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On the Intensity Changes of Basal Reflections with Relation to Barium Content in Manganoan Phlogopites and Kinoshitalite

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Abstract

Manganoan phlogopites (manganophyllite) from the Noda-Tamagawa mine contain Ba as much as 1.93 to 17.85 percent BaO. The most Ba-rich specimen which contains more Ba than K is a new brittle mica named kinoshitalite.

Relative intensities of basal reflections change with the Ba content, namely the first and the third order reflections decrease and the second order increases with the increase of the Ba content.

Electron density distributions given by Fourier syntheses normal to the basal plane confirm that Ba occupies the interlayer position in the mica and brittle mica structure. Fe^{3+} is thought to occupy the octahedral layer in Ba-rich manganoan phlogopites and kinoshitalite, which contain significant amount of Al.

Introduction

Mica minerals containing barium have been known; for example, muscovites with substantial barium content are named *oellacherites*. Some of the reported barium micas are as follows. Barium-muscovite from Franklin, New Jersey, U.S.A. has 9.89 percent BaO (Bauer and Berman, 1933); and manganobarian muscovite from the Muramatsu mine, Nagasaki Prefecture, Japan has 4.14 percent (Hirowatari, 1957). As to trioctahedral micas, "green biotite" from the Kaso mine, Tochigi Prefecture, Japan contains 4.18 percent (Yoshimura, 1938); barium-rich phlogopite from Långban, Sweden has 7.90 percent (Frondel and Ito, 1967); and lepidomelane with high barium content from Pierrefitte, Hautes-pyrénées, France has 7.5 percent (Orliac et al., 1971). And iron-rich trioctahedral barium brittle mica, anandite, from Ceylon has 20.59 to 21.50 percent BaO (Pattiaratchi et al., 1967). Synthetic study of $BaMg_3Al_2Si_2O_{10}(OH)_2$ was carried out successfully by Frondel and Ito (1967).

In the course of the study of manganoan phlogopite, named *manganophyllite*, in the Noda-Tamagawa mine, Iwate Prefecture, Japan, the specimens were found to contain as much as 1.93 to 17.85 percent BaO. The most barium-rich specimen (17.85 percent BaO) is a new mineral kinoshitalite.

It was also found in the study that the intensities of the basal reflections of X-ray powder

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patterns change with the barium content. The relation between the relative intensities of the basal reflections and the chemical compositions of micas has been studied by GOWER (1957), BRADLEY and GRIM (1961), SCHIAFFINO (1962) and others with excellent results. These works, however, concerns the Mg–Fe and/or Al–Fe ratios in the octahedral sites of mica minerals, and studies on the cations in the interlayer sites have not been undertaken for micas and brittle micas. K and Ca have not been reported to make a complete solid solution in the mica—brittle mica series. Even if there is no immiscible gap in the series, the replacement produces small effect on the intensities of X-ray diffraction, because Ca and K occupy neighboring positions in the periodic table.

In the case of micas and brittle micas containing Ba, however, the difference of the atomic number between Ba and K seems to be sufficient to produce significant difference in the X-ray powder patterns. And since Ba was inferred to replace K from the chemical data in Table 1, the intensity changes are thought to be the effect of this substitution in the interlayer site.

To discuss the relationship mentioned above, one-dimensional Fourier syntheses were attempted for several specimens of barium-bearing manganoan phlogopite and kinoshitalite from the mine.

Chemical Composition

Six specimens collected at different parts of the Noda-Tamagawa manganese ore deposit were chemically analysed. The results are shown in Table 1, and it is seen that all of the analysed specimens contain significant amount of Ba. It substitutes K, and Si is replaced by Al in accordance with this substitution to compensate for the increase of positive valence. Another substitution pair, Mn for Mg, occurs independently of the above.

