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INORGANIC INTERCALATION COMPLEXES OF HALLOYSITE: AN INFRARED STUDY

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Summary

The clay mineral "halloysite", which is a member of the kaolin family, exhibits an IR spectrum in the hydroxyl absorption region (4000-3000 cm^{-1}) similar to that for kaolinite. Certain features of the spectrum, however, depend on the amount of interlayer water present. It has been found that when the interlayer water is replaced by an ionic salt the spectrum is further modified by perturbation of the structural hydroxyl vibrations and by formation of hydrogen bonds between the intercalated meterial and the internal surfaces of the clay.

Introduction

The name "halloysite" is used to designate a clay mineral which exists in two forms. One of these is more hydrous and has a larger c-spacing than the other, which gives an X-ray pattern resembling that of kaolinite. That ideal composition of a fully hydrated halloysite is $Al_2Si_2O_5(OH)_4$. The other minerals with this formula are kaolinite, dickite, and nacrite, and these, together with halloysite, are known as the kaolin minerals.

A structural model for halloysite was suggested by Hendricks[1]. Kaolinite layers are separated by a layer of water molecules. The effect of the interposition of the water molecules is to expand the basal spacing from approximately 7.2 Å to approximately 10.1Å. Hendricks and Jefferson[2] modified the model to allow for a definite configuration for the water molecules in the interlayer region (Fig. 1).

The more hydrous and less hydrous forms of halloysite are currently termed, respectively, "halloysite (10Å)" and "halloysite (7Å)"[3]. The numbers in parentheses indicating the approximate c-spacings of the two forms.

Salt intercalation complexes of halloysite were first reported by Wada[4-6] who observed the ability of certain inorganic salts of some alkali metals to be intercalated between the halloysite layers by replacing the interlayer water, resulting in an increase in the c-axis spacing. It was found that most potassium and ammonium salts, e.g., acetate, chloride, and nitrate, were favourably intercalated while the corresponding salts of sodium, lithium, rubidium, and caesium did not complex

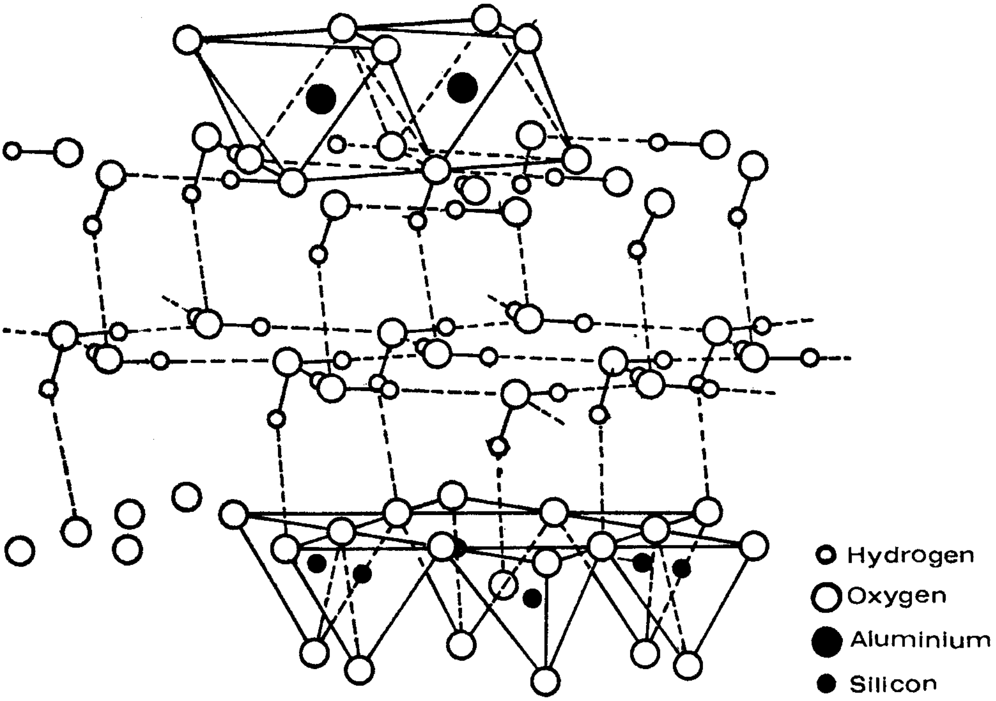

Fig. 1. Diagrammatic sketch of a portion of the halloysite(10Å) structure, showing a single layer of water molecules with the configuration suggested by Hendricks and Jefferson(2).

