STUDIES IN THE MICA GROUP: POLYMORPHISM AMONG ILLITES AND HYDROUS MICAS

A. A. LEVINSON, *College of Engineering, The Ohio State University, Columbus 10, Ohio.*

ABSTRACT

Powder and single crystal *x*-ray studies on specimens called illite or hydrous mica have demonstrated that polymorphism exists among these minerals. The 3-layer trigonal (*3T*), 2-layer monoclinic (*2M*), 1-layer monoclinic (*1M*) and 1-layer monoclinic disordered (*1Md*) structures have been identified. The commonly held concept that all illites have poorly crystallized *2M* structures is disproved. No definite correlation between the type of polymorphic crystallization and either chemical composition or geological occurrence has been observed.

INTRODUCTION

In their original description, Grim, Bray and Bradley (1937) concluded that the structure of illite from Gilead, Illinois, is closely related to that of common 2-layer monoclinic (2*M*) muscovite. Two years later Hendricks and Jefferson (1939) described the wide variety of polymorphic forms of mica. Grim, Bradley and Brown (1951, p. 145) state that the demonstration of polymorphism in biotites introduced several structural possibilities of which they had previously been unaware and note that the characterization of illite as a derivative of *2M* muscovite crystallization is based on less rigorous grounds than would be normally desired. In later papers by Grim and his colleagues, and especially in Grim (1953, p. 67), it has been pointed out that "illite" does not refer to a specific structural type of mica. Nevertheless, many persons apparently retain the early concepts as a consequence of the fact that Hendricks and Jefferson (1939) found the *2M* structure to be unique for muscovite. The degree of the dissemination of this concept may be gauged by the fact that many investigators compare material they believe to be illite or hydrous mica (these terms are here used synonomously) with the musocvite spacings reported by Nagelschmidt (1937) and others which have a *2M* structure, or assign indices on the basis of a *2M* structure, unmindful of other structural possibilities. However, the 3-layer muscovite polymorph discovered by Axelrod and Grimaldi (1949) and the lithian muscovite variation reported by Levinson (1953), demonstrate that the muscovite structure is not unique. Thus the structural interrelationship between muscovite and hydrous micas requires reëxamination.

To the writer's knowledge, the brief mention by Yoder and Eugster (1954) of a *1Md* (1-layer monoclinic disordered structure) illite has been the only published attempt to re-evaluate the *x*-ray data on illite or hydrous mica taking into account the fact that these minerals may crystallize as some polymorph other than the common *2M* muscovite. The purpose of this paper is to point out that at least three polymorphs exist among micas called illites or hydrous micas (all dioctahedral) and therefore all minerals of this type may not be considered a defect or poorly crystallized *2M* muscovite structure as many investigators have erroneously concluded from the work of Grim et al. (1937).

This work has been aided by generous gifts of illites and hydrous micas from Dr. Robert C. Mackenzie, Macaulay Institute for Soil Research, Aberdeen, Scotland, and a specimen of the hydrous mica from the Yorkshire fireclay received from Dr. A. G. Sadler of the University of Leeds, England, which has been described by Carr, Grimshaw and Roberts (1953). Professor Duncan McConnell, of this department, critically read the mansucript. Dr. H. S. Yoder kindly supplied information on the differentiation of polymorphs in addition to that available in the literature.

Identification of Polymorphs

Grim, Bradley and Brown (1951) in their discussion of mica polymorphism note (p. 145) that in the range from about 4.4 kX to 2.6 kX the most characteristic diffraction lines of the various mica polymorphs may be observed. This corresponds with 2θ for copper radiation of about 20° to 34°. They also present data (p. 166) for distinguishing the polymorphic forms of mica. This information is used as a basis for identification of the structures, although additional aid was obtained from comparison of known *1M*, *2M* and *3T* powder patterns, these structures having been first determined by single-crystal Weissenberg studies. Dr. H. S. Yoder (personal communication) pointed out that a measure of disorder in the *1M* structure may be gauged from the absence or low intensity of the $(11\bar{2})$ and (112) reflections which correspond with (approx.) $d=3.62$ Å and 3.07 Å, respectively.

