POTASSIUM SELECTIVITY OF CLAYS AS AFFECTED BY THE STATE OF OXIDATION OF THEIR CRYSTAL STRUCTURE IRON

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Abstract—The Ca–K exchange isotherms were determined at two temperatures for two highly montmorillonitic iron-rich soil clays in their oxidized and reduced states. The thermodynamic parameters **K**, ΔG_0, ΔH_0 and ΔS_0 were calculated for the exchange reactions.

It was found that the formation of K–clay from Ca–clay in both the oxidized and reduced state was accompanied by negative free energy, enthalpy and entropy changes. The results indicate that K is more strongly bound than Ca by the clay and the Ca-preference shown by the isotherms may be due to entropy changes in solution.

The oxidation of crystal structure iron resulted in an increase in K selectivity of the clay and a decrease in the free energy, enthalpy and entropy changes of the Ca–K exchange reaction. It was concluded that K is more strongly held by the oxidized clay than the reduced one, which is possibly due to a more nearly dioctahedral character in the oxidized than in the reduced state.

INTRODUCTION

It is now well-established that the oxidation of octahedral ferrous to ferric iron in soil vermiculite clays and biotites increases the potassium-fixation capacity of vermiculites and increases the difficulty of replacing interlayer potassium in biotites. (Barshad and Kishk, 1968; Robert and Pedro, 1969; Gilkes *et al.*, 1972). The increase in fixation in spite of a concurrent decrease in interlayer charge is believed to be due to a change in the orientation of the dipole of the hydroxyl ions in the octahedral layer from a perpendicular to a more inclined position to the cleavage plane. This difference in inclination of the O–H dipole places K^+ in the contracted crystal structure in a more negative environment and thus K^+ becomes more difficultly replaceable. The change in the O–H orientation upon the oxidation of Fe^{2+} to Fe^{3+} was recently confirmed by Farmer *et al.* (1968), Juo and White (1969) and Gilkes *et al.* (1972) by the use of i.r. measurements. Gilkes *et al.* (1972) demonstrated that the oxidation of biotites resulted in an ejection of interlayer and octahedral cations with little change in the tetrahedral layer and micaceous structure. The loss of iron and other octahedral cations during oxidation resulted in a change of the trioctahedral nature of biotite to a more dioctahedral character, which was confirmed by i.r. measurements. The dioctahedral nature of the oxidized biotites is responsible for their resistance to K release and weathering and the increase in their K-fixation capacity.

The clay fraction of Nile alluvial soils contains large amounts of iron-rich montmorillonite together with some 5–10 per cent vermiculites. Preliminary studies on those clays indicated that their cation exchange capacity (CEC) was dependent on the state of oxidation of their structural iron. To determine whether these changes would affect their fixation capacity for K, it was decided to study the thermodynamics of Ca–K exchange on these clays in both the oxidized and reduced states. The measurement of the selectivity coefficients, thermodynamic exchange constant, change in free energy and entropy would shed more light on the changes in the exchange properties of the clay resulting from the change in the oxidation state of the octahedral iron.

EXPERIMENTAL

Materials

Two iron-rich soil clays were used in this study. The clays ($< 2 \mu m$) were separated from two Egyptian alluvial soils by sedimentation. The chemical and mineralogical analyses of the two clays were determined by the methods described by Barshad (1965) and by Alexiades and Jackson (1966). Table 1 gives relevant information about the two clays.

