81. On a Kaolin Mineral from the Zaô Mine, Yamagata Prefecture, Japan.

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The Kaolin Mineral from the Zaô Mine.

Locality: The Zaô (sulphur) mine, Nakagawa-mura, Minami-murayama-gun, Yamagata prefecture.

Occurrence: Associated with the sulphur deposit.

Appearance: Porcelain-like mass of gray to light brownish gray colours.

Microscopic observation: Very fine powder with irregular outlines showing very weak birefringence. The refractive index: $1.560 > n > 1.556$ (16.5°C). This value is slightly lower than that of typical kaolinite, but is within the range of values for halloysite reported (Table III).

Chemical composition: The chemical composition of the mineral is as shown in Table I. The adsorbed water and the ignition loss

Table I

	(1)	(2)	(3)	(4)
SiO ₂	44.18	44.75	44.18	45.73
TiO ₂	—	—	—	1.35
Al ₂ O ₃	39.09	36.94	39.34	38.37
Fe ₂ O ₃	0.89	0.31	0.32	0.40
FeO	nd	doutful	—	—
CaO	0.10	0.11	0.30	0.56
MgO	0.05	doutful	0.03	—
Na ₂ O	nd	} 0.60	nd	—
K ₂ O	nd		nd	—
H ₂ O (+)	14.09*	14.89	14.96	13.19
H ₂ O (—)	2.40	2.53	0.96	0.50
SO ₃	—	—	—	0.16
Total	100.80	100.13	100.09	100.26

(1) The kaolin mineral from the Zaô mine, Yamagata prefecture.

* Ignition loss above 110°C, analysed by the writer.

(2) Halloysite (after C. S. Ross)⁽¹⁾.

(3) Halloysite (after C. S. Ross)⁽¹⁾.

(4) Kaolinite (after J. W. Gruner)⁽⁷⁾.

Table II

(1)		(2)		(3)		(4)	
I	d	I	d	I	d	I	d
10	7.15 A	10	7.06 A	23-24	7.1 A	4	7.42 A
b { 10	{ 4.45	6	4.39	22	4.44	10	4.42
b { 10	{ 4.28	3	4.21	19	4.17	—	—
b 5	3.97*	4	3.76	8	3.84	5	3.97
10	3.58	10	3.57	22	3.58	6	3.63
—	—	1	3.35	4	3.39	—	—
—	—	0.5	3.08	—	—	—	—
—	—	1	2.760	—	—	—	—
9	2.56	5	2.556	18	2.55	4	2.560
9	2.50	2	2.491	17	2.50	—	—
9	2.37	2	2.373	—	—	5	2.365
—	—	8	2.341	21	2.337	—	—
7	2.30	5	2.272	9	2.291	—	—
1	2.20	0.5	2.200	4	2.188	—	—
6	1.99	4	1.983	10	1.986	—	—
2	1.94	1	1.930	2	1.943	—	—
3	1.88	1	1.893	2-3	1.891	—	—
2	1.84	2	1.839	2-3	1.842	—	—
—	—	1	1.785	3	1.784	—	—
b { 4	{ 1.68	—	—	5	1.692	4	1.685
b { 6	{ 1.66	7	1.658	16-17	1.660	—	—
2	1.62	4	1.610	6	1.619	—	—
1	1.58	1	1.585	2-3	1.580	—	—
2	1.54	3	1.536	5	1.537	—	—
9	1.49	8	1.486	18	1.486	10	1.510
2	1.45	2	1.452	4-6	1.452	—	—
—	—	1	1.430	—	—	—	—
0.5	1.39	0.5	1.383	—	—	—	—
1	1.37	0.5	1.371	—	—	—	—
2	1.34	3	1.340	4	1.336	—	—
2	1.31	4	1.306	5	1.304	2	1.295
3	1.28	3	1.284	6-7	1.282	—	—
0.3	1.26	1	1.264	2-3	1.262	2	1.250
2	1.25	3	1.235	9	1.234	—	—
3	1.24	—	—	—	—	—	—

(1) The kaolin mineral from the Zaô mine, Yamagata prefecture. (Filtered Cu radiation. The radius of the camera used is 77.2 mm. No corrections are applied on the readings of the spacings. The relative intensities are compared by the naked eye, taking that of the strongest as 10.)

Weak powder lines are only recognized on the pattern taken under long exposure, but the diffuse character in the powder lines between 4.4 Å and 3.5 Å does not shows any change irrespective of exposure times.

b: Broad line.

