

THE REVERSIBLE DEHYDROXYLIZATION OF CLAY MINERALS *

EDWARD C. JONAS †

ABSTRACT

Rehydroxylation of the anhydrous modification of dioctahedral montmorillonites can be carried out under DTA conditions with controlled atmosphere techniques. The structural character of the rehydrate prepared in this way is determined from X-ray and DTA data. The mechanism of the reactions by which the rehydrate can be formed is also considered. Thermal analysis curves of the rehydrate form of several pure montmorillonite samples failed to show any large variation such as is shown by the curves of the original clays themselves. The possibility is considered that such large variations in the dehydroxylation curves of montmorillonites are related to structural instead of compositional variations within the sample. It is suggested that montmorillonites showing two reactions attributable to dehydroxylation may be mixtures of the rehydrate form and montmorillonite.

The addition of controlled-atmosphere techniques to classical differential thermal analysis (DTA) has served to stimulate new interest in its use in clay mineral research. The amount of additional information made accessible with controlled atmosphere can often make the process a profitable research tool for problems in which the classical methods would fail to reveal any useful data. Not only can the usual DTA reactions be modified by heating in a controlled atmosphere, for example, analyzing specimens rich in organic material in an atmosphere of inert gas such as argon, but also new reactions can be promoted by cooling high temperature phases in an active atmosphere.

Controlled-atmosphere DTA was applied in studying the reactions of clay minerals which involve crystalline or hydroxyl water. Standard DTA conditions of heating in an atmosphere of ordinary air at a rate of about 12° C per minute were used to produce an anhydrous form of the clay minerals. The anhydrous form was normally completely developed by 750° C, as indicated by the return of the DTA curve to base line following the endothermic reaction associated with the removal of crystalline or hydroxyl water. The anhydrous material was then cooled at a controlled rate of about 10° C per minute to a temperature of 400° C. During the cooling an atmosphere of water vapor was maintained around the sample.

The apparatus which provided these experimental conditions was similar to the one described by Stone (1952) in his thermal analysis of kaolinites,

* Published with permission of the Chief, Illinois State Geological Survey, Urbana, Illinois.

† Present address, The University of Texas, Austin, Texas.

conducted in water vapor of varying partial pressures. The essential part of the apparatus was the nickel sample holder, which was fitted with a porous refractory plate for the floor and another plate for the lid. Any gas can be streamed upward through the porous plates and the loosely packed sample during all or part of the DTA run. An auxiliary boiler was built by the Illinois State Geological Survey to be used as a source of steam of constant pressure.

Figure 1 shows a series of reactions for two clay materials. The first peak in each suite represents the endothermic dehydroxylation reaction registered during heating of the clay in air. Only the portion of the curve related to this reaction is shown (400° C-750° C). At 750° C the heating program was interrupted; superheated steam was introduced into the sample cavity while the specimen was cooled at a uniform rate to a temperature of about 400° C. The peak resulting from the exothermic reconstitution of hydroxyl water by the anhydride is shown as the second peak in each suite. The third peak is the DTA of the rehydroxylated material which was heated in an atmosphere of air under essentially the same conditions that produced the first curve in the suite for the original specimen.

Several types of clay materials were examined by this procedure. Among them were montmorillonite, kaolinite, illite, well-crystallized chlorite, well-crystallized mica, and attapulgite. Only dioctahedral three-layer minerals

