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INTERCALATION OF WATER IN KAOLIN MINERALS

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ABSTRACT

The behavior of the water intercalated into kaolin minerals after intercalation of KCH_3COO has been studied. Halloysite forms a well-known water complex with a 10.1 Å basal spacing, whereas kaolinite forms only a partial, and dickite no water complex. Nacrite forms another well-defined water complex with an 8.35 Å basal spacing. The following tabulation shows some of the other features of the two water complexes:

	Halloysite	*Nacrite*
Number of water molecule per $Si_4Al_4O_{10}(OH)_8$ unit	4	2
Frequency of OH bending vibration of water molecule	1627 cm^{-1}	1655 cm^{-1}
Peak temperature for dehydration	100–120° C.	200–210° C.

Two layer stacking sequences in which the individual water molecule is packed into the cavity of the oxygen hexagon to some extent have been proposed as models of the nacrite hydrate consistent with the *x*-ray data and other observations. The differences in hydration together with intercalation of NH_4Cl between the polymorphic varieties have been discussed in terms of the structural control over intercalation phenomena.

INTRODUCTION

The presence of kaolinite and its polymorphic varieties has posed a number of interesting problems. So far, most extensive studies have been carried out on the structural and morphological relationships between the individual members. It is established that the amount of the interlayer water is a key feature to differentiate halloysite from other minerals, yet no systematic study has been carried out on the behavior of the water molecules between the kaolin layers. This may have a potential importance in understanding hydration mechanism at the clay surface where the electric charge is relatively of minor importance. It seems interesting to know how the difference in detail of the surface structure affects hydration. Secondly, the study may throw light on the genetic relationships between the polymorphic varieties. In nature, halloysite has been the only mineral found in its hydrated form, though the reason for this occurrence has not been fully accounted for.

A main difficulty in the study has been in introduction of water molecules in between the kaolin layers. The intercalation of KCH_3COO together with water into kaolin minerals (Andrew *et al.*, 1960; Wada, 1961) opened the way to this approach. The behavior of the water molecules introduced into a dickite-nacrite, kaolinite and halloysite by washing the respective salt complexes with water has been studied by *x*-ray, infrared absorption and thermal analyses. In a preceding study (Wada, 1964b), a peculiar fixation of NH_4Cl was noticed for the same dickite-

nacrite. An attempt has therefore been made to clarify the relationships between the fixation and hydration reactions.

Materials and Methods

The minerals used are a dickite-nacrite from San Juanito, Chihuahua, Mexico, kaolinite from Birch Pit, Macon, Georgia and halloysite from Yoake, Oita. The former two were obtained from Ward's Natural Establishment Inc., New York (Dickite No. 15 and Kaolinite No. 2, Catalog No. 603).

Three set samples were prepared for the study (Table 1). The identification of the resulting complexes in this table is based on the results of the analyses presented later. The detail D of the respective preparations is given below:

Preparation A. A two gram clay sample was ground with 3.5 g of KCH_3COO in a mechanical agate mortar for 30 minutes (this procedure was omitted for halloysite) and placed with 20 ml of a saturated KCH_3COO solution in a 100 ml centrifuge tube fitted with a glass stopper. The tube was shaken for several minutes, allowed to stand for two days and centrifuged. The resulting KCH_3COO complex was washed succes-

Table 1. Description of Sample Preparation

Preparation	Mineral	Treatment[1]	Size fraction	Resulting complex
A	Dickite-nacrite	KCH_3COO (gr)—H_2O	–5, 5–20μ (2–20μ)[2]	Nacrite hydrate
A	Kaolinite	KCH_3COO (gr)—H_2O	–0.5, 0.5–2, 2–20μ (–150 mesh)	A partial hydrate of kaolinite
A	Halloysite	KCH_3COO—H_2O	–2μ (–150 mesh)	Hydrated halloysite
B	Dickite-nacrite	KCH_3COO (gr)—4 N NH_4Cl—2N NaCl—H_2O	(2–20μ)	NH_4Cl-dickite complex and nacrite hydrate
C	Dickite-nacrite	KCH_3COO (gr)—4 N NH_4Cl—5N KCH_3COO—H_2O	(2–20μ)	Nacrite hydrate

[1] Immersing or washing except for that subscribed by (gr) which notifies grinding.
[2] Size fraction before treatment.

sively with water till dispersion, and the various size fractions were collected by sedimentation or centrifugation.

Preparation B and C. After preparation of the KCH_3COO complex as described above, it was converted into an NH_4Cl complex by immersing in 4 N NH_4Cl for two weeks. The preparation was divided into two portions and suspended into 70 ml of 2 N NaCl (Preparation B) and 5 N KCH_3COO (Preparation C), respectively. After one hour, the suspensions were centrifuged, another portion of the respective extractants was added and kept for two days with occasional shaking. After centrifugation, washing with water was repeated three times. The extraction with 2 N NaCl effected only a partial extraction of interlayer NH_4Cl (fixation), whereas that with 5 N KCH_3COO resulted in a complete extraction (Figs. 2, 3; Table 6; Wada, 1964b).

