

32. PORE-WATER CHEMISTRY OF CARBONATE-RICH SEDIMENTS, LORD HOWE RISE, SOUTHWEST PACIFIC OCEAN¹

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ABSTRACT

About 200 pore-water samples were recovered and analyzed from eight sites of DSDP Leg 90. At all sites on the carbonate-rich Lord Howe Rise, Ca^{2+} concentrations increase and Mg^{2+} concentrations decrease with increasing sub-bottom depth. The value of $\Delta\text{Ca}^{2+}/\Delta\text{Mg}^{2+}$ averages -0.45 mol/mol at these sites, an unusually small negative value in comparison with sites on basaltic crust. This supports the argument that the crust of the Lord Howe Rise is siliceous. Li^+ concentrations increase and K^+ concentrations decrease with depth. Both of these constituents are affected by reactions within the sediment column. Microbial sulfate reduction occurs to a small extent at all sites. In the upper 200 m of Site 594 on the south side of the Chatham Rise, sulfate reduction and alkalinity production are more pronounced.

Carbonate recrystallization is indicated by large increases in Sr^{2+} concentrations with depth at all sites. The exact value of the Sr^{2+} maximum at each site is determined by equilibrium with respect to celestite (SrSO_4). The greater the degree of microbial sulfate reduction, the higher is the pore water Sr^{2+} concentration. The diffusive flux of Sr^{2+} out of the pore waters is consistent with an initial rate of carbonate recrystallization of $10\%/\text{m.y.}$ This recrystallization must alter the isotopic and trace elemental compositions of some carbonate components.

INTRODUCTION

Leg 90 of the Deep Sea Drilling Project consisted of a north-south transect from 26°S to 41°S along the shallow (about 1000 m deep), carbonate-rich, Lord Howe Rise between New Caledonia, New Zealand, and Australia. An additional site, Site 594, was cored on the south side of the Chatham Rise at 46°S in a region presently characterized by more hemipelagic sedimentation. The major objective of this expedition was the recovery of complete Neogene sections for high-resolution paleoceanographic studies. We also obtained an atypically large number of interstitial water samples. Combined with detailed studies of sediment isotopic, chemical, and textural composition, the chemistry of Leg 90 pore waters provides important insights into the processes and rates of carbonate diagenesis.

ANALYTICAL METHODS

All interstitial waters analyzed in this study were obtained by shipboard extraction using the procedure and equipment described by Manheim and Sayles (1974). Extraction was effected as soon as possible after sediment recovery and was conducted at laboratory ambient temperature and pressure. Comparison of this extraction method with *in situ* sampling has established previously that temperature- and pressure-of-squeezing effects on the analyzed constituents are quite small (see Gieskes, 1973, 1974).

All analyses reported in this paper were carried out ashore. Prior to analysis, samples were stored unrefrigerated in either linear polyethylene bottles or sealed polyethylene or glass ampules. On the basis of previous experience, this storage procedure is acceptable for the reported constituents. Measurements that are in progress, but not published here, include the strontium and oxygen isotopic ratios of dissolved strontium and water, respectively.

Analytical methods for determination of chloride, calcium, magnesium, silica, alkalinity, and strontium are similar to those of Gieskes

(1974) and Gieskes and Lawrence (1976). Lithium, potassium, and sulfate methodologies are similar to those of Presley (1971).

RESULTS AND DISCUSSION

All the pore-water data are shown in Table 1 and Figures 1-6. The Lord Howe Rise sites (588, 590, 591, 592, and 593) and the lower 400 m of Site 594 display increasing Ca^{2+} and decreasing Mg^{2+} concentrations with increasing sub-bottom depth. The changes in Ca^{2+} and Mg^{2+} concentrations with depth at these sites are approximately linearly correlated (Fig. 7) with an average slope $\Delta\text{Ca}^{2+}/\Delta\text{Mg}^{2+}$ of about -0.45 mol/mol . This slope is similar to those observed previously at drill sites overlying presumed siliceous basement rocks. Examples include (1) DSDP Sites 346 and 349 on the Jan-Mayen Ridge, north of Iceland, where $\Delta\text{Ca}^{2+}/\Delta\text{Mg}^{2+}$ is about -0.4 and -0.2 , respectively (Gieskes et al., 1978); (2) DSDP Site 116 on the Rockall Bank in the North Atlantic Ocean where $\Delta\text{Ca}^{2+}/\Delta\text{Mg}^{2+}$ is about -0.4 (Manheim et al., 1972); and (3) DSDP Site 237 on the Mascarene Ridge in the western Indian Ocean where $\Delta\text{Ca}^{2+}/\Delta\text{Mg}^{2+}$ is -0.57 (Sandstrom and Gieskes, 1974). By contrast, of those sites listed by McDuff (1981) in a compilation of DSDP sites displaying nonzero $\text{Ca}^{2+}/\text{Mg}^{2+}$ gradients and linear correlations of Ca^{2+} versus Mg^{2+} , not a single one overlying basaltic basement had a value of $-\Delta\text{Ca}^{2+}/\Delta\text{Mg}^{2+}$ as low as any of these on siliceous crust. A typical value of $\Delta\text{Ca}^{2+}/\Delta\text{Mg}^{2+}$ for sites on basaltic crust is -1.5 (McDuff, 1981). It has previously been shown (McDuff and Gieskes, 1976; McDuff, 1981) that linear correlation of Ca^{2+} and Mg^{2+} is usually indicative of conservative chemical behavior in the sediment column. As basement rocks alter, they take up magnesium from the pore waters and release calcium to the pore waters. Apparently, as basement rocks of the Lord Howe Rise alter, they take up more magnesium and release less calcium than do basaltic basement rocks. The implication of these observations for Leg 90 sites is sup-

¹ Kennett, J. P., von der Borch, C. C., et al., *Init. Repts. DSDP*, 90: Washington (U.S. Govt. Printing Office).

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Table 1. Interstitial water concentration data.