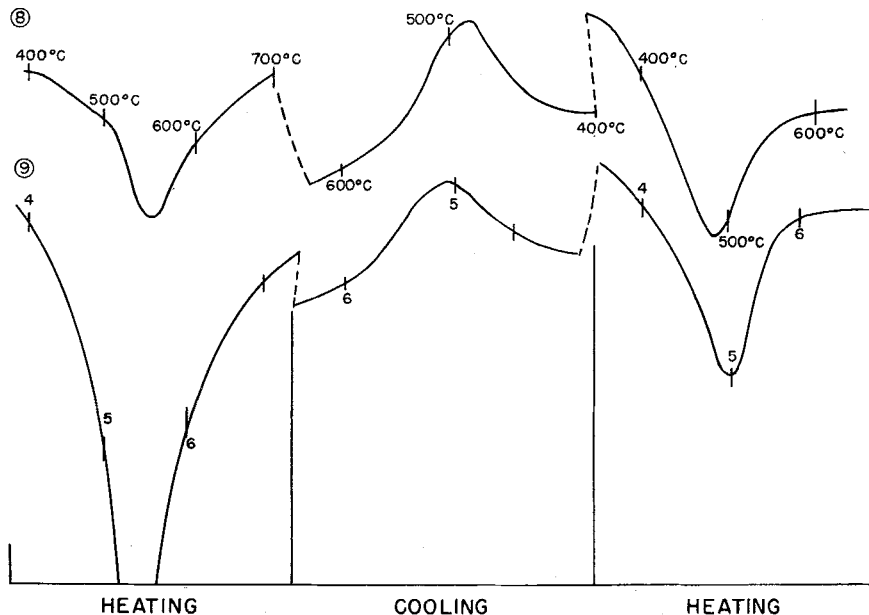


FIGURE 1.—Differential thermal analysis curves showing dehydroxylation, rehydroxylation, and dehydroxylation. (8) Illite from Fithian, Illinois. (9) Mixed illite and chlorite from Jackson County, Ohio.

produced anhydrides that would rehydroxylate under these rapid DTA conditions. The two-layer clay minerals have been shown to rehydrate under slower or more severe conditions, but the position of the reconstituted water in the structure is in question. Dehydroxylation of trioctahedral three-layer minerals produces a form which is unstable at the dehydroxylation temperature and which quickly rearranges into a structure considerably different from that of the original clay mineral and not susceptible to rehydroxylation.

Three-layer dioctahedral clay minerals, however, develop, as a result of dehydroxylation, the anhydride form, which differs only slightly from the original clay mineral structure. Figure 2a shows a schematic representation of the location of the cations in each unit-cell plane parallel to *ab* in montmorillonite. Figure 2b shows a similar representation of the cations in the anhydride form (Bradley and Grim, 1951). The rapid reaction of the anhydride form, which develops only from dioctahedral three-layer minerals with water vapor at elevated temperatures, distinguishes it from the high-temperature forms developed under similar conditions by other minerals.

The technique of controlled-atmosphere DTA can be applied in this way to furnish evidence of the presence of kaolinite, halloysite, and chlorite, which do not rehydroxylate under these conditions, in mixtures with montmorillonites or illites which will rehydroxylate. An example of such a determination is illustrated in Figure 1, which shows a series of three peaks for a pure illite from Fithian, Ill., and a similar series for the clay fraction of the Minford Silt, from Jackson County, Ohio, a mixture of illite and chlorite. Rehydroxylation of the pure illite sample, as indicated by the amplitude of the second exothermic peak, is of the magnitude of the original

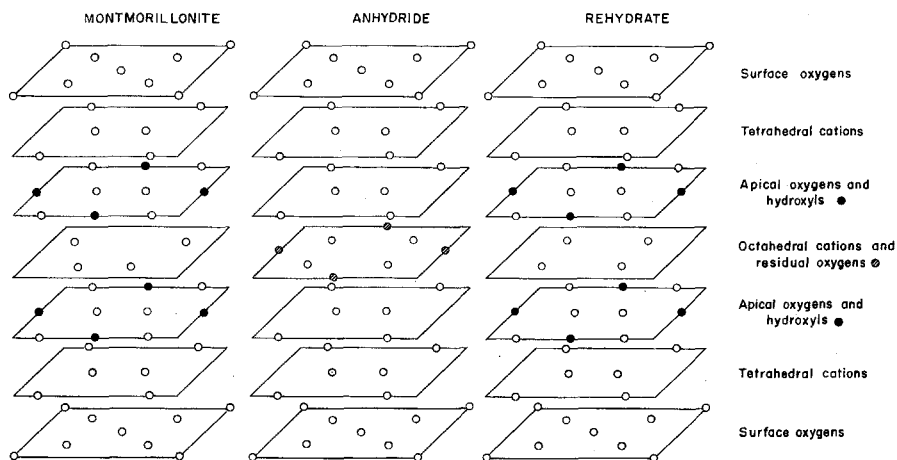


FIGURE 2. — Schematic diagram showing the locations of the atoms in the lattice planes in the original montmorillonite, the anhydride, and rehydrate.

