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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: 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%. Differential thermal and i.r. absorption analyses were similar to those of hydromuscovite. The X-ray diffraction pattern differed clearly from those of the $1M$ and/or $2M_1$ polymorphs and it was similar to that of the $2M_2$ 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 $2M_2$ 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 $2M_2$ 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 $1M$ and $2M_1$ polymorphs. Although it seems very difficult to show the existence of the $2M_2$ 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 $1M$ and $2M_1$ 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 $1M$ and $2M_1$ 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 $< 2\mu$ 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 $2M_2$ lepidolite. The reflections not recorded on the card were indexed on the basis of $a = 9{\cdot}2$ Å, $b = 5{\cdot}3$ Å, $c = 20{\cdot}2$ Å and $\beta = 98{\cdot}0°$ 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 $1M$ and $2M_1$ polymorphs than with $2M_2$ 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 $1M$ and $2M_1$ 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 $2M_2$ polymorph.

(C) Hydromuscovite from the Shakanai mine, Akita Prefecture, Japan (C in Table 2 and Fig. 1). This specimen is a mixture of $1M$ and $2M_1$ polymorphs.

(D) A 1:1 mixture of hydromuscovite with $1M$ and $2M_1$ 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 $1M$ and $2M_1$ poly-

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

1		2		3		
d(Å)	I	d(Å)	I	d(Å)	I	hkl
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*, $20\bar{2}$*
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	$11\bar{4}$
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 }				$11\bar{7}$*
2·426	15	}	20	2·421	50	023, $31\bar{4}$
2·402	14	2·40 }				117*, $20\bar{8}$*
2·285	4					$22\bar{1}$*, $11\bar{8}$*
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					$22\bar{8}$*
1·717	10	1·716	3			420*
1·694	15	1·691	5	1·687	5	$13\bar{3}$, 31·10†
1·668	15	1·667	5			422*
1·633	8	1·638	5	1·636	5	11·11, 228*, 20·$\overline{12}$*
1·614	8	1·619	3			40·$\overline{10}$*
1·585	8	1·586	5	1·575	5	135, 31·11†, 424*
1·569	5	1·565	3			$51\bar{7}$*
1·500	30	1·503	50	1·509	50	515, $60\bar{4}$†, 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 $a = 9{\cdot}2$ Å, $b = 5{\cdot}3$ Å, $c = 20{\cdot}2$ Å and $\beta = 98{\cdot}0°$ in this study.

X-ray diffractometer data are: Rigakudenki SG-2; Ni filtered Cu radiation; scanned at 1/4° 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. X-ray diffraction data of three hydromuscovites, A, B, C, and an artificial mixture, D

