X-RAY SPECTROMETER STUDY OF MICA POWDERS

Suzanne vanDijke Beatty*

ABSTRACT

The diffraction patterns of mica powders were used to test the reproducibility of various methods of powder sample preparation with a recording Geiger-counter-x-ray spectrometer. The method described proved satisfactory and is suitable for the preparation of all types of powders. The diffraction patterns of twelve micas are given and it is noted that differences occur for similar varieties obtained from different localities.

INTRODUCTION

A suitable method for the preparation of powder samples is particularly important in studies where a large flat sample area is required as with the Norelco x-ray spectrometer. In many cases, this instrument is being used to study materials having relatively weak patterns (e.g. clay minerals) so that wider slits than usual must be employed. With wider slits, however, the image of the beam upon the sample is considerably larger. Furthermore, the clay minerals have reflections at very low glancing angle (e.g. 5°) where the irradiated area is several times greater than at 30°. Thus, a large powder sample area must be obtained.

Powder samples of the pure micas are especially difficult to prepare since the cleavage planes are so very well defined. Thus an investigation of the x-ray diffraction patterns of this group of minerals was undertaken primarily to test for the most satisfactory method of powder sample preparation.

Since random orientation is so hard to achieve with the micas, it is also difficult to compare the results of different investigators using different methods of sample preparation. The present study includes the diffraction patterns of 12 micas: eastonite, 2 lepidolites, 2 muscovites, 3 biotites, 3 phlogopites and 1 zinnwaldite. Identical conditions were used to obtain the patterns so that the observed intensities may be directly compared.

SAMPLE PREPARATION AND PROCEDURE

When a large sample area must be obtained, it is important and sometime difficult to pack the powder so that it remains firm throughout the investigation. This is determined by the packing quality of the powder, the particle size and also by the shape of the aperture in the holder and the degree of packing of the powder. The preparation time of the sample often depends very largely on the grinding time of the material investigated. The preparation of a relatively large quantity of fine powder from

* Westinghouse Research Laboratories, E. Pittsburgh 30, Pa.

hard minerals e.g. bytownite or substances such as the micas requires a tremendous amount of time and effort if the grinding is done by hand. There are, however, several commercial automatic mortar grinders which are very timesaving and convenient. The machines having tungsten or boron carbide grinding surfaces are particularly worthwhile.

Two sample holders were finally used to obtain reproducible patterns. One holder with a rectangular opening $\frac{3}{8} \times 2\frac{1}{4}$ inches (.9×5.7 cm.) and a smaller one with a circular opening 9/16 inch (1.4 cm.) in diameter. It was found early in the work that any pressure across the surface of the prepared sample resulted in orientation. The method finally adopted was that proposed by G. L. McCreery (1) of the Ohio Brass Company.

The mica is ground to pass 325 mesh and deposited through a small funnel, containing a 60 mesh screen, upon a glass plate backed on the holder with scotch tape. When the holder is filled to heaping it is packed gently in vertical strokes with a spatula and a second glass plate placed over this surface. The unit is then turned over and the original plate removed exposing the prepared sample surface. The second glass plate is then secured with tape. Great care must be exercised to avoid sliding the first plate when it is removed since this is sufficient to orient the particles.

The method of sample preparation was tested through the reproducibility of the mica patterns from one packing to another. It is significant that the smaller holder gives the more reproducible mica patterns probably because the powder is more easily packed and remains more firm. The intensities may vary by a few per cent from one packing to the next but not significantly. This is not true, however, of the large holder. The intensities of the two strongest lines from the (001) cleavage plane may vary by 20 to 30 percent from a previous set of intensities. In a few cases, however, an additional weak reflection appears when the large holder is used. This seems to indicate that although the pattern obtained with the small holder is reproducible, the orientation of the particles is still not completely random. The smaller holder is probably more satisfactory when semi-quantitative and quantitative results are desired. However, in order to obtain a complete pattern for a given material it may be necessary to refer to the greater surface of the rectangular type holder for possible supplementary reflections.

