

COLLOID SCIENCE OF MONTMORILLONITES AND BENTONITES

By

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ABSTRACT

In 1847 the name "montmorillonite" was given to a rose-red, clay-like mineral forming nests in a brown clay at Montmorillon, France. The first analysis, reported by Salvétat, gave 49.4 percent to SiO_2 , 19.7 percent to Al_2O_3 , 0.8 percent to Fe_2O_3 , 0.27 percent to MgO , 1.5 percent to CaO , 1.5 percent to alkalis, and 25.67 percent to H_2O . Much later a substance which was originally called "taylorite" after William Taylor, who was the first to draw attention to it, was finally designated as "bentonite" because it was first found in the Fort Benton series of rocks in Montana. The most characteristic mineral component of bentonite is crystalline and definitely montmorillonite.

The chemical analyses of Wyoming bentonite and hectorite are compared with those of three different calcium bentonite deposits. The importance of more up-to-date crystal chemical considerations is discussed. The electrophoretic properties of bentonites are explained on the basis of the available counter ions. The formation of thixotropic bentonite gels is discussed in detail and proof is offered to show why calcium bentonites do not give thixotropic systems.

The base-exchange capacities of sodium-bentonites and of calcium-bentonites and their differences are explained on the basis of two different methods of determining this phenomenon.

Ultra- and electron photomicrographic studies reveal the difference between montmorillonites and the various types of bentonites now known. Most striking is the fact that most bentonites, specifically calcium bentonites, contain several different types of clayey minerals.

The most probable cause of the formation of bentonitic clays as well as of true montmorillonite is referred to and discussed.

The sagacious reader who is capable of reading between these lines that which does not stand written in them but is nevertheless implied, will be able to form some conception.

Johann Wolfgang von Goethe
(1749-1832)

INTRODUCTION

In 1847 the French scientist, G. Salvétat, described for the first time a rose-red claylike mineral forming nests in a brown clay at Montmorillon, France. His analysis showed that this claylike mineral was composed of: SiO_2 , 49.4 percent; Al_2O_3 , 19.7 percent; Fe_2O_3 , 0.8 percent; MgO , 0.27 percent; CaO , 1.5 percent; alkalis, 1.5 percent; and water, 25.67 percent

(total, 98.84 percent), when studied in the condition in which it was found. He gave this claylike mineral the name *montmorillonite*.

It was not until 1916 that H. Leitmeier classified as montmorillonite a yellow clayey mineral found in Bulgaria. The sample had lain in the laboratory for three years. When analyzed, it was found to contain: SiO_2 , 50.14 percent; Al_2O_3 , 19.74 percent; Fe_2O_3 , 4.14 percent; CaO , 1.26 percent; MgO , 2.28 percent; and water, 22.61 percent (total: 100.17 percent). Leitmeier (1916) assumed that part of the Fe_2O_3 was actually replacing Al_2O_3 , leaving the balance as well as MgO and CaO as impurities. On the basis of this assumption he figured the formula of the pure crystalline material to be $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 6\text{H}_2\text{O}$.

Ross and Shannon (1926) give the formula of montmorillonite as $(\text{MgCa})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$ and state that its physical form is micaceous and its crystal form orthorhombic. Their analysis, made from material which had been washed free of impurities, indicated that its composition agreed closely with material from Montmorillon, France. The only real difference was the much higher MgO content than that originally reported by Salvétat.

They also analyzed the montmorillonite obtained from Montmorillon, France, and offered the following results: SiO_2 , 38.60 percent; Al_2O_3 , 20.03 percent; Fe_2O_3 , 1.25 percent; MnO , 0.16 percent; CaO , 1.72 percent; MgO , 5.24 percent; water, 21.52 percent. They also offered the following data for the water loss of the same clay: at 100°C , 11.88 percent; at 140°C , 2.00 percent; at 450°C , 2.64 percent; and at red heat, 5.0 percent (total 21.52 percent).

In 1897 W. C. Knight described a peculiar variety of clay under the name *taylorite*. After he found that that name was already preoccupied, he proposed the name *bentonite*, since the clay was originally discovered near Fort Benton, northeast of Great Falls, Montana (Knight, 1898).

At that time colloid science had not yet become sufficiently known and established; therefore, almost no progress had been made in regard to the most important applications of bentonites. Now the situation is entirely different and important contributions have been made, particularly during the second quarter of this century. A considerable amount of basic research has been published (Bradfield, 1927, 1931; Bradley, 1945; Bradley and Grim, 1948; Foshag and Woodford, 1936; di Gleria and Zucker, 1931; Grim, 1942, 1953; Hauser, 1945; Hauser and le Beau, 1938, 1939, 1941, 1952; Hauser, le Beau, and Pevear, 1951; Hauser and Leggett, 1940; Hendricks, 1945; Marshall, 1949; Perkins, 1952; Ross and Hendricks, 1945; Williams, Neznayko, and Weintritt, 1953).

The main purpose of this contribution is to discuss the differences between sodium and calcium bentonites from a strictly colloid-scientific point of view (Hauser, 1948).

Before offering a detailed discussion of the colloid science of montmorillonites and bentonites, it seems advisable to point out why this branch of science is so important in explaining most of the phenomena of which the montmorillonites and bentonites offer the most outstanding examples of all colloidal clays.

In the case of montmorillonites and bentonites it must be borne in mind that we are dealing here with polymolecular colloids and not with simple particles.

CHEMICAL ANALYSIS

As shown in Table 1, the analysis of Wyoming bentonite compares very well with the analyses previously published by others (A.P.I., 1950; Foshag and Woodford, 1936; Grim, 1953; Hauser, 1945, 1952; Hauser and le Beau, 1946; Hillebrand, 1919; Kallmann, 1944; Marshall, 1949; Ries, 1927; Ross and Hendricks, 1945; Smith, 1871; Wiklander, 1946; Williams, 1953) and shows the purity of the tested mineral. The same holds for the analysis of hectorite.

TABLE 1. — CHEMICAL ANALYSIS

	Wyoming Bentonite (percent)	Hectorite (percent)	Cherry Lease (percent)	Princeton (percent)	Kisameet Bay (percent)
Water Loss at 110°C	13.75	14.56	13.36	7.86	4.36
SiO ₂	58.60	54.28	58.84	67.77	52.52
Al ₂ O ₃	19.59	0.68	18.39	17.13	19.40
Fe ₂ O ₃	3.19	0.10	2.82	2.12	3.77
FeO	—	—	—	—	4.52
CaO	0.37	0.50	2.29	2.92	4.35
MgO	2.51	25.25	2.12	1.84	4.53
Na ₂ O	1.69	3.19	0.91	0.42	1.57
K ₂ O	0.32	0.16	0.39	—	3.83
Li ₂ O	—	1.02	—	—	—
CO ₂	—	—	0.36	—	0.16
SO ₃	—	—	0.16	—	—
TiO ₂	—	—	0.16	—	1.12
Total	100.02	99.74	99.80	100.06	100.13

The analysis of Cherry Lease clay clearly shows that we are dealing here with a calcium bentonite which does contain, however, a comparatively high percentage of sodium. Princeton clay in its pure form must also be classified as a calcium bentonite, but it shows an excess of silica in comparison with other well-known calcium bentonites. Ultramicroscopic and electron microscopic investigations have revealed the presence of cristobalite as an impurity. The analysis of the Kisameet Bay clay deposit is nearly identical with that previously reported by W. Ure (Ross and Hendricks, 1945).

