

CRYSTALLINE SOLUBILITY IN THE MUSCOVITE
AND PHLOGOPITE GROUPS¹M. S. CROWLEY² AND RUSTUM ROY, *The Pennsylvania State
University, University Park, Pennsylvania.*

ABSTRACT

The limits of crystalline solution in the micas have been studied using hydrothermal synthesis and x-ray diffraction analysis techniques. The limit of Mg substitution into muscovite is at the phengite composition, $K_2MgAl_3(AlSi_7)O_{20}(OH)_4$. The introduction of Mg favors the development of the 3T polytype at low to moderate temperatures. The reactions for muscovite decomposition, muscovite \rightleftharpoons sanidine + corundum \rightleftharpoons sanidine + mullite + leucite, have been shown to be easily reversible and revised pressure-temperature curves for these reactions are given.

The limit of crystalline solution of Al into the phlogopite structure is at the composition $K_2Mg_4Al_2(Al_4Si_4)O_{20}(OH)_4$ which is similar to the disilic member of the chlorite family (amesite) reported as the limiting member for Al substitution in the chlorites. Substitution of Al does not seem to affect the phlogopite polytype, only the 1M variety being formed, but does lower the decomposition temperature about 100° C. The phlogopite decomposition curve found in this investigation (1120° C. at 10,000 psi), appears to be about 100° C. above the curve given by Yoder and Eugster (1954) but the results of both investigations are equivocal.

Almost 10% of ferric iron can be accommodated in the muscovite structure of composition $(K_2Al_3Fe(Al_2Si_6)O_{20}(OH)_4)$, substituting for Al. The polytype relationships are not changed but the decomposition temperature is lowered slightly. The limit of crystalline solution of ferric iron into the phlogopite structure is the composition $K_2Mg_5Fe(Fe_3Si_5)O_{20}(OH)_4$. Partial fluorine substitution in hydrothermally synthesized muscovite and phengite cannot be proven or disproven on the basis of cell dimension variations.

INTRODUCTION

The "white" and "dark" micas are common, widespread minerals. Their potential use as mineralogical indicators of geological history is widely recognized and forms part of the reason for recent experimental work. That these minerals crystallize from rocks with several ions which can be admitted into solution in their structures makes it imperative that the petrologist knows the extent of the various types of solid solutions which can occur in the micas, as well as the effects of pressure and temperature on them.

If one writes the ideal muscovite formula as



one can conceive of the following substitutions:

¹ Contribution No. 62-135, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

² Present address: American Oil Co., Whiting, Ind.

(1) K	Al ₂	AlSi ₃	O ₁₀	(OH) ₂	Ideal muscovite
(2) Na	Al ₂	AlSi ₃	O ₁₀	(OH) ₂	Extent of CS studied by Yoder and Eugster
(3) K	AlMg	Si ₄	O ₁₀	(OH) ₂	High silica substitution
(4) K _{0.5}	Al ₂	Al ₅ Si _{3.5}	O ₁₀	(OH) ₂	Illitic substitution studied concurrently (Warsaw 1960)
(5) K _{0.7} (H ₃ O) _{0.3} ⁺	Al ₂	AlSi ₃	O ₁₀	(OH) ₂	Illitic substitution studied concurrently (Warsaw 1960)
(6) K	AlMg _{1.5}	AlSi ₃	O ₁₀	(OH) ₂	Diocahedral-trioctahedral substitution
(7) K	Fe ₂ ³⁺	AlSi ₃	O ₁₀	(OH) ₂	Partial "iron muscovite"
(8) K	Fe ₂ ³⁺	FeSi ₃	O ₁₀	(OH) ₂	Complete "iron muscovite"
(9) K	Al ₂	AlSi ₃	O ₁₀	(F ₂)	Synthetic fluorine mica

Of these (3) is perhaps the most important in nature and this, along with (6), (7), and (8) received the most attention in the present study. The "illite" composition was studied simultaneously in this laboratory by Warsaw. Examples are known of appreciable crystalline solution (up to 15%) along a dioctahedral-trioctahedral join representing the partial filling of the third octahedral site; ferroso-ferric 1:1 minerals of the chamosite group (Youell, 1958) and muscovite-polyolithionite and trioctahedral mica work reported by Foster (1960A and 1960B). However, in neither case is the interpretation of the data unequivocal.

Of interest beyond the extent of solubility is, of course, the influence of the solubility on various properties of the phase. Three main properties were studied: (1) The powder *x*-ray spacings, since this is the chief diagnostic criterion in mineralogy today; (2) The thermal breakdown which affects the petrologic interpretations; (3) The influence on the polytypism in the micas in the hope that it might shed some light on whether or not there is an equilibrium between two polytypes, and if not, what determines the stacking.

Clay mineral nomenclature used in this paper follows that developed at The Pennsylvania State University over the last dozen years and recently presented by Warsaw and Roy (1961).

METHOD OF INVESTIGATION

The apparatus and techniques described by Roy and Osborn (1952), Roy and Tuttle (1956) and Koizumi and Roy (1959) were used in this study. It was found necessary to make most of the runs in sealed gold or platinum tubes to prevent the possibility of having the bulk composition changed due to preferential leaching of material. The compositions studied in the system K₂O-Al₂O₃-MgO-SiO₂-H₂O are plotted in Fig. 1. All the compositions used are listed in Table I. In the majority of cases "gels" of the desired composition formed the starting material (Roy,

1956). Some starting mixtures were made from crystalline material. The experimental procedure outlined by Warshaw (1960) was followed in making runs.