DISCUSSION OF RESULTS

Five runs were made of each sample and for each reflection the mean values of the interplanar spacings, d, and the intensities tabulated.

The slits were set at 4 mm. high and 2.3 mm. and 1 mm. wide at the x-ray and counter slits, respectively. These settings were used when

both tubes had Lindemann glass windows and correspond to the widest slit settings. When mica windows were used in both tubes, the intensity increased by a factor of 3 and similar values were obtained using the narrow x-ray slit and medium wide counter slit. These correspond to approximately .8 mm. and .5 mm. wide. The chart speed was set at $\frac{1}{2}$ inch per minute with a scanning motor speed of 1 r.p.m. Since the patterns are generally diffuse, there was no advantage in reducing the speeds.

For comparison of intensities, a sample of quartz powder was run under the same conditions so that intensities might be directly compared. The values for quartz are given in Table 1. The interplanar spacings in Angstrom units (d values) and the recorded intensities are given in Tables 2 to 7.

TABLE 1. SPECTROMETER PATTERN OF QUARTZ STANDARD

d	I	Index I	d	I	Index I
4.25	63	(25)	1.661	9	
3.35	230*	(100)	1.544	40	
2.45	32		1.454	6	
2.29	24		1.289	6	
2.24	15		1.259	9	
2.13	24		1.230	6	
1.983	16		1.202	12	
1.822	50	(25)			

* By extrapolation from weaker pattern.

On the whole, the lines are fairly wide and the angular values of the reflections should be accurate within 0.1° in 2 θ. Lines marked "w" are wide or diffuse and lines marked "vw" are very wide and in general the assigned value of 2 θ is merely the center of a band or hump. All intensities are measured above the local background and the intensity of the background proper is listed at the end of every table for the 2 θ values 70° and 8°. The latter values may serve as an indication of the relative fluorescence of the different samples.

The diffraction patterns of the micas have been obtained by Magdefrau and Hofmann (2), Nagelschmidt (3), Jackson and West (4), Hendricks (5), and others. Since their data were obtained with small powder cameras or single crystals, the spectrometer values are given here for comparison. It is evident from the A.S.T.M. index and from the present data that there are differences in the diffraction patterns of the same variety of mica obtained from different localities. The differences may be in the relative intensities of the reflections or in the d values.

In general, the reflections from the first and third orders of the cleavage

plane (001) are considerably stronger than the others and the reproducibility of their intensities is a very sensitive test for orientation in the sample. Eastonite, given in Table 2, appears to be the only exception in the group since these reflections are distinctly of secondary importance.

TABLE 2. SPECTROMETER PATTERN FOR EASTONITE, EASTON, PENNSYLVANIA

d	I	d	I
10.10	23	1.800	6 w
7.30	100	1.688	3 vw
5.06	3 w	1.538	6 w
4.61	4 w	1.508	9
3.66	79	1.463	3 vw
3.39	20	1.435	3 vw
3.17	4 w	1.375	3 vw
2.94	3 vw	1.282	5 vw
2.74	2 vw	1.222	2 vw
2.63	3 vw		
2.51	11 w	Background	
2.44	10		
2.16	7 w	14.72	17
2.03	7 w	1.342	4
1.830	6 w		

TABLE 3. SPECTROMETER PATTERNS OF LEPIDOLITE

d	Ohio City, Colorado	Hebron, Maine	d	Ohio City, Colorado	Hebron, Maine
10.10	21	8	2.00	10	10
5.01	12	6	1.702	3 vw	3 vw
4.48	10 w	10	1.639	2 vw	2 vw
3.88	3 vw	4 vw	1.588	2 vw	2 vw
3.65	10	8	1.544	4	
3.50	5	9	1.508	8 w	8 w
3.35	22	10	1.492	2 w	2
3.21	7	9	1.433	5	4
3.09	13	9 w	1.304	5 vw	5
2.99	2		1.224	6 w	4
2.90	8 w	8 w			
2.86	3	2	Background		
2.80	4 w	4 w			
2.67	2 w		14.72	28	29
2.58	21	24	1.342	8	6
2.49	4 vw	3			
2.43	5 vw	8 vw	cf. Index Cards: II—994		
2.26	4 vw	2 vw		II— 63	
2.03	10	10			

The patterns of the lepidolites given in Table 3 are similar although the two strong lines are both stronger in the sample from Ohio City, Colorado.

