13. INTERSTITIAL WATER CHEMISTRY: DEEP SEA DRILLING PROJECT, LEG 7[1,2]

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INTRODUCTION

The interstitial water received at UCLA from Leg 7 (Guam to Hawaii) consisted of forty-two samples of approximately 5 milliliters each, three samples of approximately 10 milliliters each, and three samples of approximately 100 milliliters each. These pore waters had been squeezed from sediments consisting primarily of biogenic ooze, and had been collected at five different drilling sites along the route.

All water was filtered through a 0.45-micron membrane filter immediately after squeezing. The 5-milliliter samples were sealed in plastic syringes, and were kept refrigerated except for the time in shipment to UCLA from Scripps Institute of Oceanography. The 10 and 100 milliliter samples were frozen in polyethylene bottles on board ship, and were kept frozen until analysis had begun.

Analysis was started as soon as the samples had arrived at UCLA, nevertheless as much as three months had then elapsed since collection.

EXPERIMENTAL PROCEDURES

The analytical procedures currently being used in the UCLA interstitial water program are described elsewhere (Presley, this volume; Presley and Claypool, this volume). These procedures have evolved during the course of the Deep Sea Drilling Program, as a result of attempts to obtain more and better data from the small samples available.

Although the procedures used for the Leg 7 samples are not exactly the same as those described in the references given above, most changes are too minor to warrant mention. An exception is the use of a special manometer for measuring carbon dioxide volumes, as described by Presley and Claypool. This device was used for Leg 8 and subsequent samples, but not for the Leg 7 samples, which were measured with a conventional U-tube manometer.

RESULTS AND DISCUSSION

The data obtained from the 5-milliliter samples are presented in Table 1; major cation concentrations have been omitted, because these can be found in the report by Manheim *et al.* Data obtained from the frozen samples can be found in Table 2. All frozen samples were also analyzed for phosphate, using a technique which would have detected 1 p.p.m. phosphate (PO_4), but none was found.

The trace metals iron, cobalt, nickel and copper can only be determined on relatively large volume samples by the present techniques, and these are limited in number to four or fewer on each leg by a directive from the Deep Sea Drilling Project interstitial water panel. The three samples collected on Leg 7 showed concentrations similar to those found in the biogenic oozes from Leg 6, except for the high iron value found at Site 62, and the high cobalt value at Site 66.

The significance of these high trace element concentrations is difficult to assess when so few samples are available for analysis, and when sampling and shipboard handling are not performed by the investigators. It is interesting to note, however, that the scientists on board ship made a strong complaint in the preliminary hole summaries about the abundance of iron rust from the drill pipe which contaminated all sediment collected at Site 65, yet the interstitial water from this site was not enriched in any trace metal when compared to other Pacific samples. Rather, it is the sample from Site 62, where no report of rust contamination is noted, that proved to be greatly enriched in iron.

The sediment which yielded the iron-rich interstitial water is reported to contain "shards of fresh colorless volcanic glass .... most (of which) have pyrite crystallites and rarely rosettes growing on their surfaces" (preliminary hole summary). Obviously then, there has been a mobilization of iron at this site at some time in the past, but it is not possible to say when this happened, or if conditions are still favorable for maintaining iron in solution. The UCLA data shows normal sea water sulfate in the interstitial water at all depths, thus no active reducing process is now at work that would tend to mobilize iron. Perhaps the high iron concentration is due to contamination, or to oxidative lowering of pH after coring, but the need for more work on this type of sediment is suggested.

The high cobalt value at Site 66 was accompanied by a relatively high manganese concentration, but more normal iron, nickel and copper concentrations. There is no obvious reason for the apparent cobalt enrichment.

