

THE DEFINITION AND NOMENCLATURE OF HALLOYSITES

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Abstract—This review of the literature shows that there have been many attempts to modify or revise the original definition of halloysites as distinguished from kaolinites, which was based on the greater water content of the halloysites. In general, these various attempts have arrived at definitions of halloysites as distinguished from kaolinites that are based on one or more particular instrumental or chemical techniques. Further investigations with almost all of these techniques have shown the apparently clear distinctions of this kind to be misleading. All such instrumentally—or chemically—based definitions were shown to either complicate and confuse the distinction between halloysites and kaolinites or to provide only empirical and subtle distinctions. It is concluded that only the original definition, with slight adaptations, enables clear and unambiguous distinctions to be made between halloysites and kaolinites. It is noted, however, that a distinctive structure for halloysite has been postulated as a result of electron diffraction studies. Further studies of this kind could well establish such a structure as being definitive of the mineral species.

The literature also reveals a long-standing disagreement over the nomenclature of different forms of halloysite and particularly over the nomenclature of and distinction between the two forms of halloysite at the extreme ends of the hydration series. An analysis of experimental studies of the relationship between these two and other hydration states of halloysite reveals that forms of halloysite with all possible interlayer water contents between 0 and 2 molecules H_2O per $Al_2Si_2O_5(OH)_4$ unit cell may exist and that the two end members of the hydration series may not be seen as distinct phases. The fully dehydrated halloysite is the only thermodynamically stable form of the mineral. A nomenclature system which was proposed by MacEwan in 1947 is consistent with these results. This system, amended only by the exclusion of the unnecessary term 'metahalloysite' should therefore be adopted in all studies of halloysites.

DISTINCTIONS BETWEEN HALLOYSITES AND KAOLINITES

Introduction

Halloysite was first described as a separate mineral by P. Berthier in 1826. It was originally distinguished from kaolinite (in the 19th century) on the basis of a higher proportion of water associated with it than with kaolinite (McEwan, 1947; Faust, 1955). The main effect of subsequent applications of many instrumental and chemical techniques to studies of the mineral has been to introduce not only more complicated but also more ambiguous criteria for distinguishing between the halloysite mineral species and the kaolinite species.

X-ray diffraction data

Halloysites from a number of different localities showed a distinctive pattern when first examined by X-ray powder diffraction techniques (Ross and Kerr, 1934). Halloysite appeared to have a lower crystallinity than kaolinite. This result confirmed that minerals which were given this name (or synonymous names) were different from kaolinites. Further X-ray diffraction studies which were published in the same year by Hofmann *et al.* (1934) revealed the existence of two forms of the mineral, a hydrated and a dehydrated form, with dehydration at $105^\circ C$ of the more

hydrated form leading to a material with similarities to kaolinite. Nevertheless, a clear distinction between the material which resulted from heating halloysite at $105^\circ C$ and kaolinite was recognised by Mehmel (1935).

The clarity of this distinction was shortly to be clouded by Brindley and Robinson's (1946) observation that clay minerals which were defined as kaolinites on the basis of their chemical composition nevertheless gave X-ray diffraction patterns which indicated halloysite-like random structures rather than the high crystallinity which was regarded as typical of kaolinites. Brindley and Robinson suggested that there may be a continuous series of 1:1 clay minerals, extending from highly crystalline kaolinite at one extreme to highly disordered halloysite at the other.

Electron micrographs

The first applications of electron microscopy had revealed an apparently sharp distinction between halloysites and kaolinites. Halloysites had shown a fibrous morphology which was in sharp contrast to the platy hexagonal shape that was typically exhibited by kaolinite particles (Alexander *et al.*, 1943). Bates *et al.* (1950) explained the distinctive morphology of halloysites, which they characterized as tubular, on the basis of a difference between the *b*-axis dimensions of the tetrahedral and octahedral layers comprising the mineral. Thus there is an inherent strain in the structure which causes it to curl when the restraint

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of the close proximity of adjacent layers (as in kaolinite) is lessened by the intercalation of water in halloysite. It was concluded that, as halloysites contain interlayer water (by definition) they must therefore possess a tubular morphology.

