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To the Graduate Council:

I am submitting herewith a thesis written by Joseph Houston Rule entitled "Selectivity, Fixation, and Exchange Equilibria of Potassium in Six Tennessee Soils and Soil Fractions." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agronomy.

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SELECTIVITY, FIXATION, AND EXCHANGE EQUILIBRIA OF POTASSIUM IN SIX TENNESSEE SOILS AND SOIL FRACTIONS

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

---

by

Joseph Houston Rule

August 1970

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ABSTRACT

Selected physical, chemical, and mineralogical properties were listed for reference samples from the soils from which the samples studied were obtained. Investigations were conducted to compare properties of the samples used to the properties given for the reference samples.

Six soils were used in the studies and each soil was separated into five fractions on the basis of particle size. Calcium and potassium exchange capacities were determined for all soils and soil fractions. The calcium was determined by chemical means and the potassium by the use of radioactive potassium. Calcium exchangeable potassium and the additional ammonium exchangeable potassium were determined for all soils and soil fractions.

Selectivity coefficients for the replacement of calcium by potassium on the soils were determined by the leaching column method. Potassium plus calcium solutions having a total concentration of 0.002N with three ratios of calcium to potassium were used.

Free energies, standard heats and entropies for the exchange of calcium by potassium on the soils were evaluated at two temperatures.

Selectivity coefficients for the replacement of calcium by potassium on the soils and soil fractions were determined using radioactive potassium-42 traced potassium plus calcium solutions. The solutions used had a total concentration of 0.002N and three ratios of calcium to potassium. A solution having a total concentration of

0.02N was employed, but only one ratio of calcium to potassium was used at this concentration. The potassium "fixed" against extraction by calcium was measured on part of the soils and soil fractions after determination of the selectivity coefficients.

The Iberia sand fraction was found to possess an unusually high cation exchange capacity. It was noted that most of the material in this sand fraction was concretionary. Investigations were made to determine the nature of this material. Presence of a pH dependent charge was studied, and x-ray diffractograms, specific gravity determinations, a partial elemental analysis, and an x-ray spectral analysis were run in the investigations. Photographs of the material were obtained through a microscope and features shown in the photographs were discussed.

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CHAPTER I

LITERATURE REVIEW

The amount of literature concerning studies of potassium is voluminous and its scope is tremendous. For an overview of this literature, the reader is referred to the articles by Kilmer, Younts, and Brady (editors) (30) and Reitemeier (42). Marshall (35,37) gave a review of the ionic exchange reaction of clays. The reader will find many basic concepts in or referred to in these articles.

Page and Baver (40) proposed the following theory for the fixation of K by montmorillonite type minerals. They reasoned that the potassium fixation caused by drying should be related to (1) the ionic size of potassium and (2) the contraction of the expanding lattice. The 001 spacings vary with the water content of the colloid. When fully hydrated, the sheets are far apart and ions can freely exchange in the interlayer positions. But, if the colloid is nearly dehydrated, the sheets are close together and the exchange of adsorbed ions is hindered. The rehydration process is generally thought to occur easily upon the addition of water. However, if an ion of the proper size could form a stable structure upon dehydration, the structure would not swell upon remoistening. This would thus leave the ion trapped or "fixed" in the interlayer position.

The exposed surface between the sheets of montmorillonitic minerals consists of a layer of hexagonally arranged oxygen atoms. Spaces in the center of the hexagons are the size of the oxygen

ions - 2.8Å, and the diameter of the hydrated potassium ion is 2.66Å. As such a system is dehydrated, the potassium would lose its water of hydration and the sheets could come in contact. Upon completion of the process, the ion is probably forced into the free space in the exposed surface. Once in this position, the ion should be held tightly because (a) the ion is very close to the negative charges from within the crystal, (b) these charges and the closeness of contact of the sheets should prevent re-expansion upon the addition of water, and (c) even if re-expansion should occur, the position of the ion should make it unlikely that it would move far enough away from its position to be exchanged. Larger cations could not enter these interlayer sites and smaller cations would be too small to bind the layers together.

Unhydrated ionic radii of some of the most frequently studied cations are (in Å): Li = 0.68, Na = 0.98, NH_4 = 1.21, K = 1.33, Rb = 1.48, Cs = 1.67, Mg = 0.71, Ca = 0.98, Sr = 1.15, and Ba = 1.31. The hydrated ionic radii of these ions are: Li = 6, Na = 4.3, NH_4 = 2.96, K = 3, Rb = 2.5, Cs = 3.38, Mg = 8, Ca = 6, Sr = 5.5, and Ba = 5 as calculated from the Debye-Huckel formula. Ions having hydrated radii similar to the radius of potassium are expected to behave similar to potassium, thus, articles concerning studies of ions other than potassium are reviewed.

Beckett (5) conducted equilibrium studies between K and Ca ions on the exchange surfaces in some field soils. He found that equations of the type of Gapon or Ericksson adequately described the equilibrium only when the soil already held a certain amount of exchangeable

potassium. An equation like the Langmuir adsorption isotherm best describes the exchange equilibrium involving the first quantity of exchangeable potassium. Beckett then postulated that there are sites possessing a specific binding power for potassium which hold a certain number of potassium ions. Preliminary experimental thermodynamic consideration of the exchange system also agreed with this postulate.

For a soil of low exchangeable potassium, the entropy of exchange of potassium has an abnormally high value. One reason is that the potassium ions held at specific sites have an incomplete hydration shell. A second reason is that the number of ways of distributing exchangeable ions on the surface is reduced by the presence of both specific and nonspecific adsorption sites. The specific sites may be in intra-lattice positions at the edges of the clay crystals. However, Beckett felt that this theory needs further proof.

Rich (43) and Rich and Black (44) stated that the wedge zone is important to the extent of the "catalytic" effect of this configuration in potassium selectivity. Because of the space limitations for diffusion in the wedge zone, potassium is selected from among large hydrated ions (e.g. Ca or Mg). There will be only a small amount of potassium selection if the wedge zone is near the edge of the particle. However, considerably more potassium can be selected as a result of the "catalytic" effect if the zone is deep within the particle. Selection of potassium occurs at the wedge site in very low potassium concentrations. With increasing potassium concentrations,

With increasing potassium concentrations, first, there is collapse of the silicate layer at the wedge site, and second, there is the tendency for collapse of the silicate layers at the edge of the particles where exchange is initiated resulting in entrapment of ions deeper within the crystal.

Clay-size muscovite and many soil clays have low exchange capacity. The exchange capacity would be 0.25 meq/100g for the 2μ fraction and 2.5 meq/100g for the 0.2μ fraction for the edges of these particles. High potassium selectivity of these materials cannot be explained by selection of potassium at specific sites on the edges of the particles. Thus much potassium selectivity probably occurs in the interlamellar region. In selectivity studies, it is of prime consideration to determine whether all of the specific sites occur near the edge or whether many are deep within the crystal. Studies on "planar" sites, "edge-interlattice" sites, and interlattice positions of potassium and equilibrium concerning these sites were conducted by Bolt, Sumner, and Kamphorst (7).

Tamura (48) found high selectivity of Cs by layer lattice silicates with unexpanded 10Å c-spacing. This occurred from solutions where the sodium:cesium ratio was 8000. He proposed that the cesium sorption tests can be a useful indicator of the structural conditions of the 2:1 layer lattice silicates. The sorption tests show differences within the montmorillonite series such as between Arizona and Wyoming bentonites. He further stated that the use of cesium sorption reactions may prove to be a method for detecting the presence of montmorillonites.

Jacobs (26) studied cesium sorption by hydrobiotite (called vermiculite by Jacobs) and methods to increase the fixation of the Cs. Addition of K (also Rb, Cs, and NH_4) to the influent solution resulted in "interlayer fixation" of cesium. Fixation resulted from the collapse of the lattice in the manner described by Rich (43). Previously, Jacobs and Tamura (27) had jointly described this cesium fixation process.

Dolcater, et al (13) used sodium saturated materials and mixed solutions of a total strength of 0.005N in equilibrium studies. They found that the K/divalent ion equivalent ratio (K/Ca cation exchange selectivity value) generally increased in the order: montmorillonite< vermiculite<Harpster (soil clay)<Triangle (soil clay)<biotite<muscovite. The Harpster contained approximately 43 percent vermiculite, 12 percent montmorillonite, 13 percent mica, 10 percent kaolinite, 14 percent chlorite, and three minor constituents. The Triangle contained the following amounts of the aforementioned minerals (in the same order): 29 percent, 29 percent, 13 percent, 18 percent, zero, and in addition 13 percent allophane. The above order of minerals for the K/divalent ion ratio follows the order of increasing layer charge and surface charge density. It also follows, with the exception of vermiculite, the order of decreasing CEC.

Jenny and Ayres (29) reported that potassium availability to plants was greater when calcium rather than hydrogen was the complementary ion. This was especially true at low levels of potassium saturation. Seatz and Winters (46) found that there was a greater release of potassium from calcium soils than from hydrogen soils at low levels of potassium application.

Marshall (36) stated that the activity of potassium was greater when calcium was the complementary ion than when other complementary ions were present. Barber and Marshall (2) found that increased calcium saturation greatly increased the potassium activity. Increased potassium, up to about 60 percent potassium saturation, lowered the calcium activity.

Salmon (45) stated that in soil soil-solution systems the proportion of divalent to univalent cations is decreased on diluting the solutions. Salmon discussed Schofield's 'Ratio Law' which can be expressed as

$$\frac{(a_{M_1})^{1/Z_1}}{(a_{M_2})^{1/Z_2}} = \text{a constant},$$

where M_1 and M_2 are cations of valency Z_1 and Z_2, in dilute solutions in equilibrium with adsorbed cations. In the case of soils having a predominant negative charge, and being saturated primarily by calcium, the ratio is independent of total electrolyte concentration up to 0.06M. Also, the adsorbed cations are not affected by the volume of the solution in equilibrium with the soil.

Activity ratios in soil solutions are dependent on the proportions of different exchangeable cations. However, changes in these proportions alter the activity ratios differently in different soils. These differences may reflect different cation-exchange capacities of the soils or different strengths of adsorption of the cations by the soils. Beckett (45) concluded that upon depleting the exchangeable

potassium, changes in the ratio $a_K/a_{(Ca + Mg)}^{1/2}$ in the solution were influenced more by the exchange capacity of the soil than by different strengths of adsorption. Workers such as Beckett (3,4) and Tinker (49,50) stated that the activity ratio provides a good measure for comparing soils of similar calcium status but must be used with caution with highly acid soils and those with variable calcium content. Matthews and Beckett (38) further confirmed the above statements by discussion of instantaneous potassium equilibrium. This equilibrium provides a base from which to investigate potassium fixation and release.

Several authors such as Davies (11), Gaines and Thomas (16,17), Jenny (28), Krishnamoorthy and Overstreet (31), and Vanselow(52) have offered expressions for determining the equilibrium constant for replacement reactions for soil or clay particles. Gapon, referred to by Krishnamoorthy and Overstreet (31), was among the first who offered an equation describing the replacement of one cation by another from a soil particle. His equation was a simple, straightforward mass-action type of equation. Gapon offered no correction factor for varying strengths of solutions or for different cations. Later workers including Gaines and Thomas (16,17), Krishnamoorthy and Overstreet (31), and Vanselow (52) added these correction factors to their equations.

Krishnamoorthy and Overstreet (32) offered a comparison of their equation to two others. They compared Gapon's and Vanselow's (52) equations with their own. Their equation was based on Guggenheim's theory (20,21) and included a correction term of 1.5 to be multiplied

by the amount of adsorbed divalent cation. These three equations were derived from different assumptions concerning the "activities of ions" in the adsorbed state. To test the above equations, Krishnamoorthy and Overstreet adjusted their experimental conditions so that the proportions of adsorbed ions varied over a wide range. Bentonite, synthetic resins, and three soil clays, one predominantly montmorillonitic, one of the hydrous mica type, and one largely kaolinitic were used.

For ions of equal valency, all of the proposed ion exchange equations reduce to the same relationship. Experiments dealing with monovalent-monovalent and divalent-divalent ion pairs gave very acceptable results, with the exception of hydrogen. They stated that, from unpublished results, the exchange constant for a pair of ions was independent of the mass of the adsorbent and the volume of the solution.

Gapon's equation was found to be unsuitable for monovalent-divalent ion pairs. The equation of Vanselow and the equation of Krishnamoorthy and Overstreet were found to be very satisfactory for this type except where hydrogen was one of the ions.

Gapon's equation was also found to be completely inadequate for monovalent-trivalent ion exchanges. For these pairs, Guggenheim's formulation was entirely suitable and Vanselow's equation gave somewhat less satisfactory results. Again, both cases were with the exception of ion pairs involving hydrogen. Krishnamoorthy and Overstreet further state that neither Gapon's, Vanselow's, or their equations gave satisfactory constants for mixtures of adsorbents with widely different exchange properties.

Lagerwerff and Bolt (33) reported a theoretical basis for Gapon's equation which described ion exchange equilibria in binary systems containing monovalent and divalent cations.

Ericksson (15) gave a comparison of various cation-exchange equations to those derived by regarding the exchanger phase plus solution phase as a Donnan system. According to Ericksson, Jenny (28) used statistical considerations. Jenny interpreted the constant as the ratio of the "oscillation volumes" of the two ions around the exchanger. This model is not compatible with a diffuse double layer concept.

According to Ericksson, Vanselow (52) regarded the exchanger with its ions as a mix-crystal or, better, a solid solution in deriving his equation. However, the exchanger, Z, cannot exist as Z^- as it would have to for the ideal application of the exchange equation. Therefore, the similarity between the exchanger and a solid solution is only formal.

Ericksson further stated that Krishnamoorthy and Overstreet approached the subject with the same principle as Vanselow. However, these authors altered the mole fraction term in the presence of polyvalent ions. They also assumed a relatively homogeneous exchanger phase which is not compatible with a diffuse double layer.

Ericksoon then discussed alteration of the above equations to fit his Donnan system. He stated that the experiments referred to were carried out using relatively high salt concentrations, both in the solution and collodial phases. In contrast, under most field conditions one finds rather dilute solution concentrations.

Bolt (6) reported that the exchange equilibria of Na-Ca-illite was best described on the basis of the existing double layer theory and no arbitrary constants were needed. He then implied that one can explain the relative adsorption of Na and Ca by illite as being almost completely dependent on their valences. The double-layer theory was compared with other existing theories on ion exchange equilibria. Bolt then indicated how specific interactions between clay surfaces and ions can be evaluated by exchange equilibrium data.

Gaines and Thomas (16) wished to have a formulation of equilibrium relations which was derived for a model defined in terms of directly measurable quantities. They wanted the formulation to be rigorously thermodynamic in character. A formula derived on this basis would be very clear as to the meaning of the terminology. In a given case, the applicability of the results would be determined by the quantities measured. They stated that inspection of their model reveals how closely any real system approaches the character of the model.

The proposal was then offered to obtain an adequate thermodynamic treatment of the ion exchange process on a montmorillonite clay. Their model was that the solid exchanger is to be a substance with a fixed number of exchange sites per unit mass of silicate "backbone." This exchanger is "capable of adsorbing water (and possibly other solvents) and <u>incapable</u> of adsorbing the negative ions of the surrounding solution." (16)

Gaines and Thomas (17) conducted adsorption studies on montmorillonite-cesium-strontium at temperatures from 5° to 75°C. They used an equilibrium column technique and employed isotopic tracers. It was found that the exchange capacity of the clay is independent of the temperature, the initial composition of the clay, and, to a good approximation, independent of the solution concentration.

Total solution concentration was 0.0500N. The ratio of the cesium concentration to that of the total concentration, c_{Cs}/c_o, varied from 0.0025 to 0.700. Adsorbed cesium, q_{Cs}/q_o, increased as the c_{Cs}/c_o increased, and decreased as the temperature increased.

Lewis and Thomas (34) conducted equilibrium studies on montmorillonite using the equilibrium column technique. Monovalent-monovalent (Cs - Na), divalent-monovalent (Ba - Na), and monovalent-divalent (Cs - Ba) exchanges were studied by the use of radiotracers. Equilibrium coefficients were calculated using the formulation of Gaines and Thomas. Activity coefficients of the cations on the exchanger surface were calculated. In general, the equilibrium coefficient decreased as the minor cation in the solution increased. The Cs - Na system gave the best results, the Ba - Na system gave irregular values for the equilibrium coefficient as the Ba in the solution increased.

Free energy values were calculated from the reactions and for the relation 2(Cs - Na) minus (Ba - Na) equals (Cs - Ba). The calculated value for (Cs - Ba) was in very close agreement with the experimental value (3808 calories calculated versus 3677 calories

observed). It was concluded that there were no gross undetected errors in the experiments. Deviations from ideality of the surface activity coefficients were observed in the region of high content of the selectively held component. The authors stated that a study of the temperature effect on the equilibria was needed before further meaningful discussion could be given.

Coleman, Craig, and Lewis (9) studied Cs - Ca and Cs - K sorption equilibria on montmorillonite, vermiculite, and soil clays using the leaching column technique. Cesium sorption was much larger from Ca than from K solutions. After sorption from the two ion system, leaching with 1N KCl removed 36 times as much Cs from the clays as did equal volumes of 1N $CaCl_2$. Vermiculite sorbed up to one-third of its exchange capacity of Cs from 0.001N CsCl - 1N $CaCl_2$ solutions. Most of the sorbed Cs was "fixed" against exchange with 1N $CaCl_2$, but not with 1N KCl.

Coleman, Lewis, and Craig (10) used montmorillonite, vermiculite, illite, and kaolinite in cesium sorption studies. It was found in these studies that cesium sorbed by montmorillonite, illite and kaolinite was readily displaced on leaching with 1N KCl or $CaCl_2$. Vermiculite and heated K-montmorillonite bound Cs against displacement by $CaCl_2$ and $AlCl_3$, but not KCl or NH_4Cl. The authors stated that the exchange-displacement behavior of Cs on vermiculite and heated K-montmorillonite suggests that its sorption in interlayer spaces leads to interplanar distances which admit K and NH_4, but greatly restrict the entry of Ca. They concluded that the "fixation-release" rules developed for K and NH_4 would not apply to Cs.

