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The Relation between Composition and Swelling in Clays

by

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FEB 8 1955

INTRODUCTION

The phenomenon of swelling is associated with the hydration of clays; however, all clays do not swell when hydrated. Those of the kaolin group, for example, exhibit little or no swelling on hydration. Sodium montmorillonite, on the other hand, characteristically swells in water to many times its dry volume. Calcium and magnesium montmorillonite and the hydrous micas, or so called illites, fall between these two extremes in swelling properties, but are, in general, much closer to kaolinite than to sodium montmorillonite in their increase in volume on hydration. These differences in the swelling characteristics of different clays may be related to their chemical composition, to the kind and degree of isomorphous replacements in their structure, and to the amount and nature of their associated exchangeable cations.

MECHANISM OF HYDRATION AND SWELLING

Marshall (1949) regards swelling as an osmotic property of the clays, which

"may be effected in two ways—by the interposition of solvent molecules between particles, or between the lattice units which comprise the particles themselves. In the kaolinite and mica-like clays, only the former process would operate. This, however, does not lead to extensive swelling, at least not for kaolinite, while no measurements are available for the illites. With the montmorillonite and beidellite clays swelling is a very prominent property, but the experimental data do not enable one completely to separate the interparticle effects from those occurring internally. In extreme cases, indeed, the distinction between them disappears. A montmorillonite might swell in a polar liquid until it eventually dispersed into plates of unit molecular thickness. All the surface could then be regarded as external."

The water taken up by kaolinite consists largely of water entering and filling the pore spaces between the particles. The particles are not broken down into their constituent units and the structure does not expand with increasing water content.

The hydration of sodium montmorillonite is considerably more complicated. Mering's observations (1946) on adsorption show that various levels of organization exist in montmorillonite: (a) primary particles consisting of stacks of parallel elementary sheets with an average of about 10 sheets per particle, (b) stable microaggregates formed by the association of several primary particles which are nearly parallel and joined together laterally, and (c) aggregates comprising a large number of primary particles and microaggregates. Mering has shown (figure 1) that the hydration of sodium montmorillonite passes through three successive stages as follows:

"Stage I - No swelling is produced in spite of the adsorption of 0.40 gram of water (per gram of dry material). X-ray diagrams, however, indicate that the volume of the primary particles has increased by 70 percent. Two points should be noted: (1) the apparent density of the dry aggregate was about 0.4 of the theoretical density of the dry material, that is, the texture of the aggregate has about 60 percent of empty spaces, which permits the fixation of 0.55 gram of water without any variation in the volume of the whole, and (2) the texture of the aggregates must be such that the voids adsorb the increase in volume resulting from the increase of spacings between the silicate sheets. This adsorption of the internal swelling is only possible if the primary particles are connected laterally, with no contact between their (001) faces.

"Stage II is manifested by the beginning of the plasticising and swelling of the film, (a) the increase of the spacing between the silicate sheets is relatively small and not in proportion to the swelling observed; (b) the amount of water outside the primary particles becomes larger and finally predominates. The swelling of the aggregate must therefore be ascribed to the increase in the spaces between the sheets of particles. It appears that as soon as the original spaces are filled, the water dissociates the few connections between neighboring particle sheets and forces the latter further apart; it is this which must be responsible for the plasticising of the aggregate.

"Stage III is not characterized at the onset by any peculiarity of behavior in apparent swelling. On the X-ray diagrams it is marked by progressive fading of the (001) reflections, which finally disappear altogether. The following facts show that this phenomenon is not to be interpreted in terms of a large increase of the spacing between the elementary silicate sheets: (a) while the intensity of the (001) interferences diminishes, the apparent spacing remains fixed at 20A., indicating some disorder in the primary particles rather than their expansion. This disorder in the highly swollen state may be either lack of parallelism of the layers or non-uniformity of the interlayer spacings. (b) It seems legitimate to extrapolate from the above interpretation of Stage II and to assume that the water outside the particles forms an increasingly preponderant part of the total water. (c) The aggregate can be heated with care until it reaches a state equivalent to a relative humidity of 92 percent or a little more than 0.4 gram of water per gram of material. By this treatment plasticising and swelling are prevented while the hydration and adsorption surfaces remain intact. In a relative humidity of less than 90 percent there is no distinction between the diffraction diagrams of the aggregate when so treated and the original aggregate. If placed in water, the treated aggregate produces intense (001) reflections and shows an average spacing of 20A. This indicates that swelling can be prevented by the formation of a relatively small number of indissoluble connecting links between the sheets of particles, the particles themselves retaining their freedom of expansion, thus it appears that swelling and plasticising are due to the formation of large spaces between the particles rather than to increasing separation of the elementary silicate sheets. For particles containing an average of 10 silicate sheets the mean interparticle distance at the limit of swelling is of the order of 2000 A."

Mering found that for calcium montmorillonite only Stage I exists. The change takes place first at the surface of the particles, allowing a distinction to be made between water of hydration, that is, water fixed between the elementary sheets and the water of adsorption, or water fixed between the particles. Mering concludes that the presence of calcium ions is sufficient to prevent complete dissociation of the connecting links between the sheets of particles. The fundamental spacing d reaches about 20A in water and the (001) reflections are intense. The apparent density of the films is the same as for sodium montmorillonite.

Baver and Winterkorn (1935) also found that the sorption of water by sodium saturated bentonite, as well as by lithium and potassium saturated bentonite, is a more complex phenomenon than that by barium-calcium and hydrogen saturated bentonites. Sorption of water by the latter systems is apparently about 70 percent complete at the end of 10 minutes whereas sorption by the alkali clays is less than 10 percent complete in 10 minutes and there is continued sorption after 4 days (figure 2). At the end of the period of test the alkali bentonites had swollen to a volume 8.5 to 11 times their original volume compared to a swelling of 2.5 times for the barium and calcium bentonites and of 2.2 times for the hydrogen bentonite. In the early stages of hydration, however, the alkaline earth bentonites take up more water than the alkali bentonites.

