

26. INTERSTITIAL WATER CHEMISTRY: DEEP SEA DRILLING PROJECT, LEG 6¹

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INTRODUCTION

The interstitial water received at UCLA from Leg 6 (Hawaii to Guam) consisted of forty-nine samples of approximately 5 milliliters each, four samples of approximately 100 milliliters each, and four samples of approximately 10 milliliters each. These pore waters had been squeezed from sediment consisting primarily of biogenic oozes and volcanic ash, and had been collected at fourteen sites in the NW Pacific Ocean and Phillipine Seas. All samples were filtered through a 0.45-micron filter immediately after collection. The 5-milliliter samples were sealed in plastic syringes on board ship by heat sealing the tip and pouring RTV silicon rubber around the plunger. These and the large samples, stored in polyethylene bottles, were refrigerated except for the time in shipment to UCLA from SIO. The four 10-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 after collection.

EXPERIMENTAL PROCEDURES

The experimental procedures used are essentially the same as those briefly outlined in the Leg 5 report (Presley *et al.*), but some modifications were made in an attempt to obtain more reliable data. As has been noted in previous leg reports, the small size of the samples leads to considerable analytical difficulty when data for many constituents are desired. The authors nevertheless believe that using the methods that have been developed in the course of this work they can obtain reliable concentrations for at least ten elements, sulfate and total dissolved carbonate (as well as S^{34}/S^{32} and C^{13}/C^{12} ratios) using only 5 milliliters of sample. Detailed experimental procedures are described elsewhere in this volume.

RESULTS AND DISCUSSION

The data obtained from the 5 milliliter samples are presented in Table 1, but major cation concentrations have been omitted from this report because these can be found in the report by Manheim *et al.* (this volume). The authors' data for these cations agree reasonably well with those of Manheim, with a few notable exceptions. Data obtained from the 100 milliliters and the frozen samples can be found in Table 2.

The trace metals iron, cobalt, nickel and copper can only be determined on relatively large volume samples by present techniques, and these samples are limited in number to four on each leg by a directive from the JOIDES Interstitial Water Panel. The four samples from Leg 6 showed somewhat higher concentrations of iron, cobalt and copper than were typical of previous Pacific samples (Leg 5), but similar nickel concentration. The values are also generally higher than those found in the Atlantic samples (Presley and Kaplan, Leg 4 report), and are higher than those characteristic of oxidizing sediments collected by piston coring (Brooks *et al.*, 1967).

The iron, cobalt and copper concentrations show less variation than values obtained previously. This could be due to the more uniform lithology of the Leg 6 sediments, but the small number of samples available makes any generalization difficult. It does, however, appear that biogenic oozes yield pore waters somewhat enriched in these trace metals, when compared to terrigenous-derived sediments.

The silicon values given in Table 2 are similar to those determined on previous samples, falling between saturation with respect to quartz and saturation with respect to amorphous silica. A few samples from previous legs have more closely approached saturation with respect to amorphous silica than any of the present samples do, despite the high volcanic glass content of some of these, especially those at Site 53. Manheim's silicon data for this and other sites also seem to indicate undersaturation with respect to amorphous silica. Apparently here, and in most places, dissolved silica is taken up in forming authigenic silicate minerals, preventing a buildup to saturation with amorphous silica.

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TABLE 1
Interstitial Water Chemistry, Leg 6

