31. INTERSTITIAL WATER STUDIES ON SMALL CORE SAMPLES, LEG 22[1]

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ABSTRACT

Interstitial waters from Leg 22 in the Indian Ocean revealed two unique results: Site 214, on the Ninetyeast Ridge, penetrated through a 30-meter sequence of fine-grained basalt and reentered hard, silty clay containing carbonate skeletal debris. Such a basalt layer may well have been impervious and extensive enough to seal off underlying (fossil) seawater of Paleocene age. However, except for a marked increase in calcium and a slight increase in chloride, no appreciable changes in pore fluid chemistry could be confirmed. Site 217, at the northernmost end of the Ninetyeast Ridge, demonstrated record concentrations of interstitial calcium in clayey nannofossil oozes and a relatively small but significant increment in chloride with depth. Presumably, these increments signal the existence of evaporitic sediments or evaporite-influenced brines at considerably greater depth than penetrated.

INTRODUCTION

A total of 125 sediment samples collected from eight Leg 22 sites was squeezed for interstitial water. Sediment samples were collected immediately following the recovery of the core by the removal of discrete segments of sediment-filled plastic liner (mini-cores). This sampling method is essentially the same as was used for the special geochemical studies carried out on Leg 15 (Horowitz et al., in press).

In most instances a 10-cm mini-core was cut from the top end of a 150-cm core section. This sample was first used for the resistivity measurements reported elsewhere in this volume (Chapter 32). Mini-cores were split lengthwise and one-half the available sediment was squeezed. All samples were squeezed at ambient room temperature. When soft sediments were encountered, two contiguous mini-cores were removed in order to make punch-in electrode pH measurements. pH measurements were also made on the squeezed, unfiltered pore water immediately following recovery. The fluid was injected directly from the receiver syringe into an Orion miniature flow-through electrode. The water content of all samples was determined from weight loss upon oven drying of approximately 1-g portions of sediment taken from the mini-cores prior to processing.

Analytical methods were identical to those outlined in earlier volumes of this series. Most of the analyses and data reduction were performed by John Mahoney. The analytical data are summarized in Tables 1 and 2.

[1]Contribution No. 3100 of the Woods Hole Oceanographic Institution.

RESULTS AND DISCUSSION

Rather than cover sites comprehensively, as in previous interstitial water studies, effort was concentrated on a few sites, from which a number of samples were analyzed to provide continuity of information. A total of 41 samples as selected from Site 212 in the Wharton Basin, about 1500 km northwest of Australia; Sites 214 and 217 on the Ninetyeast Ridge; and Site 218 in the southern portion of the Central Bengal Fan. A greater effort was made on this leg to squeeze pore fluid from consolidated sediment than previously. Sufficient water for analysis was obtained from moderately lithified sediments (water content as low as 18%). This may help account for the more marked evidence of diagenetic reactions, as discussed below.

Site 212

At this site, in the Wharton Basin, clayey nannofossil oozes showed moderate depletion in K, Mg, and SO_4 and a 2.5-fold increase in Ca. Alkalinity remained roughly constant at values little higher than in seawater when corrected for a systematic analytical error. The mean rate of accumulation for this site was 0.65 cm/1000 years.

Site 214

Located on the crest of the Ninetyeast Ridge, in water depth of 1655 meters, this site revealed an upper sequence of foraminiferal and nannofossil ooze, becoming glauconitic toward the base of the Eocene at about 330 meters depth below the sea floor. A remarkable series of increasingly shallow water to possibly lagoonal sediments culminated in lignitic and volcanoclastic sediments interbedded with igneous extrusive rock. Interestingly, one sample was

