THE AMERICAN MINERALOGIST, VOL. 45, SEPTEMBER-OCTOBER, 1960

AN INTERSTRATIFIED MIXTURE OF MICA CLAY MINERALS

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ABSTRACT

Various kinds of mixed-layer minerals are found in close association with the hydrothermal pyrophyllite diaspore deposit of the Yonago mine, Nagano Prefecture, Japan. The reference specimens occur as vein-shaped masses in the pyrophyllite bodies. It almost agrees with allevardite chemically: SiO_2, 43.17%; Al_2O_3, 33.54%; Fe_2O_3, 0.26%; FeO, 0.13%; TiO_2, 0.51%; CaO, 0.52%; MgO, 0.65%; K_2O, 2.84%; Na_2O, 0.38%; P_2O5, tr.; H_2O (+), 10.48%; H_2O (−) 7.75%; Total, 100.23%. *X*-ray data strongly suggest that the 26.1±1 Å spacing can be attributed to a complex combination of the 10 Å mica clay-mineral structure and its more hydrated forms. Ideally three kinds of structures can be considered as "*A*" (10 Å structure . . . a mica clay-mineral structure), "*B*" (12.48 Å structure . . . the silicate layer alternating with a single layer of water molecules), and "*C*" (15.16 Å structure . . . the silicate layer alternating with a double layer of water molecules). It can be appropriately inferred that the 26 Å spacing is nearest to that attributed to a random piling of $A+C$ and $B+C$ structures in equal proportions. It is reasonable to consider that small amounts of potassium ions are still retained even in *B* and *C* structure.

INTRODUCTION

A short time ago, a 26 Å clay mineral was found in the alteration zone around the hydrothermal gypsum deposit of the Tsutsumizawa ore body of the Hanaoka mine, Akita Prefecture, Japan (Sudo and Hayashi, 1955). More recently a 26 Å clay mineral was found in the alteration zone of the Kamikita mine, Aomori Prefecture, Japan (Sudo, Hayashi, and Yokokura, 1958), but the above workers could not provide their detailed mineralogical properties because of difficulty in obtaining pure specimens free from impurities. Subsequently the present writers found the 26° Å clay mineral from the Yonago mine (pyrophyllite diaspore deposit), Nagano Prefecture, and noticed that the mineral also agrees with the Hanaoka and Kamikita materials, and a pure natural specimen was found almost free from impurities. Thus such minerals are not so rare as we have hitherto anticipated, and the present mineral is considered appropriate for the description of its mineralogical and crystallographic properties.

MODE OF OCCURRENCE

Pyrophyllite deposits are found in many localities in Japan, usually accompaning corundum, diaspore, kaolinite, dickite, nacrite etc. Most of them are important mineral resources for the firebrick and paper industries. They are also important because of their mineralogy and geology. But many mineralogical problems remain unsolved because of their very complex mineral associations. The Yonago mine now being considered is one of the important pyrophyllite-diaspore deposits in Japan.

The area near the ore deposit consists of fine grained sandstone and shale intruded by porphyrite and andesite dykes. All of these rocks are covered by a lava flow. The ore deposit occurs along the boundary zone between the porphyrite and andesite dykes replacing both of these rocks. The ore bodies consist of diaspore, clay minerals, quartz and pyrite. Diaspore occurs as compact or powdery masses mostly cemented by pyrophyllite.

About eighty specimens were collected in the area including the ore deposit, and the amounts of the minerals in each specimen were estimated by *x*-ray analyses using an internal standard of fluorite. Standard curves were made using pure clay minerals from the other localities. The confirmed minerals are diaspore, pyrophyllite, quartz, sericite, kaolinite, halloysite, montmorillonite, and pyrite. By plotting the result of the qualitative estimations of these minerals except pyrite, zonal distributions were confirmed particularly with regard to the distributions of diaspore, pyrophyllite, and kaolin minerals. The center of the zonal distribution was confirmed in two different places; in both of which the zonal distributions were found to be (diaspore and pyrophyllite)—(kaolin minerals)—(quartz), going progressively away from the center. The mineral names written in parentheses are those of the principal minerals in each zone. The boundaries between these zones are not sharp, but gradually grade into one another. Diaspore is rather more dominant in the central area than pyrophyllite, but in most cases both of these minerals occur mixed with each other in various proportions. Pyrite crystals are dominant in the kaolin mineral zone. Sericite occurs in small amounts throughout these zones, but tends to be dominant in the silicious zone. Montmorillonite occurs locally in the silicious and kaolin mineral zones. Clay minerals showing large spacings in their powder diffraction data are frequently noted:

Type I (specimens 11 and 63): This mineral shows a 26 Å spacing and will be discussed in detail in this report. It occurs widely in the ore area, particularly dominantly in the pyrophyllite-diaspore zone, frequently as vein-shaped masses in the pyrophyllite bodies.

