ROLE OF CHEMICAL PROPERTIES OF CLAYS IN SOIL SCIENCE

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The application of petrographic and X-ray techniques to the study of minerals in colloidal clay of soils dates back over a remarkably brief span of years to 1930, when the epoch-making papers of Hendricks and Fry (1930) and Kelley, Dore, and Brown (1930) appeared independently and almost simultaneously, announcing that the inorganic colloidal material of soils was not an amorphous, indeterminate mixture of oxides, as had hitherto been supposed, but a definitely crystalline material. This important finding was, in effect, a confirmation of the results announced in 1927 by C. S. Ross (1927) to the effect that the clay minerals, notwithstanding their colloidal dimensions, exhibit definite crystallographic constants determinable with the petrographic microscope. Hendricks and Fry (1930), applying both petrographic and X-ray techniques, found that the colloidal clay from soils of many parts of the United States contained montmorillonite, Ordovician bentonite, and halloysite. Kelley, Dore and Brown (1930) in their extensive chemical and X-ray studies demonstrated with phenomenal clarity and rigor the close relationship between the crystalline character of the constituents of soil clays and their cation exchange properties. In numerous subsequent papers by these and other investigators the relationship between the mineral content of the colloidal clay and the chemistry of various soil processes has been firmly established.

Importance of Clay Chemistry in Soil Science and Technology. The clay fraction of the soil and in particular the kind and amount of the respective clay minerals present, determines in large measure the chemical and physical properties of the soil. The principal physical effects manifest themselves in soil structure and aggregation and in the movement and retention of soil moisture. By reason of its predominant role in cation and anion exchange, the clay fraction is the primary factor which controls soil acidity and alkalinity, and as such must be taken into account in any program of reclamation of alkaline and saline soils. To the extent that it influences the ease or difficulty of release of plant nutrient ions, the clay fraction is important in plant nutrition. In the field of soil morphology, Jenny and Smith (1935) have elucidated the part which the clay fraction plays in the formation of claypans. There are other respects, too, in which the clay fraction influences the character of the profile. Thus the chemistry of soil is essentially the chemistry of clay.

Chemical Properties of Clay. Chemically the colloidal clay is a highly polar, reactive system. Although its polar nature stems in considerable measure from its large surface per unit of weight, the seat of the polarity per se lies in the net charge on the crystal framework and on the openness or compactness of the lattice structure. The charge on the framework may be of relatively large dimensions, as Marshall (1937) has found, it being of the order of 4×10^{13} electrons per sq. cm in the beidellites, and 7×10^{13} in the montmorillonites. The charge may be inherent, due to lattice substitutions, or it may be accidental due to broken bonds. Thus the 1:1 and 2:1 clay minerals have varying degrees of polarity. In kaolinite the inherent charge is negligible due to the virtual absence of lattice substitution, whereas its accidental charge may be considerable. In the 2:1 minerals there may be both a high inherent and a high accidental charge. The clays behave as acids and the salts of acids and exhibit amphoterism in greater or lesser degree. Bradfield (1923) has shown that the clay acids behave as though they were monobasic. The clays sorb water and organic molecules through hydrogen bonding. Jenny and Reitemeier (1926) and Baver (1929) have shown that the clays exhibit large zeta potentials according to the size and charge of the adsorbed cation. These potentials are the primary factor in the dispersion and flocculation of clay. Underlying all of the foregoing properties is the property of cation exchange which is the dominant chemical characteristic of clay and intimately linked with nearly every important problem in soil science and technology.

Distribution of the Clay Minerals in Soils. The magnitude of the contribution of the clay minerals of soils to cation-exchange capacity, buffer capacity, cation fixation, and various physical properties depends upon the nature and amount of the various mineral species present. Attempts have been made by several investigators to estimate the quantitative proportions of the clay minerals in the superfine colloid from the results of chemical, X-ray, and thermal analyses (Alexander, Hendricks, and Nelson 1939; Buehrer, Robinson, and Deming 1949; Shaw and Humbert 1942). Alexander, Hendricks, and Nelson (1939) included in their analyses the determination of the principal lattice constituents: silica, alumina, combined ferric oxide, magnesium oxide, and potassium oxide. From the intensities of the 7.1 Å line for the second order reflection from kaolinite, the 10.0 Å line for illite, and the 15 Å line for the (001) reflection for air-dry montmorillonite, they estimated the amounts of these minerals present. Except for minerals in which iron substitutes extensively for aluminum, isomorphous replacements do not affect the diffraction pattern appreciably. Since hydrous mica is the only clay mineral having an appreciable percentage of non-exchangeable (crystal-lattice) potassium, these authors have proposed calculation of the amount of illite using an average of 6 percent K_2O as a basis. Kelley (1948), however, has pointed out that in the hydrous micas the percentage of crystal-lattice potassium varies appreciably from sample to sample, hence the calculated result can be little better than a rough approximation. Alexander et al. (1939) regard the percentage of free ferric oxide as determined chemically to be the best measure of the amount of iron oxide minerals present. They appear to attach greater significance to the result derived from X-ray analysis for hydrous mica, and indicate in their tabulated results that the values calculated from percentage of K_2O may be too low. Montmorillonite

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is difficult to estimate quantitatively by X-ray diffraction because of variation of the c-spacing with water content and because its second most intense reflection is at 3 Å, which coincides with that for the mixed-layer minerals. MacEwan (1946), who forms a complex of montmorillonite with glycerol, thereby sharpening the X-ray lines and making it possible to identify as little as one percent of the mineral with accuracy, provides a reliable method for soil scientists working in this field. Although kaolinite would seem to be easily determined quantitatively since its 7.2 Å spacing is not influenced by either adsorbed water or exchangeable cations, the determination is uncertain if the mineral is present to the extent of only 5 percent or less. Moreover, its determination by thermal decomposition is complicated by the fact that the crystal lattice water of both kaolinite and hydrous mica is given off at temperatures which lie very close to one another (610-620° C).

Kelley and Dore (1938) have devised an ingenious method of quantitative mineral analysis that consists of heating the oriented sample to 500° C prior to X-ray analysis. Upon heating to constant weight at this temperature the variable 15 Å line for montmorillonite disappears. Kaolinite and halloysite being stable at 500° C, do not decompose, and their lines can be measured with accuracy. Upon heating to temperatures above 500° C, the kaolinite and halloysite lines disappear but the (110) line at 4.49 Å for montmorillonite does not disappear until the temperature is considerably above 600° C. The lines for the more resistant minerals such as quartz can be determined from the diffraction patterns obtained by heating the clay above 600° C.

