

## 12. INTERSTITIAL WATER STUDIES, LEG 38

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### ABSTRACT

Interstitial waters recovered during Leg 38 show large changes in major ion composition and also in oxygen isotope composition. Increases in  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$  and decreases in  $\text{K}^+$ ,  $\text{Mg}^{++}$ , and  $\text{O}^{18}/\text{O}^{16}$  are interpreted in terms of extensive diagenesis of terrigenous, volcanic, or basaltic igneous materials in the sediments and underlying basalts. Slight, but well-established increases in chlorinity with depth indicate that these postulated weathering reactions involve uptake of water to a measurable extent. Interstitial waters from sites drilled on the Inner Vøring Plateau suggest the infusion of fresh waters by aquifers from the mainland of Norway.

### INTRODUCTION

Interstitial water studies of deep-sea drill cores have proven to be very useful in determining zones of reaction in the sediments and in establishing which elements are involved in such reactions (Gieskes and Lawrence, 1976a, b). With this information, a more fruitful search can be conducted in the solids to identify these reactions. This was demonstrated, in particular, by Kastner (1976), who identified from SEM and energy dispersive measurements the reactions responsible for the uptake of  $\text{Mg}^{++}$  and  $\text{K}^+$  and the production of  $\text{Ca}^{++}$  in porcelanite zones of Site 323 of Leg 35.

During Leg 38 a large number of sites were drilled (Figure 1), and preliminary work onboard ship indicated large concentration gradients in alkalinity, calcium, and magnesium in the interstitial waters of these sediments. Drilling at nine sites reached basaltic basement, whereas drilling at six sites was terminated long before reaching basement. In view of the success of Leg 35, we decided to further analyze the samples obtained during Leg 38 for the ionic composition and for the oxygen isotope ratio of the interstitial waters. At the same time, Perry et al. (this volume) studied in detail the mineralogy of the squeezed sediments and, in particular, that of the clay fraction.

This report is concerned with the analyses of the interstitial water composition, with emphasis on those sites that reached basaltic basement. Only two sites, so far, have been studied for the oxygen isotope composition, but the remainder are under study. This report is, by necessity, a preliminary one, but some of the conclusions derived will be helpful in the further study of these sediments.

### METHODS

Methods used for the chemical analysis of the interstitial waters were essentially the same as those used

by Gieskes (1974), with modifications introduced by Gieskes and Lawrence (1976b).

Chlorinity values are probably accurate to  $\pm 2\%$  ( $0.4\text{‰}$ ). However, down-hole increases and decreases are quite noticeable (Table 1). In general, the accuracy of the data is similar to that reported by Gieskes (1974).

Oxygen isotope compositions were analyzed by a method similar to that used by Gieskes and Lawrence (1976b).

### RESULTS AND DISCUSSION

All data are presented in Table 1. In addition, for all sites, except Site 337, that reached basaltic basement, the data are presented graphically in Figures 2-9. The oxygen isotope data for Sites 336 and 348 are given in Table 2 and Figure 10.

Of primary importance in the study of the chemistry of interstitial waters are sedimentation rates (Gieskes, 1974, 1975; Gieskes and Lawrence, 1976b). This is particularly true if sedimentation rates have been rapid during more recent times, which, of course, is the case for the Leg 38 drill sites. During the Plio-Pleistocene, the so-called "Glacial" period, sedimentation rates were very high, especially because of the increase of glacially derived continental material. In general, faster deposition, whether or not it is accompanied by higher contents of reactive organic carbon, will be accompanied by greater depletions in dissolved sulfate and larger increases in dissolved ammonia (Gieskes, 1974, 1975). This is mainly because depletions in sulfate and increases in ammonia cannot be completely eradicated by diffusion processes. Typically, these extrema are accompanied by maxima in alkalinity. This can be illustrated best in Sites 336 and 343. Site 336 is characterized by high sedimentation rates in Unit 1 ( $5.6 \text{ cm}/1000 \text{ yr}$ ), which is underlain by a hiatus of perhaps  $19.5 \times 10^6 \text{ yr}$  and by sediments deposited at much slower sedimentation rates. Similarly, the upper 120 meters of sediments of Site 343 were deposited at much faster rates than were the lower parts of the sediment section. Of some interest here also are the profiles of dissolved strontium and calcium (Figures 2 and 5). The strontium

