# THE RELATIONSHIP BETWEEN THE HYDRATED AND DEHYDRATED STATES OF AN HALLOYSITE

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**Abstract**— A study of the mineralogical changes taking place during the loss of interlayer water in an halloysite has been carried out in order to clarify the relationship between the most hydrated and least hydrated states of the mineral. A number of samples of halloysite which together exhibit a variety of average interlayer water capacities were obtained by the conditioning of a largely hydrated sample with different atmospheres of known relative humidities. Profiles were obtained of X-ray peaks which characterize the interlayer water capacities of halloysite samples. An attempt has been made to analyse these profiles into a sum of peaks attributable to the fully hydrated and dehydrated states of the mineral. Such an analysis does not satisfactorily explain the profile shapes. A mechanism of interstratification of hydrated and dehydrated kaolin layers in which there is a tendency towards the segregation of these layer types gives a more satisfactory explanation of these profile shapes. It is concluded that dehydration takes place through an interstratification in which there is a partial segregation of the two basic layer types. This conclusion implies that halloysites with all average interlayer water contents between 0 and 2 molecules per unit cell may exist and that fully hydrated halloysite and dehydrated halloysite are the end members of a continuous series of hydration states.

## INTRODUCTION

THE MINERALOGICAL changes taking place during the loss of the interlayer water in a New Zealand halloysite have been studied.

The study was an attempt to clarify the relationship between the fully hydrated state of halloysite and the dehydrated state of the mineral. Uncertainty over the nature of this relationship has led to debates about the nomenclature of halloysites. Mehmel (1935), Hendricks (1938) and Alexander *et al.* (1943), on the one hand, viewed these hydration states as separate mineral phases. MacEwan (1947), on the other hand, suggested that the hydrated and non-hydrated states of halloysite are members of a series which vary in their degree of hydration, and could be regarded as two forms of a single substance. He drew an analogy between halloysite and montmorillonite, another layered silicate with irregular stacking and interlayer water.

Several workers have investigated the dehydration of hydrated halloysites. One of the principal methods which has been used in these investigations is X-ray diffraction. This method was used in this particular type of study by Brindley and Goodyear (1948), Harrison and Greenberg (1962) and Hughes (1966).

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Brindley and Goodyear claimed that their data indicated that one form of halloysite ("hydrated halloysite") which exhibited basal spacings in the range 9·5–10·1 Å, gave rise to just one other form ("metahalloysite") which showed basal spacings of 7·5–7·9 Å. They interpreted the variations in the spacings of the two phases to mean that there is a small range of basal spacings at either end of the dehydration series over which interstratification of the aluminosilicate layers with water may take place. It was concluded that there were no forms of halloysite with basal spacings, and therefore, interlayer water content, intermediate between those attributable to the hydrated phase, on the one hand, and the metahalloysite phase, on the other.

Hughes obtained diffraction curves for an halloysite during dehydration which were similar in shape to those of Brindley and Goodyear and he assumed that Brindley and Goodyear's interpretation was correct.

Most of Harrison and Greenberg's traces for partially hydrated halloysites were similar in shape to those of Brindley and Goodyear. In addition, these workers obtained traces from some partially hydrated halloysites which showed no peaks at either end of the basal spacing range. Such traces contained a broad band between 7·2 and 10·1 Å. They interpreted this result to mean that many crystallites in these particular samples had some of their interlayer positions filled with water while the other interlayer positions were empty. The pos-

sibility of hydration states of halloysites with an average interlayer water content between that of the most hydrated and the dehydrated states of the mineral was thus suggested.

## MATERIAL

The particular halloysite which was studied was obtained from the same deposit as that studied by Hughes (1966). This occurs near Te Puke, New Zealand. The deposit is secondary and was probably formed by weathering and/or hydrothermal action on rhyolite and andesite.

