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THE COLLOIDAL CHEMISTRY OF CERAMIC CLAYS

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SUMMARY*

The colloidal chemistry and the structural minerology of the clay minerals are studied in detail. Deposits of kaolin and of plastic clays for white ceramics (ball clay) in the United States and England are discussed from the viewpoint of probable processes of formation. The practical consequences of the modification of the structural layer, of the associated organic material and of the flocculant salts are discussed as colloidal chemical problems. The use and abuse of deflocculants and of flocculants are considered.

The Structure of the Clay Minerals

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With the arrival of X-ray crystallography [1] it became possible for Hedding in Switzerland (1923) and Rinne in Germany (1924) to

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Since 1970 Dr. Phelps has been functioning in areas of teaching and consulting on applications of clay in ceramics. He has written a book on nonmetallic minerals and published numerous technical and scientific works.

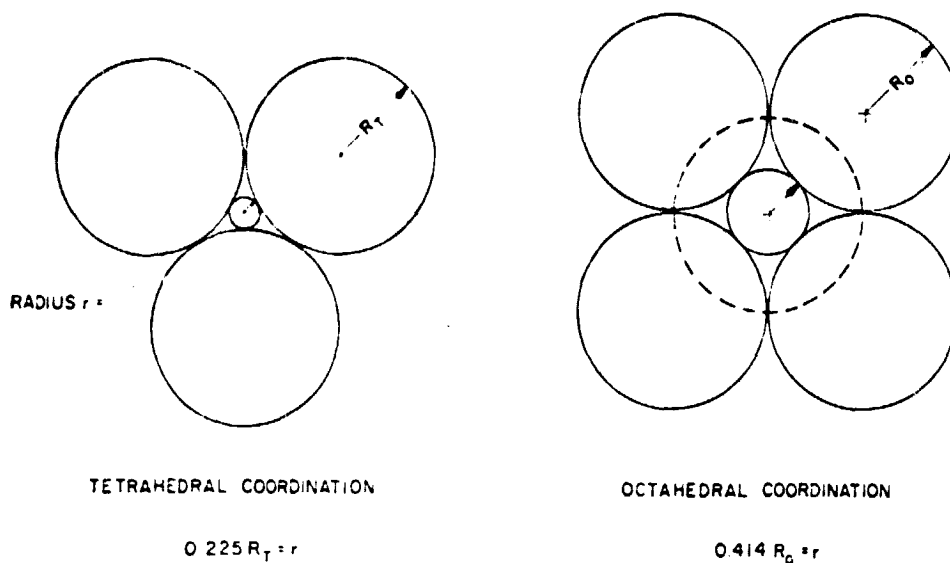
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confirm the presence of crystalline material in finer clay fractions. Around 1930 Pauling [2] was able to apply their generalizations to micas and to the structures of correlated strata, including the clay minerals.

Pauling theorized that (a) every atom forming a structural stratum has a characteristic radius, (b) the ions are bundled into a configuration producing the most stable possible arrangement, and (c) a convenient arrangement would reduce the potential energy to a minimum while satisfying the laws of valence. It was later postulated that (a) the larger ions surround the smaller ions of contrary charges as rigidly as possible with (b) the smaller size of the ions determining the arrangement of the larger ions because (c) the approach of the larger ones to one another is limited by the interaction of the electron clouds. The ratio between the radius of the larger ion and the radius of the smaller ion establishes the number of larger ions which can surround the smaller ions (i.e., the coordination number).

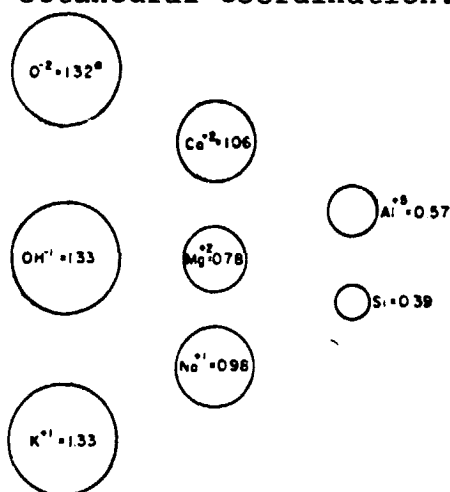
Figure 1 shows the two types of coordination most commonly found in the clay minerals and in minerals of correlative structure. /2
In the case of tetrahedral or quadruple coordination, the larger ions with an atomic radius of R_t surround a smaller atom of atomic radius $r = 0.225 R_t$. When the atomic radius of the smaller ion is large enough, six larger ions would form a tetrahedral coordination arrangement with the size of $r = 0.414 R_0$.

Figure 2 presents the atomic ratios for a number of ions appearing in various minerals of a silicate structure. The small Si^{1+} ion is located in the center of a quadruple tetrahedral figure formed by O^{2-} ions. When three oxygen atoms from each silica tetrahedron $(\text{SiO}_4)^{4-}$ are bound to similar units, a continuous lamellar structure is formed. This is the tetrahedral unit or unit in the chape of a silica lamella [3] for the clay minerals, and similarly for other correlative minerals.



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Figure 1. Quotients of two ionic radii in tetrahedral and octahedral coordination.



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RELATIVE SIZES OF CLAY, MICA AND TALC
CONSTITUENTS

* NUMBERS = RADII IN Å

Figure 2. Relative sizes of ions common in the clay minerals and in correlative ceramic materials.