A Norelco diffractometer with Cu radiation and a Ni filter was used almost exclusively to identify the phases present after synthesis. For those cases where a change in cell dimensions was measured, a small quantity of quartz or silicon was added as an internal standard to the synthesized

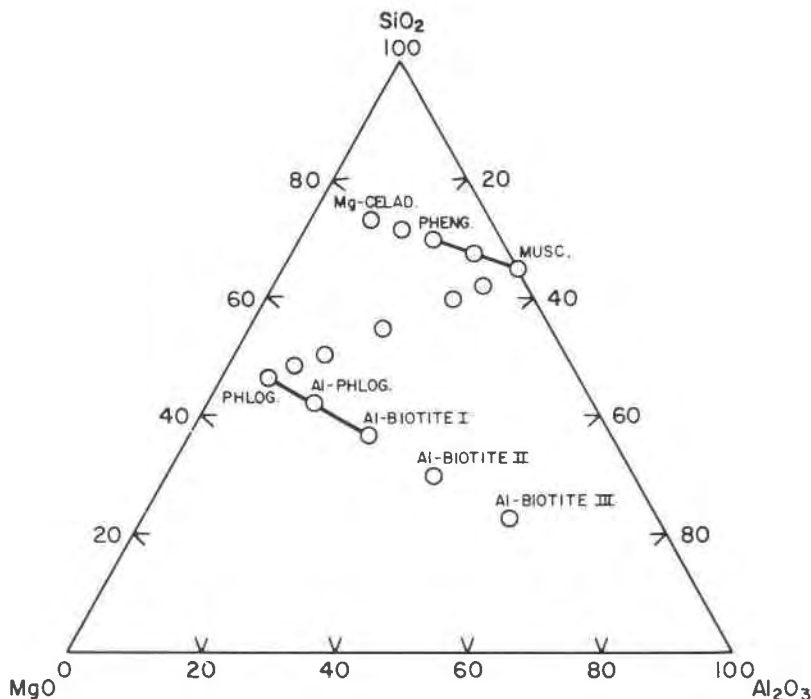


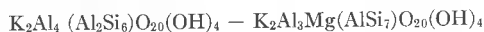
FIG. 1. 1 Mole K_2O plane.

mica smeared on a glass slide. The A.S.T.M. main peak value, measured at half peak width at half height, was used as the reference line.

Over 900 hydrothermal runs were made in this investigation.¹ The duration of the runs ranged from 14 minutes to one month, the usual run being about four days. The limits of error, as previously determined in this laboratory, are $\pm 5\%$ for pressure measurements and $\pm 5^\circ \text{C}$. for temperature measurements.

¹ No attempt is made to list extensive tables of data herein; following recent practice such tables are available to persons who are sufficiently interested from University Microfilms, Ann Arbor, Michigan, by citing the Ph.D. dissertation of M. S. Crowley, Penn State University, 1959.

RESULTS AND DISCUSSION

The Muscovite-“Phengite” Join

1. Mixtures No. 1 through No. 5 (Table I) were used to determine the extent of Mg^{2+} and Si^{4+} substitution for 2Al^{3+} in the muscovite structure. The limit of M_3^{2+} substitution is the composition $\text{K}_2\text{MgAl}_3(\text{AlSi}_7)\text{O}_{20}$

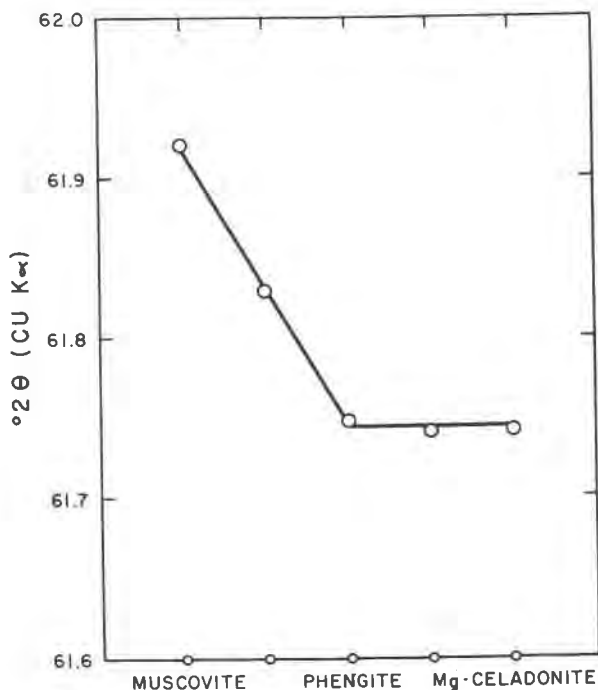


FIG. 2. Muscovite-Mg-Celadonite 060 spacings.

