

# REHYDRATION AND DEHYDRATION OF THE CLAY MINERALS†

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## ABSTRACT

Certain clay minerals, particularly the illites and montmorillonites, regain some hydroxyl water as well as adsorbed water on standing at room temperature after being dehydrated by heating to temperatures as high as 800°C. The removal of the recombined hydroxyl water may take place at slightly lower temperature than the original hydroxyl water.

Experimental data are presented showing the rehydration and loss again of the rehydration water together with a discussion of the structural significance of the rehydration.

## INTRODUCTION

In the course of the study of the character and properties of the clay minerals as revealed by differential thermal analyses, it was found that certain of the clay minerals apparently rehydrate after being dehydrated by heating to temperatures as high as 800°C. The rehydration includes both the picking up of adsorbed water and the recovery of actual lattice water hydroxyl groups. In the latter case removal of the recombined hydroxyl water may take place at a slightly lower temperature than did the removal of the original hydroxyl water. Dehydration and rehydration are important in considering the properties and the structure of the clay minerals, and may be of practical significance in the utilization of clays. The purpose of the present paper is to present some preliminary work on these matters.

## PROCEDURE

About 5 grams of minus 60-mesh material of various clay minerals were heated to temperatures up to 800°C. The samples were heated rapidly to the top temperatures and held there for at least one hour. After heating, the samples were allowed to cool to room temperature (25° to 30°C.) and kept in open dishes, but protected from dust, in the laboratory until they were studied.

The method of study was that of differential thermal analysis (1). This method is satisfactory because dehydration is accompanied by an endothermic reaction. Thermal curves, therefore, indicate any rehydration, the temperature at which the rehydrated water can be removed, and something of the energy involved.

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## EXPERIMENTAL RESULTS

*Montmorillonite*

Figure 1 presents thermal curves for a sodium montmorillonite from Wyoming bentonite, obtained on samples which had remained in the laboratory for various periods of time following heating to 500°C., 600°C., and 800°C. for one hour.

Curve B shows that a considerable amount of adsorbed water is picked up in 13 days by material heated to 500°C. This temperature is not high enough to affect the (OH) lattice water.

Heating to 600°C. for one hour (curves C-F) removes the (OH) lattice water as well as the adsorbed water. Following heating to this temperature, there is a very slow gradual pickup of adsorbed water so that a small amount is shown at the end of 268 days. Likewise there is a very slow gradual regaining of (OH) lattice water, and of great interest is the dual character of the endothermic reactions corresponding to the removal of this rehydrated water. Apparently the regained water is of two kinds or forms in the lattice. Some of this water is removed at about the same temperature as the original dehydration, and the other at about 150°C. lower temperature. Both kinds or forms of water are regained at about the same rate.

The samples heated to 800°C. (curves G-H) show no pickup of adsorbed water and only a faint trace of (OH) lattice water regained after 268 days.

The thermal reactions at about 875° to 950°C., corresponding to the destruction of the montmorillonite lattice and the development of new phases (2), are unchanged in samples heated to 600°C. In the 800°C. sample, the only effect is a very slight reduction in the intensity of the reactions.

Figure 2 shows thermal curves obtained on samples of a calcium montmorillonite from an Arizona bentonite, which had remained in the laboratory for various periods of time following heating to 500°, 600°, and 800°C. for one hour.

The curves show that this calcium montmorillonite has the same rehydration characteristics as the sodium montmorillonite shown in Fig. 1, except that the rehydration following heating to 600°C. (curves C-E) seems to be a little slower. The calcium montmorillonite that was heated to 800°C., after standing for 272 days (curve H), definitely shows some pickup of adsorbed water and of (OH) lattice water.

*Illite*

Differential thermal curves for an illite (3) purified from an underclay of Pennsylvanian age found near Fithian, Illinois, are presented in Fig. 3.

