LONG SPACING CLAY MINERAL FROM THE UKU MINE, YAMAGUCHI PREFECTURE, JAPAN*

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ABSTRACT

A white powdery clay mineral with 28.8Å. spacing was found in the kaolinite vein of the Uku mine, Yamaguchi Prefecture. The interplaner spacings of stronger X-ray powder diffraction lines of the mineral are as follows: 28.8 ± 0.1 , 14.5 ± 0.1 , 4.82 ± 0.02 and 1.4893 ± 0.0005 Å. The 14.5Å. line shifts to 15.4 ± 0.2 Å. and the 28.8Å. line to 31.0 ± 0.5 Å. after treatment with ethylene glycol. The 28.8Å. line is persistent in the temperature range from 20° to 300°C., but completely disappears above 400°C.. The 14.5Å. line is replaced by the 12.4Å. line at 400°C., which is persistent up to 600°C. but disappears above 700°C.. At 1200°C. the specimen is transformed to mullite.

It is considered that, as T. Sudo et al. have already pointed out, the unusually long spacing of 28.8Å. is the result of a regularly alternating stacking of two kinds of layer lattices; one is the ordinary montmorillonite lattice with the basal spacing of about 14.8Å. and the other is a hypothetical aluminium chlorite lattice with the basal spacing of about 14.0Å..

Introduction

The clay mineral with long spacing of about 30Å. has been found in the clays from the Kurata mine, Yamaguchi Prefecture by T. Sudo, H. Takahashi and H. Matsui⁴⁾, from the Hanaoka mine, Akita Prefecture by T. Sudo and H. Hayashi⁵⁾, and from the Kamikita mine, Aomori Prefecture by T. Sudo, H. Hayashi, H. Kodama and K. Oinuma^{**}. Recently the writer found a similar clay mineral from the

* Read at the Annual Meeting of the Mineralogical Society of Japan held in Tokyo on June 1, 1957.

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Uku mine, Abu-machi, Yamaguchi Prefecture*. In the mode of occurrence, the Uku clay especially resembles the Kurata fire clay, both occurring in veins mainly composed of kaolinite.

A detailed study of the 30Å. clay mineral was first attempted by T. Sudo et al.^{4/5)}, who interpreted that the 30Å. spacing is due to a regularly alternating stacking of two kinds of layer lattices; one is the ordinary montmorillonite layer lattice with the 15.4Å. spacing, while the other is a hypothetical one with the 14.0Å. spacing composed of a gibbsite and a pyrophyllite layers.

Mode of occurrence

As shown in Fig. 1 the ore bodies of the Uku mine are of lenti-

Fig. 1. Distribution map of country rocks and ore bodies of the Uku mine.

S: silicious rock.

A: altered zone largely composed of sericite.

L: liparite.

O: ore bodies largely composed of andalusite.

cular shape, embedded at intervals in silicious rocks which extend east and west, and they are composed of andalusite, corundum and sericite, with small amounts of pyrophyllite, quartz, rutile and pyrite. Although almost all of these minerals are unaltered, in places, aluminous silicate minerals have altered to clay materials due to later hydrothermal actions. On the basis of the differential thermal analysis and X-ray powder data, the clay materials were identified to

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be composed of kaolinite, diaspore and pyrophyllite.

The mode of occurrence of kaolinite veins including the long spacing clay mineral in question can be classified into two groups: one occurs as irregular network veinlets in flinty rocks and the other as a vein filled by powdery clay as illustrated in Fig. 2. When the

Fig. 2. Cross section of a clay vein in silicious rock.

S: silicious rock.

Se: sericite.

C: white powdery clay largely composed of kaolinite.

Sample (A) including the 29Å. clay mineral was collected in this vein.

clay mineral of the latter group was treated with saturated aqueous solution of benzidine, some of it became slightly green. It is worth noticing that montmorillonite is generally tinged with green by benzidine.

The long spacing at about 29Å. was observed in the X-ray diffraction pattern of sample (A) separated from the clay which was tinged with green by benzidine.

X-ray diffraction data

The X-ray powder patterns of the clay specimens of the Uku mine were obtained by Philips Geiger Counter X-ray Spectrometer with filtered Cu $K\alpha$ radiation. The experimental conditions were as follows: 35kV., 13mA., time constant 4 seconds, scanning speed 2° or 1/4° per minute, angular aperture 1°, receiving slit 0.006 inch.

