{20}$. A similar extent of solid solution was estimated qualitatively by Eberl and Hower (1977). Velde and Weir (1979) used alkali dissolution (Hashimoto and Jackson, 1960) to test for unreacted gel after experiments. Since run products were found to be almost insoluble by this method, it was concluded that crystallization was essentially complete and, therefore, that the bulk composition represented the approximate composition of muscovite, the only phase detected.

Although the approximate extent of muscovite solid solutions along the muscovite-pyrophyllite join has been established, these solid solutions have not been fully characterized, particularly at synthesis temperatures above 500°C. Precise characterization is required in order to distinguish between muscovite and illite and to ascertain the relationship between them.

With the development of the analytical electron microscopy (AEM), it has become possible to analyze discrete submicroscopic crystals and, thus, to determine the composition of muscovite solid solutions by direct methods. AEM analyses of 23 synthetic muscovites have been combined with X-ray data to provide a more complete assessment of the nature and stability of muscovite solid solutions in the system K_2O-Al_2O_3-SiO_2-H_2O than is available to date (Rosenberg, 1984).

PROCEDURES

Starting materials (Table 1) for most of the experiments were prepared as gels (Hamilton and Henderson, 1968) of muscovite composition or as mixtures of pyrophyllite composiiton consisting of natural pyrophyllite (Glendon, Moore Co., North Carolina) or kaolinite (API #9, Mesa Alta, New Mexico) plus quartz (Minas Gerais, Brazil) to which KOH solutions of varying concentrations were added following the procedures of Velde (1965). The molarities of these solutions, which were prepared using reagent-grade KOH (Na_2O < 0.01 wt%), were determined precisely by flame photometry. Some experiments were also carried out with kaolinite plus KOH solutions and muscovite gels to which silica or gibbsite were added.

Conventional hydrothermal equipment and techniques were used throughout this investigation. Solid starting materials were sealed along with water or KOH solutions (solid/liquid ratio ~5/1) into Au capsules and subjected to temperatures between 500 and 700°C at 2 kbar for periods of 1 to 10 weeks. Solutions were carefully weighed into Au capsules that were cooled during welding to minimize losses. After quenching, run products were identified by X-ray powder diffractometry and by optical microscopy.

Basal spacings of synthetic muscovite were determined by measurement of the X-ray reflection at approximately 45° 2θ Cu$K\alpha$ [1M (005) or 2M$_1$ (0010)] against an annealed internal standard, CdF_2, which has a reflection (220) conveniently located at 47.748° 2θ Cu$K\alpha$ (French, 1970). The muscovite (060, $\bar{3}31$) X-ray reflection at approximately 62° 2θ Cu$K\alpha$ was measured against the CdF_2 reflection ($\bar{3}11$) at 56.666° 2θ Cu$K\alpha$ (French, 1970) X-ray d spacings were obtained by averaging two or more measurements (scan rate, ¼° per minute) for each sample and are known to within 0.0002 Å (005) or (0010) and 0.0001 Å (060, $\bar{3}31$). The duration of experiments was increased until basal spacing appeared to have attained a steady state.

TABLE 1. Experimental data

Run no.*	Temp. (°C)	Time (d)	Starting composition (mol%)			Products
			Al_2O_3	SiO_2	K_2O	
Starting materials: Pyrophyllite (or kaolinite + quartz) + KOH solutions						
2085P	700	23	19.1	76.1	4.8	Muscovite + sanidine + quartz
2029P	650	19	18.9	75.6	5.5	
2028K			18.0	72.2	9.8	
2046P	600	31	19.4	77.5	3.2	
1989K		7	17.9	71.7	10.4	
2041K		31	18.6	74.1	7.3	
2077P	550	30	19.4	77.4	3.3	
2001K	500	39	18.3	73.2	8.6	
2070P	650	18	19.9	79.2	1.0	Muscovite + mullite + quartz
2067K		18	19.8	79.3	0.9	
2066K			19.7	78.8	1.6	
2048P	600	31	19.8	79.3	0.9	
2043K			19.4	77.7	2.9	
2044K			19.8	79.1	1.2	
2076K	550	30	19.8	79.3	0.9	
1983K		21	19.8	79.3	0.9	
Starting matierals: Kaolinite + KOH solutions						
2025	650	19	31.2	62.4	6.4	Muscovite + quartz
1999	500	39	30.5	60.9	8.6	
1964	600	21	33.1	66.2	0.7	Muscovite + mullite + quartz
Starting materials: Muscovite gel						
1867	600	72	30.0	60.0	10.0	Muscovite + sanidine**
1873		35				
1911	550	46				
1883	500	63				
Starting materials: Muscovite gel + silica						
2032	650	19	21.1	71.9	7.0	Muscovite + quartz + sanidine**
1952	550	60				
Starting materials: Muscovite gel + gibbsite						
2027	650	19	39.8	51.6	8.6	Muscovite + corundum
1953	550	60				

