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Hydrothermal Synthesis of Fluor-Hydroxyl Muscovite

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Fluor-hydroxyl muscovite was synthesized from a mixture of gels and chemicals of the $KAl_3Si_3O_{10}F_x(OH)_{2-x}$ composition, where $x=0$, 0.5, 1.0, 1.5 and 2.0, in the temperature range of 500—600°C under pressures ranging from 500 to 900 atm. The fluorine content of the synthetic muscovite increased with the increase in x, but the distribution coefficient of fluorine [(the fluorine content of the crystal)/(the fluorine concentration of the solution)] decreased with the increase in x, increased with the increase in the temperature of synthesis, and decreased with the increase in the pressure of synthesis. The synthetic fluor-hydroxyl muscovite crystallized mainly in 1M polymorph, and very little in 2M polymorph, at 500°C in 20 hr. The fraction of 2M muscovite increased with the increasing temperature of synthesis. The d_{005} and d_{060} lattice spacings of the mica were observed to decrease linearly with the increase in the fluorine content of the mica.

Noda and Roy¹⁾ carried out the hydrothermal treatment of fluor-phlogopite with a dilute alkali solution, intending to replace F^-ions partially by $(OH)^-$ ions; they found that hydroxyl-phlogopite formed in a separated phase and that no appreciable ion exchange between $(OH)^-$ ions in the solution and F^- ions in the mica occurred. Noda and Ushio²⁾ reported the dependence of the fluorine content of fluor-hydroxyl phlogopite on the conditions of hydrothermal synthesis, such as the fluorine content of the starting material of phlogopite composition and the temperature and pressure of the synthesis. They also found a good linearity between c_0 spacing and the fluorine content of the mica.

In this paper, the results of similar experiments on fluor-hydroxyl muscovite will be reported. The syntheses of muscovite have been reported by various investigators and reviewed briefly by Yoder and Eugster.³⁾ Yoder and Eugster determined the pressure-temperature equilibrium in the decomposition of hydroxyl muscovite. They obtained 1 M and 2 M polymorphs of muscovite and reported that 1 M muscovite transformed to 2 M muscovite at higher temperatures, the transition temperature being in the 200—350°C range at 1000 kg./cm². Crowley and Roy⁴⁾ re-examined

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1) T. Noda and R. Roy, *Am. Mineral.*, **41**, 929 (1956).

2) T. Noda and M. Ushio, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **67**, 292 (1964); *Geochem. Internatl.*, **1964** (1), 96.

3) H. S. Yoder and H. R. Eugster, *Geochim. et Cosmochim. Acta,* **8**, 225 (1955).

4) M. S. Crowley and R. Roy, *Am. Mineral.*, **49**, 348 (1964).

the temperature-pressure equilibrium of hydroxyl-muscovite and determined the limits of the substitution of Mg^{2+} and Fe^{3+} ions in the muscovite structure. They also obtained muscovite by the hydrothermal treatment of a mixture of calcined gels and $KF \cdot 2H_2O$ with the requisite composition. Eitel⁵⁾ prepared fluor-muscovite from a mixture of calcined kaoline and K_2SiF_6 in a solid state reaction. According to Yoder and Eugster,³⁾ fluor-muscovite was obtained hydrothermally from a mixture of silica glass, γ-Al_2O_3 and K_2SiF_6 in only two runs, of one hour's duration, at 500 and 600°C. In longer runs and at higher temperatures, sanidine and topaz were usually obtained. They reported that the average fluorine content of some 60 specimens of natural muscovite was 0.58% (0.124 mol./2 mol. [F+(OH)]) and that the largest fluorine content of natural muscovite was 1.28%. The presence of fluorine ions in muscovite in place of hydroxyle ions may affect the stability range of the muscovite.

Experimental

Apparatus.—A cold-sealed test tube-type bomb⁶⁾ 12 mm. in inner diameter, 50 mm. in outer diameter and 280 mm. long and made of Stellite D6-K was used for the hydrothermal experiments. Mixtures of gels, potassium hydrogen fluoride and potassium carbonate with the requisite compositions were placed in sealed platinum tubes, 10 mm. in diameter, 90 mm. long and 0.03 mm. thick, and treated hydrothermally in the bomb. The bomb was pressurized by a pump. It was kept at a fixed temperature and pressure for 20-hr. After the treatment, the bomb was taken out of the furnace and cooled by a forced draft.