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The relatively large aluminum and magnesium atoms are found in coordination with six OH^- ions, which are located in the vicinity of the ion with their centers on the six vertices of a regular octahedron. The distribution of the vertices by adjacent octahedrons results in a layered structure consisting essentially of a sandwich of two parallel planes of hydroxyl ions with Al^{3+} or Mg^{2+} between the planes. The alumina sandwich is called a gibbsite sheet, while the magnesium sandwich is analogously called a brucite sheet. When Al^{3+} is present, only two-thirds of the coordination positions are actually occupied but when Mg^{2+} is the anion, all of the positions must be occupied in order to satisfy valence requirements.

The silica tetrahedral strata and the gibbsite and brucite octahedral strata have similar dimensions and symmetry, which allows a distribution of oxygen among the strata. As a result the points "fuse with the silica, gibbsite or brucite tetrahedron oxygen stratum hydroxyls, thus producing a molecule of water and resulting in the silicon or aluminum ions sharing an oxygen atom in the sheet minerals. Two of these combinations can occur. In the case of minerals with two strata, a single tetrahedral layer is bound to a single octahedral layer. Minerals with three layers involve a bilateral fusion with the octahedral layer remaining between the two octahedral layers [sic]."

For the tetrahedral layers to be adjusted to the octahedral layer, some distortion is necessary in the location of the larger tetrahedral layer for adaptation to the smaller octahedral layer. This strain is shown by a reduction in thickness (thinning) of the single octahedral layer accompanied by a rotation of the tetrahedral layers or the basic triads of the silica layer.

The most important ceramic clays are composed essentially of the mineral of two kaolinite layers. The kaolinite structure was initially suggested by Pauling [4], developed in detail by Gruner and modified by Brindley, et al. As can be seen in the schematic

representation in Figure 3, kaolinite consists of a single silica layer combined with a single gibbsite layer in such a way that the vertices of two silica tetrahedrons and one vertex of the octahedral layers form an X of joint layers. The vertices of the tetrahedrons point in the same direction, i.e., to the center of the unit formed by the silica and alumina layers.

It is generally acknowledged that Al^{3+} is located in such a way that two atoms of Al^{3+} are separated by an OH^- above and below. This results in a hexagonal distribution of Al^{3+} in a single plane in the center of the octahedral layer. The OH^- are located in such a way that each OH^- is directly below two voids in the hexagonal structure of the O^{2-} ion of the tetrahedral layer.

The minerals of the kaolinite group consist of single sheets which are continuous in directions a and b, and heaped one above the other in direction c. There is a large number of variations in the way in which the single layers can be arranged in this heaping. This occurs with the various minerals in the kaolinite group: dickite, nactite, etc.

The kaolinite, which is the most common in ceramic use, is arranged in such a way that the adjacent sheets are in conformity with the cell dimensions determined experimentally, as is shown in Figure 4. The kaolinite has a triclinic symmetry. The oxygen atoms in one sheet and the hydroxyls in the following sheet are grouped in pairs, which suggests that the layers in the heaping are held together by means of hydrogen bonds. Other authors claim that Van der Waals forces are present and help keep the sheets united.

When kaolinite clays from different sources are examined by X-ray diffraction, variations are found in the degree of structural regularity. In some cases the triclinic angle, $= 91.8^\circ$, found

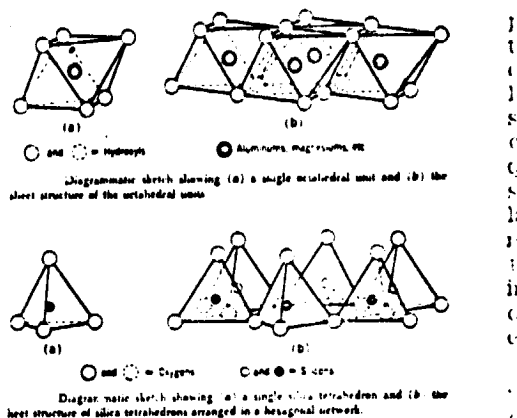


Figure 3. Diagram showing (a) the alumina octahedral unit and (b) the arrangement of the octahedrons with the tetrahedral layer. Diagrams showing (a) a single tetrahedral silica unit and (b) the arrangements of the two tetrahedrons in the tetrahedral layer. (Diagram from Grim., loc. cit., pg. 63).

in well-crystallized kaolinite becomes about 90° in some distorted forms. This can be interpreted as a function of the positions of the Al atoms and of dislocations in the case of direction b. This "distorted" kaolinite was initially found in refractory clays and is sometimes called "refractory clay mineral". In many cases, but not all, these poorly crystallized variations appear as small irregular (torn) plates.

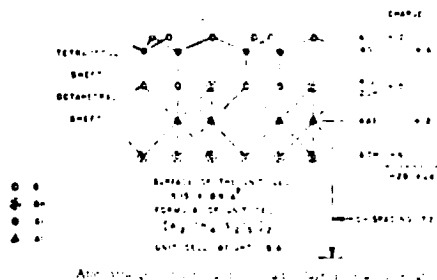


Figure 4. Diagram showing the arrangement of the tetrahedral silica sheets and the octahedral alumina layers in the single cell of a two-sheet clay mineral. (Van Olphen, loc. cit. pg. 65).

