7. INTERSTITIAL WATER STUDIES ON SMALL CORE SAMPLES. LEG 15¹

Fred L. Sayles, Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

Frank T. Manheim, U.S.G.S., Woods Hole Oceanographic Institution, Woods Hole, Massachusetts and

Lee S. Waterman, Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

ABSTRACT

Analyses of pore fluids from reducing environments demonstrate that reduction of SO₄ is accompanied by large increases in alkalinity and strong depletion of Ca and Mg. The data are compatible with a model of replacement of Fe^{3+} in clay lattices by Mg from the interstitial solutions and the precipitation of pyrite. Depletions of Na in the interstitial solutions are related to Mg losses by a ratio of approximately 1:3. Pore fluids from oxidizing pelagic sediments exhibit little SO₄ depletion. Losses of Mg are accompanied by the addition of Ca to the pore solutions on a nearly 1:1 basis. Strong Sr envichment is also found in these solutions. The magnitude of the Sr increase suggests that considerable carbonate recrystallization has occurred.

As part of an extensive interlaboratory and analytical calibration, the effect of squeezing sediment at different temperatures has been studied in depth. Samples of a variety of lithologies have been included. Enrichment of K by as much as 24 percent and depletion of Mg and Ca by up to 7 percent occurs during warming. However, no significant effect upon Cl and SO₄ could be detected. The strongest effects are seen in the minor constituents studied. On warming, Sr, Si, and B are enriched as much as 19, 40, and 60 percent, respectively. The size of the observed concentration changes varies with the mineralogy of the sediment, but is significant in all types studied, particularly with regards to Mg and K.

INTRODUCTION

The special geochemical effort of Leg 15 was initiated to provide information not usually available from the more routine operations of previous legs. The objectives specifically considered in this report include analytical checks on the effects of prolonged storage, analysis of temperatureof-squeezing artifacts observed in a variety of sediments, and the directions and pathways of diagenetic reactions affecting the major and minor constituents of interstitial solutions. Details of the procedures employed aboard the ship are presented elsewhere in this volume (Horowitz et al., this volume). The analytical procedures utilized in this laboratory are described in earlier leg reports.

Analyses of SiO_2 and alkalinity were completed onboard the *Glomar Challenger* and repeated later with aliquots of the same solutions in shore laboratories to investigate the effects of prolonged storage. Sediment samples were squeezed at 4° C and 22° C to provide quantitative data on concentration differences resulting from processing essentially identical samples at different temperatures. Data have been obtained on the size of these concentration changes for clays and calcareous and siliceous biogenic sediments. The studies, only part of which are considered here, represent a more comprehensive investigation of the composition of interstitial solutions than hitherto undertaken. This is particularly so with regard to ephemeral constituents and sampling density.

RESULTS

The major ion data for the Leg 15 samples are summarized in Tables 1 and 2 (cations and anions, respectively). Charge balances and analytical comparisons of Na determinations are presented in Table 3; water content and total dissolved solid data are listed in Table 4. The concentrations of the minor elements Ba, Sr, Mn, Li, B, and Si are given in Table 5. For most samples, analyses of the solutions from both the 4°C and 22°C processing are reported. SiO₂ concentrations determined aboard the ship and in this laboratory are compared in Table 6.

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5	bottom			w h	w h				-		
Sample	(m)	Age	Description	Na ^b Cold	Warm	K Cold	K Warm	Ca Cold	Ca Warm	Mg Cold	Mg Warm
Site 147 (1	0°42.5'N,	65° 10.5′W, wa	ater depth 892 m, Cariaco B	asin)							
147B-1-2	2.5	Pleistocene	Olive gray clay	10.9	10.9	0.33	0.39	0.24	0.64	1 25	1.14
147B-1-3	4.25	Pleistocene	Olive gray clay	10.9	10.7	0.34	0.37	0.14	0.15	1.14	1.08
147B-1-4 (15-33)	4.75	Pleistocene	Olive gray clay	10.8	10.9	0.29	0.34	0.11	0.10	1.16	1.08
147B-1-4 (35-57)	4.85	Pleistocene	Olive gray clay	10.8	10.8	0.29	0.36	0.08	0.08	1.09	1.03
147B-1-4 (57-95)	5.1	Pleistocene	Olive gray clay.	10.7	10.9	0.28	0.34	0.08	0.07	1.06	1.02
147-2-3/4	8.5	Pleistocene	Olive gray and greenish gray clay.	10.9	-	0.29	-	0.12	-	1.16	-
147B-2-2c	15	Pleistocene	Grayish olive green clay	10.9	11.0	0.35	0.39	0.37	0.37	1.33	1.32
147B-2-6	21	Pleistocene	Grayish olive green clay	10.8	11.0	0.27	0.34	0.17	0.16	1.05	0.98
147-4-3/4	28	Pleistocene	Grayish olive green clay, calcareous.	10.8		0.28	-	0.22	_	1.00	-
147B-6-2	51	Pleistocene	Grayish olive green clay, calcareous.	11.0	11.1	0.32	0.39	0.15	0.15	0.73	0.67
147-8-2/3	63	Pleistocene	Grayish olive green clay, calcareous	10.9		0.31	_	0.22	-	0.75	-
147B-7-4	63	Pleistocene	Grayish olive green clay, calcareous.	10.9	11.0	0.33	0.42	0.21	0.15	0.72	0.65
147-10-3/4	82	Pleistocene	Grayish olive green clay, calcareous, plastic.	10.9	-	0.31	-	0.24	-	0.72	-
1478-9-4	83	Pleistocene	Grayish olive green clay, calcareous.	10.7	10.8	0.31	0.38	0.10	0.06	0.67	0.61
1478-11-3	100	Pleistocene	Grayish olive green clay, calcareous.	10.7	10.7 (10.9)	0.34	0.38 (0.39)	0.08	0.12 (0.13)	0.70	0.63
147C-2-1	126	Pleistocene	Grayish olive green clay, calcareous.	10.5	10.7	0.31	0.36	0.06	0.06	0.70	0.65
147C-4-4	148	Pleistocene	Grayish olive green clay, calcareous.	10.4	10.6 (10.4)	0.34	0.37 (0.37)	0.08	0.21 (0.21)	0.62	0.57
147C-7-4	176	Pleistocene	Grayish olive green and and dark greenish gray clay, calcareous, firm and plastic.	10.3	10.3	0.27	0.32	0.16	0.11	0.60	0.54
Site 148 (1	3° 25.1'N, 6	53°43.2'W, wa	ter depth 1232 m, western o	rest o	f Aves I	Ridge)					
148-1-2	3	Pleistocene	Greenish gray foram- nanno ooze, soft and	10.8	10.8	0.39	0.46	0.39	0.38	1.30	1.05
148-1-4	6	Pleistocene	Greenish gray foram- nanno ooze, soft and plastic	10.7	10.9	0.40	0.44	0.37	0.36	1.28	1.22
148-2-1	11	Pleistocene	Greenish gray foram- nanno marly ooze, soft and plastic.	10.6	10.7 (10.5)	0.37	0.48 (0.48)	0.32	0.30 (0.29)	1.25	1.19 (1.17)
148-2-3	13	Pleistocene	Greenish gray foram- nanno marl, moderately soft and plastic.	10.7	10.8 (10.8)	0.39	0.44 (0.44)	0.31	0.30 (0.30)	1.25	1.18 (1.18)
148-3-3	22	Pleistocene	Greenish gray to light olive gray foram-nanno marl, moderately soft and plastic.	10.7	10.8	0.37	0.41	0.30	0.29	1.27	1.19
148-4-3	31	Pleistocene	Greenish gray foram- nanno marl, soft and plastic.	10.8	10.9	0.33	0.42	0.30	0.29	1.26	1.21
148-5-2	39	Pleistocene	Greenish gray foram- nanno marl moderately soft and plastic.	10.8	10.8	0.32	0.36	0.25	0.23	1.22	1.17
148-6-4	51	Pleistocene	Greenish gray foram- nanno marl, homogeneous, soft and plastic.	10.6e	10.8 (10.7)	0.326	0.40 (0.40)	0.27 ^e	0.25 (0.25)	1.21 ^e	1.11 (1.13)
148-6-4	51	Pleistocene	Greenish gray foram- nanno marl, homogeneous, soft and plastic.	10.7 ^f	-	0.34f	-	0.26f	-	1.20 ^f	-

		T.	ABLE 1			
Major	Constituents of	of Pore	Fluids,	Leg	15:	Cationsa

TABLE 1	 Continued
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Sample	Subbottom Depth (m)	Age	Description	Na ^b Cold	Nab Warm	K Cold	K Warm	Ca Cold	Ca Warm	Mg Cold	Mg Warm
148-7-3	59	Pleistocene	Greenish gray foram- nanno marl, homogeneous moderately soft and	10.7	10.7	0.30	0.36	0.24	0.22	1.14	1.05
148-8-3	67	Pleistocene	plastic. Dark greenish gray foram- nanno clay with thin ash layers scattered through- out, moderately firm, plastic	10.7	10.8	0.27	0.35	0.22	0.21	1.12	1.03
148-9-4	79	Pleistocene	Dark greenish gray foram- nanno clay, moderately firm and plastic	10.7	10.8	0.27	0.35	0.21	0.20	1.07	0.99
148-10-3	86	Pleistocene	Dark greenish gray foram- nanno clay, with faint pyritic speckling throughout, moderately firm and plastic	10.7	10.9	0.27	0.35	0.23	0.21	1.07	0.98
148-12-4	106	Pleistocene	Dark greenish gray foram nanno clay with pyritic speckling, moderately soft and plastic	10.5		0.23	-	0.25	-	0.93	-
148-14-3	122	Pliocene	Dark greenish gray foram- nanno marl and clay, pyrite specks, soft and plastic	10.5	10.8	0.23	0.29	0.27	0.24	0.96	0.86
148-16-3	141	Pliocene	Dark greenish gray foram- nanno marl, moderately	10.5	10.7	0.22	0.28	0.34	0.31	0.87	0.80
148-18-2	159	Pliocene	Dark greenish gray foram- nanno marl, with pyritic concretions throughout, firm and plastic	10.5	10.7	0.21	0.26	0.41	0.37	0.87	0.79
148-20-3	179	Pliocene	Greenish gray and dark greenish gray foram-nanno marl firm and plastic	10.5	10.7	0.21	0.27	0.44	0.40	0.84	0.78
148-23-4	209	Pliocene	Dark greenish gray to greenish gray foram- nanno marl, firm and plastic	10.4	10.6	0.22	0.29	0.43	0.38	0.87	0.80
148-26-2	232	Pliocene	Dark grayish green to olive gray foram-nanno marl firm and plastic	10.4	10.5	0.23	0.28	0.46	0.42	0.90	0.82
148-27-4	246	Pliocene	Varicolored greenish gray and olive foram- nanno marl, very com- pact, slightly plastic.	:	10.5	=	0.29	-	0.44	-	0.83
Site 149 (15° 06.2'N, 6	59° 21.8'W, wa	ter depth 3972 m, Venezue	lan Bas	sin)						
149-2-2	4	Pleistocene	Varicolored yellowish brown and grayish	10.7	10.6 (10.6)						
149-2-5	8	Pleistocene	orange foram ooze, soft. Varicolored yellowish brown and grayish orange foram ooze, soft	10.7		0.37	-	0.43	-	1.29	-
149-3-5	17	Pleistocene	Varicolored grayish orange and olive gray	10.6 (10.8)	10.7	0.38 (0.38)	0.35	0.47 (0.46)	0.48	1.22 (1.14)	1.26
149-4-3	23	Pleistocene	Grayish orange foram ooze, moderately soft and plastic.	10.7 (10.6)	10.7	0.35 (0.35)	0.39	0.48 (0.48)	0.47	1.26 (1.24)	1.21
149-5-3	32	Pleistocene	Gravish orange and greenish gray foram ooze, moderately soft and plastic.	10.6 (10.7)	10.9	0.34 (0.34)	0.40	0.54 (0.53)	0.52	1.20 (1.16)	1.18