The ideal formulas derived from the chemical data on the basis of twelve oxygens are:

$(K, Ba)(Mg, Mn^{2+}, Mn^{3+})_3Si_3AlO_{10}(OH)_2$ for nos. 1 to 5, which are manganoan phlogopites;

$(Ba, K)(Mg, Mn^{2+}, Mn^{3+})_3Si_2Al_2O_{10}(OH)_2$ for no. 6, which is kinoshitalite.

X-ray Diffraction Study

The intensities of twelve basal reflections, 001 to 00,12 were measured by an X-ray diffractometer.

Experimental conditions were as follows.

Used instrument was Rigaku Denki Geigerflex diffractometer. Nickel filtered $CuK\alpha$ radiation was used. Target input was 30 kV and 10 mA. Opening of the divergence slit was 1° for the range over 2θ 20°, (1/2)° between 20° and 10° and (1/6)° below 10° respectively. That of the receiving slit was 0.3 mm. Rotating speed of goniometer was 0.5° per minute. Scaler was 400 counts per second. Time constant was 2 second. Chart speed was 1 cm per minute.

The standard conditions mentioned above could not be used at all times. The major problem was to avoid the dead time of the GM counter. In order to keep the X-ray intensity under 1000 cps, the divergence slit opening was decreased (1/2) or (1/6)°, and when this was not sufficient, the accelerating voltage and the tube current were reduced for very strong reflections. Certain reflections were used as standards under these various conditions for comparison of the intensities.

Table 1   Chemical analyses of manganoan phlogopites and kinoshitalite from the Noda-Tamagawa mine.

No.	1	2	3	4	5	6
SiO_2	35.65	37.86	34.10	33.69	29.12	24.58
TiO_2	0.44	0.36	0.71	0.33	0.16	0.16
Al_2O_3	12.70	12.06	13.89	15.58	21.19	22.06
Fe_2O_3	2.35	1.34	1.76	0.95	0.69	0.71
Mn_2O_3	3.11	3.54	3.19	3.44	3.55	3.24
FeO	0.04	0.04	0.04	0.04	0.04	0.04
MnO	14.61	7.59	11.85	8.76	7.60	7.38
MgO	15.15	20.15	16.59	19.23	17.56	16.60
CaO	0.05	0.04	0.05	0.03	0.05	0.05
BaO	1.93	3.56	6.03	6.79	11.05	17.85
Na_2O	1.25	2.16	0.58	0.49	0.56	0.68
K_2O	8.60	7.62	7.39	7.24	5.63	3.30
F	0.15	0.39	0.14	0.33	0.27	0.21
H_2O+	3.69	3.12	3.27	2.96	2.20	2.90
H_2O-	0.18	0.20	0.15	0.18	0.18	0.20
Total	99.90	100.03	99.76	100.04	99.85	99.96
$-O=F_2$, etc.	0.06	0.16	0.06	0.14	0.11	0.09
Total	99.84	99.87	99.70	99.90	99.74	99.87

Numbers of ions on the basis of 12 (O, OH, F)

	1	2	3	4	5	6
Si	2.748	2.857	2.673	2.613	2.334	2.052
Al	1.154	1.073	1.284	1.387 / 0.037	1.666 / 0.336	1.948 / 0.223
Ti	0.025	0.020	0.042	0.019	0.010	0.010
Fe^{3+}	0.073 / 0.063	0.050 / 0.026	0.001 / 0.103	0.055	0.041	0.045
Mn^{3+}	0.183	0.203	0.190	0.203	0.217	0.206
Fe^{2+}	0.003	0.003	0.003	0.003	0.003	0.003
Mn^{2+}	0.954	0.485	0.787	0.576	0.516	0.522
Mg	1.740	2.266	1.938	2.222	2.098	2.065
Ca	0.004	0.003	0.004	0.002	0.004	0.005
Ba	0.058	0.105	0.185	0.206	0.347	0.584
Na	0.187	0.316	0.088	0.074	0.087	0.110
K	0.846	0.734	0.739	0.716	0.576	0.352
OH	1.897	1.570	1.709	1.531	1.176	1.615
F	0.037	0.093	0.035	0.081	0.068	0.055

