

TOSUDITE FROM THE HOKUNO MINE, HOKUNO, GIFU PREFECTURE, JAPAN

ATSUKO ICHIKAWA and SUSUMU SHIMODA

Geological and Mineralogical Institute, Faculty of Science, Tokyo University of Education, Tokyo, Japan

(Received 16 January 1976)

Abstract—Tosudite was found in the Hokuno pottery stone mine, Gifu Prefecture, Japan. The pottery stone ore body, altered from the Cretaceous rhyolitic rock, is composed of tosudite, interstratified illite-montmorillonite, kaolinite and quartz. Prepared by normal sedimentation method, the specimen is composed of 75.6% tosudite, 24.0% kaolinite and 0.4% quartz. The chemical composition of the specimen is SiO₂ 45.09%, TiO₂ tr., Al₂O₃ 37.31%, Fe₂O₃ 0.94%, MgO 0.41%, CaO 1.94%, Li₂O 0.45%, Na₂O 0.09%, K₂O 0.44%, H₂O(−) 1.50% and ignition loss 12.11%. After subtracting the compositions of the impurities, the structural formula of tosudite is given as: interlayer cations K_{0.23}, Na_{0.07}, Ca_{0.86} + nH₂O; 'gibbsite' layer Li_{0.76}, Mg_{0.35}, Fe_{0.29}³⁺, Al_{3.34} (OH)_{12.00}; silicate layer Al_{8.00} [Si_{13.83} Al_{2.17}] O_{40.00} (OH)_{8.00}.

Syntheses of tosudite were made from a starting material which is an interstratified illite-montmorillonite obtained from the same ore body. At 450°C, 400atm., reacting for 5 days, a tosudite-like mineral was synthesized.

INTRODUCTION

Regularly interstratified dioctahedral chlorite-montmorillonite was first found in the Kurata mine by Sudo *et al.* (1954). A similar mineral was found at the Kamikita mine by Sudo and Kodama (1956) and this chlorite component was di-trioctahedral. Regularly interstratified dioctahedral chlorite-montmorillonite was named tosudite by Frank-Kamenetsky *et al.* (1963) and at present the name tosudite is usually used for a regularly interstratified mineral with dioctahedral or di-trioctahedral chlorite component. After that tosudite has often been reported (Mitsuda, 1957; Hayashi, 1961; Kanaoka, 1968; Shimoda, 1969).

Li-bearing tosudites have been reported at Huy (Brown *et al.*, 1974) and at the Tooho mine (Nishiyama *et al.*, 1975). At the same time, syntheses of tosudite have been carried out by Matsuda *et al.* (1973). In this paper the mineralogical data of Li-bearing tosudite is given and its syntheses are discussed.

SPECIMEN

The specimen was obtained at the Shindo ore body of the Hokuno pottery stone mine, Gifu Prefecture, Japan. The pottery stone ore body is a hydrothermal alteration product of a rhyolitic rock of the Cretaceous period. The sampling points are given in Fig. 1 and the minerals found in each sample are given in Table 1. Tosudite was associated with kaolinite and found in Samples S-4 and S-5.

In this study, the specimen prepared from Sample S-5 by normal sedimentation methods was used for mineral analysis. The specimen was composed of 75.6% tosudite, 24.0% kaolinite and 0.4% quartz, determined by X-ray powder diffraction intensity measurement.

MINERALOGICAL DATA

X-ray powder diffraction data

X-ray powder diffraction data are given in Table 2. The specimen gave a reflection at 30.5 Å and higher orders. The 060 reflection appeared at 1.492 Å. The mean basal spacing calculated was 29.6 ± 0.4 Å. The regularity of the higher orders shows that the specimen is a regularly interstratified mineral of dioctahedral chlorite and montmorillonite.

After heating at 300°C for an hour, the 001 reflection disappeared and the 002 reflection shifted to about 10 Å, but rehydration quickly occurred in air and the 001 reflection appeared after 10 min. When heated to 500°C, the reflection moved to 23.6 Å and no rehydration occurred. After heating at 700°C the reflection slightly shifted to 23.1 Å.

