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Manganobarian Muscovite from the Manganese Deposit of the Muramatsu Mine, Nagasaki Prefecture, Japan*

By

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Abstract

Manganobarian muscovite, recently found in the manganese deposit of the Muramatsu mine, occurs in a braunite-rich manganese ore as a small veinlet, or as a coating on drusy cavities.

It is rose-pink to light pink in colour, while under the microscope, practically colourless. $n_X = 1.566$, $n_Y = 1.598$, $n_Z = 1.602$, $n_Z - n_X = 0.036$; $(-)2V = 36°$, op. pl. $\perp 010$ The chemical formula is

$$(K_{0.53}Na_{0.25}Ba_{0.11}Ca_{0.09})_{0.98}(Al_{1.48}Fe_{0.10}Mn_{0.20}Mg_{0.26})_{2.04}(Si_{3.02}Al_{0.98})_{4.00}O_{10.00}(OH)_{2.00}$$

The x-ray powder data confirm that polymorphic modification of this mineral agrees closely with that of the common 2-layer monoclinic structure proposed by HENDRICKS and JEFFERSON, giving the following monoclinic unit cell dimensions: $a_0 = 5.25 \pm 0.02A$, $b_0 = 9.10 \pm 0.02A$, $c_0 = 19.90 \pm 0.03A$, $\beta = 95°40'$. Using these values, most of lattice spacings have been indexed. Thus, this mineral belongs to a mica of the muscovite type (heptaphyllite), with the 2-layer monoclinic structure (common or normal muscovite structure). But it differs from the common muscovite in containing unusually high amounts of barium and manganese.

Occurrence

The manganese ore deposits of the Muramatsu mine**, about 10 kilometers north-west of Nagasaki City, Kyushu, are composed of lenticular ore bodies in the crystalline schist together with red-sericite-quartz schist and piedmontite-quartz schist both forming the wall rocks of the ore deposit.

The ores consist mainly of fine-grained braunite crystals, usually associated with beautiful rods of piedmontite and are cut by small veinlets of quartz and feldspar. The manganobarian muscovite in question, which was found by me in December of 1954, occurs in the braunite ore as a small veinlet or as a coating on drusy

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* Read at the meeting of The Mineralogical Society of Japan on Oct. 23, 1955.

** According to YOSHIMURA's genetical classification of manganese deposits in Japan (1952, 1953), the Muramatsu mine is the type locality of his "Muramatsu type"——the regionally metamorphosed manganese deposit.

cavities. Pink spherulitic aggregates made up of tiny scales of this mineral offer a splendid specimen.

Optical properties

Megascopically the mineral, hexagonal plates about 0.5 mm to 0.1 mm in diameter, is rose-pink to light pink in colour, vitreous in luster, while under the microscope it is practically colourless.

Optical data are:

The optic plane and Z are normal to 010. $n_X = 1.566$, $n_Y = 1.598$, $n_Z = 1.602$, $n_Z - n_X = 0.036$, $(-)\,2V = 36°$ (obs.), $(-)\,2V = 35°$ (calc.)

Chemical composition

The material used for chemical analysis contained no more than one per cent impurities. K. MUTA kindly examined the material spectrographically with the results that substantial amounts of Mg, Ba, Mn, Ti and Fe were determined, but V, Cr, Li, Co were not detected.

The results of my chemical analysis are given in Table 1, No. 1. Manganese determination was checked by the gravimetric and volumetric methods, whose results are in satisfactory agreement. The barium was precipitated with sulphuric acid and was weighed as $BaSO_4$. The water was determined by calcium chloride method.

The formula for the muscovite in question calculated from its chemical composition on the basis of $O_{10}(OH)_2 = 22$ is:

$$(K_{0.53}Na_{0.25}Ba_{0.11}Ca_{0.09})_{0.98}(Al_{1.48}Fe_{0.10}Mn_{0.20}Mg_{0.26})_{2.04}(Si_{3.02}Al_{0.98})_{4.00}O_{10.00}(OH)_{2.00}$$

Thus, it is evident that the mineral closely approaches the accepted theoretical formula for muscovite, namely $X_1\ Y_2\ Z_4\ O_{10}(OH)_2$, where X are K, Na, Ba, and Ca; Y are Al, Fe, Mn, and Mg; Z are Si and Al.

