TEMPERATURE EFFECTS ON POTASSIUM-CALCIUM EXCHANGE AND SELECTIVITY IN SELECTED SOILS, CLAY MINERALS, AND CATION EXCHANGE RESINS

by

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INTRODUCTION

The nature of cation exchange and selectivity has been studied extensively with respect to the components of the system, namely, the ions, the exchanger, and the solution phase. One important aspect of chemical, and some physical reactions, is that of temperature. Cation exchange, being both physical and chemical in nature, is also influenced by temperature. The extent and nature of this temperature effect on cation exchange is less understood than the effect of changes in the components of the system. The following are properties of the components: ion properties such as ionic size, polarizability, valence, oxidation state, solvation, disassociation, ionic strength, and polymerization; exchange properties such as charge density, location of charge, and steric properties; and solution properties such as pH, dielectric constant, and structure. Some of these properties can be altered by changes in temperature. Therefore, experiments carried out at ambient temperature in a laboratory may not be representative of reactions occurring in the natural environment of soils in place.

The objective of this study was to determine the effect of temperature on the exchange of two important soil cations, namely, calcium and potassium. In order to avoid some of the confounding reactions expected in soil systems, simpler exchange systems with clay minerals and synthetic cation exchangers, in addition to soils, were studied.

LITERATURE REVIEW

The temperature effects on chemical phenomena are numerous. However, in the present study the systems examined were allowed to attain equilibrium, thereby minimizing the influence of temperature on diffusion rates, viscosity, reaction velocity, etc. These systems also consisted of small amounts of exchangers in weak solution which diminishes the effects of temperature on solubility, complex formation, ion pair formation, molecular interactions, etc. The main influences of temperature in the systems studied were on kinetic energy, hydrolysis, ionization as influencing solution pH, ionic activity as influenced by hydration, and the equilibrium of exchange as related to the thermodynamic properties.

Influence of Temperature on Solution Ions

Activity coefficients: Temperature affects the activity of electrolytes in solution as observed in the coefficients for the constants in the Debye-Hückel theory (Harned and Owen, 1958, pp.59-66). These constants contain the temperature term itself as well as the dielectric constant of the medium (Babcock, 1963) which is itself temperature dependent (Harned and Owen, 1958, p.161). Generally, in weak solutions the activity coefficient decreases with an increase in temperature (Harned and Owen, 1943, pp.578-579; Robinson and Stokes, 1959, pp.480-481). However, in more concentrated solutions, with increasing temperature the activity coefficient goes through a maximum and then decreases (Harned and Owen, 1943, pp.578-579; Robinson and Stokes, 1959, pp.212 and 480-481). Temperature also affects the activity coefficient by influencing the distance of closest approach parameter through changes in the ionic hydration (Robinson and Stokes, 1949; Stokes and Robinson, 1948).

Hydration: Electrolyte solvation involving the specific ionic interactions with solvent molecules has been well documented (Robinson and Stokes, 1959, pp.239-251; Harned and Owen, 1958, pp.511-515) and the influence of temperature on hydration has been examined (Nightingale, 1959; Nightingale and Benck, 1959; Nightingale and Kuecker, 1965; Kavanau, 1964). The classical concept of hydrated ions is that they contain an electrical field at the surface of the ion sufficiently large to "adsorb" one or more layers of water molecules thus forming a peripherally hydrated ion. The activation energy of viscous flow for solutions containing these ions is greater than that of the pure solvent indicating that these species not only impede the flow of solvent but also that the relative impedence decreases with increasing temperature. Presumably, the solvent "iceberg" about the ion is "melted" to a greater extent than is the icelike structure of the bulk solvent itself (Kavanau, 1964, pp.52-78). However, large ions such as Ba and K have a relatively weak field and this limits the extent of peripheral solution and results in the exhibition of negative activation energies for viscous flow (Nightingale, 1959; Nightingale and Benck, 1959). With increasing temperature, the bonding between solvent molecules weakens and becomes more susceptible to orientation in the relatively weak field about the ion.

Solution pH: An increase in temperature generally promotes ionization of weak electrolyte solutions (Harned and Robinson, 1940; Robinson and Stokes, 1959, pp.357-358). Therefore, a temperature increase decreases the pH of pure H_2O and selected weak electrolytes (Harned and Robinson, 1940). Wiklander (1946, pp.119-125) observed a decrease in the soil pH upon heating the soil whereas Chernov (1947, p.131) reported the opposite trend.

Al hydrolysis: An increase in temperature greatly increases the hydrolysis of Al salts in aqueous solutions (Bailar, 1956, pp.448-471; Matijevic and Tezak, 1953; Thorne and Roberts, 1948, p.288). Freshly prepared solutions, or those with added acid, contained only trivalent Al ions whereas aging or heating the solution resulted in dimer formation (Matijevic and Tezak, 1953), as well as promoting the process of olation (Bailar, 1956, pp.448-471). Heating to 40C an $Al(Cl)_3$ solution that was partially neutralized with NaOH resulted in the formation of gibbsite while at 10C this product could not be detected even after 100 days (Turner and Ross, 1970).

Influence of Temperature on Exchangeable Ions

Diffusion coefficients: The diffusion coefficients in ion exchangers increase with increasing temperature (Ames, 1965; Barrer and Hinds, 1953; and Reichenbach and Rich, 1968). As a rule, the increase in mobility with temperature is somewhat greater in ion exchangers than in ordinary aqueous solutions (Boyd and Soldano, 1953; Soldano, 1953; Soldano and Boyd, 1953). Likely explanations are that with increasing temperature specific or electrostatic interactions become weaker, the matrix becomes more flexible, and the ion becomes smaller because solvation is reduced (Helfferich, 1962, p.308).

Al hydrolysis: Dry heating an Al-saturated vermiculite inhibited hydrolysis, whereas boiling an Al-vermiculite suspension produced extensive hydrolysis as evidenced by reduced NH_4 fixation, and cation exchange capacity (CEC), and the presence of a 14.1A X-ray peak for a sample heated to 400C (Rich, 1960). Heating a moist soil decreased Al extracted with KCl (Chernov, 1947, p.131; Kawamura, 1931) or 0.2N NH_4Cl at pH 4.0 (Skeen, 1964) whereas there appeared to be no effect on exchangeable Al when the soils were dry heated (Skeen, 1964). Heating also released more exchangeable Fe (Chernov, 1947, p.131; Kawamura, 1931; Meek, MacKenzie, and Grass, 1968) and Al from a previously H-saturated system (Davis, Turner, and Whittig, 1962).

General ion exchange: Temperature dependence of equilibrium in general is related to the standard enthalpy change which accompanies the reaction (Helfferich, 1962, pp.166-168). Therefore, increased temperatures inhibit reactions that occur with the evolution of heat. Ion exchange occurs as a rule with little evolution or uptake of heat for it is not a chemical reaction but a stoichometric exchange. The enthalpy changes for ion exchange processes in which no formation of covalent bonds, association, or complex formation are involved are usually smaller than 2 kcal/mole though values up to 10 kcal/mole have been observed in exceptional cases (Beckett, 1963; Bonner and Overton, 1961; Bonner and Smith, 1957; Boyd, Schubert, and Adamson, 1947; Coleman, 1952; Cosgrove and Strickland, 1950; Cruickshank and Meares, 1957a, 1957b; Deist and Talibudeen, 1967; Gaines and Thomas, 1955; Gast, 1969; Gast, Bladel, and Deshpande, 1969; Gregor and Bregman, 1951; Helfferich, 1962, pp.166-167; Hutcheon, 1966; Kressman and Kitchener, 1949a, 1949b; Samuelson, 1963, pp.85-86; Surls and Choppin, 1957). Therefore, within a limited range, temperature can be assumed to have only a slight influence upon the equilibrium (Helfferich, 1962, pp.166-167; Kelley, 1948, p.53; and Samuelson, 1963, pp.85-86).

Ion exchange may be followed by other processes which have considerable enthalpy changes (Helfferich, 1962, pp.166-167). Cation exchange of an H-saturated exchanger with a base is a typical example (Coleman, 1952; Slaraugh, 1952). Such systems are more likely to be affected by temperature changes since a large amount of heat of neutralization is liberated in the consecutive reaction.

In most systems where ions of equal valence are involved, an increase in temperature is followed by a decrease in selectivity whereas in systems that involve ions of different valence a higher temperature usually leads to increased selectivity (Bonner and Pruett, 1959a, 1959b; Coleman, 1952; Kraus and Raridon, 1959; Kraus, Raridon, and Holcomb, 1960; Loven and Thomas, 1965; Walton and Martinez, 1959).

In systems where selectivity is more pronounced, temperature has a correspondingly greater effect upon selectivity (Samuelson, 1963, pp.85-86). In most cases, selectivity results from association equilibria or complex formation in either or both the solution or exchange phases. These processes are usually inhibited by an increase in temperature (Beckett, 1963; Bonner and Pruett, 1959a, 1959b; Coleman, 1952; Deist and Talibudeen, 1967; Gaines and Thomas, 1955; Glass, 1955; Hutcheon, 1966; Kraus and Raridon, 1959; Kraus et al., 1960; Mangelsdorf, Wilson, and Daniell, 1969; Rhoads, 1967). Exceptions are found in systems that involve counter ions of different valences (Helfferich, 1962, pp.166-167; Kraus and Raridon, 1959; Muljadi, Posner, and Quirk, 1966).

Specific ion exchange: A temperature increase in a solution-exchange suspension has been shown to increase the concentration of K in solution and conversely to decrease the quantity of K on the exchanger (Beckett, 1963; Bischoff, Greer, and Luistro, 1970; Bregman, 1953; Burns and Barber, 1961; Cosgrove and Strickland, 1950; Deist and Talibudeen, 1967; Golden, 1962; Gregor and Bregman, 1951, Haagsma and Miller, 1963; Hutcheon, 1966; Mangelsdorf et al., 1969; Tucker, 1967; Wiklander, 1946, pp.119-125). A similar response was observed for NH_4, an ion which behaves similarly to K (Vanselow, 1932) and also for Na (Rhoades, 1967). In these studies, the counter ion usually involved in the exchange was Ca and/or Mg. The temperature effects of Ca equilibrium were the reverse of those of K. As temperature increased, the concentration of Ca in solution decreased

(Bischoff et al., 1970; Golden, 1962; Hutcheon, 1966; Vanselow, 1932; Wiklander, 1946, pp.119-125). The effects of Mg corresponded to those of Ca. These observed equilibrium changes with increasing temperature were accompanied with a measured decrease in total CEC (Bischoff et al., 1970; Deist and Talibudeen, 1967; Hutcheon, 1966; Vanselow, 1932) and a decrease in soil pH (Wiklander, 1946, pp.119-125).

Ion exchange to plants: Evidence has been compiled which indicates that many biological systems undergo anomalous behavior at or near the temperature where aqueous solutions undergo subtle higher order phase transitions (Drost-Hansen, 1965a, 1965b). Miller and Davey (1967) measured slight repressions in K uptake by wheat seedlings near 15 and 30C which could be due to changes in the water structure. However analyses have been published indicating that temperature-induced discontinuities in water properties do not exist but are due to contaminants (Falk and Kell, 1966; Hamann and King, 1967).

As soil temperature was increased, an increase in K uptake was shown in wheat seedlings (Miller and Davey, 1967), oats (Nielsen et al., 1960), maize seedlings (Walker, 1969), sorghum (Nielsen et al., 1961; Weber and Caldwell, 1964), bromegrass and potatoes (Nielsen et al., 1961), and soybeans (Wallace, 1957), while the Ca content decreased dramatically in maize seedlings (Nielsen et al., 1961; Walker, 1969) and soybeans (Wallace, 1957). At low soil temperatures, a significant response was obtained from K fertilization which did not occur at higher temperatures (Weber and Caldwell, 1964).

Maize seedlings demonstrated Ca deficiencies at high temperatures; however, these symptoms were not evident at lower temperatures (Walker, 1969). As temperature increased the K content of tomatoes increased at low P levels with less of an effect at high levels of P (Martin and Wilcox, 1963). The K content of corn increased with increasing temperature when fertilized with N and P but decreased when fertilized with N, P, and K (Nielsen et al., 1961). The K content of barley increased with a temperature increase from 12 to 22C but decreased with a further increase to 32C (Wallace, 1957).

MATERIALS AND METHODS

The choice of materials and methods used was dictated by the specific objective of each experiment, which in turn was related to the overall objective of determining the effect of temperature on K-Ca exchange and selectivity in selected soils, clay minerals, and resins. To this end, specific exchange materials and the experimental techniques were governed by the objective of each study. However, in each case, the K-Ca exchange isotherms were determined by the quantity-intensity (Q/I) method developed by Beckett (1964a, 1964b). The K-Ca selectivity coefficients were calculated by the Gapon equation (Babcock, 1963; Kelley, 1948, pp.45-46).

Materials

Soils: Seventeen soils located in six different states were selected for use in these studies (Table I). These soils represent a wide range in natural soil characteristics (Tables II and III).

Clays: Four different clay minerals were selected for use in these studies. These included: kaolinite from Dry Branch, Georgia, which was donated by the Georgia Kaolin Company, Elizabeth, New Jersey; Wyoming bentonite from Upton, Wyoming; Camargo bentonite, which was obtained from Dr. L.W. Reed at the Oklahoma State University, Stillwater, Oklahoma; and vermiculite from Zonolite Division, W.R. Grace Company, Travelers Rest, South Carolina.

Table I. The origin, horizon, and depth for the soil types used.

Soil Type	Horizon	Depth	Origin
		-in.-	
Bayboro peaty muck	Ap	0-10	Virginia
Portsmouth mucky loam	Ap	0-8	Virginia
Houston Black clay	A1	0-16	Texas
Carrington silt loam	Ap	0-7	Iowa
Vergennes clay	Ap	0-6	Vermont
Hadley very fine sandy loam	Ap	0-6	Vermont
Calais silt loam	Ap	0-6	Vermont
Windsor loamy fine sand	Ap	0-6	Vermont
Crosby silt loam	C	38+	Indiana
Berks silt loam	B2	10-18	Virginia
Katy fine sandy loam	B22t	28-46	Texas
Iredell silt loam	B2	11-26	Virginia
Whitestore fine sandy loam	B22t	22-31	Virginia
Nason silt loam	B2	12-23	Virginia
Tatum silt loam	B2t	27-31	Virginia
Cecil sandy loam	B2	18-46	Virginia
Oktibbeha fine sandy loam	B22t	4-16	Alabama

Table II. Exchangeable cations in the soils used.*

Soil	pH†	Exchangeable Basic Cations‡				Exchangeable Acidity§
		Na	K	Ca	Mg	
		meq/100g				
Bayboro	4.49	0.03	0.82	5.57	4.28	55.92
Portsmouth	4.68	0.19	0.32	3.54	2.16	28.42
Houston Black	8.00	0.20	1.40	58.00	0.84	0.51
Carrington	5.20	0.00	0.20	13.60	2.88	9.13
Vergennes	5.80	0.18	0.67	10.50	8.60	9.10
Hadley	6.90	0.08	0.10	10.70	0.60	2.80
Calais	6.00	0.04	0.19	4.70	0.30	13.20
Windsor	4.80	0.10	0.10	0.10	0.50	8.70
Crosby	8.30	0.01	0.13	25.25	1.29	0.00
Berks	4.69	0.03	0.10	2.65	0.36	4.57
Katy	6.50	0.37	0.22	8.00	8.28	0.68
Iredell	6.42	0.01	0.34	15.14	19.32	7.56
Whitestore	4.22	0.02	0.43	0.05	1.49	30.70
Nason	4.80	<0.01	0.21	0.30	0.87	12.06
Tatum	4.72	<0.01	0.39	0.55	0.75	14.39
Cecil	5.12	0.14	0.12	0.64	0.79	12.50
Oktibbeha	4.42	0.05	0.18	17.60	0.59	11.21

*Data from Vermont soils was obtained from personal communication with Dr. R.J. Bartlett while all other data was obtained from personal communication with Dr. C.I. Rich.

†Determined in a 1:1 ratio soil:distilled H_2O.

‡Extracted with 1:10 ratio soil:1N NH_4OAc at pH 7.

§Extracted with 1:10 ratio soil:0.5N $BaCl_2$ and 0.2N triethanolamine at pH 8.3.

Table III. Selected characteristics of the soils used.*

Soil	CEC†	Base Saturation‡	Organic Matter§	<2μ Clay¶	Dominant Clay Minerals Ψ
	meq/100g	%			
Bayboro	66.62	16.06	38.30	2.3	Mi
Portsmouth	34.63	17.93	14.88	17.0	Mo, V
Houston Black	60.95	99.16	2.65	45.6	Mo
Carrington	25.81	64.64	3.00	32.3	Mo
Vergennes	29.05	68.67	2.20	79.6	V, C
Hadley	14.28	80.39	2.51	5.8	Mi, C
Calais	18.43	28.38	5.07	6.6	Mi, C
Windsor	9.50	8.42	0.07	2.8	Mi, C
Crosby	26.68	100.00	0.30	32.7	I
Berks	7.71	40.73	0.89	45.2	I
Katy	17.55	96.13	1.16	36.5	H
Iredell	42.37	82.16	1.47	52.6	Mo
Whitestore	32.69	6.09	0.48	54.8	Mi, K
Nason	13.45	10.33	0.20	59.0	V, K
Tatum	16.09	10.59	0.30	57.7	V, K
Cecil	14.19	11.91	0.43	70.0	K
Oktibbeha	29.63	62.17	1.75	80.1	Mo

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*Data for Vermont soils was obtained from personal communication with Dr. R.J. Bartlett while all other data was obtained from personal communication with Dr. C.I. Rich.

†Sum of basic cations plus exchangeable acidity in Table II.

‡Percentage of basic cations as compared to CEC.

§Wet oxidation method (Peech et al., 1947).

¶Mineral fractionation for soils (Jackson, 1956).

ΨX-ray analysis (Jackson, 1956) where C = chlorite, H = halloysite, I = illite, K = kaolinite, Mi = mica, Mo = montmorillonite, V = vermiculite.

Cation exchange resins: Four cation exchange resins were used in these studies. These included: Rexyn 102, a weak organic acid cation exchanger from the Fisher Scientific Company. It consists of methacrylic acid containing carboxylic acid groups. It has a CEC of 12.06 meq/g of dry resin, a moisture content of 54.5%, and a mesh size of 200-400. The remaining three resins were strong acid type cation exchangers consisting of sulfonated styrene divinylbenzene beads and are products of the Dow Chemical Company. These include Dowex 50W-X1 which has a CEC of 5.3 meq/g of dry resin, a moisture content of 84.6%, and a mesh size of 50-100; Dowex 50W-X4 which has a CEC of 5.0 meq/g of dry resin, a moisture content of 67.0%, and a mesh size of 50-100; and Dowex 50W-X8 which has a CEC of 5.3 meq/g of dry resin, a moisture content of 48.0%, and a mesh size of 20-50.

Methods

Preparation of soils and clay minerals: The soil samples were air dried and passed through a U.S. Standard Sieve Series No. 35 which has an A.S.T.M. opening specification of 500μ.

The clay minerals were first treated with 1N monochloracetic acid ($CH_2ClCOOH$) to remove carbonates. The clays were then dispersed in a 5% Calgon solution and mixed for 5 minutes in a soil dispersion mixer having A.S.T.M. specifications. The clay minerals were separated into a <2μ fraction by sedimentation. This was accomplished by determining by Stokes Law the time necessary for only the 2µ particles or smaller to remain in suspension to a depth of 10 cm (Day, 1965, p.548). The upper 10 cm of the suspension was removed by suction, stored, and the process continued until sufficient clay was collected. The samples were flocculated with NaCl and then concentrated by centrifugation after repeated washing with 1N NaCl solution to remove the Calgon.

It was difficult to obtain a large quantity of the <2µ fraction of vermiculite. Therefore, this sample was wet ground in a Sorvall Omni mixer until sufficient quantity of the <2µ fraction was obtained.

Preliminary saturation of the exchange materials: Except for the Vergennes soil, cations on the exchange complex of the soil systems, prior to the K-Ca treatment were unaltered. An unaltered Vergennes soil as well as subsamples of this soil saturated with Na, K, Ca, and Al to produce homoionic systems, were studied. Wyoming bentonite was made homoionic with respect to Na, K, Ca, Mg, Fe^{3+}, and Al whereas the remaining clay minerals and resins were all Al saturated. A Dowex 50W-X8 sample was also H saturated.

Saturation of each exchange material was accomplished by equilibrating the exchanger with a minimum of 30 symmetries of a normal chloride solution of the appropriate cation.

The Vergennes soil was equilibrated with the saturating solution by means of a large Buchner funnel, attached to a suction pump. At 30-minute intervals, 1/8 of the saturating solution was slowly passed through the soil. A similar procedure was used to saturate the resins except that it was performed with Millipore filters. All clay minerals were saturated in 250-ml centrifuge bottles by shaking the clay and the appropriate solution for 15 minutes and centrifuging. After discarding the supernatant solution, the process was repeated seven more times.

The removal of excess salt was accomplished in several ways. The Vergennes soil was leached in the Buchner funnel with deionized water and the Na, K, Ca, Mg, and Al Wyoming bentonite systems, and Al vermiculite were shaken with deionized water in the centrifuge bottles until the supernatant solutions were free of Cl as indicated by the $AgNO_3$ test. All the resins, the Al-saturated kaolinite, Camargo bentonite, and the Fe^{3+}-saturated and another Al-saturated sample of Wyoming bentonite, and vermiculite, were washed eight times with 0.003N HCl. The final supernatant solution had pH values of about 2.4 with an electrical conductivity of about 2440 micromhos/cm. Washing in this manner produces the least amount of hydrolysis of the saturating cation (Barshad, 1960; Page and Whittig, 1961).

A 25 g subsample of the Al-saturated and 0.003N HCl-washed Dowex 50W-X8, Wyoming bentonite, and vermiculite were boiled for 2 hours. A reflux condenser was employed to maintain the solution volume at 1000 ml. After cooling, the samples were concentrated by centrifugation and decanting off the solution. This treatment was performed to increase the amount of Al hydrolysis (Rich, 1960).

The treated Vergennes soil was air dried and passed through a U.S. Standard Sieve Series No. 35 while the clay mineral pastes were freeze-dried and passed through this same sieve. All the resins were dried in an oven at 80C for 12 hours.

Weight corrections: All samples were stored in the laboratory and allowed to come to equilibrium with the atmosphere. Subsequently samples were weighed for each experiment and at the same time a subsample of each exchange material was taken for moisture determination. The soils and resins were dried in an oven at 110C, whereas the clay minerals were dried at 300C. All references to weight of exchange materials were corrected for the amount of moisture determined at these temperatures.

It was observed that Al-saturated Rexyn 102 and H-saturated Dowex 50W-X8 lost structural components on heating to 200C. Kunin (1958, p.321) reported that some resins are thermally unstable in the H form. The Dowex 50W-X8 was H saturated and the Rexyn 102 contained a large portion of H on the exchange even after treatment with $AlCl_3$. Little Al was adsorbed (0.289 meq Al/g) because of the weak acid character of this exchange material and the low pH (2.8) of the $AlCl_3$ solution.

In addition to the moisture correction the clay minerals and resins were also corrected by subtracting out the weight of exchangeable ions present on the exchangers from the total weight. The resulting "backbone" weight (Faucher and Thomas, 1954) of each cation-exchanger system then can be compared more accurately. The amount of exchangeable cations was determined by equilibrating 0.5 g of clay with two consecutive 50-ml portions of N NH_4NO_3 in centrifuge tubes. Each portion of extracting solution was shaken intermittently with the clay for 2 hours and then separated from the clay by centrifugation and the solution decanted off and saved. Both portions of the extracting solution were combined and analyzed for the following exchangeable ions: H, Na, K, Ca, Mg, Fe, and Al.

Experimental quantities used: The Q/I parameters were determined by varying the amounts of each soil, clay mineral, and resin that were weighed out into a series of 100-ml centrifuge tubes. Fifty ml of 0.002M $CaCl_2$ solution containing different amounts of K were added to each series of centrifuge tubes that were employed for each exchange system (Table IV).

The Gapon selectivity coefficients were determined by equilibrating 7.0 g of soil, or 0.5 g of clay mineral, or 0.2 g of resin with 50 ml of solution containing 0.002M $CaCl_2$ and 0.002M KCl with each exchange system. These were the same experimental quantities that were used for the solution in the Q/I experiments that contained the highest amount of K. After equilibrium, solutions were removed from the exchange material by centrifugation and decanting. The exchangeable cations were extracted as above. Corrections were made for Ca and K in the entrained solution phase by analysis of the Cl.

Temperature of experiments: Temperature was the main parameter examined in all these studies; therefore, care was taken to maintain uniform conditions. All equilibrium studies were performed at three temperatures: 0, 20, and 40C. These experiments were

Table IV. Experimental quantities used to determine the Q/I parameters.

Tube No.	Weight of sample			Volume added	Concentration	
	Soils	Clays	Resins		KCl	$CaCl_2$
	-g-	-g-	-g-	-ml-	-M-	-M-
1	0.5	0.0500	0.0050	50	0.0000	0.0020
2	1.5	0.1000	0.0500	50	0.0000	0.0020
3	4.5	0.3000	0.1000	50	0.0000	0.0020
4	7.0	0.5000	0.2000	50	0.0000	0.0020
5	7.0	0.5000	0.2000	50	0.0002	0.0020
6	7.0	0.5000	0.2000	50	0.0005	0.0020
7	7.0	0.5000	0.2000	50	0.0007	0.0020
8	7.0	0.5000	0.2000	50	0.0010	0.0020
9	7.0	0.5000	0.2000	50	0.0020	0.0020

conducted in Sherer Electronic Controller Transistorized Model-1-111 walk-in temperature control rooms. Throughout the experiments, these rooms had a measured solution temperature variability of less than 0.5C.

The equilibrium solutions were separated from the exchange materials by centrifugation and decanting off the solution in these temperature control rooms. Centrifugation produced less than a 0.1C change in solution temperature. All exchange studies were conducted at room temperature since it was assumed that the 1<u>N</u> NH_4NO_3 exchange solution would remove all exchangeable ions regardless of the temperature.

Time of experiment: Preliminary kinetic experiments suggested that equilibrium was complete after 1 day. No effect of equilibrating samples from 1 to 8 days could be observed on two selected exchange materials for the temperatures studied. However, due to the length of time necessary to handle all the samples studied and the random ordering for centrifugation, a time of 3 days was chosen for the equilibrium studies. The samples were continuously shaken during this entire time period on a reciprocating shaker.

The exchange studies were performed 1 day after the equilibrium solutions were removed from the exchange materials. The exchanging solution was intermittently shaken for 2 hours with the exchanger for two consecutive extractants. These two extractants were later combined for analysis.

Ion determinations: The pH of the solutions were measured with a Sergeant Model DR digital pH meter which had a Fisher microprobe electrode No. 13-639-92. The following ions were measured with a Perkin Elmer Model 303 atomic adsorption spectrophotometer: Na, K, Ca, Mg, and Fe. Aluminum was determined colorimetrically by the aluminon method (Hsu, 1963) with a Bausch & Lomb, model Spectronic 20, spectrophotometer. Chloride was measured with an Aminco-Cotlove automatic chloride titrator. Difficulty was encountered in determining Cl in the NH_4NO_3 samples that were Fe^{3+} saturated. A potential difference on the Cl titrator could not be developed due to the high Fe content. Therefore, an aliquot of these samples was passed through an H-saturated Dowex 50W-X8 resin and the Cl content of the elutriate was measured.

Activity correction and ratio calculation: In all equilibrium solutions, the concentrations of K and Ca were corrected to their chemical activities. The activity coefficients were calculated from the Debye-Hückel equation (Babcock, 1963; Harned and Owen, 1958, pp.59-66):

$$\log \phi\pm = \frac{-\kappa z^+ z^- \sqrt{\mu}}{1 + \alpha\beta\sqrt{\mu}}$$

where

$\phi\pm$ = mean activity coefficient of the electrolyte

z^+ = valency of cation

z^- = valency of anion

$$\kappa = \frac{\varepsilon^3}{2.303\ (DkT)^{3/2}} \cdot \sqrt{\frac{2\pi N}{1000}}$$

μ = ionic strength of the solution

$$\alpha = \sqrt{\frac{4\pi\varepsilon^2}{DkT} \cdot \frac{2N}{1000}}$$

β = distance of closest approach

where

N = Avogadro's number = 6.024×10^{23} molecules mole^{-1}

ε = electronic charge = 4.802×10^{-10} e.s.u.

D = dielectric constant of the medium which was H_2O

k = Boltzmann constant = 1.380×10^{-16} ergs degree^{-1} molecule^{-1}

T = absolute temperature

$\mu = 1/2\ \Sigma\ C_i z_i^2$

where

C_i = concentration of ion i in moles per liter

The κ and α constants are temperature dependent and numerical values for these constants as a function of temperature were obtained from Harned and Owen (1958, p.165) (Table V). The values of β for K and Ca were taken as 3×10^{-8} cm and 6×10^{-8} cm, respectively, for all temperatures studied (Klotz, 1964, p.417). The distance of closest approach (β) of the ions studied is known to change with temperature (Kavanau, 1964, pp.54-73; Nightingale, 1959; Robinson

Table V. Values for constants in the Debye-Hückel equation for activity coefficients in aqueous solutions as a function of temperature (Harned and Owen, 1958, p.165).