Relative Humidity (R. H.)	Total Absorption in g. of Water per g. of Dry Substance.	Average Spacing (d) in Å.	Hydration Water (Average Number of Layers).	Water on the Exterior of the Primary Particles in g. of Dry Substance.	Apparent Swelling.
I. { 0 90%	0 0.40	9.6 Å. 16.2 Å.	0 2.2	? 0.18	No swelling ↓ Beginning of swelling and plastification
II. { 96% 99%	0.60 1.00	18.5 Å. 19.5 Å.	3 3.3	0.30 0.80	About 30% swelling ↓ About 100% swelling
III. Absorption in contact with water	About 5	The apparent spacing remains fixed at 19.5-20 Å. but the (ool) reflections gradually vanish Complete disappearance of (ool) reflections			Swelling increases to about 20 times the original thickness

Figure 1. Stages in the hydration of sodium montmorillonite. (From Mering, 1946).

TABLE 3
Rate of cation uptake by bentonite saturated with various cations

WATER INTAKE (GRAMS PER 100 G.)

Time	Li	Na	K	Et	Ca	H
10	0.820	0.920	1.525	2.895		2.645
20	1.190	1.310		2.975	2.985	2.780
30				3.015	3.025	2.765
60	1.910	2.090	2.625	3.085		2.890
120	2.640	2.860	3.315		3.215	
1440	7.140	7.695	7.145	3.475		3.210
1420	11.170	11.290	9.055	3.880	3.920	3.570
5760	12.125	12.290	9.755	3.960	4.000	3.650
Ion spacing, 2m	1.540	1.290	1.200	1.260	1.500	1.170
Swelling, 2m	10.775	11.050	8.555	2.500	2.500	2.200

Figure 2. (From Bayer and Wintarkorn, 1935).

Hendricks, Nelson, and Alexander (1940), in their study of the hydration mechanism of montmorillonite saturated with various cations, obtained results which indicate that the first step in water sorption by the magnesium and alkaline earth salts is hydration of the cation with six molecules of water which is followed by completion of a water layer having a hexagonal type structure. A second water layer is taken up at high relative humidities. Similar results were obtained for the lithium salt except that only three molecules of water were required for hydration of the lithium ion. In the sodium, potassium, and cesium salts the cation is apparently not hydrated. Thus the greater uptake of water by the alkaline earth montmorillonites in the early stages of hydration is at least partially accounted for by the hydration of these cations.

THE CAUSE OF HYDRATION AND SWELLING

Wiegner (1931) and others considered that the adsorbed cations are hydrated and that a union of the solvation hulls forms the water envelope around the clay-mineral particles; also the thickness and other characteristics of the water film are a direct consequence of the hydration of the adsorbed cations present. According to this concept the greater swelling of sodium montmorillonite as compared with calcium montmorillonite is due to the greater hydration of the sodium ion. However, there was considerable divergence in the values given by different investigators for the size of the hydrated cations and for the hydration in molecules of water per ion—the measurements did not even provide strong evidence that the cations are actually hydrated. Indeed, Bernal and Fowler (1933) presented data that threw doubt on the hydration of some

cations. As has already been mentioned, Hendricks, Nelson, and Alexander (1940) later showed strong evidence that (a) the sodium ion, assumed to be most highly hydrated, is not hydrated at all and (b) magnesium and the alkaline earth cations have six molecules of water of hydration. Houwink (1937) considered that the thickness of the water film (10^2 to 10^3 \AA) was too great to be accounted for by hydration of adsorbed cations. Spiel (1940) concluded that solvation of the adsorbed cations could not fully explain the presence of the water films. Grim (1942) also concluded that the concept of cation hydration being responsible for the thickness and other characteristics of the water film was not justified and that some other cause for the development of the water film must be sought.

As data from investigations of the relation of exchangeable bases to plastic properties indicate that the character of the adsorbed cation does in some way affect the thickness of the water Grim (1942) concluded that it seems

"likely that the effect is produced by a binding action of the cations. That is to say, the cations act as bridges to bind the clay-mineral sheets together. The action is analogous to the effect of potassium in holding together the unit cells of muscovite in the direction of the c-axis. This idea does not preclude a slight hydration of certain ions, but it postulates the adsorbed cations as controlling the thickness of the film water primarily by means of the force with which they hold the sheets together."

Grim continues

"In applying this idea to montmorillonite it follows that the thickness of the water film is the result of two opposing forces: (a) the tendency of layers of water to develop on the basal planes,; and (b) the tendency of the adsorbed cation to hold the sheets together. The resulting thickness of the film is chiefly dependent on the cation."

"It is a well-known fact that Na-montmorillonite expands greatly in the presence of abundant water, whereas under similar conditions Ca-montmorillonite expands very little. According to this concept, the great swelling of Na-montmorillonite is due not to the hydration of the Na⁺ serving as a wedge to force the layers apart but to the absence of a strong bridge because of the univalent character of Na⁺ and perhaps also because of its small size enabling it to fit well in the hole of the silica sheet. The Ca-montmorillonite does not expand greatly because of the slight hydration of Ca⁺⁺ but because the divalent ion holds the layers together so that a thick series of water sheets cannot form between them."

According to Bayer and Winterkorn (1935) there are apparently two ways in which water can be associated with colloidal particles, not taking into consideration mechanically occluded water. Water molecules may be oriented at the surface as a result of the electrical properties of both the liquid and the surface. Water may also be adsorbed because of osmotic effects. The first process is associated with the release of an appreciable amount of heat and is termed by them simply "hydration." The osmotic type of hydration does not take place with the liberation of measurable quantities of heat. Mattson (1932) has shown that the osmotic type of hydration is found in highly hydrated aluminosilicates such as bentonites. In the osmotic type of hydration the hydrated ions surround the hydrated surface in a diffuse layer. These ions remain within a distance from the surface in which the mean osmotic force^{is} in equilibrium with the mean electrical attraction due to the different charges of the colloidal surface and the exchangeable ions. The apparent volume of the colloidal particle is then defined by the extent of the ionic atmosphere. The free water in which the cations are dispersed is naturally an integral part of the apparent volume of the swollen particle; and as the diffuseness of the double layer is a function of the osmotic pressure of the cations this type of swelling has been termed osmotic. The diffuseness of the ionic atmosphere is also a function of the electrical structure of the colloid surface.

The high swelling of bentonites in comparison with other clays strongly suggested to Bayer and Winterkorn that the former attract large amounts of water as a result of forces associated with the inner layer of the colloidal surface. In colloid chemical terms the nature of the inner layer and its effect on adsorption of ions and water molecules determines to a great extent the character and amount of hydration in aqueous clay systems. The kind of ion adsorbed on the surface plays an important role in simple hydration as well as in the osmotic type of hydration.

