

THE SELECTIVE ADSORPTION OF SODIUM BY CLAY MINERALS IN LAKES PONTCHARTRAIN AND MAUREPAS, LOUISIANA

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Abstract—Ion exchange analyses of the clay-sized fraction of sediments in Lakes Pontchartrain and Maurepas suggest the selective adsorption of Na at the expense of Mg. The literature suggests that Mg should be preferentially adsorbed. As the chlorinity of the lake waters increases from 300 mg/l to 3250 mg/l, the percentage of exchangeable Na increases from 13.6 to 30.6 while the percentage of exchangeable Mg decreases from 65.6–36.8. The observed exchangeable Na percentages are higher than the ones calculated from the sodium-adsorption-ratios. The difference is attributed to an increase in the Na exchange constant of the sediment and therefore an increased selectivity for Na. With an increase in chlorinity, montmorillonite increases from 47 to 61 per cent and the total of the exchangeable cations (Na, Mg, Ca, K) increases from 36 to 82 m-equiv./100 g.

INTRODUCTION

LAKES Pontchartrain (630 square miles) and Maurepas (93 square miles) lie in the southeastern corner of Louisiana (Fig. 1). The two lakes comprise about half of the Holocene Lake Pontchartrain Basin. The remainder of the basin is composed of low-lying marshes and swamps bordered on the north by the Pleistocene Port Hickey Terrace. Fresh water from several rivers and saline waters from the Gulf of Mexico mix within the lakes. The constancy of ionic ratios suggest that the mixing is accomplished by simple dilution of sea water. The direction of circulation and mixing is indicated by arrows in Fig. 1. The small size of the area and its simple hydrologic setting make it an ideal place to study natural variations in clay minerals and exchangeable ions during their movement from fresh to salt water.

In discussions pertaining to the origin of clay minerals, the process of diagenesis is cited frequently. Keller (1964, 1967) attempted to define the process of diagenesis as a stage in the rock cycle. Diagenesis is a chemical process dependent on the thermodynamic activities of ions in solution, the bonding energy of clay minerals, and the temperature and pressure. Ion exchange and fixation reactions as well as crystal structure modifications and reconstitution are ways in which the process may operate.

The results of cation exchange capacity deter-

minations by washing with various solutions (Wiklander, 1964; DeVilliers and Jackson, 1967; and Dolcater *et al.*, 1968) indicate that ion exchange and fixation is a rapid process. Isotopic exchange measurements of K and Ca indicate completion of the reaction in five minutes (Deist and Talibudeen, 1967a). It is most likely that ion exchange is the first stage in the diagenetic adjustment of clay minerals to varying chemical environments. Therefore, a knowledge of ion exchange processes in nature is essential to an understanding of the geologic distribution of clay minerals.

Several aspects of ion exchange and fixation processes have been studied and thermodynamic exchange constants have been calculated for various ion pairs. Some of the most recent work shows a preference by certain clay soils for K^+ and Ca^{2+} and Na^+ (Hutcheon, 1966; Deist and Talibudeen, 1967a, b). Calculations of chemical bonds leading to the lowest energy configurations show that with increasing hydration and increasing ionic strength, kaolinite becomes less stable and Mg^{2+} montmorillonite becomes more stable (Slaughter, 1966). The treatment of natural clay assemblages with sea water has been shown to cause a preferential sorption of Mg^{2+} over Ca^{2+} (Potts, 1959) and Na^+ (Carroll and Starkey, 1960). In this report ion exchange analyses of the clay fraction ($< 2\mu$) of sediments in Lake Maurepas and Lake Pontchartrain suggest reactions which are different from the above reported reactions. In translation from waters of "low" chloride content (300 mg/l) to waters of "high" chloride concentration (3250 mg/l), the relative abundance of Mg^{2+}