This causative connection between structural water and morphology can be disputed on the grounds of the results of studies by both Hope and Kittrick (1964) and Radoslovich (1963). Hope and Kittrick examined extremely thin particles of kaolinite which were derived from kaolinite aggregates by a chemical treatment and showed that these curled to give tubular shapes when air-dried but remained flat when freeze-dried. They claimed that halloysites had also curled during the drying process that accompanied their examination by electron microscope. Radoslovich showed, on theoretical grounds, that a misfit of dimensions between the silicon tetrahedral sheet and the aluminium octahedral sheet in kaolin minerals would be compensated, at least to some extent, by rotation of the silica tetrahedra. Such rotation could lead to a reduction in the *b*-dimension of the tetrahedral layer. A conclusion to be drawn from this work, as from Hope and Kittrick's, is that it is conceivable that halloysite may be found in a non-tubular form.

Some studies have reported kaolin minerals with a platy morphology which have interlayer water and also a high degree of disorder. A platy mineral was found by Kunze and Bradley (1954) to have a basal spacing of 7.56 Å which was increased to 7.76 Å upon the formation of a complex with ethylene glycol, while the platy kaolin investigated by Souza Santos *et al.* (1966) had a basal spacing of 10.05 Å which decreased to 7.2–7.3 Å on drying. As a further indication that tubular morphology, interlayer water and structural disorder are not necessarily connected, it is noted that Souza Santos *et al.* (1965) had reported a tubular kaolin mineral with interlayer water but with a high degree of order according to X-ray (and also electron) diffraction data.

Some later studies of halloysite electron micrographs (Chukhrov and Zvyagin, 1966; Diamond and Bloor, 1970; Askenasy *et al.*, 1973) have shown that halloysites may assume shapes other than tubes or plates. Indeed, Chukhrov and Zvyagin concluded from their studies that halloysites typically crystallise as "a combination of radial zones diverging from one axis (very close to the *b*-axis) and of elongated prismatic, mostly hollow crystallites with all the faces parallel to the *ab*-plane". Diamond and Bloor (1970) took issue with Chukhrov and Zvyagin's contention that their proposed morphology is typical of all halloysites, however.

Electron diffraction data

The fact that non-tabular kaolin minerals can display considerable 3-dimensional structural order has been indicated by the application of the techniques of electron diffraction to single crystallites by Honjo *et al.* (1954), Kulbicki (1954) and Chukhrov and Zvyagin (1966). The discovery of structural order by the

use of electron diffraction where X-ray diffraction data had suggested that it was lacking can be explained from the theory of X-ray diffraction if it is supposed that such order exists but that it is obscured by distortions of the X-ray diffraction patterns which arise from the curving of the layers (Whittaker, 1954; Waser, 1955). It is thus seen that kaolin minerals may be either tabular or non-tabular and that kaolin minerals displaying either morphology can be either ordered or disordered.

Differential thermal analyses

Results of differential thermal analyses of the minerals have also appeared to provide some criteria for differentiating between halloysites and kaolinites. The main endothermic peak occurs at a lower temperature for halloysites than for kaolinites and is considerably more asymmetric in halloysite D.T.A.'s than in those for kaolinite. Bramao *et al.* (1952) examined D.T.A. plots from a number of halloysites and kaolinites and discovered that, while the values for a quantitative measure of peak asymmetry, the 'slope ratio', varied widely over the 11 kaolinites and also over the 7 halloysites that were studied, there was no overlap of the kaolinite range (from 0.78 to 2.39) with that of the halloysites (from 2.50 to 3.80). The peak asymmetry, which is due to a low-temperature shoulder, arises from weakly-bound hydroxyls in the structure. Chukhrov and Zvyagin (1966) point out that these particular hydroxyls may derive from residual interlayer water molecules. Hence the asymmetry of the endothermic D.T.A. peak of halloysite (and also the lower temperature of the peak, which may itself be a product of peak displacement due to asymmetry) might indicate nothing about the distinctiveness of the structure of halloysite except to confirm the well-known fact that residual interlayer water is retained up to relatively high temperatures.

