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STUDIES ON THE SWELLING OF Li-TAENIOLITE WITH WATER

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Synthetic Li-taeniolite $LiMg_2Li(Si_4O_{10})F_2$ reacts with water , and nearly free swelling occurs . Its X-ray diffraction spectra show that the interlayer spacing d (001) discontinuously expands with the increase of water content , and eight crystalline swelling steps are observed .

Although Li-taeniolite $LiMg_2Li(Si_4O_{10})F_2$ was reported by R.A. Hatch and his co-workers 1) , detailed investigation with regard to its existence and swelling has been lacking . Recently we could substantially synthesize Li-taeniolite , and studied its water uptake and dehydration processes extensively , using high temperature X-ray diffraction , TG , DTA and I.R. methods .

From the melt of a special composition (LiF - SiO_2- MgO) part of lithium ions can be forced into 12-fold coordination sites of fluor-tetrasilicic mica , rather than into octahedral sites which lithium ion favours , because of its small ionic radius . Formation of Li-taeniolite was ascertained by X-ray diffraction and chemical analysis .

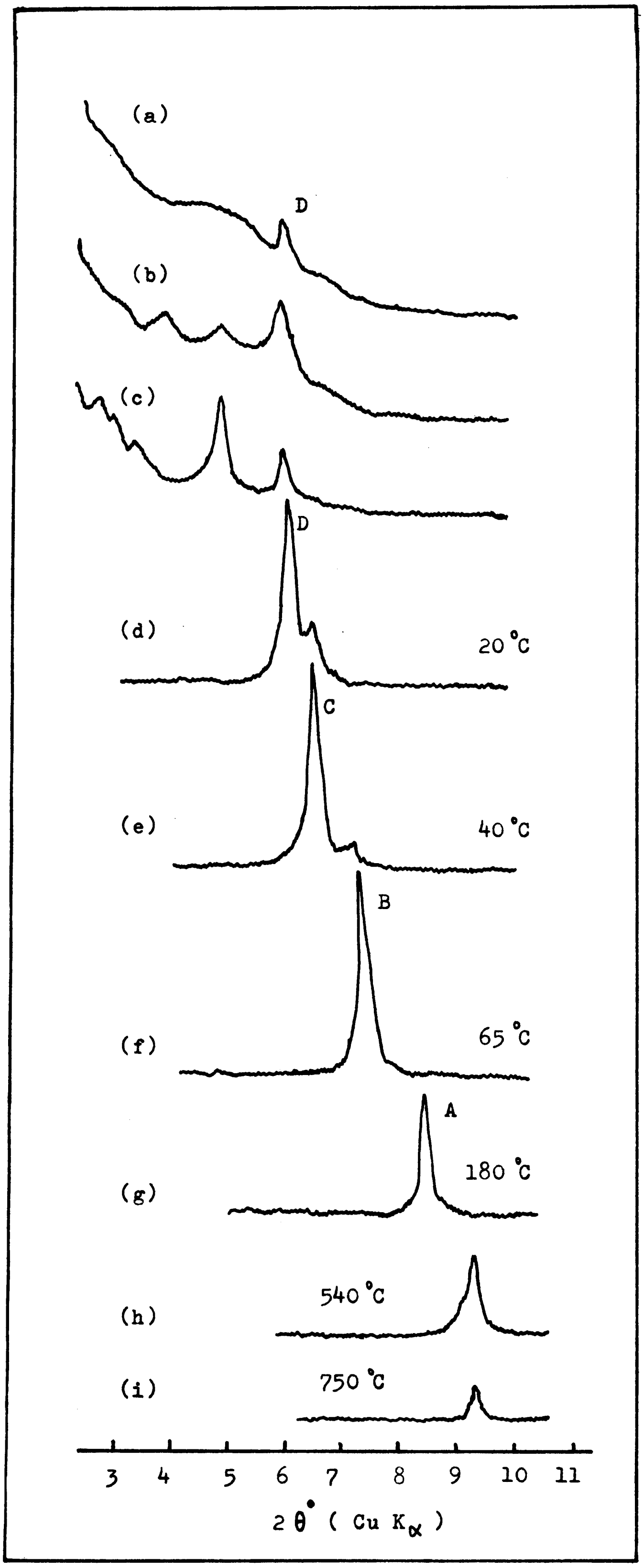
From the obtained results , it seems that hydrated Li-taeniolite might be called as lithium fluor-hectorite in respect to its swelling characteristics and chemical composition and crystal structure . In other words Li-taeniolite might be called as anhydrous lithium fluor-hectorite .

