

## EXPERIMENTAL EVALUATION OF Ca–K EXCHANGE SELECTIVITY REACTIONS IN ESTUARINE SEDIMENTS

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**Abstract**—Clay materials separated from estuarine sediments in Louisiana exhibit a selectivity for exchangeable calcium in laboratory experiments. The studies were conducted at 25°C and 60°C in mixed calcium and potassium chloride solutions in which the equivalent fraction of potassium varied from 0.12 to 0.54. Calcium selectivity was observed to increase with an increase in the equivalent fraction of potassium in the external solution and the temperature. The results suggest the possible importance of ion exchange reactions in the regulation of calcium availability during early diagenetic reactions in sediments.

### INTRODUCTION

The selective adsorption of cations by the exchange complex of soils and sediments has an important bearing on their physical and chemical properties. It is one of the processes normally operating in clay materials which is directly dependent on the mineralogy and distribution of charge deficiencies within the exchanger. A complete understanding of the variables influencing ion selectivity reactions might be useful in interpreting the chemical changes involved in the diagenesis and weathering of clay minerals.

Selective cation adsorption has been related to solution concentration, pH, temperature, ion size, ion valence, ion hydration (Wiklander, 1964) and the structure and charge properties of the exchange substrate (Dolcater *et al.*, 1968). Rich and Black (1964) and Bolt *et al.*, (1963) also related the selective adsorption of potassium by soil materials to the characteristics of the adsorbing surfaces. Kozak and Huang (1971) demonstrated the importance of hydroxy-aluminum interlayers in controlling potassium/calcium selectivity of micaceous materials.

Ion exchange selectivity also has been detected in laboratory studies of the changes in river sediments in contact with sea water. The equivalent fraction of exchangeable potassium ( $Q_K/Q_0$ ) in Missouri River clays increased from 0.016 to 0.019 after 36 hr and reached 0.032 after 86 hr of exposure to sea water. (Data from Potts, in Keller, 1963). Values reported by Russell (1970) suggest a decrease in  $Q_K/Q_0$  from 0.15 to 0.061 after two weeks of contact between sea water and Rio Ameca sediments. The experimental results yielded a value which was very close to the 0.065 ratio detected in the marine sediments of the area. Russell also detected an increase in the amount of fixed potassium and a corresponding decrease in total exchange capacity which helped to account for the changes in the potassium distribution.

Changes in the ion exchange selectivity characteristics of the exchange substrate could produce changes of the type described above. Increasing solution concentration and decreasing exchange capacity (Wiklander, 1964) also would favour the adsorption of potassium. A number of other variables including temperature changes might modify the distribution of exchangeable ions and influence the early changes accompanying the diagenesis of clay mineral-rich sediments.

This study reports the results of a laboratory investigation of the ion selectivity characteristics of the clay sized fraction of estuarine sediments from Louisiana. The most important variables studied were changes in the calcium to potassium content of the solutions in contact with the sediments and the temperature of reaction. The original clay materials are also slightly different in composition.

### MATERIALS AND METHODS

Modern sediment samples were collected from five locations in Louisiana estuaries, whose approximate locations are indicated in Figure 1. The Big Island and Bay St. Denis sites are in areas where the average salinity of the overlying waters varies from 18 to 30 ppt. Lower salinities are usually present in Lake

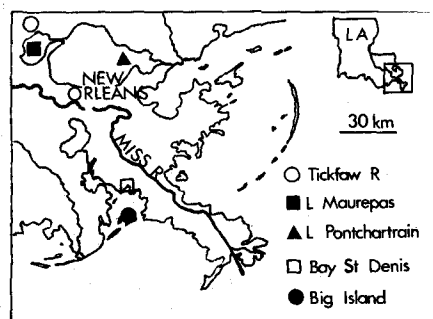


Fig. 1. Index map of approximate sample locations.

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Pontchartrain and the waters become progressively fresher in Lake Maurepas and the Tickfaw River. Typical salinities in these areas may average 10, 5 and less than 0.5 ppt, respectively. The clay-sized fractions of the sediments are complex mixtures of kaolinite, chlorite, illite, smectite and their interlayered varieties. Discrete illite and kaolinite are slightly more abundant in the samples collected in the fresher water areas (Brooks and Ferrell, 1967).