CRYSTAL CHEMICAL CONSIDERATIONS OF SILICATES

A few years ago W. A. Weyl (1951) pointed out that surface ions of silicates are exposed to an asymmetrical force field because their electronic orbits are deformed and the polarized ions therefore exert optical as well as chemical properties which differ from those of the same type of ions which happen to be located in the symmetrical force field of the interior. This statement must not be overlooked, because we are dealing here with colloidal particles of siliceous matter where the physics and the chemistry of surfaces are dominated by polarization phenomena (Fajans, 1931).

All surface units have a dipole moment and all dipoles are so oriented that their centers of positive charge point toward the interior of the crystal and their centers of negative charge point to the exterior. This orientation produces an electric double layer.

From a strictly colloidal point of view one must therefore differentiate between two possibilities, namely, what Weyl termed the "D-units" and the "E-units."

In the interior of silica the building unit would be $\text{Si}^{4+} (\frac{\text{O}^{2-}}{2})_4$. At the surface, however, we must consider two types of groups, namely, $\text{Si}^{4+} (\frac{\text{O}^{2-}}{2})_3$ and $\text{Si}^{4+} (\frac{\text{O}^{2-}}{2})_3 \cdot \text{O}^{2-}$. The first one, called "D-unit," is characterized by an excess positive charge. The second one, termed "E-unit," reveals oxygen excess over the stoichiometric ratio and therefore exhibits a negative charge. Figure 1 is a schematic picture of a crystallized form of SiO_2 showing the two types of units present in the surfaces.

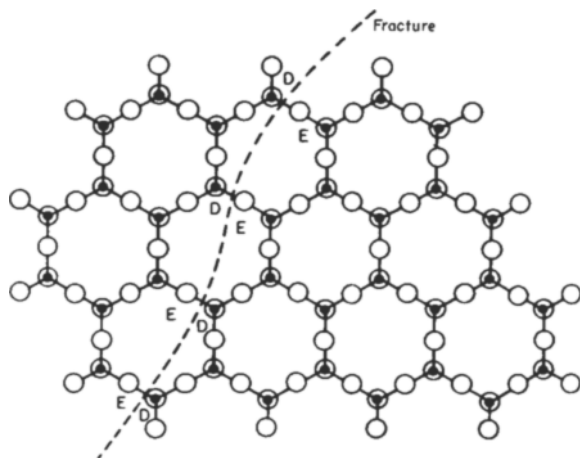


FIGURE 1.—Formation of E- and of D-units at the fracture surface of crystalline SiO_2 .

The "E-units" are stabilized by adsorbing positive ions or polar molecules which can balance the force field and thereby restore some of its original symmetry. The "E-units," however, are also likely to undergo an electron transfer, which leads to divalent silicon and atomic oxygen.

Weyl has offered factual proof for the release of atomic oxygen, using either 4,4',4''-hexamethyl-triamino-triphenyl-methane or 4,4'-tetramethyl-diamino-triphenyl-methane as an indicator. When the indicator is mixed with a clay sample in a concentration of about 10 milligrams per gram of clay and then slightly heated (in the case of the former indicator) or exposed to irradiation with ultraviolet light (in the case of the latter), a more or less pronounced blue color will appear. The intensity of the color varies with the chemical composition of the clay; e.g., sodium montmorillonite gives a very dark blue color, hectorite a medium purple color, Kisameet Bay clay a very light blue reaction, and Cherry Lease and Princeton clays a very dark blue color. Hauser, le Beau and Pevear (1951) have reported on results obtained with this indicator technique in testing colloidal siliceous matter.

Weyl has offered herewith a new atomistic interpretation of chemical reactions which involve solid surfaces and in doing so he has given the colloid scientist a very important tool for research, since colloid science deals primarily with surface phenomena.

MONTMORILLONITES AND BENTONITES AS COLLOIDAL ELECTROLYTES

All montmorillonites and bentonites have the basic structural pattern of mica, namely, two silica sheets which enclose an alumina sheet. One of the most important factors is that the spacing between the lattice units varies with the moisture content in the case of sodium bentonites. This is the reason why they are frequently referred to as the "expanding lattice" group; this group comprises four main minerals, bentonite, saponite, beidellite, and nontronite. In the clay mineral hectorite, aluminum has been largely replaced by magnesium.

In the bentonites the seat of the net charge is separated from the water layers and from the exchangeable cations by the silica sheets, which in the case of sodium bentonites appear to hinder a close association between the cations and the lattice. Marshall (1949) has already pointed out that in general, the greater dissociation of Na-bentonites than beidellites can be accounted for quantitatively.

All clays of the montmorillonite type fit very well into McBain's (1950) definition of colloidal electrolytes since, in an aqueous suspension, each lattice unit comes to equilibrium with the outer solution. On this basis it has been assumed that the base-exchange capacity should be almost independent of particle size, and Marshall confirmed this. Hauser and Reed (1936, 1937) have shown that relatively monodisperse fractions of electrolyzed sodium bentonite all give the same pH-*versus*-concentration

curve, irrespective of particle size. This strongly reinforces the suggestion that bentonites must be classified as colloidal electrolytes.

The work of most investigators so far has referred only to Na bentonites. It has been observed that all sodium bentonites and hectorite exhibit pronounced thixotropic properties. In the case of calcium bentonites a drastic difference in their behavior is immediately observed when they are placed in water; they do not have the tendency to swell to any appreciable extent but will instead settle out fairly fast. It can be proved that the calcium ions cannot be considered as part of the actual lattice because they can be exchanged. This can be accomplished by treating the calcium bentonites with a high concentration of sodium salts and then washing them carefully. The net result is then a sodium clay which, however, will not exhibit thixotropy comparable with that of the original sodium bentonites and hectorites.

