

# COMPARISON OF A NATURAL BENTONITE WITH ITS SYNTHETIC ANALOGUE

*By*

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## ABSTRACT

Comparison was made between a sample of Wyoming bentonite and its synthetic analogue. Equivalent decomposition temperatures and mineral phases were obtained in hydrothermal environments and by calcinations.

## INTRODUCTION

Many of the clay minerals have been synthesized hydrothermally over the past half century. Recent systematic studies on pure oxide systems, including the clay minerals, have provided a broad basis for research on these materials using hydrothermal techniques. In general these studies have been concerned primarily with phase equilibria determined at relatively high pressures of about 1000 atmospheres. The stability data thus obtained can be applied directly to problems of clay genesis in which the clay minerals involved undergo little isomorphous substitution in the lattice. The kaolinite group, talc, and pyrophyllite are examples.

However, the question arises whether one can apply such stability data to those clay systems where there is extensive substitution in the lattice as in the montmorillonite group. A large amount of experimental work would be required to determine the effect on the thermal stability of all cationic substitutions in the interlayer position, as well as the numerous substitutions in the octahedral and tetrahedral positions of the montmorillonite. Another unanswered question is whether one can reproduce synthetically and consistently the random interstratification and mixed-layer effects of the natural clays. This challenge to hydrothermal experimenters involves a consideration of reaction rates and nonequilibrium conditions in addition to the equilibrium studies. The bulk of hydrothermal research has been of an equilibrium nature although nonequilibrium data are accumulated incidentally in the process. In addition to equilibrium data on pure oxide systems, more work is needed on the other hydrothermal approaches. The thermal stability of natural montmorillonites and their synthetic analogues remains to be determined. This approach of using both natural and synthetic mixtures has been standard procedure for other mineral suites. The effect of interlayer cationic substitution on the crystallization might be investigated further. The latter should give additional information on the phenomenon of mixed layering. The technique of determining the thermal stabilities of natural vs. synthetic montmorillonites was selected for a brief study on one montmorillonite composition. Wyoming bentonite, a rela-

tively homogeneous clay about which much information has been accumulated, was chosen for the study.

The studies of Roy and Osborn (1954, p. 868) on pure Al-montmorillonite indicate that it is stable to 420° C. The addition of sodium adds about 60° C to the maximum stability temperature as shown by the work of Sand, Roy, and Osborn (1955). Coincidentally, the effect of magnesium substitution in the octahedral layer appears to be the same as the sodium in raising the maximum stability temperature as indicated by the studies of Roy and Roy (1955, p. 161). A pure sodium-based Al-montmorillonite with an  $\text{Al}_2\text{O}_3:4\text{SiO}_2$  ratio is close to the Wyoming bentonite in composition. Above 480° C a sodium-based montmorillonite with an  $\text{Al}_2\text{O}_3:\text{SiO}_2$  ratio of about 1:3.7 decomposes to paragonite, pyrophyllite, and mullite.

## EXPERIMENTAL

### *Apparatus*

The pressure vessels used in the investigation were of the "test-tube" type described by Roy, Roy, and Osborn (1950). It consisted of a 1 $\frac{1}{8}$  inch diameter Inconel "X" rod, with a one-fourth inch diameter drilled hole, attached to a high pressure line. Water pressure was supplied by an air-driven pump.

### *Technique*

A 0.5 g sample was enclosed in a silver envelope, inserted into the pressure vessel and a rod inserted in the remaining space before attachment to the pressure line. The vessel was maintained at the desired pressure while being brought to temperature.

$(\text{Na}_{.32}\text{K}_{.03}\text{Ca}_{.05}) (\text{Fe}_{.18}\text{Mg}_{.22}\text{Al}_{1.60}) \text{Si}_4\text{O}_{10}(\text{OH})_2$  is the formula of the Wyoming bentonite studied and is the composition used in making the synthetic material. This corresponds to an oxide ratio of one-sixth mole alkali oxide, 1 mole of alumina (or its equivalent) and 4 moles silica. The synthetic materials were made by drying solutions of ethyl ortho silicate and soluble salts of the other cations. The extraneous anions were eliminated by calcination. This method is described by Roy and Roy (1955).

## RESULTS

Table 1 presents the results of a series of hydrothermal runs on a natural Wyoming bentonite and its synthetic analogue at 15,000 psi. The material was saturated with ethylene glycol vapor for 4 hours (Brunton) before being x-rayed. The 350° C run on Wyoming bentonite produced no change. The 450° C run on Wyoming bentonite yielded a montmorillonite of a different composition, mullite, cristobalite, and partially collapsed montmorillonite. (We are defining a partially collapsed montmorillonite as a material that adsorbs only one layer of ethylene glycol vapor and gives a 13.5 Å spacing on x-ray diffraction.) The 500° C run showed mica as a phase in addition to the above mentioned phases. A run at 650° C yielded mullite, cristobalite, and mica.

The lowest- and highest-temperature runs on Wyoming bentonite and its synthetic analogue gave identical results. The differences in the intermediate runs

TABLE 1.—MINERAL PHASES AFTER HYDROTHERMAL TREATMENT OF WYOMING BENTONITE AND ITS SYNTHETIC ANALOGUE AT 15,000 PSI.

Wyoming bentonite	Degrees C	Synthetic analogue
Unchanged	350	Mont
Mont-p.c., cr, mu	450	Mont, cr
Mont-p.c., cr, mu, mi	500	Mont, cr, mu, mi
Cr, mu, mi	650	Cr, mu, mi

Mont—montmorillonite.