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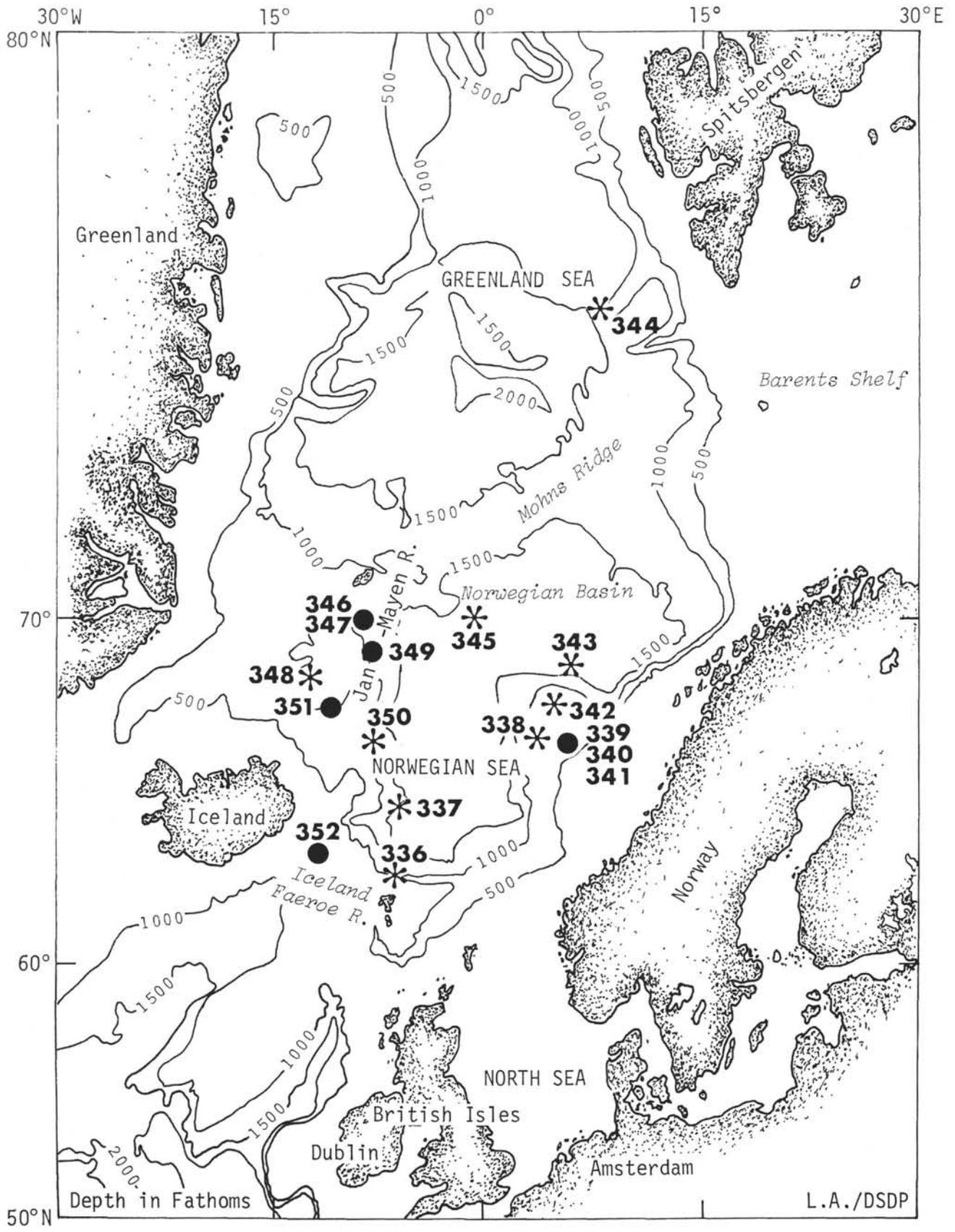


Figure 1. Map of sites drilled during Leg 38. Sites reaching basaltic basement are so indicated.

