[AMERICAN JOURNAL OF SCIENCE, VOL. 263, DECEMBER 1965, P. 886-913]

PHENGITE MICAS: SYNTHESIS, STABILITY, AND NATURAL OCCURRENCE

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ABSTRACT. The solid solutions of the dioctahedral potassic micas have been investigated for two groups of micas—phengites and glauconitic celadonites. Natural phengites are found in metamorphic and igneous rocks, whereas glauconitic celadonites are minerals produced in low-grade hydrothermal or diagenetic deposits. Both the chemical composition and the geologic environment separate these two mineral groups.

Phengites are the products of a particular type of metamorphism involving low temperatures and high pressures ($\approx P_{H_2O}$). It is probable that phengites are quite common in many metamorphic rocks, particularly in areas in which the last stage of metamorphism is produced by high pressures.

INTRODUCTION

Dioctahedral potassic micas occur in nearly all types of geologic environments. Individual micas or groups of micas have been analyzed and discussed. but no useful method has been developed that enables one to relate the geologic occurrence and chemical composition. Most discussions thus far have been concerned with the chemical compositions of natural minerals (for example, Hendricks and Ross, 1941; Grim, 1953; Weaver, 1959; Ernst, 1963b) or properties and stabilities of synthetic end members in the various mica series (for example, Yoder and Eugster, 1955; Wise and Eugster, 1964). However, the general problem of composition and environment relations for the dioctahedral potassic micas has not yet been pieced together into a unified scheme.

A series of natural mica compositions has been established which appears to include most natural dioctahedral potassic micas, $K[(Al_2)Si_3AlO_{10}(OH)_2]$–$K[(R^{+2}R^{+3})Si_4O_{10}(OH)_2]$; this is the muscovite-celadonite series of Schaller (1950) and Foster (1956). Intermediate in composition between these two end members are the phengite micas (Michel, 1953; van der Plas. 1959; Ernst, 1963b). The extent of continuous solid solution in this series defines the range of compositions given the name phengite. It is well known that muscovites form in igneous and high-grade metamorphic environments and that natural glauconites and celadonites form in sedimentary and hydrothermal alteration environments. The compositional and environmental link between the two mineral groups is the phengite group, which occurs most commonly in metamorphic rocks. A greater knowledge of these minerals would clarify the geologic significance of dioctahedral potassic micas.

It should be noted that a previous study of the MgAl celadonite–muscovite system has been published by Crowley and Roy (1964). The work closely parallels the pertinent portions of the present study. However, results from the two studies are very different, for example, Crowley and Roy (1964, p. 352, fig. 3) and this paper (fig. AI). A discussion of the experimental technique and method of analysis used by Crowley and Roy has previously been given (Velde, 1965). The present author believes his data are closer to a true picture

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of the phase relations in question, mainly as a result of much longer experiments and the successful reversal of many reactions. Determinations made in this manner should yield a much closer approach to mineral stabilities.

EXPERIMENTAL TECHNIQUE

Hydrothermal runs were made in standard cold-seal externally heated "rod bomb" type pressure vessels with the pressure maintained by static water pressures and temperatures maintained by resistance furnaces. A single experiment was performed at 10 kb in apparatus described by Yoder (1950). A detailed description of all the experimental equipment used can be found elsewhere (Velde, 1965). However, preparation and identification procedures do warrant a detailed description.

The starting materials used in this study were a natural mica (table 2, no. 30), synthetic minerals, mixtures of oxides made by the gel method (Roy, 1956), and mixtures of kaolinite and metal oxides. Bulk compositions for synthetic micas were prepared by the following two methods:

1. Natural kaolinite (<0.5 weight percent impurities) and pure metal oxides (<0.002 weight percent impurities) were dried for at least 12 hours at 120°C to a constant weight. The components were combined as molar proportions and ground under alcohol for at least 1 hour in a mechanical mortar. Variations from the intended molar compositions were considered to be less than 1 percent.

2. Homogeneous gels (identified as non-crystalline by optical and X-ray diffraction observations) were prepared in the following manner: Pure metals (Mg, 99.995 percent; Fe sponge, 99.999 percent pure) dissolved in nitric acid or metal nitrates ($Al[NO_3]_3 \cdot nH_2O$ with less than 0.03 weight percent impurities, KNO_3 with less than 0.013 weight percent impurities) were added in solution to an ammonia stabilized silica gel (less than 1.0 weight percent impurities). The solution was dehydrated at 100°C and then fired at about 1000°C for 1 hour. The resulting gel was used as an anhydrous starting material. Each metal nitrate solution was standardized by firing a representative sample to constant weight before the solutions were mixed. The metal oxide content of the nitrate solutions was determined to have a probable error of ± 1.0 weight percent. Volumetric errors due to combining the various solutions were less than 1 percent. Resultant deviations from the intended compositions were much smaller than could be detected through identification of the synthesized phases.

All solid materials were combined with distilled water in welded $Ag_{70}Pd_{30}$ capsules. The water, injected into the capsule with a microsyringe, was always present in excess of that amount necessary for any chemical reaction in the charge. The pressure inside the capsule during the runs was maintained by the excess H_2O and could be considered as $P_{H_2O} = P_{\text{total external}}$. The activity of the H_2O was subject to variations owing to solubility of silicates and non-ideal behavior of the fluid itself.

The problem of the oxidation state of the initial charge and the oxygen fugacity during the run is of importance (see Eugster and Wones, 1962, for a full discussion). The iron in the starting materials was essentially all Fe^{+3}

unless the charge was to be used in making a ferrous mica. In such a case, the ferric iron was reduced to ferrous by heating the gel to 900°C under a stream of hydrogen. No red-brown color remained after treatment. When an Fe^{+2}–Fe^{+3} gel was desired half of the charge was reduced, and the two portions were mixed by grinding. Thus each charge had a bulk composition very close to that of the mica to be synthesized.

During the runs the oxygen fugacity in the bomb (actually in the H_2O which transmitted the pressure) could be expected to influence the Fe^{+3}/Fe^{+2} ratios of the charge inside the capsule. The metal of the pressure vessel, Stellite, acts as a buffer which controls the f_{O_2} in the fluid pressure medium. As f_{H_2} is directly related to f_{O_2} in an aqueous system, the f_{H_2} is also controlled by the bomb buffering. Hydrogen migrating through the $Ag_{70}Pd_{30}$ run capsule allows the charge to come to equilibrium with the f_{H_2} induced by the bomb (see Eugster and Wones, 1962, for a complete discussion). The bomb buffer f_{O_2} is near that of the nickel–nickel oxide f_{O_2} for aqueous systems. However, the experiments were often made at such low temperatures that the f_{O_2} inside the capsule during the run was probably near that of the initial f_{O_2} of the charge, that is, little hydrogen moved through the $Ag_{70}Pd_{30}$ capsule wall. Some run products exhibited vari-colored zoning, which was interpreted as stability of the outer portion of the charge at or near the nickel–nickel oxide f_{O_2} of the bomb resulting from the *P-T* conditions of the experiment. The effect of externally imposed f_{O_2} was not explored in this study owing to experimental difficulties of low temperatures and long experimental durations. However, it is believed that the main trends of mica stabilities and solid solutions observed in this study are valid as generalizations. Justification is found in the rather close correspondence between synthetic and natural phengite compositions.

Identification of the products of each run was made by optical and X-ray diffraction methods, a combination of both methods being essential for the identification of all run products. In solid solution series such as those studied, the compositions of products are not vastly different from one another. Failure of the charge to form a homogeneous product could be undetected if X-ray identification was the only method used, since amounts of up to 15 percent of a poorly crystallized phase can be undetected in X-ray diffraction evaluations. Hence optical identification is necessary to determine the presence of small amounts of one phase in multiphase aggregates. X-ray diffraction is the only method available for the observation of structural parameters. Therefore, both optical and X-ray identification were considered necessary to determine the stability and solid solutions of the mica systems.

No attempts have been made to identify specifically the anhydrous breakdown products of the micas synthesized. The reasons for such omission are as follows. Little has been established about the X-ray and optical parameters of intermediate iron-aluminum potassium feldspars, feldspars which occur as dehydration products of these micas. Also, the extent of aluminum substitution in biotites, which also occur as products of thermal decomposition of micas, has not been established. Before complete identification of these phases could be made a detailed study of the feldspar and aluminum biotite series would be necessary. It is believed that such a study is not warranted in direct connection with an investigation of the dioctahedral mica series. Identifications have thus been limited to the general classification of feldspar and biotite as determined by X-ray diffraction. These products are listed in the tables and figures simply as sanidine, quartz, and two micas (muscovite-phengite and biotite). Identification of the feldspar and quartz was made by optical examination or by X-ray diffraction reflections in the 20° to 36° 2θ region using Cu$K\alpha$ radiation.

The existence of two micas was determined by the (060) reflections between 59° and 63° 2θ. Biotite has a peak near 60°, and muscovite-phengite between 61° and 62° 2θ. In cases where this separation of mica phases was not possible the products are listed in the table simply as "micas".

It is known from other experimental studies of iron-containing micas (Wones, 1963; Wise and Eugster, 1964) that the physical properties of the mica will vary depending upon the f_{O_2} conditions of a run. Other factors which result in variations of the physical properties of mica products are run duration and pressure (Wise, 1961; Crowley and Roy, 1964). Considering the experimental method used, it was judged as unrealistic to determine the physical properties of the mica products with greater precision (especially optical parameters and cell dimensions). Certainly, had they been determined, the applicability to natural micas would be questionable since the variations found for one mica composition and due to variations of experimental parameters would certainly overlap variations that could be attributed solely to compositional differences. Mean indices of refraction for various micas and (060) cell spacings are listed in the tables because they served as a guide to variations between minerals in a series synthesized under essentially the same conditions. These parameters could not be extrapolated to determine the compositions of natural micas.