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The arrangements of the three layers of the silica and gibbsite sheets result in three groups of laminar minerals of great interest to the ceramicist. They are: (a) the smectites [6] or expansive clay minerals (montmorillonite), and (b) the micas [7] and illites (or mica clays). The structures of these three groups of minerals are ultimately derived from a prototype structure shown in Figure 5. Variations appear in the lamellar layer because of the substitution of cations of lower valence by cations of higher valence. These substitutions can occur both in the octahedral layer and in the tetrahedral layers, or in all three at one time. The consequences of the need of electrostatic balancing are responsible for the varieties of minerals.

The diagrammatic sketch of Figure 5 presents the ideal arrangement which occurs when two tetrahedral silica layers are bound to two octahedral gibbsite layers. When no substitutions are found in the structure, the mineral formed is pyrophyllite. When the octahedral layer is in the form of magnesium, brucite, or a balanced and compacted product, it is a talc mineral.

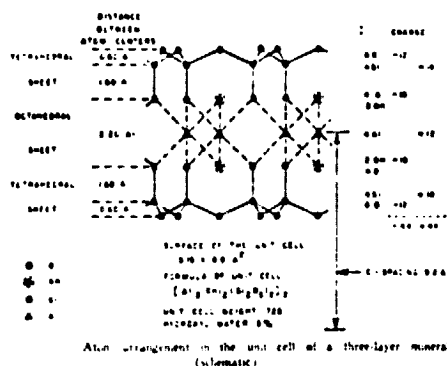


Figure 5. Diagram showing the arrangement of the silica sheet and the alumina sheet in the single cell of three-layer clay minerals. (Van Olphen, loc. cit., pg. 64).

However, if the pyrophyllite structure were to have one or 5 two aluminum atoms replaced by an Mg^{2+} ion (or some other ion of lesser valence and size close to that of Al^{2+}), the result would be an excess of negative charge which would require balancing in some way. The aluminum can be completely or partially replaced by Li^+ , Fe^{2+} , Cr^{2+} or Zn^{2+} , or the aluminum can replace Si^{4+} in the tetrahedral layers. The excess negative charge is balanced by the cations of the two basic planes of the individual layers. Such cations as Ca^{2+} , K^+ , Na^+ are generally too large to fit into the structure or into the structural voids, so that they are hardly captured by the electrostatic activity. Figure 6 shows the formulae of some types of montmorillonite clays. The positions of the variable ions are also shown.

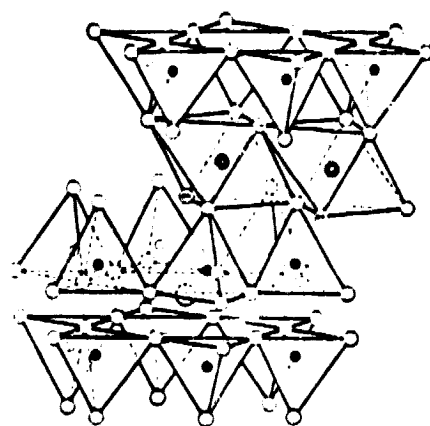
The effect of the different compensatory cations on the reaction of the smectites to water is of great importance in ceramics. For example, in the phase of montmorillonite the presence of the sodium ion between the individual layers produces a great swelling effect when the so-called sodium montmorillonite is placed in water. On the other hand, the swelling is much less pronounced when the Ca^{2+} is the variable cation. Montmorillonite also swells when it is put into contact with other polar liquids besides water, ethylene glycol, for example.

Two explanations have been given for the behavior of the polar liquid in expanding the smectite layers.

(1) The interlamellar cations become hydrated, so that the high energy involved exceeds the Van der Waals forces of attraction between the layers (in the balanced prototypes, pyrophyllite and talc do not have interlamellar ions, and for this reason there is no energy of hydration to cause the swelling).

(2) The penetrating water does not hydrate the interlamellar ions, but is adsorbed to the oxygen layers by means of hydrogen bonds (it is possible that certain geometric arrangements of the water

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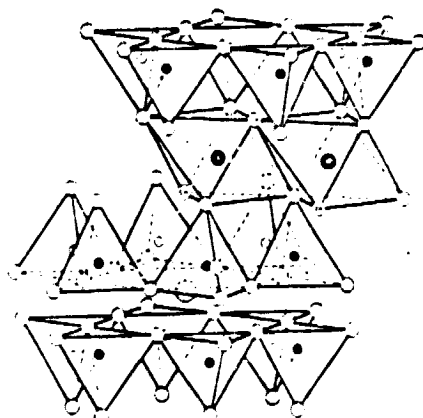


○ Oxygen, ⊖ Hydroxyl, ● Aluminum, ○ Potassium
○ and ⊖ ions (one fourth replaced by aluminum)

Diagrammatic sketch of the structure of muscovite

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Figure 6. Diagrammatic sketch of the structure of smectites (expansive clays) and a list of some members of this group, presenting a concept of the various substitutions which can occur in the structure (Grim., loc. cit., pp. 79, 83).



○ Oxygen, ⊖ Hydroxyl, ● Aluminum, ○ Potassium
○ and ⊖ ions (one fourth replaced by aluminum)

Diagrammatic sketch of the structure of muscovite

Figure 7. Diagram of the mineral structure of three muscovite layers. Compare this diagram with that of Figure 6 and notice the difference in the location of the interlamellar ions. Muscovite is a non-expansive mineral. (Grim., loc. cit., pg. 93).

favor such bonds), with the energy of hydration being too weak to overcome the Van der Waals forces which unite the layers in the prototypes, but strong enough to separate the smectite layers.

