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LITHIUM-BEARING TOSUDITE

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Abstract—Lithium-bearing tosudite was found from a brittle clayey part of the Tooho "roseki" deposit, Aichi Prefecture, Japan. The chemical composition of the Li bearing tosudite was estimated as SiO_2 41·60%, Al_2O_3 36·40%, Fe_2O_3 1·82%, MgO 0·29%, CaO 0·38%, Li_2O 1·04%, Na_2O 0·14%, K_2O 0·38%, H_2O^+ 11·12% and H_2O^- 6·87% from the chemical composition of a specimen with associated impurities. The Li-bearing tosudite has the regularly interstratified structure of montmorillonite and dioctahedral chlorite in which Li is present in a gibbsite sheet as shown in the structural formula of interlayer cations $K_{0\cdot16}$, $Na_{0\cdot09}$, $Ca_{0\cdot13}$ + 9·60 H_2O; gibbsite sheet $Li_{1\cdot36}$, $Mg_{0\cdot14}$, $Fe_{0\cdot45}$, $Al_{3\cdot59}$ $(OH)_{12\cdot00}$; silicate layer $Al_{8\cdot00}$ $(Si_{13\cdot60}, Al_{2\cdot40})$ $O_{40\cdot00}$ $(OH)_{8\cdot00}$. The 29·48 Å reflection series of the Li-bearing tosudite moves to 31·3 Å after ethylene glycol treatment and to 23·3 Å on heating to 500°C for 1 hr.

INTRODUCTION

Tosudite, a regularly interstratified mineral of di or di-trioctahedral chlorite and montmorillonite, has been found in various localities in Japan. Tosudite with di-trioctahedral type chlorite in its interstratification has been found in the Kamikita mine, Aomori Prefecture (Sudo and Kodama, 1957), the mineralized zone at Niida, Akita Pref. (Kimbara and Nagata, 1974) and the Iwami mine, Shimane Pref. (Shimoda, 1975). Tosudite having dioctahedral chlorite has been found in the Kurata mine, Yamaguchi Pref. (Sudo *et al.*, 1954), the Hanaoka mine, Akita Pref. (Sudo and Hayashi, 1956), the Uku mine, Yamaguchi Pref. (Mitsuda, 1957), Uebi, Ehime Pref. and Izushi, Hyogo Pref. (Kanaoka, 1968), the Takatama mine, Fukushima Pref. (Shimoda, 1969), the Igashima mine, Niigata Pref. (Imai and Watanabe, 1972), the Hiraki mine, Hyogo Pref., the Hokuno mine, Gifu Pref. and Amakusa, Kumamoto Pref. (Kanaoka, 1975).

Recently Brown *et al.* (1974) reported a Li-bearing aluminium regular mixed-layer montmorillonite–chlorite from Huy, Belgium. In this paper we report on a Li-bearing tosudite which has dioctahedral chlorite in its interstratification, from the Tooho mine, Aichi Pref., Japan.

SPECIMEN

This specimen was obtained from the Tooho "roseki" deposit, Aichi Pref., Japan. The dominant clay mineral distribution sequence in this deposit is pyrophyllite–allevardite–mica from the central area of alteration of the andesitic country rock. The specimen occurs in an allevardite area where it is altered secondarily to a brittle clayey part by later hydrothermal activity. The brittle clayey part has small green and white veinlets and is translucent. The specimen occurs in the green veinlets, and the white and translucent veinlets are composed of dickite and fluorite respectively.

The specimen of green color has a high plasticity in the presence of water due to the montmorillonite layer (Kanaoka, 1968) and the green color is due to the presence of iron.

The specimen used in this experiment is found in the green veinlets closely associated with allevardite. The impurities in the raw material were determined quantitatively by X-ray intensity measurement using the so-called "method of known additions" (Brindley, 1961) as 20·2% allevardite, 3·4% dickite, 2·8% quartz and 1·0% fluorite.

MINERALOGICAL DATA AND DISCUSSION

Structural features of the specimen

An oriented sample shows a regular series of basal X-ray powder diffraction reflections from a spacing of 29·5 Å (Table 1). The 29·5 Å spacing increases to 31·1 Å with ethylene glycol treatment and decreases to 23·3 Å when heated at 500°C for 1 hr. When water is added to the heated specimen, the spacing re-expands to 29·5 Å. These spacing changes resemble those of tosudite from the Takatama mine (Shimoda, 1969) and in pottery stone such as that from the Hiraki, Hokuno and Amakusa mines (Kanaoka, 1975).