X-ray diffraction patterns were obtained with powder or oriented specimens still moistened, dried at R.H. 65%, and heated progressively at 50, 100, 150 and 200° C. for two hours. Simultaneously, weight-loss was determined for 200 to 250 mg of some samples. Infrared spectra were obtained using a NaCl prism after pressing 2 to 2.5 mg of a sample kept at R.H. 60 to 70% for overnight or longer with 500 to 600 mg of KBr in a vacuum die. DTA was carried out in air with a 100 mg sample mixed with a proper amount of alumina to give a constant volume. Morphological changes after various intercalation treatments were checked by electron microscopy.

Results and Discussion

X-Ray data. The results listed in Table 2 show that the basal spacing of the mineral after KCH_3COO—water treatment differs from one mineral to another. Examination of the effect of heating on the basal spacing suggests that hydration can occur in between all the kaolin layers except for some of the dickite-nacrite, but it is different in the extent and in the reaction mechanism. No or only minor influence of the particle size was observed for the changes in the basal spacing. The halloysite forms a well-known water complex, whereas the kaolinite shows poor ability to form intercalation complex with water.

The 8.35 Å spacing observed with the dickite-nacrite deserves special attention. The corresponding reflection was sharp, and accompanied by the regular higher order reflections (Table 7). The shift to 7.2 Å upon repeated washings with methyl alcohol or acetone as well as heating gives a confirmation for formation of a water complex. Table 3 lists powder data obtained with the dickite-nacrite before and after the heat treatments together with those for reference specimens from literature. Examination

TABLE 2. BASAL SPACINGS OF KAOLIN MINERALS TREATED WITH KCH_3COO AND WASHED WITH WATER (Å)

Wet		Drying and heat treatment									
		Dried at R. H. 65%		Heated for 2 hrs. at 50° C.		100° C.		150° C.		200° C.	
					Dickite-nacrite, –2μ						
8.3	(7.5)[1]	—		—		—		—		—	
7.5	(2.5)	—		—		—		—		—	
					Dickite-nacrite, –5μ						
8.35	(7)	8.34	(7)	8.38	(6)	8.30	(5)	8.11	(2.5)		
7.25	(3)	7.16	(3)	7.20	(4)	7.14	(5)	7.17	(7.5)	7.17	(10)
					Dickite-nacrite, 5–20μ						
8.35	(6.5)	8.34	(5.5)	8.35	(5)	8.2	(3)	8.0	(2)		
7.15	(3.5)	7.13	(4.5)	7.14	(5)	7.17	(7)	7.14	(8)	7.11	(10)
					Kaolinite, –0.5μ						
7.6 7.3		12.1[2] 7.4 7.2		—		—		—		—	
					Kaolinite, 0.5–2μ						
7.5		7.48		7.40		7.25		7.17		7.14	
					Kaolinite, 2–20μ						
7.5		—		—		—		—		—	
					Halloysite, –2μ						
10.1		10.1		8.4 very 7.6 broad		7.44		7.38		7.22	

[1] Relative intensity estimated from peak height on recording chart.

[2] Due to montmorillonite as an impurity.

of the effect of heating on some reflections which can be used for differentiation of nacrite from dickite (italicized in the table) clearly indicates that hydration occurs primarily in the nacrite. The shorter basal spacing obtained with the unheated dickite-nacrite therefore indicates that the dickite has virtually no interlayer hydration capacity.

More numerous reflections appeared for the dickite-nacrite (Table 3) and kaolinite (Table 4) in comparison with the halloysite (Table 4) even after the intercalation and desorption treatments. This is important in indicating that the former higher crystalline polymorphs can retain a three-dimensional regularity in intercalation and restore some of their original structure after the expulsion of the interlayer material. Of course, there occur the displacements of the structural layers and the thinning of the crystallites. Their (*hkl*) reflections generally blurred and diffused, and were less in intensity than the original minerals. This is particularly true for the reflections in the "02, 11" band.

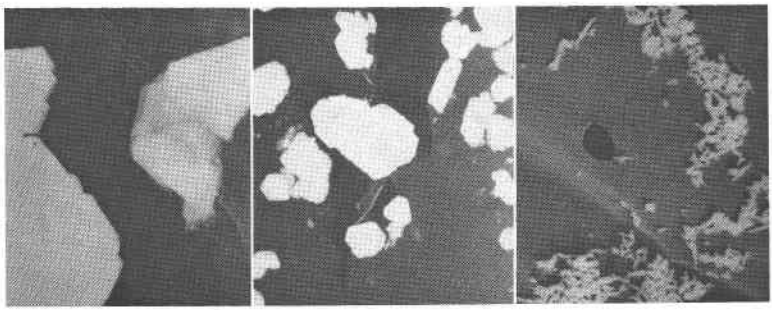

FIG. 1. Electron micrographs: a. Dickite-nacrite A, 5–20μ; b. Kaolinite A, 0.5–2μ; c. Halloysite A, -2μ. Width of print is 10μ.