Ethylene glycol treatment caused an increase of the 30.5 Å value to 32.1 Å. No shift was observed when treated with 1 N NH₄NO₃. After treatment with K⁺-solution (Brown, 1953), the 30.5 Å reflection changed to 26.8 Å and it moved to 31.0 Å by treatment with Al³⁺-solution. Each mean basal spacing is listed in Table 3.

Table 1. Associating minerals of each sample obtained from the ore body

	S-1	S-2	S-3	S-4	S-5	S-6
Quartz	⊙	⊙	⊙	⊙	⊙	⊙
Kaolin	⊙	○	○	○	⊙	⊙
Mordenite	—	—	○	△	—	—
Ill./mont.*	⊙	○	○	△	—	⊙
Tosudite	—	—	—	○	⊙	—
Montmorillonite	—	△	—	—	—	—

* Interstratified illite-montmorillonite. The symbols ⊙, ○, △, and — denote clearly observed, well observed, poorly observed and not observed, respectively by X-ray diffractometer.

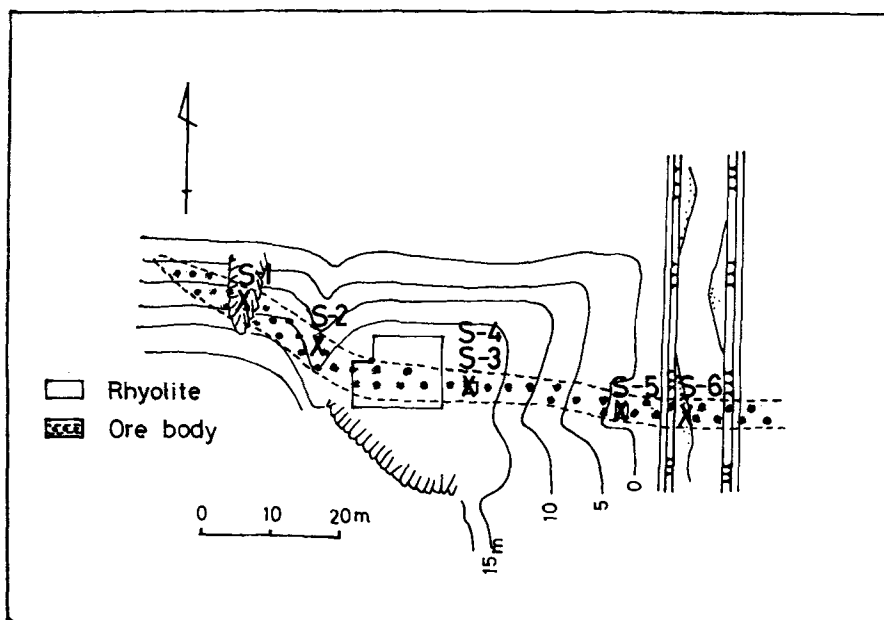


Fig. 1. The Shindo ore body at Hokuno and the sampling points.

Table 2. X-ray powder diffraction data of tosudite; oriented specimen (CuK α : 1.542 Å)

hkl	(a) natural		(b) 300°C		(c) 500°C		(d) E.G.		(e) NH ₄ NO ₃	
	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
001	30.5	254	29.4	218	23.6	77	23.1	422	30.5	103
002	14.98	196	14.73	226	11.87	148	16.07	602	14.26	238
003	9.88	7	9.82	9	8.01	4	10.11	5		
004	7.40	24			5.81	3	7.86	153		
005	5.91	1	5.91	1	4.70	10				
006	4.93	39	4.90	45			5.22	155	5.01	156
007	4.23	4	4.21	2	3.31	36B	4.46	100		
008	3.68	17	3.66	15						
009	3.28	12	3.28	19B			3.47	222	3.29	71
00.10	2.94	11	2.94	17B						
00.11			2.675	1						
00.12			2.465	0.3						

- a: Air-dried natural state.
- b: After the rehydration occurs.
- d: Ethylene glycol treatment.
- B: Broad peak.

