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STUDIES ON THE SWELLING OF Na-TAENIOLITE WITH WATER

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Synthetic Na-taeniolite $NaMg_2Li(Si_4O_{10})F_2$ reacts with water , and its X-ray diffraction spectra show that the interlayer spacing (001) discontinuously widens with the increase of water content . Four steps are observed for the water uptake processes into the interlayer sites .

The maximum crystalline swelling state for Na-taeniolite is so-called two water layers hydrated type . It seems that the swelling of Na-taeniolite is mainly due to the high hydration energy of interlayer sodium ions .

Although Na-taeniolite $NaMg_2Li(Si_4O_{10})F_2$ was reported by R. A. Hatch and his co-workers 1) , detailed investigation with regard to its swelling phenomenon has been lacking .

Recently we studied the water uptake processes and the dehydration processes of Na-taeniolite extensively , using ordinary high temperature X-ray diffraction methods and DTA and TG methods . From the obtained results , it seems that Na-taeniolite is a hybrid between mica and montmorillonite in respect to its swelling properties and crystal structures .

Mixtures of 1 mol-LiF , 1 mol-NaF , 2 mol-MgO , and 4 mol-SiO_2 , which were special grade reagents , were melted in a sealed platinium crucible at 1380 °C for 8 hrs , and then crystallized into Na-taeniolite at the cooling rate of 2 °C/min. . The cooling range was from 1380 °C down to 800 °C . The crystal aggregates thus obtained were powdered , and purified by the sedimentation in water .

Samples dried at 120 °C were then studied by the X-ray diffraction method , which showed that no foreign minerals coexisted and Na-taeniolite was substantially obtained .

Fig.1 shows the changes of X-ray diffraction patterns in the (001) reflection region of Na-taeniolite caused by the increase of water content . A in Fig. 1 is the (001) peak at no water absorption . Peak A then moves to peak B , while the sample absorbing the water vapour in the air . But this B state is unstable in relatively high humidity , and soon changes to another state showing peak C . This C state of Na-taeniolite is the most stable crystalline state in the course of swelling in air under the relative humidity of 90 - 60 % . but then changes to D state by water treatment on the sample . However , this D state is again very unstable , and rapidly changes to E state . The E swelling state is the crystalline state corresponding to maximum swelling , and a higher hydrated state was never obtained , even if samples were wetted with excess water .

The interlayer distances of each crystalline swelling state and the so-called clearance spaces , i.e. ,the differences between the interlayer distance of anhydrous Na-taeniolite and those of the hydrated ones , are shown in Table 1 .

(001) distances of crystalline swelling states of 12.4 Å and 15.4 Å were reported for Na-montmorillonite 2) . The values of C and E for Na-taeniolite are nearly the same