Marshall's method (1937) involves calculation of the ultimate analysis of the colloidal clay to gram-atoms of the individual elements on the basis of the number of oxygen atoms in the theoretical anhydrous formula of the mineral assumed to be present in predominant amount. Thereafter the elements are assigned to tetra- and octahedral positions consistent with the known positions in the mineral chosen. The deductions as to the dominant mineral species present in bentonite, Putnam clay, and Rothamsted clay, arrived at by this method, were in agreement with the results found by petrographic methods. Kelley (1945), however, has pointed out that the assignment of atoms to the various positions may be arbitrary, and the existence of interleaving and the presence of small amounts of non-exchangeable calcium, sodium, and potassium may totally vitiate the calculation.

Shaw and Humbert (1942) and Buehrer, Robinson, and Deming (1949) have made estimates from chemical and thermal data alone, based on determinations of non-exchangeable potassium, crystal-lattice water content of the colloid, and its base-exchange capacity. These calculations involve numerical values for these three properties for what are presumed to be standard mineral samples. In some instances the estimates so found have agreed very closely with those derived from X-ray determinations. The deviations may be a result of variation in potassium content of the hydrous mica due to lattice substitutions, and to possible presence of mixed-layer minerals. None of the above-mentioned authors regard the numerical values obtained as being more than rough estimates, in the absence of more precise

technique. Some remarkably suggestive deductions have grown out of such estimates, notwithstanding the relatively empirical nature of the method.

The weaknesses of the method of Shaw and Humbert (1942) have been pointed out by Kelley (1948), who states that the cation-exchange capacity of mineral mixtures is difficult to interpret and is not necessarily a simple summation of the exchange capacities of the component minerals. Calculation of mineral content by use of cation-exchange capacity can have significance only if the colloid happens to consist predominantly of only one group or type of clay mineral. The exchange capacity of any so-called standard mineral that might be chosen for these calculations is a variable depending greatly upon particle size and lattice substitutions.

Page (1943) in a thermal study of the montmorillonites found considerable variability among 12 bentonites which on the basis of X-ray patterns were considered to be largely montmorillonite. He found that they gave widely differing thermal curves, in some cases exhibiting an endothermic inflection at 850° C, a temperature considerably higher than the 800° C found generally for the removal of the last OH^- water from montmorillonite. In one instance the sample was a mixture containing considerable illite. He concludes that montmorillonite is thus not a definite entity but one whose properties depend in large measure upon lattice substitutions. He suggests that the thermal curve, nevertheless, may be of value in arriving at the nature and extent of such substitutions.

Coleman and Jackson (1946) in studies on coastal-plain soils estimated kaolinite, montmorillonite, and quartz from X-ray patterns, hydrous mica from the percentage of non-exchangeable potassium, and hematite from fusion analysis. Kelley, Dore, and Brown (1930) and Kelley, Dore, Woodford, and Brown (1939) in their extensive studies of mineral composition of California soils, obviate all of these assumptions by not reporting numerical percentages, but merely indicating whether a given clay-mineral group is present or not, and if present, whether in considerable or small amount.

The table shows that the red and yellow podzolic soil colloids are highly kaolinitic and contain considerable amounts of hydrous oxides, chiefly iron. The gray-brown podzolics contain predominant amounts of illite, and smaller amounts of kaolinite and hydrous oxides. The prairie and chernozem soil groups contain about 70 percent montmorillonite, and the remainder consists of kaolinite and illite in about equal proportions. In the alkaline desert soils the dominant constituents are montmorillonite and illite, with appreciable amounts of kaolinite, as well as quartz, hydrous oxides, and carbonates in the solonchaks. The solonetzic soil colloids similarly contain all of the mineral groups, with montmorillonite and illite predominating. Coleman and Jackson (1946) report a laterite from Puerto Rico as consisting entirely of minerals of the kaolin group.

Parent material does not appear to influence the mineral composition of colloidal clay appreciably. Under humid conditions, whether the parent material be granitic or basaltic, the dominant mineral appears to be kaolinite. Under arid conditions, montmorillonite and illite are the dominant minerals, regardless of parent

Table 1.   Estimated clay-mineral composition of soil colloids.

Soil series	Great group	Parent rock	Horizon	SiO₂/R₂O₃	Kao-linite percent	Mont-morillo-nite percent	Hy-drous mica percent	Quartz percent	Hy-drous oxides percent	References
Cecil (N.C.)	Red podzolic	Granitic	C	1.88	80	None	None		15	Alexander, Hendricks and Nelson (1939)
Decatur (Ala.)	Red podzolic	Limestone	B₂	1.95	80		10		13	
Miami (Ind.)	G. B. podzolic	Glacial till	B₂	2.69	10		80		7	
Barnes (S.D.)	Chernozem	Glacial till	B₂	2.77	30	20	40		None	
Mohave (Calif.)	Red desert	Granitic	C	2.60	20	80			2	
Denmark (W.A.)	Yellow podzolic	Granitic	23–36	1.18	60				27*	Hosking (1940)
Coolangatta	Red-brown podzolic	Basaltic	18–27	1.44	65				22*	
Gunnedah (N.S.W.)	Red-brown earth	Basalt	18–27	2.85	10	65		6	7*	
Houston (Miss.)	Rendzina	Calcareous marl	A	2.73	20	55	26	5		Coleman and Jackson (1946)
Orangeburg (Miss.)	Red podzolic	Marine sandstone	B	1.93	75	20	3	5		
Catalina (P.R.)	Laterite	Andesitic tuff	B₂		100	None	None	None		
Imperial (Calif.)	Solonchak	Sandstone-shale	0–12″	2.73	Present	Present	Present	High		Kelley, Dore, and Page, (1941)
Fresno (Calif.)	Solonetz	Granite-alluvium	0–12″	2.80	None	None	High	Present		
Redding (Calif.)	Planosol	Pleistocene, sediments	20–37″	2.05	High	Present				
Mohave (Ariz.)	Red desert	Granite	4–14″	2.48	None	34	65			Buehrer, Robinson, and Deming (1949)
Ramona (Ariz.)	Red desert	Granite	12–24″	2.04	20	33	46			
Pima (Ariz.)	Recent alluvial	Mixed	0–10″	2.63	4	57	44			
Tubac (Ariz.)	Solonetz	Mixed	10–24″	1.95	6	44	52			

* Summation of ferric, aluminum, and titanium oxides.

material. Montmorillonite is dominant in the younger soils, although there are without doubt exceptions to this rule. Coleman and Jackson (1946) found that the clay colloid from coastal-plain soils was fairly abundant in quartz illite, kaolinite, and hematite in the coarse clay fraction, but low in montmorillonite. In the fine clays, montmorillonite was the dominant mineral (50–80 percent); there were appreciable amounts of illite, kaolinite, and hematite, but there was less than 5 percent quartz.