Materials.—$SiO_2 \cdot nH_2O$ gel was prepared by the hydrolysis of pure silicon tetrachloride and dried at 110°C. The dry gel was amorphous, and its water content was 5.0%. $Al_2O_3 \cdot nH_2O$ gel was precipitated by ammonia from a aluminum chloride solution which had been prepared by dissolving pure metallic aluminum (99.99%) in hydrochloric acid. The gel was washed with water and dried at 110°C. The dry gel was identified as gibbsite by the X-ray diffraction method. Its water content was 33.4%. The potassium hydrogen fluoride and potassium carbonate used were both pure chemicals. The calculated amounts of the gels and the chemicals were well mixed in an agate mortar. The water contents of the gels were determined before every mixing. The mixture contained about 18% water.

For experiments in which the fluorine distribution between crystal and solution was investigated, two parts of water was added to one part of the original mixture of the gels and the chemicals. The resulting mixture will be called the A-mix. Because the original mixture contained ca. 18% water, the ratio of solid substance to water in the A-mix was 0.38/1.00, or the ratio of the mica composition to water was 0.39/1.00, i. e., 0.97 mol./kg. water. In order to prepare specimens for the determination of lattice spacings, the original mixture moistened with a little water was used. This mix will becalled the B-mix. For both mixes, the chemical compositions given in Table I were used.

TABLE I. THE CHEMICAL COMPOSITION OF THE STARTING MIXTURE IN $KAl_2AlSi_3O_{10}(OH)_{2-x}F_x$

x	0,	0.5,	1.0,	1.5,	2.0
Abbreviations for the designation of the composition	F_0,	$F_{0.5}$,	$F_{1.0}$,	$F_{1.5}$,	$F_{2.0}$

After the hydrothermal treatment, the pH value of the coexisting solution was measured, and then the solution was separated from the solid substance. The solid substance was suspended in Thoule's solution (mercury(II) iodide-potassium iodide solution) with a density of ca. 3.0 in order to separate the heavier impurities by a centrifuge, and then the solution was diluted to a density of ca. 2.7 in order to separate the lighter impurities. For the determination of the fluorine content of the mica, the purified mica was fused with sodium carbonate and zinc oxide, the fused mass was dissolved in water, perchloric acid was added to the solution, the fluoride in the solution was distilled as fluosilicic acid, and the distillate was titrated with a thorium nitrate ($Th(NO_3)_4$) solution.⁷⁾ The fluorine in the coexisting solution was distilled from the solution and titrated with a thorium nitrate ($Th(NO_3)_4$) solution.

Results

The Distribution of Fluorine between Crystal and Solution.—The plot of the fluorine content of the muscovite crystal vs. the fluorine content of the starting mixture (dry basis) is give in Fig. 1. The fluorine content of the muscovite increases with the increase in the fluorine content of the starting mixture, x, with some variation with the temperature and pressure of syntheses.

The plot of the mean value of the fluorine content of muscovite, C_m, vs. the mean value of the fluorine concentration of the coexisting solution, C_s, is given in Fig. 2. In general, for the same starting mixture, F_x, C_m increases and C_s decreases with an increase in the temperature at a constant pressure, while C_m decreases and C_s increases with an increase in the pressure at a constant temperature. The dependences of C_m on the temperature at a constant pressure and of C_m on the pressure at a constant temperature are more clearly shown in Figs. 4a and 4b.

The plot of C_s vs. x in F_x is given in Fig. 3. The dependences of C_s on the temperature at a constant pressure and of C_s on the pressure at a constant temperature are given in Figs. 5a and 5b. C_s

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5) W. Eitel, *Proc. Internatl. Symposium on the Reactivity of Solids, Gothenburg*, 335 (1952).

6) O. F. Tuttle, *Bull. Geol. Soc. Am.*, **60**, 1727 (1949).

7) H. R. Shell and R. L. Craig, *Anal. Chem.*, **26**, 996 (1954).

