

## 21. INTERSTITIAL WATER STUDIES ON SMALL CORE SAMPLES, DEEP SEA DRILLING PROJECT, LEG 3<sup>1</sup>

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### INTRODUCTION

Eleven samples of fluids which had been squeezed on board ship, and four, packaged sediment samples were received in our laboratories. As in Leg 2, the volumes of fluid available were scanty and did not permit multiple determinations of constituents in many of the samples; in Hole 21 the fluid available sufficed only for refractometer readings (a few tenths of a milliliter). Therefore, analytical scatter is again responsible for partially obscuring variations (and constancy) in the conservative constituents such as sodium. However, on the whole the results confirm the features which appeared in Legs 1 and 2. Central oceanic sediments display a remarkable constancy in total salinity, chlorinity and sodium concentration to the greatest depths and ages yet penetrated in the project drillings. Variations attributable to postburial reactions do occur in the remaining major ions, but they usually show little systematic trend with depth—with the exception of potassium, which will be discussed later.

Methods remain similar to those employed for Leg 2; the detailed techniques are now being prepared for submission, but a brief description may be obtained from the previous Leg reports (Manheim and Sayles, 1969; Chan and Manheim, 1970). Results from four unsqueezed samples are not complete and, therefore, do not appear here.

### RESULTS AND DISCUSSION

All measurements are reported in Table 1, together with brief sediment descriptions and ages from the preliminary log. Minor constituents could not be analyzed on Holes 20C and 21 due to the lack of sample fluid. The ocean basin samples (excluding Hole 21 on the Rio Grande Rise) showed salinities and chlorinities within 1 per cent (standard deviation) of mean values of 35.2 o/oo and 19.5 o/oo, respectively. These values are insignificantly different from the Leg 2 means (17 samples) of 35.1 o/oo and 19.7 o/oo. On the other hand, the Rio Grande Rise samples (salinity and chloride of 36.1 o/oo and 20.6 o/oo, respectively) are significantly higher than the mean.

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New results bearing on the distribution of potassium concentration in pore waters have just been communicated to the writers by J. L. Bischoff (Bischoff *et al.*, 1969). Previously Mangelsdorf *et al.* (1969) noted that the reported values of potassium in oceanic pore waters consistently exceeded the potassium concentration in open ocean water. They showed that the diffusional flux of potassium into the ocean from pore waters might exceed the supply from the continents. These authors also performed an experiment on sea water-saturated bentonite which showed that raising the equilibrium temperature during squeezing of the sediments could raise interstitial potassium concentrations appreciably. Sodium was also enriched, though to a lesser extent; whereas, magnesium and, to a lesser extent, calcium compensated for the excess cations by being depleted in the pore waters. Pressure differences in the squeezing process did not appear to cause significant changes. The experiments by Bischoff and his co-workers were performed on natural clayey sediments from Southern California offshore basins and suggested an increase in interstitial potassium concentrations of about 10 per cent for each 18-degree temperature increase (i.e., from 4.5° bottom-equivalent temperatures to 22.5°, laboratory temperatures).

The effects in question are assumed to be related to ion exchange behavior of the more reactive clay minerals, especially montmorillonite and illite. Only a minority of the Deep Sea Drilling Project samples run to date are as clay-rich as those sediments whose temperature-sensitive properties have been demonstrated to date. Nevertheless, it is clear that analytical values, especially for potassium, may be affected by the difference between *in situ* temperature (around 2 to 3°C for most of the oceanic samples) and squeezing temperatures (on the order of 21°C). Experiments are planned to explore the influence of these effects on a range of materials collected by the Project. For the time being we suggest that a part, and sometimes all of potassium excesses noted in near-surface samples may be due to the change of temperature prior to squeezing. On the other hand, only a relatively small portion of the normal magnesium depletions are attributable to temperature effects, assuming that the equivalent ionic magnesium depletion does not exceed the equivalent ionic enrichment of potassium. Ten per cent enrichment in potassium