Sample	Subbottom Depth (m)	Age	Description	Na ^b Cold	Na ^b Warm	K Cold	K Warm	Ca Cold	Ca Warm	Mg Cold	Mg Warm
149-6-4	43	Pleistocene-	Light olive gray to	10.8	10.9	0.32	0.38	0.56	0.55	1.21	1.15
		boundary	chalk, moderately firm and plastic.								
149-7-2	49	Pliocene	Light olive gray foram chalk, soft and plastic.	10.9	10.8	0.38	0.38	0.52	0.53	1.18	1.18
149-8-4	62	Pliocene	Light olive gray foram chalk, clayey, soft and plastic.	10.7	10.9	0.31	0.37	0.58	0.56	1.21	1.16
149-9-5	72	Pliocene	Light olive gray and greenish gray foram marl, very soft and plastic.	10.7	10.9	0.29	0.35	0.62	0.60	1.18	1.13
149-10-2	78	Pliocene	Medium yellowish brown clay, firm and plastic.	10.6	10.8	0.27	0.31	0.67	0.67	1.18	1.11
149-11-4	90	Pliocene	Light olive gray clay with some faint burrow mottling, firm and plastic.	10.7	10.9	0.27	0.33	0.67	0.66	1.18	1.10
149-12-5d	100	Late Miocene	Grayish orange nanno marl, small scale burrow mottling.	9.4	9.7	0.22	0.28	0.72	0.67	0.91	0.86
149-14-3	116	Middle Miocene	Grayish yellow green clay with variegated lumps of mark	10.5	10.8	0.24	0.30	0.92	0.83	1.07	1.01
149-16-4	135	Middle Miocene	Varicolored brown and gray marl, strong color mottling, firm and	10.6	11.0	0.23	0.30	0.98	1.00	0.99	0.95
149-18-3	153	Early Miocene	Pale grayish orange and yellowish gray	10.8	10.9	0.25	0.30	0.98	0.94	1.00	0.97
149-20-4	173	Early Miocene	Varicolored orange and gray foram-nanno chalk, extensive burrow mottling, firm and elightly crumbly	10.8	10.8	0.24	0.31	1.20	1.17	0.88	0.85
149-23-4	201	Early Miocene	Grayish orange foram- nanno chalk, crumbly	10.8	11.0	0.23	0.27	1.31	1.27	0.85	0.81
149-26-2	226	Oligocene	Varicolored green and gray foram-nanno chalk.	10.7	11.0	0.22	0.26	1.36	1.30	0.80	0.79
149-29-3	254	Oligocene	Yellowish gray to greenish gray nanno-rad chalk firm and crumbly	10.8	11.0	0.22	0.28	1.27	1.19	0.83	0.79
149-31-1	271	Late Eocene Eocene	Grayish orange to dark yellowish orange indu- rated rad ooze, very compact and crumbly	10.9	11.0	0.23	0.26	1.30	1.28	0.79	0.78
149-33-1	289	Middle Eocene	Grayish orange to dark yellowish orange indurated rad ooze,	10.9	10.9	0.23	0.26	1.32	1.28	0.78	0.77
149-34-2	301	Middle Eocene	Grayish orange indurated rad ooze, scattered pumice fragments.	-	11.0	<i>.</i>	0.27	-	1.38		0.77
149-35-4	313	Middle Eocene	Yellowish gray nanno rad chalk, scattered pumice fragments.	10.9	10.9	0.21	0.22	1.38	1.40	0.82	0.82
149-37-3	329	Middle Eocene	Very pale orange nanno-rad chalk, very compact and crumbly	11.0	11.0	0.20	0.22	1.44	1.46	0.79	0.78
149-40-1	354	Middle Eocene	Yellowish gray indu- rated rad ooze, compact and crumbly.	10.6	10.5	0.18	0.21	1.41	1.38	0.77	0.76

TABLE 1 – Continued

Sample	Subbottom Depth (m)	Age	Description	Na ^b Cold	Nab Warm	K Cold	K Warm	Ca Cold	Ca Warm	Mg Cold	Mg Warm
149-41-5	369	Middle Eocene	Pale yellowish gray and grayish orange indurated rad ooze, quite compact.	10.2	11.0	0.19	0.24	1.22	1.27	0.72	0.83
149-42-2	374	Middle Eocene	Yellowish gray indurated rad ooze, compact and crumbly.	10.8	10.8	0.20	0.22	1.34	1.30	0.80	0.85

TABLE 1 – Continued

^aValues in g/kg ($^{\circ}/_{\circ\circ}$) except as noted. Values in parentheses represent separate samples carried through the entire analytical process. The room temperature (warm) sample has been arbitrarily paired with the "low pH" sample in this tabulation.

bSodium determined by analysis. Values in parentheses refer to separate samples carried through the entire sampling and analytical processes.

^cBoth warm and cold samples show high Ca and SO₄ (Table 2) values indicating a contamination of the interstitial water by the drilling fluid, surface ocean water, during the coring operation.

^dMarkedly lower Na and Cl (Table 2) values indicate a contamination of the interstitial water by the drilling fluid, fresh water, during the coring operation.

e"Low pH" sample obtained from one of the cold squeezings; analyzed separately.

f"High pH" sample; analyzed separately.

Major Constituents

Changing the temperature at which the samples are processed has a significant effect upon the concentration of all the major cations. As has been reported by Mangelsdorf et al. (1969) and Bischoff et al. (1970), the univalent cations are enriched by warming while the divalent cations are depleted.² A comparison of the pairs of analyses from each sediment sample are given in Table 7. In terms of total change in milliequivalents per kilogram of solution, Mg and Na predominate (Table 8). On the basis of percent change, K is affected far more strongly than any of the other major cations; increases range to 32 percent of the 4°C concentration. Na increases on warming rarely exceed 3 percent and average slightly more than 1 percent. Depletions of Mg on warming consistently fall in the range 5 to 10 percent. The Ca data exhibit considerable scatter, particularly for Site 147. Sites 148 and 149 data are more consistent, indicating percent depletions similar to that of Mg.

The scatter of the Ca data at Site 147 may be due to precipitation of $CaCO_3$ during processing and storage. As noted by Gieskes (this volume), there is evidence that precipitation of $CaCO_3$ has occurred in some of our samples in which the alkalinity is very high, as at Site 147. Gieskes' data for Site 147 are also scattered with regard to temperature effects. Quite possibly, alteration of the interstitial solutions occurred prior to and during processing. Since Ca concentrations are low at Site 147, relatively small changes as a result of CaCO₃ precipitation would completely overshadow the temperature effects. The consistency of the data from Sites 148 and 149 leaves little doubt as to the direction and size of the temperature effect to be expected, however.

The major anions, in general, do not show systematic temperature effects. The differences seen between the 4°C and 22°C processing are attributable to sampling and analytical error in most cases. The average chloride change is about 0.4 percent, roughly equivalent to the uncertainty of the handling and analytical procedure. The number of samples showing depletion on warming is only slightly in excess of those exhibiting enrichment. The response of SO₄ to temperature change is similar to that of chloride with one exception. Nearly 80 percent of the Site 149 samples show enrichment on warming. The size of the observed enrichment is on the order of 0.5 percent. This is less than our estimated precision, but we would expect a random deviation rather than one skewed heavily in one direction. A systematic temperature effect is a possibility for these sediments, but, even if real, the size of this change is small enough to preclude significant influence on virtually all of the data. Results for alkalinity are considered in detail in this volume by Gieskes.

Variations in size of the temperature-induced concentration changes are seen at the three sites investigated. Most of these variations are relatively small, doubtless reflecting similarity in gross mineralogy. Temperature of squeezing effects on Na, K, and Mg are significantly smaller in the lower part of Site 149 (below Core 29) than in other samples. K and Mg concentration changes as a result of changes in processing temperature are largest in the samples from Site 148. The variation in temperature-induced Ca concentration change is, for the most part, within the uncertainty of the analyses.

² Sample 149-3-5 exhibits exactly the opposite behavior (see Table 6) and it is thought that the warm and cold portions of this sample have been mislabeled.

1	Subbottom										3
a i	Depth			C1.	C1.	SO4	SO4	Alk.	Alk.	HCO3b	HCO3b
Sample	(m)	Age	Description	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm
Site 147 (1	0°42.5'N, 6	65° 10.5'W, wa	ter depth 892 m, Cariaco B	asin)							
147B-1-2	2.5	Pleistocene	Olive gray clay.	20.00	20.00	0.98	2.33	7.8	2.8	0.47	0.17
147B-1-3	4.25	Pleistocene	Olive gray clay.	20.14	19.83	0.54	0.52	16.9	10.9	1.03	0.67
147B-1-4	4.75	Pleistocene	Olive gray clay.	19.93	19.93	0.32	0.26	15.5	15.1	0.94	0.92
(15-33) 147B-1-4 (35-57)	4.85	Pleistocene	Olive gray clay.	19.85	19.79	0.05	0.13	23.5	14.3	1.43	0.87
147B-1-4 (57-95)	5.1	Pleistocene	Olive gray clay.	19.88	20.02	0.03	0.02	11.4	12.4	0.70	0.76
147-2-3/4	8.5	Pleistocene	Olive gray and greenish	19.91	-	0.45	-	10.6	-	0.65	-
147B-2-2c	15	Pleistocene	Gravish olive green clay.	19.97	20.00	2.27	2.30	6.6	5.8	0.41	0.35
147B-2-6	21	Pleistocene	Gravish olive green clay.	20.02	20.09	0.03	0.04	12.2	10.0	0.74	0.61
147-4-3/4	28	Pleistocene	Grayish olive green	19.91	_	0.07		4.0	-	0.24	-
			clay, calcareous.								
147B-6-2 14	51	Pleistocene	Grayish olive green clay, calcareous	19.48	19.66	0.13	0.03	6.0	6.9	0.37	0.42
147-8-2/3	63	Pleistocene	Grayish olive green clay, calcareous.	19.19		0.09	<u>न्तः</u> स्टब्स्	10.3	-	0.63	77.1 10.100
147B-7-4	63	Pleistocene	Grayish olive green clay, calcareous.	19.07	18.95	0.04	0.03	15.8	17.0	0.96	1.04
147-10-3/4	82	Pleistocene	Grayish olive green clay, calcareous, plastic.	18.97		0.13	-	16.9		1.03	-
147B-9-4	83	Pleistocene	Grayish olive green clay, calcareous.	18.64	18.72	0.01	0.01	12.6	16.3	0.77	1.00
147B-11-3	100	Pleistocene	Grayish olive green clay, calcareous.	18.48	18.53	0.16	0.18	18.9	23.8 (21.6)	1.16	1.45 (1.32)
147C-2-1	126	Pleistocene	Grayish olive green clay, calcareous.	18.26	18.21	0.22	0.17	13.8	15.3	0.84	0.93
147C-4-4	148	Pleistocene	Grayish olive green clay, calcareous.	18.15	18.14	0.20	0.14 (0.15)	22.5	24.3 (17.7)	1.37	1.48 (1.08)
147C-7-4	176	Pleistocene	Grayish olive green and dark greenish gray clay, calcareous, firm and plastic.	17.83	17.79	2 <u>_</u> 2	0.06	10.0	16.0 (18.4)	0.61	0.98 (1.12)
Site 148 (1	3° 25.1'N, 6	3°43.2'W, wa	ter depth 1232 m, Western	crest of	Aves Rid	ge)					
148-1-2	3.	Pleistocene	Greenish gray foram- nanno ooze, soft and	19.58	19.73	2.60	2.63	2.6	4.3	0.16	0.26
148-1-4	6	Pleistocene	Greenish gray foram- nanno ooze, soft and	19.49	19.42	2.49	2.49	3.7	4.5	0.23	0.28
148-2-1	11	Pleistocene	Greenish gray foram- nanno marly ooze, soft	19.47	19.43	2.34	2.36 (2.34)	3.2	3.0 (2.9)	0.20	0.18 (0.17)
148-2-3	13	Pleistocene	Greenish gray foram- nanno marl, soft and	19.56	19.53	2.22	2.22	4.2	4.4 (4.4)	0.25	0.27 (0.27)
148-3-3	22	Pleistocene	Greenish gray to light olive gray foram-nanno marl, moderately soft and plastic.	19.48	19.61	2.04	2.12	4.5	6.0	0.28	0.37
148-4-3	31	Pleistocene	Greenish gray foram- nanno marl, soft and plastic.	19.58	19.61	2.10	2.23	4.5	6.1	0.27	0.37
148-5-2	39	Pleistocene	Greenish gray foram- nanno marl, moder- ately soft and plastic.	19.57	19.59	1.57	1.60	5.2	4.9	0.32	0.30
148-6-4	51	Pleistocene	Greenish gray foram- nanno marl, homoge- neous, soft and plastic.	19.54e	19.64	1.61 ^e	1.74	5.9e	3.8 (5.8)	0.36 ^e	0.23 (0.36)
148-6-4	51	Pleistocene	Greenish gray foram- nanno marl, homo- geneous, soft and plastic.	19.62 ^f	-	1.48 ^f		6.1 ^f		0.37 ^f	-