A number of other theories have been proposed to explain the development of water films and the great swelling of sodium montmorillonite, but none seem so satisfactory as the concept of cation dissociation.

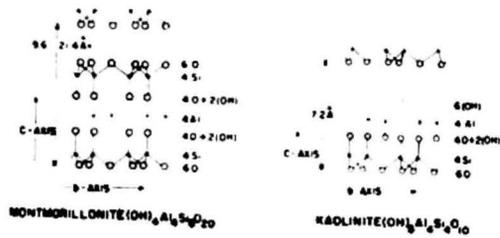
CLAYS AS COLLOIDAL ELECTROLYTES

Hartley (1935) differentiated charged colloids into two classes: those of which (1) the bulk of the particle is made up of insoluble material in regard to which there is no equilibrium and whose charge is due chiefly to preferential adsorption of foreign ions and (2) the particle is made up of a definite ionizing compound with regard to which there is true equilibrium and whose charge is due to ionization of this compound. The term "colloidal electrolytes" may be applied to this second class. From structural considerations Marshall and Krinbill (1942) concluded that the clays of the montmorillonite group may be placed in the second class and may be looked upon as colloidal electrolytes.

The montmorillonite group of clay minerals have the fundamental structural pattern of the micas,--two silica sheets bound together by an alumina sheet (figure 3). Isomorphous replacements of trivalent alumina for quadrivalent silicon in the silica sheet or of magnesium or some other bivalent or univalent ion for trivalent aluminum in the alumina sheet give rise to net residual charges on the structure, which are neutralized by cations held electrostatically. Thus the clays of the montmorillonite group fit Hartley's definition of colloidal electrolytes. When such a clay is dispersed in water each unit can come to equilibrium with the outer solution--the adsorbed cations tend to dissociate and the clay unit can be pictured as a complex anion. The suspended clay particle may be likened to a dissociated electrolyte, the size of one of its ions falling within the colloidal range of dimensions.

Dissociation of the associated cations leaves some of the structural units negatively charged. Thus charged, the units tend to repel each other, and the montmorillonite appears to swell. The more complete the dissociation and the greater the number of units carrying a charge, the greater is the swelling; the less complete the dissociation, the fewer are the units carrying a charge and the less is the swelling. The dissociated cations may be regarded as constituting the Gouy diffuse double layer.

The hydrous mica group--by some called illites - like the montmorillonites - has the fundamental structural pattern of the micas. They differ from montmorillonites in having a higher degree of isomorphous replacement in the structural sheets - although usually less than the micas - and consequently greater charges on the structural units. However, these



SCHEMATIC REPRESENTATION OF CRYSTAL STRUCTURE OF MONTMORILLONITE AND KAOLINITE

Figure 3.

Fraction active for sodium and calcium over successive ranges of neutralization of the acid clay with base*

CLAY	CONCENTRATION	NEUTRALIZATION CAPACITY BY INFUSION in a 100 gm	SODIUM		CALCIUM	
			Neutralization	Fraction Active	Neutralization	Fraction Active
Putnam < 200 m μ (beidellite)	7% (Na) 9% (Ca)	70	0-14	0.121		
			14-29	0.076	0-29	.006
			29-43	0.125	29-43	.003
			43-57	0.139	43-57	.003
			57-71	0.124	57-71	.006
			71-79	0.240	71-86	.022
			79-86	0.084	86-100	.029
86-93	0.189					
93-100	0.514					
Bentonite < 200 m μ (montmorillonite)	2.8% (Na) 3.0% (Ca)	100	0-15	0.412	0-20	.031
			15-35	0.142	20-70	<.001
			35-55	0.284	70-80	.006
			55-70	0.298	80-90	.019
			70-80	0.097	90-100	.066
			80-85	0.114		
85-100	1.20					
Kaolinite < 2 μ	10%	3.0	0-33	0.50	0-39	.043
			33-50	0.10	39-59	.049
			50-67	0.32	59-79	.156
			67-83	0.18	79-99	.195
			83-100	0.67		

* Calculated from data by C. A. Krinbill, A. D. Ayers, and C. E. Marshall

Figure 4. (From Marshall, 1948).

charges are to a large extent neutralized by potassium, which is fixed and is not exchangeable—nor does it dissociate when the particle is dispersed in water. On the outside of the particles cations, such as sodium, calcium, or magnesium, balancing the remainder of the charge, are presumably exchangeable. But as the units making up the particle are so firmly held together by the fixed potassium, exchangeable cations in the interior of a particle are inaccessible. Thus although the clays of this group possess theoretically considerable exchangeable cation capacity - some have almost as high a number of exchangeable cations as some montmorillonites - they cannot be classed as colloidal electrolytes, as the number of ionizable or exchangeable cations available is a function of particle size. Qualitatively, however, they should resemble the calcium salts of the montmorillonite group in their electrochemical behavior.

In the kaolin group the unit structure consists of a silica sheet and an alumina sheet bound together. Dickite, nacrite, and kaolinite are believed to represent merely different geometrical modifications in the relative positions of the sheets. Replacements do not generally take place in the kaolinite structure, and other variations, such as Al^{+3} vacancies in the alumina layer, appear to be balanced by O-OH changes, so that no excess or deficiency of charge develops on the structure. The outer surfaces of colloidal crystals of these minerals will consist of silica or alumina sheets with broken edges and it is to the broken bonds on these edges that the small cation exchange capacity of the kaolin group minerals is attributed. The electrochemical behavior of these minerals will, therefore, depend on the surface properties of silica and alumina sheets and on unsatisfied bonds

at the broken edges. Such material would not fall within the scope of Hartley's definition of a colloidal electrolyte; there is no stoichiometric relationship between the chemical composition of the mineral and the number of ionizable groups, as the number of cations available for ionizations varies with particle size. The cation-exchange capacity - due only to broken bonds on the edges of the particles - is usually less than 15 milliequivalents per 100 grams. Because of the small number of ionizable cations, and their situation, at the flake edges and not between the sheets, the dissociation of the cations does not pry the clay particles apart into their constituent units and there is no expansion on dispersion in water.