The 3-layer Trigonal (3*T*) Polymorph

As originally defined by Grim et al. (1937), illite is a general term for the clay-mineral constituents of argillaceous sediments belonging to the mica group. This definition has been modified in such a way that illite has been used as a general name for mica-clay minerals from other environments. Mackenzie, Walker and Hart (1949), for example, have described illite occurring in the decomposed granite at Ballater, Aberdeenshire. This mineral might possibly have been called "sericite" or "phengite" (owing to its high silica) if older terms had been employed. The fact that it is relatively low in potassium and correspondingly high in water justifies the name hydrous mica under any condition.

Specimens of this mica were obtained from Dr. Mackenzie for *x*-ray

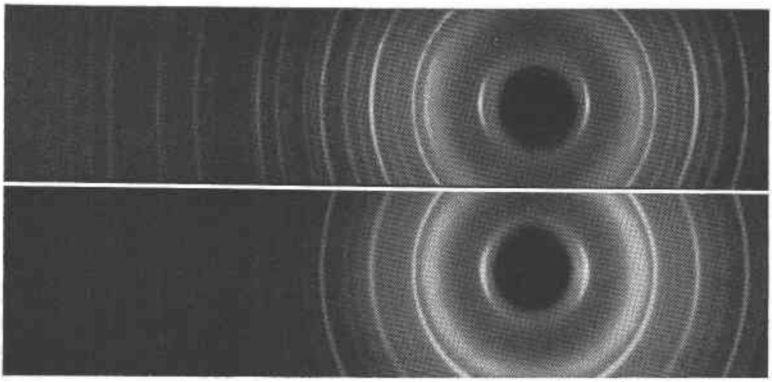

FIG. 1. Powder x-ray photographs of 3-layer trigonal (*3T*) mica polymorphs. Top: Muscovite from Sultan Basin, Washington. Bottom: Illite from Ballater, Aberdeenshire. Filtered copper radiation.

study. Powder photographs of the Ballater mica were compared with photographs of *3T* muscovite* from Sultan Basin, Washington, described by Axelrod and Grimaldi (1949). The patterns are identical (Fig. 1) and it is thus concluded that the illite from Ballater has crystallized with the *3T* structure. (This same polymorph has previously been described as 3-layer rhombohedral or hexagonal by various authors). The d-spacings for the *3T* Ballater illite are given in Table 1 along with new powder data on the *3T* muscovite from Sultan Basin. The data given by Axelrod and Grimaldi (1949) were obtained using unfiltered radiation with the result that several diffraction lines result in part or wholly from β radiation.

THE 2-LAYER MONOCLINIC (*2M*) POLYMORPH

Several examples of hydrous micas or illites crystallizing with this structure have been identified. The most interesting one is the hydrous mica from the Yorkshire fireclay described by Carr, Grimshaw and Roberts (1953) because it was possible to obtain single-crystal Weissenberg photographs from several flakes. Figure 2 is believed to be the first single crystal photograph obtained from a hydrous mica. The structure is unmistakably *2M*.

Optical studies of specimens of this mica yield different results from

* The muscovite from Sultan Basin, Washington, described by Axelrod and Grimaldi (1949), has been restudied by the Weissenberg method. The conclusion that this mica is monoclinic on the basis of differences in diffuse scattering has not been confirmed by this writer. The mica is therefore considered to be *3T*, although the 2V of as much as 15° is admittedly anomalous. Smith and Yoder (1954) reached the same conclusion regarding the structure by utilizing the precession method.

TABLE 1. X-RAY POWDER DATA FOR 3-LAYER TRIGONAL POLYMORPHS

A. 3T Muscovite		*B. 3T Illite*	
d(Å)	*I*	*d*(Å)	*I*
9.98	S	9.9	S
4.98	M	4.9	M
4.47	S	4.45	VS
4.29	VW	4.28	W
4.11	VW	4.10	W
3.87	M	3.87	M
3.60	M	3.64	MW
3.34	VS	3.35	VS
3.10	M	3.09	MW d
2.87	M	2.85	M d
2.57	VS	2.56	VS
2.47	M d	2.45	MW
2.38	M	2.39	M
2.24	W	2.235	MW
2.20	W	—	
2.13	M	2.14	M
2.05	VW	—	
2.00	MS	1.988	M
1.96	W	1.940	W
1.72	VW	—	
1.65	M	1.647	M d
1.61	VW	—	
1.52	VW	—	
1.50	M	1.497	S
1.35	M	1.342	MW d
1.30	MW	1.294	M
—		1.266	W
1.25	W	1.243	MW

