X-ray studies of halloysite and metahalloysite.

*Part III. Effect of temperature and pressure on the transition
from halloysite to metahalloysite.*

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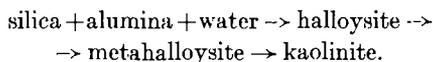J. Goodyear, Ph.D., A.Inst.P.

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THIS paper concludes the account of our experiments on halloysite
and is to be read in conjunction with the two previous parts, to
which frequent reference will be made.

Effect of temperature.

The effect of heat-treatment on metahalloysite was examined with
the primary object of ascertaining if a recrystallization or 'kaolinization'
of metahalloysite could be achieved. The question is of interest in con-
nexion with the possible formation of kaolinite according to the following
scheme:

$$\text{silica} + \text{alumina} + \text{water} \rightarrow \text{halloysite} \rightarrow$$
$$\rightarrow \text{metahalloysite} \rightarrow \text{kaolinite.}$$

The experiments, however, provide no evidence for any such reorganiza-
tion of the silicate layers. The temperature was raised progressively at
intervals of about 50° to 450° C., at which temperature the silicate layers
commence to decompose, and was maintained for several hours at each
temperature.

Attention was directed especially to the appearance of the two-
dimensional diffraction bands which would be expected to show some
change if reorganization of the layers occurs. This negative result is in
accordance with data for other layer-lattice silicates having randomly
displaced layers, cf. data for antigorite by Aruja (1945) and by Ali and
Brindley (1948) for the transition of pennine into olivine.

The effect of heat-treatment on metahalloysite is also of interest in
connexion with the dehydration of the mineral, for, as we have shown
in Part II, halloysite is only partially dehydrated in completely dry

atmospheres, and this is also true at low temperatures, such as 100° C. The continued dehydration of the mineral as the temperature is raised is shown by the change of the basal reflections, which become sharper and also change their positions. The (001) spacing diminishes progressively (fig. 1), tending finally to a minimum value of about 7·2 Å., which approximates to the basal spacing of kaolinite, 7·13 Å. As we have shown in Part II, the larger spacing normally found for the (001) reflection, about 7·5 Å., is the result of the inclusion of residual water
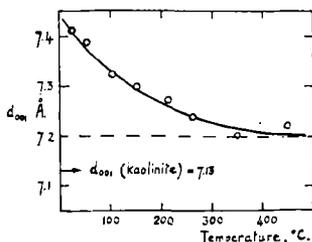

FIG. 1.   FIG. 2.

FIG. 1. Spacing of (001) reflection from metahalloysite plotted against temperature of heat-treatment. Corresponding value for kaolinite indicated by arrow.
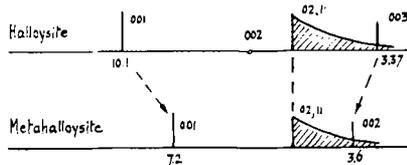
FIG. 2. Diagrammatic representation of the change of the low-order reflections when halloysite dehydrates to metahalloysite.

layers between the silicate layers. It is now seen that considerable heat-treatment is necessary to expel this residual water and, in fact, a temperature so high that the silicate layers themselves begin to decompose is necessary before the water is finally driven out. These results agree with the general picture sketched by Brindley and Robinson (1946) of water inclusions trapped between kaolinite layers. They agree also with the dehydration data of Ross and Kerr (1934, p. 140) who recorded a gradual loss of water on heating halloysite to 400° C., whereas kaolinite loses very little water up to this temperature.

The second-order basal reflection, (002), shows less change than the first order and is less accurately measurable on account of the widely spreading (02,11) diffraction band (cf. fig. 1 of Part I). We find, however, a small *increase* of the (002) spacing accompanying the *decrease* of the (001) spacing, a result which is in agreement with the theory of Hendricks and Teller (1942) as we indicate diagrammatically in fig. 2.

The sharpening of the basal reflections can arise from several causes. By eliminating the residual water inclusions, the heat-treatment produces a more regular lattice, i.e. a lattice in which only one type of layer exists instead of a statistical distribution of two types, and this alone is

sufficient to sharpen the reflections. The silicate layers may also be distorted by the presence of the water inclusions, and the removal of this distortion will also lead to a sharpening of the reflections. The smallness of the crystal size doubtless also contributes to the broadness of the basal reflections. It is scarcely possible to disentangle these combined effects and we can only draw the general conclusion that heat-treatment produces a more regular sequence of basal layers.

Effect of pressure.

The effect of pressure on the halloysite–metahalloysite transition has been examined primarily to determine whether naturally occurring metahalloysite can be produced from halloysite by application of pressure alone. Small samples of 1–2 grams of finely powdered Utah halloysite were placed between flat-faced steel plungers of 1 inch diameter (area = 0·785 sq. in. or 5·06 sq. cm.) and subjected to loads up to 60,000 lb. (27,200 kg.), i.e. pressures up to about 76,000 lb. sq. in. (5000 kg./sq. cm.) by means of hydraulic machines in the Department of Engineering of this University. This maximum pressure corresponds to the static pressure exerted by a column 17,000 metres in height of density 3 and is therefore comparable with or greater than the pressures exerted on natural deposits. In general the pressure was not maintained for longer periods than 24 hours, but in one case the test was continued for 10 days. After compression, the finely powdered material emerged as disks about 2–3 mm. thick which were examined directly by X-ray reflection from the flat faces. The following results were obtained:

(a) A partial transformation of halloysite to metahalloysite proceeds more nearly to completion as the pressure and duration of the test are increased. The process cannot be studied in as much detail as the dehydration produced by dry atmospheres because the basal (001) reflection consists of a broad band covering the whole range of spacings from about 10–7 Å., which cannot be resolved clearly into two components. Typical microphotometer curves of the (001) reflection are shown in fig. 3, and separate peaks corresponding to halloysite and metahalloysite have been tentatively sketched by broken lines.