TABLE I  
Interstitial Water Data, Leg 38

Core-Section	Depth (m)	pH	Alk (meq/l)	S (‰)	Cl (‰)	Ca (mmoles/l)	Mg (mmoles/l)	Sr (mmoles/l)	K (mmoles/l)	Mn (ppm)	SO <sub>4</sub> (mmoles/l)	NH <sub>4</sub> (μmoles/l)	SiO <sub>2</sub> (μmoles/l)
<b>Site 336</b>													
Surface seawater		8.32	2.38	34.9	19.7	10.6	54.0	0.10	11.4	0	29.4	9	7
1-4	6	7.96	3.85	34.4	19.4	10.6	50.6	0.10	9.2	0.7	27.2	1255	360
5-5	43	8.25	4.84	34.1	19.6	11.4	46.2	0.10	10.9	0.35	19.5	670	437
8-4	70	8.09	5.37	33.8	19.4	12.8	43.0	0.10	10.0	0.26	16.6	563	620
11-4	117.5	8.15	3.66	33.6	19.8	19.5	39.2	0.12	9.8	0.40	16.9	483	575
16-4	184	8.09	1.97	35.2	—	31.9	34.9	0.15	8.4	0.60	19.5	281	693
18-4	203	7.87	1.74	35.2	20.2	34.3	33.6	0.15	7.3	0.77	19.9	333	560
22-2	242.5	8.40	1.00	34.9	21.0	41.0	29.6	0.17	7.0	0.40	19.3	254	105
27-5	292	8.35	0.80	36.3	20.7	47.8	28.4	0.20	5.2	0.35	20.2	303	97
30-4	336	8.39	0.70	36.0	—	56.1	26.0	0.20	4.7	0.26	19.7	210	106
33-5	394.5	7.60	0.50	36.3	21.4	70.2	20.6	0.20	2.8	0.53	17.3	241	113
35-3	429.5	7.81	0.51	36.3	21.6	71.3	22.2	0.20	2.0	0.70	15.9	262	103
39-3	478.5	—	1.20	35.8	21.0	72.5	23.4	(0.04 0.06)	0.8	1.13	16.5	479	32
<b>Site 337</b>													
Surface seawater		8.33	2.44	34.9	19.5	10.3	53.5	0.08	10.9	0	29.7	(199)	0
1-4	6	8.05	2.81	35.2	19.7	10.7	52.4	0.10	14.0	2.45	29.8	148	165
5-3	37	7.90	2.0	35.1	19.8	11.5	52.6	0.10	13.6	0.35	29.1	58	107
10-5	92.5	7.35	1.83	35.5	19.8	11.8	53.3	0.10	13.2	0	28.6	61	827
<b>Site 338</b>													
Surface seawater		8.21	2.44	35.2	19.8	10.3	53.5	0.10	12.2	(0.35)	29.2	27	0
1-3	4.5	7.72	5.02	35.2	19.2	10.4	53.8	0.10	13.6	4.50	27.9	299	178
4-3	40.5	7.48	7.87	35.8	18.9	11.5	48.7	0.10	8.4	2.20	23.7	450	250
8-3	80.5	7.16	7.43	35.2	19.3	16.6	44.6	0.11	10.0	2.77	23.0	354	810
11-3	108.5	7.17	5.52	35.2	19.2	17.0	45.9	0.10	10.1	3.00	24.6	284	740
14-2	136	7.18	6.30	35.2	19.5	17.3	45.8	0.12	9.8	3.45	23.2	279	960
19-3	185	7.45	5.21	35.5	19.5	22.0	42.1	0.14	8.7	3.20	24.0	270	800
23-0	218.5	7.65	5.25	35.5	19.5	24.8	40.8	0.15	9.0	2.25	21.4	320	973
26-1	248.5	—	4.60	34.1	—	28.0	44.1	—	—	—	28.1	761	—
30-4	291	8.42	1.67	34.9	—	33.1	33.5	0.16	5.8	1.55	21.3	264	173
35-1	334	7.75	1.75	35.8	20.2	28.7	41.4	0.17	7.0	1.95	24.6	188	193
37-1	353	7.78	1.33	35.2	20.4	31.7	—	0.17	5.4	1.95	21.2	212	122
