

## DISTRIBUTION OF MAJOR CATIONS IN ESTUARINE SEDIMENTS

A. S. PARASHIVA MURTHY and R. E. FERRELL, JR.

Department of Geology, Louisiana State University, Baton Rouge, Louisiana 70803, U.S.A.

(Received 14 August 1972)

**Abstract**—This paper reports the measured distribution of major cations in interstitial, exchangeable and non-exchangeable phases of estuarine sediments. The observed changes in ionic ratios result from the valence and dilution effects in the Donnan equilibrium concept according to which the ion exchanger favors the sorption of divalent ions at the expense of monovalent cations and cations migrate to the outer solution. The above findings have direct application to an interpretation of diagenetic changes in clay minerals.

### INTRODUCTION

ION EXCHANGE is one of the most important chemical phenomena by which diagenetic changes occur after terrestrial sediments are deposited in the marine environment. Because of the importance of ion exchange to understanding diagenetic changes, a number of workers studied the effect of sea water on pure clay minerals and river clays (Powers, 1959; Potts, 1959; Carroll and Starkey, 1960; Russell, 1970) and observed that variations in the concentrations of potassium and magnesium affect diagenetic processes. Although considerable information is available on the effect of dilution on the distribution of ions in the soluble and exchangeable phases of soils (Reitemeier, 1946), very little is known about the effects of dilution on the distribution of ions between interstitial (soluble), exchangeable and non-exchangeable phases of natural heterogeneous sediments. This study was undertaken to assess the variability in the distribution of ions in these locations as a function of sediment-water ratio. This ratio was selected for study because it is one of the natural changes taking place during diagenesis and is likely to be one of the factors influencing inter-laboratory correlations. Of particular interest is the applicability of the Donnan equilibrium concept as used by Mattson (1929) to interpret the changes in ion concentrations upon dilution of sediments with water. Because the pH and ratios of anions in the waters in contact with these sediments essentially were constant, these aspects of the system were not investigated.

### MATERIALS AND METHODS

Information about collection and location of sediment samples was presented in detail in a pre-

vious publication by Murthy and Ferrell (1972). The samples are modern muds from three Louisiana bays, collected by dredging, and refrigerated prior to laboratory analysis.

Interstitial ions were extracted after diluting separate aliquots of the original samples with enough distilled water to obtain sediment-water ratios of 1:2, 1:5, and 1:10. The measured pH of several of these dilutions was 7.8. The solutions were separated by centrifugation and the remaining sediment used in the following extractions.

Exchangeable cations were released after 16 hr of equilibration with  $N. NH_4OAc$  adjusted to a pH of 8.2 (Bower *et al.*, 1952). Corrections were applied to account for interstitial ions remaining in the sediment. Non-exchangeable cations were determined by the method of Pratt (1965) using the  $NH_4$ -saturated samples obtained above.

All cation determinations were achieved by atomic absorption techniques. A 0.1 per cent lanthanum solution was used to suppress the possible interferences from silicon, aluminum, and phosphorus in the calcium and magnesium analyses. Appropriate standards were prepared in  $N. NH_4OAc$  and HCl to avoid any matrix interference in the exchangeable and non-exchangeable cation analyses. All results for calcium, magnesium, sodium, and potassium are expressed as milliequivalents per 100 g of sediment dried at 105°C. Exchangeable hydrogen was not measured so its contribution to the total of the exchangeable ions can not be assessed.

### RESULTS AND DISCUSSION

#### *Ion distribution as a function of dilution*

The amounts of Ca, Mg, Na and K in the interstitial solutions, and in the exchangeable and non-

exchangeable phases of the sediments as a function of increased dilution with water are presented in Table 1.

Dilution of the sediment with distilled water resulted in an increase in the total abundance of elements in the interstitial solution. Generally, the total dissolved ions should remain constant with dilution. In natural heterogeneous soils and sediments, however, there have been reports to show increase in concentration of dissolved ions on dilution due to dissolution of sparingly soluble salts (Kelley, 1938, Reitemeier, 1946, Murthy and Ferrell, 1972).

Reactions other than dissolution must also be involved. The results suggest a rearrangement of exchangeable and non-exchangeable ions because the sums of the ions in these positions decrease with increased dilution. There is a suggestion of a change which is specific for the ions involved with the exchanger because calcium and to some extent magnesium do not follow the overall pattern.