These x-ray observations accord well with the results of electron microscopy. Major morphological features of the respective minerals were also well preserved after the KCH_3COO—water treatment (Fig. 1).

The observed specificity in the hydration was further confirmed in relation to the NH_4Cl fixation in the dickite-nacrite sample. The amount of the water complex in Preparation B and C was estimated from the intensities of its basal reflections (Fig. 2). The reflections that appeared at 10.1, 8.37–8.45 and 7.15–7.2 Å were assigned to those from NH_4Cl complex, hydrated and dehydrated forms of the minerals, respectively. The amount of the water complex can be regarded as the same irrespective of the fixation of NH_4Cl. It is inferred that there exist the reaction sites specific to water and NH_4Cl. The former would correspond to the interlayer

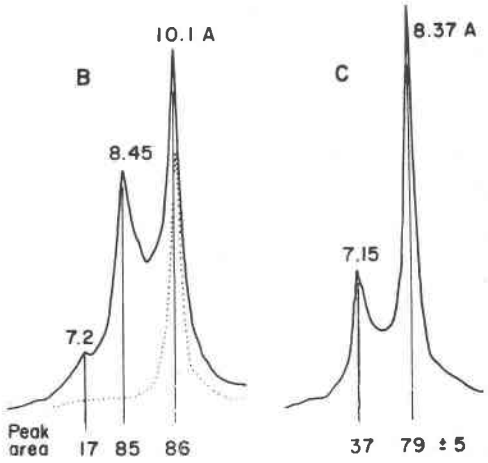

FIG. 2. X-ray patterns: Dickite-nacrite B and C (full line), and NH_4Cl complex (dotted line) from which Preparation B was obtained.

TABLE 3. *X*-RAY POWDER DATA FOR DICKITE-NACRITE

Dickite-nacrite Untreated		Dickite-nacrite KCH_3COO-H_2O -5μ				Dickite Reference[1]		Nacrite Reference[1]	
		R. H. 65%		200° C.					
d Å	I	d Å	I	d Å	I	d Å	I	d Å	I
		8.34	45						
7.18	72	7.08	22	7.16	63	7.16	10	7.17	10
4.44	25					4.44	4	4.41	7
		4.42	14	4.40	13				
4.37	36					4.37	3		
4.27	14	4.19	15			4.27	3		
4.13	38			4.12	10	4.13	7	4.12	3
3.95	11	*3.93*	7	*3.96*	6	*3.95*	2		
3.79	18	*3.80*	10	*3.79*	6	*3.79*	6		
3.59	78	3.56	25	3.58	55	3.59	10	3.58	10
3.48	10								
3.43	15	*3.43*	5	*3.43*	7	*3.43*	3		
3.23	2	3.19	7			3.27	2		
3.05	10			3.08	4B	3.10	2	3.06	1
2.93	7	*2.94*	4	*2.94*	2	*2.94*	2	*2.92*	1/2
2.80	4	*2.80*	4	*2.78*	2	*2.79*	2		
2.56	11	2.56	8	2.56	5	2.56	4	2.58	3B
2.50	16	2.49	5	2.50	6	2.51	5	2.50	
		2.46	6						
2.43	15			*2.43*	9	*2.40*	1	*2.44*	7
2.40	15			*2.39*	10	*2.38*	2	*2.40*	7
2.32	30	*2.33*	10	*2.33*	10	*2.32*	9	*2.33*	2
2.21	4	2.22	3B	2.20	1	2.21	2		
2.09	4	2.10	2	2.09	2B	2.11	1	2.10	1B
2.07	3	2.06	3B	2.05	3				
		2.02	3						
1.97	11	*1.98*	3	*1.98*	4	*1.98*	5	*1.98*	1/2
1.92	6					1.94	1	1.92	2B
1.90	5	1.91	3B	1.91	3B	1.90	2		
1.86	3					1.86	3	1.82	2
1.79	5	1.79	2	1.79	3	1.81	1	1.79	3
						1.79	1		
1.67	5							1.67	3B
1.65	11	*1.66*	5B	*1.65*	5	*1.65*	5		
1.56	5			1.55	3	1.56	4		
1.49	16	1.49	7	1.49	6	1.49	5	1.49	5
1.46	7					1.46	3	1.46	1

[1] Brindley (1961) p. 115 and 117.

I; peak height read from recording chart except for reference data.