Temperature C	κ	$\alpha \times 10^{-8}$
0	0.4883	0.3241
20	0.5046	0.3276
40	0.5241	0.3315

and Stokes, 1949). However, the effect of the range of temperatures studied on the magnitude of β as reflected in the Debye-Hückel equation was found to be insignificant (Klotz, 1964, p.418; Robinson and Stokes, 1949).

The ionic strengths of the equilibrium solutions in the Q/I experiments were calculated from the measured Na, K, Ca, and Mg concentrations. In the remaining studies involving equilibrium solutions, the ionic strength was calculated from the concentration of H, Na, K, Ca, Mg, Fe, and Al. The concentration of H was calculated as follows:

$$H = \frac{1}{\text{Antilog pH}}$$

In all cases, it was assumed that the anions were monovalent. Evidence for this assumption exists from the fact that the exchange materials were saturated with Cl solutions, the equilibrium solutions were Cl derivatives, and hydroxyls are the other major anions existing in these exchange materials.

The activity ratio (AR) of K vs. Ca and Mg was calculated as follows:

$$AR = \frac{C_K \times (\phi_{KCl})^2}{\sqrt{C_{Ca} + C_{Mg}} \times (\phi_{CaCl_2})^{3/2}} = \frac{A_K}{\sqrt{A_{Ca + Mg}}}$$

where

A_i = activity of ion i in moles per liter

It was assumed that Ca and Mg had similar properties in the exchange materials studied (Beckett, 1964b; Schofield and Taylor, 1955). The resulting unit of measurement in the AR equation is $(\text{moles/liter})^{1/2}$.

Calculation of a Q/I isotherm and related parameters: The equilibrium solutions in the Q/I experiments were calculated and plotted by the technique given by Beckett (1964a, 1964b). For each exchange material and temperature studied a series of points were obtained by plotting AR on the abscissa versus the change in K (ΔK) on the ordinate. The values for ΔK were calculated from the difference between the K concentration of the initial solution with that of the resultant solution in equilibrium with the exchange material. The unit of measure of ΔK is meq K/100g of exchanger. Thus, by plotting corresponding values of ΔK and AR, a quantity intensity (Q/I) curve was obtained which has three distinct parameters. These parameters are: (1) the equilibrium activity ratio (ARE) which is the value of AR where $\Delta K = 0$, (2) the potential buffering capacity (PBC) which is the slope of the linear portion of the curve, and (3) the standard exchangeable K (ΔK^{o}) which is the value of ΔK upon extrapolating the linear portion of the curve to $AR = 0$.

Calculation of the Gapon coefficient: The K selectivity coefficients were based on the Gapon equation as shown by Rich and Black (1964). The K selectivity coefficient $k_{K/Ca}$ was calculated as follows:

$$k_{K/Ca} = \frac{K \text{ (sorbed)}}{Ca \text{ (sorbed)}} \div \frac{K \text{ (solution)}}{\sqrt{Ca \text{ (solution)}}}$$

The sorbed cations were measured in the exchange solution and were corrected for the entrained solution by analyzing for Cl. The determined Cl was partitioned between the cations in proportion to their concentrations in the equilibrium solution and then subtracted from the values obtained for exchangeable cations. The cations in solution were determined from the equilibrium solution and were corrected to their chemical activities. The sorbed cations are expressed as meq/100g of exchanger and the cations in solution as moles/liter. Therefore the resulting unit of measurement of $k_{K/Ca}$ is $(\text{liters/mole})^{1/2}$.

RESULTS

The results are presented for seven experiments each of which had specific objectives. All of the work was related to the overall objective of determining the effect of temperature on K-Ca exchange and selectivity in selected soils, clay minerals and resins. It was first necessary to determine the time required to attain equilibrium for K-Ca exchange at the temperatures studied. The effect of temperature on K-Ca exchange was then determined on naturally occurring soils. Some soils demonstrated an effect of temperature on K-Ca exchange whereas others did not. Therefore a soil and some selected clay minerals and resins were chemically treated in an attempt to determine the influence that ions, initially on the exchange sites, had on the temperature effect in subsequent K-Ca exchange. Finally an experiment was conducted to determine the influence of temperature on selectivity of K and Ca in soils, clay minerals and resins. Subsequently these systems were analyzed further to better characterize the effects that temperature had on the exchange reactions.

In order to give some continuity to this section and to orient the reader, the purpose and the experimental procedure for each experiment is restated prior to the presentation of the results. These statements provide a brief introduction to the presentation of results for each experiment.

Kinetics of K-Ca Exchange in a Soil and Clay System at Three Temperatures

Introduction: Ion exchange is known to occur rapidly and attain equilibrium within seconds (Malcolm and Kennedy, 1969). However ion exchange is known to be temperature dependent (Kelley, 1948, p.53). The purpose of this experiment was to determine the time necessary to achieve equilibrium between K and Ca and the exchanger at the temperatures studied. The untreated Vergennes soil and the Al-saturated and water-washed vermiculite were used as the exchange materials. They were equilibrated at temperatures of 0, 20, and 40C for periods of 1, 2, 4, and 8 days and subsequently analyzed. The resulting data were plotted by the Q/I technique.

Influence of time: Equilibrium between K and Ca in solution and the Vergennes soil, and Al-saturated and water-washed vermiculite was complete by the first day at all temperatures (Figures 1 and 2). No difference could be detected between the first or the eighth day for either exchange system at any temperature. Apparently the exchange equilibrium occurring for the first 8 days was complete at the end of the first day. Subsequently it was decided that all equilibrium experiments would be conducted for a period of 3 days.

Influence of temperature: A marked change in the Q/I isotherms occurred at the temperatures studied for both the Vergennes soil and the vermiculite. These exchangers demonstrated similar responses to temperature changes. As temperature increased the amount of K

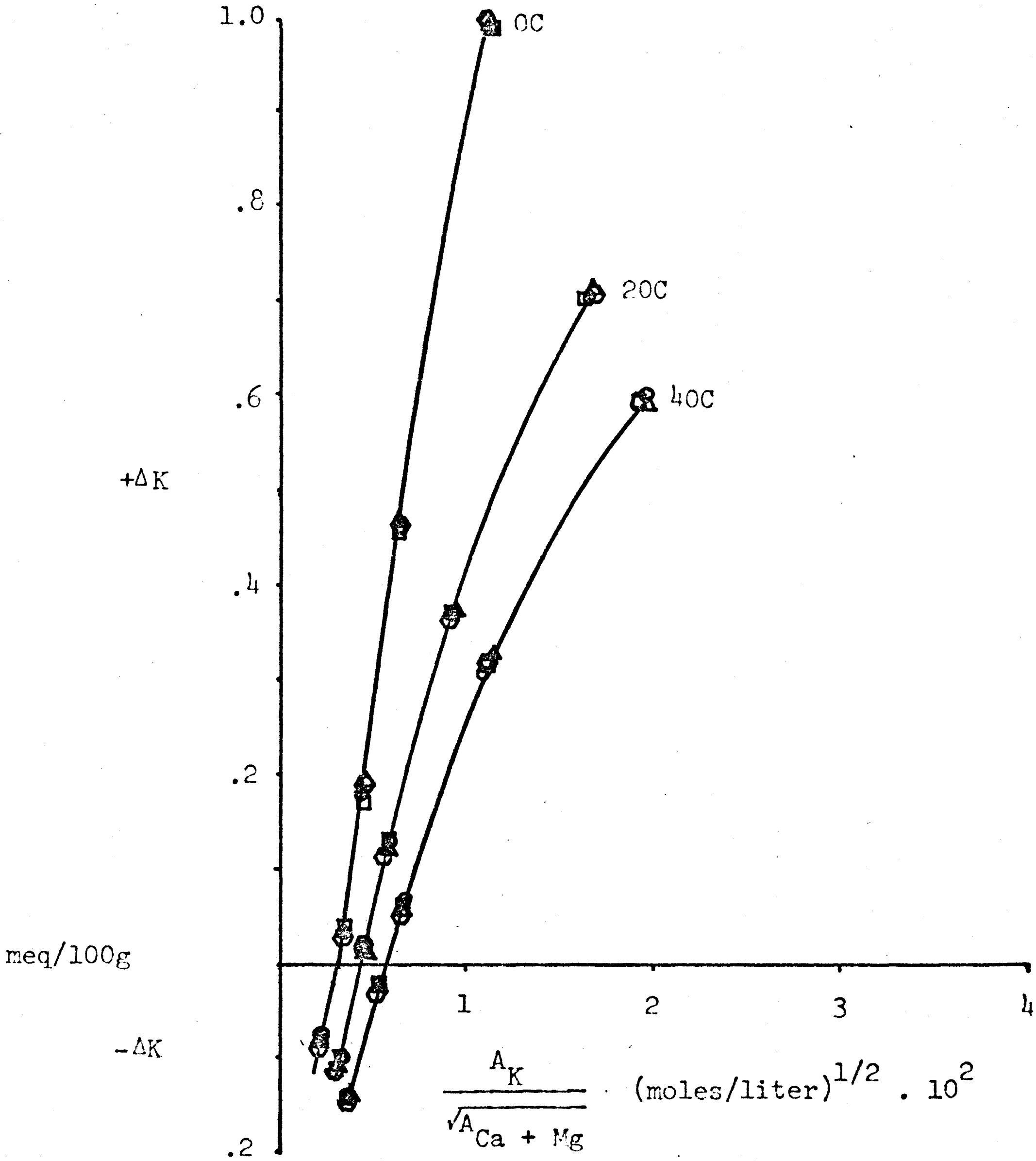

Fig. 1. The K-Ca exchange isotherms of the Vergennes Ap at 0, 20, and 40C for 1, 2, 4, and 8 days: o ,1 day; Δ ,2 days; □,4 days; O,8 days.

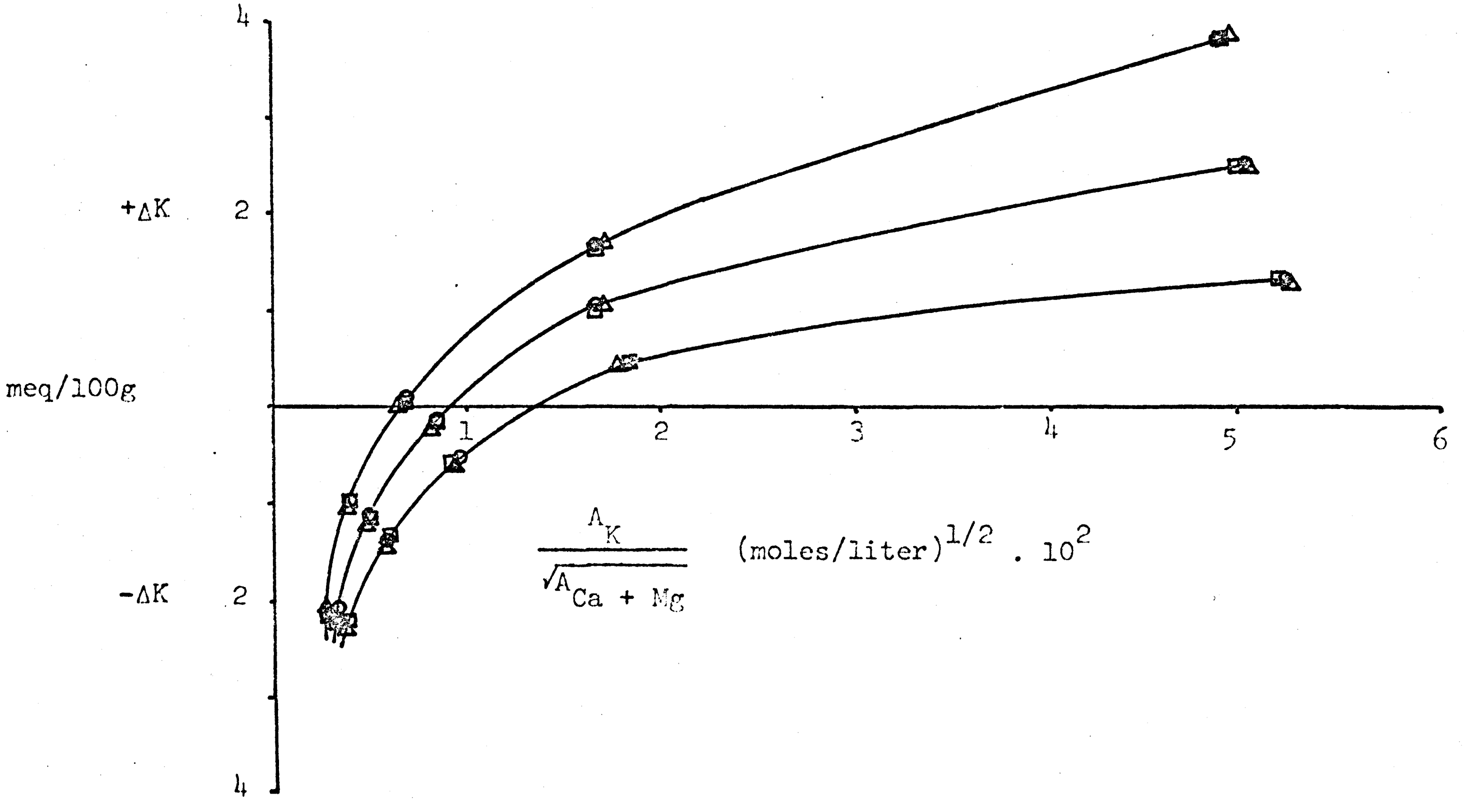

Fig. 2. The K-Ca exchange isotherms of the Al-saturated and water-washed vermiculite at 0, 20, and 40C for 1, 2, 4, and 8 days: ○,1 day; △,2 days; □,4 days; ⬡,8 days.

adsorbed by the exchangers decreased as evidenced by a lower value of ΔK for similar concentrations of the initial solution. A lower PBC was also noted as a decrease in the slope of the linear portion of the plot. However the ARE increased as noted by a larger value for the cross-over point of the isotherm on the abscissa. For similar concentrations a decrease in temperature decreased the value of ΔK while at the same time shifting the AR to the right. Therefore as temperature increased less K was adsorbed by the exchangers examined at equivalent ratios of K and Ca in solution. Stated another way, in order to maintain an equal amount of K on the exchanger with increasing temperature, a higher ratio of K relative to Ca in solution was needed.

Experimental error: Two replicates were averaged for each point on these graphs. However the magnitude of the resulting point plotted on the graph also included each of the individual values used to calculate the average. The experimental error is actually less than the error due to plotting. In fact the data was analyzed on different days and yet excellent agreement occurred for values of similar concentrations at each of the 4 days studied. The amount of variation of K-Ca exchange in these systems are minimal when analyzed and plotted by the techniques used.

Temperature Effects on K-Ca Exchange in Selected Soils

Introduction: Temperature was observed to influence K-Ca exchange in a Vergennes soil. However, the effect of temperature on exchange of these ions in other soils was unknown. The purpose of this experiment was to determine if temperature would influence K and Ca exchange in a variety of soils from many locations. Therefore 17 soils with widely different properties were selected for study. These soils were analyzed and plotted by the Q/I technique. Observing the direction and magnitude of the temperature effects on K and Ca exchange in these soils could lead to the reason or reasons for these phenomena.

Influence of temperature: It is immediately apparent from Figures 3, 4, and 5 that for three soils, namely, Calais, Windsor, and Crosby, there was no effect of temperature on K-Ca exchange. The effect of temperature on K-Ca exchange in the remaining 13 soils occurred in the same direction as that observed in the case of the Vergennes soil but at different magnitudes (Figures 6-19).

The Q/I isotherms of soils in which K and Ca exchange were not affected by changes in temperature, have either a very steep or very flat slope. The Crosby soil has a very steep slope and is the only soil which does not contain any exchangeable acidity. It is predominantly Ca saturated (Table II). However, other soils showing temperature effects have large slopes for their Q/I isotherms. These soils are Houston Black, Vergennes, Carrington, Oktibbeha, Katy, and Iredell. These soils do contain exchangeable acidity and do demonstrate an effect of temperature on K-Ca exchange. The Calais, and especially the Windsor soils, had a very flat Q/I slope (PBC). These soils do not demonstrate an effect of temperature on

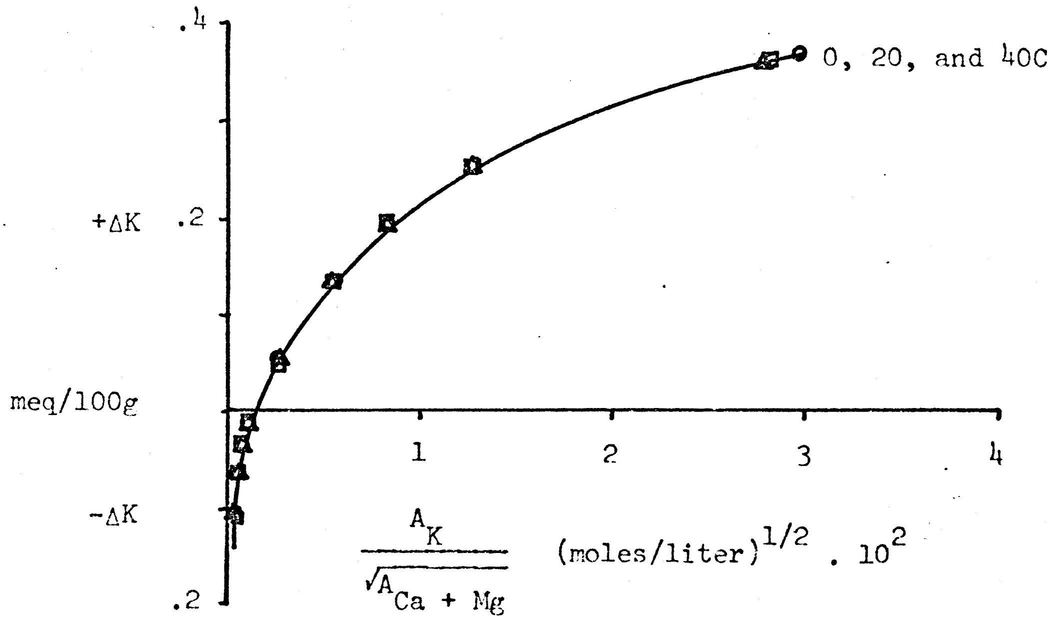

Fig. 3. The K-Ca exchange isotherms of the Calais Ap at 0, 20, and 40C: o ,0C; Δ ,20C; □ ,40C.

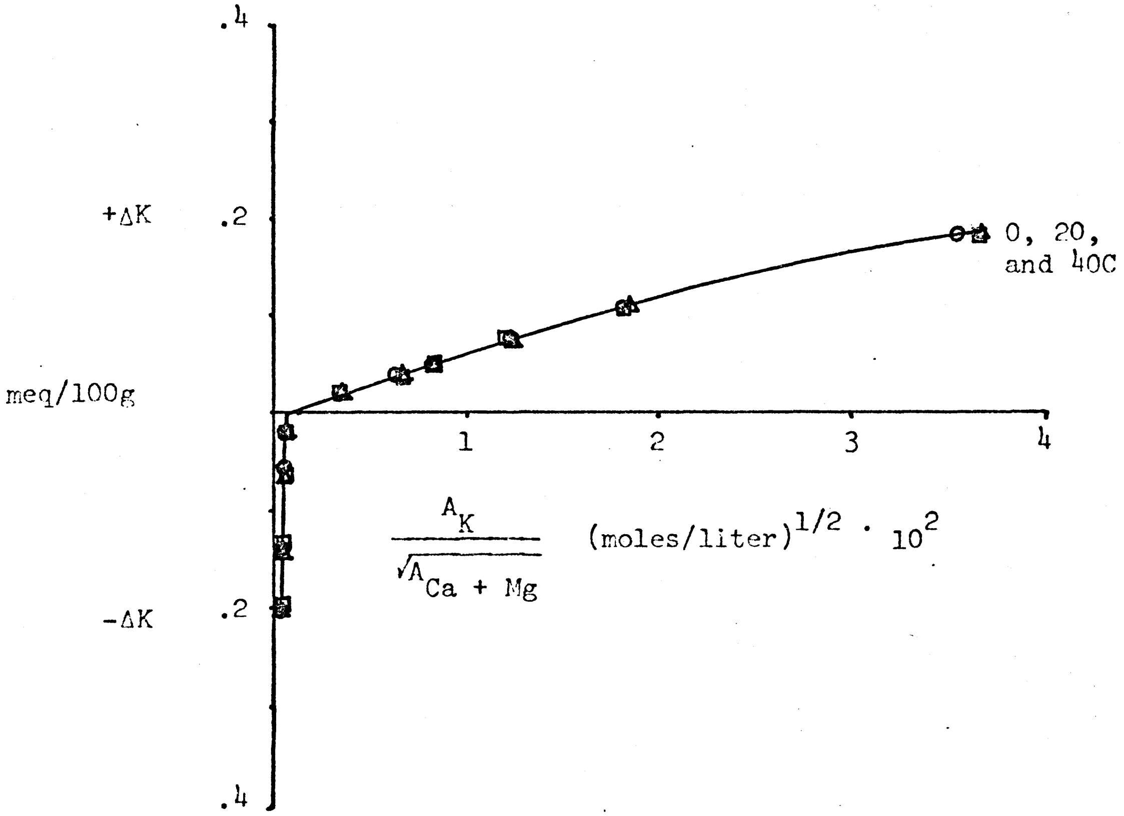

Fig. 4. The K-Ca exchange isotherms of the Windsor Ap at 0, 20, and 40C: ○,0C; △,20C; □,40C.

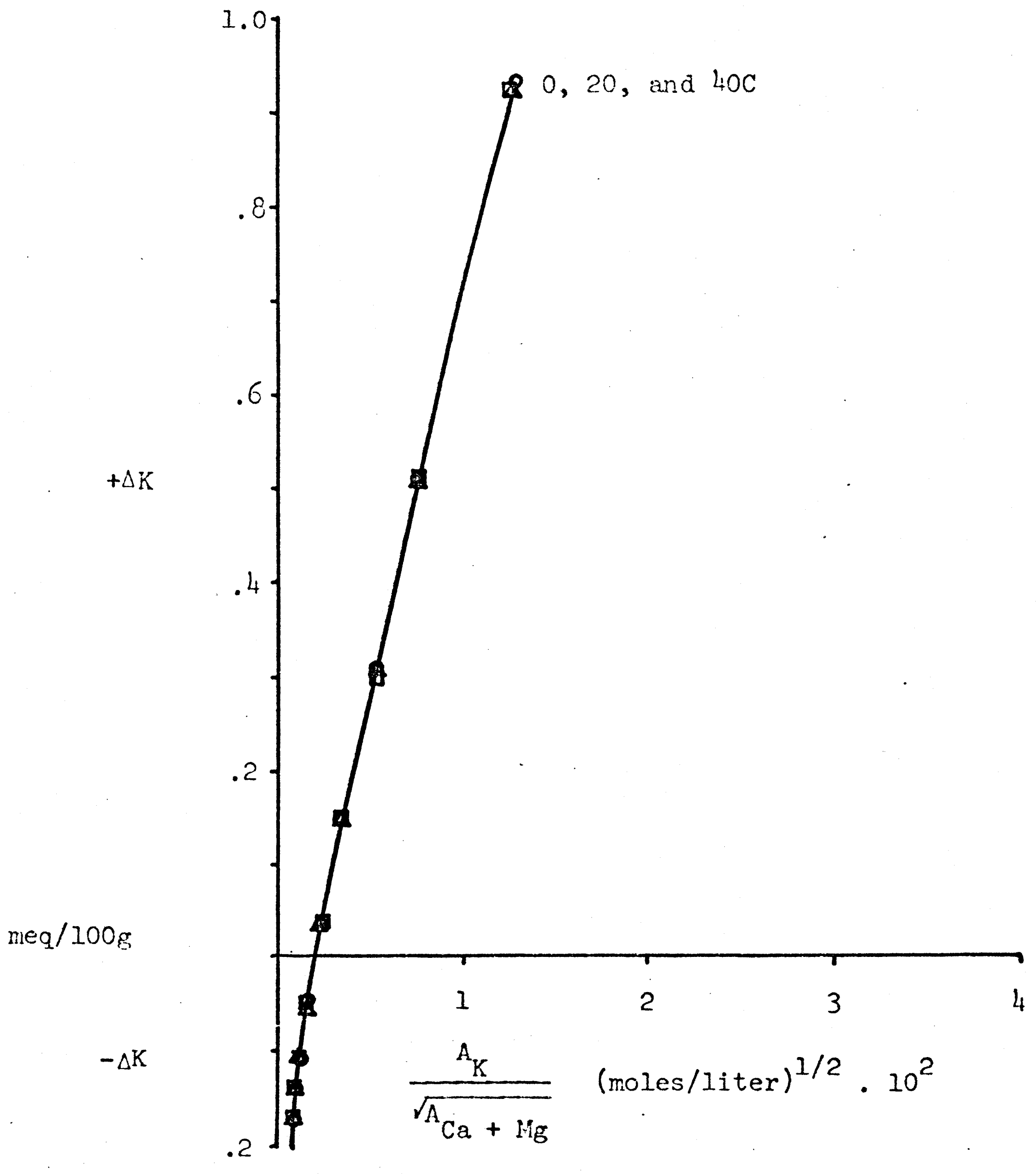

Fig. 5. The K-Ca exchange isotherms of the Crosby C at 0, 20, and 40C: ○,0C; △,20C; □,40C.

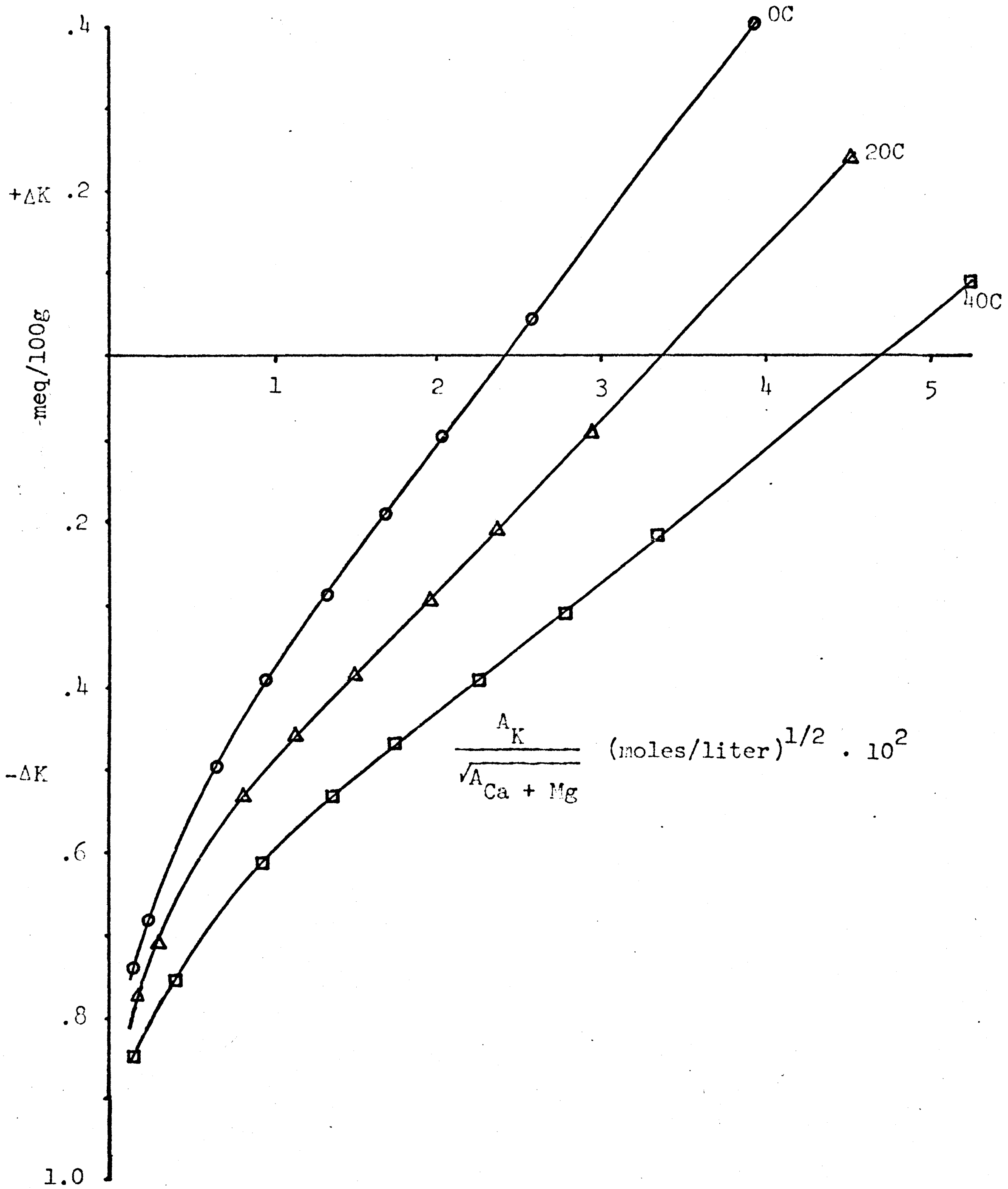

Fig. 6. The K-Ca exchange isotherms of the Bayboro Ap at 0, 20, and 40C.