Methods

1. *Clay preparation.* The clays were freed of $CaCO_3$ using 0·2 N Na_4EDTA. This method also removes

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Table 1. Chemical and mineralogical properties of the clays used

	Clay I (%)	Clay II (%)
Total chemical composition (on ignition basis)		
SiO_2	53·80	58·63
Al_2O_3	21·95	19·34
Fe_2O_3	15·70	12·10
MgO	5·10	3·02
CaO	0·75	1·11
K_2O	1·20	1·76
Na_2O	0·30	2·22
TiO_2	1·20	1·70
Cation exchange capacity (m-equiv 100^{-1} g air dry basis)		
Reduced state	75·5	68·8
Oxidized state	63·8	61·0
Mineralogical composition		
Montmorillonite	48·5	40·5
Vermiculite	5·0–10·0	5·0–8·0
Kaolinite	18·0	17·0
Soil mica	5·5	9·0
Feldspars	5·0	5·0
Quartz	2·0	4·0
Free oxides	10·5	15·0

large amounts of organic matter. Reduction of structural iron was carried out at room temperature by shaking the clays with sodium dithionate and sodium citrate in water mixture overnight. At the end of the reaction, the clays turned to a bluish–green color indicating the reduction of their iron. The clays were freed of dithionate and citrate salts, and the resulting suspensions were divided into two aliquots. One aliquot was reoxidized using H_2O_2 and the second was left in the reduced state. The reoxidized clays were left on a hot plate at 10°C for more than 18 hr until they were bleached and had regained their original color (i.e. before the reduction process.).

The two forms (oxidized and reduced) were then transferred to centrifuge tubes, washed twice with distilled water and converted to Ca-saturated clays by extracting them for 5 times with N $CaCl_2$. The excess salts were removed using two washes, distilled water adjusted to pH 9 by $Ca(OH)_2$ and neutral ethanol, repeated until the clays were freed of chloride ions. The clays were dried at 60°C, ground to pass a 200 mesh sieve, and kept in air-tight vials.

2. *Equilibrium experiments.* Duplicates of 0·1000 g samples were placed in 50 ml centrifuge tubes. To each tube aliquots of KCl solution (0·01 N) were added to give the following initial normal concentrations of potassium ions ($\times 10^{-3}$): 0, 2, 3, 4, 6, 8 and 10. These K ion concentrations correspond to approximate symmetry values of 0, 0·5, 1·0, 1·2, 1·8, 2·5 and 3·0 respectively. Aliquots of $CaCl_2$ solution were added to adjust

the initial total normality at 0·01N. The tubes were shaken by hand and kept at a constant temperature of $28 \pm 0.5°C$ for 36 hr to attain equilibrium. The same experiment was repeated at a constant temperature of $5 \pm 0.5°C$. After centrifugation, 5 ml aliquots (in duplicates) were taken for calcium determination. Calcium was determined by complexing with EDTA (0·01 N) and calver indicator. Potassium was determined by flame photometry. The CEC, which refers to the sum of adsorbed calcium and potassium, was determined by the NH_4OAc method which gave nearly identical results to the CEC determined by $CaCl_2$ on the K-saturated clays. The samples exhibited no K-fixation in the wet state. These observations justified the assumption that the CEC of the clays were nearly constant over the entire range of the exchange isotherm.

RESULTS AND CALCULATIONS

From the experimental results the exchange isotherms were constructed for the reaction;

$$Ca-clay + 2 K^+ \rightleftarrows 2 K-clay + Ca^{2+}$$
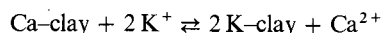
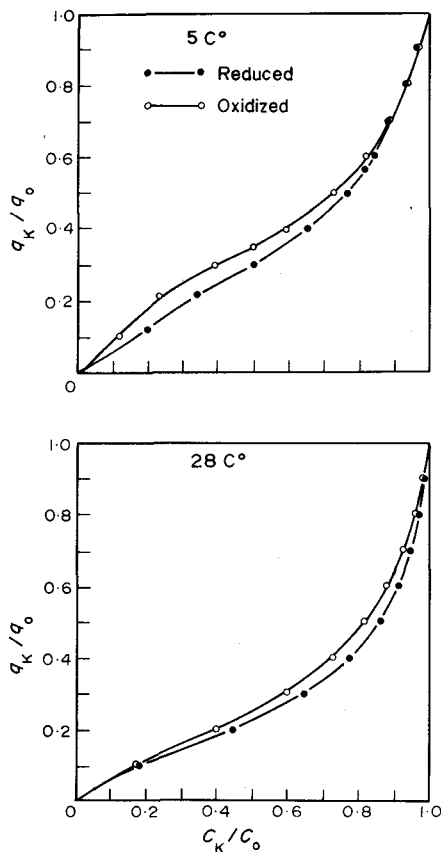as shown in Figs. 1 and 2. The isotherms show a preference for Ca in all cases.