A sample from this deposit was air dried and lightly ground. A size fractionation of the aggregate and the subsequent selection of a particle size fraction which gave an X-ray pattern showing little or no evidence of minerals other than halloysite (viz. the $0\cdot75$–$1\cdot7$ $\mu$m e.s.d. fraction) produced a suitable material for study. Size fractionation was effected using a method described by Jackson (1956). A sample of this fraction was kept under water in order to prevent the loss of interlayer water which takes place when halloysites are exposed to the atmosphere for long periods of time.

## APPARATUS

An enclosed sample holder was designed so that an halloysite sample could be equilibrated at various relative humidities and examined by X-ray diffraction with Cu$K_\alpha$ radiation while at a constant humidity. The cylindrical cover around the sample holder was made of brass but also contained windows covered with Mylar film through which X-rays passed into and out of the sample in the holder. It was connected by rubber and glass tubing to a flask containing a humidity controlling sulphuric acid solution.

The apparatus consisting of both sample holder and flask was maintained at a pressure of 20–25 mm Hg throughout the process of conditioning the sample at a constant relative humidity (R.H.) value and during the determination of the X-ray diffraction plots. The apparatus was kept at a temperature of $20°\pm1°C$ during the equilibration of the sample with the constant humidity atmosphere. It was found that the maximum variation in the density of the sulphuric acid solutions was equivalent to a maximum humidity variation of $\pm1\%$ R.H.

By comparing the shapes of the (001) peak profiles in charts recorded from samples subjected to successively longer times of treatment with an atmosphere at a particular R.H. value, it was decided that $3\frac{1}{2}$ days was the minimum time for the attainment of equilibrium between the sample and the atmosphere in this apparatus.

## METHOD OF RECORDING PROFILES

The procedure for obtaining a line profile consisted of recording the counts received by a Geiger–Müller tube over constant periods of time at angular intervals of $0\cdot05°$ $2\theta$ over the range from $5\cdot5°$ $2\theta$ to $14°$ $2\theta$. Since the standard deviation in the number of X-ray counts is equal to the square root of the total number of counts (Peiser et al., 1960, p. 222), it was desirable to have as large a number of counts as practicable.

After a complete profile had been recorded, the sulphuric acid solution was replaced by one corresponding to another relative humidity value and conditioning was carried out for a further $3\frac{1}{2}$ days or more. Diffraction traces were obtained from time to time in order to follow changes during conditioning.

All of the recorded counts were corrected for coincidence losses caused by the finite resolving time of the Geiger counter (Klug and Alexander, 1954). The shapes of peaks of different intensities could be compared after these corrections had been made.

## RESULTS

The resulting series of profiles showed that the intensities of the reflections at low angles decrease relative to those at higher angles as dehydration of halloysite proceeds. The reflections at one or the other or both ends of the profiles were more intense than the reflections in the intermediate angular range (from $9\cdot4$ to $11\cdot3°$ $2\theta$) in all of the profiles.

Trials at interpretation based on physical mixtures of two discrete phases (the fully hydrated and fully dehydrated phases) could not account for the observed profiles for halloysites with intermediate water contents. This result led to the consideration of interstratification.

## DISCUSSION

*Calculation of profiles from interstratification theory*

A computer program was written to calculate basal peak profiles from interstratifications of non-hydrated kaolin layers of $7\cdot2$ Å spacing (type $A$ layers) with hydrated kaolin layers of $10\cdot1$ Å spacing (type $B$ layers) by means of the method of MacEwan et al. (1961). Where $P_A$ is the proportion of type $A$ layers and $P_{AA}$ is the probability that a type $A$ layer follows another layer of the same type on travelling through the structure in one specified direction, plots were calculated for $P_A = 0\cdot1$, $0\cdot2$, $0\cdot3$, ..., $0\cdot9$, and, for each of these values of $P_A$, for $P_{AA} = 0$, $0\cdot1$, $0\cdot2$, $0\cdot3$, ..., $1\cdot0$. The Lorentz-polarisation factor for random powers was used in these calculations. The structure factor was derived from the kaolin layer structure (as described by Pauling, 1930).

