COMPARATIVE CHEMICAL COMPOSITION OF SEDIMENT INTERSTITIAL WATERS

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Abstract — Interstitial waters squeezed from modern sediments with a 100 psi pressure at laboratory temperature (23°C) are depleted in K and Ca and enriched in Mg when compared to the solutions obtained at *in situ* temperature (28°C). The changes are especially pronounced when the samples are refrigerated during transport back to the laboratory. The magnitude of the variation in chemical composition was dependent on the element being analyzed as well as the sediment used. The maximum observed depletion in the laboratory was about 12% per degree difference in temperature for potassium. Element ratios in the solutions were affected most seriously. The Mg/Ca and Na/K ratios increased 51 and 60% respectively.

A water extraction method using sediment to water ratios of 1:2, 1:5, and 1:10 was compared with the pressure method. The total composition of the pore fluids obtained by squeezing is greater than expected, corresponding to a sediment to water ratio less than 1:5. The artificially squeezed sediments are yielding pore fluids which are more concentrated than the "in-place" solutions.

The water extraction method yields results which are in agreement with the behavior predicted by the Donnan Principle. It is suggested that the values obtained by successive dilution analyses can be extrapolated to measured moisture contents and used to determine the elemental composition and element ratios in interstitial pore fluids.

INTRODUCTION

THE STUDY of the composition of the interstitial solutions in modern sediments can provide an understanding of the principles governing diagenesis of clay minerals. It is essential to know where the ions are in order to define the chemical changes taking place. For example, potassium may be found in 3 major sites; (1) in the interstitial solution, including soluble salts, (2) the exchangeable sites, and (3) as ions fixed in structural positions. The distribution of potassium between these sites is a function of reaction kinetics and analytical techniques. This investigation reports an attempt to assess the latter variable on the apparent distribution of the ions.

Reported variations in composition due to squeezing pressure and temperature (von Englehardt, 1961; Manheim, 1966; Presley *et al.*, 1969) have caused the interstitial water results to be viewed with a certain amount of skepticism by many geochemists. This uncertainty provided a strong impetus to the present authors to use the water extraction method generally used in soil fertility investigations (Burgess, 1922) to obtain the interstitial water composition of some modern estuarine sediments. This method provides more useful data on ion distribution during exchange and early diagenetic reactions.

The results of the present investigation comfirm the importance of temperature effects and indicate the desirability of ship-board extractions of pore fluids. Multiple dilution experiments suggest that squeezing the sediment at 100 psi to extract interstitial fluids yields a total composition which corresponds to sediment: water ratios smaller then 1:5.

MATERIALS AND METHODS

The approximate locations of sediments used in the present study are shown in Fig. 1. Two stations (St. Denis and Bird Reef) were in Barataria Bay, a large estuary about 45 miles south of New Orleans on the western side of the Mississippi River. The third station was in Euhlan Bay about 35 miles southeast of New Orleans on the eastern side of the river. The salinity of the bay waters was about $12^o/_{oo}$ sodium chloride at the Euhlan Bay and St. Denis stations and near $30^o/_{oo}$ at Bird Reef. Bottom sediment temperatures were between 28° and 30°C measured by direct probe. The consistency of the sediments precluded the possible mixing of the bay waters and interstitial waters during sampling.

Two dredge samples were taken, combined and mixed thoroughly in a plastic bucket to form a subsample. A second subsample was prepared in the same manner at each station by allowing the boat to drift about 50 yards and then repeating the dredge operation. Each subsample was split into 6
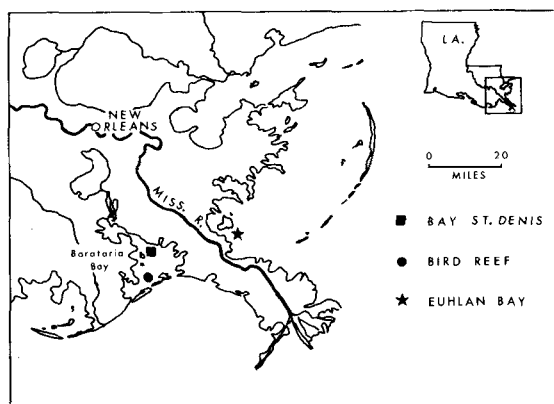
Fig. 1. Index map of sample locations.

representative aliquots and placed in screw cap plastic bottles. The first 2 of these were transferred within 5 min of collection to an apparatus like the one described by Reeburg (1967) and the interstitial water extracted by squeezing. Nitrogen gas was used to achieve a pressure of 100 psi on the diaphragm. The sample temperature was about 28°C.