ELECTROPHORETIC PROPERTIES OF BENTONITES

All colloidal clays must be classified as electrocratic sols. Their stability or instability depends on electrokinetic phenomena resulting from the presence or absence of charges on the surface of the clay particle, and the type and concentration of ions present in the dispersion medium. Differences in the lattice structure of the various clay minerals result in diffuse double layers being formed by different mechanisms. For example, the electric double layer of a sodium bentonite which exhibits high base-exchange capacity is due to the negatively charged surface of the crystallite of the inner rigid layer, the adsorbed hydrated sodium ions representing the counter ions in the diffuse outer layer. In the case of calcium bentonite the calcium ions are much more strongly adsorbed and held closer to the surface of the negatively charged clay particle, and therefore the chances of dissociation are reduced. This is shown in a much lower base-exchange capacity. Since the adsorbed counter ions are electrostatically bonded to the clay particles, complete dissociation from them is prevented. They surround the clay particle at a certain distance and thereby form an imaginary membrane. If pure water is used as a dispersion medium, osmotic imbibition of water through this hypothetical membrane occurs and the clay swells to its maximum. We know that all montmorillonites and bentonites carry a net negative charge and it is also known that the electrical forces associated with a colloidal particle arise from two sources: One set of forces arises from the ions predominantly of one sign, which are rigidly adsorbed on the surface of the particle, or belong to the particle; and the other set arises from the ions of opposite sign, which gather about the particles in an effort to neutralize this charge. Since the particle possesses a net charge one may assume that the total number of ions that gather about the particle in accordance with the Gouy concept are not sufficient to neutralize the charge on the particle. Some of these ions of opposite sign may be floating about in random

motion in the dispersion medium so that the dispersion medium has a charge opposite to that of the particle.

The cataphoretic velocity of purified, colloidal, monodisperse fractions of Na-bentonite increases with decreasing particle size. With constant particle size it decreases with increasing concentration, the drop being most pronounced with the smallest particles. In extreme dilutions (up to 0.5 percent) the cataphoretic velocity remains constant for a given particle size. The results obtained in studying the cataphoretic velocity of Wyoming bentonite sols are shown in Table 2.

TABLE 2. — CATAPHORETIC VELOCITY OF BENTONITE SOLS

Apparent Particle Diameter m μ	Concentration percent dry weight	Cataphoretic Velocity μ /volt/cm/sec	ζ -Potential mv
96	0.210	6.1	84.2
96	0.372	6.1	84.2
96	0.516	5.5	75.6
96	0.742	4.3	59.6
60	0.211	6.3	89.0
60	0.340	6.3	89.0
60	0.525	5.7	78.5
60	0.713	4.8	66.0
20	0.240	7.0	96.6
20	0.424	7.0	96.6
20	0.612	5.0	68.3
20	0.800	4.0	54.9

GELATION

It is known from experiment that to obtain the maximum gelation effects in electrocratic colloidal systems, monovalent ions possessing a sign opposite in charge to that of the sol are most suitable. A negatively charged bentonite will set to a gel by the use of lithium, sodium, potassium, hydrogen, etc., and it is important to note that the effectiveness of adsorption of the ion in the diffuse layer increases from lithium to hydrogen in the Hofmeister series. This indicates that the less strongly the ion carrying the charge opposite to that of the sol particle is adsorbed in the diffuse layer, the more powerful it is in forming gels. It must also be expected, however, that polyvalent ions will behave differently from monovalent ions. They are more strongly adsorbed in the diffuse layer because of the greater attraction; there would also be greater forces of repulsion between the ions of like sign in the dispersion medium, thus reducing any tendency of interaction of the ions to form ionic groups, making the system more diffuse. The electrocratic behavior of a sol depends in general upon the individual adsorption characteristics of the

ions in the surface of the systems and the adsorption behavior of the colloidal clay particles (Hauser and Reed, 1936, 1937).

This phenomenon has been clearly demonstrated in the production of the coherent bentonite film known as "Alsifilm" (Hauser, 1941, 1941a, 1941b, 1943, 1945, 1945a; Hauser and Dannenberg, 1946; Hauser and le Beau, 1938, 1939, 1941, 1946, 1952; Hauser, le Beau, and Pevear, 1951). For example, if a sodium bentonite sol is first converted into a gel by evaporation and the gel is spread on an appropriate support or deposited thereon directly from the sol state and then allowed to dry out completely, it is observed that the particles when forced closer together actually snap into their new location, thereby forming long interlacing filaments or fiber bundles. This is shown in Plate 1. The presence of separate reflection disks as ultramicroscopically observed in the sol and gel stages gives way to continuous threadlike aggregations which, upon continued evaporation, seemingly grow into larger crystals of highly anisometric shape. These filaments interweave and tie together by tri-dimensional cross-linkages, resulting in an absolutely coherent structure. After complete desiccation a self-supporting film is obtained which can be easily removed from its support as a coherent sheet.

We owe this phenomenon mainly to the structure of the sodium bentonite particles. It has not been possible to obtain such films from calcium bentonite. In all probability the reason for this is the divalency of the calcium ions, which are much more tightly bonded to the clay particle than are the sodium ions. They will also hydrate considerably less than the sodium ions, and this hydration is essential for film formation.

BASE-EXCHANGE CAPACITY

The determination of the base-exchange capacity of clay minerals has been carried out by many workers using various methods (Coffman, 1946; Ganguly, 1951; Graham and Sullivan, 1938; McConnell, 1950; Perkins, 1952). One is first to leach the clay with a neutral solution ($\text{NH}_4\text{COOCH}_3$) and then to determine the amount of cations present in the solution, or the amount of cations adsorbed by the clay. This method has been widely used during the last thirty years.

If one is more interested in the total base-exchange capacity than in the amount of each exchangeable cation, however, titration of the electro-dialyzed or acid-leached clay is used until a definite pH value is obtained. By the use of NaOH some have titrated the H-clay to a pH of 7. The majority of workers, however, continued the titration until a pH of 8.3 to 8.5 was attained. In most cases this corresponds to the real end point of the titration. As pointed out by Kelley (1948) and Kelley, Dore, and Brown (1931), the results of the determination of the base-exchange capacity using the H-clay titration method are always much lower with samples from certain bentonite deposits than those commonly obtained by the use of the NH_4 -acetate method.

One of the most recent methods for determining the total base-exchange capacity of different types of clays is based on the use of versenate (Perkins, 1952). This method is extremely simple, requires only very