 TABLE 2

 Major Constituents of Pore Fluids, Leg 15: Anions^a

	Subbottom Depth			Cl.	C1.	SO4	SO4	Alk.	Alk.	HCO3b	HCO3b
Sample	(m)	Age	Description	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm
148-7-3	59	Pleistocene	Greenish gray foram- nanno marl, homo- geneous, moderately	19.59	19.56	1.23	1.13	5.5	7.4	0.34	0.45
148-8-3	67	Pleistocene	soft and plastic. Dark greenish gray foram- nanno clay with thin ash layers scattered through- out, moderately firm,	19.59	19.57	0.97	0.96	6.7	7.1	0.41	0.43
148-9-4	79	Pleistocene	plastic. Dark greenish gray foram- nanno clay, moderately	19.49	19.50	0.79	0.82	5.1	5.9	0.31	-
148-10-3	8 86	Pleistocene	Dark greenish gray foram- nanno clay, with faint pyritic speckling through- out, moderately firm and plastic	19.48	19.60	0.96	0.86	4.4	5.7	0.27	0.35
143-12-4	106	Pleistocene	Dark greenish gray foram nanno clay with pyritic speckling, mod-	19.40	_	-		6.7	-	0.38	-
148-14-3	122	Pliocene	Dark greenish gray foram- nanno marl and clay, pyrite specks, soft and	19.40	19.46	0.63	0.46	3.2	5.0	0.19	0.30
148-16-3	141	Pliocene	Dark greenish gray foram-nanno marl, moderately firm and	19.26	19.53	0.29	0.33	0.4	4.0	0.02	0.24
148-18-2	159	Pliocene	Dark greenish gray foram-nanno marl with pyritic concretions throughout, firm and	19.38	19.48	0.29	0.28	1.2	9.1	0.08	0.6
148-20-3	179	Pliocene	Greenish gray and dark greenish gray foram- nanno marl, firm and plastic.	19.23	19.50		0.62	1.6	1.4	0.10	0.09
148-23-4	209	Pliocene	Dark greenish gray to greenish gray foram- nanno marl, firm and plastic.	19.49	19.45	0.31	-	2.7	2.8	0.17	0.17
148-26-2	232	Pliocene	Dark grayish green to olive gray foram- nanno marl, firm and plastic	19.39	19.46	0.41	0.38	1.1	2.6	0.07	0.16
148-27-4	246	Pliocene	Varicolored greenish gray and olive foram- nanno marl, very compact, slightly plastic.	-	19.39	-	0.37) – (2.6		0.16
Site 149	(15°0.6.2'N,	69°21.8′W, w	ater depth 3972 m, Venezue	elan Bas	in)						
149-2-2	4	Pleistocene	Varicolored yellowish brown and grayish orange foram ooze, soft.	19.38	19.46	-	2.73	2.0 (2.5)	2.3	0.12 (0.15)	0.14
149-2-5	8	Pleistocene	Varicolored yellowish brown and grayish orange foram ooze, soft.	19.45	-	2.66	<u></u>	2.0	-	0.12	
149-3-5	17	Pleistocene	Varicolored grayish orange and olive gray foram ooze, very soft.	19.50	19.42	2.62	2.69	2.2	3.3	0.13	0.20
149-4-3	23	Pleistocene	Grayish orange foram ooze, moderately soft and plastic.	19.55	19.58	2.47	2.64	1.8 (2.1)	2.3	0.11 (0.13)	0.14

 TABLE 2 – Continued

Sample	Subbottom Depth (m)	Age	Description	Cl Cold	Cl Warm	SO4 Cold	SO4 Warm	Alk. Cold	Alk. Warm	HCO3 ^b Cold	HCO3 ^b Warm
149-5-3	32	Pleistocene	Grayish orange and greenish gray foram ooze, moderately soft	19.62	19.67	2.59	2.32	2.1 (2.0)	1.7	0.13 (0.12)	0.10
149-6-4	43	Pleistocene- Pliocene boundary.	and plastic. Light olive gray to greenish gray foram chalk, moderately firm	19.65	19.63	2.44	2.56	1.4	2.2	0.08	0.14
149-7-2	49	Pliocene	Light olive gray foram chalk, soft and	19.63	19.60	2.52	2.61	0.4	1.0	0.03	0.06
149-8-4	62	Pliocene	Light olive gray foram chalk, clayey, soft and plastic	19.61	19.66	2.51	2.65	1.1	3.8	0.06	0.23
149-9-5	72	Pliocene	Light olive gray and greenish gray foram marl, very soft and plastic	19.65	19.61	2.41	2.49	1.0	1.8	0.06	0.11
149-10-2	78	Pliocene	Medium yellowish brown	19.51	19.65	2.49	2.49	1.2	2.4	0.08	0.15
149-11-4	90	Pliocene	Light olive gray clay with some faint burrow mottling, firm and plastic	19.29	19.49	2.28	2.49	1.6	1.5	0.09	0.10
149-12-5d	100	Late Miocene	Grayish orange nanno marl, small scale	17.14	17.36	2.04	2.13	0.9	1.3	0.06	0.08
149-14-3	116	Middle Miocene	Grayish yellow green clay with variegated lumps of marl.	19.45	19.54	2.32	2.47	0.1	1.9	<0.01	0.11
149-16-4	135	Middle Miocene	Varicolored brown and gray marl, strong color mottling, firm and plastic	19.53	19.96	2.13	2.14	1.0	(2.6)	0.59	(0.16)
149-18-3	153	Early Miocene	Pale grayish orange and yellowish gray	19.74	19.73	2.16	2.25	2.3	2.2	0.14	0.14
149-20-4	173	Early Miocene	Varicolored orange and gray foram-nanno chalk, extensive burrow mottling, firm and slightly crumbly.	19.87	19.84	2.22	-	2.1	2.6	0.13	0.16
149-23-4	201	Early Miocene	Grayish orange foram-	19.85	19.83	2.10	2.12	1.9	3.2	0.12	0.19
149-26-2	226	Oligocene	Varicolored green and gray foram-nanno chalk	19.86	19.95	2.09	2.22	2.3	3.1	0.14	0.19
149-29-3	254	Oligocene	Yellowish gray to greenish gray nanno- rad chalk, firm and crumbly	19.91	19.99	2.09	2.02	2.7	2.6	0.16	0.16
149-31-1	271	Late Eocene	Grayish orange to dark yellowish orange indurated rad ooze, very	20.09	20.11	2.17	2.23	3.0	3.0	0.18	0.18
149-33-1	289	Middle Eocene	Grayish orange to dark yellowish orange indurated rad ooze, firm and compact.	20.18	20.10	2.33	2.25	2.8	2.8	0.17	0.17
149-34-2	301	Middle Eocene	Grayish orange indu- rated rad ooze, scattered pumice		20.18	-	2.11	-	1.8		0.11
149-35-4	313	Middle Eocene	Yellowish gray nanno rad chalk, scattered pumice fragments.	20.04	20.08	2.15	2.25	0.2	2.0	0.01	0.12
149-37-3	329	Middle Eocene	Very pale orange nanno- rad chalk, very compact and crumbly.	20.09	20.14	2.11	2.27	1.1	3.5	0.06	0.21

TABLE 2 - Continued

THOLE & Communed	TABLE	2 -	Continued
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Sample	Subbottom Depth (m)	Age	Description	Cl Cold	Cl Warm	SO4 Cold	SO4 Warm	Alk. Cold	Alk. Warm	HCO3 ^b Cold	HCO3 ^b Warm
149-40-1	354	Middle Eocene	Yellowish gray indurated rad ooze, compact and crumbly.	19.50	19.34	2.03	2.16	1.7	2.1	0.10	0.13
149-41-5	369	Middle Eocene	Pale yellowish gray and gray ish orange indurated rad ooze, quite compact.	20.11	20.07	2.01	2.28	1.7	1.4	0.11	0.08
149-42-2	374	Middle Eocene	Yellowish gray indurated rad ooze, compact and crumbly.	20.14	20.10	2.14	2.18	1.8	3.9	0.11	0.24

^aValues in g/kg ($^{\circ}/_{\circ\circ}$) except alkalinity which is in meq/kg. The room temperature sample has been arbitrarily paired with the "low pH" sample. Values in parentheses refer to separate samples carried through the entire analytical process.

bHCO3 is calculated from total alkalinity, assuming this is entirely due to bicarbonate ion.

^cBoth warm and cold samples show high Ca (Table 1) and SO₄ values indicating a contamination of the interstitial water by the drilling fluid, fresh water, during the coring operation.

^dMarkedly lower Na (Table 1) and Cl values indicate a contamination of the interstitial water by the drilling fluid, fresh water, during the coring operation.

e"Low pH" sample obtained from one of the cold squeezing; analyzed separately.

f"High pH" sample; analyzed separately.

Minor Constituents

Strontium concentrations in the pore fluids show patterns previously encountered in Legs 4, 7, and 8 of the DSDP. Where appreciable $CaCO_3$ dissolution has taken place, as evidenced by net increase in interstitial Ca, Sr increases in parallel fashion (Figure 1). If some of the analytical scatter retained in the data could be removed, the parallelism in Figure 1 might be even more striking.

Site 148 showed little net increase in either Ca or Sr. On the other hand, Site 147 shows a drop in interstitial Ca, while Sr increases somewhat irregularly with depth. As discussed later, the diagenesis of the sediments of Site 147 appears complex and involves several concurrent reactions, including heavy methane production.

