

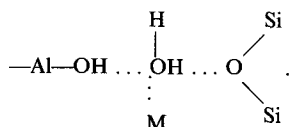
# INTERACTION BETWEEN ALKALI-HALIDES AND HALLOYSITE: I.R. STUDY OF THE INTERACTION BETWEEN ALKALI-HALIDES AND HYDRATED HALLOYSITE

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**Abstract**—Halloysite was mechanically ground in the presence of NaCl, KCl, KBr, RbCl and CsCl, and i.r. spectra were recorded after various periods of grinding, up to 10 min. Changes in the wavenumbers and sharpness of absorption bands were interpreted using assignments accepted for kaolinite. Diminution of absorption bands of OH groups and the appearance of new bands indicate formation of complexes of halloysite with KCl, KBr, RbCl, and CsCl. Water was essential in the complex formation, which may be formulated:



The amount of the complex formed depended on the salt and the time of grinding. Complex formation requires that the cation be large enough to serve as a “structure breaker” of the interlayer water sheet. Complex formation also requires that the cation be a weak electron acceptor. Grinding also led to changes in the fine structure of the tactoid.

The possibility of using the i.r. spectrum of halloysite as a finger print for identification of the mineral is discussed. It was concluded that NaCl is the most reliable dispersing agent to determine whether or not a mineral sample belongs to the kaolinite group. Disks in RbCl may be used to differentiate between kaolinite and hydrated halloysite.

## INTRODUCTION

The present communication is concerned with the effects of alkali halides on the i.r. absorption spectrum of hydrated halloysite. There are two purposes for this study:

(1) Since the publications of Wada (1959a,b) on the oriented penetration of ionic compounds between the kaolin-like layers of halloysite, no satisfactory explanation has been given as to why the interaction with the salts of  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  resulted in reversible lattice expansion, whereas smaller monovalent cations, such as Li and Na, and divalent cations Mg, Ca and Ba, gave no evidence of the reaction.

According to Garrett and Walker (1959) the ability of the cation to enter into the structure is influenced by its hydration shell. Very low hydration of the cation favors complex formation. This model fails to explain why small and divalent cations do not form this complex under low humidities.

According to Wada (1959a,b), insofar as the monovalent cation is concerned, the reaction seems to occur only with salts in which the cation does not fit into the cavity of the oxygen network. That is the geometric fitting of the cation into the surface structure of the oxygen layer of clay minerals seems to

have prime importance in the reaction. This model fails to explain the behavior of the divalent cations. In spite of the similarity of ionic radii of  $\text{Ba}^{2+}$  to  $\text{K}^+$ , there is no evidence of any reaction of the salts of this cation with the halloysite. The present study is an attempt to give an alternative explanation of this behaviour. Recently, Yariv (1975a,b) showed that i.r. studies may provide information on the mechanism of the reactions which occur during grinding of kaolinite in the presence of alkali halides. It seems plausible to compare i.r. absorption spectra of hydrated halloysite ground in the presence of various alkali-halides.

(2) The i.r. absorption spectrum of halloysite reveals some peculiar properties which differ from those of other minerals of the kaolinite group. According to Chukhrov and Zvyagin (1966), changes in the spectra can be accepted as an empirical characteristic of the degree of structural perfection. Askenasy, Dixon and McKee (1973) attributed changes in position of absorption bands and their intensities to the concentration ratio between loosely bonded (expanded) layers and platy material. Recently, Yariv and Shoval (1975) showed that when a disk of hydrated halloysite is prepared using CsCl as the dispersing agent, the i.r. spectrum differs from that of halloysite deposited by evaporation from a suspension onto supporting