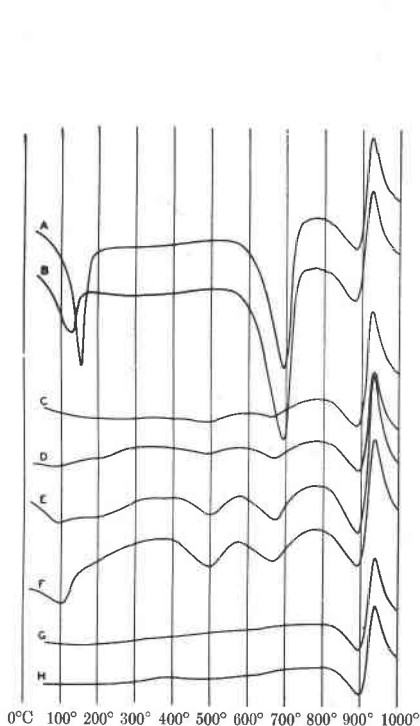


FIG. 1

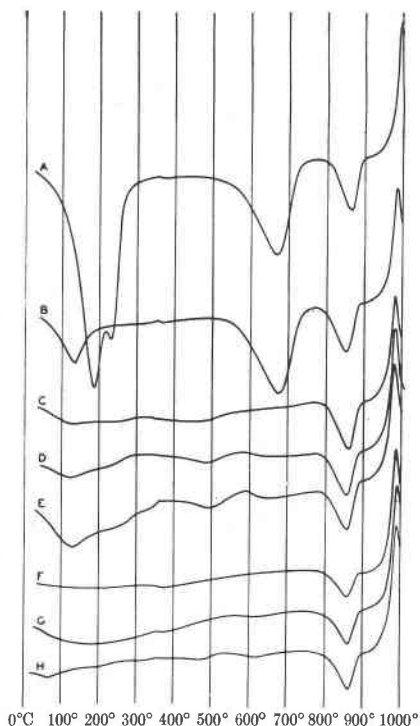


FIG. 2

FIG. 1. Differential thermal curves of sodium montmorillonite, bentonite, Clay Spur, Wyoming.

A.	Not heated.							
B.	Heated 500° C. for 1 hour, curve run after standing 13 days.							
C.	" 600° C. " 1 " " " " " " 11 "							
D.	" 600° C. " 1 " " " " " " 68 "							
E.	" 600° C. " 1 " " " " " " 146 "							
F.	" 600° C. " 1 " " " " " " 268 "							
G.	" 800° C. " 1 " " " " " " 76 "							
H.	" 800° C. " 1 " " " " " " 268 "							

FIGURE 2. Differential thermal curves of calcium montmorillonite, bentonite, Arizona.

A.	Not heated.							
B.	Heated 500° C. for 1 hour, curve run after standing 13 days.							
C.	" 600° C. " 1 " " " " " " 14 "							
D.	" 600° C. " 1 " " " " " " 68 "							
E.	" 600° C. " 1 " " " " " " 145 "							
F.	" 800° C. " 1 " " " " " " 73 "							
G.	" 800° C. " 1 " " " " " " 145 "							
H.	" 800° C. " 1 " " " " " " 272 "							