However, the problem seems to be much more complex than these two ideas. In addition to the Van der Waals forces there is certainly an electrostatic attraction between the interlamellar cations and the surface of the charged particle. It appears that the type of mineral and the type of interlamellar cation can determine whether the swelling mechanism is due to hydration of the ion or hydration of the surface.

By referring to the diagram in Figure 7 and imagining each fourth Si^{4+} of the tetrahedral layers of prototype pyrophyllite replaced by Al^{3+} , we can see that a substantial excess of negative charge is developed. If, at the same time, many K^+ ions were present, it would be possible for the relatively large K^+ to adjust itself suitably within the hexagonal spaces between the oxygen atoms of the tetrahedral layers. Taking a position between the adjacent layers, the K^+ is coordinated with the 12 oxygens, and the layers are bound to one another by electrostatic forces. What we have is muscovite mica.

The three-layer illite clays seem to be derived from mica, but the mechanism or mechanisms are still not well understood. Generally the illites contain less K^+ than muscovite and have more Si^{4+} and less Al^{3+} . The non-expansive nature of illites or hydrated micas seems to be due to the great attraction of the silicate layers across K^+ , which remains in the oxygen hexagons of the tetrahedral layers. While K^+ , as an interlamellar ion in the montmorillonites, allows them to expand, this does not happen with the illites. However, in illite the K^+ content is 1.5 times greater than in montmorillonite; in addition the charge "deficits" are concentrated in the octahedral layers of the montmorillonite and must necessarily be weaker than the tetrahedral bonds in the mica clays.

Origin and Occurrence of Clays

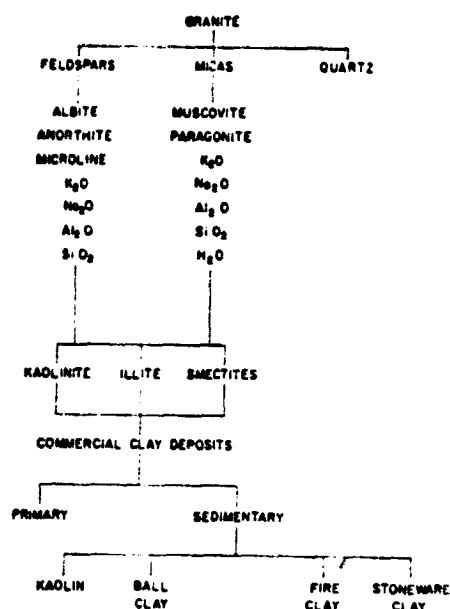
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The clay minerals can be naturally formed [8] by:

- (1) Diagenesis (or alteration) of feldspathic minerals, micas or other clays;
- (2) Genesis (or directly from solutions) under the following experimentally determined conditions:
 - (a) Acidic solutions, low temperatures and low pressures favor the formation of the kaolinite clays;
 - (b) At low temperatures and pressures, under alkaline conditions, muscovite mica or montmorillonite can be formed;
 - (c) When 0.2 to 0.4 moles of K^+ are available for one mole of Al_2O_3 , only mica will be formed;
 - (d) The presence of Mg^{2+} favors the formation of montmorillonite;
 - (3) When there is an abundance of Al_2O_3 and SiO_2 , and the temperature exceeds $350^\circ C$, pyrophyllite is formed, and, with an excess of Al_2O_3 boehmite forms;
 - (f) Under acidic conditions at high temperatures mica can be formed.

The size of the clay particles is limited by strains in the structure. When the clay is formed by alteration of mica, the structural strains in clay tend to break the particles into very small units.

Figure 8 shows granite as a source of materials from which the clay minerals can be formed by diagenesis of non-argillaceous minerals. Under special circumstances the geographic location can produce an attractive deposit as a source of raw material for ceramic purposes. The deposit can be residual and require the removal of non-argillaceous material by means of rinsing. Otherwise the clay may have been extracted by pluvial action and elutriated by vapor action, with the use of a sedimentary deposit not requiring



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Figure 8. An idealized diagram showing the minerals from which clays are formed.

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preliminary improvement to be used.

While commercial deposits of clay are not rare, really good clay-producing areas are limited to some relatively restricted regions of the United States, Great Britain and the continent of Europe. For the purposes of this discussion, I shall consider the clay-producing areas of Dorset, Devon and Cornwall in England and the southwestern United States as representatives of ball clay, and the methods by which it was formed.

Figure 9 shows the counties of Dorsetshire, Devonshire and Cornwall in southern England. Below the center of this area is a chain of granite which rises to the surface at some six or seven points. At five of these points the feldspathic rocks and the mica of the original granite have been modified, by hot solutions, into kaolinite which remains in the place of formation as a residual deposit of fine sheets of kaolinite mixed with quartz and muscovite mica, in addition to other lesser constituents. The clay and the various mica constituents are removed from the deposit by high-pressure water jets. The quartz and major mica fractions are removed in decanting basins. The clay and the fine mica, not cleansed of sandier material, are removed in mica washers, concentrated, filtered and dried.

in the past kaolin has been extracted from areas 1-6, but at the present time most of the English kaolin comes from the mass granite mines in St. Austell.