Core-Section (interval in cm)	Depth (m)	Ca ²⁺ (mM)	Mg ²⁺ (mM)	Sr ²⁺ (mM)	K ⁺ (mM)	Li ⁺ (μM)	SiO ₂ (μM)	Alkalinity (meq/l)	SO ₄ ²⁻ (mM)
Site 587									
2-3, 144-150	7.57	9.03	54.66	0.147	10.49	—	186	3.64	26.7
3-6, 0-6	20.23	8.79	55.40	0.287	11.54	—	214	3.51	28.0
5-3, 144-150	36.37	9.30	53.98	0.293	11.54	—	147	3.36	27.4
7-3, 144-150	55.57	9.74	53.54	0.306	10.68	—	—	3.28	25.7
9-1, 144-150	71.77	9.83	53.74	0.363	11.75	—	—	3.09	—
Hole 588									
1-3, 144-150	4.47	10.63	51.03	—	10.49	31.0	220	2.84	25.0
2-5, 144-150	13.07	10.47	51.23	0.249	11.76	32.8	190	2.74	26.1
3-4, 144-150	21.17	10.51	51.03	0.300	11.50	34.2	169	2.83	25.7
4-4, 144-150	30.77	10.72	51.07	0.395	11.54	36.3	149	2.77	25.8
5-4, 144-150	40.37	11.01	50.56	0.446	10.91	37.0	158	2.84	25.4
6-4, 144-150	49.97	11.20	49.95	0.523	10.75	39.0	156	3.04	24.7
7-4, 144-150	59.57	11.15	49.97	0.561	10.75	39.6	141	—	—
9-4, 144-150	78.77	11.76	49.25	0.644	10.18	41.4	152	3.06	23.3
10-4, 144-150	88.37	11.93	47.79	0.638	10.31	42.8	164	2.78	24.7
11-4, 144-150	97.97	12.10	48.04	0.701	10.23	43.6	160	2.97	23.7
12-4, 144-150	107.57	12.11	48.15	0.714	10.16	44.3	165	2.95	23.6
13-4, 144-150	117.47	12.47	47.19	0.746	10.44	46.6	201	2.90	23.6
14-3, 144-150	125.27	12.71	46.45	0.708	—	48.1	211	2.91	23.4
15-3, 144-150	134.87	12.77	46.33	0.714	10.01	47.8	182	2.86	23.3
16-3, 144-150	144.47	12.97	46.25	0.708	10.01	49.1	210	2.79	22.9
17-3, 144-150	154.07	13.17	45.80	0.708	10.12	51.1	226	2.74	23.3
18-5, 144-150	166.67	13.38	46.75	0.714	10.01	55.7	233	2.72	23.3
19-5, 144-150	176.27	13.23	45.59	0.733	9.79	54.2	226	2.71	22.6
20-3, 144-150	182.87	13.32	44.58	0.663	9.62	55.0	222	2.75	22.9
21-4, 144-150	193.97	13.36	44.91	0.689	9.63	58.7	228	2.50	22.3
22-4, 144-150	203.57	13.58	44.43	0.682	10.16	59.6	324	2.22	22.9
23-3, 144-150	211.67	13.42	43.57	0.676	10.16	61.7	258	1.98	23.4
24-3, 144-150	221.27	11.79	45.57	0.689	9.96	63.0	246	—	23.6
25-3, 144-150	230.87	11.81	45.57	0.669	10.12	66.2	284	1.90	22.9
Hole 588A									
1-4, 144-150	241.97	13.62	37.42	0.701	10.49	69.7	150	1.67	22.7
3-2, 144-150	253.57	14.28	42.30	0.714	10.15	73.9	158	1.99	22.6
5-2, 144-150	263.57	14.13	42.33	0.695	10.03	77.1	158	1.71	21.7
7-2, 144-150	273.57	14.31	42.71	0.720	9.24	80.0	169	1.78	21.6
9-2, 144-150	283.57	14.20	42.00	0.708	—	84.8	—	—	22.9
12-2, 140-150	298.55	14.31	39.95	0.701	10.35	84.5	166	0.46	22.1
14-1, 140-150	307.05	14.62	41.37	0.708	10.18	84.3	169	0.97	22.0
17-1, 140-150	326.65	—	—	0.701	—	94.0	—	0.80	23.0
Hole 588C									
1-5, 140-150	313.15	14.22	41.64	0.720	—	88.2	81	—	22.7
3-3, 140-150	329.35	14.94	40.90	0.752	9.64	92.0	105	0.80	22.4
5-4, 140-150	350.05	—	—	0.720	10.23	99.1	—	0.21	22.6
7-2, 140-150	366.25	—	—	0.740	9.84	102.2	—	0.44	22.6
9-5, 140-150	398.95	—	—	0.759	9.74	105.2	—	0.54	22.0
11-1, 140-150	403.15	—	—	0.765	8.67	107.0	—	0.59	21.7
13-3, 140-150	425.35	—	—	0.759	9.41	118.5	—	0.43	21.4
15-4, 140-150	446.05	—	—	0.822	9.79	124.3	—	0.58	22.6
17-3, 140-150	463.75	—	—	0.746	9.05	115.5	—	—	22.4
Site 589									
1-4, 140-150	5.95	10.68	52.41	0.191	12.38	34.9	252	3.70	26.3
2-5, 144-150	14.77	10.96	49.99	0.300	11.25	36.0	277	4.01	25.1
3-5, 144-150	24.37	10.70	48.84	0.402	12.62	39.2	261	3.86	24.1
4-4, 144-150	32.47	11.22	47.74	0.491	12.38	41.0	233	4.46	23.4
Hole 590									
1-3, 144-150	4.47	10.66	50.89	0.172	11.39	33.2	263	3.42	26.1
2-3, 144-150	11.47	10.85	49.59	0.300	11.23	38.1	278	4.31	25.1
3-3, 144-150	21.07	10.78	50.90	0.274	11.04	37.2	260	3.97	25.6
Hole 590A									
1-3, 144-150	30.65	11.23	47.73	0.504	11.17	38.6	241	4.84	21.7
2-3, 144-150	40.27	11.39	46.49	0.587	11.02	40.8	188	4.52	22.6
3-3, 144-150	49.87	11.48	45.13	0.657	11.02	41.4	182	4.02	21.1
4-5, 144-150	62.47	11.84	44.49	0.797	11.20	42.8	177	4.30	20.7
5-3, 144-150	69.07	12.29	44.07	0.759	10.69	42.8	175	3.77	19.7

Table 1. (Continued).