EXPERIMENTAL RESULTS

The compositions and stabilities of the micas that were synthesized are given in the tables of run data (tables A to F). Accompanying the tables are the results shown in graphical form (figs. A to E). Only those runs that establish the thermal stability of each mica series are given. Runs in each series investigated were made for compositions and temperatures at about 0.2 mole fraction and about 75°C intervals (250° to 550°C at 2 and 4.5 kb pressure). The muscovite-MgAl celadonite solid solution was determined at 10 kb by one run. Data from the eight solid solution series investigated are compiled in figure 1. Volumes defined by the lined areas represent compositions that produced one mica phase. The stabilities of muscovite and MgFe^{+3} celadonite were taken from Velde (1964) and Wise and Eugster (1964), respectively.

The upper stability of the phengites as well as the extent of solid solution was influenced by pressure in several mica series but most notably in the muscovite-MgAl celadonite series. The *P-T-x* relations for this solid solution are shown in figure 2. Obviously, increasing the water pressure increases the

EXPLANATION OF DATA TABLES A TO F

Composition: Celadonite-muscovite solid solutions are listed by the amount of celadonite and muscovite components present. The celadonite component is denoted by the ions present in the octahedral positions.

Starting materials:

Syn mica = single-phase mica produced by synthesis from the bulk composition stated.
Oxide mix = metal oxides plus kaolinite mixed by grinding in an agate mortar for 2 hours.
Syn 2 micas + san + Q = products of thermal reaction of the mica.
Gel = silicate gel made from nitrate solution of the metal ion components.

Products:

ML = mixed layer mica-montmorillonoids.
2 micas = dioctahedral + trioctahedral (phengite + biotite) as particularly identified.
San = K feldspar (± Fe^{+3}).
Q = quartz.
1Md, 1M, 2M = mica polymorphs identified by X-ray criteria of Yoder and Eugster (1955) only listed for single phase dioctahedral mica.

TABLE A

$K[(MgAl)Si_4O_{10}(OH)_2]$–muscovite

Composition	d_{060} ± 0.005 Å	Nm ± 0.003
$(MgAl)_{0.2}$–$musc_{0.8}$	1.503	1.572
$(MgAl)_{0.3}$–$musc_{0.7}$	1.505	1.570
$(MgAl)_{0.4}$–$musc_{0.6}$	1.506	—
$(MgAl)_{0.8}$–$musc_{0.2}$	1.501	—

Composition	Pressure, kb	Temp, °C	Time, days	Starting material	Product
$(MgAl)_{0.1}$–$musc_{0.9}$	2	650	10	Gel	Mica + san + Q
$(MgAl)_{0.1}$–$musc_{0.9}$	2	550	9	Gel	1M + 2M mica
$(MgAl)_{0.2}$–$musc_{0.8}$	2	375	10	Kaol + oxides	1M mica
$(MgAl)_{0.2}$–$musc_{0.8}$	2	375	61	Syn 2 micas + san + Q	1M + 2M mica
$(MgAl)_{0.2}$–$musc_{0.8}$	2	390	27	Syn mica	Mica + san + Q
$(MgAl)_{0.2}$–$musc_{0.8}$	2	400	14	Kaol + oxides	Mica + san + Q
$(MgAl)_{0.3}$–$musc_{0.7}$	2	250	55	Syn 2 micas + san + Q	2 micas + san + Q
$(MgAl)_{1.0}$–celad	2	270	90	Gel	Mont + san + Q
$(MgAl)_{1.0}$–celad	2	400	31	Gel	2 micas + san + Q
$(MgAl)_{0.1}$–$musc_{0.9}$	4.5	575	30	Gel	1M + 2M mica
$(MgAl)_{0.1}$–$musc_{0.9}$	4.5	600	11	Gel	Mica + san + Q
$(MgAl)_{0.2}$–$musc_{0.8}$	4.5	540	23	Kaol + oxides	1M + 2M mica
$(MgAl)_{0.2}$–$musc_{0.8}$	4.5	500	21	Kaol + oxides	1M + 2M mica
$(MgAl)_{0.2}$–$musc_{0.8}$	4.5	600	11	Kaol + oxides	Mica + san + Q
$(MgAl)_{0.3}$–$musc_{0.7}$	4.5	450	12	Gel	1M + 2M mica
$(MgAl)_{0.3}$–$musc_{0.7}$	4.5	440	31	Syn 2 micas + san + Q	1M + 2M mica
$(MgAl)_{0.3}$–$musc_{0.7}$	4.5	450	31	Gel	2 micas + san + Q
$(MgAl)_{0.3}$–$musc_{0.7}$	4.5	480	30	Syn mica	2 micas + san + Q
$(MgAl)_{0.4}$–$musc_{0.6}$	4.5	350	11	Kaol + oxides	Mica + san + Q
$(MgAl)_{0.4}$–$musc_{0.6}$	4.5	350	91	Syn mica	Mica + san + Q
$(MgAl)_{0.4}$–$musc_{0.6}$	4.5	300	8	Kaol + oxides	1Md mica
$(MgAl)_{0.8}$–$musc_{0.2}$	10	350	0.3	Gel	1M mica

Reaction interval $(MgAl)_{0.2}$–$musc_{0.8}$, 2 kb, 375° to 390°C . . . musc, 2 kb, 685° to 700°C
$(MgAl)_{0.3}$–$musc_{0.7}$, 4.5 kb, 440° to 480°C . . . musc, 4.5 kb, 700° to 720°C

EXPLANATION (Cont.)

Mica = one mica phase identified optically and by X-ray diffraction.
Mica + san + Q = only one mica identified, but product is not single phase.
Mont = montmorillonoid.
He = hematite.
? = doubtful identification of phase.

Pressure: Total measured external pressure with capsule containing the run.

Temperature: ±6°C.

Time: Duration of run in days.

The mean index of refraction is listed for the synthesized micas. Index is ±0.003. Also (060) structural measurements are given as determined by X-ray diffraction using CuKα filtered radiation.

The reaction interval that determines the upper stability of the dioctahedral micas is listed where the reaction was observed in both directions (equilibrium was observed). Muscovite data are from Velde (1964).

TABLE B

$K[(MgFe^{+3})Si_4O_{10}(OH)_2]$–muscovite

Composition	d_{060} ± 0.005 Å	Nm ± 0.003
$(MgFe^{+3})_{0.2}$–musc$_{0.8}$	1.508	1.578
$(MgFe^{+3})_{0.3}$–musc$_{0.7}$	1.512	1.583
$(MgFe^{+3})_{1.0}$–celad*	1.515	1.620

Composition	Pressure, kb	Temp, °C	Time, days	Starting material	Product
$(MgFe)_{0.2}$–musc$_{0.8}$	2	400	10	Oxide mix	1M mica
$(MgFe)_{0.2}$–musc$_{0.8}$	2	470	28	Syn mica	2 micas + san + Q
$(MgFe)_{0.2}$–musc$_{0.8}$	2	500	72	Syn mica	2 micas + san + Q
$(MgFe)_{0.2}$–musc$_{0.8}$	2	440	35	Syn 2 micas + san + Q	1M + 2M mica
$(MgFe^{+3})_{0.25}$–musc$_{0.75}$	2	450	20	Oxide mix	2 micas + san + Q
$(MgFe^{+3})_{0.25}$–musc$_{0.75}$	2	400	20	Oxide mix	1Md mica
$(MgFe^{+3})_{0.3}$–musc$_{0.7}$	2	375	18	Oxide mix	2 micas + san + Q
$(MgFe^{+3})_{0.3}$–musc$_{0.7}$	2	400	31	Oxide mix	2 micas + san + Q
$(MgFe^{+3})_{0.8}$–musc$_{0.2}$	2	350	30	Oxide mix	ML + san + Q
$(MgFe^{+3})_{0.9}$–musc$_{0.1}$	2	300	31	Oxide mix	ML + san + Q
$(MgFe^{+3})_{0.9}$–musc$_{0.1}$	2	350	31	Oxide mix	2 micas + san + Q
$(MgFe^{+3})_{0.2}$–musc$_{0.8}$	4.5	320	10	Gel	1M mica
$(MgFe^{+3})_{0.2}$–musc$_{0.8}$	4.5	500	11	Gel	Mica + san + Q
$(MgFe^{+3})_{0.3}$–musc$_{0.7}$	4.5	400	31	Gel	1M + 2M mica
$(MgFe^{+3})_{0.3}$–musc$_{0.7}$	4.5	420	30	Syn mica	1M + 2M mica
$(MgFe^{+3})_{0.3}$–musc$_{0.7}$	4.5	450	27	Syn mica	Mica + san + Q
$(MgFe^{+3})_{0.4}$–musc$_{0.6}$	4.5	330	31	Gel	Mica + san + Q
$(MgFe^{+3})_{0.9}$–musc$_{0.1}$	4.5	400	11	Gel	Mica + san + Q
$(MgFe^{+3})_{1.0}$–celad	4.5	400	30	Gel	1Md mica
$(MgFe^{+3})_{1.0}$–celad	4.5	450	80	Syn mica	Mica + san + Q
$(MgFe^{+3})_{1.0}$–celad	4.5	425	27	Syn 2 micas + san + Q	Mica

* Wise and Eugster (1964) for NNO buffer.

