NOTES

THE NATURE OF THE INTERACTION BETWEEN WATER MOLECULES AND KAOLIN-LIKE LAYERS IN HYDRATED HALLOYSITE

The hydration of halloysite has been the subject of many investigations. The present study is an attempt to clarify whether basal hydroxyls and oxygens are hydrogen bonded to the interlayer water.

Recently, Yariv (1975a, b) showed by i.r. spectroscopy that during the grinding of kaolinite with CsCl, delamination of the kaolinite occurred and water was sorbed from the atmosphere with hydrogen bonds being formed between the basal hydroxyl groups and the sorbed molecules. When a disk of hydrated halloysite (0·5 mg) is prepared using CsCl (125 mg) as dispersing agent, a spectrum similar to that of kaolinite–CsCl–H_2O complex is obtained (Fig. 1). Hence it is assumed that in the presence of this salt,

Fig. 1. I.r. spectrum of halloysite (a) in CsCl disk (b, c) film on AgCl window perpendicular and at 45° to the direction of the beam respectively.

hydrogen bonds are also formed between the basal hydroxyl groups and the interlayer water molecules. It seems plausible to compare i.r. absorption spectra of hydrated halloysite deposited by evaporation from a suspension onto supporting windows with those of halloysite in CsCl disks.

Hydrated halloysite from Te-Puke, New Zealand, used in the present study was kindly donated by Prof. J. B. Dixon, Texas A & M University, and described by Hughes (1966). It has a complex three dimensional structure (McKee *et al.*, 1973). Five mg of the clay was dispersed in 4 ml of H_2O and ultrasonically vibrated for 20 min in a Bransonic 12 (75 W). The suspension was evaporated on a AgCl window. I.r. spectra of the oriented specimen were recorded on a Perkin-Elmer spectrophotometer model 237, with the windows at 45° and 90° to the direction of the beam. Spectra are given in Fig. 1. The positions and assignments for the different bands of the halloysite film and the CsCl disk plus those obtained for the Georgia kaolinite (Yariv, 1975b, c) are summarized in Table 1.

Due to the morphology of this halloysite, the pleochroic behavior of bands *A* and *P* which is characteristic for oriented specimens of various kaolinites, is not clearly observed. According to McKee *et al.* (1973) there are occasional bends in the layers of Te Puke halloysite. Besides, some rolled material is also present. In such a morphology, vibrations are randomly oriented. The slight appearance of band *P* and the slight diminution of band *F* in the sample inclined at 45° to the direction of the beam (Fig. 1) may indicate the presence of some plates without curvature, which tend to settle in a prefered orientation. It also may indicate the effect of the planar part of the halloysite particle on its orientation during settling.

The band at 3550 cm^{-1}, which does not show pleochroic behavior, is interpreted as belonging to water in the interlayer space. According to Hendricks (1938) this space enables the penetration of a single molecular sheet of water molecules. Hydrogen bondings between these molecules is limited.

McKee (personal communication) by electron microscopy observed triangular interlayer separations, one having a base of 240 and a height of 72 A, in Te-Puke halloysite. Askenasy, Dixon and McKee (1973) stated that pores of these dimensions offer sufficient space for appreciable amounts of water. This space enables the penetration of several molecular sheets of water molecules. Hydrogen bonding between these molecules is favored and results in absorption at a range lower than 3550 cm^{-1}.

McKee *et al.* (1973) also observed several linear voids which have widths about twice the basal spacing which could represent space occupied by water. The band at 3330 cm^{-1} may be assigned to OH stretching of these water molecules. This band does not appear when the halloysite is ground with alkali halides and pressed into disks, since the fine morphology is affected by grinding (Yariv, in preparation). This band shows a pleochroic behavior which may indicate that the orientations of the settled particles
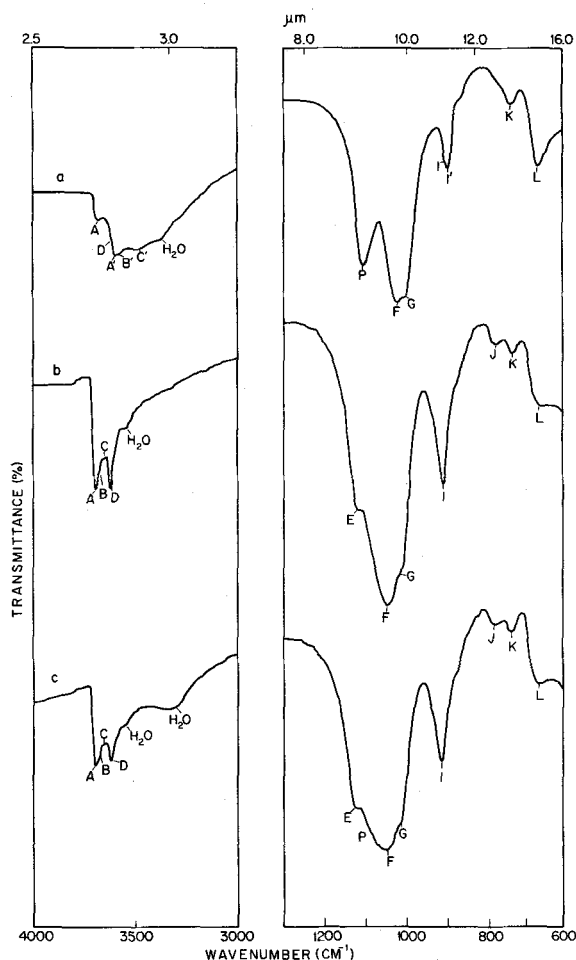
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Table 1. Wavenumbers of absorption bands (in cm^{-1}) of halloysite and kaolinite