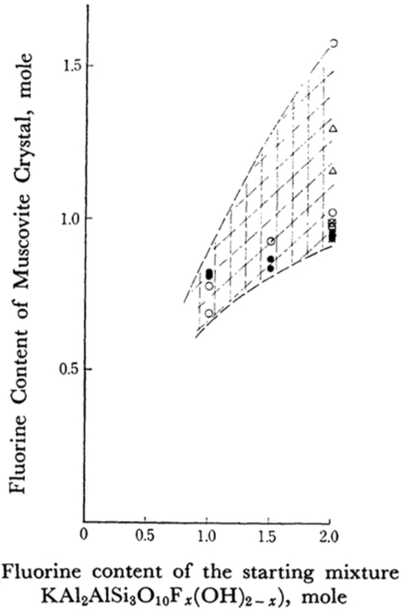

Fig. 1. Dependence of fiuorine content of muscovite crystal on the fluorine content of the starting mixture.

○ 600°C 700 atm.
● 500°C 700 atm.
□ 550°C 900 atm.
× 550°C 700 atm.
△ 550°C 500 atm.

decreases with an increase in temperature and increases with an increase in pressure. The dependences of C_s on the temperature and pressure are thus just the reverse of those of C_m. Because a definite amount of the starting mixture was used in a sealed platinum tube, thus making a closed system, the increase in C_m results in the decrease in C_s. The amount of C_m relative to C_s is determined by the distribution coefficient of fluorine between crystal and solution.

The distribution coefficient (C_m/C_s) is given in Table II.

TABLE II. THE DISTRIBUTION COEFFICIENT OF FLUORINE BETWEEN CRYSTAL AND SOLUTION

Starting mixture	Pressure atm.	Temperature, °C			(B-mix)
		500	550	600	
$F_{2.0}$	500	—	2.0	—	
	700	1.0	1.2	1.6—1.9	(1.7)
	900	—	1.1	—	
$F_{1.5}$	700	1.2	—	2.2	(1.9)
$F_{1.0}$	700	6.5	—	6.1	(5.8)

The distribution coefficient increases with the increase in temperature for $F_{2.0}$ and $F_{1.5}$, but it does not change much for $F_{1.0}$. The coefficient decreases with the increase in pressure. It decreases with the increase in x.

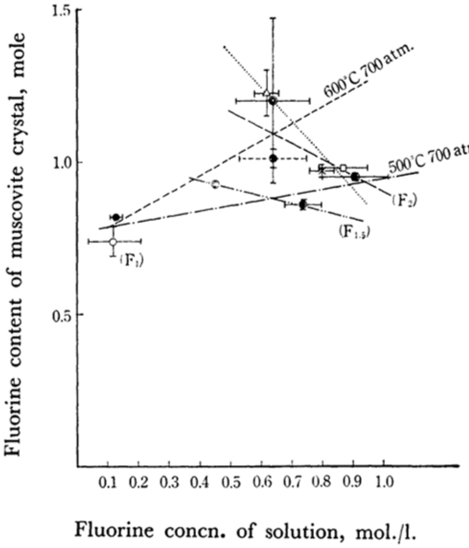

Fig. 2. Dependence of fluorine content of muscovite crystal on the fluorine concentration of solution.

○ 600°C 700 atm. (F_1)
◎ 600°C 700 atm. ($F_{1.5}$)
◎ 600°C 700 atm. ($F_{2.0}$)
● 500°C 700 atm. (F_1)
⊙ 500°C 700 atm. ($F_{1.5}$)
◉ 500°C 700 atm. ($F_{2.0}$)
□ 550°C 900 atm. ($F_{2.0}$)
× 550°C 700 atm. ($F_{2.0}$)
△ 550°C 500 atm. ($F_{2.0}$)
▨ 600°C 700 atm. ($F_{2.0}$)[a]

(a) Indicate the mean value excluding a value deviating greatly.

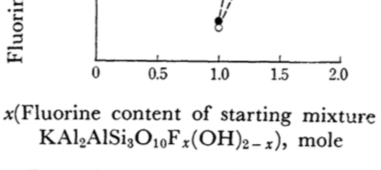

Fig. 3. Dependence of fluorine concentration of solution on the fluorine content of the starting mixture.

○ 600°C 700 atm.
● 500°C 700 atm.
□ 550°C 900 atm.
× 550°C 700 atm.
△ 550°C 500 atm.