Soil pH and the Nature of the Clay Acids.   The pH value of a soil as determined by means of the glass electrode is assumed to be a measure of, or a function of, the hydrogen- or hydroxyl-ion activity in the sense that Sorensen originally defined it. Because of the hydrolytic equilibria in soils containing various exchangeable cations that directly affect the hydrogen-ion activity of the soil-water system, because of their effects on the soil, and because of the ease of its determination with vacuum-tube pH meters, pH determination has become the popular approach to the solution of many field problems. The pH value is influenced by a variety of inherent as well as external experimental factors. Such inherent factors as the nature of the clay, the proportions of various exchangeable cations present, the presence of organic matter, carbonates, gypsum, and soluble salts, combine to form a very complex system. Variation in any one of these factors may result in appreciable variation in pH value. The conditions of measurement which involve the soil:water ratio, time of standing, and characteristics of the electrode use contribute to make this determination one of the most characteristically empirical quantities measured in soil science and technology. Numerous papers have been published in recent years dealing with these variables too extensively to justify detailed reference here. The advantage of the glass electrode in making possible direct measurement of pH on soil pastes and under direct field conditions, and the fact that it comes to equilibrium

with the soil system almost instantaneously, have put such measurements on a more reproducible basis than before.

There has, however, appeared considerable polemic thinking and writing in regard to what the glass electrode actually measures. Coleman, Williams, Nielsen, and Jenny (1951) have pointed out that the process involved in the cell reaction involves an unknown, variable, and probably indeterminable junction potential, as a result of which the actual cell process does not involve a simple diffusion through the glass membrane, but a junction potential near the surface of the calomel electrode which contains saturated KCl. The pH value is a potential measurement, hence seriously affected by the unknown junction potential when the latter becomes large. Colman et al. (1951) conclude that "Empirical correlations obtained in the past between soil pH and other variables are still valid," but a considerable error will be introduced when E_j becomes large. Empiricism is, of course, unavoidable in such a complex system, hence the discrepancies in measurement reported in the literature. The most serious problem in this connection is that soils investigators have not yet agreed upon a standard and uniform condition of measurement, particularly with reference to moisture content.

The function of the colloidal clay in these systems is to influence the H⁺ or OH⁻ ion activity by dissociation, hydrolysis, cation exchange, or buffer effects. Bradfield (1925) defines the point of maximum buffering as that at which the soil is half-saturated with cations. The underlying cause of these effects is, of course, the strength of the clay acid. Bradfield (1923) showed that the clays give buffered pH titration curves similar to those of weak acids, and that in a 1 percent colloidal suspension, the normality of an electrodialyzed clay acid lies between 0.002 and 0.004-N. For concentrations of clay between 1 percent and 12 percent, he found the value of K_A to be of the order of 3×10^{-7}, assuming it to be monobasic. The clay acid therefore exhibits a strength of the order of magnitude of carbonic acid.

Jenny (1932) termed the apparent dissociation constant of the clay acid which Bradfield had calculated from the pH value given by the clay at the point of half-neutralization, the "avidity index," on the grounds that the constant so found was not a true constant. Bradfield (1923) and Peech and Bradfield (1948) have shown that the dissociation constant so calculated for Ca- and Na-salts of a clay acid are correct if the activity of these salts is included in the equation as follows:

$$pH = pK + \log \frac{a_M\text{-}clay}{a_H\text{-}clay} + \log a_M$$

where a_M is the activity coefficient of the cation of the added base adsorbed on the clay.

Marshall (1949) points out that the clay acids are not pure H-systems but mixtures in which at low pH values aluminum plays an important part. These acids are only partially dissociated and their degree of dissociation varies with the cation present and the degree of saturation with cations. Under alkaline conditions the clay minerals decompose to a greater or lesser extent, yielding aluminates and silicates. He holds that the clay acids are not similar to the simple weak acids, nor to the simple non-mineral colloidal electrolytes. In other words, they cannot be treated as compounds with one or more sharply defined dissociation constants. Their conductivities are generally less than the sum of the conductivities of the charged clay particles and the cations which constitute the "outer atmosphere."

The shape of the pH titration curve for clay acids varies with the nature of the clay, the concentration of the clay suspension, and the base used for titration. In most instances a single inflection point is observed, corresponding to the equivalence point, as in similar titrations of the simple monobasic acids. If the suspended clay at various concentrations is so titrated, the curves obtained intersect in a common point. This has been found by Marshall (1949) to be true for beidellite, illite, and kaolinite, but not for montmorillonite. In the last-mentioned case, the higher the concentration of the suspension, the greater the base required per unit quantity of clay for neutralization, and the higher the pH value at the point of inflection. Both conductance and potentiometric studies have been made on H-saturated clays. They indicate a pH value of 2.85 for H-montmorillonite, 3.58 for H-beidellite, 3.69 for H-illite, and 4.60 for H-kaolinite under comparable conditions.

Mehlich (1942-1943) in extensive studies on the relation between base saturation of soils and their pH values investigated this relationship also for pure clay minerals and their mixtures. His results based on pH titration curves of the H-saturated minerals are in agreement with the findings of Bradfield, Jenny, and Marshall previously cited, concerning the dissociation of these clay acids. Kaolinite over the entire range of saturation percentages yields higher pH values; bentonite and bentonite-halloysite mixtures yield pH values in the lower range and exhibit greater buffering power. Illite and montmorillonite yield nearly identical titration curves but they lie within an appreciably lower pH range. A very close correlation was obtained by Mehlich between the titration curves for pure minerals and mineral mixtures and similar curves for soil clay colloids whose mineral composition had been determined.