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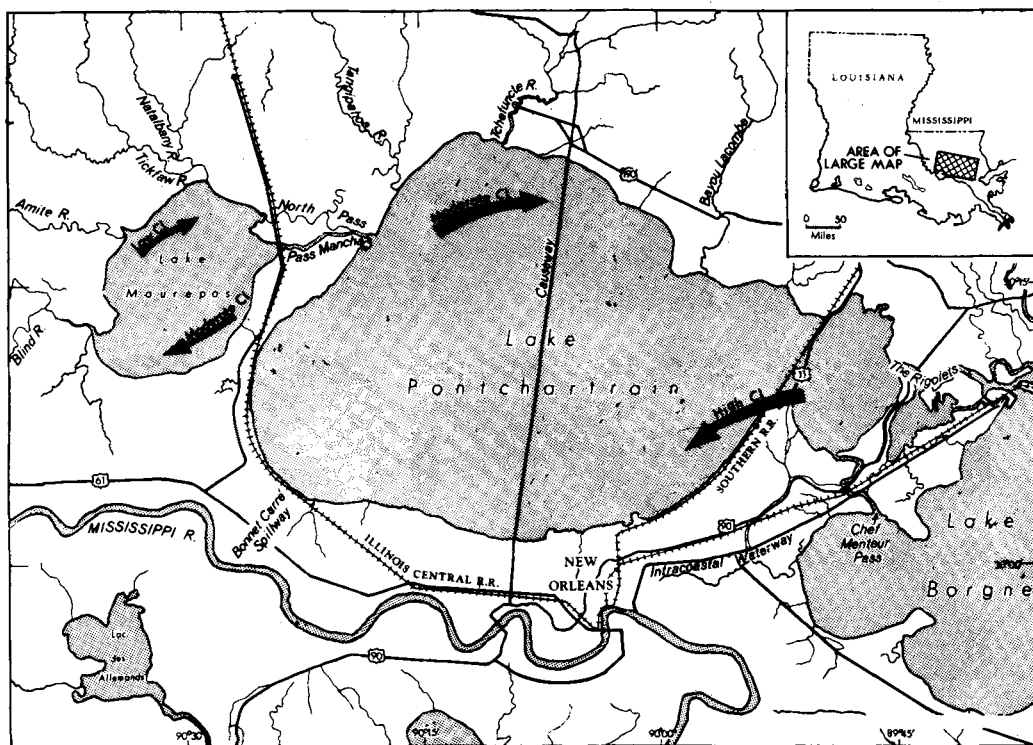


Fig. 1. Location map of Lakes Pontchartrain and Maurepas.

in the exchange position decreases sharply while Na^+ increases.

METHODOLOGY

An approximate square grid system was employed to sample the lakes systematically. Sample stations were approximately two miles apart. Initial sampling was done in August of 1967. In March, April, and May of 1968, the entire system was sampled again. Some sample stations were visited as many as 5 times to gain information on temporal variation of sediment and water characteristics.

Sampling techniques were designed to collect the most recently deposited sediments and the waters in direct contact with them. Bottom sediment samples were collected in polyethylene bottles and stored for later analysis. Samples were obtained by diving. In some cases, the water samples were collected with the sediment; in others they were collected separately. No mineralogical or chemical differences were noted among the samples collected by the two methods.

In the laboratory, the $< 2\mu$ fraction was separated by settling techniques. Determinations were made of the mineralogical composition and the

amount of Ca^{2+} , Mg^{2+} , K^+ and Na^+ occupying exchange positions in the clay fraction. These cations were also measured in each water sample taken from the sediment-water interface. Measurement was by atomic absorption spectrophotometry. The ionization interference of Na^+ with K^+ was overcome by comparing unknown samples to an aliquot with a small measured amount of additional potassium (Billings, 1965; Fishman and Downs, 1966; and Angino and Billings, 1967). Ca^{2+} and Mg^{2+} complexes with Al, Si, and P were eliminated by the addition of about 500 ppm of lanthanum (Angino and Billings, 1967).

Chloride ion concentrations were determined in all samples of water from the sediment-water interface. Measurement was made using a chloride ion specific electrode and reference solutions. The alkalinity and pH were measured by electrode methods in the field.

An adaptation of the method of Jackson (1958) was employed to determine the amounts of Mg^{2+} , Ca^{2+} , Na^+ and K^+ in exchange positions. Prior to analysis, the samples were washed three times with distilled water to remove ions associated with the interstitial water. All analyses were performed on the $< 2\mu$ size fractions. The method involves

the replacing of existing cations with NH_4^+ and measuring the amounts of the interlayer cations driven out. An outline of the revised procedure follows:

1. 1 g of the sample was placed in an Erlenmeyer flask with 30 ml of 1N NH_4OAc buffered at pH7 and shaken for a period of 24 hr.
2. The sample was centrifuged and the supernatant decanted and saved.
3. The clay material was again placed in a flask with another 30 ml NH_4OAc and shaken for 30 min.
4. The suspension was again centrifuged until clear, the supernatant was decanted and added to that of step No. 2. After one more washing, the combined volume was adjusted to 100 ml.
5. The solution was analyzed by atomic absorption and the results were reported as m-equiv./100 g of solid.