The main conclusion which follows from fig. 3 is that the transformation proceeds further with increasing time and pressure. Curve (a), corresponding to the original Utah halloysite, already shows a proportion of metahalloysite (see Part II). Curves (b), (c), and (d) show the effect of increasing the load, while curves (e), (f), (g), (d), (h), and (i) show the effect of increasing the time. While these results do not prove that

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metahalloysite is actually produced in nature by application of pressure alone, it seems very probable, when the geological time-factor is taken into consideration, that this must often have occurred.

Other points may be briefly considered. For small loads and times, curves (b), (c), (e), and (f) show a very considerable spreading of X-ray scattering towards smaller angles and the X-ray negatives almost suggest
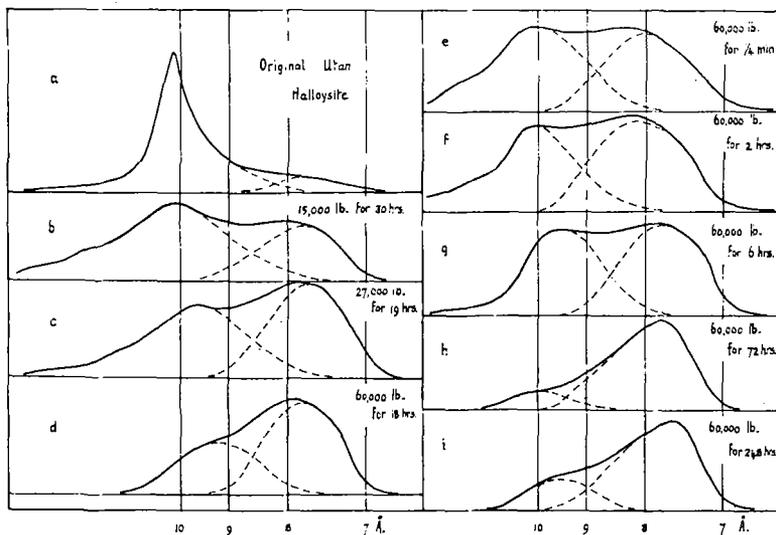

Fig. 3. Microphotometer traces of the (001) X-ray reflection from Utah halloysite before and after application of pressure. A *load* of 60,000 lb. corresponds to a *pressure* of 76,000 lb./sq. in. or 27,200 kg./sq. cm. Vertical lines indicate positions corresponding to lattice spacings of 10, 9, 8, and 7 Å.

the existence of weak broad lines in the range 12–18 Å., which appear in the photometric curves as small variations superimposed on the steady decrease of intensity. We can offer no explanation of these doubtful effects and their reality has not been established for certain. It is also seen that the peak spacings of both the halloysite and the metahalloysite components tend to decrease as the dehydration proceeds, and the process therefore resembles that discussed in Part II. The peak spacings are, however, too inaccurate to justify any detailed discussion.

(b) The intensity of the (001) reflection relative to the (02,11) band shows that under pressure a partial orientation of the metahalloysite crystals takes place. This, we believe, is the first time that an orientation

effect has been detected with halloysite or metahalloysite. Kaolinite, on the other hand, shows marked orientation very readily, for example when sedimented in water. Electron microscope pictures of halloysite reveal lath-shaped crystals which produce no obvious orientation when sedimented. When subjected to pressure, however, the (001) reflection is considerably enhanced relative to the (02,11) band. The orientation appears to be confined mainly to the surface layers of the compressed disks. There has previously been some doubt regarding the directions of the crystallographic axes relative to the lath-shaped crystals, but it is clear from this result that the a- and b-axes must lie in the plane of the lath.

Many natural metahalloysites occur in a hard porcellaneous form and it was thought that these might have been produced naturally by application of pressure. We have examined several such specimens from Lawrence County, Missouri, but without finding any clear evidence for orientation of the crystallites.

Summary and conclusions.

It is shown that heat-treatment up to temperatures at which the silicate layers decompose produces no reorganization of the randomly displaced layers in metahalloysite. No evidence is therefore obtained for the production of kaolinite from halloysite by application of heat. Detailed study of the basal reflections shows that the partial dehydration of halloysite achieved in dry atmospheres and/or at low temperatures can be largely completed by heating to the highest temperature the mineral will withstand without decomposition, about 400° C. The basal spacing then shrinks almost to the value found in kaolinite, and the sharpening of the reflections indicates a more regular sequence of basal layers. Partial transformation of halloysite to metahalloysite has been achieved by application of pressure alone, and probably under geological conditions pressure alone would be sufficient to produce the transformation.

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