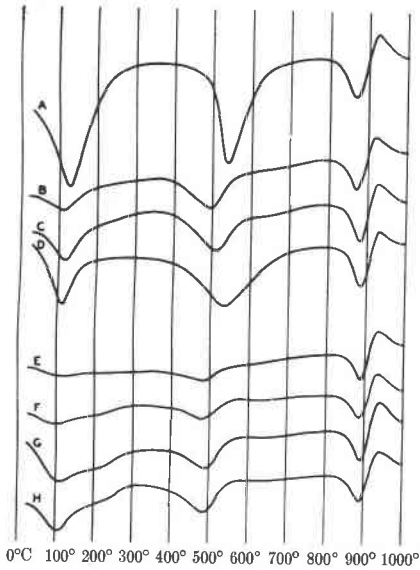


FIG. 3

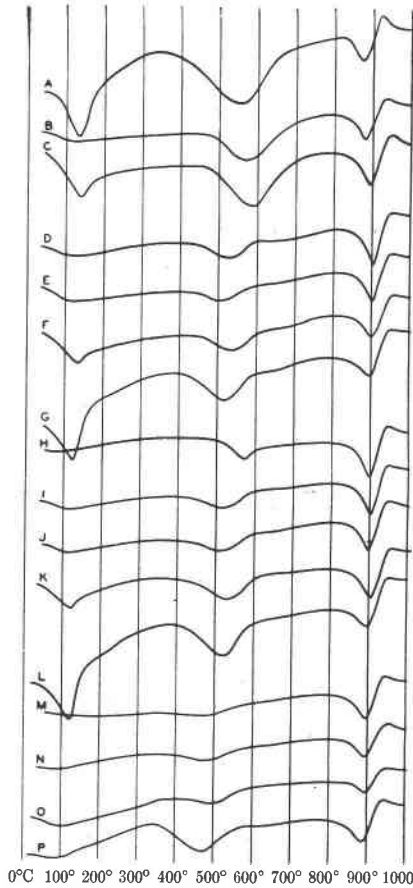


FIG. 4

FIG. 3. Differential thermal curves of illite, Fithian, Illinois.

- A. Not heated.
- B. Heated 600° C. for 3 hours, curve run after standing 2 hours.
- C. " 600° C. " 1 " " " " " 1 day.
- D. " 600° C. " 1 " " " " " 70 days.
- E. " 800° C. " 1 " " " " " 13 "
- F. " 800° C. " 1 " " " " " 70 "
- G. " 800° C. " 1 " " " " " 147 "
- H. " 800° C. " 1 " " " " " 275 "

FIG. 4. Differential thermal curve of illite, Grundy County, Illinois.

- A. Not heated.
- B. Heated 450° C. for 1 hour, curve run after standing 7 days.
- C. " 450° C. " 1 " " " " " 55 "
- D. " 550° C. " 1 " " " " " 4 "

(Legend continued on page 54)

The curves show that after heating to 600°C. (curves B–D) some pickup of adsorbed water and (OH) lattice water is very rapid. Apparently a considerable portion of both kinds of water is taken up quickly and further amounts are taken up at a slow gradual rate. The curves show also that loss of the rehydrated (OH) water begins at a lower temperature (400°C.) than that of the original (OH) water (475°C.).

On standing after heating to 800°C. (curves E–H) there is a gradual regaining of adsorbed water and (OH) lattice water. The similarities of the curves for 147- and 275-day standing periods suggest that after a certain amount of rehydration takes place, any further pickup of water is slight and very slow.

The final part of the curve, showing reactions corresponding to destruction of lattice and the formation of a new phase, is unchanged by the dehydration and rehydration.

The curves for the illite purified from the Grundy County, Illinois, clay presented in Fig. 4 shows that this sample has the same general rehydration properties as those of the previously considered illite. The rehydration of the Grundy County illite appears to be slower and without any suggestion of a lowering of the temperature required to remove the water gained on rehydration.

The rehydration characteristics of an illite from the Minford silt of Ohio are shown in Fig. 5. The adsorbed water is picked up slowly and gradually on material heated to 600°C. so that after 217 days (curve L) there appears to be more adsorbed water than there was in the original sample. Adsorbed water is picked up also after heating to 800°C. (curve M).

The curves show a slight regaining of (OH) lattice water after heating to temperatures as high as 800°C. The amount of (OH) water regained is small—considerably smaller than the previously considered illites. There is no indication that the samples heated to 500°C. (curves B, C) regained more water on rehydration than the sample heated to 800°C. (curve M).

