

A HYDROMUSCOVITE FROM THE SHAKANAI MINE, AKITA PREFECTURE, JAPAN

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Abstract—A hydromuscovite in association with gypsum and anhydrite was collected from the Shakanai mine, Akita Prefecture, Japan. Chemical composition: SiO₂ 47.14%; TiO₂ 0.34%; Al₂O₃ 37.09%; Fe₂O₃ 0.49%; MgO 0.83%; CaO 0.57%; Na₂O 0.35%; K₂O 7.10%; H₃O⁺ 5.18%; H₂O⁻ 0.99%; P₂O₅ 0.01%; total 100.09%. Differential thermal and i.r. absorption analyses were similar to those of hydromuscovite. The X-ray diffraction pattern differed clearly from those of the 1*M* and/or 2*M*₁ polymorphs and it was similar to that of the 2*M*₂ polymorph, which is known to occur in lepidolites.

INTRODUCTION

FINE-grained micaceous minerals are found associated with the Kuro-ko ore body of the Shakanai mine as alteration products of tuff and tuffaceous sediments. These minerals consist chiefly of hydromuscovite, chlorite and mixtures of the two minerals. In the course of examining many samples from the alteration area, a hydromuscovite with properties of a 2*M*₂ polymorph was noticed. Polymorphism in muscovite was studied extensively by Hendricks and Jefferson (1939), Heinrich *et al.* (1953) and Smith and Yoder (1956). The natural occurrence of a 2*M*₂ hydromuscovite was first described by Threadgold (1959), but later Radoslovich (1960) re-examined the same specimen and showed that the X-ray powder pattern was similar to that of a mixture of 1*M* and 2*M*₁ polymorphs. Although it seems very difficult to show the existence of the 2*M*₂ polymorph by the X-ray powder method, as mentioned by Radoslovich, the results obtained in this study indicate that the specimen from the Shakanai mine is not a mixture of 1*M* and 2*M*₁ polymorphs.

The present paper reports the occurrence of the hydromuscovite and its mineralogical data are described in comparison with earlier data.

MINERALOGICAL DATA

Mica minerals with the 1*M* and 2*M*₁ structures were found to be associated with the ore minerals of the kuro-ko. The specimen in question was found to be accompanied with gypsum and anhydrite in the south part of the alteration area. The < 2μ fraction separated by dispersion in distilled water was used in this study.

The X-ray diffraction data in Table 1 and Fig. 1 (upper) are similar to Threadgold's data (1959) and

those of lepidolite reported by Levinson (1953). The *hkl* indices in Table 1 were taken from ASTM card 14-11 for 2*M*₂ lepidolite. The reflections not recorded on the card were indexed on the basis of $a = 9.2 \text{ \AA}$, $b = 5.3 \text{ \AA}$, $c = 20.2 \text{ \AA}$ and $\beta = 98.0^\circ$ and marked as (*). Because Radoslovich (1960) showed that the X-ray diffraction data of hydromuscovite described by Threadgold were in better agreement with a mixture of 1*M* and 2*M*₁ polymorphs than with 2*M*₂ lepidolite, the *d*-spacings and intensities of a number of specimens were carefully examined by using a diffractometer. The following four specimens were examined under the same conditions and their data were compared with those of 1*M* and 2*M*₁ muscovite given by Yoder and Eugster (1955).

(A) Hydromuscovite in question from the Shakanai mine, Akita Prefecture, Japan (A in Table 2 and Fig. 1).

(B) Hydromuscovite from the Tsuchihashi mine, Okayama Prefecture, Japan (B in Table 2 and Fig. 1). This specimen seems to be composed chiefly of the 2*M*₂ polymorph.

(C) Hydromuscovite from the Shakanai mine, Akita Prefecture, Japan (C in Table 2 and Fig. 1). This specimen is a mixture of 1*M* and 2*M*₁ polymorphs.

(D) A 1:1 mixture of hydromuscovite with 1*M* and 2*M*₁ polymorphs from the Seshido mine, Tochigi Prefecture, Japan (Shimoda *et al.*, 1969) and from the Goto mine, Nagasaki Prefecture, Japan (Tomita and Sudo, 1968), respectively (D in Table 2 and Fig. 1).