Thermal properties

A part of the sample used for the chemical analysis were examined by a differential thermal analysis method. The result is shown in Fig. 1. The D.T.A. curve

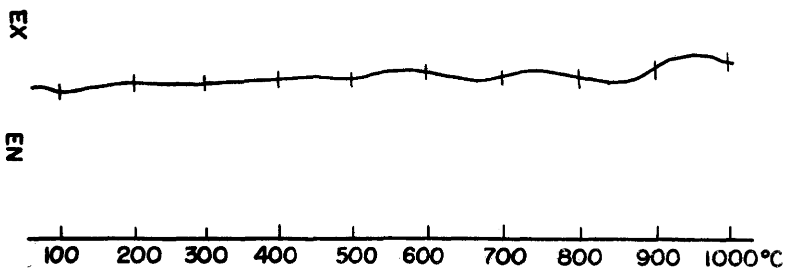

Fig. 1. Differential thermal analysis curve for manganobarian muscovite from the Muramatsu mine.

Table 1. Chemical analyses of manganobarian muscovite, muscovites and lepidolite

No.	1	2	3	4	5	6	7
SiO_2	44.93	41.37	42.59	49.44	45.7	44.95	46.86
TiO_2	0.25	—	—	—	—	0.31	0.14
Al_2O_3	30.81	32.64	30.18	26.05	34.0	33.51	21.25
Fe_2O_3	2.08	—	0.91	—	0.16	1.76	1.01
FeO	—	—	1.74	2.31	—	0.64	0.16
MnO	3.49	0.62	0.12	—	1.7	0.05	7.55
MgO	2.64	1.55	4.85	3.03	0.22	0.81	0.52
							Li_2O 5.20
BaO	4.14	9.89	4.65	5.76	0.0008		Rb_2O 1.46
							Cs_2O 0.04
CaO	1.25	0.36	1.03	1.81	1.12	0.37	0.78
K_2O	6.17	6.33	7.61	7.54	10.6	10.47	9.48
Na_2O	1.93	1.51	1.42	—	0.085	1.32	0.22
	ZnO	1.84 SrO	0.09			F 0.13	8.31
$H_2O(+)$	2.19						0.25
		4.05	4.43	4.24	—	5.30	
$H_2O(-)$	1.00						1.28
Total	100.88	100.16	99.93	100.18		99.72	104.41
						—F	3.66
							100.75

(1). Manganobarian muscovite, Muramatsu mine, Nagasaki, Japan.
Analyst: F. Hirowatari (this paper).

(2). Barium-muscovite, Franklin Furnace, New Jersey.
Analyst: L. H. Bauer (1933).

(3). Oellacherite, Ptitschthal, Tyrol.
Analyst: F. Oellacher (1858).

(4). Oellacherite, Habachtal, Tyrol.
Analyst: F. Bergman (1875).

(5). Mangan-muscovite, Mattkärr, Finland.
Spectrochemical analysis by C. E. Harvey (1955).

(6). Muscovite (average of 37 specimens), calculated by
K. Rankama and Th. G. Sahama (1950).

(7). "Lepidolite," Sakihama, Iwate, Japan.
Analyst: H. Shibata (1952).

shows two endothermic peaks, though indistinct, one at about 670°~700°C and the other 800°C~900°C.

X-ray powder data and identification of polymorphism

The powder diffraction data for CuK_α ($\lambda=1.5418$A) radiations were obtained, using a camera with 114.6 mm in diameter. The measured and calculated lattice spacings together with the visually estimated intensities are given in Table 2, Column 1, comparing with the data for normal muscovite from Chandlers Holler (Column 2; Nagelschmidt, 1937) and lithian muscovite from South Portland (Column 3; Levinson, 1953)

Table 2. X-ray powder data for manganobarian muscovite, normal muscovite and lithian muscovite