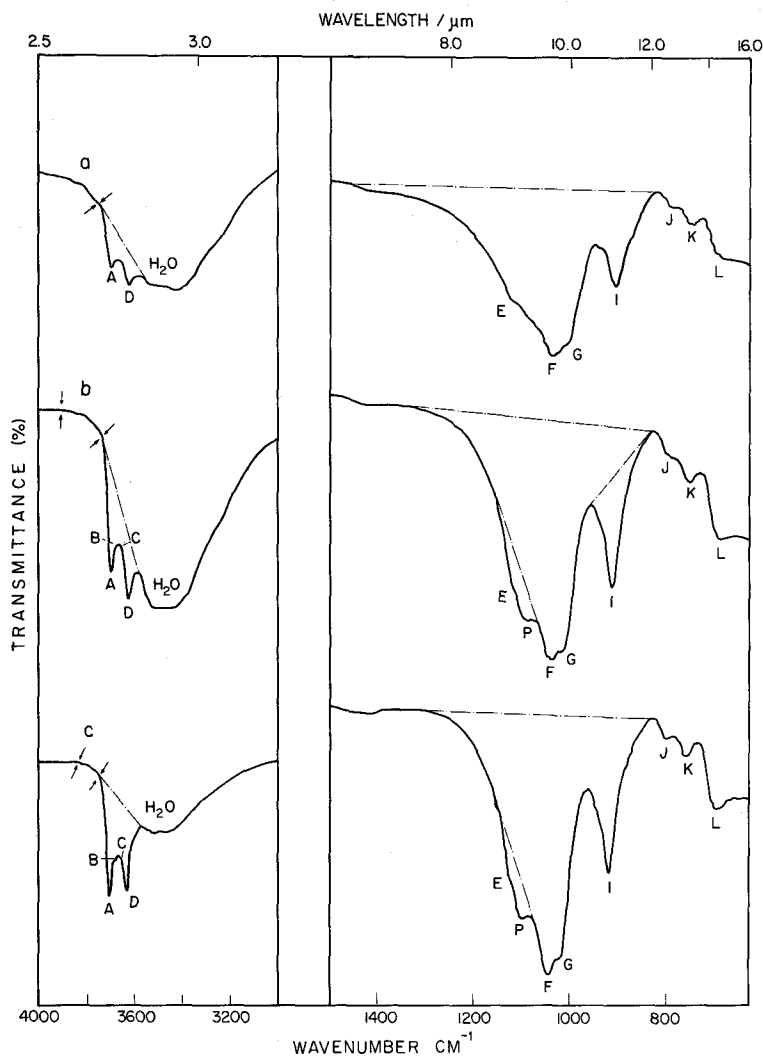


Fig. 1. I.r. spectrum of Eureka halloysite in NaCl disks (a) unground, freshly prepared (b and c) ground for 5 min, freshly prepared, and dried two months at 105°C respectively.

windows, due to a complex formation with the alkali-halide. It seems plausible to examine whether or not differences in the spectra of various halloysites reported in the literature are due to complex formation with the dispersing alkali-halides.

#### EXPERIMENTAL

The halloysites used in the present study are from Eureka, Utah, U.S.A. (Hebrew University Collection) and from Te-Puke, New Zealand (kindly donated by Prof. J. B. Dixon from Texas A & M University and described by Hughes, 1966). Both samples were in a hydrated state. The halides were analytical grade reagents. They were used after being ground for 5 min and dried overnight at 105°C.

A disk of unground halloysite was prepared from 0.8 mg of the clay and 125 mg of the salt. Disks of ground halloysite were prepared from 0.3 mg of the clay and 125 mg of the salt. The mixtures were ground

in an agate mortar for various times up to 10 min before being pressed into disks.

The spectra were run on a Perkin-Elmer 237 spectrophotometer immediately after preparation of the disks and also after drying the disks at 105°C for various periods of time. Parallel experiments were carried out with dehydrated halloysites.

#### RESULTS

Some of the spectra obtained with mixtures of halloysite from Eureka are shown in Figs. 1-3. Similar curves were obtained using halloysite from Te-Puke. The wavenumbers of the absorption bands maxima are listed in Table 1, together with the assignments of the bands.

As will be discussed later, the maxima of the bands F, G, L and P depend on the time of grinding and the alkali halide used. Grinding periods longer than 10 min result in broadening and diminution of bands