Some 10 to 15 million years ago pluvial activity removed the clay from the kaolinized granite from the granite mass of Dartmoor and transported it to a sedimentation zone in an estuary in the region, near what is now Poole Harbor in the country of Dorsetshire [10]. In the process of transportation the clay was freed of all impurities except for some finer particles of clay and mica; the clay from this area under study is normally devoid of sand and is extremely fine. The mineral structure is predominantly poorly crystallized kaolinite with 20 to 40% micaceous particles. In a probable earlier deposition, near Bovey Tracey in South Devon, this type of clay was mixed with organic material. The clay particles adsorbed colloids originating in the remains of plants and, after erosion, were redeposited in Dorsetshire, where the organic material remained adsorbed to the clay to produce the Dorset clays with a characteristic ashy-blue color.

Some six to eight million years ago the clay was again removed to the Dartmoor granite area, elutriated by vapor activity and deposited in the fresh water lakes in Devon in the south, near Bovey Tracy, and in Devon in the north at Torrington. During this period large amounts of organic material, consisting mainly of sequoia and cinnamon trees, were removed from the neighboring hills and carried by water to the lakes. As a result of the earlier modification of the material from these plants, the deposits of clay and adjacent areas were associated with thick layers of lignite. Most of the plastic clay (ball clay) from southern Devon is covered by lignite and thus the clay was modified into black plastic clay (dark ball clay). Except for the presence of about 2 to 10% of organic material, the clays from northern and southern Devon are made up of normal kaolinite elutriated and mixed with very fine mica inclusions.

1. LANDS END GRANITE
2. ST. GERMONE GRANITE
3. CARN MARSH GRANITE
4. ST. AUSTELL GRANITE
5. BODMIN MOOR GRANITE
6. DART MOOR GRANITE
7. SOUTH DEVON BALL
8. NORTH DEVON BALL
9. DORSET BALL

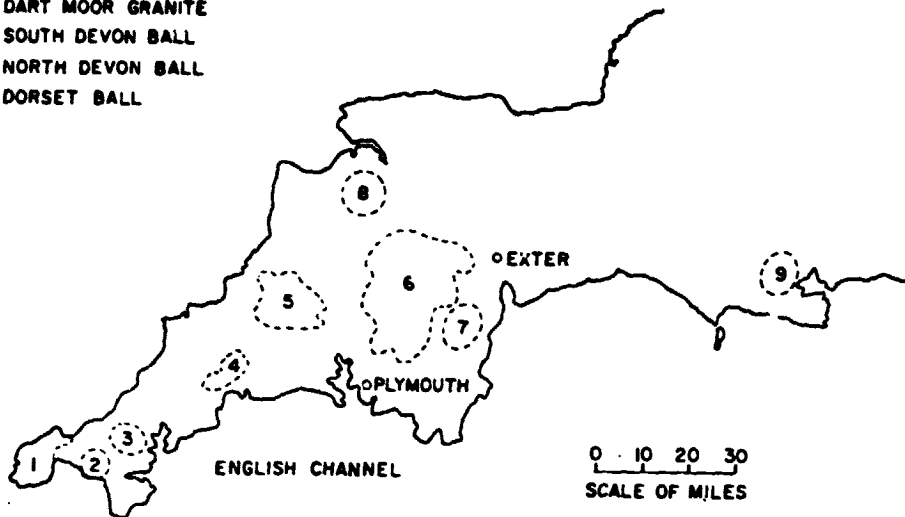


Figure 9. Contour map of the Cornwall peninsula and neighboring Devonshire and Dorsetshire in England, showing the location of the principal deposits of kaolin primarily derived from granite, and the locations of the Devon and Dorset "ball clays" derived from the Dartmoor granite by pluvial activity and deposited in sediment at points 7, 8 and 9.

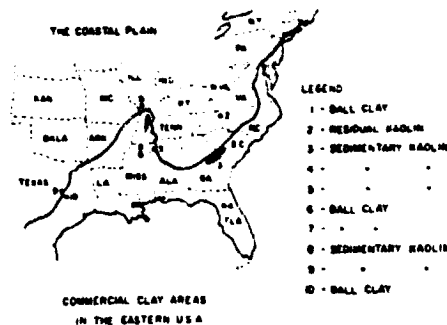


Figure 10. Contour map of the United States region showing the location of the principal commercial deposits of clay. Attention is directed to the general association of the deposits of sedimentary clay and of ball clay at the dividing line between the coastal plain and the adjacent piedmont.

Figure 10 shows the contour of the coastal plain which extends along the Atlantic Coast from New England to Florida and from the Gulf of Mexico coast as far as Texas. The map shows a large number of commercially explored deposits of plastic clay (ball clay) and of kaolin, and it can be seen that all of the deposits, with two exceptions, are found in or near the line dividing the coastal plain from the piedmont and the mountainous zones farther north. The location of these sedimentary deposits has special significance which we shall now consider.

The only residual deposit of kaolin, perhaps with a commercial value of some importance, in the United States is in the Great Smoky Mountains in western North Carolina [11]. These deposits are probably the result of the decomposition of a dike of pegmatite or of pegmatite granite, caused by temperature changes on the surface. The clay is extracted by means of successive washings, more or less like that performed with the English kaolins.

In a belt more or less 30 to 50 miles wide, extending from near Columbia, Carolina to the south near Macon, Georgia, and then running down the fault separating the coastal plain from the piedmont, we find many kaolin deposits. These deposits do not form a continuous chain, but appear as lenses with a size variation from several centimeters in thickness and several meters in length to enormous 15 meter beds and larger covering many acres [12].