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E.	"	550° C.	"	1	"	"	"	"	"	17	"
F.	"	550° C.	"	1	"	"	"	"	"	55	"
G.	"	550° C.	"	1	"	"	"	"	"	221	"
H.	"	600° C.	"	1	"	"	"	"	"	1	"
I.	"	600° C.	"	1	"	"	"	"	"	9	"
J.	"	600° C.	"	1	"	"	"	"	"	17	"
K.	"	600° C.	"	1	"	"	"	"	"	53	"
L.	"	600° C.	"	1	"	"	"	"	"	223	"
M.	"	800° C.	"	1	"	"	"	"	"	12	"
N.	"	800° C.	"	1	"	"	"	"	"	70	"
O.	"	800° C.	"	1	"	"	"	"	"	146	"
P.	"	800° C.	"	1	"	"	"	"	"	278	"

In some of the Minford silt samples, illite occurs associated with a chlorite. Although no chlorite was apparent by  $\alpha$ -ray diffraction or optical examination of the sample used in this study, it is not unlikely that the variations of these curves from those of the other illites are nevertheless due to the admixture of undetected chlorite.

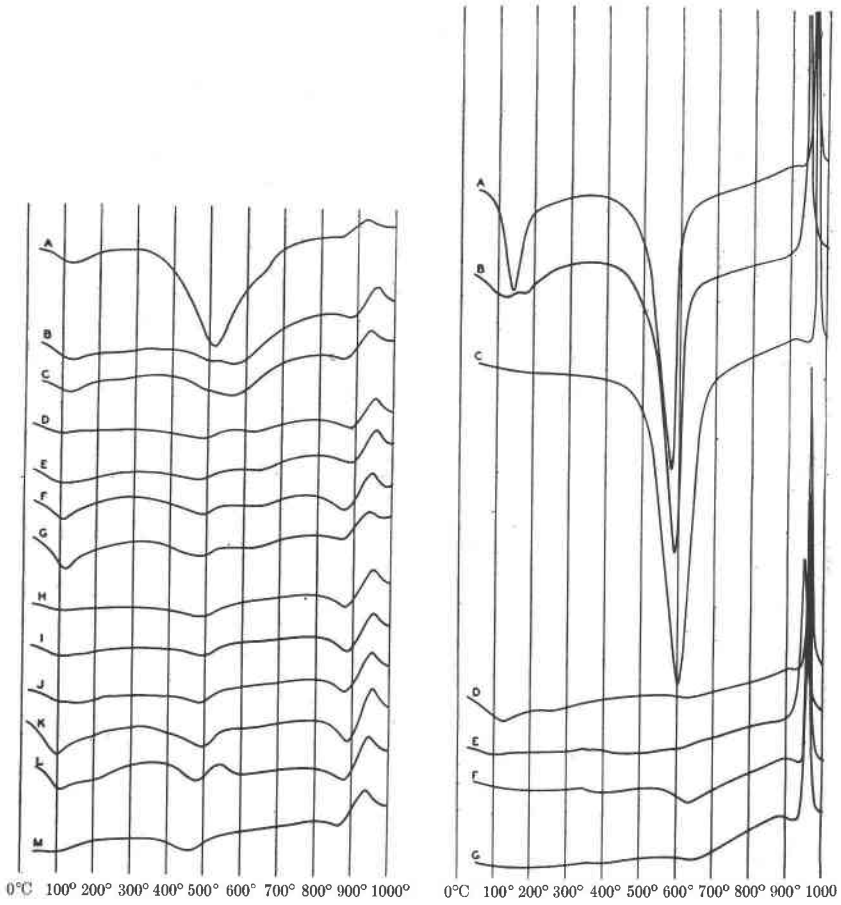


FIG. 5

FIG. 6

FIG. 5. Differential thermal curves of illite from Minford silt, Ohio.