A. 3T muscovite, Sultan Basin, Wash., described by Axelrod and Grimaldi (1949). Spacings remeasured using filtered copper radiation and 114.59 mm. diameter camera. $CuK\alpha = 1.5418$ Å.

B. 3T illite, Ballater, described by Mackenzie, et al. (1949). Spacings from original paper. FeK_{α} radiation.

those reported by Carr, et al. (1953). Particularly, the optic angle was reported as small (between 5° and 10°) whereas the optic angles observed by the writer were considerably larger than 10°. In some cases the retardation on flakes in horizontal positions is high and distinct interference figures indicate a 2V of approximately 30° (est.). One index on these flakes was found to be as high as 1.590 whereas 1.578 is reported in the original paper. Thus it seems likely that two phases exist in the hydrous mica from the Yorkshire fireclay although the powder *x*-ray data given by Carr, et al. (1953) suggest the *2M* polymorph.

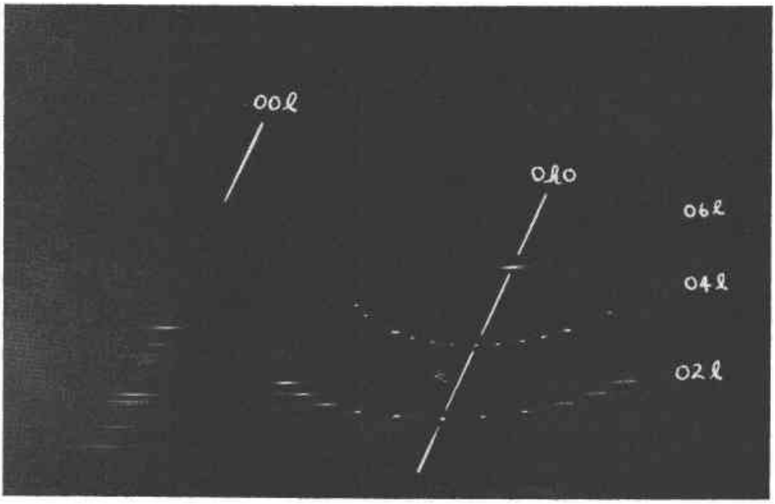

FIG. 2. Zero-level *a*-axis Weissenberg photograph obtained from hydrous mica described by Carr, et al. (1953) showing 2-layer monoclinic (*2M*) polymorph. Unfiltered copper radiation. (020), (021), (022) and (04*l*) reflections were retouched for better reproduction.

Another example of a *2M* structure is furnished by a specimen of illite from Fithian, Illinois, which has been described in the American Petroleum Institute reports as *A.P.I.* specimen number 35. The specimen is a coarse fraction and thus the powder patterns show some quartz lines. Nevertheless the *2M* polymorph can be definitely established. Another specimen from this locality with a *1Md* structure will be described below. Powder diffraction data for the *2M* muscovite polymorph have been reported by several investigators. Those of Nagelschmidt (1937) or Grim, et al. (1937) may be used to identify this structure.

TABLE 2. ANALYSIS OF ILLITE FROM ST. AUSTELL, CORNWALL

SiO_2	53.3
Al_2O_3	26.0
Fe_2O_3	2.5
TiO_2	0.01
MgO	4.4
CaO	0.2
K_2O	8.3
Na_2O	0.3
loss on ign.	5.7
	100.71

Analyzed at the laboratories of English Clays Lovering Pochin and Co. Ltd., St. Austell, Cornwall, England. Mr. I. H. Warren kindly gave permission to publish this analysis.