Core-Section (interval in cm)	Depth (m)	Ca^{2+} (mM)	Mg^{2+} (mM)	Sr^{2+} (mM)	K^+ (mM)	Li^+ (μM)	SiO_2 (μM)	Alkalinity (meq/l)	SO_4^{2-} (mM)
Hole 590A (cont.)									
6-3, 144-150	78.67	12.93	43.31	0.848	—	—	186	3.90	—
7-3, 144-150	88.27	12.78	43.12	0.880	10.71	42.6	177	4.56	18.4
8-3, 144-150	97.87	12.66	41.25	0.854	11.09	43.6	181	3.63	19.1
10-3, 144-150	117.07	13.64	40.17	0.842	10.71	41.6	192	2.96	18.3
11-3, 144-150	126.67	13.81	40.21	0.880	—	40.7	194	2.53	—
12-3, 144-150	136.27	13.76	38.84	0.874	10.61	40.8	201	2.95	17.4
13-3, 144-150	145.87	14.54	38.58	0.880	10.73	40.5	214	3.36	17.3
14-3, 144-150	155.47	13.99	38.63	0.854	9.88	39.7	216	2.46	17.3
15-3, 144-150	165.07	14.71	36.73	0.893	10.31	40.2	235	—	16.1
16-3, 144-150	174.67	14.89	37.72	0.880	10.27	39.7	246	3.65	16.4
17-3, 144-150	184.27	14.75	36.11	0.880	10.42	39.5	260	2.89	15.7
18-3, 144-150	193.87	15.50	37.10	0.893	—	39.8	284	3.09	16.6
19-3, 144-150	203.47	15.37	34.96	0.905	—	45.6	310	2.19	16.6
20-3, 144-150	213.07	15.72	37.00	0.899	10.06	47.2	337	2.38	15.1
21-3, 144-150	222.67	15.70	34.95	0.905	10.66	42.1	395	2.17	14.4
23-3, 144-150	241.87	16.17	33.88	0.842	10.49	46.0	504	2.04	15.4
24-3, 144-150	251.47	16.64	33.92	0.848	10.71	47.7	609	—	15.6
25-3, 144-150	261.07	16.37	34.06	0.842	10.39	48.9	781	2.17	15.9
26-3, 144-150	270.67	17.27	33.56	0.822	10.07	51.0	899	—	16.0
27-2, 144-150	278.77	16.68	33.63	0.829	9.92	53.7	976	1.99	14.9
Hole 590B									
33-5, 140-150	304.95	17.52	33.36	0.842	10.30	65.8	1035	—	16.0
35-4, 140-150	322.65	18.23	32.59	0.829	10.23	79.6	1060	—	15.7
37-4, 140-150	341.85	18.72	31.89	0.867	10.37	92.4	1135	2.12	15.9
39-5, 140-150	362.55	19.73	32.57	0.854	10.30	104.4	840	—	16.4
41-5, 140-150	381.75	19.98	32.38	0.867	9.92	115.5	622	2.22	17.0
43-3, 140-150	397.95	19.45	31.69	0.848	10.01	125.2	574	—	16.3
45-4, 140-150	418.65	20.44	31.65	0.886	9.77	137.5	672	—	16.6
47-6, 140-150	440.85	20.24	31.53	0.867	9.73	148.7	647	1.80	16.6
49-4, 1401-50	457.05	19.28	33.06	0.791	9.59	143.2	357	—	17.6
51-3, 140-150	474.75	19.52	33.37	0.835	9.88	135.2	361	1.91	17.7
53-4, 1401-50	495.45	19.42	34.06	0.822	9.76	131.7	378	—	18.1
Hole 591									
2-3, 144-150	7.87	10.53	50.88	0.198	11.95	34.5	354	4.44	24.3
4-3, 144-150	27.07	11.35	49.94	0.389	11.81	33.4	492	3.21	22.7
6-3, 144-150	46.27	11.28	44.81	0.548	12.76	35.2	497	3.87	21.4
8-3, 144-150	65.47	12.24	45.15	0.759	11.90	34.6	583	4.68	20.7
10-3, 144-150	84.67	13.20	41.89	0.829	12.00	33.4	672	5.05	19.6
12-3, 144-150	103.87	12.98	40.59	0.880	11.40	30.5	700	4.32	18.7
14-2, 144-150	121.27	13.27	39.70	0.925	12.14	29.6	831	3.30	18.9
16-4, 144-150	142.87	14.04	37.63	0.931	12.31	27.0	935	2.52	17.3
18-4, 144-150	161.47	15.29	36.52	0.925	12.07	27.1	950	2.64	18.0
20-2, 144-150	177.27	14.60	36.16	0.944	12.18	25.3	988	—	17.9
22-4, 144-150	199.27	15.27	36.15	0.918	12.09	24.9	1001	2.58	17.0
24-3, 144-150	216.57	15.99	34.39	0.931	12.18	25.5	1026	2.34	16.9
26-3, 144-150	235.57	15.31	34.01	0.969	12.03	28.9	1236	—	15.7
28-3, 144-150	254.77	16.53	32.14	0.969	12.04	27.3	1048	—	16.9
30-2, 144-150	272.27	17.74	31.59	0.950	11.97	26.6	1073	2.21	16.7
Hole 591B									
2-3, 140-150	284.67	18.64	31.74	0.925	12.06	29.6	1056	1.84	17.0
4-3, 140-150	303.85	18.36	31.56	0.931	11.54	28.7	1037	—	—
6-3, 140-150	322.65	18.61	31.33	0.912	11.87	31.7	1071	1.85	—
10-2, 140-150	359.35	19.13	31.59	0.905	11.23	42.1	1005	—	—
12-1, 140-150	377.05	19.44	29.79	0.912	11.87	46.2	1039	2.15	—
14-1, 140-150	396.25	19.96	31.02	0.899	11.45	52.2	1082	1.86	—
18-3, 140-150	437.65	20.32	30.07	0.918	11.72	66.1	980	—	—
20-3, 140-150	456.85	20.02	29.09	0.889	—	70.9	1012	2.26	—
22-4, 140-150	477.55	19.63	28.91	0.880	12.10	76.1	990	2.43	—
24-4, 140-150	496.75	19.58	29.42	0.867	11.85	76.4	—	2.23	—
Hole 592									
2-3, 144-150	8.97	11.14	50.72	0.185	11.16	33.9	—	2.85	27.3
4-4, 144-150	29.67	11.39	—	0.370	11.26	—	207	3.39	26.0
6-3, 144-150	47.37	11.89	47.56	0.497	10.67	40.1	—	3.32	24.9
8-3, 144-150	66.57	12.26	46.91	0.580	10.49	41.4	184	3.90	24.3
10-3, 144-150	85.77	13.15	45.38	0.676	10.69	44.3	186	3.84	22.9
12-3, 144-150	104.97	13.23	45.58	0.752	10.12	46.1	190	4.00	22.4
14-3, 144-150	124.17	13.65	44.25	0.769	9.21	48.3	199	4.12	22.7
16-3, 144-150	143.37	14.15	43.99	0.784	9.81	49.2	213	4.04	21.6

Table 1. (Continued).

