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AN INTERLAYER COMPLEX OF HALLOYSITE WITH AMMONIUM CHLORIDE

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ABSTRACT

An NH_4Cl-halloysite complex with a basal spacing of 10 Å was prepared by drying halloysite from an NH_4Cl solution or by dry mixing it with NH_4Cl crystals. In addition to the change in basal spacing, orientation of NH_4Cl between the silicate layers caused variations in the relative intensities and peak shapes of some of the *hk* bands. The oriented NH_4Cl no longer gives *x*-ray reflections as does the normal salt, and shows some distinctive features, such as loss of the transformation at 185° C., and the shift of the thermal decomposition to a temperature 30 to 50° C. higher. The orientation maximum of NH_4Cl is estimated at 325 to 330 m. mols. per 100 gms. of air-dried clay (2 molecules of NH_4Cl per unit cell of halloysite). Two molecules of the interlayer water are replaced by one molecule of NH_4Cl in the first stage of the complex formation.

INTRODUCTION

Earlier studies (6, 7) have shown that the basal spacing of hydrated halloysite will expand from 5 to 45% when dried from certain K, NH_4, Rb and Cs salt solutions, but not from Li and Na solutions. Since the reaction is reversible, and specific for certain pairs of cations and anions, a type of intermolecular complex formation has been suggested. The data indicate that an important factor controlling the reaction is the relation of the cation size to the size of the cavity in the oxygen network of the Si-O sheet. It is here proposed that the cation penetrating between the silicate layers is trapped in this cavity. The anions orient themselves around the trapped cation to neutralize its excess positive charge, forming a two-dimensional ionic layer.

If the complex forms through this reaction mechanism, the number of the salt molecules per unit cell should be two, provided the size of the anion allows for the two anions to orient per unit cell. The first purpose of this study is to estimate the number of the salt molecules oriented per unit cell of halloysite, utilizing the fact that the oriented form no longer contributes to *x*-ray diffraction as the normal salt (6). The oriented salt is also expected to differ from the normal salt in respect of thermal transformations. In view of the bond formation and possible steric hindrance, it seems worth while to know what effects appear on the thermal transformations of the interlayer material. The second purpose is to illustrate this on DTA curves. The third is to study the behavior of the interlayer water upon penetration of the salt molecules into the interlayer spaces. It might give a better understanding of the nature of the reaction together with that of the interlayer water. An NH_4Cl-halloysite complex with a 10.5 Å basal spacing (6) is adopted as the subject of this study on account of its simple composition and stability.

MATERIALS AND METHODS

Experiments were made on hydrated halloysite from Yoake, Oita, Japan (1) (6), and on metahalloysite prepared by heating it at 300° C. Half gram samples of the clay (<150 mesh) were soaked in 1 ml. NH_4Cl solutions containing from 0 to 3.00 m.mols of NH_4Cl, and allowed to dry at 30° C. in an atmosphere with relative humidity of 65% for two weeks. The samples were then weighed and their water content determined.

X-ray diffraction patterns were obtained by means of a Philips diffractometer with Cu-Kα radiation. Flat plates of the samples were mounted according to McCreey's procedure (4). DTA was carried out on a portion of each sample corresponding to 100 mg. of the untreated air-dry clay at the heating rate of 10° C. per minute.

RESULTS AND DISCUSSION

Characteristics of the X-ray Pattern of the NH_4Cl-Halloysite Complex

X-ray diffraction patterns of halloysite and NH_4Cl-treated halloysite (400 m.mols. NH_4Cl per 100 gms. air dried clay) are shown in Fig. 1. The (001) and (003) reflections of halloysite shift from 10.1 and 3.36 Å to 10.5 and 3.49 Å, respectively. These reflections of the NH_4Cl-halloy-