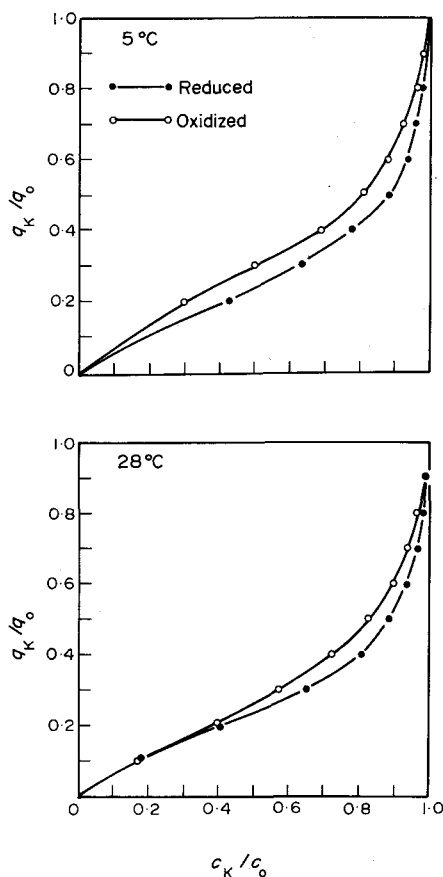Fig. 1. Isotherm of Ca–K exchange (clay No. 1).

Fig. 2. Isotherm of Ca–K exchange (clay No. II).

The uncorrected selectivity coefficient, K'_c, is;

$$K'_c = \frac{(q_K/q_0)^2 (1 - C_K/C_0)}{(1 - q_K/q_0) C_0 (C_K/C_0)^2}, \quad (1)$$

where C_0 is the total electrolyte concentration in equivalents per liter. C_K/C_0 and q_K/q_0 are the equivalent ion fractions of K^+ in solution and exchangeable K^+ respectively.

From the smoothed 'best fit' curves drawn through the plotted experimental results, values of C_K/C_0 were determined for fixed values of q_K/q_0. K'_c the uncorrected selectivity coefficient for the reaction, was then calculated from equation (1) at each value of q_K/q_0.

The selectivity coefficient, K_c was obtained from the expression:

$$K_c = K'_c (f_{\pm CaCl_2}/f^2_{\pm KCl}), \quad (2)$$

where $f_{\pm KCl}$ and $f_{\pm CaCl_2}$ are the mean rational activity coefficients of KCl and $CaCl_2$ in solution, calculated from Debye–Hückel equation.

The equilibrium constant **K** is expressed by:

$$\mathbf{K} = K_c (\bar{f}^2_K/\bar{f}_{Ca}), \quad (3)$$

where $\bar{f}_{Ca}$ and $\bar{f}_K$ are the activity coefficients of the Ca and K on the clay. According to the thermodynamic treatment of ion exchange developed by Gaines and Thomas (1953), the equilibrium constant is approximated by averaging the selectivity coefficients over the entire range of saturation of the exchanger:

$$\ln \mathbf{K} = -(Z_K - Z_{Ca}) + \int_0^1 \ln K_c \, d(q_K/q_0)$$

$$= 1 + \int_0^1 \ln K_c \, d(q_K/q_0), \quad (4)$$

where z is the valence of ions. Thus, the values of In K_c were graphed against surface composition (q_K/q_0) to calculate the equilibrium constant by graphical integration (Figs. 3 and 4). The area under the curve was measured and the value of the thermodynamic constant **K** calculated by using equation (4) at the two temperatures.

