### 15. INTERSTITIAL WATER STUDIES ON SMALL CORE SAMPLES, DEEP SEA DRILLING PROJECT, LEG 2<sup>1</sup>

K. M. Chan, Woods Hole Oceanographic Institution, Woods Hole, Mass. and F. T. Manheim<sup>2</sup>, U.S. Geological Survey, Woods Hole, Mass.

### **INTRODUCTION**

Pore water samples from Leg 2 form a natural continuation to the samples from Holes 4, 5, 6, and 7 from Leg 1-providing coverage across the central North Atlantic Ocean. The samples from Leg 1 are included in this report in summarizing the main features of pore water composition which have emerged from these results. In general, concentrations of the "conservative" elements chlorine and sodium and, also, total salinity confirm the relative constancy of total salt content and chlorinity in deep ocean sediments which was tentatively inferred from the results of the Guadalupe Mohole (Rittenberg et al., 1963), and Holes 4, 5, 6, and 7 in Leg 1 (Manheim and Sayles, 1969).

With one exception, only waters squeezed aboard ship (i.e., no specially-packaged sediments for squeezing and treatment in the laboratory) were available from Leg 2. Thus, no porosity and water content information could be obtained. Also, the small volumes of fluid, which ranged from about 3 milliliters to less than 1 milliliter, did not permit multiple determinations of constituents. This and the need for taking minimum workable quantities of fluid for the several analytical procedures contributed to analytical scatter. Such scatter is not regarded as particularly significant for calcium, potassium, magnesium and the minor constituents (except boron), in comparison with natural variations. For constituents such as sodium and chloride (and also total salinity), however, the authors believe that scatter due to sample manipulations and analytical error partly obscures natural variations or constancy.

No material was available from Site 12, north of the Cape Verde Islands. This is regrettable since recent seismic reflection studies reveal diapiric features which may be salt bodies at over 5000 meters depth, northwest of the Cape Verde Islands (Schneider, 1969). In line with the marked increases in pore water salinity above evaporite beds in the Gulf of Mexico (Manheim and Bischoff, 1968, Manheim and Sayles, 1969), analvsis of pore waters from cores in Site 12 would have tested the salt diapir hypothesis.

The analytical techniques utilized in Leg 1 were partly modified for Leg 2. Calcium and magnesium were determined only by atomic absorption, and alkalinity was determined by the indirect titration method of Buch and Wattenberg (see Koroleff, 1966). As before, sodium and potassium were determined by atomic absorption spectroscopy, minor constituents were analvzed by spark emission spectrometry, sulfate was determined microgravimetrically (after Shishkina, 1956), and chloride was determined by gravimetric titration. Eau Normale (Copenhagen) served as primary standard for the major cations and chloride, and served to check the gravimetric factor and sulfate and the accuracy of the minor element determinations for strontium, lithium and boron. Refractometer determinations of total salt content were helpful, as before, to confirm salt concentration in a drop of pore liquid. These determinations facilitated preparation of standards and calculation of aliquots.

Two samples, one each from Holes 9 and 10, had evidently evaporated prior to sealing, or were improperly sealed; all constituents in these two samples showed anomalously large increases, of the same magnitude, over the concentration levels in the other samples and in open ocean water. These samples are not included in the analytical tables. The authors wish to thank D. Spencer and P. Brewer for allowing them the use of atomic absorption equipment.

### RESULTS

### **Major Constituents**

The two samples from Hole 11, though separated by more than 200 meters of sediments, and more than 10 million years, had concentrations for most major constituents which were remarkably close to each other and to the concentration levels in standard ocean water. The deviation for chloride, for example, was not significant with respect to the estimated analytical scatter for samples from this leg, which was 0.1 °/° (Table 1). This station was in the central North Atlantic, approximately equidistant from the American and European continents. Chloride concentrations in Holes 8 through 10 had greater variations, but showed no observable trends with depth, and remained constant within a standard deviation of about 2 per cent around a median value of about 19.7 °/00. Some of the deviations must be assumed to be due to sample manipulation by the