B; broad reflection.

space of nacrite and the latter to that of dickite. This view was also supported from examination of the change in some reflections upon various heat treatments (Table 5). Actually, the assignment of the molecules intercalated on dickite and nacrite was done on the basis of the appear-

TABLE 4. *X*-RAY POWDER DATA FOR KAOLINITE AND HALLOYSITE

Kaolinite						Halloysite			
Untreated 2–20μ		KCH_3COO–H_2O 0.2–5μ				KCH_3COO–H_2O –2μ			
		R. H. 65%		200° C.		R. H. 65%		200° C.	
d	I	d	I	d	I	d	I	d	I
Å		Å		Å		Å		Å	
						10.1	23		
7.14	41	7.49	19	7.15	44			7.22	17
4.46	16	4.44	12	4.42	11	4.45	16	4.42	22
4.35	18			4.35	14				
4.18	17	4.19	11	4.19	11				
3.97	15								
3.58	40	3.56	20	3.57	42			3.60	15
3.38	2			3.40	5	3.36	9		
3.14	2								
				2.80	2				
2.56	11	2.56	8	2.56	9	2.56	7	2.56	7
2.53	10			2.52	8				
2.50	13	2.50	8	2.50	11				
2.39	7	2.40	3	2.38	6B				
2.34	23	2.34	12B	2.34	15			2.33	7
2.30	12			2.30	9				
2.24	5								
2.19	4	2.20	2B	2.19	2B				
2.07	1								
1.99	8	2.01	3B	1.99	5				
1.94	8			1.89	2				
1.84	3								
1.79	3			1.79	3				
1.73	4								
1.68	4					1.69	3	1.68	4
1.66	9	1.66	5B	1.66	7B				
1.62	4	1.62	3	1.62	3B			1.63	3
1.58	9								
1.54	3			1.54	1B				
1.49	11	1.49	7	1.49	7	1.48	5	1.49	3

I; peak height read from recording chart.
B; broad reflection

TABLE 5. SOME REFLECTIONS FROM DICKITE-NACRITE INTERCALATION COMPLEXES

Preparation and treatment	Intercalated molecules on		d Å (I)						
	dickite	nacrite							
Untreated	None	None	—	—	2.43 (30)	2.40 (30)	—	2.32 (60)	—
NH_4Cl complex	NH_4Cl	NH_4Cl	—	2.45 (5)	—	—	2.38 (5)	—	2.30 (5B)
B; R. H. 65%	NH_4Cl	H_2O	2.47 (10)	2.45 (9)	—	—	2.35 (8B)	—	—
B; 200° C.	NH_4Cl	None	—	—	2.43 (14)	2.40 (14)	—	—	2.31 (4B)
B; 450° C.	None	None	—	—	2.44 (16)	2.40 (16)	—	2.33 (14)	—
C; R. H. 65%	None	H_2O	2.48 (14)	2.46 (14)	—	—	—	2.33 (21)	—
Dickite[1]	None	None	—	—	—	2.41 (2)	2.39 (15)	2.32 (95)	—
Nacrite[1]	None	None	—	—	2.43 (60)	2.40 (40)	—	2.32 (15)	—

I; peak height read from recording chart except for reference data.
[1] Bailey (1963); also see reference data quoted in Table 3.

ance and disappearance of the reflections characteristic to the respective minerals.

A random and intimate intergrowth of dickite and nacrite in the same sample was reported by Molloy and Kerr (1961). In view of the present result, the two minerals are believed to be fairly well segregated and respond separately to the respective intercalation treatments. However, this does not mean that the sample is a mechanical mixture of the two. For example, the appearance of the two reflections at 10.1 and 8.45 Å (Fig. 2) suggests that a random mixing of 10.2 Å (NH_4Cl-dickite)/8.35 Å (nacrite hydrate) layer structures, and hence of dickite/nacrite, occurs to some extent. A noticeable enrichment of nacrite in finer fractions after treatments (Table 2) suggests that nacrite may dominantly occur in peripheral portions.

Infrared spectra. All the water intercalated in the kaolin minerals exhibited a broad band in the 3540—3500 cm^{-1} region due to its OH stretching vibration (Fig. 3). Heating at 200° C. resulted in some decrease in absorbance of this region. A peculiar variation, however, appeared in the OH inplane deformation band. The nacrite hydrate in both Preparation B and C shows a fairly sharp, strong absorption at 1655 cm^{-1}