- A. Not heated.
- B. Heated 500° C. for 1 hour, curve run after standing 14 days.
- C. " 500° C. " 1 " " " " " 163 "
- D. " 550° C. " 1 " " " " " 2 "
- E. " 550° C. " 1 " " " " " 16 "
- F. " 550° C. " 1 " " " " " 52 "
- G. " 550° C. " 1 " " " " " 218 "

(Legend continued on page 56)

*Halloysite and kaolinite*

The kaolinite represented by curve B in Fig. 6 is rather poorly crystallized, whereas that represented by curve C is very well crystallized (4). The curves for these two kaolinites show pronounced differences (*a*) in the intensity of the reactions, (*b*) in the presence of an initial endothermic reaction in the poorly crystallized kaolinite, and (*c*) in the presence of a slight endothermic reaction at about 930°C. in the well crystallized sample.

The thermal curve D in Fig. 6 shows that after heating to 600°C. there is a very slight pickup of adsorbed water by the halloysite sample, but in the light of the known highly porous condition of halloysite aggregates, it is probable that this represents merely adsorbed rather than crystalline water. There is also a suggestion of the regaining of a trace of (OH) lattice water.

Curve E for the poorly crystallized kaolinite suggests the pickup of a trace of adsorbed water, but there is no positive indication of the regaining of any (OH) water.

The well crystallized kaolinite (curves F and G) shows a distinct pickup of a very small amount of (OH) lattice water after heating to 600°C.

The final part of the curves are substantially unchanged by heating to 600°C. It is significant that the halloysite and well crystallized kaolinite which show an endothermic reaction at about 920–930°C. show some regaining of (OH) lattice water, whereas the poorly crystallized kaolinite which shows no final endothermic reaction also shows no regaining of (OH) lattice water.

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H.	"	600° C.	"	1	"	"	"	"	"	2	"
I.	"	600° C.	"	1	"	"	"	"	"	7	"
J.	"	600° C.	"	1	"	"	"	"	"	16	"
K.	"	600° C.	"	1	"	"	"	"	"	52	"
L.	"	600° C.	"	1	"	"	"	"	"	217	"
M.	"	800° C.	"	1	"	"	"	"	"	6	"

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FIG. 6. Differential thermal curves of kaolinites and halloysite.

- A. Halloysite (partially hydrated form), Eureka, Utah. Not heated.
- B. Kaolinite, Anna, Illinois, not heated.
- C. Kaolinite, Dry Branch, Georgia, not heated.
- D. Halloysite heated 600° C. for 1 hour, curve run after standing 70 days.
- E. Kaolinite, Anna, Illinois, heated 600° C. for 1 hour, curve run after standing 70 days.
- F. Kaolinite, Dry Branch, Ga., heated 600° C. for 1 hour, curve run after standing 70 days.
- G. Kaolinite, Dry Branch, Ga., heated 600° C. for 3 hours, curve run after standing 7 days.

## DISCUSSION OF RESULTS

Quite a surprising number of common minerals, not otherwise so obviously related, are based upon variations of a single characteristic assemblage of oxygen and hydroxyl ions coordinated about various combinations of particular cations. This structural unit, with the proportion of 20 oxygen ions to 4 hydroxyl ions, is encountered in the crystallizations of the micas, talc, pyrophyllite, the chlorites, the montmorillonite group minerals, the illites and probably several others.

For the better crystallized examples of this structural type the hydroxyl water is not very readily removed by firing, and any approach to equilibrium conditions at a given temperature is so slow that they do not lend themselves to thermal analysis. For the two fine-grained groups, however, the illites and the montmorillonites, the thermal expulsion of this water has become a well-known diagnostic feature in numerous thermal analysis studies, and it has been generally noted that the illites lose this water at about 100–150°C. lower temperature than do the montmorillonites.

It has been remarked before (5, 6) that this type of fundamental structural unit is able to survive the abstraction of its hydroxyl water with only moderate readjustment, but detailed analysis has not been attempted.