as readily. Intercalation of inorganic salts of divalent cations, such as magnesium, calcium, and barium, was not observed. It was of interest that no complex was obtained when salts of lithium and sodium were used, whose ionic radii are less than about 1.35 Å which is the approximate radius of the hexagonal cavity. Furthermore, it appeared that a variety of ammonium and potassium salts behaved differently with respect to the tendency to form an intercalation complex. It was concluded that the intercalation reaction depended on the size and charge of the cation and anion, and, to a certain extent, on the amount of the complexing salt. It was also noted that inorganic salt-halloysite complexes could be formed either by soaking halloysite (10Å) in concentrated solutions of the appropriate salts or by dry-grinding of the hydrated clay with the solid salts. Wada estimated that approximately two molecules of salt were intercalated per unit cell ($Al_4Si_4O_{10}(OH)_8$) of halloysite, the stability of the complex being controlled partly by the geometrical relationship between the interlayer material and the internal surface structure of halloysite. Similar studies made by Garrett and Walker[7] showed that cations with low ionic potentials (i.e., charge-to-radius ratios) tended to complex very readily.

It has been observed[8] that potassium acetate intercalated in halloysite could be replaced by many complexing agents by washing the potassium acetate-halloysite complex with the appropriate solutions.

Completely dehydrated halloysite(7Å) was observed to form intercalation compounds with potassium and ammonium acetate and several methylated amides by direct contact[9]. In all cases halloysite(10Å) could be regenerated by washing with water.

There have been relatively few IR studies on intercalation complexes of halloysite. The usual conclusion is that hydrogen bonds play a major role in the complex formation[10-12]. This report attempts to verify the above conclusion by examining infrared spectra of halloysite and its complexes, particularly in the hydroxyl absorption region.

Materials and Methods

Halloysite samples from the Kauri Mountain, Northland, New Zealand were used. These were fully hydrated and contained a small amount of quartz. For comparison, a sample of kaolinite from Bang Rin, Ranong, Thailand was also used in the infrared measurements.

Preparation of complexes. Salt complexes of halloysite were prepared by soaking approximately 2 g of clay in a concentrated salt solution ($\sim$6 mol dm^{-3}), mixing thoroughly for 10 minutes with a magnetic stirrer, and filtering through a Buchner funnel. Formation of the complex was confirmed by chemical analysis. The resulting complex was air-dried for the infrared study.

Preparation of partially intercalated clay. Partial intercalation of halloysite was achieved by soaking approximately 2 g of clay in the appropriate salt solution ($\sim$3 mol dm^{-3}), mixing and filtering as in the preparation of complexes above. The clay was then air-dried for the infrared study.

Fully or partially complexed halloysite could be rehydrated by washing with distilled water through a Buchner funnel until the filtrate was free of the complexing salt.

Infrared measurements. A small amount of dry, complexed clay was mulled with a drop of Nujol, lightly ground, and mounted between two sodium chloride infrared windows. Samples of halloysite(7Å) and kaolinite are similarly treated for infrared measurements.

A Beckman IR-20A infrared spectrophotometer was used. Infrared transmittance of the samples was recorded as a function of frequency (in wavenumber units) within the region from 4000 to 3000 cm^{-1}.

Results and Discussion

Infrared spectra of halloysite and kaolinite in the hydroxyl absorption region are shown in Fig. 2. Generally there are two prominent absorption peaks at 3695 and 3620 cm^{-1} whose relative intensity varies with the degree of dehydration. These two absorptions correspond respectively to the two maxima at 3704 and 3623 cm^{-1} reported by Fripiat[13] for halloysite. There is a gradual intensity increase of the 3695 cm^{-1} absorption in passing from fully hydrated halloysite(10Å) to the completely dehydrated form, while the peak at 3620 cm^{-1} remains unchanged. It has been found that the presence of interlayer water or other intercalated materials causes a reduction in intensiy of the 3695 cm^{-1} absorption[14]. The slope of the line joining the two corresponding maxima in kaolinite has been used as a measure of the degree of intercalation[10]. The 3695 cm^{-1} absorption can thus be assigned to hydroxyl groups with axes normal or nearly normal to the layer plane, and is believed to consist of contributions from OH bonds which are directed towards hexagonal holes on the other side of the interlayer space (cf. ref. 14). These hydroxyl groups are therefore expected to be perturbed by the presence of any interlayer material besides water molecules. Inspection of the infrared spectra of several salt complexes of halloysite, shown in Fig. 3–6, confirms this. It can be seen that in all cases intercalation resulted in an intensity reduction of the 3695 cm^{-1} peak. (The extent of this reduction apparently depends on the degree of intercalation).

It is noted that the peak at 3620 cm^{-1} remained more or less unaltered after intercalation, indicating that the hydroxyl groups giving rise to this peak are not involved in interlayer bonding. In a manner analogous to that in which the corresponding peak in kaolinite has been assigned[14], this peak can be attributed to hydroxyl groups pointing to unoccupied octahedral sites.