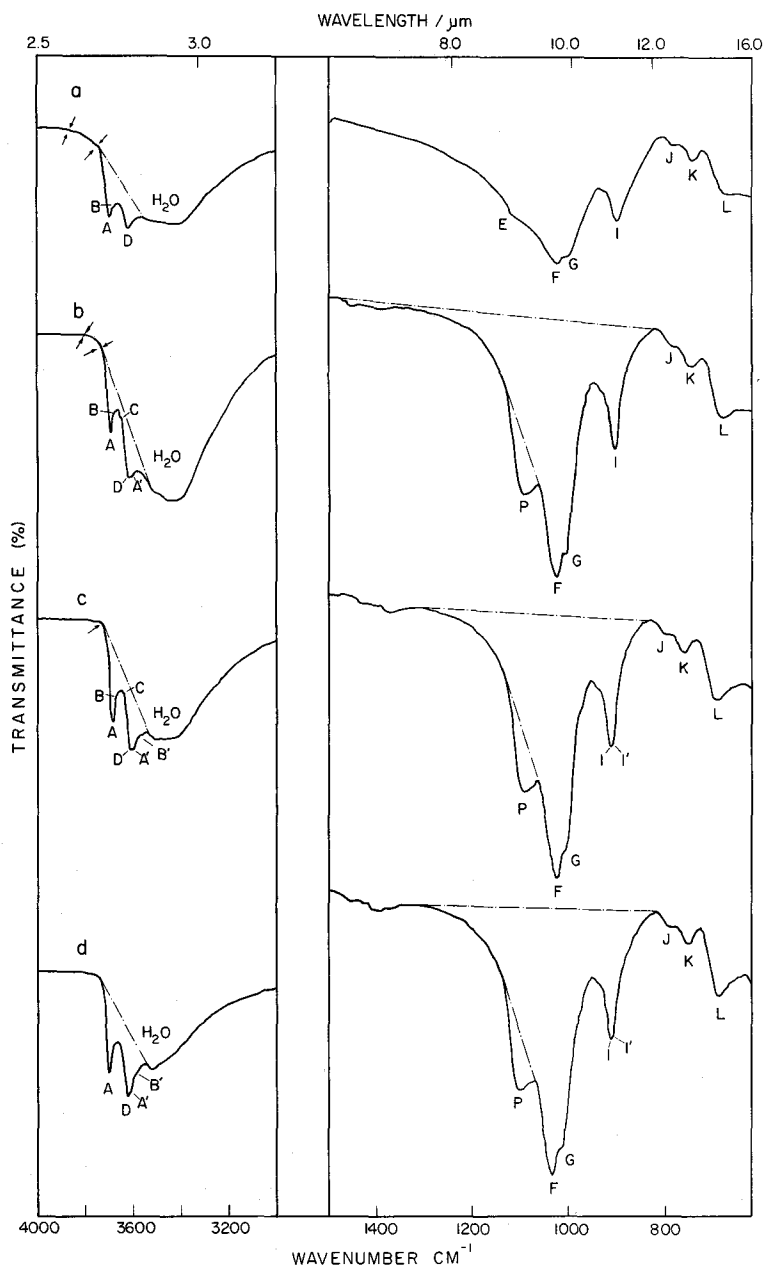


Fig. 2. I.r. spectrum of Eureka halloysite in KCl disks (a) unground, freshly prepared (b, c and d) ground for 10 min, freshly prepared, dried 3 weeks and 2 months at 105°C respectively.

belonging to the kaolin-like layers due to the transformation of the mineral into amorphous material. They are not further discussed.

Disks of halloysite hold water much more firmly than disks of kaolinite. Water bands were clearly observed with all samples even after drying the disks for two months. Wavenumbers of the stretching bands are listed in Table 2.

Changes in water content can be observed in both the stretching and the bending vibrations of H<sub>2</sub>O. The sorbed water content increased with a longer time of grinding. The disks lost considerable amounts

of water after being dried at 105°C for 24 hr. On further heating the disks progressively lost more water, but the band at 3500–3525 cm<sup>-1</sup> did not decrease. With KCl, RbCl and CsCl, this band increased with increasing time of grinding.

#### INTERPRETATION OF THE SPECTRA

The effects of grinding on the absorption frequency of the various vibrations and the intensity and sharpness of the bands can give some information on the processes occurring during grinding.