The next 2 splits of each subsample were placed in an ice chest and kept refrigerated until the interstitial water could be extracted. The remaining 2 aliquots were returned to the laboratory at ambient temperatures. The same apparatus was used to obtain the pore fluids in the laboratory, but the temperature at the time of squeezing was close to 23°C. Thus, 12 different solutions were analyzed from each of the 3 stations. The analyses reported in Table 1 are the mean values obtained by determining the ionic abundances in 4 solutions extracted on the boat at 28°C, 4 solutions extracted in the laboratory at 23°C after refrigeration, and 4 solutions extracted in the laboratory at 23°C with no refrigeration during transport. The refrigerated samples were also used in the water extraction procedure.

Briefly, the water extraction method consisted of adding appropriate amounts of recently boiled and cooled distilled water to moist sediments to give a 1:2, 1:5, and 1:10 sediment to water weight ratio. The suspensions were shaken on a wrist-action shaker for 6 hr and then centrifuged immediately at 8000 rev/min for 10 min. The supernatant solution was saved for analysis. The remaining sediment was saved to determine the exchangeable and nonexchangeable ions. The results of which will be published elsewhere.

The concentrations of Ca, Mg, K, and Na in both types of interstitial waters were determined by atomic absorption methods after appropriate dilution. A 0·1% La solution was used to suppress the interferences from Si, Al, and P on Ca and Mg. The results are expressed as meq of the element per 100g of sediment dried at 105°C in order to compare the techniques.

RESULTS AND DISCUSSION

Effect of temperature on the composition of interstitial waters

The sediment samples squeezed on the boat at 28°C produced pore fluids which contain more K and Ca and less Mg than the sediments extracted in the laboratory (Table 1). The results for Na are variable, some were enriched slightly, others severely depleted. The unrefrigerated samples were not as different from the "on-board" ones as were the sediments which were refrigerated prior to analysis. The Euhlan Bay samples, especially, were sensitive to refrigeration. Storage at low temperatures produces irreversible changes in the composition of the pore fluids which can be extracted at 100 psi.

At the lower laboratory temperatures, apparently K and Ca are taken up by the sediment and Mg released. The temperature effect on K is similar to that reported by Bischoff *et al.* (1970) for ocean bottom sediments but the direction of change is reversed because estuarine bottom sediments are warmer than the laboratory atmosphere. There were 2 cases in which Na was depleted, severely. It was affected only slightly in the others. The decreased selectivity of the sediment at *in situ* temperatures for K and Ca may be due to the blocking effect of inorganic Mg-hydroxide interlayers, or for the latter element by carbonate equilibria. (Our X-ray diffraction analyses of the -2μ clays confirm the existence of interlayers in these sediments similar to those reported earlier by Lynn and Whittig, 1966; Rich, 1968).

The element ratios are also affected by the temperature of storage and squeezing. The Mg/Ca and Na/K ratios are increased as much as 51 and 60%, respectively. The changes in these ratios vividly illustrate the differences in the composition of pore fluids extracted at various temperatures.

Comparison of dilution and pressure extraction methods

The pressure method produced greater individual amounts of cations as well as totals of the ions extracted than the dilution method for sediment to water ratios of 1:2 and 1:5 (Table 2). The chemical composition of the squeezed water is similar to that of samples with sediment to water ratios between 1:5 and 1:10. This was an especially surprising result because our consideration of ion exchange equilibria had predicted higher values for all dilute samples because of increased hydrolysis

Table 1. Chemical composition of sediment interstitial waters obtained by squeezing at 100 psi