Core-Section (interval in cm)	Depth (m)	Ca^{2+} (mM)	Mg^{2+} (mM)	Sr^{2+} (mM)	K^+ (mM)	Li^+ (μM)	SiO_2 (μM)	Alkalinity (meq/l)	SO_4^{2-} (mM)
Hole 592 (cont.)									
18-3, 144-150	162.57	14.50	43.07	0.784	8.61	50.9	222	3.92	20.9
20-3, 144-150	181.77	15.00	42.65	0.740	9.36	51.9	224	3.99	21.1
22-3, 144-150	200.97	15.38	41.36	0.778	9.58	54.7	199	3.98	20.9
24-3, 144-150	220.17	15.70	40.90	0.784	9.81	57.5	190	3.63	20.3
26-3, 144-150	239.37	15.86	40.67	0.797	9.05	58.6	196	3.65	20.9
28-3, 144-150	258.57	15.66	40.75	0.784	9.47	60.7	211	3.28	20.7
31-3, 140-150	287.35	16.10	39.60	0.791	8.61	62.7	286	2.71	19.7
33-3, 140-150	306.55	16.71	38.54	0.771	8.93	65.2	465	3.02	20.1
35-3, 140-150	325.75	17.16	38.08	0.791	8.35	66.4	—	—	19.7
37-3, 140-150	344.95	17.20	38.04	0.797	8.49	77.4	925	3.29	19.1
39-3, 140-150	364.15	17.34	37.44	0.797	8.37	80.0	1033	3.27	18.7
41-3, 140-150	383.35	17.54	36.86	0.797	8.30	83.0	946	3.18	18.9
Site 593									
1-4, 144-150	5.97	10.56	51.96	0.166	11.07	31.6	—	3.42	27.0
4-3, 144-150	28.77	10.54	51.42	0.236	11.74	29.2	405	3.34	27.1
6-3, 144-150	47.97	10.68	49.99	0.338	11.30	32.6	—	3.34	26.4
8-1, 144-150	62.37	10.74	49.90	0.389	10.92	35.8	182	3.36	25.0
12-3, 144-150	105.57	11.24	48.99	0.529	10.81	38.3	—	4.12	24.9
14-3, 144-150	124.77	11.66	48.69	0.671	10.08	39.4	—	3.35	25.0
16-3, 144-150	143.17	11.62	48.23	0.631	9.95	39.6	177	3.94	25.0
18-3, 144-150	163.17	11.74	47.97	0.657	9.91	41.0	—	3.54	24.1
20-3, 144-150	182.37	12.18	46.37	—	10.12	42.5	—	—	24.6
22-3, 144-150	201.57	12.15	46.82	0.701	9.33	45.5	254	3.55	23.9
24-3, 144-150	220.77	12.64	46.06	0.733	9.44	45.1	241	3.78	24.3
26-3, 144-150	239.97	12.79	45.91	0.720	9.65	47.3	203	3.14	23.1
28-3, 144-150	259.17	13.17	44.02	0.733	9.37	49.8	190	2.73	22.6
30-3, 144-150	278.37	13.44	43.04	0.752	9.35	51.5	—	—	23.1
32-2, 144-150	296.07	13.84	42.68	0.695	9.16	53.1	—	2.99	23.4
34-2, 144-150	315.27	13.94	42.67	0.759	9.16	54.3	171	2.81	22.4
36-2, 144-150	334.47	14.16	42.93	0.714	9.09	57.3	—	2.28	22.4
38-3, 144-150	355.17	14.31	41.73	0.752	9.02	58.2	162	2.93	21.4
40-3, 144-150	374.37	14.77	40.57	0.733	8.51	61.0	—	2.91	21.6
42-3, 144-150	393.57	14.81	39.48	0.759	—	62.8	—	2.64	21.0
44-3, 144-150	412.77	15.46	38.69	0.765	8.30	68.4	—	2.52	21.9
46-3, 144-150	431.97	15.86	37.65	0.771	8.49	71.6	—	2.44	21.4
47-3, 144-150	441.57	15.49	—	0.746	9.28	71.9	—	1.99	21.9
48-3, 144-150	451.17	15.71	37.24	0.733	8.45	69.7	186	—	22.1
50-3, 144-150	470.37	15.69	36.60	0.759	9.21	95.5	—	2.08	21.3
54-2, 144-150	507.27	16.71	34.13	0.708	8.72	83.8	459	—	20.9
56-3, 144-150	527.97	17.12	33.50	0.746	—	—	—	—	20.6
58-1, 140-150	544.15	16.02	34.81	0.714	8.84	88.3	425	2.14	21.4
60-3, 144-150	566.37	15.14	30.16	0.689	7.79	179.5	—	—	—
Hole 594									
2-3, 144-150	10.37	6.45	51.80	0.070	11.52	32.3	689	9.57	19.6
4-3, 144-150	29.57	6.46	47.66	0.064	12.16	34.2	761	9.83	15.3
6-3, 144-150	48.77	5.83	45.45	0.070	11.54	36.1	859	14.94	10.1
8-3, 144-150	64.97	3.96	44.53	0.102	12.18	—	—	—	9.0
10-1, 144-150	84.17	5.03	41.96	0.134	10.85	43.7	808	13.06	—
12-3, 144-150	106.37	5.14	41.84	0.140	11.63	47.7	819	9.38	10.6
15-3, 144-150	135.17	5.90	43.82	0.191	11.04	40.4	931	9.28	13.3
18-3, 144-150	163.97	8.01	44.03	0.306	10.88	—	—	7.80	16.3
20-3, 144-150	183.17	9.24	43.17	0.338	10.67	31.5	954	5.62	18.0
24-3, 144-150	221.57	12.44	41.07	0.555	9.01	27.6	1039	4.84	18.9
26-3, 144-150	240.77	14.17	39.63	0.620	9.51	—	—	—	20.1
28-3, 144-150	259.97	15.02	38.88	0.657	9.70	24.8	1137	2.48	19.4
30-3, 144-150	279.17	16.34	38.62	0.720	9.23	—	1043	2.97	20.3
34-3, 144-150	316.57	17.83	36.33	0.759	9.46	—	—	—	19.1
36-3, 144-150	335.77	18.31	35.25	0.797	7.79	24.8	—	2.44	19.0
38-2, 144-150	353.47	19.31	33.98	0.810	8.23	26.1	—	2.23	19.3
40-3, 144-150	374.17	20.05	32.34	0.816	8.54	27.9	1205	—	19.6
42-3, 144-150	394.37	20.49	32.66	0.835	8.65	30.8	—	3.16	19.0
44-3, 144-150	414.57	21.44	29.63	0.861	8.16	35.5	1139	3.22	18.3
46-1, 144-150	429.77	22.00	29.07	0.861	6.58	39.8	1173	3.18	19.1
48-2, 144-150	450.47	22.58	28.94	0.867	7.24	43.7	1196	3.06	18.9
Hole 594A									
11-3, 144-150	202.37	12.08	40.89	0.478	—	30.2	908	3.11	17.6
12-1, 138-144	496.91	24.82	24.59	0.931	7.10	52.1	1364	2.99	17.1
14-3, 140-150	519.15	24.76	25.49	0.931	6.82	56.5	1340	2.68	17.0
16-3, 140-150	538.35	24.56	25.43	0.937	—	59.7	1132	2.82	17.6
19-1, 140-150	564.15	25.23	23.83	0.976	6.44	63.1	795	1.99	16.6

Table 1. (Continued).