Lithium remains constant in Site 148, but shows an intermediate maximum of about 0.4 mg/kg at 200 meters depth at Site 149 and a consistent increase toward the bottom of Site 147, reaching 0.8 mg/kg. The patterns in the latter two sites definitely point toward continuing release of Li from some solid phases in the sediment. Previous observation of substantial increases in Li in clayey strata suggest that Li may desorb from sheet silicates, but biogenic materials may also supply this element.

As might be expected, Ba is most enriched at Site 147, where SO_4 is nearly totally depleted. Its behavior with regard to temperature of squeezing is erratic and unpredictable, however, and we have no explanation for these patterns.

Manganese reaches highest levels in Site 149, where alkalinities are low. Although the patterns observed are complex, reprecipitation of Ca appears to play a significant role in limiting Mn in solution. The rather smooth transitions in Mn concentrations (except near the detection limit of about 0.5 mg/kg) suggest that absorption/ desorption phenomena occur relatively slowly, allowing time for smooth diffusion gradients to develop in these sediments.

Boron, as a small highly charged ion, shows a strong positive correlation with temperature of squeezing for the clayey sediments (Sites 147 and 148), but much smaller changes for the more biogenic sediments at Site 149 (Table 9). The changes are partly obscured by analytical scatter for the latter. The boron data exhibit a large degree of scatter and appear to be systematically high. Consequently, only the data pertinent to temperature of squeezing effects are reported. Because temperature data in Table 9 represent differences between 4°C and 22°C samples and are averages, the values reported are deemed valid.

Silicon concentrations are enhanced in all of the sediments as a consequence of warming, confirming observations recently reported for surficial piston cores from the Cariaco Basin by Fanning and Pilson (1971). The normal changes increase from 1 to 2 mg/kg for the lower concentration observed (about 2-4 mg/kg) to as much as 4 mg/kg for pore water concentrations of 27 to 30 mg/kg which are noted in the deeper radiolarian oozes in Site 149. A part of this effect would have been expected to be due to the greater solubility of silica at higher temperatures, but we note that the radiolarian ooze samples from the lowest part of Site 149 show no net silica increase, based on colorimetric measurement. In terms of net absolute changes, Holes 147, 148, and upper 149 show an increase of 2.1, 2.2, and 1.3 mg/kg Si respectively, while in the lower part of Hole 149 the increase is variable (Table 9).

The analyses of dissolved SiO_2 carried out aboard the ship and in this laboratory demonstrate that storage of 3 months has no appreciable effect upon the samples. There is a systematic difference in the samples from Site 148. In view of the agreement at Sites 147 and 149, this discrepancy is probably due to a small systematic error in analysis. The analyses in this laboratory were run in two groups with a random distribution of samples from each site in both groups. Aboard the ship, the samples from each site were run separately. An error in the pre-prepared reagents used

Sample	Total Cations Cold	Total Anions Cold	Nab	Nac	Total Cations Warm	Total Anions Warm	Na ^b	Na ^c
147P 1 2	500	502	10.9	10.0	610	615	11.0	10.0
14/D-1-2	590	592	10.8	10.9	576	581	10.0	10.9
147D-1-5	304	390	11.4	10.9	570	301	10.9	(10.9)
147B-1-4	577	584	10.9	10.8	578	583	11.0	10.9
(15-33)	511	501	10.7	10.0	570	000	11.0	10.5
147B-1-4 (35-57)	570	578	11.0	10.8	566	575	11.0	10.8
147B-1-4	564	573	10.9	10.7	570	578	11.1	10.9
(37-95) 147-2-3/4	592	597	10.9	10.0			25.51	
147-2-3/4 147B-2-2	502	502	10.0	10.9	618	618	11.1	11.0
147B-2-6	571	577	10.9	10.9	576	577	11.0	11.0
147-4-3/4	570	567	10.7	10.8	_	-		-
147B-6-2	554	558	11.1	11.0	555	562	11.2	11.1
147-8-2/3	555	553	11.4	10.9			-	-
147B-7-4	552	551	10.9	10.9	550	552	11.0	11.0
147-10-3/4	553	555	10.9	10.9	 :	-		-
147B-9-4	536	539	10.8	10.7	533	544	11.1	10.8
147B-11-3	535	543	10.9	10.7	536	550	11.2	10.7
						(548)	(11.1)	(10.9)
147C-2-1	526	533	10.7	10.5	529	532	10.7	10.7
147C-4-4	516	539	10.9	10.4	528	539	11.1	10.6
				10000	035722	(532)	(10.8)	(10.4)
147C-7-4	512	-		10.3	517	519	10.4	10.3
						(521)	(10.4)	
148-1-2	608	609	10.8	10.8	589	616	11.4	10.8
148-1-4	597	605	10.8	10.7	603	604	10.9	10.9
148-2-1	590	601	10.8	10.6	585	600	11.0	10.7
						(600)	(10.9)	(10.5)
148-2-3	593	602	10.9	10.7	594	602	11.0	10.8 (10.8)
148-3-3	594	597	10.8	10.7	595	603	11.0	10.8
148-4-3	595	600	10.9	10.8	599	606	11.0	10.9
148-5-2	590	590	10.8	10.8	587	591	10.9	10.8
148-6-4d	582	590	10.8	10.6	583	594	11.0	10.8
148.6.48	596	500	10.9	10.7		(596)	(11.1)	(10.7)
148-7-3	578	584	10.0	10.7	572	583	11.0	10.7
148-8-3	574	580	10.0	10.7	573	570	10.9	10.7
148-9-4	570	571	10.0	10.7	572	574	10.9	10.8
148-10-3	572	574	10.7	10.7	575	576	11.0	10.0
148-12-4	552	-	10.7	10.7	515	-		
148-14-3	556	564	10.7	10.5	560	564	10.9	10.8
148-16-3	550	550	10.5	10.5	556	562	10.9	10.7
148-18-2	553	554	10.5	10.5	554	559	10.8	10.7
148-20-3	551	1000000 2773		10.5	557	564	10.9	10.7
148-23-4	551	559	10.6	10.4	553	-	-	10.6
148-26-2	556	556	10.4	10.4	553	559	10.7	10.5
148-27-4	0.000	-	100	-	555	557	10.6	10.5
149-2-2	600	-	-	10.7	595	608	10.9	10.6 (10.6)
149-2-5	602	606	10.8	10.7		-	π.	—
149-3-5	595	607	11.0	10.6 (10.8)	602	607	10.8	10.7
149-4-3	599	605	10.8	10.7	598	610	11.0	10.7
149-5-3	596	609	11.0	10.6	607	605	10.8	10.9
149-6-4	606	606	10.8	10.8	604	609	11.0	10.9
149-7-2	608	607	10.9	10.9	605	608	10.9	10.8
149-8-4	601	606	10.8	10.7	607	614	11.1	10.9
149-9-5	601	605	10.8	10.7	607	607	10.9	10.9
149-10-2	599	603	10.7	10.6	600	608	10.9	10.8
149-11-4	602	593	10.5	10.7	604	603	10.8	10.9
149-12-5	525	527	9.5	9.4	533	535	9.8	9.7
149-14-3	597	597	10.5	10.5	603	604	10.8	10.8

TABLE 3Ion Concentrations,² Leg 15

	Total	Total			Total	Total		
Sample	Cold	Cold	Nab	Nac	Warm	Warm	Nab	Nac
149-16-4	598	596	10.6	10.6	614	610	10.9	11.0
149-18-3	607	604	10.7	10.8	609	606	10.8	10.9
149-20-4	608	609	10.8	10.8	608	-	-	10.8
149-23-4	609	606	10.7	10.8	613	607	10.8	11.0
149-26-2	604	606	10.7	10.7	615	612	10.9	11.0
149-29-3	607	608	10.8	10.8	610	608	11.0	11.0
149-31-1	610	615	11.0	10.8	613	617	11.1	11.0
149-33-1	610	620	11.2	10.9	608	616	11.1	10.9
149-34-2					619	615	10.9	11.0
149-35-4	617	610	10.8	10.9	617	615	10.8	10.9
149-37-3	619	612	10.8	11.0	620	619	10.9	11.0
149-40-1	601	594	10.5	10.6	595	593	10.5	10.5
149-41-5	568	611	11.2	10.2	616	615	11.0	11.0
149-42-2	608	614	11.0	10.8	610	616	11.0	10.8

TABLE 3 - Continued

^aThe room temperature (warm) sample has been used for calculating the Na by difference with both pH samples. Cation and anion totals expressed in milli-equivalents.

^bSodium determined by differences between anions and cations (excluding Na (g/kg)

^CSodium determined by analysis. Values in parentheses refer to separate samples carried through the entire sampling and analytical processes. The total cation values shown are determined using these values and means of duplicate determinations, where available (g/kg)

d"Low pH" sample.

e"High pH" sample.

at Site 148 could account for the systematic difference observed. The samples from Site 148 could have behaved differently and the concentration differences could be real, but we think this is very unlikely. Sample alteration during storage does not appear to be significant.

DISCUSSION

Temperature-Induced Effects

Changes in the composition of interstitial fluids in response to changes in the temperature at which the samples are processed have been noted previously in clays and clay-rich sediments by Mangelsdorf et al. (1969) and Bischoff et al. (1970). Investigation of predominantly calcareous and siliceous biogenic sediments has not previously been conducted to our knowledge. The data from Leg 15 demonstrate that temperature-induced compositional artifacts in predominantly calcareous and siliceous biogenic sediments are important. The effects found in clayey sediments are larger than those reported previously (see Tables 7 and 8).

Preliminary X-ray diffraction analyses and smear slide descriptions make some examination of the relation between mineralogy and temperature effects possible. Previous studies (e.g., Mangelsdorf et al., 1969) have attributed the observed concentration changes to temperature-induced shifts in ion exchange equilibria. One would expect the magnitude of changes observed to strongly correlate with mineralogy. Specifically, we would expect concentration changes in relatively pure CaCO₃ sediments to be markedly less than those observed in clay-rich sediments. The data in Table 7 demonstrate, however, that temperature effects are only slightly greater in clayey and marly sediments than in "chalks." For example, the size of the K increase in the upper calcareous sections of Site 149 is only slightly less than that found at Site 147, which is described as consisting of "calcareous clay" or "marl." The Na increase is as large in the calcareous section of Site 149 as that found at Site 147. Ca depletions are largest at Site 149 (in terms of Δ milliequivalents), although one should add that these depletions could be related to precipitation reactions rather than ion exchange. Only the change in Mg concentration on warming is markedly decreased in the calcareous section of Site 149, i.e., only 50 to 60 percent of the changes noted at Sites 147 and 148. We do not know the actual sites of the observed exchange reactions. The smallest temperature effects are found in the samples from the lower section of Site 149 (below 271 meters). These sediments are described as calcareous radiolarian oozes in which the siliceous component dominates; although the effects are only 20 to 50 percent of those in Sites 147 and 148, they are still significant. Temperature effects on Na at Site 149 were less than the precision of our analyses. More quantitative mineralogical data will be required to establish definitive temperature effect correlations, but our data suggest that one cannot rule out such effects for minerals other than clays.

The observed temperature-induced K enrichments in clays and marls are roughly equivalent to the largest enrichments reported in earlier pore water studies such as those by Shishkina (1964) and Bischoff and Ku (1970).