The procedure was repeated four consecutive times on each of six samples to evaluate the precision of the method. The standard deviation for the analysis of each element is given in Table 1. Less than 4 per cent of the amount of cations removed in the first washing remained in the second, and only traces of Mg^{2+} , Ca^{2+} , K^+ and Na^+ were observed in three succeeding extractions. Because organic matter was not separated from the sample some of the exchanged cations may have been extracted from it.

Table 1. Ammonium acetate exchange precision tests

Cation	\bar{X}	N	S^2	S	Designation
Ca^{2+}	19.2	6	1.26	1.12	15H (Sample)
Mg^{2+}	31.7	6	6.79	2.60	15H (Sample)
K^+	2.3	6	1.88	1.37	15H (Sample)
Na^+	23.4	6	2.75	1.65	15H (Sample)

\bar{X} = mean; N = number of samples; S^2 = variance; S = standard deviation.

CHEMICAL AND MINERALOGICAL DISTRIBUTION PATTERNS

The areal distribution patterns of chloride concentration in water from the sediment-water interface vary from day to day in both lakes. Nevertheless, the same general pattern is always recognizable in Lake Maurepas (Fig. 2) and Lake Pontchartrain (Fig. 3). The chloride concentration shows a general increase from west to east in Lake Maurepas. In Lake Pontchartrain, there is

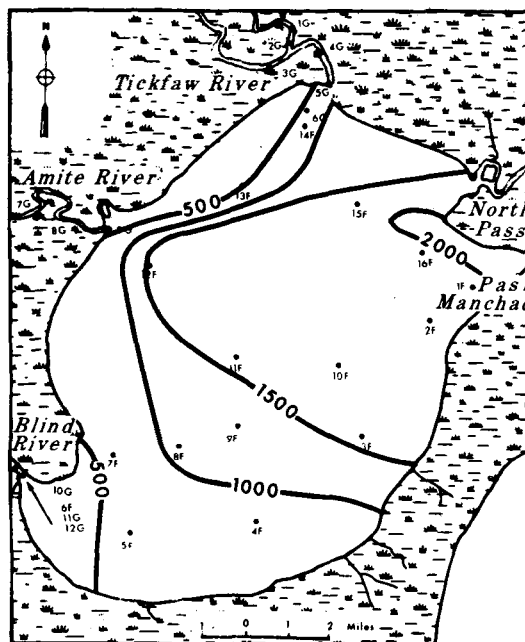


Fig. 2. Chloride concentration in Lake Maurepas (mg/l) March 28, April 2, 1968.

usually a poorly defined north to south increase in chloride concentration.

The distribution patterns for the concentration of Na^+ , K^+ , Mg^{2+} and Ca^{2+} , the smectite content of the clay fraction, and the exchange capacity are very similar to the distribution pattern of the chloride ion. All of the above increase as chlorinity increases. The kaolinite distribution pattern is similar, but varies inversely with chloride concentration. The distribution of $< 2\mu$ illite is similar to the distribution of chloride, but is less well defined (Brooks, 1969). The details of each pattern may change daily, but the general trends appear fairly constant.

The mineralogical variations were determined by X-ray diffraction techniques (Brooks and Ferrell, 1970). Uncertainties in the method of interpretation may produce inaccurate results, but the precision of the analyses allows one to say that the relative changes are real. There are no detectable variations in the fine details of the X-ray diffractograms that may be related to particle size distribution, degree of crystallinity, or type of interstratification. Changes in peak intensity ratios are thought to be related to varying weight percent. The exchange capacity measurements support this interpretation, because as smectite increases so do the exchangeable ions.

The differential settling velocities of clay

Table 2. Selected analyses of lake water and sediments at various chloride concentrations