	Manganobarian muscovite, Muramatsu mine			Normal muscovite, Chandler Holler			Lithian muscovite, S.P.	
hkl	$d(A)_{calc.}$	$d(A)_{obs.}$	I*	$d(KX)_{calc.}$	$d(KX)_{obs.}$	I*	$d(A)_{obs.}$	I*
002	9.92	9.93	m	9.95	9.98	s	9.95	m
004	4.96	4.97	m	4.97	5.00	s	5.01	m
020 110	4.55 4.53	4.51	m	4.50 4.48	4.49	s	4.50	m
112	4.01						3.95	vvw
$11\bar{3}$	3.89	3.91	w	3.86	3.91	w	3.87	vvw
023	3.75	3.70	w	3.72	3.73	w	3.71	w
$11\bar{4}$	3.49	3.50	w	3.48	3.50	m	3.46	w
024	3.36	3.38	w	3.35				
006	3.32	3.31	vs	3.31	3.33	vs	3.32	ms
114	3.22	3.19	w	3.20	3.20	m	3.21	m
025	2.99	2.98	m	2.98	3.00	m	2.98	m
115	2.88	2.84	ms	2.86	2.88	m	2.84	s
$11\bar{6}$	2.77	2.77	w	2.779	2.80	m	2.755	w
131 $20\bar{2}$ 116	2.587 2.585 2.583	2.59	msB	2.568 2.566 2.565	2.57	vs	2.571	ms
008 $13\bar{3}$ 202	2.481 2.477 2.476	2.48	wB	2.485	2.475	wB	2.474	m
133 $20\bar{4}$	2.404 2.402	2.390	wB	2.380 2.382	2.385	m	2.387	m
134 $20\bar{5}$ 040 $22\bar{1}$ 041	2.279 2.278 2.275 2.268 2.265	2.264	vwB	2.270	2.28	w	2.247	vw
$22\bar{3}$ 028	2.202 2.181	2.194	vw	2.180	2.19	w	2.196	vvw
043 135 $20\bar{6}$	2.152 2.147 2.145	2.139	wB	2.142	2.134	s	2.132	mw
$13\bar{6}$ 223	2.105 2.096						2.081	m
136 029 00,10	2.010 1.987 1.980	1.980	vs	1.986 1.990	1.995	vs		
206	1.951						1.951	vw
02,10	1.822	1.822	vvw	1.821				
208	1.728	1.729	vvw	1.714	1.730	vw	1.742	w
$20,\bar{1}\bar{0}$ 00,12	1.653 1.650	1.643	mB		1.651	sB	1.644	m

13,$\bar{1}$0 228 049	1.612 1.615 1.610	1.601	vvw				1.596	vvw
13,10	1.552			1.550	1.546	vw	1.557	vvw
315	1.525			1.531	1.523	vw		
060 33$\bar{1}$	1.512 1.515	1.517	mB	1.500 1.499	1.500	s	1.510 1.500	vvw w
063	1.478	1.480	vvw	1.463			1.487	w
333 064 33$\bar{5}$	1.450 1.450 1.449	1.449	vvwB	1.440	1.450	vw	1.453	vvw
00,14 334 33$\bar{6}$ 065	1.421 1.416 1.416 1.415	1.418	vvwB	1.428	1.421	vw	1.427	vw
31.$\bar{1}$0	1.356	1.347	w	1.355	1.356	m		
067 336	1.338 1.337	1.337	w		1.337	m	1.340	w
260 40$\bar{2}$	1.312 1.312	1.318	vvw	1.298				
400 068 40$\bar{3}$ 401 337 33$\bar{9}$	1.307 1.295 1.304 1.297 1.294 1.293	1.302	vwB	1.293 1.283	1.296	m	1.296	vvw

* vs: very strong, s: strong, ms: middle strong, m: middle, mw: middle weak, w: weak, vw: very weak, vvw: very very weak, B: broad line.

Polymorphism of the micas was first pointed out by HENDRICKS and JEFFERSON (1939), who also stated that the muscovite type micas usually crystallize with the 2-layer monoclinic structure (2M polymorphs). However, further x-ray studies of polymorphism in the mica group made by AXELROD & GRIMALDI (1949), MAKENZIE et al. (1949), LEVINSON (1953, 1955), HEINRICH & LEVINSON (1955), and SMITH & YORDER (1954) tell us that the micas of the muscovite type crystallize not only with the 2M polymorphs, but also with five polymorphs, such as 6M, 3H, 3T, 1M, and 1Md*.

All of these polymorphic modifications were determined by the Weissenberg method. GRIM and BRADLEY (1951) presented a paper on the method of distinguishing the polymorphic forms in the micas. They state: "In all of the mica powder diffraction diagram the region of clearest import is the range from about 4.4 KX to 2.6 KX which includes only 02*l* and 11*l* reflections." Supposing this suggestion to be used as the basis for the identification of polymorphism, I examined several

* 6M: 6-layer monoclinic structure. 3H: 3-layer hexagonal structure. 3T: 3-layer trigonal structure. 1M: 1-layer monoclinic structure. 1Md: 1-layer disordered monoclinic structure.

x-ray powder data for the muscovite type micas from various localities and found that 6M, 3H, 3T, 2M, 1M, and 1Md polymorphs could be discriminated by this method.