TABLE 4 Total Dissolved Solids and Water Content

Sample	Depths (m)	Sum ^a Cold	Sum ^a Warm	Water ^b Content
147B-1-2	2.5	34.2	35.6	_
147B-1-3	4.25	34.2	33.4	-
147B-1-4	4.75	33.6	33.5	
(15-33)				
147B-1-4	4.85	33.6	33.1	
(35-57)				
14/B-1-4 (57.05)	5.1	32.1	33.1	100
147.2.3/4	8 5	335	1.11	65
147B-2-2	15		33.7	47
147B-2-6	21	33.1	33.2	47
147-4-3/4	28	32.5		44
147B-6-2	51	32.2	32.4	39
147-8-2/3	63	32.1	-	36
147B-7-4	63	32.2	32.2	36
147-10-3/4	82	32.3		34
147B-11-3	100	31.2	31.0	33
147C-2-1	126	30.8	31.1	20
147C-4-4	148	31.2	31.2	37
147C-7-4	176	_	30.2	30
148-1-2	2	25.2	25.2	51
148-1-4	6	35.0	35.5	51
148-2-1	11	34.6	34.5	45
148-2-3	13	34.7	34.7	45
148-3-3	22	34.4	34.8	45
148-4-3	31	34.6	35.0	47
148-5-2	39	34.0	34.0	41
148-6-4	51	33.9c	34.2	41
148-0-4	51	34.0u	22.5	41
148-8-3	67	33.3	33.5	39
148-9-4	79	32.3	33.1	30
148-10-3	86	33.0	33.3	40
148-12-4	106	-	-	34
148-14-3	122	32.2	32.4	34
148-16-3	141	31.5	32.2	33
148-18-2	159	31.7	32.5	33
148-20-3	179	21.0	32.4	32
140-25-4	209	31.9	22.0	35
148-27-4	232	51.9	32.0	-
110 27 4	240		52.0	-
149-2-2	4	25.0	35.0	50
149-2-5	17	35.0	25.1	41
149-4-3	23	34.9	35.1	42
149-5-3	32	35.0	35.1	40
149-6-4	43	35.1	35.3	39
149-7-2	49	35.2	35.2	-
149-8-4	62	35.0	35.5	38
149-9-5	72	34.9	35.2	39
149-10-2	78	34.8	35.2	38
149-11-4	100	34.0	35.1	42
149-14-3	116	34.5	35.1	41
149-16-4	135	35.1	35.5	37
149-18-3	153	35.1	35.2	38
149-20-4	173	35.3		37
149-23-4	201	35.3	35.5	34
149-26-2	226	35.2	35.7	-
149-29-3	234	35.3	35.4	54
149-33-1	289	35.0	35.0	54
149-34-2	301	-	35.8	-
149-35-4	313	35.5	35.8	50

TABLE 4 – Continued

Sample	Depths (m)	Sum ^a Cold	Sum ^a Warm	Waterb Content
149-37-3	319	35.7	36.1	-
149-40-1	354	34.6	34.5	51
149-41-5	369	34.6	35.8	51
149-42-2	374	35.5	35.7	49

^aThe sum (gm/kg) incorporates the Na values determined by analysis and means of replicate values where available. Minor constituents are not included but, with the exception of strontium in some samples, contribute less than $0.1^{\circ}/_{\circ\circ}$ to the sum. Cold was 4°C, warm 22°C.

^bWater contents (% by weight) are taken from shipboard summaries. In most instances they represent core barrel averages utilizing all the determinations which were reported.

^c"Low pH" sample.

d"High pH" sample.

Our data suggest that it is possible that most, if not all, of the previously observed K enrichments are due to temperature-of-squeezing artifacts rather than to real enrichments. Mg depletions have been noted in the aforementioned interstitial water studies. These depletions appear to be larger than those which could be attributed to temperature effects. However, it seems likely that the real depletions are considerably smaller than that suggested by the uncorrected data of earlier studies. Temperatureinduced concentration changes have not seriously prejudiced results as regards Na and Ca. Lithologic control over the size of the temperature responses does not appear to be very strong, but at this point, generalizations should be made cautiously as our understanding of the effect is incomplete.

The net changes in total cation concentration (meq/kg) occurring as a result of sample warming are essentially zero. Only the "net Δ meq" value for the calcareous sections of Site 149 is more than one standard deviation from zero. This suggests that the effect of temperature upon the concentrations of Na, K, Ca, and Mg is due entirely to shifting ion exchange equilibria. The absence of any significant changes in Cl and SO₄ concentrations as a result of warming supports this conclusion. Changes in alkalinity were noted (Gieskes, this volume) but these do not exceed 0.5 meq/kg and are usually less than 0.25 meq/kg. Such small values do not affect the conclusion that virtually all of the changes in concentration of the major cations are due to ion exchange. Let us emphasize that this conclusion does not apply to the minor elements.

Deviations from Sea Water Composition

1. A significant decrease in the concentration of interstitial Na, Cl and total dissolved solids appears in the deeper parts of Site 147. The decrease reaches about 10 percent with respect to seawater. It cannot be attributed to contamination during drilling, manipulation, and recovery because of the transitional nature of the fresher influence with depth, as well as the fact that the drilling fluid was

	TABLE 5		
Minor	Constituents, ^a	Leg	15

	Subbottom			185.5		13.13.4						Si .	Si .	Si	Si
Sample	Depth (m)	Age	Description	Ba Colđ	Ba Warm	Li Cold	Li Warm	Mn Cold	Mn Warm	Sr Cold	Sr Warm	col.b Cold	col Þ Warm	spec Cold	.c spec.c Warm
Hole 147,	147B and 14	47C													
147B-1-2	2.5	Pleistocene	Olive grav clay.	<03	< 0.3	0.16	0.18	< 0.1	< 0.1	9.1	8.5	17	12	16	19
147B-1-3	4.25	Pleistocene	Olive gray clay.	<0.3	< 0.3	0.17	0.15	< 0.1	< 0.1	6.9	6.3	20	19	22	19
147B-1-4	4.75	Pleistocene	Olive gray clay	<0.3	<04	0.17	0.17	<01	< 0.1	7.7	8.4	8.9	9.5	13	(10)
(15-33)		- 10101000110	onie gruy only.	-0.5		0.17	0.17	-0.1			0	0.5			(10)
(13-33) 147B-1-4 (35-57)	4.85	Pleistocene	Olive gray clay.	<0.3	0.3	0.18	0.14	< 0.1	< 0.1	7.5	5.8	5.9	7.8	7	10
(33-37) 147B-1-4 (56-95)	5.1	Pleistocene	Olive gray clay.	< 0.3	्रत्त	(0.14)	0.14	< 0.1	<0.1	8.3	7.6	3.8	7.2	7	9
147-2-3/4	8.5	Pleistocene	Olive gray and greenish	<0.3	0.4	0.20	<u> </u>	<0.1	< 0.1	9.6	<u> </u>	14	14	11	110
147B 2.2	15	Plaistagana	Crewish alive groop alay	0.2	0.4	0.10	0.16	<01	<01	0 0	8.0	11	12	10	12
147D-2-2	15	Pleistocene	Gravish clive green clay.	0.5	0.4	0.19	0.16	<0.1	<0.1	0.0	0.0	16	22	16	22
147 4 2/4	21	Pleistocene	Grayish olive green clay.	0.3	0.5	0.21	0.10	< 0.1	_	9.0	9.0	10	22	10	22
147-4-5/4	20	Pleistocene	calcareous.	0.3	-	0.21	-	< 0.1	-	10.8	-	17	-	0	0
147B-0-2	51	Pleistocene	calcareous.	<0.3	≤0.3	0.29	0.22	<0.1	<0.1	13.0	13.1	9.4	5.9	(10)	-
147-8-2/3	63	Pleistocene	Grayish olive green clay, calcareous.	0.7		0.36		<0.1		13.8	-	6.9	-	6	10
147B-7-4	63	Pleistocene	Grayish olive green clay, calcareous.	0.7	0.6	0.43	0.34	<0.1	< 0.1	16.5	14.2	5.0	8.4	6	10,
147-10-3/4	4 82	Pleistocene	Grayish olive green clay, calcareous, plastic.	0.8	-	0.56		<0.1	14	19.1	14	13	111	12	
147B-9-4	83	Pleistocene	Grayish olive green clay, calcareous.	<0.3	0.4	0.49	0.43	<0.1	0.1	8.6	7.2	6.0	8.8	8	10
147B-11-3	100	Pleistocene	Grayish olive green clay, calcareous.	0.6	1.0	0.49	0.57	< 0.1	< 0.1	5.6	13	5.7	8.0 7.9	6	9
147C-2-1	126	Pleistocene	Grayish olive green clay, calcareous.	0.8	0.4	0.30	0.43	<0.1	<0.1	7.5	4.0	6.4	10	6	12
147C-4-4	148	Pleistocene	Grayish olive green clay, calcareous.	0.5	1.8 1.4	0.85	0.82	< 0.1	< 0.1	4.9	14 16	20	-	19	25 26
147C-7-4	176	Pleistocene	Grayish olive green and dark greenish gray clay, calcareous, firm and plastic.	1.1	<0.5 <0.5	0.57	0.54	<0.1	<0.1	1.1	6.2 6.1	6.0	7.1	6	8 8
Site 148															
148-1-2	3	Pleistocene	Greenish gray foram- nanno ooze, soft and plastic.	<0.1	<0.1	0.20	0.16	1.5	1.4	9.4	8.8	8.8	13	8	(13)
148-1-4	6	Pleistocene	Greenish gray foram- nanno ooze, soft and	<0.1	<0.1	0.19	0.16	(1.3)	2.7	9.2	10.2	7.1	10	5	(15)
148-2-1	11	Pleistocene	Greenish gray foram- nanno marly ooze, soft	< 0.1	<0.1 <0.1	0.16	0.17	1.0	<0.1 <0.1	7.1	7.2 6.9	7.1	7.6	8	10 8
148-2-3	13	Pleistocene	Greenish gray foram- nanno marl, soft and	< 0.1	<0.1 <0.1	0.18	0.18 0.18	1.2	$^{1.0}_{< 0.1}$	7.3	6.8 8.0	5.8	7.4	8	9 9
148-3-3	22	Pleistocene	plastic. Greenish gray to light olive gray foram-nanno marl, moderately soft	<0.1	<0.1	0.20	0.17	<0.1	<0.1	9.5	0.8	7.0	8.7	5	-
148-4-3	31	Pleistocene	and plastic. Greenish gray foram- nanno marl, soft and plastic.	<0.1	<0.1	0.18	0.18	1.0	1.4	9.2	8.8	7.5	8.7	7	12
148-5-2	39	Pleistocene	Greenish gray foram- nanno marl moderately	<0.1	<0.1	0.20	0.17	<0.1	<0.1	9.2	7.8	6.3	7.5	5	9
148-6-4d	51	Pleistocene	Greenish gray foram- nanno marl, homogeneous	<0.1 8,	<0.1 <0.1	0.19	0.18 0.19	<0.1	<0.1 <0.1	7.6	7.2 7.5	5.7	5.7 5.4	7	8 9
148-6-4 ^e	59	Pleistocene	Greenish gray foram- nanno marl, homogeneous soft and plastic.	<0.1 8,	-	0.18	-	<0.1	-	8.0	-	5.3	-	7	-