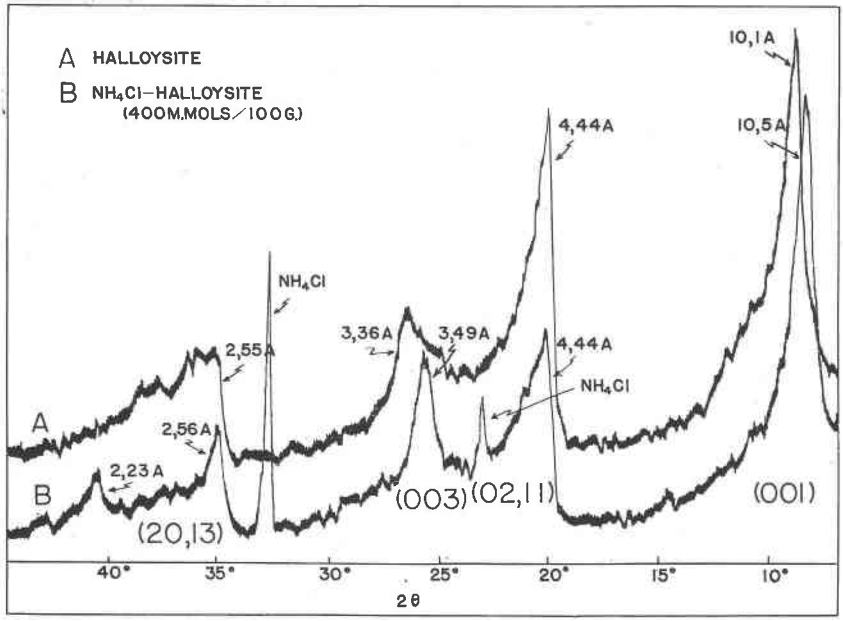

FIG. 1. X-ray diffraction patterns of halloysite and NH_4Cl-treated halloysite.

site complex are estimated to be about 1.3 to 1.5 times as strong as those of halloysite, after making allowance for a dilution effect due to the presence of NH_4Cl not oriented in the treated sample. The basal reflections of the original halloysite spread slightly on the high-angle side probably due to partial dehydration, while the symmetry of these peaks increases remarkably as the result of the complex formation. It might be interpreted in terms of penetration of NH_4Cl into the interlayer spaces partially dehydrated. Otherwise, there would be a shifting of the 10.5 Å (001) reflection towards 7-Å, indicating a random interstratification of 10.5- and 7-Å layers.

While (*hk*) reflections show no essential change in spacings for their low-angle termination upon penetration of NH_4Cl, considerable variations are found in their relative intensities and peak shapes (Fig. 1). The height of the low-angle termination of the (02, 11) band shows remarkable reduction, even taking the dilution effect into consideration. Further, two rather symmetrical peaks appear in the (20, 13) band at 2.56 Å. and 2.22 Å., while the (24, 31, 15) and (33, 06) bands are hardly affected. The reaction causes no alteration in the cell dimension a_0 and b_0 of halloysite, but clearly does produce a definite change in its structure factor, implying that the interlayer NH_4Cl probably assumes a regular configuration. In further studies, it might be possible to deduce the configuration of the salt molecules oriented between the silicate layers from such variations in the (*hk*) bands together with those in the (00*l*) reflections. Similar variations in the *x*-ray pattern were not observed for the NH_4Cl-treated metahalloysite.

Estimation of the Amount of NH_4Cl Oriented on Halloysite

The salt oriented two-dimensionally on halloysite no longer contributes to the *x*-ray diffraction as the salt (6). If diffraction intensities of NH_4Cl are measured on the NH_4Cl-treated samples, it is possible to estimate the amount of NH_4Cl not oriented on halloysite or metahalloysite (free NH_4Cl), and hence find the amount oriented by subtraction. Estimation of the free NH_4Cl was made according to the procedure of Alexander and Klug (4) using quartz as an internal standard. The diffraction intensities were measured from the peak height on automatic recording charts after calibration of the recorder response.

The observed intensity ratio of the 2.72 Å NH_4Cl and the 1.54 Å quartz lines (I_1/I_s) is plotted against the rate of NH_4Cl addition in Fig. 2. The weight fraction of the free NH_4Cl was calculated by multiplying the intensity ratio I_1/I_s by an empirical factor 0.0229 (weight fraction of quartz: 0.25), and then the amount of NH_4Cl oriented (Fig. 3) was calculated from this, taking the water content of the samples (Fig. 6) into consideration.

The 10.5 Å spacing of the NH_4Cl-halloysite complex fully develops with salt addition corresponding to 300 m. mols per 100 g. of air-dried clay. The orientation maximum of NH_4Cl is estimated at 325 m.mols per 100 g. of air-dried clay on the basis of the data in Fig. 3. Taking the unit cell of halloysite as $Al_4Si_4O_{10}(OH)_8 \cdot 4\ H_2O$, this corresponds to 1.93 molecules of NH_4Cl per unit cell of halloysite, suggesting that two molecules of NH_4Cl orient per unit cell either on the internal or on the external surface. The value accords well with that expected from the reaction mechanism proposed at the beginning of this paper, that is, the geometrical fitting of the cation into the cavity of the oxygen hexagon allows the reaction. In view of the geometrical fitting, it seems fair to assume that NH_4^+ probably orients into the cavity and Cl^- lies on the oxygen hexagon forming a monomolecular salt layer, though the relation between the changes in the peak shape (Fig. 1) and the arrangement of the interlayer NH_4^+ and Cl^- is as yet not clear.