Apart from the intensity reduction of the 3695 cm^{-1} peak, intercalation in halloysite also produced new absorptions at lower frequencies corresponding to the formation of new hydrogen bonds between the interlayer species and the internal surfaces of the clay[10]. For example, intercalation of dipotassium hydrogenphosphate

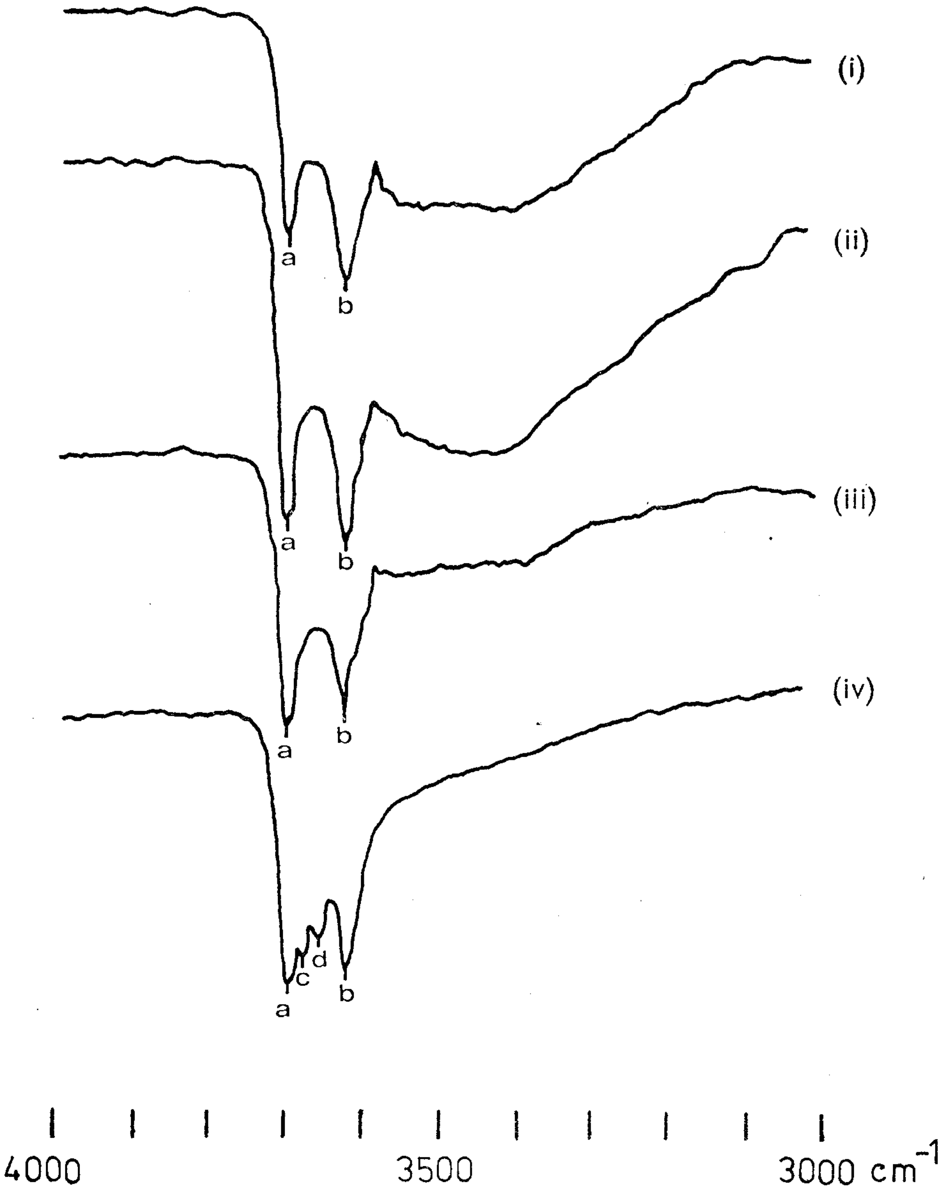

Fig. 2. OH stretching bands:

(i) Kauri halloysite(10Å) air dried for 2 hours.

(ii) Kauri halloysite(10Å) air dried for 3 days.

(iii) Kauri halloysite(7Å).

(iv) Bang Rin kaolinite.

Maximum absorptions are situated at

(a) 3695 cm^{-1}; (b) 3620 cm^{-1};

(c) 3670 cm^{-1}; (d) 3650 cm^{-1}.

