22. INTERSTITIAL WATER CHEMISTRY: DEEP SEA DRILLING PROJECT, LEG 14

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INTRODUCTION AND PROCEDURES

The interstitial water received at UCLA from Leg 14 (Lisbon, Portugal to San Juan, Puerto Rico) consisted of thirty-one samples of 5 milliliters each intended for carbon isotope and minor element constituents. No large volume samples for trace element analysis were collected. The samples were obtained at six different drilling sites, and from a variety of sediment types.

All water was forced through a 0.45μ 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 essentially those 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 provided by the Deep Sea Drilling Program. Therefore, in some instances, the procedures used for Leg 14 may be modifications of those described in the references, but any changes considered are not sufficiently significant to warrant a separate description here.

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, as they are discussed in the report by Sayles et al., this volume. The shipboard total carbon-dioxide (ΣCO_2) values which were given in our previous reports have been omitted here, because, as on previous legs, the laboratory and shipboard values show a 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 milliliter of water, and there was in no case, 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 value. The data show very pronounced trends in chloride and bromide concentration, suggesting that they (Cl/Br ratios) are geochemically significant, and should be considered when reconstructing the geological history of this area.

Samples from three sites, 137, 141 and 142, show chloride and bromide values differing only slightly from

values typical of average present-day sea water. This is in spite of the fact that the samples were recovered from as deep as 429 meters, and were reportedly as old as Cretaceous. Samples from Sites 139, 140 and 144 show a pattern of increasing chloride and bromide concentration with depth in the sediment column. The trend is most pronounced at Site 139 where Early Miocene siliceous ooze from 660 meters depth gave pore water with a chloride concentration of 45 parts per thousand, and bromide of 158 parts per million. Thus, both constituents show a greater than twofold enrichment over average sea water. This results in a Cl/Br ratio of 285, which is probably insignificantly different from the sea water value of 289.

The deepest pore waters at Sites 140 and 144 were enriched in chloride and bromide by a factor of 1.4, relative to normal sea water, in contrast to the 2.3 enrichment factor at Site 139, but at these sites, too, the Cl/Br ratio remains close to that of sea water. The ratio drops to 275 in the two deepest samples at Site 144. This represents an approximate 5 per cent decrease and is larger than our usual analytical error, however it is still too small to warrant any speculation as to its significance. It seems likely that the high salinity pore water resulted from a simple evaporative concentration of sea water at some time in the geologic past, and that no evaporite precipitation or solution, which would alter the Cl/Br ratio, was involved. It is also possible that diffusion may be occurring from entrapped brines—but presently we have no information to support this possibility.

Pore water from Site 139 showed other unusual characteristics in addition to its high chloride and bromide content. For example, it was found to be highly enriched in ammonia. Ammonia concentrations increased with depth to a value of 12 millimolar in the deepest sample analyzed. This same sample had less than 4 millimolar total dissolved carbon dioxide, so one can see the importance of ammonia in determining alkalinity in this case. Similar instances have been noted previously, for example in some Leg 11 samples.

The phenomenon of ammonia being much higher in concentration than carbon dioxide deserves comment, because in the decomposition of marine organic matter, more than six times as much carbon dioxide as ammonia should be produced. It thus appears that large amounts of carbon dioxide have been removed from the pore waters, even if ammonia has been completely inert. The most obvious assumption is that the lost carbon dioxide was involved in authigenic carbonate formation within the sediment column, although we have no direct proof of this. One can easily show that the pore waters are greatly super-saturated with calcium carbonate, especially at Sites 137, 139, 141 and 144, where calcium-ion concentration

TABLE 1
Selected Major and Minor Constituents and δC^{13}, Interstitial Water, Leg 14