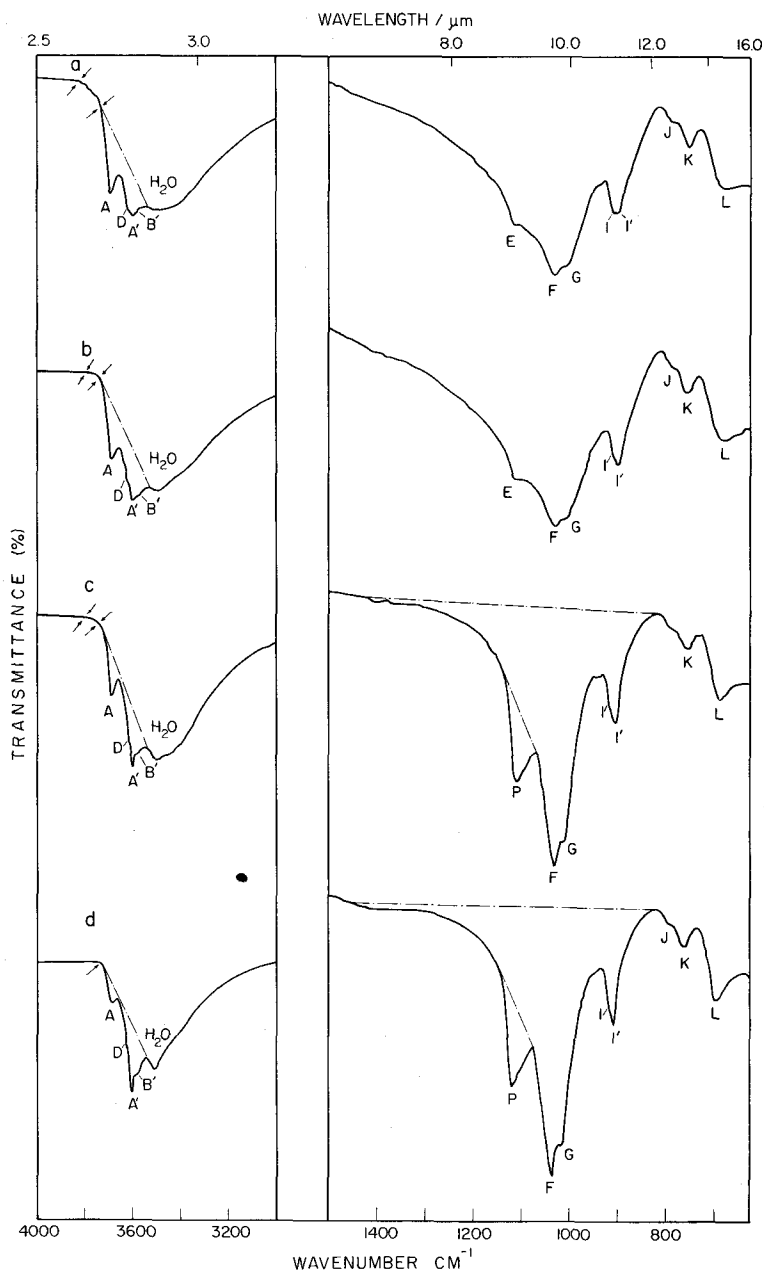


Fig. 3. I.r. spectrum of Eureka halloysite in RbCl disks (a and b) unground, freshly prepared and dried 3 weeks at 105°C respectively (c and d) ground for 5 min, freshly prepared and dried 2 months respectively.

$N_i$ , the ratio between the intensity of band  $i$  and that of a reference band  $R$ , is given by

$$N_i = \frac{\log(T_{bi}/T_i)}{\log(T_{bR}/T_R)} = \frac{A_i - A_{bi}}{A_R - A_{bR}}$$

where  $T_i$  and  $T_{bi}$  are the percent transmission values measured for the band peak and for an extrapolated base-line, at the same frequency, respectively.  $A_i$  and  $A_{bi}$  are the values of absorbance obtained for the band peak and the extrapolated baseline.

#### *Indications of complex formation.*

Diminution of absorption bands of OH groups, resulting in the appearance of bands  $A'$  and  $B'$ , may serve to indicate formation of complexes of halloysite with alkali-halides.

Grinding in the presence of NaCl did not lead to any shift in the frequencies of these bands. They appeared at wavenumbers similar to those observed with unground halloysite deposited on AgCl windows (Yariv and Shoval, 1975). On the other hand, grinding

Table 1. Wavenumbers of i.r. absorption bands (in  $\text{cm}^{-1}$ ) of Eureka halloysite in disks of alkali halides: (unless stated values are given for mixtures which were ground for 5 min and dried for 24 hr)

Band assignment	Symbol	NaCl disk	KCl disk	RbCl disk	CsCl disk
OH stretching	A	3700	3700	3688 v.w.	3688 v.w.
	B	~3675 sh.	~3675 sh.	—	—
	C	~3650 sh.	~3650 sh.	—	—
	D	3629	3629	~3629 w.sh.	~3629 w.sh.
	A'		(3606 sh.)*	3606	3606
	B'		(3578 sh.)*	~3578	~3578 sh.
Si-O stretching	E†	1120 sh.	1120 sh.	1115 sh.	—
	F	1035	1031	1030	1024
	G‡	1013*	1012	1009	1004
	I, I'	912	912	903	901
Al-OH deformation	J	790 sh.	790 sh.	790 w.sh.	—
	K	748	745	753	752
	L	685 sh.	688	690	690

v.—very, w.—weak, sh.—shoulder, \* 10 min. grinding, † unground, ‡ 2 months drying.

with KCl or KBr led to changes in the spectrum of halloysite; these changes were enhanced by drying the disk at  $105^\circ\text{C}$ . A new band and a shoulder were developed at 3606 and  $3578\text{ cm}^{-1}$ , respectively. These effects are similar to those observed in the spectra obtained with kaolinites ground with CsCl (Yariv, 1975c). Interaction with interlayer water molecules causes perturbation of the basal OH groups, causing shifts in bands A, B and C to give A' and B'.

The effects were much more drastic when RbCl and CsCl were used as diluents. In this case, bands A' and B' were observed even with disks of unground mixtures. Furthermore, band A not only decreased in intensity but shifted from 3700 to 3688 and  $3685\text{ cm}^{-1}$  for Eureka and Te-Puke halloysites, respectively. The band at  $3688\text{--}3685\text{ cm}^{-1}$  is due to these basal OH groups which do not react with interlayer water.