(OH)₄. This was determined on the basis of the shift in the 060 d-spacing (Fig. 2) and the phases present (Fig. 3). The 005 spacing measurements agree with the 060 measurements in determining that this composition is the limiting member. The phase assemblages shown in Fig. 3 are binary only in the lower left-hand corner of the diagram, where a single dioctahedral mica exists. The decomposition reactions, which mixtures No. 1 through No. 5 undergo, are listed in Table II, and the p-t curve for the decomposition of the most magnesian phase is shown in Fig. 4.

The various mica polytypes encountered in this investigation were identified by using the data published by Smith and Yoder (1956). The effect of the conditions of pressure and temperature formation on

phengite polytypism is listed in Table III and is shown in Fig. 3. It is seen that Mg^{2+} substitution markedly tends to promote the formation of the 3T polytype at low temperatures. No sharp transition temperatures could be found for any composition, and there is no experimental basis for stating that a particular polytype is "stable" under any given conditions.

2. The results of this investigation on the decomposition of muscovite are compared with the earlier work in this laboratory and the results of

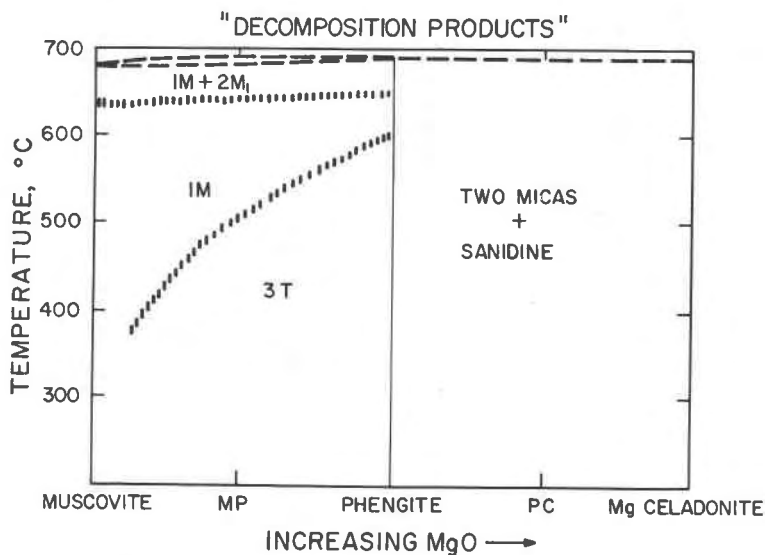


FIG. 3. Phase assemblages formed on the muscovite—"Mg celadonite" join as a function of temperature (at 1000 atm.). Solid decomposition products actually found above 900° C. as follows: MP→Sanidine, mullite, leucite, phlogopite; Phengite→Sanidine, mullite, quartz, phlogopite; PC→Sanidine, mullite, quartz, phlogopite; Mg-celadonite→Sanidine, quartz, phlogopite.

Yoder and Eugster (1955) in Fig. 5. It can be seen that the results of the investigation agree fairly well in the range of 5000 psi to 30,000 psi. At the higher pressures (55,000 psi) the present data indicate that the equilibrium curve is somewhat steeper than shown by Yoder and Eugster. By using the decomposition products as starting materials (*i.e.*, sanidine and corundum, etc.) it was possible to form muscovite in just a few minutes at temperatures between 500 and 600° C. (Table V). The data for the runs shown in Fig. 5 are listed in Table IV.

Since the "dry" equilibrium diagram for the $K_2O-Al_2O_3-SiO_2$ system by Schairer and Bowen (1955) shows that the assemblage "leucite, sanidine

and mullite" is stable just below the eutectic temperature, 1140° C., it is clear that there must be a reaction (corundum + sanidine \rightleftharpoons leucite + sanidine + mullite) between about 650° and 1140° C. DeVries and Roy (1958) have already pointed out the structural prejudice provided by the

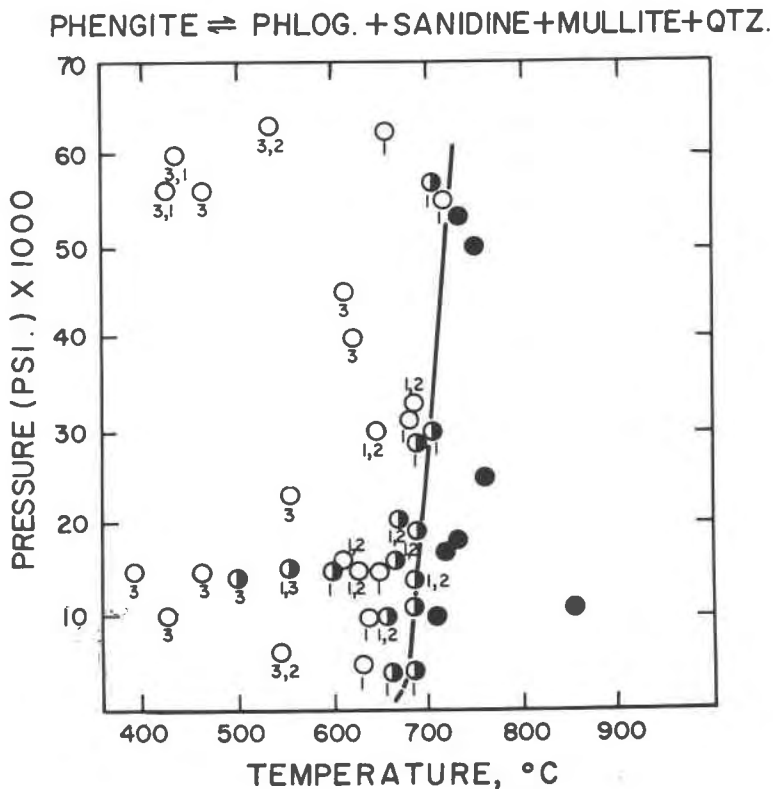


FIG. 4. P-t curve for the dissociation of the most-magnesian muscovite. Open circles represent the mica phase and closed circles the "decomposition" products. The numbers below the mica-containing runs indicate the polytype formed (3=3T, 2=2M, 1=1M); the predominance of the 3T form in these compositions is a distinctive feature.