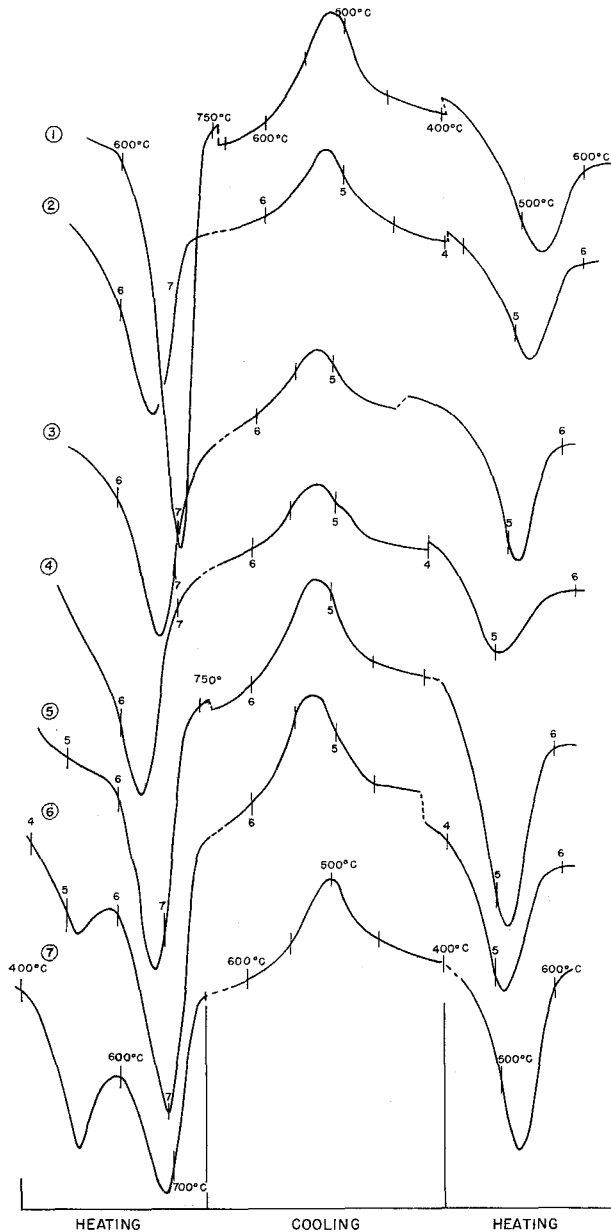


FIGURE 3. — Differential thermal analysis curves showing dehydroxylation, rehydroxylation, and dehydroxylation. (1) Montmorillonite from Belle Fourche, South Dakota. (2) Montmorillonite from Chambers, Arizona. (3) Montmorillonite from Santa Rita, New Mexico. (4) Montmorillonite from Otay, California. (5) Montmorillonite from Smithville, Mississippi. (6) Montmorillonite from Tatatilla, Vera Cruz, Mexico. (7) Montmorillonite from Montmorillon, France.

dehydroxylation shown by the first endothermic peak. Minford Silt, however, shows a large endothermic peak followed by a much smaller exothermic rehydroxylation. In this sample, dehydroxylation occurs simultaneously for the entire material, the illite portion and the brucite part of the chlorite portion, causing a large peak. Only the illite portion is available for rehydroxylation, hence the much smaller exothermic reaction.

Figure 3 shows the same series of three peaks for 7 pure montmorillonite samples. The first peak in each series, which indicates the dehydroxylation of the original clay sample, is quite variable. Wyoming bentonite shows a sharp dehydroxylation peak at about 700° C; 3 montmorillonites, from Chambers, Ariz., Santa Rita, N.M., and Otay, Cal., show peaks as low as 640° C; and 3 montmorillonite samples, from Smithville, Miss., Tatatilla, Vera Cruz, Mexico, and Montmorillon, France, show two dehydroxylation reactions. One peak occurs near 700° C in all of the double-peak samples, and a lower temperature reaction (when well resolved from the more intense higher temperature reaction) occurs at about 525° C, lower than normally expected even for illite.

The exothermic peaks, indicating rehydroxylation of the anhydride form, are all remarkably similar. The slight differences in peak temperature and amplitude are insignificant compared with the differences in the original dehydroxylation reactions. Even those samples which show two dehydroxylation peaks develop only one exothermic rehydroxylation.

The third peak in each series, indicating the dehydroxylation of the rehydroxylated samples, is closely related to the exothermic rehydroxylation peak in both temperature and amplitude. The third peaks are all remarkably similar to each other compared with the original dehydroxylation reactions, and they appear only as single peaks at 510° C-525° C.