Spacings of the principal powder lines with 2 θ angle lower than 8° were accurately determined either by recording the reflection lines under scanning speed 1/8° per minute with angular aperture

$1/4^\circ$, or by calibrating their angles by referring to the powder lines of quartz or silicon, and further by counting their intensities at the fixed time of 64 seconds with scale factor 8.

X-ray powder diffraction at room temperature

The X-ray powder diffraction patterns of sample (A) are depicted in Fig. 3 and correlated in Table 1 to those of kaolinite, sericite, pyrophyllite and quartz except the 28.8 and 14.5Å. lines. The reliability factors of their spacings are shown in Table 2.

The results are summerized as follows:

Fig. 3. X-ray diffraction patterns of sample (A).

a_1 , a_2 : 001 reflections from a basal spacing of 28.8Å.

K: kaolinite, q: quartz, S: sericite, P: pyrophyllite.

(1) It is clear that sample (A) is mainly composed of kaolinite with basal reflection of $7.17\text{\AA}$. (001), $3.578\text{\AA}$. (002) and $2.390\text{\AA}$. (003), which is of slightly disordered type as revealed by unification of the close doublet, $(1\bar{1}\bar{1})$ and $(11\bar{1})$.

(2) The 14.5 , 4.81 , 4.61 and $2.30\text{\AA}$. lines approximate to the reflections of montmorillonite, while the 14.5 , 7.17 and $4.81\text{\AA}$. lines approximate to the subsequent reflections of the $28.8\text{\AA}$. line.

(3) The 4.26 and $3.34\text{\AA}$. lines imply the presence of small amounts of quartz, 10.0 , 5.00 and $3.34\text{\AA}$. lines, that of sericite, and the $9.24\text{\AA}$. line that of pyrophyllite.

(4) The spacing of (06) or (060) is $1.489\text{\AA}$., which is similar to that of kaolinite and/or montmorillonite. It indicates that the principal clay minerals in sample (A) are of the dioctahedral type and that the number of aluminium ions in the tetrahedral coordination in the silica layer is quite small.

Effect of heat treatment

To ascertain the nature of the X-ray reflection of $28.8\text{\AA}$. spacing, the effect of heat treatment on X-ray powder pattern was investigated. Sample (A) was heated for one hour at every hundred degree interval between 100° and 1200°C . and each of the heated sample was examined by X-ray powder method after cooling to room temperature in the air.

The results obtained are shown in Fig. 3 and Table 1, and summarized as follows:

(1) It is the most important feature that the $28.8\text{\AA}$. spacing is unaffected up to 300°C ., and on further heating at 400°C . the $28.8\text{\AA}$. line disappears completely and the $14.7\text{\AA}$. line is replaced by the $12.4\text{\AA}$. line, which is preserved up to 600°C . but absolutely disappears above 700°C ..

(2) The pattern of kaolinite almost disappears at 600°C . and completely at higher temperatures.

(3) In the temperature range of $20^{\circ}\sim 900^{\circ}\text{C}$., the structures of

Table 1. X-ray diffraction data for sample (A)

$d(\text{calc.})$ for $d(00l) = 28.85\text{\AA}$	S	P	K	Q	20°C		300°C	
	hkl	hkl	hkl	hkl	$d(\text{\AA})$	I	$d(\text{\AA})$	I
28.85 $\text{\AA}$					28.8 ₅ **	6	28.8*	5
14.43					14.5 ₂ **	17s	14.4*	9s
	002				10.0 ₄ *	8s	10.1	6s
9.62		002			9.2 ₄ *	5s	9.2	4
7.21			001		7.17 ₂ *	200s	7.16	170s
5.77	004				5.00 ₆ *	15s	5.01	10s
4.81					4.81 ₉ *	13	4.83	9
					4.61 ₅ *	6	4.60	5
	110		020		4.45 ₇ *	40s	4.45	40
			110		4.37 ₉ *	22	4.37	30
				100	4.26 ₉ *	27	4.25	28
4.12			111)		4.14 ₂ *	15	4.14	14
3.606			002		3.57 ₈ *	180s	3.58	150s
		113		101	3.340*	15s	3.34	10s
2.885	115)				2.976*	15s	2.97 ₆	11s
	025)							
	202		201)		2.575*	20	2.57 ₅	23
			130)		2.540*	4		
			131)		2.505*	16	2.508	20
			200		2.440*	11	2.400	10b
			003		2.390*	20	2.396	20
			202)		2.342*	28	2.351	25
			131)					
			203)		2.301*	11	2.301	14
			132)		2.00*	10b	2.000	10b
			133		1.943*	4	1.948	4
			004		1.792*	10	1.795	7
			204		1.662*	14	1.666	13b
			133)				1.659	11b
			310)		1.622*	5	1.622	7b
			203		1.545*	5	1.544	4b
			060)					
			131)		1.489*	17s	1.489	20s