Manganese concentrations are, as has been the case with samples from previous legs, highly variable and apparently independent of location or depth in the sediment column. The authors have noted previously that pure calcareous oozes give pore water with low manganese concentrations, and that relationship holds for the present samples. Only where appreciable clay is mixed with the calcareous ooze, such as the tops of Holes 62 and 63, has manganese enrichment been found. Some of the radiolarian oozes, such as those in Hole 66, show high concentrations of dissolved manganese, but perhaps here too, something other than the skeletal material contributed the manganese.

Boron concentrations tend to be somewhat higher than is typical of seawater, but there is no evidence for either contributions from depth or uptake by clays.

The chloride and bromide values are in all cases close to those typical of seawater, although some samples seem to be enriched in both by a few percentage. This enrichment is most likely the result of evaporation during storage and handling of samples, that is, both of these elements are relatively inert to diagenetic changes occurring in the sediment column. Only where there is evidence of the presence of evaporites, such as in the Gulf of Mexico, have chloride and bromide concentrations been found to be significantly different from those of the overlying seawater.

The first column of total carbon dioxide values (ΣCO_2) given in Table 1 were obtained by a manometric measurement of the carbon dioxide evolved from an acidified sample of water. The small sample size makes accurate measurement with a conventional manometer difficult, nevertheless, with a few exceptions there is moderately good agreement between the authors' values and those of Takahashi (personal communication) for the samples that both groups analyzed. There is also good agreement, again with a few exceptions, between the UCLA laboratory values and the values from the shipboard gas chromatograph (Table 1). The shipboard determination is made using only 0.2 milliliter of water, therefore, analytical scatter is difficult to avoid. Considering the difficulties in both measurements, the ± 10 per cent agreement shown by most samples is as good as can be expected. The precision and accuracy of the UCLA laboratory measurement is expected to improve on future samples when a specially-designed manometer will be used. Hopefully, the shipboard measurements can also be made more precise.

As can be seen from Table 1, most of the Leg 7 interstitial waters proved to be somewhat enriched in carbon dioxide compared to normal seawater, but only in Hole 64 was the enrichment by as much as a factor of 2. Samples from previous legs have often shown a tendency for depletion of carbon dioxide at depth, and this can be seen at Site 62. The concentration at other Leg 7 sites is almost constant with depth, however, and the factors necessary to cause a carbon dioxide depletion, probably by carbonate precipitation, are unknown.

The C^{13}/C^{12} ratios of the total dissolved carbonate from the Leg 7 samples show relatively minor variation with depth and position, compared to the large isotopic variations found in interstitial water from near shore sediments by Presley and Kaplan (1968). These authors show how biological degradation of organic matter continues after burial, leading to an increase in total dissolved carbonate and a lowering of the C^{13}/C^{12} ratio.

The δC^{13} of the Leg 7 interstitial water carbonate carbon is generally somewhat lower than the +0.5 per mille characteristic of deep ocean water (Deuser and Hunt, 1968) except for a few samples from below 100 meters depth in the sediment column. This seems to indicate a small but measurable contribution of carbon dioxide from oxidizing organic matter, a conclusion which is consistent with the slight enrichment in dissolved carbonate shown by most samples. It is probably unrealistic to place much significance on small changes in the isotope ratio with depth, in view of the possibilities of contamination or fractionation of the small samples during handling. Nevertheless, some of these changes may be real, and if so, give further proof of gradients being maintained despite diffusion.

REFERENCES

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TABLE 1
Selected Major and Minor Constituents and δC^{13}, Interstitial Water, Leg 7