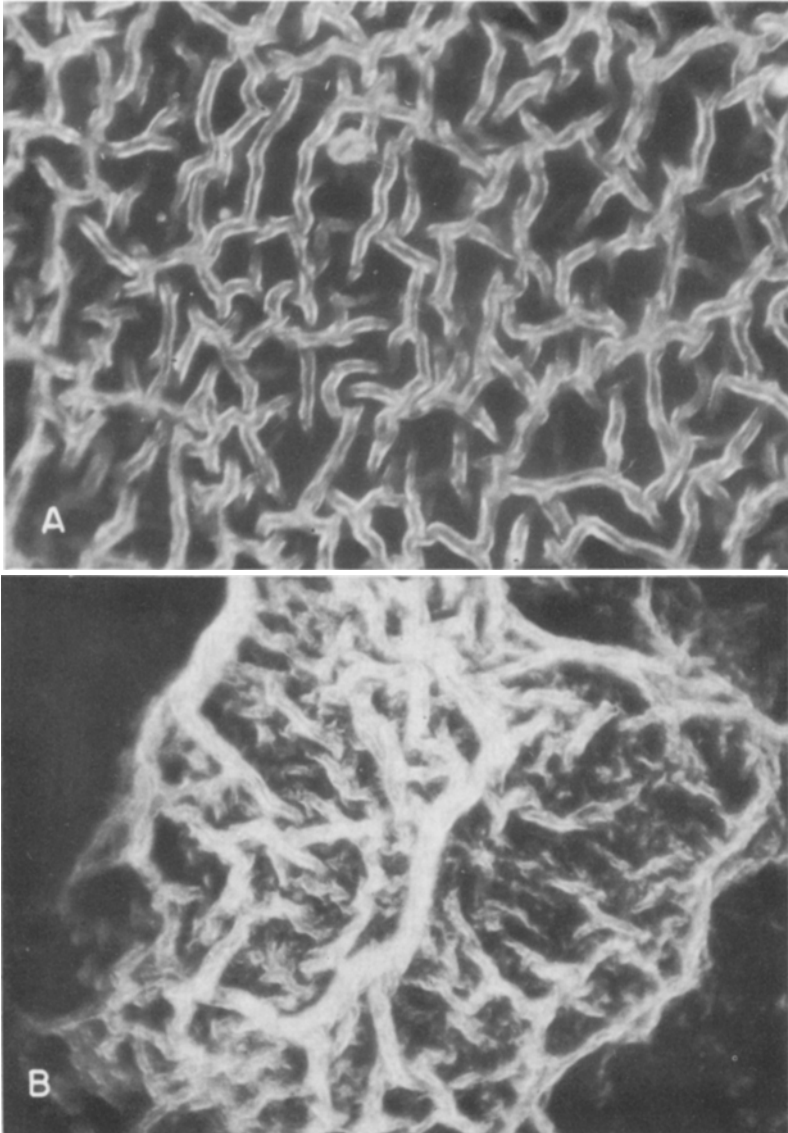


PLATE 1. — Ultraphotomicrographs of (A) "Alsifilm" obtained from Wyoming bentonite (Orig. magn. 550x; present magn. 3,300x); and (B) film formed from hectorite gel (orig. magn. 550x; present magn. 3,300x).

simple equipment, and in the majority of cases offers results which are in excellent agreement with those obtained by the NH_4 -acetate method.

We have carried out the base-exchange capacity determinations by both the H-clay titration method and the versenate method. With the calcium clays we found that the results obtained with the potentiometric titration method were lower than those obtained with the versenate method.

In carrying out base-exchange capacity determinations with the H-clay titration method we preferred to transform the clay into H-clay by leaching it with diluted HCl instead of by applying electro dialysis. Several authors have pointed out that electro dialysis may effect a decomposition of the clay unless extremely low potentials are applied.

Table 3 offers the results obtained by both methods.

TABLE 3. — BASE-EXCHANGE CAPACITY DETERMINATIONS

Clay	H-clay Titration	Versenate
Wyoming bentonite	86.1	88
Hectorite	67.5	68
Cherry Lease	59.5	72
Princeton	42.0	54
Kisameet Bay	20.1	24

When base-exchange reactions are determined, care must be taken that only particles of a given size are subjected to investigation and that no agglomerates are present. This is most easily assured by subjecting a dispersion of the clay to supercentrifuging and then selecting only the fine portion of the deposit. This is of primary importance in studying calcium bentonites because they have the tendency to agglomerate quite strongly. Such agglomerates do not allow exchange reactions to be carried out to the limit.

The Cherry Lease composite and the Princeton clay were converted into sodium clays by first exhaustively leaching them with a 3*N* NaCl solution, and then by treating them with a concentrated solution of NaCl at a temperature of 50°C for 30 hours. Thereafter the base-exchange capacities of these sodium clays were determined. Owing to the substitution of sodium for calcium and even for some of the magnesium, a marked increase over the original base-exchange capacities could be recorded. The results are clearly seen in Table 4.

TABLE 4. — BASE-EXCHANGE CAPACITY DETERMINATIONS

Clay	Titration	Versenate
Cherry Lease Composite	66.5	80
Princeton	46.5	60

Figure 2 offers a visual demonstration of the change in base-exchange capacity with varying pH.

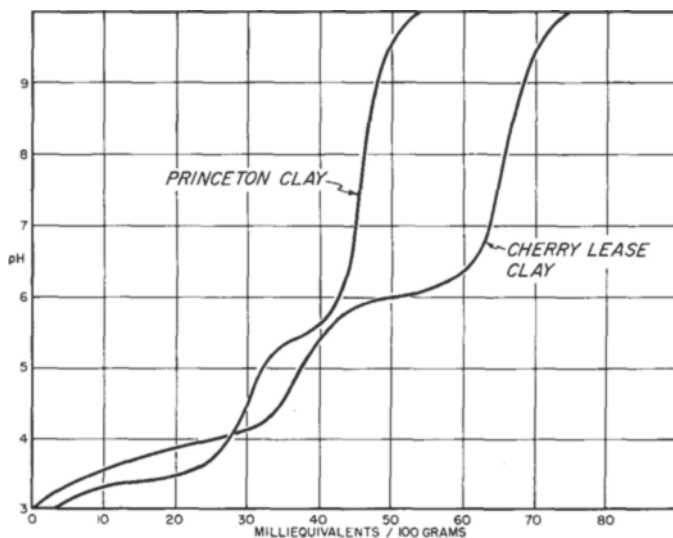


FIGURE 2. — Change in base-exchange capacities of Princeton clay and Cherry Lease clay with varying pH.

Ultramicroscopy and electron microscopy have revealed that the particle sizes of Na-bentonites are extremely small. What has not yet been accurately reported, however, is the actual surface area of bentonite particles involved. J. Hall of Godfrey L. Cabot, Inc., carried out for us some tests on hectorite after it had been oven dried at 105°C and then evacuated at 80°C for 45 minutes. A measurement of the surface adsorption of N₂ revealed a surface area of 70.8 square meters per gram of sample. This information may prove to be of value for further research pertaining to other bentonites, or even to other types of clays.

DIFFERENTIAL THERMAL ANALYSIS

Figure 3 represents the differential thermal analyses of Wyoming bentonite, Cherry Lease clay, Princeton clay, and Kisameet Bay clay.