Sample	Squeezing Conditions	Potassium (meq/100g)	(% change)	Sodium (meq/100g)	(% change)	Calcium (meq/100g)	(% change)	Magnesium (meq/100g)	(% change)	Sum. (meq/100g)	(% change)	Mg/Ca (meq/100g)	(% change)	Na/K (meq/100g)	(% change)
Bay St. Denis	On boat at 28°C	0·7		20·6		1·0		4·9		27·2		4·9		29·4	
	Lab at 23°C no refrigeration	0·6	−14	17·4	−15	0·9	−10	4·9	NC	23·8	−13	5·4	+10	29·0	−1
	Lab at 23°C refrigerated	0·5	−29	20·6	0	0·9	−10	5·7	+16	27·7	+2	6·3	+23	41·2	+40
Bird Reef	On boat at 28°C	1·2		33·1		2·1		8·2		44·6		3·9		27·6	
	Lab at 23°C no refrigeration	1·0	−17	33·7	+2	1·7	−19	9·0	+10	45·4	+2	5·3	+36	33·7	+22
	Lab at 23°C refrigerated	0·9	−25	32·9	−1	1·5	−29	8·8	+7	44·1	−1	5·9	+51	36·5	+33
Euhlan Bay	On boat at 28°C	0·8		21·7		1·4		5·7		29·6		4·1		27·1	
	Lab at 23°C no refrigeration	0·7	−12	22·8	+5	1·2	−14	6·6	+16	31·3	+6	5·5	+34	32·6	+20
	Lab at 23°C refrigerated	0·3	−63	13·0	−40	0·7	−50	3·8	−33	17·8	−40	5·4	+32	43·3	+60

Table 2. Comparison of interstitial water compositions extracted by pressure and water dilution methods*

Ion concentration in meg/100g	St. Denis				Bird Reef				Euhlan Bay			
	Pressure method	Sediment:water			Pressure method	Sediment:water			Pressure method	Sediment:water		
		1:2	1:5	1:10		1:2	1:5	1:10		1:2	1:5	1:10
Ca	0·9	0·6	0·7	0·7	1·5	0·8	0·8	0·9	0·7	0·3	0·3	0·5
Mg	5·7	3·1	3·3	3·6	8·8	4·7	4·6	4·2	3·8	1·6	1·6	1·9
Na	20·6	15·2	20·8	25·7	32·9	22·2	27·9	33·3	13·0	10·4	14·4	15·5
K	0·5	0·5	1·0	1·3	0·9	0·8	1·2	1·5	0·3	0·5	0·7	0·9
Sum	27·7	19·4	25·8	31·3	44·1	28·5	34·5	39·9	17·8	12·8	17·0	18·8
% change†		−30	−7	+13		−35	−22	+9		−3	−4	+5
								+10		−28		+6

*All samples were refrigerated prior to analysis.
†Refers to percentage change in the sum of cations extracted by pressure method.

of exchange sites and dissolution of precipitated salts. These data suggest that the pressure extraction method does not yield a pore fluid composition that is representative of the *in situ* values. Squeezing the sediment at 100 psi produces an interstitial water that is enriched in the ionic constituents. The degree of enrichment is dependent on the characteristics of the sediments and ions. Abrasion of sediment particles created by the applied pressure may increase solution concentration of the ions by dissolution of the freshly exposed surfaces. Or this may be evidence also for the pressure dependence of ion exchange equilibria.

A decrease in the sediment to water ratio results in an increase in the concentration of a given cation in the water extract. These results are in agreement with the observations of Eaton and Sokoloff (1935) and Lagerwerff (1956). The monovalent ions, K and Na, increase the most, whereas Ca and Mg values are almost constant. At Bird Reef, the most saline sample locality, the magnesium values actually decrease with dilution. This effect is attributed to the removal of ions in excess of those interstitial to the sediment particles by the excess solvent. Furthermore, dilution resulted in a decrease in the Ca/K ratios. The results are thus in general agreement with the predictions of the Donnan Principle (Marshall, 1964).

CONCLUSIONS

The experiments discussed above demonstrate the desirability of extracting pore fluids from modern sediments within minutes of their collection and at *in situ* temperatures. Storage of samples, especially refrigeration of estuarine sediments, produces irreversible changes in the composition of the interstitial solutions. Squeezing the sediment at 100 psi to obtain the fluids should be avoided because the elemental abundances are too high and

the elemental ratios are different from the actual ones. It is suggested that pore fluid compositions can be obtained best by the water extraction methods common in soil fertility investigations and similar to the dilution technique of Mangelsdorf *et al.* (1969). The 'in place' values of ions in the interstitial solutions and the element ratios can be assessed by extrapolation of the dilution data to observed moisture contents of fresh sediment samples because Donnan Equilibria are the major controls on the distribution of ions in clayey sediment–water systems.

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Résumé – Les solution interstitielles chassées de sédiments modernes sous une pression de 100 psi à la température du laboratoire (23°C) sont plus pauvres en K et Ca et plus riches en Mg que les solutions obtenues à la température *in situ* (28°C). Les changements sont particulièrement prononcés quand les échantillons sont réfrigérés pendant le transport au laboratoire. L'amplitude de la variation de la composition chimique dépend de l'élément analysé aussi bien que du sédiment utilisé. Pour la potassium, la diminution maximum observée au laboratoire est environ de 12% par degré de différence de température. Ce sont les rapports des éléments dans la solution qui sont affectés le plus sérieusement. Les rapports Mg/Ca et Na/K augmentent respectivement de 51 et 60%.