42-1	400.5	8.17	1.00	35.2	20.5	43.1	32.9	(0.11 0.12)	4.7	0.87	20.1	648	110
<b>Site 339</b>													
Surface seawater		8.24	2.37	34.4	19.4	10.3	53.0	0.10	11.5	0	28.7	9	5
1-4	6	7.74	6.35	35.2	19.1	10.0	50.2	0.10	12.9	5.60	25.8	316	260
3-3	21.5	7.72	8.13	33.0	18.3	8.2	46.8	0.10	11.9	0.87	20.2	581	270
6-3	50.5	7.46	14.47	29.7	16.3	7.3	37.5	0.10	9.8	0.77	8.3	674	545
8-3	69.5	7.74	11.08	30.0	16.5	7.6	37.6	0.10	9.9	1.03	8.1	634	652
12-2	106	7.59	11.50	29.7	16.3	8.1	39.4	0.08	8.6	0.35	8.7	727	1100
<b>Site 340 (offset from Site 339)</b>													
2-2	12.5	8.00	4.04	35.2	19.5	11.3	53.0	0.10	14.0	2.15	28.8	272	465
5-1	39.5	7.65	4.13	35.2	19.5	11.1	52.4	0.10	13.7	2.35	27.8	206	670
10-4	91.5	7.77	3.70	35.2	19.6	11.2	53.1	0.12	12.4	0.87	29.1	181	770
<b>Site 341</b>													
Surface seawater		8.21	(1.91)	35.2	19.3	10.5	53.7	0.10	12.3	0	28.9	(1620)	5
2-2	12.5	7.77	8.28	33.3	19.2	7.5	48.2	0.12	11.9	1.70	16.2	(1517)	235
7-4	72.5	7.56	9.36	33.0	18.9	7.1	43.8	0.10	8.6	0	5.4	1843	625
12-5	113	7.35	5.49	33.0	19.5	8.7	41.3	0.10	6.7	0	7.7	2540	412
17-1	163	7.53	4.47	33.6	—	9.4	40.4	0.10	5.9	0.10	17.1	2406	315
20-4	243.5	7.85	7.23	31.6	18.5	6.5	26.3	0.45	6.2	0.10	2.8	3187	403
23-5	311.5	8.01	11.42	32.2	18.1	7.1	20.6	0.13	(9.2 8.8)	0	2.4	2932	393
27-5	377.5	—	26.08	33.0	—	8.9	26.2	0.08	5.8	0	3.2	2660	468
32-5	434	7.35	26.50	32.4	16.1	10.0	22.6	0.13	(8.9 9.2)	0.10	2.3	2760	855
<b>Site 342</b>													
Surface seawater		8.20	2.38	35.2	—	10.7	53.7	0.10	11.7	0	28.4	(117)	4
1-4	6	7.60	4.46	35.2	19.6	10.6	51.0	0.10	10.6	4.75	26.5	421	785
2-3	42	7.77	7.46	34.4	19.3	10.8	45.0	0.10	10.7	0.77	19.1	772	276
3-3	89.5	7.52	5.76	34.6	19.4	13.4	53.2	0.10	9.2	0.95	18.2	701	681
4-1	124.3	7.48	4.60	34.9	20.0	18.7	41.0	0.11	9.5	1.40	18.0	478	800
<b>Site 343</b>													
Surface seawater		8.22	2.38	34.5	19.2	10.4	52.9	0.10	9.2	0	28.9	24	5
1-1	1.5	7.38	3.13	35.5	19.7	10.9	51.6	0.10	13.7	0.60	28.0	207	115
3-4	56.5	7.50	8.23	35.2	19.5	12.8	49.7	0.10	7.9	0.17	18.2	1034	280
4-2	104	7.41	8.37	34.9	19.2	15.3	46.3	0.10	7.8	1.90	19.2	802	215
5-5	152.8	7.73	5.09	35.2	19.4	22.9	44.2	0.14	(10.2 8.7)	7.80	22.6	297	605
7-2	205.5	7.66	1.03	35.5	20.1	34.9	34.1	0.16	(10.0 8.4)	3.37	24.2	225	80
15-2	272	7.41	0.37	36.6	20.5	51.8	25.1	0.16	(8.0 7.2)	0.70	24.4	213	83