mica structure towards forming sanidine + corundum. Hence, it was necessary to establish not only that leucite, sanidine and mullite could form at high temperature, but that they could be reconverted to corundum + sanidine. Both these points were established experimentally and the p-t curve for this reaction is also shown in Fig. 5 (Yoder and Eugster also presented a quite different curve for this reaction but it does not appear to have been based on many data).

The Phlogopite—Al Biotite Series

1. Mixtures No. 7 through No. 11 (Table I) were used in determining that the limit of Al^{3+} substitution into phlogopite is the composition $\text{K}_2\text{Mg}_4\text{Al}_2(\text{Al}_4\text{Si}_4)\text{O}_{20}(\text{OH})_4$. The limit of substitution was determined by the shift in cell parameters as shown in Fig. 6 and the phases present (Fig. 7). This corresponds with the limit of Al^{3+} substitution into chlorites

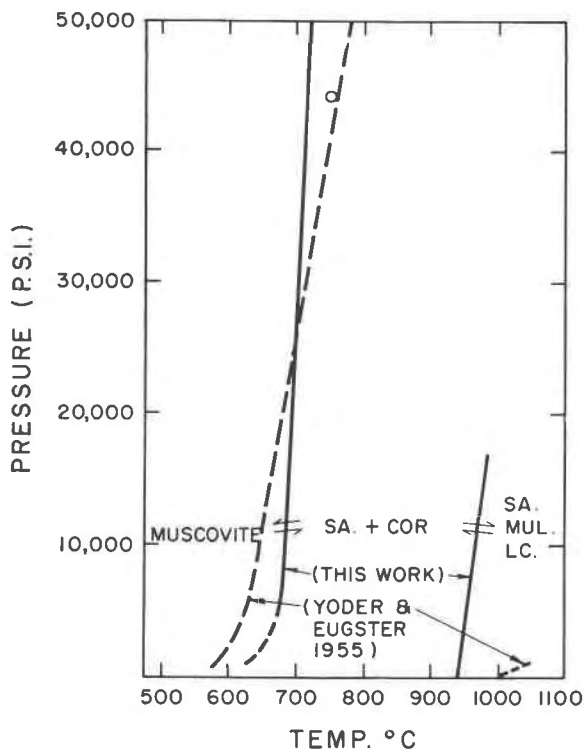


FIG. 5. Muscovite decomposition curve.

as reported by Nelson and Roy (1958), in that the limit is reached at the amesite member, *i.e.*, when the numbers of Al and Si ions in the tetrahedral layer become equal.

2. The pressure-temperature decomposition curve for phlogopite is shown in Fig. 8 and compared therein are the data of Yoder and Eugster (1954) with the findings of this investigation. The data for Fig. 8 are listed in Table VI. Our data *indicate* that the equilibrium decomposition curve is much higher than that shown by Yoder and Eugster. Their data were far from unequivocal. However, even the many repeated runs with

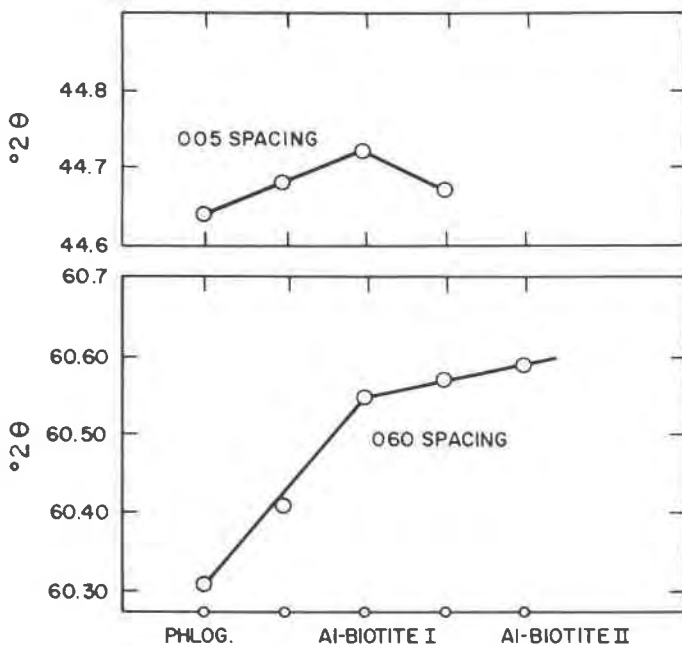


FIG. 6. Phlogopite—"Al-Biotite" spacing.