Woodruff (53,54,55) used free energies of exchange of Ca and K to evaluate the status of these ions in the soil. Solution activity ratios were used in calculating the free energies of exchange. He defined a range of free energy values for the replacement of calcium by potassium which defines potassium deficient (-3,500 to -4,000 cal.), "ideal" (-2,500 to 3,000 cal.) and calcium deficient (<-2,000 cal.) soils. Free energy was found to be related to the amount of exchangeable potassium in soils.

CHAPTER II

METHODS AND PROCEDURES

Six Tennessee soils with different properties from various regions of the state were used in the studies. The soil types were Baxter cherty silt loam, Hartsells loam, Iberia silty clay, Maury silt loam, Memphis silt loam, and Sequoia silt loam. Selected properties of these soils are given in Table I. The exact locations of the sample sites are given in the Appendix.

Soils Descriptions

The Baxter soil is a typic paleudult - clayey, mixed, mesic. The site of the sample used is located in the Highland Rim region of Middle Tennessee. It is a deep, well-drained upland soil derived from cherty limestone. This soil has a low natural fertility, is medium to strongly acid, and has a moderately low available water holding capacity (22).

The Hartsells soil is a typic hapludult - fine loamy, siliceous, thermic. The sample site is located in the Cumberland Plateau region of East Tennessee. It is a moderately deep, well-drained upland soil developed from level-bedded, acid sandstone and sandy shale. This soil has a low natural fertility, is strongly acid, and has a moderate to moderately high available water holding capacity (23).

The Iberia soil is a vertic haplaquoll - fine, montmorillonitic, noncalcareous, thermic. The sample site is located in the Central Basin in Middle Tennessee. It is a deep, poorly drained basin soil

TABLE I

SELECTED PHYSICAL AND CHEMICAL PROPERTIES OF THE SOILS[a]

U.S.D.A. Particle Size Dist. (%)					Chemical Analysis				
Sand 2.0-.05mm	Silt .05-.002mm	Clay <.002mm	Gravel >2.0mm (Whole soil)	Mineralogical Analysis	pH (1:1 H_2O)	Percent O.M.	CEC (meq/100g)	Total Bases (meq/100g)	Percent Base Saturation
				Baxter Cherty silt loam					
9.4	78.2	12.5	5.0	$V_2K_2I_2Q_2$	4.8	1.29	4.94	0.83	16.8
				Hartsells loam					
41.4	44.7	14.0	0.1	$V_1K_2Q_2I_3$	4.9	0.82	4.85	1.19	24.5
				Iberia silty clay					
7.0	43.7	49.3	0	$M_2K_2Q_1$	6.3	3.01	40.80	33.30	82.0
				Maury silt loam					
15.3	60.6	24.0	0.4	$V_2(V/M_2)K_2I_2Q_3$	6.1	2.57	17.50	14.92	85.3
				Memphis silt					
10.6	79.3	10.0	0	$M_2I_2K_2Q_3$	6.9	1.89	13.78	16.08	116.7
				Sequoia silt loam					
7.6	72.0	20.4	2.9	$V_2K_2M_2Q_2$	4.8	1.86	8.62	2.74	31.8

[a]Department of Agronomy, University of Tennessee, Knoxville, Unpublished Data.

developed from alkaline clayey alluvium. This soil has a high natural fertility, is medium acid to mildly alkaline and noncalcareous, and has a moderate available water holding capacity (39).

The Maury soil is a typic paleudult - clayey, mixed, mesic. The sample site is located in the Outer Basin region of Middle Tennessee. It is a deep, well drained, upland soil developed from weathered residuum of phosphatic limestone. This soil is highly productive, high in phosphorus, moderately acid, and moderate in available water holding capacity (51).

The Memphis soil is a typic hapludalf - fine - silty, mixed, thermic. The sample site is located in the Deep Loess region of West Tennessee. It is a deep, well drained upland soil, developed from loess. This soil is highly productive, slightly to strongly acid, and high in available water holding capacity (8).

The Sequoia soil is a typic hapludult - clayey, mixed, mesic. The sample site is located in Blount County in East Tennessee. It is a moderately deep, well drained upland soil developed from leached or acid shale bedrock. This soil is low in fertility, medium to strongly acid, and moderate in available water holding capacity (14).

All soil samples had been previously collected with the exception of the Iberia, which was collected by the author. The Ap or A_2 horizons of the soils were used. All samples were air dried, crushed, and passed through a 20 mesh (1.0mm) sieve.

Particle Size Separation

The procedure used was a modification of the one described by Jackson (24) and is briefly described as follows. Approximately 100g of each soil was treated with 30 percent H_2O_2 to remove the organic matter, then with 2 percent Na_2CO_3 to aid in dispersion. Dispersion was accomplished by the use of a malt mixer after which the sands were separated by wet sieving on a 300 mesh screen, washed, dried, and stored. Silt and clay suspensions of each sample were maintained below a one percent level during separation. Clay fractions were separated by the sedimentation process. Silt fractions were then subdivided by sedimentation and the clays were subdivided by the use of a Sorvall continuous flow supercentrifuge. Silt and clay fractions were Mg saturated, washed salt free with 95 percent ethanol, and dried at 50°C. All samples were then reground and stored until used. The soil fractions and their size ranges were: Sand (1000-50μ); coarse silt (50-20μ); fine silt (20-2.0μ); coarse clay (2.0-0.2μ); and fine clay (<0.2μ). The silt and clay size fractions will hereafter be identified by the adjectives coarse and fine.

X-Ray Diffraction Analysis of the Soil Clays

Dried clay samples were dispersed in water and saturated with the desired cation after which the suspensions were dried on glass slides. Four x-ray diffractograms were made on each clay fraction. The diffractograms were made after the following treatments:

1. Mg saturated, air dried.

2. Mg saturated, ethylene glycol solvated by exposure to glycol vapors for three to four days at room temperature.
3. K saturated, air dried.
4. K saturated, heated to 500°C.

The slides were x-rayed with a Norelco vertical goniometer, x-ray diffractometer utilizing CuKα radiation on which kilowatt and milliamp settings were 30 and 18, respectively. The basal spacings were determined from charts for the solution of Bragg's equation (41).

Vermiculite Content of the Iberia Clay

The percent vermiculite in the Iberia clay was determined according to the procedure of Alexiades and Jackson (1).

Organic Matter Determination of the Soils

The organic matter content of the soils was determined using the acid chromate digestion procedure (47).

Soil pH Determination

The pH of the soils was determined on a 1:1 soil-water suspension using a glass electrode pH meter.

Whole Soil Cation Exchange Capacity Determinations

One set of values was determined using Ca (as 0.1N $CaCl_2$) as the saturating cation and Na (as 0.1N NaCl) as the extracting cation. A second set of values was determined using Ca (as 1.0N $CaCl_2$) as the saturating cation and NH_4 (as pH 7, 1N CH_3COONH_4) as the extracting cation. Each soil was replicated twice in both determinations.

Elemental chemical determinations for all procedures were made with a Perkin Elmer Model 303 atomic absorption spectrophotometer.

Cation Exchange Capacity Determinations of the Soil Fractions

Three one gram samples for each soil fraction were weighed into 50 ml. centrifuge tubes. Samples were Ca saturated by four centrifuge washings of 0.05N $CaCl_2$. The samples were allowed to stand overnight in the first aliquot of the $CaCl_2$. Excess electrolyte was removed by centrifuge washing with water, followed with 95 percent ethanol until the supernatent gave a negative test for Cl by the use of $AgNO_3$. The samples were then extracted with 0.05N Na as NaCl, made to volume and the Ca determined as previously described.

Calcium Exchangeable Potassium and the Additional Ammonium Exchangeable Potassium of the Soils and Soil Fractions

Saturation and initial extraction was carried out the same manner as for the Ca CEC determinations, using, in this case, 1N K (as KCl) as the saturating cation and 1N Ca (as $CaCl_2$) as the first extracting cation. One set of soil minus organic matter samples were dried in the presence of K before extractions were made. They were treated as follows: After K saturation and one washing with water, the samples were resuspended in a minimum amount of water and allowed to dry at room temperature. After drying, they were resuspended in 95 percent ethanol and further treated as all other samples. After the K extraction by Ca for calculation of the calcium exchangeable potassium, (Ca - ex - K), the samples were washed twice with 95 percent

ethanol to remove excess $CaCl_2$. The samples were then extracted four times by centrifuge washing with a total of 40ml 1N NH_4Cl, the extract made to volume and the K determined as previously described. The amount of K determined by this extraction was called the additional ammonium exchangeable potassium, (NH_4 - ex - K).

Potassium Selectivity Studies on the Soils Using Leaching Columns

Leaching columns were prepared using from 1:1 to 1:4 soil to cellulose powder mixtures, the ratio used for each soil being determined by its texture and cation exchange capacity. The ratios were such that all mixtures would leach at about the same rate and the cation exchange capacity of the columns were similar.

Appropriate amounts of soil and cellulose powder were placed into an evaporating dish, moistened, and thoroughly mixed. After drying at 60°C, the mixture was lightly ground with a pestle to obtain a fine, uniform mixture. The leaching columns were glass and were an average of 1.6 cm in inside diameter and 22 cm in length. A plug of glass wool and approximately 0.75 g of cellulose powder was placed in the bottom of each column after which the soil and cellulose powder mixture was added and packed to a uniform density. Cellulose powder and a glass wool plug were then added to the top of the mixture. The columns were placed into a vacuum, wetted slowly from the bottom, with 1N NaCl, to reduce the number of air bubbles in the wetted columns. OneN NaCl was leached through the columns to insure removal of all other ions and to insure Na saturation. Soil columns were

then leached slowly (1.5 - 2 ml per minute) with the appropriate 0.002N (Ca + K) solution (see below). Leaching continued until equilibrium (the concentration of effluent Ca was the same as influent Ca) was reached. Fifty ml of 95 percent ethanol was added to remove the excess electrolytes. Approximately 100 ml of 1N NaCl (for Set I) or 1N $BaCl_2$ (for Set II and Set III) was used to extract the Ca and K. Extracts were made to volume and the Ca and K determined as previously described. The (Ca + K) solutions (Ca as $CaCl_2$ and K as KCl) were:

Set	(Ca + K), N	Ca, N	c_{Ca}/c_o	K, N	c_K/c_o	%K
I	0.002	0.0019	0.95	0.0001	0.05	5
II	0.002	0.0018	0.90	0.0002	0.10	10
III	0.002	0.0016	0.80	0.0004	0.20	20

For these studies, the free energy studies, and the potassium-42 studies, equilibrium selectivity coefficients for the reaction

$$2K^+ + CaM_2 \rightleftarrows 2KM + Ca^{++}$$

were determined. Two coefficients were calculated. The first, K_c', called the "rational equilibrium coefficient," was determined by

$$K_c' = \frac{(q_K/q_o)^2 \ (c_{Ca}/c_o)}{(q_{Ca}/q_o) \ (c_K/c_o)}$$

where q_K/q_o = (meq K /100g) / [meq(Ca + K)/100g] and c_K/c_o = (N of K in solution) / [N of (Ca + K) in solution]. A second equilibrium coefficient, K_c'', was calculated using the formulation of Gaines and

Thomas (16) where

$$K_c'' = \frac{1}{2c_o} \frac{[1-(q/q_o)]^2 (c/c_o)}{(q/q_o)[1-(c/c_o)]^2},$$

the values of c/c_o and q/q_o were for Ca. Methods of calculation are the same for both coefficients, the latter values being larger by a factor of 250 for c_o=0.002N and 25 for c_o=0.02N values. Reasons for using both values will be discussed in the results and interpretations.

Determination of the Free Energies, Enthalpies and Entropies of Exchange for the Replacement of Calcium by Potassium on the Soils

Soil columns were prepared, wetted, leached, and extracted in the same manner as previously described for the potassium selectivity studies. In this case, however, Ba, as 1N $BaCl_2$, was the initial saturating cation and pH 7.0, 1N CH_3COONH_4 was the extracting solution. The leaching solution was 0.002N (Ca + K) with c_K/c_o=0.10. Temperatures used were 8°C and 23°C and the temperature variation was ± 1.0°C.

Equilibrium selectivity coefficients were calculated using the method of Gaines and Thomas (16). Free energies of exchange, $\Delta G°$, were calculated by $\Delta G° = -RT \ln K_c''$. Standard heats of exchange (enthalpy), $\Delta H°$, were determined from a graph of $R \ln K_c''$ versus 1/T using the relationship $(d \ln K_c'') / (d\ 1/T) = -\Delta H°/R$ at $dP = 0$. $\Delta H°$ must be assumed to remain constant over the temperature range for the relationship to be correct. Standard entropies of exchange, $\Delta S°$, were then calculated from $\Delta G° = \Delta H° - T\Delta S°$ where T is the absolute temperature.

A means of determining K_c'' values at any given temperature for each soil was derived as follows:

1. $\frac{d}{dT}\left(\frac{\Delta G^\circ}{T}\right) = -\frac{\Delta H^\circ}{T^2}$, at $dP = 0$.

2. $d\frac{\Delta G^\circ}{T} = -\frac{\Delta H^\circ}{T^2}\,dT$

3. Integrate equation 2

4. $\frac{\Delta G^\circ}{T} = \frac{\Delta H^\circ}{T} + I$, where I is the constant of integration

5. $\Delta G^\circ = \Delta H^\circ + IT$

Equation 5 was solved for I for each of the soils. Since ΔH° is a constant, for each soil, one may solve for ΔG° for any temperature, T, and thus determine the equilibrium selectivity coefficient, K_c'', for that temperature.

Potassium Selectivity as Determined from Potassium-42 Labeled (Ca + K) Equilibrium Studies

The total strength of the solutions was 0.002N (Ca + K). Solutions with varying amounts of K were used and were the same as described for the leaching column studies. A second study involved the use of 0.02N (Ca + K) but only at the 5 percent level of K.

The samples were weighed into 15 ml tubes, with three replications for each sample. Sample amounts were:

Sample	g/sample
soils	0.5000
sands	1.0000
silts	0.5000
clays	0.1000

All samples were Ca saturated by treatment with 5 ml portions of 1N $CaCl_2$ by centrifuge washing. Excess electrolyte was removed by centrifuge washing with 5 ml portions of 95 percent ethanol. Radioactive potassium-42 (K-42) was added to the (Ca + K) solutions in tracer amounts. A 5 ml portion of the desired (Ca + K) - (K-42) solution was added to each sample. The samples were then placed in a horizontal shaker for approximately five hours after which they were centrifuged and the clear supernatent discarded into a K-42 waste container. The samples were centrifuge washed with 5 ml portions of ethanol to remove the excess electrolyte. Potassium-42 remaining on the samples was determined with a nuclear Chicago Analyzer/Scaler model 8725 with a solid NaI(Tl) scintillation crystal. The amounts of potassium calculated from this determination was the total sorbed potassium. Solution K was determined by subtraction of this value from the amount of K originally present. These amounts were used in the calculation of the selectivity coefficients, K_c' and K_c''.

Activities and activity ratios were calculated for the equilibrium solutions. Average activity coefficients were calculated for each of

the concentration levels using the Debye-Huckel formula where $\log \gamma = -0.509\ (Z^2)\ \sqrt{I}$, $I = \frac{1}{2} \Sigma\ (\underline{M}\ Z^2)$ and the activity, a, = $\underline{M}\ \gamma$. The average activity coefficients are given in Table A-VIII in the Appendix.

Activity ratios for the reaction studied, as written, are given by the expression $(a_{Ca})/a_K)^2$. However, the ratios were calculated as $a_K/(a_{Ca})^{1/2}$. Thus, a comparison can be made to $\Delta G°$ values given by Woodruff (53,54,55) in evaluating the Ca and K status of a soil. Free energies were calculated using K'_c, K''_c, and activity ratio values. All values were calculated by the general expression $\Delta G° = RT \ln a$.

The samples were then centrifuge washed with 5 ml portions of 1$\underline{N}$ $CaCl_2$ to remove all exchangeable potassium. Amounts of K-42 remaining on the samples were determined and the "fixed" K was calculated. Standards for each (Ca + K) solution and for sample tubes of different geometric configurations were prepared. These standards were used to construct decay curves for the K-42. K concentrations on the samples were computed by using the K-42 decay curves and the initial solution concentrations. The K-42 was carrier free, free of other radioactive substances, and initial purity of the source was 99.9 percent.

Potassium exchange capacity values were determined by using K-42 labeled 1$\underline{N}$ KCl and the same procedure as described above was used for determining the sorbed K.

Fractionation of the Iberia Sand

For reasons discussed in the results and discussion section, the Iberia sand fraction was subjected to a more thorough study than any of the other sands. The sand fraction was divided into the following separates by the procedure given in the Soil Survey Investigations Report No. 1, p. 9 (47): 2-1mm, 1.0-0.5mm, 0.5-0.25mm, 0.25-0.10mm, and 0.10-0.05mm.

Cation Exchange Capacity Determination of the Iberia Sand Separates

The samples were Ca saturated using pH 7.0, 0.5N $CaCl_2$ and extracted with NH_4 as pH 7.0, 0.5N CH_3COONH_4. There were three replications for each separate.

Specific Gravity Separations of the Iberia Sand

Separates of the Iberia sand were subdivided on the basis of specific gravity by the heavy liquid procedure given by Jackson (24, pp. 473-480). The specific gravity groups were: >2.96, 2.96-2.72, 2.72-2.65, 2.65-2.60, and <2.60.