* P, pyrophyllite starting material; K, kaolinite + quartz starting materials.

** Sanidine present in minor amounts; detected by optical microscopy but not by X-ray diffractometry.

Identification of muscovite polymorphs was difficult because of interference caused by coexisting phases and because of the weakness of diagnostic X-ray reflections. However, the polymorphic forms of most synthetic muscovites are known with reasonable certainty based on the identification of at least two diagnostic X-ray reflections (Velde, 1965).

Partial analyses of muscovite crystals were obtained using a Phillips EM400T analytical electron microscope (AEM) in the transmission mode and an EDAX energy-dispersive analysis system that permits quantitative determination of elemental ratios (Champness et al., 1982). Thin isolated muscovite crystals (thickness <0.1 μm, estimated by transparency under TEM) were easily resolved and analyzed at magnifications of 16 000 and 22 000 ×. Analyzed crystals remained stable and were virtually unchanged after repeated exposure to the beam. Muscovite compositions are based on averages of 10–27, 60-s, random-point analyses. The presence of MgO, CaO, TiO_2, and Fe_2O_3 in trace amounts, derived from the natural starting materials, has been neglected. Relative percentages of Al_2O_3, SiO_2, and K_2O were calculated from count-rate data using conversion factors based on analyses of mineral standards (Champness et al., 1982). Atomic proportions were calculated assuming 12 oxygen atoms

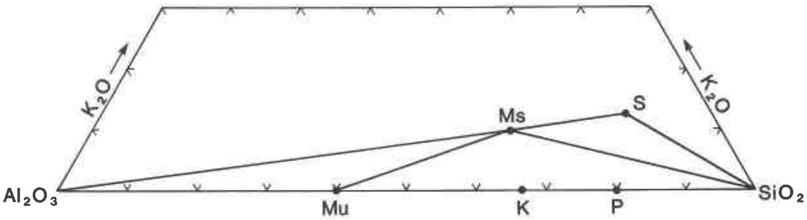

Fig. 1. Chemographic relations in the system K_2O-Al_2O_3-SiO_2 projected from H_2O. Starting compositions expressed in this system given in Table 1. Ms, Muscovite; Mu, mullite; S, Sanidine; K, Kaolinite; P, pyrophyllite.

per unit cell; the number of protons was selected so that sufficient Al would be available to complete the tetrahedral site and to fill ⅔ of the octahedrally coordinated sites in muscovite.

RESULTS

Synthesis of assemblages

Experimental data are summarized in Table 1. Starting compositions were calculated from the weights of solid mixtures and solutions used in each experiment. Excess water was present in all experiments. Four solid-phase assemblages were synthesized (Fig. 1).

1. Muscovite + sanidine + quartz. This assemblage was synthesized from pyrophyllite bulk compositions (pyrophyllite or kaolinite + quartz mixtures) to which K was added as KOH solutions in amounts approaching that in stoichiometric muscovite and also from a mixture of muscovite gel and 25 wt% silica. Kaolinite with similar amounts of K, added as KOH solutions, yielded the assemblage muscovite + quartz with little or no sanidine.

2. Muscovite + mullite + quartz. This assemblage was synthesized from the same pyrophyllite bulk compositions or kaolinite to which smaller amounts of K were added as KOH solutions.

3. Muscovite with minor amounts of sanidine. Muscovite gels were used to synthesize this assemblage. Sanidine was not detected by X-ray diffractometry but was observed under the polarizing microscope. The sanidine often appeared corroded, particularly in the products of the longer experiments, suggesting metastable early crystallization.