TABLE 1 – Continued

Core-Section	Depth (m)	pH	Alk (meq/l)	S (‰)	C1 (‰)	Ca (mmoles/l)	Mg (mmoles/l)	Sr (mmoles/l)	K (mmoles/l)	Mn (ppm)	SO <sub>4</sub> (mmoles/l)	NH <sub>4</sub> (μmoles/l)	SiO <sub>2</sub> (μmoles/l)
<b>Site 344</b>													
Surface seawater		8.15	2.36	35.2	–	10.4	52.7	0.09	10.9	0	28.9	12	2
2-1	3.0	7.29	4.19	33.8	–	10.8	42.5	0.10	8.7	0.60	16.6	805	265
6-4	45.5	7.79	6.09	32.4	19.3	12.1	31.7	0.10	5.5	0	5.0	1706	227
11-1	88.5	7.67	4.68	32.4	19.7	19.9	24.3	0.12	4.1	0	6.7	1966	230
15-5	132.5	7.32	4.15	33.0	19.4	23.9	23.7	0.14	3.2	0.6	9.6	2066	412
21-1	183.5	–	2.88	31.9	19.5	26.8	15.9	0.12	1.6	0	2.4	2293	98
27-2	242.0	–	2.22	32.4	19.7	29.2	14.2	0.13	0.9	0	4.4	2289	65
									1.5				
31-1	316.5	7.55	1.38	32.4	19.7	34.5	9.2	0.18	1.7	0.35	3.1	1400	77
33-1	373.5	7.38	0.99	33.3	19.3	37.7	9.5	0.18	2.9	0.60	7.4	1612	412
<b>Site 345</b>													
Surface seawater		8.15	2.31	35.2	19.6	10.3	53.1	0.07	10.6	0	29.4	12	6
1-1	15	7.41	3.23	34.9	19.2	11.3	53.2	0.10	12.6	0.87	29.1	87	150
4-1	28	7.44	3.99	35.2	19.6	13.3	48.6	0.09	11.9	5.60	27.4	324	190
7-1	76	8.13	3.07	35.2	19.9	14.9	45.7	0.09	11.2	8.35	24.7	317	395
10-4	137.5	7.34	2.33	34.6	19.6	18.	40.5	0.13	9.0	~12	20.6	401	405
14-3	250	–	1.97	33.3	–	26.6	27.6	0.10	1.2	2.27	13.5	736	105
16-5	338	8.03	1.67	33.6	20.2	31.4	21.4	0.20	4.8	0.87	11.3	758	70
19-4	451	8.61	1.09	32.7	19.9	41.7	12.0	0.24	1.6	0.60	8.4	897	51
20-2	486	8.72	0.77	32.7	19.5	41.8	11.5	0.23	3.3	0	8.3	(37?)	45
21-4	527	8.88	0.90	33.0	20.0	49.4	7.2	0.27	2.7	0	7.4	876	51
23-5	604.5	–	0.54	34.9	20.9	56.9	5.9	(0.19 0.21)	1.0	0	7.6	844	40
<b>Site 346</b>													
Surface seawater		8.15	2.37	35.2	19.4	10.3	52.1	0.08	10.9	0	–	12	2
1-4	6	7.44	3.05	34.6	19.1	11.3	52.2	0.10	13.8	0.87	29.1	15	200
4-4	31.5	8.32	3.94	34.9	19.9	12.9	49.1	0.09	13.5	5.55	28.4	91	416
6-4	50.5	7.47	3.54	35.2	–	13.1	47.9	0.13	12.7	4.20	26.7	128	368
9-5	80.5	7.27	3.45	35.2	–	14.2	47.5	0.17	9.7	2.54	25.7	171	430
12-3	106	7.74	3.58	38.2	19.4	14.4	40.4	0.15	10.3	2.00	24.2	224	554
15-4	136	7.95	2.00	35.2	–	14.9	44.9	0.18	10.0	0.87	24.0	296	105
17-1	150.5	–	1.88	35.2	–	16.1	39.8	0.16	3.8	0.35	21.5	566	55
<b>Site 348</b>													
Surface seawater		8.06	2.30	34.6	19.6	10.5	52.5	0.10	10.5	0	28.4	55	0
1-4	6	7.51	2.82	34.6	19.0	13.6	49.2	0.10	12.1	5.04	28.0	124	208
4-2	40.5	7.72	2.36	34.4	–	28.8	34.9	0.11	8.6	3.93	21.6	392	257
7-3	80	7.60	2.06	34.9	20.0	38.5	25.6	0.14	6.8	2.83	17.1	464	532
9-2	116.5	8.27	1.83	35.5	21.3	42.4	24.3	0.13	7.2	1.17	17.6	642	355
12-5	168.5	7.61	1.81	34.9	21.0	52.6	15.1	0.13	5.8	2.00	13.7	676	675
16-5	235	7.39	1.71	35.2	20.3	58.4	13.0	0.16	4.0	2.00	12.7	635	875
20-5	282.5	7.21	0.19	35.2	–	68.6	8.2	0.14	4.4	0.35	11.1	928	77
24-5	349.0	7.82	0.26	35.2	20.8	85.9	4.7	0.20	2.2	0	9.7	635	76
29-5	491.5	7.02	0.21	36.0	21.1	110.7	0.8	0.22	1.0	0	8.8	699	68
32-2	525	7.74	0.23	36.3	20.6	115.2	–2.8	0.22	1.2	0	8.8	756	95
<b>Site 349</b>													
Surface seawater		8.11	2.31	34.6	19.5	10.2	52.5	0.10	10.8	0	29.4	12	3
1-3	4.5	7.43	3.19	34.9	19.4	11.1	51.2	0.08	11.6	3.10	29.1	93	387
2-5	61	7.91	3.42	34.6	19.7	13.0	45.5	0.08	11.3	3.37	24.9	257	406
5-4	116.5	7.75	2.71	34.4	20.1	12.7	48.0	0.08	9.5	0.30	25.6	254	145
10-5	194	7.82	1.32	34.1	19.8	13.9	34.2	0.05	7.7	0	18.0	608	105
<b>Site 350</b>													
Surface seawater		8.10	2.30	34.4	19.3	10.2	51.5	0.08	10.9	0	28.4	65	2
1-2	3	7.46	2.64	35.2	19.3	12.3	49.8	0.10	12.9	3.65	29.0	114	115
4-2	87	7.95	1.41	34.9	19.4	19.3	44.4	0.17	10.2	1.70	24.7	229	165
8-2	201	7.73	0.87	35.5	20.2	28.3	42.5	0.25	7.9	0.60	22.7	185	88
10-3	259.5	6.98	0.47	35.5	20.2	37.5	41.7	0.30	4.7	0.60	21.2	254	81
12-2	315	6.61	0.38	36.0	20.4	45.2	39.6	0.34	4.9	0.87	19.3	387	74
<b>Site 352</b>													
Surface seawater		8.13	2.31	35.2	–	10.5	52.9	0.08	12.3	0	28.9	(132)	2
2-4	14.5	7.79	1.50	35.2	–	18.8	44.6	0.10	9.2	1.45	29.6	223	229
<b>Site 352 (Hole 352A)</b>													
3-1	114.5	7.27	0.45	35.5	–	23.6	40.0	0.17	7.2	0	26.9	345	395

appears to have a source in the deeper sediment layers. The data suggest no significant gradients in Sr<sup>++</sup> in the Pleistocene section in both sites. Similarly, dissolved calcium data show increased curvature, affected by both the increased sedimentation rate and the possible precipitation of calcium carbonate. At a sedimentation rate of 5.6 cm/1000 yr (Site 336) and with a diffusion coefficient of dissolved Sr<sup>++</sup> of about  $1 \times 10^{-6}$  cm<sup>2</sup>/sec (Li and Gregory, 1974), the so-called "communication"

depth (Gieskes, 1975) will be about 60 meters. This means that the strontium gradient is in a steady state to about 60 meters above the lower boundary of Unit 1. Above that, no steady state exists, and hence normal seawater values or concentrations very close to these are observed. Similar arguments apply to Site 343.

