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NEW DATA FOR TOSUDITE

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Abstract—Tosudite from the Takatama mine is found as an alteration mineral of the wall rocks (tuff and tuffaceous sediments of Tertiary age) of gold–silver–quartz veins. A specimen free from impurities was obtained by the sedimentation method. Chemical composition: SiO_2 42·14%; Al_2O_3 37·38%; Fe_2O_3 0·30%; MgO 0·08%; CaO 1·65%; Na_2O 0·15%; K_2O 1·40%; H_2O^+ 11·22%; H_2O^- 6·16%; total 100·48%. A negligible amount of MgO indicates that both octahedral sheets of the chlorite structure are dioctahedral. Structural formula is given as $(K_{0.58}\ Na_{0.09}\ Ca_{0.57})(Mg_{0.04}\ Fe^{3+}_{0.07}\ Al_{12.05})(Al_{2.28}\ Si_{13.72})\ O_{40.00}(OH)_{20.00}8.88H_2O$.

A reflection at 30 Å with its higher order reflections and another reflection at 1·493 Å are observed. After heating at 300°C, a 27 Å phase has appeared, in which a single plane of water molecules was confirmed as the interlayer water of montmorillonite. The structures in air-dried state and in dehydrated steps were proved by comparing the calculated and observed F-values, and by Fourier synthesis. The DTA and TG curves and the i.r. absorption spectrum are reported in this paper.

INTRODUCTION

REGULAR dioctahedral chlorite–montmorillonite was first found from the Kurata mine by Sudo *et al.* (1954), and after that other localities in Japan were reported by Sudo and Hayashi (1956). Although these samples contain some amounts of kaolinite, which could not be removed, the amounts of magnesium in these samples were shown to be negligible even when the amounts of kaolinite were estimated by X-ray and the chemical compositions corresponding to these amounts were subtracted from the chemical compositions of the raw materials. The same type of interstratification was found in the Honko ore body of the Kamikita mine by Sudo and Kodama (1957). It was reported to have about 6% MgO and the chlorite in this interstratification was shown to be of the di/trioctahedral type. Frank-Kamenetsky *et al.* (1963) showed that the minerals designated as alushtite from Crimea in some cases are of the same type of interstratification consisting of coupled pyrophyllite sheets, connected through the hydroargillite sheets; for this mineral they proposed the name tosudite, after the name of the first researcher Professor Dr. Toshio Sudo. Based upon this principle, the chlorite structure of tosudite may be of the di/dioctahedral type; however, the approximate crystallochemical formula of the specimen from Crimea shows the octahedral magnesium content as $(Al_{5.0}Mg_{1.0})$ which is close to that of the Kamikita material chemically.

The present paper reports the occurence of tosudite consisting of di/dioctahedral chlorite and montmorillonite structures, and its mineralogical data are described in comparison with earlier data, particularly with the Kamikita material.

MINERALOGICAL DATA

The Takatama mine, Fukushima Prefecture, has been worked as one of the gold–silver mines in Japan. In this mine, numerous gold–silver–quartz veins intersect the wall rocks (Tertiary tuff and tuffaceous sediments), which have been intensely altered to clay minerals consisting largely of kaolinite. Recently, tosudite has been found as one of the principal clay mineral components.

The specimen in question is free from impurities, having been obtained by the sedimentation method.

As given in Table 1, the X-ray diffraction data and the effects of thermal and chemical treatments reveal that the specimen is a regular dioctahedral chlorite-montmorillonite interstratification. A 30 Å reflection and its higher order reflections are clearly observed. After heating at 300°C for an hour the 30 Å reflection shifted to 27 Å which is due to dehydration of the interlayer water from double planes to a single plane of water molecules. After heating at 300°C for five hours the 27 Å reflection disappeared, and the 13·5 Å reflection shifted to 12 Å. A 23 Å reflection appeared after heating at 500 and 600°C for 1 hr. The firing product at 800°C is composed of mullite and γ-alumina. A 1·493 Å reflection indicates that the specimen is of the dioctahedral type. After treatment with ethylene glycol the 30 Å reflection shifted to 31·9 Å. After

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Table 1. X-ray diffraction data of the Takatama specimen