As given in Table 2 and Fig. 1, the X-ray diffraction data of the Shakanai specimen (A) and the Tsuchihashi specimen (B) clearly differ from the data of the artificial mixture of 1*M* and 2*M*₁ poly-

Table 1. X-ray diffraction data of the Shakanai specimen, $2M_2$ hydromuscovite and $2M_2$ lepidolite

1		2		3		<i>hkl</i>	
<i>d</i> (Å)	I	<i>d</i> (Å)	I	<i>d</i> (Å)	I		
10.25	55	10.0	80	10.0	60	002	
5.06	42	5.01	40	5.00	50	004	
4.49	60	4.48	90	4.50	50	$11\bar{1}, 110^*, 200^*$	
4.37	15	4.39	5			$111^*, 202^*$	
4.31	5	4.27					$11\bar{2}^*$
3.966	5					$202^*, 112^*$	
3.921	21	3.89	30	3.85	30	$11\bar{3}$	
3.681	43	3.66	40	3.62	50	$113, 20\bar{4}$	
3.520	33	3.50	35	3.48	50	114	
3.348	58	3.34	60	3.32	50	006	
3.211	28	3.20	40	3.20	50	114, 204	
3.066	40	3.06	35	3.08	50	$11\bar{5}$	
		3.01	5				
2.946	15	2.93	5			115^*	
2.869	22	2.87	30	2.89	50	$20\bar{6}$	
2.812	18	2.81	3	2.780	50	116	
2.583	90	2.58	100	2.577	100	$311, 116^*$	
2.513	10					$206^*, 008^*$	
2.450	16	2.46	20			$11\bar{7}^*$	
2.426	15				2.421	50	$023, 31\bar{4}$
2.402	14	2.40					$117^*, 20\bar{8}^*$
2.285	4					$22\bar{1}^*, 118^*$	
2.252	8	2.25	10	2.252	5	118, 221	
2.210	7					314^*	
2.186	7	2.19	5	2.194	5	$222, 31\bar{6}$	
		2.14	3				
2.082	20	2.08	15			208^*	
2.055	15			2.043	20	$22\bar{5}, 11\bar{9}$	
2.006	30	1.983	43	1.989	80	00.10	
1.750	3					228^*	
1.717	10	1.716	3			420^*	
1.694	15	1.691	5	1.687	5	$13\bar{3}, 31.10\ddagger$	
1.668	15	1.667	5			422^*	
1.633	8	1.638	5	1.636	5	$11.11, 228^*, 20.12^*$	
1.614	8	1.619	3			40.10^*	
1.585	8	1.586	5	1.575	5	$135, 31.11\ddagger, 424^*$	
1.569	5	1.565	3			517^*	
1.500	30	1.503	50	1.509	50	$515, 60\bar{4}\ddagger, 600^*$	
1.481	4	1.480	3			$33\bar{4}^*, 426^*$	

1. The Shakanai specimen; 2. $2M_2$ hydromuscovite (Threadgold, 1959); 3. $2M_2$ lepidolite (Levinson, 1953).

hkl: ASTM card 14-11. †: Additional indices are possible. *: Obtained on the basis of $a = 9.2 \text{ \AA}$, $b = 5.3 \text{ \AA}$, $c = 20.2 \text{ \AA}$ and $\beta = 98.0^\circ$ in this study.

X-ray diffractometer data are: Rigakudenki SG-2; Ni filtered Cu radiation; scanned at $1/4^\circ$ per min; recorded on chart paper at 1 cm per minute; silicon powder (Rigakudenki Si standard) used as standard.

morphs (D), particularly the reflections marked from 1 to 18 in Fig. 1. The specimen from the Shakanai mine (C) resembles the artificial mixture (D) and the data for the natural (C) and artificial (D) mixtures show considerably better agreement with those of $1M$ and $2M_1$ muscovite given by

Yoder and Eugster (1955). Although it is very difficult to show the existence of the $2M_2$ polymorph by powder methods (Radoslovich, 1960), careful study of the *d*-spacings and intensities indicates the probable presence of the $2M_2$ structure in the specimen in question.

Table 2. (cont.)

	A		B		C		D		1M muscovite*		2M ₁ muscovite*	
	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
							1.730	3			1.736	6
13	1.717	10	1.719	7								
	1.694	15	1.694	11	1.698	6	1.691	2			1.699	6
14	1.668	15	1.668	11	1.668	13	1.666	8	1.668	16	1.670	12
					1.649	10	1.646	10	1.653	12	1.653	17
15	1.633	8	1.635	9	1.635	4			1.635	12		
16	1.614	8	1.615	5								
17	1.585	8	1.584	5							1.602	7
18	1.569	5	1.569	3								

A, The specimen in question from the Shakanai mine; B, Hydromuscovite from the Tsuchihashi mine; C, Hydromuscovite from the Shakanai mine; D, A 1:1 mixture of hydromuscovite with 1M and 2M₁ polymorphs; A, B, C and D correspond to those used in Fig. 1. The reflections appearing in Fig. 1 are listed in this table and numbers from 1 to 18 correspond to those in Fig. 1.