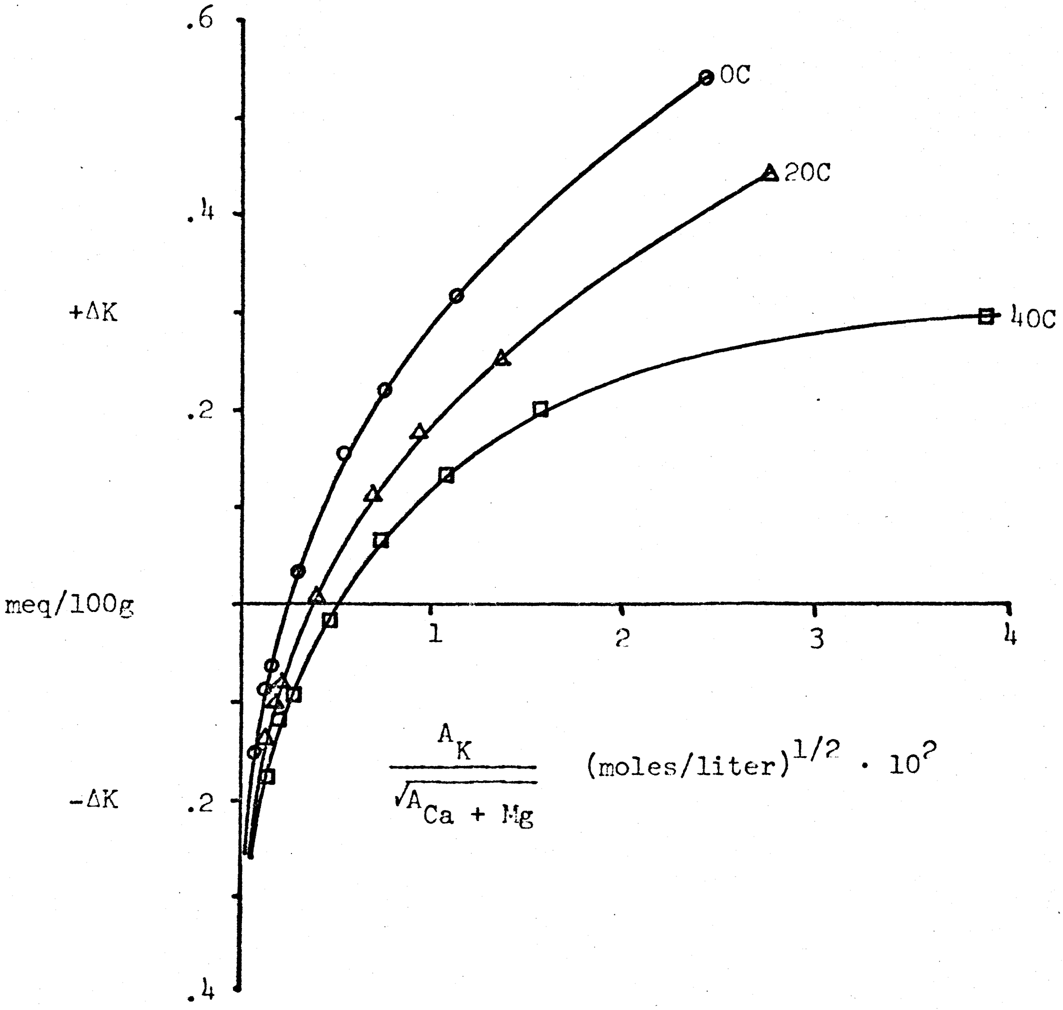

Fig. 7. The K-Ca exchange isotherms of the Portsmouth Ap at 0, 20, and 40C.

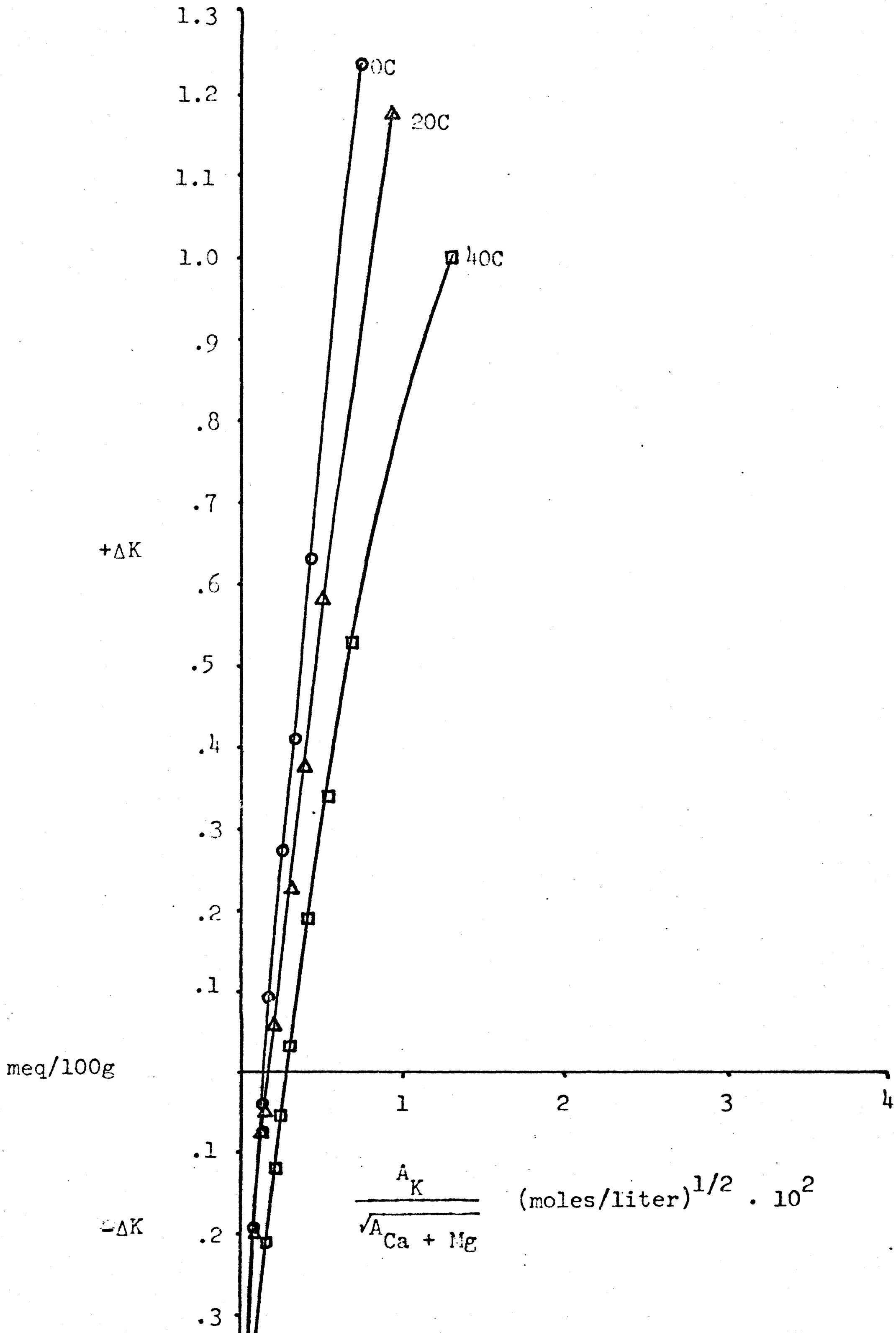

Fig. 8. The K-Ca exchange isotherms of the Houston Black A1 at 0, 20, and 40C.

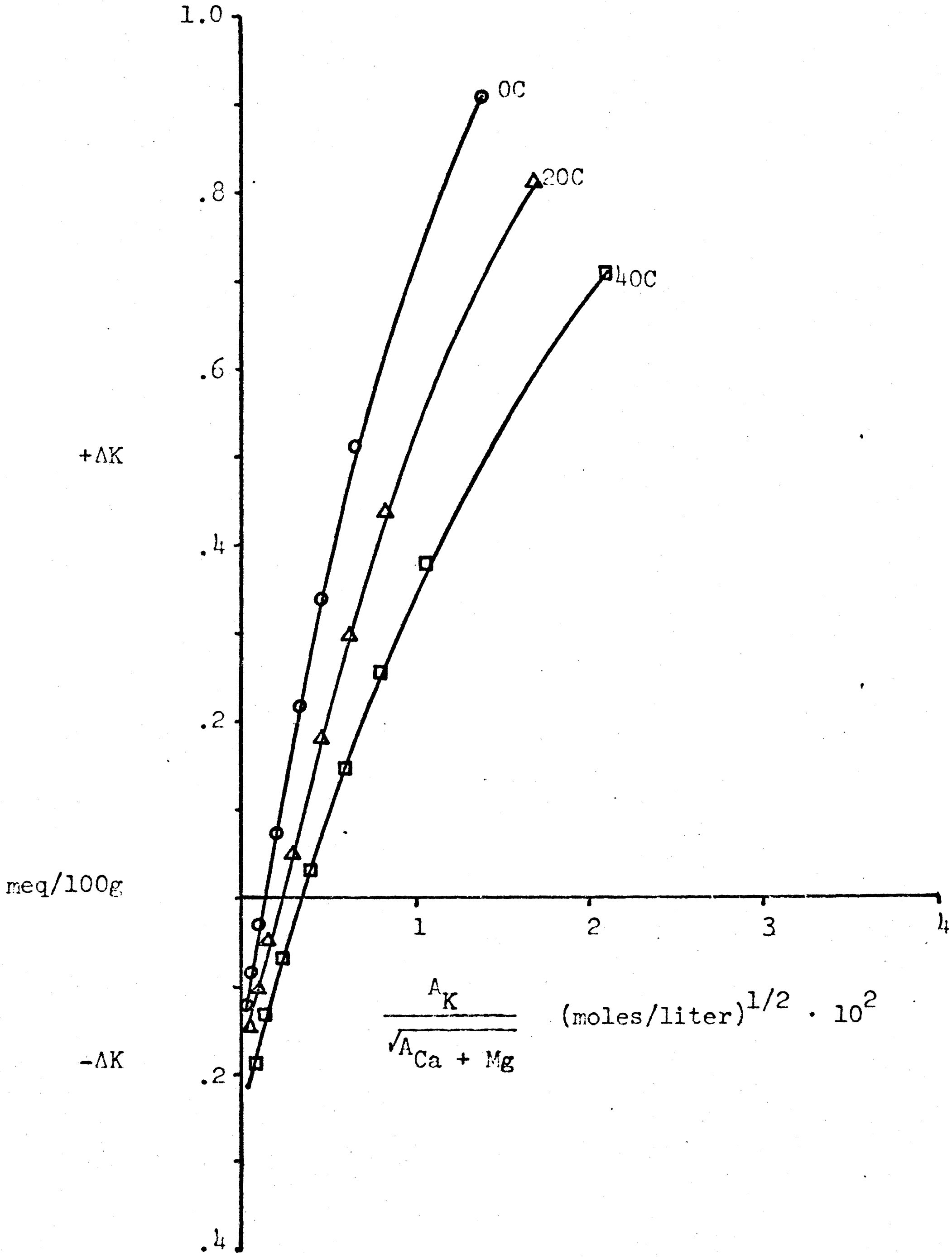

Fig. 9. The K-Ca exchange isotherms of the Carrington Ap at 0, 20, and 40C.

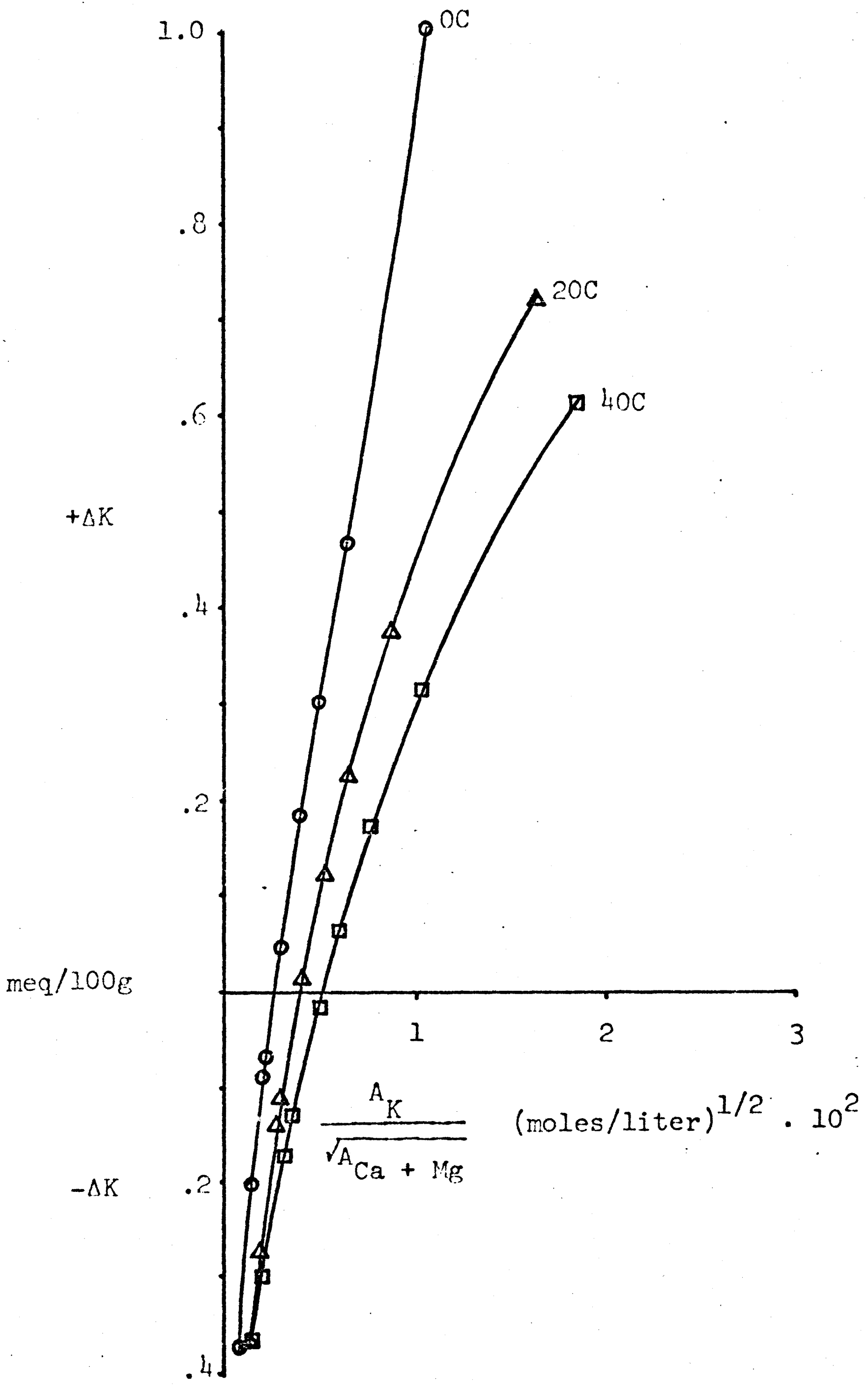

Fig. 10. The K-Ca exchange isotherms of the Vergennes Ap at 0, 20, and 40C.

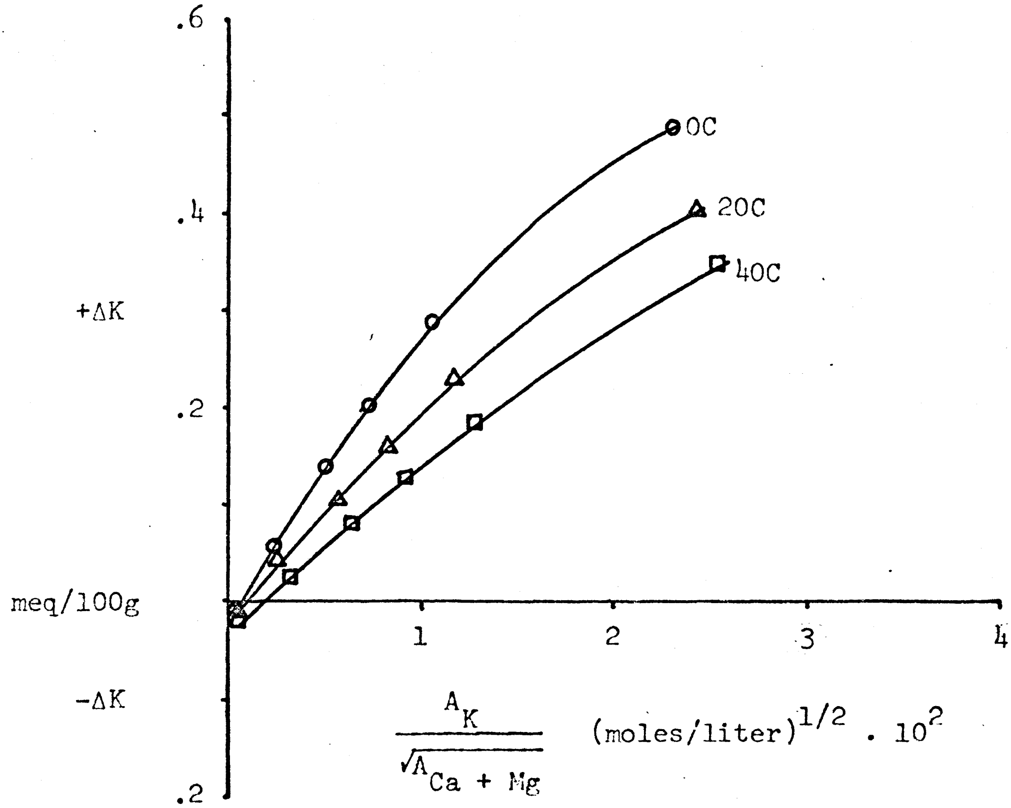

Fig. 11. The K-Ca exchange isotherms of the Hadley Ap at 0, 20, and 40C.

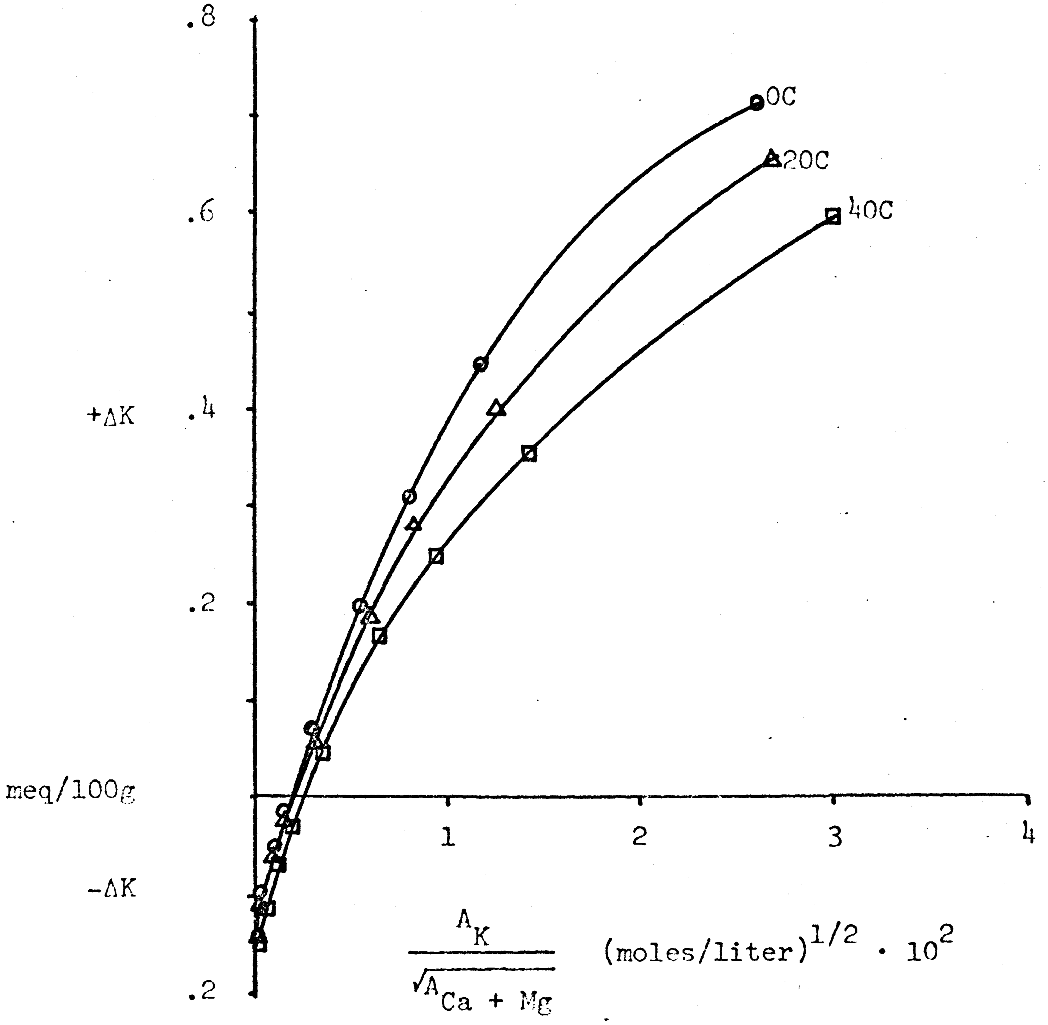

Fig. 12. The K-Ca exchange isotherms of the Berks B2 at 0, 20, and 40C.

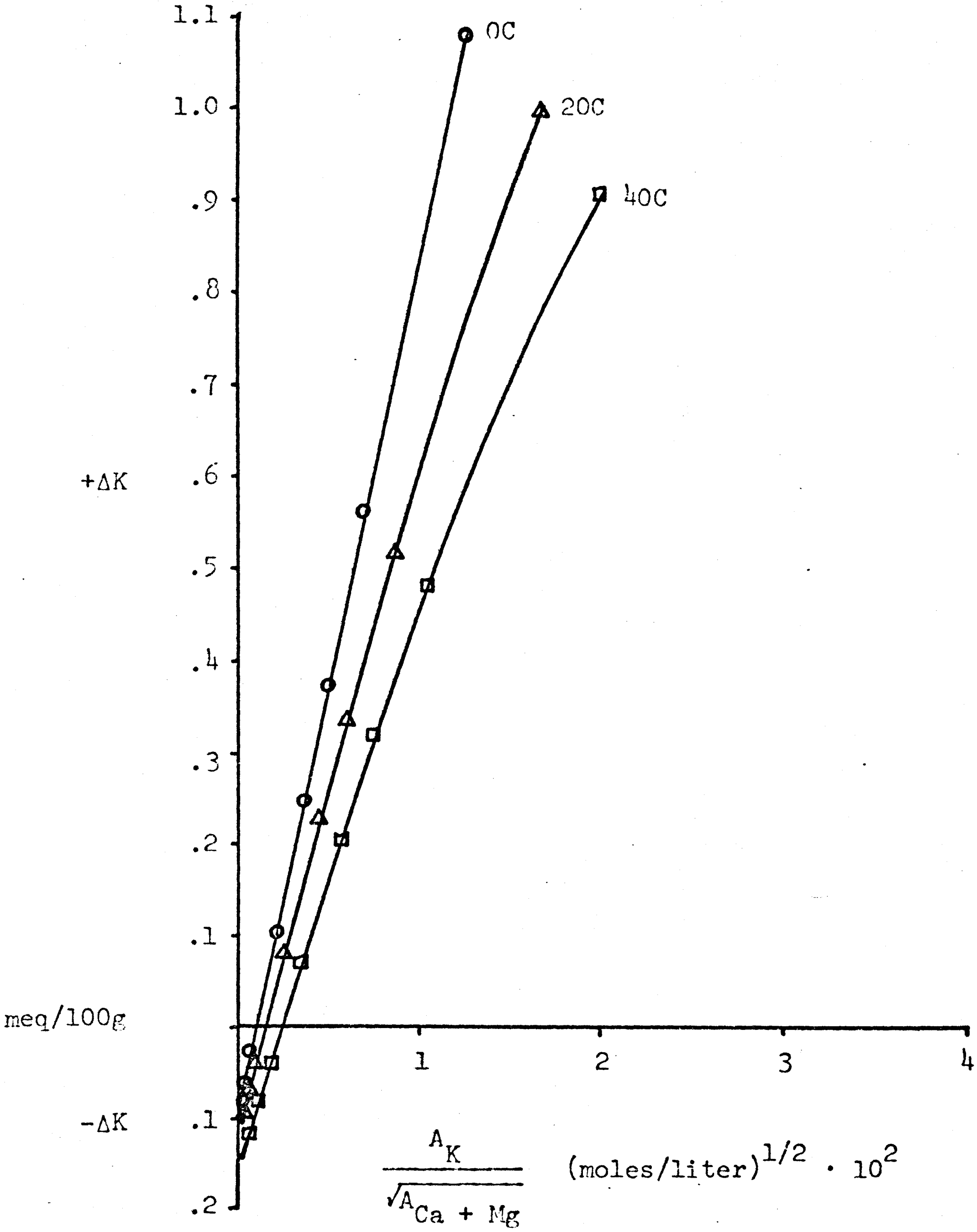

Fig. 13. The K-Ca exchange isotherms of the Katy B22t at 0, 20, and 40C.

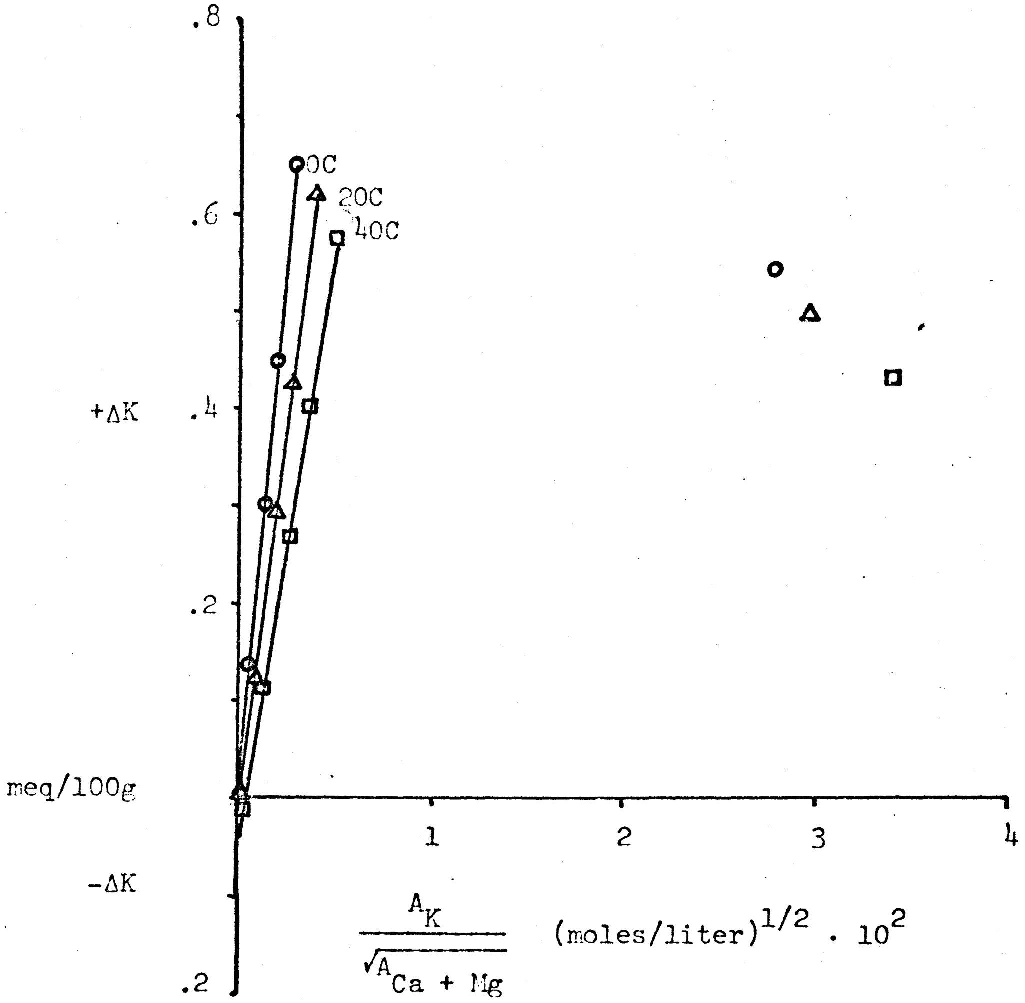

Fig. 14. The K-Ca exchange isotherms of the Iredell B2 at 0, 20, and 40C.