TABLE	5 -	Continued

Sample	Subbottom Depth (m)	Age	Description	Ba Cold	Ba Warm	Li Cold	Li Warm	Mn Cold	Mn Warm	Sr Cold	Si Sr Warm	Si col. ^b Cold	Si col. ^b Warm	Si spec. Cold	Si ^c spec, ^c Warm
148-7-3	59	Pleistocene	Greenish gray foram- nanno marl, homogene- ous, moderately soft	<0.1	<0.1	0.17	0.18	<0.1	1.1	7.9	7.1	7.0	8.6 8.8	<6	10
148-8-3	6.7	Pleistocene	and plastic. Dark greenish gray foram-nanno clay with thin ash layers scattered throughout, moderately firm plastic	<0.1	<0.1	0.18	0.18	<0.1	<0.1	9.5	8.4	5.6	8.2	<6	8
148-9-4	79	Pleistocene	Dark greenish gray nanno clay, moderately firm and plastic	<0.1	<0.1	0.16	0.15	<0.1	<0.1	10.1	9.6	3.9	4.9	<6	7
148-10-3	86	Pleistocene	Dark greenish gray foram nanno clay, with faint pyritic speckling through- out, moderately firm and plastic.	- <0.1	<0.1	0.16	0.15	< 0.1	<0.1	10.1	8.8	4.2	6.2	<6	9
148-12-4	106	Pleistocene	Dark greenish gray foram nanno clay with pyritic speckling, moderately soft and plastic	1.9	-	0.15		<0.1	-	9.5	-	4.4	-	<6	-
148-14-3	122	Pliocene	Dark greenish gray foram-nanno marl and clay, pyrite specks, soft and plastic.	0.4	1.3	0.14	0.15	<0.1	<0.1	10	10.2	6.3	8.9	<6	11
148-16-3	141	Pliocene	Dark greenish gray foram-nanno marl, mod- erately firm and plastic.	1.3	1.9	0.14	0.14	<0.1	<0.1	10.5	9.1	3.8	6.0	<6	>10
148-18-2	159	Pliocene	Dark greenish gray foram-nanno marl with pyritic concretions throughout, firm and plastic.	2.7	3.5	0.14	0.16	<0.1	<0.1	9.6	9.4	5.1	7.4	6	>10
148-20-3	179	Pliocene	Greenish gray and dark greenish gray foram- nanno marl, firm and plastic.	0.6	0.7	0.16	0.14	<0.1	<0.1	10.0	9.3	5.8	12	6	9
148-23-4	209	Pliocene	Dark greenish gray to greenish gray foram- nanno marl, firm and plastic	1.1	>3	0.14	0.16	<0.1	<0.1	9.7	9.4	4.5	4.3	<6	<6
148-26-2	232	Pliocene	Dark grayish green to olive gray foram- nanno marl, firm and	1.8	0.5	0.20	0.20	<0.1	<0.1	10.6	10.2	2.0	5.4	<6	<6
148-27-4	246	Pliocene	Varicolored greenish gray and olive foram- nanno marl, very compact, slightly plastic.	~	-	1	5 7 0	<0.1	<0.1		-	-	7.7		
Site 149															
149-2-2	4	Pleistocene	Varicolored yellowish brown and grayish orange	< 0.1	<0.1 <0.1	0.18	0.20	1.6 1.8	1.9	9.1 8.8	8.8	3.5 3.5	4.4	<6 <6	6
149-2-5	8	Pleistocene	Varicolored yellowish brown and grayish orange foram ooze	<0.1	-	0.18	-	3.0	-	9.6	-	3.8	-1	<6	
149-3-5	17	Pleistocene	Varicolored grayish orange and olive gray foram ooze, very soft.	<0.1	<0.1	0.14 0.14	0.15	5.2 5.1	5.0	10.6 10.3	10.7	3.4	3.1	<6 <6	<6
149-4-3	23	Pleistocene	Grayish orange foram ooze, moderately soft and plastic.	<0.1	<0.1	0.12 0.12	0.20	5.3 5.3	6.3	10.1 10.1	10.0	2.9 3.1	3.7	<6 <6	<6
149-5-3	32	Pleistocene	Grayish orange and greenish gray foram ooze, moderately soft and plastic.	<0.1	<0.1	0.23 0.14	0.14	3.5 3.5	3.9	11.8 12.7	13.8	2.6 3.0	3.5 3.5	<6 <6	<6

TABLE 5	- Continued
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Sample	Subbottom Depth (m)	Age	Description	Ba Cold	Ba Warm	Li Cold	Li Warm	Mn Cold	Mn Warm	Sr Cold	Sr Warm	Si col. ^b Cold	Si col. ^b Warm	Si spec. ^G Cold	Si spec.c Warm
149-6-4	43	Pleistocene- Pliocene boundary	Light olive gray to greenish gray foram chalk, moderately firm	< 0.1	< 0.1	0.18	0.15	2.1	2.7	13	12	2.0	3.6	<6	<6
149-7-2	49	Pliocene	and plastic. Light olive gray foram	< 0.1	<0.1	0.17	0.15	2.5	2.9	12	12.5	3.6	2.1	<6	<6
149-8-4	62	Pliocene	Light olive gray foram chalk, clayey, soft and plastic	< 0.1	<0.1	0.15	0.17	2.1	2.2	11	13	3.8	4.4	1	<6
149-9-5	72	Pliocene	Light olive gray and greenish gray foram marl, very soft and plastic.	<0.1	<0.1	0.19	0.18	2.6	3.2	11	13	2.5	3.7	<6	8
149-10-2	78	Pliocene	Medium yellowish brown clay firm and plastic	< 0.1	< 0.1	0.21	0.17	6.5	6.5	14	16	4.1	3.2	(8)	(8)
149-11-4	90	Pliocene	Light olive gray clay with some faint burrow mottling, firm and plastic.	< 0.1	<0.1	0.19		4.9	7.3	15	15	2.2	3.3		<6
149-12-5	100	Late Miocene	Grayish orange nanno marl, small scale hurrow mottling	-0.1	<0.1	0.26	0.18	5.3	7.4	15	16	2.9	4.7	<6	6
149-14-3	116	Middle Miocene	Grayish yellow green clay with variegated	< 0.1	<0.1	0.28	0.23	6.2	6.5	21	23	2.5	3.9	6	-
149-16-4	135	Middle Miocene	Varicolored brown and gray marl, strong color mottling, firm and	< 0.1	<0.1	0.28	0.30	5.5	6.7	23	24	4.8	7.2	~6	8
149-18-3	153	Early Miocene	Pale grayish orange and yellowish gray foram	<0.1	<0.1	0.34	0.28	4.6	5.3	24	24	7.6	9.2	(9)	9
149-20-4	173	Early Miocene	Varicoloram. Varicoloram-nanno chalk, extensive burrow mottling firm and slightly crumbly	<0.1 g,	<0.1	(0.41)	0.39	4.4	4.4	32	32	9.9	11	9	10
149-23-4	201	Early	Grayish orange foram-	< 0.1	< 0.1	(0.42)	0.40	1.4	1.3	37	39	19	23	17	23
149-26-2	226	Oligocene	Varicolored green and	<0.1	< 0.1	(0.42)	0.30	1.2	1.1	46	45	25	28	16	23
149-29-3	254	Oligocene	Yellowish gray to green- ish gray nanno-rad chalk,	<0.1	< 0.1	0.32	0.32	1.1	1.4	46	42	23 23	27 27	24	29
149-31-1	271	Late Eocene	Grayish orange to dark yellowish orange indurated rad ooze, very compact and crumbly.	<0.1	<0.1	0.30	0.33	1.5	1.9	47	47	27	28	27	32
149-33-1	289	Middle Eocene	Grayish orange to dark yellowish orange indurated rad ooze, firm and compact	<0.1	< 0.1	0.26	0.24	1.5	1.4	43	43	-	28 28	29	29
149-34-2	301	Middle Eocene	Grayish orange indurated rad ooze, scattered pum- ice fragments.	<0.1	< 0.1	-	0.19	-	1.7	-	42	-	32	=:	-
149-35-4	313	Middle Eocene	Yellowish gray nanno- rad chalk, scattered pum- ice fragments.	< 0.1	< 0.1	0.20	0.20	1.9	1.4	43	41	26	25	26	31
149-37-3	329	Middle Eocene	Very pale orange nanno- rad chalk, very compact and crumbly.	<0.1	< 0.1	0.20	0.21	1.4	1.8	46	41	28	27	24	21
149-40-1	354	Middle Eocene	Yellowish gray indurated rad ooze, compact and crumbly.	< 0.1	<0.1	0.19	0.17	1.8	0.9	39	40	26	30	29	30
149-41-5	369	Middle Eocene	Pale yellowish gray and grayish orange indurated rad ooze, quite compact.	0.1 0.1	0.1	0.19 0.20	0.20	1.8	-	46 42	43	-	-	30 27	31

 TABLE 5 - Continued

Sample	Subbottom Depth (m)	Age	Description	Ba Cold	Ba Warm	Li Cold	Li Warm	Mn Cold	Mn Warm	Sr Cold	Sr Warm	Si col. ^b Cold	Si col. ^b Warm	Si spec. ^C Cold	Si spec. ^c Warm
149-42-2 1	374	Middle Eocene	Yellowish gray indurated rad ooze, compact and crumbly.	0.1 0.1	0.1	0.20		1.4	-	43 45	44		-	30 26	28

^aThe room temperature (warm) sample has been arbitrarily paired with the "low pH" sample in this tabulation. A pair of values, one listed beneath the other, refer to separate samples carried through the entire analytical process. Values in parentheses indicate suspect concentrations determined on the basis of analytical scatter. Concentrations in mg/kg (ppm).

bCol. = Colorimetric determination.

^cSpec. = Emission spectrographic determination.

d"Low pH" sample.

e"High pH" sample.

Caribbean surface water. Since chloride is only a trace component in most minerals and reacts with them to an insignificant degree for present purposes (i.e. cannot be adsorbed or otherwise removed by them), we assume that the decrease reflects some bulk process involving water itself. Possible mechanisms include retention of fresher "fossil water," dilution by introduced less saline solutions, in situ production of fresh water by oxidation of organic matter, and release of bound water from sediments.

Fossil water having fresher character seems unlikely because Pleistocene seawater should have been generally saltier than at the present by several percent and earlier DSDP cores penetrating thick Pleistocene sediments (e.g. Site 26, Sayles et al., 1970) did not show appreciable chloride decreases with depth.

Submarine discharge of fresh waters from land has been shown to affect strata far from shore (Manheim and Chan, 1972, and work cited therein) where a suitable pressure gradient and aquifer system exist. The Cariaco Basin is close enough to shore for such a possibility, but the existence of permeable/impermeable strata and suitable structural continuity has not been established.

Oxidation of organic matter with the simultaneous reduction of sulfate can produce primary water. Although substantial organic matter was available at Site 147 in the form of methane as well as solid organic matter, we believe it unlikely that sufficient reaction could have occurred to produce the observed decrease of Cl. The maximum interstitial SO₄ available for reaction corresponds to about 1 gm of H₂O per kg of solution or a dilution of 0.1 percent. No additional sources such as SO₄ minerals have been detected in these sediments. Diffusion cannot have supplied sufficient SO₄, for it is only at depth that depletion is noted, whereas the SO₄ gradients are greatest in the upper few meters.

Dehydration of clays may also produce significant quantities of water as well as lead to the removal of cations from solution. However, the loss of the interlayer water from clays has been reported only for depths and temperatures far in excess of those encountered at Site 147 (Burst, 1969).

We thus have no acceptable explanation of reactions producing the observed Na and Cl depletions. We favor a hypothesis of dilution but as yet have found no promising source of the fresher solutions.