*Yoder and Eugster (1955).

The chemical analyses and the numbers of ions on the basis of 24(O,OH) of the Shakanai specimen (A) and the Tsuchihashi specimen (B) are given in Table 3 together with that of hydromuscovite

given by Threadgold (1959). Lithium could not be detected by spectroscopic analysis. The most noticeable features of analyses are that the content of the alkali metals was lower and the H₂O⁺ higher

Table 3. Chemical analyses of hydromuscovites

	A	B	T	Numbers of ions on the basis of 24(O,OH)			
SiO ₂	47.14	45.95	45.65	Si	6.17	6.03	6.00
TiO ₂	0.34	tr.	tr.	Al	1.83	1.97	2.00
Al ₂ O ₃	37.09	38.68	36.03	Al	3.92	4.01	3.58
Fe ₂ O ₃	0.49	0.09	1.80	Ti	0.04		
FeO			0.13	Fe ⁺³	0.05	0.01	0.18
Cr ₂ O ₃			0.25	Fe ⁺²			0.01
MgO	0.83	0.12	0.52	Cr			0.03
MnO		0.03		Mg	0.16	0.02	0.10
CaO	0.57	0.82	0.23	Mn		0.00	
BaO			0.22	Ca	0.08	0.12	0.03
Na ₂ O	0.35	0.53	1.23	Ba			0.01
K ₂ O	7.10	9.02	8.18	Na	0.09	0.13	0.31
H ₂ O ⁺	5.18	5.12	5.27	K	1.19	1.50	1.37
H ₂ O ⁻	0.99	0.34	0.68				
P ₂ O ₅	0.01						
FeS ₂			0.27				
Total (%)	100.09	100.70	100.46				

A, The specimen in question from the Shakanai mine.

B, Hydromuscovite from the Tsuchihashi mine.

T, 2M₂ hydromuscovite (Threadgold, 1959).

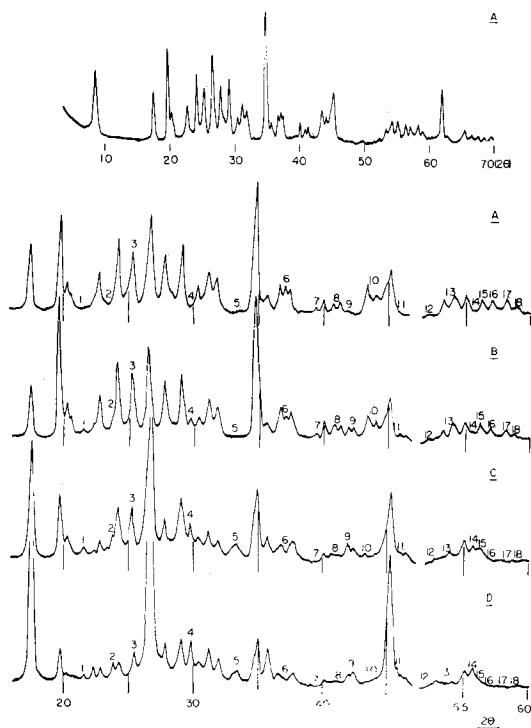


Fig. 1. X-ray diffraction patterns of four hydromuscovites. A. The specimen in question from the Shakanai mine. B. Hydromuscovite from the Tsuchihashi mine. C. Hydromuscovite from the Shakanai mine. D. A 1:1 mixture of hydromuscovite with $1M$ and $2M_1$ polymorphs. A, B, C, and D correspond to those used in Table 2.

than in muscovite. These properties are similar to those of hydromuscovite and differ from those of lepidolite.

DTA curves of the Shakanai specimen (A), Tsuchihashi specimen (B) and the mixture of $1M$ and $2M_1$ polymorphs from the Shakanai mine (C) in Fig. 2 were obtained by heating in air at a rate of 10°C per min. They show an endothermic reaction at about 615°C , due to the loss of hydroxyl water. These curves are closely similar to that of hydromuscovite found in the literature.

The infrared absorption spectrum is close to those of $1M$ and $2M$ polymorphs of illite reported by Oinuma and Hayashi (1968); it shows absorption bands 3638 , 1020 , 926 , 830 , 756 , 536 , 480 , 406 and 346 cm^{-1} .