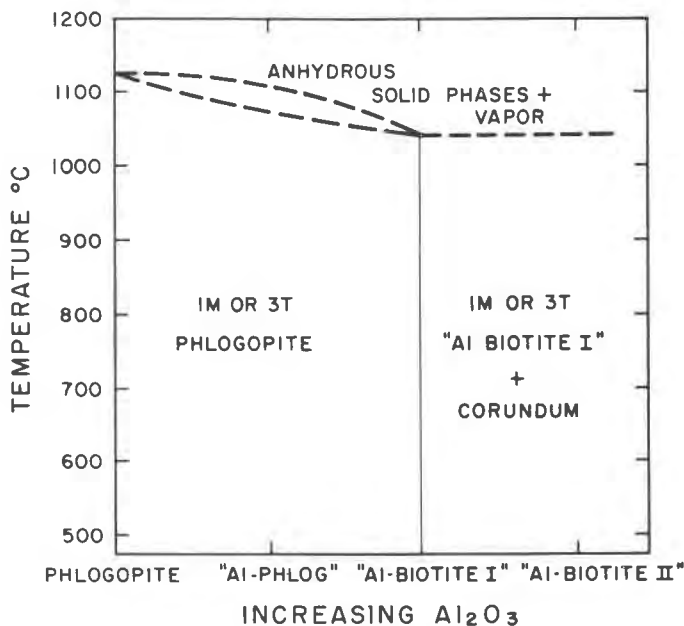


FIG. 7. Phase assemblages formed on the phlogopite—"Al-Biotite" join as a function of temperature (at 1000 atm.) H₂O pressure. Anhydrous phases formed at highest temperature as follows: Al-Phlog:→Forsterite, leucite, spinel, MgO; Al-Biotite I→Leucite, spinel, MgO; Al-Biotite II→Leucite, spinel, KAlO₂.

various starting materials in the present study failed to produce unequivocal results. Difficulties in interpretation of the data are the result of (1) metastable growth of some or all of the decomposition products below the decomposition curve, (2) metastable persistence of mica above its decomposition temperature, (3) possible melting of the phlogopite or any combination of the decomposition products with the water, or (4) growth of phlogopite during quenching. The reversibility of the phlogopite decomposition reaction was proven by holding the decomposition products

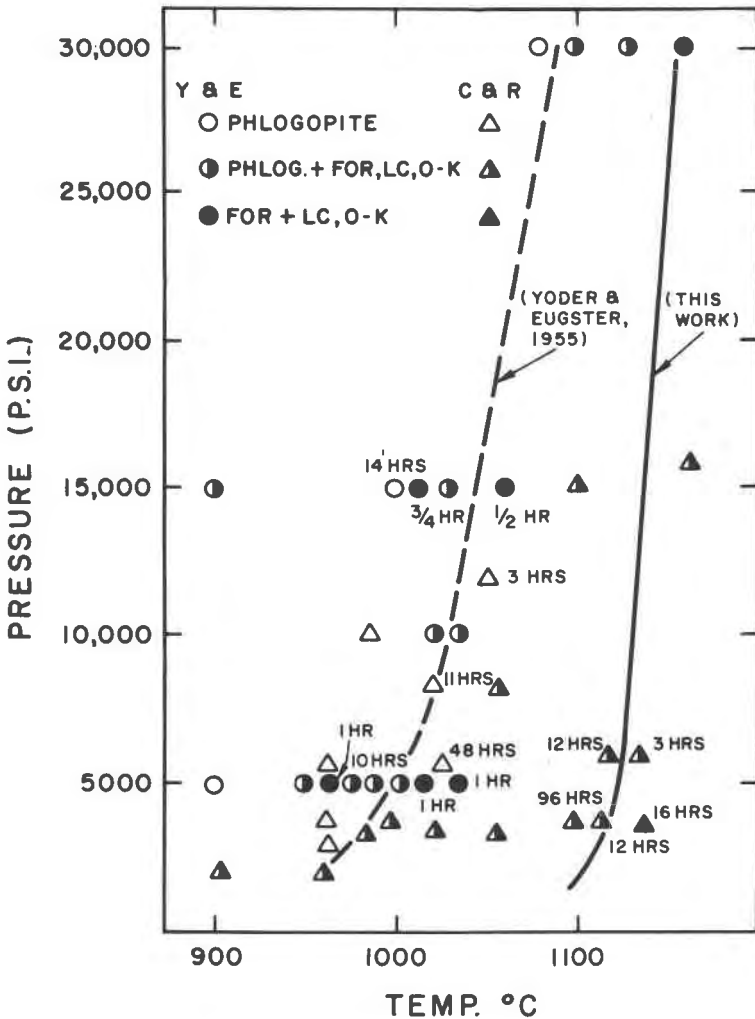


FIG. 8. Phlogopite decomposition curve.