TABLE 3. X-RAY POWDER DATA FOR 1-LAYER MONOCLINIC POLYMORPHS

1. *1M Lepidolite*		2. *1M Illite*		3. *1M "Hydromuscovite"*		4. *1Md Illite*		5. *1Md Illite*	
d(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
9.98	MS	10.1	S	10.1	S	10.1	S	10.0	VS
4.98	MS	4.98	M	4.98	W	4.98	W	5.0	M
4.53	M	4.50	S	4.48	S	4.48	S	4.46	VS
4.34	VW	4.35	VW	—		—		—	
4.12	VW	4.10	VW	4.09	VW	—		—	
3.86	VW	3.85	VW	3.87	VW	—		—	
3.62	S	3.62	MS	3.65	M	—		—	
3.33	VS	3.32	S	3.34	S	3.33	S	3.32	VS
3.07	S	3.08	MS	3.07	M	3.07	VW	2.97	VW
2.86	M	2.89	MW	2.88	VVW	2.85	VW	2.80	VW
2.68	W	2.67	W	2.67	MW	—		—	
2.58	S	2.57	VS	2.56	S	2.57	VS	2.55	VS
2.48	W	2.47	W	2.46	W	2.46	W d	2.44	W
2.39	MW	2.38	M	2.38	MW	2.38	W d	2.37	WM
2.26	W	2.25	MW	2.25	W	2.25	W d	2.23 }	W
—		—		—		—		2.17 }	
2.14	MW	2.14	M	2.13	MW	2.14	W d	2.14	M
1.99	MS	1.99	S	2.00	M d	1.99	W d	1.98	M
1.96	VVW	—		—		—		—	
1.72	VW	1.71	VW	—		—		—	
1.65	M d	1.65	M d	1.64	W d	1.65	W d	1.64	M
1.58	VW	1.58	VVW	—		—		—	
1.51	S	1.50	S	1.50	MS	1.50	S	1.49	VS
1.43	VW	—		—		—		—	
1.38	VW	1.38	VVW	—		—		—	
1.35	VW	—		—		—		—	
1.34	W	1.34	W d	1.34	W	1.34	W d	1.34	W
1.30	M	1.30	M	1.29	W	1.30	MW	1.29	M
1.25	VW	1.25	W	1.25	VW	1.25	W	1.24	W

Data for samples 1 through 4 obtained using filtered copper radiation and 114.59 mm. diameter camera. $CuK\alpha = 1.5418$ Å.

1. *1M* Lepidolite, Brown Derby pegmatite, Colorado.
2. *1M* Illite, St. Austell Clay, Cornwall.
3. *1M* "Hydromuscovite" from decomposed granite, Aberdeenshire.
4. *1Md* Illite, Fithian, Illinois.
5. *1Md* Illite, South Wales, described by Nagelschmidt and Hicks (1943). Spacings from original paper: CoK_α radiation.

THE 1-LAYER MONOCLINIC (*1M*) POLYMORPH

A previously undescribed illite from the St. Austell China Clay deposits, Cornwall, was supplied by Dr. R. C. Mackenzie. Data furnished by Dr. Mackenzie indicate that this material is dioctahedral, that it gives a *D.T.A.* curve very similar to the Ballater illite discussed above (which has been shown to have a *3T* structure) and that the deposit from which it comes is not of sedimentary origin. An analysis of this illite is presented in Table 2; noteworthy is the high K_2O content.

X-ray study of this Cornwall illite shows that the material is pure and has an essentially well ordered *1M* structure. When compared with *1M* lepidolite the patterns are practically identical except that the illite gives slightly more diffuse lines, as would be expected (Fig. 3). Spacings for this *1M* illite are given in Table 3 and are compared with a *1M* lepidolite as well as other *1M* illites or hydrous micas described below.

Another specimen received from Dr. Mackenzie is the hydromuscovite mentioned by MacEwan (1951, the "*HM*" in Table 4, p. 133). Inasmuch as identification apparently depends on how these terms are defined, illite would also be a suitable name for this material. Dr. Mackenzie notes that it gives a *D.T.A.* peak of the illite type and that it originated from a boulder of decomposed granite in glacial drift in Aberdeenshire. The *x*-ray patterns show a small amount of quartz contamination but this does not interfere with the identification of the polymorph. The structure is *1M* and the pattern compares closely with that of the Cornwall illite described above. The most noticeable difference is the low intensity of the reflection with $d=2.88$ Å on the former as compared with the medium intensity of this reflection in the latter (Fig. 3).