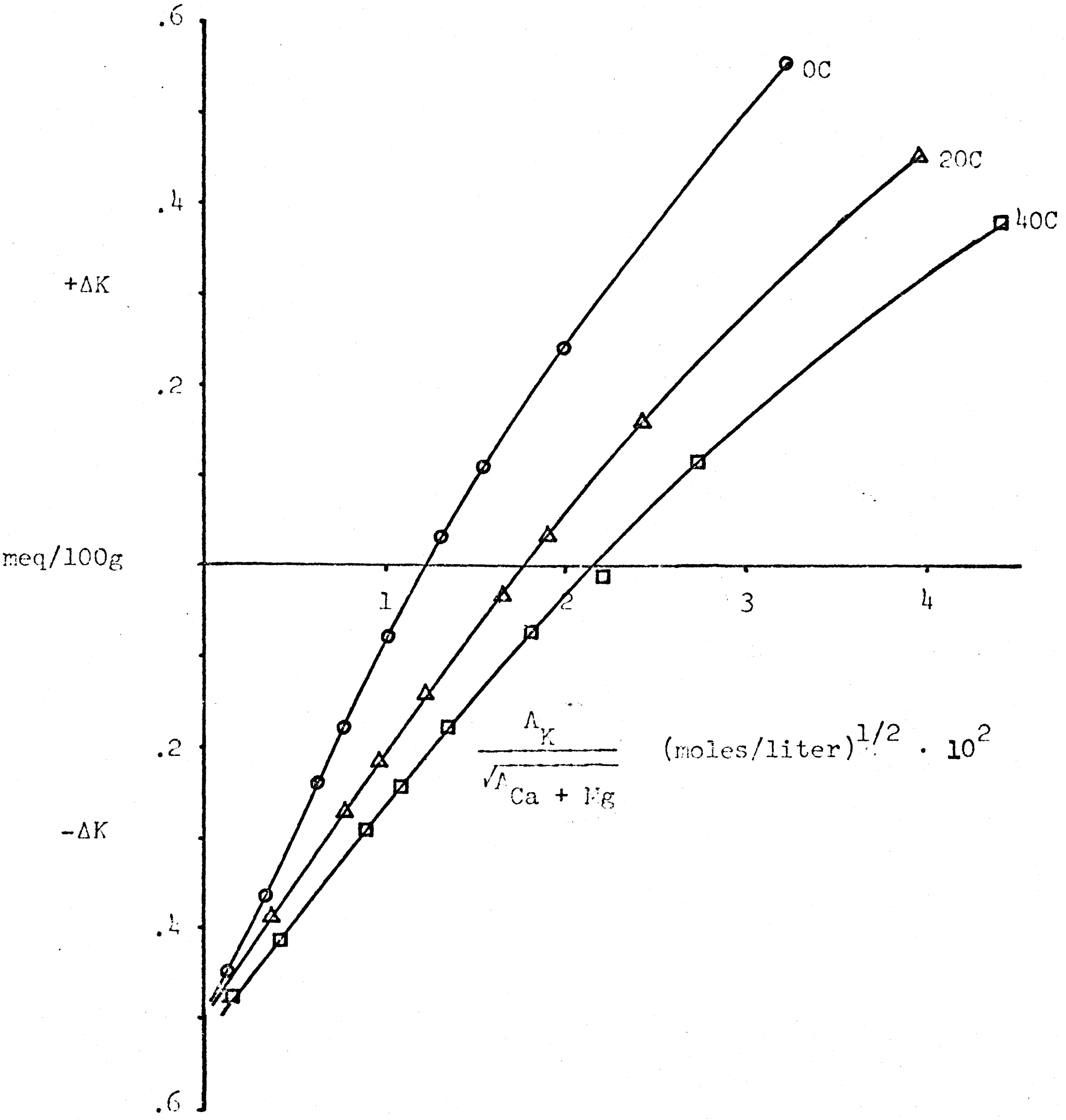

Fig. 15. The K-Ca exchange isotherms of the Whitestore B22t at 0, 20, and 40C.

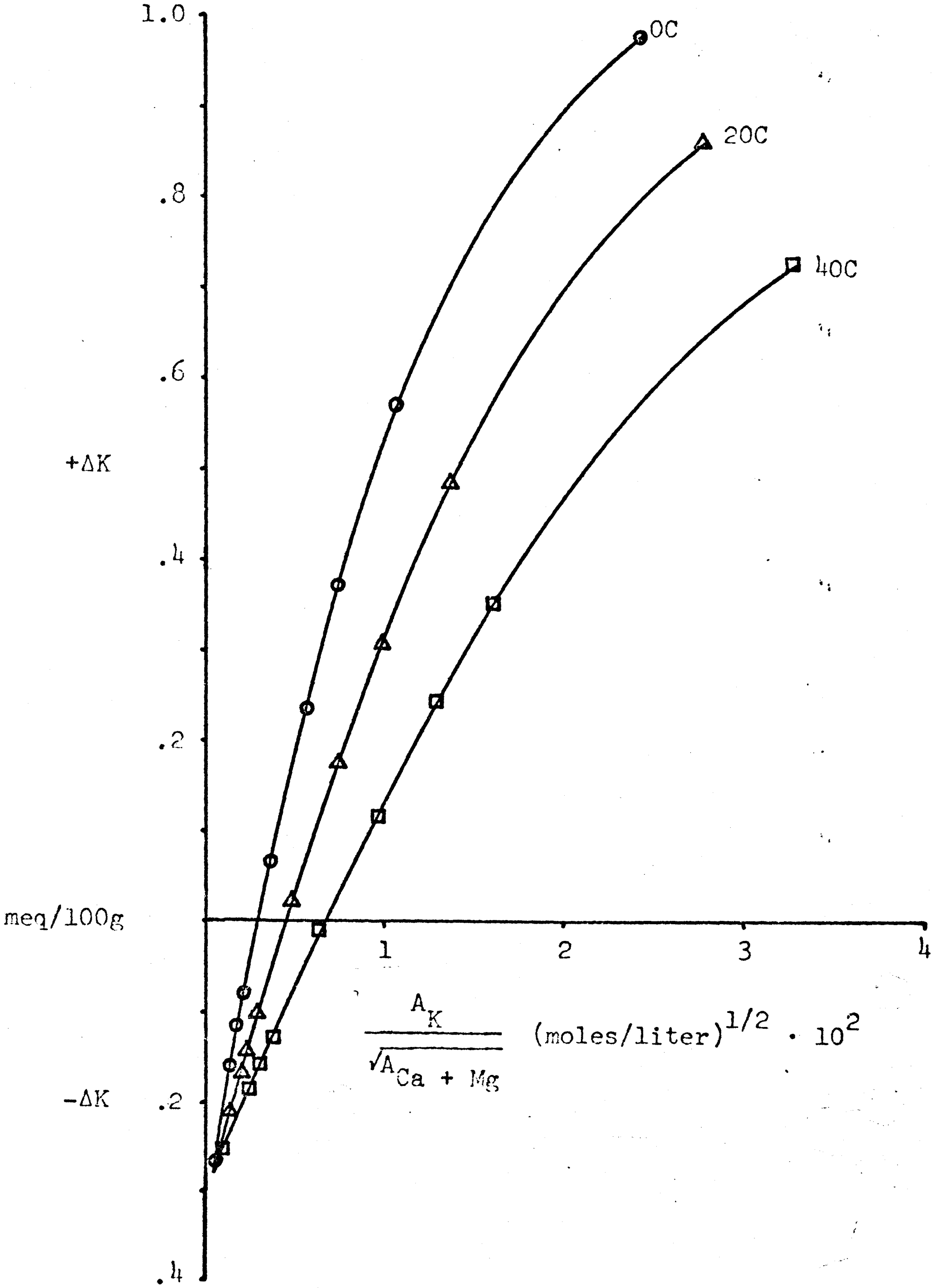

Fig. 16. The K-Ca exchange isotherms of the Nason B2 at 0, 20, and 40C.

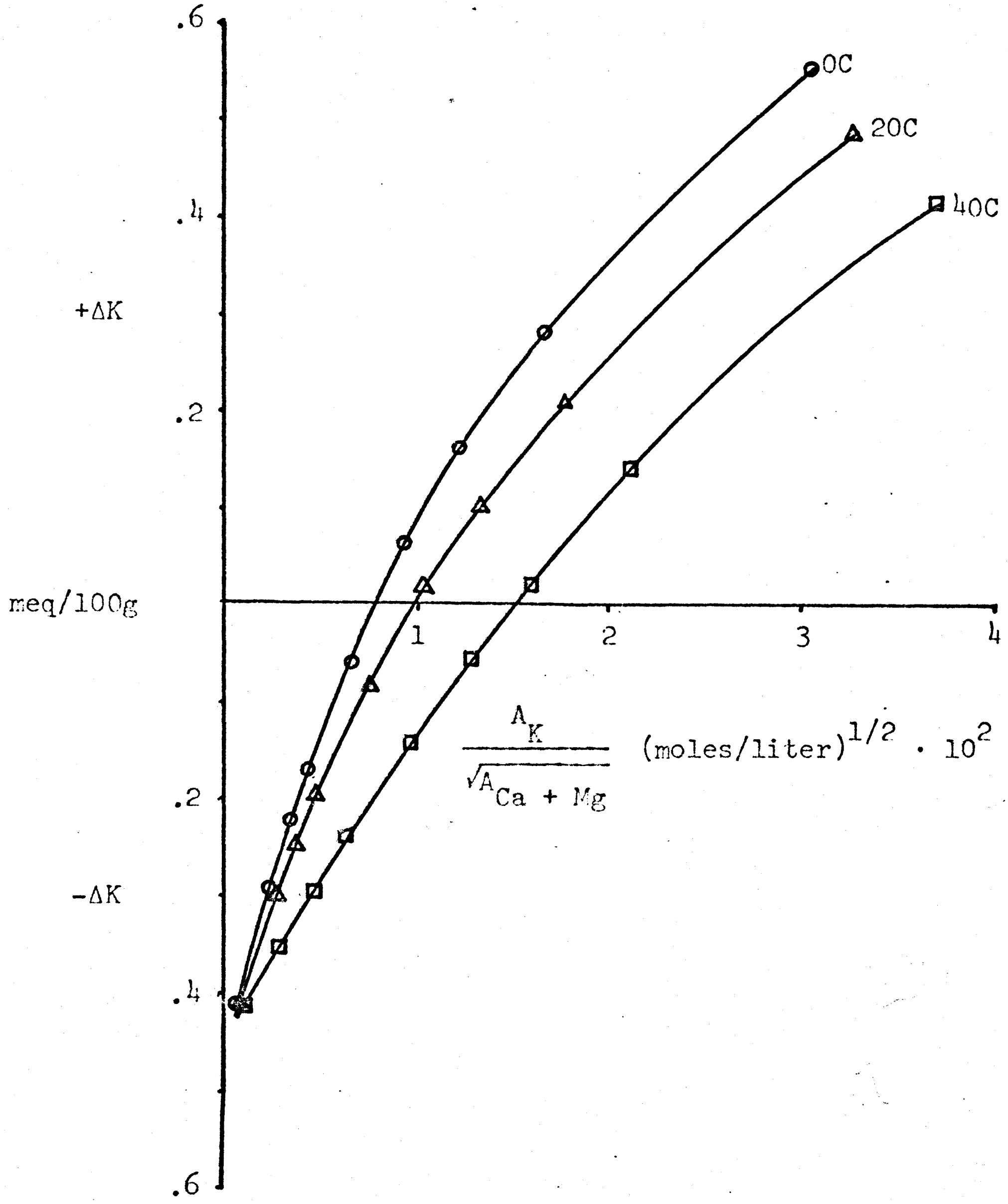

Fig. 17. The K-Ca exchange isotherms of the Tatum B2t at 0, 20, and 40C.

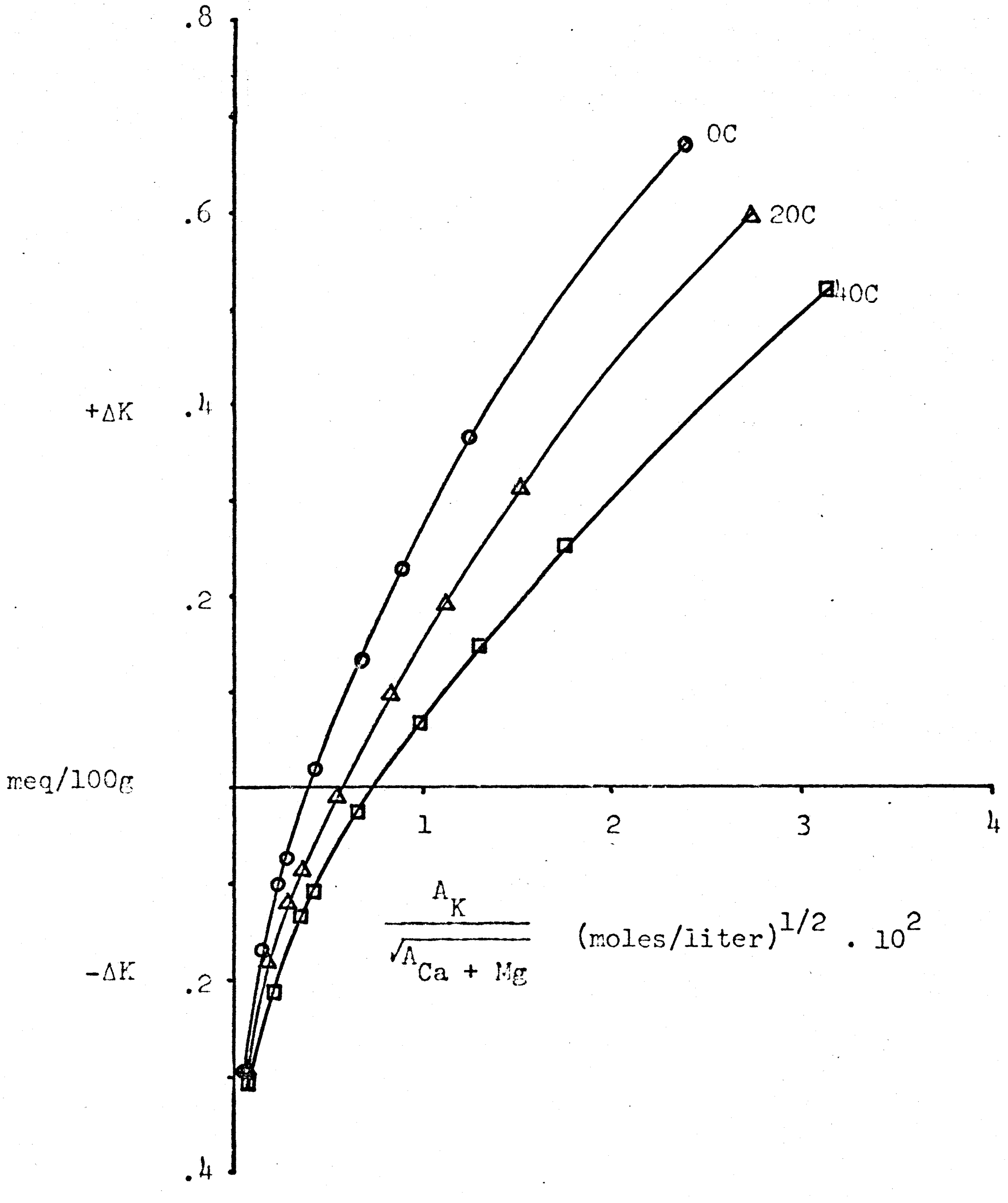

Fig. 18. The K-Ca exchange isotherms of the Cecil B2 at 0, 20, and 40C.

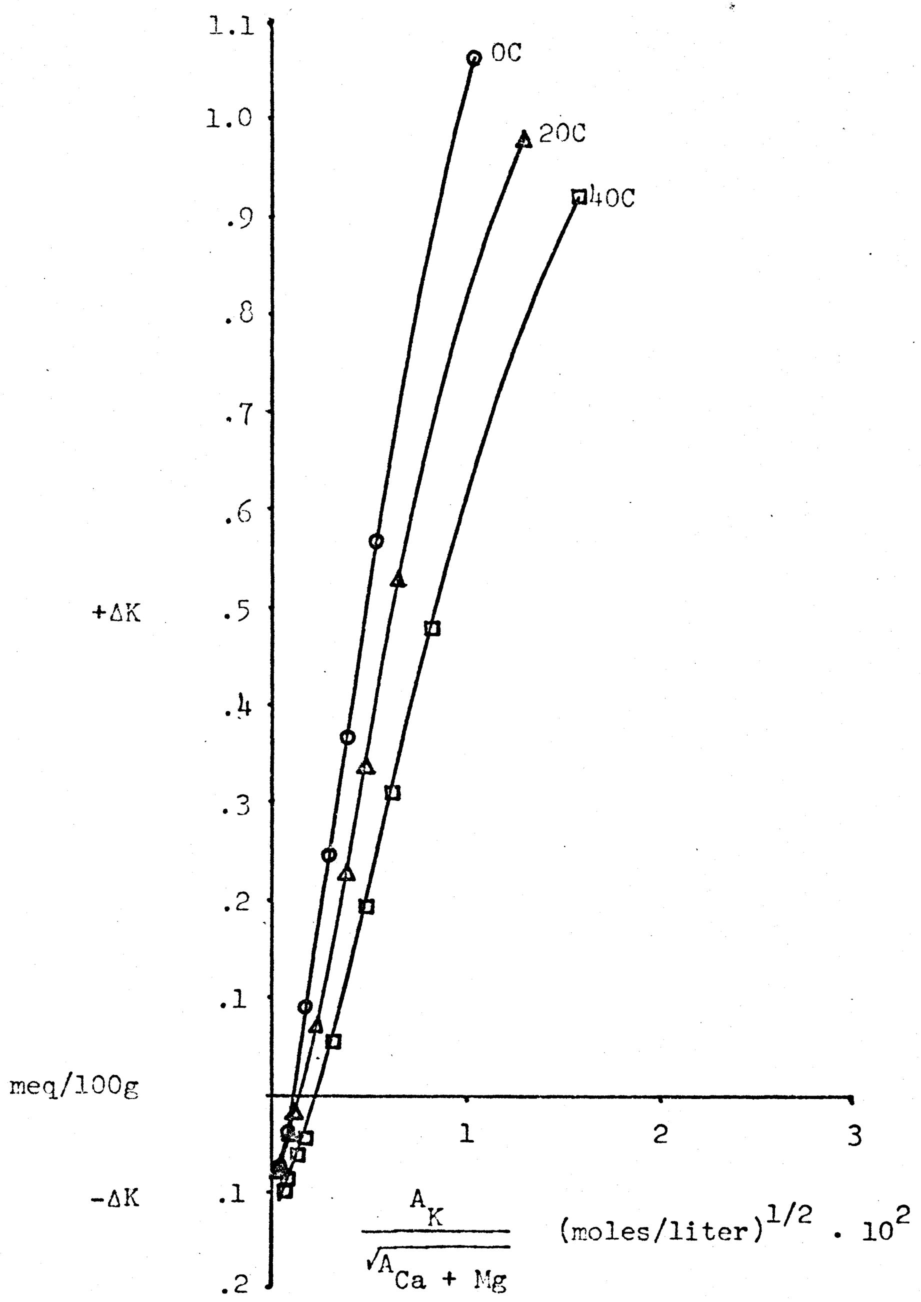

Fig. 19. The K-Ca exchange isotherms of the Oktibbeha B22t at 0, 20, and 40C.

K-Ca exchange although they do contain appreciable amounts of exchangeable acidity.

The largest effects of temperature on K-Ca exchange occurred with the Bayboro soil. This soil was highest in organic matter and exchangeable acidity for the soils studied. Sizeable effects of temperature on K-Ca exchange were also noted on the following soils: Portsmouth, Whitestore, Nason, Tatum, Cecil, Vergennes, Oktibbeha, and Carrington. These soils vary in the amount of organic matter present but all contain appreciable quantities of exchange acidity.

The effects of temperature on K-Ca exchange increased with increasing concentrations of K. Temperature produced the greatest divergence in the Q/I isotherms at the upper portion of the curve. It is also observed that these curves are typical Q/I curves as reported by Beckett (1964a, 1964b), although they do exhibit more bending at higher concentrations of K and tend to bend downward. In the case of the Iredell soil at the highest concentration of solution K, the experimental points do not associate with the curve although the relative order within the temperatures studied is maintained. No reason for this discontinuity is apparent.

Increasing temperature either had no effect on K-Ca exchange, or it decreased the amount of K adsorbed by the soil. This is evidenced by a lower value of ΔK for similar concentrations of K and Ca in the original solution. A lower PBC (Table VI) with an increase in temperature was noted whereas the ARE increased (Table VII). Temperature had little effect on ΔK^{o} (Table VIII).

Table VI. The influence of temperature on the PBC parameter of the Q/I isotherm for the soils studied.

Soil	Temperature 0C	20C	40C
	— meq K/100g · (moles/liter)$^{-1/2}$ —		
Bayboro	26.3	22.2	15.8
Portsmouth	77.1	49.7	38.6
Houston Black	197.5	179.1	118.2
Carrington	95.8	71.2	54.1
Vergennes	121.1	83.1	59.4
Hadley	46.8	20.6	16.0
Calais	27.4	27.4	27.4
Windsor	6.5	6.5	6.5
Crosby	87.6	87.6	87.6
Berks	51.4	46.2	45.0
Katy	100.0	72.4	61.5
Iredell	218.8	145.8	105.9
Whitestore	41.1	28.4	24.1
Nason	86.0	56.7	40.6
Tatum	46.9	40.4	25.1
Cecil	56.2	36.7	26.5
Oktibbeha	134.7	105.8	81.2

Table VII. The influence of temperature on the ARE parameter of the Q/I isotherm for the soils studied.

Soil	Temperature		
	0C	20C	40C
	—— (moles/liter)$^{1/2}$ x 10^{2} ——		
Bayboro	2.41	3.40	4.75
Portsmouth	0.27	0.39	0.55
Houston Black	0.15	0.16	0.27
Carrington	0.13	0.22	0.29
Vergennes	0.25	0.34	0.45
Hadley	0.05	0.08	0.17
Calais	0.11	0.11	0.11
Windsor	0.09	0.09	0.09
Crosby	0.20	0.20	0.20
Berks	0.15	0.20	0.24
Katy	0.10	0.15	0.25
Iredell	0.00	0.00	0.02
Whitestore	1.20	1.77	2.19
Nason	0.30	0.48	0.63
Tatum	0.77	1.00	1.53
Cecil	0.40	0.60	0.75
Oktibbeha	0.10	0.13	0.22

Table VIII. The influence of temperature on the ΔK^{o} parameter of the Q/I isotherm for the soils studied.

Soil	Temperature 0C	 20C	 40C
	meq K/100g		
Bayboro	0.64	0.79	0.75
Portsmouth	0.21	0.20	0.20
Houston Black	0.30	0.33	0.32
Carrington	0.14	0.14	0.19
Vergennes	0.32	0.33	0.30
Hadley	0.01	0.01	0.02
Calais	0.03	0.03	0.03
Windsor	0.09	0.09	0.09
Crosby	0.20	0.20	0.20
Berks	0.10	0.10	0.10
Katy	0.15	0.13	0.16
Iredell	0.00	0.00	0.02
Whitestore	0.51	0.50	0.51
Nason	0.29	0.27	0.28
Tatum	0.38	0.39	0.39
Cecil	0.25	0.21	0.20
Oktibbeha	0.18	0.17	0.20

Temperature Effects on K-Ca Exchange in a Homoionic Na, K, Ca, or Al Vergennes Soil

Introduction: It was observed that temperature had a pronounced effect on K-Ca exchange in many soils. This effect appeared to be related to the ions on the exchange complex. A system that is mainly Ca saturated such as the Crosby soil gave no effect of temperature on K-Ca exchange whereas the temperature effect was pronounced in many soils that contained a large portion of exchangeable acidity. The purpose of this experiment was to determine if the cations on the exchange complex of a Vergennes soil could account for the observed temperature effects of K-Ca exchange in this soil. Individual samples of the Vergennes soil were saturated with Na, K, Ca, or Al and washed free of excess salts with H_2O. Subsequently, the samples were treated according to the Q/I technique.

Influence of temperature: The effect of temperature on K-Ca exchange in the Vergennes soil was lost when this soil was Na, K, or Ca saturated (Figures 20-22), whereas increasing the temperature decreased the amount of K adsorbed on the sample that was Al saturated and water washed (Figure 23).

The slopes of the Q/I curves were low for the Na-saturated soil and high for the Ca-saturated soil. The slopes of the isotherms for the Al-saturated soil was intermediate between the Ca and Na systems. The slope of the unaltered Vergennes soil (Figure 10) was intermediate between the Ca-and the Al-saturated soil. The

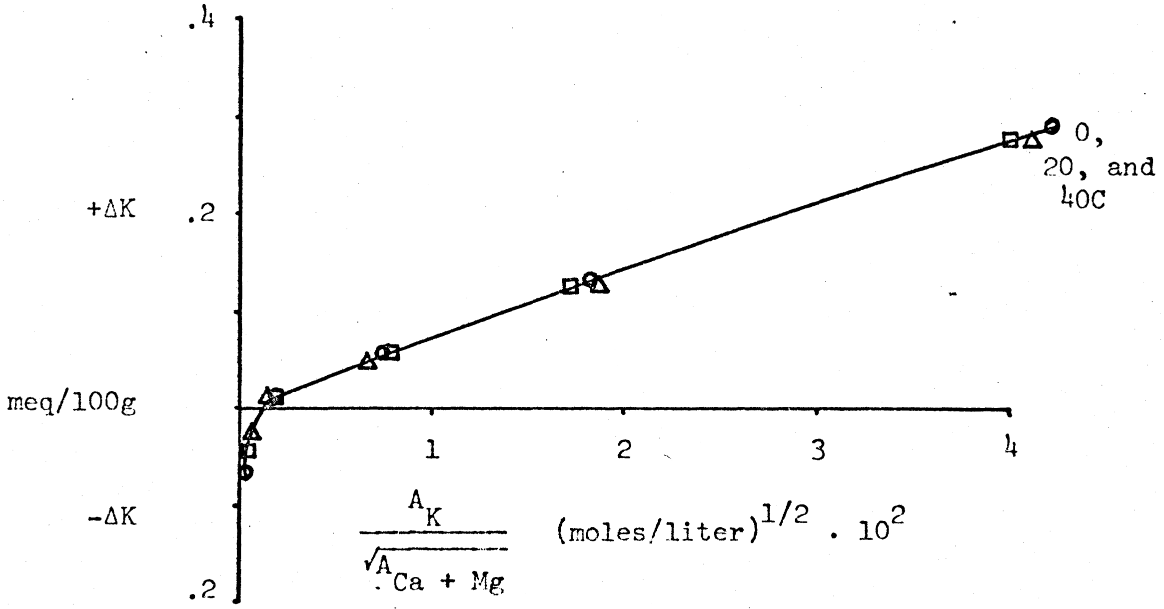

Fig. 20. The K-Ca exchange isotherms of the Na-saturated and water-washed Vergennes Ap at 0, 20, and 40C: ○ ,0C; △ ,20C; □ ,40C.

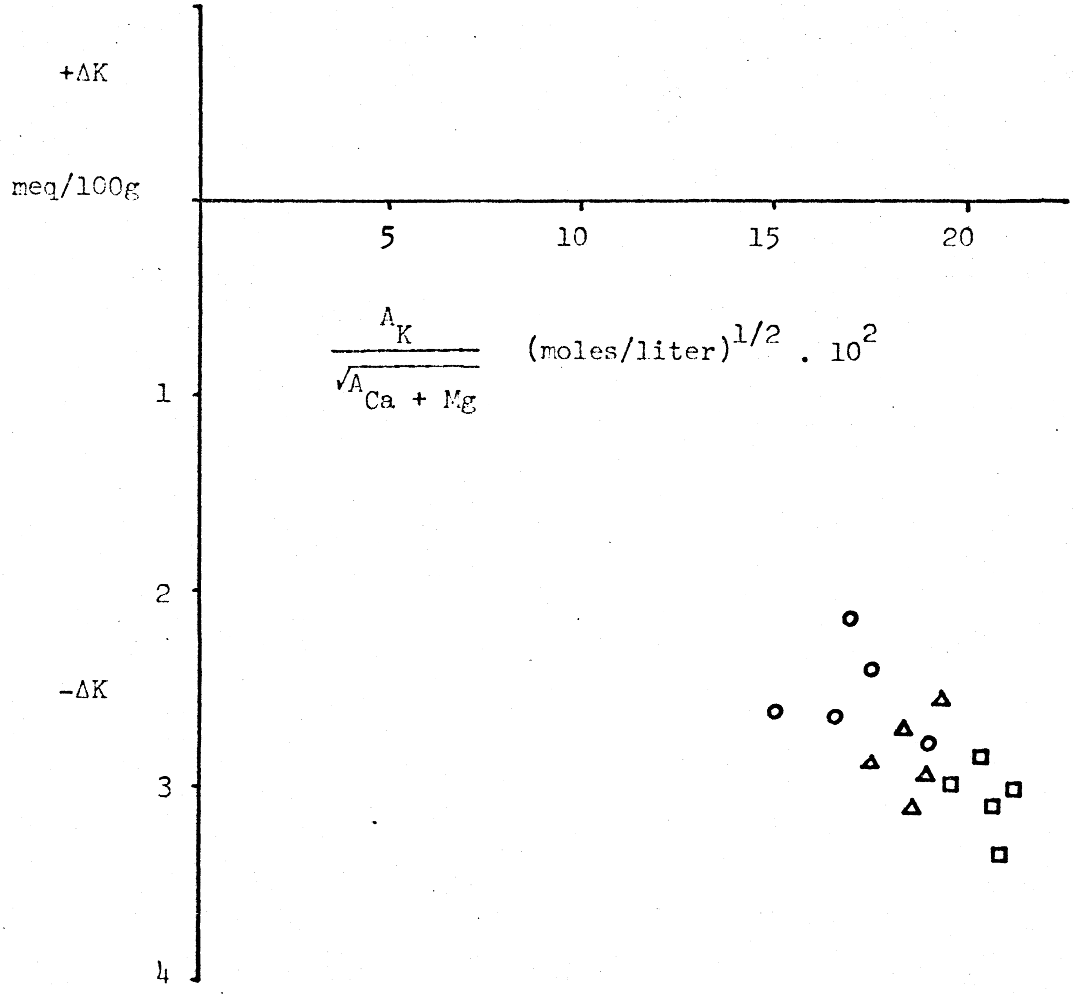

Fig. 21. The K-Ca exchange isotherms of the K-saturated and water-washed Vergennes Ap at 0, 20, and 40C: ○,0C; △,20C; □,40C.