Core-Section (interval in cm)	Depth (m)	Ca^{2+} (mM)	Mg^{2+} (mM)	Sr^{2+} (mM)	K^+ (mM)	Li^+ (μM)	SiO_2 (μM)	Alkalinity (meq/l)	SO_4^{2-} (mM)
Hole 594A (cont.)									
21-1, 140-150	583.35	24.94	23.10	0.956	6.34	68.1	—	—	15.9
23-2, 140-150	604.05	—	—	—	—	—	—	—	—
25-2, 140-150	623.25	25.11	23.05	0.963	5.48	69.0	692	1.81	16.1

Note: Dashes indicate that no analysis was performed.

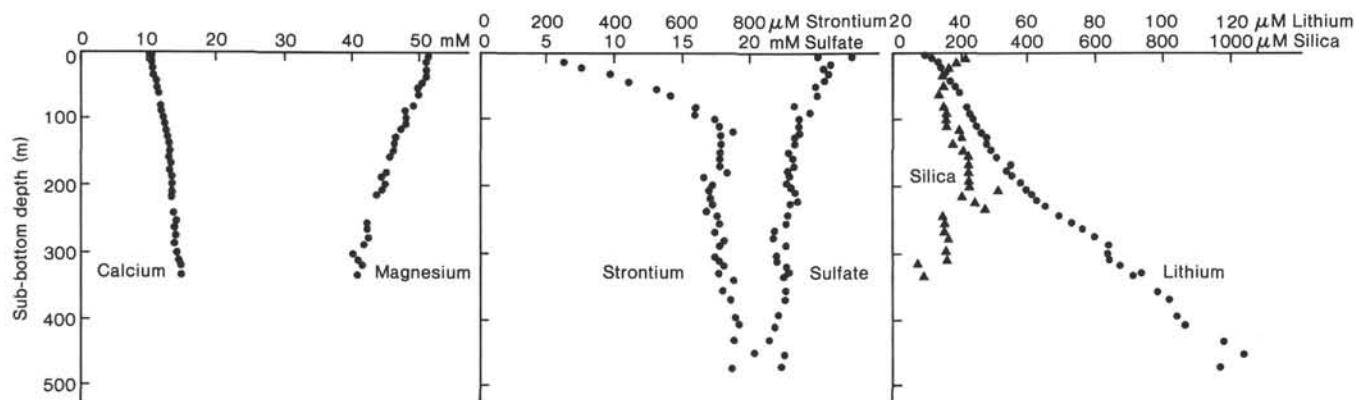


Figure 1. Pore-water concentrations of calcium, magnesium, strontium, sulfate, lithium, and silica as a function of sub-bottom depth of Site 588.

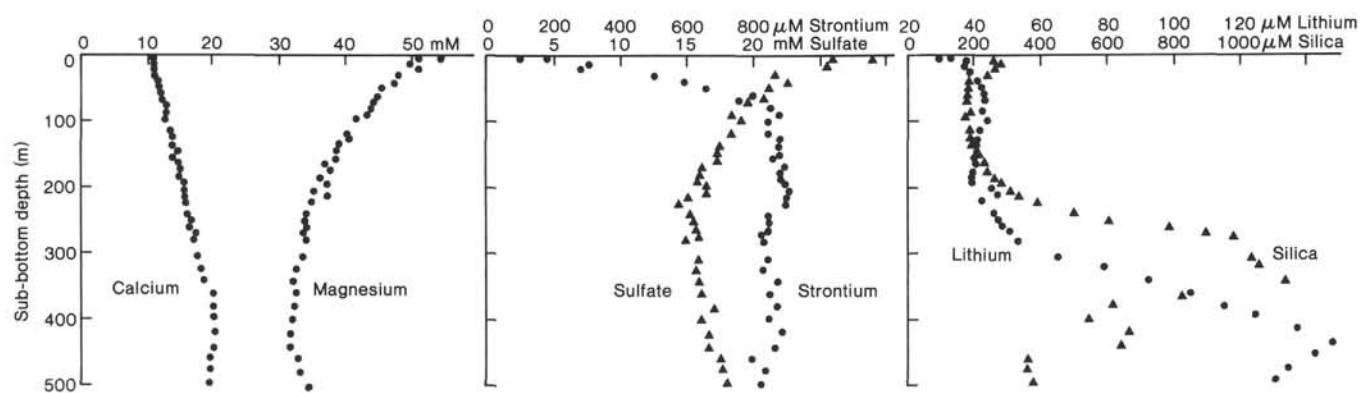


Figure 2. Pore-water concentrations of calcium, magnesium, strontium, sulfate, lithium, and silica as a function of sub-bottom depth at Site 590.

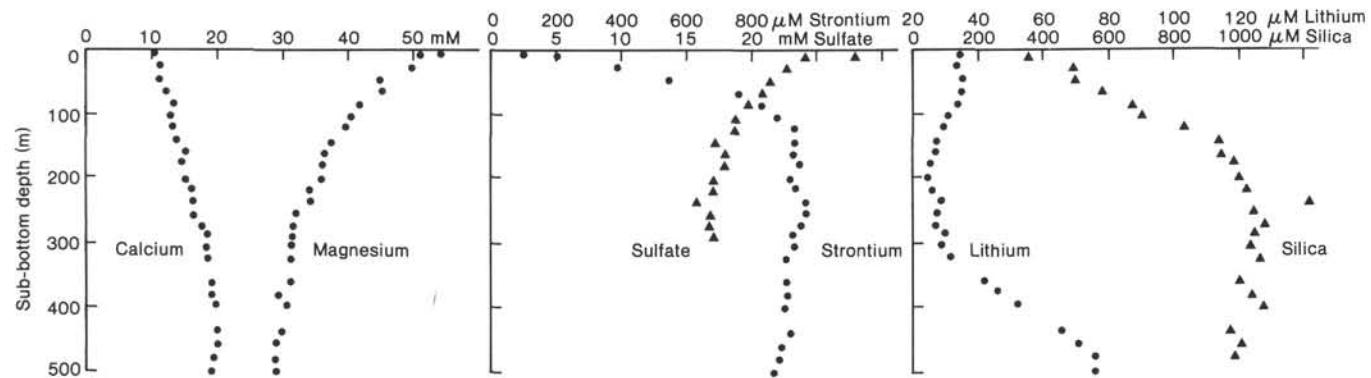


Figure 3. Pore-water concentrations of calcium, magnesium, strontium, sulfate, lithium, and silica as a function of sub-bottom depth at Site 591.