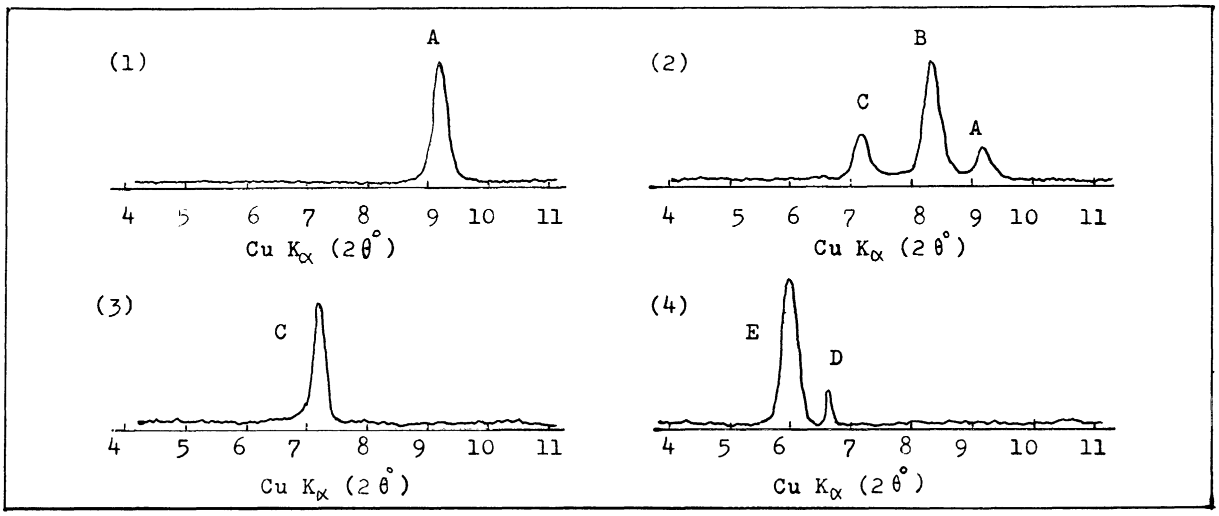

Fig. 1 Changes of X-ray diffraction patterns in (001) reflection region for Na-taeniolite with water content .

Table 1 Descriptions of four different crystalline states of hydrated Na-taeniolites

Crystalline swelling state	Interplanar distance (001)	Clearance space (C.S.)	C.S. / 2.76
A	9.61 (Å)	---------	--------
B	10.57 (Å)	0.96 (Å)	0.35
C	12.26 (Å)	2.65 (Å)	0.96
D	13.38 (Å)	3.77 (Å)	1.37
E	14.96 (Å)	5.35 (Å)	1.94

as these , although Na-montmorillonite is known to swell indefinitely with water .

The ratios of clearance space to 2.76 (Å) , which is the OH-O distance in ice crystal 3) , are also shown in Table 1 . As seen in Table 1 , the ratios of clearance space to 2.76 (Å) for C and E are nearly 1 and 2 , respectively . It can be seen from these facts that C and E correspond to the so-called one water layer hydrated type and two water layers hydrated type , respectively . It is probable that the interlayer water molecules in C and E are co-ordinated to the oxygen layers of Na-taeniolite by hydrogen bonds as shown by Hendricks for montmorillonite 4) , i.e. , planar hexagonal water networks were imposed in the interlayer spaces parallel to the silicate layers . Sodium ions are then postulated to exist at the centers of hexagonal water network for the former , and at the middle of two hexagonal water networks for the latter .

The states B and D can not be explained by Hendricks model as described hitherto . Similar swelling states have not been reported for Na-montmorillonite or any other substances which swell with water . As to the B state , it seems that a hydrated shell of sodium ion exists in the 12-fold co-ordination site , because the difference between the size of an H_2O molecule and that of a sodium ion is calculated to be about 0.7 - 0.8 Å , which is nearly equal to the clearance space of the B state . The D state is then assumed to be the mixed state of B and C . The B swelling step seems to be the transition process to the C step , and the D step also seems to be the transition process to the E step . The reason why B and D swelling processes exist in the case of Na-taeniolite and the corresponding processes can not be observed for Na-montmorillonite might be ascribed to the difference in the number of interlayer sodium ions , because Na-taeniolite contains much more (3 times) sodium ions than idealized montmorillonite 5) .

The high temperature X-ray diffraction studies on hydrated Na-taeniolite revealed nearly the same results as descrived before . But the D swelling state could not be observed , because it was too rapidly changed to the C step to observe .

DTA and TG curves for the two water layers hydrated type of Na-taeniolite were recorded by the thermobalance at the same time . It is obvious from Fig. 2 that the TG curve consists of two stages , and DTA curve shows two endothermic peaks , corresponding to the weight losses at TG curve . The first stage in TG curve is due to the dehydration process from E to C , in accordance with the high temperature X-ray diffraction studies . The DTA peak temperature for this dehydration process is 35°C . Thus the second stage in TG curve is attributed to the dehydration process from C to anhydrous Na-taeniolite . The DTA peak temperature (78°C) for the second stage is higher than that for the first stage . If the heating rate of DTA measurements was delayed to 1°C/min - 3°C/min , the second DTA peak was obscurely splitted into two peaks . This split on DTA peak suggests that C → A dehydration step is separated into two stages , i.e. , C → B and B → A dehydration processes , at the moderate dehydration rate . However , it was impossible to separate the first peak into two peaks like the second peak .