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 (mM/Kg)	δC^{13} (PBD)
137-1-5	60	Unknown age; brown silty clay	19.5	68	6.3	7.9	6.9	0.3	0.25	1.85	−0.58
137-2-1	100	Unknown age; red silty zeolitic clay	20.0	72	5.3	10.7	3.6	1.3	0.24	1.52	−0.79
137-2-CC	101	Unknown age; red silty zeolitic clay	19.7	68	4.4	17.7	4.1	1.3	0.26	1.71	−1.51
137-3-6	144	Unknown age; brown slightly zeolitic clay	19.7	68	5.2	13.8	9.1	3.1	0.34	1.07	+0.30
137-6-CC	225	Late Cretaceous; brown zeolitic clay	19.6	69	2.4	25.7	11.3	3.7	0.38	0.88	−2.85
137-7-CC	265	Late Cretaceous; banded CaCO$_3$-pyrite-clay	19.8	69	1.8	2.4	−	1.2	0.47	0.13	−11.22
137-8-CC	274	Late Cretaceous; foraminiferal-nannofossil chalk	20.2	72	3.3	8.2	6.1	2.3	0.42	0.88	−5.48
137-9-5	280	Late Cretaceous; foraminiferal-nannofossil chalk	20.1	70	2.9	5.0	4.0	1.7	0.39	0.41	−5.34
137-10-5	290	Late Cretaceous; nannofossil marl/chalk	20.0	69	2.6	7.7	18.6	1.7	0.47	0.37	−5.47
139-1-2	117	Early Pliocene; nannofossil chalk ooze, H$_2$S	23.7	79	5.2	24.3	61.0	<0.2	−	10.97	−8.27
139-2-4	231	Early Pliocene; nannofossil chalk ooze	29.8	99	6.7	13.1	98.0	<0.2	1.14	9.01	−
139-3-CC	354	Middle Miocene; nannofossil marl/chalk	36.7	123	6.8	19.3	156.0	<0.2	2.65	5.36	+1.99
139-4-CC	463	Middle Miocene; silty nannofossil marl	40.1	136	6.3	14.1	212.0	<0.2	2.78	3.98	+4.36
139-7-3	660	Early Miocene; siliceous, ooze, nannofossils	45.0	158	8.1	19.7	−	<0.2	3.16	6.03	+9.69
140-1-6	98	Pliocene; white chalk ooze	20.7	72	5.3	3.8	12.6	<0.2	0.30	3.58	−
140-2-6	210	Early Miocene; gray silty diatom ooze	23.0	77	5.2	24.8	16.2	0.7	0.68	4.50	−10.84
140A-2-6	244	Middle Eocene; siliceous clay, sand lenses	23.5	83	4.2	24.6	14.1	1.3	0.77	5.00	−8.77
140-3-2	314	Middle Eocene; siliceous gray silty clay	25.4	87	3.8	19.3	24.2	1.0	0.96	3.76	−
140-4-3	372	Middle Eocene; gray-green silty clay	26.0	−	−	21.0	26.6	−	0.74	4.14	−30.20
140-6-CC	519	Late Cretaceous; banded silty clay, dolomite	27.7	93	5.3	18.9	41.8	<0.2	0.44	2.17	−
141-1-6	14	Early Pleistocene; chalk ooze	19.6	69	5.0	−	3.8	<0.2	0.18	1.97	−3.00
141-2-5	21	Late Pliocene; chalk ooze	19.6	70	4.9	2.9	3.3	<0.2	0.18	1.75	−
141-4-4	38	Early Pliocene; chalk ooze	19.7	70	5.4	3.3	1.5	<0.2	0.19	1.77	−
141-7-6	88	Unknown age; brown silty clay	19.4	70	6.3	6.8	0.7	1.9	0.24	1.72	−2.95
141-9-5	198	Unknown age; mottled zeolitic clay	19.3	68	6.4	9.4	6.7	2.3	0.34	0.98	−9.07
142-1-6	116	Pleistocene; dark clayey silt and sand	19.1	65	4.0	4.2	35.0	<0.2	0.05	3.91	−
142-2-4	216	Pleistocene; dark silty sand	19.2	67	3.5	4.9	46.0	<0.2	0.07	2.80	−1.85
142-3-CC	301	Pleistocene; nannofossil marl with sand	19.4	66	3.7	3.1	38.0	<0.2	0.11	1.91	−3.88
142-4-3	370	Pliocene; varicolored chalk ooze	19.7	68	4.1	2.4	30.0	<0.2	0.34	2.21	−2.65
142-5-CC	429	Pliocene; CaCO$_3$ clay and sand, detrital sand	19.8	68	4.3	2.4	26.0	<0.2	0.44	1.93	−3.93
144B-1-6	9	Middle Oligocene; foraminiferal-nannofossil chalk	19.3	67	4.7	11.0	1.8	0.6	0.19	2.18	−0.18
144B-2-5	17	Middle Oligocene; foraminiferal-nannofossil chalk	19.8	67	4.5	20.0	3.6	<0.2	0.23	2.43	−1.80
144A-1-2	23	Middle Oligocene, nannofossil-foraminiferal chalk	19.9	70	3.8	13.1	2.6	<0.2	0.28	1.30	−
144A-2-6	47	Early Oligocene; nannofossil-foraminiferal chalk	20.4	71	3.4	−	5.0	<0.2	0.35	1.20	−3.56
144-1-6	65	Middle Eocene; chalk-marl ooze, SiO$_2$	20.7	71	4.0	19.6	4.7	<0.2	0.40	3.12	−1.29
144A-5-CC	189	Late Cretaceous; interbedded shale and lime	26.7	97	6.9	16.9	17.5	<0.2	1.08	1.66	−
144-4-3	217	Late Cretaceous; laminated limestone	27.7	101	6.7	14.5	19.2	<0.2	1.12	2.79	−2.53