Cationic Activity of Clays and Soils. The dissociation of clay salts is of great importance in plant nutrition since it determines the rate at which cations on the colloidal clay can be released for absorption by the plant. The term "available" plant nutrient is usually defined in terms of that portion which is water-soluble and that which is exchangeable. The degree of dissociation is a function of the character of the ionizing surface, hence related directly to the nature of the minerals which make up the colloidal system. The bonding energies with which cations are held in equilibrium with the ionizing surface are expressed quantitatively in terms of cation activity as measured by Marshall (1951) by means of clay-membrane electrodes. They are no doubt also involved in the oscillation volumes of exchangeable cations taking part in contact exchange in terms of the theory of Jenny (1936). By use of clay membranes prepared from different clay minerals and a cell arrangement similar to that of the glass electrode, in which the clay membrane performs essentially the same function as the glass membrane, Marshall and his co-workers have determined what they consider to be the activity coefficient of various clay minerals for various uni- and di-valent cations. Their work is too extensive for detailed discussion at this point. Reference to the most significant findings will, however, be made. Marshall and Bergman (1942) have studied the dissociation of montmorillonite, beidellite, illite, and kaolinite saturated to various degrees with potassium and ammonium ions. For beidellite in 2-4 percent suspension, they report an activity coefficient for Ca^{++} ion to be 0.01-0104, for K^+ ion, 0.18, for NH_4^-, 0.08, Na^+ ion, 0.09, and H^+ ion 0.04, from which the relative ease of dissociation may be deduced. Marshall (1948), comparing the dissociation of Na-, K-, and NH_4-salts of kaolinite and montmorillonite, found that the kaolinite salts, in contradistinction to those of montmorillonite, are quite highly dissociated, to an extent of 20-30 percent. The order of the minerals as to activity coefficient of the cation is:

kaolinite > montmorillonite > beidellite > illite

with respect to the univalent cations other than hydrogen. For the same clays saturated with hydrogen ion, the order is:

montmorillonite > beidellite > illite > kaolinite.

The feeble dissociation of the kaolinite acid and its strong dissociation as a salt is interpreted in terms of the lattice structure. Kaolinite has a compact structure with no unbalanced inherent charge on the lattice. Dissociation of OH^- groups is feeble and hence the hydrogen-ion activity is low. In the form of its salt, however, the cations are on the outer edges of the crystal and readily accessible. In montmorillonite, beidellite, and illite, dissociation is enhanced by lattice substitutions. As a result, their acids are much stronger than that of kaolinite, despite the fact that secondary reactions liberating aluminum occur. The salts, however, are feebly dissociated because of the strong attractive forces holding the cations to the lattice, and of penetration of certain cations into the silica layers.

The nature of the cation-exchange reaction, principles and quantitative equations relating to the equilibrium involved, and the numerous respects in which this important reaction enters into soil science and technology have been set forth in comprehensive form by Kelley (1948) and for reasons of space limitation will not be treated here.

Fixation and Release of Potassium in Soils. One of the most challenging problems in soil fertility that engaged the attention of soils investigators as far back as 1848 is the fixation and availability of potassium. Its importance is indicated by the large number of papers, some 200 or more, listed in the scholarly review of the subject by Reitemeier (1951) in *Advances in Agronomy.* A full hundred or more papers on both field and laboratory studies on this problem were not included in his review.

Potassium occurs in soils in the form of primary minerals (to the extent of 90-98 percent as the feldspars and micas), in the clays and other secondary minerals, and in water-soluble form. In the clays it exists in both exchangeable and non-exchangeable form, the latter being generally greatly in the predominance. A sample distribution of potassium in its various forms in calcareous and non-calcareous soils, as found by McGeorge (1933), is shown in table 2.

Table 2.   Distribution of potassium in calcareous desert soils.*
(p.p.m. K on dry soil basis)

Soil	Total K (fusion)	Water-soluble	CO_2-soluble	Ex-change-able	Non-ex-change-able	Neubauer value
Litchfield	23,100	83	200	670	22,350	188
Kyrene	30,100	134	440	1,730	28,240	308
Laveen	26,400	75	70	260	26,060	154
Tucson	25,500	60	130	910	24,530	300
Tempe	21,800	69	310	1,310	21,600	240
Peoria	24,400	48	110	320	24,030	198
Mesa	19,200	60	130	910	18,230	340

* McGeorge, W. T., 1933.

The data in table 2 illustrate the fact that by far the greatest proportion of the potassium is non-exchangeable, as measured by replacement with ammonium acetate, this form ranging between 90 and 99 percent of the total potassium present. The CO_2-soluble fraction represents the amount of potassium replaced at a pH value of about 6 in a 1:5 water suspension of the soil and, as would be expected, is considerably greater than the amount soluble in water alone. The Neubauer values in most instances exceeded even the amount of potassium brought into solution by saturated carbonic-acid solution, but were in some cases considerably less than the total exchangeable potassium. On this basis McGeorge concluded that the potassium supply of desert soils is of such a magnitude that this element will not need to be applied in fertilizers for some years to come. Very few mixed fertilizers sold in the State of Arizona carry potassium, and in few instances have crop responses to its application been reported.

On the other hand, the fixation of potassium in an unavailable form is a problem that has assumed great importance in recent years. Volk (1933) was apparently the first to demonstrate what happens when potassium becomes fixed in non-exchangeable form in soils. He showed that when the 0.3 micron fraction of Hagerstown silt loam was treated with KCl solution and evaporated to dryness, the potassium became fixed, whereas little potassium was fixed while the soil was kept moist. Thirty-two wetting-and-drying cycles at 70°C resulted in fixation of 75 percent of the potassium added. X-ray examination yielded a diffraction pattern which resembled that of muscovite so closely that he announced fixation to be due to the synthesis of muscovite. Subsequent research has indicated that the mineral identified was not native muscovite but hydrous mica, or illite.

A surprisingly large proportion of arable soils fix potassium in a form unavailable as measured by ordinary cation-replacement methods. It is fixed primarily by the 2:1 group of clay minerals with expanding or partially expanding lattice and not by the kaolin group. By reason of its stable 12-coordination as in the micas, as well as in a 14-coordination, potassium has now been definitely shown to be fixed in the variable spacing of the expanding-lattice minerals.

A series of fundamental researches subsequent to Volk's announcement have served to elucidate the mechanism of the fixation of potassium. Truog and Jones (1938) found that the fixation of potassium reduced the cation exchange capacity as was to be expected if the binding together of layer packages reduced the number of exchange spots on the lattice of the mineral. A brief summary of their data, obtained after removal of organic matter from the soil sample, saturating with K^+ and subjecting it to 20 wetting-and-drying cycles at 80°C, is shown in table 3. It is evident that the num-

Table 3.   Reduction in cation-exchange capacity of soils and clay minerals accompanying potassium fixation.*

Soil type or mineral	Horizon of treatment	K fixed me./100 g	Reduction in C.E.C. me./100 g
Miami silt loam	A	1.5	1.9
	B	4.7	4.8
Carrington silt loam	A	2.7	2.7
	B	3.4	3.2
Richfield clay	A	4.0	3.8
	B	5.0	5.1
Bentonite, powd. 20 cycles @ 80°C		14.8	14.5
Bentonite <0.1μ 20 cycles @ 80°C		49.4	51.7
Bentonite, powd. 75 hrs. @ 110°C		27.0	28.0
Nontronite <0.1μ 10 hrs. @ 145°C		31.5	34.0

* Truog, E., and Jones, R. J., 1938.

ber of milliequivalents of K^+ fixed is equal to the number of milliequivalents by which the cation-exchange capacity was reduced; a fact particularly striking in the case of bentonite under a variety of conditions. Martin, Overstreet, and Hoagland (1946), working with Vina and Ramona colloidal clay, found that the reduction in exchange capacity was considerably less than the amount of K^+ fixed in the coarse clay fraction, but equivalent to it in the clay size fraction. When the whole soil was considered, the amount of K^+ fixed was found to be

equal to the sum of the exchangeable bases liberated during fixation.