Sample[a] Designation	Depth[b] (m)	Age and Description of Sediment	Cl (g/kg)	Br (mg/kg)	B (mg/kg)	Mn (mg/kg)	ΣCO_2 (mM/kg)	ΣCO_2[c] (mM/kg)	δC^{13} (ΣCO_2)	pH[d]
62.1-1-3	10	Upper Pleistocene; marly calcareous ooze	19.8	69	6.3	1.55	—	2.02	—	7.38
62.1-4-6	42	Upper Pleistocene; marly calcareous ooze	19.5	69	5.8	0.10	—	—	-3.93	7.63
62.1-6-5	62	Upper Pleistocene; chalk ooze, trace SiO_2 and pyrite	19.5	68	6.3	0.10	2.28	2.10	-2.46	7.27
62.1-8-5	80	Lower Pleistocene; chalk ooze, trace SiO_2 and pyrite	20.3	71	—	0.10	2.55	2.32	-5.30	7.24
62.0-1-2	94	Lower Pleistocene; chalk ooze, trace SiO_2, ash	19.3	—	—	0.10	3.34	3.34	-0.69	7.69
62.1-14-5	137	Lower Pleistocene; chalk ooze, trace SiO_2, ash	19.5	67	6.7	0.07	1.86	1.76	-2.77	7.46
62.1-16-5	155	Upper Miocene; chalk ooze, trace SiO_2, and chalk	19.8	69	—	0.07	2.08	2.02	-1.71	7.26
62.1-18-2	166	Upper Miocene; chalk ooze, trace SiO_2, and chalk	19.8	69	6.0	0.07	2.37	2.10	-1.40	7.56
62.1-20-5	194	Upper Miocene; chalk ooze, trace SiO_2, and chalk	19.9	71	—	0.07	2.46	2.28	-1.04	7.43
62.0-2-2	208	Upper Miocene; chalk ooze, trace SiO_2, and chalk	19.5	68	6.5	0.07	3.11	2.85	-0.01	7.48
62.1-24-5	233	Upper Miocene; chalk ooze, trace SiO_2, and chalk	19.7	69	6.8	0.07	2.80	2.15	-1.46	7.51
62.1-26-2	248	Upper Miocene; chalk ooze, trace SiO_2, and chalk	19.9	70	—	0.07	2.39	2.32	—	7.49
62.1-28-5	269	Upper Miocene; chalk ooze, trace SiO_2, and chalk	19.6	65	6.3	0.07	2.99	2.98	-1.58	7.41
62.0-3-2	301	Upper Miocene; indurated chalk	20.0	65	—	0.07	—	2.21	—	6.72
62.1-34-5	325	Upper Miocene; indurated chalk	19.9	70	—	0.07	—	1.09	—	7.96
62.1-36-2	339	Upper Miocene; indurated chalk	19.5	66	4.3	0.07	—	0.98	—	8.10
62.0-4-4	400	Lower Miocene; indurated chalk	19.5	67	4.9	0.07	1.64	1.53	-2.86	7.50
63.0-1-5	8	Quaternary; mottled yellow-brown clay, manganese nodules	19.0	67	5.5	4.40	2.96	2.21	-2.21	7.57
63.2-2-3	23	Lower Pleistocene; mottled gray-green marly ooze, FeS	19.8	68	5.5	1.40	—	—	—	—
63.0-2-3	64	Upper Miocene; light green chalk ooze, FeS_2	20.4	—	6.3	0.15	2.73	3.11	—	7.41
63.1-5-2	103	Upper Miocene; mottled chalk ooze, trace ash	20.1	69	5.5	0.15	3.07	3.47	+0.09	7.34
63.0-3-2	139	Middle Miocene; mottled chalk ooze, trace ash	20.2	70	—	0.15	—	3.56	-1.41	7.28
63.1-9-2	140	Middle Miocene; mottled chalk ooze, trace ash	19.7	69	5.9	0.15	—	2.61	—	7.27
63.1-11-5	161	Middle Miocene; mottled chalk ooze, trace ash	19.7	—	5.4	0.10	3.06	3.66	+1.70	7.47
63.1-13-3	177	Lower Miocene; mottled chalk ooze, trace ash	19.5	66	5.8	0.15	—	4.68	—	7.36
63.0-4-2	233	Lower Miocene; light pyritic chalk	19.8	—	5.5	0.15	3.26	2.58	+0.31	7.41

