X-ray studies of halloysite and metahalloysite.

Part II. The transition of halloysite to metahalloysite in relation to relative humidity.

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THE experiments described below on the dehydration of halloysite were largely carried out in the Laboratoire Central des Services Chimiques de l'État, Paris, where we enjoyed not only the excellent facilities of the laboratory but also the advice of Monsieur J. Méring and Mlle R. Glaser who had made similar studies of montmorillonite. The use of a Guinier-type focusing camera with strictly monochromatic radiation was especially useful. These experiments were undertaken because little was known about the dehydration process beyond the recognition that it occurs very readily in dry atmospheres and at low temperatures. The main experimental difficulty lies in differentiating between water adsorbed on external surfaces of the clay particles (adsorbed water) and water internally absorbed between the kaolin layers (interlayer water). Experiments by Alexander *et al.* (1943) in which the changes of weight were determined when halloysite was brought to equilibrium firstly at 75% humidity, then at a lower humidity, and finally at 75% humidity again were difficult to interpret, as they themselves recognized. They also dried the mineral at 300° C. before returning it to 75% humidity and found that only about half the total water lost was regained, from which it was clear that the adsorbed and interlayer water contents were of comparable importance.

Our own experiments have followed up this latter line of inquiry and parallel X-ray studies have shed considerable light on the mechanism of the processes which occur. The halloysite used also came from Eureka, Utah, which was the source of the material used by Alexander *et al.* Weighing experiments were carried out as follows: Two equal samples of halloysite of about 0·5 gram weight were prepared, one of which was then heated to 300° C. for 2–3 hours to remove adsorbed and interlayer water, cooled in a desiccator and reweighed. Let w_1 be the initial mass, w_2 the mass after heating and cooling. The two samples were now placed over a solution of H_2SO_4 and H_2O adjusted to give the required relative humidity. After two days and again after four days they were reweighed; generally there was no significant difference between these weights, so that presumably equilibrium had been attained. If w_3 is the new mass of the unheated sample and w_4 that of the heated sample, then (w_3-w_4) will measure the interlayer water corresponding to the chosen humidity, provided (*a*) no interlayer water returns to the lattice after baking at 300° C., and (*b*) the adsorbed water is the same for the heated and unheated samples. X-ray evidence indicates that (*a*) is true or very nearly true.

If any interlayer water should return to the heated material, then (w_3-w_4) will be *less* than the mass of interlayer water at the chosen humidity; we return to this point later when discussing results. As regards (*b*), provided the heat-treatment does not change the total surface area, the adsorbed water at any chosen humidity will probably not be changed. With this assumption, (w_4-w_2) measures the adsorbed water.

An additional complication arises in practice because the original material contains a small percentage of gibbsite, $Al_2O_3.3H_2O$, which dehydrates to boehmite, $Al_2O_3.H_2O$, at about 200° C. Alexander *et al.* make no reference to gibbsite in their Utah halloysite though they mention it as a possible impurity in halloysite used by Hofmann, Endell, and Wilm (1934). We have estimated the gibbsite impurity from X-ray intensity measurements to be $3{\cdot}6\pm0{\cdot}7$ %, and this has been confirmed by Dr. R. W. Grimshaw who by thermal analysis methods has obtained $2{\cdot}9\pm0{\cdot}2$ %. The original material also contains an admixture of metahalloysite, the effect of which on the interpretation of the results will be considered later.

Results of the dehydration measurements.

These are set out in table I and are scaled to correspond to an initial sample of exactly 0·500 gram. They have been corrected systematically for the presence of 3·6 % gibbsite; the original mass, w_1, therefore appears as $0{\cdot}500-0{\cdot}018 = 0{\cdot}482$ gram. The table itself is self-explanatory.

The following features are shown more clearly in fig. 1: as the humidity increases the adsorbed water (curve *a*) rises from almost zero rapidly at first but more slowly at higher humidities. The interlayer water (curve *b*) rises slowly at first from a value *not equal to zero* and more

TABLE I. *Dehydration data for halloysite* (Eureka, Utah).

w_1 = mass of original sample = $0{\cdot}482_0$ gram.
w_2 = mass of sample after baking at 300° C. = $0{\cdot}419_7$ gram.
w_3 = mass of unheated sample after standing in relative humidity, R %.
w_4 = mass of heated sample after ,, ,, ,, R
(w_3-w_4) = mass of interlayer water after ,, ,, ,, R
(w_4-w_2) = mass of adsorbed water after ,, ,, ,, R