4. Muscovite + corundum. A mixture of muscovite gel and 25 wt% alumina in the form of gibbsite yielded this assemblage.

The electron microscope revealed idiomorphic platelets generally similar in size and shape to those shown in scanning-electron micrographs by Chatterjee and Johannes (1974). In general, many smaller (1–2 μm in diameter), thinner (~0.01 μm), imperfectly formed crystals were produced from starting compositions high in K, whereas some larger (5–10 μm in diameter), thicker (~0.1 μm), well-formed crystals were synthesized from starting compositions low in K. All mineral assemblages crystallized from starting compositions containing pyrophyllite are distinctly coarser grained than those synthesized from other materials. Many muscovite crystals in these assemblages are close to 10 μm in diameter and >0.1 μm in thickness.

X-ray data

X-ray measurements for the synthetic muscovites are given in Table 2. The 1M polymorph was synthesized from bulk compositions with stoichiometric or near-stoichiometric amounts of K (except sample 2027, which contains subordinate amounts of the $2M_1$ polymorph); the $2M_1$ polymorph predominates in muscovites synthesized from bulk compositions low in K. Basal spacings (Table 2) are the largest in muscovites synthesized from stoichiometric gels, somewhat smaller in sanidine-rich assemblages, and still smaller in mullite-bearing assemblages (Table 1).

Basal spacings (d_{005}) of the 1M muscovites synthesized between 500 and 700°C are shown in Figure 2. Two groups of 1M muscovites can be distinguished on the basis of their d_{005} values: (1) muscovites synthesized from stoichiometric gels (Fig. 2, filled circles) and (2) muscovites synthesized from mineral mixtures (both kaolinite and pyrophyllite bulk composition) and KOH solutions (Fig. 2, open triangles and hexagons). However, after experiments of short duration, d_{005} values of all 1M muscovites lie within the gel muscovite group (Fig. 2, filled triangle; no. 1989, Tables 1 and 2). Basal spacings of muscovites synthesized from silica-rich mineral mixtures and KOH solutions become smaller during the course of the experiments, suggesting that muscovites with larger basal spacings may be metastable. The addition of excess silica to muscovite gels (Fig. 2, circles with X; Tables 1 and 2,

TABLE 2. X-ray data

Run no.:	2029	2028	2046	1989	2041	2077	2001	2070	2067	2066	2048	2043
d_{005} or d_{0010}	2.0065	2.0068	2.0056	2.0101	2.0059	2.0058	2.0051	2.0028	2.0038	2.0052	2.0015	2.0042
$d_{(060,331)}$	1.4992	1.4982	n.m.	1.4987	1.4973	n.m.	1.4985	n.m.	n.m.	1.4986	n.m.	n.m.
Polymorph	?	1 M	1 M	1 M	1 M	1 M	?	2M (1M)	2M (1M)	2 M	?	?

Note: Uncertainties for d_{005} and d_{0010} values and for $d_{(060,331)}$ are ±0.0002 and 0.0001, respectively. n.m. = not measurable. Polymorphs shown in parentheses are subordinate.

nos. 1952 and 2032) results in muscovite d_{005} values comparable to those obtained for muscovite crystallized in the same assemblage (muscovite + sanidine + quartz) from different starting materials having similar bulk compositions, whereas the presence of excess alumina (Fig. 2, open circles; Tables 1 and 2, nos. 1953 and 2027) has no apparent effect on d_{005} of gel muscovites.

The d_{005} spacings of 1M muscovites (Fig. 2, filled squares) synthesized from stoichiometric mineral mixtures by Eugster et al. (1972) are quite similar to those prepared from similar starting materials in this study. A 1M muscovite synthesized from a gel at 603°C and 2 kbar by Velde and Weir (1979) lies within the group of gel muscovites of the present study (Fig. 2, open square).