The standard free energy (ΔG_0), enthalpy (ΔH_0) and entropy (ΔS_0) changes were calculated from:

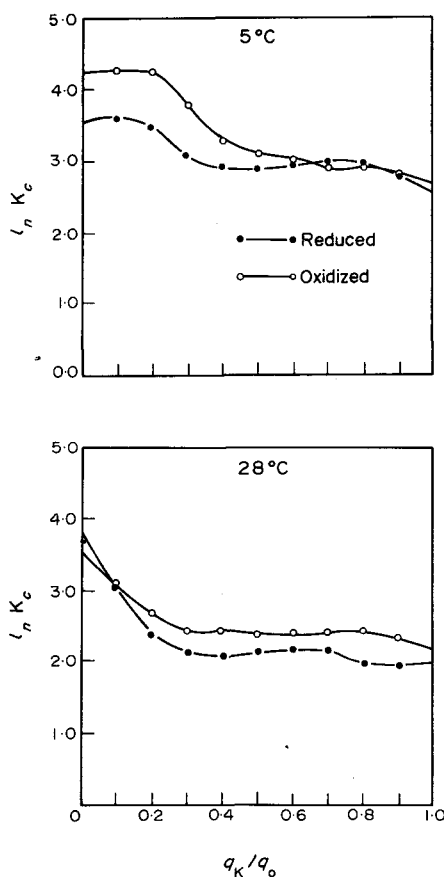$$\Delta G_0 = -RT \ln \mathbf{K}, \quad (5)$$

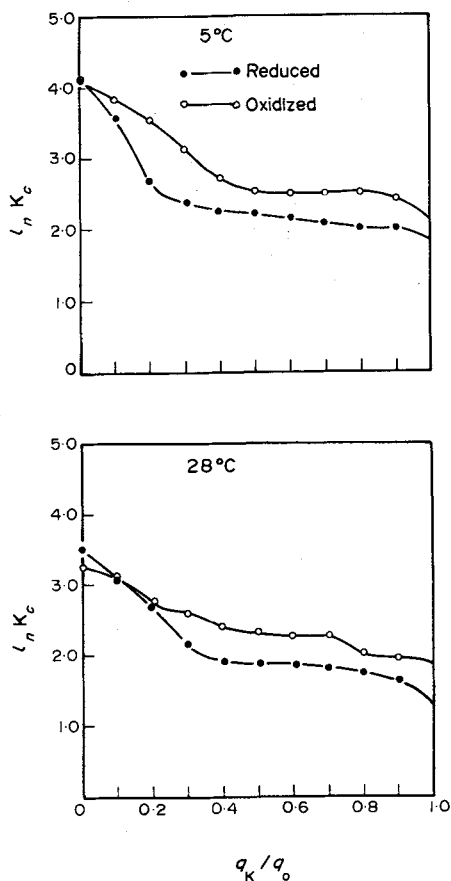Fig. 3. Natural logarithms of selectivity coefficients as a function of equivalent ionic fraction of K in clay No. I.

Fig. 4. Natural logarithms of selectivity coefficients as a function of equivalent ionic fraction of K in clay No. II.

The activity coefficients of the exchangeable ions were calculated from:

$$\ln \bar{f}_K^2 = (1 - q_k/q_0)(1 - \ln K_c) + \int_{q_K/q_0}^{1} \ln K_c \, d(q_K/q_0)$$
(8)

$$\ln \bar{f}_{Ca} = -(q_K/q_0)(1 - \ln K_c) - \int_0^{q_K/q_0} \ln K_c \, d(q_K/q_0),$$
(9)

which reflect the relative freedom of adsorbed ions at various K-saturations.