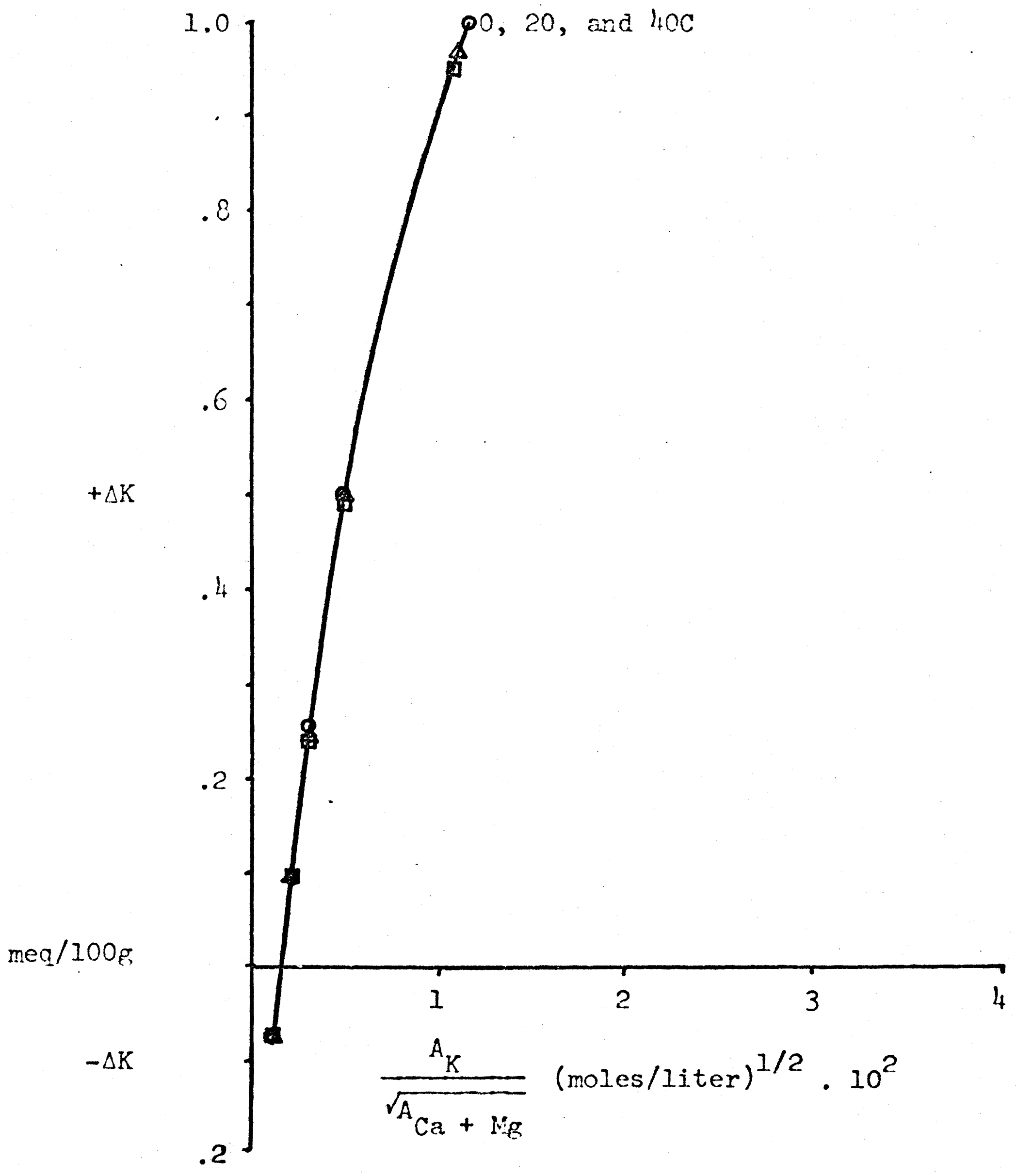

Fig. 22. The K-Ca exchange isotherms of the Ca-saturated and water-washed Vergennes Ap at 0, 20, and 40C: ○, 0C; △,20C; □,40C.

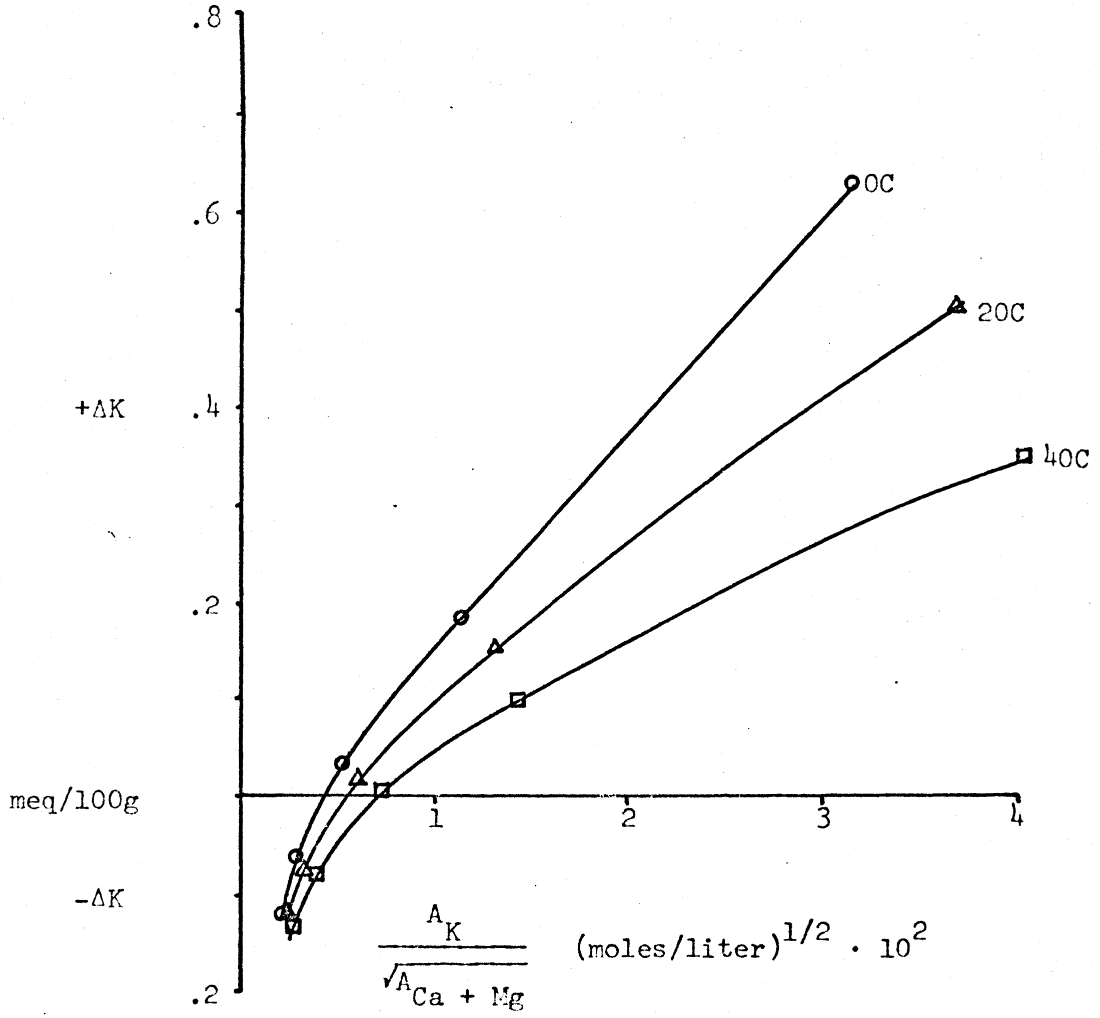

Fig. 23. The K-Ca exchange isotherms of the Al-saturated and water-washed Vergennes Ap at 0, 20, and 40C.

Vergennes soil is mainly a Ca and Al system (Table II). A Q/I isotherm could not be obtained from the K-saturated Vergennes soil for K was released to all solutions used, thereby producing a common cluster of points.

Temperature Effects on K-Ca Exchange in a Homoionic Na, K, Ca, Mg, Fe, or Al Wyoming Bentonite

Introduction: The type of ions on the exchange complex was observed to change the effect of temperature on K-Ca exchange. However salt saturation of the Vergennes soil drastically altered this soil by solubilizing the organic matter which was subsequently removed from the system. The purpose of this experiment was to determine if the cations on the exchange complex of another inorganic exchanger, such as Wyoming bentonite, would influence the effect of temperature on K-Ca exchange. Wyoming bentonite was saturated with Na, K, Ca, Mg, Fe, or Al. The Na-, K-, Ca-, and Mg-saturated bentonites were washed free of salts with water whereas the Fe and Al systems were washed free of salt with dilute acid (0.003N HCl). This procedure was used to keep hydrolysis at a minimum. These systems were analyzed and plotted by the Q/I technique.

Influence of temperature: The effect of temperature on K-Ca exchange did not occur in the Wyoming bentonite saturated with Na, K, Ca, Mg, Fe, or even Al (Figures 24-29). No effect of temperature on K-Ca exchange occurred in any system, even the Al-saturated clay.

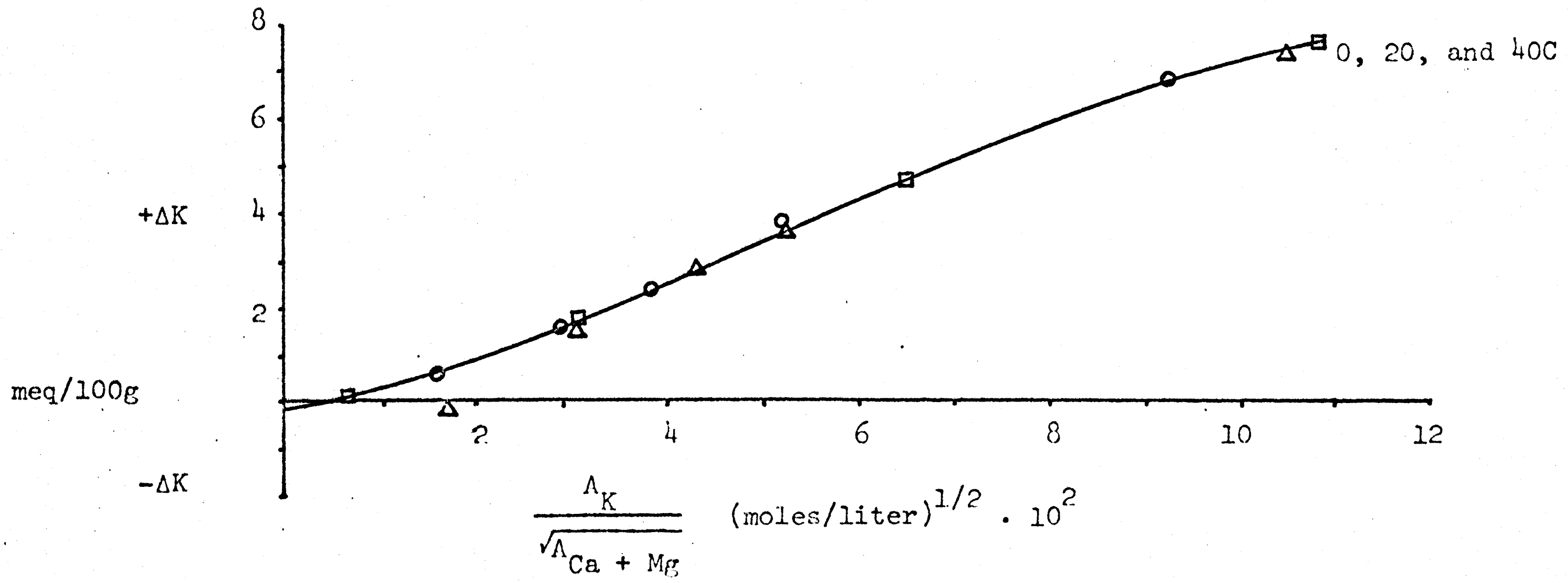

Fig. 24. The K-Ca exchange isotherms of the Na-saturated and water-washed Wyoming bentonite at 0, 20, and 40C: ○, 0C; △, 20C; □, 40C.

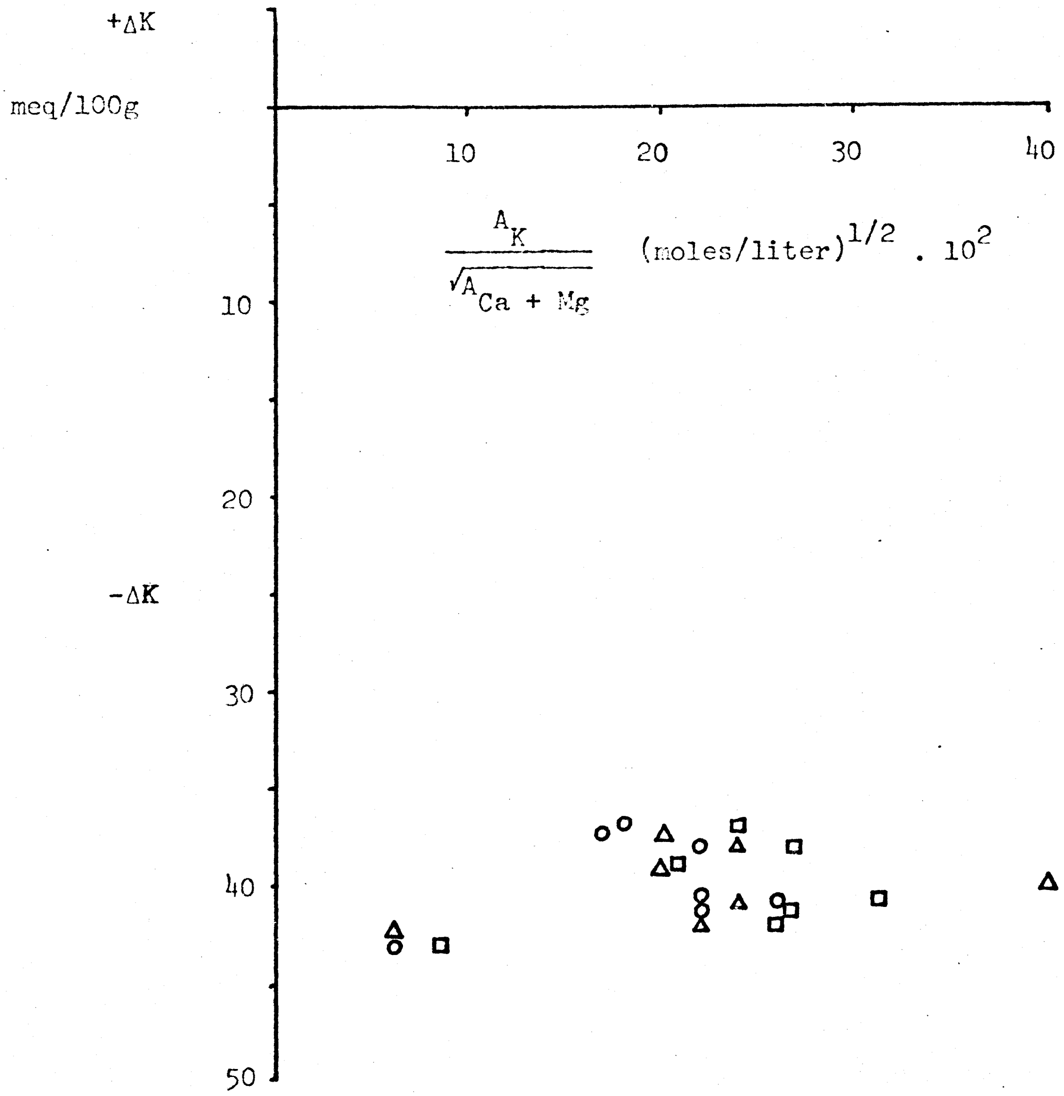

Fig. 25. The K-Ca exchange isotherms of the K-saturated and water-washed Wyoming bentonite at 0, 20, and 40C: ○,0C; △,20C; □,40C.

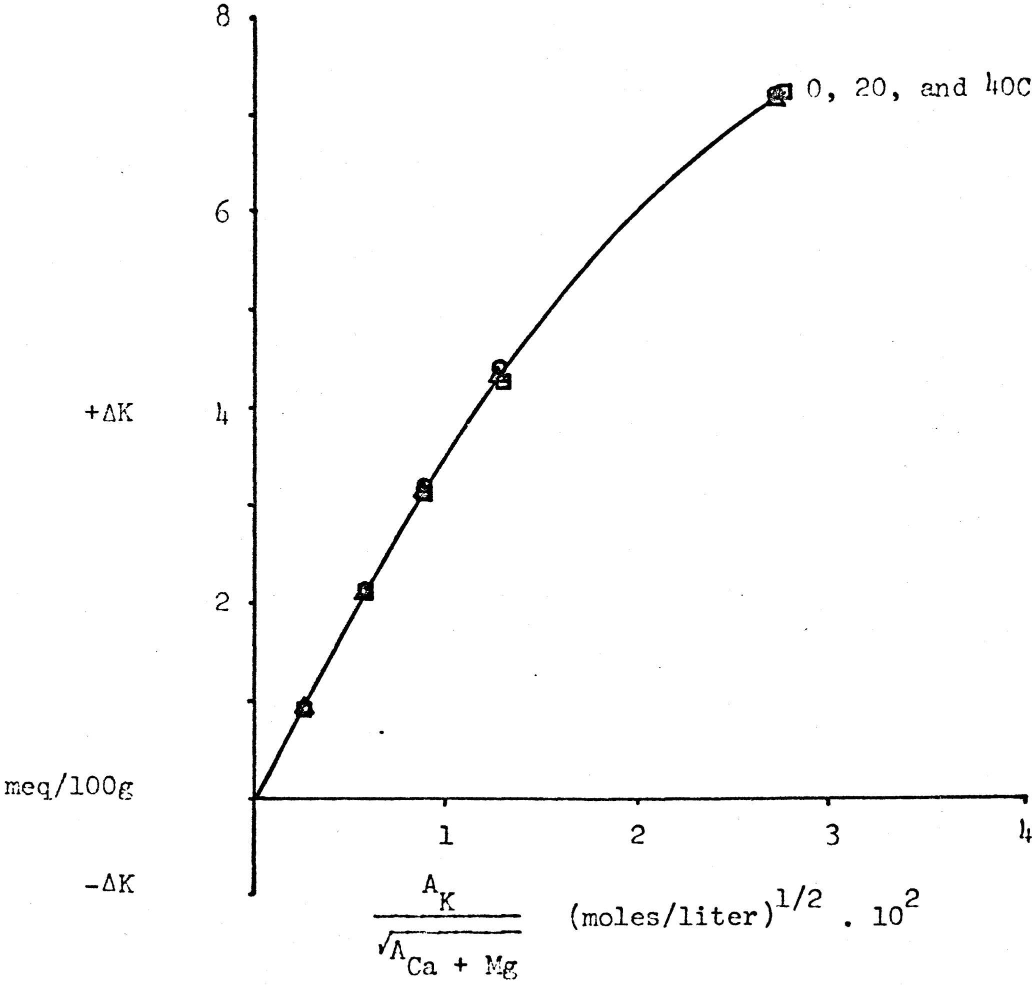

Fig. 26. The K-Ca exchange isotherms of the Ca-saturated and water-washed Wyoming bentonite at 0, 20, and 40C: ○, 0C; △, 20C; □, 40C.

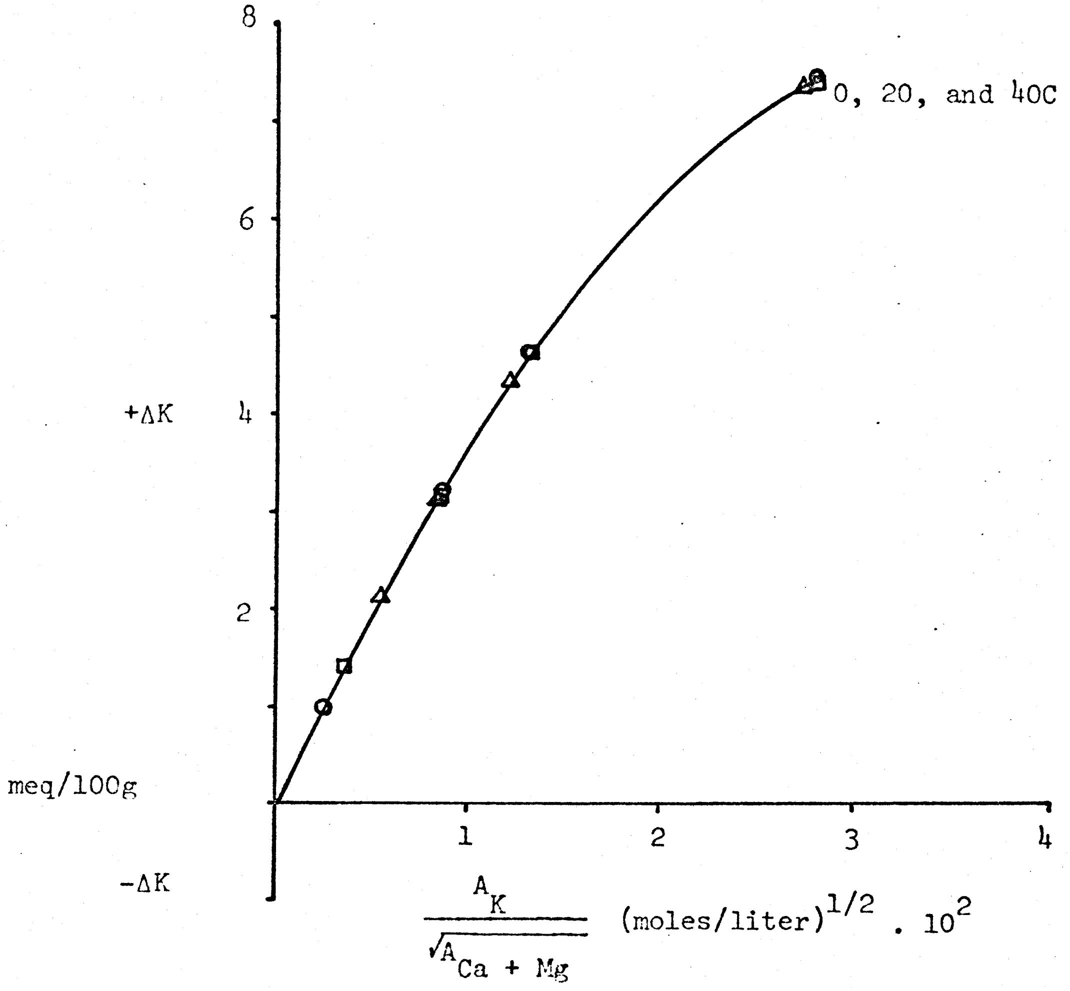

Fig. 27. The K-Ca exchange isotherms of the Mg-saturated and water-washed Wyoming bentonite at 0, 20, and 40C: o, 0C; △, 20C; □, 40C.

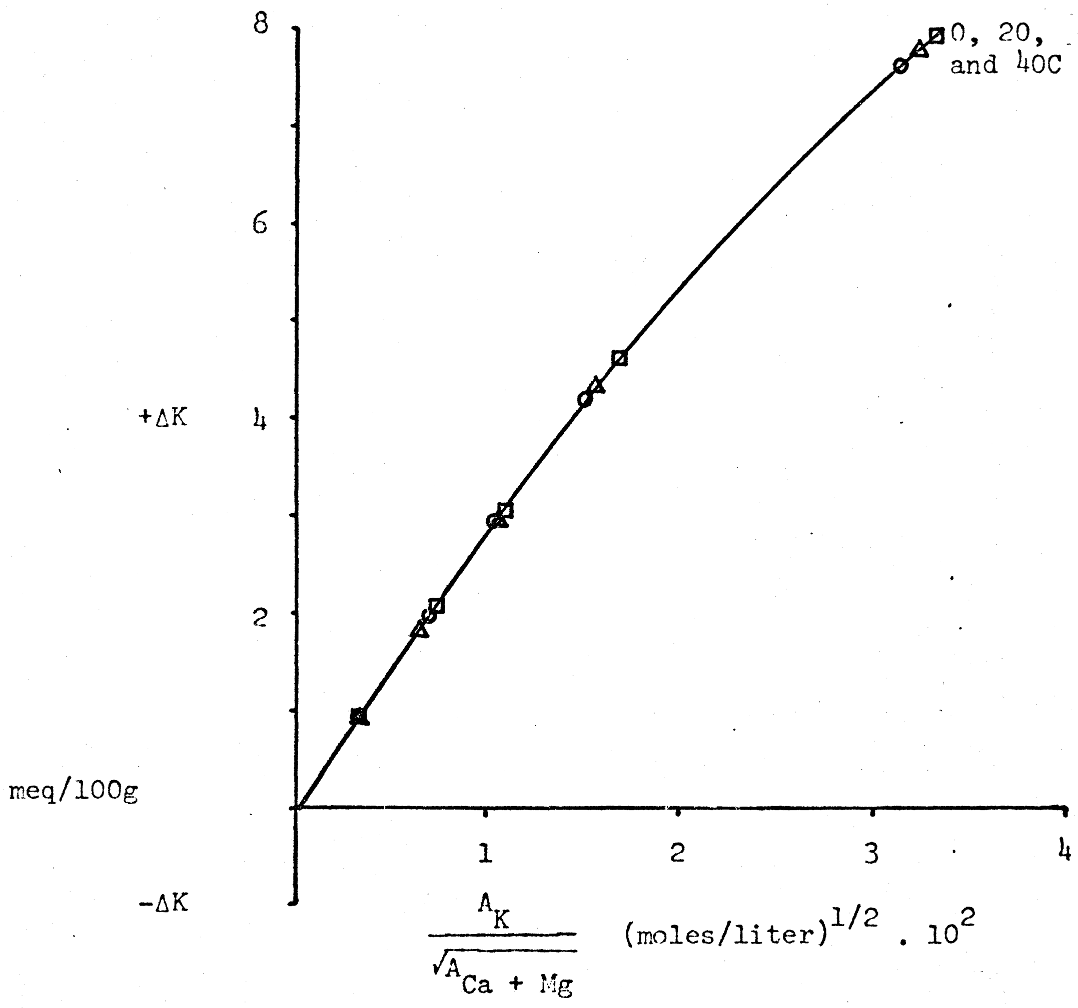

Fig. 28. The K-Ca exchange isotherms of the Fe^{3+}-saturated and 0.003N HCl-washed Wyoming bentonite at 0, 20, and 40C: ○, 0C; △, 20C; □, 40C.