Table 3. Lattice spacings, $d(001)$ Å, of tosudite before and after various treatments

Condition of the specimen	$d(001)$ Å	Component layer	
		chl.	mont.
A: Air-dried, natural state	29.6 ± 0.4	14.2	15.4
B: 300°C, 1 hour	29.5 ± 0.1		
C: 500°C, 1 hour	23.5 ± 0.3	14.0	9.5
D: 700°C, 1 hour	23.1 ± 0.2		
E: Ethylene glycol treatment	31.6 ± 0.4	14.2	17.4*
F: NH ₄ NO ₃ treatment	29.6 ± 0.7	14.2	15.4*
G: K ⁺ -clay	26.6 ± 0.1	14.2	12.4*
H: Al ³⁺ -clay	30.4 ± 0.2	14.2	16.2*

- B: After the rehydration occurs.
- F: After boiling in 1 N NH₄NO₃ for 10 min.
- G: After boiling in 1 N KOH + 1 N KCl for 5 hr.
- H: After boiling the K⁺-clay in 1 N AlCl₃ for 1 hr.
- * Not estimated by the Fourier synthesis.

Table 4. Chemical analyses of the specimen and related minerals

	1	2	3	4	5
SiO ₂	45.09	44.20	42.14	41.60	39.74
TiO ₂	tr.	tr.			0.01
Al ₂ O ₃	37.31	36.65	37.38	36.40	35.87
Fe ₂ O ₃	0.94	1.24	0.30	1.82	0.98
FeO					2.77
MgO	0.41	0.54	0.08	0.29	3.08
CaO	1.94	2.56	1.65	0.38	0.06
Li ₂ O	0.45	0.60		1.04	0.51
Na ₂ O	0.09	0.12	0.15	0.14	0.12
K ₂ O	0.44	0.58	1.40	0.38	0.62
H ₂ O(-)	1.50	1.97	6.16	6.87	15.70
lg. !	12.11	11.54	11.22	11.12	
P ₂ O ₅					0.10
Total	100.28%	100.00%	100.48%	100.04%	99.56%
Structural formula					
2 Interlayer cations		K _{0.23} , Na _{0.07} , Ca _{0.86} + nH ₂ O			
'Gibbsite' layer		Li _{0.76} , Mg _{0.25} , Fe _{0.29} ³⁺ , Al _{3.34} (OH) _{12.00}			
Silicate layer		Al _{8.00} [Si _{13.83} Al _{2.17}] O _{40.00} (OH) _{8.00}			
3 Interlayer cations		K _{0.58} , Na _{0.09} , Ca _{0.57} + 8.88H ₂ O			
'Gibbsite' layer		Mg _{0.04} , Fe _{0.07} ³⁺ , Al _{4.05} (OH) _{12.00}			
Silicate layer		Al _{8.00} [Si _{13.72} Al _{2.28}] O _{40.00} (OH) _{8.00}			
4 Interlayer cations		K _{0.16} , Na _{0.09} , Ca _{0.13} + 9.6H ₂ O			
'Gibbsite' layer		Li _{1.36} , Mg _{0.14} , Fe _{0.45} , Al _{3.59} (OH) _{12.00}			
Silicate layer		Al _{8.00} [Si _{13.60} Al _{2.40}] O _{40.00} (OH) _{8.00}			

1: The specimen in this paper.

2: The specimen in this paper after subtracting the compositions of the impurities.

3: The Takatama specimen (Shimoda, 1969).

4: The Tooho specimen (Nishiyama *et al.*, 1975).

5: The Huy specimen, Mg-saturated specimen. (Brown *et al.*, 1974).

Chemical analysis

Chemical analyses of the specimen and some related minerals are given in Table 4. The structural formula is shown after subtracting the compositions of the impurities. As seen in the structural formula, the two octahedral sites of the chlorite component are dioctahedral and this tosudite contains a small amount of Li. Chemically the specimen resembles the specimens from Huy (Brown *et al.*, 1974) and the Tooho mine (Nishiyama *et al.*, 1975) as given in columns 5 and 4 of Table 4.

I.r. absorption data

I.r. absorption data of tosudite are given in Table 5 together with some data found in the literature. The OH absorption bands of tosudite appeared at 3630 cm⁻¹ and 3535 cm⁻¹. The 3630 cm⁻¹ band persisted up to 550°C, but the band at 3535 cm⁻¹ disappeared at 550°C. Therefore the former may be attributed to the OH stretching in the silicate layer and the latter to that in the 'gibbsite' layer. The 750 cm⁻¹ band, which disappeared at 550°C, also seems to be related to the gibbsite layer. These data are closely similar to those of tosudite composed of dioctahedral chlorite and montmorillonite, but differ slightly from those of tosudite with di-trioctahedral chlorite as a component layer (Shimoda, 1975).