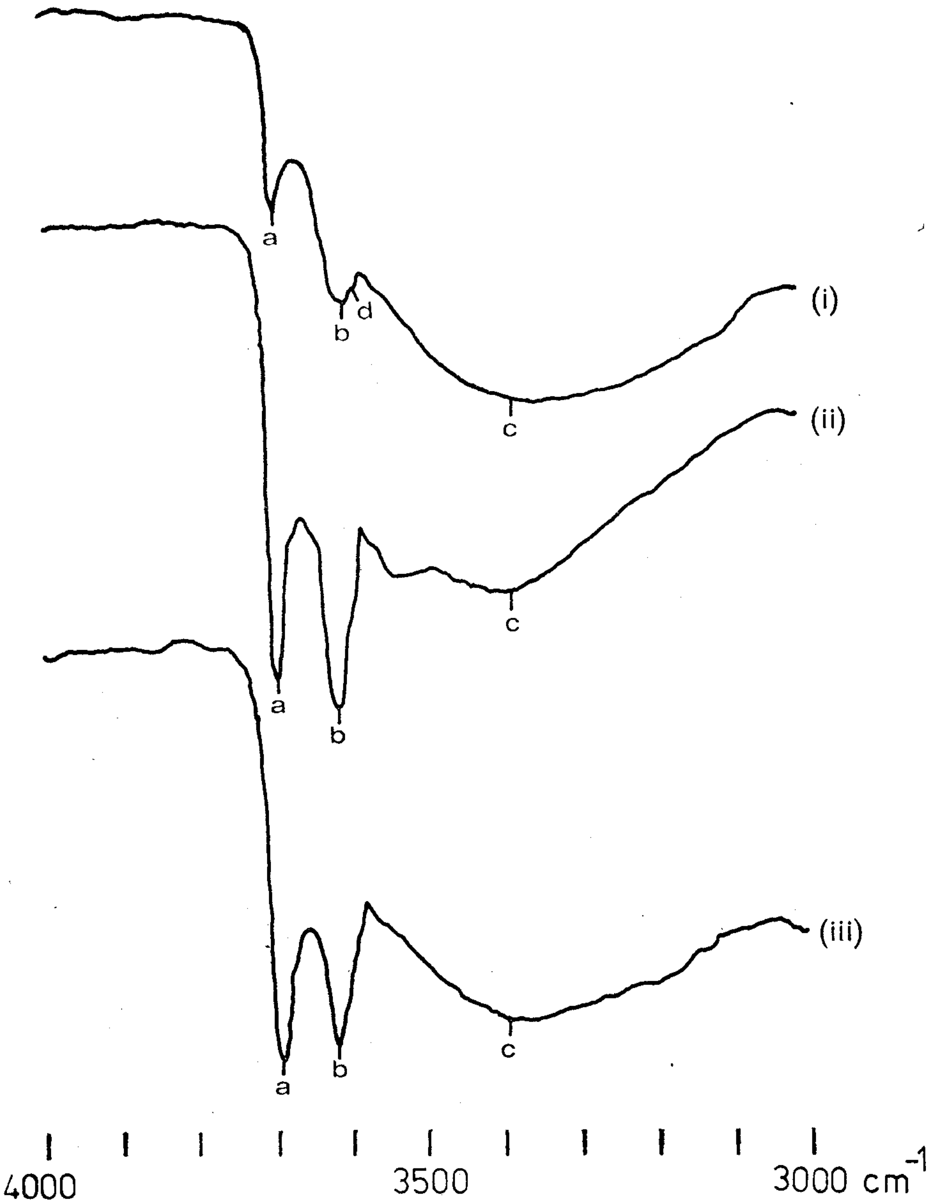

Fig. 3. OH stretching bands of Kauri halloysite:
(i) K_2HPO_4 complex;
(ii) partial K_2HPO_4 intercalation;
(iii) halloysite (7Å)–K_2HPO_4 mixture.
Maximum absorptions are situated at
(a) 3695 cm^{-1}; (b) 3620 cm^{-1};
(c) ~3400 cm^{-1}; (d) 3610 cm^{-1}.