DISCUSSION AND CONCLUSIONS

Although single crystal methods should be used to determine the polymorphs unequivocally, the powder diffraction technique was used because of

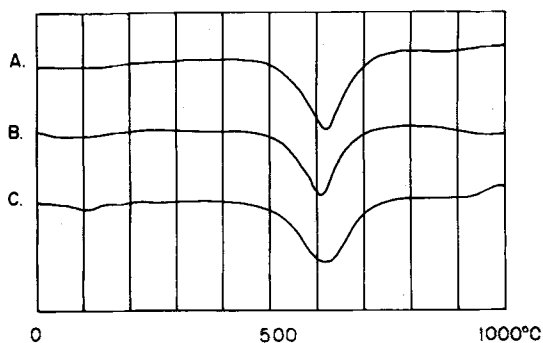


Fig. 2. DTA curves of hydromuscovites. A. The specimen in question from the Shakanai mine. B. Hydromuscovite from the Tsuchihashi mine. C. Hydromuscovite from the Shakanai mine. A, B, and C correspond to those used in Fig. 1 and Table 2.

the fine grained nature of the specimens. These powder methods have been used to distinguish between $1M$ lepidolites, $2M_2$ lepidolites and $2M_1$ lithium muscovites. For the specimen in question, the X-ray powder pattern resembles that of a $2M_2$ lepidolite and is clearly different from those of the $1M$ and/or $2M_1$ polymorphs. Chemically, the specimen differs from lepidolite, and is similar to certain hydromuscovites. It deviates from the ideal muscovite composition in regard to high water and low alkali content. Therefore, it is highly probable that the specimen is hydromuscovite with a $2M_2$ structure, although further studies are required to establish the crystal structure.

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Résumé—Une hydromuscovite en association avec du gypse et de l'anhydrite a été recueillie de la mine de Shakanai, Préfecture d'Akita, Japon. Composition chimique: SiO_2 47,14%; TiO_2 0,34%; Al_2O_3 37,09%; Fe_2O_3 0,49%; MgO 0,83%; CaO 0,57%; Na_2O 0,35%; K_2O 7,10%; H_2O 5,18%; H_2O^- 0,99%; P_2O_5 0,01%; total 100,09%. Les analyses différentielles thermiques et d'absorption d'infra-rouge étaient similaires à celles de l'hydromuscovite. Un modèle de diffraction des rayons X différait nettement de ceux des polymorphes $1M$ et/ou $2M_1$ et était identique à celui du polymorphe $2M_2$ qui est connu pour se produire dans les lépidolites.

Kurzreferat—Ein Hydromuskowit begleitet von Gips und Anhydrit wurde aus den Shakanai Minen, Akita Prefektur, Japan bezogen. Die chemische Zusammensetzung war wie folgt: SiO_2 47,14%; TiO_2 0,34%; Al_2O_3 37,09%; Fe_2O_3 0,49%; MgO 0,83%; CaO 0,57%; Na_2O 0,35%; K_2O 7,10%; H_2O 5,18%; H_2O^- 0,99%; P_2O_5 0,01%; insgesamt 100,09%. Die differentiellen Wärme- und Infrarotabsorptionsanalysen waren ähnlich denen des Hydromuskowits. Das Röntgenbeugungsbild unterschied sich deutlich von jenen des $1M$ und/oder $2M_1$ Polymorphs und war ähnlich dem des $2M_2$ Polymorphs, das bekanntlich in Lepidoliten vorkommt.

Резюме—Гидромусковит в ассоциации с гипсом и ангидритом обнаружен в месторождении Шаканай, префектура Акита, Япония. Химический состав минерала: SiO_2 —47,14%; TiO_2 —0,34%; Al_2O_3 —37,09%; Fe_2O_3 —0,49%; MgO —0,83%; CaO —0,57%; Na_2O —0,35%; K_2O —7,10%; H_2O^+ —5,18%; H_2O^- —0,99%; P_2O_5 —0,01%; сумма 100,09%.

Данные дифференциально-термического анализа и инфракрасной спектроскопии сходны с результатами, полученными ранее для других гидромусковитов. Порошковые диаграммы обнаруживают явное отличие от таковой полиморфных модификаций $1M$ и/или $2M_1$ и сходны с порошковыми диаграммами порошка полиморфной модификации $2M_2$, которая характерна для некоторых лепидолитов.