Grouping sums:

- Si+Al+Ti+Fe³⁺: 4.000 (nos. 1, 2, 3); 4.000 (nos. 4, 5, 6)
- Mn³⁺+Fe²⁺+Mn²⁺+Mg (with Fe³⁺): 2.943 (1), 2.983 (2), 3.021 (3), 3.115 (4), 3.221 (5), 3.074 (6)
- Ca+Ba+Na+K: 1.095 (1), 1.158 (2), 1.016 (3), 0.998 (4), 1.014 (5), 1.051 (6)
- OH+F: 1.934 (1), 1.663 (2), 1.744 (3), 1.612 (4), 1.244 (5), 1.670 (6)

Nos. 1 to 5: manganoan phlogopite, no. 6: kinoshitalite
Analysis: K. MAEDA, M. YOSHIDA (F in nos. 1 to 5) and K. NAGASHIMA (F in no. 6).

Table 2 Relative intensities of basal reflections and d-values for manganoan phlogopites and kinoshitalite.

hkl	1	2	3	4	5	6
001	5580	3810	3700	3320	1670	507
002	61	27	112	82	194	527
003	2390	2040	2200	1910	1320	1040
004	356	338	455	417	380	556
005	385	445	436	496	410	566
006	113	87	119	102	100	156
007	77	56	52	46	30	22
008	65	60	65	54	58	86
009	10	5	6	4	2	0
00, 10	18	13	17	14	13	23
00, 11	15	10	10	8	5	6
00, 12	6	7	7	5	7	11
d_{200}	2.634 Å	2.623	2.637	2.634	2.627	2.632
d_{060}	1.551 Å	1.543	1.548	1.546	1.546	1.546
d_{005}	2.029 Å	2.018	2.023	2.021	2.020	2.020
$\frac{Ba}{Na+K+Ca+Ba}$	5.3%	9.1	18.2	20.6	34.2	55.6
$\frac{Mn}{Mg+Mn+Fe}$	37.7%	22.7	32.3	25.5	25.5	25.6

Heights of the diffraction curves measured on the chart were a good approximation of the intensities.

The results are shown in Table 2.

The powder data for all of six specimens are able to be indexed as $1M$ polytype. The details will be reported in the near future.

It is seen from the analytical results that specimens 2, 4, 5 and 6 have similar Mn/(Mg+Mn+Fe) ratios ranging from 22.7 to 25.6 percent. It is inferred that the effect of this difference on the X-ray reflection intensities is very small, although any discussions have not been made in the case of manganese rich phlogopite in previous papers.

The data plotted in Fig. 1 show that the intensity ratio of the first and the third order basal reflections to the fifth one decreases markedly with the increase of Ba, and those of the second to the fifth increases with the increase of Ba.

Thus it seems logical to use these samples to study the relation between the Ba content and the X-ray diffraction intensities of the minerals of this series.