2. The depletion of interstitial K occurs in all three sites. Heretofore, marked depletion of K has been prominent in sediments which contained an appreciable terrigenous clay component, and was assumed to be due to aggradation or reconstitution of clays degraded during weathering (Powers, 1959; Dunoyer de Segonzac, 1970, and references cited in these works). Uptake of magnesium also may occur in part in this way.

3. Strong depletion of interstitial SO₄ and Ca and enrichment in alkalinity (HCO₃) are characteristic of Site 147, even in the uppermost samples. As in previous cores investigated by us, the bacterial reduction of SO₄ and consequent evolution of HCO₃ has evidently led to the precipitation of CaCO₃. This reaction may be coupled with the reaction of sulfide (formed from sulfate) with Fe from the clays, causing a substitution of Mg for Fe in the clay lattices (Drever, 1971). As demonstrated by Gieskes (this volume), NH₄ formation contributes significantly to the alkalinity at Site 147. Berner et al. (1970) have quantitatively demonstrated similar controls (except the Drever reaction) in nearshore anoxic sediments. Details of these reactions are given later in the discussion.

4. Increases in interstitial Ca and Sr have been frequently observed in carbonate-rich sediments (especially those characterized by coccolith-foraminiferal oozes) that are accumulated relatively rapidly (more than 1 cm/103 y). At Site 149 (Figure 1), Ca and Sr increase in parallel fashion. In the absence of other probable sources (see discussion in Manheim and Sayles, 1971), we assume that both Ca and Sr variations are chiefly influenced by carbonate equilibria, especially dissolution of CaCO3. However, Ca/Sr ratios in planktonic carbonate organisms (chiefly coccoliths and forminifera) are about 250. Therefore, the large strontium anomalies in the pore water cannot be due to simple dissolution of biogenic carbonates, since dissolution of calcium carbonate sufficient to provide 2000 mg/kg extra Ca would yield only about 8 mg/kg additional Sr. However, as shown by Manheim and Sayles (1971), solution and reprecipitation of calcite containing lower concentrations of Sr can explain some of the previously described Sr variations in the interstitial waters.

TABLE 6 Si Concentration.^d Leg 15

	Shipboard Analysis	Laboratory Analysis
Sample	(ppm)	(ppm)
147B-1-2	18	17
147B-1-3	20	20
147B-1-4(15-33)	9.1	8.9
147B-1-4(35-57)	5.6	5.9
147B-1-4(57-95)	5.3	3.9
14/-2-3/4 147B-2-2	15	14
147B-2-2	16	16
147-4-3/4	18	17
147B-6-2	3.1	9.4
147-8-2/3	7.4	6.9
147B-7-4	5.6	5.0
147-10-3/4	14(13) ^c	13
147B-9-4	6.0	6.0
14/B-11-3	4.3	5.7
147C-2-1	20(20)0	20
147C-7-4	4.6	6.0
148-1-2	10	8.9
148-1-4	8.6	7.2
148-2-1	10	7.1
148-2-3	7.0	5.8
148-3-3	10	7.0
148-4-3	9.0	7.5
148-5-2	8.0	6.3
148-6-4a	7.1	5.7
148-0-40	0.5	5.5
148-8-3	1.5	5.6
148-9-4	5.0	3.9
148-10-3	5.1	4.2
148-12-4	5.3	4.4
148-14-3	7.0	6.3
148-16-3	5.1	3.8
148-18-2	4.3	5.1
148-20-3	6.8	5.8
148-23-4	5.8	4.5
140-20-2	5.5	2.1
149-2-2	2.5	3.5(3.5) ^c
149-2-5	2.7	2.9
149-3-3	2.8	2 9(3 1)0
149-9-3	2.2	2.6(3.0)°
149-6-4	1.7	2.0
149-7-2	1.9	3.6
149-8-4	3.2	3.8
149-9-5	2.8	2.5
149-10-2	1.5	4.1
149-11-4	2.5	2.2
149-12-3	2.8	2.9
149-16-4	2.7	4.8
149-18-3	8.2	7.6
149-20-4	10	9.8
149-23-4	19	19
149-26-2	24	25
149-29-3	24	23(23) ^c
149-31-1	25	-
149-33-1	30	29
149-37-3	27	28
149-40-1	27	26
149-41-5	29	10 ST.
11/14-4	20	

a"Low pH" sample.

b"High pH" sample.

^cDuplicate samples analyzed separately.

^dComparison of Si concentration as determined on board the *Glomar Challenger* and in the laboratory after storage. For Site 149, dissolution and near complete reprecipitation of carbonate equivalent to at least 10,000 mg/kg calcium carbonate must have occurred to supply the observed Sr. Such a quantity is a minimum because it assumes unrealistically that the recrystallized $CaCO_3$ phase contains no Sr. Note that according to this mechanism, dissolution of carbonate may account for Sr enrichments even though no Ca enrichments are evident.

Gains in interstitial Ca at Site 149 are accompanied by Mg losses on a nearly 1:1 basis. This correspondence is suggestive of dolomite formation although there is no direct evidence of dolomite at this site.

5. Many of the diagenetic reactions occurring in marine sediments under reducing conditions appear to be related to the bacterial reduction of SO₄ and simultaneous production of H_2S and HCO_3 . Berner (1970) studied pore waters of nearshore anoxic sediments and showed that, assuming a starting pore fluid having seawater composition, alkalinity increases could be accurately calculated (predicted) from depletions of SO₄, Ca, and Mg and increases of NH₄ in the analyzed pore fluid. This system is represented by a simple charge balance:

$$\Delta Ca + \Delta Mg + NH_4 - \Delta SO_4 = \Delta HCO_3$$
(1)

where the gain in cations less the gain in sulfate equals the remaining major anion, bicarbonate. Other constituents such as chloride, sodium, potassium, and borate are assumed or demonstrated to be nonreactive (remain unchanged) and hence may be ignored. The Δ convention used here refers to the difference between observed concentrations of an interstitial ion (in milliequivalents) and the concentration of that ion in seawater having chlorinity comparable to the sample in question. The Δ for NH₄ may be dropped since normal seawater has negligible ammonia concentration for the present purposes.

The data reported here show that changes in K and Na do occur and these ions should be included in the charge balance. Thus,

$$\Delta Na + \Delta K + \Delta Ca + \Delta Mg + NH_4 - \Delta SO_4 - \Delta HCO_3 = 0$$
(2)

Within the overall electroneutrality of the system, the ratios of the various ions are governed by the specific reactions between the fluid and the sediments and we may use our data to determine which reactions dominate. We postulate the following type reactions:

$$Ca^{+2} + 2HCO_3^{-} \rightleftharpoons CaCO_3 + H_2O + CO_2$$
(3)

$$Mg^{+2} + 2HCO_3^{-} \rightleftharpoons MgCO_3 + H_2O + CO_2$$
(4)

where MgCO₃ is incorporated either in calcite or dolomite.

(kaolinite)
A1₂Si₂O₅(OH)₄ + 5Mg⁺² + 10 HCO₃⁻ + SiO₂
$$\rightleftharpoons$$

N

(chlorite)
$$Mg_5A1_2Si_3O_{10}(OH)_8 + 10 CO_2 + 3 H_2O$$
 (5)

 $SO_4^{-2} + 2 CH_2 O \rightleftharpoons H_2 S + 2 HCO_3^-$ (6)

027			Na	1	К		Ca	Mg		
Sample	Depth (m)	% Change ^b	∆(meq/kg) ^C	% Change ^b	Δ(meq/kg) ^C	% Change ^b	∆(meq/kg) ^C	% Change ^b	Δ(meq/kg) ^c	ΣΔ(meq)
147B-1-2	2.5	-0.5	-2	+18	+1.5	+155		-9	-9.1	-
147B-1-3	4.25	+0.6	+3	+8	+0.7	+6	+0.4	-5	-4.4	-0.7
147B-1-4	4.75	+1.5	+7	+21	+1.5	-16	-0.9	-7	-6.7	+0.9
(15-33)										
147B-1-4	4.85	-0.3	-1	+25	+1.8	0	0	-6	-5.0	-0.5
(35-57)										
147B-1-4	5.1	+2.2	+10	+25	+1.7	-10	-0.4	-4	-3.3	+8.0
(37-95)	9.5							1000		
147-2-3/4 147B-2-2	0.5	+1.3	+6	+11	+1.0		+0.2	-	1.0	+6.4
147B-2-6	21	+1.9	+9	+25	+1.0	-3	-0.2	-7	-5.9	+4.6
147-4-3/4	28	-	_	- 25	-	-	-	· · ·	_	-
147B-6-2	51	+0.8	+4	+24	+1.9	+1	+0.1	-7	-4.4	+1.5
147-8-2/3	63	(-)	-	-	-	-	-	-	-	-
147B-7-4	63	+1.3	+6	+27	+2.3	-28	-2.9	-9	-5.3	+2.0
147B-10-3/4	82	-	-		-		-	-	-	-
147B-9-4	83	+0.6	+3	+21	+1.7	-40	-0.9	-8	-4.5	-2.1
147B-11-3	100	+1.1	+5	+14	+1.2	+54	+2.2	-14	-7.9	+0.7
147C-2-1	126	+1.4	+6	+14	+1.1	-10	-0.3	-6	-3.7	+3.6
147C-4-4	148	+0.8	+4	+10	+0.9	+158		-9	-4.5	-
147C-7-4	176	+0.5	+2	+16	+1.1	-31	-2.5	-10	-5.1	-4.3
148-1-2	3	+0.2	+1	+14	+1.5	-3	-0.6	-9	-4.9	-3.0
148-1-4	6	+2.0	+9	+19	+1.8	-3	-0.6	-4	-4.6	+5.7
148-2-1	11	0	0	+25	+2.5	-8	-1.2	-6	-6.2	-4.9
148-2-3	13	+0.9	+4	+20	+1.9	-3	-0.4	-6	-6.1	-0.3
148-3-3	22	+1.2	+6	+24	+2.0	-3	-0.5	-6	-6.8	+0.4
148-4-3	31	+1.2	+6	+25	+2.2	-3	-0.5	-4	-4.1	-3.4
148-5-2	39	+0.3	+1	+13	+1.0	-8	-1.0	-4	-3.8	-2.5
148-6-44	51	+0.6	+2	+24	+1.9	-5	-0.6	-7	-7.2	-3.5
148-0-4	51	+0.5	+2	+19	+1.9	-3	-0.6	-/	-1.2	-3.5
140-7-3	59	+1.2	+1	+22	+1.6	-0	-0.8	-8	-7.5	-5.8
148-9-4	79	+1 4	+6	+20	+2.0	_4	-0.5	-0	-7.2	-2.0
148-10-3	86	+2.1	+10	+30	+2.0	-12	-1.5	_9	-7.7	+2.4
148-12-4	106	-	-		-	-	-	-	-	
148-14-3	122	+2.9	+13	+25	+1.5	-8	-1.2	-11	-8.8	+4.5
148-16-3	141	+2.5	+11	+27	+1.5	-8	-1.4	-8	-5.9	+5.5
148-18-2	159	+1.8	+8	+23	+1.3	-10	-2.0	-9	-6.2	+1.3
148-20-3	179	+2.3	+10	+29	+1.5	-8	-1.8	-7	-4.8	+5.3
148-23-4	209	+2.5	+11	+32	+1.8	-12	-2.5	-9	-6.2	+4.4
148-26-2	232	+1.2	+5	+23	+1.4	-9	-2.0	-9	-6.8	-2.2
148-27-4	246	-	-	_	_	-	-	-	-	-
149-2-2	4	-0.3	-1	+13	+1.3	-1	-0.3	-3	-3.0	-3.3
149-2-5	8	-	-	-		-	-	-	-	-
149-3-5	17	-0.6	-3	-7	-0.7	+2	+0.5	+3		8 <u>—</u>
149-4-3	23	+0.6	+3	+13	+1.2	-2	-0.5	-3	-3.3	0.0
149-5-3	32	+2.4	+11	+17	+1.5	-4	-0.9	0	-0.2	+11.3
149-6-4	43	+0.6	+3	+20	+1.6	-3	-0.8	6	-5.5	-1.7
149-7-2	49	-0.6	-4	0	0	+0.2	+0.5	0	+0.1	-3.0
149-8-4	02	+1.9	+9	+20	+1.6	-4	-1.0	-4	-4.2	+5.1
149-10-2	72	+1.2	+10	+23	+1.7	-3	-1.0	-4	-5.5	+0.8
149-11-4	90	+1.5	+7	+15	+1.0	+0.2	-0.6	-6	-5.5	+2.5
149-12-5	100	+2.9	+12	+27	+1.5	-2	-0.0	-0	-3.5	+7.0
149-14-3	116	+3.0	+17	+25	+1.5	_9	-4.3	-6	-4.9	+9.7
149-16-4	135	+3.6	+16	+28	+1.7	+2	+0.8	-4	-3.2	+15.8
149-18-3	153	+0.9	+4	+21	+1.3	-4	-1.8	-2	-1.9	+1.9
149-20-4	173	+0.1	+0.4	+32	+1.9	-2	-1.2	-4	-2.3	-1.2
149-23-4	201	+1.9	+9	+21	+1.2	-4	-2.3	-4	-2.7	+4.9
149-26-2	226	+3.2	+15	+21	+1.2	-5	-3.2	-2	-1.3	+11.5
149-29-3	254	+1.2	+6	+25	+1.4	-6	-3.9	-6	-3.8	-0.7
149-31-1	271	+0.6	+3	+12	+0.7	-2	-1.3	-2	-1.2	+0.8
149-33-1	289	+0.6	+3	+12	+0.7	-2	-1.3	-2	-1.0	+1.0
149-34-2	301		_	-				-		
149-37-3	319	0	0	+11	+0.5	+1	+0.8	-1	-0.5	+0.8