The predominantly $2M_1$ muscovites synthesized from highly K-deficient compositions, resulting in the presence of mullite rather than sanidine, have d_{0010} spacings ranging from 2.0052 to 2.0010 Å (Tables 1 and 2). The maximum value lies close to the minimum for 1M muscovite (Fig. 2). This d_{0010} spacing (2.005 Å), which corresponds to a $2M_1$ muscovite synthesized at 650°C (Tables 1 and 2, no. 2066) in the present study, was also reported for a $2M_1$ muscovite crystallized at 650°C by Chatterjee and Johannes (1974).

The (060, $\bar{3}31$) X-ray reflection was carefully measured wherever possible (Table 2), but most of the values obtained are almost constant and differences are not clearly related to other variables.

Muscovite analyses

Chemical compositions and atomic proportions (Table 3) are based on averages of 10 to 27 point analyses for seven elements. Compositional variability from point to point in any sample is due both to real variations, which appear to be quite significant on a submicrometer scale, and to random error. Limits of error (1σ) for the 17 AEM point analyses of muscovite in sample 2029 are typical of all samples: MgO, 0.42 ± 0.50; Al_2O_3, 37.90 ± 1.49; SiO_2, 49.15 ± 2.26; K_2O, 10.04 ± 0.92; CaO, 0.52 ± 0.40; TiO_2, 0.08 ± 0.19; Fe_2O_3, 1.91 ± 1.21 wt%.

The analytical results (Table 3) reveal that muscovites crystallized in assemblages with sanidine and quartz or mullite and quartz (Table 1) are silica rich and K deficient with respect to end-member muscovite. This is true even for samples with starting compositions having stoichiometric muscovite $Al_2O_3:SiO_2$ ratios (e.g., no. 1964, Tables 1 and 3). Muscovites synthesized from stoichiometric gels and gels with excess alumina (Table 1) are slightly silica and K deficient.

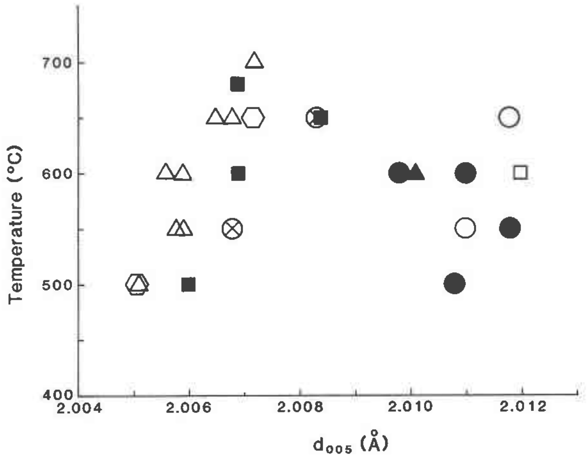

Fig. 2. Variation of muscovite (1M) d_{005} (Å) with temperature. Stoichiometric muscovite gels, open circles; muscovite gel + silica, circles with X; muscovite gel + gibbsite, filled circles. Pyrophyllite or kaolinite + quartz + KOH solutions, triangles (open, longer-duration; filled short-duration expeiments). Kaolinite + KOH solutions, hexagons. Eugster et al. (1972), filled squares; Velde and Weir (1979), open square.

Although the small variations in proton-content inferred for most of the muscovites crystallized from mineral mixtures and KOH solutions may be due to analytical error, several muscovites synthesized from gels (nos. 2027, 1867, 1873, 1953, Tables 1 and 3) appear to contain significant H^+ excesses, probably in the form of H_3O^+ or $(OH)^-$.

Relationship between chemical composition and basal spacings

The relationships between muscovite composition and basal spacings inferred previously (Rosenberg, 1973) have been confirmed for the 1M muscovites synthesized in this study. An approximately linear relationship exists between Si/(Si + ^{IV}Al) and d_{005} (Fig. 3). Neglecting sample 1989, the product of a short-term experiment (Fig. 3, filled triangle) and assuming a linear model, which may not provide the best possible fit to the data, regression analysis yields a correlation coefficient of −0.80, implying that almost ⅔ of the observed variation can be accounted for by this relationship. The series of partially ordered 1M polytypes synthesized by Velde and Weir (1979, Table 5) show a very similar, though slightly displaced linear relationship between Si/(Si + ^{IV}Al) and d_{005}. Values of Si/(Si + ^{IV}Al) greater than 0.75 represent silica-