Sample ^a Designation	Depth ^b (m)	Age	Description	Cl (g/kg)	Br (mg/kg)	B (mg/kg)	Mn (μ g/kg)	Zn (μ g/kg)	Li (μ g/kg)	Total CO ₂ (mm/kg)	Total ^c CO ₂ (mm/kg)
45.1-1-1	3	Unknown	Brown zeolitic clay, 5% ferric oxide	19.2	62	7.0	100	545	200	2.89	—
47.0-1-3	4	Pleistocene	Layered gray-yellow-brown foraminiferal-nannoplankton ooze	19.0	70	4.8	870	660	176	2.91	2.24
47.2-2-3	22	Lower Pleistocene	Nannoplankton-foraminiferal ooze, 25% volcanic ash	19.4	65	3.6	340	585	156	2.16	2.01
47.2-4-3	40	Upper Pliocene	Nannoplankton-foraminiferal ooze, 5-10% glass	19.6	—	3.5	430	900	171	2.12	—
47.2-7-1	64	Lower Eocene	Nannoplankton-foraminiferal ooze	19.7	64	4.3	440	840	156	3.21	1.94
47.2-10-2	93	Lower Paleocene	Nannoplankton-foraminiferal ooze	19.5	—	4.1	175	1170	161	4.09	2.10
48.2-1-2	54	Lower Pliocene-Upper Miocene	Nannoplankton chalk ooze	19.7	69	3.3	245	600	161	1.56	0.94
49.0-1-2	3	Pleistocene	Brown mud, up to 20% glass	19.4	—	3.6	<50	540	185	2.87	1.94
49.1-1-3	7	Cretaceous (?)	Brown zeolitic mud, manganese nodule, limonite	19.3	71	4.9	105	440	200	3.29	2.18
50.1-1-4	9	Pleistocene	Light yellow-brown nannoplankton clay, siliceous fossils, 20%	19.1	—	2.1	210	530	180	2.58	2.44
50.1-3-5	30	Unknown	Dark yellow zeolitic clay, 20% limonite	19.4	69	5.0	<50	560	200	2.97	1.98
51.1-1-5	25	Pleistocene	Gray-brown sandy diatom-radiolarian volcanic mud	19.4	75	2.2	9415	320	176	1.85	1.91
51.0-1-4	120	Miocene	"Drilling breccia" fragments, zeolitic clay	19.1	—	6.8	215	1070	234	1.37	2.04
52.0-1-4	6	Unknown	Brown ashey clay, 20% glass, 5% zeolite	19.7	—	3.2	215	845	171	2.21	1.70
52.0-3-2	20	Unknown	Light red-brown clay, 8% glass, 4% zeolite	19.1	62	3.4	4085	680	180	—	1.77
52.0-5-3	40	Unknown	Dark gray-brown clay, 20% glass, 5% zeolite	19.2	75	6.1	370	490	195	2.96	1.57
53.1-1-4	6	Unknown	Dark yellow-brown zeolitic clay, limonite, etc., 10%	19.3	—	6.7	100	575	215	1.71	1.54

TABLE 1 – Continued

Sample ^a Designation	Depth ^b (m)	Age	Description	Cl (g/kg)	Br (mg/kg)	B (mg/kg)	Mn (µg/kg)	Zn (µg/kg)	Li (µg/kg)	Total CO ₂ (mm/kg)	Total ^c CO ₂ (mm/kg)
53.2-1-4	18	Upper Miocene	Brown radiolarian silt and volcanic glass	19.7	70	4.8	2800	560	268	1.24	0.61
53.1-2-5	28	Upper Miocene	Dark gray-brown sandy-to-clayey ash, with Radiolaria	20.0	–	4.3	4225	605	224	–	0.77
53.1-3-4	60	Middle to Upper Miocene	Gray silty-to-clayey volcanic ash	19.4	75	4.9	2100	590	185	0.63	0.23
53.0-1-2	102	Upper Middle Miocene	Firm gray sandy-silty volcanic ash	19.7	–	1.7	775	240	195	0.46	0.25
53.0-3-1	137	Lower to Middle Miocene	Gray to black silty-to-muddy ash	19.3	–	1.4	320	240	220	–	0.33
53.0-4-1	166	Lower Oligocene to Lower Miocene	Red to black silty-to-muddy ash	19.8	–	1.5	270	610	325	–	0.33
53.0-6-2	195	Lower Oligocene to Lower Miocene	Hard gray-green volcanic rock chalk	19.4	69	5.5	180	575	365	0.43	0.30
54.0-2-3	142	Lower Middle Miocene	Gray calcareous sandy volcanic ash	19.1	–	3.2	725	295	107	1.16	0.54
54.0-4-2	206	Lower Middle Miocene	Very firm gray calcareous sandy volcanic ash	–	71	2.3	620	250	122	1.37	0.47
54.0-6-4	227	Lower Middle Miocene	Firm gray calcareous silty ash	19.3	67	3.0	530	300	122	1.03	0.44
54.0-7-2	264	Lower Middle Miocene	Dark gray-brown silty calcareous ash	19.4	–	3.6	320	535	137	2.90	1.70
55.0-1-3	4	Pleistocene	Light brown nannoplankton-foraminiferal ooze	19.1	63	4.7	<75	455	171	3.55	1.80
55.0-3-3	22	Upper Pliocene	Light foraminiferal-nannoplankton ooze	19.3	70	4.0	<75	550	166	3.16	2.15
55.0-5-3	40	Lower Upper Miocene	Nannoplankton ooze, 90% discoaster	19.7	–	4.7	<75	290	166	2.85	2.31
55.0-7-3	58	Lower Middle Miocene	White nannoplankton-foraminiferal ooze	18.9	70	3.8	<75	300	195	2.84	2.15
55.0-10-3	85	Lower Miocene	Light brown nannoplankton radiolarian-foraminiferal ooze	–	67	3.3	<75	320	156	1.85	2.10
55.0-12-3	106	Upper Oligocene to Lower Miocene	White nannoplankton ooze, Radiolaria, foraminifera	19.6	–	4.1	<75	875	161	2.51	2.10
56.2-1-6	82	Upper Miocene	White nannoplankton-foraminiferal ooze	19.1	62	4.4	<75	880	151	3.62	2.21
56.2-4-4	106	Middle Miocene	White nannoplankton-foraminiferal ooze	19.1	66	3.9	<75	505	146	–	2.15