Band I diminished with increasing grinding time. At the same time, a sharp band I' developed at a lower frequency, which is a perturbed Al-OH deformation vibration.

Band J is a Si-O-Si vibration and an out-of-phase vibration of the hydroxyl group of the gibbsite-like layer. This band disappeared after a short period of grinding halloysite with CsCl. It became very weak however it was still detectable even after 10 min of grinding with RbCl.

Ratios  $N_A$  and  $N_{A'}$ , using band D as a reference standard, and baselines as those shown in Figs. 1-3, are given in Table 3. The reduction in intensity of band A, which is apparent with KCl, RbCl and CsCl, is correlated with the appearance and increase of band A'. The highest proportion of complex is obtained with CsCl and decreases with RbCl. It decreases further with KCl and is not formed at all with NaCl.

The paired bands F and G (shoulder) are Si-basal oxygen in-plane vibrations. A spectrum of halloysite film deposited on a AgCl window showed band F at 1033 and  $1039\text{ cm}^{-1}$  for the Eureka and Te-Puke halloysite, respectively, and a shoulder at  $1008\text{ cm}^{-1}$

(band G). Freshly prepared disks of unground mixtures showed the same band maxima. On grinding with NaCl, band F was not affected but was perturbed by the other salts. The amount of perturbation was greatest with CsCl and decreased with RbCl and KCl, respectively. Perturbation of the bands increased upon drying the disks. From Table 1 it is obvious that the same salts caused perturbation of band G. These results indicate that during the formation of the complex, hydrogen bonds are formed between interlayer water molecules and basal oxygens.

#### Indications of changes in the microstructure of the tactoid

As was previously shown for kaolinite (Yariv, 1975), the changes observed for band P may indicate changes in the size of the tactoid. This is an Si-O out-of-plane vibration of the kaolin-like layer. In spectra of disks of unground mixtures, band P appeared as a tail on the left side of band F. This corresponds to absorption by randomly oriented tactoids. Upon grinding, sharpening and shifting of band P to higher frequencies is observed, indicating that delamination of the tactoid occurred.

Baselines were drawn for the peaks as shown in Figs. 1-3. If such baselines are used, changes in  $N_p$ , the ratio between the intensity of band P and that

Table 2. Absorption stretching bands (in  $\text{cm}^{-1}$ ) of  $\text{H}_2\text{O}$  in spectra of Eureka halloysite

Dispersing salt	Immediately after grinding	2 months after grinding (dried)
NaCl	3525-3430	~3525, 3460-3440
KCl	3525 sh., 3440-3400	3520 br., †
RbCl	3510 br., 3440 sh., 3390 sh.	3510 br., †
CsCl	3500 br. (3370 sh.)*	3500 br., 3370 sh.

br.—broad; sh.—shoulder; †—tail, absorption at wavenumber  $< 3500\text{ cm}^{-1}$ . A maximum on a shoulder could not be defined.

\* Observed only with ground samples.

Table 3. Effects of time of grinding and drying at 105°C on ratios  $N_A$  and  $N_{A'}$  between intensities of bands A and A' respectively and of band D in spectrum of Eureka halloysite

Dispersing salt	Time of grinding	Immediately after grinding		1 day after grinding		1 week after grinding		3 weeks after grinding		2 months after grinding	
		$N_A$	$N_{A'}$	$N_A$	$N_{A'}$	$N_A$	$N_{A'}$	$N_A$	$N_{A'}$	$N_A$	$N_{A'}$
NaCl	min.	$N_A$	$N_{A'}$	$N_A$	$N_{A'}$	$N_A$	$N_{A'}$	$N_A$	$N_{A'}$	$N_A$	$N_{A'}$
	0	1.21	0.00	1.14		1.09		1.20		1.15	
	5	1.21	0.00	1.12		1.15		1.31		1.28	
KCl	10	1.45	0.00	1.35		1.33		1.45		1.40	
	0	1.31	0.00	1.25	0.00	1.34	0.00	1.32	>0.00	1.25	>0.00
	5	1.17	>0.00	1.17	>0.00	1.23	0.80	1.11	0.88	1.16	0.88
RbCl	10	0.92	0.81	0.99	0.85	1.05	0.90	1.10	0.86	1.00	0.85
	0	1.29	0.92	1.12	1.03	1.20	1.05	1.12	1.22	1.06	1.23
	5	0.87	1.52	0.83	1.65	0.85	1.69	0.52	2.39	0.48	2.23
CsCl	10	0.48	1.92	0.56	2.17	0.45	2.12	0.42	3.40	0.37	3.60
	0	1.02	1.06	0.93	1.19	0.77	1.41	0.73	1.89	0.59	1.76
	5	0.84	1.82	0.65	2.37	0.46	2.57	0.45	2.59	0.29	2.43
	10	0.51	2.15	0.48	2.65	0.31	3.44	0.27	3.98	0.09	3.80

of the reference standard, band F, can give information on changes in the sharpness of the band. Changes in wavenumber and sharpness of the band caused by different times of grinding and heating at 105°C are summarized in Table 4. From Table 4 it is obvious that delamination results from grinding, but heating the disk has no further effect. The highest proportion of single sheets is obtained with CsCl and RbCl. This decreases further with KCl and NaCl, respectively.