R %	w_3 gram.	w_4 gram.	w_3-w_4 gram.	w_4-w_2 gram.	$(w_3-w_4)/w_3$ %	$(w_4-w_2)/w_3$ %
0	$0{\cdot}431_3$	$0{\cdot}423_0$	$0{\cdot}008_3$	$0{\cdot}003_3$	1·92	0·77
5	$0{\cdot}437_3$	$0{\cdot}430_1$	$0{\cdot}007_2$	$0{\cdot}010_4$	1·65	2·38
10	$0{\cdot}440_1$	$0{\cdot}431_4$	$0{\cdot}008_7$	$0{\cdot}011_7$	1·98	2·66
15	$0{\cdot}445_0$	$0{\cdot}432_6$	$0{\cdot}012_4$	$0{\cdot}012_9$	2·79	2·90
20	$0{\cdot}448_2$	$0{\cdot}433_3$	$0{\cdot}014_9$	$0{\cdot}013_6$	3·32	3·04
25	$0{\cdot}454_0$	$0{\cdot}433_3$	$0{\cdot}020_7$	$0{\cdot}013_6$	4·56	3·00

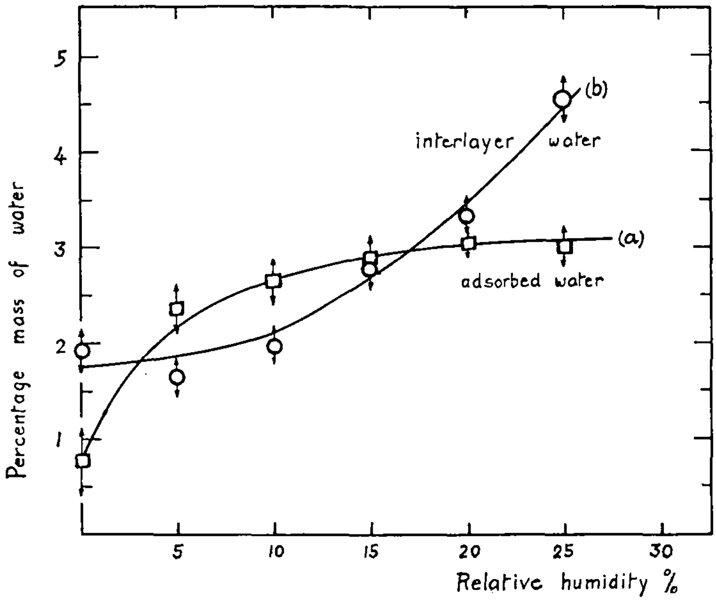

FIG. 1. Adsorbed water, curve (*a*), and interlayer water, curve (*b*), associated with halloysite at various relative humidities; the water masses are expressed as percentages of the mass of mineral, halloysite+water, in equilibrium at each humidity.

rapidly at higher humidities. That curve (*a*) does not diminish exactly to zero at zero humidity may be due to experimental error, but there seems no question that the residual interlayer water shown by curve (*b*) is a real effect, and indeed the X-ray results lead to a similar conclusion. The estimated probable errors arising from the weighings are shown by vertical lines in fig. 1.

Méring (1946) finds a similar curve for the adsorbed water on montmorillonite for the lower range of humidities, though the amount is much greater, being about 10 % at a 20 % humidity compared with 3 % for halloysite. This difference is not surprising since montmorillonite probably possesses a much larger specific surface. The interlayer water curve for montmorillonite shows no residual water at small humidities such as we find for halloysite, but Dr. Méring has pointed out in a private communication that the method used would not enable any residual interlayer water to be measured, but that X-ray measurements, similar to those described in the next section, indicate such residual water in montmorillonite at small humidities.

X-ray study of the dehydration of halloysite.

Specimens prepared for X-ray examination were subjected to various relative humidities at the same time as the experiments already described were in progress. After standing 2–4 days in atmospheres of known humidity, the specimens were quickly sealed between thin mica flakes and transferred directly to an X-ray camera of the Guinier type. In fig. 2 microphotometer traces of the X-ray photographs are shown for the intensity distribution in the first-order basal reflection (001). The second-order reflection is of little use for following the changes which occur since it is unobservable for halloysite, while the third order from halloysite almost coincides with the second order from metahalloysite.