(formed in a previous run and checked by *x*-ray analysis at a temperature below the curve) and reforming mica. The run at 1098° C. at 4000 psi for 96 hours, in which phlogopite persisted, is considered one of the best indications that the true phlogopite decomposition curve is considerably higher in temperature than that presented by Yoder and Eugster (1954)

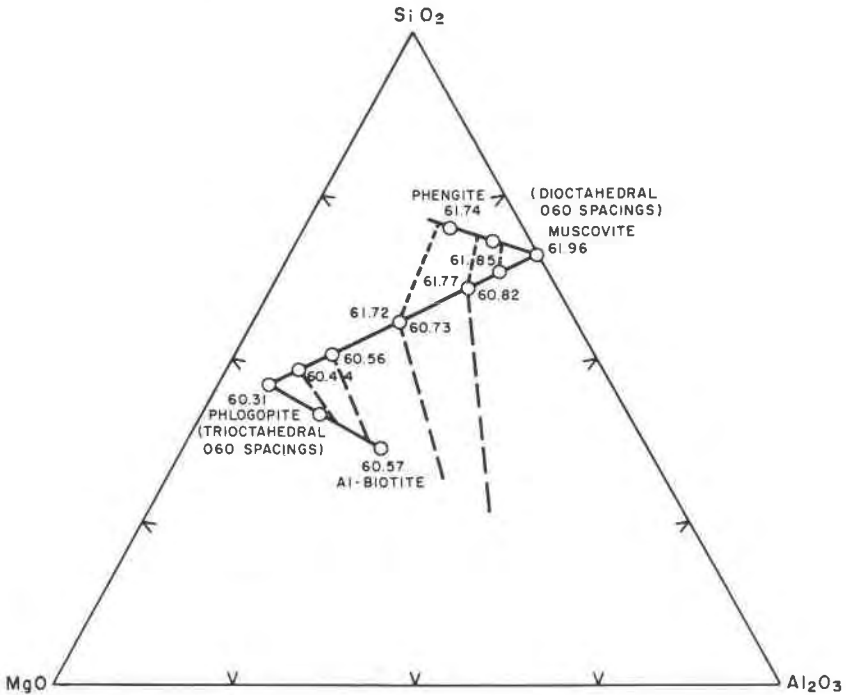


FIG. 9. Muscovite-phlogopite 060 spacing relationships.

Muscovite-Phlogopite Join

A few cases have been reported by Foster (1960A, B) of appreciable solubility between corresponding dioctahedral and trioctahedral clay minerals (muscovite-polyolithionite). A study of the data on mixtures lying directly on the muscovite-phlogopite join force one to the conclusion that this crystalline solution must be quite extensive. Reference to Fig. 9 will reveal why these binary mixtures alone are insufficient to actually determine the extent of the solid solution. Various compositions along the join may react to form either two crystalline solutions lying on the join or to a mixture of two crystalline solutions, each of which will be a binary crystalline solution member of either the phengite or biotite

series described above. On the other hand they may yield two ternary crystalline solutions, or any combination of a binary and ternary crystalline solution. Fortunately the cell dimension changes listed in Table VII make it clear that we are not dealing with the simple binary phengite or biotite series solutions, and the crystalline solution must involve some of the trioctahedral-dioctahedral type substitution.

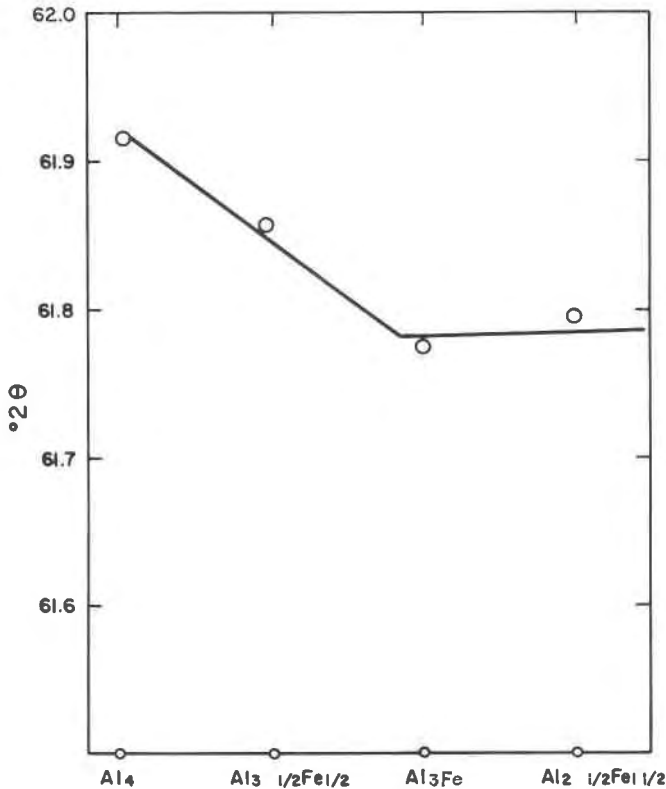


FIG. 10. Fe-muscovite spacing 060 peak.