TABLE 1A  
Major Constituents in Interstitial Waters of Leg 3 Cores<sup>a</sup>

Sample Designation	Depth Below Sea Bed (m) <sup>b</sup>	Age	Description	Na	K	Ca	Mg	Total Cations (meq/kg) <sup>e</sup>	Cl	SO <sub>4</sub>	Alk.	HCO <sub>3</sub> <sup>d</sup>	Total Anions (meq/kg) <sup>e</sup>	Sum	Salinity <sup>f</sup>
Hole 13 (6°02.4'S., 18°13.7'W., water depth 4685 m)															
2-4	23	Lower Pliocene	Brown silty zeolitic clay, Mn-stained	10.7 <sup>c</sup>	0.47	0.45	1.24	(603)	19.5	2.26	5.6	0.34	603	35.0	35.2
3-3	140	Middle Eocene	Gray-yellow-green sandy to silty radiolarian ooze	10.7 <sup>c</sup>	0.37	0.78	1.24	(614)	19.8	2.27	8.2	0.50	614	35.6	35.8
Hole 15 (30°53.4'S., 17°59.0'W., water depth 3927 m)															
3-5	(40)	Pliocene	White nannofossil chalk	11.0 <sup>c</sup>	0.42	0.40	1.29	615	19.7	2.59	5.6	0.3 <sup>f</sup>	(615)	35.0	-
9-5	136	Lower Miocene	Dark brown marly nannofossil chalk ooze	10.8	0.43	0.42	1.20	600	19.1	2.44	6.1	0.37	596	34.5	-
Hole 19 (28°32.1'S., 23°40.6'W., water depth 4677 m)															
1-5	7	Miocene (?)	Dark red-brown zeolitic clay	10.8	0.49	0.38	1.23	602	19.3	2.68	5.8	0.35	606	35.2	-
8-4	110	Middle Eocene	Light yellow-brown nannofossil chalk ooze	11.0	0.44	0.38	1.23	610	19.6	2.53	4.0	0.24	609	35.4	-
11-3	136	Middle Eocene	Yellow-brown nannofossil chalk ooze	10.8 <sup>c</sup>	0.45	0.38	1.23	605	19.2	2.21	15 <sup>d</sup>	0.9 <sup>d</sup>	(605)	35.2	-
Hole 20C (28°27'S., 26°58'W., water depth approx. 4500 m)															
1-5	8	Oligocene	Light yellow to brown marly nannofossil chalk ooze, zeolitic-hematitic in part	11.0 <sup>c</sup>	0.49	0.35	1.24	610	19.6	2.60	3.3 <sup>d</sup>	0.20	(610)	35.5	-

TABLE 1A - Continued

Sample Designation	Depth Below Sea Bed (m) <sup>b</sup>	Age	Description	Total Cations				Total Anions				Sum	Salinity <sup>f</sup>		
				Na	K	Ca	Mg	(meq/kg) <sup>e</sup>	Cl	SO <sub>4</sub>	Alk.			HCO <sub>3</sub> <sup>d</sup>	(meq/kg) <sup>e</sup>
3-1	37	Eocene	As above	10.8 <sup>c</sup>	0.46	0.36	1.28	(603)	19.4	2.51	3.8	0.23	603	35.0	-
Hole 21	(28°35.1'S., 30°35.8'W., water depth 2113 m)														
5-2	100	Upper Cretaceous (Campion)	Pink foraminifera-nannofossil ooze	-	-	-	-	-	(20.6)	-	-	-	-	-	36.2
8-3	130	Upper Cretaceous (Campion)	Yellow-gray nan-nofossil-foraminiferan chalk	-	-	-	-	-	(20.5)	-	-	-	-	-	36.1

<sup>a</sup>All values are in g/kg unless otherwise noted. Standard deviations of reproducibility of the results are: Na 0.8, Cl 0.1, K 0.01, Ca 0.01, Mg 0.02, SO<sub>4</sub> 0.03, Alkalinity 0.1. The above estimates are subject to modification, partly as noted below. As noted in previous reports NH<sub>4</sub>, though not determined here, is not thought to contribute significant error to the cation-anion balances, except possibly in Sample 19-11-3 (very high alkalinity).