A		B		C		D	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
30·4	320	27·8	20			24·0	10
15·2	240	13·6	90				
		11·8	5	12·0	60	11·9	60
10·00	20	9·02	22				
				8·158	25		
7·557	20						
5·980	3					5·824	6
		5·336	18				
5·006	70			4·818	70		
4·480	95	4·480	70	4·502	45	4·525	90
4·247	15						
		4·168	5				
		3·798	5			3·864	5b
3·705	20						
				3·424	40		
3·297	24	3·336	20			3·302	27
2·954	20	2·947	8	2·966	15	2·928	7
2·562	40	2·565	35	2·568	25	2·588	20
				2·513	15		
2·354	6	2·336	6	2·354	12		
2·302	5	2·247	4			2·257	7
2·189	4	2·179	3	2·178	3	2·174	5
2·026	7	2·034	10	1·994	10	2·034	4b
1·971	6						
1·691	10	1·688	8	1·682	7	1·697	7b
1·688	10	1·641	7	1·650	8		
1·493	40	1·496	28	1·496	20	1·505	6

b indicates a broad reflection.
A: Air-dry, natural state.
B: After 1 hr at 300°C.
C: After 5 hr at 300°C.
D: After 1 hr at 500°C.

treatment with ammonium nitrate solution by boiling for ten minutes the 30 Å reflection shifted to 26·5 Å, which may be due to contraction of the montmorillonite structure. The basal spacings of the specimen after various treatments are recorded in Table 2-a.

F-values were calculated from various models of the combinations of chlorite (magnesium-free type) and montmorillonite in which the interlayer water is completely dehydrated or exists as two-plane or single-plane water. The results are given in Table 2-b. Good agreement between calculated and observed values is noticed, although in the case of the dehydrated form the R-factor did not fall in the range of good agreement. Fourier synthesis diagrams, as shown in Fig. 1, also prove the structures in air-dried state and in dehydration steps.

The DTA-curve, as shown in Fig. 2, shows three endothermic peaks. Two distinct steps of weight loss are observed in the TG-curve in Fig. 2. The first weight loss below 300°C is about 6·8 per cent, which is due to dehydration of interlayer water. The second weight loss between 400°C and 650°C is about 7·8 per cent, which is due to dehydration of the hydroxide sheet of the chlorite structure. Gradual and small weight loss can be observed above 650°C, which is attributable mainly to dehydration of the hydroxyl of the silicate layer.

Chemical analysis, as given in Table 3, shows a negligible amount of magnesium. Hence the two octahedral sheets of the chlorite structure are of the dioctahedral type. As shown in Table 3, the structural formula reveals that the composition of the hydroxide sheet of the chlorite agrees with that of gibbsite.

The i.r. absorption spectrum is close to that of dioctahedral chlorite reported by Oinuma and Hayashi (1968); it shows absorption bands 3650, 3525, 3375, 1613, 1000, 920, 812, 735, 530 and 462 cm^{-1}, of which the bands 3375 and 1613 cm^{-1} are due to the interlayer water molecules.

COMPARISON WITH EARLIER DATA

Chemically the present material agrees with the Kurata material, i.e. both of the octahedral sheets of the chlorite structure are dioctahedral, differing

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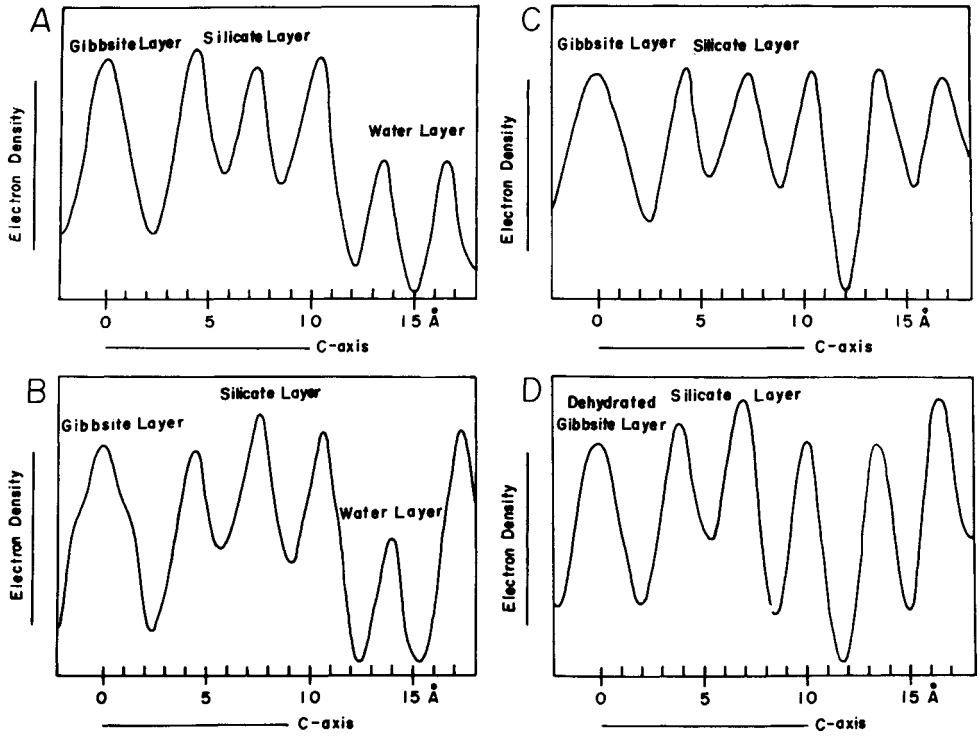