Fig. 2 shows that as the relative humidity is reduced there is a progressive growth of metahalloysite accompanied by a gradual disappearance of halloysite. The lattice spacings of the peaks diminish with the humidity, the halloysite spacing decreasing from about 10·1 to 9·5 Å., and the metahalloysite spacing from about 7·9 to 7·5 Å. From the areas of the component peaks approximate quantitative data can be obtained for the increase of one mineral and the decrease of the other. This entails a consideration of the relative intensities of the two reflections, the details of which are separately discussed in an appendix to the paper. There we show that in a mixture of halloysite and metahalloysite, the reflected intensity of the (001) reflection per unit mass of halloysite is **4·28** times as great as that of the (001) reflection of metahalloysite.[1] In consequence of this large ratio, the diagrams of fig. 2 at first sight overemphasize the halloysite content compared with the metahalloysite content. There is, for example, about 40 % of metahalloysite in the naturally occurring material, a result which would not be suspected from the appearance of the curve.

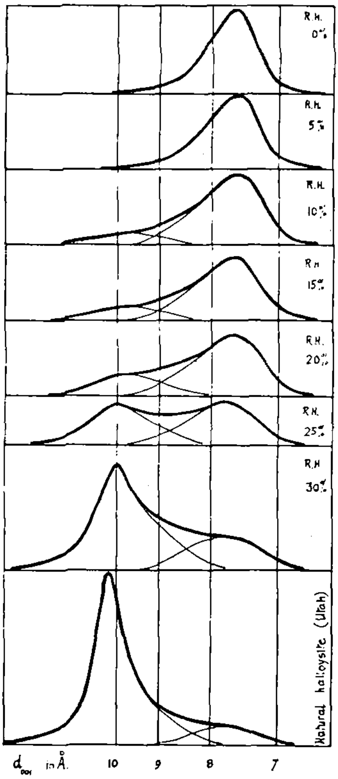

FIG. 2. Microphotometer curves of X-ray powder diagrams of halloysite in equilibrium at various relative humidities. The curves show the (001) reflections from halloysite and metahalloysite. The lowest curve corresponds to the original Utah 'halloysite'.

In fig. 3 the spacings and percentage amounts (A_H and A_M) of the two minerals are plotted against the relative humidities; the corresponding data are also shown for the original material before treatment. The rapid decay of halloysite and growth of metahalloysite below 30 % humidity are clearly shown. Halloysite which has not changed over to metahalloysite shows a partial shrinkage to a spacing of 9·5 Å., but the process cannot be followed beyond this point. Metahalloysite when first formed has an expanded lattice presumably due to the inclusion of residual water layers which are partially expelled as the humidity decreases to zero. We have been unable to obtain evidence for the existence of intermediate stages with spacings between 9·5 and 7·9 Å. It appears that even at 0 % humidity all the residual water is not removed because the spacing is still markedly greater than that of metahalloysite baked at 300° C., namely, 7·2 Å. This is in general agreement with the results from the weighing experiments.

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[1] This value, 4·28, is obtained from comparisons of reflections from specimens having spacings 10·1 and 7·4 Å. Whether we are strictly justified in applying this result when the spacings differ from these values is questionable, but at present there is no obvious alternative.

X-ray diffraction by layer silicate minerals with randomly interposed water layers.

On the basis of a theory developed by Hendricks and Teller (1942) we may estimate the content of interlayer water in halloysite and metahalloysite from their observed lattice spacings. Brindley and Robinson (1946) have already made a simple correlation of the excess water found in chemical analyses of metahalloysite with the expanded lattice spacing by calculating the mean lattice spacing resulting from the insertion of a number of water layers randomly amongst the silicate layers. A more satisfactory approach to the problem, however, is on the basis of the Hendricks–Teller theory.

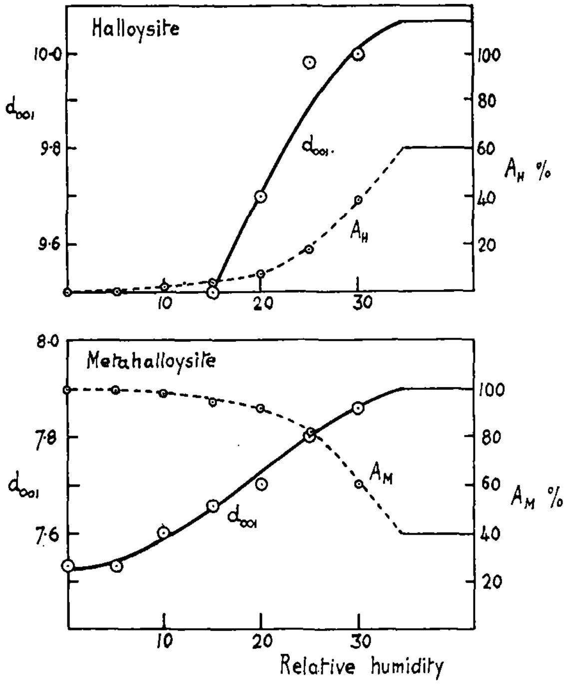

FIG. 3. Basal spacings (full curves) and percentage amounts of halloysite and metahalloysite (dashed curves) in equilibrium at various relative humidities. Horizontal lines at right-hand side give data for the original material which is a mixture of halloysite and metahalloysite.