Mont-p.c.—partially collapsed montmorillonite.

Cr—cristobalite.

Mu—mullite.

Mi—mica.

probably are due to the slower transformations of the existing crystal structure as compared with direct synthesis from a gel.

Figure 1 compares the x-ray diffraction patterns of the natural and synthetic runs made at 350° C. These were run on a Norelco Buerger-type camera with unfiltered chromium radiation. The samples were solvated with ethylene glycol and mounted in Lindemann capillary tubes. The x-ray patterns are identical, with the exception of minor differences in relative intensities.

Figure 2 shows the differential thermal analysis patterns of the natural and synthetic materials. There is a general similarity, with the synthetic material apparently releasing its adsorbed water at a higher temperature and having a less pronounced peak upon release of the hydroxyls. The exothermic crystallization of the synthetic material is at a slightly higher temperature.

The base-exchange capacity of the synthetic clay was 65 meq Mn<sup>2+</sup>/100g as compared to 92 meq for the Wyoming bentonite sample used. Both the D.T.A. curves and base-exchange capacity determination indicate that complete crystallization was not obtained in the hydrothermal synthesis and that longer runs should have been made. The 350° C run was held for 6 days.

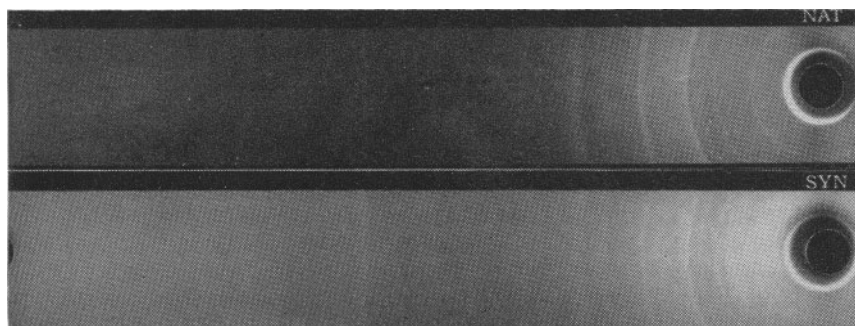


FIGURE 1.—X-ray diffraction patterns of Wyoming bentonite (NAT) and its synthetic analogue (SYN) after hydrothermal treatment at 350° C. Cr, unfiltered radiation.

TABLE 2.—MINERAL PHASES AFTER CALCINATION

Wyoming bentonite	Degrees C	Synthetic analogue
Mont-p.c.	400	Mont-p.c.
Mont-p.c.	500	Mont-p.c.
Mont-anhy, Q	650	Mont-anhy
Mont-anhy, Q	850	Mont-anhy, Q

Mont-p.c.—partially collapsed montmorillonite.

Mont-anhy—anhydrous montmorillonite.

Q—quartz.

Table 2 compares the products resulting from calcination of the natural and synthetic montmorillonites. The results are analogous through 500° C and indicate that the material has adsorbed only one layer of ethylene glycol. These results are compatible with those of Earley, Milne, and McVeagh (1953, p. 776). At 650° C quartz appears with the anhydrous montmorillonite as a calcination product from the Wyoming bentonite but not from the synthetic clay. At 850° C the calcination products are identical. The presence of quartz, according to Bradley and Grim (1951, p. 197), indicates that there is little substitution of Al for Si in the tetrahedral layer and the composition approaches a ratio of  $Al_2O_3:4SiO_2$ . If so, little or no aluminum entered tetrahedral coordination during synthesis from the gel.

### CONCLUSIONS

Although it is obvious from the results that a complete identity of the synthetic with the natural montmorillonite was not obtained, close similarities in many properties are noted. The study was made on only one synthetic preparation. It is reasonable to assume that with other starting materials, temperature, time, and pressure, a closer identity would be realized. It was noted, for instance, that the iron did not enter completely into the structure. Base-exchange determinations made on a pure sodium-based aluminum montmorillonite gave the same base-exchange capacity as the natural Wyoming bentonite and D.T.A. patterns of such synthetics show identity with Wyoming bentonite.

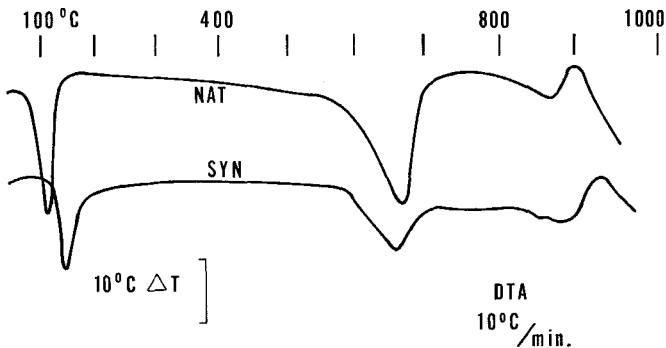


FIGURE 2.—Differential thermal analysis patterns of Wyoming bentonite (NAT) and its synthetic analogue (SYN).

The maximum thermal stability of Wyoming bentonite under 15,000 psi water pressure is about 380° C as shown by the hydrothermal runs on both the bentonite and its synthetic analogue. An aluminum bentonite composition intermediate between a beidellite ( $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ) and a montmorillonite ( $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ) composition is the most stable.

It is believed that montmorillonites can be synthesized which are very similar in structure and properties to their natural counterparts. While this study was made arbitrarily on a relatively simple clay it is felt that the technique is applicable to more complex clay systems.

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