Mixtures of 2mol-LiF , 4mol-SiO_2 , and 2mol-MgO , which were special grade reagents , were melted in a sealed platinium crucible at 1350°C for 6 hrs , and then crystallized into Li-taeniolite at the cooling rate of 3 °C/min. . The crystal aggregates thus obtained were immersed into water . The samples rapidly absorbed water and bloated into a stable suspension . The suspension was then purified by centrifugation .

The samples dried at 140°C were then studied by the X-ray diffraction method , which showed that the purification was effective . The samples , which were not purified by centrifugation , showed the coexistence of foreign minerals , i. e. , high temperature form of SiO_2 and an unknown fluor-tremolite-like mineral (characteristic line d = 8.34 Å) . Formation of such foreign minerals can be prevented by controlling the fluorine content of the batches , i. e. , by adding some excess fluoride to the batches taking defluorination into account . It is also important to prevent defluorination by sealing the platinium crucible .

Fig. 1 shows the changes of X-ray diffraction patterns in the (001) reflection region of Li-taeniolite caused by the decrease of water content . Li-taeniolite gel showed no diffraction peak except a weak one at 15.2 Å (D in Fig. 1 (a)) . It seems that the band scattering at the low diffraction angle in Fig. 1 (a) is caused by random water uptake into the interlayer sites of Li-taeniolte . It is obvious from this diffraction pattern

Fig. 1 Changes of X-ray diffraction patterns in (001) reflection region with water content of Li-taeniolite .



that nearly free swelling occurs in Li-taeniolite - H_2O system . While Li-taeniolite gel was dried , X-ray diffraction patterns varied from Fig. 1 (b) to Fig. 1 (c) . It is clear from Fig. 1 (b) that Li-taeniolite becomes more and more crystalline with the decrease of water content . The crystalline swelling state D is relatively stable at the room temperature and humidity , but easily changes to the swelling state C as shown in Fig. 1(e) with a little temperature increase .
The high temperature X-ray diffraction spectra show that the interlayer spacing d (001) discontinuously shortens with the decrease of water content . The peak in Fig. 1 (h) is (001) line of anhydrous Li-taeniolite .

The interlayer distance of each crystalline swelling state and the so-called clearance spaces , i.e. , the differences between the interlayer distance of anhydrous Li-taeniolite and those of hydrated ones , are shown in Table 1 . The ratios of clearance space to 2.76 (Å) , which is the OH-O distance in ice crystal 2) , are also shown . As seen in Table 1 , the ratio of clearance space to 2.76 for each crystalline swelling state is nearly represented by 0.5n (n = 1 , 2 , 3 ,.....) .
It has been reported that the planar oxygen anions of the expanding layer silicates are normally separated by one or more layers of water molecules 3) .

So these facts seem to show that the B and D states correspond to the so-called one-layer hydrated type and two-layer hydrated type , respectively , because 0.5n is 1 for B state , and 2 for D state , respectively .

It is probable that the interlayer water molecules in B and D are coordinated to the oxygen layers of Li-taeniolite by hydogen bonds as shown by Hendricks and Jefferson for vermiculite , i.e. , planar hexagonal water molecule rings are imposed with the

Table 1 Descriptions of eight different crystalline swelling states for Li-taeniolite

crystalline swelling state	interplanar distance d (001)	clearance space (C. S.)	(C. S.)/ 2.76
anhydrous	9.50 (Å)	-------	-------
A	10.40	0.90 (Å)	0.33
B	12.23	2.73	0.99
C	13.90	4.40	1.59
D	15.23	5.73	2.08
E	18.99	9.49	3.44
F	26.0	16.5	6.0
G	30.4	21.0	7.6
H	38.4	29.0	10.5

oxygens of each water being tetrahedrally bonded to neighbouring oxygens through hydrogen atoms 4) . But no previsions for the positions of interlayer lithium ions can be deduced from Hendricks model . Recent studies on crystal structure of two-layer Mg-vermiculite by Shirozu and Bailey 5) show that the exchangeable cations lie midway between the talc sheets and are postulated to exist vertically between the ordered Al tetrahedra of the talc sheets above and below . It seems that the negative charge is distributed over the surface oxygens evenly and local charge balance , which is necessary for the most stable configuration as described before for Mg-vermiculite , can not be attained in Li-taeniolite crystal , because no tetrahedral substitution occurs in Li-taeniolite . Interlayer lithium ions are then postulated to exist in the midway of two water layers for two-layer hydrated Li-taeniolite . This prevision of position for interlayer hydrated lithium ions seems to be most probable from the viewpoint of charge balance and crystal structure . A 10.3 (Å) phase has been reported for Mg-saturated hectorite and vermiculite , which retains one water molecule per one exchangeable cation (monohydrate ion) 6) . The swelling state A in Table 1 seems to correspond with this 10.3 (Å) phase of hectorite ; This point is also confirmed by thermogravimetry (see below) . It is believed that monohydrate ion of lithium is formed by the coulombic interaction between strong dipole moment of water molecule and large positive charge density of lithium ion . The C state is then assumed to be the mixed state of A and B states . In other words it might be assumed that the trihydrate ions of lithium exist in the interlamellar region for C swelling state . The A and C states seem to be the transition states between one-layer hydrated Li-taeniolite and anhydrous one , and two-layer hydrated Li-taeniolite and one-layer hydrated one , respectively .