Type II (specimen 1): This mineral also shows a spacing of about 26 Å and occurs only in the kaolinite zone. Because of difficulty in obtaining a pure sample, we could not ascertain its detailed mineralogical properties, but it seems to agree with rectorite (Bradley, 1950), or the 26 Å clay mineral found from the Honami pyrophyllite deposit, Nagano Prefecture (Kodama, 1958).

Type III (specimen 38): This is found rarely in the silicious zone as thin crusts covering silicious rock fragments. The silicious area usually shows brecciated structures consisting of silicious rock fragments. Because of difficulty in obtaining a pure sample, we could not determine its detailed mineralogical and properties, but it seems to agree with the aluminian mixed-layer mineral recently found from the Kamikita mine, Aomori Prefecture (Sudo and Kodama, 1957).

26 Å CLAY MINERAL (TYPE I)

Macroscopic properties: This mineral occurs as white compact masses with greasy luster resembling the pyrophyllite masses, and is associated with the pyrophyllite-diaspore zone. We could not determine its detailed mode of occurrence, but some of it surely occurs as vein-shaped masses in pyrophyllite bodies.

By x-ray testing, we found specimens almost free from impurities, and obtained the following data from the crude specimens. Their x-ray reflections consist of the clear and sharp 26 Å reflection and its higher orders except the weak 4.27Å reflection which is probably due to a small amount of impurity. On close examination of the 26 Å reflection under various experimental conditions as studied with a slow scanning speed, or using the internal standard of α-stearic acid, the spacing appears to vary slightly from specimen to specimen. Basal spacings obtained from nine reference specimens and also the mean values of each set of basal reflections are given in Table 1. From each of these mean value the 001 spacings were calculated, and 26.1 ± 1 Å was obtained as the final mean value.

TABLE 1. BASAL SPACINGS OF THE 26 Å CLAY-MINERAL FROM THE YONAGO MINE

001	1		2		3		4		5		6	
	d	I	*d*	I	*d*	I	*d*	I	*d*	I	*d*	I
001	28.5 Å	61 s	27.6 Å	66 s	26.8 Å	91 vs	26.8 Å	91 vs	28.5 Å	44 m	26.8 Å	60 s
002	12.8	52 vs			13.0	83 vs	13.0	83 vs	13.0	47 s	12.5	50 s
005	5.12	25 s			5.09	39 s	5.12	40 vs	5.12	27 vs	5.06	34 s
008	3.24	30 s			3.27	48 s	3.24	42 m	3.27	40 vs	3.25	34 m
00.10	2.57	26 s			2.57	32 s	2.57	32 s	2.57	42 vs	2.57	35 s

	7		8		9		Mean	d(001)
	d	I	*d*	I	*d*	9	*d*	
001	27.6 Å	50 m	27.6 Å	20 b	28.5 Å	21 b	27.6 Å	27.6 Å
002							12.9	25.8
005							5.10	25.5
008							3.25	26.0
00.10							2.57	25.7
								Mean 26.1 ± 1 Å

Worthy of notice is that the 26 Å reflection is usually accompanied by a tailed reflection on its small angle side, but we could not find reflections attributable to superstructures of the 26 Å one.