DISCUSSION

The two clays used in this study are highly montmorillonitic and exhibited no K fixation in the wet state. Their nearly constant CEC over the entire range of the Ca–K exchange isotherm justified the use of Gaines and Thomas thermodynamic treatment. Even with small changes in the CEC of the clay, Gaines and Thomas (1955) found that their isotherms were not affected.

The exchange isotherms show a preference of Ca in all cases. However the selectivity for K was higher in the oxidized than in the reduced clays. The thermodynamic equilibrium constant was also higher for the oxidized state than the reduced indicating that the oxidation of crystal lattice iron increased the selectivity of the clays for K. The free energy change ΔG_0 (Table 2) was more negative in the oxidized clay than in the reduced clay indicating that the oxidized state favors the formation of K–clay from Ca–clay.

In all cases, the formation of K–clay from Ca–clay was accompanied by a decrease in free energy which would indicate that K–clay should form spontaneously. Although the isotherms showed a preference by the clay for Ca over K, the calculated free energy change was negative. This is a consequence of

$$\ln(K_2/K_1) = -(\Delta H_0/R)(1/T_2 - 1/T_1),$$
(6)
and
$$\Delta G_0 = \Delta H_0 - T\Delta S_0.$$
(7)

The calculated thermodynamic parameters are shown in Table 2.

Table 2. Thermodynamic parameters for K^+ ion exchange with Ca–clay as affected by the state of oxidation of crystal structure iron

Thermodynamic parameter	Oxidized (Fe^{3+})		Reduced (Fe^{2+})	
	5°C	28°C	5°C	28°C
		Clay I		
K	80·2	35·2	58·2	26·8
ΔG_0 (cal mole^{-1})	−2420	−2126	−2243	−1965
ΔH_0 (cal mole^{-1})		−6070	−5700	
ΔS_0 (cal deg^{-1} mole^{-1})		−13·15	−12·41	
		Clay II		
K	48·5	30·5	31·4	22·3
ΔG_0 (cal. mole^{-1})	−2142	−2040	−1905	−1855
ΔH_0 (cal mole^{-1})		−3415	−2540	
ΔS_0 (cal deg^{-1} mole^{-1})		−4·58	−2·28	

the fact that $2K^+$ ions are exchanged for each Ca ion. Stated another way the thermodynamic equilibrium constant **K** is related to the calcium ion concentration divided by the potassium ion concentration squared $([Ca]/[K]^2)$. This situation is characteristic of all exchange reactions involving ions of unequal valencies. Similar data showing negative free energy changes for the formation of monovalent cation–montmorillonite from divalent cation–montmorillonite, in spite of the preference by the clay for the divalent cation, have been reported by Gaines and Thomas (1955), Hutcheon (1966), Diest and Talibudeen (1967), Laudelout et al. (1968), Gilbert (1969) and Gilbert and Van Bladel (1970).

The K–clay was formed from Ca–clay with a decrease in enthalpy (ΔH_0) in all cases, (Table 2). The negative enthalpy changes for the formation of K–clay from Ca–clay points to stronger binding of K. Since the enthalpy changes of the oxidized clays reaction were more negative than in the reduced clays, it is suggested that K is bound more strongly to the surface of the oxidized clay than to the surface of the reduced one.

With regard to the entropy change (ΔS_0) it is noticed that the formation of K–clays from Ca–clays is accompanied by a decrease in entropy. The effect of oxidation of the structural iron on the change in entropy (ΔS_0) was not very large, though it was in the expected direction. The ΔS_0 is more negative in the oxidized state indicating that K ions may be more ordered in the oxidized than in the reduced clays.