DTA and TG curves

DTA and TG curves are shown in Fig. 2. The endothermic peaks at 80 and 180°C are due to the

dehydration of the interlayer water. The endothermic peak at about 500°C with a shoulder at 700°C is due to the dehydroxylation of the gibbsite and silicate layers. The shoulder at 700°C seems to be caused by

Table 5. I.r. absorption data of tosudite and some related minerals

	Natural	550°C	700°C	T	K
	3670 Inf	3650 MB		3670 Inf	3660 Inf
	3630 S			3640 S	3630 S
	3535 S			3545 S	3540 S
			3400 S		
	3375 M			3390 SB	3380 SB
	1625 M		.620 M	1640 M	
				1404 W	
		1055 SB	1055 SB	1055 Sh	
	1030 S			1035 SB	1030 SB
	1005 S				
	940 W			950 Inf	940 Inf
	830 W			820 W	827 W
	750 S			750 S	
				705 Sh	704 S
	629 M			630 Sh	
		550 Sh	555 M	544 S	540 S
	533 S			523 Sh	
				478 S	478 S
	465 S	465 S	470 S		
	425 M				

T: The Takatama specimen (Shimoda, 1975).

K: The Kamikita specimen (Sudo and Kodama, 1957).

S: Strong M: Medium W: Weak Inf: Inflection.

Sh: Shoulder B: Broad.

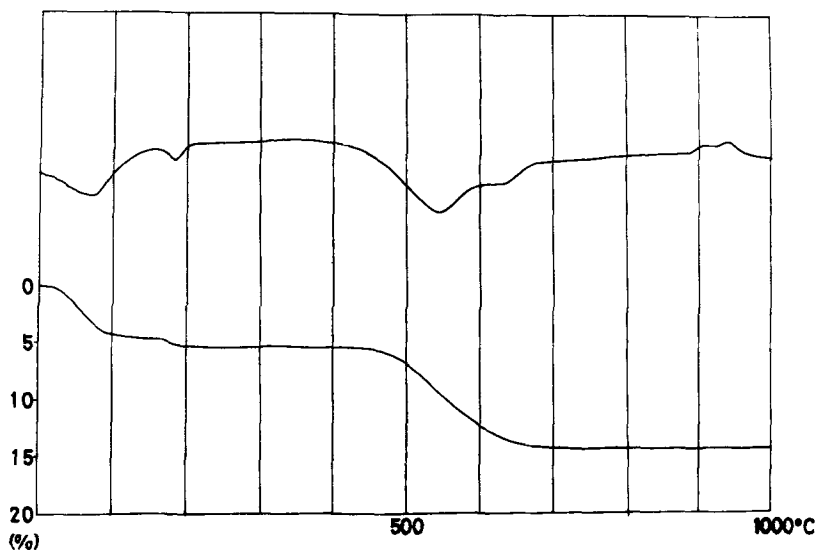


Fig. 2. DTA and TG curves of the specimen.

Table 6. *F*-values of the (00 l) reflections of tosudite, natural state and after heating at 500°C for 1 hr

00 l	natural state				500°C			
	Hokuno F cal	Ta. F obs.	To. F obs.	To. F obs.	Hokuno F cal	Ta. F obs.	To. F obs.	To. F obs.
001	77	58	61	48	-39	22	22	43
002	-94	99	85	100	-52	60	82	29
003	34	28	29	23	9	14	18	
004	7	71	20	35	0	17	34	8
005	13	12	9	10	70	40	27	26
006	110	138	89	88	35		32	37
007	38	49	59	28	117	111	148	21
008	67	123	62	62	-71	46	74	17
009	104	119	107	70				100
00.10	-133	125	92	83				58
00.11								13
00.12				42				

Ta.: The specimen from Takatama.
To.: The specimen from Tooho.