Of these four samples, Wyoming bentonite and Kisameet Bay clay show a pronounced minimum at a temperature of about 175°C. Although this minimum is also present with Princeton clay, but at a somewhat higher temperature, it is much weaker than that of the other two clays. Cherry Lease clay not only shows a much stronger minimum, but at a temperature of about 155°C a slight intermediate decrease in that minimum is found. Kisameet Bay clay shows the strongest minimum in that region. Between 300°C and 600°C Wyoming bentonite and Princeton clay are practically constant. At about 725°C Wyoming bentonite shows an endothermic peak, which is even more pronounced with Princeton clay and the Kisameet Bay clay. Cherry Lease clay shows a slightly

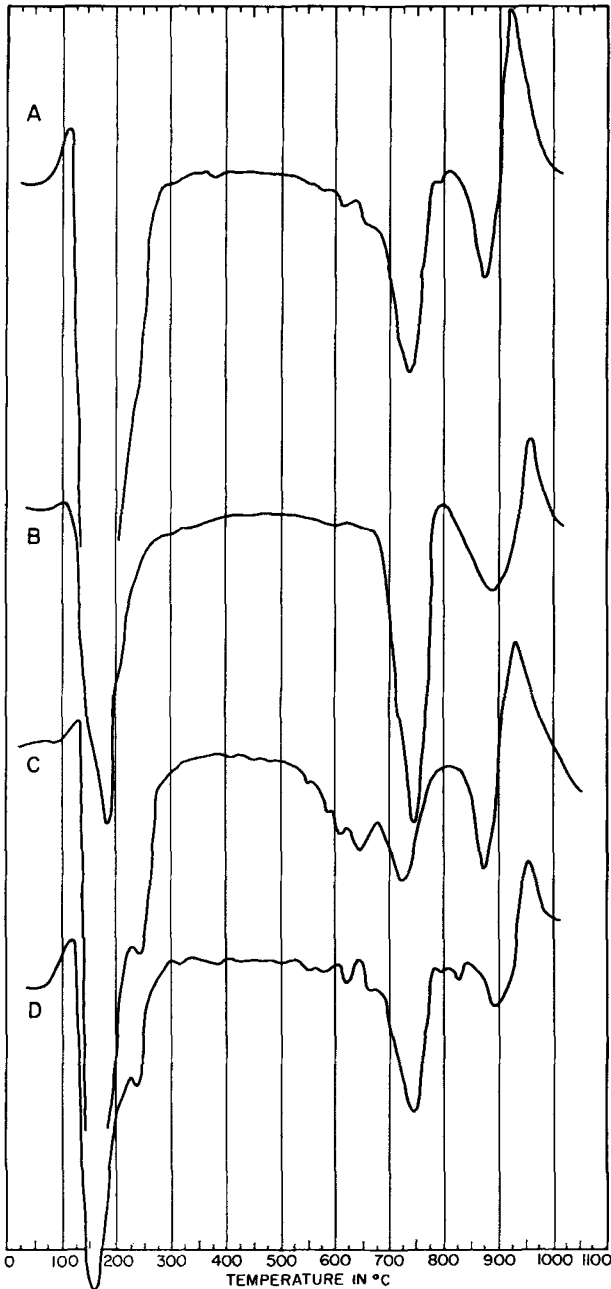


FIGURE 3.—Differential thermal analysis curves. (A) Kisameet Bay, B.C., clay deposit; (B) Princeton, B.C., calcium bentonite; (C) Cherry Lease Composite calcium bentonite; (D) Wyoming bentonite.

endothermic reaction in that region. Princeton clay and Kisameet Bay clay show a slight endothermic peak at about 875°C. All four clays tested show more or less pronounced exothermic peaks at temperatures between 900°C and 950°C. This reaction is in all probability associated with the formation of spinel (Grim and Rowland, 1942; Hauser, le Beau, and Pevear, 1951). These results indicate clearly that the initial endothermic peak must be attributed to adsorbed water located on the surface of the material. The most pronounced second endothermic peaks refer to the loss of lattice water, and the last endothermic peaks, where present, seem to correspond to a breakdown of the lattice itself.

Infrared absorption spectra of sodium bentonite films have revealed distinct absorption bands at a reciprocal wave length of 3,700 cm^{-1} due to free hydroxyl groups, and between 3,600 and 3,200 cm^{-1} due to associated hydroxyl groups or adsorbed water. Whereas increasing the temperature of drying the films reduces the second absorption band, the first remains practically unchanged (Hauser, le Beau, and Pevear, 1951).

ULTRA- AND ELECTRON MICROSCOPIC RESULTS

Unsubstituted montmorillonite will adsorb counter ions only where broken edges are present, and will not, as is the case with the substituted bentonite, adsorb counter ions as a result of its unbalanced crystal lattice. Plate 2A shows a montmorillonite from Combe Hay, Somersetshire, England; it is unquestionably one of the most typical montmorillonites. In contrast thereto, the Wyoming bentonites and hectorite have a pronounced base-exchange capacity and are therefore quite different from ideal montmorillonite in most of their properties. The film-forming property of Wyoming bentonite has been discussed above ("Gelation" section). Such films are also obtainable with hectorite. The electron photomicrograph of hectorite is shown in Plate 2B; here the available magnification clearly shows the alignment of the individual particles which then form a coherent structure.

The ultra- and electron photomicrographs of Cherry Lease clay are shown in Plates 3 and 4. They clearly indicate that this clay is very difficult to disperse completely unless it first undergoes certain chemical treatments, e.g., the use of trisodium phosphate. This can easily be demonstrated by comparing A and B, Plate 3.

As has already been shown in the chemical analysis, Princeton clay differs pronouncedly from Cherry Lease clay. The difference in SiO_2 content is particularly striking. Careful comparison of electron photomicrographs of Princeton clay with those of Cherry Lease clay shows that Princeton clay contains mica and in all probability also quartz particles (Pl. 5). Therefore not all of the deposit can be classified as calcium bentonite.

In its natural condition Princeton clay displays a high degree of aggregation, as is shown in Plate 6. After trisodium phosphate is mixed