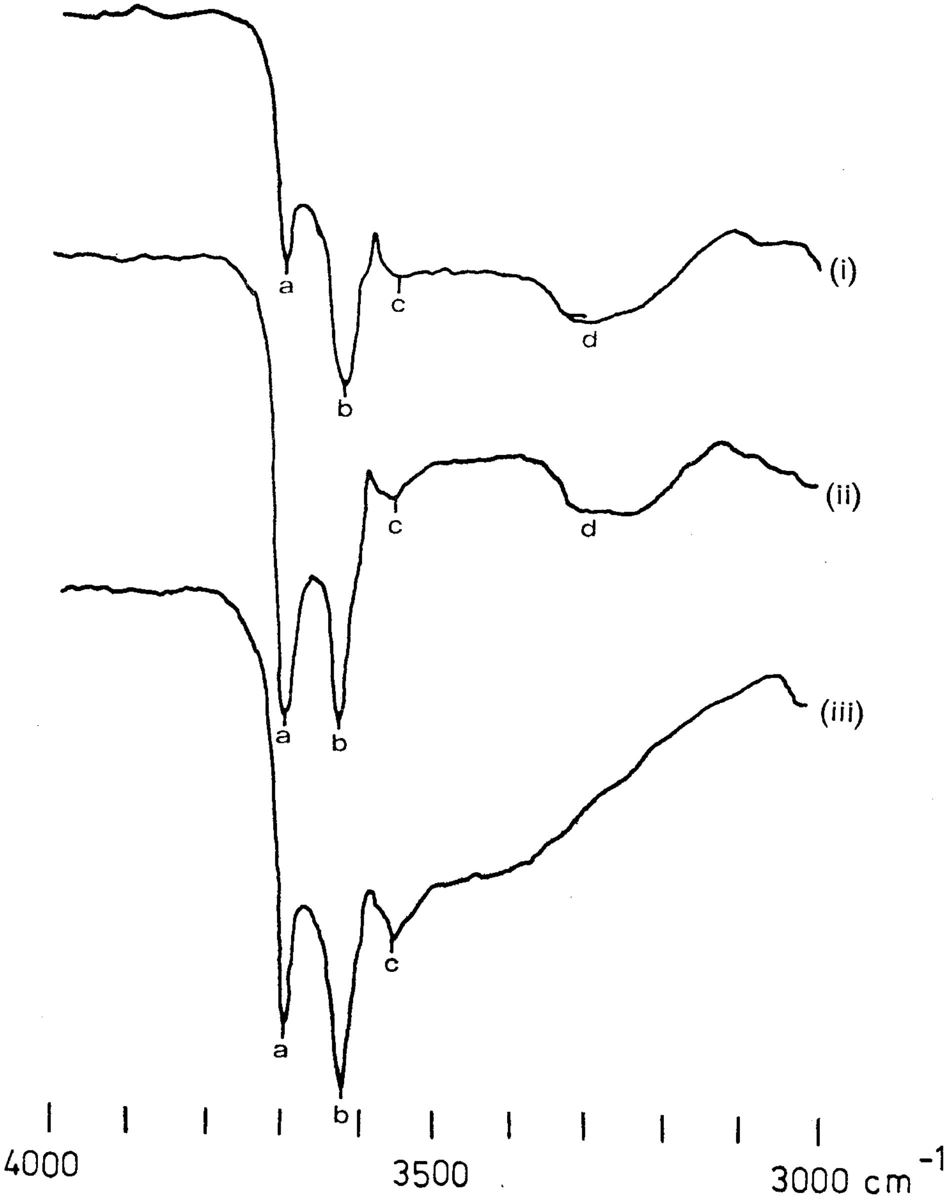

Fig. 4. OH stretching bands of Kauri halloysite;
(i) NH_4F complex;
(ii) halloysite (7Å)–NH_4F mixture;
(iii) rehydrated halloysite.
Maximum absorptions are situated at
(a) 3695 cm^{-1}; (b) 3620 cm^{-1};
(c) 3550 cm^{-1}; (d) ~3280 cm^{-1}.