Effects of heat (Table 2): The specimen analysed by *x*-ray diffraction was heated at each of the temperatures 300° C., 500° C., 700° C., 900° C., and 1000° C. for one hour and sealed into a glass tube immediately after cooling, and kept in the sealed glass tube until it was studied by *x*-rays. In the specimen heated at 300° C. for one hour, the 26 Å reflection was just visible, and its higher order reflections were somewhat weakened. The 13 Å reflection shifted to a 10.3 Å reflection, and the 5.10 Å reflec-

TABLE 2. *X*-RAY DIFFRACTION DATA FOR THE AIR-DRYED 26 Å CLAY MINERAL (CuKα, 1.5418 Å)

Room temp.		300° C.		500° C.		700° C.		900° C.		1000° C.	
d	I	*d*	I	*d*	I	*d*	I	*d*	I	*d*	I
26.7 Å	40 vs					24.5 Å	3 vb				
								18.4 Å	2 b		
13.0	33 vs										
				11.5 Å	5 b	11.8 Å	7 b				
		10.3 Å	12 b	10.9	5 b	10.4	8 b	10.3	15 s	10.3 Å	2 b
				9.9	6 b	10.0	10 b				
9.3	3 b										
5.10	16 s	5.01	8 m	5.07	5 b	5.04	9 s	5.07	10 s	5.09	3 m
4.48	19 s	4.51	20 vs	4.53	22 s	4.51	38 vs	4.51	42 vs	4.50	8 m
4.27	10 vs	4.29	21 vs	4.31	3 s	4.27	7 vs				
						3.87	4 vb	3.92	6 b		
								3.80	6 b		
		3.52	3 vb					3.55	5 b		
3.47	3 b										
										3.40	8 vb
3.35	6 s			3.35	10 m	3.34	27 vs	3.35	30 s		
3.27	6 s	3.29	11 b	3.29	8 s	3.24	7 vs	3.27	9 vs	3.25	4 s
								3.10	4 b		
						3.03	2 vb	3.08	4 b		
						2.84	2 vb	2.88	3 b		
										2.70	2 b
2.56	13 s	2.58	15 s	2.59	9 m	2.59	10 b	2.59	11 m		
						2.51	3 vb	2.52	5 b	2.54	3 vb
2.49	3 b	2.46	4 vb	2.49	5 b	2.48	3 vs	2.49	4 b		
2.44	4 b			2.42	3 vb	2.41	3 vb	2.41	4 b		
2.39	4 b					2.35	4 b				
		2.25	3 b	2.26	3 vb			2.26	6 m	2.21	3 b
2.19	3 vb										
2.13	3 vb	2.14	3 b			2.13	4 vs	2.13	2 b	2.13	2 vb
		2.03	2 b			2.01	4 vb	2.01	5 b		
1.99	5 b										
		1.79	4 b	1.72	3 b	1.72	3 vb				
1.69	3 b	1.69	3 b	1.63	3 vb	1.67	3 vb	1.69	5 b	1.68	3 b
		1.65	3 vb								
		1.55	5 s								
1.49	7 m	1.50	9 m	1.51	3 b	1.51	4 b	1.52	4 b		

vs: very sharp. s: sharp. m: medium. b: broad. vb: very broad.

tion was replaced by a 5.01 Å reflection. The 3.27 Å reflection became broader, and its spacing was replaced by a slightly larger spacing of 3.29 Å. In the specimen heated at 500° C., the 26 Å reflection was still just visible. Its higher order reflections became weaker than in the case of the specimen heated at 300° C. The 3.27 Å reflection was replaced by a broad reflection with a slightly larger spacing of 3.35 Å. Worthy of special attention is that the 10 Å reflection acquired a tail toward its low angle side. A very broad reflection at about 11.5 Å could be recognized on its tailed reflection. Such behaviour is closely similar to that of the tailed reflection accompanying the 10 Å reflection in the crude specimen of the Kamikita material. After heating to 700° C., the weak and broad 2.45 Å reflection appeared; the intensities of the 10 Å and 5 Å reflection became somewhat more intense, but the 3.34 Å and 4.51 Å reflections became remarkably intense. The tailed reflection was still confirmed. After heating to 900° C., the intensities of the 10 Å, 5 Å, 4.5 Å and 3.35 Å are similar to those in the specimen heated at 700° C., but the 26 Å reflection as well as the tailed reflection completely disappeared, and the very weak 19 Å reflection appeared. In the specimen heated at 1000° C., the reflections were weakened, except the 4.50 Å and 3.40 Å reflections. The result obtained above suggests that the 26 Å spacing seems to be related to hydrous states of the 10 A structure.