Since band L is also due to a perpendicular vibration of the kaolin-like layer, delamination of the tactoid by grinding caused this band to sharpen and to be displaced to higher frequencies. Rate of sharpening increased in the order NaCl < KCl < RbCl < CsCl. A spectrum of halloysite film deposited on a AgCl window showed this band at 680 cm<sup>-1</sup> (Yariv and Shoval, 1975). A shoulder at 680 cm<sup>-1</sup> was observed with unground halloysite in NaCl and KCl. A weak and broad peak, which sharpened on heating at 105°C, was observed at the same frequency with unground RbCl and CsCl. With samples ground with NaCl and CsCl for 10 min and left 7 days at 105°C, band L sharpened and appeared at 690 and 695 cm<sup>-1</sup> respectively.

Band A had a tail at 3720–3800 cm<sup>-1</sup>, which clearly appeared in the spectra of unground halloysite with each of the alkali-halides examined (see arrows in

Figs. 1–3). This tail diminished slowly on grinding. It further diminished on drying the disks at 105°C. Its diminution depended on the salt used. The rate of diminution increased in the order NaCl < KCl < RbCl < CsCl. The changes observed can be interpreted according to previous work on grinding kaolinite (Yariv, 1975b). The tail corresponds to some basal hydroxyl groups which are inclined at angles differing from those of the bulk hydroxyls, due to some kind of tension existing in the layer when it is part of a tactoid. The diminution of the tail, which is associated with the increase in the intensity of band A, corresponds to the turning of the hydroxyls to their ideal positions. This is due to the release of tension as a result of the delamination of the tactoid, or the disintegration of curved or bent layers. The increment in absorbance of band A can be seen from the ratios  $N_A$  for halloysite in NaCl, which increased after 10 min grinding (Table 3). It cannot be observed from  $N_A$  values obtained for the other halides, because of the interaction of the basal hydroxyls with interlayer water molecules. Due to curvatures and bending of the kaolin-like layers in halloysite, this tail is much bigger in the spectrum of halloysite than in the spectrum of kaolinite. Furthermore, its diminution requires longer periods of grinding.

Table 4. Effects of time of grinding and drying at 105°C on the maximum (in cm<sup>-1</sup>) of band P and on ratio  $N_P$  between intensities of band P and of band F in spectrum of Eureka halloysite

Dispersing salt	Time of grinding	Immediately after grinding		1 day after grinding		1 week after grinding		2 months after grinding	
		cm <sup>-1</sup>	$N_P$	cm <sup>-1</sup>	$N_P$	cm <sup>-1</sup>	$N_P$	cm <sup>-1</sup>	$N_P$
NaCl	5	1085 (1093 sh.)	0.11*	1091	0.14	1093	0.15	1093	0.17
	10	1090	0.16	1095	0.18	1095	0.19	1095	0.19
KCl	5	1085 (1093 sh.)	0.08*	1086 sh.	0.08	1095 sh.	0.11	1095 sh.	0.10
	10	1100	0.22	1100	0.22	1100	0.24	1095	0.19
RbCl	5	1106	0.30	1106	0.30	1110	0.30	1112	0.32
	10	1110	0.44	1112	0.42	1112	0.42	1112	0.44
CsCl	5	1112	0.33	1112	0.32	1115	0.31	1112	0.32
	10	1112	0.41	1115	0.43	1115	0.40	1112	0.42

\* Calculated for absorbance at 1085 cm<sup>-1</sup>. sh.—shoulder.



The sharpness of band G may give information as to whether the hexagonal sheet is more or less uniform. This is usually very sharp in the spectra of kaolinites but it only appears as a shoulder or a weak band in the spectra of halloysites. This band is slightly sharpened upon grinding (Figs. 1–3). In the tactoid, disturbing effects, such as bends existing in the layers, may cause basal oxygens to move from their ideal positions. Sharpening of this band by grinding may be the result of the movement of more and more oxygens to their ideal positions. This may be related to the release of tension in the layer as a result of delamination and breaking of bent layers.