The electrochemical study of clays really began with Bradfield's (1923) potentiometric and conductometric titrations of clay acids prepared by electro dialysis. Broadly, the titration curves of electro dialyzed beidellite and montmorillonite were found to be similar to those of ordinary soluble weak acids like acetic. Marshall (1948) points out that titration curves of clay acids are, however, in some respects quite different from those of soluble weak acids at the extreme acid and the alkaline end of the range. At the acid end it is also evident that ionized aluminum is present; and in extremely alkaline solutions soluble silicates are formed. Yet even though the soil constituents might show complex properties as acids, there seemed, by analogy with the behavior of soluble acids and salts, no reason to expect wide differences in bonding energy for single metallic ions. Exchange reactions between soil constituents and salt solutions were therefore formulated as though all reactants were completely ionized.

EXTENT OF IONIZATION

Some investigators, Mattson (1929), Baver (1929), and others, however, obtained good evidence that the "clay salts" were not completely ionized. Direct measurements of the degree of ionization of the cations most commonly present in clays - calcium, magnesium, sodium, and potassium - were lacking until Marshall and associates began their work on the ionization of soil colloids. The great difficulty in making such measurements was that these cations are all so electropositive that metallic electrodes were not adapted to the measurement of the small ionic activities to be expected in soil colloids.

Marshall and Gupta (1933) first investigated cations for which electrodes were available--such as silver and thallium. Serious limitations in their use were encountered, although in the case of silver it was clearly evident that only a small fraction of the exchange ions were ionized. Marshall then undertook the development of membrane electrodes. He and his associates have succeeded in developing such membranes of preheated clay films with which they have determined the ionization of the single cations - potassium, ammonium, sodium, calcium, and magnesium - in the concentration range where they naturally fall in soil systems or in colloidal suspensions of soil constituents. Also fairly complete studies of four important clay types - montmorillonite, beidellite, hydrous mica, and kaolinite - have been made with potassium, ammonium, sodium, and calcium. In the case of sodium the conclusions have been checked by conductivity measurements.

The numerical differences in the active fraction which arise over the course of titration of Putnam clay (mineralogically a beidellite), Wyoming bentonite (mineralogically a montmorillonite) and kaolinite with NaOH and $\text{Ca}(\text{OH})_2$ is shown in figure 4. These data are taken from Marshall (1948) and represent tabulation of the values calculated from different parts of the titration curves. For sodium on Putnam clay the values for the active fraction range from 0.08 to 0.50, for calcium from 0.003 to 0.03. On bentonite the range is even wider, for sodium from 0.007 to 1.20, and for calcium from less than 0.001 to 0.066. On kaolinite the range is from 0.10 to 0.67 for sodium and from 0.043 to 0.195 for calcium. These figures show that there are great qualitative differences between fractions active for sodium and calcium in the Putnam clay and in the bentonite, but that there are no such wide qualitative differences between sodium and calcium in the kaolinite.

In the montmorillonite and beidellite clays the fraction that is active varies abruptly for sodium and for calcium at different stages of neutralization. Sodium shows a narrow zone and calcium a broad zone of very low activity. Kaolinite shows a fairly steady rise in fraction active for both cations as the amount of base is increased.

These differences in active fraction reflect large differences in differential heat of adsorption of the cation in different regions of the titration curves. Exchange ions of a given kind are thus held with a wide range of bonding energies. Marshall points out that

"...kaolinite can be compared qualitatively with a weak acid having a series of dissociation constants of diminishing magnitude (Pauli's concept of colloidal acids in general). Its behavior approaches that of a soluble weak acid in several respects. The salts, both of Na and Ca, are much more highly ionized than for montmorillonite, beidellite, and illite, and they differ less from each other. When pH curves are drawn for the titration of different concentrations of kaolinite with sodium hydroxide they lie close together, being nearer in character to those of soluble acids, whereas the montmorillonite clays give widely spaced curves reminiscent of strong acids."

The results of these studies show that the exchange cations of kaolinite are more extensively ionized than those of the montmorillonite clays—except in bentonite near the point of neutralization. But because of the very low exchangeable cation capacity of kaolinite and because the cations are not located between the sheets, but at the broken edges where they are not effective in prying the units apart, this greater ionization does not lead to any great amount of swelling.

Between the sodium and calcium bentonite near the point of neutrality (90 to 100 percent) there is almost a 20-fold difference in degree of ionization—1.20 fraction active for sodium as against 0.066 fraction active for calcium. As most of these ions are between the unit sheets, this great difference in ionization is fully capable of accounting for the great difference in the swelling of sodium and calcium montmorillonite.

EFFECT OF IONIC SUBSTITUTION ON THE SWELLING OF MONTMORILLONITES

Most studies on the swelling of montmorillonite have been on the effect of the exchangeable cation, although Kelley (1943) observed that the swelling of sodium saturated montmorillonites from different sources is not always proportional to cation exchange capacity and that, on the

other hand, those having approximately equal cation-exchange capacity may swell very differently. Grim (1935) pointed out some years ago, that the physical properties of clays may be ascribed to two factors-- the character of the exchangeable cation and the composition of the clay mineral. By composition Grim referred to the makeup of the clay mineral, particularly with regard to substitution within the structure.

Specifically, Grim stated

"Two montmorillonites, identical except for differences in Mg replacements for Al in gibbsite positions, may be expected to impart different physical properties to clays containing them. In other words the physical properties depend not only on the presence of montmorillonite, but on the composition of the particular montmorillonite."

Differences in the physical properties of two montmorillonites identical in composition except for differences in Mg replacements for Al in gibbsite positions might be attributed to differences in cation exchange capacity except for Kelley's observation that sodium-saturated montmorillonites having approximately equal cation exchange capacity may swell quite differently.

The difference in swelling between a montmorillonite and a beidellite (an aluminian montmorillonite) of equal exchange capacity has been attributed by Marshall (1936) to the fact that in one the seat of the charge is in the middle or alumina layer and in the other it is in the outer silica layers. An excess negative charge originating in the outer silica layers is presumed to be strong enough to hold the units closely together and to prevent the entrance of water and expansion. An excess negative charge originating in the middle alumina layer is, on the other hand, generally thought to have the strength to hold exchangeable cations but not the strength necessary to hold the units closely together and prevent expansion and the entrance of water.

Interpreted by the concept of ionization, the cations associated with a charged alumina layer are presumed to be more easily dissociated than the cations associated with a charge originating in the silica layers, as they are physically separated from the seat of the charge by the silica layers and are consequently less strongly held. The degree of dissociation of a montmorillonite and consequently the swelling would, therefore, be expected to be greater than that of a beidellite having the same charge.