Reaction interval $MgFe^{+3}$ celad, 2 kb, 400° to 420°C (Wise and Eugster, 1964).
$MgFe^{+3}$ celad, 4.5 kb, 425° to 450°C
$(MgFe^{+3})_{0.2}$–musc$_{0.8}$, 2 kb, 440° to 470°C . . . musc, 2 kb, 685° to 700°C

TABLE C

$K[(Mg_{1.0}Fe_{0.5}{}^{+3}Al_{0.5})Si_4O_{10}(OH)_2]$–muscovite

Composition	$d_{060} \pm 0.005$ Å	Nm ± 0.003
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.2}$–musc$_{0.8}$	1.509	1.578

Composition	Pressure, kb	Temp, °C	Time, days	Starting material	Product
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.2}$-musc$_{0.8}$	2	300	30	Gel	ML + mica
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.2}$–musc$_{0.8}$	2	370	30	Gel	Mica + san + Q
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.2}$–musc$_{0.8}$	2	440	30	Gel	Mica + san + Q
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{1.0}$–celad	2	300	31	Gel	Mica + san + Q
				No significant solid	solution at 2 kb
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.2}$–musc$_{0.8}$	4.5	375	31	Gel	Mica + san + Q
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.2}$–musc$_{0.8}$	4.5	330	31	Syn 2 micas + san + Q	Mica
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.2}$–musc$_{0.8}$	4.5	330	30	Gel	Mica
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.2}$–musc$_{0.8}$	4.5	300	30	Syn 2 micas + san + Q	Mica
$(MgFe_{0.5}{}^{+3}Al_{0.5})_{0.3}$–musc$_{0.7}$	4.5	300	30	Gel	2 micas + san + Q

Reaction interval musc, 4.5 kb, 700° to 720°C.

TABLE E

$K[(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+3}Fe_{0.5}{}^{+2})Si_4O_{10}(OH)_2]$–muscovite

Composition	$d_{000} \pm 0.005$ Å	Nm ± 0.003
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	1.503	1.573

Composition	Pressure, kb	Temp, °C	Time, days	Starting material	Product
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.4}$–musc$_{0.6}$	2	295	30	Gel	ML + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	2	295	30	Gel	Mica
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	2	375	31	Gel	2 micas + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	2	360	27	Syn mica	Mica + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	2	370	31	Syn 2 micas + san + Q	Mica + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	2	340	30	Syn 2 micas + san + Q	1M mica
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	2	340	31	Syn mica	1M mica
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{1.0}$–celad	2	300	31	Gel	Mica + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	4.5	300	30	Syn 2 micas + san + Q	Mica
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	4.5	295	30	Gel	1M + 2M mica
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	4.5	375	31	Syn mica	Mica + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	4.5	440	31	Syn mica	Mica + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$	4.5	370	30	Syn 2 micas + san + Q	Mica + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.4}$–musc$_{0.6}$	4.5	300	31	Gel	Mica + san + Q
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})$–celad	4.5	300	31	Gel	Mica + san + Q

Reaction interval $(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$, 2 kb, 340° to 360°C . . .
musc, 2 kb, 685° to 700°C
$(Mg_{0.5}Al_{0.5}Fe_{0.5}{}^{+2}Fe_{0.5}{}^{+3})_{0.2}$–musc$_{0.8}$, 4.5 kb, 300° to 370°C . . .
musc, 4.5 kb, 700° to 720°C

TABLE D

$K[(Fe_{0.5}^{+2}Mg_{0.5}Al)Si_4O_{10}(OH)_2]$–muscovite

Composition	d_{060} ± 0.005 Å	Nm ± 0.003
$(Mg_{0.5}Fe_{0.5}^{+2}Al_{1.0})_{0.3}$–musc$_{0.7}$	1.505	1.569, 1.576

Composition	Pressure, kb	Temp, °C	Time, days	Starting material	Product
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	2	300	30	Gel	1M mica
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	2	375	30	Gel	Mica + san + Q
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	2	340	31	Syn mica + san + Q	Mica
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	2	340	27	Syn mica + san + Q	Mica + san + Q
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	2	370	27	Syn mica	Mica + san + Q
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.5}$–musc$_{0.5}$	2	300	31	Syn mica	Mica + san + Q
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.5}$–musc$_{0.5}$	2	370	30	Syn mica	Mica + san + Q
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	4.5	300	32	Gel	Mica
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	4.5	370	30	Gel	1M + 2M mica
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	4.5	440	31	Gel	Mica + san + Q
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$	4.5	420	27	Syn mica	Mica + san + Q
$(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.5}$–musc$_{0.5}$	4.5	300	32	Gel	Mica + san + Q

Reaction interval $(Fe_{0.5}^{+2}Mg_{0.5}Al)_{0.3}$–musc$_{0.7}$, 2 kb, 300° to 340°C
musc, 2 kb, 685° to 700°C

TABLE F

$K[(Fe^{+2}Fe^{+3})Si_4O_{10}(OH)_2]$–muscovite

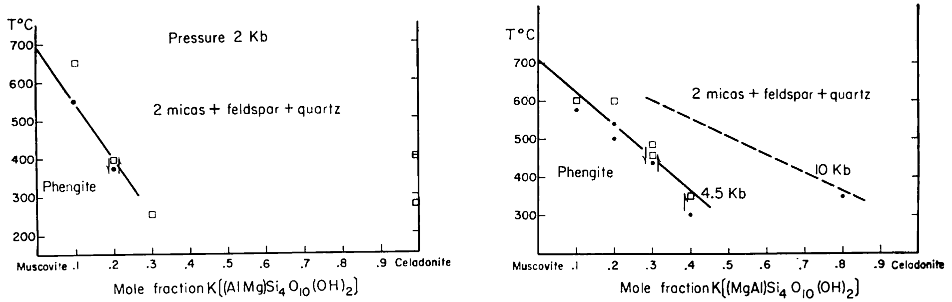
Composition	Pressure, kb	Temp, °C	Time, days	Starting material	Product
$(Fe^{+2}Fe^{+3})_{1.0}$–celad	2	350	50	Gel + oxides	ML + san + Q + He
$(Fe^{+2}Fe^{+3})_{0.25}$–musc$_{0.75}$	2	300	30	Kaol + oxides	ML + san + Q + He
$(Fe^{+2}Fe^{+3})_{0.25}$–musc$_{0.75}$	2	350	30	Kaol + oxides	ML + san + Q + He
$(Fe^{+2}Fe^{+3})_{0.25}$–musc$_{0.75}$	2	440	31	Kaol + oxides	2 micas + san + Q
$(Fe^{+2}Fe^{+3})_{0.75}$–musc$_{0.25}$	2	300	30	Kaol + oxides	ML + san + Q + He
$(Fe^{+2}Fe^{+3})_{0.75}$–musc$_{0.25}$	2	350	30	Kaol + oxides	ML + san + Q + He
$(Fe^{+2}Fe^{+3})_{0.75}$–musc$_{0.25}$	2	440	31	Kaol + oxides	2 micas + san + Q
					No apparent solid solution
$K[(Mg_{0.4}Fe_{0.6}^{+2}Fe_{1.0}^{+3})Si_4O_{10}(OH)_2]$–muscovite					
$(Mg_{0.4}Fe_{0.6}^{+2}Fe_{1.0}^{+3})_{0.88}$–musc$_{0.12}$	2	300	31	Gel	2 micas + san + Q
$(Mg_{0.4}Fe_{0.6}^{+2}Fe_{1.0}^{+3})_{0.88}$–musc$_{0.12}$	2	370	31	Gel	2 micas + san + Q
$(Mg_{0.4}Fe_{0.6}^{+2}Fe_{1.0}^{+3})_{0.88}$–musc$_{0.12}$	2	440	31	Gel	2 micas + san + Q
					No apparent solid solution
$K[(FeAl)Si_4O_{10}(OH)_2]$–muscovite					
$(FeAl)_{1.0}$–celad	2	350	40	Gel + oxides	Mica + Q
$(FeAl)_{0.2}$–musc$_{0.8}$	2	295	31	Gel	Mica + san + Q
$(FeAl)_{0.2}$–musc$_{0.8}$	2	440	30	Gel	Mica + san + Q
$(FeAl)_{0.2}$–musc$_{0.8}$	4.5	310	30	Gel	Mica + san + Q
$(FeAl)_{0.2}$–musc$_{0.8}$	4.5	400	32	Gel	Mica + san + Q
$(FeAl)_{0.2}$–musc$_{0.8}$	4.5	300	32	Syn 2 micas + san + Q	2 micas + san + Q
					No apparent solid solution

EXPLANATION OF FIGURES A to E

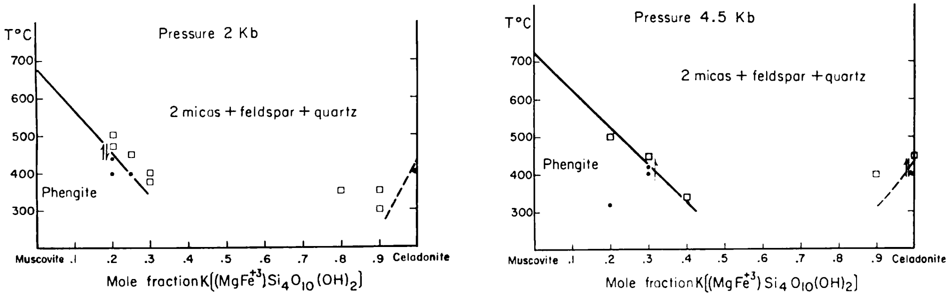
Diagrams represent the determined stability relations of phengite micas and their breakdown products, $P_{\text{total}} \cong P_{H_2O}$. Arrows represent the direction of the reaction when observed. In cases where only synthesis products were obtained, no arrow is indicated. Phengite products were considered as such when a run produced < 10 percent non-mica phases and the mica was homogeneous to X-ray and optical examination. Solid circles represent phengite products; squares represent two micas, feldspar, and quartz products or other phases. Lines representing field boundaries are drawn as a most reasonable fit to the reaction intervals observed by synthesis, breakdown, or reaction reversals.

The 10 kb curve in figure AII is based on a single synthesis run and hence is dashed.

Data for the reversed reaction muscovite $\rightleftarrows$ sanidine + corundum + water are from Velde (1965).