The mixing functions were calculated for 14

layer thick particles. A calculation which was made using the Scherrer equation (Klug and Alexander, 1954, p. 491), and, as a standard, the breadth of a peak at $11 \cdot 1° 2\theta$ from a complex of nickel (NiN$_4$-C$_6$H$_{10}$·C$_2$O$_5$·3H$_2$O) in which all particles are $> 70$ Å and therefore too large to produce peak broadening. This calculation, which was approximate, showed that the sample of halloysite which was studied consisted of particles with an average thickness of about 20 layers. Fourteen layers was a practical maximum for the program which was used, however. MacEwan *et al.* (1961) showed that, while variations in the assumed thicknesses of particles had only a minor effect on the shapes of profiles which were calculated, the assumption of a smaller than actual average layer thickness leads to an underestimate of peak heights and an overestimate of the intensity and angular spread of the background underneath the peaks.

*Comparison of experimental and calculated profiles*

The most significant features of the partially hydrated halloysite peak profiles are, (1) the spread of intensity over the entire basal spacing range in all profiles other than those from the more dehydrated samples, and (2) the appearance of maxima in only two narrow ranges at either ends of the profiles. Profiles calculated for cases of either complete or partial alternation of layers and for completely random interstratifications all show one maximum which varies in position throughout the range of basal spacings as $P_A$ is varied. Furthermore, plots calculated for the case of the complete segregation of layers all show two sharp peaks which are invariant in both position and breadth as $P_A$ is varied from $0 \cdot 1$ to $0 \cdot 9$. None of these types of interstratification is therefore able to account for the series of experimental plots. Only those plots which were calculated for interstratifications in which there is a partial segregation of layers (i.e. those cases for which $P_A < P_{AA} < 1 \cdot 0$) reproduce those characteristic features of the group of experimental curves which are noted above.

The right hand series of curves in Fig. 1 have been calculated for interstratifications of this kind for successively higher values of $P_A$. At each value of $P_A$, a $P_{AA}$ value was chosen which gives the plot with essential features such as peak position and angular spread of intensity above background most similar to those in the experimental plots. It was observed that only changes of $\geqslant 0 \cdot 1$ in $P_{AA}$ reflected significant changes in the shapes of these curves and in the positions of the maxima when $P_A$ was low. Thus, the effect of change in $P_{AA}$ by increments of only $0 \cdot 1$ were tested for $P_A \leqslant 0 \cdot 5$ while the effect of changes in $P_{AA}$ of $< 0 \cdot 1$ were observed

for $P_A > 0 \cdot 5$. Plots were also calculated for $P_A = 0 \cdot 95$ in order to try to reproduce the form of the experimental curves for the most dehydrated samples.

This series of calculated curves is compared with the series of experimental plots on the left hand side of Fig. 1. Individual experimental and calculated curves may not be compared on the basis of a common ratio of dehydrated layers to hydrated layers as the starting material was partly dehydrated to an undetermined extent. Consequently, the degree of hydration of the samples used to obtain the experimental plots is not known.

The characteristic features of the experimental curves which have been mentioned above are shared by this series of calculated curves. All of these calculated plots show a spread of intensity above background over the whole range of basal spacings. In addition, the series of plots which is presented on the right hand side of Fig. 1 shows maxima in only two narrow ranges at either ends of the profiles.

The probability coefficients which gave rise to these curves were chosen by a trial-and-error process. It was observed in the course of this process that the values of $P_{AA}$ which gave the curves with essential features which were most similar to those of the experimental plots changed throughout the series in such a way that $(P_{AA} - P_A)$ decreased as $P_A$ increased. It was then discovered that the sets of probability factors throughout the series were related to each other by closely similar values for the "degree of segregation" as defined by Cesari *et al.* (1965). "Degree of segregation" $S$ is given by

$$S = 1 - \frac{1 - P_{AA}}{1 - P_A}.$$

Each value of $P_{AA}$ which gave a curve with a "best fit" to the characteristics of the group of experimental curves was related to its associated $P_A$ value by an $S$ value of between $0 \cdot 2$ and $0 \cdot 3$. Table 1 gives values of $P_{AA}$ at each value of $P_A$ which are predicted when $S = 0 \cdot 2$ and $S = 0 \cdot 3$, together with the value which is selected for the "best fit" by the trial-and-error method. Those values of $P_{AA}$ closest to the selected values at each $P_A$ which were tested and then rejected because they gave a less satisfactory fit to the group of experimental plots are also given in Table 1.