TABLE 1
Major Constituents of Pore Fluids

Sample	Depth (m)	Age	Description	Na[a] (g/kg)	Na[b] (g/kg)	K (g/kg)	Ca (g/kg)	Mg (g/kg)	Total Cations (meq/kg)	Cl (g/kg)	SO_4 (g/kg)	Total Anions (meq/kg)	Sum[c] (g/kg)	Salinity[d]	H_2O (%)[e]	pH[e]
Site 212 (19°11.3′S, 99°17.8′E, water depth 6243 m, Wharton Basin)																
Surface ocean water				10.7	10.5	0.37	0.42	1.27	591	19.2	2.69	601	34.9	34.6	–	–
212-2-3	12	Early Pliocene	Medium brown iron-bearing clay with 2-5% silt	10.9	10.7	0.46	0.45	1.20	599	19.5	2.54	607	35.3	34.6	58	7.1
5, CC	70	Upper Miocene	Very pale orange, foram-bearing nanno ooze	10.9	10.6	0.40	0.42	1.18	591	19.4	2.44	602	35.0	34.1	–	7.6
11-3	196	Early middle Miocene	Dusky yellow clay-rich nanno ooze	11.0	10.7	0.36	0.53	1.06	586	19.6	2.17	599	34.9	34.4	25	7.2
13-3	253	Early middle Miocene	Very pale orange, foram nanno chalk	11.1	10.7	0.33	0.61	1.01	586	19.6	2.28	603	35.2	34.1	32	7.2
25-5	389	Middle Eocene	Very light gray and pinkish gray nanno chalk	–	10.7	0.29	0.79	0.98	595	20.0	–	–	–	34.6	15	6.9
37, CC	506	(?)	Medium brown to dusky yellow brown clay-rich zeolite	10.6	10.4	0.29	1.01	0.88	583	19.2	2.15	591	34.4	33.6	13	7.0
Site 214 (11°20.2′S, 88°43.1′E, water depth 1665 m, crest of Ninetyeast Ridge)																
Surface ocean water				10.6	10.3	0.37	0.40	1.26	583	18.9	2.66	592	34.4	34.1	–	–
214-1-5	8	Pleistocene	White foram nanno ooze	10.8	10.6	0.41	0.44	1.26	595	19.4	2.66	606	35.2	34.9	–	7.5
39-3	364	Paleocene	Grayish olive green silty sand	11.0	10.7	0.32	1.19	0.80	604	20.1	1.90	610	35.4	34.6	28	7.8
41-3	384	Paleocene (?)	Grayish green silty sand	10.8	10.7	0.28	1.33	0.82	604	20.3	1.64	610	35.3	35.5	25	7.1
42, CC	400	Paleocene (?)	Grayish black lignite	10.7	10.6	0.24	1.34	0.82	601	20.2	1.64	608	35.1	34.6	–	6.7
46-3	424	Paleocene (?)	Dark greenish gray clay pebble conglomerate	10.0	10.0	0.22	1.56	0.80	582	19.6	1.34	585	33.7	33.8	36	7.1
52, CC	486	Paleocene (?)	Grayish blue green silty clay, very hard	9.6	9.9	0.14	3.19	0.49	636	21.3	0.97	623	35.8	37.1	–	7.2

Site 217 (8°55.6'N, 90°32.3'E, water depth 3020 m, east flank of Ninetyeast Ridge)