F-values of the (00ℓ) reflections were calculated from various models of a combination of chlorite and montmorillonite layers having the structural formula mentioned later, For the specimen heated at 500°C for 1 hr a model was assumed in which interlayers of montmorillonite and chlorite are completely dehydrated and partially dehydroxylated from the evidence of i.r. and DTA analyses. The results, listed in Table 2, show good agreement between observed

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Table 1. X-ray powder diffraction data for the specimen from the Tooho mine, before and after various treatments

	a			b		c		d		e	
hkℓ	$d(00\ell)$ (Å)	$d(00\ell) \times \ell$ (Å)	I	$d(00\ell)$ (Å)	I	$d(00\ell)$ (Å)	I	$d(00\ell)$ (Å)	I	$d(00\ell)$ (Å)	I
001	29·4	29·4	100	27·6	24	23·1	33	29·4	83	31·6	100
002	14·66	29·31	60	14·66	100	11·76	100	15·07	100	15·56	49
003	9·825	29·48	2·6	9·807	10	7·766	1·0			10·163	0·3
004	7·417	29·67	3·4	7·403	8·7	5·826	5·9	7·460	0·2	7·789	6·1
005	5·905	29·53	0·2	5·909	0·5	4·690	1·4	5·937	1·3		
006	4·921	29·53	9·2	4·939	34	3·880	0·6	4·910	1·6	5·185	6·9
007			0·7		3·7		26	4·154	0·4	4·450	5·1
008	3·691	29·53	2·5	3·698	7·4	2·919	16	3·652	0·2	3·882	4·2
009	3·271	29·44	2·4	3·286	8·1	2·586	2·8	3·276	5·2	3·453	7·1
00·10	2·937	29·37	2·7	2·952	8·1	2·332	1·0	2·932	1·4		0·1
00·11				2·695	1·0			2·660	0·1	2·826	2·8
00·12	2·455	29·46	0·5								
mean $d(00\ell)$	29·48 ± 0·19Å			29·54 ± 0·22Å		23·32 ± 0·22Å		29·50 ± 0·60Å		31·09 ± 0·60Å	

(a) Air-dry, natural state; (b) After 1 hr at 300°C; (c) After 1 hr at 500°C; (d) Rehydration after 1 hr at 500°C; (e) Ethylene glycol treatment.
* is calculated except the value of $d(00\ell)$.

and calculated F-values, although further modification may be necessary for the treated samples. Figure 1 shows the electron density curves along the *c*-axis of this specimen, after various treatments, calculated by Fourier synthesis using the observed F-values and the calculated signs. From these each component layer spacing of chlorite and montmorillonite is obtained, Table 3. The chlorite layer has a 13·9 Å spacing which does not change with ethylene glycol treatment and heat treatment at 300°C for 1 hr. At 500°C for 1 hr the spacing changes to 13·6 Å and the electron density of the "gibbsite" sheet becomes low due to dehydroxylation. The montmorillonite layer has a 15·6 Å spacing which expands to 17·0 Å with ethylene glycol treatment. The spacing does not change at 300°C, but at 500°C the interlayer water is completely removed and the spacing shrinks to 9·7 Å. It re-expands to 15·8 Å with rehydration.

The spacing of the chlorite layer of this specimen is about 0·4 Å smaller than that of the Takatama specimen and rather similar to that of the Huy specimen (Brown *et al.*, 1974). After heating at 300°C for 1 hr the $d(001)$ Å spacing of the specimen quickly rehydrates under ambient room conditions but under drier conditions the spacing shrunk to 24·4 Å after the same heat treatment. This means that the montmorillonite layer spacing varies sensitively with humidity. Therefore we could not easily compare the montmorillonite layer spacing with that of other specimens.