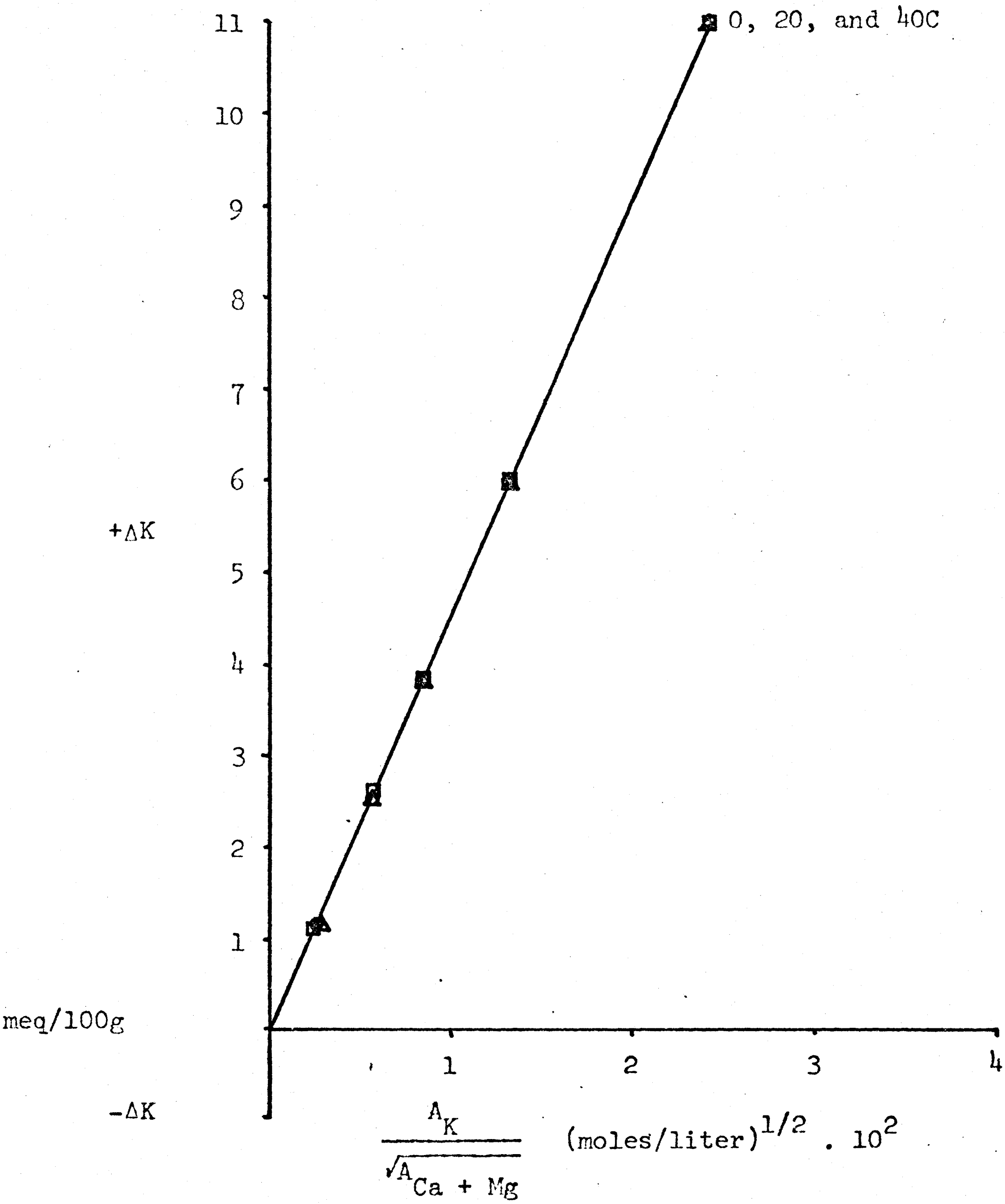

Fig. 29. The K-Ca exchange isotherms of the Al-saturated and 0.003N HCl-washed Wyoming bentonite at 0, 20, and 40C: ○ ,0C; △ ,20C; □ ,40C.

It is noted that this Al system was washed free of excess salts with 0.003N HCl thereby keeping hydrolysis at a minimum.

The lowest slope occurred in the Na-saturated bentonite while the largest occurred for the Al system. The Al-saturated and dilute acid-washed bentonite even had a steeper slope than the Ca-saturated system. This result is opposite to that observed for the Vergennes systems. The Ca- and Mg-saturated bentonite behave similarly with respect to K-Ca exchange with this type of Q/I plot. As in the K-saturated Vergennes soil, the K-saturated Wyoming bentonite released K to all solutions used thereby producing a cluster of points.

Temperature Effects on K-Ca Exchange in Al Saturated Clay Minerals

Introduction: It is apparent that the type of Al present on the exchange material is important in determining the influence of temperature on K-Ca exchange. The Al-saturated Vergennes soil and vermiculite that were water washed demonstrated a decrease in K adsorption with increasing temperature whereas the Al-saturated Wyoming bentonite which was washed with 0.003N HCl gave no temperature effect on K-Ca exchange. The purpose of this experiment was to determine the influence that the form of Al present on the exchange complex had on the temperature effect in subsequent K-Ca exchange. Kaolinite, Camargo bentonite, and vermiculite were Al saturated and washed with 0.003N HCl. Subsamples of the Al-saturated and acid -

washed Wyoming bentonite and vermiculite were boiled in water whereas still another subsample of each of these Al-saturated minerals were washed with water. These systems were analyzed and plotted by the Q/I technique.

Influence of temperature: There was no response of K-Ca exchange to temperature changes in the Al-saturated and acid-washed kaolinite (Figure 30). However, in the remaining systems an increase in temperature decreased the amount of K adsorbed (Figures 31-36). The temperature effect on K-Ca exchange was greater in the Al-saturated and acid-washed vermiculite than in the Camargo bentonite although no effect was observed in the previous Wyoming bentonite systems that had been treated somewhat differently. Decreased K adsorption with increasing temperatures occurred in the Wyoming bentonite systems that were Al saturated and acid washed but then boiled or just water washed. A significant decrease in the slope of the Q/I isotherms are observed between the Wyoming bentonite that was acid washed and those that were boiled or water washed. The Al-saturated vermiculite that was boiled had a steeper slope and a smaller ARE than the water washed samples.

Temperature Effects on K-Ca Exchange in Selected Cation Exchange Resins

Introduction: The effect of temperature on K-Ca exchange is dependent on the type of Al present on the exchange complex which itself is dependent on the charge density of the exchanger. The

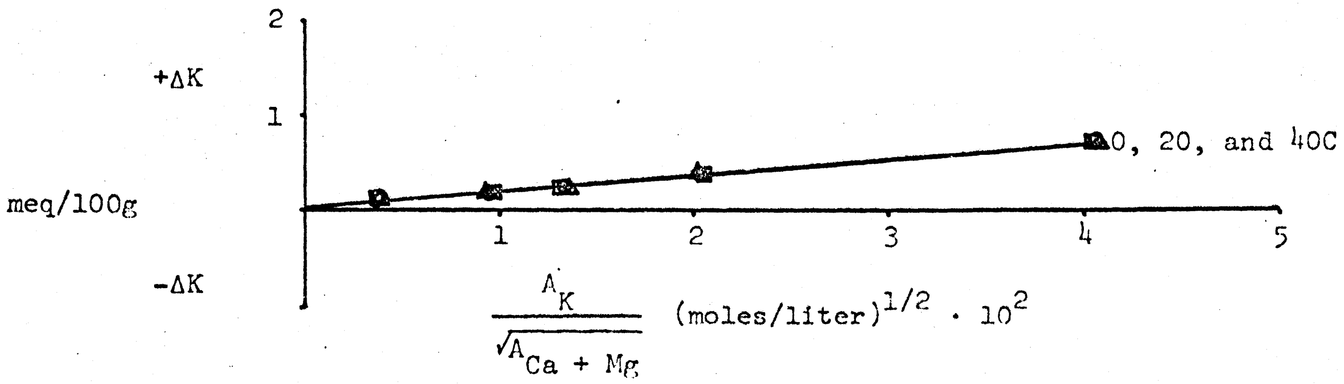

Fig. 30. The K-Ca exchange isotherms of the Al-saturated and 0.003N HCl-washed kaolinite at 0, 20, and 40C: ○, 0C; △, 20C; □, 40C.

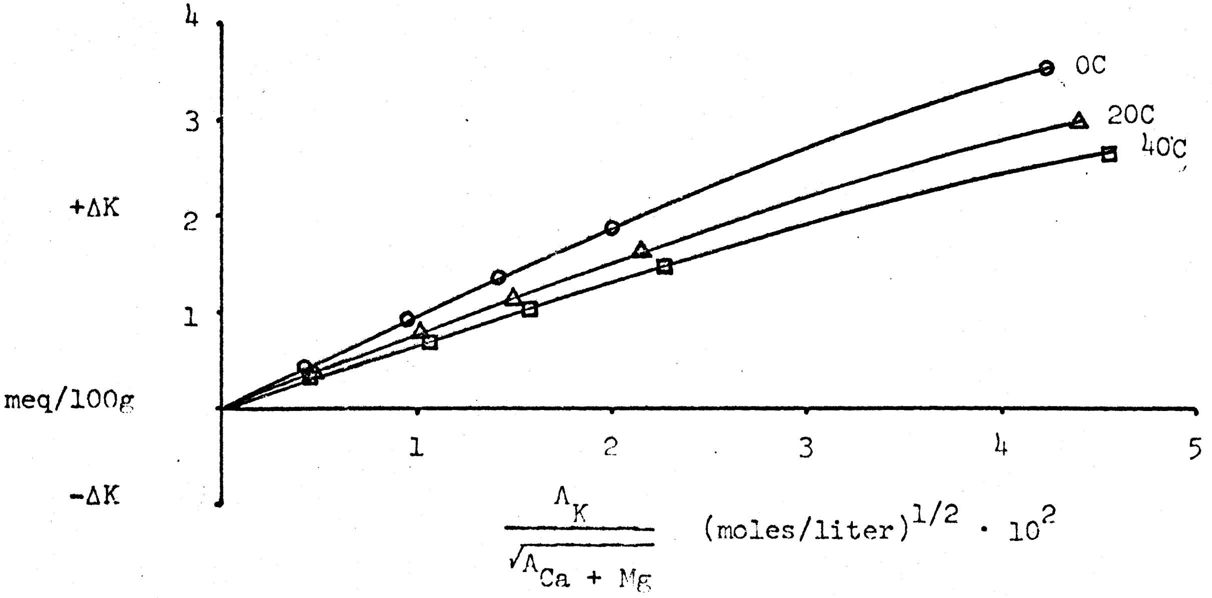

Fig. 31. The K-Ca exchange isotherms of the Al-saturated and 0.003N HCl-washed Camargo bentonite at 0, 20, and 40C.

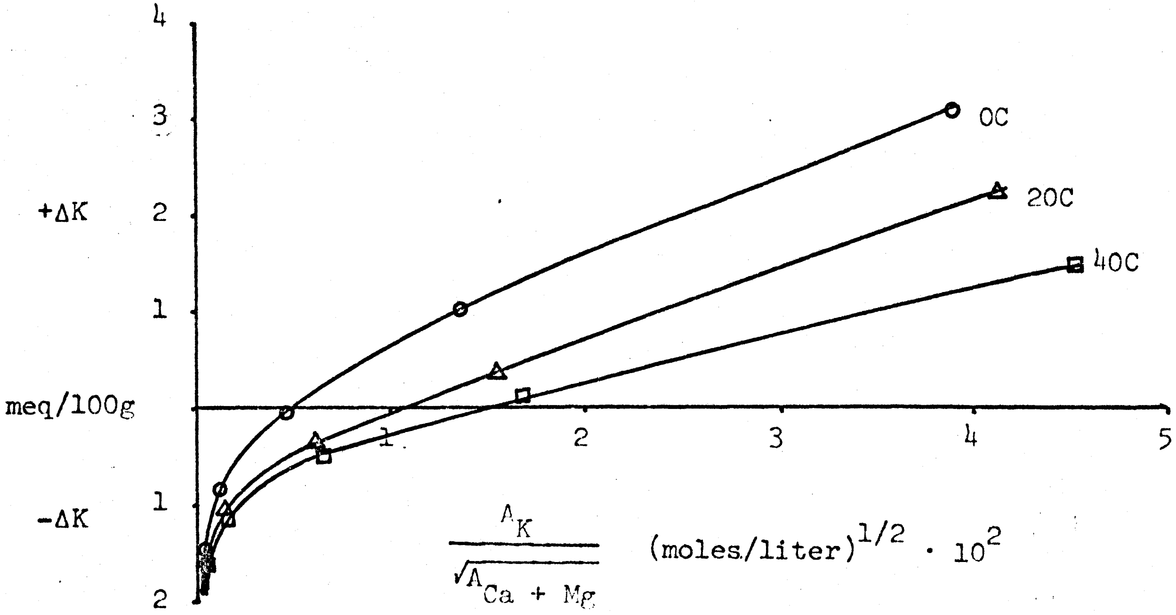

Fig. 32. The K-Ca exchange isotherms of the Al-saturated and 0.003<u>N</u> HCl-washed vermiculite at 0, 20, and 40C.

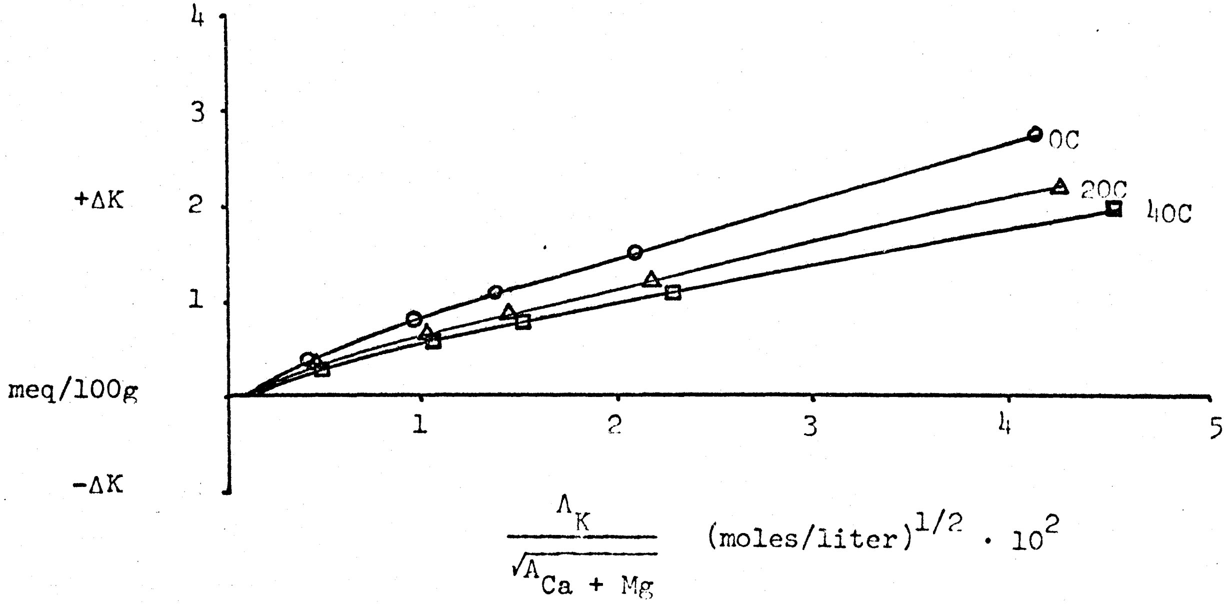

Fig. 33. The K-Ca exchange isotherms of the Al-saturated, 0.003N HCl-washed, and boiled Wyoming bentonite at 0, 20, and 40C.

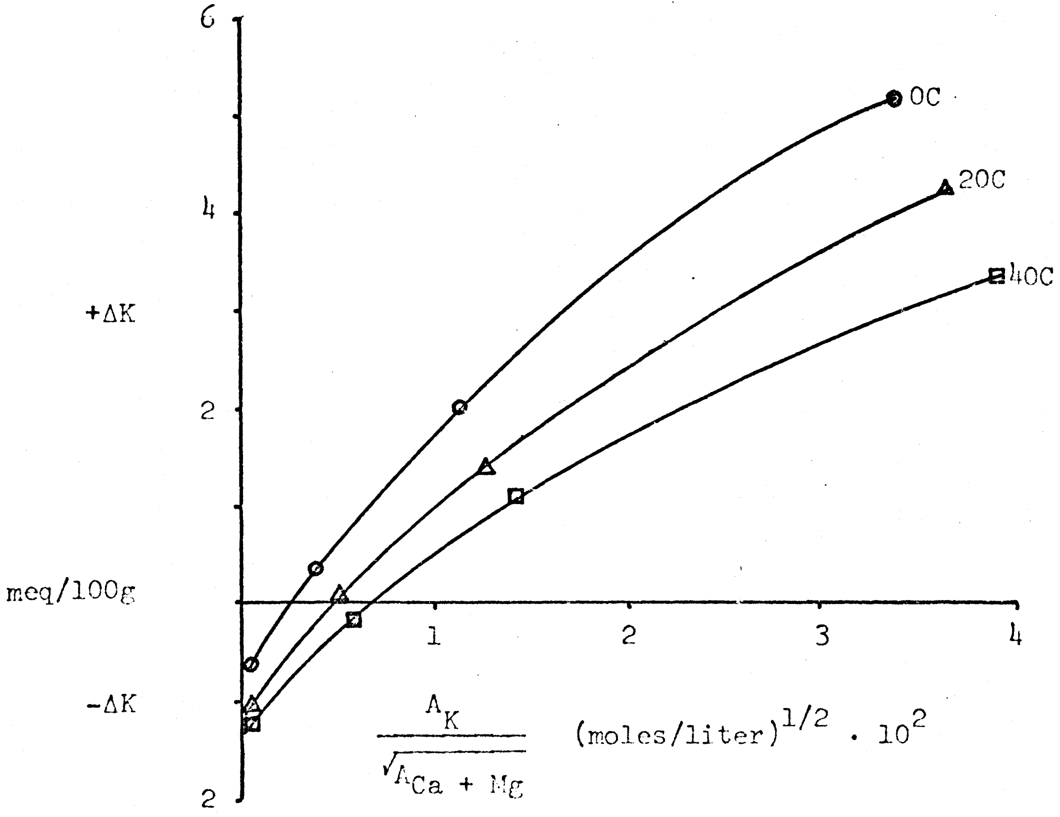

Fig. 34. The K-Ca exchange isotherms of the Al-saturated, 0.003N HCl-washed, and boiled vermiculite at 0, 20 and 40C.

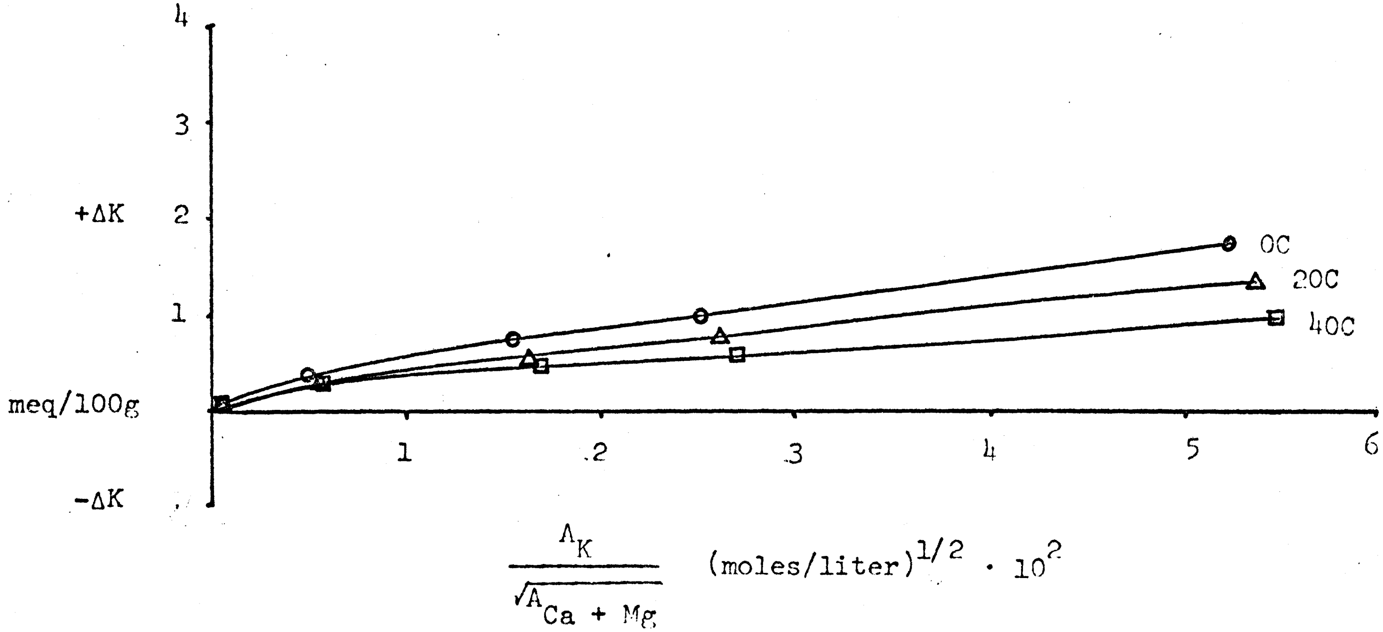

Fig. 35. The K-Ca exchange isotherms of the Al-saturated and water-washed Wyoming bentonite at 0, 20, and 40C.

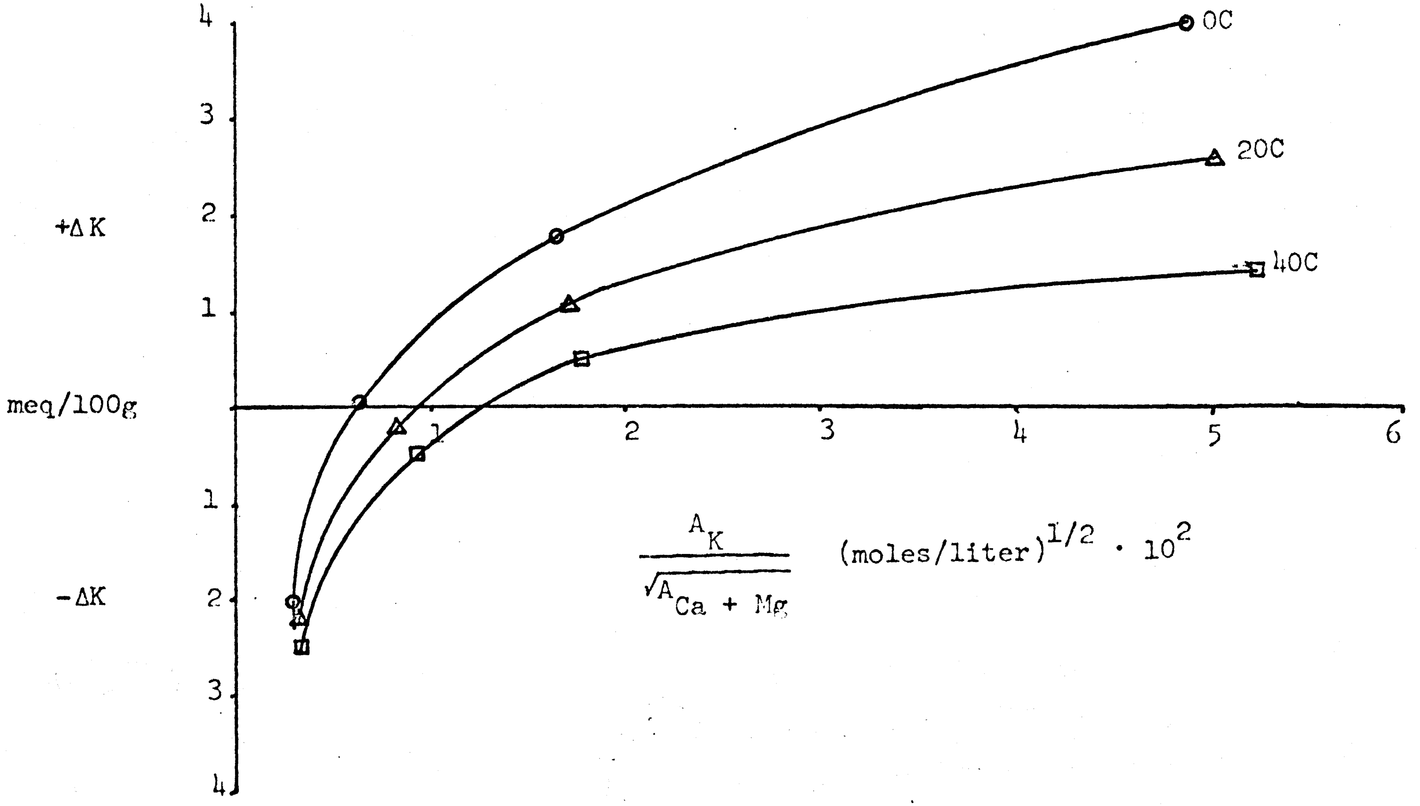

Fig. 36. The K-Ca exchange isotherms of the Al-saturated and water-washed vermiculite at 0, 20, and 40C.

purpose of this experiment was to determine the influence of temperature on K-Ca exchange in two Al-saturated exchange resins, one a weak acid type and the other a strong acid type, and to determine the effect of cross linkage in the strong acid type. Rexyn 102 was chosen as the weak acid cation exchanger and Dowex 50W as the strong acid cation exchanger. The Dowex 50W resin used had cross linkages of X1, X4, and X8. These samples were Al saturated and washed with 0.003N HCl. A subsample of the Dowex 50W-X8 was boiled and another subsample was H saturated. These systems were analyzed and plotted by the Q/I technique.

Influence of temperature: Temperature affected K-Ca exchange in all systems studied (Figures 37-42). As before an increase in temperature decreased the amount of K adsorbed on all systems containing Al on the exchange sites. The magnitude of the temperature effect on K-Ca exchange occurred to a smaller degree in the Rexyn 102 resin than in the Dowex 50W resins and was observed to bend upward rather than downward. Neither increasing cross linkage nor boiling had an apparent consistent influence on K-Ca exchange in the Dowex 50W resins. The effects of temperature on K-Ca exchange in the H-saturated Dowex 50W-X8 resin was opposite to those effects observed in the Al systems. As temperature increased, more K was adsorbed by the exchange resin. However no apparent differences occurred between the 20 and 40C treatments.

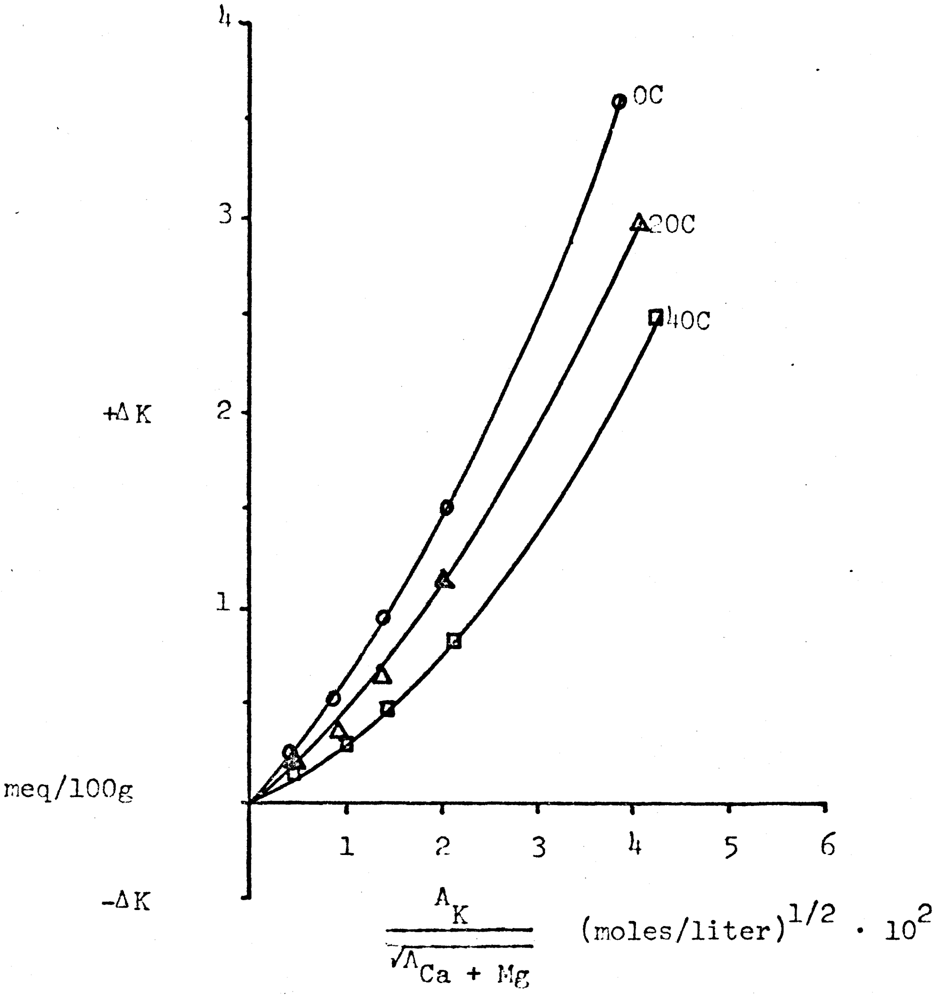

Fig. 37. The K-Ca exchange isotherms of the Al-saturated and 0.003N HCl-washed Rexyn 102 at 0, 20, and 40C.