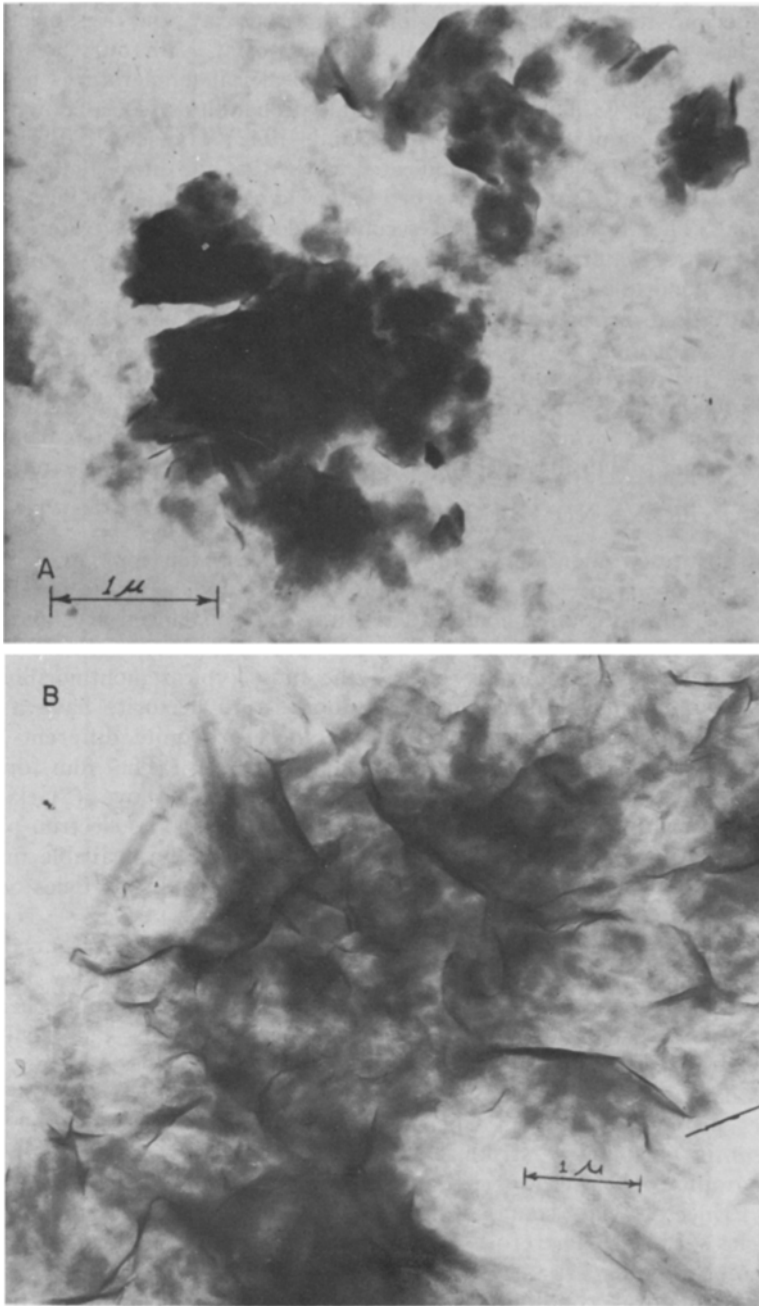


PLATE 2.—Electron photomicrographs of (A) montmorillonite (Combe Hay, England) (orig. magn. 10,100x); and (B) lectorite (orig. magn. 10,100x).

with the Princeton clay in sufficiently high concentration, approximately 80 percent of the available calcium ions are replaced by sodium ions; furthermore the phosphate ions are adsorbed on the broken edges of the crystal lattices, thereby aiding in causing maximum dispersion.

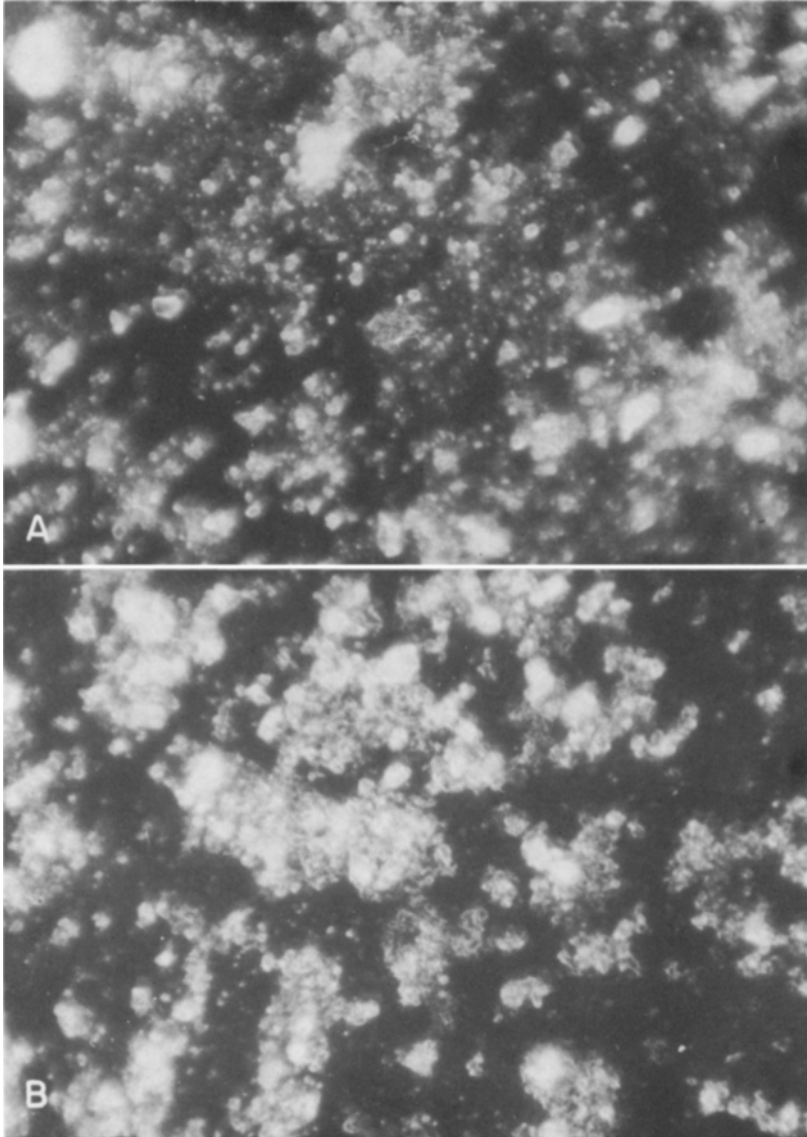


PLATE 3.—Ultraphotomicrographs of (A) Cherry Lease clay (orig. magn. 550x; present magn. 3,300x); and (B) Cherry Lease clay plus $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (orig. magn. 550x; present magn. 3,300x).