	A		B		C		D		1*M* muscovite*		2M_1 muscovite*	
	d(Å)	I	*d*(Å)	I	*d*(Å)	I	*d*(Å)	I	*d*(Å)	I	*d*(Å)	I
	5·06	42	5·06	35	5·04	78	5·02	100†	5·04	37	5·02	55
	4·49	60	4·50	90	4·49	42	4·48	20	4·49	90	4·48	55
											4·46	65
	4·37	15	4·37	20	4·37	12	4·38	3	4·35	27	4·39	14
	4·31	5	4·31	10			4·29	2			4·30	21
			4·13	2	4·13	5	4·11	4	4·11	16	4·11	14
1	3·966}	5}	3·983	5	3·990	3	3·983	7			3·973	12
	3·921}	21}	3·900	25	3·897	8	3·895	6			3·889	37
					3·735	5	3·728	10			3·735	32
2	3·681	43	3·683	45	3·675	30	3·660	10	3·66	60		
	3·520	33	3·517	36	3·517	30	3·497	10			3·500	44
3	3·348	58	3·354	58	3·342	100	3·336	100†	3·36	100	3·351	100
	3·211	28	3·209	33	3·206	15	3·206	16			3·208	47
	3·066	40	3·071	36	3·071	28	3·066	19	3·07	50		
			3·005	5	3·000	13	2·999	18			2·999	47
4	2·946	15	2·947	6	2·942	5	2·938	5	2·926	6		
	2·869	22	2·873	20	2·869	11	2·864	15			2·871	35
	2·812	18	2·810	19	2·803	7	2·796	12			2·803	22
					2·672	10	2·680	6	2·689	16		
5											2·589	50
	2·583	90	2·580	92	2·583}		2·583}		2·582	50	2·580	45
					2·569}	45	2·562}	28	2·565	90	2·562	90
									2·550	22		
	2·513	10	2·520	7	2·511	10	2·506	21			2·514	20
	2·450	16	2·450	20	2·450	10	2·460	5	2·450	11	2·458	19
											2·446	12
	2·426	15	2·421	14								
6	2·402	14	2·402	17					2·405	4	2·396	10
					2·384	13	2·381	7	2·380	12	2·380	24
							2·336	2				
	2·285	4	2·279	3								
7	2·252	8	2·250	10	2·249	7	2·247	4	2·246	8	2·247	12
											2·236	5
	2·210	7	2·206	8	2·215	4	2·200	2	2·219	7	2·201	5
	2·186	7	2·184	8					2·191	4	2·184	7
8			2·151	6	2·151	10	2·150	7	2·156	20	2·149	10
9			2·134	5	2·130	7	2·130	10			2·132	23
									2·109	6		
10	2·082	20	2·084	15	2·088	3						
	2·055	15	2·054	12							2·051	6
	2·006	30	2·010	26	1·983	45	2·002	80	2·013	32	2·010	75
			1·978	3	1·971	3	1·975	3			1·975	14
11			1·956	3	1·951	5	1·947	4	1·957	7		
12	1·750	3	1·751	2								

Table 2. (*cont.*)

	A d(Å)	A I	B d(Å)	B I	C d(Å)	C I	D d(Å)	D I	1M muscovite* d(Å)	1M muscovite* I	$2M_1$ muscovite* d(Å)	$2M_1$ muscovite* I
							1·730	3			1·736	6
	1·717	10	1·719	7								
13												
	1·694	15	1·694	11	1·698	6	1·691	2			1·699	6
	1·668	15	1·668	11	1·668	13	1·666	8	1·668	16	1·670	12
14					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								
											1·602	7
17	1·585	8	1·584	5								
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 $2M_1$ 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 H_2O^+ higher

Table 3. Chemical analyses of hydromuscovites

	A	B	T
SiO_2	47·14	45·95	45·65
TiO_2	0·34	tr.	tr.
Al_2O_3	37·09	38·68	36·03
Fe_2O_3	0·49	0·09	1·80
FeO			0·13
Cr_2O_3			0·25
MgO	0·83	0·12	0·52
MnO		0·03	
CaO	0·57	0·82	0·23
BaO			0·22
Na_2O	0·35	0·53	1·23
K_2O	7·10	9·02	8·18
H_2O†	5·18	5·12	5·27
H^2O^-	0·99	0·34	0·68
P_2O_5	0·01		
FeS_2			0·27
Total (%)	100·09	100·70	100·46

Numbers of ions on the basis of 24(O,OH)	A	B	T
Si	6·17	6·03	6·00
Al	1·83	1·97	2·00
Al	3·92	4·01	3·58
Ti	0·04		
Fe^{+3}	0·05	0·01	0·18
Fe^{+2}			0·01
Cr			0·03
Mg	0·16	0·02	0·10
Mn		0·00	
Ca	0·08	0·12	0·03
Ba			0·01
Na	0·09	0·13	0·31
K	1·19	1·50	1·37

A, The specimen in question from the Shakanai mine.
B, Hydromuscovite from the Tsuchihashi mine.
T, $2M_2$ hydromuscovite (Threadgold, 1959).