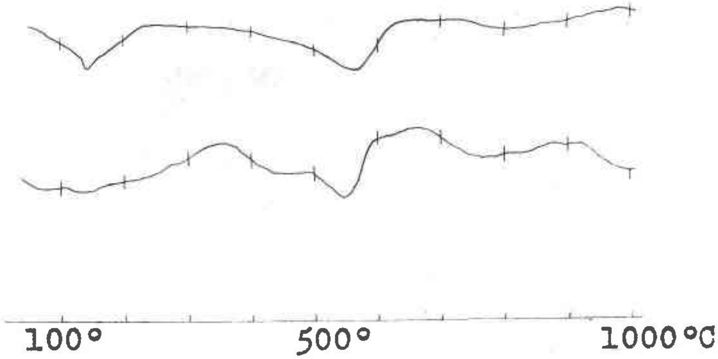

FIG. 1. D.T.A. curves of the 26 Å clay mineral from the Yonago mine. Above: specimen in natural state. Below: specimen treated with piperidine.

Differential thermal analysis curve: The differential thermal analysis curve of the specimen analysed by *x*-rays shows the broad endothermic peaks at about 600° C., and also between 700° C. and 800° C., except a clear endothermic peak between 100° C. and 200° C. (Fig. 1, above). The specimen was soaked in piperidine for about 10 minutes, and dried on a water-bath. The specimen thus pretreated was analysed thermally (Fig.

1). Its thermal curve shows an additional exothermic peak between 600° C. and 700° C. as in the case of montmorillonite or vermiculite.

Chemical composition: The specimen analysed thermally and by *x*-rays was also analysed chemically. Its chemical composition is as follows: SiO_2 43.17%; Al_2O_3, 33.54%; TiO_2, 0.51%; Fe_2O_3, 0.26%; FeO, 0.13%; CaO, 0.52%; MgO, 0.65%; K_2O, 2.84%; Na_2O, 0.38%; P_2O_5, tr.; H_2O (+) 10.48%; H_2O (−) 7.75%, Total, 100.23%. It is worthy of notice that the mineral almost agrees with allevardite (Caillère, Mathieu-Sicaud, and Hénin 1950; Brindley, 1956), except that the amount of potassium is slightly larger and the amount of sodium is smaller in the present material than in the case of allevardite. The structural formula was constructed on the basis of the number of ions in the octahedral and tetrahedral positions as 12 for the sake of comparison with that of allevardite.

$$(Na_{0.16}K_{0.52}Ca_{0.08})(Al_{3.82}Fe'''_{0.02}Fe''_{0.02}Mg_{0.08})(Si_{6.13}Al_{1.87})O_{17.68}(OH)_{7.44}$$

Treatment with water or ethylene glycol gave no unique results; they seem to vary slightly even from portion to portion in a hand specimen. Treatment with water always caused the 26 Å reflection to be replaced by the 29.2 ± 1 Å reflection, but treatment with ethylene glycol caused no expansion in some specimens, yet clear expansion to about 28 Å in others. Treatment with ammonium nitrate solution (1 N) by boiling for 10 minutes caused no remarkable change except the 26 Å and 13 Å reflections became somewhat broad.

X-ray analysis: In general, the powder reflections are somewhat broad, and we could obtain only five basal reflections for crystallographic considerations even with a slide of well-oriented aggregates. Therefore we could not obtain reliable data for Fourier synthesis of the electron density or the Fourier transform (MacEwan 1956). But we could suggest the probability of occurrences of spacings of about 10 Å, 13 Å, and 16 Å.

DISCUSSION

The present material has mineralogical properties almost agreeing with those of allevardite, but the following slight differences exist between them, which must be considered in drawing a conclusion:

(1) For allevardite, the largest spacing obtained was 24.12 Å in air-dry unheated material, and very many basal reflections were found. In the present case the *x*-ray powder reflections are generally broad, and only five basal reflections are available. The 26 Å spacing varies slightly from specimen to specimen, and even from portion to portion in a hand specimen, and is accompanied by a tailed reflection on its low angle side. But

we could not find reflections due to super-structures by the small-angle scattering technique.

(2) The intensities of the x-ray powder reflections of the specimen heated at 900° C. almost agree with the calculated intensities for the regular piling of the 10 Å mica clay-mineral structure and its silicate layer. But the 10 Å reflection is stronger than its calculated value, which implies that the 10 Å structure may be also produced in the firing product.

