35. INTERSTITIAL WATER CHEMISTRY: DEEP SEA DRILLING PROJECT, LEG 11

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INTRODUCTION AND PROCEDURES

The interstitial water received at UCLA from Leg 11 (Miami to Hoboken) consisted of fourteen samples of 5 millimeters each intended for carbon isotope and minor constituent work. No large volume samples for trace element work had been received when this report was written. The samples had been collected at six different drilling sites, and from a variety of sediment types.

All water was forced through a 0.45-micron membrane filter on board ship immediately after squeezing. The samples were then sealed in plastic syringes, and were kept refrigerated, except for time in shipment. Analysis was started as soon as the samples arrived at UCLA; nevertheless, as much as three months had then elapsed since collection.

The analytical procedures currently being used in our pore water program are described in some detail elsewhere (Presley, 1971; Presley and Claypool, 1971). These procedures have evolved as we have sought to obtain more and better data from the small samples available from the Deep Sea Drilling Program. Therefore, the procedures used for Leg 11 may not be exactly as described in the references, but any changes are too minor to warrant mention here.

In addition to pore water, 20 samples of gas taken from Leg 11 sediments were sent to UCLA for analysis. These had been collected by puncturing gas pockets visible through the core liner, and allowing the gas to enter a sealed evacuated tube. Analytical work, including carbon isotope analysis, on these gases is now in progress, and will be reported elsewhere. We will, however, comment briefly in this report on the shipboard gas chromatography performed on these gases.

RESULTS AND DISCUSSION

All data that we have obtained to date from the water samples is given in Table 1, except major cation concentrations, which were omitted since they can be found in the report by Manheim *et al.* (this volume). The pH determination made on board ship is also

given, but the shipboard Σ CO_2 values have been omitted, because, as on previous legs, the laboratory and shipboard values show moderately good agreement, and the laboratory values are more reliable.

The chloride and bromide values given in Table 1 were each determined on approximately 0.2 millimeter of water, and there was in no case a sufficient sample for replicate determinations. For this reason some scatter in the data is to be expected, and one might legitimately question an isolated odd number, such as, the high bromide in the only sample analyzed from Site 104. However, the values for nearby Site 102, where six samples were analyzed, present quite a different case. Here chloride and bromide are found in near-sea-water concentrations in the uppermost sample, but with increasing depth chloride shows a slight decrease in concentration, and bromide a very strong increase. This results in a chloride to bromide ratio of only 40 per cent—that of sea water at 424 meters depth. Our deepest sample from this site came from a depth of 619 meters, and it had more chloride and less bromide than the sample from 424 meters. Thus, the sediment responsible for the extremely low chloride to bromide ratios must be between these depths.

Other constituents—for example, boron, silica, ammonia, and manganese—also show concentrations at a depth of 619 meters which contrast with smooth trends established in shallower samples. This adds confidence to the chloride and bromide values and must indicate some fundamental but unknown change in sediment type or environment somewhere between 424 and 619 meters into the sediment column.

It is unfortunate that we did not receive more samples from Holes 103 and 104 in order to more clearly delineate the changes found at Site 102. This cluster of three holes was drilled into rather unusual sediments containing abundant organic matter which has led to sulfate reduction and pyrite formation. Siderite and other authigenic minerals were also reportedly common. We have asked the Manheim group to analyze the samples they received from Holes 103 and 104 for bromide, and perhaps when their work is completed, and more data is available on mineralogy, some mechanisms for production of this unusual pore water can be suggested. At present we can do little more that point out the phenomenon.