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Sample Designation	Depth Below ion Sea Bed (m) <sup>b</sup>	Age	Description	Na	K	Ca	Mg	Total Cations (meq/kg)	Cl	SO4	Alk (meq/kg)	HCO3	Total Anions <sup>c</sup> (meq/kg)	Sum
Hole 8	(35° 23.0'N., 67° 33.2'W, w	vater depth 5154 m)												
1-1 (150) 2-3 (0-3)	260 175	Middle Miocene Eocene	Gray-green mud Quartz and siliceous silt	10.8 10.5	0.31 0.30	0.65 0.59	1.08 1.04	602 579	20.0 20.0	1.70 <sup>d</sup> 1.14	2.52	0.15	(566) (587)	34.5 (33.6)
Hole 8A	A (35° 23.0'N, 67° 33.2'W,	water depth 5169 m)												
1-1 (0-2)	279	Eocene	Olive, siliceous silt with mud breccia; clayey	10.8	0.35	0.58	1.05	597	20.0	1.60 <sup>d</sup>	1.06	0.06	(562)	34.3
Hole 9	(32°46.4′N, 59°11.7′W, wa	ter depth 4965 m)												
5-1 (147-150) 7-4 (125-150)	) 32 201	Quaternary Lower Pliocene	Coccolith marl ooze Olive marly ooze	10.7 11.3	0.45 0.28	0.30 0.38	1.16 1.03	588 603	19.8 20.8	1.78 1.10	2.13	0.13	596 608	34.3 34.9
Hole 10	) (32°51.7′N, 52°12.9′W, w	ater depth 4697 m)												
1-1 (140-150	30	Pliocene	Pale brown coccolith	11.2	0.47	0.45	1.23	626	19.9	1.67	2.60	0.16	618	36.1
2-4 (135-145)	47	Miocene	Yellow-brown, zeolitic coccolith ooze	10.7	0.44	0.47	1.21	603	19.4	2.59	2.91	0.18	603	35.0
3-2 (140-150)	53	Oligocene	Yellow-brown, zeolitic coccolith ooze	10.8	0.43	0.49	1.24	610	19.7	2.59	2.92	0.18	609	35.5
5-2 (140-150)	77	Oligocene	Nannofossil ooze (coccolith)	10.9	0.42	0.51	1.26	615	19.9	2.59	-	0,10 <sup>e</sup>	(613)	35.7
7-3 (140-145)	96	Middle Upper Eocene	Yellow-brown, zeolitic coccolith chalk ooze	10.3	0.46	0.49	1.14	576	18.5	2.49	-	0.20 <sup>e</sup>	(573)	33.5
9-1 (140-150	). 244	Lower Eocene	Brown radiolarian/nanno- fossil (siliceous) ooze	10.9	0.42	0.49	1.20	608	19,4	2.54	3.05	0.19	603	35.1
10-4 (146-150)	) 297	Upper Cretaceous	Light olive coccolith- foraminifera ooze	10.7	0.38	0.50	1.13	593	19.5	2.00	2.04	0.12	593	34.3

 TABLE 1

 Major Constituents of Samples from Leg 2, Reported in g/kg (unless otherwise indicated)<sup>a</sup>

### TABLE 1 – Continued

Sample Designation	Depth . Below Sea Bed (m) <sup>b</sup>	Age	Description	Na	K	Ca	Mg	Total Cations (meq/kg)	Cl	SO4	Alk (meq/kg)	HCO3	Total Anions <sup>c</sup> (meq/kg)	Sum
Hole 10 (32°51.7'N, 52°12.9'W, water depth 4697 m) (Continued)														
11-3 (140-150)	385	Upper Cretaceous (Lower Maestrichtian)	Light gray foraminifera/nanno- fossil chalk ooze	10.8	0.45	0.50	1.19	605	19.5	2.45	2.36	0.14	603	35.1
15-2 (90-100)	423	Upper Cretaceous (Lower-middle Campanian)	Pale brown foraminifera/nanno- fossil chalk ooze, zeolitic	10.9	0.45	0.46	1.21	609	19.8	2.48	2.55	0.16	611	35.5
17-3 (135-145)	440	Upper Cretaceous (Lower-middle Campanian)	Dolomitic marl ooze	11.0	0.41	0.58	1.27	618	20.1	2.63			(620)	36.0
18-2 (144-150)	445	Upper Cretaceous (Lower-middle Campanian)	Dolomitic marl ooze, coccolith ooze	10.7	0.40	0.39	1.31	603	19.3	2.58		0.40 <sup>e</sup>	(597)	35.1
18-5 (125-135)	450	Upper Cretaceous (Lower-middle Campanian)	Dolomitic foraminifera chalk ooze	11.0	0.41	0.40	1.21	610	19.6	2.57	2.87	0.18	609	35.4
Hole 11 (29°	°56.6'N, 44°44.8'W, wat	er depth 3556 m)												
1-2 (130-145)	19	Quaternary	Pale brown foraminifera/nanno- fossil ooze	10.9	0.41	0.39	1.29	608	19.7	2.25	2.04	2.04	600	34.9
Hole 11A (2	9°56.6'N, 44°44.8'W, w	ater depth 3556 m)												
4-3 (0-15)	266	Middle Miocene	Nannofossil-foraminifera ooze	10.8	0.41	0.41	1.29	608	19.6	2.53	2.31	0.14	607	35.2
			Mean Seawater (Culkin, 1965)	10.8	0.39	0.41	1.29	608	19.4	2.71		(0.14)	607	35.0

<sup>a</sup>Standard deviation of analyses is given by the following (g/kg): Na 0.3, K 0.01, Ca 0.01. Mg 0.02, CI 0.1, SO<sub>4</sub> 0.02, HCO<sub>3</sub> 0.003. Values of SO<sub>4</sub> and HCO<sub>3</sub> in parentheses are approximate values determined by difference from the cation-anion balance, where insufficient sample did not permit direct determination. The small amount of sample available on this leg contributed analytical scatter. As a result, standard error for sodium is large enough to affect cation-anion balance calculations appreciably. Omission of the minor elements, boron and strontium, leads to error of considerably smaller magnitude. Ammonia was not determined, but the data of Shishkina and Bykova (1961) on pore water from piston cores in Atlantic bottom sediments suggests that NH<sub>4</sub> should probably not exceed 0.5 meq/kg for alkalinities of the order obtained here.