TABLE 2.—*Continued*

2044	2076	1983	2025	1999	1964	2027	1867	1873	1953	1911	1883	2032	1952
2.0032	2.0039	2.0021	2.0072	2.0051	2.0021	2.0118	2.0098	2.0110	2.0110	2.0118	2.0108	2.0083	2.0068
n.m.	n.m.	n.m.	1.4983	1.4976	n.m.	n.m.	1.4987	1.4992	1.4995	1.4999	1.4981	n.m.	1.4969
?	?	2 M	1 M	1M (2M)	2 M	1M (2M)	1 M	1 M	?	1 M	1 M	1M (2M)	?

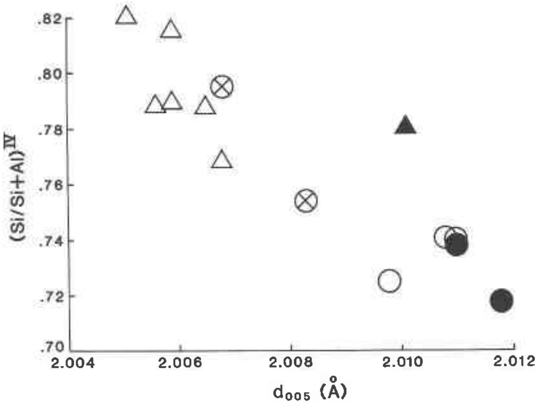

Fig. 3. Variation of Si/(Si + ^{IV}Al) with muscovite (1M) d_{005} values. Symbols as in Figure 2.

rich muscovites, whereas values below 0.75 are alumina-rich relative to the end-member composition.

No relationship between chemical composition and basal spacings has been found for 2M$_1$ (or predominantly 2M$_1$) muscovites. Since all 2M$_1$ muscovites synthesized in this study are associated with mullite + quartz assemblages, it is probable that other muscovites of unknown polymorphism in similar assemblages are also predominantly the 2M$_1$ variety. Despite a wide range in d_{0010} values, the Si/(Si + ^{IV}Al) ratios of these muscovites are nearly constant, varying between 0.785 and 0.803. The number of K$^+$ ions per half-cell varies from 0.82 to 0.71 (Table 3). Thus, the synthetic 2M$_1$ muscovites, like their 1M counterparts, are silica rich and K deficient.

Observed variations in d_{0010} values are accounted for by differences in grain size rather than differences in chemical composition. Apparent enlargement of mica d_{005} and d_{0010} values is observed in crystals less than 10 layers thick (Ross, 1968). Larger, thicker 2M$_1$ muscovite crystals with smaller basal (d_{0010}) spacings were synthesized from starting compositions containing pyrophyllite and/or having relatively low K$^+$ content. For example, in samples 2048 and 2070, muscovite crystals with d_{0010} values of 2.0015 and 2.0028 Å, respectively (Table 2), have diameters up to 10 μm and appear to be relatively thick (>0.1 μm), as compared to sample 2066 in which muscovite crystals with a d_{0010} of 2.0052 Å (Table 2) average 1–2 μm in diameter and are much thinner (~0.01 μm). Since the molal volume of the 2M$_1$ polymorph is slightly smaller than the 1M polymorph (Blencoe, 1977), smaller basal spacings are to be expected for the 2M$_1$ polymorph. Therefore, the smallest d_{0010} value observed, 2.0015 Å (no. 2048, Table 2), probably represents the closest approach to the actual value for 2M$_1$ muscovite, whereas larger spacings may be artifacts due to the presence of large numbers of very thin platelets in most samples. Extrapolated to end-member composition, the basal spacings of 34 carefully analyzed natural, slightly alkali-deficient 2M$_1$ muscovites yield a value for d_{0010} of 2.0012 Å (Evans and Guidotti, 1966), which is in close accord with the value inferred from the present study.