Iron Substitution in Micas

1. Mixtures No. 12 through No. 16 (Table 1) were used to determine the limit of ferric iron substitution in muscovite. The end member as determined by cell dimension spacings and appearance of other phases (shown in Fig. 10), is the composition $K_2Al_3Fe(Al_2Si_6)O_{20}(OH)_4$. This composition has almost 10% (wt.) Fe_2O_3 , which is twice as much as the high iron analysis listed by Foster (1956). However, Foster's combined

foreign ions totaled over 8% and the effects of divalent iron may drastically alter the limit of trivalent iron substitution. There was no significant change in the polytypism of muscovite when iron was introduced. The 1M form is the predominant type with some mixed 1M and 2M polytypes appearing in areas close to the decomposition curve. The main effect of

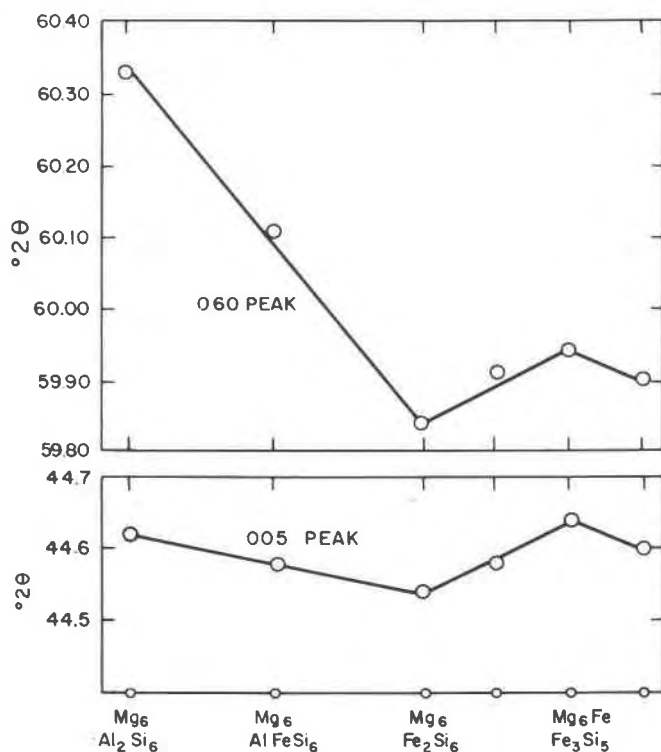


FIG. 11. Phlogopite-“Al-Biotite” spacing.

iron substitution into the muscovite structure is to lower the decomposition temperature by about 20° C.

2. In determining the extent of ferric iron substitution for Al and Mg+Si in phlogopites, mixtures No. 17 through No. 22 (Table 1) were used. The composition $K_2Mg_5Fe(Fe_3Si_5)O_{20}(OH)_4$ represents the limit of ferric iron substitution in a phlogopite type structure. The effect of ferric iron substitution on the cell size can be seen in Fig. 11 which shows the variation in the 005 and 060 peaks as a function of composition. An unusual feature of this series is the fact that the first atom of iron enters the tetrahedral layer substituting for Si, instead of entering the octahedra

layer to substitute for Mg. One can conclude that the iron must go into the tetrahedral layer, otherwise mixture No. 18 could not form a mica since it contains no Al. Further confirmation on the location of the initial iron atoms is obtained from a comparison of the 005 and 060 curves in Fig. 11; it is seen that the slope of the 060 curve for the first 3 mixtures is much greater than the slope of the 005 curve. Since the "b" axis is more dependent on the tetrahedral layers than the "c" axis, a change in the tetrahedral ion size will result in a larger shift for the "b" axis than the "c" axis.

The iron substitution, like the Al substitution, appears to have little effect on the polytypism of the phlogopite but the decomposition temperature is apparently lowered. Melting of the iron phlogopites was found in several runs and this complicated the picture on iron phlogopite stability, and no effort was made to determine the phase relations exactly.

Fluorine Substitution in Dioctahedral Micas

Roy (1949), and Noda and Roy (1956) were unable to make muscovite and partially F substituted phlogopites by solid state reaction, and Yoder and Eugster (1955) reported that they were unable to make fluoromuscovite by hydrothermal reactions. However, since many natural micas contain fluorine and numerous investigators have made mica "dry" using fluorine as a substitute for hydroxyl ions, some exploratory work on the effect of fluorine in hydrothermally synthesized micas seemed warranted.

The starting mixtures were made in the usual manner except that the salt $\text{KF} \cdot 2\text{H}_2\text{O}$ was used as the source of potassium and fluorine, and was ground in alcohol with the pre-calcined gel. It was felt that this procedure minimized the possibility of losing fluorine or silica as the volatile SiF_4 . Contrary to expectations, the introduction of fluorine into the mixtures did not increase the degree or rate of crystallization; however, the dark grey color of the charges, and the presence of topaz reported by Yoder and Eugster (1955) were found, indicating that fluorine was in the gel during the hydrothermal runs.

While this area was not investigated extensively, a sufficient number of runs were made to indicate that there is no (or very little) fluorine for hydroxyl substitution in muscovite or phengite at points intermediate between the "F" and "OH" end members. Precise peak measurements showed a very slight increase ($0.04^\circ 2\theta$) in the 005 and 060 spacings of "F" mica as compared to "OH" mica. However, it remains to be proven whether the fluorine substitutes for hydroxyl or oxygen ions or both, or if the substitutions will result in an appreciable shift in cell dimensions.

CONCLUSIONS

1. The limit of Mg substitution into muscovite is the phengite composition, $K_2MgAl_3(AlSi_7)O_{20}(OH)_4$, and the introduction of Mg enhances the formation of the 3T polytype at low temperatures. The decomposition reactions, muscovite \rightleftharpoons sanidine + corundum \rightleftharpoons sanidine + mullite + leucite have been shown to be easily reversible and revised p-t curves are presented for the reactions.