Infrared examination shows that the expandable

Table 2. F-value of (00ℓ) reflections of the specimens from the Tooho, the Takatama and the Kamikita mines, before and after various treatments

	a				b		c				d	
	Tooho		Ta*	Ka†	Tooho	Ta*	Tooho		Ta*	Ka*	Tooho	
hkℓ	F_{cal}	F_{obs}	F_{obs}	F_{obs}	F_{obs}	F_{obs}	F_{cal}	F_{obs}	F_{obs}	F_{obs}	F_{cal}	F_{obs}
001	49	48	61	57	15	25	−36	16	22	17	23	43
002	−64	100	85	89	57	99	−27	53	82	73	−46	29
003	27	23	29	41	27	62	3	7	18	20	11	
004	30	35	20	49	35	17	23	26	34	28	7	8
005	18	10	9	20	10	67	64	50	27	61	9	26
006	86	88	89	131	100	99	50	13	32	30	60	37
007	22	28	59	29	39	52	99	100	148	125	14	21
008	78	62	62	62	60	124	−88	90	74	104	58	17
009	74	70	107	89	75	99	6	42			57	100
00·10	−87	83	92	100	85		−29	29			−62	58
00·11	−11				32						−6	13
00·12	−41	42										

(a) Air-dry, natural state; (b) After 1 hr at 300°C; (c) After 1 hr at 500°C; (d) Rehydration after 1 hr at 500°C.
Ta: The Takatama specimen. Ka: The Kamikita specimen.
* Shimoda (1969). † Sudo and Kodama (1957).

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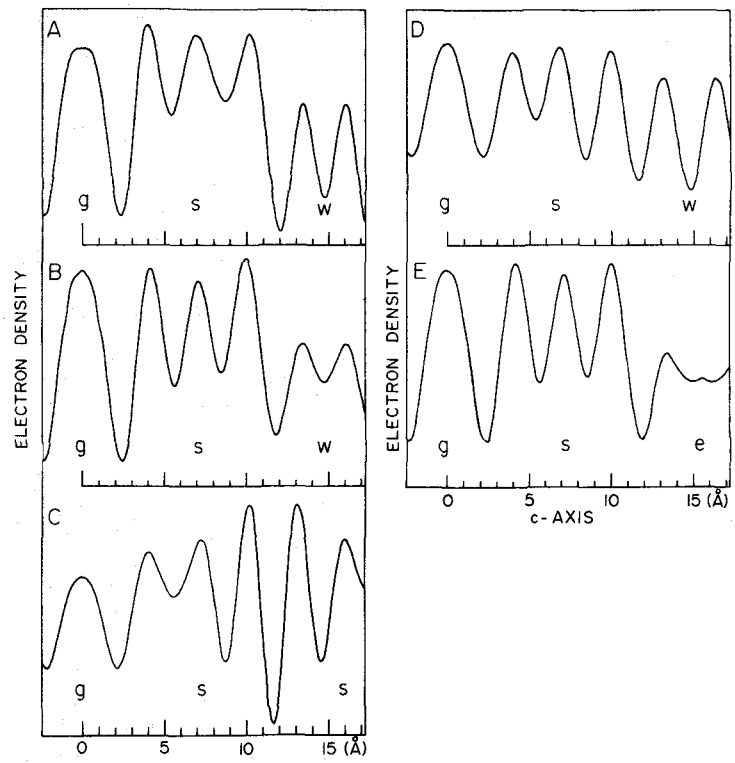


Fig.1. Electron density curves along *c*-axis of the specimen from the Tooho mine before and after various treatments. (a) Air-dry, natural state. (b) After 1 hr at 300°C. (c) After 1 hr at 500°C. (d) Rehydration after 1 hr at 500°C. (e) Ethylene glycol treatment. *g*, gibbsite sheet. *s*, silicate layer. *w*, interlayer water. *e*, interlayer ethylene glycol.

layer in this specimen is a normal montmorillonite layer, rather than a vermiculite layer, from the behavior of the absorption band at 1400 cm^{-1} assigned to an adsorbed NH_4^+ as shown in Fig. 2 (Sato *et al.*, 1974). That is, the adsorption band appeared on the NH_4^+ treated specimen disappears on the K^+ following NH_4^+ treated specimen.

Differential thermal analysis and thermogravimetric analysis patterns of the specimen are shown in Fig. 3. The DTA curve shows a double endotherm peak (126 and 207°C) which is attributed to dehydration of absorbed and interlayer water of the montmorillonite layer. An endothermic peak at 527°C is attributed to dehydroxylation of the chlorite interlayer. These reactions start at lower temperatures. Exothermic peaks which appear at 930 and 955°C can be attributed to recrystallization of the specimen and of associated dickite respectively. This specimen does not show a clear endothermic peak due to dehydroxylation of the silicate layer. These results are very similar to those of the Takatama specimen (Shimoda, 1969).