In connection with a related study of heat effects (6), occasion has arisen to examine several montmorillonites after ignition to temperatures just above those necessary to remove the hydroxyl water. X-ray diffraction diagrams obtained from such material are found to be consistent with effects to be anticipated from the relatively simple layer rearrangement illustrated in Fig. 7. The two packed layers of octahedrally co-

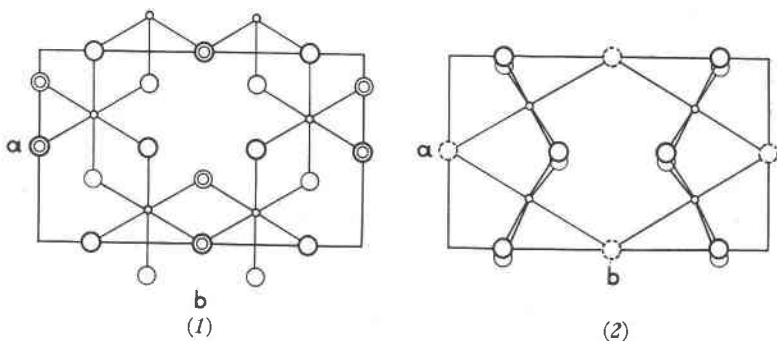


FIG. 7. Schematic representation of the configurations in the layers of octahedral coordination (1) before and (2) after condensation of the (OH) lattice water of the three-layer silicates. Large circles represent oxygen, double circles hydroxyl, and small circles aluminum or magnesium.



ordinated ions are merely shifted from the packed position to one of direct apposition, with each pair of hydroxyl ions being replaced by a single residual oxygen ion set between two hydroxyl positions.

It is noted that the described arrangement affords a reasonably adequate disposition for four octahedrally coordinated cations per unit cell per layer as in a heptaphyllite type, but would demand a highly unreasonable sequence of shared coordination octahedron faces for an octaphyllite type mineral. Neither the 500°–700°C. endothermic peak nor the characteristically modified diffraction diagram is observed for the one certain example of octaphyllite clay (the "hectorite") which was available in the study referred to above.

The quantity of hydroxyl water taken into recombination by these montmorillonites amounts to only about one-fourth the original hydroxyl water and does not afford any clear cut *x*-ray diffraction inference, but in the light of the anhydrous configuration illustrated, it seems reasonable to assume that only a small part is recombined into the original configuration, with an additional significant amount attaining only some other bonding of lower energy.

The nature of the micas is such that they do not afford even the limited data that are obtainable from the montmorillonites. The pairing of layers in the muscovite structure, which is presumably also present in illites, reduces the natural  $\beta$  angle so nearly to 90° that such a shift as the one described for montmorillonites results in too slight an effective shift for the double layer to be clearly observable in the diffraction diagrams. For this same reason, however, we can feel that the more intimate association of adjacent layers not only permits easier abstraction of the interior hydroxyl water, as evidenced by the lower temperature of the endothermic reaction, but also promotes the reversibility of the recombination and reabstraction of such water.

The structural unit upon which the crystallization of the kaolinite minerals is based is less stable and does not survive the loss of its (OH) water as a conventional crystal. Some degree of order does persist however, the state being commonly designated as "metakaolin." The thermal curves for the two-layer clay minerals indicate that a noticeable amount of (OH) lattice water rehydration takes place for the halloysite and the well crystallized kaolinite, but that none takes place in the poorly crystallized kaolinite. It is significant that the samples showing rehydration also show the small endothermic reaction at about 930°C. Although not well shown by the curves presented herein, differential thermal analyses of a very large number of kaolinites have shown that when the endothermic peak at about 930°C. is present, there is also a definite upward slope to the curve between the endothermic peak at about 600°C. and

the 930°C. peak, and that when the 930°C. endothermic reaction is not present the curve is horizontal between the 600°C. endothermic peak and the final exothermic reaction. The best interpretation of the foregoing observations seems to be that in the case of at least some halloysites and in well crystallized kaolinites, the structural remnant which makes up the "metakaolin" retains sufficient regularity to recombine at least minor amounts of (OH) water, and that some of this structure persists even up to about 930°C.

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