A comparison of the two muscovites in Table 4 shows that the sample from Irwin, Tennessee, has a far richer pattern than that from Chester, Pennsylvania. The intensities of the two strong lines are greater in the former and their ratios are reversed.

TABLE 4. OBSERVED PATTERNS OF MUSCOVITE

d	Chester, Pennsylvania	Irwin, Tennessee	d	Chester, Pennsylvania	Irwin, Tennessee
10.00	8	60	1.546		3 vw
5.01	4	14	1.528	2 vw	5 vw
4.50	8 w	16	1.510	6 w	9 w
4.31		5	1.459	2 vw	2 vw
3.90	5 w	8	1.433	3 vw	5 w
3.75	4 w	8	1.391		2 vw
3.52	5 w	10	1.368		3 vw
3.35	15	48	1.354	4 vw	6 vw
3.22	5 w	14	1.342		3 vw
3.00	7	14	1.322		2 vw
2.88	4 w	9	1.298		5 vw
2.80	4 w	15	1.279		3 vw
2.58	15	21	1.265		3 vw
2.51		8 w	1.224		7
2.47		5			
2.40	5 w	8		Background	
2.15	5 vw	6			
2.14		9 w	14.72	33	34
2.06	2	2	1.342	14	13
2.03	10	10			
2.00	7	3	cf. Index Cards: II—2177		
1.979	3 w			II—2109	
1.664		7 vw		II—1026	
1.653	6 vw	10 vw		II— 71	
1.610	3 vw	3 vw		II— 67	
1.563		3 vw			

The relative intensities of the lines from the cleavage plane are similar in the three biotites given in Table 5. It is evident, however, that small differences occur between the samples from Franklin, New Jersey, and Tromo, Norway. The biotite from Nahant, Massachusetts, is strikingly different with a very high background and only the strongest lines appearing. This sample was also run using an Fe target but the background remained high and little change was found.

TABLE 5. SPECTROMETER PATTERNS OF BIOTITE

d	Franklin, N. J.	Tromo, Norway	Nahant, Mass.
10.04	45		25
9.93		36	
4.64	4 vw		
4.57		4 vw	
4.28		5 vw	
3.65	4 w	4 vw	
3.54	3 w		
3.37	34		17
3.35		22	
3.29	3 w		
3.14		5 vw	
3.07			3 vw
3.04	6 w		
2.93	3 vw	3 vw	
2.83	5		
2.63	18		8 w
2.61		19	
2.53	5	5 vw	2 w
2.45	10		5 w
2.43		9 w	
2.28	4 w		
2.19	9 w		2 vw
2.17		7	
2.03	5	5	6
1.991		5	
1.912	2 vw		
1.744	3 vw		
1.682	10	7	3 vw
1.634	3 vw		
1.608	3 vw		
1.550			5 vw
1.544	13 w		
1.537		11 w	
1.528	4 w		
1.517		3 w	
1.433	8	5 w	5
1.368	4 w	5 w	
1.332	2 w		
1.221	8	7 w	8