This unexpected result of entropy changes for a spontaneous reaction which must be positive is attributed to the entropy changes of solution phase which may exceed the entropy change of the solid phase. This effect may be responsible for the Ca-preference reflected by the isotherms, since the calculated standard entropy changes (ΔS_0) of the system is a sum of entropy changes of the solid phase and the entropy changes of solution phase (Diest and Talibudeen, 1967)

Activity coefficients of adsorbed ions. According to the Gaines and Thomas treatment, the calculated activity coefficients of the adsorbed cations are relative to the values in the standard state of mono-ion solid. These activity coefficients are integral values of the activity coefficients of an ion species at different compositions of the exchanger and they also reflect the relative freedom of adsorbed ions at various K-saturations.

Figures 5 and 6 represent the activity coefficients of the adsorbed ions (f_K, f_{Ca}). It can be shown that f_K increases with increasing K-saturation up to 40 per cent and then decreases. On the other hand, f_{Ca} decreases continuously with increasing K-saturation. Diest and
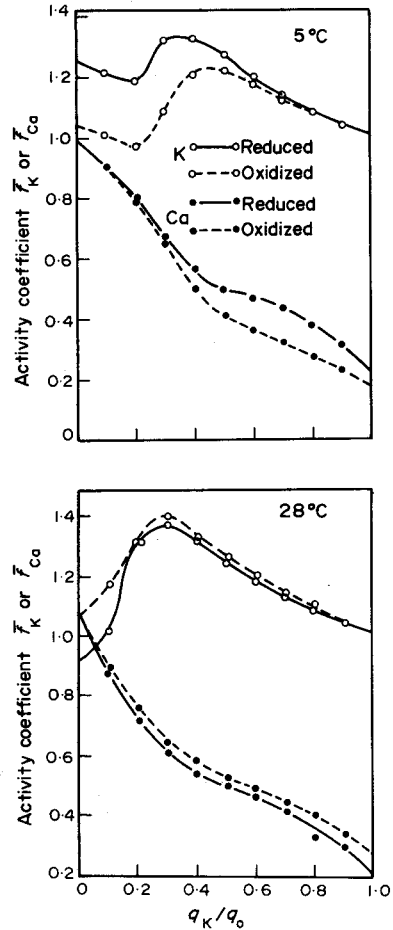

Fig. 5 Activity coefficients of the adsorbed ions as a function of K fraction in the clay (clay No. I).

Talibudeen (1967) regard the behavior of the individual activity coefficients of absorbed ions f_{Ca} and f_K a reflection of their relative freedom at various compositions, which is brought about by two balancing factors: one relating their relative distribution in Gouy and Stern layers; and the other being manifested by variations in interlayer spacing with composition.

The effect of oxidation of crystal lattice iron manifested itself at the lower temperature. $\bar{f}_K$ was lower in the oxidized state than in the reduced. At the higher temperature the situation was reversed and complex. No definite conclusion was drawn from these calculated activity coefficients as to the effect of oxidation–reduction of crystal lattice iron.

CONCLUSIONS

The state of oxidation of structural iron in the iron-rich clays affects their selectivity for K. The Ca–K
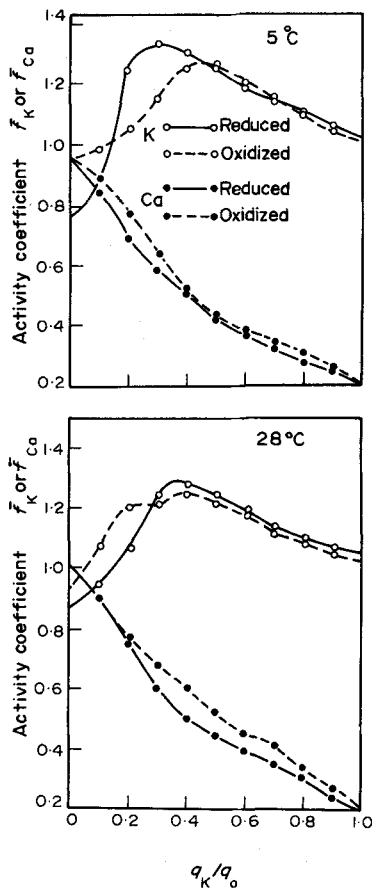
Fig. 6. Activity coefficients of the adsorbed ions as a function of K fraction in the clay (clay No. II).