Page and Baver (1940), in a study of fixation of K^+ by bentonite and Miami clay on drying at 105°C, found that NH_4^+, Rb^+, Cs^+, and Ba^{++} can undergo similar fixation. The results of their studies are summarized in

Table 4. *Fixation of cations by Miami colloid as a function of ionic size.**

| Cation | Ionic diameter Å | Percent replaceable | | Difference | Percent of exchangeable ion fixed by drying |
		Moist	Dry		
Li+	1.36	89.7	74.6	15.1	16.8
Na+	1.96	89.4	72.4	17.0	19.0
NH4+	2.42	71.7	34.6	37.1	51.7
K+	2.66	77.0	35.1	41.9	54.5
Rb+	2.96	54.4	26.7	18.7	51.0
Cs+	2.34	43.8	24.1	19.7	45.2
Mg++	1.42	65.0	46.1	18.9	29.1
Ca++	1.96	82.0	68.7	13.3	16.2
Sr++	2.30	59.5	43.2	16.3	27.4
Ba++	2.62	72.4	38.3	34.1	47.2

* Page, J. B., and Baver, L. D., 1939.

table 4. They found that ions which were of such a diameter that they could fit into the hexagonal O-cavity whose "diameter" was 2.80 Å, could become fixed. Thus the cations whose ionic diameters were of the order of 2.80 Å can fit snugly into such positions and be firmly held, whereas much smaller cations such as Li^+, Na^+, Mg^{++}, and Ca^{++} are loosely held and therefore remain in large measure replaceable. Wear and White conclude (1951) from studies on Wyoming bentonite that the charge resulting from substitutions in the tetrahedral layer of montmorillonite is responsible for the fixation. Beidellitic and illitic clays have more tetrahedral substitution than does montmorillonite, hence show a greater fixation capacity. Wear and White hold that during fixation some of the interlayers remain contracted upon re-wetting, while the remainder expand.

Stanford (1948) in a study of calcareous soils found that potassium may become fixed immediately upon its addition to the soil, even without drying. Working with electrodialyzed illite and acid-washed bentonite, and a constant level of added potassium, he varied the pH value of a series of samples with NaOH, thereafter determining the amount of exchangeable potassium on the moist and dry soil. He found that illite fixes potassium in increasing amounts as the pH increases from 3 to 10, whether the soil was moist or dry. Bentonite fixed no potassium in the moist state, but on drying, the amount of potassium fixed was 5 me. per 100 g at pH 3, the amount decreasing to a limiting value of 2 me. per 100 g at neutrality, and thereafter remaining constant. Thus illite fixes potassium in calcareous soils even under moist conditions, and its capacity to fix potassium is increased by drying. Acid illite fixes relatively little potassium because hydrogen, iron, and aluminum ions, present in the inter-layer, appear to inhibit fixation. Removal of these ions by addition of a base, a phosphate or fluoride, increased the capacity of illite to fix potassium. Fluoride increases fixation by montmorillonite, through removal of aluminum which blocks the exchange

positions at the interplanar surfaces. In acid soils, hydrogen, iron, and aluminum must be replaced before potassium can be fixed. In calcareous soils, Ca^{++}, Mg^{++}, and Na^+ are replaced readily by potassium, hence the latter is fixed readily even under moist conditions. Stanford thus holds that potassium fixation by illitic clay is essentially an exchange reaction.

The question as to whether the so-called fixed potassium can again become exchangeable and available to plants has likewise engaged the attention of investigators. McGeorge[1] cites the case of Superstition sand near Yuma, Arizona, which contains potassium which cannot be released in the ordinary cation-exchange procedures but which is extensivley available to plants as indicated by Neubauer determinations. This soil has an exchange capacity of 4 me. per 100 g. Only 0.7 me. potassium per 100 g is found to be exchangeable. For 12 years this soil has been cropped to alfalfa, yielding 6 tons of alfalfa per acre per year, and the crop removing 225 lbs of potassium per acre per year. To date, 2,700 lbs of potassium have been thus removed, yet the soil originally contained only 2,320 lbs of exchangeable potassium per acre to a 2-foot depth. This soil has never shown a response to potash fertilizer in terms of increased yield of alfalfa. McGeorge concludes that the non-exchangeable potassium must gradually be becoming exchangeable.

Fine, Truog, and Bailey (1941) have found that alternate freezing and thawing will release fixed potassium. Hoagland and Martin (1933), Drake and Scarseth (1940), Reitemeier, Brown, and Holmes (1951), and others have found by Neubauer determinations that plants can extract more potassium from soils containing fixed potassium than can be extracted by replacement with ammonium acetate, dilute nitric acid, and other solutions. Heating to 200°C, alternate wetting and drying and electrodialysis release more potassium than can be replaced by cation exchange.

Williams and Jenny (1952), in experiments with plants grown on Ramona loam, a non-calcic brown soil with high potassium-fixing capacity, find large amounts of non-exchangeable potassium to be absorbed, indicating that such a conversion takes place. In leaching experiments at various pH values of the leaching solution, it was found that the potassium replaced between pH 3 and 7 is that which is present in normally replaceable form in the soil. Below pH 3, however, more potassium appears in the leachate, which they conclude must be part of that potassium which is non-exchangeable. Hence the pH value of the leaching solution appears to be one of the controlling factors in this release. In leaching experiments with the chlorides of H^+, Na^+, Li^+, Mg^{++}, Ca^{++}, and NH_4^+, Williams and Jenny found that all of the cations except ammonium are able to release considerable amounts of non-exchangeable potassium.

Ammonium Ion Fixation. The first report on the possibility of ammonium-ion fixation by soils was in 1917 by McBeth, who found that not all of the ammonium ion with which a soil had been treated could be removed either by distillation with alkali or extraction with 10 percent HCl. Bower (1951) observed that the subsoil of an alkali soil showed an exchangeable-sodium content

[1] Private communication.