Background

14.72	40	40	59
1.342	18	17	39

cf. Index Cards: II—2010
II— 70
II— 56

SUZANNE VAN DIJKE BEATTY

TABLE 6. SPECTROMETER PATTERNS OF PHLOGOPITE

d	Clark Hill, N. Y.	Vromans Lake, N. Y.	Burgess, Ontario
10.04	26	19	33
5.05		3.5 vw	
5.01	4 w		
4.62		5 vw	7 vw
4.60	6 vw		
4.31	6		
4.27			2 vw
4.04	2 vw		
3.95	3 vw	3 vw	5 vw
3.69		4 vw	
3.68			10
3.66	5 w		
3.36	45	30.5	21 (w)
3.15	11	8.5	7
3.05	6	5	3 w
2.94			7 w
2.93		6	
2.92	8		
2.80		3 w	
2.79	2 w		
2.73			5 w
2.72	5	3	
2.63	16	22	20
2.53	8	7	5 w
2.46	9		
2.45		6	
2.44	10	10	8 w
2.30	6	3 vw	2 vw
2.27	3	9 w	
2.18			7 vw
2.17	8	11	
2.13	5		
2.10	3	4	
2.04			7
2.03	8	6	
2.01			5 vw
2.00	12	10	
1.983	5		
1.908	2 vw	2 vw	
1.878	2 vw		
1.829	6	2 vw	
1.744		7	
1.702	2 vw		2
1.679			7 w
1.673	12	12 w	
1.651	2 vw		3 vw

TABLE 6. (*Cont.*)

d	Clark Hill, N. Y.	Vromans Lake, N. Y.	Burgess, Ontario
1.621	2 vw	3 vw	
1.573		2 vw	2 vw
1.537	14 w	16	13
1.523			4 vw
1.519	3 w	5 vw	
1.503		2 vw	1 vw
1.479		2 vw	2 vw
1.435	5 w	3 vw	3 vw
1.398		2 vw	
1.377	6 vw		
1.368			3 vw
1.363	5 vw	5 vw	
1.328	3 vw	3 vw	4 vw
1.310	3 vw	2 vw	3 vw
1.259	3 vw		
1.224	4	7 w	4 w
Background			
14.72	30	22	26
1.342	6	8	5
cf. Index Card: II—65			

The patterns of the phlogopites given in Table 6 are the richest of the group and the tendency of the powder to become oriented was most pronounced.

TABLE 7. SPECTROMETER PATTERN OF ZINNWALDITE, WINTERHAM, VIRGINIA

d	I	d	I
10.04	20	2.29	3 vw
4.57	6 w	2.17	6 vw
4.19	3 vw	2.04	4 vw
3.88	3 w	1.991	6
3.68	6 vw	1.682	5
3.34	17	1.667	6 vw
3.25	3	1.526	6 vw
3.12	9		
3.05	3	Background	
2.93	6 w		
2.70	3	14.72	35
2.62	18	1.342	25
2.56	3		
2.49	4	cf. Index Card: II—66	
2.43	5 w		

Zinnwaldite in Table 7 has a high background although not as great as the Nahant biotite.

TABLE 8. PATTERN OF CLEAVED MICA SURFACE

d	Order	d	Order
10.0	1	2.0	5
5.0	2	1.67	6
3.33	3	1.43	7
2.5	4		

CONCLUSIONS

Reproducible diffraction patterns can be obtained for powder samples by the method outlined earlier. In the vast majority of cases it should be possible to achieve completely random orientation of the particles. In the case of the most difficult type of sample to prepare, namely the micas, it is still possible to achieve reproducibility and to approximate random orientation.

The diffraction patterns of the micas studied show that the d values and intensities of the reflections differ from one variety of mica to another and within the same variety.

The intensities of the reflections at $d = 10.0$ and 3.3 are strongly affected by slight orientation in the sample. It might be useful to describe the patterns of mica by means of a secondary set of intensities where the reflections of the cleavage plane are omitted. This should remove considerable distortion in the intensity ratios when the orientation, though slight, is sufficient to influence the strongest reflections.

REFERENCES

(1) Paper, Fifth Annual Pittsburgh Conference on X-Ray and Electron Diffraction, Nov., 1947.
(2) *Zeit. Krist.*, **98,** 31–59 (1937).
(3) *Zeit. Krist.*, **87,** 120–145 (1934); *Zeit. Krist.*, **97,** 514–521 (1937).
(4) *Zeit. Krist.*, **76,** 211–227 (1930).
(5) *Am. Mineral.*, **24,** 729–771 (1939).