TABLE 1 – *Continued*

Sample[a] Designation	Depth[b] (m)	Age and Description of Sediment	Cl (g/kg)	Br (mg/kg)	B (mg/kg)	Mn (mg/kg)	ΣCO_2 (mM/kg)	ΣCO_2[c] (mM/kg)	δC^{13} (ΣCO_2)	pH[d]
64.0-1-3	4	Quaternary; nannofossil chalk ooze, trace radiolarians	20.0	–	6.3	0.53	4.19	3.43	–	7.82
64.0-2-2	101	Lower Pliocene; nannofossil chalk ooze, trace radiolarians	19.5	66	5.1	<0.07	4.08	4.92	-1.20	7.72
64.0-3-4	207	Upper Miocene; nannofossil chalk ooze, trace radiolarians	19.5	66	5.9	<0.07	5.27	5.88	-0.33	7.46
64.0-4-5	311	Middle Miocene; nannofossil chalk ooze, trace radiolarians	19.7	70	6.6	<0.07	4.57	4.42	-0.39	7.49
64.1-1-6	441	Lower Miocene; chalk-chalk ooze, trace radiolarians	19.8	70	7.5	<0.07	5.30	5.05	+1.39	7.41
65.0-3-4	25	Lower Pliocene-Upper Miocene dark brown radiolarian ooze	19.8	70	4.8	0.42	2.50	3.79	-1.84	7.51
65.0-9-6	82	Lower Miocene; light brown radiolarian ooze	19.8	70	5.5	0.48	2.03	3.36	-5.28	7.70
65.0-11-5	98	Lower Miocene; dark brown radiolarian ooze	19.3	67	6.0	0.19	3.80	3.61	–	7.68
65.0-16-5	144	Upper Eocene radiolarian ooze, rock chips	19.6	66	–	<0.07	3.80	3.06	-0.81	7.69
65.1-4-5	160	Middle Eocene; radiolarian ooze, rock chips	19.8	70	5.2	<0.07	3.63	3.73	-1.98	7.69
66.1-2-4	26	Pliocene; light yellow-brown radiolarian ooze	19.2	67	5.9	<0.07	3.01	–	-1.69	7.58
66.1-6-5	64	Middle Miocene; light yellow-brown radiolarian ooze	19.3	67	5.3	1.65	3.11	3.19	-0.86	7.59
66.0-2-2	82	Middle Miocene; light yellow-brown radiolarian ooze	19.5	71	5.1	1.85	–	3.52	-2.04	7.65
66.0-3-5	124	Lower Miocene-Upper Oligocene; radiolarian ooze	19.4	–	5.8	2.45	3.38	3.52	+2.40	7.53
66.0-6-3	169	Oligocene; stiff zeolitic (?) brown clay	19.6	71	–	0.48	3.24	3.32	+0.26	7.79
66.0-9-3	191	Cretaceous; Fe-Mn clay, volcanic debris	19.3	69	5.3	0.24	2.92	3.10	-0.82	7.66
Surface Sea Water			19.7	67	4.8	0.002	2.60	2.60	0.00	8.10

[a] Hole, core and section sampled.
[b] Refers to depth in sediment column.
[c] Data from UCLA gas chromatograph on board ship.
[d] Data obtained on board ship using UCLA equipment.

TABLE 2
Trace Constituents of Interstitial Water, Leg 7, From Large Volume ($\approx$ 100 ml) Squeezing

Sample Designation	Depth In Column (m)	Fe μg/kg	Co μg/kg	Ni μg/kg	Cu μg/kg	Mn μg/kg	Si mg/kg
62.1-12-2	111	105	2.1	30	20	100	24.4
65.0-9-6	82	20	1.0	11	19	345	26.7
66.0-7-4	178	19	7.4	29	18	1000	8.8
Sea Water[a]	0	10	0.1	2	3	2	3.0

[a]Goldberg, 1965.