The sediment samples were treated with sodium acetate at pH 5.0 (Jackson, 1969) to remove the carbonates. The considerable quantity of organic matter which is normally present was oxidized and removed with sodium hypochlorite of pH 9.5 (Anderson, 1963). Free iron oxides were removed by the dithionite-citrate-bicarbonate method of Jackson (1969). The samples were dispersed in pH 9.5 sodium carbonate and fractionated to obtain the less than 2  $\mu\text{m}$  size fraction. The fine clays were flocculated with a saturated solution of sodium chloride, washed free of salt, and then freeze-dried prior to use in the laboratory experiments. These pretreatments were used to make sure that the other constituents normally present in sediments did not interfere with the ion selectivity determination.

Selectivity measurements were performed on duplicate Na-saturated clay samples from each of the five locations. The clays were equilibrated with solutions containing various mixtures of potassium and calcium chloride, to produce the equivalent fractions of potassium indicated in Table 1. The salt solutions were always prepared with a total concentration of the above cations of 0.02 m which approximates their abundance in sea water. The average ionic strength of the solutions was approximately 0.25.

The samples were prepared at sediment to water ratios of one to five on a weight basis, and reacted in a thermostatically controlled water bath at 25°C or 60°C, for a period of 40 hr. The procedures of Dolcater *et al.* (1968) which do not require drying of the sample, were utilized to extract the adsorbed ions. The ions were displaced with  $\text{N.NH}_4\text{OAc}$  at pH 8.0 to more closely approximate reaction with sea water. The extracted ions were measured by atomic absorption techniques and the results are tabulated in Table 1.

## RESULTS AND DISCUSSION

The exchange equilibrium data (Table 1) for Ca-K exchange on estuarine clays reveal a general preference for calcium and the selective adsorption of calcium is greater at 60°C than at 25°C. The preference for calcium also becomes stronger as the equivalent fraction of potassium in solution increases. These differences are illustrated by the adsorption isotherms on Figures 2 and 3.

At 25°C, all but one of the experimental values fall below the line of no preference on the adsorption plot of Figure 2 and within the field where calcium

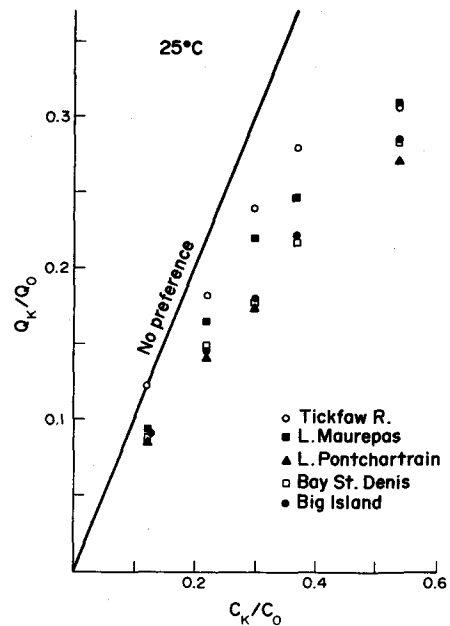


Fig. 2. Adsorption plot of K-Ca exchange reactions at 25°C.

is preferred. All the samples from the more marine parts of the estuaries have about the same degree of preference for calcium adsorption by the exchange complex. The Lake Maurepas samples exhibited less preference for calcium. Samples from the Tickfaw River were still lower in their preference for calcium and one value indicated no preference. All adsorption isotherms demonstrate an increased preference for calcium as the equivalent fraction of calcium decreased. When the calcium and potassium ions in solution were of equal normality, more equivalents of calcium were adsorbed than potassium.

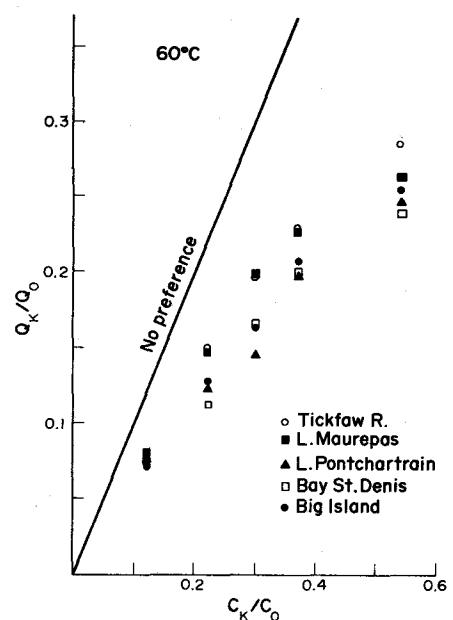


Fig. 3. Adsorption plot of K-Ca exchange reactions at 60°C.