Fig. 1 One-dimensional structural projection of the specimen. A: air-dry, natural state; B: after 1 hr at 300°C; C: after 5 hr at 300°C; D: after 1 hr at 500°C.

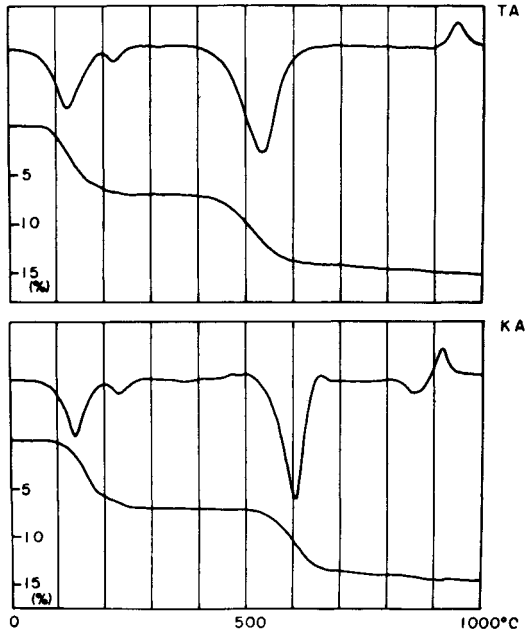


Fig. 2 DTA and TG curves of the Takatama and the Kamikita specimens. TA: Takatama specimen; KA: Kamikita specimen.

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Table 2. Lattice spacings, $d(001)$, of the specimen after various treatments and the F-values of the 00*l* reflections of the four distinct hydration states

a.

Condition of mineral	$d(001)$ Å	Component layer chl.	mont.
Air-dry, natural state (A)	30·0 ± 0·5	14·5	15·5
After 1 hr at 300°C (B)	27·0 ± 0·8	14·5	12·5
After 5 hr at 300°C (C)	24·0 ± 0·6	14·5	9·5
After 1 hr at 500°C (D)	23·5 ± 0·3	14·0	9·5
After 1 hr at 600°C	23·5 ± 0·3	14·0	9·5
Ethylene glycol treatment	31·9 ± 0·8	14·5	17·4*
NH_4NO_3 treatment	26·5 ± 1·0	14·5	12·0*

b.

	A			B		C		D	
		T	K†		T		T	T	K‡
	$F_{cal.}$	$F_{obs.}$	$F_{obs.}$	$F_{cal.}$	$F_{obs.}$	$F_{cal.}$	$F_{obs.}$	$F_{obs.}$	$F_{obs.}$
001	56	61	57	46	25	−9	10	22	17
002	−90	85	89	−40	99	−38	42	82	73
003	39	29	41	58	62	35	36	18	20
004	21	20	49	33	17	5	11	34	28
005	18	9	20	40	67	89	77	27	61
006	79	89	131	102	99	21	20	32	30
007	40	59	29	27	52	83	103	148	125
008	67	62	62	122	124	−104	74	74	104
009	91	107	89	−81	99	30	—	—	—
00·10	−115	92	100	11	—	30	—	—	—

A, B, C and D indicate the condition of minerals, as given in Table 2-a. T and K indicate the specimens from the Takatama and the Kamikita mines, respectively.