#### I.R. SPECTRUM OF DEHYDRATED HALLOYSITE

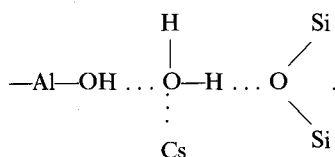
These clay samples were dried three days at 105°C before mixing with alkali-halides. Infrared spectra of Te-Puke halloysite, ground 1 min with alkali-halides and recorded immediately after pressing the disks, are shown in Fig. 4. Drastic differences between the spectra of hydrated and dehydrated halloysite were obtained only for potassium halide. When dehydrated halloysite was dispersed, either in KCl or in KBr, no complex was formed even after prolonged grinding.

When dehydrated halloysite is ground with RbCl and CsCl the absorption spectra obtained are similar to those obtained for hydrated halloysites, except that the complex formation and delamination occur more slowly. In the case of NaCl, the effect of grinding on the sorption of water by the disk was very small. It should be remembered that this effect was very great when hydrated halloysite was ground with NaCl.

#### DISCUSSION

##### *Interaction between alkali-halides and halloysite*

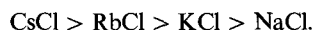
The i.r. spectra reveal that the penetration of K, Rb and Cs salts into the interlayer space of the halloysite results in hydrogen bonding between the water molecules and the kaolin-like layers. The mechanism of formation of this complex is similar to that previously described by Yariv (1975a,c) for the complex formed between CsCl, water and kaolinite. Water molecules coordinate with the alkali cations. At the same time they may interact with basal hydroxyls and basal oxygens of two adjacent parallel kaolin-like layers. The three way interaction may be formulated as follows:



The water molecule in this association must be situated in such an orientation that will enable it to

interact at the same time with both kaolin-like layers and the alkali cation.

Electron donation properties of water coordinated with alkali metal and hydrogen bondings to basal hydroxyls are affected by the salts in the following decreasing order:



Stretching absorption bands of H<sub>2</sub>O are compatible with this model.

From a consideration of polarization effects it would be expected that the strength of hydrogen bonding formed between interlayer water and basal oxygens of kaolin-like layers will increase with decreasing atomic weight of the alkali cation. From bands F and G it is obvious that the opposite is correct. Bonner *et al.* (1973, 1974) found that the effect of alkali metals in modifying the water structure in solutions falls in the order Cs > Rb > K > Na. They explain this phenomenon by the size of the sodium ion which is such that it can apparently fit into the interstitial cavities of water with minimum disruption of the water structure. The same explanation can be adopted to describe changes in the interlayer single sheet of water in hydrated halloysite. In the absence of any salt the orientation of water molecules inhibits hydrogen bonding to the basal oxygens. There is distorted hydrogen bonding between these molecules, resulting in an absorption band at 3550 cm<sup>-1</sup>. Sodium ions can fit into the interstitial water cavities. The structure of the interlayer water sheet is not disrupted and hydrogen bonding with basal oxygens or basal hydroxyls does not occur. Hydrogen bonding between water molecules in the sheet may be enhanced, resulting in absorption in a region lower than 3550 cm<sup>-1</sup> (Table 2). Due to electrostatic repulsions, this complex is not stable and is not formed under the conditions described by Wada (1959a,b). Bigger ions, which cannot fit into the cavities, may be considered as structure breakers of the water sheet. A new structure is developed which is stabilized by hydrogen bonding of the sheet with kaolin-like layers on both sides.

According to Cruz, Jacobs and Fripiat (1973) the main contribution to the interaction between the layers in minerals of the kaolinite group is electrostatic. In the presence of liquid inside the interlayer spaces (even a few molecules), the electrostatic attractive force is strongly decreased by the high increase of the dielectric constant, and intercalation may take place. Their hypothesis is in line with our observations on the effect of drying the halloysite on its ability to form complexes. No potassium complex was formed with dry halloysite, even after prolonged grinding. The previous discussion leads to the following conclusions: (1) Interlayer water molecules take part in complex formation between alkali-halides and halloysite; (2) The cation must be large enough to serve as a "structure breaker" of the interlayer water sheet; (3) The cation must be a weak electron accep-