TABLE 1 – Continued

Sample ^a Designation	Depth ^b (m)	Age	Description	Cl (g/kg)	Br (mg/kg)	B (mg/kg)	Mn (µg/kg)	Zn (µg/kg)	Li (µg/kg)	Total CO ₂ (mm/kg)	Total ^c CO ₂ (mm/kg)
56.2-6-4	193	Lower Miocene- Upper Oligocene	White nannoplankton- foraminiferal ooze	19.8	63	2.6	100	475	151	3.39	2.15
56.2-8-4	212	Upper Oligocene	White nannoplankton- foraminiferal ooze, yellow bands	19.2	–	1.2	75	675	180	2.83	1.94
56.2-10-4	229	Upper Oligocene	Mottled brown-white silty foraminiferal sand, ash	19.4	68	4.5	75	260	146	3.22	2.33
57.2-1-1	10	Upper Pliocene	White nannoplankton chalk ooze	19.7	65	3.8	115	1070	166	1.54	1.37
57.1-1-4	50	Upper Miocene	White nannoplankton chalk ooze	19.2	–	4.2	110	550	161	2.32	1.24
57.0-1-1	299	Upper Oligocene	Mixed gray-yellow-green nannoplankton marl	19.5	68	2.3	<75	300	127	1.08	0.23
57.1-2-2	309	Upper Oligocene	Light blue-green banded chalk	19.2	67	3.0	160	200	127	1.26	0.30
57.1-4-4	326	Upper Oligocene	Nannoplankton ooze with ash bands	19.3	–	2.3	335	300	132	1.00	–
58.1-1-2	3	Pleistocene	Light brown silty chalk ooze	19.3	67	4.6	105	500	245	3.32	1.67
58.2-1-3	139	Upper Oligocene	Brown-yellow nannoplankton ooze, with radiolarians	19.3	68	2.3	765	755	140	1.89	1.10
59.1-3-3	55	Quaternary	Dark yellow-brown zeolitic clay	19.4	72	5.8	910	550	205	2.39	–
59.2-2-3	103	Lower Miocene	Dark yellow-brown siliceous ooze, clay, ash	19.4	72	5.0	60	775	185	2.24	2.53
60.0-1-1	53	Upper Middle Miocene	Banded yellow-brown volcanic sand	19.6	66	3.4	500	725	190	1.89	1.57
Seawater	0	(Goldberg, 1965)		19.0	65	4.6	2	10	170	2.7	2.7

^aSample number refers to hole, core and section. Location of holes, water depth, etc. can be found elsewhere in this volume.

^bDepth refers to depth below sediment-water interface.

^cData from shipboard gas chromatography using 0.2 milliliter aliquots of sample.

TABLE 2
Trace Constituents of Interstitial Water, Leg 6, from Large Volume (100 ml) Squeezing

Sample Designation	Depth Below Sea Bed (m)	Fe ($\mu\text{g}/\text{kg}$)	Co ($\mu\text{g}/\text{kg}$)	Ni ($\mu\text{g}/\text{kg}$)	Cu ($\mu\text{g}/\text{kg}$)	Si ^a (mg/kg)
47.2-10-5	98	28	2.6	22	35	9.2
50.1-1-2	6	20	1.3	8	27	6.1
53.2-1-5	20	20	2.9	14	19	14.5
55.0-10-5	89	16	1.0	8	20	20.6
Seawater ^b	0	10	0.1	2	3	3.0

^aSeparate split of water, kept frozen from time of collection.

^bGoldberg, 1965.

Manganese and zinc concentrations could be determined on nearly all samples without pre-concentration, as has been the case on previous legs. These values are given in Table 1, along with other minor elements which could be similarly determined. The authors again suspect that the zinc concentrations, which are uniformly much higher than sea water values, may be the result of contamination during drilling, squeezing, or storage.