On the presumption that the difference in swelling between a montmorillonite and a beidellite is due to the source of the charge, whether in the alumina or silica layers, two montmorillonites of equal charge but differing in the proportion of the charge originating in the alumina and silica layers would be expected to swell differently. And two montmorillonites with approximately equal exchange capacity originating in the same degree in the alumina and silica layers would be expected to swell to the same degree. Thus the composition of a montmorillonite, especially with respect to substitutions in the structure that contribute to total charge and to the relative distribution of charge between the outer and inner layers, would be expected to have a significant influence on the swelling volume. As trivalent iron substituted for aluminum does not change the charge on the inner layer, it would not be expected to affect the swelling volume.

In order to test these assumptions, I (1953) made a comparison of the free swelling volumes in water of 12 sodium-saturated montmorillonites that differed considerably in extent of iron and magnesium substitution in the alumina layer, in total exchange capacity, and in the relative distribution of charge between the alumina and silica layers. The results revealed unexpected relationships.

The range in swelling volume - from 21 to 66 milliliters per gram - strongly supported the assumption that the swelling of montmorillonites is greatly influenced by factors other than the exchangeable cation, which was the same, that is, sodium, in all the specimens. As the amount of sodium present varied with the total cation exchange capacity, it seemed possible that the differences in swelling volume might be due to differences in the amount of sodium present as a result of difference in exchange capacity. However, comparison of cation-exchange capacity with swelling volume (figure 5), indicated that although the Santa Rosa sample, which had the highest cation-exchange capacity, had also the highest swelling volume and the Aberdeen sample, which had the lowest exchange capacity, had the lowest swelling volume, a more detailed examination of the data showed certain discrepancies. For example, the Aberdeen, Nieder-Bayern and Amargoso Valley samples had approximately the same swelling volumes, 23, 23, and 21 milliliters per gram, respectively, although they had quite different exchange capacities, 0.77, 0.94, and 1.11 milliequivalents per gram, respectively. On the other hand, the Amargosa Valley and Greenwood samples had almost the same exchange capacities, 1.11 and 1.14 milliequivalents per gram, respectively, but their swelling volumes were quite different, 21 and 50 milliliters, respectively. Consequently there seems to be no direct relationship between total exchange capacity and swelling volume.

A comparison of the swelling volumes of other pairs of samples gives some information as to the supposedly greater ability of a charge originating in the tetrahedral layer to prevent expansion and swelling. The Fort Steel and Belle Fourche samples have almost the same total charge, 0.39 and 0.38, respectively. (See figure 7) In the Fort Steel

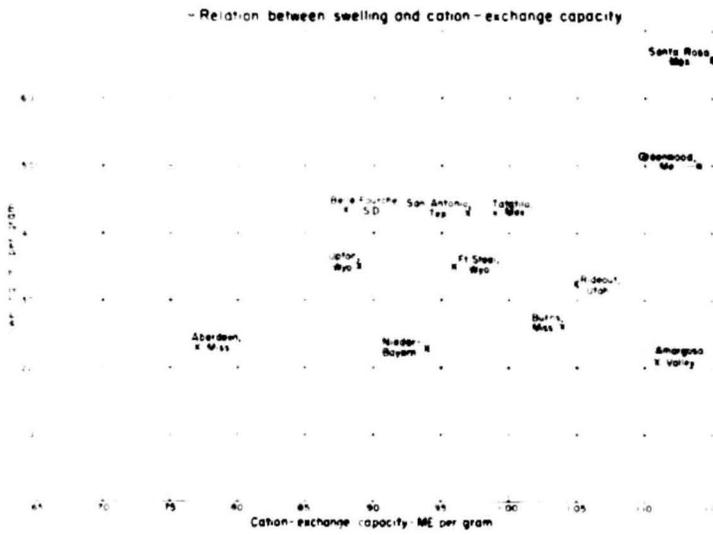


Figure 5. (From Foster, 1953).

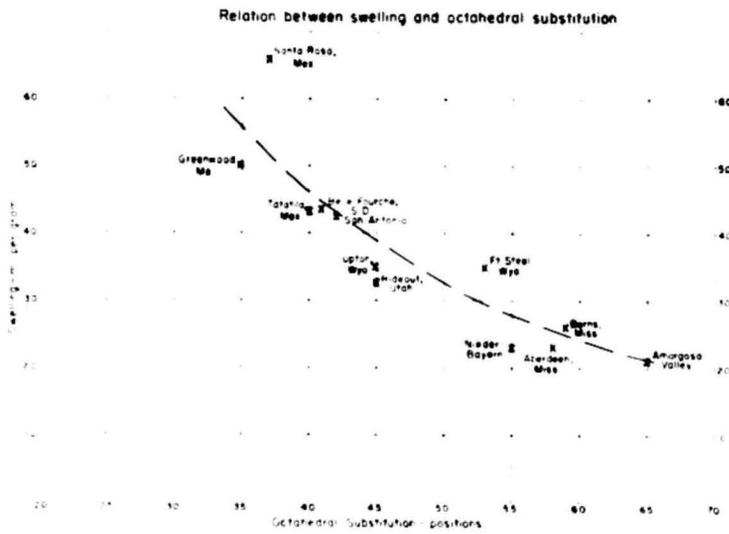


Figure 6. (From Foster, 1953).

sample this charge originates almost wholly in the octahedral layer, but in the Belle Fourche sample almost half the charge originates in the tetrahedral layer. Yet the Belle Fourche sample had a swelling volume of 43.5 milliliters, whereas the Fort Steel sample had a swelling volume of only 35 milliliters. Similarly the Greenwood sample, with 0.17 tetrahedral charge, swelled more than the Amargosa Valley sample with only 0.04 tetrahedral charge. Other samples with the same total charge and the same tetrahedral charge, as for example, the Nieder-Bayern and San Antonio samples, had quite different swelling volumes. Thus either the amounts of tetrahedral charge found in the montmorillonites has little effect in preventing swelling, or some other factor overcomes its effect.

Inspection of the formulas of the last-mentioned pair of samples - Nieder-Bayern and San Antonio - showed that although the charge-inducing substitutions in the tetrahedral layer and in the octahedral were about the same in both samples, the amount of total substitution, that is, trivalent iron plus bivalent magnesium, in the octahedral layer, was quite different, being 0.55 and 0.43, respectively, and that the sample with the greater total octahedral substitution had the lower swelling volume. Examination of other pairs of samples that have been mentioned showed the same relationship--the sample with the higher octahedral substitution had the lower swelling volume.