I. Fig. A. II.



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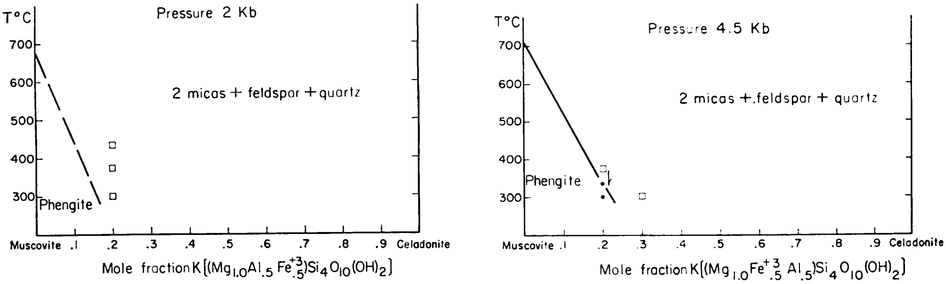
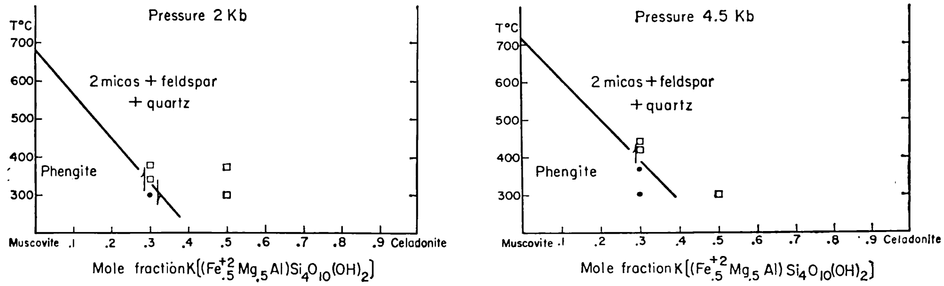
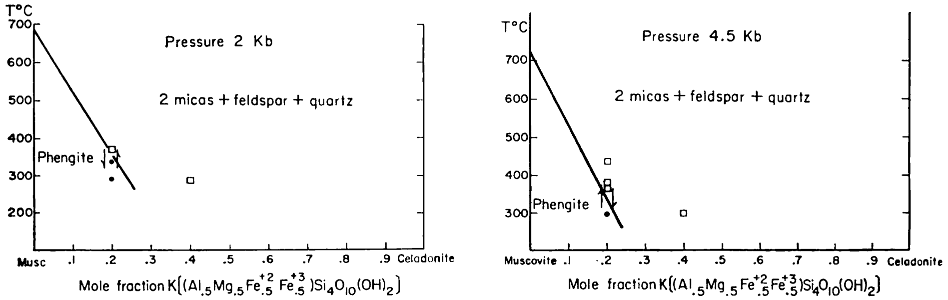


I. Fig. C. II.



I. Fig. D. II.



I. Fig. E. II.

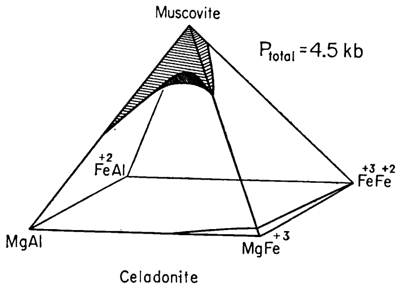


Fig. 1.

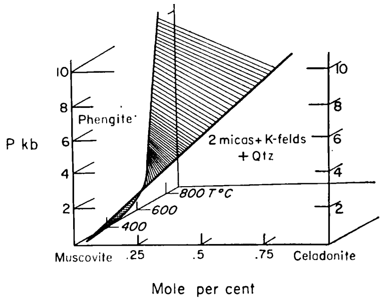


Fig. 2.

Fig. 1. Composite diagram representing the extent of solid solution in the muscovite-celadonite compositions found in this study at 4.5 kb and 300°C.

Fig. 2. *P-T-x* relationships on the muscovite-MgAl celadonite join. $P_{H_2O} \cong P_{total}$. Based on data in table A.

amount of solid solution. The volume to the left of the lined surface represents mica (phengite) stability. All data were collected for conditions where $P_{fluid} \cong P_{total}$.

The upper stability of a natural phengite was determined, using a mica from the Alps (analysis no. 30 in table 2) described by Michel (1953) (table 1). This mica is approximately one-third celadonite and two-thirds muscovite. The R^{+3} component of the celadonite is Al^{+3}, and R^{+2} is about equally divided between Fe^{+2} and Mg^{+2}.[1]

The stability of the natural phengite can be compared with the stability of a similar synthetic mica. The stability of synthetic micas in the $(Fe_{0.5}{}^{+2}Mg_{0.5}Al_{1.0})$ celadonite–muscovite series is given as an approximation to the natural phengite (fig. 3). The stability range of the natural mica is more closely defined for the 2 kb pressure than 4.5 kb. The reaction at the

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[1] A new value for K_2O was determined by M. D. Foster of the U. S. Geological Survey. The new values are K_2O, 11.00; CaO, 0.08; Na_2O, 0.00 weight percent.

TABLE 1

Natural phengite (no. 30, table 2)

Composition of phengite (natural)	Pressure, kb	Temp, °C	Time, days	Starting material	Product
$(Mg_{0.2}Fe_{0.1}Al_{0.3})_{0.3}$–musc$_{0.7}$	2	300	30	Natural mica	Mica
$(Mg_{0.2}Fe_{0.1}Al_{0.3})_{0.3}$–musc$_{0.7}$	2	350	31	Natural mica	Mica + san + Q
$(Mg_{0.2}Fe_{0.1}Al_{0.3})_{0.3}$–musc$_{0.7}$	2	340	53	Syn 2 micas + san + Q	Mica
$(Mg_{0.2}Fe_{0.1}Al_{0.3})_{0.3}$–musc$_{0.7}$	4.5	350	30	Natural mica	Mica
$(Mg_{0.2}Fe_{0.1}Al_{0.3})_{0.3}$–musc$_{0.7}$	4.5	400	30	Natural mica	Mica
$(Mg_{0.2}Fe_{0.1}Al_{0.3})_{0.3}$–musc$_{0.7}$	4.5	420	31	Natural mica	Mica + san?
$(Mg_{0.2}Fe_{0.1}Al_{0.3})_{0.3}$–musc$_{0.7}$	4.5	450	53	Natural mica	2 micas + san + Q

Reaction interval at 2 kb, 340° to 350°C.
Reaction interval at 4.5 kb, 400° to 450°C.
Abbreviations as in tables A to F.

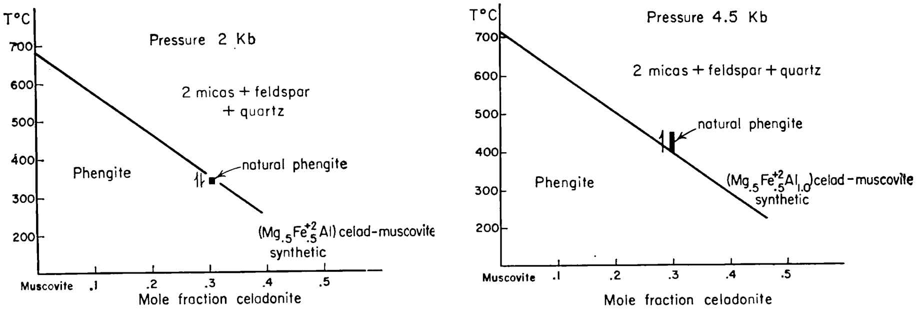
former pressure was reversed by using thermal breakdown products of the natural phengite as starting material.

It can be concluded that the experimental procedure is valid for stabilities of synthetic and natural micas of the same composition. Thus, extrapolation of the experimental conditions to describe the natural conditions under which phengites form is warranted. It must be remembered that the water pressure in the experimental systems was approximately equal to total pressure, a condition that may or may not be fulfilled in natural systems. However, the data can be considered as representing maximum stability limits for the phengitic micas (see Yoder, 1955, and Thompson, 1955, for a discussion of the significance of the water pressure as related to total pressure in natural petrologic systems).

Mica polymorphism, most recently discussed by Radoslovich (1960), was considered in the present synthetic mica study. Conclusions are very tentative because of the slow nature of mica crystallization. A detailed study of synthetic muscovite polymorph stabilities (Velde, 1965) revealed that starting materials can greatly affect the nature of the products of an experiment. Therefore, no conclusions drawn from the present investigation can be considered as definitive. Reactions were very slow, run durations were 3 months at the most, and equilibrium was attained only very slowly for the upper stability of the micas. Only polymorphs produced near the mica upper stability limit are considered as being an approach to the stable polymorph for a given mica composition.

Natural micas which have compositions near those studied here occur in three polymorphs—1M, $2M_1$, and 3T (Yoder and Eugster, 1955). In general, the low-temperature minerals such as natural glauconites and celadonites have a 1M polymorph. Phengites have most commonly a $2M_1$ polymorph, as does muscovite, but occasionally a 3T polymorph appears (reviewed by Ernst, 1963b).

From the experimental data it appears that celadonite micas have 1Md or 1M polymorphs. This is reasonable because natural celadonites and the closely related glauconites are found to have only these two polymorphs (Hower, 1961; Wise and Eugster, 1964). The synthetic phengites appear to



A. Fig. 3. B.

Fig. 3. Comparison of the upper stability of a natural phengite (Michel, 1953) with a similar synthetic mica. The synthetic micas are in the series muscovite-$Mg_{0.5}Fe_{0.5}^{+2}Al$ celadonite. $P_{H_2O} \cong P_{total}$.

have $2M_1$ polymorphs near the muscovite composition, but at compositions distant from that of muscovite (which can only be formed at 10 kb) only the 1M polymorph is present. It is possible that a compositional-pressure relation for the stable polymorph exists; however, insufficient data are available from the experimental work to make a definitive statement. The presence of the 3T polymorph in natural micas is quite puzzling, since 3T micas were never encountered in this experimental investigation. It is interesting to note that the natural phengite used in the study had a 3T polymorph (as described by Yoder and Eugster, 1955). This polymorph persisted as long as the mica was stable.

Crowley and Roy (1964) synthesized 3T, $2M_1$, and 1M micas in the muscovite–MgAl celadonite series. According to these authors all three forms were stable. The discrepancy between their work and the present study is unexplained.