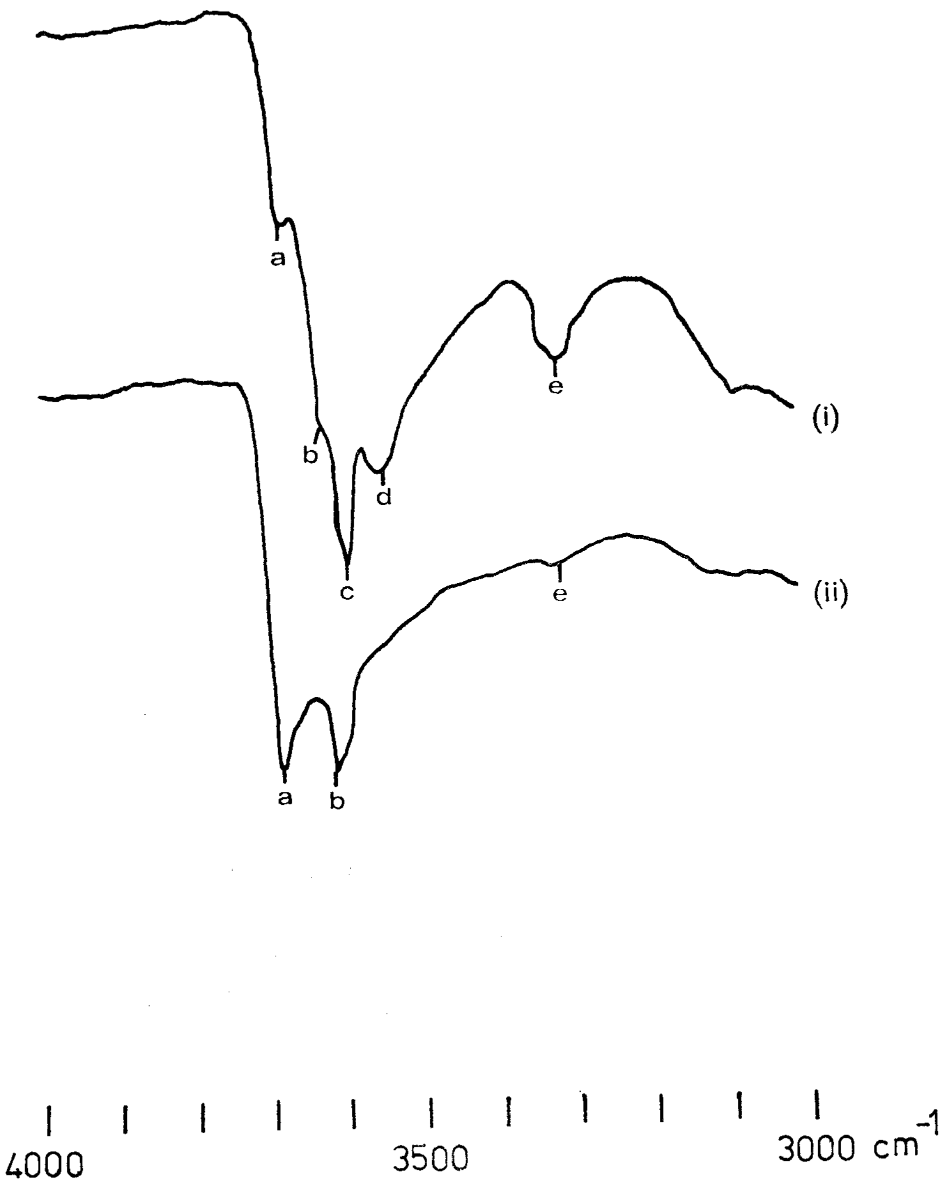

Fig. 5. OH stretching bands of Kauri halloysite:

(i) NH_4Cl complex;

(ii) halloysite (7Å)–NH_4Cl mixture.

Maximum absorptions are situated at

(a)	3695 cm^{-1};	(b)	3620 cm^{-1};
(c)	3610 cm^{-1};	(d)	3570 cm^{-1};
(e)	~3300 cm^{-1};		