Elemental Analysis of the Iberia Sand Separates

Selected separates of the Iberia sand size fraction and specific gravity separations were totally digested by the method given by Jackson (25, pp. 272-284). The sample size fractions used were: 1-0.05mm, 2-1mm, 1-0.5mm, 0.5-0.25mm, 0.25-0.1mm, and 0.1-0.05mm. In addition, the following size fractions of the material having a specific

gravity of <2.96 were also analyzed: 2-1mm, 1-0.5mm, 0.5-0.25mm, and 0.25-0.1mm. Fe, Mn, Na, K, Mg, An, and Ca were determined as previously described.

Cation Exchange Capacity Variation with pH in the Maury and Iberia Sands

The Maury sand fraction (1.0-0.5mm) and the 1.0-0.5mm, 2-1mm and 1.0-0.5mm separates of the Iberia sand were subjected to the following study. One gram portions, with three replications for each sample, were placed in small leaching tubes with the samples being divided into two sets. One set was leached with 100 ml of 1N, pH 8.5 $(CH_3COO)_2Ca$, and a final pH of 7.4 was reached on this set of samples. The second set of samples was leached with 100 ml of 1N, pH 4.5 $(CH_3COO)_2Ca$ (the pH adjusted with CH_3COOH). A final pH of 4.5 was reached on this set of samples. Fifty ml of 1N CaCl was leached through each of the samples. All samples were then washed with 50 ml of ion free water and finally with 95 percent ethanol until the leachate was Cl free. The Ca was extracted with 100 ml of 0.5N NaCl, and determined by the method previously described.

CHAPTER III

RESULTS AND DISCUSSION

Table II presents the results of the x-ray analysis of the soil clay fractions. Comments pertinent to each fraction are presented in the table. The term "vermiculite" is used to describe the 14Å mineral that does not expand upon glycolation, gives a 10 to 14Å spacing upon K saturation and a 10Å peak upon heating to 500°C. It is felt that the term "soil vermiculite" or "vermiculite" enclosed in quotations is best for this soil mineral as it does not seem to behave as the true mineral vermiculite. "Illite" is the name given the stable 10Å component of the soil clays. This term is often misused, misunderstood, and misdefined. Perhaps the term a "micaceous 10Å component" is best suited for an analysis such as the one conducted in which clay mineral identification was not of major emphasis and study.

Many diffraction patterns indicated the presence of wide (25-35Å) spaced material. However, the technique employed was not such that any definite identifications can be made of this material. In several instances the 7.15Å peak was shifted toward a slightly higher spacing or there was a shoulder or plateau on the high spacing side of the peak. This shift of shoulder possibly indicates the presence of halloysite or metahalloysite. Specific investigations are needed to confirm or deny this hypothesis.

TABLE II

RESULTS OF THE X-RAY ANALYSIS OF THE SOIL CLAYS

Soil Clay and Fraction	Clay Minerals Identified	Comments
Baxter, <0.2μ	kaolinite	large component
	"vermiculite"	large component
	"illite"	presence questionable
	quartz	minor component
		The 14Å peak is not completely collapsed to 10Å at 500°C, there appears to be >10Å interstratified material.
Baxter, 2.0-0.2μ	kaolinite	large component
	"vermiculite"	14Å peaks better defined than in <0.2μ
	"illite"	minor component
	quartz	more than in <0.2μ fraction
		There are shoulders on the low angle sides of the 10 and 14Å peaks indicating interstratification.
Hartsells, <0.2μ	"vermiculite"	major component
	kaolinite	large component
	quartz	trace
		After heating to 500°C, the 14Å ("vermiculite") peak is collapsed to a rounded peak centered at 11Å.
Hartsells, 2.0-0.2μ	"vermiculite"	large component
	kaolinite	large component
	quartz	more than is in the <0.2μ fraction
		As in the <0.2μ fraction, after heating to 500°C, the 14Å peak is collapsed to a rounded peak centered at 11Å.

TABLE II (continued)

Soil Clay and Fraction	Clay Minerals Identified	Comments
Iberia, <0.2μ	montmorillonite kaolinite	With the Mg - air dry material, there is a 7-9Å shoulder leading up to a 12Å peak. Upon glycolation the 7-9Å shoulder widens to 7-11Å and there is a broad region of expansion from 11-22Å. A micaceous component (10.5-11Å) is indicated by the K treatments. This strongly suggests the presence of inter-stratified material being comprised of any two or all of the minerals montmorillonite - "illite" "vermiculite."
Iberia 2.0-0.2μ	montmorillonite kaolinite quartz	less than in <0.2μ fraction With the Mg - air dry treatment, there are 10 and 14Å peaks with shoulders on the low angle sides and a plateau from 14-22Å which might indicate an illitic compo-nent. Upon glycolation there are peaks (14, 16, 18.8Å) which suggest some sort of the same interstrati-fication as mentioned in the <0.2μ fraction of Iberia.
Maury <0.2μ	kaolinite montmorillonite "vermiculite" "Illite" quartz	 small amount small amount Some evidence of a 29-32Å spaced material.

TABLE II (continued)

Soil Clay and Fraction	Clay Minerals Identified	Comments
Maury 2.0-0.2μ	kaolinite	
	montmorillonite	small amount
	"vermiculite"	
	"illite"	a 10Å mineral
	quartz	
		Evidence of interstratified components of montmorillonite-"vermiculite"-"illite." Also some evidence of high spaced (30-32Å) material.
Memphis, <0.2μ	kaolinite	
	montmorillonite	Some interstratification of these minerals as indicated by a plateau from 7-22Å in all but K - 500°C treatment.
	"vermiculite"	
	"illite"	
	quartz	small amount
Memphis, 2.0-0.2μ	kaolinite	
	montmorillonite	Same type of interstratification indicated as in Memphis, <0.2μ.
	"vermiculite"	
	"illite"	
	quartz	
Sequoia, <0.2μ	"vermiculite"	
	"illite"	
	kaolinite	possibly metahalloysite or halloysite
	quartz	small amount
	montmorillonite	possibly present, identification difficult
Sequoia 2.0-0.2μ	"vermiculite"	
	"illite"	
	kaolinite	
	montmorillonite	possibly present, identification difficult

Alexiades and Jackson's (1) chemical test for vermiculite was performed on the Iberia clay fractions. The results gave 14 percent "vermiculite" in the 2.0-0.2μ fraction and 15 percent in the <0.2μ fraction. There are two assumptions made by the authors of the above method which need pointing out. A CEC of 154 meq/100g is used for the vermiculite. It is doubtful that soil formed vermiculite has a CEC of this magnitude. Also, drying at 100°C is used to "fix" potassium in one case to obtain a differential of exchangeable potassium in reference to another determination. One must remember that montmorillonite also irreversibly "fixes" potassium upon drying and the Iberia soil contains a significant amount of montmorillonite.

In general, the results of the x-ray analysis of the clay fractions agree with the analysis on previous samples (see Table I, p. 15). As one might expect, much evidence of interstratified and degraded materials is present in almost every diffraction pattern. Interpretation, at best, is difficult and no attempt at identifying specific interstratified components was attempted.

Results of the determination of pH, organic matter (O.M.), and cation exchange capacity (CEC) for the soils are given in Table III. These values may be compared to those in Table I, p. 15, to note any differences in the samples used and the characterization samples. CEC values were determined in unbuffered systems with two different extracting solutions.

Table IV lists the CEC values of the soils and soil fractions as determined by using Ca as the saturating cation and Na as the

TABLE III

CATION EXCHANGE CAPACITY, pH AND ORGANIC MATTER CONTENT OF THE SOILS

Soils	pH (1:1 H_2O)	Percent O.M.	CEC[a] meq/100g	CEC[b] meq/100g
Baxter	5.5	2.43	3.3	3.4
Hartsells	6.9	4.14	4.8	9.3
Iberia	6.2	3.60	17.1	31.8
Maury	6.2	1.52	8.7	13.6
Memphis	7.0	1.20	5.0	6.5
Sequoia	5.2	2.37	4.2	4.2

[a] 0.1N Ca saturated, 0.1N Na extracted.

[b] 1.0N, pH 7 Ca saturated, 1.0N, pH 7 CH_3COONH_4 extracted.

TABLE IV

CATION EXCHANGE CAPACITY OF SOILS AND SOILS FRACTIONS
USING CALCIUM AS THE SATURATING CATION

Soil name	Soil	Soil -O.M.	Sand	Coarse Silt	Fine Silt	Coarse Clay	Fine Clay
	meq/100g						
Baxter	2.5	2.1	0.30	0.45	0.30	11.0	25.0
Hartsells	4.3	2.1	0.05	0.40	1.60	14.0	28.5
Iberia	24.0	7.5	2.80	0.17	2.00	23.0	24.5
Maury	10.0	6.2	2.40	1.20	3.00	15.0	21.5
Memphis	3.5	2.7	0.40	1.30	1.70	21.7	32.5
Sequoia	3.7	3.3	2.00	0.40	1.20	13.5	16.0

displacing cation. This type of determination gives a value for the CEC of the soil or soil fraction at the pH at which most studies were conducted.

The calcium exchangeable potassium, (Ca-ex-K), was determined for the soils and soil fractions (Table V). Differences in the (Ca-ex-K) values for the whole soil and soil minus organic matter (soil-O.M.) are shown and can be attributed to the organic matter. The additional ammonium exchangeable potassium, (NH_4-ex-K), values for each soil in these two groups are nearly identical, indicating that the K in this category is not affected by the organic matter.

(Ca-ex-K) values for the soil-O.M. were reduced up to 67 percent by drying in the presence of K before extraction by Ca. The (NH_4-ex-K) was reduced up to 65 percent by drying before extraction.

(Ca-ex-K) values for the Iberia, Sequoia, and Maury sands are most unexpected. These sands also have relatively high CEC values, and, as will be seen below, show a high selectivity for K. All of the fine silts have (Ca-ex-K) values larger than their corresponding coarse silt fractions. This possibly indicates "vermiculite" and/or "illite" minerals in the fine silts. Of the clay fractions, the Iberia has the highest (Ca-ex-K) values.

Results of the leaching column equilibrium studies on the soils are presented in Table VI. With one exception, the equilibrium selectivity coefficient, K_c'', decreased with increasing K in the leaching solution, c_K/c_o. The Iberia soil had the highest K_c'' value at c_K/c_o=0.05. Maury had the highest K_c'' values at c_K/c_o=0.10 and 0.20.

TABLE V

CALCIUM EXCHANGEABLE POTASSIUM, (Ca-ex-K), AND THE ADDITIONAL AMMONIUM EXCHANGEABLE POTASSIUM, (NH_4-ex-K), OF THE SOILS AND SOILS FRACTIONS

	Baxter	Hartsells	Iberia	Maury	Memphis	Sequoia
	meq/100g					
Whole soil						
(Ca-ex-K)	3.72	8.400	34.20	14.40	6.60	6.20
(NH_4-ex-K)	0.24	0.450	0.89	0.89	0.23	0.41
Soil-O.M.						
(Ca-ex-K)	3.46	4.700	26.03	11.13	4.74	5.51
(NH_4-ex-K)	0.29	0.440	1.04	0.83	0.24	0.43
Soil-O.M. (dried)						
(Ca-ex-K)	2.43	2.170	18.90	9.20	2.04	3.97
(NH_4-ex-K)	0.13	0.170	0.55	0.56	0.09	0.15
Sand						
(Ca-ex-K)	0.71	0.000	14.71	8.60	0.18	7.75
(NH_4-ex-K)	0.05	0.001	1.20	0.88	0.05	0.94
Coarse silt						
(Ca-ex-K)	0.53	0.650	1.10	1.15	0.93	0.60
(NH_4-ex-K)	0.08	0.140	0.13	0.30	0.11	0.06
Fine silt						
(Ca-ex-K)	1.21	4.950	3.21	7.14	3.23	3.14
(NH_4-ex-K)	---	---	---	---	---	---
Coarse clay						
(Ca-ex-K)	17.50	23.300	25.20	23.50	20.30	17.90
(NH_4-ex-K)	---	---	---	---	0.63	---
Fine clay						
(Ca-ex-K)	28.00	28.400	38.00	29.70	36.50	26.50
(NH_4-ex-K)	1.07	1.100	---	---	0.89	---

TABLE VI

VALUES FOR THE EQUILIBRIUM REACTION $2K^{+} + CaM_2 \rightleftarrows 2KM + Ca^{++}$ ON THE SOILS AT c_o=0.002N, 23°C, AS DETERMINED FROM LEACHING COLUMN STUDIES

c_K/c_o=0.05			c_K/c_o=0.10			c_K/c_o=0.20		
q_K/q_o	K''_c	$\Delta G°$[a]	q_K/q_o	K''_c	$\Delta G°$[a]	q_K/q_o	K''_c	$\Delta G°$[a]
				Baxter				
.0526	277.5	-3304	.0646	100.5	-2711	.0847	39.0	-2152
				Hartsells				
.0332	108.2	-2752	.0515	63.0	-2434	.0638	21.7	-1811
				Iberia				
.1190	1526.0	-4310	.0714	123.5	-2828	.0915	46.0	-2252
				Maury				
.0478	246.2	-3175	.0848	176.7	-3040	.1120	71.5	-2505
				Memphis				
.0562	321.0	-3393	.0623	93.0	-2664	.0919	46.5	-2258
				Sequoia				
.0821	697.5	-3851	.0490	56.8	-2376	.1070	64.0	-2446

[a] $\Delta G°$=cal./2 moles

A large K_c'' value indicates a large capacity to adsorb K from solution even when the K is present in small amounts. This type of adsorption indicates the presence of sites on the soil particles which are "specific for K." That is, K is preferentially adsorbed over the Ca ions in the solution. The soils listed in order of their decreasing K_c'' values are:

at c_K/c_o=0.05 - Iberia>Sequoia>Memphis>Baxter>Maury>Hartsells

at c_K/c_o=0.10 - Maury>Iberia>Baxter>Memphis>Hartsells>Sequoia

at c_K/c_o=0.20 - Maury>Sequoia>Memphis>Iberia>Baxter>Hartsells

Free energies of exchange, $\Delta G°$, for the reactions were calculated from the relationship $\Delta G°=-RT\ln K_c''$, with $\Delta G°$ in calories per two moles. Since $\Delta G°$ depends upon $\ln K_c''$, the $\Delta G°$ values also decrease with increasing K in solution. Evaluation of the above reaction by $\Delta G°$ as calculated from the two equilibrium coefficients and solution activity ratios is given a more thorough consideration below.

Table VII lists the free energies ($\Delta G°$) standard heats ($\Delta H°$) and entropies ($\Delta S°$) of reaction for the replacement of calcium by potassium on the soils. $\Delta G°$ values were calculated from $\ln K_c''$ as previously described. $\Delta H°$ values for each soil were obtained from the slopes of the lines in Figure 1. Values for $\Delta S°$ were obtained from the relationship $\Delta G°=\Delta H°-T\Delta S°$. Gast, et. al. (19) reported that exchange of a nonpreferred for a preferred cation, $\Delta G°$, $\Delta H°$, and $\Delta S°$ were always negative. Ion pairs used in their work were alkali metals. The alkali-alkaline earth ion pair discussed here does not follow this behavior for all soils. The absolute values of these three

TABLE VII

FREE ENERGIES, STANDARD HEATS AND ENTROPIES OF EXCHANGE FOR THE REPLACEMENT OF CALCIUM BY POTASSIUM ON THE SOILS AT c_o=0.002N, c_K/c_o=0.10

	q_K/q_o		K''_c		$\Delta G°$[a]		$\Delta H°$[a]	$\Delta S°$[b]
Soils	T=281	T=296	T=281	T=296	T=281	T=296	---	---
Baxter	0.192	0.132	1,022	454	-1932	-1798	-4478	-9.05
Hartsells	0.087	0.076	187	138	-1460	-1449	-1680	-0.78
Iberia	0.186	0.189	960	993	-1916	-2028	177	7.45
Maury	0.206	0.168	1,202	763	-1979	-1951	-2520	-1.92
Memphis	0.041	0.046	39	50	-1028	-1150	1260	8.15
Sequoia	0.062	0.049	92	57	-1262	-1189	-2648	-4.93

[a] cal./mole K

[b] e.u./mole K

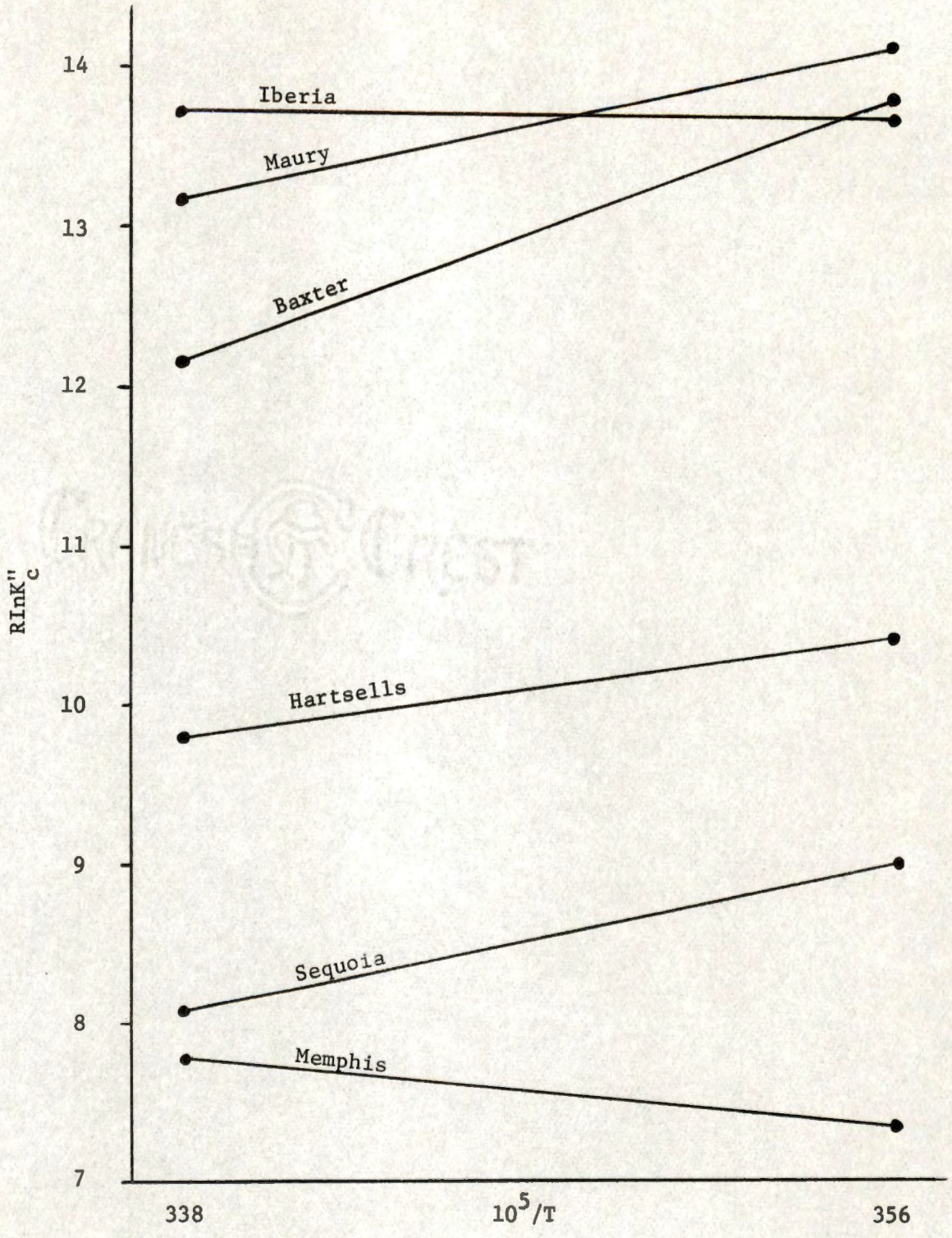

Figure 1. Temperature dependence of K''_c, the equilibrium constant.

terms increase with the degree of selectivity. The K_c'' values of all of the soils give negative $\Delta G°$ values at both temperatures. However, the absolute value of $\Delta G°$ increased with an increase in temperature on the Iberia and Memphis resulting in positive $\Delta H°$ and $\Delta S°$ values for these two soils. The other four soils show a decrease in absolute value of $\Delta G°$ and negative values for $\Delta H°$ and $\Delta S°$.