Formerly it was thought that such deposits were formed by clay transporting a deposit of residual kaolin formed in the granite in the northeastern mountains or in the piedmont feldspar and mica below the mountains. It was thought that the clay was carried along by currents of water and deposited in fresh or salt water lagoons behind the elevated banks along the seacoast of the times. These ideas have recently been revised [13] and one hypothesis states that the clay in these deposits from Georgia and South Carolina were formed by modification of the mica and feldspathic sand in aquifer deposits a short distance inland.

The clay varies in quality from deposits of well-crystallized kaolinite with comparatively large particles to very poorly crystallized kaolin with very fine particles. It has been suggested that those deposits which were set down in fresh and acidic pools developed a typical face-edge structure [12] which is open and allows continuous water percolation; the effect of this is to remove the iron oxide and some silica, and probably to assist in the recrystallization of the clay in a more regular form of larger grains. These kinds of clay were deposited in the vicinity of salt water with high pH which caused face-to-face flocculation of the fine particles and formed a somewhat imperfect structure resisting percolation and permitting the clay to retain its original composition with excess iron and silica. It is a fact that the hardest and finest deposits have a higher iron and silica content, and are deposits much more poorly crystallized than large, clear particles.

Farther south, in northern and central Florida, there are very fine deposits of kaolinite appearing as a grainy cover surrounded by very pure silica. It was originally thought that this clay was residual, but now there is reason to believe that the clay was transported from farther north and deposited in the current layers of silica sand.

In location 5, northeastern Alabama, there are deposits of sedimentary kaolin similar to the deposits of the Georgia and South Carolina Fault, and probably formed in the same way. Location 8, in southern Illinois, has deposits of very hard and extremely fine kaolinite, very similar to those of Georgia. Location 9, in Texas, has a very fine kaolinite deposit mixed with pure silica sand resembling the Florida deposits.

A narrow emergence of tertiary layers appears along the border of the coastal plain in a very broad arc through the southern Mississippi Valley states. This arc delineates the structural basin

resulting from alluvium in Cretaceous and Tertiary times, allowing the Gulf of Mexico to advance northward to its present limits. This extension is called the Mississippi Bay. A large number of closed bays, swamps and lagoons developed around the edges of the bay. Clay deposits are found in these depressions. There is a particularly large concentration of clay deposits in the counties of Weakley, Henry and Carroll in northeastern Tennessee [15] and in the adjacent county of Calloway in southeastern Kentucky [16].

This forms the largest productive area of plastic clay for white ceramics (ball clay) in the United States.

The origin of the clay in these deposits has still not been definitely solved. Opinions [17] vary; they range from (a) disintegration of "chert" and limestone removal from the nearest rock to (b) clay from crystalline rocks of the southern Appalachian Mountains borne by an ancestor of the Tennessee River or (c) erosion of the redeposition of old sediments from the east and north.

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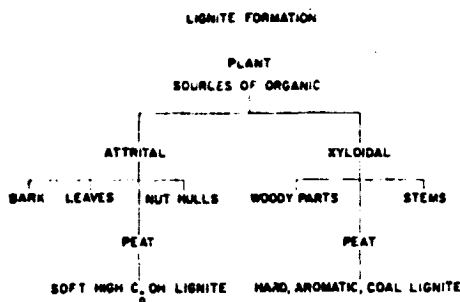


Figure 11. Diagram showing the dependence of the type of lignite on the sources of organic substances from which it is formed. Types of soft lignite and with a high carboxylic content are more susceptible to the activity of alkaline hydroxides and hydrolyzable alkaline salts in the formation of humus.

We can imagine the transportation of sediment from some place in the north or east, perhaps 15 million years ago, to be deposited in lagoons or marshes close to the margin of the bay under semi-tropical conditions. A considerable length of time must have passed

because there are two geological formations in the deposits. As is the case with the English deposits of South Devon, many of the Tennessee and Kentucky deposits contain significant colloidal deposits of organic material derived from lignite formed from tree trunks washed down to the lakes and marshes, and later transformed into deposits of plastic clay for white ceramics (ball clay).

The term "lignite" refers to a stage in the geochemical progression from turf to coal. Petrographically lignites can be classified [18] (see Figure 11) as either (a) attrital or (b) xyloidal, depending on whether the vegetation is "attritus" (foliage, bark, nut shells, cork, pollen, etc.) or pieces of wood (xyloidal). The low oxygen content in attrital material contributed to a slower formation of aromatic compounds, so that attrital lignite is normally less "carboniferous", and less reactive to alkalis than is xyloidal lignite or lignite of a similar age. A line drawn from northwest to southeast through the boundaries of the counties of Weakley and Henry in Tennessee divides the clays remaining in the younger Grenada formation from those of older Holly Springs in the north; in addition the attrital lignite in the deposits of Holly Springs, Tennessee and southeastern Kentucky are much "softer" and more soluble in alkalis than are the younger and more carboniferous xyloidal lignites from the Grenada deposits in Weakley County.

The colloidal humic acid coming from the ground and from different sources of lignite is spherical particles [19] or ellipsoidal particles [20] capable of forming layers of groups of phenolic or carboxylic hydroxyls by means of hydrogen bonds. The colloidal humus in the plastic clay (ball clay) is concentrated in the finest fraction of the clay [21], to which it is connected [22] by hydrogen bonds and/or lateral electrostatic attraction.