The series of calculated curves shown in Fig. 1 differs from the adjacent series of experimental curves in some respects. The backgrounds are much steeper in this series than in that of the experimental plots. The calculation of these plots does not take into account the chief factors con-
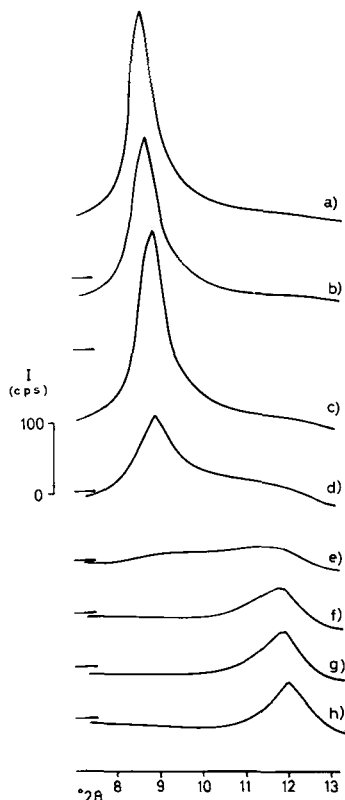
Fig. 1a. Series of partially hydrated halloysite basal peak profiles. R. H. values at which profiles were obtained: (a) 100%, (b) 75%, (c) 54%, (d) 35%, (e) 18%, (f) 9%, (g) 4%, (h) 0%.

Fig. 1b. Series of curves which are calculated for the values of $P_A$ and $P_{AA}$ that are shown. Intensity scale in counts per second applies to experimental profiles only.

Table 1. Comparison of probability coefficients for "best fits" and calculated coefficients

| $P_A$ | $P_{AA}$ for "best fit" | $P_{AA}$ for rejected plots | $P_{AA}$ calculated for $S = 0.2$ | $P_{AA}$ calculated for $S = 0.3$ |
|---|---|---|---|---|
| 0·3 | 0·5 | 0·4; 0·6 | 0·36 | 0·51 |
| 0·4 | 0·5 | 0·4; 0·7 | 0·52 | 0·58 |
| 0·5 | 0·6 | 0·5; 0·7 | 0·60 | 0·65 |
| 0·6 | 0·7 | 0·68;0·8 | 0·68 | 0·70 |
| 0·7 | 0·77 | 0·75;0·8 | 0·76 | 0·79 |
| 0·8 | 0·85 | 0·84;0·86 | 0·84 | 0·86 |
| 0·9 | 0·93 | 0·92;0·95 | 0·92 | 0·93 |
| 0·95 | 0·96 | 0·97 | 0·96 | 0·965 |

tributing to the background in the experimental cases, viz. incoherent scattering of X-rays, the scattering of white radiation, and fluo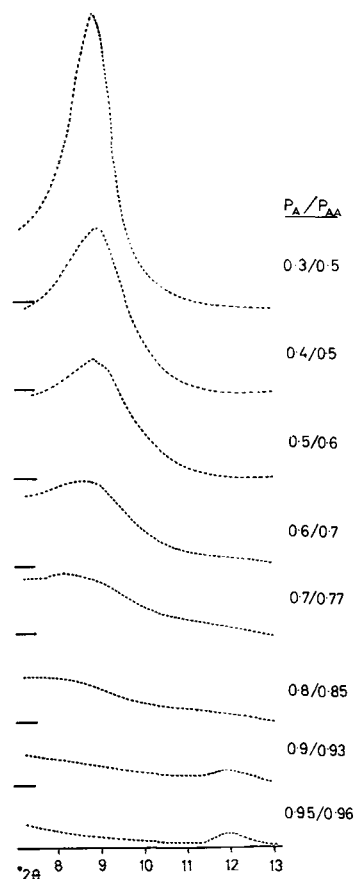rescence (Nuffield, 1965, p. 188). As a result, the back-grounds which are calculated are much lower than actual backgrounds at the higher angles. Furthermore, as observed earlier, the assumption that the size of the particles is smaller than the actual size produces an enhanced background intensity at the lower angles, particularly in plots for low values of $P_A$. The steep background effects a shift in peaks towards lower angles.