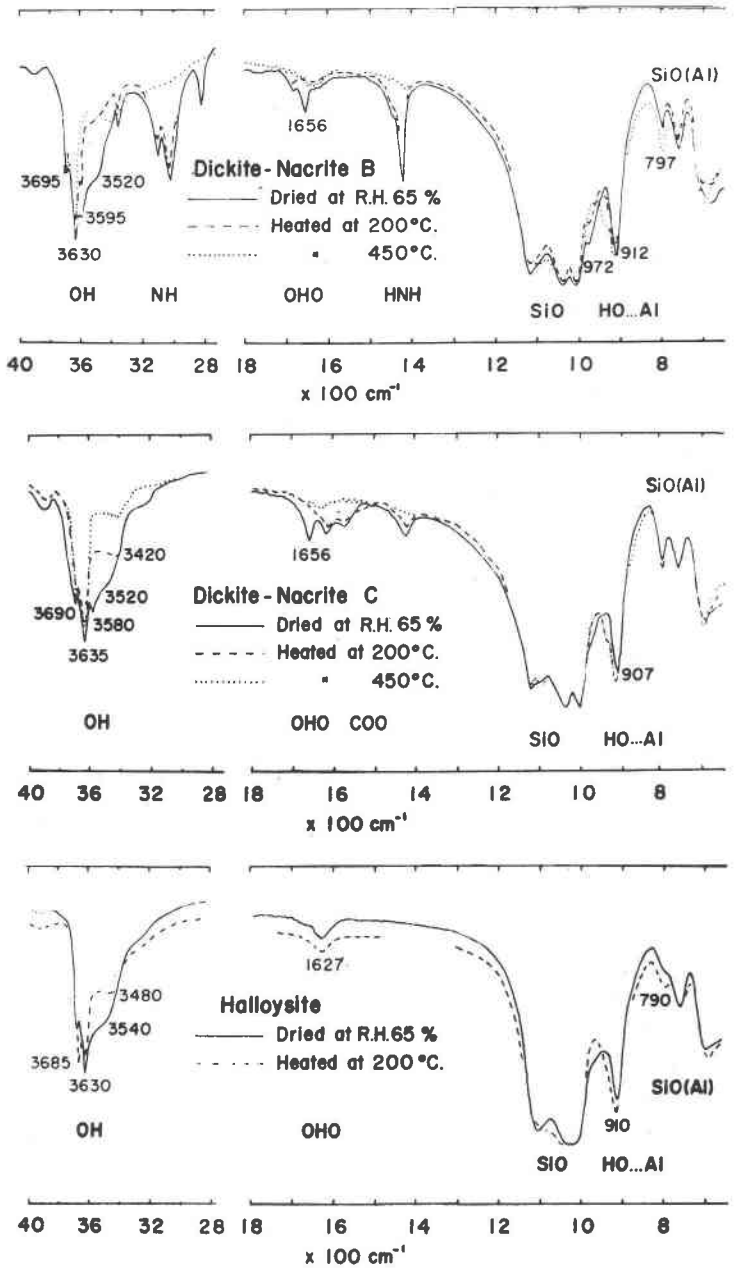

FIG. 3. Infrared spectra: a. Dickite-nacrite B; b. Dickite-nacrite C; c. Halloysite A.

in comparison with a relatively broad one at 1627 cm^{-1} for the hydrated halloysite. The absorption at 1655 cm^{-1} disappears, whereas the absorptions due to the remaining salts persist after heating at 200° C. The band at about 1630 cm^{-1} is common to the water adsorbed on the clay surface.

In the case of the water dissolved in various solvents, its deformation band shifts progressively upward as the base strength of the solvent increases. The following frequency series was noted by Greinacher, *et al.* (1955):

States or solvents	*(Vapor)*	CH_3NO_2	$(CH_3)_2CO$	*Dioxane*	*(Liquid)*	*Pyridine*	*(Solid)*
δ	1595	1623	1631	1638	1637	1650	1644
ν ass	——	3510	3440	3430	3428	3412	3256

δ; deformation band, ν ass; stretching band associated.

In the case of clay hydrates, so far as the author is aware, only the water assumed to be bound in the form of $Mg\text{-}OH_2$ in sepiolite gives a clear absorption around 1650 cm^{-1} probably due to its OH deformation (Shimoda, 1964). In both the cases, however, the upward shift of the OH deformation band associates much more downward shift for the stretching band due to strong hydrogen bond formation. Therefore, the result for the nacrite hydrate strongly suggests a unique and definite orientation of the water molecule intercalated.

The expulsion of the interlayer material upon heating restored almost all features of the infrared spectra of the original mineral. Only an exception is some increase in the absorbance of the 3400–3500 cm^{-1} region of the dickite-nacrite (Figs. 3a, b). This effect is particularly remarkable for Preparation B heated at 450° C., and may have a bearing on the lowering of the dehydroxylation temperature observed in DTA (Fig. 4). Extra adsorption of water may occur due to production of some defects possibly at the interlayer edge portions after expulsion of the interlayer material.

The modifications caused by intercalation have some important implications on the structural assignment of the OH groups in the original mineral (Serratosa *et al.*, 1963; Ledoux and White, 1964a, b; Wada, 1964a). However the effect of intercalation on the structural OH groups is generally less pronounced for water molecules in comparison with other salt and organic molecules. In the dickite-nacrite, a small peak appeared at 3580 to 3595 cm^{-1} (Figs. 3a, b) probably due to OH-O (H_2O) interaction in the nacrite. A partial shift of the structural OH deformation band from 935 to 970 cm^{-1} also associates with hydration. No noticeable change was found for the kaolinite, whereas the halloysite exhibited most remarkable change in the OH stretching vibrations (Fig. 3c).The direc-