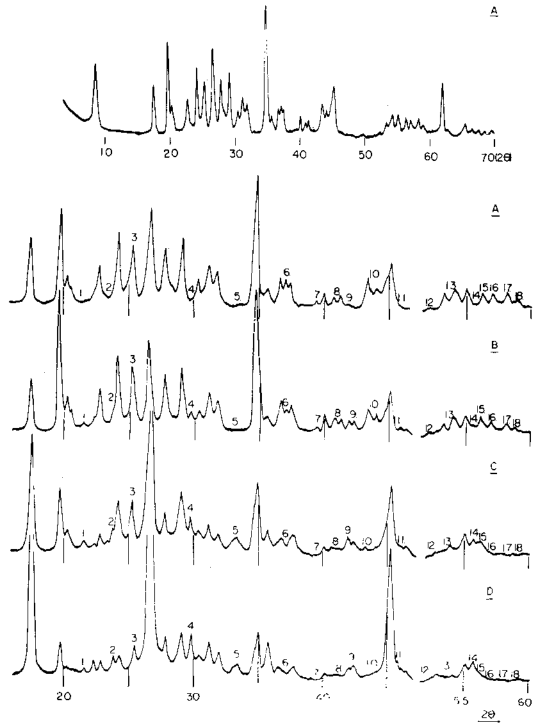

Fig. 1. X-ray diffraction patterns of four hydromuscovites. A. The specimen in question from the Shakanai mine. B. Hydromuscovite from the Tsuchihashi mine. C. Hydromuscovite from the Shakanai mine. D. A 1 : 1 mixture of hydromuscovite with $1M$ and $2M_1$ polymorphs. A, B, C, and D correspond to those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

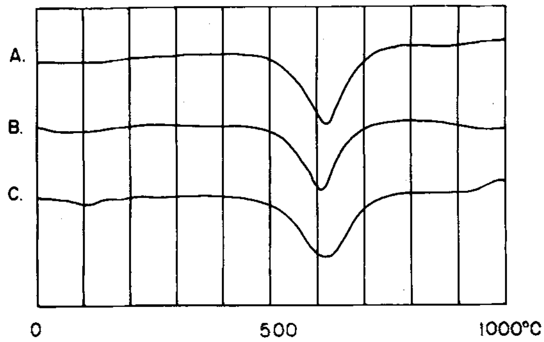

Fig. 2. DTA curves of hydromuscovites. A. The specimen in question from the Shakanai mine. B. Hydromuscovite from the Tsuchihashi mine. C. Hydromuscovite from the Shakanai mine. A, B, and C correspond to those used in Fig. 1 and Table 2.

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 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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REFERENCES

Heinrich, E. W., Levinson, A. A., Levandowski, D. W. and Hewitt, C. H. (1953) Studies in the natural history of micas: University of Michigan Engineering Res. Inst. project M. 978.

Hendricks, S. B. and Jefferson, M. (1939) Polymorphism of the micas, with optical measurments: *Am. Mineralogist* **24**, 729–771.

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

Oinuma, K. and Hayashi, H. (1968) Infrared spectra of clay minerals: *J. Toyo Univ. General Education (Nat. Sci.)* **9**, 57–98.

Radoslovich, E. W. (1960) Hydromuscovite with the $2M_2$ structure—A criticism: *Am. Mineralogist* **45**, 894–898.

Shimoda, S., Sudo, T. and Oinuma, K. (1969) Differential thermal analysis curves of mica clay minerals: *Proc. Intern Clay Conf., Tokyo, Vol. 1*, 197–206.

Smith, J. V. and Yoder, H. S. (1956) Experimental and theoretical studies of the mica polymorphs: *Mineral. Mag.* **31**, 209–235.

Threadgold, I. M. (1959) A hydromuscovite with the $2M_2$ structure, from Mount Lyell, Tasmania: *Am. Mineralogist* **44**, 488–494.

Tomita, K. and Sudo, T. (1968) Interstratified structure formed from a pre-heated mica by acid treatments: *Nature* **217**, 1043–1044.

Yoder, H. S. and Eugster, H. P. (1955) Synthetic and natural muscovite: *Geochim. et Cosmochim. Acta* **8**, 225–280.

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. Порошкограммы обнаруживают явное отличие от таковой полиморфных модификаций $1M$ и/или $2M_1$ и сходны с порошкограммами порошка полиморфной модификации $2M_2$, которая характерна для некоторых лепидолитов.