The following tentative summary is made concerning mica polymorphs: The glauconite-celadonite micas have 1M polymorphs, whereas the muscovite–phengite micas can have 2M or 3T polymorphs. It is questionable whether synthetic phengite 1M polymorphs represent stable structures. This conclusion is drawn by analogy with similar studies of muscovite polymorphism in a synthetic system (Velde, 1965).

MICA STRUCTURAL FORMULA

One problem arising in the study of phengitic micas is the scarcity of reliable analyses in the literature. In chemical analyses of mica minerals the calculated electrostatic charge relations of the ions and the total numbers of ions present should meet certain requirements consistent with the mica structure. The ionic charge and site occupancy relationships disqualify most mica analyses in the literature from serious consideration. Using the present knowledge of the mica structure, still largely based on the work of Pauling (1930), the following criteria have been established here for selecting dioctahedral mica analyses.

A mica formula calculated from a chemical analysis of metal oxides on the basis of twelve O^{-2} ions must show the following relations between the seven cations present per formula unit:

1. Interlayer ions must have a total charge of 1.00 ± 0.10.
2. Occupancy of the octahedrally coordinated sites cannot exceed 2.00 ± 0.10 ions.
3. The total charge of cations in octahedral and tetrahedral coordination must be 21.00 ± 0.10.
4. The total charge imbalance of the structure (negative charge of structure = 22) cannot exceed ±0.10, that is, the sum of the interlayer, octahedral, and tetrahedral ion charges = 22.00 ± 0.10.

The above conditions define true dioctahedral micas. It is probable that in many natural minerals the calculated charge will vary or ion site occupancy will differ significantly from the above requirements, though the formula will still represent a valid mineral species; such minerals cannot be considered true dioctahedral micas by the author's criteria. Thirty-three analyses that fulfill the above criteria are listed in table 2.

COMPOSITIONS OF IMPORTANT DIOCTAHEDRAL MICAS

Because mica compositions can vary by means of several different ionic substitutions, end members must be chosen as a frame of reference for the dioctahedral phengite micas. The following arguments eliminate many less important mica types or less important ionic substitution series.

A broad division of micas can be made by considering the numerical occupancy of the layer of cations that are octahedrally coordinated with oxygen and hydroxyl anions. Charge relations of the normal hydrated mica structure, $(OH)_2$, allow a total of +6 ionic charges per cell, whereas structural restrictions allow positions for three ions. Micas usually have $2R^{+3}$ or $3R^{+2}$ ions present in these positions. Micas with approximately three octahedrally coordinated ions form the trioctahedral biotite series. The dioctahedral micas considered in the present paper always have very nearly two ions per unit cell (Foster, 1956, 1960). Deviations from this number are small and infrequent except in cases where lithium is present. Since lithium is a rather infrequent constituent of micas (Foster, 1960) and lithium-bearing micas are rather rare in nature, they will not be considered here. Occupancy of the octahedral ion position by two ions per formula establishes requirement (2), as stated above.

The general approach to selecting the important features of the dioctahedral micas is based upon structural considerations and prevalent compositions of natural micas. In this respect, the significance of interlayer ion occupancy can be treated by a consideration of the structural importance of the ionic species that could be present.

The interlayer ion position can be occupied by one M^+ ion or $1/2M^{+2}$ ion. The most important interlayer cations are potassium and sodium, which are present in the end members—muscovite, $K[(Al_2)Si_3AlO_{10}(OH)_2]$, and paragonite, $Na[(Al_2)Si_3AlO_{10}(OH)_2]$. Partial solid solution between the two "end members" of this series is often reported in the literature, but complete solid solution has not yet been established (Eugster and Yoder, 1955; Zen and Albee, 1964; Iiyama, 1964). A structural study of a coexisting muscovite–paragonite mineral pair gives insight into the relative importance of interlayer ion occupancy with respect to the influence it exerts on the whole mica structure. Burnham and Radoslovich (1964) found that the structures of the muscovite–paragonite minerals (Ms_{65} and Ms_{15}) were very similar in dimension and symmetry. Certainly little distortion was noted that would cause a unique geometry in any portion of the structure. Thus, a particular interlayer ion occupancy (either K or Na) would not be expected to influence the species of ion that would occupy any other structural site. Na and K can then be considered as interchangeable as far as any effect on the structure is concerned. The temperature dependence of the Na-K substitution is indicated in studies by Eugster and Yoder (1955) and Iiyama (1964). Zen and Albee (1964) have discussed the relations found in natural minerals. The mica structure influences the abundance of interlayer ion species and not vice versa.

In summary, two generalizations can be made about the micas studied here. They can be assumed to be dioctahedral, 2.00 ± 0.10 ions per formula, and the nature of occupancy of the interlayer position will have little influence upon the rest of the structure. Two types of natural micas that fit the above

Table 2

Mica analyses

No.	Octahedral				Interlayer			Σ oct. ion	Σ oct. chg.	Σ inter-layer chg.	Σ tet. chg.	Total chg.
	Fe^{+3}	Fe^{+2}	Mg^{+2}	Ti^{+4}	K^{+}	Na^{+}	Ca^{+2}					
1	0.26	0.03	0.26	0.02	0.86	0.04	0.02	2.03	0.21	0.94	0.73	-0.00
2	0.28	0.03	0.26	0.05	0.83	0.03	0.02	2.03	0.18	0.90	0.70	+0.02
3	0.10	0.04	0.55	0.03	0.80	0.12	0.01	2.08	0.37	0.94	0.62	-0.03
4	0.05	0.09	0.50	0.01	0.87	0.07	0.02	2.08	0.42	1.00	0.61	-0.03
5	0.13	0.09	0.08	0.02	0.89	0.09	0.01	2.04	0.15	1.00	0.93	-0.08
6	—	—	0.01	—	0.85	0.08	—	0.96	0.01	0.93	0.96	-0.04
7	0.19	0.15	0.29	0.06	0.74	0.13	0.08	1.99	0.40	1.06	0.60	+0.06
8	0.38	0.05	0.36	0.04	0.91	0.05	0.03	2.01	0.36	1.02	0.64	+0.02
9	0.06	0.20	0.27	0.02	0.78	0.08	0.04	2.04	0.37	0.94	0.58	+0.01
10	0.19	0.13	0.29	0.03	0.78	0.09	0.03	2.04	0.28	0.93	0.67	-0.02
11	0.16	0.12	0.36	0.08	0.85	0.07	0.01	2.02	0.36	0.94	0.64	-0.06
12	0.04	0.04	0.09	—	0.90	0.07	0.01	1.01	0.11	0.99	0.89	-0.02
13	—	0.01	0.06	—	0.85	0.09	0.01	2.00	0.07	0.96	0.88	+0.01
14	—	0.08	0.22	—	0.93	0.08	—	2.00	0.30	1.01	0.72	-0.01
15	0.07	0.02	0.24	—	0.82	0.25	—	1.96	0.28	1.07	0.71	+0.08
16	0.15	0.07	0.28	—	0.83	0.13	—	2.00	0.36	0.96	0.60	0.00
17	—	0.33	0.25	—	0.82	—	0.05	2.03	0.49	0.92	0.43	0.00
18	0.93	0.24	0.77	—	0.92	0.02	0.01	2.01	1.01	0.96	—	-0.05
19	0.42	0.15	0.19	—	0.94	0.02	—	2.03	0.25	0.96	0.73	-0.02
20	0.80	0.29	0.64	—	0.41	0.55	—	2.03	0.87	0.96	0.12	-0.03
21	1.17	0.39	0.33	—	0.92	0.03	0.05	2.03	0.66	1.05	0.39	0.00
22	1.05	0.24	0.44	—	0.69	0.24	0.07	2.01	0.66	1.04	0.33	+0.05
23	0.88	0.28	0.42	—	0.73	0.20	—	2.05	0.57	0.93	0.31	+0.05
24	1.11	0.21	0.44	—	0.84	0.07	—	2.00	0.65	0.91	0.26	0.00
25	0.12	0.11	0.08	0.04	0.88	0.12	—	2.02	0.19	1.00	0.74	-0.07

TABLE 2 (Continued)

No.	Octahedral				Interlayer			Σ oct. ion	Σ oct. chg.	Σ interlayer chg.	Σ tet. chg.	Total chg.
	Fe^{+3}	Fe^{+2}	Mg^{+2}	Ti^{+4}	K^{+}	Na^{+}	Ca^{+2}					
26	0.21	0.13	0.13	0.04	0.93	0.05	—	2.07	0.08	0.98	0.86	+0.04
27	0.08	0.12	0.16	0.04	0.86	0.15	0.03	2.08	0.40	1.07	0.68	-0.01
28	0.11	0.10	0.15	0.04	0.76	0.18	0.06	2.07	0.35	1.06	0.67	+0.04
29	0.13	0.08	0.14	0.04	0.79	0.12	0.02	1.99	0.20	0.95	0.80	-0.05
30	—	0.12	0.22	—	0.95	—	—	2.06	0.22	0.95	0.69	-0.06
31	1.25	0.16	0.48	—	0.69	0.26	0.05	2.00	0.64	1.05	0.40	+0.01
32	0.15	0.06	0.41	0.04	0.83	0.18	—	2.00	0.43	1.01	0.62	-0.04
33	0.77	0.21	0.68	—	0.84	0.01	0.03	2.02	0.85	0.91	0.10	-0.04

Calculated formulas taken from the literature.

Σ oct. chg. = 6 – charge on the octahedral ions.

Σ interlayer chg. = charge total of interlayer ions.

Σ tet. chg. = 12 – charge on the ions in tetrahedral coordination (Si and Al) or ΣAl^{IV} ions.

The restrictions that the calculated formulas must fulfill are discussed in the text. Only analyses with the following elements present were considered: Al, Si, Fe, Mg, K, Na, Ca.