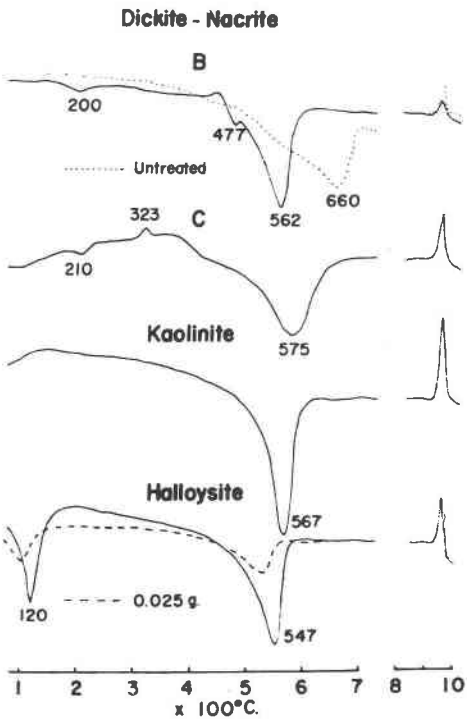

FIG. 4. DTA curves: Dickite-nacrite B,C, kaolinite A, 0.5—2μ and halloysite A, -2μ.

tion of the change is that expected for OH-O (H_2O) interaction resulted from a closer contact between OH and O (H_2O) in the hydrate than that between OH and O in an adjacent layer in the dehydrated form. The similar and the reverse changes in the relative intensity of the OH stretching vibrations were noted for halloysite upon glycerol solvation and heating, respectively (Serratosa *et al.*, 1963; Hayashi and Oinuma, 1963).

No particular strong interaction between OH and O (H_2O) or OH and Cl (NH_4Cl) is noted from the infrared spectra in bonding between water and nacrite or NH_4Cl and dickite in the respective complexes. The hydrogen bonding may not have primary importance in determining the stability of the resulting interlayer complex.

Thermal analyses data. The number of water and salt molecules intercalated can be calculated per $Si_4Al_4O_{10}(OH)_8$ unit from the thermogravimetric data (Table 6). The allocation of the weight loss in a temperature range to the respective components is based partly on the *x*-ray (Table 2) and the infrared data (Fig. 3), and partly on the result of the preceding study on the NH_4Cl complex (Wada, 1964b). Therefore, this allocation

TABLE 6. WATER AND SALT CONTENTS OF KAOLIN INTERCALATION COMPLEXES ESTIMATED FROM WEIGHT-LOSS DATA UPON HEATING (NUMBER OF MOLECULES PER $Si_4Al_4O_{10}(OH)_8$ UNIT)

Heating temperature range	Assignment	Mineral and preparation					
		Dickite-nacrite				Kaolinite	Halloysite
		Untreated 2–20μ	A –5μ	B 2–20μ	C 2–20μ	A 0.5–2μ	A –2μ
Room temperature (R. H. 65%) –200° C.	*Adsorbed water:* Total	tr.	1.31	1.25	1.75	0.78	4.35
200° C.—room temperature (R. H. 65%) Rehydration	External	tr.	0.28	0.30	0.48	0.30	1.29
	Interlayer[1]	tr.	1.03	0.95	1.27	0.48	3.06
200–400° C.	*Salt:* KCH_3COO	—	0.26	—	0.33	0.007 (0.04)[2]	0.07 (0.38)[2]
200–450° C.	NH_4Cl	—	—	0.92	—	—	—
400 or 450° C. —ignition	*Hydroxyl water*	4.12	4.20	4.36	4.23	4.02	3.63

[1] Total—External.

[2] Calculated as water molecule.

is sometimes approximate in nature due to an overlapping of the reactions as seen in the higher and lower hydroxyl content of the treated dickite-nacrite and halloysite, respectively.

The amount of the water intercalated in the dickite-nacrite is in the range of 0.95 to 1.27 on the molecular basis. The fact that this amount is essentially independent of the fixation of NH_4Cl again suggests that the site for the respective reaction has a specificity. The higher values noted for Preparation A and C may indicate association of some water molecules with KCH_3COO which remained in spite of repeated washings.

In the preceding study (Wada, 1964a), the intercalation capacity for NH_4Cl in the dickite-nacrite as a whole was estimated nearly two on the molecular basis. On the other hand, the saturation of the intelayer space with respect to water and NH_4Cl in Preparation B has been known to be

80 to 85% or more (Fig. 2). With these figures in mind, it may be inferred from the data for Preparation B (Table 6) that the intercalation capacity for water in the nacrite as well as that for NH_4Cl in the dickite is close to two on the molecular basis, and that the dickite-nacrite ratio in the sample is nearly 1 to 1. The *x*-ray data show that some strong reflections which can be used for differentiation between dickite and nacrite are comparable in their relative intensity with those expected for a 1 to 1 mixture of reference nacrite and dickite (Tables 3, 5).