The above observations serve as an important reminder that steady-state diffusion calculations cannot be readily applied to sediments with sedimentation

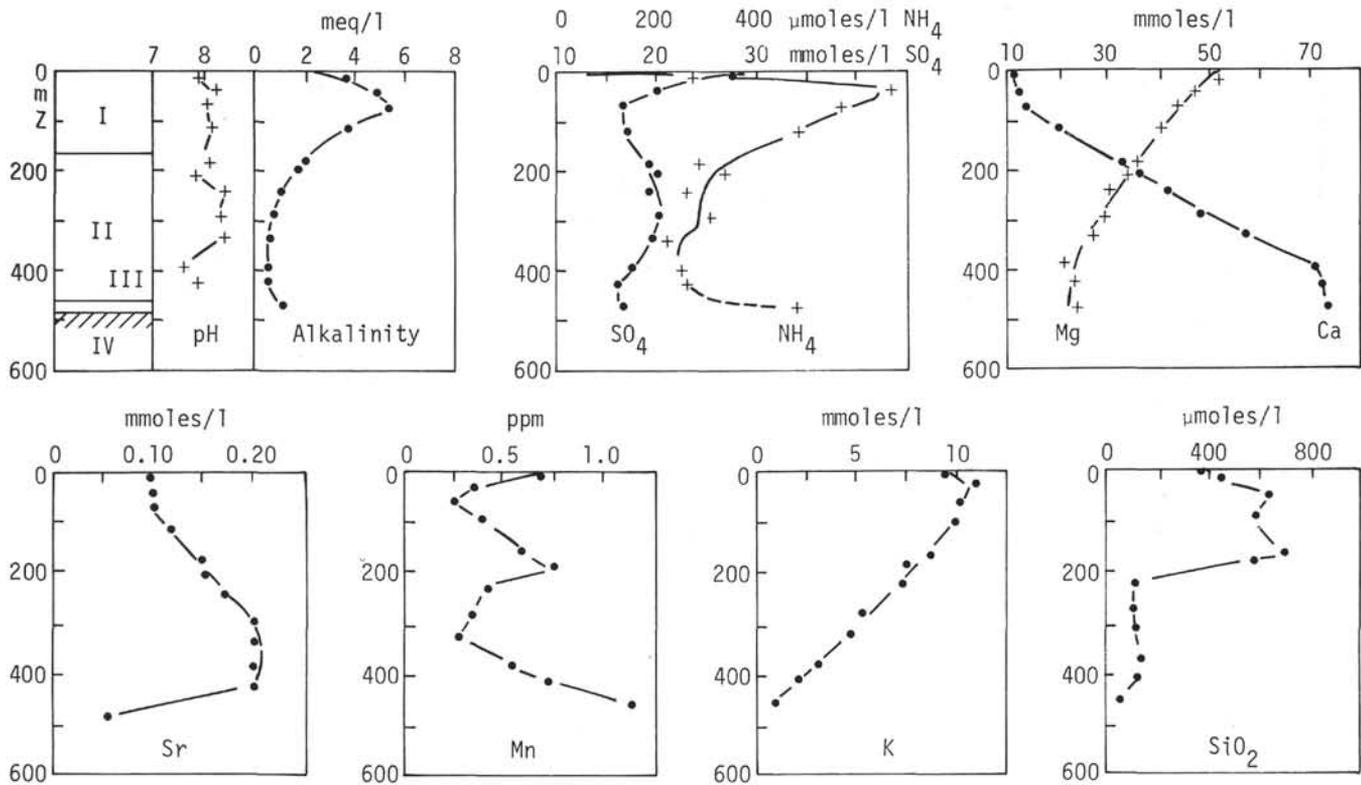


Figure 2. Interstitial water data, Site 336, (I): gray mud, sandy mud, clay-Pleistocene; (II): olive and dusky yellow mud, clay and mudstone, sandy mudstone and claystone-upper-middle Eocene, upper Oligocene (?); red, black-red clay, claystone, volcanic rubble-Eocene (?); (IV): basalt.

rates higher than 2 cm/1000 yr (Gieskes, 1975). Minima in dissolved sulfate imply that no steady state exists for this component in the deeper sediment layers. As soon as we have more precise information on sedimentation rates and on the diffusional characteristics of these sediments, we shall attempt to model these processes, in order to gain some insight into the rates at which reactions proceed in these sediments.