When the swelling volumes of the samples were plotted against octahedral substitution (figure 6), there is apparent a much closer relationship than when swelling volumes were plotted against cation-exchange capacity. The Burns and Aberdeen samples, with quite different cation-exchange capacities - 1.04 and 0.77, respectively - had nearly the same

amount of octahedral substitution - 0.59 and 0.58 - and nearly the same swelling volumes - 26 and 23 milliequivalents per gram. The Amargosa Valley sample, which had the highest octahedral substitution - 0.65 - had the lowest swelling volume, and the Greenwood sample, which had the lowest octahedral substitution - 0.35 - had the highest swelling volume.

The significant effect of trivalent iron substitution on swelling is apparent when the formulas and swelling volumes of the Tatatila, Fort Steel, and Burns samples are compared (figure 7). In these samples the amount of trivalent iron substitution increases from 0.00 in the Tatatila sample, to 0.10 in the Fort Steel sample, and to 0.16 in the Burns sample and the swelling volumes decrease from 43 milliliters for the Tatatila sample, to 35 milliliters for the Fort Steel sample, and to 26 milliliters for the Burns sample. As the makeup of the tetrahedral layers is the same in all three samples, and as the amount of magnesium substitution in the octahedral layers is essentially the same, it seems reasonable to conclude that the differences in trivalent iron substitution are responsible for the differences in swelling. For these three samples, an increase of 0.16 in trivalent iron substitution was accompanied by a decrease of 17 milliliters in swelling volume.

The Belle Fourche and Aberdeen samples similarly show a decrease in swelling volume with increase in trivalent iron substitution, other substitutions being essentially the same. In this pair of samples an increase of 0.15 in trivalent iron substitution is accompanied by a decrease of 20.5 milliliters in swelling volume.

Effect of R^1 substitution in octahedral group on swelling volume, other substituents being constant.		
		Swelling volume
Tetralin	$\left[\frac{a_{1,1}^{R^1} \rho_{1,1}^{R^1} \mu_{1,1}^{R^1}}{a_{1,2}^{R^1} \rho_{1,2}^{R^1} \mu_{1,2}^{R^1}} \right] \left[\frac{a_{1,3}^{R^1} \rho_{1,3}^{R^1} \mu_{1,3}^{R^1}}{a_{1,4}^{R^1} \rho_{1,4}^{R^1} \mu_{1,4}^{R^1}} \right] \rho_{1,1}^{R^1} (\sigma)_{1,1}$	4.51
Portulacal	$\left[\frac{a_{1,1}^{R^1} \rho_{1,1}^{R^1} \mu_{1,1}^{R^1}}{a_{1,2}^{R^1} \rho_{1,2}^{R^1} \mu_{1,2}^{R^1}} \right] \left[\frac{a_{1,3}^{R^1} \rho_{1,3}^{R^1} \mu_{1,3}^{R^1}}{a_{1,4}^{R^1} \rho_{1,4}^{R^1} \mu_{1,4}^{R^1}} \right] \rho_{1,1}^{R^1} (\sigma)_{1,1}$	35
Burns	$\left[\frac{a_{1,1}^{R^1} \rho_{1,1}^{R^1} \mu_{1,1}^{R^1}}{a_{1,2}^{R^1} \rho_{1,2}^{R^1} \mu_{1,2}^{R^1}} \right] \left[\frac{a_{1,3}^{R^1} \rho_{1,3}^{R^1} \mu_{1,3}^{R^1}}{a_{1,4}^{R^1} \rho_{1,4}^{R^1} \mu_{1,4}^{R^1}} \right] \rho_{1,1}^{R^1} (\sigma)_{1,1}$	26
Solid Polystyrene	$\left[\frac{a_{1,1}^{R^1} \rho_{1,1}^{R^1} \mu_{1,1}^{R^1}}{a_{1,2}^{R^1} \rho_{1,2}^{R^1} \mu_{1,2}^{R^1}} \right] \left[\frac{a_{1,3}^{R^1} \rho_{1,3}^{R^1} \mu_{1,3}^{R^1}}{a_{1,4}^{R^1} \rho_{1,4}^{R^1} \mu_{1,4}^{R^1}} \right] \rho_{1,1}^{R^1} (\sigma)_{1,1}$	35.5
Acetylene	$\left[\frac{a_{1,1}^{R^1} \rho_{1,1}^{R^1} \mu_{1,1}^{R^1}}{a_{1,2}^{R^1} \rho_{1,2}^{R^1} \mu_{1,2}^{R^1}} \right] \left[\frac{a_{1,3}^{R^1} \rho_{1,3}^{R^1} \mu_{1,3}^{R^1}}{a_{1,4}^{R^1} \rho_{1,4}^{R^1} \mu_{1,4}^{R^1}} \right] \rho_{1,1}^{R^1} (\sigma)_{1,1}$	23
Effect of R_2 substitution in octahedral group on swelling volume, other substituents being constant.		
Vanillin	$\left[\frac{a_{1,1}^{R_2} \rho_{1,1}^{R_2} \mu_{1,1}^{R_2}}{a_{1,2}^{R_2} \rho_{1,2}^{R_2} \mu_{1,2}^{R_2}} \right] \left[\frac{a_{1,3}^{R_2} \rho_{1,3}^{R_2} \mu_{1,3}^{R_2}}{a_{1,4}^{R_2} \rho_{1,4}^{R_2} \mu_{1,4}^{R_2}} \right] \rho_{1,1}^{R_2} (\sigma)_{1,1}$	3
Anisole	$\left[\frac{a_{1,1}^{R_2} \rho_{1,1}^{R_2} \mu_{1,1}^{R_2}}{a_{1,2}^{R_2} \rho_{1,2}^{R_2} \mu_{1,2}^{R_2}} \right] \left[\frac{a_{1,3}^{R_2} \rho_{1,3}^{R_2} \mu_{1,3}^{R_2}}{a_{1,4}^{R_2} \rho_{1,4}^{R_2} \mu_{1,4}^{R_2}} \right] \rho_{1,1}^{R_2} (\sigma)_{1,1}$	23

Figure 7. (From Foster, 1953).