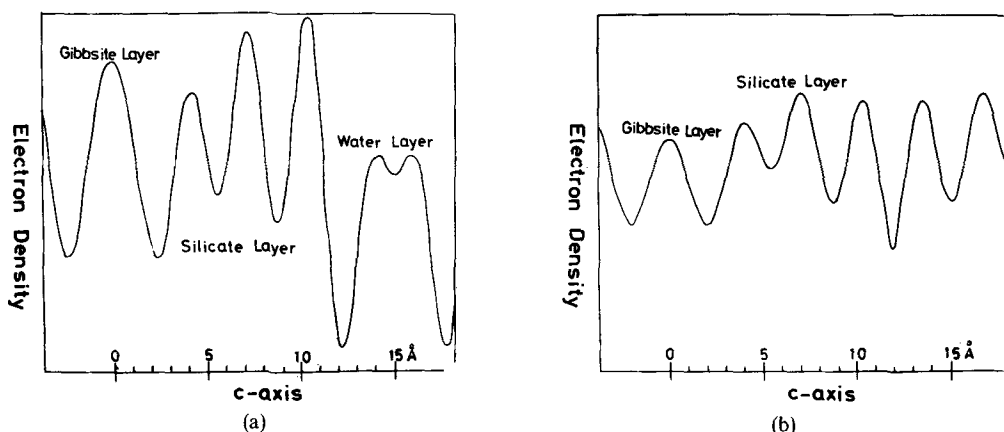


Fig. 3. One-dimensional Fourier synthesis curves. (a) Air-dried, natural state. (b) After heating at 500°C for 1 hr.

Table 7. Chemical analysis of the starting material

SiO ₂	46.42
TiO ₂	0.14
Al ₂ O ₃	32.65
Fe ₂ O ₃	4.67
MgO	0.65
CaO	1.44
Li ₂ O	0.26
Na ₂ O	0.20
K ₂ O	2.13
H ₂ O(-)	1.65
Ig. loss	10.23
Total	100.44%

the dehydroxylation of kaolinite, which may be dickite contained as an impurity. TG curve showed two weight losses. The first 5.3% loss below 200°C corresponds to the endothermic peaks at 80 and 180°C in DTA. The 8.3% loss between 300 and 700°C corresponds to the dehydroxylation.

Fourier analysis

The structure amplitudes were obtained from the intensities of the basal reflections, as given in Table 6. The signs were derived from an interstratification of dioctahedral chlorite and montmorillonite. In air-dried natural state montmorillonite was considered to have 4 water molecules and 0.16 K⁺ per single layer in the interlayer. After heating at 500°C for an hour, no water molecules were considered. R-factors are 0.26 for the natural state and 0.35 for the dehydrated specimen. One-dimensional Fourier synthesis curves are shown in Fig. 3.

These X-ray data show that tosudite found at the Hokuno mine is nearly regularly interstratified dioctahedral chlorite-montmorillonite which contains a small amount of Li.

SYNTHESES OF TOSUDITE

At the Hokuno mine, tosudite is found in the central area of the ore body surrounded by an interstrati-

Table 8. I.r. spectra data of the starting and synthesized materials

SM	1	2	3	4	
	3715 M	3710 M			kaolin
3680 S	3680 M	3670 M	3680 S	3680 M	
	3650 M	3650 M	3660 M	3660 Sh	kaolin
	3640 M	3635 M	3640 M	3640 Sh	
3620 S					
3450 S		3440 MB	3440 MB	3430 MB	
	3415 WB				
1615 MB	1615 MB	1620 MB	1620 MB	1615 MB	
1400 WB	(1405 WB)		(1470 WB)		
1100 Sh	1105 Sh	1115 Sh	1120 Sh	1120 Sh	
1030 S	1030 S	1025 S	1065 Sh	1030 S	
1005 M		945 Sh	1040 S	945 Sh	
			945 Sh		
910 S	910 M				
820 M		815 WB	825 WB	815 M	
795 M	795 M				
750 S	750 M	750 M	740 WB	740 M	
690 S	690 M	695 M	685 W	695 M	
530 S	530 S	530 S	530 S	530 S	
460 S	465 S	465 S	470 S	465 S	
420 M	425 M	415 M	415 M	415 M	

SM: The starting material obtained from Sample S-2.

1-4: The synthesized material given in Table 9.