Infra-red spectra

Studies of the i.r. spectra of halloysites have indicated that many of the main features of the spectra occur at similar frequencies to those in kaolinite spectra. The principal differences between the spectra of the two types of minerals are that these features are often more diffuse in halloysite spectra than in kaolinite spectra and that the relative intensities of the various peaks are different (e.g. Lyon and Tuddenham, 1960; Farmer and Russell, 1964). Halloysites also show peaks which can be attributed to the i.r. vibrations of interlayer water (Pampuch and Blaszcak, 1964; Wada, 1965). The relatively more diffuse nature of the absorption bands and the type of difference between relative band intensities in halloysite spectra compared with kaolinite spectra tend to support the indication of early X-ray diffraction data (e.g. Ross and Kerr, 1934) that most halloysites, at least, have more disordered structures than most kaolinites, although there are marked variations between different halloysites in these features of the i.r. spectra (Chukhrov and Zvyagin, 1966).

Chemical reactivities

Early studies which showed that certain organic compounds were intercalated by halloysites but not by kaolinites (MacEwan, 1946) suggested that this type of chemical distinction between the two minerals could be made. Halloysites were later shown to intercalate particular ionic salts as well (Wada, 1959). Andrew *et al.* (1960) then showed that not only halloysite but also kaolinite could form intercalation complexes with ionic salts, while Weiss *et al.* (1963) showed that kaolinites as well as halloysites could form intercalation complexes with a number of organic compounds. Range *et al.* (1969) determined that the different kaolins varied in their abilities to form complexes with different organic compounds and devised a scheme for classifying kaolin samples either as one of four different 'types' of kaolinite or as halloysite. All kaolin minerals had basal spacings of 7.2–7.4 Å when dried at 110°C. Halloysites were expanded by treatment with hydrazine hydrate, remained expanded when the hydrazine was replaced with water by washing and had this water replaced by treatments with both ethylene glycol and glycerol. None of the types of kaolinite underwent all of these expansion and replacement reactions, with the different types undergoing different numbers of these reactions and with a mineral of each type participating in one or more of the particular reactions to a characteristic degree of completion. Range *et al.* also report that different halloysites show considerable differences in their behaviour towards certain other organic compounds, e.g. dimethyl sulfoxide and formamide and hence they conclude, like Chukhrov and Zvyagin (1966), that different halloysites exhibit a range of properties, probably as a result of there being different degrees of randomness and order within the halloysite mineral species.

A novel method of investigating the relationship between halloysites and kaolinites was applied by Hughes and Foster (1970). They discovered that there was the same strong correlation between the 'extractable material content' (an empirical measure of chemical reactivity) and the 'moisture content at fixed relative humidity' for all kaolin clays. Although results for halloysites tended to fall into a different area of the correlation curve from results for kaolinites there appeared to be no discontinuity between the two groups.

Conclusions and definition

A study of the literature thus shows that any attempt to modify or revise the original definition of halloysite is likely to be frustrated rather than aided by the application of the many instrumental and chemical techniques which have been applied to this problem in the past. Kaolin minerals which are characterized as halloysites by X-ray diffraction methods may appear to be typical kaolinites in electron micrographs (e.g. Kunze and Bradley, 1954; Souza Santos *et al.*, 1966) and vice versa (e.g. Souza Santos *et al.*,

1965). Electron diffraction results serve to further confuse the issue when kaolin minerals exhibiting a shape that is thought to be typical of halloysites and giving a characteristic halloysite basal spacing according to X-ray diffraction, have yet been shown to have considerable 3-dimensional order (e.g. Honjo *et al.*, 1954). DTA and i.r. data for kaolinites and halloysites have shown a difference on degree but not a difference in the nature of certain characteristic features of these charts and spectra for the two mineral types. The chemical reactivities of the various kaolin minerals have also been shown to differ only in degree so that chemically based distinctions between kaolinites and halloysites can only be made on the empirical grounds of their relative abilities to react with certain specified chemical compounds while the mechanisms of these reactions remain poorly understood (e.g. Carr and Hwa Chih, 1971).