Band assignment	Symbol	Te Puke halloysite		Eureka halloysite		Georgia kaolinite	
		Film	CsCl Disk	Film	CsCl disk	KBr disk	CsCl-$H_2$0 complex
OH stretching	A	3700	3685 w.	3700	3688 w.	3700	3682 m.
	B	3675 sh.	--	3675 sh.	-.--	3674 sh.	----
	C	3653 v.v.w.	--	3650 v.v.w.	--	3657 v.w.	----
	D	3629	3624 w.sh.	3629	3629 w.sh.	3627	3624 sh.
	A'	--	3606	--	3606	--	3606
	B'	--	3578 sh.	--	3578 sh.	--	3588 sh.
	C'	--	3502 br.	--	3502 br.	--	3507
$H_2$0 interlayer space		3550 br.w.	3370 sh.	3550 v.br.	3370 sh.	--	3375
$H_2$0 in linear voids		3330 br.	--	3330 br.	--	--	----
$H_2$0 bending		1600 br.	1645, 1660	1600 br.	1635, 1660	--	1666
SiO stretching	E	1115 sh.	--	1115 sh.	--	1115 v.w.	----
	P	--	1107	--	1107	1098	1114
	F	1039 v.br.	1024	1033 br.	1023	1031	1026
	G	1008 sh.	1003	1008 sh.	1004	1007	1005
AlOH deformation	H	--	--	--	--	937 w.	----
	I	912	910 sh.	912	910 sh.	912	910 sh.
	I'	--	901	--	901	--	900
	J	780-790 w.br.	--	788 w.br.	--	785 w.	----
	K	743 w.	752 m.	743 w.	752 m.	750 w.	758 m.
	L	680 m.v.br.	688	680 m.v.br.	688	694 m.br.	690

w – weak; m – medium; br – broad; sh – shoulder; v – very.

are related to the orientations of the hydrated interlayer separations.

All bands which are associated with either basal OH groups (*A*, *B*, *C*, and *I*) and basal oxygens (*F* and *G*), or interlayer water appear in the spectrum of CsCl disk at wavenumbers lower than those in the spectra of the halloysite film. Furthermore, a Si–O out of plane vibration (band *P*) becomes very sharp indicating delamination of the mineral. These effects are similar to those observed by comparing the spectrum obtained for kaolinite with that obtained for a kaolinite–CsCl–H_2O complex. Therefore it may be concluded that bands which characterize the presence of hydrogen bonds between water molecules and basal hydroxyls or oxygens are not present in the spectra of halloysite films. The interaction forces between water sheets and kaolin-like layers in halloysite are primarily due to dipole attraction and not due to hydrogen bonds.

X-ray powder diffraction patterns of the oriented specimen were recorded on a Seifert Iso-Debyeflex III A diffractometer before and after the recording of the i.r. spectra. The same *c* spacing (7·4–9·8 Å) was obtained in both cases, and the peaks showed that the halloysite was only slightly dehydrated during the i.r. study. Furthermore, Churchman, Aldridge and Carr (1972) showed that every interlayer space in a partially hydrated halloysite sample from Te-Puke is considered to be either completely full of water or completely empty. Hence, our conclusions are distinctive despite the fact that the halloysite was partly dehydrated.

Serratosa, Hidalgo and Vinas (1963) studied the effects on the i.r. spectrum before and after drying a film of halloysite. In agreement with our conclusions, they did not find any shift in the frequencies of the various vibrations. In their paper they stated that a marked increase in intensity of the absorption band *A* was observed in passing from the hydrated to the dehydrated form without change in the *D* band. However, from Fig. 5 of their article, it can be seen that if extrapolated base-lines are drawn to the bands similar to those previously drawn by Yariv (1975a, b and c), almost no change in the ratio of the intensities of the two bands occur after drying.

Similar observations were obtained with a tubular halloysite from Eureka, Utah (Table 1).

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