Fourier Syntheses

One-dimensional Fourier syntheses normal to the basal plane were carried out from the relative intensities in Table 2. For the calculation of structural factor (Fc), STEINFINK (1962)'s z parameters for phlogopite were chosen, and Ba was added at the interlayer position as shown in Table 3.
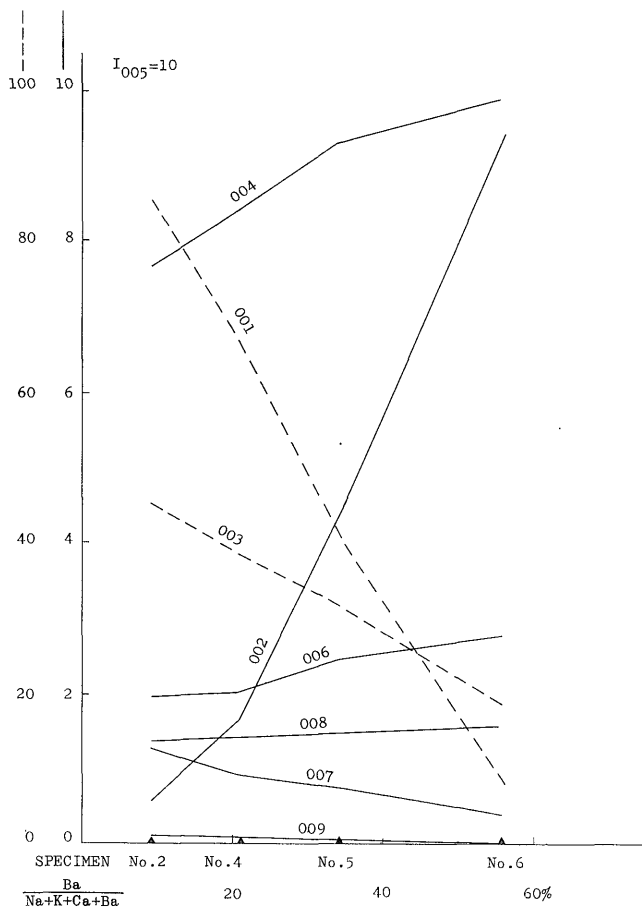
Figure 1   Relationship between basal intensities and Ba content on the basis of I_{005}

Table 3   Z parameters of phlogopite crystal (After
STEINFINK, 1962)

Atom	$\dfrac{z}{c}$
Na	0
K	0
Ca	0
Ba	0
O_1	.1692
O_2	.1700
Si	.2261
Ti	.2261
Al	.2261
Fe	.2261
O_3	.3900
OH	.3955
Mg	.5000
Mn	.5000

Note: Ba was added in this study. Structure factors (Fc)
were calculated using above parameters for nos.
1. to 4 in Table 4; and parameter of Fe was
changed to 0.5000 for nos. 5 and 6.

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The model was good for the Ba-poor specimens (nos. 1 to 4); but the reliability factors (R):

$$R = \frac{\sum ||Fo|| - |Fc||}{\sum |Fo|}$$

improved for the Ba-rich specimens when Fe^{3+} was moved to the octahedral site, namely it decreased from 0.10 to 0.05 in no. 5 and from 0.09 to 0.08 in no. 6 (kinoshitalite) respectively. Final reliability

Table 4 Observed and Calculated Structure Factors for 00*l*.

| No.	1		2		3		4		5		6	
hkl	|Fo|	Fc	|Fo|	Fc	|Fo|	Fc	|Fo|	Fc	|Fo|	Fc	|Fo|	Fc
001	57	−65	47	−52	46	−53	44	−49	33	−36	18	−17
002	12	11	8	8	16	16	14	15	23	21	38	40
003	115	−115	107	−102	110	−105	103	−101	92	−91	81	−73
004	61	66	60	60	69	68	66	66	68	77	82	89
005	82	87	88	93	87	94	93	96	91	103	107	117
006	55	50	49	47	57	52	53	53	56	54	70	67
007	55	−52	47	−45	45	−46	43	−44	37	−37	32	−33
008	59	61	57	57	59	62	54	61	61	61	73	71
009	26	−20	18	−16	20	−16	16	−15	12	−8	0	−3
00, 10	36	36	31	33	35	36	32	36	33	33	44	41
00, 11	31	−26	25	−22	26	−22	23	−19	19	−16	21	−13
00, 12	17	21	18	19	18	21	15	21	19	18	24	24
R	0.08		0.05		0.07		0.06		0.05		0.08	
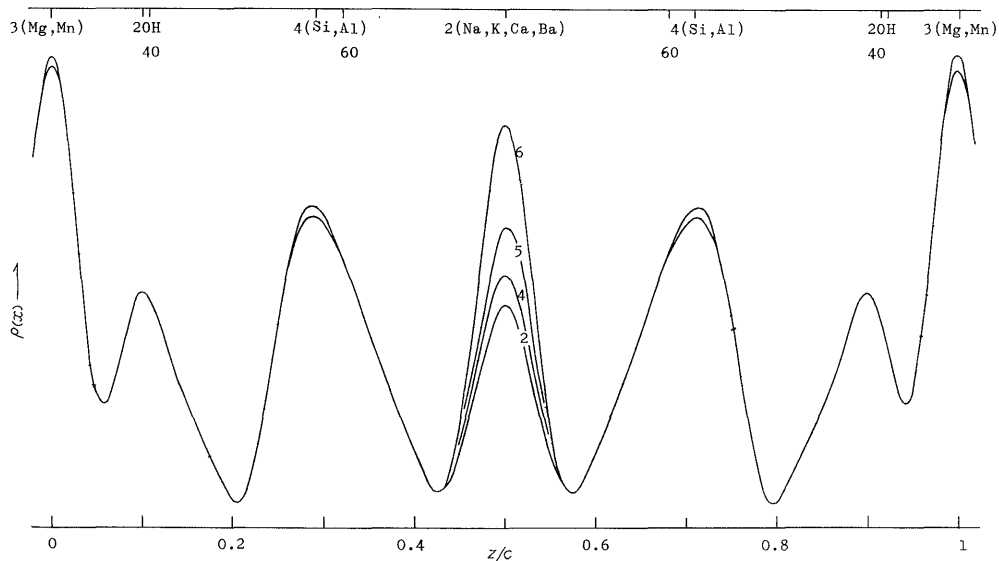
Figure 2 Distribution of the electron density normal to the basal planes for manganoan phlogopites and kinoshitalite. Electron density for specimen 2, 4, 5 and 6 changes markedly at the interlayer site, but it is less distinct at other sites.