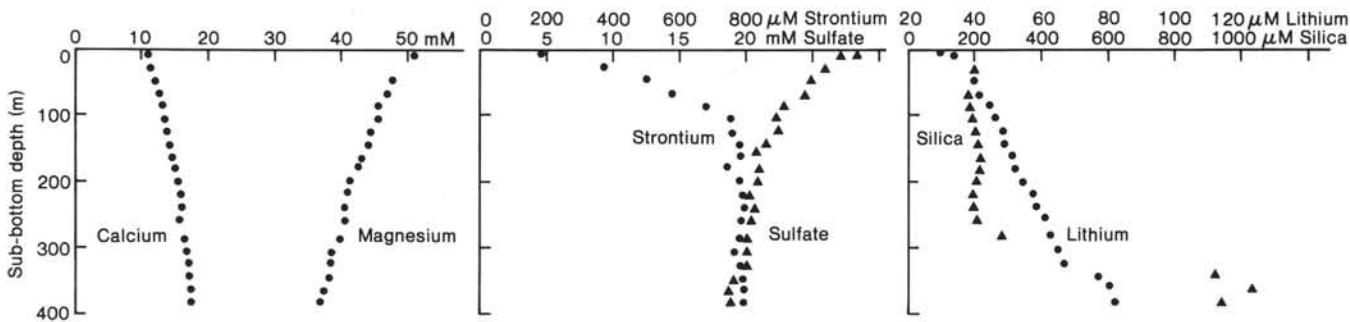


Figure 4. Pore-water concentrations of calcium, magnesium, strontium, sulfate, lithium, and silica as a function of sub-bottom depth at Site 592.

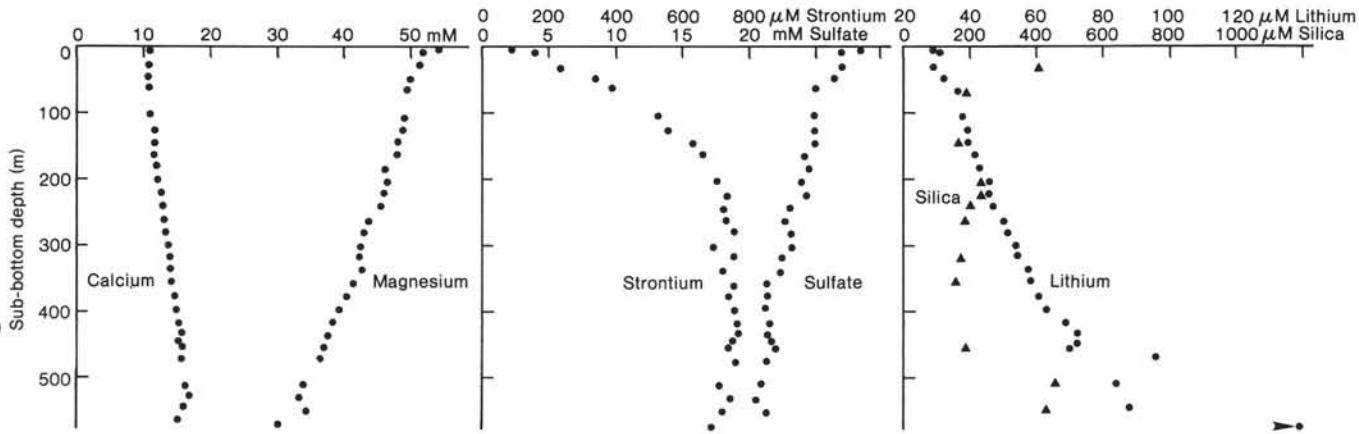


Figure 5. Pore-water concentrations of calcium, magnesium, strontium, sulfate, lithium, and silica as a function of sub-bottom depth at Site 593.

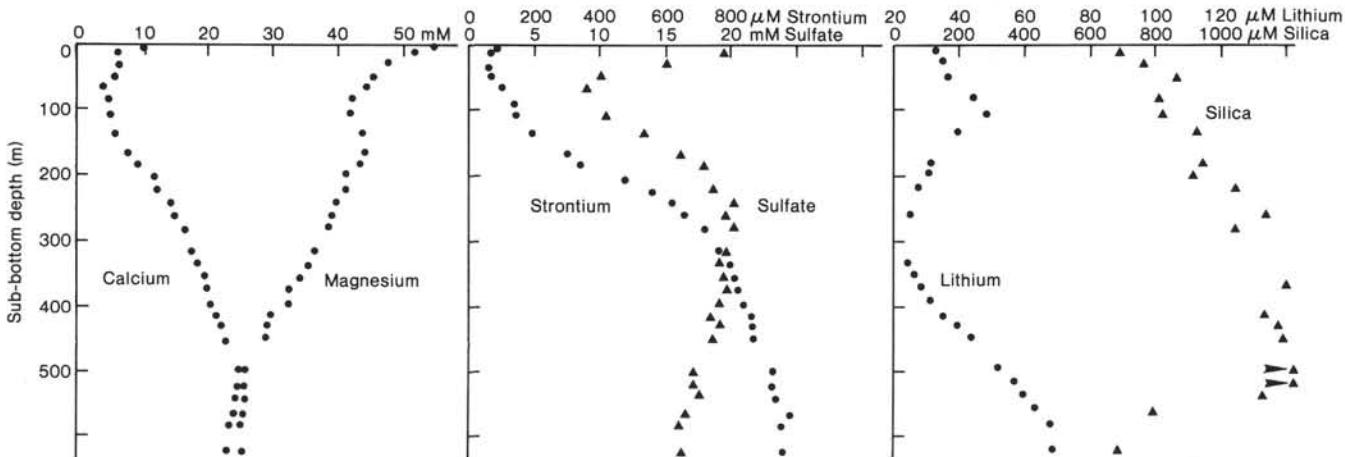


Figure 6. Pore-water concentrations of calcium, magnesium, strontium, sulfate, lithium, and silica as a function of sub-bottom depth at Site 594.

port for the hypothesis that the entire Lord Howe Rise has an affinity with continental crust (van der Lingen, 1973; Willcox et al., 1980). The minor amount of curvature (toward lower magnesium values) displayed in Figure 7 is consistent with some volcanic ash alteration within the sediment column (Gieskes and Lawrence, 1981), particularly at Sites 590 and 591.

The alkali metals, lithium and potassium, exhibit trends similar to those observed at many other DSDP sites (e.g., Gieskes, 1983). At all sites except Site 591 there is a

slight tendency for potassium concentrations to decrease and lithium concentrations to increase with increasing burial depth. It is clear from the shapes of the lithium concentration-depth curves, that sources and sinks for lithium must occur within the sediment column. At the present time, the nature of these sources and sinks is unknown (Gieskes, 1983).