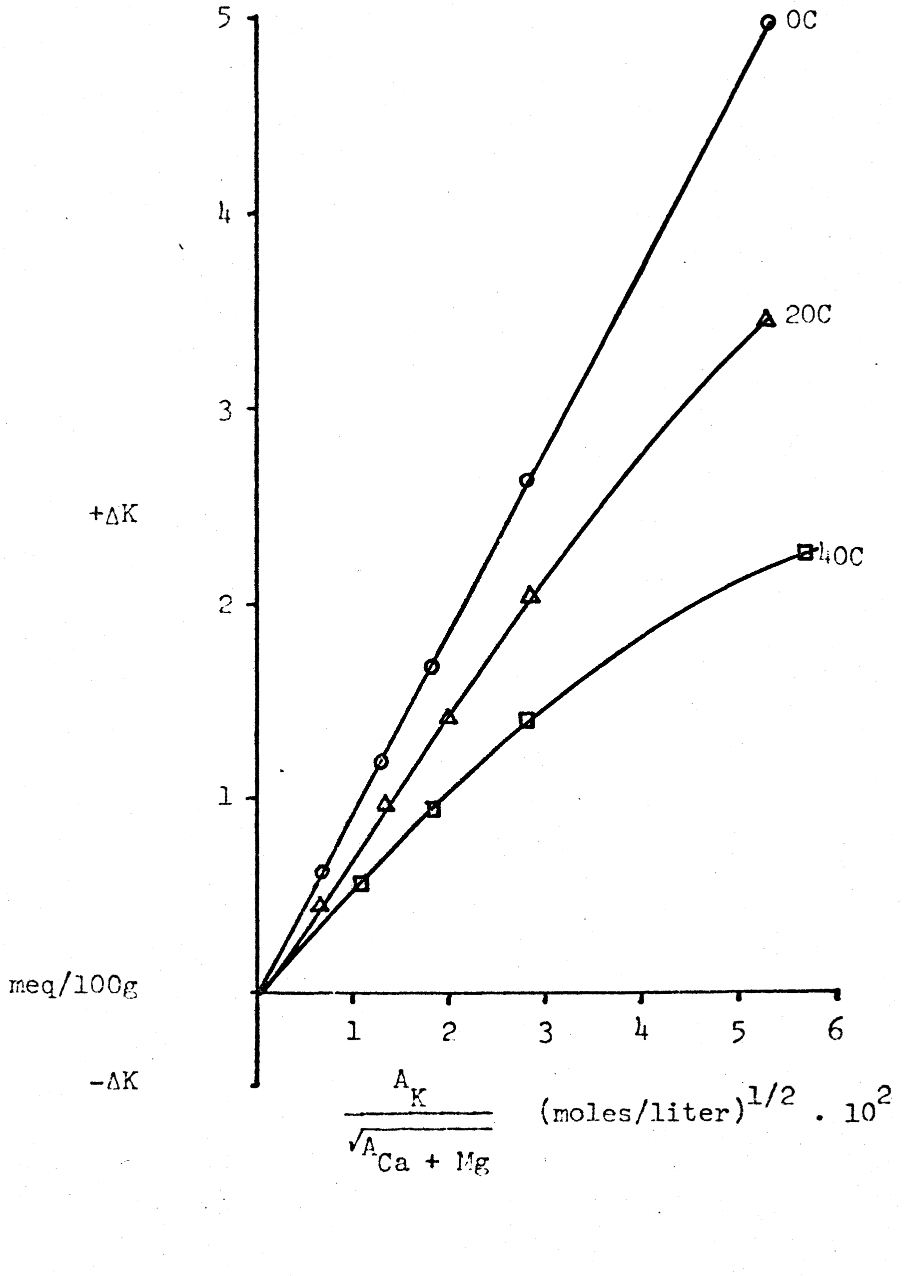

Fig. 38. The K-Ca exchange isotherms of the Al-saturated and 0.003N HCl-washed Dowex 50W-X1 at 0, 20, and 40C.

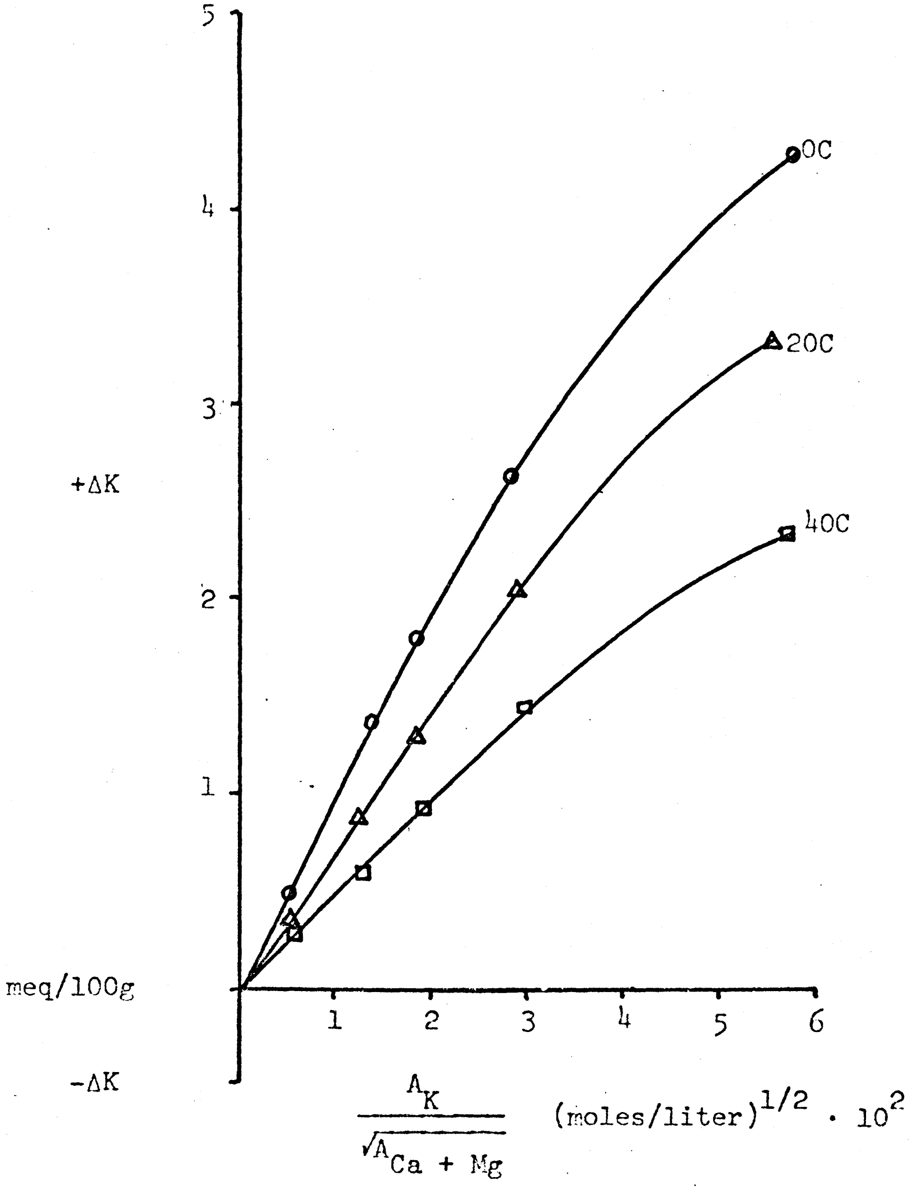

Fig. 39. The K-Ca exchange isotherms of the Al-saturated and 0.003N HCl-washed Dowex 50W-X4 at 0, 20, and 40C.

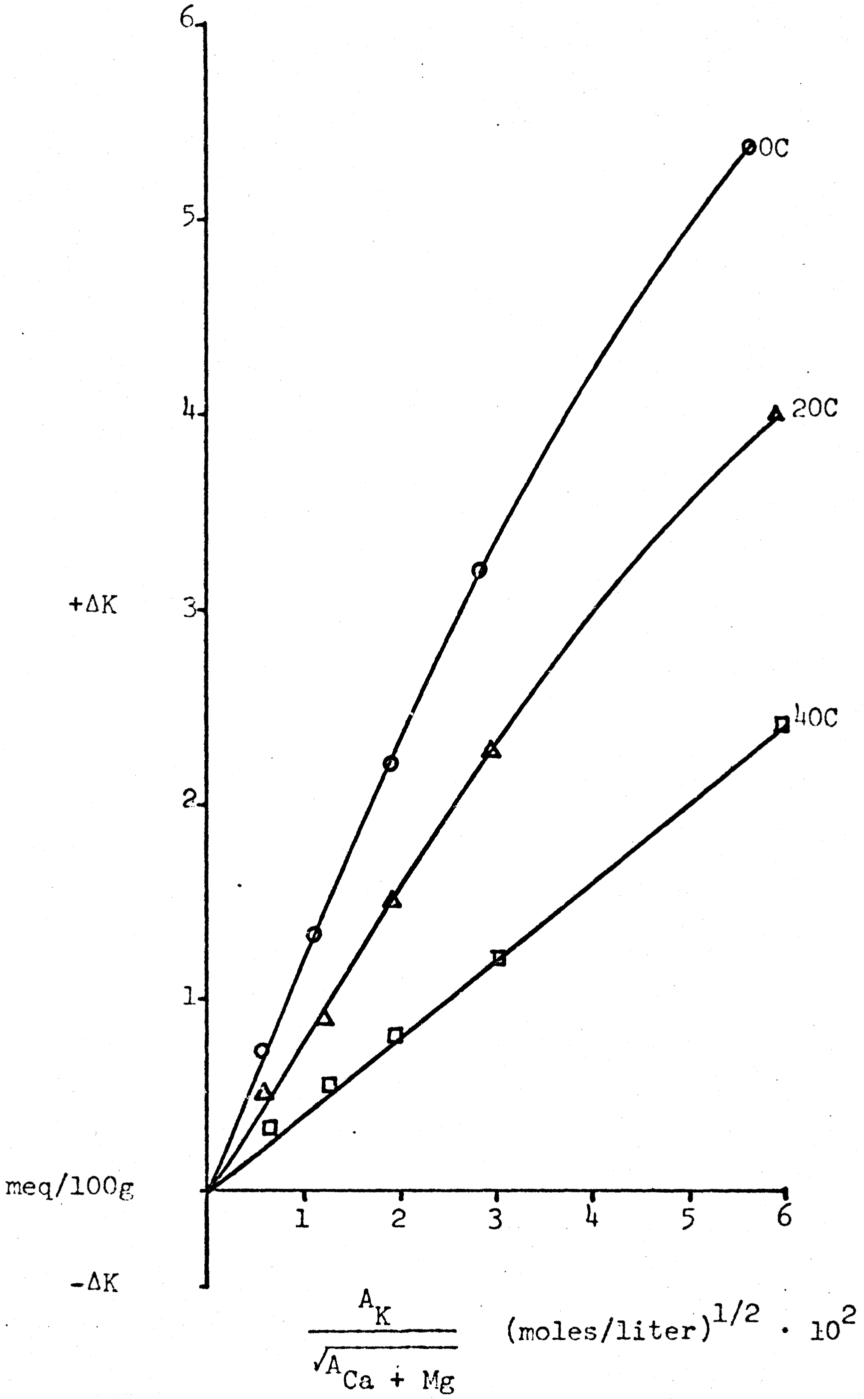

Fig. 40. The K-Ca exchange isotherms of the Al-saturated and 0.003N HCl-washed Dowex 50W-X8 at 0, 20, and 40C.

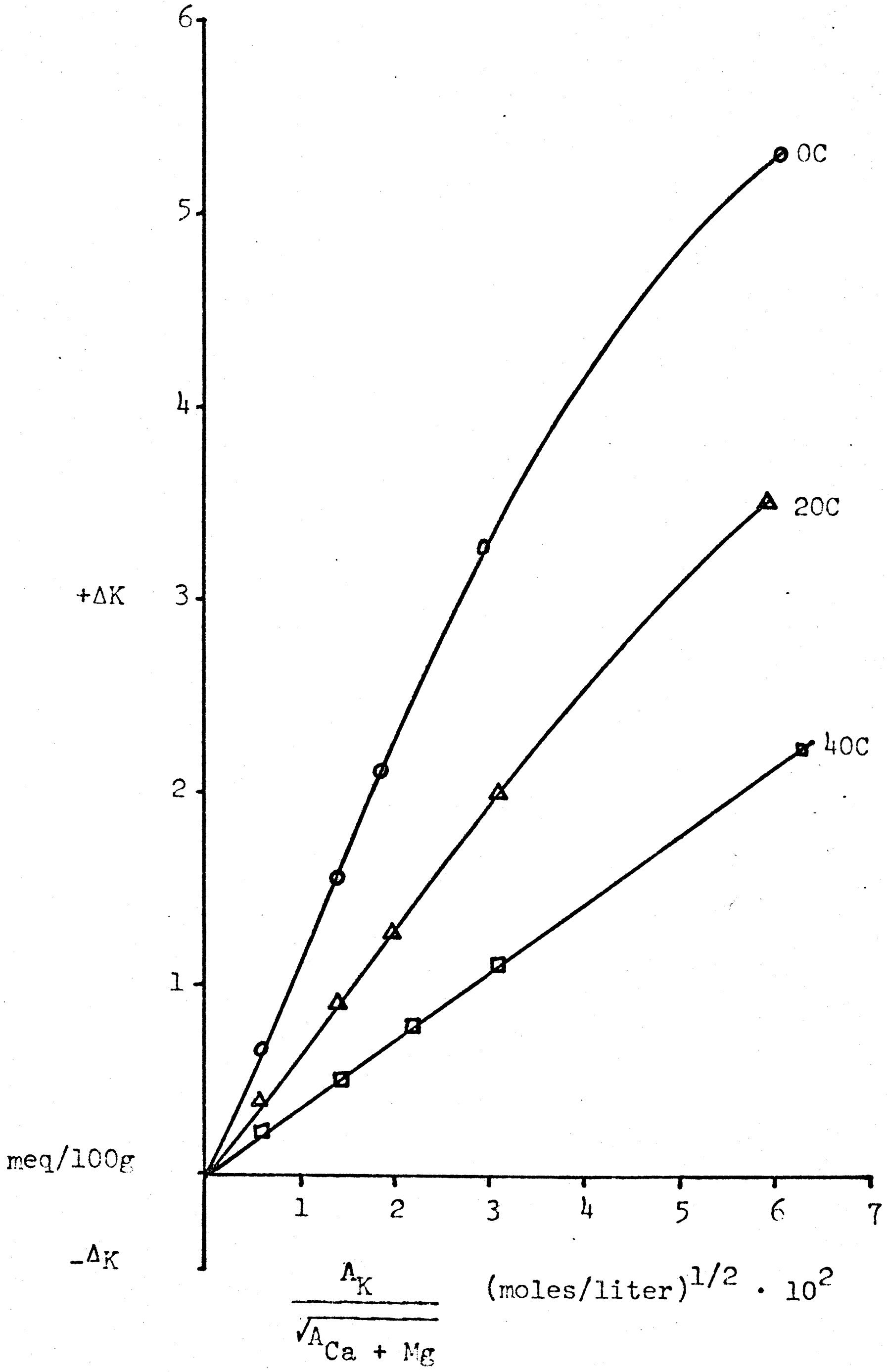

Fig. 41. The K-Ca exchange isotherms of the Al-saturated, 0.003N HCl-washed, and boiled Dowex 50W-X8 at 0, 20, and 40C.

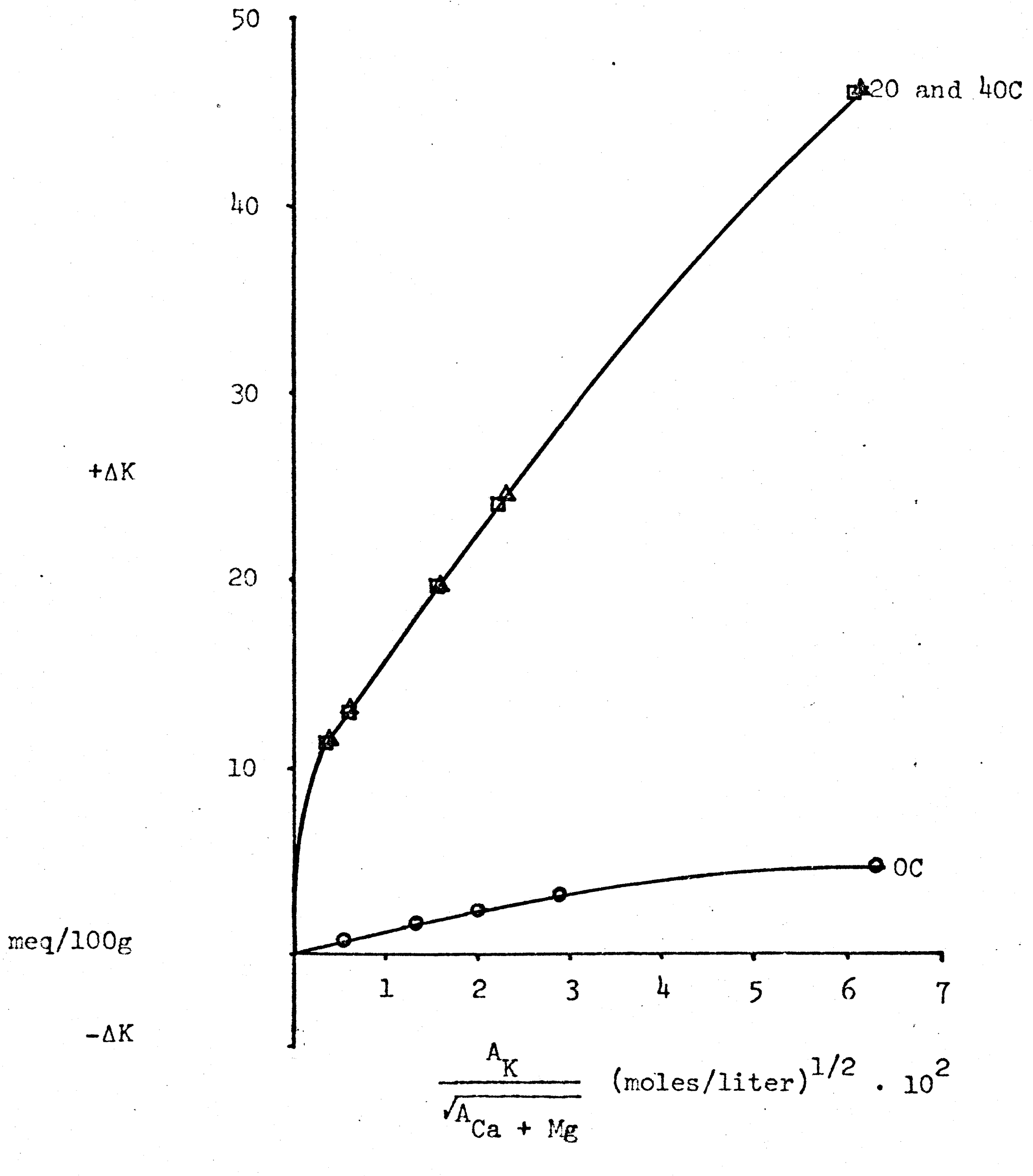

Fig. 42. The K-Ca exchange isotherms of the H-saturated and 0.003N HCl-washed Dowex 50W-X8 at 0, 20, and 40C: ○,0C; △,20C; □,40C.

Temperature Effects on K-Ca Selectivity in Selected Soils, Clay Minerals, and Cation Exchange Resins

Introduction: It is observed that temperature affects K-Ca exchange in soils, clay minerals and cation exchange resins containing hydroxy-Al groups on the exchange complex. However the effects of temperature on K selectivity and other properties of the exchange system are unknown. In fact the values for ΔK were obtained by measured differences in concentration between the original and final experimental solutions. However little was known about the actual ratio of ions on the exchange sites. The purpose of this experiment was to determine the influence of temperature on K selectivity in the selected soils, clay minerals and cation exchange resins that were previously studied and reported in this dissertation. These include the unaltered soils, the clay minerals, and cation exchange resins. They were treated in the same manner as before. The exchangeable ions were extracted with 1N NH_4NO_3 after the equilibrating solutions were separated from the exchanger. The CEC was determined by summing the measured concentrations of Na, K, Ca, Mg, Fe, and Al. Temperature effects will be related to measured changes in exchangeable K, Ca, Al, and total CEC, and in changes in the pH of the system.

Influence of temperature on K selectivity: Increasing temperature decreased K selectivity in all soils studied (Table IX). Increasing temperature from 0 to 40C decreased K selectivity almost six times

Table IX. The influence of temperature on K selectivity in the soils used.

Soil	Temperature 0C	20C	40C
	—— (liter/mole)$^{1/2}$ ——		
Bayboro	3.30	1.78	1.29
Portsmouth	5.25	3.82	3.14
Houston Black	3.27	2.59	1.89
Carrington	6.04	4.61	3.20
Vergennes	11.41	6.44	4.64
Hadley	3.06	2.64	2.23
Calais	10.81	10.17	8.38
Windsor	11.57	8.88	5.41
Berks	21.20	16.98	12.29
Katy	9.83	8.10	5.90
Iredell	3.08	2.60	1.97
Whitestore	99.46	64.84	39.15
Nason	263.67	131.12	58.03
Tatum	203.46	95.01	35.76
Cecil	110.75	47.93	31.49
Oktibbeha	6.98	5.02	4.06

in the Tatum soil and over four times in the Nason soil. These soils also gave the highest selectivity coefficient for K. The lowest specificity for K was given by Bayboro, Hadley, and Iredell.

Increasing temperature decreased the K selectivity in all the clay minerals and cation exchange resins studied except the Fe^{3+}-saturated Wyoming bentonite, Al-saturated Rexyn 102 and, the H-saturated Dowex 50W-X8 (Table X). Temperature had little effect on K selectivity in Al-saturated Rexyn 102. With rise in temperature K selectivity increased in the H-saturated Dowex 50W-X8 at 20 and 40C and in the Fe^{3+}-saturated Wyoming bentonite at 40C.

The selectivity of K in a Wyoming bentonite system increased with the following order of ions on the exchange sites: $K < Na < Ca < Mg < Fe^{3+} < Al$. The K selectivity increased in the Al-saturated clay minerals as the CEC of the clay minerals increased. Selectivity was lowest for kaolinite followed by Wyoming bentonite, and Camargo bentonite, and was largest for vermiculite. The K selectivity was observed to decrease as the cross linkage in the Dowex 50W increased. Boiling the Al-saturated clay minerals decreased K selectivity in all but the Al-saturated Wyoming bentonite at 40C. However this treatment had little effect on the Al-saturated Dowex 50W-X8 system.

<u>Influence of temperature on ions adsorbed</u>: Increasing temperature decreased the amount of K adsorbed in all of the soils studied except Calais (Table XI). The least effect of temperature on the amount of K adsorbed occurred in the Windsor, and Calais soils. These soils gave no effect of temperature on K exchange by the

Table X. The influence of temperature on K selectivity in the clay minerals and cation exchange resins used.

Exchanger	Saturating Cation	Treatment	Temperature 0C	20C	40C
			$(liter/mole)^{1/2}$		
Wyoming bentonite	Na	-	2.25	1.50	1.50
Wyoming bentonite	K	-	1.85	1.07	1.52
Wyoming bentonite	Ca	-	2.80	2.65	2.39
Wyoming bentonite	Mg	-	6.18	5.35	4.97
Wyoming bentonite	Fe^{3+}	-	7.92	5.47	78.10
Wyoming bentonite	Al	-	30.41	19.66	8.01
Wyoming bentonite	Al	boiled	13.55	12.13	11.25
Camargo bentonite	Al	-	34.24	25.65	15.93
Kaolinite	Al	-	12.37	5.62	3.96
Vermiculite	Al	-	96.55	68.29	36.92
Vermiculite	Al	boiled	15.67	10.67	6.50
Rexyn 102	Al	-	3.83	3.86	3.68
Dowex 50W-X1	Al	-	7.80	6.66	4.72
Dowex 50W-X4	Al	-	6.74	5.50	4.02
Dowex 50W-X8	Al	-	5.20	4.70	2.77
Dowex 50W-X8	Al	boiled	5.73	4.08	2.90
Dowex 50W-X8	H	-	6.33	8.87	8.65

Table XI. The influence of temperature on NH_4NO_3 exchangeable K after equilibrating the soils with a $KCl-CaCl_2$ (each 0.002M) solution.

Soil	Temperature		
	0C	20C	40C
	meq/100g		
Bayboro	1.28	1.09	0.98
Portsmouth	0.68	0.58	0.53
Houston Black	1.42	1.42	1.40
Carrington	1.09	0.96	0.90
Vergennes	1.19	1.04	1.00
Hadley	0.48	0.44	0.39
Calais	0.47	0.50	0.50
Windsor	0.20	0.18	0.17
Berks	0.52	0.49	0.45
Katy	0.98	0.92	0.83
Iredell	0.98	0.76	0.77
Whitestore	0.91	0.83	0.75
Nason	1.24	0.67	0.18
Tatum	0.63	0.60	0.53
Cecil	0.92	0.69	0.59
Oktibbeha	1.25	1.14	1.10

Q/I technique. The change in K adsorbed with temperature changes was also small for the Hadley and Houston Black soils. Increasing temperature from 0 to 40C decreased the amount of K adsorbed on the Nason soil about seven times. This soil gave the largest decrease in adsorbed K by increasing temperature.

As in the case of soils, increasing temperature decreased the amount of K adsorbed by all the Al-saturated clay minerals and cation exchange resins (Table XII). Increasing temperature increased the K adsorbed by Fe^{3+}-saturated bentonite and especially for the H-saturated Dowex 50W-X8. These systems had the lowest pH. The amount of K adsorbed by the Wyoming bentonite systems changed in the following order of ions on the exchange site: K > Na > Mg > Ca > Fe = Al. The quantity of K adsorbed by Al-saturated clay minerals changed in the following order: Kaolinite < Wyoming bentonite < Camargo bentonite < vermiculite. Boiling increased the amount of K adsorbed in the Al-saturated vermiculite but decreased the amount adsorbed in the Al-saturated Wyoming bentonite except for the highest temperature. Boiling had no effect on the amount of K adsorbed by Dowex 50W-X8 saturated with Al.

In general the amount of Ca adsorbed by the exchange systems studied increased with increasing temperature (Tables XIII and XIV) although there are several which changed little, decreased, or showed no consistent change. The largest increase in adsorbed Ca with increasing temperature occurred for H-saturated Dowex 50W-X8 while the greatest percent decrease occurred for Fe^{3+}-saturated Wyoming

Table XII. The influence of temperature on NH_4NO_3 exchangeable K after equilibrating the clay minerals and cation exchange resins with a KCl-$CaCl_2$ (each 0.002<u>M</u>) solution.

Exchanger	Saturating Cation	Treatment	Temperature 0C	20C	40C
			meq/100g		
Wyoming bentonite	Na	-	7.24	6.14	6.56
Wyoming bentonite	K	-	16.15	14.41	16.36
Wyoming bentonite	Ca	-	3.58	3.78	3.62
Wyoming bentonite	Mg	-	4.27	3.93	3.76
Wyoming bentonite	Fe^{3+}	-	1.97	2.10	2.82
Wyoming bentonite	Al	-	2.07	1.92	1.81
Wyoming bentonite	Al	boiled	1.89	1.89	1.87
Camargo bentonite	Al	-	3.46	3.01	2.96
Kaolinite	Al	-	0.48	0.30	0.28
Vermiculite	Al	-	4.29	3.15	2.98
Vermiculite	Al	boiled	5.75	4.99	4.81
Rexyn 102	Al	-	1.98	1.88	1.36
Dowex 50W-X1	Al	-	4.60	4.25	3.22
Dowex 50W-X4	Al	-	4.34	3.63	2.80
Dowex 50W-X8	Al	-	5.59	3.98	2.74
Dowex 50W-X8	Al	boiled	5.53	3.93	2.87
Dowex 50W-X8	H	-	6.21	48.51	48.08

Table XIII. The influence of temperature on NH_4NO_3 exchangeable Ca after equilibrating the soils with a KCl-$CaCl_2$ (each 0.002*M*) solution.

Soil	Temperature		
	0C	20C	40C
	meq/100g		
Bayboro	12.66	13.14	14.45
Portsmouth	5.40	5.46	5.63
Houston Black	54.74	56.79	58.17
Carrington	12.47	12.15	13.30
Vergennes	10.38	9.89	11.49
Hadley	6.82	6.73	6.76
Calais	1.54	1.70	2.04
Windsor	0.49	0.55	0.88
Berks	0.94	1.06	1.22
Katy	7.87	8.69	6.90
Iredell	11.22	9.69	11.55
Whitestore	0.26	0.32	0.43
Nason	0.21	0.22	0.24
Tatum	0.10	0.18	0.41
Cecil	0.33	0.52	0.59
Oktibbeha	17.12	17.02	17.37

Table XIV. The influence of temperature on NH_4NO_3 exchangeable Ca after equilibrating the clay minerals and cation exchange resins with a KCl-$CaCl_2$ (each 0.002<u>M</u>) solution.

Exchanger	Saturating Cation	Treatment	Temperature 0C	Temperature 20C	Temperature 40C
			meq/100g	meq/100g	meq/100g
Wyoming bentonite	Na	-	34.62	34.53	33.99
Wyoming bentonite	K	-	32.39	32.98	34.30
Wyoming bentonite	Ca	-	47.92	51.37	52.78
Wyoming bentonite	Mg	-	24.47	25.27	25.45
Wyoming bentonite	Fe^{3+}	-	7.91	11.35	1.47
Wyoming bentonite	Al	-	2.88	4.01	4.84
Wyoming bentonite	Al	boiled	3.32	3.56	4.01
Camargo bentonite	Al	-	2.37	3.31	4.03
Kaolinite	Al	-	0.97	1.31	1.80
Vermiculite	Al	-	1.12	1.10	1.10
Vermiculite	Al	boiled	10.89	12.76	16.06
Rexyn 102	Al	-	13.04	11.68	6.47
Dowex 50W-X1	Al	-	10.75	10.59	11.49
Dowex 50W-X4	Al	-	11.76	11.76	11.76
Dowex 50W-X8	Al	-	18.22	14.19	16.07
Dowex 50W-X8	Al	boiled	15.89	15.89	15.89
Dowex 50W-X8	H	-	16.15	84.39	84.39

bentonite. Similar variations occurred for the amount of Al present on the exchange at the three temperatures (Tables XV and XVI). The effect of temperature on CEC is small considering the extent to which the other ions changed with temperature (Tables XVII and XVIII). On boiling the Al-saturated vermiculite suspension, the CEC decreased to almost one half of the initial value whereas the CEC of the boiled Al-saturated Wyoming bentonite increased slightly.