References:

1 to 2, Caillère and Michard (1962); author's nos. S12, S19.
3 to 6, Ernst (1963b); author's nos. 6, 9, 12, 14.
7 to 11, Ernst (1964); author's nos. E-4, E-7, E-11, E-15a, E-16.
12 to 18, Foster (1956); author's nos. 2, 3, 7, 9, 10, 12, 14, 17.
19, Foster, Bryant, and Hathaway (1960), p. 845.
20 to 24, Hendricks and Ross (1941); authors' nos. 4, 5, 21, 23, 28.
25 to 29, Lambert (1959); author's nos. 352, 635, 646, 684, 992.
30, Michel (1953), p. 173, analysis corrected for 11.00 percent K_2O.
31, Pirani (1963); author's no. 39.
32, Van der Plas (1959), p. 477.
33, Wise and Eugster (1964); author's no. 15.

generalizations remain, muscovites and celadonite glauconites. The generalized formulas are as follows:

$$K[R_2^{+3})Si_3AlO_{10}(OH)_2], \text{ muscovite}$$
$$K[(R^{+2}R^{+3})Si_4O_{10}(OH)_2], \text{ celadonite}$$

These, as previously mentioned, can be treated as end members of a series of compositions (Schaller, 1950; Foster, 1956) that include most dioctahedral potassic micas.

Muscovite.—The criteria for naming a mica muscovite are that over half of the interlayer ions are K^+ (Zen and Albee, 1964) and the tetrahedrally coordinated ions are Si_3R^{+3}. Si_3 is considered a fixed quantity (Foster, 1956, 1960). The R^{+3} component is always most easily accounted for by Al^{+3} ions. The remaining positions in the muscovite structure that could contribute to chemical variability are the two octahedrally coordinated R^{+3} sites. Kanehira and Banno (1960), after calculation of structural formulas of muscovite from analyses of natural micas, found that there were no micas having more than 25 percent of the octahedrally coordinated R^{+3} positions filled by Fe^{+3}. Essentially, all of the remaining ions in that position were Al^{+3}. The present investigation determined similar limits of substitution through synthesis—a maximum of 25 percent substitution of Fe^{+3} for Al^{+3} in the octahedral position. This limited substitution of "iron muscovite" in aluminous muscovite will be referred to later. Muscovite will be treated as having essentially the composition $K[(Al_2)Si_3AlO_{10}(OH)_2]$. The variations that occur in natural muscovite (Na–K and Al–Fe^{+3} substitutions) are considered to be of minor importance to the main trend of mica solid solutions. The resultant simplified composition is very useful when dealing with synthetic mica systems.

Celadonites.—The formula $K[(R^{+2}R^{+3})Si_4O_{10}(OH)_2]$ is an ideal mineral group formula for a series of micas. Foster (1956) cites only one natural mineral that has a calculated formula very near that of this ideal mica, a celadonite found in a basalt near Reno, Nevada. Thus, the theoretical mica with four silicon atoms per unit formula is called celadonite by analogy with the analyzed natural mineral. In the present study micas with four silicon atoms are called celadonite micas if they meet the requirements for a calculated dioctahedral mica formula previously enumerated. Natural minerals similar in composition are called natural celadonites in this paper; they need not have calculated formulas that fit mica requirements. The distinction is made to avoid confusion and to refrain from adding new names to mineral taxonomy.

Possible theoretical celadonite mica end members deduced from combinations of the most commonly occurring ions in natural celadonites are:

$$K[(Fe^{+2}Al^{+3})Si_4O_{10}(OH)_2]$$
$$K[(Mg^{+2}Al^{+3})Si_4O_{10}(OH)_2]$$
$$K[(Fe^{+2}Fe^{+3})Si_4O_{10}(OH)_2]$$
$$K[(Mg^{+2}Fe^{+3})Si_4O_{10}(OH)_2]$$

The $K[(Mg^{+2}Fe^{+3})Si_4O_{10}(OH)_2]$ celadonite[2] is the only pure end member which has been synthesized (see Wise and Eugster, 1964, for a complete ac-

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[2] For simplicity celadonite end members will be referred to by the composition of the octahedral ions, for example, $MgFe^{+3}$ celadonite = $K[(Mg^{+2}Fe^{+3})Si_4O_{10}(OH)_2]$.

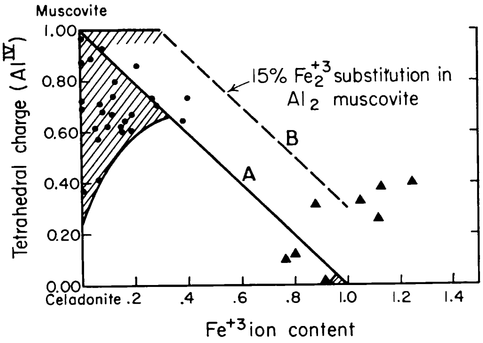

Fig. 4.

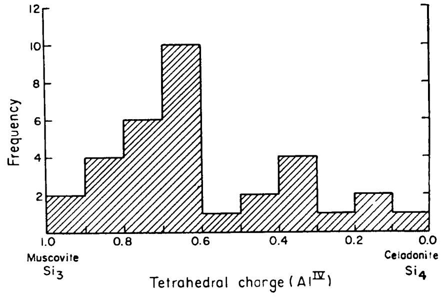

Fig. 5.

Fig. 4. Plot of natural mica compositions with respect to tetrahedral charge (Al^{IV} content) and Fe^{+3} ions. Circles are phengites and triangles glauconite celadonites. Data from table 1. Line *A* is the boundary for theoretical compositions in the series Al_2 muscovite–$R^{+2}Fe^{+3}$ celadonite. Line *B* (dashed) shows the solid solution limit $Fe_2^{+3} \longrightarrow Al_2^{+3}$ in muscovite and its effect on the muscovite-celadonite theoretical compositions. Line *B* represents a theoretical limit of Fe^{+3} ion content in dioctahedral micas. The lined areas indicate the micas synthesized in this investigation.

Fig. 5. The data of table 1 (and fig. 4) plotted to show the continuous substitution of Si_3 for Si_4 in the dioctahedral micas. This represents a projection of the muscovite-celadonite mica series.

count of this mineral's stability under experimental conditions). The few analyses of "true mica" celadonites in the literature, that is, those that meet ionic occupancy and charge requirements for micas, are near this composition.

Phengites.—The remaining micas, phengites, are complex solid solutions between muscovite and celadonite compositions. Muscovite and any one or several celadonite compositions can form a solid solution series.

If the Si^{+4} ion content (plotted as tetrahedral charge) of natural micas is plotted against Fe^{+3} ion content, a rather significant grouping appears (fig. 4). Two main mineral groups predominate—celadonite glauconites and phengites. Phengites, found most often as metamorphic minerals (Michel, 1953; Ernst, 1963b), form the group near the muscovite composition. The frequency distribution of tetrahedral charge (fig. 5) is shown, a rather continuous series of compositions similar to that reported by Foster (1956). The calculated structures representing natural glauconite-celadonite micas show a high Fe^{+3} content which is characteristic of these mineral groups (Hendricks and Ross, 1941; Pirani, 1963; Wise and Eugster, 1964).

It appears that two natural mica groups can be defined by both geologic occurrence and chemical composition—phengites and glauconite celadonites. However, twenty-eight chemical analyses are not sufficient to show the precise difference. In order to test the proposition of two major mica groups as defined by composition, the synthesis study was undertaken in the aluminous muscovite–celadonite systems.

The discussion of the experimental data in the synthetic muscovite–celadonite systems and the conclusions which can be drawn from them will be restricted here to the phengitic micas. The glauconitic celadonites are discussed in more detail in another paper (Velde, in preparation). However, one observation on the mica system as a whole can be made. The range of synthetic mica compositions is in good agreement with the analysis of natural mica compositions. The division of the natural dioctahedral micas into two groups, phengite (plus muscovite) and celadonites, on the basis of their distribution in an Fe^{+3} versus Si^{+4} plot appears to be valid (fig. 4). The observed experimental and natural solid solution between $Fe_2{}^{+3}$ muscovite and Al_2 muscovite is defined by line *A* in figure 4. Natural micas, in some instances, have compositions that exhibit more solid solution than the synthetics. This could be explained as being due to more favorable conditions during formation (for example, bulk composition, time). However, it is doubtful that any continuous series between the phengitic micas and iron-rich celadonites exists because of the rather large compositional gap separating both synthetic and natural micas (figs. 1 and 4).

The phengitic compositions that resulted in single-phase micas are notably iron-deficient. Both the $Fe^{+2}Fe^{+3}$ celadonite and $Fe^{+2}Al$ celadonite–muscovite series show no solid solution in muscovite. Moderate amounts of solid solution were noted in the $MgFe^{+3}$ celadonite-muscovite series. $MgFe^{+3}$ celadonite was the only end member composition that formed a single-phase mica. The MgAl celadonite-muscovite series did, however, show significant solid solution. This was especially marked at higher pressures (4.5 and 10 kb).

The importance of water pressure in the formation of the phengitic micas can be appreciated by considering the following possible reactions among minerals common in pelitic rocks.