[a]Hole, core, section.

[b]Depth in sediment column.

[c]From preliminary hole summaries.

increases sharply with depth (see report by Sayles *et al.* this volume) leading to greater super-saturation.

Calcium ion increase with depth, accompanied by decreases in magnesium and potassium, have been a common pattern throughout the Deep Sea Drilling Project work, but the mechanisms of the changes are still not known. If they are due to silicate reactions which release calcium and take up magnesium and potassium then this calcium could react with dissolved carbonate to produce solid carbonate phases, resulting in the decrease in total dissolved carbon dioxide commonly observed. On the other hand, dolomite formation by replacement of calcite could take up magnesium, release calcium, and lower total carbon dioxide due to the low solubility of dolomite.

Where large amounts of biogenic carbon dioxide are being produced in the sediment column, calcium-ion concentration can be lowered below that found in sea water. This is seen in our shallowest sample—Site 139. Site 139, although 117 meters deep and Pliocene in age, still shows strong biological influence by retaining about four times the sea water value of total carbon dioxide which in addition is isotopically light (Presley and Kaplan, 1968). Isotopically heavy CO_2 (δC^{13} = +9.69) is not often found in interstitial water. Its presence has been explained by Nissenbaum *et al.* (1972) as resulting from the formation of methane by hydrogenation of carbon dioxide according to the following equation:

$$CO_2 + 4H_2 \qquad CH_4 + 2H_2O$$

This follows a kinetic relationship with an isotope effect equal to 1.05-to-1.06 and probably follows a Rayleigh distillation-type relationship. Thus, the released methane will be isotopically light, whereas the residual carbon dioxide will become enriched in C^{13}. This may also be partially responsible for the depletion of dissolved carbon dioxide. If this methane should become oxidized near the surface water interface, the resulting carbon dioxide will be anomalously light. A mixture of this C^{12}-enriched carbon dioxide with normal dissolved carbon dioxide may be the cause for the δC^{13} value in Sample 140-4-3.

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 abundant in the solid phase.

Lithium concentration increases with depth in the sediment column as found at previous sites. The strongest enrichment in this element was found in the deepest samples analyzed from all Leg 14 cores with the exception of those from Site 140. The extremely high enrichment in lithium found at Site 139 (up to thirty-fold) may be related to the development of the high salinity water found at this site.

Boron concentrations show no pronounced trends in these samples, and differ from typical sea water values by less than a factor of two in all cases.

As usual, manganese is highly unpredictably variable in concentration. Sites 139 and 142 give yet another example of a phenomenon which we have pointed out many times, that is a low concentration of dissolved manganese in reducing sediments. It is not yet clear whether this is due to low content of manganese in the solid phase of reducing sediments or possible removal of solubilized manganese at an early state in sedimentation.

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