The ionization of the two mentioned functional groups of absorbed organic material depends on the nature of the group [23]. The phenolic hydroxyl in the aromatic rings requires a higher pH

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	ENGLISH CHINA	GA SED BALL	TEMP BALL	KENTUCKY BALL	DEVON BALL	DORSET BALL
PARTICLE - SIZE						
% 44 μ	99.9	98.6	98.1	97.9	96.3	96.8
20	99.7	92.3	93.3	93.4	95.5	96.9
10	87.5	80.2	88.2	92.6	92.2	97.3
5	85.5	66.0	82.5	86.5	86.8	94.1
2	42.5	47.0	74.0	72.0	77.0	87.0
1 μ	30.0	32.0	64.0	60.1	65.5	78.0
0.5	15.0	14.8	49.0	43.4	48.0	65.5
0.2	3.8	2.7	23.5	27.0	30.0	40.0
CHEMICAL ANALYSIS						
% SiO ₂	46.76	45.24	55.03	49.11	45.54	50.98
Al ₂ O ₃	37.93	38.39	28.18	30.62	34.84	32.87
Fe ₂ O ₃	0.69	0.28	0.67	1.06	0.91	0.94
TiO ₂	0.07	1.35	1.73	1.73	0.88	1.25
CaO	0.08	0.16	0.32	0.20	0.46	0.48
MgO	0.15	0.18	0.34	0.60	0.36	0.60
H ₂ O	1.42	0.06	0.68	0.37	1.82	3.00
Na ₂ O	0.06	0.14	0.33	0.43	0.14	0.24
Zn	12.73	13.82	12.69	15.59	15.80	9.16
DYE INDEX mgg/100gm	2.4	2.1	8.7	8.3	8.9	12.5

Figure 12. Basic physical and chemical data for typical English and American ceramic clays. The greatest firing losses in the Devon and Kentucky clays are caused by the presence of substantial quantities of adsorbed organic material. The low firing loss of Dorset ball clay is due to the presence of very fine muscovite mica.

for ionization than a carboxylic group with an aliphatic peripheral chain. It has been confirmed that, as the source of the colloidal humic acid of plastic clay (ball clay) proceeds from the turf stage to the sub-bituminous coal stage, the aromatic fraction of the humic material increases at the cost of the aliphatic fractions [24].

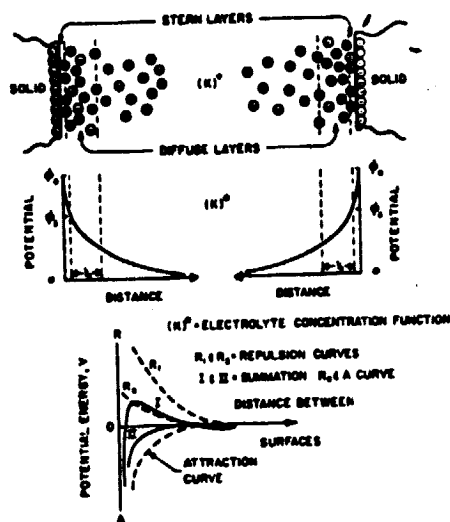
A plastic clay (ball clay) is resultantly an elutriated clay consisting mainly of kaolinite mineral [25] in different degrees of order or disorder, associated with small amounts of montmorillonite and/or micaceous material to which various humic colloidal contents, originating in lignitic plant residue, have been adsorbed. The plastic clay (ball clay) can be diluted by the presence of very fine free quartz and contents ranging from 1% to 30% or more.

The presence in the plastic clay of pyritic material and of lignite containing sulfur provides a source of soluble sulfates which,

through exposure to the oxidizing air, tends to increase during storage under humic conditions.

Figure 12 compares a typical English kaolin with a typical large-particle sedimentary kaolin from Georgia. However, it should be pointed out that there are sedimentary clays in Georgia which are much finer and less pure than those shown in Figure 12. In the same way some English kaolins are not as fine, and others contain more mica (indicated by the very high K_2O content). The highest dye index value of the Dorset plastic clay (ball clay) is a result of its extraordinary fineness. Dorset clay reveals relatively small fire losses. The presence of about 30% mica is responsible for this value (muscovite has a fire loss of 4.6%, while kaolin's is 14.0%). The high fire loss of Devon clay is due to the presence of a large amount of adsorbed lignite. Both the plastic clay (ball clay) from Tennessee and from Kentucky contains substantial amounts of free quartz, as is well noted in analyses. The low K_2O content of the two clays can be observed well, as can the high organic material content of the plastic clay (ball clay) from Kentucky.

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THE DIFFUSE DOUBLE-LAYER AND ATTRACTION-REPLICATION

Figure 13. Diagram showing the essence of DLVO from the theory of interaction of the double diffuse layers shifting the forces of attraction between the colloidal particles and preventing or retarding coagulation. (Redrawn from Shaw, loc. cit., pp. 117-152).

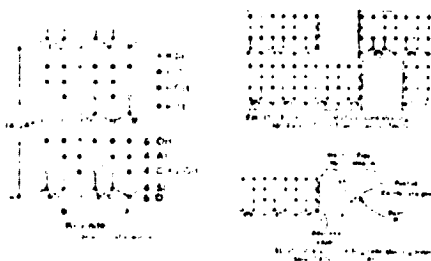
Modern Theories of Clay Deflocculation

All of the modern theories on clay deflocculation are definitively based on the double diffuse layer proposed by Gouy [27] and Chapman [28], and modified by Stern [29] and Grahame [30]. The clay minerals are lyophobic [31] and the stability of colloidal clay suspensions can be faced in terms of the theory of complete interaction and of attraction-repulsion of the double layer proposed initially by Derjaguin and Landau [32] and, later, by Verwey and Overbeck [33]. This theory is illustrated in the diagrams of Figure 13.