Baxter, Iberia, and Maury exhibit selection of potassium over calcium ($q/q_o > c/c_o$). Iberia shows an increase in selectivity with an increase in temperature. The amount of increase (shown indirectly by the slope of the Iberia line in Figure 1, p. 40) is slight and it is felt that additional determinations are needed before the situation is fully evaluated. The Memphis soil, while not exhibiting selection for potassium, adsorbs more potassium with an increase in temperature. The soils in order of most to least negative $\Delta H°$ and $\Delta S°$ values (highest to lowest absolute numbers) are Baxter>Sequoia>Maury>Hartsells>Memphis>Iberia. Gast (18) indicates that $\Delta S°$ is important in evaluating selectivity reactions because of its relation to the electrical charge on the clays and ion hydration. Clays with high charges are able to dehydrate solution cations and adsorb them more strongly than clays with weaker charges. The system with the more strongly adsorbed cations would thus give higher (more negative) absolute $\Delta S°$ values than those systems of less strongly adsorbed cations. Thus one would expect the charge strengths of the clays to follow the same order as the above $\Delta H°$ and $\Delta S°$ values.

The relationship $\Delta G^\circ = \Delta H^\circ + IT$, derived previously, was solved to determine the constant of integration, I, for each soil. I values for each soil were substituted into the above general equation giving an expression allowing the calculation of ΔG° for each soil at any temperature. From the ΔG° value thus calculated, the equilibrium coefficient K_c'' for the temperature in question may be calculated. The expressions for the individual soils are:

$$\Delta G^\circ_{\text{Baxter}} = -4478 + 9.05\ T$$

$$\Delta G^\circ_{\text{Hartsells}} = -1680 + 0.78\ T$$

$$\Delta G^\circ_{\text{Iberia}} = 177 - 7.45\ T$$

$$\Delta G^\circ_{\text{Maury}} = -2520 + 1.92\ T$$

$$\Delta G^\circ_{\text{Memphis}} = 1260 - 8.15\ T$$

$$\Delta G^\circ_{\text{Sequoia}} = -2648 + 4.93\ T$$

and will give ΔG° in cal/mole K.

Results of the equilibrium studies utilizing potassium-42 (K-42) on the soils and soils fractions at $c_o = 0.002\underline{N}$ are presented in Table VIII through Table X. Data from which these values were calculated are in Appendix Tables A-III through A-V. The amounts of adsorbed potassium (q_K/q_o) increased with increasing solution potassium (c_K/c_o) on all soil fractions. Table XI gives the results of the equilibrium study at $c_o = 0.02\underline{N}$, initial $c_K/c_o = 0.05$. The increase in this solution concentration from the $c_o = 0.002\underline{N}$, initial $c_K/c_o = 0.005$ solution was by a factor of 10. The q_K/q_o values at $c_o = 0.02\underline{N}$ do not show a consistent increase by any one constant or value from the q_K/q_o values at $c_o = 0.002\underline{N}$.

TABLE VIII

VALUES FOR THE EQUILIBRIUM REACTION $2K^{+} + CaM_2 \rightleftarrows 2KM + Ca^{++}$ ON THE SOILS AND SOILS FRACTIONS FROM THE POTASSIUM-42 STUDIES AT c_o=0.002N, 23°C, INITIAL c_K/c_o=0.05

	c_K/c_o	q_K/q_o	$a_K/a_{Ca}^{1/2}$	K'_c	K''_c
Soils					
Baxter	0.0334	0.0101	0.00244	0.0992	22.3
Hartsells	0.0296	0.0110	0.00216	0.1359	34.0
Iberia	0.0096	0.0028	0.00070	0.0832	20.8
Maury	0.0171	0.0126	0.00124	0.5390	134.8
Memphis	0.0288	0.0121	0.00206	0.1796	44.9
Sequoia	0.0249	0.0139	0.00181	0.3072	76.8
Sands					
Baxter	0.0430	0.0052	0.00315	0.0141	3.5
Hartsells	0.0467	0.0029	0.00343	0.0036	0.9
Iberia	0.0240	0.0077	0.00174	0.1007	25.2
Maury	0.0280	0.0086	0.00204	0.0923	23.1
Memphis	0.0447	0.0046	0.00328	0.102	2.5
Sequoia	0.0290	0.0107	0.00211	0.1340	33.5
Coarse Silts					
Baxter	0.0450	0.0053	0.00330	0.0133	3.3
Hartsells	0.0435	0.0056	0.00319	0.0157	3.9
Iberia	0.0385	0.0111	0.00282	0.0808	20.2
Maury	0.0380	0.0128	0.00278	0.1106	27.6
Memphis	0.0395	0.0113	0.00289	0.0975	24.4
Sequoia	0.0440	0.0065	0.00321	0.0209	5.2
Fine Silts					
Baxter	0.0420	0.0092	0.00308	0.0459	11.5
Hartsells	0.0335	0.0121	0.00244	0.1276	31.9
Iberia	0.0300	0.0122	0.00219	0.1624	40.6
Maury	0.0270	0.0134	0.00196	0.2428	60.7
Memphis	0.0350	0.0158	0.00256	0.1999	50.0
Sequoia	0.0375	0.0116	0.00274	0.0932	23.3
Coarse Clays					
Baxter	0.0222	0.0255	0.00161	1.3428	335.7
Hartsells	0.0252	0.0235	0.00183	1.0229	255.7
Iberia	0.0053	0.0154	0.00038	8.5311	2132.8
Maury	0.0214	0.0205	0.00155	0.9177	229.4
Memphis	0.0212	0.0204	0.00154	0.9250	231.2
Sequoia	0.0209	0.0225	0.00152	1.1578	289.4

TABLE VIII (continued)

	c_K/c_o	q_K/q_o	$a_K/a_{Ca}^{1/2}$	K'_c	K''_c
Fine Clays					
Baxter	0.0173	0.0129	0.00125	0.5538	138.4
Hartsells	0.0185	0.0167	0.00134	0.8140	203.5
Iberia	0.0069	0.0100	0.00050	2.1069	526.7
Maury	0.0136	0.0189	0.00098	1.9411	485.3
Memphis	0.0154	0.0126	0.00111	0.6680	167.0
Sequoia	0.0151	0.0148	0.00109	0.9607	240.2

TABLE IX

VALUES FOR THE EQUILIBRIUM REACTION $2K^{+} + CaM_2 \rightleftarrows 2KM + Ca^{++}$ ON THE SOILS AND SOILS FRACTIONS FROM THE POTASSIUM-42 STUDIES AT c_o=0.002N, 23°C, INITIAL c_K/c_o=0.10

	c_K/c_o	q_K/q_o	$a_K/a_{Ca}^{1/2}$	K'_c	K''_c
Soils					
Baxter	0.0815	0.0110	0.00599	0.01690	4.22
Hartsells	0.0744	0.0110	0.00545	0.02040	5.10
Iberia	0.0305	0.0048	0.00218	0.02410	6.02
Maury	0.0553	0.0170	0.00400	0.09080	22.70
Memphis	0.0741	0.0140	0.00542	0.03350	8.38
Sequoia	0.0716	0.0160	0.00523	0.04710	11.78
Sands					
Baxter	0.0920	0.0059	0.00680	0.00376	9.40
Hartsells	0.0960	0.0035	0.00711	0.00120	0.30
Iberia	0.0550	0.0130	0.00399	0.05350	13.38
Maury	0.0680	0.0120	0.00496	0.02940	7.35
Memphis	0.0936	0.0061	0.00693	0.00390	0.98
Sequoia	0.0710	0.0148	0.00519	0.04100	10.25
Coarse Silts					
Baxter	0.0920	0.0087	0.00680	0.00820	2.05
Hartsells	0.0890	0.0087	0.00657	0.00870	2.18
Iberia	0.0800	0.0190	0.00588	0.05290	13.22
Maury	0.0810	0.0200	0.00595	0.05720	14.30
Memphis	0.0830	0.0180	0.00611	0.04390	10.98
Sequoia	0.0900	0.0110	0.00655	0.01370	3.42
Fine Silts					
Baxter	0.0880	0.0140	0.00649	0.02340	5.85
Hartsells	0.0735	0.0190	0.00540	0.06320	15.80
Iberia	0.0625	0.0230	0.00455	0.12990	32.48
Maury	0.0590	0.0240	0.00428	0.15950	39.88
Memphis	0.0740	0.0280	0.00542	0.13640	34.10
Sequoia	0.0785	0.0200	0.00576	0.06100	15.25
Coarse Clays					
Baxter	0.0957	0.0390	0.00709	0.15630	39.08
Hartsells	0.0960	0.0350	0.00711	0.12450	31.12
Iberia	0.0269	0.0250	0.00192	0.86200	215.50
Maury	0.0556	0.0320	0.00403	0.32320	80.82
Memphis	0.0528	0.0340	0.00382	0.40660	101.60
Sequoia	0.0519	0.0370	0.00875	0.50040	125.10

TABLE IX (continued)

	c_K/c_o	q_K/q_o	$a_K/a_{Ca}^{1/2}$	K'_c	K''_c
Fine Clays					
Baxter	0.0421	0.0230	0.00303	0.29260	73.15
Hartsells	0.0504	0.0260	0.00364	0.25290	64.88
Iberia	0.0205	0.0180	0.00146	0.76900	192.20
Maury	0.0400	0.0310	0.00288	0.59500	148.80
Memphis	0.0377	0.0230	0.00271	0.36660	91.65
Sequoia	0.0381	0.0270	0.00274	0.49650	124.10

TABLE X

VALUES FOR THE EQUILIBRIUM REACTION $2K^{+} + CaM_2 \rightleftarrows 2KM + Ca^{++}$ ON THE SOILS AND SOILS FRACTIONS FROM THE POTASSIUM-42 STUDIES AT c_o=0.002N, 23°C, INITIAL c_K/c_o=0.20

	c_K/c_o	q_K/q_o	$a_K/a_{Ca}^{1/2}$	K'_c	K''_c
Soils					
Baxter	0.1585	0.0250	0.01205	0.0215	5.38
Hartsells	0.1550	0.0240	0.01175	0.0208	5.20
Iberia	0.0710	0.0089	0.00514	0.0147	3.68
Maury	0.1080	0.0350	0.00797	0.0971	24.28
Memphis	0.1565	0.0240	0.01188	0.0203	5.08
Sequoia	0.1375	0.0350	0.01033	0.0579	14.15
Sands					
Baxter	0.1840	0.0120	0.01420	0.0035	0.88
Hartsells	0.1940	0.0050	0.01507	0.0005	0.12
Iberia	0.1220	0.0230	0.00908	0.0319	7.98
Maury	0.1400	0.0230	0.01053	0.0238	5.95
Memphis	0.1890	0.0095	0.01464	0.0021	0.52
Sequoia	0.1410	0.0300	0.01061	0.0401	10.02
Coarse Silts					
Baxter	0.1910	0.0098	0.01481	0.0022	0.55
Hartsells	0.1880	0.0100	0.01455	0.0026	0.65
Iberia	0.1775	0.0220	0.01365	0.0129	3.22
Maury	0.1735	0.0380	0.01331	0.0221	5.52
Memphis	0.1785	0.0230	0.01373	0.0140	3.50
Sequoia	0.1880	0.0130	0.01455	0.0039	0.98
Fine Silts					
Baxter	0.1865	0.0150	0.01442	0.0053	1.32
Hartsells	0.1670	0.0240	0.01276	0.0176	4.40
Iberia	0.1550	0.0270	0.01176	0.0264	6.60
Maury	0.1420	0.0340	0.01069	0.0509	12.72
Memphis	0.1670	0.0350	0.01276	0.0379	9.48
Sequoia	0.1750	0.0230	0.01344	0.0146	3.65
Coarse Clays					
Baxter	0.1486	0.0470	0.01123	0.0894	22.35
Hartsells	0.1515	0.0430	0.01147	0.0714	17.85
Iberia	0.1143	0.0300	0.00847	0.0629	15.72
Maury	0.1410	0.0420	0.01601	0.0796	19.90
Memphis	0.1411	0.0420	0.01062	0.0794	19.85
Sequoia	0.1437	0.0440	0.01083	0.0840	21.00

TABLE X (continued)

	c_K/c_o	q_K/q_o	$a_K/a_{Ca}^{1/2}$	K'_c	K''_c
Fine Clays					
Baxter	0.1125	0.0350	0.00833	0.0890	22.35
Hartsells	0.1212	0.0420	0.00902	0.1102	27.55
Iberia	0.0824	0.0270	0.00600	0.1013	25.32
Maury	0.1163	0.0440	0.00863	0.1323	33.08
Memphis	0.1188	0.0300	0.00822	0.0579	14.48
Sequoia	0.1101	0.0390	0.00814	0.1162	29.05

TABLE XI

VALUES FOR THE EQUILIBRIUM REACTION $2K^{+} + CaM_2 \rightleftarrows 2KM + Ca^{++}$ ON THE SOILS AND SOILS FRACTIONS FROM THE POTASSIUM-42 STUDIES AT c_o=0.02N, 23°C, INITIAL c_K/c_o=0.05

	c_K/c_o	q_K/q_o	$a_K/a_{Ca}^{1/2}$	K'_c	K''_c
Soils					
Baxter	0.0454	0.0280	0.01334	0.374	9.35
Hartsells	0.0446	0.0282	0.01311	0.392	9.80
Iberia	0.0236	0.0183	0.00686	0.598	14.95
Maury	0.0361	0.0531	0.01056	2.202	55.05
Memphis	0.0430	0.0387	0.01263	0.804	20.10
Sequoia	0.0426	0.0411	0.01250	0.929	23.22
Sands					
Baxter	0.0463	0.0280	0.01361	0.359	8.98
Hartsells	0.0487	0.0110	0.01433	0.049	1.22
Iberia	0.0249	0.0740	0.00724	9.300	232.50
Maury	0.0313	0.0730	0.00913	5.684	142.10
Memphis	0.0478	0.0190	0.00141	0.153	3.82
Sequoia	0.0326	0.0890	0.00951	7.915	197.90
Coarse Silts					
Baxter	0.0490	0.0103	0.01444	0.042	1.05
Hartsells	0.0486	0.0115	0.01432	0.054	1.35
Iberia	0.0472	0.0275	0.01387	0.333	8.32
Maury	0.0470	0.0326	0.01381	0.475	11.88
Memphis	0.0474	0.0275	0.01396	0.329	8.22
Sequoia	0.0487	0.0141	0.01433	0.081	2.02
Fine Silts					
Baxter	0.0486	0.0161	0.01430	0.106	2.65
Hartsells	0.0462	0.0280	0.01358	0.360	9.00
Iberia	0.0448	0.0321	0.01314	0.508	12.70
Maury	0.0420	0.0470	0.01230	1.262	31.55
Memphis	0.0460	0.0428	0.01350	0.865	21.62
Sequoia	0.0470	0.0280	0.01382	0.348	8.70
Coarse Clays					
Baxter	0.0444	0.0517	0.01303	1.368	34.20
Hartsells	0.0455	0.0395	0.01337	0.749	18.68
Iberia	0.0397	0.0354	0.01164	0.790	19.75
Maury	0.0429	0.0508	0.01260	1.412	35.30
Memphis	0.0430	0.0493	0.01265	1.320	33.00
Sequoia	0.0438	0.0481	0.01285	1.213	30.32

TABLE XI (continued)

	c_K/c_o	q_K/q_o	$a_K/a_{Ca}^{1/2}$	K'_c	K''_c
Fine Clays					
Baxter	0.0367	0.0529	0.01073	2.116	52.9
Hartsells	0.0387	0.0528	0.01134	1.886	47.2
Iberia	0.0304	0.0456	0.00888	2.278	56.9
Maury	0.0377	0.0644	0.01102	3.006	75.2
Memphis	0.0355	0.0531	0.01037	2.282	57.0
Sequoia	0.0367	0.0571	0.01073	2.473	61.8

At c_o=0.002N, the q_K/q_o values for the coarse clays were higher than for the fine clays at all c_K/c_o levels. However, at c_o=0.02N, the q_K/q_o for the fine clays was higher than for the coarse clays.