<sup>b</sup>Depths below sediment surface are given to the nearest meter because of positional uncertainties owing to incomplete recovery of core. In some cases, the margin of uncertainty may be even greater.

<sup>C</sup>Anion sum comprising Cl. SO<sub>4</sub> and HCO<sub>3</sub> ions; values in parentheses are incomplete anion sums.

<sup>d</sup>Sulfate determined by difference in cation-anion balance.

<sup>e</sup>HCO<sub>3</sub> determined by difference, assuming anion excess over cations is entirely due to bicarbonate alkalinity.

## TABLE 2

# Minor Constituents in Leg 2 Interstitial Waters

	Depth Below Sea Bed					
Sample Designation	(m)	Li	Sr	Mn	Ba	В
Hole 8						
1-1 (150)	160	0.49	7.6	5.1	0.09	4
2.3 (0-3)	175	0.84	11.2	8.3	0.04	6
Hole 8A						
1-1 (0-2)	279	0.76	9.9	5.1	<0.04	3
Hole 9						2
5-1 (147-150)	32	0.16	5.8	2.6	<0.04	7
7-4 (125-155)	201	0.17	8.3	2.6	0.09	6
Hole 10						
1-1 (140-150)	30	0.23	11.8	0.9	<0.04	11
2-4 (135-145)	47	0.36	11.5	0.5	<0.04	10
3-2 (140-150)	53	0.30	11.4	0.1	<0.04	10
5-2 (140-150)	77	0.17	8.4	0.1	<0.04	9
7-3 (140-148)	96	0.38	12.9	0.7	<0.04	9
9-2 (140-150)	244	0.27	10.0	0.4	<0.04	7
10-4 (146-150)	297	0.19	6.6	0.3	<0.04	4
11-3 (140-150)	385	0.23	8.5	0.5	<0.04	4
15-2 (90-100)	423	0.13	6.3	0.8	< 0.04	3
1/-3(133-143) 19 2 (144 150)	440	0.10	6.2 5.0	1.2	<0.04	9
18-5 (125-135)	443	0.17	6.9	1.4	<0.04 <0.04	6
Hole 11				5		
1-2 (130-145)	19	0.20	10.9	1.0	0.04	10
Hole 11A						
4-3 (0-15)	266	0.26	20.0	0.3	0.04	9

onboard team and the laboratory workers, and to analytical scatter. Salinity (total salt content) varies somewhat more widely, partly due to analytical scatter for the various constituents, but also due to the ionic changes attributable to diagenetic reaction with the enclosing sediments.

A significant increase in concentration variability on approaching the North American continent occurred for all constituents, but especially for calcium, magnesium and sulfate. Magnesium was consistently depleted with respect to standard sea water by as much as 25 per cent in Holes 4 through 10, especially in the more clayey and siliceous sediments. An exception to the depletion corresponded with the occurrence of dolomitic sediments from 440 to 450 meters in Hole 10.

Potassium tended to show excesses over standard sea water in the upper parts of the sediment column. These excesses diminished irregularly with depth, and as the continent was approached (e.g. Hole 8, near the Hudson Canyon fan off New York, showed depletions comparable to those found in some Gulf of Mexico landderived clays, as reported in Leg 1 (Manheim and Sayles, 1969). These data confirm earlier reports of excesses of potassium in pore waters as noted by Mangelsdorf *et al.* (1969), but also point the way to an explanation of how the inferred losses of potassium to the ocean by diffusion may be compensated by corresponding absorption. The absorption sites may be geosynclinal sediments of terrigenous origin.

### **Minor Constituents**

Among the trace elements, lithium concentrations correspond rather closely to open ocean values (0.19 mg/kg) in Hole 11, and in the deeper levels of Hole 10. Lithium concentrations increase as the continent is approached, as do those of manganese. Barium in excess of 0.05 mg/kg occurs only where sulfate is appreciably depleted in the waters-as in Hole 8. The depletions perhaps correlate with higher organic concentrations and accumulation rates, which may favor sulfate reduction processes. Strontium fluctuates relatively slightly around its sea water value of about 8 mg/kg, whereas boron tends to be enriched in pelagic oozes rich in zeolite components. There is no evidence of an increase in boron concentration with depth, which might bespeak added hydrothermal boron from subsediment rocks.

### CONCLUSIONS

Chloride concentrations in interstitial waters of drill cores from the North Atlantic cluster about 19.7  $^{\circ}/_{\circ\circ}$ and vary with depth from less than 1 per cent to about 2 per cent through Upper Cretaceous sediments. Ionic proportions in the pore waters are closest to those in the present open ocean in the central part of the ocean, and become progressively more divergent as the continents and terrigenous influences are approached. Magnesium is generally depleted in the presence of clayey or siliceous sediments, except in dolomitic sediments; potassium is frequently enriched in the upper sediment column. Except for boron, minor element concentrations (strontium, barium, magnesium, lithium) increase on approaching the continents.

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