A specimen of illite from Fithian, Illinois, was purchased from Ward's Natural Science Establishment. Powder *x*-ray photographs were extremely poor and show only a few discernible reflections in addition to several orders of the basal pinacoidal reflections (Fig. 3). In the range of approximately $d=4.48$ Å to $d=2.57$ Å, for example, there is little more than a faint haze with the exception of the strong basal reflection at $d=3.33$ Å. (112) and ($11\bar{2}$) reflections ($d=3.07$ and 3.62 Å) are either extremely weak or absent. The absence or low intensities of these reflections is the yardstick used by Dr. Yoder (personal communication) for designation of the *1Md* (disordered *1M*) structure, resulting from random stacking of the mica layers. This specimen of illite from Fithian is thus interpreted as a *1Md* structure and is analogous to disordered kaolinite recently described by Robertson, Brindley and Mackenzie (1954). The *1Md* structure has been noted in illite from Illinois by Yoder and Eugster (1954). Another polymorph, the *2M*, from the same general locality has been described above.

A specimen of the illite (fine fraction) described by Nagelschmidt and Hicks (1943) from South Wales has also been obtained for study. *X*-ray studies gave essentially identical results with those reported in the original paper. However, a few weak reflections observed only on aggregate

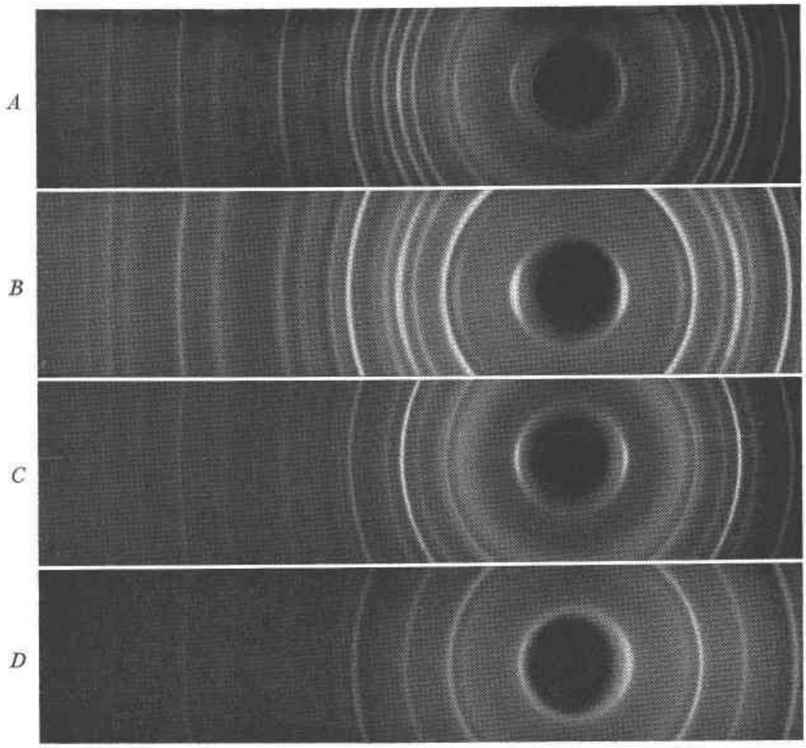

FIG. 3. Powder x-ray photographs of 1-layer monoclinic (*1M*) mica polymorphs. Filtered copper radiation. *A. 1M* lepidolite, Colorado. *B. 1M* illite, St. Austell Clay, Cornwall. *C. 1M* "hydromuscovite," Aberdeenshire. (Small amount of quartz contamination.) *D. 1Md* (disordered) illite, Fithian, Illinois.

diagrams by Nagelschmidt and Hicks (1943) were observed on the powder diagrams in the present investigations; they consist of the kaolinite reflections at 7.1 and 3.55 Å. The x-ray powder photographs appear very similar to those obtained from the *1Md* illite from Fithian, Illinois. (112) and ($11\bar{2}$) reflections are extremely weak or absent; the structure is therefore considered another example of a *1Md* illite.