Dissolved silica concentrations reflect the amount of biogenic silica present in the surrounding sediments (e.g., Gieskes, 1981). Thus, high values of dissolved silica are

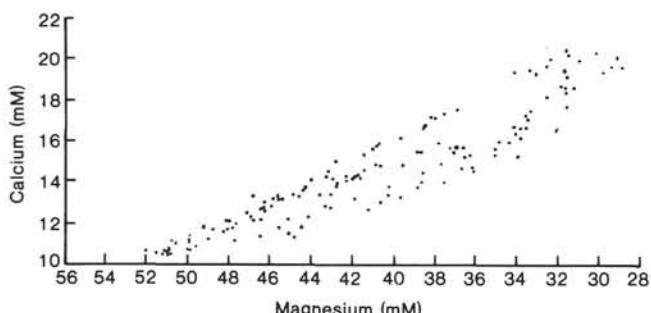


Figure 7. Pore-water concentrations of calcium and magnesium for every sample from the Lord Howe Rise Sites 588, 590, 591, 592, and 593. The data from Sites 590 and 591 lie beneath the general trend.

found at Sites 591 and 594, the two sites that contain the most abundant solid silica. Elsewhere, silica concentrations increase at depth at Sites 590 and 592. The transformation of biogenic silica to opal-CT is associated with a decrease in dissolved silica as observed at Sites 590, 592, and 594. This "silica front" occurs at depths of about 350, 375, and 550 m at the respective sites. Chert was recovered at 335 and 380 m sub-bottom at Site 592, but was not identified at Sites 590 or 594.

Because of the relatively high rates of carbonate sedimentation, microbial sulfate reduction occurs to some degree at all sites of Leg 90. There is some correlation between the degree of sulfate reduction and the rate of sedimentation, with Sites 590 and 591 having slightly lower sulfate concentrations and higher sedimentation rates than at other sites. Site 594, with its thick hemipelagic Pleistocene section, has a much greater degree of sulfate reduction than any of the Lord Howe Rise sites. At Site 594 an increase in alkalinity accompanies the decrease in sulfate. In turn, the alkalinity increase causes the precipitation of calcium carbonate and a decrease in the Ca^{2+} concentration.

The strontium concentration profiles are a product of two reactions: carbonate recrystallization and celestite (SrSO_4) precipitation. As previously shown by Baker et al. (1982), the calcium carbonate tests of foraminifers and coccoliths are enriched in strontium relative to recrystallized calcium carbonate precipitated during burial diagenesis. As a result, there is a net input of strontium to the pore waters of carbonate-rich sediments during the calcite dissolution-reprecipitation reaction. The amount of strontium incorporated into diagenetic carbonate is predicted by the product of the distribution coefficient of strontium in calcite, k_{sp} , and the ratio of dissolved strontium to dissolved calcium $\text{Sr}^{2+}/\text{Ca}^{2+}$:

$$\left(\frac{\text{Sr}}{\text{Ca}}\right)_{\text{calcite}} = k_{\text{sp}} \left(\frac{\text{Sr}^{2+}}{\text{Ca}^{2+}}\right).$$

As the amount of recrystallization increases in older and deeper carbonate sediments, the Sr^{2+} concentration increases, more strontium is incorporated into the reprecipitated calcite, and eventually a steady-state plateau concentration of Sr^{2+} is achieved.

The Sr^{2+} concentration at the plateau is typically 0.4 to 0.7 mM in deep-sea carbonate porewaters (Baker et al., 1982). The relatively high sedimentation rates at the Leg 90 sites has led to higher plateau concentrations, ranging from 0.7 mM at Site 588 to 0.9 mM at Sites 591 and 594. As a consequence of these higher concentrations, celestite precipitation occurs. Small nodules of celestite were recovered at Sites 590, 591, and 592. The observed concentration product of strontium sulfate at depth in all the Leg 90 sites averages about 15.2×10^{-6} mol²/l². The exact value of the Sr^{2+} concentrations are controlled by celestite precipitation and thus, by the degree of sulfate reduction at each site.

The concentration gradients of Sr^{2+} versus depth over the upper 100 m of core at Sites 588, 590, 591, and 592, average 7×10^{-11} mol $\text{Sr}^{2+}/\text{cm}^4$. The average diffusive flux of Sr^{2+} out of the pore waters at these sites can be calculated simply from Fick's law:

$$\text{Flux} = -D \frac{dc}{dx}$$

where D is the diffusion coefficient of Sr^{2+} in pore waters and dc/dx is the average concentration-depth gradient of Sr^{2+} . Substituting a value of 4×10^{-6} cm²/s for D , we calculate an average flux of Sr^{2+} out of the sediments of 2.8×10^{-16} mol/cm² per s or 8.8×10^{-3} mol/cm² per m.y. In a column of sediment that is 100 m thick, with a porosity of 67%, an average carbonate content of 90% and an average Sr/Ca ratio in the carbonate of 2.0×10^{-3} (Baker et al., 1982), there are about

$$(0.9 \times 5 \times 10^3 \text{ cm}^3 \text{ CaCO}_3) \left(\frac{2.7 \text{ g CaCO}_3}{\text{cm}^3 \text{ CaCO}_3} \right)$$

$$\left(\frac{1 \text{ mol Ca}}{100 \text{ g CaCO}_3} \right) \left(\frac{2.0 \times 10^{-3} \text{ mol Sr}}{\text{mol Ca}} \right)$$

$$= 0.24 \text{ mol Sr in the solid phase per cm}^2 \text{ of pore water.}$$

The average age of the sediments at 100 m sub-bottom is about 3 m.y. The diffusive flux of Sr^{2+} over a 3-m.y. time span amounts to a loss to seawater of 0.026 mol or 11% of the total amount of strontium contained in the original sediment. Thus, the *minimum* rate of recrystallization of the surface sediments is 11% in 3 m.y. However, much of the strontium released during the dissolution of biogenic calcite is immediately sequestered during the reprecipitation of authigenic calcite. In fact, the "efficiency" of strontium release is probably only about one-third in the upper 100 m of sediment (and almost zero below 100 m). This implies that as much as 30–35% of the carbonate in the upper 100 m of sediment is recrystallized!