Averaged results of determinations		Low chloride (300 mg/l)	Av. chloride concn. Moderate chloride (1200 mg/l)	High chloride (3250 mg/l)
Cation conc. in water	Mg ²⁺	14.8 mg/l	69.0 mg/l	172.8 mg/l
	Ca ²⁺	3.4 mg/l	38.9 mg/l	71.3 mg/l
	Na ⁺	160.2 mg/l	581.7 mg/l	1560.6 mg/l
	K ⁺	11.5 mg/l	31.5 mg/l	30.6 mg/l
Cations in exchange position	Mg ²⁺	23.6 m-equiv./100g	26.2 m-equiv./100g	36.8 m-equiv./100g
	Ca ²⁺	5.8 m-equiv./100g	6.6 m-equiv./100g	15.6 m-equiv./100g
	Na ⁺	4.9 m-equiv./100g	12.1 m-equiv./100g	24.9 m-equiv./100g
	K ⁺	1.8 m-equiv./100g	2.7 m-equiv./100g	5.0 m-equiv./100g
Sodium adsorption ratio (SAR)		7.8	13.1	23.1
Exchangeable sodium percentage (ESP)		9.4 (calc.) 13.6 (obs.)	15.3 (calc.) 25.4 (obs.)	24.7 (calc.) 30.6 (obs.)
Potassium adsorption ratio (PAR)		0.3	0.4	0.3
Exchangeable potassium percentage (EPP)		6.6 (calc.) 4.8 (obs.)	7.4 (calc.) 5.8 (obs.)	6.0 (calc.) 6.0 (obs.)
Mineralogy of < 2μ fraction (%)		47 Montmorillonite 3 Illite 50 Kaolinite	54 Montmorillonite 9 Illite 37 Kaolinite	61 Montmorillonite 8 Illite 31 Kaolinite

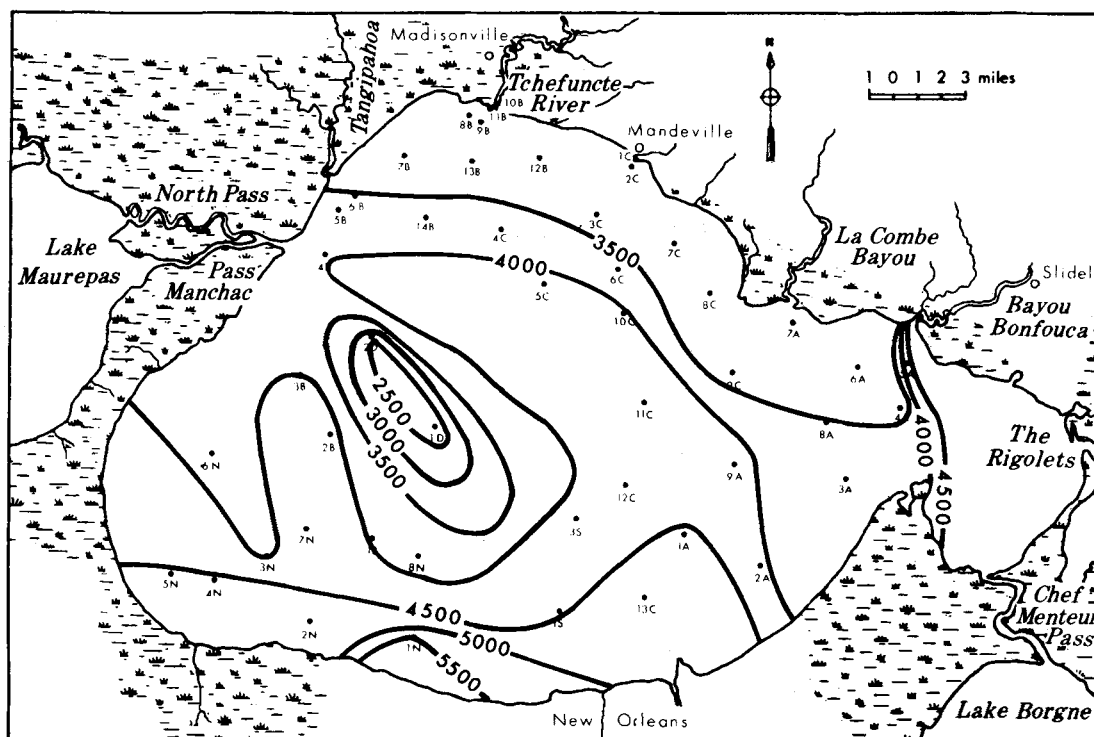


Fig. 3. Chloride concentration in Lake Pontchartrain (mg/l) Aug. 1-9, 1967.