Table 9. Data of the synthesized materials

Starting material	Temperature (°C)	Days	Synthesized materials
1 SM(50 mg) + H ₂ O(0.05 ml)	400	2	montmorillonite Ill/mont.-mineral* kaolin*
2 SM(50 mg) + H ₂ O(0.05 ml)	450	5	tosudite Ill/mont.-mineral* kaolin*
3 SM(50 mg) + H ₂ O(0.05 ml)	480	2	Ill/mont.-mineral
4 synthesized montmorillonite at 400°C (No. 1)	450	4	tosudite Ill/mont.-mineral*
5 SM(50 mg) + AlCl ₃ (25 mg) + H ₂ O(0.05 ml)	450	4	pyrophyllite
6 SM(50 mg) + AlCl ₃ (25 mg) + NaOH(0.05 ml)	450	4	pyrophyllite
7 SM(50 mg) + NaOH(0.05 ml)	450	4	Ill/mont.-mineral

* Probably not transformed from the starting material.

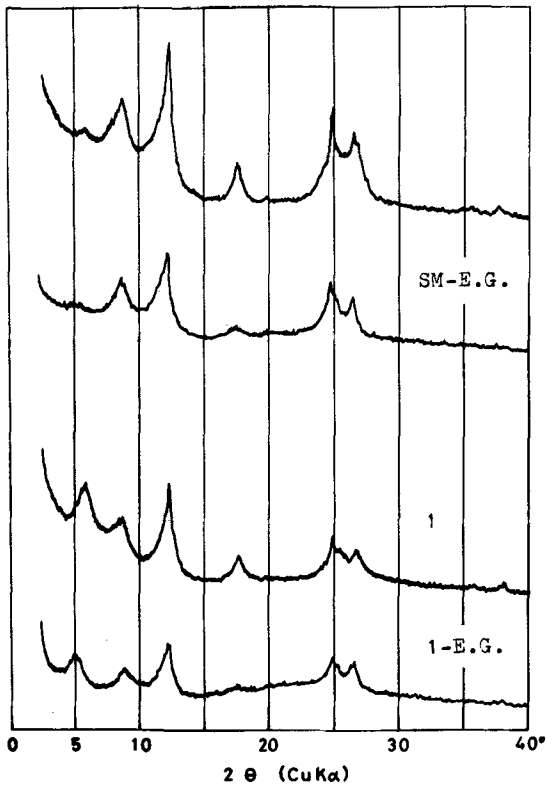


Fig. 4(a). X-ray powder diffraction patterns of the starting and synthesized materials. SM: The starting material obtained from Sample S-2. 1: 400°C, 2 days. E.G.: After ethylene glycol treatment.

fied illite-montmorillonite zone as shown in Table 1. The same distribution pattern of tosudite and interstratified illite-montmorillonite can be seen at the Kakitani pottery stone mine, Izushi, Hyogo Prefecture. Tosudite described by Nishiyama *et al.* (1975) is closely associated with interstratified illite-montmorillonite. Accordingly, to study the transformation from interstratified illite-montmorillonite to tosudite, syntheses were tried in the autoclave using the method of Matsuda *et al.* (1973).

The $< 2 \mu$ fractions of Sample S-2 were used as the starting material. The fractions are composed of interstratified illite-montmorillonite, kaolinite and a small amount of montmorillonite. Chemical analysis and i.r. absorption data of the material are given in Tables 7 and 8. Although it contains a small amount of Li, X-ray and i.r. absorption data indicate no presence of tosudite.

The starting material (50 mg) with distilled water (0.05 ml) was sealed in Ag-tubes and then the tubes were placed in the autoclave (Sakashita D-type). Pressure was kept at 400 atm, by water vapor and temperature was controlled at 400, 450 and 480°C.

The materials obtained were examined mainly by X-ray diffractometry. The results are listed in Table 9. As seen in Fig. 4, the material obtained at 400°C gave a 15.24 Å reflection and it expanded to 17.67 Å by ethylene glycol treatment. Though there were a

small amount of montmorillonite in the starting material, the reflection became much stronger. This indicates the formation of a montmorillonite-like material from the interstratified mineral. In fact the i.r. absorption bands are very similar to that of montmorillonite (Table 8-1).