Now, the above-mentioned x-ray powder data for the Muramatsu muscovite was found to be in close agreement with normal muscovite of the 2M polymorphs distinguished from those of 6M, 3H, 3T, IM, and 1Md polymorphs. The most noticeable characteristics of the Muramatsu muscovite (2M polymorphs) as compared with the other polymorphs are as follow: the (023), $(11\bar{4})$, (114), (025), and $(11\bar{6})$ reflections which respectively correspond to d=3.70±0.02A, 3.50±0.02A, 3.20±0.02A, 2.98±0.02A and 2.78±0.02A are distinct, while the reflections corresponding to d=4.3A, 4.1A, 3.60±0.02A and 3.10±0.02A are absent. Thus the muscovite in question has a 2-layer monoclinic structure with the monoclinic unit cell dimensions given below.

Unit cell dimensions

The d_{001} dimension was determined by using the (008), (00,10) (00,12) and (00,14) reflections. The d_{010} dimension was obtained by taking the (060) reflection for d=1.517A. The d_{100} dimension and β were determined by using the (336), $(33\bar{5})$ and $(33\bar{1})$ reflections. The results are summarized in Table 3.

Table 3. Unit cell dimensions of manganobarian muscovite from the Muramatsu mine

d_{100}= 5.23±0.02A	....	a_0= 5.25±0.02A
d_{010}= 9.10±0.02A	....	b_0= 9.10±0.02A
d_{001}=19.80±0.03A	....	c_0=19.90±0.03A
β=95°40′	....	β=95°40′

The cell dimensions of the manganobarian muscovite from the Muramatsu mine, those of the normal muscovite from Chandler Holler, and those of the lithian muscovite from South Portland will be compared with each other in Table 4.

Table 4. Cell dimensions of the 2-layer monoclinic muscovites

	Manganobarian muscovite	Normal muscovite	Lithian muscovite
a_0	5.25±0.02A	5.2KX	5.2A
b_0	9.10±0.02A	9.0KX	9.0A
c_0	19.90±0.03A	20.0KX	20.0A
β	95°40′	95°30′	95°30′
Author	HIROWATARI (this paper)	HENDRICKS & JEFFERSON (1939)	LEVINSON (1953)

Using the cell dimensions, most of lattice spacings were calculated and indexed with results given in Table 2.

Nomenclature

Muscovite with substantial amount of barium (BaO 4–5%) from Ptitschthal, Tyrol, has been called "oellacherite" by DANA (1914, p. 614). Afterwards, a micaceous mineral with 8.89% BaO from Franklin Furnace, New Jersey, was called "barium-muscovite" by BAUER and BERMAN (1933).

On the other hand, a lepidolite containing very high amount of manganese (MnO 7.55%; Table 1, No. 7) has been reported from the Sakihama-pegmatite, Japan (SHIBATA, 1952). Recently a mangan-muscovite has been found from the Mattkärr, Finland (HEINRICH and LEVINSON, 1955), but this mineral contains only 1.7% MnO (Table 1, No. 5).

Chemically, the muscovite from the Muramatsu mine shows similarities to "oellacherite" or barium-muscovite with respect to the high BaO content on one hand, and to mangan-muscovite on the other.

Structurally, both barium-muscovite and mangan-muscovite have the 1-layer monoclinic structure, while the Muramatsu muscovite and oellacherite the normal 2-layer monoclinic structure, though HEINRICH & LEVINSON (1955a) put forth the opinion that the barium-muscovite can not be considered as a variety of normal muscovite.

The Muramatsu muscovite, chemically one kind of barium-muscovite and structurally of normal muscovite, may be called either "manganobarian muscovite" as a variety of normal muscovite or "manganoan oellacherite" as a variety of oellacherite. In this connection the noteworthy view of HEINRICH & LEVINSON (1955a) should be taken into account that "the oellacherite from the type locality (Ptitschtal, Tyrol) has crystallized with the 2-layer monoclinic structure, but a flame test for Ba negative results and, therefore, the validity of this specimen is in doubt."

Therefore, I wish to propose a name "manganobarian muscovite" as a new variety of normal muscovite for the mineral from the Muramatsu mine.

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