In Preparation A and C, a significant amount of KCH_3COO remained against repeated washings with water (Table 6, Fig. 3b). In *x*-ray analysis, however, the position of KCH_3COO thus fixed remained unidentified. No similar phenomenon was noted for kaolinite and halloysite (Table 6, Fig. 3c).

The water content of the kaolinite at interlayer space corresponding to about one eighth in the ideal hydrated halloysite is in accord with the observed spacing of 7.5 Å (Table 2). According to the picture of random mixing, this spacing corresponds to that of a mixture of the dehydrated layer (7.15 Å) with the hydrated one (10 Å) in proportion in between 9:1 to 8:2 (MacEwan *et al.*, 1961).

The hydrated halloysite exhibited a water content of 4.35 H_2O in total and of 3.06 H_2O at interlayer space. No exact value for intercalation capacity as comparable with that of the nacrite is not known, but 4 H_2O in the ideal composition may be a good estimate taking consideration of relatively large external surface area.

The extra stability of the water intercalated in the nacrite has been shown in *x*-ray analysis (Table 2). In DTA, the dehydration peak appeared at about 200° C. for the nacrite and at 100 to 120° C. for the halloysite (Fig. 4), although the endothermic effect is less pronounced for the former than the latter even taking consideration of the amount of the water (*cf.* 0.025 g curve of halloysite). Some similar differences were noted upon thermal dissociation of NH_4Cl; NH_4Cl fixed in the dickite exhibited thermal dissociation peak at about 480° C., whereas the same peak appeared at 360 to 380° C. for NH_4Cl merely intercalated in the nacrite, kaolinite and halloysite, and at 330 to 340° C. for "free" NH_4Cl (Wada, 1964b).

The intercalation and subsequent expulsion of the interlayer material can cause some modifications on dehydroxylation reaction. This has been noted for urea-kaolinite (Weiss *et al.*, 1963), NH_4Cl-dickite, nacrite and kaolinite but not for NH_4Cl-halloysite (Wada, 1964b). In DTA, the intercalation of NH_4Cl resulted in remarkable decrease in the peak temperature together with increase in the symmetry of the peak shape for the former higher crystalline polymorphs (*e.g.*, dickite-nacrite B in Fig. 4).

The result was interpreted in terms of the rate of nucleation that will increase with increasing number of imperfection resulting from intercalation and subsequent expulsion of the interlayer material. In addition to this, the present curves indicate that the magnitude of the effect is also dependent on the material intercalated. Water again exhibited less pronounced effect than did NH_4Cl. This may possibly occur due to difference in creation of defects at the interlayer edge portions. The corresponding difference between Preparation B and C in the infrared spectra has been already discussed.

Water-kaolin complexes. The nature and configuration of water molecules in hydrated halloysite were discussed by Hendricks and Jefferson as early as in 1938. According to them, the water molecules are arranged in a hexagonal pattern, linked to each other and to the adjacent silicate layers by hydrogen bonding. On this view, the differences found here between the halloysite and other higher crystalline polymorphs in hydration are interesting. In the Hendricks-Jefferson picture, the stability of the water layer in hydrated halloysite arises mainly from its geometrical relationship to the oxygen atoms and hydroxyls of the silicate framework. Several significant distortions from the ideal geometry have recently been postulated for dickite (Newnham, 1961) and indicated by inference for kaolinite and nacrite (Brindley and Nakahira, 1958; Newnham, 1961; Bailey, 1963; Radoslovich, 1963). Thus, the observed trend in hydration may suggest that the fitness and misfit in the geometry in the resulting configuration primarily determine the stability of the "halloysite type" water complex.

The structure of the nacrite hydrate should at first comply with its observed basal spacing 8.35 Å and intercalation capacity, two water molecules per unit $Si_4Al_4O_{10}(OH)_8$. On this view, two most probable configurations A and B are worked out. Their atomic arrangement along the *c*-axis is depicted in Fig. 5 together with that postulated for hydrated halloysite (Hendricks and Jefferson, 1938). In A, the water molecule lies flat onto the cavity of the oxygen hexagon, whereas in B, the oxygen of the water molecule shows a slight upheaval on the one end and the OH bond directs slantingly downward. Both the configurations A and B show a good agreement in the (*OOl*) intensities between the observed and calculated (Table 7). A structure with a 16.7 Å basal spacing that consists of a single water layer per two kaolin layers may be considered[1], but this

[1] This line of interpretation has been advanced by W. F. Bradley (CIPEA Congress, Stockholm, 1964) for the 8.4 Å hydrate of the Juanito dickite. His picture is that of undulations in the water layers over regions of a few hundred Å units in the *b*-direction (Pers. comm., Dr. H. van Olphen).