DISCUSSION

Substitutions in synthetic muscovite

Assuming that ⅔ of the octahedral sites are occupied by Al^{3+}, tetrahedral charge due to variations in Si/(Si + ^{IV}Al) ratios in muscovite solid solutions must be balanced by substitutions involving K$^+$ and/or H$^+$. Thus, the muscovite-pyrophyllite join and synthetic muscovite solid solutions can be shown on a diagram with the proportion of tetrahedral Si^{4+} and the sum of H$^+$ and K$^+$ as coordinates (Fig. 4). Since these coordinates are not independent variables, Figure 4 serves only as an illustration of the extent of solid solution along the join.

Silica-rich, K-deficient, 1M muscovites (Fig. 4, open symbols) represent solid solution from end-member muscovite toward pyrophyllite. Muscovite compositions synthesized from gels (Fig. 4, filled circles) are K and Si deficient and H rich with respect to end-member muscovite. H$^+$ in excess of stoichiometric amounts may be present as H$_3$O$^+$ substituting for K$^+$ (Eugster et al., 1972) or as additional (OH)$^-$ (Forbes, 1972). Synthetic 2M$_1$ muscovites lie within the narrow range indicated by the heavy line. Muscovite compositions lie on the join because H$^+$ = K$^+$ substitutions are also taken into account in this diagram. However, a small amount of excess water appears to be present in one gel muscovite (Table 3, no. 1953) that lies above the join (Fig. 4). Excess water has also been observed in synthetic muscovites by Velde and Weir (1979).

The observed compositional variations in synthetic muscovite can be accounted for by the substitutions (1) Al^{3+} + K$^+$ = Si^{4+}, yielding muscovite-pyrophyllite solid solutions having the formula $K_{1-x}Al_2(Si_{3+x}Al_{1-x})O_{10}(OH)_2$; (2) Si^{4+} = Al^{3+} + H$^+$, leading to Si-deficient, OH-rich muscovites of the type $KAl_2(Si_{3-x}Al_{1+x})O_{10-x}(OH)_{2+x}$; (3) K$^+$ = H$^+$, yielding K-deficient, proton-rich muscovites in which H$^+$ in excess of the stoichiometric amounts may

TABLE 3. Muscovite compositions (mol%) and atomic proportions

Run no.:	2029	2028	2046	1989	2041	2077	2001	2070	2067	2066
Al_2O_3	28.69	29.45	28.72	28.84	27.19	28.43	26.99	28.27	28.49	27.78
SiO_2	63.09	62.02	63.17	62.37	64.56	63.72	64.90	63.51	63.28	64.21
K_2O	8.22	8.53	8.12	8.80	8.25	7.85	8.11	8.23	8.18	8.01
No. of analyses	17	15	11	10	12	12	13	13	13	12
Si/(Si + ^{IV}Al)	0.788	0.768	0.788	0.780	0.815	0.790	0.820	0.793	0.790	0.803
K$^+$	0.82	0.85	0.81	0.88	0.83	0.78	0.82	0.82	0.82	0.80
H$^+$	2.0	2.1	2.0	2.0	1.9	2.1	1.9	2.0	2.0	2.0

be present as H_3O^+ (Eugster et al., 1972) or as additional $(OH)^-$ (Forbes, 1972), resulting in the formulas $K_{1-x}(H_3O)_xAl_2(Si_3Al)O_{10}(OH)_2$ or $K_{1-x}Al_2(Si_3Al)O_{10-x}(OH)_{2+x}$, respectively.

Substitution 1 characterizes muscovites synthesized from mineral mixture + KOH solutions that yield the assemblage muscovite + sanidine or mullite + quartz and solution. Substitution 2 takes place in gel muscovites owing, in part, to the crystallization of metastable sanidine that effectively removes K^+ and Si^{4+} from the bulk composition and results in the departure of muscovite compositions from the muscovite-pyrophyllite join (Fig. 4). Substitution 3 appears to represent a degree of disequilibrium that also results in muscovite compositions that are displaced from the muscovite-pyrophyllite join.