Table 3. Lattice spacings of *d*(001) and component layers of the specimens from the Tooho mine, the Takatama mine and Huy before and after various treatments

	Tooho			Takatama*			Huy†
		Component layer			Component layer		
	d(001) (Å)	chl. (Å)	mont. (Å)	*d*(001) (Å)	chl. (Å)	mont. (Å)	*d*(001) (Å)
a	29·5 ± 0·2	13·9	15·6	30·0 ± 0·5	14·5	15·5	28·9
b	29·5 ± 0·2	14·1	15·4	27·0 ± 0·8	14·5	12·5	23·8§
c	23·3 ± 0·2	13·6	9·7	23·5 ± 0·3	14·0	9·5	23·4
d	29·5 ± 0·6	13·7	15·8				
e	31·1 ± 0·6	14·1	17·0	31·9 ± 0·8	14·5	17·4‡	31·1

(a) Air-dry, natural state; (b) After 1 hr at 300°C; (c) After 1 hr at 500°C; (d) Rehydration after 1 hr at 500°C; (e) Ethylene glycol treatment.

* Shimoda (1969). † Brown *et al.* (1974), Mg-saturated. ‡ Not estimated from the Fourier synthesis. § At 315°C.

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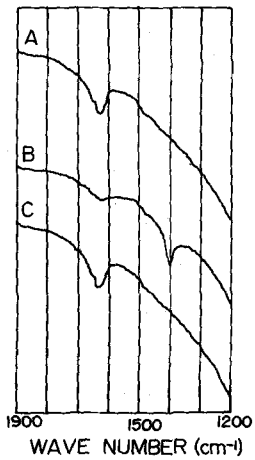


Fig. 2. I.r. absorption spectra of the specimen from the Tooho mine before and after treatment with NH_4NO_3 solution. (a) Air-dry, natural state. (b) After boiling in 1N NH_4NO_3 solution for 15 min. (c) 1N KCl treatment for 22 hr at room temperature after 1N NH_4NO_3 treatment.

Li-*bearing tosudite*

Chemical analysis data for the specimen in question are listed in Table 4. The most probable chemical composition of the specimen was calculated after subtracting the chemical composition of other impurities all of which are estimated to have ideal chemical compositions except allevardite. For the chemical composition of allevardite we used the analysed data of the allevardite which occurs in the brittle clayey part closely associated with the green veinlets of this Tooho deposit (Table 4). As the structure of allevardite is similar to that of mica, it may contain Li in its silica layer but no evidence was obtained for the presence of Li in the allevardite structure. When the result is compared with those of the Takatama specimen (tosudite having dioctahedral chlorite layer) and the Kamikita specimen (tosudite having di-trioctahedral chlorite layer; Sudo and Kodama, 1957), the chemical composition of this specimen resembles that of the Takatama specimen regarding the high aluminium and low magnesium content (Table 4). Therefore this tosudite has a dioctahedral chlorite layer in its interstratification like the Takatama specimen. This is estimated from the *d*(060) spacing of 1·492 Å by X-ray powder diffraction. This specimen characteristically contains lithium (Li_2O, 1·04%) and has a lower potassium and calcium content than that of the Takatama specimen. It resembles the Huy specimen (Table 4).

To know the presence of Li as interlayer cation, exchangeability of Li^+ by NH_4^+ ions was measured. But when the specimen was dispersed in the 1N NH_4Ac solution, which had been adjusted to pH 7, at room temperature for 24 hr, exchanged Li was 0·01% for Li_2O. Even when the dispersed solution was heated at 93°C for 30 min, the exchanged Li was only 0·02% for Li_2O. This result shows that Li in this specimen is nonexchangeable rather than exchangeable and that it occupies an octahedral site of the silicate layer and/or gibbsite sheet rather than an interlayer position in the montmorillonite layer.

The *d*(060) spacing of this specimen increased from 1·492 to 1·493 Å with heat treatment at 350°C for 1 hr and that of the Takatama specimen also increased from 1·491 to 1·492 Å with the same heat treatment. But after the Takatama specimen was treated with 1N LiCl solution, its *d*(060) spacing no longer changed with the heat treatment. This result suggests that the exchanged Li ion migrates into empty octahedral sites of the silicate layer following heat treatment (Calvet and Prost, 1971) and it resists an increase in the *b*-dimension of the silicate layer