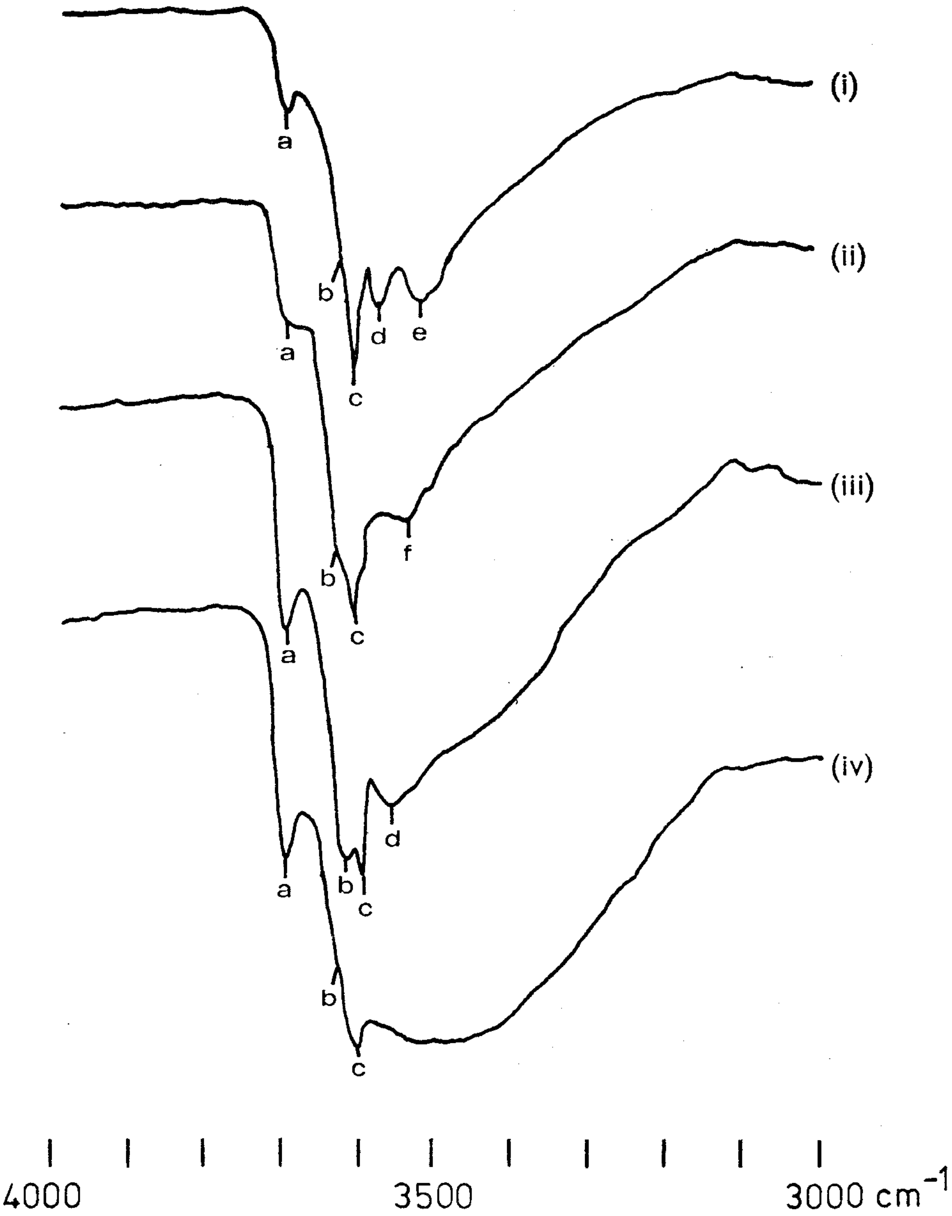

Fig. 6. OH stretching bands of Kauri halloysite:

(i) KCl complex; (ii) KBr complex;
(iii) KI complex; (iv) KOAc complex.

Maximum absorptions are situated at

(a)	3695 cm^{-1};	(b)	3620 cm^{-1};
(c)	3610 cm^{-1};	(d)	3570 cm^{-1};
(e)	3520 cm^{-1};	(f)	~3530 cm^{-1};

resulted in an additional, weak absorption at ~3600 cm^{-1} (Fig. 3). The shift of the IR absorption peak to lower frequency indicates a stronger association of hydroxyl groups with the interlayer material via hydrogen bonds.

Infrared spectra of the ammonium fluoride-halloysite complex show a broad and diffuse absorption at ~3280 cm^{-1} (Fig. 4). This band probably arises from the stretching vibration of the NH_4^+ group. Supporting evidence is given by the presence of a similar, broad band at 3300 cm^{-1} in the infrared spectrum of the ammonium chloride complex (Fig. 5) and by the close agreement between the above frequencies and those obtained by Wada[11] and the values cited by Bellamy[15] for N-H stretching vibrations.

Infrared spectra of intercalation complexes of halloysite with some potassium salts are shown in Fig. 6. For these complexes the diminution of the 3695 cm^{-1} peak was always accompanied by the appearance of one or more absorptions at lower frequencies. Common to all is the peak at ~3610 cm^{-1} which may be attributed to the stretching frequency of the hydroxyl groups which are perturbed by the presence of the interlayer cation and anion. It is noted that when halloysite is in the hydrated state this perturbation is minimised and the peak appears as a shoulder of the 3620 cm^{-1} band. This observation seems to support the assignment of the 3695 cm^{-1} peak to hydroxyl groups directed towards hexagonal cavities of the opposite oxygen sheet[14]. It is believed[5] that following salt intercalation the cation of the salt fits into the hexagonal cavity while the anion is oriented in the interlayer space. Consequently, the vibration of these hydroxyl groups is strongly perturbed and the frequency shift to a lower value results. The corresponding peak at 3600 cm^{-1} observed by Ledoux and White[10] for the potassium acetate complex of kaolinite was assigned to the hydrogen bond between the $-COO^-$ group and the hydroxyl surface of the clay. However, this assignment cannot explain the appearance of infrared bands at the same frequency for the chloride, bromide, and iodide complexes of halloysite. Wada[11] has suggested hydrogen bonding of the type $O-H\cdots Cl$ in KCl intercalates, but this explanation seems unlikely in view of the known inability of chlorine atoms to form strong hydrogen bonds. Hence, the appearance of additional, weak bands between 3600 and 3500 cm^{-1} may not be due to new hydrogen bonds formed between the intercalated salts and the clay structure. These bands are probably due to the stretching vibrations of water molecules associated with the intercalated ions or molecules.

The peak at ~3550 cm^{-1} is often present for both the 7Å– and 10Å–forms of halloysite and has been assigned to O–H bonds associated with surrounding oxygens[16] and to stretching vibrations of interlayer water[17]. This band has also been observed by Serratosa *et al.*[14] and Churchman[18]. The validity of either of the above assignments, however, has not been unequivocally established because of the unpredictable appearance of the band and the fact that this band is usually obscured by a broad band centred at ~3400 cm^{-1}.