The observed decrease in the sum of the major exchangeable cations is similar to the findings of Carroll and Starkey (1960) and Russell (1970) during controlled reaction of clays with sea water. Much of this decrease is generally thought to be due to fixation of the ions, especially K, within the interlayers of expansible layer silicates. However, these analyses do not support this contention. There is a strong suggestion that the "fixed" ion population also decreases. If any ion is fixed, it is most likely calcium.

#### *Comparison of ionic abundances in interstitial and exchange positions*

Sodium is more abundant in the interstitial solutions than in exchange positions of these sediments. Exchangeable K is 1–5 times as abundant as interstitial K (Table 1). The sums of the exchangeable divalent ions (Ca + Mg) are 3–8 times as abundant as Ca + Mg ions in interstitial solution. The low concentration of K in interstitial solution of sediments compared to higher concentration of K in the exchangeable and non-exchangeable phases of sediments suggests the greater specificity of the clay minerals for this element.

Na and Mg are more concentrated than K and Ca in interstitial and exchangeable phases of marine sediments, probably because of their greater overall abundance. The relatively large quantities of Mg in the interstitial solution may move into octahedral positions of clay minerals and result in the formation of chlorite, vermiculite and/or mixed layer mica-montmorillonite over a period of time.

The importance of cation exchange in the reaction of sediments with water, and in the understanding of diagenesis of clay minerals, is evident in the specific attraction of the clays for K and probably Mg.

#### *Constancy of overall chemical composition*

Although dilution resulted in considerable rearrangement of individual ions, the overall chemical composition of the sediments essentially remained unchanged. The grand totals of the analyses of these three samples were the same regardless of the dilution involved. The most radical changes in the detected distribution of an ion are between the interstitial and exchange phases (Table 1).

These analyses indicate the possibility of considerable variation in the measured abundances of exchangeable ions as a function of the analytical technique. It would be extremely difficult to determine the *in situ* distribution of ions between the interstitial solution and exchange sites of a modern sediment. These data confirm the suggestion of Devine (1971) that the "total pore solution" composition is the more reliable indicator of ionic abundance in modern sediments. The total pore solution is a combination of interstitial and exchangeable ion analyses.

#### *Effect of dilution on ionic ratios*

The variation of the ionic ratios with dilution is shown in Table 2. As the ratio of (Ca + Mg)/(Na + K) in interstitial solution decreased with increased dilution, the ratio of (Ca + Mg)/(Na + K) increased on the exchange sites. The observed sorption of ions of higher valence (Ca and Mg) at the expense of the ions of low valence, (Na and K) is in accord with the valence dilution effect in the Donnan equilibrium concept.

The ratio of K/Na in interstitial solutions ranges from 0.03–0.06 compared to 0.20–0.37 in exchange positions and 1.0 in the non-exchangeable positions. The higher K/Na ratio in exchangeable and non-exchangeable positions compared to interstitial solutions suggests that K is bound more strongly than Na to the negatively charged sites, and that the K is hard to exchange using simple cation exchange procedures. The observation is in accord with the theory that for ions of equal valence, the one with the smallest hydrated radius will be held most strongly by the sediment.

#### CONCLUSIONS

The observed changes in ionic ratios with increased dilution of estuarine sediments with water

Table 1. Distribution of major cations in the interstitial, exchangeable and non-exchangeable phases of estuarine sediments as a function of sediment-water ratio. (All reported values are m-equiv/100 g)