A number of schemes have been suggested for the classification of minerals in the halloysite-kaolinite series into more than two subdivisions. Schemes which propose three subdivisions within this series, i.e. kaolinites, hydrated halloysites and dehydrated halloysites are not uncommon, but some have involved even more than three. These include Range *et al.*'s (1969) classification, with its chemical basis and also a scheme of Brindley and Souza Santos (1966) wherein these minerals are subdivided according to: (a) the particle morphology; (b) the state of hydration; and (c) the degree of crystalline order. According to this scheme, at least six names are required to specify all of the minerals which had previously been known as kaolinites or halloysites.

In complete contrast, it is observed that an exhaustive review of the subject by Douillet and Nicolas (1969) led these authors to conclude that the difficulties of formulating definitions of mineral types within the kaolinite-halloysite series could only be resolved if all minerals in the series were named 'kaolinite'. A description of the particular mineral under investigation from the points of view of hydration, morphology and degree of crystallinity would be used to specify it as a certain type of kaolinite, e.g. 'hydrokaolinite' would denote minerals with interlayer water and hence a 10 Å spacing. The term 'halloysite' would be dispensed with under this particular scheme.

The results of a number of studies (e.g. Mehmel, 1935; Honjo *et al.*, 1954; Chukhrov and Zvyagin, 1966) indicate that halloysites may be unique, however. Consequently, in order both to avoid unnecessary complications with superfluous nomenclature and also to ensure that the bulk of the studies of halloysites in the literature retain their relevance, we consider that halloysites should be simply defined as: *those minerals with a kaolin layer structure which either contain interlayer water in their natural state or for which there is unequivocal evidence of their formation by dehydration from kaolin minerals containing interlayer water.*

Evidence for the intercalation of water in a kaolin mineral is relatively easy to obtain, e.g. by the X-ray

diffraction identification of a basal spacing of > 7.2 Å which collapses to 7.2 Å irreversibly on drying at 110°C . By comparison, a strong argument for a particular non-hydrated kaolin mineral sample having a history of intercalation of water is probably only obtained when a number of different investigational techniques all give indications of the major kinds of structural effects which could be expected to derive from the earlier presence of water in the mineral. Thus, if a particular sample gives relatively diffuse X-ray diffraction and i.r. absorption spectra, has irregular, non-hexagonal shaped particles according to electron micrographs, gives a main endothermic peak that has a high 'slope ratio' in D.T.A. plots, is easily expanded with a number of organic compounds and ionic salts and then shows a basal spacing of 10.1 Å when the complexing agent is removed with water, then it may be characterized as a halloysite with a high degree of confidence. The results of a number of subsidiary measurements may also reflect a present or prior intercalation of water in a kaolin mineral and therefore aid in its identification as a halloysite. These include surface areas (generally higher for halloysites than for kaolinites), densities (generally lower for halloysites) and dielectric constants (generally higher for halloysites) (Grim, 1968). Furthermore, as pointed out by Brindley (1961), an X-ray diffraction pattern from a parallel oriented sample of an unknown kaolin mineral can reveal not only the degree of crystallinity of the mineral, but also the extent of curvature of its particles. Brindley suggests that strong evidence for a halloysite is obtained when the ratio of the (001) peak intensity to that of the 020,111) peak near 4.4 Å is less than 2:1. This method of distinction is based on observations that particles of halloysites are usually curved while those of kaolinites are usually flat. The limitations of this method in giving definitive indications of kaolin mineral types are revealed in the present review where there is shown to be no necessary correlation between particle morphology and the presence of interlayer water in a kaolin mineral.