*Not estimated from the Fourier synthesis.

†Sudo and Kodama (1957).

‡The data obtained by this study.

from the Kamikita material in which the hydroxide sheet of the chlorite structure is close to the trioctahedral type (Table 3). This difference in chemical composition is reflected in the DTA and TG curves. As shown in Fig. 2, the temperature of dehydroxylation of the chlorite structure of the Kamikita material is about 80°C higher than that of the present material. The Kamikita material shows a small endothermic peak at about 850°C which accompanies a step of small weight loss. It is reasonably considered that this small peak is due to dehydroxylation of the silicate layer. In the present material, the peak is obscure. The X-ray intensities of the Kamikita material verify that the hydroxide sheet is rather trioctahedral and the silicate layer is dioctahedral in the chlorite structure. Nevertheless, the Kamikita material is slightly different from the present material with respect to the peak due to dehydroxylation of the silicate layer. This remains a problem for future study.

NOMENCLATURE

Chlorites and also interstratifications with chlorite structures pose a problem in nomenclature. There is special confusion in the nomenclature of dioctahedral chlorite (Brown, 1955; Brindley and Gillery, 1956; Brydon *et al.*, 1961). Müller (1963) has proposed the name sudoite as a group name for dioctahedral chlorite. Mackenzie and Mitchell (1966) accepted the name as a species name in their classification scheme of clay minerals. Recently the Subcommittee of CIPEA suggested that the term dioctahedral chlorite should include all species with 4–5 octahedral cations per formula unit. Eggleton and Bailey (1967) emphasized the importance of di/tri- or tri/dioctahedral types and proposed that the name sudoite should be given to the di/trioctahedral chlorite as a species name, not as a group name.

As for the nomenclature of the interstratification, Brown (1955) noted that a specific name should be given, if the interstratification is regular and the nature of the sheets is established. According to this principle, the specimen in this paper, a regular interstratification of di/dioctahedral chlorite with montmorillonite, should be given a specific name.

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Table 3. Chemical analyses of the Takatama and the Kamikita specimens

	Takatama	Kamikita
SiO_2	42·14	39·94
TiO_2		0·74
Al_2O_3	37·38	33·17
Fe_2O_3	0·30	1·34
FeO		0·18
MgO	0·08	6·44
MnO		tr.
CaO	1·65	1·30
Na_2O	0·15	0·52
K_2O	1·40	0·24
H_2O^+	11·22	11·64
H_2O^-	6·16	4·39
P_2O_5		0·08
Total (%)	100·48	99·98*

Structural formula

Takatama

Interlayer cations $K_{0·58}, Na_{0·09}, Ca_{0·57} + 8·88H_2O$

Gibbsite sheet $Mg_{0·04}, Fe^{3+}_{0·07}, Al_{4·05}(OH)_{12·00}$

Silicate layer $Al_{8·00}(Si_{13·72}, Al_{2·28})O_{40·00}(OH)_{8·00}$

*Kamikita**

Interlayer cations $K_{0·10}, Na_{0·34}, Ca_{0·46} + 8H_2O$

Gibbsite sheet $Al_{2·32}, Mg_{3·19}(OH)_{12·00}$

Silicate layer $Al_{8·00}(Si_{13·30}, Al_{2·70})O_{40·00}(OH)_{8·00}$

*Includes S 0·69%, Sudo and Kodama (1957).

In this report the name tosudite is considered as a regular interstratification of dioctahedral chlorite with montmorillonite, and the specimen described in this paper is a species of tosudite.

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Résumé—La Tosudite de la mine de Takatama existe sous la forme d'un minéral d'altération sur les parois rocheuses (tuf et sédiments tufacés de l'époque tertiaire) des veines de quartz aurifère et argentifère. Un spécimen absolument pur a été obtenu par la méthode de sédimentation.

Composition chimique: SiO_2 42·14%; Al_2O_3 37·38%; Fe_2O_3 0·30%; MgO 0·08%; CaO 1·65%; Na_2O 0·15%; K_2O 1·40%; H_2O^+ 11·22%; H_2O^- 6·16%; Total 100·48%.