** : Spacing determined on the basis of the data of fixed time operation.

* : Spacing read on the chart recorded under the scanning speed 1/4° per minute.

Other spacings were read on the chart recorded under the scanning speed 2° per minute.

Relative intensities were estimated by amplitudes of peaks.

500°C		600°C		900°C		1000°C		1200°C	
$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I
12.4*	8b	12.4*	10b					5.41 ₃	26s
10.1	8s	10.1	10s	10.2	5			4.27 ₅	10
9.24	4s							4.09 ₉	31s
7.16	170s	7.16	15s					3.42 ₉	67
5.01	90s	5.01	8s	5.05	10s			3.40 ₃	63
								2.89 ₈	15s
?	?							2.70 ₀	27s
4.47	32s	4.50	30s	4.50	20s			2.55 ₀	33s
4.37	20	4.37	20					2.43 ₈	8
4.24	20	4.24	20	4.24	18	4.25	17	2.29 ₂	11
4.14	14							2.208	40
3.58	160s	3.58	20					2.127	15
3.34	25s	3.34	25s	3.34	45s	3.14	13vb	1.891	6
2.97	12	3.1	8b	3.11	11s	3.11	7	1.844	7
2.57	18	2.59	7			2.70	6b	1.712	11
2.508	15					2.53	5b	1.602	11
2.433	10					2.46	5b	1.527	26s
2.390	20							1.460	5
2.341	20							1.445	13
2.301	8								
2.000	12	2.000	6						
1.948	4								
1.795	7								
1.666	12b								
?	?								
?	?								
1.487	13					1.445	6		

s: sharp, b: broad, vb: very broad.

Q: quartz, K: kaolinite with indices after G. W. Brindley¹⁾,

P: pyrophyllite with indices after J. W. Gruner³⁾,

S: sericite with indices after R. E. Grim²⁾.

sericite, pyrophyllite and quartz are not destroyed.

(4) The powder pattern [of the sample heated at 1200°C. is similar to those of mullite.

Effect of treatment with ethylene glycol and/or water

Fig. 4. Basal X-ray diffraction patterns for sample (A).

A: natural, B: complexed with ethylene glycol, C: complexed with water.

The original sample (A) was pulverized, then covered completely with a few drops of ethylene glycol and/or water on slide-glass. The treated samples were studied by X-ray powder method, and the results obtained are shown in Fig. 4 and Table 2; they may be summarized as follows:

(1) The 14.5Å. spacing expands to 15.4Å. with ethylene glycol; this amount of expansion is less than that of the montmorillonite with two sheets of water molecules. While,

Table 2. Basal X-ray diffraction data for long spacing clays.

	Kurata ⁴⁾		Hanaoka ⁵⁾		Uku	
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
(001)	29.8±0.5 Å	10s	29.6±0.2Å	10s	28.8±0.1Å	6
(002)	14.7±0.2	15s	14.7±0.1	18s	14.5±0.1	17s
(003)	10.3?	4b	9.8±0.1	3		
(004)	7.18±0.04	20s	7.32±0.02	5	7.17±0.02	200s
(005)	?		5.99?	3	?	
(006)	4.95±0.05	10s	4.91±0.02	10s	4.82±0.02	13
(009)	3.32±0.02	6b	3.30±0.02	5	?	
(00, 10)	3.03±0.06	4b	2.97±0.06	2	2.97±0.01?*	15s
(060, 331)	1.4919±0.0002	15s	1.5057±0.0008	8s	1.4893±0.0005	17s

* The spacing 2.97Å is superposed by that of sericite.