1. $$\underset{\text{muscovite}}{3K[(Al_2)Si_3AlO_{10}(OH)_2]} + \underset{\text{biotite}}{K[R_3{}^{+2})Si_3AlO_{10}(OH)_2]} + \underset{\text{K feldspar}}{2KAlSi_3O_8} + \underset{\text{quartz}}{3SiO_2} + \underset{\text{water}}{2H_2O} \rightleftarrows$$
$$\underset{\text{phengite}}{6K[(R_{0.5}{}^{+2}Al_{1.5})Si_{3.5}Al_{0.5}O_{10}(OH_2]} \quad \text{(van der Plas, 1959).}$$

2. $$\underset{\text{muscovite}}{5K[(Al_2)Si_3AlO_{10}(OH)_2]} + \underset{\text{biotite}}{3K[R_3{}^{+2})Si_3AlO_{10}(OH)_2]} + \underset{\text{quartz}}{7\,SiO_2} + \underset{\text{water}}{4H_2O} \rightleftarrows$$
$$\underset{\text{phengite}}{8K[(R_{0.5}{}^{+2}Al_{1.5})Si_{3.5}Al_{0.5}O_{10}(OH)_2]} + \underset{\text{chlorite}}{R_5{}^{+2}Al_2Si_3O_{10}(OH)_8} \quad \text{(Ernst, 1964).}$$

3. $$\underset{\text{chlorite}}{R_5{}^{+2}Al_2Si_4O_{10}(OH)_8} + \underset{\text{pyrophyllite}}{4Al_2Si_4O_{10}(OH)_2} + \underset{\text{K feldspar}}{10KAlSi_3O_8} + 2H_2O \rightleftarrows$$
$$\underset{\text{phengite}}{10K[(R_{0.5}{}^{+2}Al_{1.5})Si_{3.5}Al_{0.5}O_{10}(OH)_2]} + 26SiO_2$$

Water is a chemical constituent of each of the reactions; thus its activity in the system is an important factor (see Greenwood, 1961, for a discussion of the importance of water fugacity in experimental systems). Assuming that the solids are only slightly soluble in the fluids, the variables of the experimental system are then f_{H_2O}, temperature, and total pressure (Thompson, 1955).

Phengites or phengite assemblages would be favored by high H_2O pressure or high f_{H_2O}.

Calculation of the molar volumes of the solid phases (reduced to volume/formula unit) for the upper stability equilibria of several hydrous minerals also yields interesting results. Cell volume data for each mineral involved and net volume changes of solid phases for the reactions are given in table 3. The net volume change of the solids for the reactions involving the micas annite, phlogopite, and muscovite is negative. However, ΔV_S for the breakdown of phengite (table 3, equation 4) is positive. The phengite appears to be more dense than the solid phases of the higher temperature assemblage, and other micas appear to be less dense than their high-temperature breakdown products.

The cell volume data are not precise enough to make an absolute statement on the matter. ΔV_S for one phengite formula is about 1 percent of the total volume of the solids involved; this is well within the limits of error of the original cell measurements. However, the comparison between phengite and other micas indicates that it is a more dense type of mica than others which are alternative—muscovite and biotite. It is apparent that phengites are favored by conditions of high total pressure.

Mineral associations including kyanite, jadeite, and aragonite led Banno (1958) to the conclusion that the *P-T* conditions responsible for the general mineral assemblages in the glaucophane (and phengite) schists of Japan were between 6 and 12 kb pressure and 200° and 300°C. Glaucophane itself probably represents conditions of high total pressure (Ernst, 1961, 1964). The upper stability limits of kyanite, jadeite, muscovite, and phengite are shown in

TABLE 3

Cell volume relations of several reactions

Mineral	cc/mole	Cell data source
Annite	152	Eugster and Wones (1962)
Phlogopite	149	Yoder and Eugster (1954)
Phengite	140	Ernst (1963b)
Muscovite	140	Yoder and Eugster (1955)
Corundum	25	Deer, Howie, and Zussman (1962)
Quartz	23	Frondel (1962)
Microcline	108	Finney and Bailey (1964)
Forsterite	43	Deer, Howie, and Zussman (1962)
Fayalite	46	Deer, Howie, and Zussman (1962)
Leucite	96	Deer, Howie, and Zussman (1962)
Kalsilite	60	Deer, Howie, and Zussman (1962)

1. 2 annite → 3 fayalite + leucite + kalsilite + 2 water
   ΔV_S/mica formula = –5 cc/mole
2. 2 phlogopite → 3 forsterite + leucite + kalsilite + 2 water
   ΔV_S/mica formula = –7 cc/mole
3. muscovite → sanidine + corundum + water
   ΔV_S/mica formula = –7 cc/mole
4. 6 phengite → 3 muscovite + phlogopite + 2 microcline + 3 quartz + 2 water
   $6K[(Mg_{0.5}Al_{1.5})Si_{3.5}Al_{0.5}O_{10}(OH)_2] \rightarrow 3K[Al_2Si_3AlO_{10}(OH)_2] + KMg_3Si_3AlO_{10}(OH)_2 + 2KAlSi_3O_8 + 3SiO_2 + 2H_2O$
   ΔV_S/mica formula = 1 cc/mole.

figure 6. The glaucophane schists of Japan can, in general, be attributed to physical conditions of low temperature and high pressure, with water contributing a significant portion of the total pressure. Ernst (1963a) discussed the petrogenesis of glaucophane schists in greater detail. Van der Plas (1959) and Müller (1958) also find kyanite and glaucophane associated with the general phengitic mineral assemblages of the areas they studied in the European Alps. Thus field occurrences, in general, substantiate the pressure relations of phengite stability.

THE PETROLOGY OF PHENGITE MICAS

Phengitic micas have been described in metamorphic rocks of several areas: Japan (Banno, 1958; Kanehira and Banno, 1960), California (Ernst, 1963a,b), North Carolina (Foster, Bryant, and Hathaway, 1960), the European Alps (Michel, 1953; van der Plas, 1959), and Scotland (Lambert, 1959). Mineral associations in Japan and the Alps suggest that the metamorphism that produced the minerals was one of high pressure and relatively low temperature. In three of the above studies, the mineral associations are rather simple, and general petrographic evidence indicates clearly the phase relations and mineral transformations that have proceeded during the metamorphism that produced the phengite-bearing assemblage.

The following descriptions and analyses are made in order to indicate common mineral associations and reactions likely to produce phengite-bearing mineral assemblages. The petrographic model is simplified in order to focus on the origin of phengite. This, of course, leads to many errors which a more rigorous approach would eliminate. However, in the instances cited, the proposed petrographic model appears well suited.

There are two commonly occurring types of mineral assemblages which are likely to have been the progenitor of phengitic metamorphic rocks—sedimentary and gneissic. Examples of the gneissic progenitor follow.

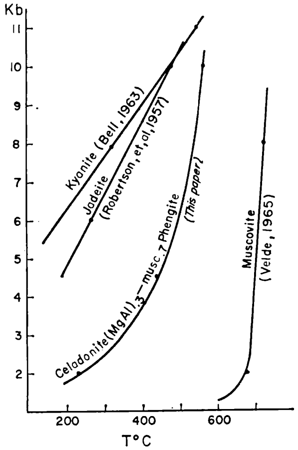

Fig. 6. Upper stability of some minerals commonly found in phengite schists and associated rocks.

Micas of phengitic composition have been known in the European Alps for quite a long time, the first chemical analysis being made in 1891 by Schmidt (quoted from Michel, 1953). Several petrographic investigations have been made detailing the mineral associations and geologic settings in areas where retrograde metamorphism produced phengite-bearing rocks. Two types of phengite mineral associations will be discussed here. The first type was described by Müller (1958) and van der Plas (1959), and the second by Michel (1953).

In brief summary, the first occurrence is that of phengitic gneisses which are often found as bands or isolated bodies within a muscovite–biotite gneiss country rock. There is little evidence to support the hypothesis that the phengite gneisses were formed as a result of local compositional variation. Van der Plas (1959) proposed the following reaction to explain the occurrence of phengite mica:

$$\text{Muscovite} + \text{biotite} + \text{K feldspar} + \text{quartz} + H_2O \rightarrow \text{phengite}$$

The equation, as written, suggests a retrograde metamorphic reaction, the muscovite-biotite assemblage representing an upper greenschist facies rock stable above the limits of phengite stability. From the experimental results of the present study one can surmise that, if pressure (P_{total} and P_{H_2O}) were kept constant and temperature lowered, the reaction would take place as written. This can be seen by the relations of figure 2, which show equilibrium for the reaction in the muscovite–MgAl celadonite system. In situations where the rocks were not able to maintain a high partial water pressure, the original two-mica assemblage would remain. The water pressure in a system is probably a critical factor in determining the mineral assemblage muscovite + biotite + K feldspar or phengite.

Figure 7C,D shows the reaction as plotted on a modified K–R^{+2}–R^{+3} diagram (after Ernst, 1963b); quartz and water are considered in excess for all reactions. Several obvious simplifications are inherent to such a representation of rock assemblages. First, not all the important chemical elements are considered; notably absent are Na and Ca. Second, Mg and Fe^{+2} are considered as playing homologous roles in the mineral reactions. Discussion of the effects of such omissions and improper simplifying assumptions would be lengthy. However, when the compositions of the rocks discussed here are plotted on such a diagram, the mineral phases in them appear to follow the pattern of relations proposed. This is entirely an empirical approach and is not expected to work in all cases. Nevertheless, it is a useful approximation to consider that the rock compositions can be plotted in the system described by figure 7. If micas and chlorites are the only major phases that contain Mg and Fe, the system can be applied to natural examples. Bulk compositions of two-mica gneisses and associated phengite gneisses reported by van der Plas (1959) can be approximated by the point marked *A* in the feldspar (KR^{+3})–pyrophyllite ($2R^{+3}$)–talc–chlorite ($3R^{+2}$) diagram (fig. 7C,D). The composition marked by *B* is that of the dioctahedral mica stable under low-pressure (muscovite) conditions, and *B′* the high-pressure mica (phengite) where $P_{H_2O} = P_{\text{total}}$. The muscovite–biotite–K feldspar assemblage is changed to one of