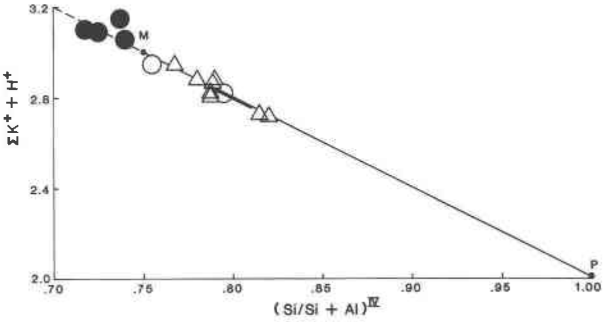

Fig. 4. Variation of Si/(Si + ^{IV}Al) with $\Sigma(K^+ + H^+)$ for synthetic muscovites. Gel muscovites, filled circles; gel muscovite + quartz, open circles. Mineral mixtures + KOH solutions, 1M muscovites, open triangles; $2M_1$ muscovite, heavy line. M, muscovite; P, pyrophyllite.

Muscovite-pyrophyllite solid solutions and their implications

The mole percentages of SiO_2 and K_2O in the starting compositions (Table 1) and in the muscovites synthesized from them (Table 3) are compared at 650, 600, and 550°C in Figures 5a, 5b, and 5c, respectively. Micaceous phases lying below the muscovite-pyrophyllite join are silica deficient and have excess protons, whereas those lying above the join contain excess silica and are proton deficient with respect to end-member muscovite.

Phase compositions synthesized from starting compositions having higher and lower SiO_2 and K_2O contents (Figs. 5a, 5b, 5c) approach the muscovite-pyrophyllite join, but some do not lie on it, suggesting that chemical equilibrium was not fully attained in these experiments. Crystallization of metastable sanidine from muscovite gels may be responsible for the synthesis of muscovite compositions that diverge from the join. In the absence of sanidine, these muscovite compositions would probably approach a Si-rich, K-deficient composition on the join similar to those synthesized by Velde and Weir (1979).

Assuming that stable phases lie along the join, a series of solid solutions from Ms_{100} to about $Ms_{80}Py_{20}$ may be inferred. A series of similar extent was proposed at lower temperatures (300–400°C) by Velde and Weir (1979). However, the interstratified "illite-smectite" phases synthesized by them from compositions with a pyrophyllite content greater than 20 mol% are apparently not stable at the higher temperatures of the present investigation. Highly K-deficient starting compositions yield the end-member solid solution $K_{0.8}Al_2(Si_{3.2}Al_{0.8})O_{10}(OH)_2$ $(Ms_{80}Py_{20})$; starting compositions having higher K contents than the end-member solid solution yield solid solutions of intermediate composition (Figs. 5a, 5b, 5c).

Synthetic compositions extending from muscovite toward pyrophyllite have X-ray diffraction patterns much like muscovite; they show no evidence of expansion on glycolation or contraction on heating and, thus, appear to represent single-phase solid solutions. A similar range of solid solutions exists in nature. Beaufort and Meunier (1983) reported hydrothermal micaceous phases that display a complete range of alkali-site occupancies from 0.80 to 1.0 calculated on the basis of 10O and 2OH.

Recent studies by Środoń et al. (1986) suggest that illite is composed of at least two kinds of layers, one of which has a composition approaching 1.0K calculated on the basis of 10O and 2OH. Furthermore, multiphase solubility has been observed in natural illites by Sass and Rosenberg (1984 and unpub. data). Assuming an R^{2+}-free stoichiometry, the inferred components of these illites include a mica-like phase having (on the same basis) 0.90K. Solubility studies by Kittrick (1984) also suggest that multiple phases exist in illite, but it is not possible to determine phase compositions from these data. Thus, it appears that illite is a multiphase material containing as one of its phases a high-K, mica-like mineral that is K deficient and Si rich relative to muscovite. The nonexpandable, $2M_1$ clay mineral with an alkali-site occupancy of $0.87(K,Na)_{0.87}$ per 10O and 2OH from the Kaube mine, Nara Prefecture, Japan, is the best natural example of a mica-like illite end member (Środoń and Eberl, 1984).