If a sample shows some, but not all, of the major kinds of structural effects expected to derive from water intercalation as listed above, then the possibility that it is a mixture of halloysite and kaolinite (Brindley *et al.*, 1963), of kaolinite and smectite, or even that it contains a mixed layer interstratified kaolinite-smectite mineral of the type described by Wiewiora (1971, 1972) must first be considered. Otherwise the mineral will be classified as a kaolinite. Further research could reveal that there are distinctive structural features of halloysites that are detectable by electron diffraction (Chukhrov and Zvyagin, 1966—see discussion below). It is possible that reclassification (as halloysites) of some of the minerals which are defined by the above scheme as kaolinites would be justified on this structural basis.

It is noted that the intercalation of water into the interlayers of kaolin minerals via the removal by washing of another substance forming an interlayer

complex with the mineral may effect considerable changes in the structure of these minerals (Wiewiora and Brindley, 1969; Churchman and Carr, 1973). As a result of these changes the properties of the minerals, including dehydrated forms of halloysite, which have been treated in this way are likely to be atypical of halloysites. Hence the products of these treatments should not be classified as halloysites.

It has been suggested by some workers (Fieldes, 1955; Parham, 1969) that, with time, halloysites may transform to kaolinites in nature. The occurrence of such transformations could lead to some kaolinites which may have been formed in this way being classified as halloysites according to the basis for the classification that is proposed in this present paper. Nevertheless, these speculative suggestions which are supported by only circumstantial evidence are discounted to some extent at least by the fact that halloysites have been found in Jurassic or Cretaceous sediments which have derived from Precambrian granite-gneisses. Hence these halloysites have been stable for long periods of time (Parham, 1969). Parham also points out, conversely, that kaolinites are found in recent weathering products.

Chukhrov and Zvyagin (1966) concluded from a detailed study of a number of halloysites using electron diffraction, i.r. absorption and differential thermal analyses that this mineral type is comprised of a series of minerals encompassing a range of structural order. Kaolinites form a separate series on the same basis. The two mineral types are characterized by quite different and distinctive structures, with halloysites being monoclinic and having a 2-layer periodicity. They state "it can be inferred that all the characteristics of halloysites (water in the structure, radial zonality of prismatic crystals and a distinctive monoclinic two-layer structure in the anhydrous state) are not independent but are intimately interconnected and depend upon the conditions of formation of the mineral". More specifically it could be that the peculiar structural and morphological features of halloysites are a result of the fact that they contain water or have contained water in their interlayers. The fact that halloysites contain or have contained interlayer water could alternatively arise from pre-existing structural and morphological features.

A particular generalization by Chukhrov and Zvyagin which is most relevant to the clarification of the definition of halloysites is that concerning the distinctiveness of the monoclinic 2-layer structure to halloysites. Although this awaits confirmation by further extensive electron diffraction studies, it could conceivably provide the key to the absolute characterization of a mineral as a halloysite, whether it be hydrated or not.

It is concluded from an analysis of the literature that the one characteristic feature of halloysite which is indisputably established at this stage is the intercalation or the history of intercalation of water between its layers. This basis alone is both necessary and sufficient for distinguishing halloysites from kaolinites.

DISTINCTIONS BETWEEN DIFFERENT FORMS OF HALLOYSITE

Introduction

There have been many debates over the distinction between and nomenclature of different forms of halloysite (e.g. MacEwan, 1947; Brindley, 1951; Faust, 1955; Mackenzie, 1963). In particular, there has been considerable disagreement over the nature of the relationship between fully hydrated halloysite and fully dehydrated halloysite and hence over the nature of the relationship of these extreme forms of the halloysite hydration series to halloysites with intermediate interlayer water contents.