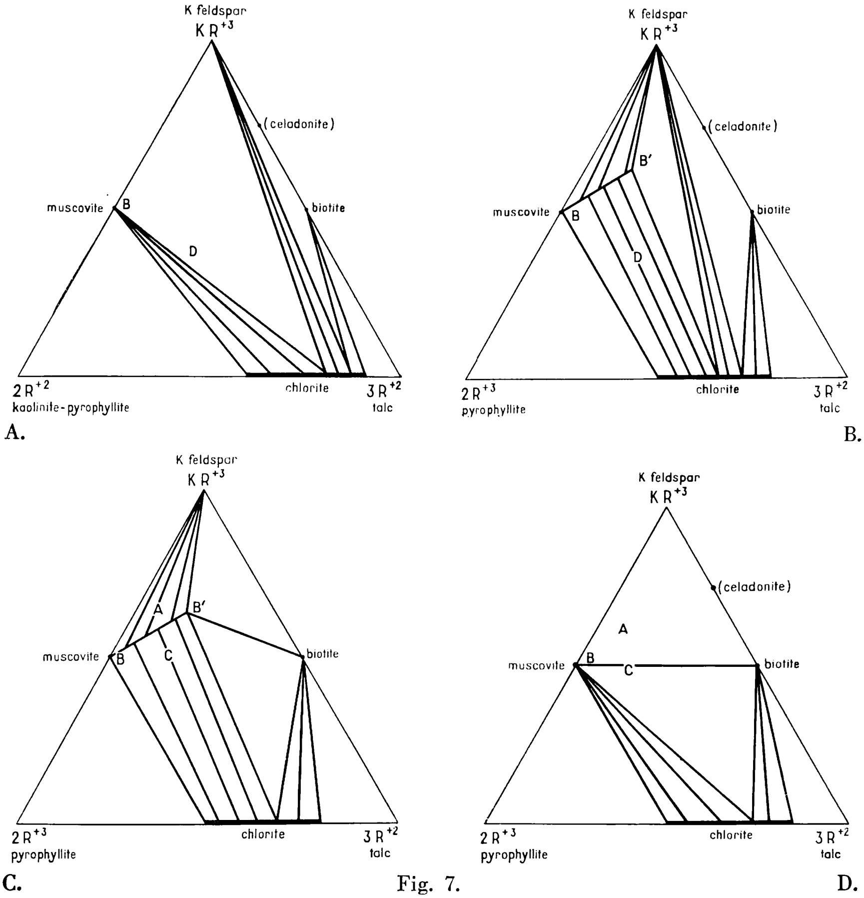

Fig. 7.

Fig. 7. Phase relations in a portion of the system K–3R^{+2}–2R^{+3} with H_2O and SiO_2 present in excess quantities. The sequence of *P-T* conditions represented is: (*a*) *P* and *T* low, (*b*) *P* high and *T* low, (*c*)*P* and *T* high, and (*d*) *P* low and *T* high. Compositions represented by points *A*, *C*, and *D* are discussed in the text. *B* and *B′* represent muscovite and phengite compositions of the solid solution series.

phengite-K feldspar as the phengite solid solution increases toward celadonite. Figure 7D could represent high-temperature phases, and figure 7C the corresponding lower temperature assemblage as well as representing a change of pressure.

Probably the first study of phengite-producing metamorphism was conducted by Michel (1953) in the Franco-Italian Alps. Here a late-stage metamorphism of migmatites and gneisses produces a primarily albite–chlorite–phengite assemblage. Michel gives petrographic evidence to support the view that the phengite–chlorite–albite assemblage was produced by the following reaction:

Muscovite + biotite + quartz + H_2O → phengite + chlorite

(This type of reaction is also discussed by Yoder, 1959, and Ernst, 1963b)

This, again, represents a retrograde type metamorphism. However, chlorite, which was minor or absent in the rocks previously discussed, is an important constituent in these rocks. Explanation for the presence of chlorite in the rocks described by Michel can be easily made by referring to figure 7C,D. The bulk compositions of the rocks are much lower in K_2O content than those of van der Plas and Müller (about 3 percent as compared with 6 percent). The phengite-chlorite rocks can be plotted by the approximate bulk composition (based upon analyses given by Michel, 1953) shown by point *C*. The mineral assemblages representative of higher temperatures or low pressures are similar in both Alpine studies, but upon "phengitization" they differ.

An interesting aspect of the mica relationships involves coexisting micas —dioctahedral and trioctahedral—in biotite facies rocks. In pelitic metamorphosed rocks where K feldspar is present, the composition of the dioctahedral mica could be used as an indication of the *P-T* conditions which formed the mineral assemblage. By plotting the bulk composition of the rocks in the diagram (fig. 7D) one can determine whether the phengite composition represents the maximum solid solution allowed by the bulk composition of the rock or whether *P-T* conditions limited the solid solution. If the latter is true, an estimation of these conditions can be made.

Michel (1953) describes a phengite-bearing metamorphic assemblage produced by Alpine metamorphism in a series of Mesozoic sediments. The original argillaceous and argillocarbonate rocks were metamorphosed into an albite–phengite–chlorite–quartz assemblage. Structural and stratigraphic evidence suggest that the metamorphism involved was that of a prograde type only, that is, the original sedimentary mineral assemblage was transformed directly into the present one.

A brief consideration of the mineralogy of argillaceous sediments in general indicates the reactions that would be pertinent to the formation of phengite during metamorphism of normal sediments. It has been well established that sedimentary rocks contain chlorite and illite as major argillaceous components (Weaver, 1959; Velde and Hower, 1963). These minerals are equivalent to an assemblage of muscovite + chlorite + quartz when subjected to very low-grade metamorphic conditions. It is reasonable to consider that K feldspar is a common mineral in these rocks, since the occurrence of K feldspar in sedimentary and low-grade metamorphic argillaceous rocks is well known (Harrison and Campbell, 1963; Reynolds, 1963). Thus, the mineral assemblage muscovite (illite) + chlorite + K feldspar + quartz would be very probable in a series of sedimentary rocks. If, at low temperature, the pressure is high ($P_{H_2O} = P_{total}$), the following reaction is likely to take place:

$$\underset{\text{illite (muscovite)}}{K[(Al_2)Si_3AlO_{10}(OH)_2]} + \underset{\text{chlorite}'}{R_{6.0}{}^{+2}Si_{4.0}O_{10}(OH)_8} + \underset{\text{feldspar}}{KAlSi_3O_8} + \underset{\text{water}}{H_2O} \rightleftarrows$$

$$\underset{\text{chlorite}''}{R_{5.0}{}^{+2}Al_2Si_3O_{10}(OH)_8} + \underset{\text{phengite}}{2K[(R_{0.5}Al_{1.5})Si_{3.5}Al_{0.5}O_{10}(OH)_2]} + \underset{\text{quartz}}{SiO_2}$$

Figure 7A,B indicates the general phase relations for such a reaction. The figures are similar to those of Ernst (1963b) except that the mineral pair chlorite-K feldspar is indicated as stable. The problem of their coexistence in experimental systems has not yet been solved (preliminary experiments have been reported by Fawcett, 1964), but the coexistence of these minerals in nature is well documented in the literature.[3]

This particular reaction involves the complementary change of composition for the mica and chlorite phases. The mica becomes enriched in an R^{+2} component whereas the chlorite is impoverished. Data from synthetic chlorites (Fawcett and Yoder, 1962) indicate that the chlorites stable at high pressures have a lower R^{+2} content than those stable at low pressures. Thus both the dioctahedral mica and chlorite present in a high-pressure assemblage have characteristic compositions.

In figure 7A,B the bulk composition of the rocks reported by Michel (1953) is represented by point *D*. *B-B′* are points representing the solid solution muscovite–celadonite as pressure is increased. Tie lines between micas or mica-like minerals (illite) and chlorites are inferred.

THERMAL METAMORPHISM OF PHENGITES

From examination of figure 2 conclusions can be drawn regarding the trend of mica compositions during prograde thermal metamorphism. It can be seen that at constant water pressure conditions higher temperatures lead to stable dioctahedral micas containing smaller amounts of celadonite in solid solution. Thus, as thermal metamorphism progresses, the phengitic micas will come closer to muscovite in composition. Data by Lambert (1959) illustrate this conclusion. Higher grade metamorphic mineral assemblages in the Moine area of Scotland contain micas with fewer R^{+2} ions, that is, approaching $(K,Na)Al_2Si_3AlO_{10}(OH)_2$ in composition. However, a parallel substitution takes place in the interlayer ion position. Na is found in larger amounts in micas from higher grade rocks. Experimental results reported by Eugster and Yoder (1955) and Iiyama (1964) indicate that the muscovite structure can accommodate more Na at higher temperatures. Thus, it can be deduced qualitatively that phengites with considerable amounts of Na in the interlayer position would have been produced by higher temperature conditions than phengites of similar R^{+2} composition but containing less Na. Any direct interpolation of *P-T* data from the above information is likely to fail, however, because little is known about the effect of increased pressure upon Na-K substitution.

GENERAL CONCLUSIONS

The upper thermal stability of phengitic micas has been determined experimentally and correlated with the geological conditions that were probably responsible for the production of the natural minerals. It can be concluded that high pressure is probably responsible in most cases for dioctahedral micas of phengite composition. Future petrographic studies of areas where such conditions have occurred should consider the possibility of finding phengitic white micas.

The upper stability relations of the phengitic micas under various pressures should be an aid to determining the physical conditions that formed a

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[3] For pertinent bibliographical references see appendix.

mineral assemblage containing them. The presence of phengites is indicative of metamorphism under conditions of significant water pressures although P_{H_2O} need not equal P_{total}. The usefulness of phengites as indicators of specific physical conditions of metamorphism should become apparent as they are discovered or proved absent in future petrographic studies.

ACKNOWLEDGMENTS

This work was carried out at the Geophysical Laboratory of the Carnegie Institution of Washington. The author is indebted to Dr. P. H. Abelson, Director of the Laboratory, for providing the opportunity to pursue this study. The experimental portion of the study was performed with the help of D. H. Lindsley, to whom many thanks are given.

The manuscript was critically reviewed by D. H. Lindsley, M. D. Foster, D. R. Wones, and W. G. Ernst. These reviewers aided greatly in the correction and formulation of many aspects of the paper.

The author is also indebted to R. Michel, who provided the analyzed natural phengite, and to J. J. Fawcett and H. S. Yoder, Jr., for performing the 10 kb experiment.

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APPENDIX

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