* This broad line may separate into four lines in kaolinite, 021, 02 $\bar{1}$, 11 $\bar{1}$, and 1 $\bar{1}\bar{1}$.

(2) Kaolinite (after J. W. Gruner)⁷⁾.

(3) Kaolinite (after J. Ch. L. Favejee)⁸⁾.

(4) Halloysite (after C. S. Ross)¹⁴⁾.

above 110°C in this mineral are slightly more than in the typical kaolinite. The chemical composition corresponds to that of halloysite reported (Table I). The mineral powder is treated with about 3% solution of potassium hydroxide on the water-bath for about one hour, then about 52% are dissolved. The solubility of this mineral is greater than that of the typical kaolinite (about 2-3%).

X-ray powder pattern: The powder lines are more in number than those of halloysite reported as shown in Table II. The powder photograph approaches to that of the kaolinite type, for example in appearance of the lines of 7.1 Å and 1.99 Å. However, the pattern is partly somewhat diffuse than that of the typical kaolinite. For example, on close examination, the diffuse character of the powder lines between 3.4 Å and 4.4 Å is always clearly recognized. In this point it approaches to that of halloysite described by C. S. Ross⁽¹⁾.

Thermal properties: The type of the dehydration curve is near to that of kaolinite, but the amount of water dehydrated at each temperature is slightly larger than that of typical kaolinite (Zettlitz

Fig. 1. The dehydration curve of the kaolin mineral from the Zaô mine (Za), and Zettlitz kaolinite (Ze).

L: Ignition loss
T: Temperature (°C)

Fig. 2. Differential thermal analysis curve of the kaolin mineral from the Zaô mine (Za), and Zettlitz kaolinite (Ze).

NR: Endothermic reaction
XR: Exothermic reaction
T: Temperature (°C)

Fig. 3. (Ca. $\times 50,500$)
Electron micrograph of the kaolin mineral from the Zaô mine; bladed habit.

Fig. 4. (Ca. $\times 40,000$)
Electron micrograph of Zettlitz kaolinite; hexagonal outline.

kaolinite) (Fig. 1). This fact is due to a slightly more water content, in this mineral than in typical kaolinite as shown in the chemical analysis. The type of differential thermal analysis agrees with that of kaolinite except the small endothermic peak at about 100°C (Fig. 2). These data agree with the curve of halloysite⁶⁾.

Electron micrograph: Under the electron microscope, the crystals of bladed and acicular habits are clearly recognized, decidedly differing from the hexagonal habit of the typical kaolinite (Zettlitz kaolinite) (Fig. 3). In the bladed to acicular habits, they agree well with those of halloysite recently reported by L. T. Alexander¹⁾ etc.

History of Halloysite Studies. (Table III)

P. Berthier²⁾ first described a secondary mineral with an ideal chemical formula ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) found in Carboniferous limestone of the lead and zinc deposits of Angleur, Liège, Belgium, as the mineral *halloysite*. It is almost optically isotropic. Thereafter it was recognized that such mineral is widespread in clay and soil⁽⁴⁾⁽⁸⁾⁽¹¹⁾. Next, U. Hofmann etc.¹⁰⁾ described the mineral from Djebel, Debar, Libya, which is the more hydrous species ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \cdot 2\text{H}_2\text{O}$) than the original species, and called the hydrous species "*halloysite*".

This conclusion caused the confusion of the nomenclature of halloysite. Next, M. Mehmél¹²⁾ accepted the nomenclature by U. Hofmann and proposed the crystal structure of "*Hofmann's halloysite*", which is built up of alternate layers of $(\text{Al}_2(\text{OH})_6)_n$ and $(\text{Si}_2\text{O}_5(\text{OH})_2)_n$, and concluded that the dehydrated species from "*Hofmann's halloysite*" has somewhat different crystal structure from that of typical kaolinite, and Mehmél¹²⁾ called the dehydrated species, "*metahalloysite*".

C. S. Ross and P. F. Kerr¹⁴⁾ first tried a reexamination on the mineralogical properties of the original halloysite as to the optical, chemical, and thermal properties as well as X-ray powder pattern, and concluded that the original halloysite must be recognized as a mineral species having the disordered lattice of normal kaolinite. S.B. Hendricks⁹⁾ reexamined the crystal structure of the original halloysite and also "*Hofmann's halloysite*". He pointed out that the crystal structure proposed by M. Mehmél does not explain exactly the intensities of powder lines, and proposed a new idea about the crystal structure of "*Hofmann's halloysite*", which is built up of alternate layers of $[\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4]_n$ and water layer $[\text{H}_2\text{O}]_n$. Hendricks concluded that "*Hofmann's halloysite*" corresponds to hydrous variety of original halloysite, and gave the name "*hydrohalloysite*" to "*Hofmann's halloysite*".