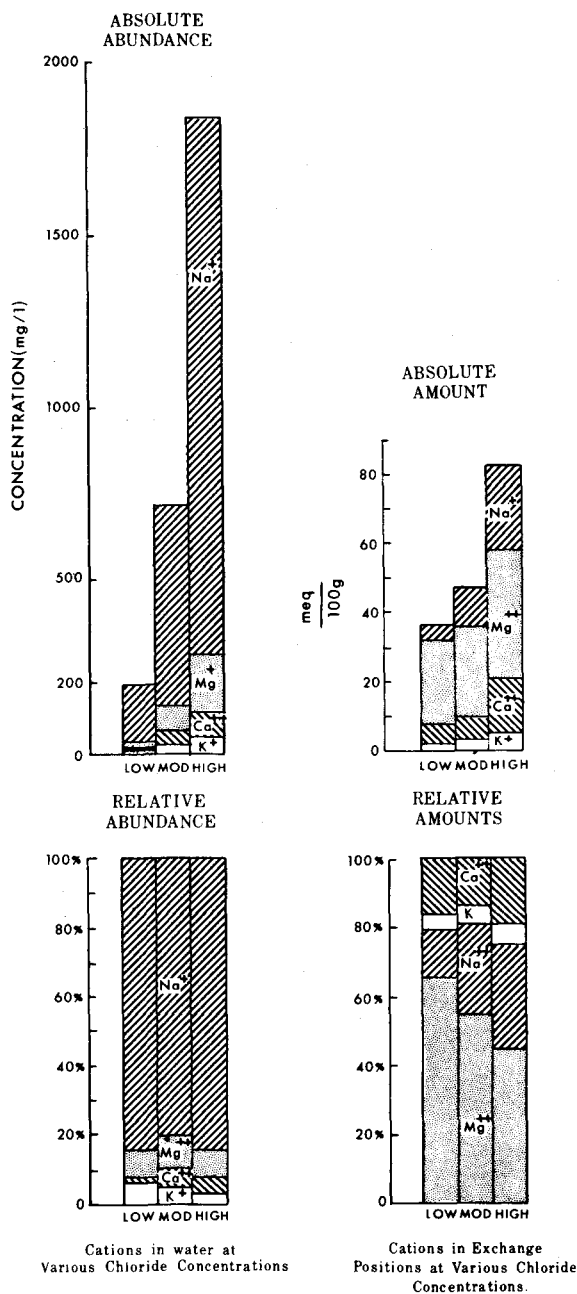


Fig. 4. Comparison of cationic concentrations and relative abundances in lake waters of varying chloride concentrations.

minerals in aqueous suspensions are the principal mechanisms responsible for creating changes in the areal distribution of kaolinite and smectite. The soils around the lakes contribute varying amounts of the two minerals. Kaolinite is ac-

cumulated to a greater degree in the fresher waters because it settles more rapidly than smectite. The sediment distribution patterns and the exchangeable ions associated with the clay minerals in the sediment are both related to the ionic concentrations in the lake waters.

The concentrations of ions in the lake waters increase with the chloride content. This increase is probably due to simple mixing of saline waters in the lakes because the proportions of all ions remain fairly constant. The total ionic strength is quite low and no activity adjustments were made for the concentrations reported. Exchangeable ions are most abundant in samples with high chloride contents. The relative abundance of Na⁺ is doubled, K⁺ and Ca²⁺ increase slightly, and Mg²⁺ is about two-thirds as abundant in high chloride waters as it is in samples associated with low chloride waters. The average ionic and mineralogic composition of samples collected in arbitrarily designated high, moderate, and low chloride waters are presented in Table 2. The pH is always between 7.9 and 8.2.

The ionic interactions can be seen best in the graphical comparison of the results depicted in Fig. 4. Absolute amounts of all ions increase in all cases. In this system an increase in concentration of an ion in the water at the sediment-water interface causes increased quantities of the ion to be adsorbed. Increased exchange capacity is probably due to the concurrent increase in smectite.

CATION SELECTIVITY

The lower bar diagrams in Fig. 4 compare the relative variations in the ionic constituents. This allows one to assess the selectivity of the clay minerals for various ions. One of the most striking changes is the selective increase in exchangeable Na⁺. It appears to become more abundant at the expense of Mg²⁺ in the exchange position. Potassium occupies about the same relative number of sites even though its relative abundance decreases in the overlying solution. Exchangeable Ca²⁺ appears to increase markedly in samples from high chloride waters. The small amount of this element in the intermediate samples suggests that its absorption may be dependent on total ionic strength in addition to relative abundance.