Manganese concentrations are, as has been the case with samples from previous legs, highly variable and independent of location or depth in the sediment column. There are no obvious correlations with sediment type, depth, Eh, pH or other variables, with the exception that those white, nearly pure, nannoplankton-foraminiferal oozes all give low manganese concentrations. This did not appear to be the case with the Leg 5 samples, but there the lithologies were less uniform with depth, and vertical migration of manganese could well have obscured any correlations with sediment type. Site 53 appears to give an excellent example of such migration. There, the concentration at 28 meters depth proved to be more than 4 ppm, and a uniform decrease in concentration was noted above and below this depth. It is not possible at this time to identify the solid phase or phases which are releasing manganese, but if such a concentration gradient is maintained for even a relatively short time geologically, a significant redistribution of the total manganese in the sediment column will occur.

There is very poor agreement between the boron concentrations given in Table 1 and those determined by Manheim *et al.* This is rather surprising in view of the fact that the agreement was generally good for the Leg 5 samples. The boron concentrations found here

are similar to those found on previous legs. That is, most of the values are somewhat lower than the normal sea water values, but there is considerable variation with location and depth. The authors' data gives no evidence for contribution of boron from depth; rather uptake, probably by clays, seems to be the dominant mechanism at almost every site.

Pore waters have tended to show enrichment in lithium with depth at most sites on previous legs, especially where samples from near the "basement" were recovered. This trend is less pronounced in Leg 6 samples than in samples from previous legs, but samples from Site 53, where a reportable "baked" contact was encountered at depth, do show a significant enrichment in lithium. Several other samples, especially those from Site 54, appear to be slightly depleted in lithium. No explanation can be offered here as to why these sediments, which are largely volcanic ash, should remove lithium from the interstitial water.

Both the chloride and bromide values show slightly more scatter than the authors believe to be real, although, as can be seen, all samples differ very little from average seawater values. It seems likely that there is practically no change in the concentration of either with depth, that is, both are relatively inert to diagenetic changes occurring in the sediment column. Only where there is evidence of evaporites in the column, such as in the Gulf of Mexico, have these two elements shown concentrations significantly different from the overlying seawater in these studies.

The total carbon dioxide values given in the next-to-the-last column of 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 there is moderately good agreement between our values and those of Takahashi (this volume) for those samples analyzed by both groups. Most of the values differ by less than 10 per cent, and the differences seem to be random rather than biased one way or the other. The agreement between the authors' laboratory and shipboard measurements is not as good as desired, but generally follows the same trends. Subsequent shipboard analyses are proving to be more reliable, as the techniques improve. Although the data is presented in this report (last column, Table 1) for the sake of completion and comparison, the authors advise that the laboratory data be used for reference and calculation. Despite their confidence in the laboratory data for total dissolved carbon dioxide, they believe that some of the laboratory values may include a small contamination from laboratory air, which was enriched in carbon dioxide due to the large amounts of dry ice used in the laboratory. Very small amounts of this isotopically light carbon dioxide significantly affects the carbon isotope ratios, therefore no isotope data is included in this report. Both the problem of atmospheric contamination and that of measuring very small volumes have now been solved, and it is hoped that future leg reports will be more complete and more reliable.

The outstanding feature of the carbon dioxide distribution in the Leg 6 samples is the extremely low concentrations found at depth at Site 53. A decrease in dissolved carbonate and a resultant decrease in alkalinity was noted at some of the Leg 5 sites, but the decreases were not nearly as pronounced as that at Site 53. Measurements here show about 0.4 mm/kg total carbon dioxide at depth, and both Takahashi and the shipboard gas chromatograph found even lower values for these samples.

This remarkable depletion in dissolved carbonate is accompanied by an equally remarkable increase in dissolved calcium, as reported by Manheim (this volume) and confirmed by the authors' own measurements.

There is, in fact, an approximately 7-fold decrease in dissolved carbonate corresponding to an approximately 7-fold increase in dissolved calcium. This is exactly what would be expected if the interstitial water is maintaining equilibrium with a solid carbonate phase while the dissolved calcium increases, due to release from some other solid phase.

The calcium increase is balanced by a decrease in dissolved magnesium and potassium, but the exact nature of this "ion exchange" reaction is not clear. Neither is it clear how long such a process has been operating. The very steep concentration gradients now existing would result in a considerable transfer of matter if long maintained. Perhaps much of the re-crystallized calcite reported by shipboard observers (preliminary hole summary) has resulted from seawater carbonate diffusing down through the interstitial water and reacting with calcium leached from volcanic ash. Magnesium and potassium could also be supplied by diffusion, ultimately radically altering the nature of the sediments.

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