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exchange isotherms indicated that K becomes more selectively adsorbed on the clay when the octahedral iron is in the oxidized state. These results are a further confirmation of the previous findings that K becomes more difficulty exchangeable after the oxidation of biotites and other micaceous minerals.

Résumé—Les isothermes d'échange Ca–K ont été déterminés à deux températures pour deux argiles de sol à haute teneur en montmorillonite, riches en fer soit à l'état oxydé, soit à l'état réduit. Les paramètres thermodynamiques **K**, ΔG_0, ΔH_0 et ΔG_0 ont été calculés pour les réactions d'échange.

On a trouvé que la formation d'argile K à partir d'argile Ca à la fois à l'état oxydé et à l'état réduit était accompagnée par des variations négatives d'énergie libre, d'enthalpie et d'entropie. Les résultats indiquent que K est plus fortement retenu que Ca par l'argile et la sélectivité pour Ca observée sur les isothermes peut être due à des variations d'entropie en solution.

L'oxydation du fer de consitution entraîne une augmentation de la sélectivité de l'argile pour K et une diminution des variations d'énergie libre, d'enthalpie et d'entropie de la réaction d'échange Ca–K. On en conclut que K est retenu plus fortement par l'argile oxydée que par l'argile réduite, ce qui peut être dû à un caractère plus typiquement dioctaédrique à l'état oxydé qu'à l'état réduit.

Kurzreferat—Die Ca–K–Austauschisothermen wurden bei zwei Temperaturen für zwei stark montmorillonithaltige, eisenreiche Bodentone in oxidiertem und reduziertem Zustand bestimmt. Die thermodynamischen Parameter **K**, ΔG_0, ΔH_0 und ΔS_0 wurden für die Austauschreaktionen berechnet.

Es wurde festgestellt, daß die Bildung von K–Ton aus Ca–Ton sowohl im oxidierten als auch im reduzierten Zustand von negativen Veränderungen der freien Energie, Enthalpie und Entropie begleitet sind.

Die Ergebnisse deuten darauf hin, daß K durch den Ton fester gebunden wird als Ca, und daß die durch die Isothermen angezeigte Ca–Präferenz ihre Ursache in Entropieänderungen in der Lösung haben kann.

Die Oxidation von Eisen im Kristallgitter hatte einen Anstieg der K–Selektivität des Tons und eine Abnahme der Veränderungen der freien Energie, der Enthalpie und der Entropie der Ca–K–Austauschreaktionen zur Folge. Es wurde der Schluß gezogen, daß K von dem oxidierten Ton fester gebunden wird als von reduziertem, was möglicherweise auf einen im Vergleich zum reduzierten Zustand stärker dioktaedrischen Charakter des oxidierten Tons zurückzuführen ist.

Резюме — Определяли изотермы обмена К–Са при двух температурах двух монтмориллонитовых глинистых пород богатых содержанием железа в окисленном и восстановленном состояниях. Для реакции обмена высчитали термодинамические параметры K, ΔG_0, ΔH_0 и ΔS_0.

Нашли, что образование К-глины из Са–глины как в окисленном, так и в восстановленном состояниях сопровождалось негативной свободной энергией и переменами энтальпии и энтропии. Результаты указывают, что К связан глиной сильнее, чем Са и предпочтение изотермами Са, очевидно, происходит вследствие изменения энтропии в растворе.

Окисление железа кристаллической структуры ведет к повышению избирательности глиной К; к понижению свободной энергии и к перемене в энтальпии и энтропии реакции обмена Са–К. В заключение решили, что К удерживается лучше окисленной глиной, чем восстановленной, явление происходящее, возможно, вследствие более диоктоэдральной характеристики глины в окисленном состоянии, чем в восстановленном.