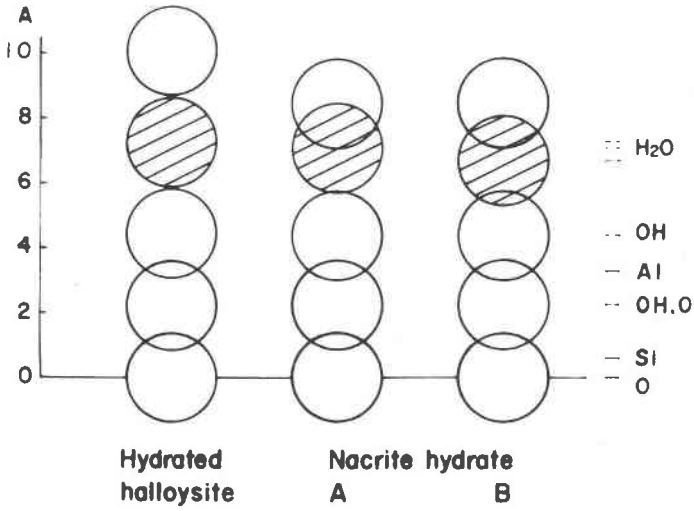

FIG. 5. A schematic presentation of layer stacking sequences for hydrated halloysite (Hendricks and Jefferson, 1938) and nacrite hydrate.

is eliminated on account of a total lack of the corresponding odd-order reflections.

In both the configurations A and B, the respective water molecules fit in someway into layer surface structure and are isolated. This picture seems to accord with the observed stability of the water in the nacrite hydrate and the smaller endothermic effect in the dehydration upon heating. Two "bent" long hydrogen bonds will be formed in both the configurations, although in general such deviations from linearity is not

TABLE 7. SPACINGS AND INTENSITIES CALCULATED AND OBSERVED FOR SOME (00l) REFLECTIONS FROM NACRITE HYDRATE

Order	$d_{calc.}$	$d_{obs.}$	$F^2\phi(\theta)\times10^{-3}$ Configuration		$I_{obs.}$[1]
			A	B	
1	8.35 Å	8.35 Å	340	316	300
2	4.18	4.18	81	60	84
3	2.78	2.80	4	14	16
4	2.09	2.11	13	17	16

[1] Estimated from peak area on recording chart.

Values of z parameters; 60:0, 4Si:0.07, 40+20H:0.26, 4Al:0.39, 60H:0.52, $2H_2O$:0.84(A), 0.79(B).

TABLE 8. INTERCALATION OF KCH_3COO, NH_4Cl AND WATER IN KAOLIN MINERALS AND BASAL SPACINGS OF RESULTING COMPLEXES (Å)

Mineral	KCH_3COO and Water	NH_4Cl		Water
		Intercalation	Fixation	
Nacrite	+(14)	+(10.2)	–	+(8.35)
Dickite	+(14)	+(10.2)	+(10.2)	–
Kaolinite	+(14)	+(10.2)	±(9.8)	±(7.5)
Halloysite	+(14)	+(10.4 −10.5)	–	+(10.1)

±; partial reaction.

energetically favored for formation of hydrogen bond in crystals (Pimentel and McClellan, 1960). Presumably a unique orientation of the water molecule involving these deviations may have a bearing on the observed abnormal OH bending vibrations in the infrared spectra, but no relevant data has been available at hand.

Table 8 gives a summary of the studies made so far on the intercalation phenomena in the kaolin minerals in relation to their polymorphic structure. Miller and Keller (1963) tried ethylene glycol solvation of KCH_3COO-treated kaolin clays. Since this was done following washings with water, their result could be used as a check to the formation of the water complex. Halloysite yielded 10.4 to 10.9 Å basal spacing, whereas kaolinite yielded 7.1 to 7.6 Å. The lower values were obtained with kaolin minerals in various fire clays including a ball clay. The Colorado dickite gave 7.2 Å basal spacing, while a small 10.7 Å peak together with the 7.1 Å one was noticed for the San Juanito dickite same as that used here as the dickite-nacrite. This response was interpreted as being due to intermixed halloysite but not to nacrite. In view of the present result, an interaction of ethylene glycol and nacrite seems more likely, and actually this possibility has been confirmed by direct washings of the KCH_3COO complex with ethylene glycol. Both the nacrite and dickite can form well-defined ethylene glycol complex of 10.8 Å basal spacing. Fifty per cent conversion occurred within 3 days, although then the reaction slowed down and did not complete even after 3 months.

The observed differences in intercalation between the polymorphic varieties (Table 8) may be taken as an indication of a structural control over the intercalation since factors other than the structural one such as the presence of interlayer cations can not have importance here. This view is consistent with the previous conclusions (*e.g.*, Wada, 1964a) that the intercalation is in nature a molecular association and that the geo-

metrical relationships between the interlayer material and mineral surface structure is of primary importance. Thus, some intercalation could be used as an indicator showing similarity and dissimilarity of the detailed layer structure of the kaolin minerals. The result summarized in Table 8 indicates a partial resemblance of the kaolinite structure either to the halloysite or to the dickite one, and a uniqueness of the nacrite structure. A broad parallelism may be noted between this and a recent structural analysis on the polymorphism of kaolin minerals by Bailey (1963).

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