We consider halloysite and metahalloysite to be composed of silicate layers with randomly interposed water layers; when the ratio of silicate layers to water layers, x, tends to unity, the mineral is termed halloysite and has a spacing of the order of 10 Å., and when x is greater than about 3, the mineral is metahalloysite and has a spacing between about 7·2 and 8 Å. The theory of Hendricks and Teller will be applied in the same simple manner as they themselves have applied it to the corresponding problem for montmorillonite. The randomly interposed water layers create phase shifts between reflections from the silicate layers but do not themselves contribute appreciably to the scattered (or reflected) intensity. There are then two phase shifts to consider between reflections from successive silicate layers, viz.:

$\phi_1 = 4\pi(7{\cdot}13)(\sin\theta)/\lambda$, when there is no interposed water layer[1]

and $\phi_2 = 4\pi(10{\cdot}1)(\sin\theta)/\lambda$, when there is an interposed water layer.

The probabilities p_1 and p_2 of these phase shifts occurring are respectively

$$p_1 = (x-1)/x \quad \text{and} \quad p_2 = 1/x.$$

The theory expresses the average intensity I scattered in a direction θ as

$$I \simeq (1-C^2)/(1-2C\cos\bar{\phi}+C^2), \tag{1}$$

where

$$C = \sum_n p_n \cos(\phi_n-\bar{\phi}), \tag{2}$$

$\bar{\phi}$, denoting an average value, is defined by

$$\sum_n p_n \sin(\phi_n-\bar{\phi}) = 0, \tag{3}$$

and p_n is the probability of a phase shift ϕ_n. For numerical calculations where only two phase shifts are involved, a more convenient expression for I can be developed as follows:

If we put $$p_1\sin\phi_1+p_2\sin\phi_2 = A$$

and $$p_1\cos\phi_1+p_2\cos\phi_2 = B,$$

then from equation (3) $\tan\bar{\phi} = A/B$, and from equation (2) we find

$$C = A\sin\bar{\phi}+B\cos\bar{\phi} = B/\cos\bar{\phi}.$$

Substituting in equation (1) we obtain

$$I \simeq (1-A^2-B^2)/(1-2B+A^2+B^2)$$

$$= \frac{(x-1)\{1-\cos(\phi_2-\phi_1)\}}{(x^2-x+1)+(x-1)\cos(\phi_2-\phi_1)-x\{(x-1)\cos\phi_1+\cos\phi_2\}}.$$

This final expression for I, though apparently more complex than equation (1), is now in a form which allows I to be calculated directly as a

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[1] 7·13 Å. is the layer spacing of kaolinite and may be taken as the thickness of the kaolinite layers in 'contact' with each other.

function of $(\sin\theta)/\lambda$ for any chosen value of x. Such intensity distributions have been calculated from this expression for a range of values of x from 1 to 20, and the results for the variation of mean lattice spacing with water content are shown graphically in fig. 4.

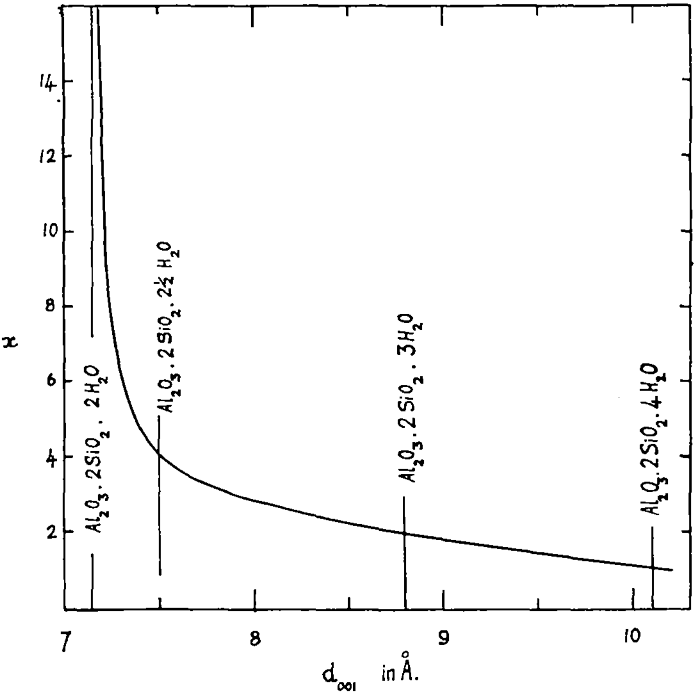

FIG. 4. Variation of mean lattice spacing of halloysite and metahalloysite with water content; x is the ratio of silicate layers to water layers.