In the following we will discuss each site separately, at least those sites that reached basaltic basement. The other sites will be considered only briefly, in a separate section.

#### Site 336 (Figure 2)

In the previous section we have discussed the influence of the sedimentation rate on the dissolved sulfate and ammonia profiles.

Below 120 meters, concentration gradients of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  are essentially linear to about 400 meters. Similarly,  $\text{K}^+$  decreases are approximately linear to the bottom of the hole. Changes in chlorinity (Table 1) appear real and amount to about 5%-8%. Of interest is the calculation of the concentration of  $\text{Na}^+$  by mass balance at about 394.5 meters (336-3-5) using differences from present-day seawater values:  $\Delta$  cations = +46 meq;  $\Delta \text{SO}_4^{--} = -24$  meq. If  $\text{Cl}^-$  were constant, this would imply  $\Delta \text{Na}^+ = -70$  mmoles/l, but the increase in  $\text{Cl}^-$  is about equal to  $35 \pm 10$  mmoles/l, so that  $\Delta \text{Na}^+ = -35$ . Thus we conclude that reactions oc-

curing in the sediments between 120 and 400 meters, or below this, involve an exchange of  $\text{Ca}^{++}$  for  $\text{Mg}^{++}$  and  $\text{K}^+$  ions, with a slight increase in the  $\text{Cl}^-$  concentration with depth, presumably due to water uptake by alteration products. Although little net concentration change has occurred in  $\text{Na}^+$ , the  $\text{Na}^+/\text{Cl}^-$  ratio must have decreased because of the measured  $\text{Cl}^-$  increase. Thus, some uptake of  $\text{Na}^+$  must also have occurred during the alteration processes, presumably by uptake through ion exchange on possible alteration products (clay minerals?).

A more detailed study of the physical properties, presently planned by us, will serve in an investigation of the nature of the concentration gradients of  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{K}^+$ . This will determine whether any significant reactions occur in the sediment column between 120 and 400 meters, or in the section below this.

The concentration changes below 400 meters become almost zero. Sediments below this depth show extreme lithification. Perhaps the process of lithification involves alteration reactions of igneous material, volcanic or terrigenous, that cause the release of  $\text{Ca}^{++}$  and the uptake of  $\text{Mg}^{++}$ ,  $\text{K}^+$ , and maybe  $\text{Na}^+$ . Oxygen isotope changes are relatively large (Figure 10), an observation that has previously led to the suggestion that igneous material of basaltic or volcanic origin is involved in the above-mentioned alteration reactions (Lawrence et al., 1975, 1976). That substantial alteration has occurred is