The weight loss at the second stage attained to 8 -9 % , which was nearly the same value as 9.02 % of the calculated value from Hendricks model , according to which one water layer type can be expressed in the form of $NaMg_2Li(Si_4O_{10})F_2 \cdot 2H_2O$. These facts seem to support Hendricks model and the chemical formula derived from it . Thus the two water layers hydrated type might be reasonably expressed as $NaMg_2Li(Si_4O_{10})F_2 \cdot 4H_2O$, which is analogous to

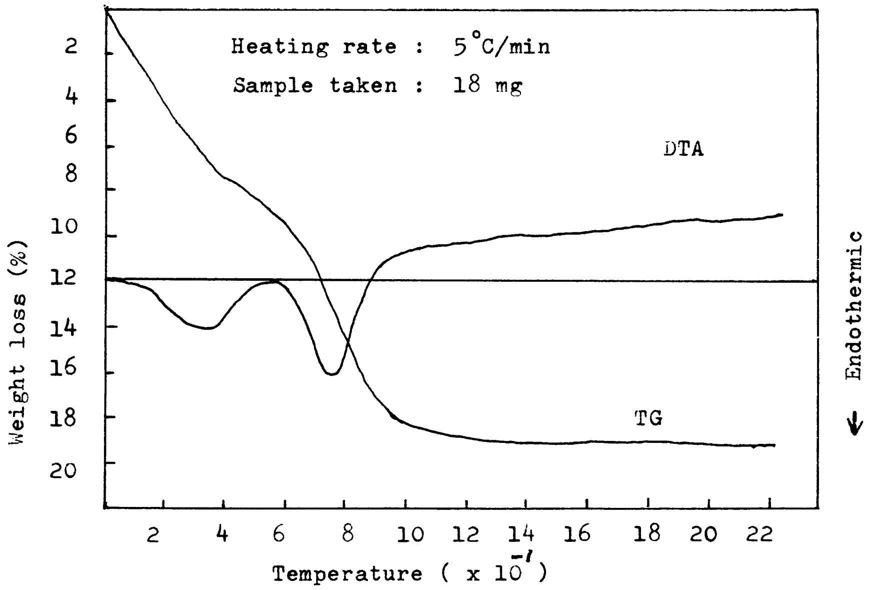

Fig. 2 DTA and TG curves for two water layers hydrated type of Na-taeniolite

the formula of vermuculite $(Mg,Fe)_3(Al,Si)_4(OH)_2\cdot 4H_2O$. From the discussions mentioned above B and D might be expressed as $NaMg_2Li(Si_4O_{10})F_2\cdot H_2O$, $NaMg_2Li(Si_4O_{10})F_2\cdot 3H_2O$, respectively .

It is interesting to study why Na-taeniolite can swell with water . The potassium substituted analogue of Na-taeniolite , i.e. , taeniolite $KMg_2Li(Si_4O_{10})F_2$ does not show any crystalline swelling with water . It seems probable that the swelling is due to the weakness of the attraction between the silicate layers . Thermal expansion can be considered to be nearly inversely proportional to the strength of chemical bonding . Therefore thermal expansion perpendicular to (001) plane seems to the parameter of the interlayer attraction .

The thermal expansion perpendicular to silicate layers were measured by the high temperature X-ray diffraction method for both taeniolites , and the comparisons were made . The peaks used for the measurements were (003) and (005) . The coefficient of thermal expansion measured from room temperature to 445 °C , of Na-taeniolite was $19 \times 10^{-6} deg^{-1}$, and that measured from room temperature to 540 °C, of taeniolite was also $19 \times 10^{-6} deg^{-1}$. These values suggest that the attraction between the silicate layers is equal for both taeniolites . However , these values of thermal expansion for both taeniolites are somewhat larger than that of fluor-phlogopite $KMg_3(AlSi_3O_{10})F_2$ (17×10^{-6} deg^{-1}) , which does not show any crystalline swelling with water 6) . So we can not help considering the difference of sodium ion and potassium ion , especially in relation to their hydration abilities , as the reason why swelling occurs only in the case of Na-taeniolite . The hydration energy of sodium ion (120.3 kcal/mol) is remarkably higher than that of potassium ion (76.5 kcal/mol) , and the hydration characteristics of sodium ion is known to be very different from that of potassium ion . In other words sodium ion is called structure forming ion , whereas potassium ion is called structure breaking ion 7) . Thus the strong hydration power of sodium ion might be the predominant reason why Na-taeniolite swells with water .

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