Surface ocean water				10.3	10.1	0.36	0.40	1.22	569	18.5	2.58	579	33.6	33.3	–	–
217-1-3	7	Pleistocene	Greenish gray foram-bearing clay-rich nanno ooze	10.8	10.6	0.49	0.41	1.22	594	19.3	2.63	602	35.1	34.4	49	7.3
3-2	73	Late Miocene	Light bluish gray foram clay-bearing nanno ooze	10.6	10.4	0.45	0.73	1.09	589	19.6	2.16	600	34.8	34.6	42	7.1
5-1	155	Middle Miocene	Yellowish gray clay-bearing nanno ooze	10.5	10.3	0.42	1.15	1.01	600	19.9	2.04	607	35.2	35.2	35	7.0
7-4	234	Oligocene	Very light gray foram clay-bearing nanno chalk	10.1	10.0	0.38	1.55	0.98	603	20.0	1.91	606	35.1	35.5	25	7.0
10-4	348	Late Eocene	Yellowish gray calcite Radiolaria-bearing nanno chalk	9.7	9.7	0.32	2.20	1.08	633	20.8	1.83	628	36.1	37.1	24	6.9
12-CC	383	Paleocene	Pale yellowish brown foram-bearing nanno chalk	9.4	9.4	0.32	2.46	1.08	628	21.1	1.62	630	36.1	–	26	6.8
14-4	397	Paleocene	Yellowish gray foram-bearing nanno chalk	9.0	9.1	0.30	2.70	1.03	625	20.7	1.48	618	35.4	36.6	21	6.9
20-4	454	Maastrichtian	Yellowish gray nanno chalk	(8.6)	8.9	0.28	3.32	0.99	640	21.2	(1.4)	(629)	(35.9)	38.0	20	7.7
25-4	502	Maastrichtian	Light gray and very light gray foram clay calcite-bearing nanno chalk	8.1	8.6	0.28	4.52	0.82	673	22.0	1.37	651	37.2	39.6	18	6.7

Site 218 (8°00.4'N, 86°17.0'E, water depth 3759 m, Central Bengal Fan)

218-2-4	8	Quaternary	Light gray foram clay-rich nanno ooze	10.9	10.6	0.44	0.32	1.15	584	19.4	1.87	595	34.6	34.1	36	8.0
3-2	20	Quaternary	Dark olive gray silt with sand and clay	10.9	10.7	0.44	0.32	1.13	587	19.3	1.80	593	34.5	34.1	31	7.9
4-2	48	Quaternary	Dark gray graded silt	10.6	10.6	0.35	0.25	1.00	565	19.5	<0.01	567	32.7	32.4	29	7.6
5-2	77	Quaternary	Dark gray clayey silt	10.8	10.6	0.34	0.18	0.94	558	19.5	0.14	567	32.8	32.2	29	7.8
6-1	114	Quaternary	Very dark gray nanno-bearing silty clay	10.9	10.6	0.37	0.12	0.92	554	19.7	0.14	564	32.5	31.9	40	7.7
8-3	192	Quaternary	Gray clayey silt	10.9	10.9	0.26	0.32	0.79	560	19.7	0.03	563	32.4	31.9	35	7.7
9,CC	232	(?)	Dark gray clayey silt	10.9	10.8	0.24	0.35	0.80	557	19.7	0.16	564	32.5	32.2	23	7.6
11-2	304	Early Pliocene	Dark gray silt	10.9	10.8	0.30	0.37	0.85	566	19.8	0.34	572	32.9	32.4	32	7.6
13-2	376	Upper Miocene	Grayish olive green nanno ooze	11.6	11.4	0.18	0.44	0.77	586	20.8	0.19	595	34.2	33.6	25	7.5
14,CC	422	Upper Miocene	Olive gray clayey silt and silty clay	11.4	11.4	0.14	0.52	0.68	581	20.6	0.01	583	33.4	33.0	23	7.9