The clay minerals are negatively charged when they are dispersed in water, and are susceptible to flocculation when the total ionic solution concentration (the Greek letter k indicates the effect of the valence and concentration of ions of the total solution) or the valence of these ions, or both, exceeds any critical point [34]. The slower the reduction in potential with the particle surface distance, the greater will be the force of repulsion between the particles. The attraction curve proceeds from the Van der Waals forces of attraction and diminishes exponentially. Roman numeral I of the summary curve between the curve of repulsion R_1^- and the inherent curve of attraction would show an attraction peak which must be overcome by the kinetic energy of the approaching particles if coagulation is to occur. The Brownian movement is responsible for this kinetic energy. Summary curve II does not have a peak, and coagulation must occur since the particles fall into the attraction force zone. For a given double layer thickness (conventionally expressed as $1/k$), the more concentrated the suspension and the finer the particles, the greater will be the opportunity for the particles to cross the energy barrier and form aggregates.

In 1941 Johnson and Norton [35] proposed a mechanism for the deflocculation of kaolinite, suggesting that the negative charge of the kaolinite particles was due to the hydroxyl ions adsorbed onto unsaturated positive valences (see Figure 14) at the edges of the clay particles and to the hydroxyl ions adsorbed onto the basic

surfaces by hydrogen bonds. The argument for this is that the OH^- fits into the structure agreeing with Fajans Hans' rule, postulating preferential adsorption of the ions best included in the structure. The lower valence ions of the alkali group with pH 7 or above are necessary to deflocculate natural clays, considered as occurring when polyvalent cations were displaced by monovalent cations and precipitated as a more or less insoluble salt. The relative efficiency of the different sodium deflocculants was explained by the solubility of a respective polyvalent cation salt produced in an exchange product, the greater the deflocculant effectiveness.



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Figure 14. Evolution of the kaolinite surface charge in agreement with the theory proposed by Johnson and Norton. (See reference [35] quoted in this article).

Schofield and Samson [36] criticized the pH 7.0 and the other requirements for deflocculation proposed by Johnson and Norton [35]. They demonstrated that kaolinite could be deflocculated with various poly-electrolytes, organic and inorganic, at pH below 7, and proposed that kaolinite be considered as having an inherent negative charge due to the absence of about 1 cation per 400 in the structure. In addition, under low pH conditions (see Figure 5), the anions exposed at the sides of the kaolinite structure would absorb protons and become positively charged. These positively charged sides would be able to attract the basic negatively charged surfaces, so that flocculation of the face-edge type could take place. With poly-electrolytes present in a low pH, they could be adsorbed by the positive side, and thus make the particle totally negative and cause

deflocculation. Okuda and Williamson [37] demonstrated face-edge flocculation of kaolinite, Cashen [38] experimentally tested Schofield-Samson's theory, and Phelps [39] demonstrated low pH deflocculation by using various polyanions.

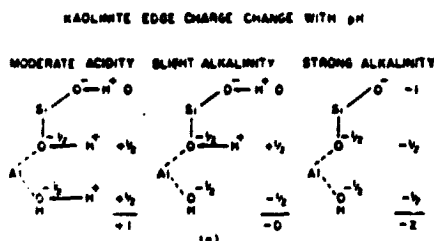


Figure 15. Diagram illustrating the theory of Schofield and Samson relating to the nature of the edge charge of the kaolinite sheets. (See [36] quoted in this article).

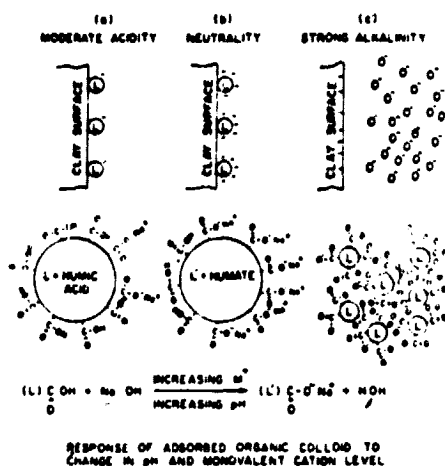


Figure 16. Diagram of the idea according to which adsorbed colloidal humic acid is first charged with increased contents of alkali and pH, and then dislodged from clay as electrically charged kinetic units.

Phelps [39] showed that where polyanions are adsorbed onto kaolinite, the increase in pH above 7 dislodges such polyanions and transfers them in suspension as units free of a kinetic charge. Figure 16 details a concept according to which the organic colloid

derived from lignite is adsorbed onto the clay particles by hydrogen bonds and/or edge adsorption. In the absence of monovalent alkaline cations and with low pH, the functional groups of the adsorbed layer are very slightly ionized. Increasing the pH and having monovalent alkaline cations available, some of the exposed groups are ionized and the clay particles with their adsorbed layers develop a negative surface charge and a double layer. With a subsequent increase in pH and alkaline cations, some of the adsorbed layers are dislodged and disperse as negatively charged free colloids. At even higher pH, the adsorbed material is completely dislodged and disperses as an organic salt. The clay particles develop a negative edge charge at the same time and thus deflocculate completely.

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The organic colloid dispersion can be reduced by the presence of divalent alkaline earth cations which form salts with the functional groups slightly ionized at higher pH. Polyvalent anions, such as SO_4^{2-} , reduce the organic colloid dispersion.

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