40 percent greater than the exchange capacity of the soil as determined by replacement with neutral ammonium acetate. This anomaly pointed to the possibility of error in the determination of exchange capacity using ammonium ion as the replacing cation, and to fixation of the ammonium ion by the clay. He found that a fairly high percentage fixation occurs under moist-soil conditions. Analogous to observations of other investigators working on the fixation of potassium, Bower found that the amounts of K^+ and NH_4^+ ions fixed by the same soils were practically identical in magnitude, suggesting that this could occur only if the mechanism of the fixation were substantially the same. He observed that a reduction in cation-exchange capacity accompanies the fixation of ammonium ion and concluded from this that fixation is itself an ion-exchange reaction or involves cation exchange somewhere in the process. As to the mineral responsible for the fixation, Bower holds that the amount of illite present in the colloidal clay would not account for its magnitude. It appears likely that another clay mineral is responsible for it.

Stanford and Pierre (1947) find that the calcareous soils of Iowa fix considerable amounts of ammonium ion under moist conditions. They showed that if the soil is saturated in part with K^+ ion prior to addition of NH_4^+ ions, the amount of NH_4^+ ion fixed was reduced; likewise the amount of potassium fixed by the soil is reduced by prior fixation of ammonium.

The mechanism of the fixation of NH_4^+ ions has been studied by Allison, Doetch, and Roller (1951) who find that the fixation which occurs under moist conditions involves interaction with illite whereas the additional fixation brought about by drying at 100°C (six times as much being fixed on drying as under moist conditions) must be attributed to montmorillonite and illite.

Barshad (1948) has shown that vermiculite, heated repeatedly to 70° C, in presence of normal ammonium salt solutions, fixes large amounts of NH_4^+ ion which is not replaceable by K^+, Rb^+, or Cs^+, but readily replaced by Li^+, Na^+, Mg^{++}, Ca^{++}, and Ba^{++}. It is apparent that the ions which are smaller than NH_4^+ are able to replace it from the position where it is fixed in the lattice, whereas the large cations cannot. Barshad therefore concludes that fixation involves the orientation of the NH_4^+ ion in the hexagonal openings between the layer packages of montmorillonite analogous to the manner in which fixed potassium is held. Barshad (1951) further found that in replacing the adsorbed NH_4^+ ions from a soil, distillation with a base is more effective than leaching with a salt solution. The difference between the amounts of NH_3 obtained by distillation with NaOH and KOH respectively, represents the fixing capacity of a soil for NH_4^+ ion.

The results of these studies are rather far-reaching, since they cast doubt upon validity of conclusions based upon many hundreds of cation exchange capacity determinations that have been made in the past, in which neutral normal ammonium acetate replacement, followed by distillation of the adsorbed ammonium, has been accepted as a standard method. Since such a distillation results in the liberation of both exchangeable and non-exchangeable ammonium, the exchange-capacity values so obtained must in many instances have been much too high. Bower, Reitemeier, and Fireman (1952) have

sought to obviate the difficulty by using sodium acetate as the replacing reagent, and determining the number of me. per 100 g of Na^+ ion adsorbed by the colloid. However, Larson and Allaway (1950) find that Na^+ ion can likewise become fixed in non-replaceable form under certain conditions.

Phosphate Fixation. The subject of phosphate fixation in soils has been comprehensively reviewed by Dean (1949). In view of the extensive literature on the subject, the present discussion will be limited to the mechanism of phosphate fixation only. Murphy (1939), Stout (1940), Coleman (1945), Dean and Rubins (1947), Low and Black (1948), McAuliffe et al. (1948), and others have shown that phosphate can enter into anion exchange-reactions with clay. The mechanism of the fixation has, however, been a subject of some controversy in recent years.

Dean and Rubins (1947) have shown that anion exchange in soils increases with clay content and specific surface, and involves the lattice cations that are located at the broken edges of the mineral crystals. Clays have a definite anion-exchange capacity, as shown by the fact that they can alternately exchange arsenate and phosphate groups. Phosphate enters into such reactions and is readily exchanged by F^-, OH^-, tartrate, borate, and silicate ions. Exchange from kaolinite is rapid with dilute solutions of phosphate, and there is evidence to show that the exchange occurs between the phosphate ions and the free -Al-OH groups at the crystal edges. In the case of the kaolinitic clays, and anion- and cation-exchange capacities are approximately equal to one another. This is as might be expected, since the -Si-OH groups at the edges are responsible for cation exchange, and the -Al-OH groups for anion exchange. In montmorillonite and illite clays, anion adsorption is only a small fraction of the cation-exchange capacity, since the latter is the result of ionization which occurs at the planar surfaces. In the kaolin clays there is no charge resulting from lattice substitutions, hence the adsorption of both cations and anions is attributed to the accidental charges due to broken bonds.

Stout (1940), on the basis of chemical and X-ray evidence with phosphated kaolinites, found that the OH^- groups made accessible by grinding must have reacted with the phosphate ions, as evidenced by the loss of water at 150°C. Kaolinite lost 13.5 percent water, halloysite 21.2 percent, and bentonite only 0.2 percent, indicating that the interaction must have occurred between the phosphate and OH^- groups of the —Al—OH groups of the gibbsite layer of kaolinite. There being no corresponding OH^- groups available in montmorillonite, there was no interaction. Further, the equilibrium shifted to a more alkaline pH value as would be expected if OH^- groups were liberated in the interchange. The X-ray pattern of the fraction greater than 1 micron gave the characteristic pattern of kaolinite. However, when the <1 micron fraction was examined, the kaolinite pattern was destroyed, and the phosphated kaolinite was amorphous to X-rays. When the phosphated kaolinite was dephosphated, the X-ray pattern was the same as that of the original material. Stout therefore concluded that the amorphous character of the pattern for the phosphated kaolinite indicated that there had

been a disruption of the kaolinite layer packages resulting from the substitution of larger phosphate ions for OH ions within each cleavage plane. Restoration of the pattern on dephosphating indicated that the original alumino-silicate units of the kaolinite lattice had not been destroyed.

Thus the X-ray evidence obtained by Stout pointed to the fact that the fixation process was reversible. This fact was further confirmed by a calculation, from the altitude of the PO₄ tetrahedron and the diameter of OH⁻ ion, of the plane of repetition in kaolinite, and the value found was 9.4 Å.