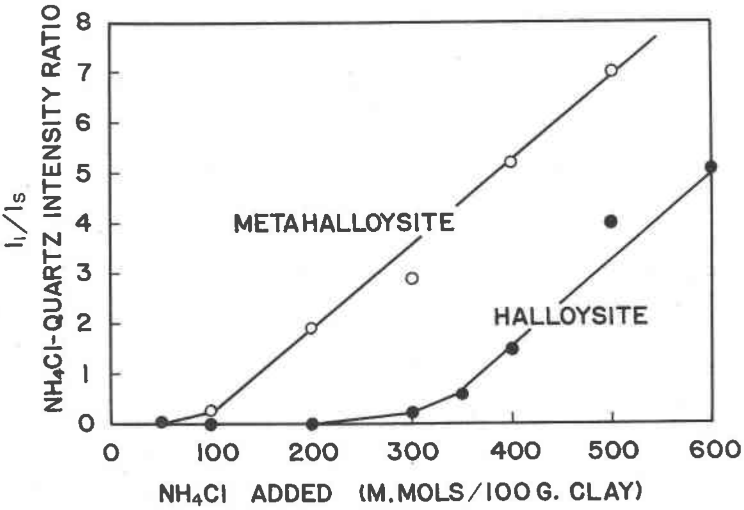

FIG. 2. NH_4Cl-quartz diffraction intensity ratio for NH_4Cl-treated halloysite and metahalloysite.

It may seem curious that NH_4Cl also orients on the external surface, but, if the same reaction mechanism is assumed, a monolayer of NH_4Cl should be formed on the exposed SiO-sheet. Actually the orientation maximum of NH_4Cl is estimated at 140 m.mols per 100 g. of air-dried clay in the case of metahalloysite (Fig. 3). It may be allocated to the NH_4Cl oriented on the external surface of halloysite, and the difference between halloysite and metahalloysite (185 m.mols), to that oriented between the silicate layers of halloysite. This assumes that the external surface of halloysite is not affected by heating at 300° C., and the same heat treatment completely precludes the entry of NH_4Cl into the interlayer spaces. The plausibility of the assumption will be discussed later.

Thermal Transformations of NH_4Cl Oriented on Halloysite

DTA curves of halloysite and metahalloysite treated with 100 and 400 m.mols of NH_4Cl are reproduced in Fig. 4 with those of NH_4Cl diluted with α-alumina for comparison. The effect of orientation appears at first on the endothermic peak due to the transformation of NH_4Cl from α to β at 185° C. Although the appearance of the peak is considerably affected by mere physical grinding of the NH_4Cl crystals, it appears safe to conclude that the α-β transformation can not occur in the oriented NH_4Cl as is expected in view of the orientation-induced-polymorphism.

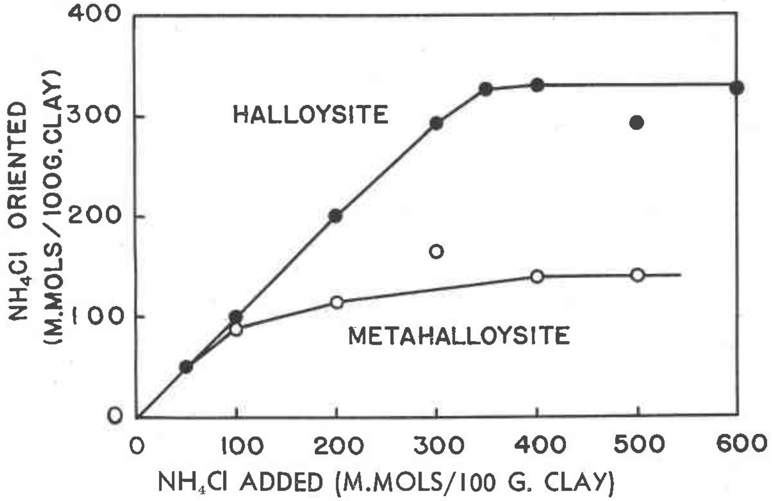

FIG. 3. Estimation of NH_4Cl oriented on halloysite and metahalloysite on the basis of the x-ray data.