Complexed with ethylene glycol

	Kurata	Hanaoka	Uku
(001)'	$32.3 \pm 0.5 \text{ \AA}$	$31.6 \pm 0.2 \text{ \AA}$	$31.0 \pm 0.5 \text{ \AA}$
(002)'	15.6 ± 0.3	15.6 ± 0.1	15.4 ± 0.2

the $28.8 \text{ \AA}$. spacing expands to $31.0 \text{ \AA}$. at the rate twice as great as in the case of the $14.5 \text{ \AA}$. spacing.

(2) Upon treatment with water, the $14.5 \text{ \AA}$. spacing expands to about $16 \text{ \AA}$. and that of $28.8 \text{ \AA}$. to $31 \sim 32 \text{ \AA}$.

These facts suggest that $28.8 \text{ \AA}$. and $14.5 \text{ \AA}$. lines may be related to the presence of the montmorillonite lattice.

Differential thermal analysis curve

Heating rate for differential thermal analysis was 10°C . per minute. The differential thermal analysis curve of sample (A), as shown in Fig. 5, displays the following peaks:

(1) A clear endothermic peak in the temperature range of $100^\circ \sim 200^\circ\text{C}$. and a weak one in $200^\circ \sim 300^\circ\text{C}$.

(2) A sharp endothermic peak at about 600°C . and a broad weak one in the temperature range of $700^\circ \sim 800^\circ\text{C}$.

(3) Finally, a sharp exothermic peak in the range of $900^\circ \sim 1000^\circ\text{C}$. Those peaks reveal that sample (A) includes both kaolinite and montmorillonite.

Fig. 5. Differential thermal analysis curve for sample (A).

Chemical analysis

The chemical analysis of sample (A) gave the following results: SiO_2 45.83, Al_2O_3 40.37, Fe_2O_3 0.61, TiO_2 0.11, CaO 0.15, MgO 0.07, K_2O

and Na_2O trace, $\text{H}_2\text{O}(+)$ 12.49, $\text{H}_2\text{O}(-)$ 0.85, total 100.48% (analyst, Goro Shibuya).

Taking into consideration the fact that the intensity of the $7.17\text{\AA}$. line of sample (A) is the strongest as well as the chemical composition of the sample, it may be concluded that the most dominant component of the Uku clay is kaolinite.

Discussion

The observed spacings of the long spacing clay minerals from Kurata⁴⁾, Hanaoka⁵⁾ and Uku are compared in Table 2. They are generally in good agreement with each other, but differ slightly with regard to their relative intensities as well as to the spacing of (001).

The spacing of (001) of the clay mineral from Uku is a little smaller than that from Kurata or Hanaoka. It may be considered that the montmorillonite layer composing the clay minerals from Kurata and Hanaoka have the basal spacing of $15.4\text{\AA}$. with two sheets of water molecules, whereas that from Uku, $14.8\text{\AA}$.. Actually, a certain specimen from the same locality as sample (A) produced a diffraction line at $14.8\text{\AA}$. while lacking the long spacing of about $29\text{\AA}$.. The $14.8\text{\AA}$. spacing of this specimen was identified as the basal spacing of montmorillonite by means of X-ray and thermal studies.

Accepting T. Sudo's idea on the $30\text{\AA}$. clay mineral, the long spacing observed for the sample from the Uku mine may be interpreted as follows:

The long spacing of $28.8\text{\AA}$. is caused by a regularly alternating stacking of two kinds of layer lattices: one is the usual montmorillonite lattice with about two sheets of water molecules and a cell height of $14.8\text{\AA}$. which is expected to decrease to $10.8\text{\AA}$. by dehydration and to expand to about $17.0\text{\AA}$. by the treatment with ethylene glycol; the other is an aluminium chlorite lattice with a cell height of about $14.0\text{\AA}$. which is expected to be unaffected by the treatment with ethylene glycol and/or water and may be persistent at least up to 600°C ..

Acknowledgements

The writer is greatly indebted to Professor Zyunpéi Harada, Hokkaido University, for reading this manuscript and offering significant suggestions. Thanks are due to Professor Toshio Sudo, Tokyo University of Education, for helpful suggestions, and to Mr. Goro Shibuya, Yamaguchi University for chemical analysis. The writer also acknowledge to Mr. Hiroshi Noguchi, the President of the Nihon Firebrick Company for affording facilities for field survey.

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Manuscript received September 28, 1957.