Black (1942) and later Coleman (1945) in studies of phosphate fixation have reported evidence to show that the sorption of phosphate might be due to the presence of aluminum hydroxide on the surfaces of the kaolinite crystals. Both of these investigators removed the hydroxides and found that not only did the purified kaolinite adsorb negligibly small amounts of phosphate, but that the adsorption was not greatly dependent upon the pH value. Other clay minerals, montmorillonite, halloysite, and illite gave the same results, although on long standing, kaolinite gave a much higher adsorption at pH 3 than at pH 7. These investigators therefore concluded that Stout's results were less a property of the kaolinite, per se, than of the material that had resulted from the fine grinding.

Stout (1940) had found that the solution at equilibrium was less acid after phosphation. Coleman (1945) observed, however, that after removal of the ferric and aluminum hydroxides, there was little or no increase in pH value, and in most instances the pH value actually decreased. Hence he concluded that there had been little or no anion exchange between phosphate ion in solution and the OH groups on the clay minerals. Coleman's curves of phosphate fixed by montmorillonitic and kaolinitic clay, respectively, as related to the final pH value of the phosphate-clay mixture, show that these clays are able to fix only a small portion of the phosphate which was fixed before the free iron and aluminum hydroxides were removed. The phosphated clays were then extracted with Truog's reagent and the amounts of aluminum and iron hydroxides so removed were determined. The results showed that the phosphate was removed simultaneously with the hydroxides, and further, that the amounts of each were equivalent to one another, indicating that the fixation was the result of a simple interaction between the phosphate and the hydroxides of iron and aluminum. Moreover, the clay minerals themselves did not break down either during or after removal of the hydroxides, indicating that the hydroxides were not an integral part of the mineral lattice. Black (1942) assuming that during contact with the phosphate the clay might decompose, liberating soluble aluminum that might fix phosphate, treated the clay with acetic acid at the same pH as that of the phosphate solution used. The aluminum rendered soluble was far too small to account for the phosphate fixed. Hence the fixation must be attributed to the hydroxides natively present in the soil.

Low and Black (1948) obtained evidence to show that the phosphate does, in fact, react with kaolinite, but the product formed is not a phosphated kaolinite; instead, it is aluminum phosphate. If this were true, it would necessitate the liberation of silicic acid during the reaction. They assume a solubility product as follows:

$$[Al(OH)^{+\cdot}\gamma]^2 \cdot [Si_2O_5^{--}\cdot\gamma] = K_{SP}$$

in which the concentrations are molar concentrations, and γ the activity coefficient. Any ion capable of reducing the activity of either ion represented in the equation should therefore cause the clay to dissociate. Low and Black accordingly digested kaolinite at 60°C for 20 hrs with a solution containing 8-hydroxy-quinoline buffered to a pH of 4.7, and the determined amount of silica which appeared in the filtrate. They found silica to be released by this treatment, the amount increasing continuously to a maximum of 105 mg per 100 g of clay. This amount was over twice that obtained with ammonium chloride extraction, which does not precipitate the aluminum at 10 times the concentration and twice the time of digestion. The evidence is conclusive that kaolinite dissociates and yields aluminum which is then free to combine with any phosphate added, forming aluminum phosphate.

McAuliffe, Hall, Dean, and Hendricks (1948) have studied this problem by use of the isotopic exchange with $P^{32}O_4^{---}$. When a clay or soil is suspended in a phosphate solution, there should be an equilibrium established between the PO_4^{---} ions in solution and those associated with the solid phase. If $P^{32}O_4^{---}$ is introduced, keeping the total PO_4^{---} concentration constant, it should be possible to determine the equilibrium existing between the PO_4^{---} ions on the surface and those in the solution. Since this is a simple isotopic interchange, the equilibrium constant should be unity. Knowing the total $P^{32}O_4^{---}$ added and the $P^{32}O_4^{---}$ and $P^{31}O_4^{---}$ in solution, it should be possible to calculate the amount of $P^{31}O_4^{---}$ in solution. They found that two distinct changes are involved in the interaction between the phosphate in solution: the first is rapid and reaches equilibrium in 32 hours. It corresponds with the exchange of phosphate in solution with the phosphate on the surface. In the second stage, which is much slower, the ratio of P^{32} in the surface to the P^{32} in solution increases continuously with time. The phosphate which comes to equilibrium rapidly at the surface in the first step, correlates closely with the amount of available phosphate as determined by Truog's method and Neubauer determinations.

McAuliffe et al. (1948) reasoning that this difference in rate of phosphate adsorption must be related to the extent of the hydroxylic surface as well as to the lability of the OH-groups, measured the specific hydroxylic surface by way of an isotopic reaction involving deuterium oxide. Total surface was determined by ethane adsorption after the method of Brunauer, Emmett, and Teller. Their results show that in kaolinite and halloysite the percentage of hydroxylic surface relative to the total surface is about 2/3 of that which may be expected from the crystal structure of these minerals. The high values for the other (2:1) minerals probably result from diffusion of deuterium into the lattice where the deuterium atoms exchange with labile hydrogens. Hence these measurements indicate something as to the lability of the OH-groups within the crystal lattice. A comparison was

also made between the readily exchangeable P^{31} and the NaOH-soluble phosphorus. The data show that the percentage of the total surface occupied by P^{31} atoms is very small, which makes it appear that the fixation of phosphate by kaolinite does not occur by way of simple anion exchange with the soil colloid. Only a small fraction of the phosphorus that was presumed to be present as exchangeable anions was in direct equilibrium with the phosphorus in the soil solution. Since such an equilibrium apparently does not exist, it is not justifiable to conclude that phosphate is fixed by anion exchange on the kaolinite lattice.

DISCUSSION

W. P. Kelley:

In soil chemistry we are probably dealing, in a great many and perhaps all soils, with mixtures of clay minerals together with a great variety of other substances. Very commonly these clay minerals, particularly the layer types, are either interleaved or else so intimately mixed that separation is practically impossible; with the result that we rarely find good specimens of pure clay minerals. There is evidence that they do exist, but almost always they are associated with something else. That association is very likely to lead to some considerable variation in properties as contrasted with the properties of the relatively pure materials. We always have to bear in mind that the effect of the associated minerals on the soil will cause different properties than we would anticipate from a mere determination of which clay minerals are present. In addition, the alteration layers around the soil grains may very well influence the overall properties of the system. If we undertake to make an artificial soil from bentonite with quartz or with secondary minerals, we find that they have properties that are not exactly matched with those commonly found in soils. We are not therefore dealing with pure clay minerals or pure igneous silicates, but with silicates which have undergone more or less alteration, and clay minerals intermixed, perhaps interleaved. In other words, whether we deal with soil from the standpoint of agriculture or engineering we are sure to encounter differences in behavior from those that we would prophesy from mechanical mixtures of pure materials.