In contrast to these curves are those of Grim and Bradley (1948), who prepared the rehydrated forms of some heated clay minerals by allowing them to stand for long periods of time (up to 278 days) in contact with atmospheric moisture. Their montmorillonite samples rehydrated in such a way as to show two dehydroxylation reactions regardless of the character of the original dehydroxylation peak. One peak reached a maximum near 700° C (about the same as the original clay), the other, at about 550° C.

These observations led Grim and Bradley to conclude that the structure of the rehydroxylated material was different from that of the original clay mineral, at least in the portion that showed a dehydroxylation reaction at a temperature so much lower than the original montmorillonite. As their specimens were mixtures of the high-temperature peak material (presumably identical with the original montmorillonite) and the new form showing a low temperature dehydroxylation, along with some unreacted anhydride they did not furnish any very clear diffraction data. The character of the new form could not be determined.

Rapid reaction of the anhydride form with water vapor under controlled

atmosphere DTA conditions results in the development of only one rehydroxylated phase immediately after preparation. This material when allowed to stand for a period of two months in a closed container shows a DTA curve with two dehydroxylation peaks, a large one at 525° C and a small peak developing at about 150° higher in temperature instead of the single dehydroxylation peak at 525° C. The rehydroxylated anhydride characterized by a 525° C peak is an unstable form at room temperature and spontaneously reverts back to the original montmorillonite structure which dehydroxylates at a much higher temperature.

The complete reversible dehydroxylation reaction for dioctahedral three-layer clay minerals includes the following steps:

1. Formation of the anhydride form by dehydroxylation of the clay as a result of heating.
2. Reconstitution of hydroxyl water by the anhydride on cooling in the presence of water vapor and consequent formation of the rehydrate form.
3. Spontaneous reversion of the rehydrate form to the original clay structure.

The material developed by the slow rehydroxylation procedure used by Grim and Bradley was a mixture of all three forms, the anhydride, the rehydrate, and some of the original clay that had reverted from the rehydrate form. Rehydroxylation carried on under rapid DTA conditions did not allow time enough for any of the rehydrate to revert to the original clay structure and therefore resulted in a mixture of the rehydrate form with only the unreacted anhydride.

This two-component sample was sufficiently concentrated in the rehydrate form to furnish some diffraction data characteristic of its structure. Figure 2c shows a schematic representation of the structure of this rehydrate form suggested by the X-ray diffraction and DTA data. It has a composition identical with the original dioctahedral three-layer clay mineral, but its structure is more nearly that of the anhydride. Because of the general similarity among the three forms, it would be expected that transitions from one to another could be induced rather easily.

Natural montmorillonites which show two dehydroxylation reactions have DTA curves that resemble the rehydroxylated anhydride samples of Grim and Bradley. The dehydroxylation temperature of the rehydrate form is the same as the low-temperature peak of natural double-peak montmorillonites. The higher temperature peak occurs near 700° C as it frequently does in single-peak montmorillonites. Thus it is possible that double-peak montmorillonites may be mixtures of the rehydrate form and some material that has reverted to the ordinary montmorillonite structure.

Conditions under which montmorillonite is generally believed to be developed in nature are not compatible with the high temperatures necessary to develop the anhydride. If the rehydrate form exists as a natural material, it must have developed as a result of some process other than rehydroxylation of the anhydride. In this respect it is interesting to observe that the

clay fractions of some incompletely devitrified volcanic ash contain montmorillonite with two dehydroxylation peaks. It is suggested that the rehydrate form exists in nature as an intermediate in the development of montmorillonite from volcanic ash. Some of the material with the rehydrate form spontaneously rearranges into the more stable montmorillonite configuration. A double-peak montmorillonite has not completed the rearrangement from the rehydrate form to ordinary montmorillonite and represents a transitional mixture of the two structural phases.

REFERENCES

- Bradley, W. F., and Grim, R. E. (1951) *High temperature thermal effects of clay and related minerals*: Am. Mineral., vol. 36, pp. 182-201.
- Grim, R. E., and Bradley, W. F. (1948) *Rehydration and dehydration of the clay minerals*: Am. Mineral., vol. 33, pp. 50-59.
- Stone, R. L. (1952) *Apparatus for differential thermal analysis under controlled partial pressures of H₂O, CO₂, or other gases*: Jour. Am. Cer. Soc., vol. 35, pp. 76-82.