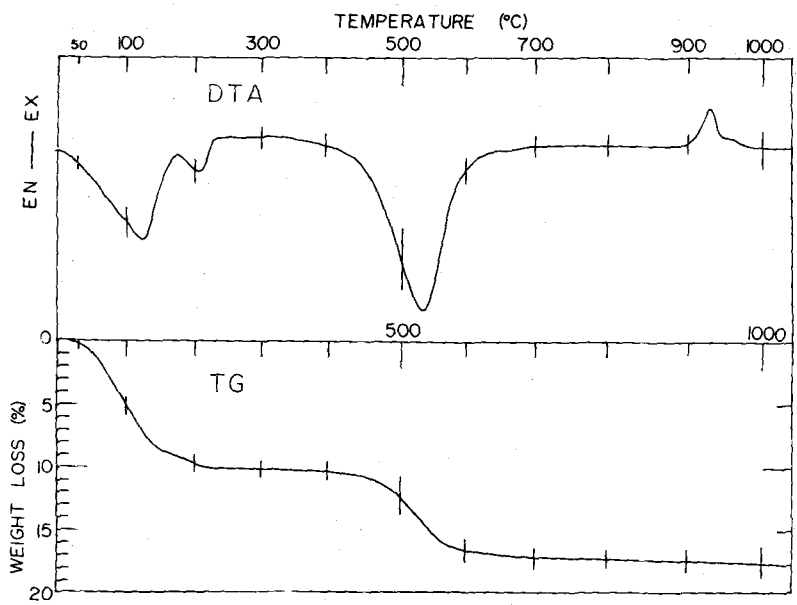


Fig. 3. DTA and TG curves of the specimen from the Tooho mine.

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Table 4. Chemical analyses of the specimens from the Tooho mine, the Takatama mine, the Kamikita mine and Huy

	(1) (%)	(2) (%)	(3) (%)	(4) (%)	(5) (%)	(6) (%)
SiO_2	44·40	47·46	41·60	42·14	39·94	39·74
TiO_2					0·74	0·01
Al_2O_3	34·25	31·52	36·40	37·38	33·17	35·87
Fe_2O_3	1·55	1·08	1·82	0·30	1·34	0·98
FeO					0·18	2·77
MgO	0·25	0·19	0·29	0·08	6·44	3·08
MnO					tr.	
CaO	1·78	2.44	0·38	1·65	1·30	0·06
Li_2O	0·77	0·07	1·04			0·51
Na_2O	0·44	1·68	0·14	0·15	0·52	0·12
K_2O	0·43	0·76	0·38	1·40	0·24	0·62
H_2O^+	10·07	7·11	11·12	11·22	11·64	15·70
H_2O^-	6·47	7·20	6·87	6·16	4·39	
P_2O_5					0·08	0·10
S					0·69	
Total	100·41	99·51	100·04	100·48	100·67	99·56

(1): The Tooho specimen associating impurities. (2): Allevardite from the Tooho mine. (3): The Tooho specimen after subtracting the chemical components of impurities. (4): The Takatama specimen (Shimoda, 1969). (5): The Kamikita specimen (Sudo and Kodama, 1957). (6) The Huy specimen, Mg-saturated specimen (Brown *et al.*, 1974).

(Leonard and Weed, 1967; Lahav and Bresler, 1973). The Li of this specimen is nonexchangeable and the *d*(060) spacing expanded by the heat treatment, therefore the Li in this specimen is not present in interlayer of the montmorillonite. No expansion of the *d*(060) spacing by the heat treatment also indicates that the Li may not occupy its position in octahedral sites of the silicate layer.

From these results we estimate the structural formula of this specimen as follows.

interlayer cations $K_{0.16}$, $Na_{0.09}$, $Ca_{0.13}$ + 9·60 H_2O

gibbsite sheet $Li_{1.36}$, $Mg_{0.14}$, $Fe_{0.45}$, $Al_{3.59}$ $(OH)_{12.00}$

silicate layer Al_{800} $(Si_{13.60}, Al_{2.40})$ $O_{40.00}$ $(OH)_{8.00}$.

As mentioned above, the correctness of this formula is supported by the calculated *F* values based on this structural formula (Table 3). The Li position in the structure could not be determined in detail because the structure factor is almost unaffected by Li atoms.

From these results, this specimen is a regularly interstratified clay mineral of Li-bearing dioctahedral chlorite and dioctahedral type montmorillonite. The name tosudite has been used for a regularly interstratified clay mineral of di or di-trioctahedral chlorite and montmorillonite by Frank-Kamenetsky *et al.* (1963). Therefore we conclude that this specimen is a Li-bearing tosudite.

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