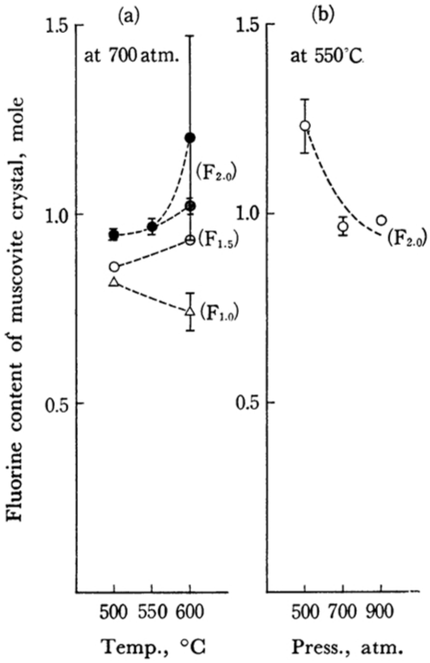

Fig. 4. Dependence of fluorine content of muscovite crystal on (a) temperature and (b) pressure of synthesis.

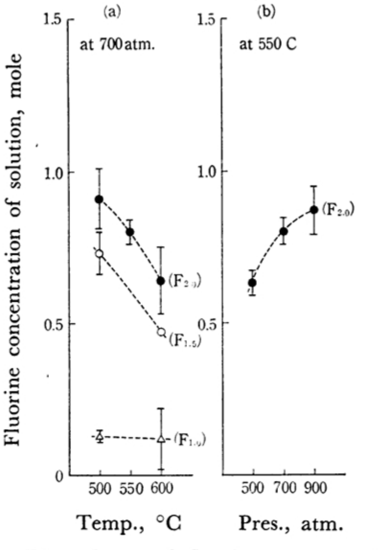

Fig. 5. Dependence of fluorine concentration of solution on (a) temperature and (b) pressure of synthesis.

Almost the same results were obtained in the experiments using the B-mix. The series experiments were carried out at 600°C under 700 atm. The dependence of C_m on x given in Fig. 6 is almost identical with that found in the A-series experiments carried out at 600°C under 700 atm. One could estimate the C_s values of B-series experiments from the C_s vs. x curve of the A-series experiments at the same temperature and pressure. The C_m/x vs. x ratio of the B-mix is shown in Fig. 7. One can see that the ratio decreases with the increase in x. Using the C_s values of Fig. 3 and the C_m values of Fig. 6, the distribution coefficients were obtained; they are given in parentheses in Table II.

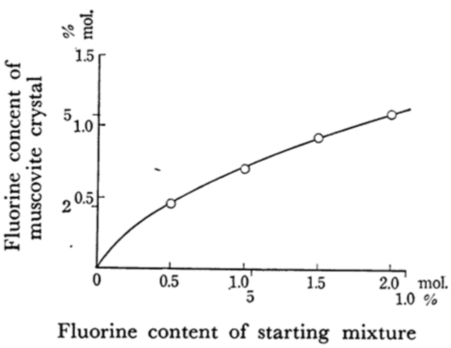

Fig. 6. Dependence of fluorine content of muscovite crystal on fluorine content of starting mixture (B-Series).

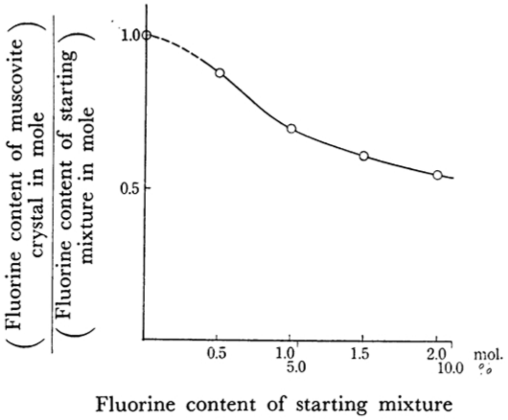

Fig. 7. Dependence of the ratio [(Fluorine content of muscovite crystal)/(Fluorine content of starting mixture)] on fluorine content of starting mixture.