Although the peak temperature of the thermal decomposition peak of NH_4Cl varies with the amount of NH_4Cl involved in the samples (Fig. 5), it clearly shifts to the higher temperature side in the case of the NH_4Cl-treated halloysite (Fig. 4). When more than 300 m.mols of NH_4Cl is added, another peak, probably due to the presence of the free NH_4Cl, appears on the lower temperature side, and two apexes are clearly found on the shifted peak, although the reason for this is not understood at present.

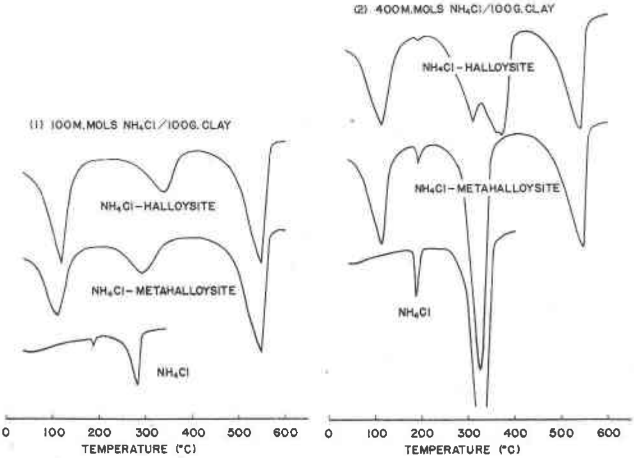

FIG. 4. DTA curves of NH_4Cl-treated halloysite and metahalloysite.

The shift of the peak temperature is characteristic of the interlayer NH_4Cl, whereas the peak shape is affected, even in the case of metahalloysite (Fig. 4), where the peak is broadened and increases in symmetry in comparison with the NH_4Cl alone. This tendency, however, becomes obscured with the increase in the rate of NH_4Cl addition, as is shown in comparison between the treatments with 400 and 100 m.mols of NH_4Cl. In the NH_4Cl-treated halloysite, more asymmetrical peaks are shown, and even if there is a composite effect of the interlayer and external NH_4Cl, the decrease in the degree of symmetry seems still to remain as a characteristic of the interlayer NH_4Cl.

Since treating halloysite with NH_4Cl hardly affects the endothermic peak due to the dehydroxylation of halloysite (Fig. 4), possibilities that NH_4Cl or its thermal decomposition products react with halloysite and bring about alterations of the DTA curve, may be excluded. Also, it is unlikely that the reaction scheme in the thermal decomposition changes due to the orientation. Thus, observed variations of the DTA curve may be treated as variations in the rate of the thermal decomposition vs. temperature behavior, since all empirical factors that may possibly contribute to alterations of the DTA curve are maintained fixed in this case.

In general, the reaction rate for this type of solid decomposition can be described by an equation

$$\frac{dx}{dt} = A(1 - x)^n e^{-E/RT}$$

where dx/dt is the reaction rate, A is the frequency factor, x is the fraction reacted, n is the empirical order of the reaction, and E is the activation energy. The shift of the reaction to the higher temperature side on the DTA curve as shown with the interlayer NH_4Cl means the decrease in the reaction rate at a given temperature. It may result either from the decrease in the frequency factor A or from the increase in the activation energy E. The former would be expected from a steric hindrance that is conceivably probable as the site of the reaction is confined to the interlayer spaces, and the latter, from a stabilizing effect, as a new bond is formed between halloysite and NH_4Cl.

Stone (5) explained the shape of an endothermic peak on a DTA curve by that of the distribution curve of the energy of a bond concerned in the reaction. Kissinger (3) demonstrated the effect of varying order of the reaction on the degree of symmetry of a peak. Although these explanations can not directly be applied to the present variations in the peak shape, observations are of interest in showing that the shape of the DTA curve is clearly affected by the state of the distribution of NH_4Cl.

Estimation of the Orientation Maximum of NH_4Cl on Halloysite (DTA)

The orientation maximum of NH_4Cl on halloysite was also estimated by DTA. The sum of the interlayer and external orientation was determined by assuming that the endothermic peak on the lower temperature