Alternative nomenclatures

The earliest workers on halloysite, e.g. Mehmel (1935), Hendricks (1938), Alexander *et al.* (1943) viewed the most hydrated halloysite and the most dehydrated halloysite as distinctly separate mineral phases. The fully hydrated halloysite was named 'halloysite' by Mehmel, 'hydrated halloysite' by Hendricks and 'endellite' by Alexander *et al.* Mehmel gave the name 'metahalloysite' to the dehydrated phase while this phase was designated 'halloysite' by Alexander and co-workers.

MacEwan (1947), on the other hand, suggested that the hydrated and non-hydrated forms of halloysite are members of a series which vary in the degree of hydration and that they could be regarded as two forms of a single substance rather than as entirely separate substances. The bases for this assertion were: (a) the observation that the space between adjacent kaolin sheets could be filled by other molecules besides water, e.g. by polar organic molecules; (b) the observation that the dehydrated form of halloysite was not uniform. Variations in the strength of binding between the structural sheets had been shown to exist; (c) a study of the analyses of naturally occurring halloysites which were published in the literature prior to 1934. This study showed that the whole range of composition of interlayer water between that corresponding to a formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and that appropriate to a formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ was covered in these analyses; and (d) the study of X-ray diagrams obtained from naturally occurring halloysites revealed evidence for the existence of intermediate forms of the mineral.

These results led MacEwan to draw on analogy between halloysite and montmorillonite. The implication for the nomenclature of different types of halloysite was that 'halloysite', like 'montmorillonite' in the analogous case, should serve as the name of the whole group of hydrates and of complexes with other compounds which are associated with the basic aluminosilicate layer $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The state of hydration of a particular sample or the name of the material intercalated between the aluminosilicate layers would be specified by a prefix, according to this scheme of nomenclature. Thus 'hydrated halloysite' would designate the high-water form, 'non-hydrated' or 'meta-hal-

loysite' (which was to be retained as a name for convenience) the dehydrated form and 'partly hydrated halloysite', the intermediate forms. The complex of halloysite with glycerol, for instance, would be known as 'glycerol-halloysite'.

Another nomenclature system involves adding the basal spacing '-7 Å' or '-10 Å' as a suffix to 'halloysite' in order to indicate the state of hydration (Brindley, 1951; Grim, 1968). This system appears to have had fewer adherents than the others which have been discussed.

Experimental studies

The understanding of the process of dehydration of the form of halloysite at the high-water end of the hydration series is of fundamental significance in defining the relationship between the two end members. Brindley and Goodyear (1948) carried out an extensive study of the process, following the changes in basal spacing and in the weight of a halloysite sample on dehydration. They found that the basal plane 001 peaks in the X-ray diffraction patterns of the halloysite at each stage of the dehydration process appeared in either or both of two narrow regions of the spectrum viz. those regions corresponding to basal spacings of 9.5–10.1 Å and/or 7.5–7.9 Å. They interpreted this result to mean that one form of halloysite ('hydrated halloysite', with a basal spacing between 9.5 and 10.1 Å) gave rise to just one other form ('metahalloysite', with a basal spacing between 7.5 and 7.9 Å). They explained the variations in the spacings of the two phases to mean that there is a limited amount of interstratification of the aluminosilicate layers with water towards either end of the hydration series. It was concluded that there were no forms of halloysite with basal spacings and therefore interlayer water contents intermediate between those attributed to the hydrated halloysite phase, on the one hand and the metahalloysite phase, on the other. The suggested possibility of a discontinuity in the dehydration process was also supported by a change of slope at a low r.h. in Brindley and Goodyear's plots of weight loss against r.h.

Harrison and Greenberg (1962) also carried out a close study of the dehydration process and like Brindley and Goodyear (1948) observed that X-ray diffraction traces obtained from halloysites during the dehydration process displayed peaks in only the two most extreme ranges of possible spacings. They suggested, nevertheless, that dehydration may take place through forms of halloysite with water contents that are intermediate between those of the most hydrated and least hydrated forms of the mineral.