After treated at 450°C, a weak reflection appeared in the region of 30–34 Å. Its higher orders were detected regularly. The mean basal spacing calculated was 30.5 ± 1.6 Å and it became 32.2 ± 1.0 Å by the treatment with ethylene glycol. The results are very similar to the properties of the tosudite specimen found in nature at the Hokuno mine (Fig. 4b). The i.r. absorption data (Table 8-2) also show that the tosudite-like material is the same as the natural tosudite. The lack of 3535 cm^{-1} band may be due to the incomplete crystallinity of the gibbsite layer of tosudite.

The expandable layer synthesized at 400°C changed to the tosudite-like mineral at 450°C, 400 atm. This seems to show that the transformation of interstrati-

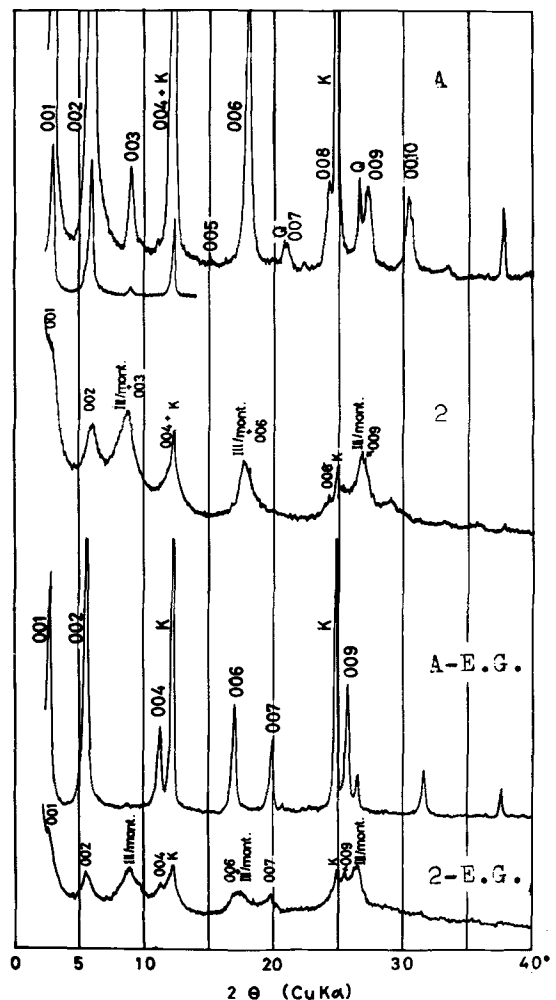


Fig. 4(b). X-ray powder diffraction patterns of the synthesized material and natural tosudite. 2: 450°C, 5 days. A: The specimen of tosudite obtained from Sample S-5. E.G.: After ethylene glycol treatment.