Neglecting the small proportion of R^{2+} cations in octahedral coordination in the natural materials, the mus-

Table 3.—*Continued*

2048	2043	2044	2076	1983	1964	2027	1867	1873	1953	1883	2032	1952
28.92	28.36	28.22	28.58	29.08	28.76	32.13	31.69	30.96	31.47	30.60	30.22	28.32
63.91	64.09	64.23	64.17	63.69	63.48	58.69	59.21	60.27	60.76	59.69	61.22	63.65
7.17	7.55	7.55	7.25	7.23	7.76	9.18	9.10	8.77	7.77	9.69	8.56	8.03
18	13	26	10	10	13	25	11	12	10	13	27	10
0.793	0.795	0.800	0.793	0.785	0.788	0.718	0.725	0.740	0.738	0.740	0.754	0.795
0.71	0.75	0.75	0.72	0.71	0.77	0.90	0.89	0.86	0.75	0.96	0.85	0.80
2.15	2.1	2.0	2.1	2.1	2.1	2.2	2.2	2.2	2.4	2.1	2.1	2.0

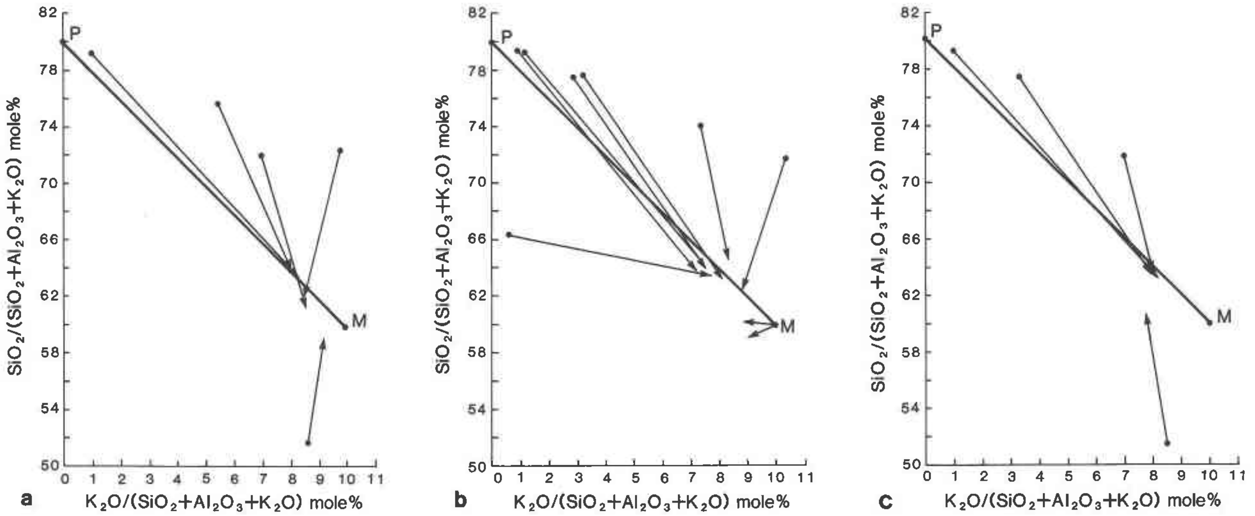

Fig. 5. Mole percentage of SiO_2 and K_2O in starting compositions (dots) and in corresponding synthetic muscovites (arrows). M, muscovite; P, pyrophyllite. (a) 650, (b) 600, (c) 550°C.

covite-pyrophyllite solid solutions synthesized in this study are represented in nature by discrete micaceous phases and, more commonly, by components of mixed-layer (mixed-phase) illites. These solid solutions form in nature as the end product of the diagenesis of smectite or directly by crystallization from hydrothermal solutions (Środoń and Eberl, 1984).

CONCLUSIONS

Muscovite solid solutions toward and away from pyrophyllite, due to substitutions of the type $Si^{4+} = Al^{3+} + H^+$ or K^+, are possible in muscovite. Al- and proton-rich solid solutions synthesized from stoichiometric gels appear to be metastable, whereas Si-rich and K-deficient compositions synthesized from mineral mixtures + KOH solutions appear to be stable under the conditions of these experiments.

At high temperatures (>300°C), muscovite-pyrophyllite solid solutions form a series that extends from end-member muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2(Ms_{100})$ to approximately $K_{0.8}Al_2(Si_{3.2}Al_{0.8})O_{10}(OH)_2(Ms_{80}Py_{20})$. These solid solutions are represented in nature by discrete micaceous minerals and, more commonly, by components of mixed-layer (mixed-phase) illites.

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