Table 1. K-Ca exchange equilibrium data for estuarine clays

Sediment Location	Temperature (°C)	$C_K^1/C_0$	CES <sup>2</sup>	$Q_K^3/Q_0$	$Q_K^4$	$Q_{Ca}^5$	CEC <sup>6</sup>
Lake Maurepas	25	0.12	0.10	0.0881	3.74	38.70	42.44
		0.22	0.20	0.1659	6.89	34.63	41.52
		0.30	0.28	0.2188	9.64	34.40	44.04
		0.37	0.33	0.2482	10.83	32.86	43.63
		0.54	0.45	0.3100	12.56	27.95	40.51
	60	0.12	0.10	0.0880	3.54	36.65	40.19
		0.22	0.17	0.1476	5.91	34.11	40.02
		0.30	0.25	0.1968	8.55	34.89	43.44
		0.37	0.29	0.2266	9.41	32.11	41.52
		0.54	0.36	0.2623	11.16	31.18	42.54
Tickfaw River	25	0.12	0.14	0.1230	4.33	30.84	35.17
		0.22	0.22	0.1829	6.35	28.36	34.71
		0.30	0.32	0.2407	8.08	25.48	33.56
		0.37	0.39	0.2805	10.11	25.93	36.04
		0.54	0.44	0.3046	11.02	25.12	36.17
	60	0.12	0.08	0.0744	2.42	30.06	32.48
		0.22	0.18	0.1503	4.50	25.42	29.92
		0.30	0.24	0.1955	6.12	25.17	31.29
		0.37	0.31	0.2384	6.47	20.66	27.13
		0.45	0.40	0.2846	9.05	22.74	31.79
Bay St. Denis	25	0.12	0.10	0.0876	3.74	38.91	42.65
		0.22	0.18	0.1499	6.11	34.65	40.76
		0.30	0.22	0.1784	7.59	34.95	42.54
		0.37	0.28	0.2180	9.97	35.77	45.74
		0.54	0.40	0.2843	13.48	33.93	47.41
	60	0.12	0.08	0.0750	3.55	43.76	47.31
		0.22	0.13	0.1115	5.26	41.90	47.16
		0.30	0.20	0.1652	7.85	39.65	47.50
		0.37	0.25	0.1987	9.18	37.02	46.20
		0.54	0.31	0.2376	11.34	36.37	47.71
Big Island	25	0.12	0.10	0.0912	3.76	37.45	41.21
		0.22	0.17	0.1452	5.76	33.90	39.66
		0.30	0.21	0.1765	7.59	35.39	42.98
		0.37	0.29	0.2228	10.49	36.58	47.07
		0.54	0.39	0.2820	13.51	34.39	47.90
	60	0.12	0.08	0.0763	3.63	43.94	47.57
		0.22	0.14	0.1246	6.04	42.41	48.45
		0.30	0.21	0.1728	8.70	41.64	50.34
		0.37	0.26	0.2064	9.98	38.35	48.33
		0.54	0.34	0.2550	12.24	35.75	47.99
Lake Pontchartrain	25	0.12	0.09	0.0837	3.53	38.63	42.16
		0.22	0.16	0.1410	5.52	33.61	39.13
		0.30	0.17	0.1748	7.51	35.44	42.95
		0.37	—	—	—	—	—
		0.54	0.37	0.2707	12.17	32.78	44.95
	60	0.12	0.08	0.0779	3.49	41.30	44.79
		0.22	0.14	0.1218	5.33	38.42	43.75
		0.30	0.17	0.1441	6.41	38.05	44.46
		0.37	0.26	0.2077	9.83	37.48	47.31
		0.54	0.33	0.2463	9.89	30.25	40.14

1—Equivalent fraction of potassium in the external solution

2—Cation exchange selectivity ( $Q_K/Q_{Ca}$ )

3—Equivalent fraction of exchangeable potassium

4—Milliequivalents of exchangeable potassium per 100 g

5—Milliequivalents of exchangeable calcium

6—Cation exchange capacity ( $Q_K + Q_{Ca}$ )

The same general relationships are present in adsorption isotherms for the clay materials at 60°C. The Tickfaw River samples have the lowest preferences for calcium and the more marine ones the greatest. There are smaller differences in the magnitude of the selectivity exhibited by the various samples at 60°C in comparison to 25°C. The magnitude of the preference for calcium is also greater at the higher temperature. The selective adsorption of calcium increases as the concentration of calcium in solution decreases.