The data of fig. 4 may be applied directly to the observed lattice spacings to find the ratio x of silicate to water layers and hence to find the content of interlayer water in the two minerals as a function of the humidity.

Assuming the structure and density of the water layers are as given by Hendricks and Jefferson (1938), i.e., two molecules of H_2O for each kaolinite 'molecule' $Al_2O_3.2SiO_2.2H_2O$, we have

$$\frac{\text{Mass of interlayer water}}{\text{Mass of silicate layers}} = \frac{2\ (\text{Molecular weight of } H_2O)}{x\ (\text{Molecular weight of kaolinite 'molecule'})}$$

$$= \frac{36}{x \times 258}.$$

But the mass of the silicate layers in the 0·5 gram samples used in the dehydration experiments was the quantity designated w_2 which had the value 0·4197 gram (see table I). Hence

$$\text{Mass of interlayer water} = \frac{36 \times 0{\cdot}4197}{x \times 258} = \frac{0{\cdot}0586}{x}.$$

If in a mixture of halloysite and metahalloysite there is a proportion A_H of halloysite with spacing corresponding to x_H, then the interlayer water in the halloysite component is $0{\cdot}0586 A_H/x_H$ and similarly in the metahalloysite component is $0{\cdot}0586 A_M/x_M$. Values of A_H and A_M are obtained from the data of fig. 3, while x_H and x_M are obtained directly from the observed lattice spacings with the aid of fig. 4.

TABLE II. Comparison of interlayer water in halloysite and metahalloysite from X-ray data and from direct weighing experiments.

Relative humidity	Halloysite.			Metahalloysite.			Interlayer water in 0·5 gr. sample.			
	d_{001}	x_H	A_H %	d_{001}	x_M	A_M %	in halloysite component.	in metahalloysite.	Total.	$w_3 - w_4$ table I.
0 %	—	—	–	7·53	4·0	100	..	0·0147	0·0147	$0{\cdot}008_3$
5	—	—	—	7·53	4·0	100	..	0·0147	0·0147	$0{\cdot}007_2$
10	—	—	—	7·60	3·6	98	....	0·0160	0·0160	$0{\cdot}008_7$
15	9·52	1·45	4·7	7·66	3·4	95	0·0019	0·0164	0·0183	$0{\cdot}012_4$
20	9·69	1·32	7·4	7·70	3·3	93	0·0033	0·0165	0·0198	$0{\cdot}014_9$
25	9·98	1·11	18·0	7·80	$3{\cdot}1_5$	82	0·0095	0·0152	0·0247	$0{\cdot}020_7$
30	10·0	1·10	39·0	7·86	3·0	61	0·0208	0·0119	0·0327	—

Hence the total interlayer water in a mixture of the two forms of the mineral can be obtained and the results compared directly with those from the weighing experiments. The numerical data are given in table II and the variations of interlayer water content with humidity obtained by the two methods are compared in fig. 5.

Discussion of results for interlayer water in halloysite and metahalloysite.

Since the errors and assumptions involved in the two methods of finding the interlayer water are wholly unconnected with each other, the large measure of agreement found between the results suggests that a fairly truthful account of the amount of water between the silicate layers in the two forms of halloysite has been obtained.

The X-ray method has the advantages (*a*) of showing the presence of both forms of the mineral for humidities exceeding about 15 %, and (*b*) of enabling the interlayer water in both forms to be determined. Table II shows that x increases from unity to about 1·5 in halloysite before this form completely disappears; $x = 1{\cdot}5$ means that on the average there are three silicate layers to two water layers, or one out of every three water layers of halloysite has disappeared. The corresponding formula is $Al_2O_3.2SiO_2.3\frac{1}{3}H_2O$. Beyond this stage the water seems to emerge so rapidly that we cannot observe any further stage until we come to a state when x is about 3, i.e. three silicate layers to one water layer, which corresponds to $Al_2O_3.2SiO_2.2\frac{2}{3}H_2O$. The water now emerges