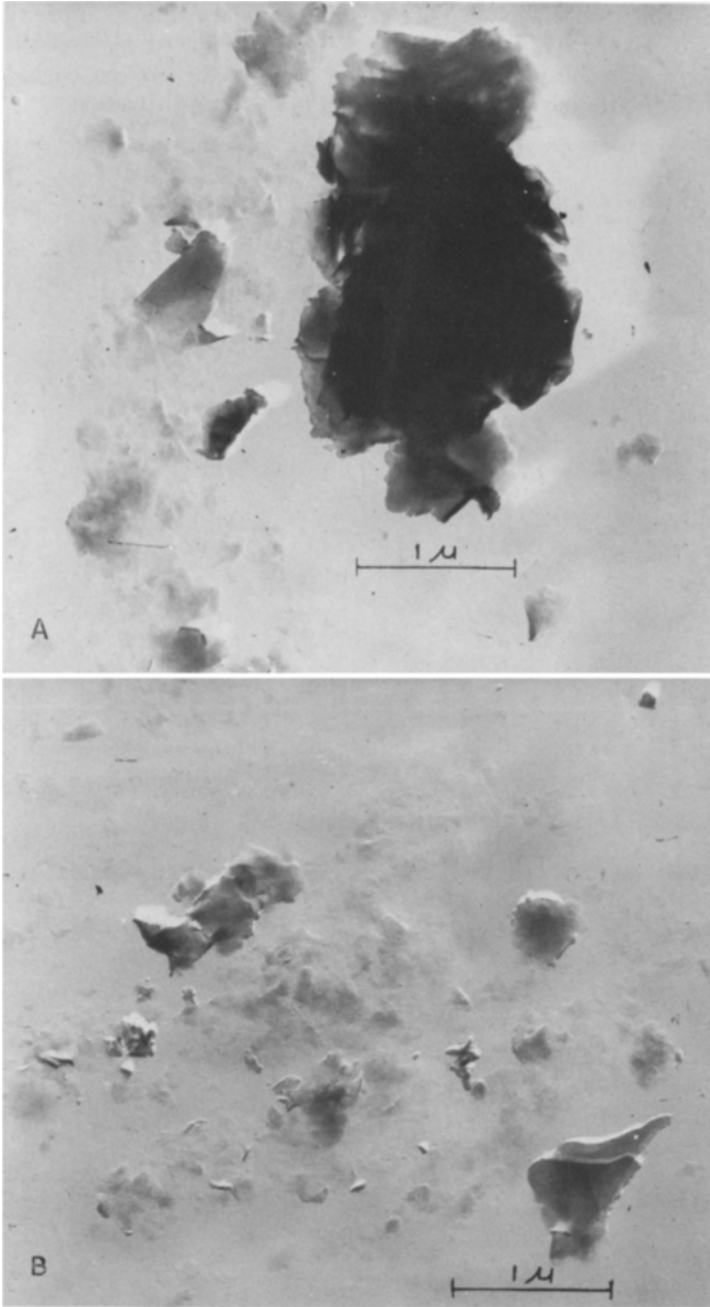


PLATE 4.— Electron photomicrographs of Cherry Lease clay; mounted dry; shadowed, 45° angle (orig. magn. 10,100x).

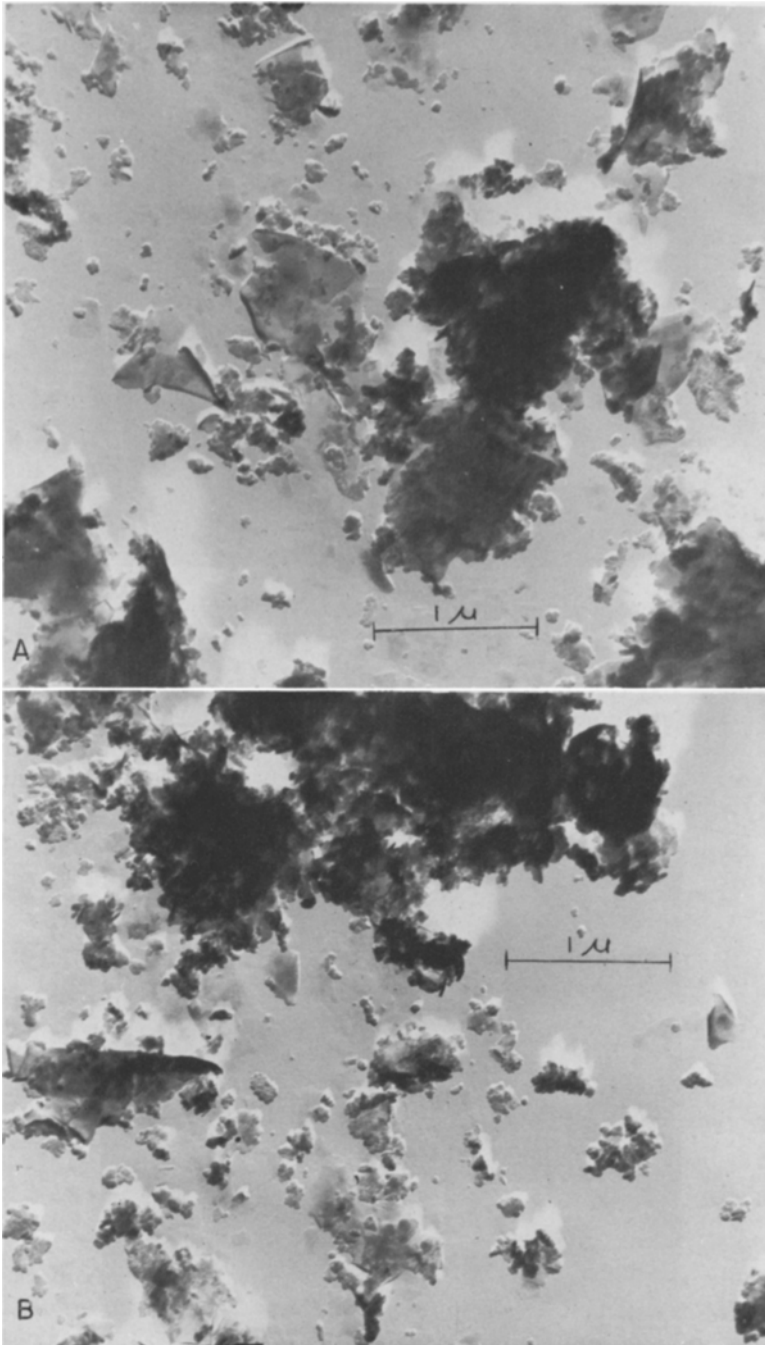


PLATE 5. — Electron photomicrographs of (A) Princeton, B.C., clay; mounted dry; shadowed, 45° angle (orig. magn. 10,100x); and (B) Princeton, B.C., special clay; mounted dry; shadowed, 45° angle (orig. magn. 10,100x).

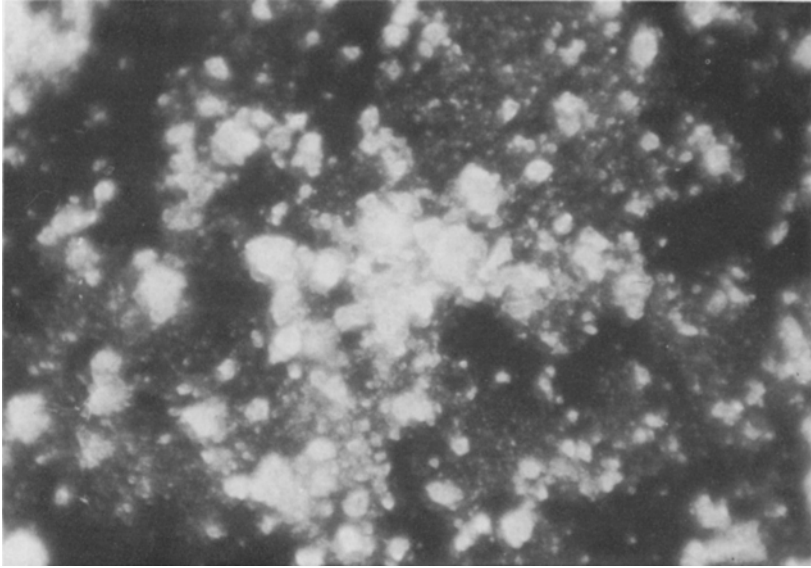


PLATE 6.—Ultraphotomicrograph of Princeton, B.C., clay (orig. magn. 550x; present magn. 3,300x).