The assumption of a smaller particle size than that pertaining to the particular halloysite sample being examined also results in considerable broadening of the maxima relative to those in the profiles obtained experimentally.

A further difference between the conditions of derivation of the series of experimental plots and that of the calculated plots arises from the fact that the shapes of the former include the effect of broadening by instrumental causes and from structural disordering while no account is taken of these fac-

tors in obtaining the latter. Peaks are broadened either symmetrically or asymmetrically by these factors (Stokes, 1960) but it is unlikely that such effects are significant by comparison with the particle size broadening of the calculated peaks.

## CONCLUSIONS

None of the (001) X-ray peak profiles obtained from partially hydrated samples of the halloysite which was studied resembled those of a mineral with a single basal spacing or those of a mixture of two mineral phases, each with a different basal spacing. Thus the dehydration of this halloysite could not be explained either by a single step mechanism in which a fully hydrated phase gives rise to a fully dehydrated phase without the formation of intermediates or by a completely random interstratification of the two phases in the course of the dehydration process. The characteristic features of the halloysite peak profiles were shown to be closely reproduced throughout the range of possible interlayer water contents by profiles calculated from interstratification theory for the case of partially segregated mixtures of the basic layer types. Every interlayer space in a partially hydrated halloysite sample is considered to be either completely full of water or completely empty and it is concluded that the loss of the interlayer water takes place through an interstratification in which there is a partial segregation of the component hydrated and dehydrated kaolin layers.

The conclusions of this study may be compared with those of Brindley and Goodyear's (1948) study. Brindley and Goodyear considered that all halloysite samples comprise a mixture of some zones of largely hydrated layers with other zones of largely dehydrated layers and that there is a separation between these two types of zones in each of these mixtures. By comparison, the present study concludes that the partially hydrated forms of the mineral are comprised of layers, which, while tending to segregate into some zones of hydrated halloysite and other zones of dehydrated halloysite, also show significant randomness in their mixing. The slight difference between these two interpretations of the mixing of layer types in partially hydrated halloysites leads to an important difference between the ranges of possible compositions of halloysites which are consistent with these interpretations. Brindley and Goodyear conclude that halloysites may not exhibit average interlayer water contents within a certain range of values (i.e. between 0·66 and 1·33 $H_2O$ molecules per unit cell). In contrast, the mechanism derived from the present study implies that halloysites with average interlayer water contents encompassing all values between 0 and 2 molecules per unit cell are possible.

The results of this study indicate that the fully hydrated and fully dehydrated states of this halloysite should be considered as the end members of a continuous series of hydration states of the mineral. Churchman and Carr's (1972) results strongly suggest that the different hydration states of this halloysite corresponding to each of the various average interlayer water contents betwen 0 and 2 molecules of $H_2O$ per unit cell have similar relative stabilities, that each one of these hydration states is the unique product of hydrothermal treatment at a particular temperature and pressure, and that each is stable at that temperature and pressure for a significant period of time (at least 36 days).

The X-ray profiles which were obtained during the dehydration were similar in shape to those which have been obtained for other halloysites by different workers (e.g. Brindley and Goodyear, Hughes, and Harrison and Greenberg). This suggests that the conclusions drawn from this study may be applicable to halloysites in general.