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TABLE 1
Selected Major and Minor Constituents and C^{13}, Interstitial Water, Leg 11

Sample[a] Number	Depth[b] (m)	Age and Description of Sediment[c]	Cl (g/kg)	Br (mg/kg)	B (mg/kg)	Si (mg/kg)	NH_3 (mg/kg)	Mn (mg/kg)	Li (mg/kg)	ΣCO_2[d] (mM/kg)	δC^{13} (PDB)	PH[e]
99A-1-4	5	Pleistocene clayey foram–nanno ooze	19.2	66	–	6.6	7.0	<0.20	0.19	2.24	–	7.4
101-2-3	73	Late Miocene hemipelagic clay, pyrite streaks	19.3	64	4.7	10.9	24.3	0.72	0.37	11.00	-15.3	7.7
101A-1-3	123	Middle Miocene hemipelagic clay, pyrite and siderite	19.7	64	3.9	16.0	38.5	0.69	0.43	10.80	-19.7	7.7
101A-3-2	202	Middle Miocene hemipelagic clay, pyrite and siderite	19.7	64	4.9	7.1	22.5	0.73	0.39	6.08	-17.1	7.7
102-1-5	6	Pleistocene hemipelagic mud with black Fe sulfide	19.1	66	5.4	19.0	16.0	2.00	0.14	18.40	-26.4	–
102-2-5	25	Pleistocene hemipelagic mud, diatoms, Fe sulfide, pyrite	19.3	74	6.4	19.8	10.5	0.82	0.11	23.50	-21.8	7.8
102-4-4	101	Pleistocene hemipelagic mud, nanno-fossils, Fe sulfide	19.4	89	4.8	14.9	14.5	<0.20	0.15	16.20	-1.1	7.9
102-7-5	187	Early Pleistocene hemipelagic clay, SiO_2, $CaCO_3$ fossils	19.1	110	3.6	22.3	47.0	<0.20	0.20	12.40	+3.0	8.1
102-12-4	424	Middle Pliocene firm hemipelagic clay, nannofossils, siderite	18.3	160	1.5	10.2	170.0	<0.20	0.59	5.65	-0.8	7.9
102-17-1	619	Late Miocene indurated clay, nannofossils, pyrite	19.1	100	2.9	17.4	72.0	0.45	0.80	4.54	+1.2	7.4
103-1-5	7	Early Pliocene firm green hemipelagic mud, H_2S, FeS	18.9	66	–	6.5	2.6	0.55	0.18	3.11	-16.7	7.9
104-2-5	44	Middle Miocene soft hemipelagic mud, H_2S, FeS_2	19.3	77	–	14.2	6.3	<0.20	0.54	21.30	-19.9	7.5
106-1-2	2	Quaternary soft hemipelagic mud, FeS layers	19.1	66	5.5	16.1	3.5	3.75	0.16	4.54	- 8.5	7.5
106-3-4	115	Early Pleistocene soft clay with green sand	19.1	71	5.2	11.6	40.0	<0.20	0.12	7.08	-11.3	8.0
Average Sea Water			19.4	67	4.5	0-3	0(?)	0.002	0.17	2.60	0.0	8.1

[a]Hole, core, section.

[b]Depth in sediment column.

[c]From preliminary hole summaries.

[d]Laboratory measurement.

[e]Shipboard measurement.

An easily detectable amount of ammonia was present in all samples received from Leg 11; this is in itself an unusual circumstance. Furthermore, the ammonia in many samples accounted for a considerable percentage of the total alkalinity. In fact, the sample at 424 meters depth in Hole 102 has more than twice as much ammonia (NH_3) as dissolved carbonate on a molar basis. In the decomposition of organic matter, more than six times as much carbon dioxide (CO_2) as ammonia (NH_3) should be produced. It thus appears that large amounts of carbon dioxide have been removed from the pore water. Much of this probably went into authigenic carbonates; we find calcium to be greatly depleted in these waters (see also the chapter by Manheim *et al.*, this volume), and authigenic siderite is a common component of the sediment.

The tendency for carbon-dioxide depletion at depth in the sediment column has been noted at many of the sites from previous legs. However, this loss is usually accompanied by an increase rather than a decrease in calcium concentration. This seems most likely to result from a breakdown or leaching of silicates which releases calcium and supersaturates the pore water with respect to $CaCO_3$ or perhaps dolomite. The formation of authigenic dolomite would also explain the commonly observed decrease in magnesium concentration. The opposite effect, that is, excess of carbon dioxide and resulting calcium depletion occurs only where organic matter is abundant and is being biologically degraded.