R. E. Grim:

In some soils the analytical data obtained add up to 100 percent, that is, it is felt that substantially everything that is in the soil has been identified. The lines in the X-ray diffraction pattern, for example, are of sufficient intensity that one feels that all the components are revealed. There are frequently other soils, however, in which one is convinced that there are constituents which may be amorphous to X-rays. Perhaps the pendulum has swung too far in considering that all argillaceous materials are 100 percent crystalline. I think there are some soils which contain a fair amount of material which has a low degree of crystallinity or is amorphous.

R. C. Mielenz:

A separation of an Ione California clay was made recently, and the amount of minerals apparent in X-ray diffraction analysis did not add up to 100 percent. This was particularly true of the fraction which appeared microscopically to be virtually all quartz with a particle size of 50 to 20 microns. According to our standard X-ray diffraction procedure the amount of quartz, in terms of the intensity, appeared to be only 35 to 40 percent of that fraction, and no other mineral was present. Has anyone else had this experience?

R. E. Grim:

Not specifically as applied to quartz, but we have had it with soils. For such materials the DTA method is frequently more sensitive than X-ray diffraction. It will detect smaller amounts of material with beginnings of nucleation, and in smaller particle sizes, than will X-ray diffraction.

W. D. Keller:

Some of the soils in Missouri are composed of partially altered primary minerals. That alteration may be chemical, or it may be mechanical pulverization, as in glacial flour. In weathering, groups of silica tetrahedra and other units are formed and appear amorphous to the X-ray. Will electron diffraction, which is said to have a higher degree of resolution, indicate some periodicity? Murata (1946) pointed out that silica gels form more readily with a certain alumina-silica ratio. These "alumina-silica wreckages" could be missed by the soil mineralogist; they may help to explain some phenomena in plant nutrition.

I feel that bacteria may play a very important part in the degradation of illite. This may be the reason for the difficulties encountered in identifying minerals in shales. Similar problems are encountered from a ceramic viewpoint. The different clays, such as china clay and ball clay, have characteristic properties which are difficult to explain on the basis of mineralogical composition. I suggest that some of these clays contain some partially weathered material which is utilizable by bacteria, but which is unrecognized mineralogically. Our instrumentation is not sufficiently precise to recognize differences in the clays, but bacteria are more sensitive than our laboratory instruments, and they do differentiate between them.

B. B. Osthaus:

Keller mentioned the breakdown of the amorphous or gelatinous material of some of these soils. The cation-exchange capacity of some of the different fractions of a montmorillonite that I mentioned in my paper, *Interpretation of Chemical Analyses of Montmorillonites* (herein), might relate to this problem. The original montmorillonite had a higher cation-exchange capacity than the first fraction, which started at about 1600 millimicrons. As we went down the particle-size scale, the cation-exchange capacity increased and reached a maximum which was above that of the original montmorillonite.

T. F. Buehrer:

In regard to the availability of fixed potassium: some interesting observations have been made by McGeorge on Superstition sand of the Yuma Mesa, in Arizona. Much new land in this area has been brought under cultivation by extensive irrigation developments from the Colorado River. The soil is 96 percent sand, and has an exchange capacity of 4 me. per 100 g. The amount of exchangeable potassium as determined by replacement with sodium ion is of the order of 0.7 me. per 100 g. The fine clay fraction consists of montmorillonite and hydrous mica in approximately equal proportions. Notwithstanding this soil has been continuously cropped for some 12 years, there has been no response observed in crops as a result of potash fertilization. The only conclusion is that potassium is being released for plant use from the nonexchangeable form. Plant studies have also shown that much of the potassium in finely ground orthoclase is available, apparently as a result of fracturing of the mineral.

R. L. Stone:

While I was at Ohio State University several years ago, we proposed to study the rate at which the alkali ions were removed from the surfaces of pulverized potassic and sodic feldspars, nepheline syenite, and anorthoclase when introduced into distilled water.

A paraffin-lined glass jar, filled with distilled water, was equipped with pH electrodes and a high-speed propeller. The open surface of the water was flooded with argon; the propeller was started and the L. & N. pH meter balanced. The powder was then released, and much to our surprise, the rate of change of pH was much faster than that type of electrode could follow. The pH changed from 6.9 (the water) to 9.5 in a fraction of a second for a potash feldspar. It continued to rise for a period of at least three weeks, when the pH was 9.8.

J. L. Gring:

Oblad (1951), of Houdry Process Corporation, wrote of the exchange of oxygen in calcined silica-alumina cracking catalysts. This would ordinarily be considered a very stable structure. I think the material had been given the usual calcination (1100° F) which gives a thorough dehydration. By using water that contained oxygen 18 instead of oxygen 16, in the form of steam going past the cracking catalyst, he found a very rapid exchange between the oxygen in the silica-alumina lattice and that which was in the steam going past. It is of interest that even in such a stable structure the oxygen is quite mobile and free to exchange between steam and a solid structure.

E. C. Henry:

In regard to the degradation of illite as a source of potash in soil, C. D. Jeffries made a very thorough study of the soils of Puerto Rico where he had an example of almost every type of soil, and where records had been kept for many generations (Jeffries, Bonnet and Abruna 1952). He showed an excellent correlation between the plant yield, the potash availability, and the amount of feldspar in the soil. Although illite was largely absent in Puerto Rican soils, the potash made available by the weathering of feldspars apparently would have made it unnecessary to call upon the degradation of illite even if both had been present.

T. F. Bates:

Leonard Sand, a former graduate student at Pennsylvania State College, has just completed a thesis on the weathering of feldspars and other minerals to kaolinite and halloysite in the Spruce Pine district of North Carolina (Sand 1952). A large proportion of the clay in that region is endellite, yet there is a considerable amount of coarse mica. Sand has established that in this area the kaolinite is formed directly from the mica, which is either primary in the pegmatites of the district, or formed by alteration of some of the feldspar. Under conditions of optimum leaching all of the feldspar went directly to halloysite. It is apparent that structural control imposed by the platy mica was the dominant factor which caused the formation of kaolinite under conditions more suitable for the formation of endellite.

When these clay minerals exist in such very fine particles, as I believe they may, it seems possible that the individual particles may be entirely crystalline and yet be so very small and with such tremendous surface area that they may act in relation to many processes as very poorly crystallized materials. As far as the particular particle is concerned, however, the lattice may be well developed.

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