A summary of the equilibrium coefficients, K'_c, for the c_o=0.002N studies is given in Table XII. In most cases, the K'_c values decreased with increasing potassium in the solution, as was expected. At initial c_K/c_o=0.05, the Iberia soil had the lowest K'_c value, yet it removed over 96 percent of the potassium from the solution. This soil also had low K'_c values from the equilibrium at c_K/c_o=0.10 and 0.20, yet again depleted the solution of a large amount of potassium. The high exchange capacity of Iberia requires that a large amount of potassium must be adsorbed in order to obtain large K'_c values. Maury had the highest K'_c value of any of the soils at all three levels of solution potassium.

Iberia, Maury, and Sequoia sands have K'_c values much higher than any of the three other sands at all three levels of solution potassium. The nature and behavior of these sands are discussed below.

The fine silts gave larger K'_c values than did the coarse silts indicating the possibility of clay minerals in the fine silts. X-ray analysis showed the presence of "vermiculite" and/or "illite" in many of the clays. Thus, one might expect some of this material in the fine silt fractions. For both silt fractions, Maury had the highest K'_c values at all levels of solution potassium.

With the initial c_K/c_o at 0.05 and 0.10, the Iberia coarse and fine clays had the highest K'_c values, but at initial c_K/c_o=0.20,

TABLE XII

SUMMARY OF THE EQUILIBRIUM COEFFICIENTS, K', FOR THE SOILS AND SOILS FRACTIONS FROM THE POTASSIUM-42 STUDIES AT c_o=0.002N

	Soil	Sand	Coarse Silt	Fine Silt	Coarse Clay	Fine Clay
			Initial c_K/c_o=0.05			
Baxter	0.0892	0.0141	0.0133	0.0459	1.3428	0.5538
Hartsells	0.1359	0.0036	0.0157	0.1276	1.0229	0.8140
Iberia	0.0832	0.1007	0.0808	0.1624	8.5311	2.1069
Maury	0.5390	0.0923	0.1106	0.2428	0.9177	1.9411
Memphis	0.1796	0.0102	0.0975	0.1999	0.9250	0.6680
Sequoia	0.3072	0.1340	0.0209	0.0932	1.1578	0.9607
			Initial c_K/c_o=0.10			
Baxter	0.0169	0.0038	0.0082	0.0234	0.1563	0.2926
Hartsells	0.0204	0.0012	0.0087	0.0632	0.1245	0.2595
Iberia	0.0241	0.0535	0.0529	0.1299	0.8620	0.7690
Maury	0.0908	0.0294	0.0572	0.1595	0.3233	0.5950
Memphis	0.0335	0.0039	0.0439	0.1364	0.4066	0.3666
Sequoia	0.0471	0.0410	0.0137	0.0610	0.5004	0.4965
			Initial c_K/c_o=0.20			
Baxter	0.0215	0.0035	0.0022	0.0053	0.0894	0.0890
Hartsells	0.0208	0.0005	0.0026	0.0176	0.0714	0.1102
Iberia	0.0147	0.0319	0.0129	0.0264	0.0629	0.1013
Maury	0.0971	0.0238	0.0221	0.0509	0.0796	0.1323
Memphis	0.0203	0.0021	0.0140	0.0379	0.0794	0.0579
Sequoia	0.0579	0.0401	0.0039	0.0146	0.0840	0.1162

K_c' values for the two Iberia clay fractions were below those for several other clays. At the initial c_K/c_o=0.05, the coarse clays gave higher K_c' values than their corresponding fine clay with the exception of the Maury. The values were mixed at c_K/c_o=0.10 and at c_K/c_o=0.20, four of the six fine clays had higher K_c' values than their corresponding coarse clay.

For the three c_o=0.002N solutions, the order of the K_c' values for a given fraction at any one level of solution potassium was not the same at any other level of potassium in all cases. The values for the clay fractions mentioned above is a good example of this inconsistency. This indicates that the K:Ca ratio had an effect on selectivity for potassium. As the K:Ca solution ratio increased, the q_K/q_o of the soils and soils fractions decreased, and there was a shift in the order of q_K/q_o values within each fraction.

A summary of the equilibrium coefficients, K_c'', is given in Table XIII. The K_c'' values are larger than their corresponding K_c' values by a factor of 250. In the K_c'' values, a term, $\frac{1}{2c_o}$, has been introduced to correct for the effect of the solution on the equilibrium constant. The relative order of the K_c' and K_c'' values are the same, but as shown below, the absolute number of an equilibrium coefficient is sometimes important.

Activity ratios of the equilibrium solutions for the soils and soils fractions are summarized in Table XIV. As mentioned above, the activity ratio for the equilibrium reaction as written is given by a_{Ca}/a_{K^2}. However, for reasons discussed later, the ratio was

TABLE XIII

SUMMARY OF THE EQUILIBRIUM COEFFICIENTS, K_c'', FOR THE SOILS AND SOILS FRACTIONS FROM THE POTASSIUM-42 STUDIES AT c_o=0.002N

	Soil	Sand	Coarse Silt	Fine Silt	Coarse Clay	Fine Clay
			Initial c_K/c_o=0.05			
Baxter	22.30	3.52	3.32	11.48	335.70	138.40
Hartsells	33.97	0.90	3.92	31.90	255.72	203.50
Iberia	20.80	25.18	20.20	40.60	2132.78	526.70
Maury	134.75	23.08	27.65	60.70	229.40	485.30
Memphis	44.90	2.55	24.38	49.98	231.20	167.00
Sequoia	76.80	33.50	5.22	23.30	289.40	240.20
			Initial c_K/c_o=0.10			
Baxter	4.22	0.94	2.05	5.85	39.08	73.15
Hartsells	5.10	0.30	2.18	15.80	31.12	64.88
Iberia	6.02	13.38	13.22	32.48	215.50	192.20
Maury	22.70	7.35	14.30	39.88	80.82	148.80
Memphis	8.38	0.98	10.98	34.10	101.60	91.65
Sequoia	11.78	10.25	3.42	15.25	125.10	124.10
			Initial c_K/c_o=0.20			
Baxter	5.38	0.88	0.55	1.32	22.35	22.25
Hartsells	5.20	0.12	0.65	4.40	17.85	27.55
Iberia	3.68	7.98	3.22	6.60	15.72	25.32
Maury	24.28	5.95	5.52	12.72	19.90	33.08
Memphis	5.08	0.52	3.50	9.48	19.85	14.48
Sequoia	14.48	10.02	0.98	3.65	21.00	29.05

TABLE XIV

SUMMARY OF THE ACTIVITY RATIOS, $a_K/a_{Ca}^{1/2}$, FOR THE SOILS AND SOILS FRACTIONS FROM THE POTASSIUM-42 STUDIES AT c_o=0.002N

Soil	Sand	Coarse Silt	Fine Silt	Coarse Clay	Fine Clay
		Initial c_K/c_o=0.05			
Baxter	0.00244	0.00315	0.00330	0.00308	0.00161	0.00125
Hartsells	0.00216	0.00343	0.00319	0.00244	0.00183	0.00134
Iberia	0.00070	0.00174	0.00282	0.00219	0.00038	0.00050
Maury	0.00124	0.00204	0.00278	0.00196	0.00155	0.00098
Memphis	0.00206	0.00328	0.00289	0.00256	0.00154	0.00111
Sequoia	0.00181	0.00211	0.00321	0.00274	0.00152	0.00109
		Initial c_K/c_o=0.10			
Baxter	0.00599	0.00680	0.00680	0.00649	0.00709	0.00303
Hartsells	0.00545	0.00711	0.00657	0.00540	0.00711	0.00364
Iberia	0.00218	0.00399	0.00588	0.00455	0.00192	0.00146
Maury	0.00400	0.00496	0.00595	0.00428	0.00403	0.00288
Memphis	0.00542	0.00693	0.00611	0.00542	0.00382	0.00271
Sequoia	0.00523	0.00519	0.00655	0.00576	0.00375	0.00274
		Initial c_K/c_o=0.20			
Baxter	0.01205	0.01420	0.01481	0.01442	0.01123	0.00833
Hartsells	0.01175	0.01507	0.01455	0.01276	0.01147	0.00902
Iberia	0.00514	0.00908	0.01365	0.01176	0.00847	0.00600
Maury	0.00797	0.01053	0.01331	0.01069	0.01061	0.00863
Memphis	0.01188	0.01464	0.01373	0.01276	0.01062	0.00882
Sequoia	0.01033	0.01061	0.01455	0.01344	0.01083	0.00814

written as $a_K/a_{Ca}^{1/2}$. Thus, the activity ratios of a given fraction increase as the solution potassium increases.

If a comparison is made of each soil fraction using K_c'' values and $a_K/a_{Ca}^{1/2}$ values (Table XV), some differences can be seen in the order of the values for the fractions. As previously mentioned, the Iberia soil gave a low K_c'' value, yet the activity ratio of its equilibrium solution was the lowest of any of the soils. It is believed that, in this instance, the activity ratio is the better of the two values in evaluating the equilibrium situation. For the type of equilibrium being studied, one is most interested in the amount of potassium that the soil or soil fraction is able to adsorb from the solution. The activity ratio of the solution is the best measurement when one knows the amount of K which has been adsorbed from the solution as well as the amount remaining in solution.

For many of the other fractions, the K_c'' and $a_K/a_{Ca}^{1/2}$ values give a very similar order. In these instances, either value would be acceptable in evaluating the equilibrium. In all studies of this type, however, the solution activities should be considered in the evaluation.

The results of a tenfold increase in total concentration, as compared to Tables XII-XIV, pp. 52, 54-55, is shown in Table XVI. Summaries of the equilibrium coefficients, K_c' and K_c'', and solution activity ratios, $a_K/a_{Ca}^{1/2}$, are given for c_o=0.02N, initial c_K/c_o=0.05. The order of the K_c' or K_c'' values from highest to lowest in a given fraction are not the same for the two c_o values. This suggests selectivity variation with concentration.

TABLE XV

RANKING OF THE SOILS AND SOILS FRACTIONS USING THE EQUILIBRIUM COEFFICIENTS, K_c'', AND ACTIVITY RATIOS, $a_K/a_{Ca}^{1/2}$, FROM THE POTASSIUM-42 STUDIES AT c_o=0.002N

K_c'' values (decreasing order)			$a_K/a_{Ca}^{1/2}$ (increasing order)		
Initial c_K/c_o			Initial c_K/c_o		
0.05	0.10	0.20	0.05	0.10	0.20
	Soils			Soils	
Ma[a]	Ma	Ma	Ib	Ib	Ib
Se	Se	Se	Ma	Ma	Ma
Me	Me	Ba	Se	Se	Se
Ha	Ib	Ha	Me	Me	Ha
Ba	Ha	Me	Ha	Ha	Me
Ib	Ba	Ib	Ba	Ba	Ba
	Sands			Sands	
Se	Ib	Se	Ib	Ib	Ib
Ib	Se	Ib	Ma	Ma	Ma
Ma	Ma	Ma	Se	Se	Se
Ba	Me	Ba	Ba	Ba	Ba
Me	Ba	Me	Me	Me	Me
Ha	Ha	Ha	Ha	Ha	Ha
	Coarse silts			Coarse silts	
Ma	Ma	Ma	Ma	Ib	Ma
Me	Ib	Me	Ib	Ma	Ib
Ib	Me	Ib	Me	Me	Me
Se	Se	Se	Ha	Se	Se
Ha	Ha	Ha	Se	Ha	Ha
Ba	Ba	Ba	Ba	Ba	Ba
	Fine silts			Fine silts	
Ma	Ma	Ma	Ma	Ma	Ma
Me	Me	Me	Ib	Ib	Ib
Ib	Ib	Ib	Ha	Ha	Ha
Ha	Ha	Ha	Me	Me	Me
Se	Se	Se	Se	Se	Se
Ba	Ba	Ba	Ba	Ba	Ba

TABLE XV (continued)

K''_c values (decreasing order)			$a_K/a_{Ca}^{1/2}$ (increasing order)		
Initial c_K/c_o			Initial c_K/c_o		
0.05	0.10	0.20	0.05	0.10	0.20
	Coarse clays			Coarse clays	
Ib	Ib	Ba	Ib	Ib	Ib
Ba	Se	Se	Se	Se	Ma
Se	Me	Ma	Me	Me	Me
Ha	Ma	Me	Ma	Ma	Se
Me	Ba	Ha	Ba	Ba	Ba
Ma	Ha	Ib	Ha	Ha	Ha
	Fine clays			Fine clays	
Ib	Ib	Ma	Ib	Ib	Ib
Ma	Ma	Se	Ma	Me	Se
Se	Se	Ha	Se	Se	Ba
Ha	Me	Ib	Me	Ma	Ma
Me	Ba	Ba	Ba	Ba	Me
Ba	Ha	Me	Ha	Ha	Ha

[a]Ba - Baxter
Ha - Hartsells
Ib - Iberia
Ma - Maury
Me - Memphis
Se - Sequoia

TABLE XVI

SUMMARY OF THE EQUILIBRIUM COEFFICIENTS, K_c', K_c'', AND THE ACTIVITY RATIOS, $a_K/a_{Ca}^{1/2}$, FOR THE POTASSIUM-42 EQUILIBRIUM STUDIES AT c_o=0.02N, INITIAL c_K/c_o=0.05

	Soil	Sand	Coarse Silt	Fine Silt	Coarse Clay	Fine Clay
			K_c' coefficients			
Baxter	0.374	0.359	0.042	0.106	1.368	2.116
Hartsells	0.392	0.049	0.054	0.360	0.749	1.886
Iberia	0.598	9.300	0.333	0.508	0.790	2.278
Maury	2.202	5.684	0.475	1.262	1.412	3.006
Memphis	0.804	0.153	0.329	0.865	1.320	2.282
Sequoia	0.929	7.915	0.081	0.348	1.213	2.473
			K_c'' coefficients			
Baxter	9.350	8.980	1.050	2.650	34.200	52.900
Hartsells	9.800	1.220	1.350	9.000	18.680	47.200
Iberia	14.950	232.500	8.320	12.700	19.750	56.950
Maury	55.050	142.100	11.880	31.550	35.300	75.150
Memphis	20.100	3.820	8.220	21.620	33.000	57.050
Sequoia	23.220	197.900	2.020	8.700	30.320	61.820
			$a_K/a_{Ca}^{1/2}$ values			
Baxter	0.01334	0.01361	0.01444	0.01430	0.01303	0.01073
Hartsells	0.01311	0.01433	0.01432	0.01358	0.01337	0.01134
Iberia	0.00686	0.00724	0.01387	0.01314	0.01164	0.00888
Maury	0.01056	0.00913	0.01381	0.01230	0.01260	0.01102
Memphis	0.01263	0.01406	0.01396	0.01350	0.01265	0.01037
Sequoia	0.01250	0.00951	0.01433	0.01382	0.01285	0.01073

Most fractions show an increase in the K_c' values with the concentration increase, but several show approximately the same value at both concentrations. The sand fractions of the Iberia, Maury, and Sequoia have the highest K_c' value of any of the fractions at c_o=0.02N. Comparison of the K_c'' values shows that the values at c_o=0.02N are noticeably lower than at c_o=0.002N. In contrast, K_c' values increase from c_o=0.002N to c_o=0.02N, primarily as a function of the total concentration increase. Thus, K_c'' values give a better comparison of values at different concentrations. There are three very noticeable exceptions to the statements concerning the K_c'' values at c_o=0.02N. These are the Iberia, Maury, and Sequoia sand fractions whose K_c'' values are much higher than their corresponding K_c' values and are the highest K_c'' values of all fractions at c_o=0.02N.

A comparison of the K_c', K_c'', and the equilibrium solution $a_K/a_{Ca}^{1/2}$ values for the soils from the K-42 equilibrium studies using their respective $\Delta G°$ values is shown in Tables XVII and XVIII. Woodruff (53,54,55) used $\Delta G°$ values calculated from $a_K/a_{Ca}^{1/2}$ values to evaluate the potassium status of a soil. He gave the ranges for $\Delta G°$ of

potassium deficient = -3500 to -4000 cal/mole

"ideal" = -2500 to -3000 cal/mole

calcium deficient = -2000 cal/mole

in describing the calcium-potassium balance in soils. To evaluate the data presented by free energy, $a_K/a_{Ca}^{1/2}$ values are the most appropriate unless one wishes to redefine the range of $\Delta G°$ values.