TABLE 1 – *Continued*

Sample	Depth (m)	Age	Description	Na[3] (g/kg)	Na[b] (g/kg)	K (g/kg)	Ca (g/kg)	Mg (g/kg)	Total Cations (meq/kg)	Cl (g/kg)	SO_4 (g/kg)	Total Anions (meq/kg)	Sum[c] (g/kg)	Salinity[d]	H_2O (%)[e]	pH[e]
218-15-1	455	Upper Miocene	Dark gray clayey silt and silty clay	11.1	10.9	0.14	0.52	0.72	561	19.8	0.45	571	32.9	32.7	19	7.4
16-2	466	Upper Miocene	Dark gray clayey silt	11.3	11.2	0.14	0.54	0.71	575	20.2	0.38	580	33.5	32.7	21	7.8
18, CC	488	Upper Miocene	Dark gray silt	11.4	11.2	0.11	0.56	0.65	573	20.3	0.17	579	33.4	33.0	21	7.4
21-3	542	Upper Miocene	Dark gray clayey silt and silt intervedded	11.4	11.3	0.11	0.60	0.67	579	20.2	0.41	582	33.6	33.0	18	7.4
22-2	580	Upper Miocene	Dark gray silt interbedded with fine sand and clayey silt	11.3	11.2	0.14	0.64	0.64	574	20.2	0.34	578	33.4	32.4	23	7.4
23-2	618	Upper Miocene	Dusky yellow green clay-bearing nanno ooze	11.8	11.6	0.08	0.73	0.61	594	21.0	0.33	600	34.6	34.1	21	–
24-2	656	Upper Miocene	Dusky yellow green clay carbonate-bearing nanno ooze	11.6	11.6	0.08	0.76	0.57	591	20.8	0.27	592	34.2	34.1	19	–
25-2	694	Middle Miocene	Dark gray silt and sandy silt	11.4	11.4	0.11	0.71	0.56	579	20.4	0.30	582	33.6	33.0	25	7.9
26-2	732	Middle Miocene	Dark gray sandy silt	11.4	11.3	0.06	0.74	0.55	574	20.2	0.25	579	33.4	33.0	17	7.6
27-2	770	Middle Miocene	Dark gray clayey silt	11.4	11.2	0.08	0.72	0.54	571	20.1	0.46	579	33.4	33.0	20	8.0

Note: Alkalinities are not shown because of systematic contamination of the alkalinity subsamples in the laboratory. However, some remarks on qualitative changes in alkalinity are offered. Sites 212 and 214 showed relatively constant alkalinities on the order of sea-water values, except for the bottommost sample (below the basalt) in 214, where alkalinity is less than 1 meq/kg. Site 217 alkalinities decrease with increasing depth from seawater to very low levels in the high calcium waters. Site 218 alkalinities show an increase to about 15 meq/kg at 48 m depth, decrease thereafter to seawater levels or below at depths greater than 400 m. Sums and total anions were calculated using alkalinity values, which are believed to be too high by about 1.5 to 2 meq/kg.

[a]Sodium determined by difference between anions and cations excluding Na.
[b]Sodium determined by atomic absorption analysis.
[c]The sum incorporates the sodium values determined by difference.
[d]Salinity of pore fluids taken from heat-sealed sections of plastic pipe prior to subdivision of samples for analysis. Salinity values determined with Goldberg temperature compensated refractometer.
[e]pH and water content taken from shipboard summaries.

TABLE 2
Si Determined Colorimetrically

Sample	Depth (m)	Age	Description	Si (ppm)
		Site 212		
				<0.1
212-2-3	12	Early Pliocene	Medium brown iron-bearing clay with 2-5% silt	3.6 3.6
5, CC	70	Upper Miocene	Very pale orange, foram-bearing nanno ooze	2.9
11-3	196	Early middle Miocene	Dusky yellow clay-rich nanno ooze	4.2
13-3	253	Early middle Miocene	Very pale orange, foram nanno chalk	3.7
25-5	389	Middle Eocene	Very light gray and and pinkish gray nanno chalk	17
37, CC	506	(?)	Medium brown to dusky yellow brown clay-rich zeolite	12
		Site 214		
				<0.1
214-1-5	8	Pleistocene	White foram nanno ooze	9.8
39-3	364	Paleocene	Grayish olive silty sand	7.1
41-3	384	Paleocene (?)	Grayish green silty sand	6.5
42, CC	400	Paleocene (?)	Grayish black lignite	4.2
46-3	424	Paleocene (?)	Dark greenish gray clay pebble conglomerate	1.9
52, CC	486	Paleocene (?)	Grayish blue green silty clay	2.4
		Site 217		
				0.9
217-1-3	7	Pleistocene	Greenish gray foram-bearing clay-rich nanno ooze	12.0
3-2	73	Late Miocene	Light bluish gray foram clay-bearing nanno ooze	16.0
5-1	155	Middle Miocene	Yellowish gray clay-bearing nanno ooze	15.0
7-4	234	Oligocene	Very light gray foram clay-bearing nanno chalk	20.0
10-4	348	Late Eocene	Yellowish gray calcite Radiolaria-bearing nanno chalk	20.0
12, CC	383	Paleocene	Pale yellowish brown foram-bearing nanno chalk	12.0
14-4	397	Paleocene	Yellowish gray foram-bearing nanno chalk	13.0