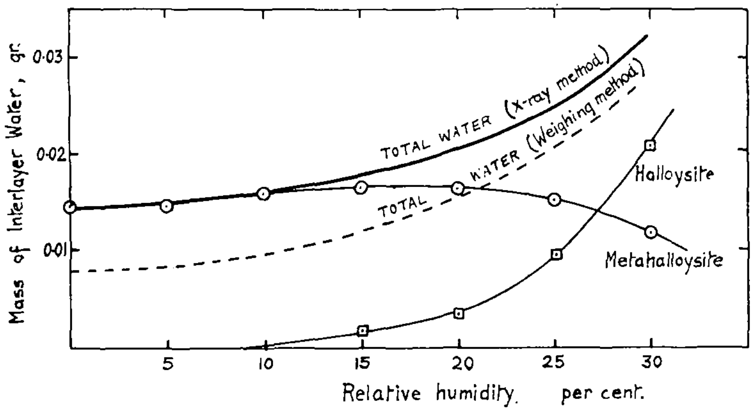

FIG. 5. Mass of interlayer water per half-gram sample of Utah halloysite brought to equilibrium at various relative humidities. Full lines obtained by X-ray measurements of basal spacings, dashed line obtained from direct weighing experiments.

much less easily, and in the driest atmospheres x has not increased beyond about four corresponding to $Al_2O_3.2SiO_2.2\frac{1}{2}H_2O$. These values of x are based on the observed X-ray spacings and the formulae assume the H_2O molecules in the water layers to be packed in the manner described by Hendricks and Jefferson (1938).

Now for humidities less than 15 %, where only metahalloysite occurs, the results from the weighing experiments give for the interlayer water 0·08 gram per half-gram sample (see table I) which corresponds to $x = 6$ and a formula $Al_2O_3.2SiO_2.2\frac{1}{3}H_2O$, a result which is in close agreement with that deduced from the X-ray measurements.

As regards the result that the X-ray measurements indicate rather more interlayer water at the lowest humidities than the direct weighing experiments, the following observations may be made. In the first place, if the water molecules in the residual water layers are less closely packed than in the full hydrated mineral, then the *number* of water layers given by the X-ray measurements would correspond to a *smaller* water content. Secondly, when describing the weighing experiments, we stressed that if any interlayer water re-entered the sample baked at 300° C., this would lead to an *under*-estimate of the interlayer water. There are therefore good reasons why the X-ray method may give high values and the weighing experiments low values for the interlayer water.

Comparison of present results with published analyses of halloysite and metahalloysite.

It is of interest to compare the present results with various chemical analyses. In a recent discussion of the nomenclature of these minerals, MacEwan (1947) has listed the number of water molecules, n, obtained from a series of analyses published from 1816 onwards. He has rejected data 'for which the SiO_2:Al_2O_3 ratio differed markedly from 2' (p. 39) and has calculated n with reference to one Al_2O_3 group per 'molecule'. The values of n lie in two main groups, (i) between 3·5 and 4·5, (ii) between 2·2 and 2·7, corresponding presumably to (i) halloysite and (ii) metahalloysite with residual water layers. Out of 27 values of n, four only lie between 2·7 and 3·5. There appears to be a definite avoidance of values around $n = 3$. While noting these results, we cannot be very certain of their precise significance. MacEwan describes the analyses as relating to 'air-dry or lightly dried material'. If the material was dried at room-temperature in an atmosphere of 15 % humidity or less, then the present experiments show that it would pass to metahalloysite; we cannot dry halloysite, i.e. remove adsorbed water, without also losing interlayer water. It seems very probable that in all the analyses where n lies in the range 3·5–4·5, the water is partly due to surface adsorption. There is also the question of whether the materials analysed were partly halloysite and partly metahalloysite, as we have found to be the case for the Utah halloysite. For these reasons we consider that, as regards the present work, not much significance can be attached to the amount of water shown in chemical formulae based on early analyses.[1]

The more recent data of Ross and Kerr (1934) are in a different category. Their analyses record H_2O+ and H_2O-, the former presumably being water driven off above 100° C. or thereabouts, though the temperature is not stated. In calculating the number of water molecules, n, corresponding to the H_2O+ content, it is difficult to know whether to refer the calculation to two molecules of SiO_2 or one molecule

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[1] This, of course, does not imply any criticism of MacEwan's paper; he was concerned with showing that for a period of a century or more the term 'halloysite' has been used for material containing approximately $2H_2O$ and approximately $4H_2O$ per formula.

of Al_2O_3, because the $SiO_2 : Al_2O_3$ ratio departs from the ideal value 2 rather considerably in some cases. If this is due to an excess of some aluminous material, then the silica-water ratio will be the more reliable basis, but Ross and Kerr could not find, either optically or by X-rays, any impurities to substantiate this view. In table III are listed the values of n calculated from the twelve analyses, nos. 2–13, given by Ross and Kerr based on both the silica and the alumina contents, together with the silica/alumina ratio. The values based on silica are probably the more reliable.