On this basis, it may be inferred that the 26 Å spacing is not necessarily attributed to a unique regular piling of the 10 Å structure and its more hydrated one, but to a more complex mixed-layer mineral; it is strongly suggested that the 26 Å spacing is due to a random piling of two structures with spacings near to 26 Å.

Table 3. Observed Values of Spacings and Intensities of some Basal Reflections Compared with their Calculated Values Obtained from a Random Mixed-Layer Structure of A+C and B+C Structures

	Observed values		Calculated values	
	d	I	*d*	I
001	26.1 Å	1	26 Å	1
002	12.9	0.52	12	0.40
005	5.10	0.18	5	0.15
008	3.25	0.32	3.1	0.30

As already shown by Brindley (1956), the cell heights of the hydrated forms of the mica clay-mineral structure are as follows:

A: 9.98 Å—mica clay-mineral structure.

B: 12.48 Å—potassium ions are completely replaced by a single layer of water molecules.

C: 15.16 Å—potassium ions are completely replaced by a double layer of water molecules.

Of course these three models are ideal ones. We can consider intermediate states as potassium ions are still associated with water layers. But since the amount of potassium associated with the water layers is small, the fluctuation of these cell heights may be small, and the principal cell heights can be grouped at about 10 Å, 13 Å, and 16 Å, which were already suggested by Fourier-transform diagram.

Various combinations were considered and finally it was shown that the structure of a random piling of 25.1 Å ($A+C$) and 27.6 Å ($B+C$) in equal proportions, gave the calculated intensity values nearest to observed ones (Table 3). Actually, it may be more appropriate to consider that some potassium is still preserved even in the *B* and *C* structures because, as shown above, it seems that the firing product at 900° C. is not solely composed of a regular piling of the 10 Å mica clay-mineral structure, its silicate layer, but also of some amounts of the 10 Å structure.

Worthy of special attention is that a tailed reflection appears associated with the 10 Å reflection on heating. This fact suggests that various spacings slightly different from the 10 Å spacing occur on heating, and also suggests that dehydration did not occur uniformly throughout all the layers on heating. Furthermore in relation to this fact, it is also worthy of notice that effects of treatments with ethylene glycol are not unique. This fact implies that the crystallochemical behavior of the potassium ions is not unique; some of them are exchangeable and others not.

ORIGIN

On the basis of the model, it seems likely that the mineral now in question is a mica clay mineral partially altered by hydration and leaching, the degree of which may vary from place to place, as shown by variation of cell heights and organic complexes. It is believed that with increase of hydration and leaching, potassium ions decrease and the number of layers of water molecules increases. Thus, although potassium ions are still preserved in the water layers, the amount can be expected to be less in the case of a double layer than in the case of a single layer. If the mineral is an alteration product of the 10 Å mica clay mineral it is possible that the mineral is not necessarily represented by the ideal model, but small amounts of potassium ions are still preserved in *B* and *C* structures.

The above statement can be supported by the mode of occurrence of this mineral, namely, in the central area of the deposit closely associated with pyrophyllite-diaspore which may have been formed in a leaching environment. In the case of the Kamikita material, the 26 Å minerals are dominant in the central area of the deposit associating with pyrophyllite and pyrite, and the 10 Å mica clay mineral is rather dominant on going outward.

Recently one of the writers emphasized the concept of the intermediate mineral in clay mineralogy (Sudo, 1957). It means a mineral which behaves as mineral "*a*" in some of its properties but as mineral "*b*" in the other properties. These minerals have frequently been found between certain principal clay minerals such as montmorillonite and chlorite. It is frequently noticed that some of these intermediate minerals have a mixed-layer structure with two kinds of minerals. Thus the present material may be described as an intermediate mineral, formed during the hydration of the 10 Å mica clay mineral.

ACKNOWLEDGMENTS

The writers are indebted to Mr. Miura and S. Ota of the Chugai-mining Company, and Mr. J. Takahashi, of the Yonago Mine, for help of Geological survey. Thanks are due to the officials of the Department of Education for their kindness in granting funds for this study.

The writers wish to express their deep appreciation to Professor G. W. Brindley of the Pennsylvania State University, for critically reading of this manuscript.

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Manuscript received June 19, 1959.