factors for the six specimens were 0.05 to 0.08 in this study. This can be seen from the results of chemical analyses alone. For example, in specimens 5 and 6 all Fe ions must be treated together with octahedral cations, while in sample 1 almost half of Fe^{3+} must be included in the tetrahedral position in order to form four tetrahedral cations. In other words, the increase of Ba is accompanied by the increase of Al to compensate for the difference in valence and which seems to result in the movement of Fe into the octahedral position.

Obtained structure factors are shown in Table 4.

The distribution of electron densities for the specimens 2, 4, 5 and 6 normal to the basal plane is shown in Fig. 2. The figure shows that the electron density at the interlayer position changes markedly. This is thought to be caused by the subsitution of Ba for K. The change of electron density at tetrahedral site where Si is replaced by Al is less distinct.

Sobax ICC 2700 micro computer was used for the calculations with several computation programs made by one of the writers (M. Y.).

Conclusion

Fe^{3+} is located at the tetrahedral site in phlogopite structure (STEINFINK, 1962), but it is inferred that Fe^{3+} occupies the octahedral site in case of Ba-rich phlogopite and kinoshitalite, both of which have significant amount of Al.

Ba content in manganoan phlogopite and kinoshitalite results in variation of the relative intensities of the basal reflections. Also the calculation of the Fourier syntheses showed that Ba is in the interlayer site of the structure.

It would be interesting to determine quantitatively the relation between the content of the two metals and the basal reflection intensities, but this is much more complex than in case of phlogopite—biotite shown by GOWER (1957) and others, as Mg–Fe–Mn variation must also be taken into account.

Acknowledgment

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マンガン金雲母と木下石における Ba 含有量と X 線底面反射強度との関係

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要　旨

野田玉川鉱山産のマンガン金雲母（マンガノフィライト）には，BaO 1.93〜17.85% の Ba が含まれる．このなかには Ba>K となるものがあり，これは新鉱物木下石 (Kinoshitalite) である．

X線の底面反射強度は Ba の量と関係し，Ba の増加とともに，001，003 が減少し，002 は増加する．Z方向のフーリエ合成により，Ba は層間位置を占め，Fe^{3+} は木下石と Ba に富むマンガン金雲母では八面体位置を，Ba に乏しいマンガン金雲母では四面体位置をそれぞれ占めるらしいことが，判明した．