The pH values of the coexisting solution increase with the increase in C_s, although there is a considerable scattering of points, as is shown in Fig. 8. There are approximate proportionalities of pH with C_s among the experiments made at 500, 550 and 600°C under 700 atm., and among the experiments made at 500, 700 and 900 atm. at 550°C for the F_2 composition. There is also an approximate proportionality of pH with x among the experiments using $F_{2.0}$, $F_{1.5}$, $F_{1.0}$ at 500°C under 700 atm. However, there are too few points to establish a definite relationship for each set of experimental conditions.

The Polymorphism and Lattice Spacing of Fluor-Hydroxyl Muscovite.—The muscovite crystals hydrothermally synthesized from the mixture

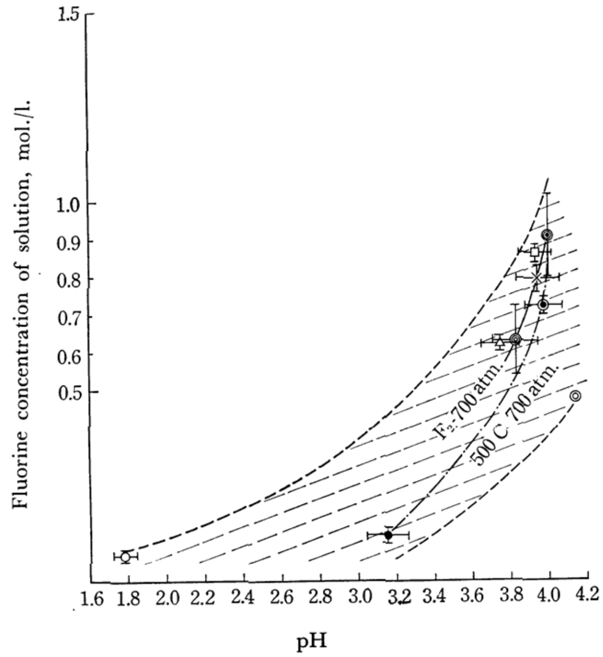

Fig. 8. Plot of fluorine concentration of solution vs. pH of solution.

○ 600°C 700 atm.($F_{1.0}$) ◎ 600°C 700 atm.($F_{1.5}$) ◎ 600°C 700 atm.($F_{2.0}$)
● 500°C 700 atm.($F_{1.0}$) ⊙ 500°C 700 atm.($F_{1.5}$) ◉ 500°C 700 atm.($F_{2.0}$)
☐ 550°C 900 atm.($F_{2.0}$) × 550°C 700 atm.($F_{2.0}$) △ 550°C 500 atm.($F_{2.0}$)

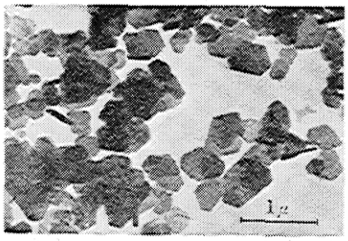

Plate I. Fluor-hydroxyl muscovite synthesized from $F_{2.0}$-composition at 600°C, 700 atm.

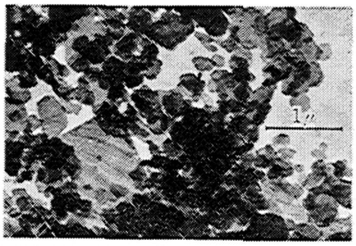

Plate III. Fluor-hydroxyl muscovite synthesized from $F_{1.0}$-composition at 600°C, 700 atm.

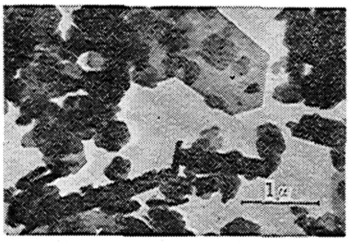

Plate II. Heavy fraction of synthetic product from $F_{2.0}$-composition at 600°C, 700 atm.

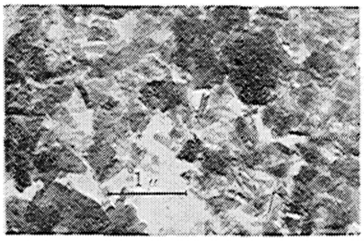

Plate IV. Hydroxyl muscovite synthesized from $F_{0.0}$-composition at 600°C, 700 atm.

of gels of silica and alumina and potassium fluoride in muscovite composition were accompanied by small amounts of topaz and feldspar. Topaz was concentrated in the heavier fraction separated by centrifuging the mixture in Thoule's solution. Topaz crystals are seen as columnar crystals in the electron micrographs shown in Plates I and II.