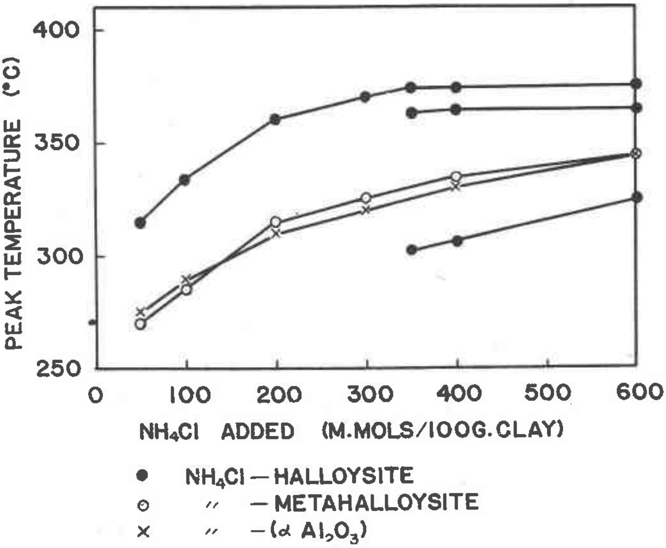

FIG. 5. Effect of orientation on the peak temperature of the thermal decomposition of NH_4Cl.

side (Fig. 4 & 5) appeared only after the sites for orientation were saturated by NH_4Cl. Although this assumption is rather arbitrary, because NH_4Cl oriented on the external surface also contributes to this peak at least potentially, the minimum rate of the NH_4Cl addition necessary to cause this, 330 ± 10 m.mols per 100 g. of air-dried clay, shows a good agreement with the orientation maximum 325 m.mols obtained on the basis of the x-ray data.

Interlayer orientation of NH_4Cl was determined as follows: as is already described, a peak appears on the lower temperature side when more than 330 m.mols of NH_4Cl is added per 100 g. of air-dried clay (Fig. 4 & 5). If it is allowed to allocate this peak to the NH_4Cl oriented on the external surface and to the free NH_4Cl, its peak temperature would give a measure of the amount of NH_4Cl not oriented between the silicate layers, because there is a relation between the NH_4Cl content of the samples and the peak temperature as shown in Fig. 5. Thus, the interlayer orientation maximum of NH_4Cl was estimated at 240 50 m.mols per 100 g. of air-dried clay, which is considerably higher than the value 185 m.mols estimated on the x-ray data. The reason for this difference will be discussed later in comparison with the third estimate for this value.

Wet and Dry Preparation of the NH_4Cl-Halloysite Complex

It was previously shown (6) that merely grinding hydrated halloysite with NH_4Cl crystals in an agate mortar for 10 to 15 minutes (dry preparation) produces the same 10.5 Å. of basal spacing. DTA curves of thus prepared samples (100 and 400 m.mols NH_4Cl per 100 g. of air-dried clay) are entirely identical to those of wet preparations shown in Fig. 4, indicating that both preparations are the same also in the quantitative aspect of the formation of the NH_4Cl-halloysite complex. It is of interest in dry preparation that NH_4Cl disperses very rapidly from visible crystals to the monomolecular state in the absence of free water molecules, although a stickiness develops on grinding, probably due to the replacement of the interlayer water. Since the similar reaction does not occur with metahalloysite and probably not with kaolinite, dry preparation can be utilized for differentiation of halloysite (hydrated or partially hydrated) from these 1:1 minerals on DTA curves on account of its rapidity and simplicity.

Replacement of the Interlayer Water

Effects of the NH_4Cl-treatment on the water content of halloysite and metahalloysite are shown in Fig. 6. Determination of the water content was carried out on the samples equilibrated at a relative humidity of 65 per cent, that was selected on the basis of the fact that the water content of metahalloysite and halloysite showed nearly constant values in the range of R.H. 60 to 80 per cent, avoiding possible dehydration or condensation.

The water content of halloysite at first decreases rapidly and then gradually with the increase of the rate of NH_4Cl addition. The first reduction of the water content indicates that approximately two molecules of the interlayer water are replaced by one molecule of NH_4Cl. *X*-ray analysis and DTA have shown that two molecules of NH_4Cl orient per unit cell of halloysite. Hence the 2/1 ratio implies that four molecules of water orient per unit cell of halloysite in accordance with Hendricks and Jefferson's "hexagonal net theory" (2). The following slower reduction suggests that NH_4Cl orients also on the external surface as well as on the interlayer surface with the increasing rate of NH_4Cl addition. Even on the interlayer surface, the replacement ratio may differ on its periphery from its central portion, but as a whole, it is very nearly one to one. For metahalloysite, the NH_4Cl-treatment results in increase in the water content apparently at the rate of 1 to 1 (Fig. 6), suggesting that NH_4Cl orients together with the extra water on the external surface.