The effect of trivalent iron substitution on swelling volume is similar to that of magnesium substitution. Thus, between the San Antonio and Amargosa Valley samples there is a difference of 22 milliliters in swelling volume for a difference of 0.19 in magnesium substitution, all the other substitutions being essentially identical.

Thus, although trivalent iron does not contribute to the charge on the structure or to the cation-exchange capacity, it does seem to have an effect on the swelling volume similar to that of magnesium, which does contribute to the charge and cation-exchange capacity. On the other hand, aluminum substituted for silicon in the tetrahedral layers appears to have little effect on the swelling volume, although it does contribute to the cation-exchange capacity and gives rise to a charge on the tetrahedral or outer layers, where a charge had been supposed to be more effective than a charge originating in the middle layer in preventing expansion.

The relative effect of trivalent and divalent iron on swelling volume is indicated by a comparison of the swelling volumes of two specimens of bentonite that were identical in chemical composition but that differed in the proportionate amounts of divalent and trivalent iron present.

In natural exposures and near the surface the bentonite that is commonly known as the "Wyoming" swelling bentonite is pale olive-green or cream in color. However, under a few feet of cover many of the blocks, which have formed by drying and shrinking of bentonite, have a central core of blue-gray material. Analyses of the blue-gray and olive-green phases of the same block showed that the two color phases

were essentially identical in chemical composition, except for the state of oxidation of the iron. The total iron content of the two phases was the same, but in the blue-gray material two-thirds of the iron was present as ferrous iron, one-third as ferric; in the olive-green material the reverse relationship was found; only one-third of the iron was present as ferrous iron, whereas two-thirds was present as ferric iron. Tests showed that the blue-gray phase swelled to only two-thirds the volume of the olive-green phase—40 milliliters as against 60 milliliters. Reexamination of the blue-gray material 11 months later showed that it had oxidized to such an extent that the ferrous-ferric iron relationship was the same as that of the olive-green material originally. It swelled to a volume of 66 milliliters, compared to 60 milliliters for the original olive-green material. These data indicate that ferrous iron in octahedral positions has a greater depressing effect on the swelling volume than ferric iron.

The significant effect of ferric iron substitution on the swelling volume suggests that the apparent relation between octahedral substitution and swelling is not due to the charge induced on the unit by the substitution but rather to some other change in electrochemical properties brought about by the substitution.

If swelling is assumed to be related to ionic dissociation, the decrease in swelling volumes found to accompany increase in octahedral substitution suggests that these substitutions in some way affect the degree of dissociation of the exchangeable cations, even though the substitution does not affect the charge. In other words, the substitution in some way affects the strength of the clay unit as an anion.

Because of differences in polarizing power the substitution of any ion for another must cause a change in the polarization of neighboring ions.

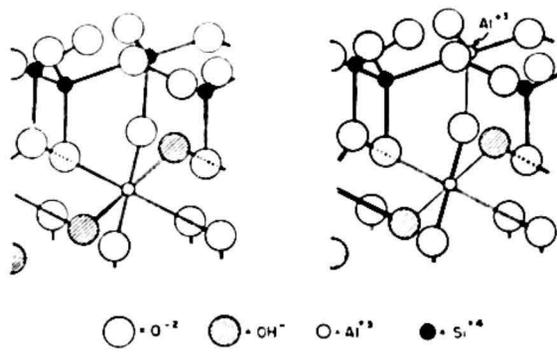
Moreover, it is reasonable to suppose that the effect of any substitution should be felt not only by the nearest neighbors but would be reflected throughout the structure, thus altering the energy relationships of the whole. In a recent study on the effect of aluminum substitution for silicon in the tetrahedral layers on the chemical bonding characteristics and, in consequence, on the physical properties and especially the temperature of dehydroxylation of clays, Johns and Jonas (1954) observe

"One method of analyzing bond type involves recognition of types intermediate between extreme ionic and extreme covalent bonds. The use of Pauling's electronegativity values and the concept of resonance are based on this kind of reasoning. This approach offers a method of determining gradational bond types, but it is difficult to arrive at any quantitative value for bond strength. An alternative method useful for largely ionic crystals is the concept of polarization as utilized by Goldschmidt (1926) and Fajans (1931). In the ideal ionic crystal there is a spherical distribution of the electrons around the center of each ion. Small charged cations, such as Al^{+3} and Si^{+4} , have a distorting or polarizing effect on the electron atmospheres of larger, less highly charged anions, like oxygen, which is considered to be highly polarizable. If the relative polarizing power and polarizability of interacting ions are known, it is possible to determine qualitatively the deviation from pure ionic bonding resulting from various combinations of these ions. The two concepts of bond character are qualitatively compatible; however, the polarization approach is more amenable to mental visualization."

Johns and Jonas continue

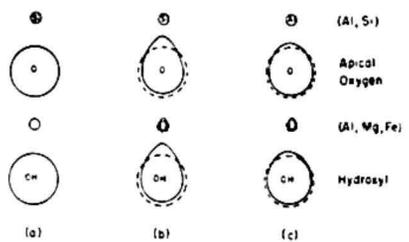
"The sequence of bonds involved in this discussion is $(Al, Si)-O-(Al, Mg, Fe)-OH$. The symbol (Al, Si) represents the cations that commonly occupy the tetrahedral position in the structure. The common ions in the octahedral position are (Al, Mg, Fe) . As shown in figure 1 [figure 8, this paper] three of the oxygens in the tetrahedral portion of a layer silicate are identically bonded coplanar ions, each of which is bonded by two tetrahedrally coordinating ions in two neighboring tetrahedra. The fourth oxygen - the apical oxygen of the tetrahedron - is bonded to a tetrahedral cation and to an octahedral cation. The $(Al, Si)-O$ bond to be considered here refers to the bond between the tetrahedral ion and the apical oxygen.

"Figure 2a [figure 9a, this paper] shows a schematic representation of the sequence under discussion with ideal spherical electron distribution. However, it is reasonable to suppose that ions would never assume a spherical character under the



Configuration of a portion of a layer silicate showing spatial relations between tetrahedral and octahedral coordination systems. Changes of bond strength when Al proxies for Si are shown by weight of line. Heavy lines represent bonds which are strengthened, light lines are weakened bonds.

Figure 8. (From Johns and Jonas, 1954).