Fluor-hydroxyl muscovite crystallized from fluorine-containing compositions mainly in 1 M or 1 Md polymorph, and very little in 2 M polymorph, at 500°C in 20 hr. (cf. the X-ray diffraction patterns shown in Fig. 9, Nos. 1, 4 and 7). The fraction of 2 M muscovite gradually increased with the increase in the temperature of synthesis (Fig.

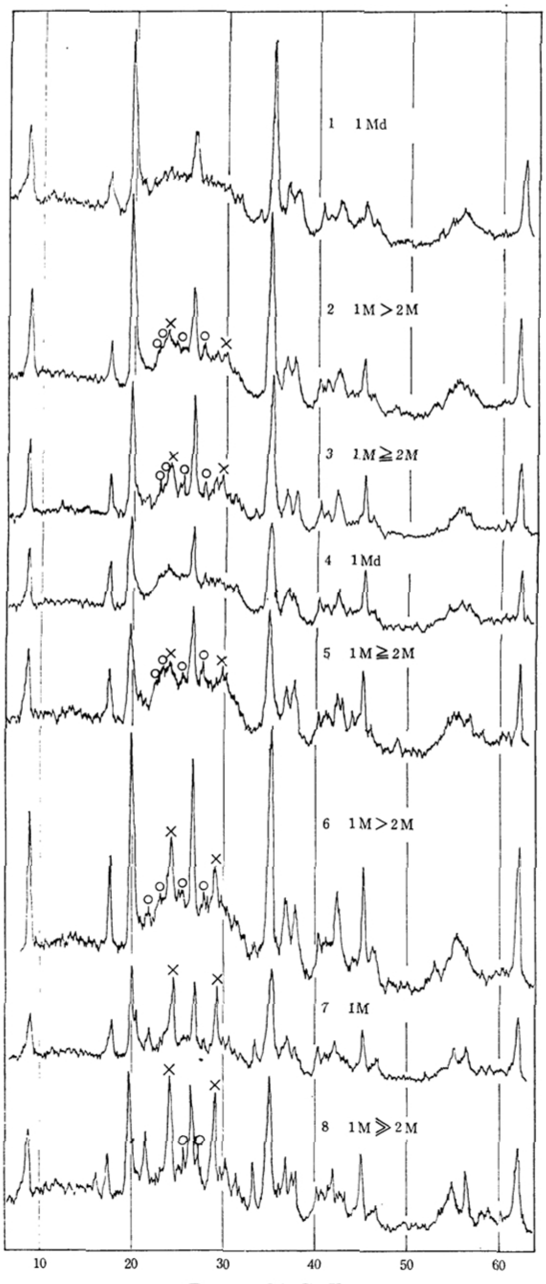

Fig. 9. X-ray powder patterns of fluor-hydroxyl muscovites prepaperd from

1. $F_{2.0}$-composition at 500°C 700 atm.
2. $F_{2.0}$-composition at 550°C 700 atm.
3. $F_{2.0}$-composition at 600°C 500 atm.
4. $F_{1.5}$-composition at 500°C 500 atm.
5. $F_{1.5}$-composition at 600°C 500 atm.
6. $F_{1.0}$-composition at 600°C 500 atm.
7. $F_{0.5}$-composition at 500°C 500 atm.
8. $F_{0.5}$-composition at 600°C 500 atm.