The broad band observed at approximately 3480 cm^{-1} for the 10Å– and, occasionally, 7Å–forms of the clay has been attributed to vibrations of O–H bonds of externally adsorbed water (cf. ref. 19). However, the study of dehydration effects on the O–H stretching vibrations by De Keyser, Wollast, and De Laet[20] led to the conclusion that this wide band was due partly to the humidity water and partly to OH groups situated at structural defects. Olejnik *et al.*[12] attributed the band to interlayer water. In view of the results obtained in this study, however, it seems appropriate to assign this absorption peak, at least partly, to O–H bonds of externally adsorbed water; the presence of this band in the infrared spectrum of the potassium acetate complex (Fig. 6) due to the hygroscopic nature of the salt seems to support this assignment. Interlayer water molecules may also contribute to this vibration. The width of the absorption band probably suggests an overlap of individual peaks due to interlayer and externally adsorbed water.

Conclusion

In the formation of salt intercalation complexes of halloysite, weak hydrogen bonds between the interlayer water and the internal surfaces of the clay are broken and stronger hydrogen bonds are formed between the internal hydroxyl groups of the clay and the complexing salts. Vibration of these hydroxyls is perturbed and the vibrational frequency shifts to lower wavenumbers. Other species which may give rise to vibrations in this region include NH_4^+, externally adsorbed water, and residual interlayer water.

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References

1. Hendrick, S.B. (1938) *Am. Mineralogist* **23**, 295.
2. Hendrick, S.B. and Jefferson, M.E. (1938) *Am. Mineralogist* **23**, 863.
3. Brindley, G.W. (Chairman) (1975) *Clays Clay Minerals* **23**, 413.
4. Wada, K. (1958) *Soil and Plant Food* **4**, 137.
5. Wada, K. (1959) *Am. Mineralogist* **44**, 153.
6. Wada, K. (1959) *Am. Mineralogist* **44**, 1237.
7. Carrett, W.G. and Walker, G.F. (1959) *Clay Minerals Bull.* **4**, 75.
8. Miller, W.D. and Keller, W.D. (1963) *Clays Clay Minerals, Proc. 10th Natl. Conf.* **12**, 244.
9. Hoffmann, U. and Reingraber, R. (1969) *Z. Anorg. Allg. Chem.* **369**, 208.
10. Ledoux, R.L. and White, J.L. (1966) *J. Colloid Interface Sci.* **21**, 127.
11. Wada, K. (1964) *Clay Sci. (Tokyo)* **2**, 43.
12. Olejnik, S., Aylmore, L.A.G., Posner, A.M., and Quirk, J.P. (1968) *J. Phys. Chem.* **72**, 241.
13. Fripiat, J.J. (1960) *Groupe Francais Des Argiles., Bull.* **12**, 25.
14. Serrrtoza, J.M., Hidalgo, A., and Vinas, J.M. (1963) *Proc. Intern. Clay Conf., Stockholm*, 17.

15. Bellamy, L.J. (1975) *The IR Spectra of Complex Molecules*, v. 1, 3rd ed., Chapman and Hall, p. 266.
16. Kodama, H. and Oinuma, K. (1963) *Clays Clay Minerals, Proc. 11th Natl. Conf.* **13**, 236.
17. Pampuch, R. and Blaszczak, K. (1964) *Pol. Akad. Nauk. Oddzal Krakowie, Pr. Kom. Nauk. Tech. Ceram.* **3**, 5.
18. Churchman, C.J. (1970) Interlayer Water in Halloysite, Ph.D. Thesis, Otago Univ. New Zealand.
19. Wolff, R.G. (1965) *Am. Mineralogist* **50**, 240.
20. De Keyser, W.L., Wollast, and De Laet, L. (1963) *Proc. Intern. Clay Conf., Stockholm* **2**, 75.

บทคัดย่อ

Halloysite เป็นแร่ชนิดหนึ่งในกลุ่มของดินขาว IR spectrum ของ halloysite ในช่วงความถี่ 4000–3000 cm^{-1} มีลักษณะคล้ายคลึงกับ IR spectrum ของ kaolinite แต่เนื่องจากใน halloysite อาจมี interlayer water อยู่ด้วย ปริมาณของ interlayer water นี้จึงเป็นผลให้ลักษณะบางอย่างแตกต่างไปจาก spectrum ของ kaolinite จากการทดลองพบว่า ถ้า interlayer water ถูกแทนที่ด้วยเกลือไอออนนิคบางชนิด vibrations ของ OH groups ในโครงสร้างของ halloysite จะถูกรบกวน นอกจากนี้ยังอาจเกิด hydrogen bond ระหว่าง interlayer salt กับผิวภายในของ halloysite ด้วย ผลก็คือ infrared spectrum จะมีลักษณะเปลี่ยนไปจากเดิม