Kisameet Bay clay reveals electron-microscopically the presence of some foreign matter (mica and quartz) (Pl. 7). If the clay is subjected to fractionation by supercentrifuging, definite proof can be offered for the presence of such foreign matter. This is clearly evidenced by comparing Plate 7 with Plate 8, A and B.

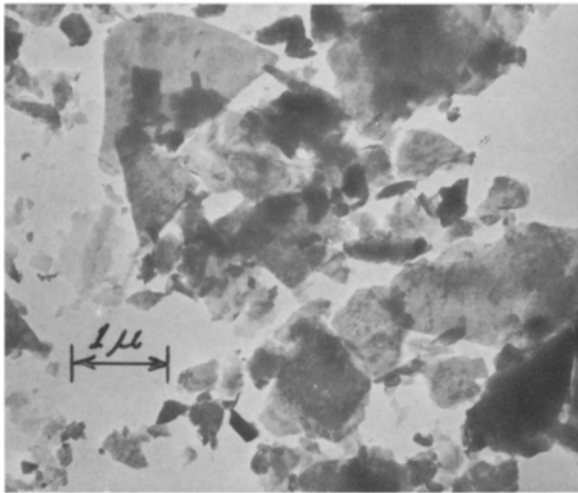


PLATE 7.—Electron photomicrograph of coarse fraction of Kisameet Bay clay deposit (orig. magn. 10,100x).

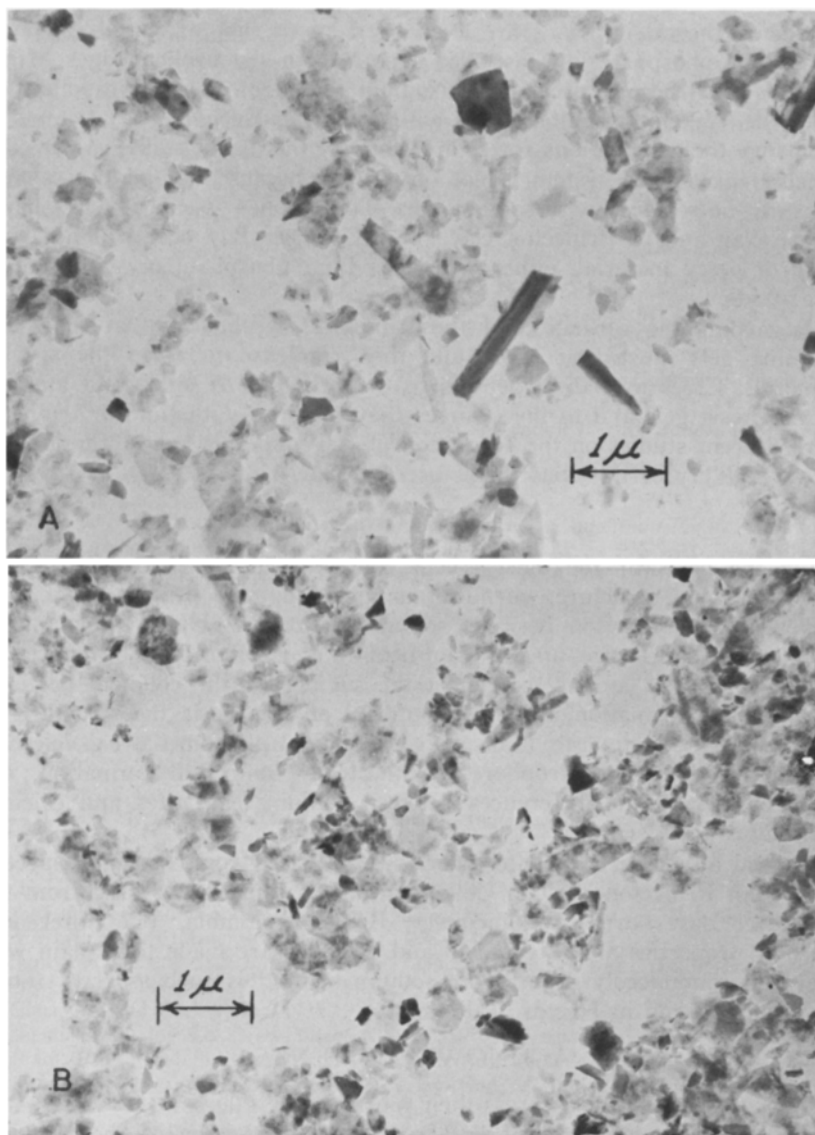


PLATE 8.— Electron photomicrographs of (A) Kisameet Bay, B.C., clay deposit (orig. magn. 10,100x); and (B) fine fraction of Kisameet Bay, B.C., clay deposit (orig. magn. 10,100x).

It has not been possible to produce truly thixotropic systems with these clays, however, particularly in the low concentrations for which Wyoming bentonites and hectorite are famous. The reason for this, in all probability,

is that if the calcium ions are exchanged by the use of trisodium phosphate, the phosphate ions are also adsorbed on the broken edges of the crystals and thereby prevent the sodium ions from reacting as they do with the Wyoming bentonites or with hectorite. Even if one attempts to exchange the calcium ions for sodium ions by the use of sodium hydroxide a truly thixotropic system is not obtainable, because not all the calcium ions can be replaced with sodium ions. This applies specifically to Cherry Lease clay and to Princeton clay. The Kisameet Bay clay will not even form a pasty material, either with trisodium phosphate or with sodium hydroxide.

Regarding the formation of these minerals we believe that silica and alumina gels must first react, and then condense to form the specific minerals. Clays owe their genesis to the presence of silica and alumina or magnesia gels and to the changes they undergo with time or temperature. Recent studies on the formation of clay minerals have offered proof of the validity of this theory (Hauser, 1952).

SUMMARY

On the basis of the most recent contributions of colloid science in evaluating the structure, chemical composition, and properties of clay minerals, a comparison between sodium bentonites, which carry an unbalanced crystal lattice, and calcium bentonites is offered. The importance of the release of atomic oxygen at the surface of the colloidal particles during their formation is pointed out and on this basis the structure of the various clay minerals is discussed. Colloidal phenomena, e.g., electrokinetic properties, electrophoresis, thixotropy, and film formation, are referred to and the differences between sodium bentonites and calcium bentonites are discussed.

Special attention is paid to Cherry Lease clay from Texas, Princeton clay from Princeton, British Columbia, and Kisameet Bay clay from the Kisameet Bay, north of Vancouver, British Columbia. The differences in their properties are referred to and attempts are made to explain why they so pronouncedly differ from sodium bentonites such as clays found in Wyoming and in Hector, California.

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