TABLE III. Water molecules per formula, n, corresponding to H_2O+ derived from analyses of metahalloysite by Ross and Kerr (1934), based on (*a*) silica content, (*b*) alumina content.

Specimen no.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
SiO_2/Al_2O_3 ...	2·06	1·80	1·95	2·01	1·91	1·93*	1·82*	1·96	1·95	1·70*	1·90*	1·82*
n (*a*) ...	2·22	2·64	2·22	2·27	2·23	2·23	2·35	2·23	2·16	2·93	2·26	2·30
n (*b*) ...	2·28	2·38	2·16	2·28	2·13	2·16	2·14	2·19	2·11	2·50	2·15	2·09

* The values for these ratios given by Ross and Kerr appear to have arithmetical errors: the values given in the table are re-calculated from the published analyses.

For the most part n lies between 2·2 and 2·4, which is entirely in accordance with our own conclusion that for material dried at room-temperature and at humidities less than 10 %, n lies in the range $2\frac{1}{3}$–$2\frac{1}{2}$. As regards the slightly lower values from the data of Ross and Kerr, it must be remembered that their analyses are for material heated (presumably) to 100° C.; data which we give in the following paper, Part III, show that the basal spacing of metahalloysite is appreciably reduced by heating at even so low a temperature as 100° C.; this diminution of spacing indicates a smaller interlayer water content.

We consider, therefore, that our findings are entirely in accordance with the analytical results collected by MacEwan and also with the analyses of Ross and Kerr.

Summary and conclusions.

Two entirely different methods are described for determining the interlayer water content in halloysite and metahalloysite in relation to relative humidity. The first is a direct weighing method in which samples of natural material and material baked at 300° C. are brought to equilibrium at different humidities. With certain assumptions, which are discussed, it is possible to determine both the adsorbed water and the interlayer water separately. The second method involves measuring the basal spacing of the mineral and applying the Hendricks–Teller theory of X-ray diffraction by a statistical arrangement of water and silicate layers. This method has the advantage of giving separately the interlayer water in halloysite and in metahalloysite when both components are present. The results obtained by the two methods are shown to be in satisfactorily close agreement. It is found that when the natural material is placed in atmospheres of decreasing humidity, not only does the halloysite component change to metahalloysite, but also both components show progressive shrinkage, so that halloysite has a basal 001 spacing in the range 9·5–10·1 Å. and metahalloysite in the range 7·5–7·9 Å. There are corresponding variations in water content, so that in the formula $Al_2O_3.2SiO_2.nH_2O$, n lies between $3\frac{1}{2}$–4 for halloysite and $2\frac{1}{3}$–$2\frac{2}{3}$ for metahalloysite. The fact that $n > 2$ for metahalloysite dried at room-temperature means that it retains an appreciable number of water layers, of the order of one water layer to six silicate layers. These results are shown to be in general agreement with chemical analyses of halloysite collected by MacEwan and of metahalloysite given by Ross and Kerr.

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APPENDIX

Comparison of intensities of (001) reflections from halloysite and metahalloysite.

In order to carry out the investigation described in this paper it was necessary to know the relative intensities of the (001) reflections from these minerals. It was deemed undesirable simply to assume without proof the layer structure of halloysite given by Hendricks in order to calculate this ratio; conversely, a quantitative measurement of the ratio would provide additional evidence for or against Hendricks's view of the structure. The experimental determination proved more difficult than was anticipated, mainly because the original halloysite already contained a large admixture of metahalloysite. Mixtures of the original material with additional metahalloysite were studied, but the results obtained were very variable. A method involving separate exposures of the original material and of metahalloysite was therefore used (cf. Brindley and Spiers, 1938). A powder holder was constructed containing two flat shallow cavities, each filled with one of the minerals, and the two specimens were brought alternately into the incident X-ray beam, each for a period of five minutes, one specimen reflecting to the right and the other to the left of the beam. The process was continued for a period of about four hours, i.e. two hours for each specimen, while the X-ray tube was operated as steadily as possible in the hope that any fluctuations of X-ray output would cancel out. The two photographs were recorded side by side on a single strip of film so that both had identical photographic treatment. This method has an advantage over a mixture method in that the background scattering from the two substances is not superimposed.