TABLE XVII

COMPARISON OF FREE ENERGIES OF EXCHANGE AS CALCULATED FROM K_c', K_c'', AND $a_K/a_{Ca}^{1/2}$ FOR THE POTASSIUM-42 SOIL EQUILIBRIUM STUDIES AT c_o=0.002N

Soils	K_c'	$\Delta G°$	K_c''	$\Delta G°$	$a_K/a_{Ca}^{1/2}$	$\Delta G°$
			Initial c_K/c_o=0.05			
Baxter	0.0892	1420	22.3	-1825	0.00244	-3537
Hartsells	0.1359	1173	34.0	-2070	0.00216	-3604
Iberia	0.0832	1461	20.8	-1876	0.00070	-4269
Maury	0.5390	363	134.8	-2881	0.00124	-3928
Memphis	0.1796	1011	44.9	-2234	0.00206	-3634
Sequoia	0.3075	695	76.8	-2553	0.00181	-3710
			Initial c_K/c_o=0.10			
Baxter	0.0169	2393	4.2	-847	0.00599	-3010
Hartsells	0.0204	2287	5.1	-958	0.00545	-3058
Iberia	0.0241	2187	6.0	-1052	0.00218	-3604
Maury	0.0908	1411	22.7	-1834	0.00400	-3275
Memphis	0.0335	1993	8.4	-1252	0.00542	-3063
Sequoia	0.0471	1793	11.8	-1452	0.00523	-3087
			Initial c_K/c_o=0.20			
Baxter	0.0215	2258	5.4	-994	0.01205	-2599
Hartsells	0.0208	2270	5.2	-970	0.01175	-2610
Iberia	0.0147	2481	3.7	-770	0.00514	-3105
Maury	0.0971	1370	24.3	-1876	0.00797	-2840
Memphis	0.0203	2287	5.1	-958	0.01188	-2605
Sequoia	0.0579	1658	14.5	-1576	0.01033	-2687

TABLE XVIII

COMPARISON OF FREE ENERGIES OF EXCHANGE AS CALCULATED FROM K'_c, K''_c, AND $a_K/a_{Ca}^{1/2}$ VALUES FOR THE SOILS FROM THE POTASSIUM-42 EQUILIBRIUM STUDIES AT c_o=0.02N

	Initial c_K/c_o=0.05					
Soils	K'_c	$\Delta G°$	K''_c	$\Delta G°$	$a_K/a_{Ca}^{1/2}$	$\Delta G°$
Baxter	0.374	578	93.5	-2670	0.01334	-2540
Hartsells	0.392	550	98.0	-2693	0.01311	-2546
Iberia	0.598	302	149.5	-2940	0.00686	-2946
Maury	2.202	-464	550.5	-3710	0.01056	-2675
Memphis	0.804	128	201.0	-3116	0.01263	-2570
Sequoia	0.929	43	232.2	-3205	0.01250	-2575

All of the soils at equilibrium with c_o=0.002N, initial c_K/c_o=0.05 solutions are potassium deficient as indicated by the $\Delta G°$ values from the activity ratios. Most soils at initial c_K/c_o=0.10 are slightly potassium deficient and at initial c_K/c_o=0.20 all soils except the Iberia are in the "ideal" range. At all c_K/c_o levels, the Iberia has a noticeably more negative (higher absolute number for) $\Delta G°$ than do any of the other soils.

At c_o=0.02N (Table XVIII, p. 62), the $\Delta G°$ values determined from the $a_K/a_{Ca}^{1/2}$ values indicate that the potassium-calcium status for all soils is "ideal." The K_c'' values give some $\Delta G°$ values which are in the "ideal" range, but also others which are not. Thus $\Delta G°$ values calculated from equilibrium solution ratios are among the best means for evaluating the calcium-potassium status of a soil after the potassium-42 type (fixed amount of soil material and solution) of equilibrium studies. These ratios should be used in conjunction with the equilibrium constant in selectivity or equilibrium studies.

Time and material prevented determination of the potassium "fixed" against removal by calcium after the equilibrium from the K-42 studies for all of the soils and soils fractions. Table XIX presents the "fixed K" on the soils at c_o=0.002N, initial c_K/c_o=0.10. Table XX lists the "fixed" K for the soils and soils fractions at c_o=0.002N, initial c_K/c_o=0.20. Although more K was adsorbed at initial c_K/c_o=0.20, less was "fixed" than at initial c_K/c_o=0.10 in percentage and meq/100g on four of the six soils. No explanation for this can be given.

TABLE XIX

POTASSIUM "FIXED" AGAINST REMOVAL BY CALCIUM ON THE SOILS AFTER THE POTASSIUM-42 EQUILIBRIUM STUDY AT c_o=0.002N, INITIAL c_K/c_o=0.10

Soils	Sorbed K	"Fixed" K	Percent "Fixed"	"Fixed" K as Percent of CEC
	------meq/100g------			
Baxter	0.037	0.0061	16.49	0.18
Hartsells	0.041	0.0076	18.54	0.20
Iberia	0.139	0.1031	74.17	0.36
Maury	0.090	0.0228	25.33	0.44
Memphis	0.052	0.0081	15.58	0.22
Sequoia	0.057	0.0116	20.35	0.32

TABLE XX

POTASSIUM "FIXED" AGAINST REMOVAL BY CALCIUM ON THE SOILS AND SOILS FRACTIONS AFTER THE POTASSIUM-42 EQUILIBRIUM STUDY AT c_o=0.002N, INITIAL c_K/c_o=0.20

	Sorbed K	"Fixed" K	Percent "Fixed"	"Fixed" K as Percent of CEC
	------meq/100g--------			
Soils				
Baxter	0.0827	0.0072	8.67	0.22
Hartsells	0.0897	0.0078	8.74	0.22
Iberia	0.2585	0.0778	30.11	0.27
Maury	0.1839	0.0223	12.16	0.43
Memphis	0.1045	0.0070	6.65	0.20
Sequoia	0.1249	0.0153	12.25	0.42
Sands				
Baxter	0.0164	0.0011	6.73	0.08
Hartsells	0.0064	0.0004	6.79	0.04
Iberia	0.0788	0.0249	31.62	0.73
Maury	0.0601	0.0113	18.86	0.44
Memphis	0.0106	0.0006	5.94	0.05
Sequoia	0.0592	0.0089	15.04	0.46
Coarse silts				
Baxter	0.0180	0.0011	6.31	0.06
Hartsells	0.0238	0.0017	7.25	0.07
Iberia	0.0450	0.0036	7.93	0.17
Maury	0.0526	0.0037	7.03	0.20
Memphis	0.0429	0.0026	6.14	0.14
Sequoia	0.0235	0.0013	5.40	0.07
Fine silts				
Baxter	0.0270	0.0027	10.52	0.17
Hartsells	0.0662	0.0095	14.41	0.35
Iberia	0.0899	0.0170	18.86	0.46
Maury	0.1162	0.0153	13.18	0.45
Memphis	0.0658	0.0067	10.24	0.36
Sequoia	0.0496	0.0048	9.61	0.22
Coarse clays				
Baxter	0.5047	0.0536	10.63	0.49
Hartsells	0.4853	0.0464	9.56	0.45
Iberia	0.8573	0.2500	29.18	0.86
Maury	0.5902	0.0604	10.23	0.43
Memphis	0.5893	0.0619	10.51	0.44
Sequoia	0.5630	0.0533	9.48	0.42

TABLE XX (continued)

	Sorbed K	"Fixed" K	Percent "Fixed"	"Fixed" K as Percent of CEC
	------meq/100g--------			
Fine clays				
Baxter	0.8746	0.0799	9.13	0.32
Hartsells	0.7877	0.0711	9.02	0.38
Iberia	1.1760	0.2188	18.60	0.51
Maury	0.8373	0.1006	12.03	0.52
Memphis	0.9210	0.0858	9.32	0.32
Sequoia	0.8984	0.0785	8.74	0.50

"Fixed" K on the soils and soils fractions at c_o=0.02N, initial c_K/c_o=0.05 is given in Table XXI. In relation to the previous values (Table XX), these are from a system of 10 times greater total concentration with a reduction of .15 in the c_K/c_o. The amount of "fixed" K is greatest at c_o=0.02N for all fractions. At c_o=0.002N, the fine clays "fixed" more potassium than the coarse clays of corresponding soils excepting Iberia. At c_o=0.02 all of the fine clays "fixed" more K than the coarse clays of corresponding soils. The clays "fixed" more K than any other fraction at either concentration, with one exception. The Iberia soil at c_o=0.02N "fixed" more K than any of the clay fractions excepting the Iberia fine clay. At c_o=0.002N, initial c_K/c_o=0.20 the fractions in the average order of decreasing "fixed" K are fine clays>coarse clays>soils>fine silts>sands>coarse silts. For c_o=0.02N, the "fixed" K decreased in the order: fine clays>coarse clays>soils>sands>fine silts>coarse silts. Each fraction "fixed" similar percentages of K at c_o=0.002N and c_o=0.02N. At both c_o values, the "fixed" K (in meq/100g) for the fine clays decreased in the order: Iberia>Maury>Memphis>Baxter>Sequoia>Hartsells. The percent "fixed" K followed the same order with Hartsells and Sequoia being reversed. "Fixed" K (in meq/100g) for the coarse clays decreased in the order: Iberia>Memphis>Maury>Baxter>Sequoia>Hartsells. The percent "fixed" K followed the same order as did the fine clays. One might expect that the "vermiculite" and/or "illite" components of the clays would decrease in the same order as does the "fixed" K. However, experimental results presented herein do not agree with this hypothesis.

TABLE XXI

POTASSIUM "FIXED" AGAINST REMOVAL BY CALCIUM ON THE SOILS AND SOILS FRACTIONS AFTER THE POTASSIUM-42 EQUILIBRIUM STUDY AT c_o=0.02N, INITIAL c_K/c_o=0.05

	Sorbed K	"Fixed" K	Percent "Fixed"	"Fixed" K as Percent of CEC
	------meq/100g--------			
Soils				
Baxter	0.183	0.0236	12.89	0.72
Hartsells	0.214	0.0258	12.04	0.70
Iberia	1.056	0.4770	45.17	1.65
Maury	0.556	0.0887	15.94	1.69
Memphis	0.278	0.0289	10.40	0.80
Sequoia	0.296	0.0448	15.12	1.24
Sands				
Baxter	0.037	0.0030	8.11	0.22
Hartsells	0.013	0.0010	7.77	0.10
Iberia	0.251	0.0563	22.36	1.66
Maury	0.187	0.0374	19.93	1.47
Memphis	0.022	0.0014	6.48	0.12
Sequoia	0.174	0.0279	16.06	1.43
Coarse silts				
Baxter	0.038	0.0030	7.98	0.17
Hartsells	0.054	0.0048	8.94	0.21
Iberia	0.114	0.0069	6.05	0.33
Maury	0.122	0.0083	6.85	0.45
Memphis	0.103	0.0070	6.76	0.38
Sequoia	0.052	0.0022	4.28	0.13
Fine silts				
Baxter	0.056	0.0071	12.55	0.41
Hartsells	0.152	0.0252	16.56	0.93
Iberia	0.211	0.0222	10.52	0.68
Maury	0.322	0.0363	11.27	1.06
Memphis	0.162	0.0154	9.50	0.81
Sequoia	0.120	0.0108	8.93	0.50
Coarse clays				
Baxter	1.126	0.1104	9.80	1.02
Hartsells	1.108	0.0984	8.92	0.84
Iberia	2.055	0.3345	16.29	1.15
Maury	1.412	0.1324	9.38	0.95
Memphis	1.390	0.1333	9.57	0.95
Sequoia	1.241	0.1028	8.19	0.78

TABLE XXI (continued)

	Sorbed K	"Fixed" K	Percent "Fixed"	"Fixed" K as Percent of CEC
	------meq/100g--------			
Fine clays				
Baxter	2.662	0.2132	8.00	0.85
Hartsells	2.257	0.1778	7.89	0.94
Iberia	3.911	0.4824	12.31	1.12
Maury	2.466	0.2637	10.69	1.38
Memphis	2.901	0.2341	8.05	0.85
Sequoia	2.661	0.1990	7.47	0.88

For example, the Hartsells clay has a large "vermiculite" component (Table II, p. 29), yet "fixes" the least amount and second from the least percentage of K. This could be due to (1) a low charge density on the "vermiculite" requiring drying before large amounts of K will be "fixed," or (2) additions of K to the soil prior to sampling were large enough to satisfy most of the positions which "fix" K. No correlation was found between "fixed" K and the equilibrium coefficients. High selectivity of K at low levels of solution K could have resulted primarily from "fixation" but no data on "fixation" at the low solution levels of K is available. The most unexpected values for "fixed" K are those for Iberia, Maury, and Sequoia sands. Values for these sands are greater than for most of the coarse and fine silts and many of the soils. "Fixation" of potassium is probably due to the existence of pores in the sand materials which cause restricted movement of potassium and calcium. The "fixation" of potassium in these sands should be termed "entrapment" of potassium so as not to confuse the process here with that of the one in layer silicates. Only for a few fractions at c_o=0.02N did the "fixed" K amount to greater than one percent of the total exchange capacity.

Potassium exchange capacities, KEC, for the soils and soils fractions as determined by K-42 labeled, 1N KCl are given in Table XXII. The reader may wish to compare these values to the calcium exchange capacity (CEC) values in Table IV, p. 34. Potassium exchange capacity values decrease in the order: fine clays>coarse clays>soils>fine silts>coarse silts>sands. The Iberia, Maury, and Sequoia sands again show unusually high values.

TABLE XXII

POTASSIUM EXCHANGE CAPACITY VALUES OF THE SOILS AND SOILS FRACTIONS AS DETERMINED BY POTASSIUM-42 LABELED, 1N KCl

Soils Name	Soils	Sands	Coarse Silts	Fine Silts	Coarse Clays	Fine Clays
	meq/100g					
Baxter	3.29	1.34	1.84	1.75	10.87	25.22
Hartsells	3.70	1.14	2.34	2.72	10.51	18.86
Iberia	28.96	3.38	2.07	3.27	29.01	42.92
Maury	5.22	2.56	1.87	3.43	13.92	19.16
Memphis	3.59	1.15	1.85	1.89	14.09	27.35
Sequoia	3.60	1.96	1.84	2.14	12.92	23.45

Studies on the Iberia sand in addition to those performed on the other soil fractions were prompted by the unusually high CEC values (Table XXIII) of the sand. Table XXIII also gives the percent composition of the Iberia sand separates in respect to the soil (<2mm material) and to the sand size material (2-0.05mm). Initial CEC determinations had given enormously high values. It was then discovered that complete removal of excess electrolyte took much longer than for any other soil fraction. This sand fraction contains a large amount of concretionary material and the ensuing investigations were made to determine the nature of this material. The Maury and Sequoia sand fractions also contain large amounts of concretionary material. Although the physical appearance of the three sands differs somewhat, their behavior is similar.

One initial theory as to the source of the charge for cation exchange in the Iberia sand sized material was that of clay trapped in the concretions. X-ray analysis, both from powder camera and powder and water oriented diffractometer samples, failed to show the presence of any clay mineral. X-ray analysis showed quartz to be the only crystalline substance present which could be identified. No quantitative determination or estimate of quartz or SiO_2 was made from the x-ray analysis.

The Iberia and Maury sand fractions were shown to exhibit a significant pH dependent CEC as shown in Table XXIV. De Villiers and Jackson (12) studied CEC variations with pH in soil clays. They attributed this phenomenon to deprotonation of M_xOH_y groups. They

TABLE XXIII

CATION EXCHANGE CAPACITY OF THE IBERIA SAND FRACTION AND SEPARATES AND THEIR RESPECTIVE PERCENTAGES OF THE SOIL (<2mm) AND SAND (2-0.05mm)

Fraction and Separates Size, mm	Percent of the <2mm Material	Percent of the 2-0.05mm Material	CEC meq/100g
1-0.05	4.6	65.7	8.6
2-1	2.4	34.3	9.2
1-0.5	1.8	25.7	12.2
0.5-0.25	0.7	10.0	12.3
0.25-0.1	1.0	14.3	10.5
0.1-0.05	1.1	15.7	7.8

TABLE XXIV

THE pH DEPENDENT CHARGE OF THE MAURY AND IBERIA SANDS

Sand	Size (mm)	pH	CEC (meq/100g)	Percent Decrease of CEC
Maury	1-0.05	7.4	7.92	
	1-0.05	4.5	5.62	29.0
Iberia	2-1	7.4	5.60	
	2-1	4.5	4.21	24.8
Iberia	1-0.5	7.4	8.21	
	1-0.5	4.5	5.56	32.3
Iberia	1-0.05	7.4	8.50	
	1-0.05	4.5	5.83	31.4

were most concerned with the hydroxy alumina ($-AlOH_2$) groups in the soil clay minerals. It is possible that this material has hydroxy groups present. Chemical analysis of the material and further elaboration on this point are discussed below.

Results of the specific gravity separations of the Iberia sand separates are given in Table XXV. An average of 60 percent of the material in all size separates had a specific gravity of greater than 2.96 and 72 percent had a specific gravity of greater than 2.72. The majority of the concretions are in these two groups and little, if any, material other than concretionary was observed in these two groups.

Elemental analysis of the Iberia sand separates, reported as oxides of the elements in Table XXVI, shows that the largest constituent, by far, is $Fe_2\ O_3$. It accounts for 41 to 48 percent of the separates of the concretionary material (that material having a specific gravity of >2.96). One interesting observation is that of the amount of Na_2O present and the lack of any CaO. The soil is high in exchangeable Ca and if the concretions were formed in place, as is thought, one would expect some entrapment of Ca with the Na in the material.

X-ray spectral analysis of the 1.0-0.05mm material having a specific gravity of >2.96 showed Fe and Mn to be the major and minor constituents, respectively, and a possibility of small amounts of As and Cr. Presence of Zr was listed as questionable from this analysis. The x-ray spectral analysis was not sensitive to any element below number 22, Ti.