Location	Sediment: H <sub>2</sub> O ratio	Interstitial			Exchangeable			Non-exchangeable			*Grand total						
		Ca	Mg	K	Ca	Mg	K	Ca	Mg	K							
Bay St. Denis	1:2	0.6	3.1	15.2	0.5	19.4	2.4	10.1	13.6	2.8	28.9	6.3	40.0	48.7	53.6	148.6	196.9
	1:5	0.7	3.3	20.8	1.0	25.8	3.0	8.2	8.0	1.5	20.7	7.6	50.1	48.2	42.0	148.0	194.5
	1:10	0.7	3.6	25.7	1.3	31.3	4.5	9.8	4.6	1.0	19.9	10.2	45.6	45.0	40.6	141.4	192.6
Bird Reef	1:2	0.8	4.7	22.2	0.8	28.5	8.4	10.8	19.5	2.5	41.2	17.5	48.5	43.1	49.0	158.1	227.8
	1:5	0.8	4.6	27.9	1.2	34.5	8.0	10.9	11.7	1.9	32.5	13.7	54.4	44.5	46.5	159.1	226.1
	1:10	0.9	4.2	33.3	1.5	39.9	9.4	11.6	8.1	1.8	30.9	19.2	50.4	45.2	42.9	157.7	228.5
Euhlan Bay	1:2	0.3	1.6	10.4	0.5	12.8	4.5	10.9	9.2	1.7	26.3	12.2	44.7	45.2	48.0	150.1	189.2
	1:5	0.3	1.6	14.4	0.7	17.0	4.8	7.9	6.0	1.4	20.1	11.4	49.8	44.8	46.0	152.0	189.1
	1:10	0.5	1.9	15.5	0.9	18.8	5.5	8.5	3.8	1.4	19.2	9.7	49.7	45.2	42.6	147.2	185.2

\*Sum of cations in interstitial, exchangeable and non-exchangeable phases.

Table 2. Effect of dilution on the ratios of cations in estuarine sediments

Location	Sediment-water ratio	Interstitial		Exchangeable		Non-exchangeable	
		$\frac{\text{Ca} + \text{Mg}}{\text{Na} + \text{K}}$	$\frac{\text{K}}{\text{Na}}$	$\frac{\text{Ca} + \text{Mg}}{\text{Na} + \text{K}}$	$\frac{\text{K}}{\text{Na}}$	$\frac{\text{Ca} + \text{Mg}}{\text{Na} + \text{K}}$	$\frac{\text{K}}{\text{Na}}$
Bay St. Denis	1:2	0.24	0.03	0.76	0.20	0.45	1.1
	1:5	0.18	0.04	1.18	0.19	0.64	0.9
	1:10	0.16	0.05	2.55	0.21	0.65	0.9
Bird Reef	1:2	0.24	0.03	0.87	0.13	0.71	1.1
	1:5	0.18	0.04	1.39	0.16	0.75	1.0
	1:10	0.14	0.04	2.12	0.22	0.79	0.9
Euhlan Bay	1:2	0.17	0.05	1.41	0.18	0.61	1.0
	1:5	0.12	0.05	1.71	0.23	0.67	1.0
	1:10	0.14	0.06	2.69	0.37	0.67	0.9

can be described by the Donnan theory. The clay particles in estuarine sediments are micro-Donnan systems. With increased dilution, this theory predicts a migration of ions from the inner solution to the outer solution similar to the observations of this study. Dilution displaces the ratios of ions in the exchangeable positions to favor the increased sorption of divalent ones. These changes are referred to as the dilution effect and the cation selectivity effect by Wiklander (1964) in his discussion of the Donnan equilibrium. He presents also a quantitative treatment of the concept. Wider application of this theory by sedimentologists should clarify and expand the applicability of the Donnan equilibrium to an understanding of sediment-water systems and early stage diagenesis. Other treatments (i.e. the Gouy Theory) also may predict the distribution of the cations in these systems. The choice of the best model is left for the future.

Considerable rearrangement of individual ions occurs as a result of valence-dilution effects. The total non-exchangeable ions and/or the sum of interstitial plus exchangeable and non-exchangeable ions do not change significantly during dilution. Their constancy augurs well for their acceptance as a uniform way to report results of sediment-water analysis.

#### RECOMMENDATIONS

If this report and our earlier one withstand the scrutiny of the scientific community, we feel there are certain steps which should be followed in future analyses of sediment-water systems:

1. We heartily support the work of others which demonstrates the need for immediate analyses of modern systems at conditions approaching those of the *in situ* state. The temperature is especially critical.

2. The multiple dilution treatment is the best

way to obtain the distribution of ions between the interstitial and exchangeable positions in sediments. The values can be obtained by extrapolation of the dilution measurements to the original moisture content. These extractions should be accomplished immediately after sample collection.

3. Combined reporting of the interstitial and exchangeable ions as the composition of the total pore solution should be considered if time does not permit all the analyses required by multiple dilution. The interstitial ions' abundances should be determined by a one-step dilution method rather than by squeezing.