Une méthode d'extraction à l'eau utilisant des rapports sédiment sur eau de 1/2, 1/5 et 1/10 a été comparée à la méthode par pression. La teneur totale en ions des fluides contenus dans les pores et obtenus par pression est plus grande que prévue, et elle correspond à un rapport sédiment sur eau inférieur à 1/5. Les sédiments artificiellement traités par la pression fournissent des fluides contenus dans les pores, qui sont plus concentrés que les solutions "en place".

La méthode d'extraction à l'eau fournit des résultats en accord avec le comportement prédit par le principelde Donnan. On suggíre que les valeurs obtenues par des analyses de dilution successive puissent être extrapolées aux teneurs en eau mesurées et soient utilisées pour déterminer la composition en éléments et le rapport de ces derniers dans les fluides interstitiels des pores.

Kurzreferat – Zwischenräumliche Wasser, die aus neuzeitlichen Ablagerungen bei einem Druck von 100 psi unter Laboratoriumstemperatur. (23°C) ausgepresst wurden, sind arm an K und Ca und angereichert an Mg im Vergleich mit Lösungen, die bei *in situ* Temperaturen (28°C) erhalten wurden. Die Änderungen sind besonders auffallend wenn die Proben während des Rücktransportes zum Laboratorium gekühlt werden. Das Ausmass der Änderung in der chemischen Zusammensetzung war abhängig von dem untersuchten Element sowie von der verwendetn Ablagerung. Die maximale im Laboratorium beobachtete Verarmung war etwa 12% pro Grad Temperaturunterschied für Kalium. Die Verhältnisse der Elemente zu einander in den Lösungen wurden sehr beträchtlich beeinflusst. Die Mg/Ca und Na/K Verhältnisse sich um 51 bzw. 60%.

Ein Wasserextraktionsmethode unter Verwendung von Sediment zu Wasser Verhältnissen von 1:2, 1:5 und 1:10 wurde verglichen mit dem Druckverfahren. Die Gesamtzusammensetzung der durch Auspressen erhaltenen Porenflüssigkeiten ist grösser als erwartet, entsprechend einem Sediment-Wasserverhältnis von weniger als 1:5. Die künstlich gepressten Sedimente ergeben Porenflässigkeiten, die konzentrierter sind als die *in-situ* Lösungen.

Die Wasserextraktionsmethode liefert Ergebnisse, die mit dem aus dem Donnanprinzip vorausgesagten Verhalten übereinstimmen. Es wird angenommen, dass die durch fortlaufende Verdünnungsanalysen erhaltenen Werte auf gemessene Feuchtigkeitsgehalte extrapoliert werden können und zur Bestimmung der Elementarzusammensetzung und der Elementarverhältnisse in zwischenräumlichen Porenflüssigkeiten verwendbar sind.

Резюме — Внедренные воды выжатые из осадков под давлением 100 фунт/дюйм² при лабораторной температуре (23°C) истощаются K и Ca и обогащаются Mg по сравнению с растворами выжатыми при температуре *in situ* (28°C). Эти перемены особенно заметны при рефрижерации образцов во время транспортировки в лабораторию. Степень вариаций в химической композиции зависит как от анализируемого элемента, так и от используемого осадка. В лаборатории максимальное наблюдаемое истощение было в порядке 12% на градус разницы температуры для калия. Соотношение элементов в растворах было очень серьезно затронуто. Относительное содержание Ma/Ca и Na/K повысилось на 51 и 60 процентов, соответственно.

Метод экстракции воды при котором относительное содержание осадков к воде — 1:2, 1:5 и 1:10 сравнивался с методом экстракции под давлением. Общая пропорция выжатой из пор жидкости была выше, чем ожидали, соответствуя относительному содержанию осадков к воде менее 1:5. Исскуственно выжатые осадки дают жидкости, которые более концентрированы, чем растворы *in situ*.

Экстракция воды дает результаты, которые сходятся с поведением предсказанным по принципу Доннана. Предполагают, что значения получаемые анализом повторных разбавлений, можно экстраполировать к измеренному содержанию влаги и применять для определения композиции элементов и их относительного содержания во внедренных в порах жидкостях.