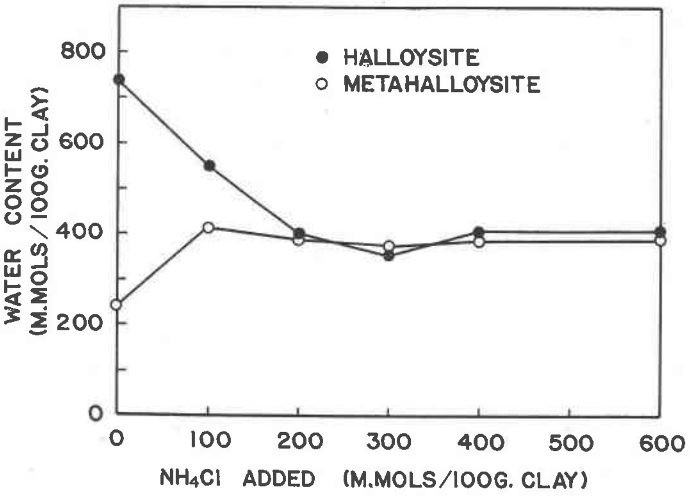

FIG. 6. Water content of NH_4Cl-treated halloysite and metahalloysite.

Providing the ratios of 2/1 and 1/1 are assumed in the replacement and adsorption of the water on the interlayer and external surfaces, a calculation affords an approximate estimate for the interlayer orientation maximum of NH_4Cl (x).

$$\underset{\substack{\text{Orientation maximum}\\ \text{on halloysite}\\ \text{(x-ray \& DTA)}}}{2x-(330-x)} = \underset{\substack{\text{Total reduction of}\\ \text{water content of halloysite}\\ \text{(Fig. 6)}}}{340}$$

$$x = 220 \text{ m.mols/100 g. of air-dry clay}$$

This is comparable to the 240 m.mols estimated by DTA, but x-ray data have shown a little lower value (185 m.mols) on the assumption that the area of the external surface is the same for halloysite and metahalloysite. Therefore, the simple subtraction of the orientation value for metahalloysite from that for halloysite seems likely to induce an overestimation for the area of the external surface. When halloysite is heated at 300° C., a part of the interlayer surface may be exposed as a new external surface owing to the peeling off of the curved sheet of halloysite, and/or the interlayer spaces may not completely close to the penetration of NH_4Cl.*

The replacement of the interlayer water by NH_4Cl is indicative of the greater strength in bonding between NH_4Cl and halloysite than that between water and halloysite. Upon drying halloysite from the solutions, the molar ratio of NH_4Cl to water in the bulk solution is not likely to exceed that in the saturated solution of NH_4Cl, namely, 1/7.75 at 30° C. Although the interlayer NH_4Cl is leached out again by washing with water (6), if only a mass action effect is assumed, it seems difficult to account for the observed replacement of the interlayer water.

CONCLUSION

It is concluded that two molecules of NH_4Cl per unit cell, in the form of a monomolecular layer, orient on the SiO-sheet of the silicate layer, probably mainly owing to the geometrical fitting of NH_4^+ in the cavity of the oxygen hexagon in the SiO-sheet. The bonding forces between

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* A recent study (**) has shown that grinding metahalloysite with NH_4Cl for 1 hour causes a shift of the 7.3 Å reflection to 10.3–10.4 Å, indicating penetration of NH_4Cl between its silicate layers. Sample preparation in this study involves manual grinding of NH_4Cl-treated halloysite and metahalloysite for 10–15 minutes to obtain powder samples fine enough for quantitative x-ray analysis. Reexamination of the x-ray pattern of the NH_4Cl-treated metahalloysite has revealed a slight shift of the 7.3 Å reflection towards 10 Å. Partial penetration of NH_4Cl into metahalloysite may largely account for the overestimation for the external surface area. The true orientation maximum on the external surface has been estimated at 40 m.mols per 100 g. of air-dry clay.

** "Use of salt complex for differentiation of halloysite from kaolinite," Read at the Second Annual Meeting of the Clay Mineral Group of Japan (Tokyo), December, 1958.

NH_4Cl and halloysite at the interlayer spaces are greater than those between the interlayer water and halloysite.

Oriented NH_4Cl no longer contributes to the *x*-ray diffraction as the normal salt, and shows some distinctive structural and thermochemical features depending on the orientation site. The preparation of the NH_4Cl-treated-clay samples, by either drying from an NH_4Cl solution or dry grinding with NH_4Cl crystals could be utilized for differentiation of halloysite (hydrated or partially dehydrated) from metahalloysite and kaolinite.

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