○ 2 M × 1 M

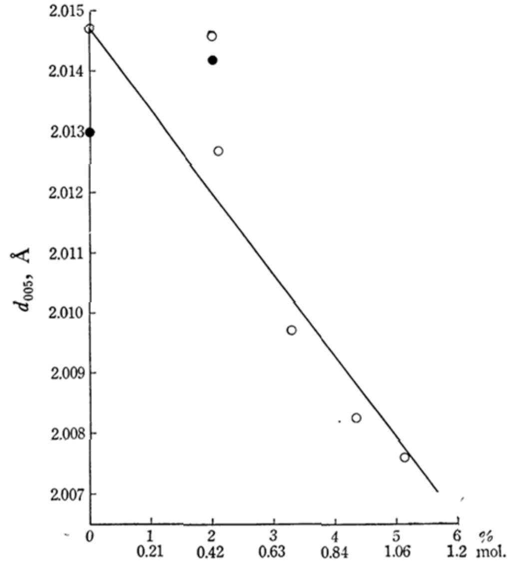

Fig. 10. Dependence of lattice spacing d_{005} on fluorine content of muscovite.
○ Experimental value
● Yoder and Eugster (1955)

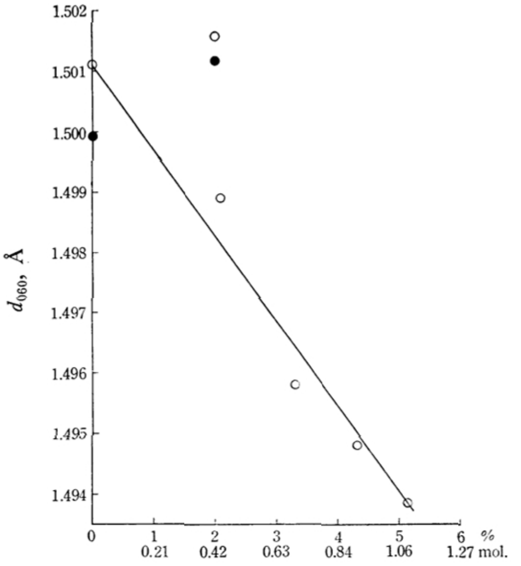

Fig. 11. Dependence of lattice spacing d_{060} on fluorine content of muscovite.
○ Experimental value
● Yoder and Eugster (1955)

9, Nos. 1, 2 and 3 for $F_{2.0}$, Nos. 4 and 5 for $F_{1.5}$, and Nos. 7 and 8 for $F_{0.5}$). The X-ray diffraction patterns of some of the muscovite specimens synthesized at 500°C from $F_{2.0}$ and $F_{1.5}$ compositions were found to be that of the 1 Md structure (Fig. 9, Nos. 1 and 4), while that of muscovite synthesized at 500°C from a $F_{0.5}$ composition was found to be of the 1 M structure (Fig. 9, No. 7). The muscovite synthesized at 600°C from $F_{2.0}$ and $F_{1.5}$ compositions was composed of almost equal amounts of 1 M and 2 M polymorphs (Fig. 9, Nos. 3 and 5), while muscovite synthesized at 600°C from $F_{1.0}$ and $F_{0.5}$ compositions (Fig. 9, Nos. 6 and 8) contained a smaller fraction of 2 M polymorph than those obtained from $F_{2.0}$ and $F_{1.5}$ compositions. It seems that muscovite containing a larger amount of fluorine tends to crystallize more in 2 M polymorph than those containing a smaller amount of fluorine at higher temperatures. Hydroxyl-muscovite which had crystallized at 600°C in 20 hr., was 1 M polymorph. Well-developed hexagonal crystals with the prism faces on the basal plate were observed in muscovite specimens synthesized from $F_{2.0}$ and $F_{1.0}$ compositions by an electron microscope (Plates I and III). Hydroxyl-muscovite crystals had less well-developed plates (Plate IV). Also, in the case of synthetic fluor-hydroxyl phlogopite,⁸⁾ fluorine-containing mica crystallized in a better-developed form than did hydroxyl-phlogopite.

The lattice spacings of synthetic muscovite were determined by an X-ray diffractometer with copper radiation and a nickel filter, using extra pure silcon powder as an inner standard.

The plots of d_{005} and d_{060} vs. C_m are given in Figs. 10 and 11. The spacings change linearly with the change in the fluorine content of muscovite, and both plots have the same slope. The deviation of a point from the straight line may mostly be caused by an error in the determination of the fluorine content in the mica. The linear dependence of the spacings on the fluorine content in muscovite is very obvious, although Crowley and Roy⁴⁾ observed a very slight increase in the spacings of "F" mica as compared with those of "OH" mica.

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8) T. Noda and N. Yamanishi, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **67**, 289 (1964); *Geochem. Internatl.*, **1964** (1), 90.