Calculation of the sodium-absorption-ratio (SAR)* and exchangeable-sodium-percentage (ESP) helps to illustrate the selectability of the clays in the higher chloride waters for sodium. The

*Computation of SAR, ESP, PAR, and EPP follows the procedure described on p. 26 of Agriculture Handbook 60, Richards (1954).

predicted percentages of exchangeable sodium are less than the observed values (Table 2). The ESP is calculated from the concentration values of the elements in solution. It does not account for variations in the exchange constant of the clay materials.

The potassium-absorption-ratio (PAR) and the calculated exchangeable potassium percentage (EPP) provide an approximation of the distribution of potassium ions in lake waters and bottom sediments. The generally close agreement between predicted and observed exchangeable potassium values suggest no change in the selectivity of the clays for potassium. There is a slight indication that exchangeable potassium is not in equilibrium with potassium in intermediate chloride waters.

SUMMARY

With increasing salinity across Lakes Pontchartrain and Maurepas the smectite content increases and, as a direct consequence, the exchange capacity increases. A slight increase in illite and a considerable decrease in kaolinite is observed as the chloride concentration in the water increases. As the exchange capacity increases the amount of each cation measured— K^+ , Na^+ , Ca^{2+} , and Mg^{2+} —increases; however, the relative amounts of the individual cations do not increase at the same rates. The rate of Mg^{2+} sorption is the least, and the relative abundance of Mg^{2+} falls off sharply with increasing salinity. The relative amount of Na^+ increases as the clay is exposed to waters with higher dissolved salt contents. Ca^{2+} also increases, and K^+ shows a slight increase in relative abundance.

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Résumé—L'étude des échanges ioniques concernant la fraction argile granulométrique de sédiments des lacs Pontchartrain et Maurepas, suggère une adsorption sélective de Na aux dépens de Mg. La littérature indique que Mg devrait être adsorbé préférentiellement. Lorsque la teneur en chlorure des eaux des lacs monte de 300 mg/l à 3250 mg/l, le pourcentage de Na échangeable augmente, en passant

de 13,5 à 30,6, alors que le pourcentage de Mg échangeable diminue, en passant de 65,5 à 36,8. Les pourcentages de Na échangeable observés sont plus élevés que ceux que l'on calcule à partir des rapports d'adsorption du Na. La différence est attribuée à une augmentation de la constante d'échange du Na dans le sédiment, et donc, à une sélectivité accrue pour Na. Lorsque la teneur en chlorure augmente, la montmorillonite passe de 47 à 61%, et la somme des cations échangeables (Na, Mg, Ca, K) augmente en passant de 36 à 82 m-équil./100 g.

Kurzreferat— Ionenaustauschanalysen der Tongröße fraktion von Ablagerungen in den Pontchartrain und Maurepas Seen deuten auf die selektive Adsorption von Na auf Kosten von Mg hin. Nach der Literatur sollte das Mg vorzugsweise adsorbiert werden. Mit Zunahme der Chlorinität der Seewässer von 300 mg/l auf 3250 mg/l, steigt der Prozentgehalt an austauschbarem N von 13,6 auf 30,6 während der Prozentgehalt von austauschbarem Mg von 65,5 auf 36,8 absinkt. Die beobachteten Prozentgehalte an austauschbarem Na sind höher als die aus dem Natrium-adsorptionsverhältnissen berechneten. Der Unterschied wird einer Zunahme in der Na-Austauschkonstanten der Ablagerung und damit einer erhöhten Selektivität für Na zugeschrieben. Mit Zunahme der Chlorinität erhöht sich der Montmorillonit von 47 auf 61% und die Gesamtmenge der austauschbaren Kationen (Na, Mg, Ca, K) steigt von 36 auf 82 mÄq/100 g.

Резюме — Определение ионно-обменных свойств глинистых фракций осадков озер Понтчартрейн и Маурепас позволило установить избирательное поглощение Na по сравнению с Mg; литературные данные указывают на предпочтительное поглощение Mg. По мере того, как содержание хлора в озерной воде возрастает от 300 мг/л до 3250 мг/л, содержание обменного Na увеличивается от 13,6 до 30,6%, в то время как содержание обменного Mg падает с 65,5 до 36,8%. Наблюдаемые количества обменного Na выше, чем вычисленные из отношения натрия — адсорбент. Подобное различие является признаком увеличения константы ионного обмена Na осадка и, следовательно, увеличения избирательной адсорбции Na. С увеличением содержания хлора в воде содержание монтмориллонита возрастает с 47 до 61%, а общее содержание обменных катионов (Na, Mg, Ca, K) увеличивается от 36 до 82 мэкв/100 г.