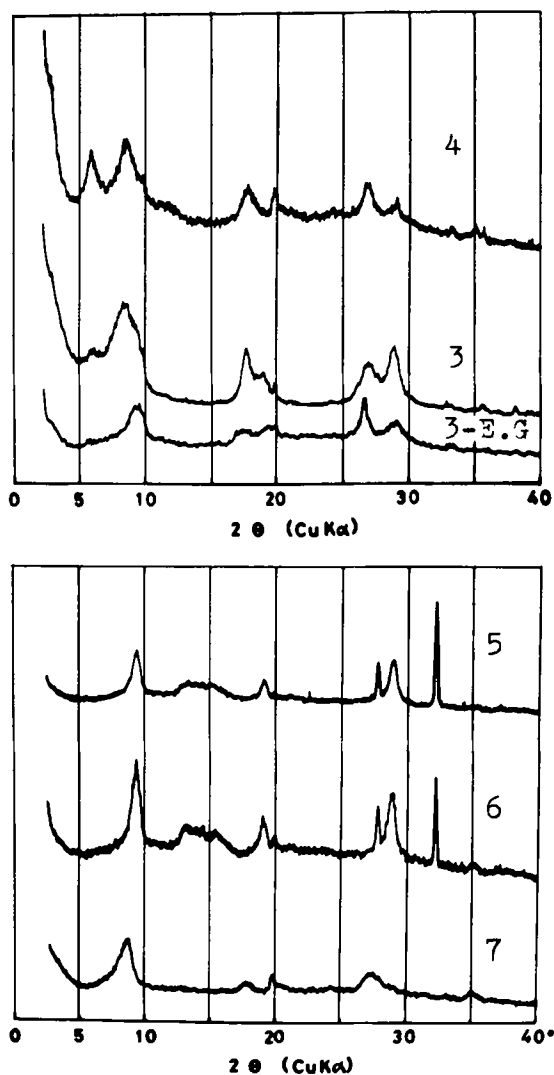


Fig. 4c. X-ray powder diffraction patterns of the synthesized materials. 3: 480°C, 2 days. 4: Treating the synthesized montmorillonite of No. 1 to 450°C. 5: Synthesized with AlCl_3 , 6: Synthesized with $\text{AlCl}_3 + \text{NaOH}$. 7: Synthesized with NaOH . E.G.: After ethylene glycol treatment.

fied illite-montmorillonite to a tosudite-like mineral passes through an expandable phase such as montmorillonite and Al^{3+} was supplied from the decomposed kaolinite mineral.

Interstratified illite-montmorillonite can be transformed to tosudite at 450°C, 400 atm. Though it is impossible to directly apply the result obtained here to the origin of tosudite, tosudite seems to be formed from the interstratified illite-montmorillonite.

Acknowledgements—The writers would like to thank Dr. S. Kanaoka, Dr. K. Shimosaka and Dr. T. Nishiyama for helping our geological survey and for their valuable comments. The writers also thank the Pottery Research Institute of Gifu Prefecture for their assistance.

REFERENCES

- Brown, G. (1953) The dioctahedral analogue of vermiculite: *Clay Min. Bull.* **10**, 64–69.
- Brown, G., Bourguignon, P. and Thorez, J. (1974) A lithium-bearing aluminium regular mixed montmorillonite-chlorite from Huy, Belgium: *Clay Minerals* **10**, 135–144.
- Frank-Kamenetsky, V., Logvinenko, N. and Drits, V. (1965) Tosudite—a new mineral forming the mixed-layer phase in alushtite: *Proc. Int. Clay Conf.* pp. 181–186. Stockholm, Sweden, Pergamon Press.
- Hayashi, H. (1961) Mineralogical study on alteration products from altered aureole of some “kuroko” deposits: *Min. J. Japan* **5**, 12–18.
- Kanaoka, S. (1968) Long spacing clay mineral in Uebi stone from Ehime Prefecture and Izushi stone from Hyogo Prefecture: *J. Ceram. Ass., Japan* **11**, 116–123.
- Matsuda, T. and Henmi, K. (1973) Hydrothermal behavior of an interstratified mineral from the mine of Ebara, Hyogo Prefecture, Japan. (An example of changes from randomly interstratified clay mineral to regular one): *J. Clay Science Soc., Japan* **13**, 87–94.
- Mitsuda, T. (1957) Long spacing clay mineral from the Uku mine, Yamaguchi Prefecture, Japan: *Min. J., Japan* **2**, 169–179.
- Nishiyama, T., Shimoda, S., Shimosaka, K. and Kanaoka, S. (1975) Lithium-bearing tosudite: *Clays & Clay Minerals* **23**, 337–342.
- Shimoda, S. (1969) New data for tosudite: *Clays & Clay Minerals* **17**, 179–184.
- Shimoda, S. (1975) X-ray and i.r. studies of sudoite and tosudite: *Contributions to Clay Mineralogy in Honor of Professor Toshio Sudo*; pp. 92–96.
- Sudo, T. and Hayashi, H. (1955) New types of clay minerals with long spacings at about 30 Å found from the altered area developed around certain ore bodies of the Hanaoka mine, Akita Prefecture: *Science Reports, Tokyo Kyoiku Daigaku*, **3**, 281–294.
- Sudo, T. and Kodama, H. (1957) An aluminian mixed-layer mineral of montmorillonite-chlorite: *Zeit. Krist.* **190**, 379–387.
- Sudo, T., Takahashi, H. and Matsui, H. (1954) A long spacing at about 30 KX, confirmed from a fireclay: *Nature, Lond.* **173**, 261–262.