DTA and TG curves for C hydrated type of Li-taeniolite were recorded by the thermobalance at the same time . It is obvious from Fig. 2 that TG curve consists of four stages , the last stage of which (IV) being due to the thermal decomposition of the sample . Thus the dehydration occurs with three stages , which correspond with three endothermic peaks in DTA curve . The first stage (I) in TG curve is due to the dehydration process from C state to B state , in accordance with the high temperature X-ray diffraction studies . The second stage (II) can also be ascribed to the dehydration process from B state to A state . The third stage (III) on weight loss curve is then attributed to the dehydration process from B state to anhydrous Li-taeniolite . The DTA peak temperatures for (I) , (II) and (III) dehydration processes are about 49 °C , 136 °C , 156 °C , respectively . If the heating rate of DTA measurements was accelerated to 10 °C/min. , the second DTA peak and the third one were duplicated . The total weight loss attained 16 % , which was nearly the same value as 14.5 % of the calculated value of trihydrated type of C state , chemical composition of which might be reasonably expressed as $\mathrm{LiMg_2Li(Si_4O_{10})F_2\cdot 3H_2O}$. On the other hand , if the starting state of the sample was two-layer type , the total weight loss of the sample attained 22 % , which also showed fairly good agreement with the calculated value of 19.3 % based on the chemical formula of $\mathrm{LiMg_2Li(Si_4O_{10})F_2\cdot 4H_2O}$. The weight loss of the third step in TG curve attained 4.4 % , which showed good coincidence with the theoretical value of $\mathrm{LiMg_2Li(Si_4O_{10})F_2\cdot H_2O}$. Thus the existence of monohydrate state is confirmed .

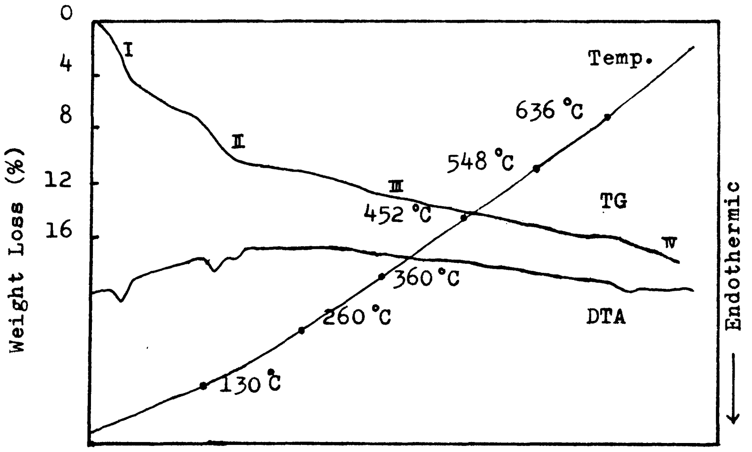


Fig. 2 TG and DTA curves of trihydrated Li-taeniolite

It is interesting to study why Li-taeniolite can swell with water. Taeniolite $\mathrm{KMg_2Li(Si_4O_{10})F_2}$ does not show any crystalline swelling with water , while sodium substituted analogue of taeniolite shows limited swelling with water . The maximum crystalline swelling state for Na-taeniolite is two-layer hydrated type 7) .

Two factors might be reasonably considered as qualitative explanation of this problem .

The first factor is hydration characteristics of interlayer cation . Hydration energies of potassium , sodium and lithium ions are 76.5 , 96.5 , 120.3 kcal/mol , respectively . The greater the hydration energy of the interlayer cation is , the more vigorous swelling with water occurs . Lithium and sodium ions are called structure forming ion , whereas potassium ion is called structure breaking ion in respect to effects on water structure around them in aqueous solution . The second factor is the ionic size effect of interlayer cations on the configurational stability in interlamellar region . The potassium ions justly fit to 12-fold coordination sites in micas , and the stable configuration is achieved, whereas the small lithium ion can not establish contacts with surface oxygens as effectively as the potassium ion does . Because of the small size of lithium ion , there will be a close approach between the surface oxygens of the upper and lower layers , so that the repulsion between anions will be considerable . Thus the hydration will tend to occur, by means of which a close approach between anions can be avoided , and the energy is lowered . The repulsion between $\mathrm{Si^{4+}}$ and $\mathrm{Li^{+}}$ can also be reduced by hydration .

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