TABLE 2 – *Continued*

Sample	Depth (m)	Age	Description	Si (ppm)
217-20-4	454	Maastrichtian	Yellowish gray nanno chalk	3.3
25-4	502	Maastrichtian	Light gray and very light gray foram clay calcite-bearing nanno chalk	2.4
		Site 218		
218-2-4	8	Quaternary	Light gray foram clay-rich nanno ooze	10.0
3-2	20	Quaternary	Dark olive gray silt with sand and clay	5.5
4-2	48	Quaternary	Dark gray graded silt	4.1
5-2	77	Quaternary	Dark gray clayey silt	7.6
6-1	114	Quaternary	Very dark gray nanno-bearing silty clay	7.4
8-3	192	Quaternary	Gray clayey silt	7.3
9, CC	232	(?)	Dark gray clayey silt	2.7
11-2	304	Early Pliocene	Dark gray silt	3.5
13-2	376	Upper Miocene	Grayish olive green ooze	2.2
14, CC	422	Upper Miocene	Olive gray clayey silt and silty clay	2.5
15-1	455	Upper Miocene	Dark gray clayey silt and silty clay	2.8
16-2	466	Upper Miocene	Dark gray clayey silt	2.9
18, CC	488	Upper Miocene	Dark gray silt	2.1
21-3	542	Upper Miocene	Dark gray clayey silt and silt interbedded	2.9
22-2	580	Upper Miocene	Dark gray silt inter-bedded with fine sand and clayey silt	2.8
23-2	618	Upper Miocene	Dusky yellow green clay-bearing nanno ooze	1.6
24-2	656	Upper Miocene	Dusky yellow green clay carbonate-bearing nanno ooze	2.0
25-2	694	Middle Miocene	Dark gray silt and sandy silt	2.4
26-2	732	Middle Miocene	Dark gray sandy silt	2.3
27-2	770	Middle Miocene	Dark gray clayey silt graded with sandy silt	1.8

obtained from hard, clayey sediment below a 30-meter, fine-grained intermediate differentiated flow. This sample could represent isolated Plaeocene seawater if the flow is of appreciable lateral continuity and provides a relatively impermeable barrier to diffusion. While the cationic composition differs from present seawater, it is similar to overlying pore fluids (suprabasalt) except as regards Ca^{++} (enriched to 3.19 g/kg). The observed compositional changes (relative to present-day seawater) are explainable in terms of previously observed diagenetic modification of pore fluids and cannot be attributed to different seawater composition during the Paleocene. This somewhat anti-climactic result should not, however, reduce the potential importance of igneous rock-sealed sediments for evaluating paleoceanic pore fluids.