*Acknowledgements*—The authors wish to acknowledge the financial support of the L.S.U. Department of Geology and the National Science Foundation through the University Science Development program. Appreciation is expressed to Mrs. I. Self and Mr. R. Abshire for their assistance in the laboratory. Discussions with Dr. S. B. Devine especially were helpful during this study.

#### REFERENCES

- Bower, C. A., Reitemeier, R. F. and Fireman, M. (1952) Exchangeable cation analysis of saline and alkali soils: *Soil Sci.* **73**, 251–261.
- Carroll, D. and Starkey, H. C. (1960) Effect of sea water on clay minerals: *Clays and Clay Minerals* **7**, 80–101.
- Devine, S. B. (1971) Mineralogical and geochemical aspects of the surficial sediments of the deep Gulf of Mexico. Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana, 160 pp.
- Kelley, W. P. (1938) Effect of dilution on the water-soluble and exchangeable bases of alkali soils and its bearing on the salt tolerance of plants: *Soil Sci.* **47**, 367–375.
- Mattson, S. (1929) The laws of soil colloidal behavior—I: *Soil Sci.* **28**, 179–220.
- Murthy, A. S. Parashiva and Ferrell, R. E. Jr. (1972) Comparative chemical composition of sediment interstitial waters: *Clays and Clay Minerals* **20**, 317–321.
- Potts, R. H. (1959) Cationic and structural changes in Missouri River clays when treated with ocean water:

- M.S. Thesis, University of Missouri, Columbia, Mo.
- Powers, M. C. (1957) Adjustment of land-derived clays to the marine environment: *J. Sed. Petrol.* **27**, 355–372.
- Pratt, P. F. (1965) Digestion with hydrofluoric and perchloric acids for total potassium and sodium: *Methods of Soil Analysis* (Edited by C. A. Black) Part 2, pp. 1019–1021.
- Reitemeier, R. F. (1946) Effect of moisture content on the dissolved and exchangeable ions of soils of arid regions: *Soil Sci.* **61**, 195–214.
- Russell, K. L. (1970) Geochemistry and halmyrolysis of clay minerals, Rio Ameca, Mexico: *Geochim. Cosmochim. Acta.* **34**, 893–907.
- Wiklander, L. (1964) Cation and anion exchange phenomena. In *Chemistry of the Soil* (Edited by F. E. Bear) pp. 160, 163–205. ACS Mono.

**Résumé**—Cet article décrit la distribution des cations majeurs que l'on peut mesurer dans les phases interstitielles, échangeables et non échangeables des sédiments d'estuaires. Les variations observées dans les rapports ioniques proviennent des effets de valence et de dilution, en utilisant le concept de l'équilibre de Donnan, selon lequel l'échangeur d'ions favorise la fixation des ions divalents aux dépens des cations monovalents et des cations qui migrent dans la solution extérieure. Les résultats précités ont une application directe dans l'interprétation des modifications diagénétiques des minéraux argileux.

**Kurzreferat**—Die Arbeit berichtet über die in Flußmündungssedimenten gemessene Verteilung der wichtigsten Kationen auf Porenlösung sowie austauschbare und nichtaustauschbare Form. Die beobachteten Veränderungen der Ionenverhältnisse sind das Ergebnis von Wertigkeits- und Verdünnungseffekten im Sinne des Donnan-Gleichgewichtes. Sie haben zur Folge, daß der Austauscher 2 wertige Kationen auf Kosten der einwertigen bevorzugt sorbiert, und daß Kationen in die Außenlösung übergehen. Die dargestellten Ergebnisse haben einen direkten Bezug zur Deutung diagenetischer Veränderungen in Tonmineralen.

**Резюме** — В этой работе излагается измеренное распределение главных катионов во внедренных, обменных и необменных фазах эстуарийных отложений. Изменения замеченные в ионных отношениях происходят вследствие эффектов валентности и разбавления по концепции равновесия Доннана, согласно которой ионный обмен способствует сорбции дивалентных ионов за счет моновалентных катионов и катионы мигрируют во внешний раствор. Данные полученные выше можно применять непосредственно к интерпретации диагенетических изменений в глинистых минералах.