<sup>b</sup>Depths below sediment surface are given to the nearest meter due to some uncertainty in position.

<sup>c</sup>Analytical error for Na was frequently large enough to distort anion-cation balances. Where the disparity exceeded 4 meq/kg, the Na values were obtained either by use of mean Na/Cl ratios and Cl values, or by difference. The use of the former method is based on the fact that Cl is the most accurately known constituent in our analysis series and Na/Cl ratios appear to show no systematic changes with depth in the open ocean samples beyond the first few meters of sediment, insofar as would appreciably affect the present results.

No values having superscript "c" have been determined by these methods.

<sup>d</sup>HCO<sub>3</sub><sup>-</sup> is calculated from alkalinity, assuming that the alkalinity is entirely due to bicarbonate. This assumption is not strictly correct, due to the influence of borate, phosphate, silicate, carbonate, or other possible weak acids, but errors from this source are probably less than uncertainties associated with squeezing the waters from the cores, etc. Samples marked with "d" are determined by difference in cation-anion balance.

<sup>e</sup>Total cations and anions, where shown in parentheses, are assumed to be equal to the oppositely charged species for the purpose of determining a constituent by difference.

<sup>f</sup>Salinity determined by refractometer on shipboard immediately following the squeezing of effluents. Salinities determined by refractometry in the laboratory showed close relationship with determined chlorinity values, and were used in Hole 21 samples to extrapolate chlorinity values.

**TABLE 1B**  
**Minor Constituents in Leg 2 Interstitial Waters Composition (mg/kg)<sup>a</sup>**

Sample Designation	Depth Below Sea Bed (m)	Sr	Li	Mn	Ba	B	Si
Hole 13							
2-4	23	7.6	0.28	2.9	0.19	7.0	9
3-3	140	11.0	0.18	1.7	0.10	3.0	29
Hole 15							
3-5	(40)	13.4	0.19	2.9	0.25	3.0	26
9-5	136	13.0	0.25	0.9	0.15	2.0	10
Hole 19							
1-5	7	12.6	0.25	1.3	0.10	8.0	10
8-4	110	13.6	0.15	1.5	0.27	5.5	12

<sup>a</sup>The reliability of the minor element determination is indicated approximately by the rounding of the data.

equals 1 meq/kg. A compensating depletion in magnesium would amount to only 0.01 o/oo or less than 1 per cent of total magnesium.

The observations by Mangelsdorf *et al.* (1969) and Bischoff *et al.* (1969) must be taken account of in another effect which has been noted: the rather characteristic decrease of potassium concentrations in deeper layers. Thermal gradient data for deeper strata in the Atlantic are not available, but assuming they are roughly equivalent to those in geosynclinal sedimentary basins (about 3°C/100 meters) laboratory or shipboard temperatures would be approached at around 600 meters (1968 feet) depth. Moreover, bottom waters during earlier Tertiary time have been stated to be warmer than at present. Cooling of bottom waters in Pliocene-Recent time should, therefore, have also altered the temperature and interstitial ionic ratios of subbottom sediments to an increasing extent with proximity to the sediment-water interface.

Among the minor elements strontium and lithium show values equal to or moderately higher than sea water concentrations. Barium and manganese values are substantially higher than in Northern Atlantic sediments. Many of the samples displayed prominent brownish casts and other evidences of appreciable manganese concentrations; Hole 20 even bottomed in manganese nodules at only 6 meters (20 feet) depth. Therefore, it seems logical to assume that the relatively high manganese values are a result of partial reduction and solubility of high-manganese oxide layers on the surfaces of sediment particles. Since samples were all squeezed immediately after core recovery and the membrane (0.45 microns) filtered, the authors believe that the

values are not an artifact of sample extraction or core-handling procedures. Boron shows typically erratic values, within a factor of 2, of sea water concentrations; Silicon, obtained by emission spectrometry for the first time in the work on the Deep Sea Drilling Project cores, reveals values much higher than in overlying bottom waters, but it is typical for interstitial waters of oceanic sediments (e.g. Zaitseva, 1966). The influence of temperature effects on minor constituents remains unknown but will be investigated by the authors.

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