Site 217

This site was located on the extreme northern end of the Ninetyeast Ridge, less than 200 km west of the southernmost Andaman Islands. Notable at this site was the continuous increase in calcium with depth, reaching values of 4.52 g/kg, more than 10 times the mean value for seawater. Concurrent with this increase are substantial depletions in Mg, K, and Na. At 502 meters, the deepest sample, the difference between observed and surface water calcium (presumed original) is 205 meq/kg. About 40% of this increase is compensated for by a depletion in Na, which is assumed to be taken up in silicate minerals. However, as shown in Figure 1, even after subtracting from excess calcium all depletions in Mg, Na, and K, there still remains a net enrichment in Ca of 80 meq/kg. This excess Ca corresponds, within the agreement between cations and anions, to the net increases in chloride with depth. Diffusion of chlorides into sediment overlying evaporites has been previously observed; however, this has always been seen almost entirely as NaCl diffusion. It is difficult to explain solution and diffusion from an underlying evaporite of $CaCl_2$ without NaCl. A likely explanation is that NaCl diffusion is occurring rather than $CaCl_2$, but the Na is taken up in silicate lattices. Reactions of this type, commonly referred to as "reverse weathering," consume alkalinity and thus could lead to the solution of $CaCO_3$ as Na is incorporated in silicates. This would produce a $CaCl_2$ enrichment. It should also produce CO_2 but, as has been observed in earlier studies, the required quantities were not found. Although the pH values do drop as low as 6.7, this is not sufficient to account for the required CO_2. Consequently, although diffusion of NaCl with consequent uptake of Na and release of Ca is believed to be the most likely, this interpretation is subject to uncertainty in the absence of an adequate explanation of the low CO_2 content.

Site 218

This site, in predominantly terrigenous silts and clays of Neogene age, yielded a pore-water composition rather typical for continental rise sediments at similar relative positions. K and Mg are depleted to one-third and one-half mean seawater values, respectively. Ca at first is depleted to 114 meters; but then increases with depth. This trend has been explained by Manheim and Sayles (in press) as superimposition of precipitation of $CaCO_3$ on a basic trend

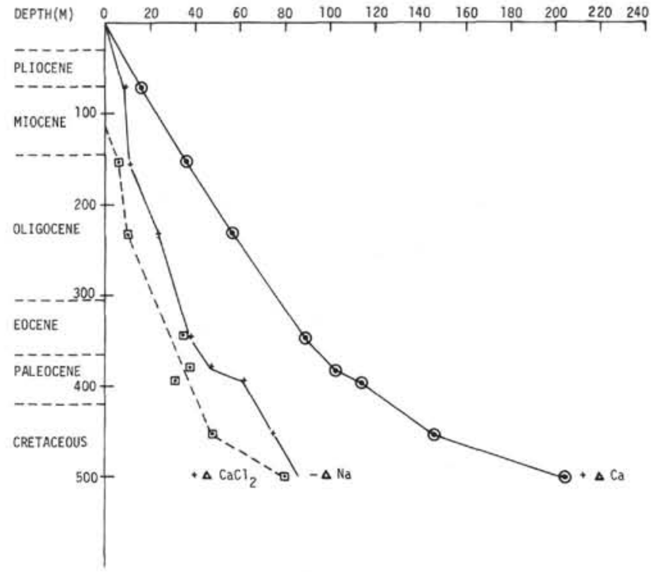

Figure 1. *Dynamic changes in composition of interstitial waters from Site 217. ΔCa refers to difference between observed interstitial Ca and that originally buried with sediments. ΔNa refers to corresponding loss of Na in silicate phases. $\Delta CaCl_2$ refers to incremental addition of chloride calcium to pore fluid residual calcium gain after compensation for exchange of Ca for Na, Mg, and K.*

toward Ca enrichment in pore fluids with depth. An alkalinity peak occurs somewhat higher in the section. Sulfate is largely depleted below 20 meters, and it is conceivable that the remaining sulfate may be an artifact owing to oxidation of iron sulfides in the sediment in the period prior to squeezing the cores. If absence of the sulfate is assumed, then it is somewhat surprising that methane production was not detected. No separation of cores owing to exsolution of gas on lowering ambient pressure was observed onboard ship, and no methane was obtained in gas chromatographic probes of air associated with the cores. The accumulation rate of sediment was 5.9 cm/1000 yr; a rate which, in other DSDP cores, is associated with appreciable preservation of organic matter in the sediments.

REFERENCES

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