When reflections from two substances, denoted by subscripts 1 and 2 for halloysite and metahalloysite respectively, are recorded in this manner, the ratio of the reflected intensities is given (cf. Brindley and Spiers (1938) p. 29) as:

$$\frac{I_1}{I_2} = \frac{p_1 N_1^2 F_1^2 \phi(\theta_1) A_1 \mu_2 t_1}{p_2 N_2^2 F_2^2 \phi(\theta_2) A_2 \mu_1 t_2},$$

where $\phi(\theta) = (1+\cos^2 2\theta)/(\sin\theta \sin 2\theta)$,

$$A = \sin(2\theta-\alpha)/[\sin(2\theta-\alpha)+\sin\alpha],$$

p is the multiplicity factor for a reflection, N the number of unit cells per unit volume of crystalline material, μ the linear adsorption coefficient of the crystalline material (not of the powder specimen), t the exposure time, θ the Bragg angle, and α the angle between the incident X-ray beam and the flat powder surface. In the present case $p_1 = p_2$, $t_1 = t_2$, $N_1/N_2 = 7{\cdot}2/10{\cdot}1$, $\theta_1 = 4^\circ\, 22'$, $\theta_2 = 6^\circ\, 8'$, $\mu_1 = 59{\cdot}4$, $\mu_2 = 79{\cdot}6$ when Cu-$K\alpha$ radiation is used; the angle α was generally taken to be 3°. Assuming the sequence of atomic layers given by Hendricks and Jefferson (1938) and using the atomic F-values of Bragg and West (1928), we find $F_1^2 = 10{\cdot}96\times10^3$, $F_2^2 = 3{\cdot}19\times10^3$; F_1^2 (i.e. for halloysite) is much greater than F_2^2, mainly because the halloysite reflection occurs at an appreciably smaller angle. The final calculated value of I_1/I_2 *under the conditions presupposed* is $(I_1/I_2)_{\mathrm{calc}} = \mathbf{4{\cdot}04}$.

The admixture of metahalloysite in the original material complicates the experimental determination of (I_1/I_2). If

$$\begin{aligned} \text{area of halloysite peak} &= H, \\ \text{area of metahalloysite impurity peak} &= m, \\ \text{area of metahalloysite peak from separate mineral} &= M, \\ \text{and if } I_1 \text{ (halloysite)}/I_2 \text{ (metahalloysite)} &= k, \end{aligned}$$

then in the absence of any metahalloysite impurity, the halloysite peak would have the area $(H+km)$ and therefore

$$k = (H+km)/M, \quad \text{i.e. } k = H/(M-m) = (I_1/I_2)_{\mathrm{Expt.}}$$

From four separate determinations, we find

$$\begin{aligned} (I_1/I_2)_{\mathrm{Expt.}} &= 3{\cdot}3,\ 3{\cdot}4,\ 3{\cdot}6, \text{ and } 5{\cdot}1 \\ &= \mathbf{3{\cdot}8 \pm 0{\cdot}6}. \end{aligned}$$

The observed value is therefore probably somewhat smaller than the calculated value, but the experimental accuracy hardly justifies us attaching any significance to the difference. The experiments have been carried out with all possible care, but there are unavoidable sources of error inherent in such experiments which make the measurement of the intensities subject to considerable uncertainty, namely: (i) the reflections are broad and the peaks do not stand out sharply above the general background; (ii) the reflection from the metahalloysite impurity overlaps considerably that from the halloysite, and in the expression for k, the quantity m is about 40 % of M. The agreement is perhaps as good as can be expected in view of these difficulties. The result, however, tends to support Hendricks's structure for halloysite.

With this justification for the calculated ratio $(F_1/F_2)^2 = 10{\cdot}96/3{\cdot}19$, we now use it to calculate (I_1/I_2) for different experimental arrangements. In the first place, for a mixed powder in which the mass ratio is (g_1/g_2) we have (see Brindley and Spiers (1934); Brindley (1945)):

$$\frac{I_1}{I_2} = \frac{N_1^2 F_1^2 \phi(\theta_1) A_1 g_1 \rho_2}{N_2^2 F_2^2 \phi(\theta)_2 A_2 g_2 \rho_1}$$

when the powder specimen is in the form of a flat block, and ρ_1 and ρ_2 are the densities, respectively 2·10 and 2·59, calculated from the cell dimensions and contents. Then with $\alpha = 3°$, we find

$$\frac{I_1}{I_2} = 3{\cdot}73 \frac{g_1}{g_2}.$$

When photographs are taken by transmission of X-rays through thin layers, as in the dehydration experiments described earlier, then provided the radiation has practically equal paths for the two reflections under consideration—and this condition is amply satisfied in the present investigation—we have

$$\frac{I_1}{I_2} = \frac{N_1^2 F_1^2 \phi(\theta_1) g_1 \rho_2}{N_2^2 F_2^2 \phi(\theta_2) g_2 \rho_1} = 4{\cdot}28 \frac{g_1}{g_2}.$$

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