Table III

	$2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	$2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	$2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	
P. Berthier G. Nagelschmidt U. Hofmann M. Mehmel C. S. Ross S. B. Hendricks S. L. Alexander	 Halloysite Halloysite Hydrohalloysite Endellite	Halloysite Halloysite Metahalloysite Halloysite Halloysite Halloysite	Kaolinite	The kaolin mineral from The Zaô mine
Refractive indices	1.526-1.542 (M. Mehmel) 1.540-1.552 (A.L. Alexander) 1.490*	1.515-1.551 (G. Nagelschmidt) 1.543-1.567 (mean, 1553) (C. S. Ross) 1.551-1.556** (A.L. Alexander)	$\alpha = 1.553-1.566$ $\beta = 1.569-1.559$ $\gamma = 1.560-1.570$ (C. S. Ross)	1.560 $>n>$ 1.556 (16.5°C)
X-ray powder pattern (in the important part for discriminating these three minerals)	I ; d sst; 10.1A } st ; 4.46 } m ; 3.40 } (M. Mehmel)	I ; d 4; 7.42A } 10; 4.42 } 5; 3.97 } 6; 3.63 } (C. S. Ross)	I ; d*** 10; 7.06-7.16A 10; 4.46 10; 4.194 } 5; 3.874 } 6; 3.614 } 5; 3.424 } (Ross)	I ; d 10; 7.15A 10; 4.45 10; 4.28 5; 3.97 10; 3.58
$\text{SiO}_2/\text{Al}_2\text{O}_3$	1.92**** (SiO_2 ; 38.97) (Al_2O_3 ; 34.43)	1.65-2.06 (mean 1.87) (C. S. Ross)	1.85-2.94***** (C. S. Ross)	1.92
H_2O (+) or ignition loss above 110°C	24.66	14.38-17.52 (C. R. Ross)	10.98-14.22 (C. S. Ross)	14.09
H_2O (-)		0.96-4.45 (C. S. Ross)	0.08-1.38 (C. S. Ross)	2.40
Electron micrograph	Bladed habit	Bladed habit	Hexagonal plate	Bladed habit

I: Intensity, d: spacing, sst: very strong, st: strong, m: medium.

* According to A. L. Alexander etc., endellite commonly mixes with halloysite; and this fact may partially account for the fluctuation of refractive index. The refractive index of pure endellite may be 1.490.

** The refractive index of endellite dehydrated at 100°-110°C.

*** After G. Nagelschmidt¹³), J. Ch. L. Favejee⁶), J. W. Gruner⁷), and M. Mehmel¹²).

**** Endellite from Hoshimata, Tsumagoi-mura, Azuma-gun, Gumma prefecture. (Bladed habit of crystals is clearly shown under the electron microscope.)

***** Anauxite.

Recently, A. L. Alexander, G. T. Faust etc.¹⁾, studied halloysite from mineralogical properties as well as the crystal habit under the electron microscope and found that "*Hofmann's halloysite*" and original halloysite show bladed habit which is clearly different from hexagonal habit of the typical kaolinite. Their conclusions are as follows: The original halloysite is derived from "*Hofmann's halloysite*" by dehydration of $2\text{H}_2\text{O}$ at about 50°C, and the original halloysite corresponds to the species having imperfect crystal structure of

kaolinite, the imperfection of the crystal structure causing some difference in mineralogical properties from the typical kaolinite. A. L. Alexander and his collaborators proposed the name "*endellite*" for "*Hofmann's halloysite*" named from the original investigator K. Endell.

Conclusion.

Although there is a confusion in nomenclature of halloysite, the facts of this mineral may be summarized as follows: (1) From the chemical composition, continuous change is recognized from endellite to halloysite by dehydration, but from X-ray powder pattern, discontinuous change is recognized by the dehydration of endellite; namely, the characteristic powder line about 10 Å becomes weaker and the powder line about 7 Å appears. (2) Halloysite is derived from endellite by dehydration, and has disordered crystal lattice of kaolinite; and this imperfection of crystal structure is a cause of slight difference in mineralogical properties from kaolinite.

The kaolin mineral from the Zaô mine, now under consideration, is a variety of halloysite showing higher crystallinity than ordinary halloysite.

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