TABLE XXV

SPECIFIC GRAVITY SEPARATES OF THE IBERIA SAND SEPARATES AS DETERMINED BY USING HEAVY ORGANIC LIQUIDS

Specific gravity	2-1mm	1-.5mm	.5-.25mm	.25-.10mm	.10-.05mm
	percent				
>2.96	89.6	79.5	67.8	44.3	16.9
2.96-2.72	4.6	13.8	16.6	16.9	12.4
2.72-2.65	3.4	3.6	10.8	16.6	13.8
2.65-2.60	2.2*	1.8	3.1	19.8	54.2
<2.60		1.4	1.6	2.4	2.6

*<2.65

TABLE XXVI

ELEMENTAL ANALYSIS OF THE IBERIA SAND SEPARATES

Size, mm	Fe_2O_3	MnO	Na_2O	K_2O	MgO	ZnO	CaO	Total
	Material separated by size only							
	percent							
1-0.05	31.6	1.60	0.41	0.57	0.25	0.01	0.00	34.44
2-1	42.5	1.50	0.33	0.59	0.27	0.03	0.00	45.22
1-0.5	38.3	1.50	0.36	0.64	0.26	0.03	0.00	41.09
0.5-0.25	31.3	1.88	0.43	0.69	0.26	0.01	0.00	34.57
0.25-0.1	24.4	1.70	0.27	0.56	0.23	0.01	0.00	27.17
0.1-0.05	12.7	0.97	0.19	0.48	0.20	0.01	0.00	14.55
	Material having a specific gravity of >2.96							
	percent							
2-1	48.3	0.72	3.17	0.84	0.89	0.03	0.00	53.95
1-0.5	44.9	0.96	2.33	0.76	0.72	0.03	0.00	49.70
0.5-0.25	43.1	1.40	3.10	0.89	0.89	0.03	0.00	49.41
0.25-0.1	40.9	1.58	1.33	0.69	0.54	0.03	0.00	45.07

There are indications of a large internal surface area in the concretions. After the specific gravity separations (above), difficulty was encountered in removing the organic liquid from the material. Washings with acetone, heating to 50-60°C, and a vacuum were used in attempting to remove the organic liquid. After all attempts, enough of the liquid remained adsorbed for the presence of Br (from tetrabromoethane) to be detected from the x-ray spectral analysis. Figures 2 through 5 show photographs of particles from a thin section of the Iberia concretions. Particles were embedded in a plastic disc, the plastic block was ground on one side until the particles were dissected, and this side of the disc was mounted on a glass slide. The top of the plastic was ground until a thickness of about 30-50μ was obtained and the photographs were taken using plane polarized light. Figure 2 shows fan-shaped striation-like lines transversing the length of the particle. This particle is not characteristic of most of the ones observed but it is much thinner (no estimate of thickness) than most of the other particles. It is believed that these lines indicate the direction of pores in this specimen. The particle in Figure 3 is characteristic of most of the concretions in the thin section, in overall appearance and in the nature of the pores (the light spots within the particle). Shaded areas on several of the pores indicate that they all are not perpendicular to the plane of the paper. Note the lighter, straited-like material in the upper right edge of the concretion. This material is thinner than the rest of the particle and is similar to the particle in Figure 2.

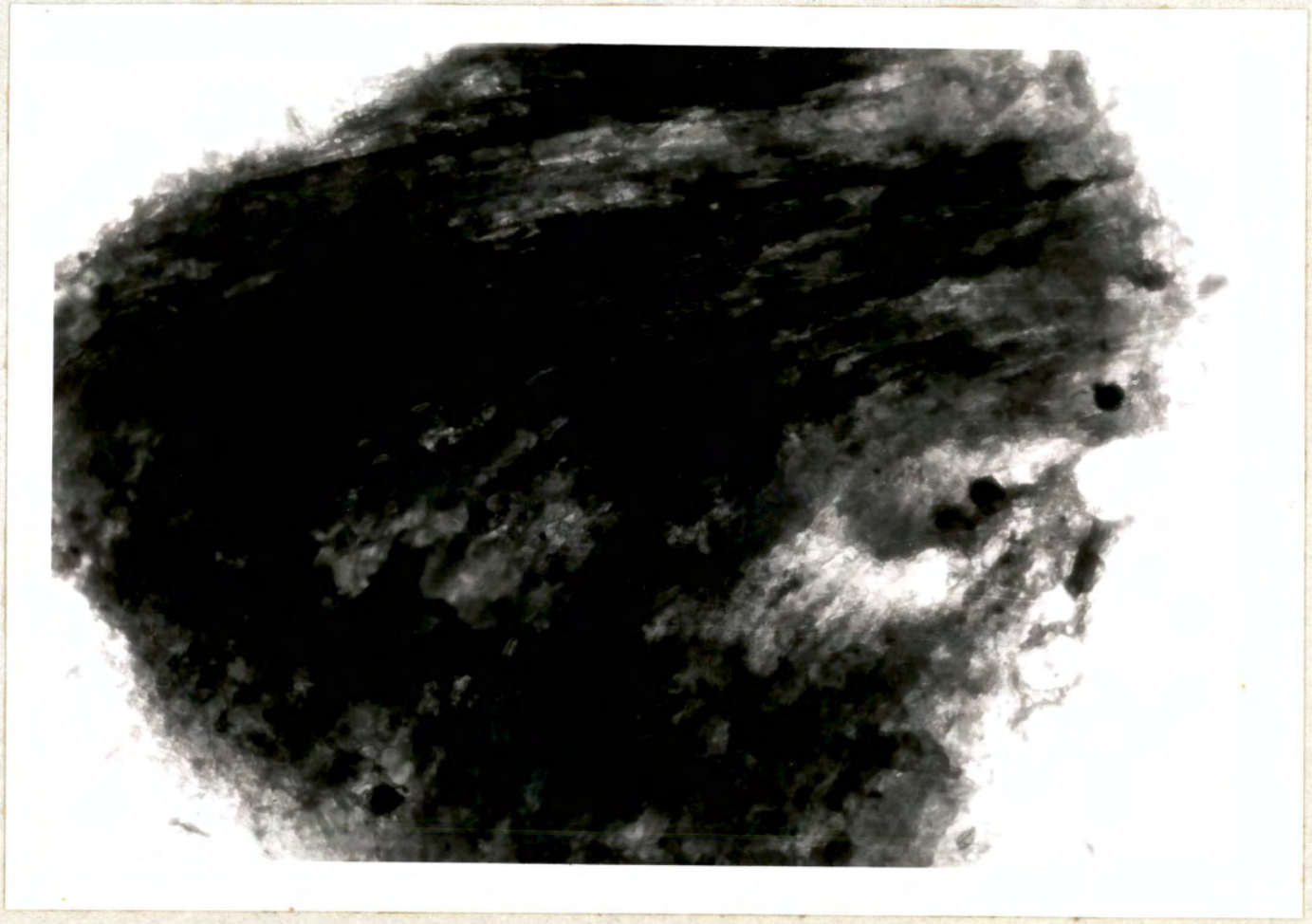

Figure 2. Iberia concretion showing longitudinal striation-like lines. Plane polarized light, 220X.



Figure 3. Iberia concretion showing pores (light areas) and inclusion of material having striation-like lines. Plane polarized light, 220X.



Figure 4. Iberia concretion showing angular direction of a pore. Plane polarized light, 220X.

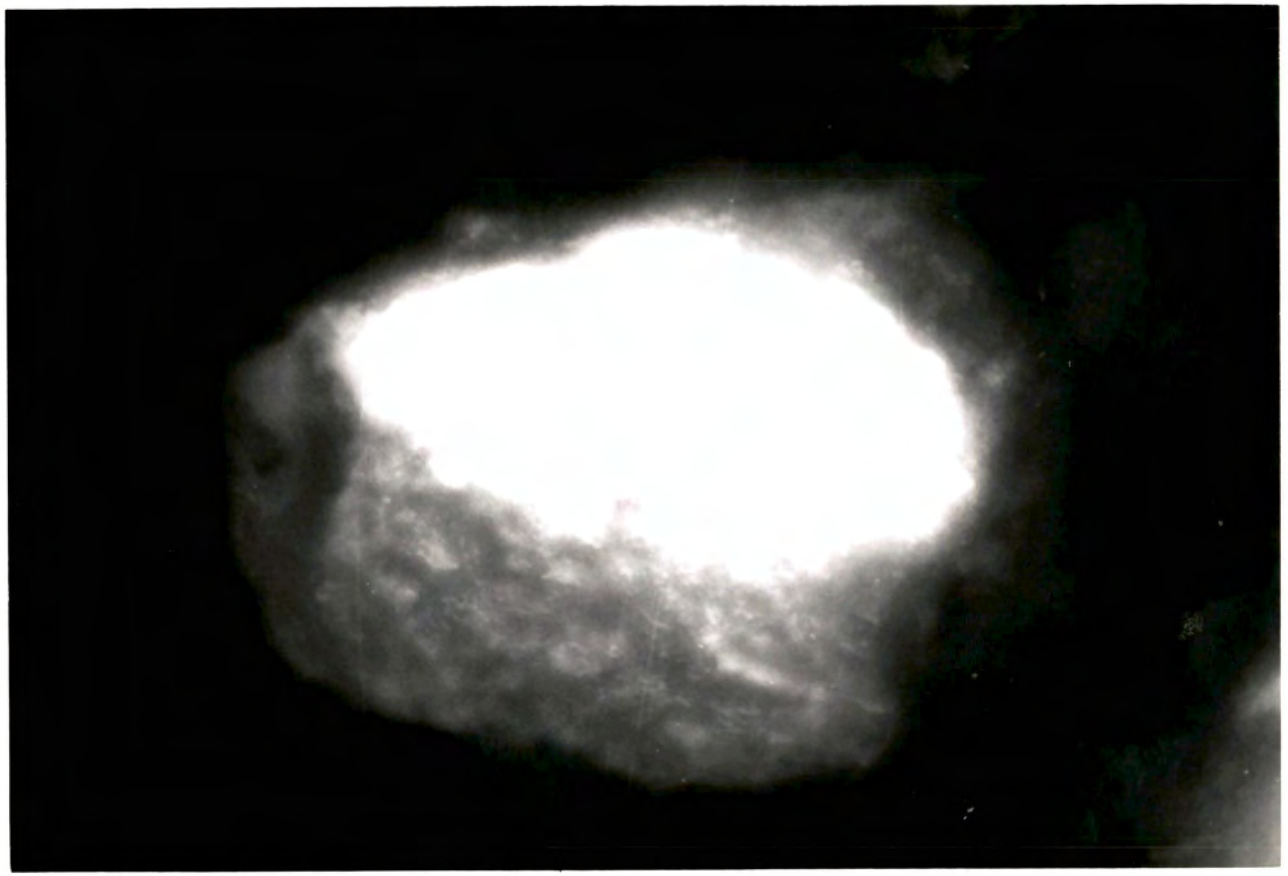

Figure 5. Close-up view of the angular pore of an Iberia concretion. Plane polarized light, 800X.

Figure 4, p. 81, shows a well defined pore in the upper center of the particle. The outline of the pore is distinct and a dimension of depth is given. This pore clearly shows that it could not have resulted from the grinding or polishing of the thin section. A closer view of this pore is shown in Figure 5, p. 82, and one can see the pitted nature of the edge of the pore. This rough texture adds to the internal surface area of the concretions. The pores shown in these photographs are 'macropores' and one may doubt that their contribution in internal surface area is sufficient to cause the type of reactivity discussed in this paper. Recent observations of these particles at 600X magnification have shown large numbers of micropores to be present, thus proving the existence of a large internal surface area in these concretions.

Upon observation of the material, members of the geology department have suggested that the concretions are limonite, goethite or a combination of the two. Absence of Ti in the x-ray spectral analysis eliminates ilmenite as being present. Present interpretation is that the concretions consist primarily of amorphous iron oxides or hydroxides. If hydroxide forms are present, at least a partial source of the negative charge of the material could be explained. The pH dependent charge possibly indicates the presence of OH groups. Fine or microcrystalline quartz is incorporated into the concretions as indicated by x-ray analysis and by microscopic observation, but no quantative estimate of Si or SiO_2 has been attempted.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Certain chemical and mineralogical properties of the samples used differed from those of reference samples from the same site. Changes in soil conditions from the time of collecting the reference samples to that of collecting the samples used in the present studies explain some differences such as pH and organic matter content. No explanation other than experimental conditions is given to the differences in some of the measured cation exchange capacity values. Current interpretations of the x-ray analysis of the soil clay fractions were in general agreement with previous interpretations. Terminology of soil clay minerals and some problems in interpretation of the results were discussed.

Cation exchange capacities of the soils were measured in unbuffered systems using two different extracting cations. Differences in values from the two measurements were attributed to the extracting cations. Cation exchange capacities of the soils and soils fractions were measured with unbuffered solutions because most studies were conducted using unbuffered solutions.

Ammonium removed additional potassium after an initial extraction by calcium from the soils and soils fractions decreased, and there was matter in the whole soil samples. Drying the soil in the presence of potassium reduced the calcium exchangeable potassium by as much as 67 percent and the additional ammonium exchangeable potassium as

much as 65 percent. The Iberia, Sequoia, and Maury sands exhibited an unusually high value for calcium exchangeable potassium.

Leaching column equilibrium studies on the soils gave the following order of equilibrium selectivity coefficients (highest to lowest):

at c_K/c_o=0.05 - Iberia>Sequoia>Memphis>Baxter>Maury>Hartsells

at c_K/c_o=0.10 - Maury>Iberia>Baxter>Memphis>Hartsells>Sequoia

at c_K/c_o=0.20 - Maury>Sequoia>Memphis>Iberia>Baxter>Hartsells

The above order of values is not the same at any two of the three potassium solution levels. As the K:Ca solution ratio increased, the q_K/q_o of the soils and soils fractions decreased, and there was a shift in the order of q_K/q_o values within each fraction. Three of the six soils were selective for potassium over calcium in the determination of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for exchange of calcium by potassium. These were Baxter, Iberia, and Maury, the basis of selectivity being that $q_K/q_o > c_K/c_o$. Four of the soils gave negative values for $\Delta H°$ and $\Delta S°$ the Iberia and Memphis gave positive $\Delta H°$ and $\Delta S°$ values. On the basis of $\Delta S°$, the soils show the following order of charge density: Baxter>Sequoia>Maury>Hartsells>Memphis>Iberia, with the latter two soils having positive $\Delta S°$ values.

The derivation of general expression $\Delta G° = \Delta H° + IT$ was shown. This expression allows calculation of $\Delta G°$ which in turn allows calculation of the equilibrium coefficient, K''_c, at any temperature. The constant of integration, I, was determined for each soil and the

following expressions were given:

$\Delta G^\circ_{Baxter} = -4478 + 9.05\ T$

$\Delta G^\circ_{Hartsells} = -1680 + 0.78\ T$

$\Delta G^\circ_{Iberia} = 177 - 7.45\ T$

$\Delta G^\circ_{Maury} = -2520 + 1.92\ T$

$\Delta G^\circ_{Memphis} = 1260 - 8.15\ T$

$\Delta G^\circ_{Sequoia} = -2648 + 4.93\ T$

where T is the absolute temperature and ΔG° is in cal/mole K.

The study of the equilibrium $2K^+ + CaM_2 \rightleftarrows 2KM + Ca^{++}$ using radioactive potassium-42 gave equilibrium selectivity coefficients for all soils and soils fractions at c_o=0.002N with three levels of solution potassium. Selectivity coefficients were also obtained at c_o=0.02N, but with only one level of solution potassium.

The equilibrium coefficient K_c' (or K_c'') is not always the best evaluation of the equilibrium as was shown with the Iberia soil. It was concluded that the activity ratios of the equilibrium solution should be considered in the evaluation.

At c_o=0.002N the K_c' values decreased in the following order:

at c_K/c_o=0.05 - coarse clays>fine clays>soils>fine silts>sands>coarse silts

at c_K/c_o=0.10 - fine clays>coarse clays>fine silts>soils>coarse silts>sands

at c_K/c_o=0.20 - fine clays>coarse clays>soils>fine silts>sands>coarse silts

At c_o=0.02N, the K_c' values decreased in the following order:

at c_K/c_o=0.05 - sands>fine clays>coarse clays>soils>fine silts>coarse silts

One can see from the above orders that there was variation among the fractions as to the K_c' values within one total concentration as well as between concentrations. This variation could result from selectivity differences at different K:Ca ratios as well as at different concentrations, but the cause is not definitely known.

Free energies of exchange were calculated from K_c', K_c'', and $a_K a_{Ca}^{1/2}$ values for the soils. Free energy values obtained from $a_K/a_{Ca}^{1/2}$ measurements gave ΔG° values within the ranges set by Woodruff (53,54,55) for describing the potassium status of the soil. These values gave the best evaluation of the reactions in the potassium-42 type of equilibrium determinations.

Data for potassium "fixed" against removal by calcium after the potassium-42 selectivity studies are incomplete. In the date presented, more potassium was "fixed" from systems having the highest initial concentration of solution potassium. There were, however, unexplained exceptions to the above statement in the soils at c_o=0.002N, initial c_K/c_o=0.10.

Potassium exchange capacities for the soils and soils fractions as determined by potassium-42 labeled KCl showed varying degrees of correlation to corresponding values determined for calcium exchange capacities. Generally, values from the two determinations were similar for corresponding fractions.

The Iberia, Maury, and Sequoia sand fractions exhibited cation exchange properties unexpected of sands. These properties were first noticed when cation exchange capacity (CEC) measurements were conducted. All three sands contain large amounts of concretionary materials. The Iberia exhibited the highest CEC and had the greatest number of concretions, therefore it was chosen for additional study. Both the Maury and Iberia have a pH dependent CEC. Reductions in CEC of 29 percent in the Maury and 31 percent in the Iberia occurred when the saturating solution was reduced from pH 7.4 to pH 4.5.

Material in the Iberia sand separates having a specific gravity >2.96 ranged from 89 percent in the coarse sand to 17 percent in the very fine sand. An average of 60 percent of the entire sand fraction (2-0.5mm) had a specific gravity of >2.96. Elemental analysis of the separates determined that Fe_2O_3 accounts for 41 to 48 percent of the concretions. Only a partial elemental analysis was conducted, but x-ray spectral analysis did not detect any additional significant elements in addition to the chemical determinations.