The high ammonia concentration seems not to have greatly affected the pH of the pore waters. This observation has been made before, and a discussion of the effects of metabolic products on pore water pH can be found in Presley (1969), and in an expanded and slightly modified form in Ben-Yaakov (in preparation).

The δC^{13} values at shallow depths where very high concentrations of total dissolved carbon dioxide are found show a strong biological influence as we have noted in previous studies (Presley and Kaplan, 1968). Furthermore, the tendency noted on previous legs for the dissolved carbon dioxide to become isotopically heavier with depth is very clearly shown at Sites 101 and 102. When more samples are analyzed, and when isotope work on the solid phases is conducted, the mechanism for this light isotope depletion with depth may be determined. At present we can only suggest that it is most likely related to exchange with solid carbonate phases and dissolved hydrocarbon gases.

The interstitial gas determinations made on board ship have been summarized in Table 2. These values were obtained by simply summing the peak heights shown on the chromatograms and finding what percentage of that sum is accounted for by each individual peak. This assumes that the chromatograph is equally sensitive to

TABLE 2
Shipboard Analysis of Gases Released by Leg 11 Sediment

Sample	Depth (m)	Age	"Air" %	CH_4 %	C_2H_6 %	CO_2 %
103-3	100	Late Miocene	48	51	0.01	0.5
103-4	175	Late Miocene	36	63	0.01	1.1
103-5	252	Middle Miocene	41	58	0.02	0.6
104-2	40	Middle Miocene	44	53	0.01	2.2
104-3	67	Middle Miocene	26	72	0.01	1.8
104-4	138	Middle Miocene	38	61	0.01	2.6
104-6	224	Middle Miocene	39	59	0.03	2.4
104-7	300	Middle Miocene	41	57	0.04	1.9
104-8	405	Middle Miocene	40	56	0.03	3.5
104-9	500	Middle Miocene	41	56	0.04	3.2
106B-2	455	Early Pliocene	42	58	0.01	0.3
106B-4	760	Middle Miocene	44	50	0.04	0.5
106B-5	940	Middle Miocene	58	41	0.05	1.0

all gases, and should therefore be considered only a rough estimate of the actual composition of the injected gas. Furthermore, the injected gas may be quite different from the actual sample gas, because in this procedure there is no provision for either knowing or controlling the pressure of the gas. Thus, if the gas is under a reduced pressure, air will be sucked into the sampling syringe and become part of the injected sample.

A few samples have now been injected into a chromatograph for oxygen determination. If we make the reasonable assumption that this oxygen represents atmospheric contamination during sampling, the air peaks shown by the shipboard chromatograph are considerably too high. An adjustment would, however, little affect the CH_4 to C_2H_6 to CO_2 ratios, which are the primary concern in this study. These ratios have now been determined in the laboratory for a few samples, and in general give values close to those in Table 2. This laboratory data will be reported in detail when the analyses are completed.

This preliminary work on the interstitial gases shows the Leg 11 samples to be somewhat richer in CO_2 than those from Leg 10, and to contain much less C_2H_6 than some of the Leg 10 samples.

The silicon values shown in Table 1 are probably too high due to a temperature of squeezing effect, but it is not possible at this time to estimate the magnitude of the effect. The values found here are similar to those found on previous legs, being much higher than sea water, and approaching saturation with respect to amorphous silica where it is reportedly abundant.

Lithium concentrations have typically increased with depth in the sediment column at previous sites, and a very strong enrichment was found in the deepest samples analyzed from Leg 11. However, at Site 102 a lithium depletion was found at intermediate depths, a phenomenon for which we have no explanation. Boron was also depleted at depth at this site, as it has been at a number of sites on previous legs.

Manganese, as usual, is highly and unpredictably variable in concentration. Site 106 gives yet another example of a phenomenon which we have pointed out many times, that is, a high dissolved manganese concentration in reducing sediments at greater depth. This once again shows that the often proposed model of manganese mobilization at depth, and an upward migration and precipitation, appears to be unworkable in many environments.

ACKNOWLEDGEMENTS

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