A schematic representation of electron distribution in the sequence (Si,Al)-O-(Al,Mg,Fe)-OH. Line a shows the distribution for ideal ionic bonding, b and c show variation from ideal due to polarization when Si and Al, respectively, occupy the tetrahedral position.

Figure 9. (From Johns and Jonas, 1954).

influence of neighboring ions in a crystal. The degree of departure from the ideal sphericity would be related to the increase in bond strength over the pure electrostatic attraction.

"In the clay mineral groups montmorillonite and illite, the highly charged Si ion (figure 2b) [figure 9b, this paper] has a great polarizing effect on the electron atmosphere of the apical oxygen of the silica tetrahedron. As a result of this polarization, there is an increase in the electron density between the Si ion and the apical oxygen. A corresponding decrease occurs in the contribution by the apical oxygen to the electron density between the apical oxygen and the octahedral ion. Although the electron atmospheres of the octahedral cations are less susceptible to polarizing influences than those of oxygen, there can be no doubt that they are still influenced by their environment. The cation electrons will be concentrated next to the apical oxygen in an attempt to compensate partially for the decrease in electron density resulting from the polarization of the apical oxygen by Si.

"Substitution of the less highly charged Al ion (figure 2e) [figure 9c, this paper] exerts less influence over the apical oxygen electron atmosphere so that the probability of an electron's occurring at the point of interaction between Al and apical oxygen will be less than between Si and the apical oxygen. As a result, an increased electron density occurs between the apical oxygen and the octahedral cation over that expected in the same position prior to substitution.

"The electron density between the octahedral cation and the hydroxyl group is mainly a result of electrons contributed by the oxygen of hydroxyl, in spite of the reduced polarizability of oxygen by the tightening of its electron atmosphere upon combining with a proton. The least polarized octahedral cation will afford the least distortion of hydroxyl, with correspondingly lower electron density toward the cation."

These authors further state

"...when considering identical structural environments, an increase in electron density corresponds to a relative increase in the covalent character of the ionic bond and an increased bond strength. Therefore, the decrease in electron density and the increased ionic character of the (Al,Mg,Fe)-OH bond,

caused by the substitution of Al for tetrahedral Si will result in decreased bond strength. Likewise, Al substitution results in a weaker (Al,Si)-O bond and a stronger O-(Al,Mg,Fe) bond."

Similarly, the substitution of iron or magnesium for aluminum would cause a redistribution of the electron atmospheres of neighboring ions and this redistribution is reflected throughout the whole structure. And such an alteration in the electron distribution in the structure would be expected to affect the ionization constant of the clay unit as an anion. Although a colloidal electrolyte like montmorillonite cannot be strictly compared with a soluble electrolyte, the change in the ionization constant of acetic acid (figure 10) brought about by the substitution of one or more of the H ions by positive or negative ions or groups - such as Cl, Br, CN, OH or CH_3 - and the increase in strength of ammonium hydroxide as a base caused by the substitution of one or more of the H atoms by CH_3 groups are examples of the way in which the degree of dissociation of a weak acid or base can be affected by substitutions.

The decrease in swelling volumes found to accompany increase in octahedral substitution seems to indicate that the effect of these substitutions is in the direction of decrease in the degree of dissociation of the montmorillonite.

Ionization Constants of
Substituted Acetic Acids*

Acid	Ionization Constant, 25°
Acetic, CH_3COOH	0.00018
Chloroacetic, CH_2ClCOOH	0.00155
Bromoacetic, CH_2BrCOOH	0.00138
Cyanoacetic, CH_2CNCOOH	0.00370
Glycollic, CH_2OHCOOH	0.000152
Propionic, $\text{CH}_3\text{CH}_2\text{COOH}$	0.000013

(From *Outlines of Theoretical Chemistry*, Getman, F. H., and Daniels, F.,
John Wiley & Sons, Inc. London, 1931, p. 403)

Figure 10.

CONCLUSION

The significant relation between clay composition and swelling is most satisfactorily explained by the concept of cation dissociation. According to this concept, when a clay of the montmorillonite group is dispersed in water, the associated cations that are located, for the most part, between the structural sheets, tend to dissociate, prying the particles apart and leaving some of the structural units negatively charged. Thus charged, the units tend to repel each other, and, if enough units are so charged, the repulsive effect is great enough to give the clay particles the appearance of swelling. When calcium is the associated cation, the degree of dissociation is not great enough to cause a significant degree of swelling; whereas when sodium is the dominant associated cation, the degree of dissociation is much greater and sodium montmorillonites are characterized by their swelling properties.

On the assumption that swelling is related to dissociation, the decrease in the swelling volumes of sodium montmorillonites found to accompany increase in octahedral substitution of iron or magnesium or both for aluminum suggests that these substitutions affect the degree of dissociation of the clay unit. It has been postulated that the substituted ions, because of their different polarization properties as compared with aluminum, have caused a redistribution of electrons throughout the structure, thus affecting the binding energy and ionization constant of the clay unit. The decrease in swelling volumes found to accompany increase in octahedral substitution indicates that the effect of the substitutions is in the direction of

decrease in dissociation of the clay unit. This interpretation of the effect of substitutions in the structure on the swelling of sodium montmorillonite is, admittedly, speculative, and further work is required to clarify the relation between substitutions in the montmorillonite structure and swelling.

Hydrous mica, with the same structure as montmorillonite, is characterized by an even greater degree of isomorphous substitutions, and consequently, a greater charge. However, a large part of this charge is neutralized by fixed potassium, nonexchangeable and nonionizable, which holds the units so tightly together that any exchangeable and ionizable cations present are largely inaccessible. Hence the hydrous micas are characterized by a low degree of swelling. It is probable also that, as the substitutions in the hydrous mica structure are considerably greater than in the montmorillonite structure, they have an even greater depressing effect on dissociation, and consequent swelling.

In the kaolinite group, in which there are generally no replacements, the small number of exchangeable cations associated with the clay structure are presumed to be held by broken bonds on the edges of the sheets. And even though Marshall has shown kaolinite to be more highly ionized than montmorillonite, this greater ionization, because of the small number of cations present and their location at the edges of the sheets, cannot pry the units apart or leave the units with sufficient charge to enable the clay particles to exhibit the phenomenon of swelling.

Thus the concept of cation dissociation satisfactorily interprets the difference in swelling exhibited by different kinds of clays and correlates these differences with their composition.

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