The observed preference for calcium instead of potassium is different from the results obtained by others (Potts and Russell). The Rio Ameca clays studied by Russell even produced some non-exchangeable potassium. This should not be very surprising because the original mineralogy and the laboratory techniques were not the same. Drying during the exchangeable ion measurements is one of the procedures which was avoided because of its possible effect on potassium fixation. The results of our study also were produced in a simple system free from the influence of sodium and magnesium.

The calculated cation exchange capacity does not exhibit a simple dependence on temperature or an increase in the equivalent fraction of potassium available in the external solution. In some cases, the sum of the exchangeable calcium and potassium increases with an increase of the equivalent fraction of potassium in solution while in others the CEC decreases or remains approximately constant. In two of the five samples studied, the CEC is higher at 25°C than at 60°C while the inverse relationship is attained in the other samples. The samples from the more marine parts of the estuaries (St. Denis, Big Island and Pontchartrain) are the ones which have a slightly higher average exchange capacity after reaction at the higher temperature.

The increased calcium selectivity with increasing concentration of potassium can be predicted by consideration of the unequal valence effect on ion distribution described by the law of mass action (Wiklander, 1964). One of the most important factors influencing the quantity of the ion adsorbed (the relative replacing power) is the rate of change in the activity coefficients of the adsorbed species as a consequence of decreasing concentration or ionic strength. According to the Debye-Huckel formula for calculating activity coefficients, the rate of change in the coefficients is greater for ions of higher valence, because the coefficient varies inversely with the square root of the valence of the ion. The activity coefficients were not directly determined in the above experiments, but the changes in the ratio of the adsorbed ions are in agreement with the general considerations of the theory.

The temperature increase appears to produce a slight increase in the calcium selectivity of the clay minerals in these sediments. This probably can be related to the ease of dehydration of the cations in

solution. From electrostatic considerations, the divalent calcium ion with 8–10 water molecules per ion is probably easier to dehydrate than the monovalent potassium ion with approximately 2.5 water molecules per ion. The magnitude of the change is largest for the Tickfaw River samples, which may suggest that changes are occurring in the exchange characteristics of the clay materials as a function of temperature. The surface characteristics of the exchanger may also be changing with the temperature. These findings are in agreement with the general discussion of exchange equilibria in sediments presented by Devine *et al.* (1973).

## CONCLUSIONS

This study demonstrates a preference for calcium to be adsorbed more readily than potassium by the exchange complex of estuarine sediment samples. The results obtained after cleaning the clays and allowing them to react in mixed potassium and calcium chloride solutions illustrate that there are original differences in the selectivity of the clay minerals for calcium and that the selectivity increases with decreasing calcium concentration and temperature increases from 25 to 60°C.

It is difficult to assess directly how these findings influence halmyrolysis and diagenesis of clays in the more complex natural environment, but some generalisation can probably be made. The preferential adsorption of calcium by the clays used in these experiments demonstrate the possible importance of ion exchange reactions in controlling calcium availability for diagenesis and/or carbonate precipitation in the interstices of sediments. The most abundant ion on the clay is probably calcium and its importance in the early diagenetic reactions must not be overlooked.

The results of these studies, which were conducted at a sediment to water ratio of 1:5, suggest that only one out of five, or fewer, exchange sites are occupied by potassium ions in clay water suspensions which approximate the solid content of freshly deposited muds. In a more dilute suspension, such as seawater, or in an open system being flushed by groundwater, one would expect the proportion of K-occupied exchange sites to be even smaller. Exchangeable potassium probably would become more abundant as the sediment is dewatered during burial or following an increase in the total salt content of the interstitial water.

These results may be specific for the types of clay studied, but there is a possibility that the relationships exhibited are typical of sedimentary materials with charge deficiencies produced by prolonged weathering of silicate materials. Weathering materials with higher charge densities could exhibit a preference for potassium. The assessment of ion selectivity reactions on the diagenetic pathways followed by clay materials of different origins is an intriguing topic for future research.

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