Influence of temperature on ions in solution: Increasing temperature decreased the pH of the equilibrium solution in all but three soils, namely, Bayboro, Vergennes, and Iredell (Table XIX). In these soils increasing temperature from 0 to 40C increased the pH of the equilibrium solution. Increasing temperature also decreased the solution pH of the Al-saturated clay minerals and resins except for Rexyn 102 in which there was little change with increasing temperature (Table XX). Boiling the Al-saturated Wyoming bentonite, vermiculite, and Dowex 50W-X8 systems increased the pH of the equilibrium solutions.

Increasing temperature changed the concentration of Al in the equilibrium solutions of the soils (Table XXI), clay minerals and cation exchange resins (Table XXII). However the effect of temperature on concentrations of Al in solution vary with each exchange system. These variations will be considered in the Discussion.

Table XV. The influence of temperature on NH_4NO_3 exchangeable Al after equilibrating the soils with $KCl-CaCl_2$ (each 0.002M) solution.

Soil	Temperature		
	0C	20C	40C
	meq/100g		
Bayboro	4.95	4.51	4.50
Portsmouth	5.62	3.69	3.37
Houston Black	0.23	0.11	0.35
Carrington	0.03	0.03	0.03
Vergennes	0.03	0.01	0.00
Hadley	0.00	0.00	0.00
Calais	0.55	0.43	0.35
Windsor	0.81	0.45	0.33
Berks	3.59	3.05	3.12
Katy	2.11	1.54	1.13
Iredell	0.20	0.00	0.00
Whitestore	3.32	1.68	0.57
Nason	22.06	19.09	18.90
Tatum	4.23	4.21	4.47
Cecil	7.81	8.03	7.66
Oktibbeha	15.39	13.92	14.26

Table XVI. The influence of temperature on NH_4NO_3 exchangeable Al after equilibrating the clay minerals and cation exchange resins with a $KCl-CaCl_2$ (each 0.002M) solution.

Exchanger	Saturating Cation	Treatment	Temperature 0C	Temperature 20C	Temperature 40C
			meq/100g	meq/100g	meq/100g
Wyoming bentonite	Na	-	1.81	0.92	0.45
Wyoming bentonite	K	-	5.18	1.19	1.87
Wyoming bentonite	Ca	-	0.46	0.48	0.48
Wyoming bentonite	Mg	-	1.96	1.20	2.96
Wyoming bentonite	Fe^{3+}	-	33.67	30.42	27.45
Wyoming bentonite	Al	-	29.77	29.69	28.97
Wyoming bentonite	Al	boiled	33.34	32.18	35.76
Camargo bentonite	Al	-	94.07	92.15	97.51
Kaolinite	Al	-	2.85	0.00	3.35
Vermiculite	Al	-	70.98	86.30	76.93
Vermiculite	Al	boiled	30.40	18.35	16.46
Rexyn 102	Al	-	18.6	20.3	26.1
Dowex 50W-X1	Al	-	523.0	469.0	524.0
Dowex 50W-X4	Al	-	446.0	416.0	465.0
Dowex 50W-X8	Al	-	357.0	337.0	376.0
Dowex 50W-X8	Al	boiled	361.0	343.0	333.0
Dowex 50W-X8	H	-	0.0	0.0	0.0

Table XVII. The influence of temperature on CEC after equilibrating the soils with a KCl-$CaCl_2$ (each 0.002*M*) solution.

Soil	Temperature		
	0C	20C	40C
	meq/100g		
Bayboro	23.54	24.73	24.63
Portsmouth	13.13	11.15	10.95
Houston Black	57.24	59.18	60.79
Carrington	16.21	15.55	16.84
Vergennes	13.38	12.64	14.39
Hadley	7.64	7.50	7.48
Calais	2.70	2.76	2.95
Windsor	1.54	1.19	1.41
Berks	5.18	4.74	4.93
Katy	15.63	16.00	12.22
Iredell	38.54	32.01	37.76
Whitestore	5.50	3.87	2.92
Nason	23.23	19.80	19.60
Tatum	5.12	5.21	5.69
Cecil	9.77	10.07	9.61
Oktibbeha	34.50	32.81	33.31

Table XVIII. The influence of temperature on CEC after equilibrating the clay minerals and cation exchange resins with a KCl-$CaCl_2$ (each 0.002<u>M</u>) solution.

Exchanger	Saturating Cation	Treatment	Temperature 0C	Temperature 20C	Temperature 40C
			meq/100g	meq/100g	meq/100g
Wyoming bentonite	Na	-	52.34	49.42	48.74
Wyoming bentonite	K	-	55.46	50.02	53.54
Wyoming bentonite	Ca	-	52.36	56.14	57.34
Wyoming bentonite	Mg	-	64.29	59.80	58.89
Wyoming bentonite	Fe^{3+}	-	45.59	45.22	36.53
Wyoming bentonite	Al	-	35.04	35.85	35.70
Wyoming bentonite	Al	boiled	38.53	37.50	41.64
Camargo Bentonite	Al	-	100.09	99.62	104.64
Kaolinite	Al	-	4.28	2.58	4.30
Vermiculite	Al	-	94.40	93.61	103.03
Vermiculite	Al	boiled	58.80	48.40	50.27
Rexyn 102	Al	-	33.6	33.9	34.0
Dowex 50W-X1	Al	-	538.6	493.6	538.9
Dowex 50W-X4	Al	-	462.5	431.2	479.3
Dowex 50W-X8	Al	-	382.4	355.3	395.4
Dowex 50W-X8	Al	boiled	381.9	362.6	352.1
Dowex 50W-X8	H	-	352.9	332.9	312.8

Table XIX. The influence of temperature on solution pH of soils equilibrated with a KCl-$CaCl_2$ (each 0.002M) solution.

Soil	Temperature		
	0C	20C	40C
Bayboro	3.43	3.48	3.56
Portsmouth	5.05	4.55	4.50
Houston Black	7.34	7.35	7.33
Carrington	6.46	6.13	5.80
Vergennes	6.68	7.49	7.81
Hadley	7.11	6.94	6.85
Calais	6.77	4.82	4.73
Windsor	5.12	4.66	4.17
Berks	4.55	4.11	3.81
Katy	5.10	4.89	4.55
Iredell	6.16	6.92	7.09
Whitestore	3.74	3.57	3.35
Nason	3.92	3.77	3.53
Tatum	4.42	4.25	4.07
Cecil	3.99	3.80	3.74
Oktibbeha	5.02	3.97	3.79

Table XX. The influence of temperature on solution pH of clay minerals and cation exchange resins equilibrated with a KCl-$CaCl_2$ (each 0.002M) solution.

Exchanger	Saturating Cation	Treatment	Temperature 0C	20C	40C
Wyoming bentonite	Na	-	4.94	5.82	5.14
Wyoming bentonite	K	-	4.61	6.20	4.75
Wyoming bentonite	Ca	-	4.57	4.57	5.18
Wyoming bentonite	Mg	-	4.51	4.30	4.22
Wyoming bentonite	Fe^{3+}	-	2.88	2.81	2.75
Wyoming bentonite	Al	-	3.45	3.34	3.22
Wyoming bentonite	Al	boiled	3.62	3.50	3.23
Camargo bentonite	Al	-	3.49	3.42	3.18
Kaolinite	Al	-	3.95	3.88	3.77
Vermiculite	Al	-	3.71	3.55	3.35
Vermiculite	Al	boiled	4.11	3.90	3.82
Rexyn 102	Al	-	3.34	3.35	3.33
Dowex 50W-X1	Al	-	3.32	3.29	3.16
Dowex 50W-X4	Al	-	3.43	3.25	3.15
Dowex 50W-X8	Al	-	3.52	3.30	3.07
Dowex 50W-X8	Al	boiled	3.60	3.42	3.29
Dowex 50W-X8	H	-	3.48	2.32	2.26

Table XXI. The influence of temperature on the concentration of Al in solution extracted from soils equilibrated with a $KCl-CaCl_2$ (each 0.002<u>M</u>) solution.

Soil	Temperature 0C	 20C	 40C
		µmoles/liter	
Bayboro	66.7	82.3	95.6
Portsmouth	30.0	41.5	43.7
Houston Black	8.2	9.6	7.4
Carrington	9.6	8.9	3.0
Vergennes	6.7	9.3	11.9
Hadley	3.0	2.2	5.6
Calais	14.8	10.4	6.7
Windsor	8.9	9.3	9.3
Berks	63.0	54.9	59.3
Katy	1.9	0.7	0.0
Iredell	5.2	4.4	0.7
Whitestore	199.0	202.0	219.4
Mason	143.8	139.0	117.9
Tatum	77.8	100.1	86.7
Cecil	148.2	144.5	133.4
Oktibbeha	11.9	40.0	57.1

Table XXII. The influence of temperature on the concentration of Al in solution extracted from clay minerals and cation exchange resins equilibrated with a KCl-CaCl$_2$ (each 0.002*M*) solution.

Exchanger	Saturating Cation	Treatment	Temperature		
			0C	20C	40C
			µmoles/liter		
Wyoming bentonite	Na	-	31.5	27.8	21.5
Wyoming bentonite	K	-	13.7	9.3	13.0
Wyoming bentonite	Ca	-	10.0	3.0	1.5
Wyoming bentonite	Mg	-	1.5	0.0	4.4
Wyoming bentonite	Fe^{3+}	-	92.7	80.4	255.7
Wyoming bentonite	Al	-	213.1	365.1	402.1
Wyoming bentonite	Al	boiled	339.1	296.5	296.5
Camargo bentonite	Al	-	407.7	402.1	355.8
Kaolinite	Al	-	83.4	46.3	27.8
Vermiculite	Al	-	352.1	339.1	302.2
Vermiculite	Al	boiled	92.7	135.3	157.5
Rexyn 102	Al	-	0.0	9.6	14.8
Dowex 50W-X1	Al	-	796.8	908.0	1037.7
Dowex 50W-X4	Al	-	852.4	759.8	726.4
Dowex 50W-X8	Al	-	945.1	908.0	796.8
Dowex 50W-X8	Al	boiled	945.1	876.5	778.3
Dowex 50W-X8	H	-	0.0	0.0	0.0

DISCUSSION

This section relates all seven experiments to the overall objective of determining the influence of temperature on K-Ca exchange in selected soils, clay minerals, and cation exchange resins. The results are related to the literature to support a proposed mechanism explaining the variation in K-Ca exchange with temperature. The significance of these findings and their practical implications are also discussed.

Temperature Effects on K-Ca Exchange and Selectivity

General effects: Temperature was found to affect the relative amounts of K and Ca adsorbed by some soils but not others. The studies with soils, clay minerals, and cation exchange resin systems indicate that where Al as hydroxy-Al groups occupied cation exchange sites, the ratio of K-Ca adsorbed by the exchanger decreased with increasing temperature within the range of 0 to 40C. These hydroxy-Al groups may be present naturally as in the case of soils, may form during Al-saturation followed by washing with water to remove excess salts, or may form on these sites during the K-Ca exchange after the initial cation saturation. The effects of temperature on K-Ca exchange did not occur when other ions such as Na, K, Ca, Mg, Fe^{3+}, or Al^{3+} were present on the exchange complex.

The form of Al on the exchange sites of clay minerals was dependent on exchange properties and temperature. A low CEC, nonrestricted cation exchange sites, or acid-washing suppressed hydrolysis in the systems examined. Consequently in such systems a temperature effect on K-Ca exchange did not occur. A high CEC, confined cation exchange sites, such as in the narrow interlayer space of vermiculite, or water-washing apparently promoted hydrolysis of Al in place in the systems studied. Surface exchange sites, low CEC, such as in kaolinite, and small particle size tended to be associated with normal exchange of Al^{3+}.

Proposed mechanism: It is proposed that the mechanism involved in the experimentally observed temperature dependence of K-Ca is as follows: With an increase in temperature there is (1) an increase in hydrolysis of Al in place with the formation of H_3O^+ at the exchange site, (2) an increase in the hydrated size of K and a decrease in the size of Ca ions, and (3) an increase in the kinetic energy of the system with increased temperature which changes ion mobility and thereby selectivity.

It is imperative to restrain Al, thereby restricting exchange and promoting hydrolysis in place. Aluminum is either restrained by size or position. Restricting Al exchange results in increased hydrolysis and the greater displacement of protons rather than Al^{3+} ions themselves. This mechanism is accelerated at higher temperatures. In clay minerals, Al-polymers can prop open interlayer spaces thereby producing "wedge sites" which are specific for K (Rich, 1964). Polymetric growth on surfaces of exchangers can also cause steric hindrance through a sieving action thereby inhibiting the diffusion of large hydrated cations such as Ca and causing selectivity in exchange reactions.

Increasing temperature decreases the hydration of Ca while at the same time increases the relative strength of the K-water bond relative to the water-water bond. Therefore increasing temperature would result in relatively smaller Ca ions and larger K ions. Ion size is important in exchange due to mobility and special relationships. Smaller ions move faster and are more effective in penetrating to confined sites of exchange.

If it is assumed that specific sites do exist for K exchange but are unavailable for Ca exchange, then increasing temperature would decrease K selectivity relative to Ca due to: (1) increase in the degree of vibration of K at exchange sites which consequently could then be occupied more easily by Ca, (2) increase in effective K size relative to Ca due to temperature changes on hydration status, and (3) increase in hydrolysis which would (a) produce a larger polymer thereby forcing the "wedge" open and eliminating the specific site for K, and (b) increase in H_3O^+ concentration which due to its similar size could replace K from specific sites.

Specific influence on soils: Soils naturally low in exchangeable acidity or saturated with basic cations gave no effect of temperature on K-Ca exchange as measured by the Q/I isotherm. It is apparent that K-Ca exchange in the Houston Black soil was affected by temperature whereas this soil is basic and contains little exchangeable Al. Some Al was present in the extracting solution and although increasing temperature did not change the amount of K adsorbed it did increase the quantity of Ca adsorbed thereby changing the Q/I isotherm. This soil contained the largest quantity of exchangeable Ca and also contains $CaCO_3$. Temperature may increase the adsorption of Ca through an increase in the solubility of $CaCO_3$.

The Calais and Windsor soils also gave no temperature effects on K-Ca exchange, although both soils contain appreciable quantities of exchangeable acidity. The pH of the Windsor soil is low which could keep the Al in the trivalent form and probably more important is the fact that the clay content and CEC are very low thereby decreasing the possibility of hydrolysis. The Calais soil contains an appreciable quantity of organic matter and the exchangeable acidity may be H^+. It is known that high organic matter content decreases interlayer formation (Rich, 1968).

The remaining soils all demonstrated a decrease in K adsorption with increasing temperature from 0 to 40C. These soils contained appreciable quantities of exchangeable acidity and very likely contain some type of hydroxy-Al polymers. Jeffries, Rolfe, and Kunze (1953), Klages and White (1957), and Rich and Obenshain (1955) have observed that certain acid soils contain a vermiculite-like clay mineral that exhibits variable collapse on K saturation. The mineral is now considered to be a vermiculite that contains variable amounts of charged Al-hydroxy-polymers adsorbed in the interlayer space. The occurrence of partially hydroxy-Al interlayered expansible layer silicated have been reported in many soils and sediments (Rich, 1968).

Specific influence on clay minerals: Jackson (1960) proposed the idea of "steric pinching" in the interlayer space of clays which would promote hydrolysis and olation, resulting in a higher degree of polymerization. Kaddah and Coleman (1967) showed that the displacement of Al from Al-saturated vermiculite with salt solutions promoted hydrolysis of the Al. Hydrolysis of Al was greater where KCl was used. In this case K tended to collapse the interlayers at the edge of the vermiculite particles, thereby restricting exchange of the large hydrated Al ion. Since protons are more easily displaced than Al, hydrolysis was increased (Rich, 1968). However, Cotton (1965) found that the degree of hydrolysis increased as the degree of cross-linkage (and charge density) in Dowex 50W decreased. This infers that hydrolysis would be less in vermiculite than in montmorillonite due to the higher charge density of the former. However in the resin, the pore size decreased with increasing cross-linkage which may limit the polymer size. This effect would not occur in clays.

Increasing temperature decreased the amount of K adsorbed by Al-saturated vermiculite which was washed with 0.003N HCl, whereas this effect did not occur in the comparable Wyoming bentonite system. It is thought that the charge density of vermiculite was sufficient to promote hydrolysis in this system even when washed in dilute acid. The charge density of Wyoming bentonite is lower than that of vermiculite and the 0.003N HCl-wash treatment inhibited hydrolysis. Upon boiling the dilute acid-washed Al-saturated Wyoming bentonite, or simply water-washing, this system was sufficient to hydrolyze the Al as evidenced by a decrease in K adsorbed with increasing temperature. Camargo bentonite has a CEC intermediate between Wyoming bentonite and vermiculite and it produced a small K decrease with an increase in temperature. Apparently a clay mineral with a CEC of about 100 meq/100g will promote Al hydrolysis even when washed with 0.003N HCl. The slope of the Q/I isotherm for the Al-saturated and dilute acid-washed vermiculite which was boiled was greater than those for the comparable systems that were not boiled or just water washed. Boiling this system may have promoted hydrolysis to the extent that some Al precipitated as $Al(OH)_3$. The Al-saturated and dilute acid-washed kaolinite gave no effect of temperature on K-Ca exchange. Kaolinite has a low CEC and the structure of the mineral plates provides no interlayer space which is necessary to restrict Al movement. Therefore hydrolysis in place is negligible. It should be noted that the charge density per unit area of kaolinite is comparable to that of bentonite although the charge per unit volume is much less.

Specific influence on resins: Increasing temperature decreased the amount of K adsorbed on all cation exchange resins containing Al on the exchange sites. The magnitude of the temperature effect on K-Ca exchange occurred to a smaller degree in the Rexyn 102, which is a weak type cation exchange resin, than in the Dowex 50W systems, which are strong acid cation exchangers. Neither increasing cross linkage nor boiling had a apparent consistent influence on K-Ca exchange in the Dowex 50W resins. Apparently the charge density is sufficiently large to promote hydrolysis even at the highest cross linkage studied. It is also known that increasing temperature increases the void size in resins (Wiklander, 1946). These results are confounded because there is a variation in the mesh sizes of the Dowex 50W resins examined. Little exchange of K or Ca occurred with the H-saturated Dowex 50W-X8 resin at 0C. However, the exchange was extensive at the higher temperatures. At 0C the H-saturated resin may orient water molecules to the extent that an "ice-like" structure forms and inhibits exchange reactions. Temperature may also influence the bond strength or mobility of H to a greater degree than is the case for K or Ca.

Specific influence on Q/I isotherms: Several workers (Beckett, 1963a, 1964a, 1964b, 1964c, 1965; Beckett and Nafady, 1967a, 1967b; LeRoux, 1966; Moss, 1963a, 1963b, 1963c, 1967) have successfully employed the Q/I technique to measure the quantity and intensity of soil potassium. This method provides an excellent estimate of plant availability of soil K. This technique allows variables, which are closely correlated with plant uptake and the complex properties of soil minerals, to be measured.

Changes in temperature were observed to change the Q/I isotherm for the exchange systems containing hydroxy-Al polymers. Increasing temperature generally decreased the PBC, increased the ARE, but had little effect on ΔK^o. Beckett (1963) showed an increase in ARE with increasing temperature. Beckett and Nafady (1967a) reported that an increase in the amount of exchangeable Al, as produced through the addition of Cetyl trimethyl ammonium bromide, would displace Ca and reduce the PBC. These results are comparable with earlier work (Beckett, 1964b) which shows that the PBC increased when the positive charges carried by exchangeable Al were reduced.

In terms of the Q/I parameter these findings indicate that with increasing temperature less K was adsorbed by the systems studied (lower ΔK), the CEC of the exchanger had decreased or become less base saturated (lower PBC), there was no influence on labile K (no change in ΔK^o), and that the plant availability of K had increased (larger ARE).

These results suggest that care must be maintained in the experimental procedure in order to equate experiments conducted at different locations or times when temperature changes may occur. Although the temperature range studied represented extremes in soil systems, the Q/I parameters were observed to vary more for a given soil examined between 0 and 40C than many of the soil systems varied between themselves.

The cation exchange resins and all the clay mineral systems except vermiculite gave no downward curvature for the Q/I isotherm at low values of AR. This tendency to approach the ordinate asymptotically did occur for vermiculite and for most of the soil systems. These results support the premise that the bending is due to specific sites or selective adsorption of K (Beckett and Nafady, 1967a; LeRoux, 1966). It should be noted that although 30 symmetries of 1$\underline{N}$ $AlCl_3$ was equilibrated with the vermiculite some K still remained in the system.

Specific influence on K selectivity: Increasing temperature decreased K selectivity in the exchangers studied. The greatest effects occurred in the soil systems. The soil systems also demonstrated a larger selectivity for K than the clay minerals or cation exchange resins systems. This phenomenon was also observed by Rich and Black (1964) and Schwertmann (1962a, 1962b). The temperature variation in K-selectivity over the temperature range of 0 to 40C was as great as the variation observed between the different soils. The selectivity of K in the saturated bentonite systems increased according to the following order of ions on the exchange: $K < Na < Ca < Mg < Fe^{3+} < Al$, and within clay minerals it increased in the order of increasing CEC: Kaolinite < Wyoming bentonite < Camargo bentonite < vermiculite. It was also observed that K selectivity increased as the cross linkages decreased in the Al-saturated and 0.003N HCl-washed Dowex 50W systems. Potassium selectivity increased in all systems in the same direction that Al-hydrolysis would be expected to increase.

Rich and Black (1964) found that boiling an Al-saturated vermiculite increased the K selectivity while decreasing the total quantity of K adsorbed. However this report found that boiling an Al-saturated and 0.003N HCl-washed vermiculite apparently decreased the K selectivity coefficient. This could be due to the fact that NH_4NO_3 was used as the extractant because NH_4 ions are known to collapse vermiculite layers and trap exchangeable ions. If it is assumed that the loss of K and Ca from the equilibrium solution is due to adsorption of these ions, then another K selectivity coefficient could be calculated from the loss in Ca-K. This new K selectivity value, was found to be 42.91, 27.22, and 11.62 for the unboiled Al-saturated vermiculite at 0, 20, and 40C while they were found to be 60.48, 40.79, and 25.86, respectively, when boiled. The selectivity of K is now observed to increase with temperature.

Specific influence on properties of the exchanger: It was found that increasing temperature decreased the amount of exchangeable K while at the same time decreasing solution pH. An increase in temperature could promote hydrolysis which would increase the H ion concentration and replace exchangeable K. The influence of pH on K exchange has been reported (Murdock and Rich, 1965; Rich, 1964; Rich and Black, 1964; Schachtschabel, 1940; Tucker, 1967). This phenomena could account for the observed decrease in K exchange and selectivity with respect to Ca at higher temperatures. In many cases the amount of exchangeable Ca increased with an increase in temperature. However this was not consistent.

It was observed that the Fe^{3+}-saturated Wyoming bentonite was in reality an Al system. Apparently the Fe^{3+} hydrolyzed completely to form H and Fe precipitated. The H ions attacked the clay to release Al and the clay became Al-saturated. The pH of this system was about 2.80. This type of transfer has been reported by Coleman and Thomas (1964).

The measured concentration of Al adsorbed and in suspension is observed to change with temperature, however the direction of change was not consistent. This is also true in the case of the measured

CEC. Attempts can be made to relate the influence of temperature on Al chemistry as expressed in the CEC. However problems develop in the determination of Al if Al-polymers are forming or dissolving.

> "It is obvious that hydrolysis of Al^{3+} ions in water is a complex process. The hydrolysis and polymerization near clay surfaces is an even more complex problem." (Rich, 1968)

Practical Implications

It is apparent that increasing temperature decreases K exchange and selectivity relative to Ca in exchange systems containing hydroxy-Al polymers. This could account for one of the variables in comparing K-Ca fertility experiments conducted in the greenhouse with those conducted in the field. Soils in the greenhouse could become much warmer than those in the field thereby releasing more K and less Ca for plant uptake. Conversely a lack of K response in the greenhouse would not insure that K deficiencies could not occur in the field. This phenomena may be an important consideration when considering fall and winter fertilization vs. summer application of fertilizers. The cool climate in the fall and winter should result in greater adsorption of K thereby reducing leaching losses. It is interesting to note that the greatest demands for K occur when the ground is warm and the soil has a better chance to release K for plant uptake. All other things being equal the greatest amount of K loss should occur in a warm climate and in the summer. This phenomena may relate to K availability and different responses of warm and cool season plants.

This finding would be an important consideration if one was interested in K-Ca exchange from exchange materials removed from one entirely different area and examined in another. It would cast some doubt on the results obtained for the exchange of these two ions from tropical or arctic regions where the work was performed in U.S. laboratories, or for systems completely removed from their environment, such as sea sediment. These results may apply to soil testing if climate differs drastically in a given test area or through the year.

CONCLUSION

It is concluded that temperature affects the relative amounts of K and Ca adsorbed by some soils and not others. The studies with soils, clay minerals, and cation exchange resins indicate that where Al as hydroxy-Al groups occupy cation exchange sites the ratio of K-Ca adsorbed by the exchanger decreases with increasing temperature within the range 0-40C. An increase in temperature decreases the amount of K adsorbed, decreases pH of the equilibrium solution and increases adsorbed Ca. This effect of temperature on K-Ca exchange did not occur when other ions such as Na, K, Ca, Mg, Fe^{3+}, or Al were present on the exchange complex. Increased temperature also decreased K selectivity.

The form of Al on the exchange sites of clay minerals was dependent on properties of the exchanger and temperature. A low CEC, nonrestricted cation exchange sites, or acid washing suppressed hydrolysis in the systems examined. Consequently in such systems a temperature effect on K-Ca exchange did not occur. A high CEC, confined cation exchange sites or water-washing promoted hydrolysis in the systems studied thereby giving the temperature effect on K-Ca exchange.

It is proposed that the mechanism involved in the experimentally observed temperature dependence of K-Ca exchange include: (1) an increase in Al-hydrolysis in place with increased temperature with the formation of H_3O^+ on the exchange sites, (2) an increase in the hydrated size of the K and a decrease in the size of Ca ions, and (3) an increase in the kinetic energy of the system with increased temperature which changes ion mobility and thereby selectivity.

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ABSTRACT

Temperature Effects on Potassium-Calcium Exchange and Selectivity in Selected Soils, Clay Minerals, and Cation Exchange Resins

by

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Temperature was found to affect the relative amounts of K and Ca adsorbed by some soils but not others. The studies with soils, clay minerals, and cation exchange resin systems indicate that where Al as hydroxy-Al groups occupied cation exchange sites the ratio of K-Ca adsorbed by the exchanger decreased with increasing temperature within the range of 0 to 40C. An increase in temperature decreased the amount of K adsorbed, decreased pH of the equilibrium solution and increased adsorbed Ca. These hydroxy-Al groups may be present naturally as in the case of soils, may form during Al-saturation followed by washing with water to remove excess salts, or may form on these sites during the K-Ca exchange after the initial cation saturation. The effects of temperature on K-Ca exchange did not occur when other ions such as Na, K, Ca, Mg, Fe^{3+}, or Al^{3+} were present on the exchange complex.

Increased temperature also decreased K selectivity. The greatest decrease in K selectivity with increasing temperature occurred with soils followed by clay minerals and cation exchange resins. The selectivity for K relative to Ca also decreased in this same order: soils > clay minerals > cation exchange resins. Increasing Al-hydrolysis increased the selectivity for K in all exchangers.

The form of Al on the exchange site of clay minerals was dependent on exchange properties and temperature. A low CEC, non-restricted cation exchange sites, or acid-washing suppressed hydrolysis in the systems examined. Consequently in such systems a temperature effect on K-Ca exchange did not occur. A high CEC, confined cation exchange sites, such as in the narrow interlayer space of vermiculite, or water-washing apparently promoted hydrolysis of Al in place in the systems studied. Surface exchange sites, low CEC, such as in kaolinite, and small particle size tended to be associated with normal exchange of Al^{3+}. Consequently in such systems a temperature effect on K-Ca exchange did not occur.

It is proposed that the mechanism involved in the experimentally observed temperature dependence of K-Ca is as follows: With an increase in temperature there is (1) an increase in hydrolysis of Al in place with the formation of H_3O^+ at the exchange site, (2) an increase in the hydrated size of K and a decrease in the size of Ca ions, and (3) an increase in the kinetic energy of the system with increased temperature which changes ion mobility and thereby selectivity.