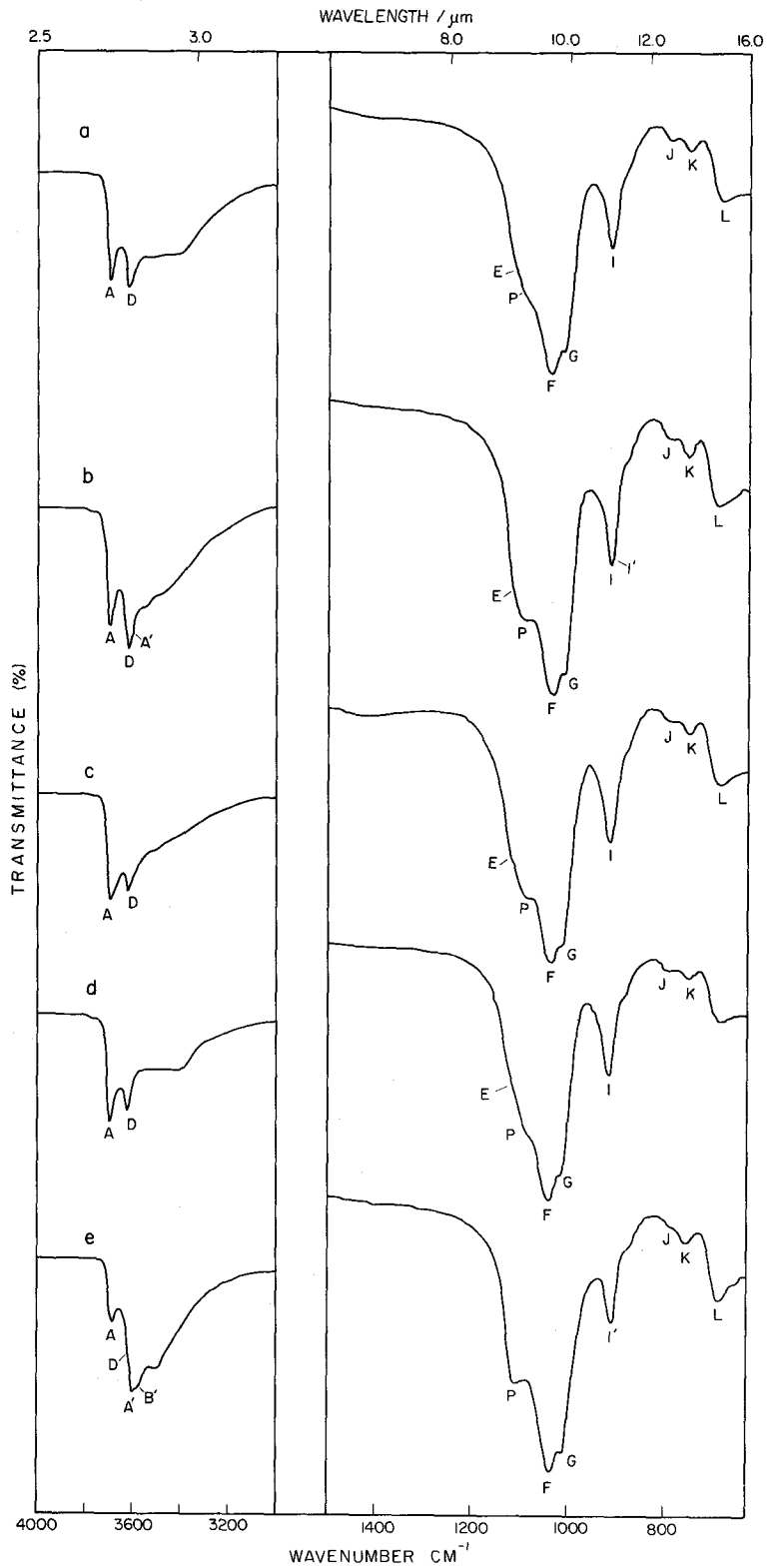


Fig. 4. I.r. spectrum of Te-Puke halloysite (a and b) in KCl and KBr respectively, ground for one minute, freshly prepared (c, d and e) powder dried three days at 105°C and ground for one minute in KBr, NaCl and RbCl respectively, freshly prepared.



tor, to enable the water molecule to accept a proton from basal hydroxyls. The effect of anions which are also important "structure breakers" were not studied at this stage.

*The possibility of using i.r. spectra of halloysite as fingerprints for the identification of the mineral*

In the foregoing paragraphs it was shown that complex formation of halloysite with the dispersing agent could account for some features of the i.r. spectra. It appears that the differences in the spectra of various samples reported in the literature are due to the amount of the complex that has been formed. This amount depends on the alkali-halide used and the mode of preparation of the disk. It also appears that some authors were mistaken in considering band A' to be band D. The spectra obtained by Askenasy, Dixon and McKee (1973, Fig. 6) for Alotenango spheroidal halloysite in a KBr disk is typical for complexed halloysite, while that obtained for Indiana halloysite shows only a slight complex formation. Considering that the disks were prepared under the same conditions, it seems that differences in morphology lead to differences in the strength of the electrostatic attraction between kaolin-like layers in the two samples, resulting in differences in the probability of complex formation. Considering these results the following conclusions may be drawn:

(1) NaCl seems to be the most reliable dispersing agent for determining whether a mineral sample belongs to the kaolinite group by i.r. spectroscopy.  
 (2) RbCl seems to be a reliable dispersing agent for differentiating between kaolinite and hydrated halloysite.

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