 TABLE 7

 Concentration Changes Due to Temperature of Squeezing Changes^a

Sample	Depth (m)	Na		K		Ca		Mg		
		% Changeb	∆(meq/kg) ^c	ΣΔ(meq)						
149-40-1	354	-0.8	-0.8	+14	+0.6	-2	-1.4	-1	-0.3	-5.0
149-41-5	369	+6.5	+6.5			+4	-	+16.1		-
149-42-2	374	-0.1	+0.1	+14	+0.7	-3	-1.9	+6.4	-	-

TABLE 7 – Continued

^aConcentration changes in response to changes in the temperature of squeezing, expressed as per cent of the 4°C concentration. $b(\Delta \times 100)/(4^{\circ}C \text{ value})$.

 $^{c}\Delta = (22^{\circ}C \text{ value}) - (4^{\circ}C \text{ value}).$

d"Low pH" sample.

e"High pH" sample.

TABLE 8 Mean Value of Temperature Effects^a

	Site 147		Site 148		Site 149		Site 149	
	Clays and Marls		Clays and Marls		Calcareous ^b		Siliceous Biogenic ^c	
Element	% change	Δ meq.	% Change	Δ meq.	% Change	Δ meq.	% Change	Δ meq.
K	+18	+1.4	+24	+1.8	+16	+1.2	+12	+0.6
Na	+0.9	+4.4	+1.3	+5.9	+1.0	+4.3	+0.5	+1.0
Ca	-	-0:4	-6.5	-1.1	-3.1	-1.3	-1.0	-1.1
Mg	-7.3	-5.1	-7.3	-6.2	-3.1	-2.6	-1.4	-0.7
Net \triangle meq.		+0.3		+0.4		+1.6		-0.2

^aPositive denotes enrichment on warming; negative, depletion.

^bCores 2-8, 17-30.

^cCores 31-42.

$$CO_{2}$$

$$CH_{2}NH_{2}COOH (glycine) + 2 (H^{+}) + H_{2}O \rightleftharpoons$$

$$NH_{4}^{+} + HCO_{3}^{-} + CH_{4}$$
(7)

A variety of aluminosilicates may be used in Equation (5) and analogous reactions may be written for K and Na. The important feature is that the reaction results in cation-Al silicates, and equivalent amounts of cations and HCO₃ are required. The organic compounds in Equations (6) and (7) represent appropriate sources of C and N, and it has been shown that, at least in pure cultures, methane producing bacteria (Equation 7) require hydrogen and CO₂ as a substrate. These are produced by fermentation breakdown of organic matter in the absence of oxygen (Wolfe, 1971) even though hydrogen is normally consumed so rapidly that it is rarely detected in natural sediments. Drever (1971) has proposed that under reducing conditions sulfide may react with trivalent iron in clays, causing Mg to substitute for the lost Fe:

$$2 \operatorname{Fe}_{clay}^{+3} + 3 \operatorname{Mg}_{aq}^{+2} + 4 [S] \rightleftharpoons 3 \operatorname{Mg}_{clay}^{+2} + 2 \operatorname{FeS}_2$$

(8)

where S is a reduced form of sulfur such as S^{-2} and or S⁰ (unspecified). The ultimate product is pyrite and magnesium clay, pyrite perhaps forming by reaction of FeS and

S (Berner, 1970). The significant point is that whereas in Equations (4), (5), and (6) 1 equivalent of magnesium reacts with the reduction products of 1 equivalent of sulfate, Equation (8) calls for 1 equivalent of magnesium to react with the reduction products of 1.33 equivalents of sulfate.

We cannot test the applicability of the Drever reaction accurately by direct comparison of ΔMg and ΔSO_4 because the analyses in Tables 1 and 2 show that losses and gains in constituents other than Mg are important in accounting for SO₄ depletion and must be considered. The high concentration of sodium means that an analytical uncertainty of 1 percent produces an absolute uncertainty in ΔNa values greater than that from all other major constituents combined, and an undesirably large scatter in comparisons including ΔNa . To reduce scatter from this source we have used a rearranged form of Equation (2), excluding ΔNa for the moment:

$$\Delta Mg = \Delta SO_4 + \Delta Alk - NH_4 - \Delta CA - \Delta K \qquad (9)$$

The data for Sites 147, 148, and 149 are plotted in Figures 2a and 2b according to Equation (9). For samples from Site 147 down to a depth of 28 meters and for most samples from Site 148, the data plot is close to a ΔMg coefficient of 1.33. A least squares analysis of all of the Site 148 samples yields a coefficient of 1.32. The least squares fit of the Site 149 data yields a coefficient of 1.25 and an



Figure 1. Co-variation of Mn, Sr, and Ca at Site 149. Note particularly the correspondence between Ca and Sr.

(10)

Component	Site 147	Site 148	Site 149 (Carbonate)	Site 149 (Siliceous)
В	+30	+61	+7°	
Sib	+26	+41	+27	0
K	+18	+24	+16	+12
Na	+0.9	+1.3	+1.0	+1.0
Li	-3(?)	0.0	0.0 ^c	
Ca	variable	-6.5	-3.1	-1.1
Mg	-7.3	-7.3	-3.1	-1.4
Sr	-19	-7	0.0	
Cl	< 0.5	< 0.5	< 0.5	< 0.5
SO4	< 0.5	< 0.5	< 0.5	< 0.5

TABLE 9

^aPer cent change = [(22°C extraction) – (4°C extraction)]/4°C extraction)

^bColloidal.

^cTotal site.

intercept of 2.2 meq/kg. These data are compatible with the Drever type of reaction as written in Equation (8).

The fit of the data to Equation (9) and the requirement of electrical neutrality (Equation 2) demonstrate that for the samples investigated a correspondence exists between Δ Mg and Δ Na. This may be seen in subtracting a rearranged form of Equation (2) from Equation (9) with a coefficient of 1.3 derived from Figure 2:

$$1.3 \Delta Mg = \Delta SO_4 + \Delta Alk - NH_4 - \Delta Ca - \Delta K \qquad (9a)$$

$$\Delta Mg = \Delta SO_4 + \Delta Alk - NH_4 - \Delta Ca - \Delta K - \Delta Na$$

$$0.3 \Delta Mg = \Delta Na \tag{11}$$

Such a relationship is not apparent from the Mg and the Na data alone, because, although there is a consistent net loss of Na, the scatter is too great to provide a reliable ratio. We note that Shishkina (1958) obtained losses of Na as well as Mg in reducing (organic-rich) sediments from the Pacific and far eastern seas, whereas oxidizing sediments did not show the depletions. Shishkina's direct observations on sodium anomalies were made possible by the fact that she utilized a gravimetric method for determining sodium, and in general obtained a high degree of precision in her interstitial water analyses.

There are still many unknowns in the system we have considered. We should emphasize that while the data appear compatible with the requirement of a reaction such as that proposed by Drever (1971), the data do not prove that this reaction occurs. The Drever reaction is not a unique explanation of the relationship demonstrated in Figure 2. Samples below 28 meters at Site 147 plot well away from the rest of the data and indicate quite different processes. Further, equation (8) is incomplete as written. We do not know the precise nature of the Mg-Fe replacement reaction, the phases involved, the manner of formation of FeS₂ or the importance of other products, such as HCO_3^- , that may take part in the reactions.

SUMMARY

Major and some minor chemical constituents were studied in pore fluids of 123 samples from three drill sites in the Caribbean Sea. Site 147 (Cariaco Basin) yielded pore fluids resembling those from other clayey and rapidly deposited sediment accumulations near shore. Strong depletions in SO₄ and substantial depletions in K, Ca, and Mg accompany increases in alkalinity. Toward the bottom of the site, a decrease in the normally "conservative" (i.e. unreactive) constituents, Na and Cl, reached nearly 10% of about 180 meters depth. The cause of this apparent



Figure 2. A plot of the analytical data in terms of the proposed model relating changes in ionic components of pore waters, Sites 147 to 149. Δ refers to concentration in pore water minus the concentration in standard seawater. Data are samples squeezed at 4°C. Abscissa and ordinate scales correspond to either of side equation(s). Lines 1 and 2 are generated by the use of Δ Mg coefficients of 1 and 1.33 respectively. The dotted line in 2b is a linear least squares fit of the data.

dilution is still unknown, but it resembles similar dilutions found in other rapidly deposited sediment pockets influenced by proximity to continental masses.

At Sites 147, 148, and 149 concentration changes of Ca, Mg, K, HCO₃, and SO₄ in most samples are compatible with a reaction model based on sulfate reduction, uptake of magnesium on clays, and precipitation of carbonates. Losses of Mg at these sites is accompanied by Na depletion in the ratio $\Delta Mg/\Delta Na \approx 3$. Site 149 (Venezuela Basin), dominated by biogenic oozes, shows strong parallel increases in Ca and Sr, accompanied by Mg decreases which correspond closely to a 1.1:1 Ca-gain/Mg-loss ratio. The strontium increases imply dissolution and reprecipitation of at least ten times as much CaCO₃ as needed to supply the excess Ca (nearly 1000 mg/kg).

The temperature of squeezing affects cation results in all sites, as indicated in the summary (Table 9). Greatest relative influence of temperature of squeezing occurred for boron, with nearly +50 percent increase in clayey-marly strata. In contrast to previous expectations, temperature-related anomalies were only slightly lower for highly calcareous sediments such as chalks than for sediments described as clays and marls.

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