Une quantité négligeable de MgO indique que les deux feuilles octaédriques de la structure de chlorite sont dioctaédriques. La formule de constitution a été donnée comme suit: $(K_{0·58}\ Na_{0·09}\ Ca_{0·57})(Mg_{0·04}\ Fe^{3+}_{0·07}\ Al_{12·05})(Al_{2·28}\ Si_{13·72})\ O_{40·00}\ (OH)_{20·00}\ 8·88H_2O$.

Une réflexion à 30 Å avec ses réflexions supérieures et une autre réflexion à 1·493 Å sont observées. Après chauffage à 200°C, une phase de 27 Å a fait son apparition, dans laquelle un seul plan de molécules d'eau était confirmé comme étant l'eau de la couche intermédiaire de montmorillonite. On démontre ensuite les structures à l'état d'air sec et en phases deshydratées en comparant les valeurs F calculées et observées, et en utilisant la synthèse de Fourier. Les courbes DTA et TG et le spectre d'absorbtion i.r. sont exposés dans ce document.

Kurzreferat—Es wurde gefunden, dass der Tosudit aus der Takatama Grube ein Veränderungsmineral der Wandgesteine (Tuff und tuffartige Ablagerungen aus dem Tertiär) von Gold-Silber-Quarz Adern darstellt. Durch die Sedimentationsmethode konnte eine von Verunreinigungen freie Probe erhalten werden. Sie hatte folgende chemische Zusammensetzung: SiO_2 42,14%; Al_2O_3 37,38%; Fe_2O_3 0,30% MgO 0,08%; CaO 1,65%; Na_2O 0,15%; K_2O 1,40%; H_2O^+ 11,22%; H_2O^- 6,16%; insgesamt 100,48%.

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Die geringfügige Menge von MgO deutet darauf hin, dass beide oktaedrische Platten des Chloritgefüges dioktaedrisch sind. Die Strukturformel ist $(K_{0,58}\ Na_{0,09}\ Ca_{0,57})(Mg_{0,04}\ Fe^{3+}_{0,07}\ Al_{12,05})(Al_{2,28}\ Si_{13,72})\ O_{40,00}\ (OH)_{20,00}\ 8{,}88\ H_2O$.

Es wurde eine Reflexion bei 30 Å mit Reflexionen höherer Ordnung, sowie eine weitere Reflexion bei 1,493 Å beobachtet. Nach Erwärmung auf 300°C, erschien eine 27 Å Phase, in welcher eine einzelne Ebene von Wassermolekülen als Zwischenschichtwasser des Montmorillonits erkannt werden konnte. Die Strukturen im lufttrockenen Zustand und in dehydratisierten Stufen wurden durch Vergleich der berechneten und beobachteten *F*-Werte, sowie durch Fourier Synthese bestätigt. Die vorliegende Arbeit enthält DTA und TG Kurven sowie das Infrarot-Absorptionsspektrum.

Резюме—Тосудит в руднике Такатама представляет продукт изменения боковых пород (туф и туфовидные осадки третичного возраста) золото-серебряных кварцевых жил. Образец, свободный от примесей, был получен седиментационным методом. Химический состав этого образца (в%): $Si0_2$—42,14; $A1_20_3$—37,38; Fe_20_3—0,30; $Mg0$—0,08 ;$Ca0$—1,65; Na_20—0,15; K_20—1,40; H_20^+—11,22; H_20^-—6,16; сумма—100,48. Незначительное содержание $Mg0$ указывает на то, что обе октаэдрические сетки хлоритового пакета являются диоктаэдриче скими. Структурная формула хлорита: $(K_{0,58}Na_{0,09}Ca_{0,57})\ (Mg_{0,04}Fe_{0,07}A1_{12,05})\ (A1_{2,28}\ Si_{13,72})\ 0_{40,00}\ (OH)_{20,00}\ 8{,}88\ H_20$.

На порошкограммах имеется рефлекс при 30А, его более высокие порядки, а также рефлекс при 1,493 А. После прогревания при 300°С появилась фаза с рефлексом 27А, в которой имеется мономолекулярный слой воды, соответствующий межслоевой воде монтмориллонита. Структура воздушно-сухих веществ и продуктов их ступенчатой дегидратации были определены сравнением вычисленных и измеренных значений F, а также с помощью синтеза Фурье. Приведены кривые ДТА, ТГА и спектры поглощения инфракрасных лучей.

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