There was thus a clear-cut disagreement between those, like Mehmel (1935), Hendricks (1938), Alexander *et al.* (1943), Brindley and Goodyear (1948) and also Faust (1955), who thought that halloysites could be classified into one of two distinct phases and those, like MacEwan (1947) and Harrison and Greenberg (1962), who thought that there is a continuous series of hydration states of halloysite which extends from

the most hydrated form of the mineral $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}]$ to the fully dehydrated form $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$.

Churchman *et al.* (1972) carried out a detailed study, using X-ray diffraction techniques, of the mineralogical changes taking place during the process of the loss of water from a naturally hydrated halloysite at room temperature. The X-ray profiles of partially hydrated halloysites at the various stages of the dehydration process show peaks in only two narrow basal spacing regions, as noted earlier by Brindley and Goodyear (1948) and Harrison and Greenberg (1962). Nonetheless, none of the profiles of the dehydrated samples could be analysed into a sum of two peaks, where one peak is attributed to the fully hydrated form and the other to the fully dehydrated form of the mineral. The complete series of experimental profiles were very similar to a series of profiles which were calculated using the theory of diffraction for cases of interstratification of the fully hydrated and fully dehydrated layer types in which there is a particular low but constant degree of partial segregation into the separate types of layers. These workers therefore concluded that halloysites with all possible interlayer water contents between 0 and 2 molecules per unit cell may exist and that fully hydrated halloysite and dehydrated halloysite are not distinct species but are merely the end members of a continuous series of hydration states. The results of this study were in complete agreement with the ideas of MacEwan (1947) and Harrison and Greenberg (1962).

In addition, Churchman and Carr (1972), in a study of the stability of halloysites at high temperatures and pressures, obtained results which strongly suggested that each hydration state of halloysite (corresponding to each possible interlayer water content) is stable over a long period of time, at least, under conditions of temperature and pressure which are unique to that particular hydration state of the mineral. It was concluded from the results of this study and also from the results of Churchman *et al.*'s (1972) room temperature study that the dehydration of halloysite does not take place via a single phase transformation but rather through the formation and then destruction of each member of a continuous series of hydration states of the mineral which accompanies the loss of each successive increment of interlayer water. Churchman and Carr (1972) noted, however, that the irreversibility of the dehydration process implies that the fully dehydrated form is the only stable phase among the halloysite dehydration series.

Churchman (1970) reports results of studies of the loss of weight and of changes in the intensities of i.r. absorptions which characterize adsorbed water (including interlayer water) during the room temperature dehydration of a naturally hydrated halloysite. These results support those of Churchman *et al.* (1972) and Churchman and Carr (1972) in that they are consistent with a continuous loss of interlayer water during the dehydration of hydrated halloysites. This interpretation of the weight loss plots differs

from that of Brindley and Goodyear (1948), who correlated a change of slope at low r.h. in a plot of 'interlayer water content' against r.h. with parallel changes in their X-ray data that had suggested a phase change (the disappearance of the 'hydrated' phase) at the same low r.h. It is noted, however, that Brindley and Goodyear had separated the interlayer water content from the content of water reversibly adsorbed on the surface by a method which involved the questionable assumption that the nature of the clay surface towards adsorption does not change on dehydration. Churchman (1970) observed a change of slope in the lower humidity portion of the plot of the total water content of a halloysite against r.h. and also pointed out that a change of slope need not represent any abrupt change in the process. Hughes (1966) had observed the same type of change of slope in the weight loss curve for a halloysite and had suggested that such an inflexion need only indicate a change in the rate of dehydration of a hydrated halloysite.

Conclusions and nomenclature

The results of the various studies by Churchman and co-workers support the basis for MacEwan's (1947) nomenclature of halloysites although MacEwan's proposed retention of the term 'metahalloysite' is considered to be unnecessary. This nomenclature was based on the existence of a continuous series of hydration states of halloysite. According to this particular system, a prefix is associated with the term 'halloysite' in order to indicate the state of hydration of the mineral or the material with which the halloysite is complexed. Such a system is consistent with the indication that the fully dehydrated form of halloysite is the only thermodynamically stable form of the mineral.

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