2. The limit of Al substitution into phlogopite is the composition $K_2Mg_4Al_2(Al_4Si_4)O_{20}(OH)_4$ which corresponds with the limit of Al replacement in chlorites reported by Nelson and Roy (1958). The introduction of Al has no effect on the polytypism but lowers the decomposition temperature about 100° C. The phlogopite decomposition curve determined in this work was found to be about 100° C higher than the literature value but the results are not unequivocal.

3. The limit of iron substitution into muscovite is $K_2Al_3Fe(Al_2Si_6)O_{20}(OH)_4$. The introduction of iron does not affect the polytypism of muscovite but does lower the decomposition temperature slightly.

4. The composition $K_2Mg_5Fe(Fe_3Si_6)O_{20}(OH)_4$ represents the limit of ferric iron substitution into phlogopite. Iron phlogopite is an example of a mica with no Al^{3+} and illustrates that Fe^{3+} can go easily into tetrahedral coordination as well as octahedral coordination.

5. Partial fluorine substitution in muscovite and phengite cannot be proven on the basis of cell dimension variations. Fluorine is known to be in the starting material but its effect on the micas is unknown and it could not be ascertained whether fluorine substitutes for hydroxyl or oxygen ions in the structure.

ACKNOWLEDGMENT

This research was supported by the American Petroleum Institute, Project 55. It appeared as Technical Report Number 1 (1958-59) of A.P.I. Project 55, dated January 26, 1959.

REFERENCES

- BRINDLEY, G. W. (1951) *X-ray Identification and Structure of Clay Minerals*. Mineral. Soc. Great Britain, Monograph, London.
- CROWLEY, M. S. AND R. ROY (1960) The effect of formation pressures on sheet structures—a possible case of Al-Si ordering. *Geochim. Cosmochim. Acta*, **18**, 94-100.
- DEVRIES, R. C. AND R. ROY (1958) The influence of ionic substitution on the stability of micas and chlorites. *Econ. Geol.* **53**, 958.
- FOSTER, M. D. (1956) Correlation of dioctahedral potassium micas on the basis of their charge relations. *U. S. Geol. Survey Bull.* **1036-D**, 57-67.
- (1960A) Interpretation of the composition of trioctahedral micas. *U. S. Geol. Survey Prof. Paper* **354-B**.

- FOSTER, M. D. (1960B) Interpretation of the composition of lithium micas. *U. S. Geol. Survey Prof. Paper* **354-E**.
- GRIM, R. E. (1953) *Clay Mineralogy*, McGraw-Hill Book Co., Inc., New York.
- HEINRICH, E. WM., *et al.* (1953) Studies in the natural history of micas. *Engr. Res. Inst. Univ. Michigan, Ann Arbor, Michigan, Rept.*
- NELSON, B. W. AND R. ROY (1958) Synthesis of the chlorites and their structural and chemical constitution. *Am. Mineral.* **43**, 707-725.
- NODA, T. AND R. ROY (1956) OH-F exchange in fluorine phlogopite. *Am. Mineral.* **41**, 929-931.
- ROMO, L. A. AND R. ROY (1957) Studies of the substitution of OH⁻ by F⁻ in various hydroxylic minerals. *Am. Mineral.* **42**, 165-177.
- ROY, D. M. AND R. ROY (1957) A redetermination of equilibria in the system MgO-H₂O and comments on earlier work. *Am. Jour. Sci.* **255**, 573-582.
- ROY, R. (1949) Decomposition and re-synthesis of the micas. *Jour. Am. Ceram. Soc.* **32**, 202.
- (1956) Some simple aids in hydrothermal experimentation II: The preparation of mixtures. *Jour. Am. Ceram. Soc.* **39**, 145-156.
- AND E. F. OSBORN (1952) Some simple aids in hydrothermal investigation of mineral systems. *Econ. Geol.* **47**, 717-721.
- AND O. F. TUTTLE (1956) Investigations under hydrothermal conditions. Chap. 6, *Physics and Chemistry of the Earth*, 1, Pergamon Press, New York.
- SCHAIRER, J. F. AND BOWEN, N. L. (1955) The system K₂O-Al₂O₃-SiO₂. *Amer. Jour. Science*, **253**, 681-746.
- SMITH, J. V. AND H. S. YODER (1956) Experimental and theoretical studies of the mica polymorphs. *Mineral. Mag.* **31**, 209-235.
- WARSHAW, C. M. (1960) Experimental studies of illite. *Proc. Seventh Natl. Clay Conf.*, p. 303-316, Pergamon Press, London.
- AND R. ROY (1961) The classification and scheme for the identification of layer silicates (in press).
- YODER, H. S. AND H. P. EUGSTER (1954) Phlogopite synthesis and stability range. *Geochim. Cosmochim. Acta.* **6**, 157-185.
- (1955) Synthetic and natural muscovites. *Geochim. Cosmochim. Acta.* **8**, 225-280.
- YOUELL, R. F. (1958) A clay mineralogical study of the ironstone at Easton Neston, Northamptonshire. *Clay Min. Bull.* **3**, 264-269.

Manuscript received, July 25, 1963; accepted for publication, November 26, 1963.