Quartz was the only constituent of the concretions which could be identified from x-ray diffraction analysis. An initial theory as to the source of reactivity of the concretions was that of entrapped clay minerals. X-ray powder and diffractometer analyses did not detect any type of clay or clay mineral. The concretions are thought to have a large internal surface area and evidence of this fact was presented. The characterization of this material is far from complete, but considerable progress has been made into the study.

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APPENDIX

SITE LOCATIONS OF THE SOIL SAMPLES USED IN THE STUDIES

The Baxter soil was sampled in Robertson County, Tennessee, from the Joel Bradly farm, one mile N. E. of the intersection of highways Tenn. 41-A and Tenn. 49. The site is off highway 41-A, ten feet north of the road bank in the woodland. The present sample was taken very close to the old sampling site and there had been no change in the area. The reference soil sample from this site is identified by the University of Tennessee Agronomy Department laboratory number 111.

The Hartsells soil sample was obtained in Fentress County, Tennessee, from the Wright Frogge farm. The site is south of Jamestown off Tenn. highway 28, 1.4 miles east of the highway and about 10 feet north of the field road. There had been a pasture established with 400 pounds of 6-12-12 and six tons of lime applied per acre prior to the sampling date. The University of Tennessee Agronomy Department laboratory number 101 identifies the reference soil sample from this site.

The Iberia soil sample was taken in Rutherford County, Tennessee, on the Little farm. The farm is on Highway 99 one mile east of Eagleville. The site is about 50 yards north of the road from a utility pole on the east side of the bridge. The sample was taken within ten feet of the location of the characterization sample site. The vegetation at the time of sampling was soybeans. There is no University of Tennessee Agronomy Department laboratory number for this soil.

The Maury soil was sampled in Maury County, Tennessee, on the J. P. Due farm, three and one-half miles N. E. of Mt. Pleasant. The sample was taken from a field of permanent fescue pasture. The University of Tennessee Agronomy Department laboratory number for the reference sample of this soil is 73.

The Memphis soil sample was obtained in Fayette County, Tennessee, from the James Kilby, Jr., farm. The farm is located 13 miles N. E. of Sommerville and the sample was taken 25 feet east of the south wing of the residence. The reference sample from this site has the University of Tennessee Agronomy Department laboratory number 52.

The Sequoia soil sample was taken in Blount County, Tennessee, on the A. M. Hornbuckle farm, 1.25 miles south of Alnwick. The site is located in a triangular-shaped tract of idle land in the forks of two gravel roads. The University of Tennessee Agronomy Department laboratory number 17 identifies the reference soil sample taken from this site.

Tables A-I through A-VII present the data from which values for the major experiments presented in the text were calculated.

TABLE A-I

DATA FROM THE EQUILIBRIUM $2K^{+} + CaM_2 \rightleftarrows 2KM + Ca^{++}$ ON THE SOILS AT c_o=0.002N, 23°C, AS DETERMINED FROM THE LEACHING COLUMN STUDIES

c_K/c_o=0.05			c_K/c_o=0.10			c_K/c_o=0.20		
Ca+K	Ca	K	Ca+K	Ca	K	Ca+K	Ca	K
meq/100g								
				Baxter				
3.61	3.42	0.19	3.56	3.33	0.23	4.01	3.67	0.34
				Hartsells				
7.21	6.97	0.24	5.63	5.34	0.29	5.48	5.13	0.35
				Iberia				
29.16	25.70	3.46	24.07	22.35	1.72	25.33	23.01	2.32
				Maury				
12.13	11.55	0.58	10.14	9.28	0.86	10.45	9.28	1.17
				Memphis				
6.04	5.70	0.34	6.28	5.87	0.39	5.87	5.33	0.54
				Sequoia				
4.87	4.47	0.40	5.50	5.23	0.27	5.07	4.53	0.54

TABLE A-II

DATA FOR THE CALCULATION OF FREE ENERGIES, STANDARD HEATS AND ENTROPIES OF EXCHANGE FOR THE REPLACEMENT OF CALCIUM BY POTASSIUM ON THE SOILS

	T=281(8°C)			T=296(23°C)		
Soils	Ca+K	Ca	K	Ca+K	Ca	K
	meq/100g					
Baxter	4.28	3.46	0.825	4.61	4.00	0.608
Hartsells	9.42	8.60	0.820	8.95	8.27	0.686
Iberia	31.95	26.00	5.950	33.30	27.00	6.300
Maury	13.35	10.60	2.750	13.22	11.00	2.220
Memphis	7.04	6.75	0.295	7.86	7.50	0.360
Sequoia	5.67	5.32	0.350	5.50	5.23	0.270

TABLE A-III

DATA FROM THE EQUILIBRIUM STUDIES UTILIZING POTASSIUM-42 AT c_o=0.002N, INITIAL c_K/c_o=0.05

	Exchangeable Cations			Equilibrium Solution	
	Ca+K	Ca	K	Ca	K
	meq/100g			meq/l	
Soils					
Baxter	3.290	3.260	0.0331	1.9331	0.0669
Hartsells	3.700	3.650	0.0408	1.9408	0.0592
Iberia	28.960	28.880	0.0807	1.9807	0.0193
Maury	5.220	5.170	0.0658	1.9658	0.0342
Memphis	3.590	3.550	0.0433	1.9433	0.0567
Sequoia	3.600	3.560	0.0502	1.9502	0.0498
Sands					
Baxter	1.344	1.337	0.0070	1.9140	0.0860
Hartsells	1.144	1.141	0.0033	1.9066	0.0934
Iberia	3.382	3.356	0.0260	1.9520	0.0480
Maury	2.562	2.540	0.0220	1.9440	0.0560
Memphis	1.152	1.147	0.0053	1.9106	0.0894
Sequoia	1.957	1.936	0.0989	1.9420	0.0580
Coarse Silts					
Baxter	1.839	1.829	0.0100	1.9100	0.0900
Hartsells	2.340	2.327	0.0130	1.9130	0.0870
Iberia	2.070	2.047	0.0230	1.9230	0.0770
Maury	1.872	1.848	0.0240	1.9240	0.0760
Memphis	1.852	1.831	0.0210	1.9210	0.0790
Sequoia	1.847	1.835	0.0120	1.9120	0.0880
Fine Silts					
Baxter	1.747	1.731	0.0160	1.9160	0.0840
Hartsells	2.719	2.686	0.0330	1.9330	0.0670
Iberia	3.273	3.233	0.0400	1.9400	0.0600
Maury	3.426	3.381	0.0460	1.9460	0.0540
Memphis	1.893	1.863	0.0300	1.9300	0.0700
Sequoia	2.145	2.120	0.0250	1.9250	0.0750
Coarse Clays					
Baxter	10.886	10.608	0.2780	1.9556	0.0444
Hartsells	10.513	10.265	0.2480	1.9496	0.0504
Iberia	29.013	28.566	0.4470	1.9894	0.0106
Maury	13.923	13.637	0.2860	1.9572	0.0428
Memphis	14.093	13.805	0.2880	1.9576	0.0424
Sequoia	12.923	12.632	0.2910	1.9528	0.0418

TABLE A-III (continued)

	Exchangeable Cations			Equilibrium Solution	
	Ca+K	Ca	K	Ca	K
	meq/100g			meq/l	
Fine Clays					
Baxter	25.220	24.893	0.3270	1.9654	0.0346
Hartsells	18.860	18.545	0.3150	1.9630	0.0370
Iberia	42.923	42.492	0.4310	1.9862	0.0138
Maury	19.160	18.796	0.3640	1.9728	0.0272
Memphis	27.350	27.004	0.3460	1.9692	0.0308
Sequoia	23.455	23.106	0.3490	1.9698	0.0302

TABLE A-IV

DATA FROM THE EQUILIBRIUM STUDIES UTILIZING POTASSIUM-42
AT c_o=0.002N, INITIAL c_K/c_o=0.10

	Exchangeable Cations			Equilibrium Solution	
	Ca+K	Ca	K	Ca	K
	meq/100g			meq/l	
Soils					
Baxter	3.292	3.255	0.037	1.8370	0.1630
Hartsells	3.696	3.655	0.041	1.8512	0.1488
Iberia	28.962	28.823	0.139	1.9390	0.0610
Maury	5.234	5.144	0.089	1.8895	0.1105
Memphis	3.594	3.542	0.052	1.8519	0.1481
Sequoia	3.601	3.544	0.057	1.8569	0.1431
Sands					
Baxter	1.345	1.337	0.008	1.8160	0.1840
Hartsells	1.144	1.140	0.004	1.8080	0.1920
Iberia	3.380	3.336	0.045	1.8900	0.1100
Maury	2.562	2.530	0.032	1.8640	0.1360
Memphis	1.153	1.146	0.006	1.8128	0.1872
Sequoia	1.957	1.928	0.029	1.8580	0.1420
Coarse Silts					
Baxter	1.839	1.823	0.016	1.8160	0.1840
Hartsells	2.340	2.319	0.022	1.8220	0.1780
Iberia	2.070	2.030	0.040	1.8400	0.1600
Maury	1.872	1.834	0.038	1.8380	0.1620
Memphis	1.852	1.818	0.034	1.8340	0.1660
Sequoia	1.847	1.827	0.020	1.8200	0.1800
Fine Silts					
Baxter	1.748	1.723	0.024	1.8240	0.1760
Hartsells	2.719	2.666	0.053	1.8530	0.1470
Iberia	3.273	3.198	0.075	1.8750	0.1250
Maury	3.427	3.345	0.082	1.8820	0.1180
Memphis	1.893	1.841	0.052	1.8520	0.1480
Sequoia	2.145	2.102	0.043	1.8430	0.1570
Coarse Clays					
Baxter	10.887	10.460	0.427	1.8085	0.1914
Hartsells	11.393	10.995	0.398	1.8080	0.1920
Iberia	29.013	28.282	0.731	1.9462	0.0538
Maury	13.923	13.479	0.444	1.8888	0.1112
Memphis	14.093	13.621	0.472	1.8944	0.1056
Sequoia	12.923	12.442	0.481	1.8962	0.1038

TABLE A-IV (continued)

	Exchangeable Cations			Equilibrium Solution	
	Ca+K	Ca	K	Ca	K
	meq/100g			meq/l	
Fine Clays					
Baxter	25.220	24.641	0.579	1.9158	0.0842
Hartsells	18.860	18.364	0.496	1.8992	0.1008
Iberia	42.923	42.128	0.795	1.9590	0.0410
Maury	19.160	18.560	0.600	1.9200	0.0800
Memphis	27.350	26.727	0.623	1.9246	0.0754
Sequoia	23.303	22.684	0.619	1.9238	0.0762

TABLE A-V

DATA FROM THE EQUILIBRIUM STUDIES UTILIZING POTASSIUM-42
AT c_o=0.002N, INITIAL c_K/c_o=0.20

	Exchangeable Cations			Equilibrium Solution	
	Ca+K	Ca	K	Ca	K
	meq/100g			meq/l	
Soils					
Baxter	3.292	3.209	0.083	1.6830	0.3170
Hartsells	3.696	3.606	0.090	1.6900	0.3100
Iberia	28.962	28.704	0.258	1.8580	0.1420
Maury	5.234	5.050	0.184	1.7840	0.2160
Memphis	3.594	3.507	0.087	1.6870	0.3130
Sequoia	3.601	3.476	0.125	1.7250	0.2750
Sands					
Baxter	1.345	1.329	0.016	1.6320	0.3680
Hartsells	1.144	1.138	0.006	1.6120	0.3880
Iberia	3.380	3.302	0.078	1.7560	0.2440
Maury	2.562	2.502	0.060	1.7200	0.2800
Memphis	1.153	1.142	0.011	1.6220	0.3780
Sequoia	1.957	1.898	0.059	1.7180	0.2820
Coarse Silts					
Baxter	1.839	1.821	0.018	1.6180	0.3820
Hartsells	2.340	2.316	0.024	1.6240	0.3760
Iberia	2.070	2.025	0.045	1.6450	0.3550
Maury	1.872	1.819	0.053	1.6530	0.3470
Memphis	1.852	1.809	0.043	1.6430	0.3570
Sequoia	1.847	1.823	0.024	1.6240	0.3760
Fine Silts					
Baxter	1.748	1.721	0.027	1.6270	0.3730
Hartsells	2.719	2.653	0.066	1.6660	0.3340
Iberia	3.273	3.183	0.090	1.6900	0.3100
Maury	3.427	3.311	0.966	1.7160	0.2840
Memphis	1.893	1.827	0.066	1.6660	0.3340
Sequoia	2.145	2.095	0.050	1.6500	0.3500
Coarse Clays					
Baxter	10.887	10.373	0.514	1.7028	0.2972
Hartsells	11.393	10.908	0.485	1.6970	0.3030
Iberia	29.013	28.156	0.857	1.7714	0.2286
Maury	13.923	13.333	0.590	1.7180	0.2820
Memphis	14.093	13.504	0.589	1.7178	0.2822
Sequoia	12.923	12.360	0.563	1.7126	0.2874

TABLE A-V (continued)

	Exchangeable Cations			Equilibrium Solution	
	Ca+K	Ca	K	Ca	K
	meq/100g			meq/l	
Fine Clays					
Baxter	25.220	24.345	0.875	1.7750	0.2250
Hartsells	18.860	18.072	0.788	1.7576	0.2424
Iberia	42.923	41.747	1.176	1.8352	0.1648
Maury	19.160	18.323	0.837	1.7674	0.2326
Memphis	27.350	26.538	0.812	1.7624	0.2376
Sequoia	23.303	22.404	0.899	1.7798	0.2202

TABLE A-VI

DATA FROM THE EQUILIBRIUM STUDIES UTILIZING POTASSIUM-42
AT c_o=0.02N, INITIAL c_K/c_o=0.05

	Exchangeable Cations			Equilibrium Solution	
	Ca+K	Ca	K	Ca	K
	meq/100g			meq/l	
Soils					
Baxter	3.292	3.200	0.092	19.0920	0.9080
Hartsells	3.696	3.589	0.107	19.1070	0.8930
Iberia	28.962	28.434	0.528	19.5280	0.4720
Maury	5.234	4.956	0.278	19.2780	0.7220
Memphis	3.594	3.455	0.139	19.1390	0.8610
Sequoia	3.601	3.453	0.148	19.1480	0.8520
Sands					
Baxter	1.345	1.308	0.037	19.0740	0.9260
Hartsells	1.144	1.131	0.013	19.0260	0.9740
Iberia	3.380	3.129	0.251	19.5020	0.4980
Maury	2.562	2.375	0.187	19.3740	0.6260
Memphis	1.153	1.131	0.022	19.0440	0.9560
Sequoia	1.957	1.783	0.174	19.3480	0.6520
Coarse Silts					
Baxter	1.839	1.820	0.019	19.0190	0.9810
Hartsells	2.340	2.313	0.027	19.0270	0.9730
Iberia	2.070	2.013	0.057	19.0570	0.9430
Maury	1.872	1.811	0.061	19.0610	0.9390
Memphis	1.852	1.801	0.051	19.0510	0.9490
Sequoia	1.847	1.821	0.026	19.0260	0.9740
Fine Silts					
Baxter	1.748	1.720	0.028	19.0280	0.9720
Hartsells	2.719	2.643	0.076	19.0760	0.9240
Iberia	3.273	3.168	0.105	19.1050	0.8950
Maury	3.427	3.266	0.161	19.1610	0.8390
Memphis	1.893	1.812	0.081	19.0810	0.9190
Sequoia	2.145	2.085	0.060	19.0600	0.9400
Coarse Clays					
Baxter	10.887	10.325	0.562	19.1124	0.8876
Hartsells	11.393	10.943	0.450	19.0900	0.9100
Iberia	29.013	27.986	1.027	19.2054	0.7946
Maury	13.923	13.216	0.707	19.1414	0.8586
Memphis	14.093	13.398	0.695	19.1390	0.8610
Sequoia	12.923	12.301	0.622	19.1244	0.8746

TABLE A-VI (continued)

	Exchangeable Cations			Equilibrium Solution	
	Ca+K	Ca	K	Ca	K
	meq/100g			meq/l	
Fine Clays					
Baxter	25.220	23.888	1.332	19.2664	0.7336
Hartsells	18.860	17.733	1.127	19.2254	0.7746
Iberia	42.923	40.968	1.955	19.3910	0.6090
Maury	19.160	17.927	1.233	19.2466	0.7534
Memphis	27.350	25.898	1.452	19.2904	0.7096
Sequoia	23.303	21.973	1.330	19.2660	0.7340

TABLE A-VII

COMPARISON OF CATION ACTIVITY AND MOLARITY OF THE EQUILIBRIUM SOLUTIONS IN THE POTASSIUM-42 SELECTIVITY STUDIES

c_o=0.002N

Initial c_K/c_o	γ_{Ca}	a_{Ca}	M_{Ca}
0.05	0.777	0.0075100	0.0009660
0.10	0.782	0.0007110	0.0009090
0.20	0.790	0.0006650	0.0008420

Initial c_K/c_o	γ_K	a_K	M_K
0.05	0.990	0.0000662	0.0000669
0.10	0.985	0.0001790	0.0001820
0.20	0.980	0.0003110	0.0003170

c_o=0.02N

Initial c_K/c_o	γ_{Ca}	a_{Ca}	M_{Ca}
0.05	0.452	0.0043200	0.0095500

Initial c_K/c_o	γ_K	a_K	M_K
0.05	0.965	0.0008760	0.0009080

VITA

Joseph Houston Rule was born on February 22, 1943, in Knox County, Tennessee. He attended public schools in Blount County, Tennessee, and graduated from Everett High School in 1961. Entering the University of Tennessee, Knoxville, in 1962, he obtained his Bachelor of Science degree in Agriculture with a major in Agronomy in the spring of 1967. He then entered the University in the spring of 1967 as an assistant in Agronomy working towards his Master of Science degree.

He is married to the former Betsy Jo Peeden of Knoxville, Tennessee.