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**Résumé** — Une étude des changements minéralogiques qui apparaissent pendant le départ de l'eau interfeuillet d'une halloysite a été effectuée afin de clarifier la relation entre l'état le plus hydraté et l'état le moins hydraté de ce minéral. Un certain nombre d'échantillons d'halloysite montrant une grande variété de capacités moyennes en eau interfeuillet a été obtenu en conditionnant un échantillon fortement hydraté avec différentes atmosphères d'humidité relative connue. Les profils des pics de rayons X obtenus caractérisent les capacités en eau interfeuillet des échantillons d'halloysite. Une tentative a été faite pour analyser ces profils comme une somme de pics attribuables aux états totalement hydraté et déshydraté du minéral. Une telle analyse n'explique pas d'une façon satisfaisante la forme des profils. Un schéma d'interstratification de feuillets de kaolin hydraté et déshydraté dans lequel il y a une tendance à la ségrégation de ces types de feuillet donne une explication plus satisfaisante de la forme de ces profils. On en conclut que la déshydratation se fait par l'intermédiaire d'une interstratification dans laquelle il y a une ségrégation partielle de deux types de feuillets de base. Cette conclusion implique que les halloysites avec tous les contenus moyens en eau interfeuillet compris entre 0 et 2 molécules par maille peuvent exister et que l'halloysite totalement hydratée et l'halloysite totalement déshydratée sont les termes extrêmes d'une série continue d'états d'hydratation.

**Kurzreferat** — Zur Aufklärung der Beziehungen zwischen den meisthydratisierten und mindesthydratisierten Zuständen eines Halloysite wurde eine Untersuchung der mineralogischen Veränderungen, die im Laufe des Verlustes von Zwischenschichtwasser in dem Mineral stattfinden, durchgeführt. Durch Konditionierung einer weitgehend hydratisierten Probe mit verschiedenen Atmosphären bekannter relativer Feuchtigkeiten wurde eine Reihe von Halloysitproben erhalten, die gemeinsam eine Vielzahl von durchschnittlichen Zwischenschichtwasservermögen aufweisen. Es wurden Profile von Röntgenspitzen erhalten, die die Zwischenschichtwasservermögen von Halloysitproben kennzeichnen. Es wurde versucht diese Profile in eine Anzahl von Spitzen entsprechend den voll hydratisierten und dehydratisierten Zuständen des Minerals auszuwerten. Eine derartige Auswertung stellt keine befriedigende Erklärung der Profilformen dar. Ein Mechanismus der Zwischenlagerung von hydratisierten und dehydratisierten Kaolinschichten, bei welchem eine Neigung zur Absonderung dieser Schichtarten herrscht, gibt eine befriedigendere Erklärung dieser Profilformen. Es wird geschlossen, dass Dehdratisierung durch eine Zwischenlagerung stattfindet bei welcher eine teilweise Absonderung der beiden grundlegenden Schichtarten erfolgt. Dieser Schluss bedeutet, dass Halloysite mit allen durchschnittlichen Zwischenschichtwassergehalten zwischen 0 und 2 Molekülen pro Einheitszelle existieren können, und dass voll hydratisierter Halloysit und dehydratisierter Halloysit die Endglieder einer kontinuierlichen Reihe von Hydrationszuständen darstellen.

**Резюме** — Исследовались минералогические изменения происходящие в галлуазите во время потери межслоевой воды для выяснения соотношения между сильно гидратированным и слабо гидратированным состоянием минерала. Получили несколько образцов галлуазита с различной средней межслойной влагомерностью путем кондиционирования крупногабаритного гидратированного образца в различных атмосферах при известной относительной влажности. Пропусканием рентгеновских лучей получили максимальные профили, характеризирующие межслойную влагомерность образцов галлуазита. Пытались анализировать эти профили. Анализ не дал удовлетворительного объяснения формам профилей. Механизм впластования гидратированного и дегидратированного слоев каолина у которых имеется тенденция обособления слоев этих типов, объясняет более удовлетворительно профили этого типа. В заключение решили, что галлуазиты, с общим средним содержанием межслоевой воды между 0 и 2 молекул на элементарную ячейку, могут существовать, и что полностью гидратированный галлуазит и дегитратированный галлуазит являются конечными членами непрерывного состояния гидрации.