Values for the distribution coefficient, k_{sp} , have previously been derived mostly from experimental studies. A limiting value also can be derived in the following manner. The amount of strontium incorporated into authigenic calcite cannot exceed the average amount of stron-

tium in the biogenic calcite. The latter value, as used, is about 2×10^{-3} mol Sr/mol Ca. At the Sr^{2+} concentration plateau:

$$2 \times 10^{-3} \geq k_{\text{sr}} \left(\frac{\text{Sr}^{2+}}{\text{Ca}^{2+}} \right)_{\text{plateau}}$$

Using an average value of 5×10^{-2} mol/mol for the $(\text{Sr}^{2+}/\text{Ca}^{2+})_{\text{plateau}}$, yields a value of $k_{\text{sr}} \leq 0.04$. This number agrees very well with the results of Katz et al. (1972) and Baker et al. (1982). In the latter paper, we predicted a value of $k_{\text{sr}} \approx 0.04$ at 5°C and 0.08 mM Sr^{2+} .

CONCLUSIONS

In summary, we can make the following statements on the basis of the observed pore-water chemistry of Leg 90 drill sites. (1) The calcium and magnesium concentration-depth gradients are dominated by silicate alteration reactions occurring mostly at depth beneath the sampled sediments. The unusual value of $\Delta\text{Ca}^{2+}/\Delta\text{Mg}^{2+} \approx -0.45$ mol/mol is consistent with the observation that the entire Lord Howe Rise is underlain by siliceous rocks. Some volcanic ash alteration can be detected within the sediments at Sites 590 and 591. (2) Minor amounts of microbial sulfate reduction occur at all sites on the Lord Howe Rise. A much higher amount of sulfate reduction occurs in the hemipelagic sediments at Site 594. (3) Strontium pore-water concentrations are determined by carbonate recrystallization reactions. Dissolved strontium concentrations increase downcore until celestite precipitation occurs. At greater depths, strontium concentrations are controlled by thermodynamic equilibrium with respect to celestite, thus Lord Howe Rise sites with lower rates of sulfate reduction have lower concentrations of dissolved strontium. (4) The diffusive flux of strontium in the upper 100 m of the pore waters can only reasonably be explained by recrystallization of the bulk carbonate sediment at an initial rate of about 10%/m.y. To verify paleoceanographic conclusions based on isotopic and/or chemical compositions of the carbonate constituents therefore will require detailed study of the relative reaction rates of different sediment components.

ACKNOWLEDGMENTS

This work has benefited from detailed reviews by Joris M. Gieskes and Douglas B. Kent. In addition, I thank Paul M. Stout and James V. Gardner for their helpful discussions. Jim Pine extracted all the pore waters aboard the *Glomar Challenger*. Support was provided for this work by NSF-OCE-8219917.

REFERENCES

- Baker, P. A., Gieskes, J. M., and Elderfield, H., 1982. Diagenesis of carbonates in deep-sea sediments—evidence from Sr/Ca ratios and interstitial dissolved Sr^{2+} data. *J. Sediment. Petrol.*, 52:71–82.
- Gieskes, J. M., 1973. Interstitial water studies, Leg 15—alkalinity, pH, Mg, Ca, Si, PO_4 , and NH_4 . In Heezen, B. C., MacGregor, I. D., et al., *Init. Repts. DSDP*, 15: Washington (U.S. Govt. Printing Office), 813–829.
- _____, 1974. Interstitial water studies, Leg 25. In Simpson, E. S. W., Schlich, R., et al., *Init. Repts. DSDP*, 25: Washington (U.S. Govt. Printing Office), 361–394.
- _____, 1981. Deep-sea drilling interstitial water studies: implications for chemical alteration of the oceanic crust, layers I and II. *SEPM Spec. Pub.*, 32:149–167.
- _____, 1983. The chemistry of interstitial waters of deep sea sediments: interpretation of deep sea drilling data. In Riley, J. P., and Chester, R. (Eds.), *Chemical Oceanography* (Vol. 8): London (Academic Press), pp. 221–269.
- Gieskes, J. M., and Lawrence, J. R., 1976. Interstitial water studies, Leg 35. In Hollister, C. D., Craddock, C., et al., *Init. Repts. DSDP*, 35: Washington (U.S. Govt. Printing Office), 407–423.
- _____, 1981. Alteration of volcanic matter in deep sea sediments: evidence from the chemical composition of interstitial waters from deep sea drilling cores. *Geochim. Cosmochim. Acta*, 45:1687–1703.
- Gieskes, J. M., Lawrence, J. R., and Gallecky, G., 1978. Interstitial water studies, Leg 38. In Talwani, M., Uditsev, G., et al., *Init. Repts. DSDP*, Suppl. to Vols. 38, 39, 40, and 41: Washington (U.S. Govt. Printing Office), 121–133.
- Katz, A., Sass, E., Starinsky, A., and Holland, H. D., 1972. Strontium behavior in the aragonite-calcite transformation: an experimental study at 40–98°C. *Geochim. Cosmochim. Acta*, 36:481–496.
- Manheim, F. T., and Sayles, F. L., 1974. Composition and origin of interstitial waters of marine sediments based on deep sea drill cores. In Goldberg, E. D. (Ed.), *The Sea* (Vol. 5): New York (Wiley-Interscience), 527–568.
- Manheim, F. T., Sayles, F. L., and Waterman, L. S., 1972. Interstitial water studies on small core samples, Deep Sea Drilling Project, Leg 12. In Laughton, A. S., Berggren, W. A., et al., *Init. Repts. DSDP*, 12: Washington (U.S. Govt. Printing Office), 1193–1200.
- McDuff, R. E., 1981. Major cation gradients in DSDP interstitial waters: The role of diffusive exchange between seawater and upper oceanic crust. *Geochim. Cosmochim. Acta*, 45:1705–1713.
- McDuff, R. E., and Gieskes, J. M., 1976. Calcium and magnesium in DSDP interstitial waters: diffusion or reaction? *Earth Planet. Sci. Lett.*, 33:1–10.
- Presley, B. J., 1971. Techniques for analyzing interstitial water samples. I. Determination of selected minor and major inorganic constituents. In Winterer, E. L., Riedel, W. R., et al., *Init. Repts. DSDP*, 7, Pt. 2: Washington (U.S. Govt. Printing Office), 1749–1755.
- Sandstrom, M., and Gieskes, J. M., 1974. Interstitial water studies, Leg 24. In Fisher, R. L., Bunce, E. T., et al., *Init. Repts. DSDP*, 24: Washington (U.S. Govt. Printing Office), 799–810.
- van der Lingen, G. J., 1973. The Lord Howe Rise rhyolites. In Burns, R. E., Andrews, J. E., et al., *Init. Repts. DSDP*, 21: Washington (U.S. Govt. Printing Office), 523–540.
- Willcox, J. B., Symonds, P. A., Hinz, K., and Bennett, D., 1980. Lord Howe Rise, Tasman Sea—preliminary geophysical results and petroleum prospects. *B.M.R. J. Aust. Geol. Geophys.*, 5:225–236.

Date of Initial Receipt: 18 June 1984

Date of Acceptance: 31 October 1984