DISCUSSION

It has been shown that minerals which have been called illite, hydromuscovite and hydrous mica have crystallized as the 3-layer trigonal (*3T*), 2-layer monoclinic (*2M*), 1-layer monoclinic (*1M*) and 1-layer monoclinic disordered (*1Md*) mica polymorphs. The demonstration of polymorphism in these "clay-micas" makes untenable the commonly held concept that all dioctahedral micas of this type are poorly crystallized *2M* muscovite. Caution must be exercised in indexing powder diffraction patterns because, for example, the 10.0 Å line corresponds with

(001) in *1M* and *1Md* polymorphs, (002) in the *2M* polymorph and (003) in the *3T* polymorph. The reader is referred to Grim, Bradley and Brown (1951, p. 166) for the correct indices of some reflections common to all polymorphs.

The cause of these polymorphic variations is not known. They do not appear to be related to any evident geological, environmental or chemical variations. It is interesting to note that both the *2M* and *1Md* polymorphs have been observed in illites from Fithian, Illinois. The *3T* and *1M* polymorphs have been observed only in non-sedimentary environments, specifically in decomposed granites. The *2M* and *1Md* polymorphs studied were found in micas only from sedimentary environments.

Mackenzie, et al. (1949) have noted that the Ballater illite gives a *D.T.A.* curve different from that of any previously described illite or hydrous mica. It would be logical to suggest, therefore, that some variations among such curves may be caused by differences inherent in the various polymorphic modifications.

References

Axelrod, J. M., and Grimaldi, F. S. (1949), Muscovite with small optic axial angle: *Am. Mineral.*, **34**, 559–572.

Carr, K., Grimshaw, R. W., and Roberts, A. L. (1953), A hydrous mica from Yorkshire fireclay: *Mineral. Mag.*, **30**, 139–144.

Grim, R. E. (1953), Clay Mineralogy: McGraw-Hill, New York.

Grim, R. E., Bray, R. H., and Bradley, W. F. (1937), The mica in argillaceous sediments: *Am. Mineral.*, **22**, 813–829.

Grim, R. E., Bradley, W. F., and Brown, G. (1951), The mica clay minerals; *X*-ray identification and crystal structures of clay minerals: Chapter V, pp. 138–172, *Mineralogical Society of Great Britain.*

Hendricks, S. B., and Jefferson, M. E. (1939), Polymorphism of the micas: *Am. Mineral.*, **24**, 729–771.

Levinson, A. A. (1953), Studies in the mica group; Relationship between polymorphism and composition in the muscovite-lepidolite series: *Am. Mineral.*, **38**, 88–107.

MacEwan, D. M. C. (1951), The montmorillonite minerals (montmorillonoids): *X*-ray identification and crystal structures of clay minerals: Chapter IV, pp. 86–137, *Mineralogical Society of Great Britain.*

Mackenzie, R. C., Walker, G. F., and Hart, R. (1949), Illite occurring in decomposed granite at Ballater, Aberdeenshire: *Mineral. Mag.*, **28**, 704–713.

Nagelschmidt, G. (1937), *X*-ray investigations on clays. Part III. The differentiation of micas by *x*-ray powder photographs: *Zeit. Krist.*, **97**, 514–521.

Nagelschmidt, G., and Hicks, D. (1943), The mica of certain coal-measure shales in South Wales: *Mineral. Mag.*, **26**, 297–303.

Robertson, R. H. S., Brindley, G. W., and Mackenzie, R. C. (1954), Mineralogy of kaolin clays from Pugu, Tanganyika: *Am. Mineral.*, **39**, 118–138.

Smith, J. V., and Yoder, H. S. (1954), Theoretical and *x*-ray study of the mica polymorphs (abstract): *Am. Mineral.*, **39**, 343–344.

Yoder, H. S., and Eugster, H. P. (1954), Syntheses and stability of the muscovites (abstract): *Am. Mineral.*, **39**, 350–351.

Manuscript received Dec. 16, 1953