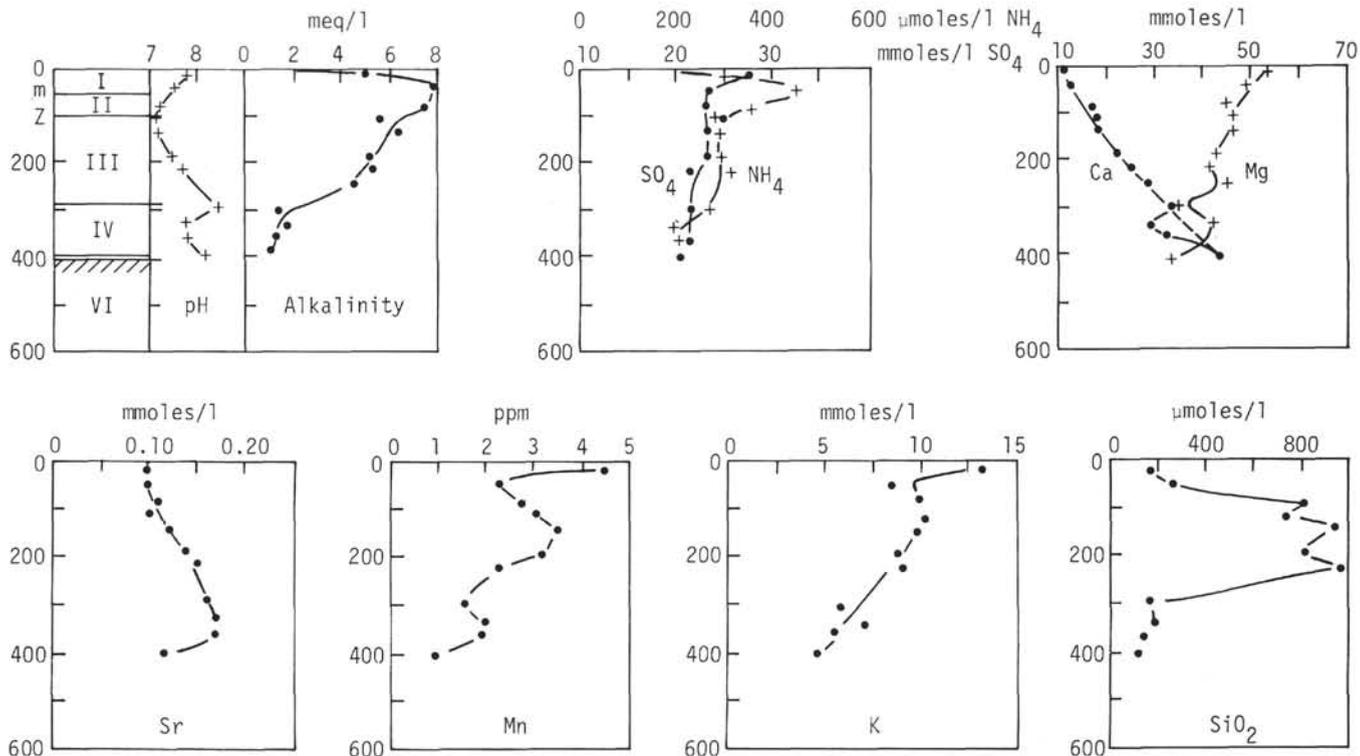


Figure 3. Interstitial water data, Site 338, (I): olive-gray sandy mud, fine pebbles—"Glacial"; (II): olive-black-gray transitional radiolarian ooze-Miocene; (III): yellow-gray siliceous biogenic (diatoms/radiolarians) oozes to 223 meters Calcareous ooze around 150 meters siliceous to lower boundary-late Eocene, middle Oligocene, lower Miocene; (IV): glauconitic sand followed by gray silt, sandy mud; (V): 32-cm limestone over 76-cm basaltic breccia; (VI): basalt.

also evident from the relatively large chloride concentration increases.

Of great interest here is the dissolved strontium gradient. It appears that between 300 and 420 meters  $\text{Sr}^{++}$  concentrations are constant. Below that, a sharp drop occurs in the basaltic breccia. Apparently there is a significant sink for this component in this breccia, probably by ion exchange. The  $\text{Sr}^{++}$  profile could be interpreted in terms of a maximum at about 400 meters, with sinks above and below. The precision of the data does not allow ruling out this possibility. At 400 meters, Perhaps other phases, for instance the postulated altering igneous materials, serve as a source of strontium.  $\Delta\text{Sr}^{++} = 0.1$  mmoles/l and  $\Delta\text{Ca}^{++} = 60$  mmoles/l, yielding  $\Delta\text{Sr}^{++}/\Delta\text{Ca}^{++} = 16 \times 10^{-4}$ , i.e., equal to the atomic ratio found in deep-sea carbonate oozes ( $20 \times 10^{-4}$ , Sayles and Manheim, 1975; Warner and Gieskes, 1974). Even with the change in sulfate (12 mmoles/l) added to  $\text{Ca}^{++}$  (assuming the equivalent amount of  $\text{HCO}_3^-$  precipitated as  $\text{CaCO}_3$ ), one obtains a ratio of about  $13 \times 10^{-4}$ . On this basis, the question can be raised of whether the increase in  $\text{Ca}^{++}$  and  $\text{Sr}^{++}$  in the interstitial waters is due to dissolution of calcium carbonate at depth. Any alkalinity increase due to this could then be decreased by the formation of silicates containing  $\text{Mg}^{++}$  and  $\text{K}^+$ , but high values of  $\text{CO}_2$  would result, an observation not made in this study. In fact, decreases in alkalinity and constant pH values ( $25^\circ\text{C}$ , 1 atm) suggest also decreases in total dissolved carbon

dioxide. We intend to study the solid phases in order to establish the sources of strontium in these sediments.

Dissolved manganese shows a variable distribution, with high values in the upper sediment layers, a maximum at the base of the siliceous sediments, and, finally, increasing values toward the base of the hole.

Dissolved silica values reflect the lithology, with the highest values in the transitional siliceous oozes in Core 18 (203 m). Below this, values are very low, at about  $100 \mu\text{moles/l}$  or less.

#### Site 337

This site shows relatively slow sedimentation rates of about 1 cm/1000 yr. The data show relatively little change in interstitial water concentrations (Table 1). This indicates that little reaction is occurring in these sediments that would affect the chemical composition of the interstitial fluids.

#### Site 338 (Figure 3)

Data are somewhat scattered at this site but, again, as at Site 336, increases in  $\text{Ca}^{++}$  and decreases in  $\text{Mg}^{++}$  and  $\text{K}^+$  are observed. Overall sedimentation rates were lower than at Site 336 and concentration-depth gradients are less pronounced.  $\text{Ca}^{++}$  increases to just above basement, but dissolved  $\text{Sr}^{++}$  again shows a decrease here. Calcium carbonate dissolution as a source of calcium is unlikely in these sediments, as authigenic carbonate is commonly observed. Basalts

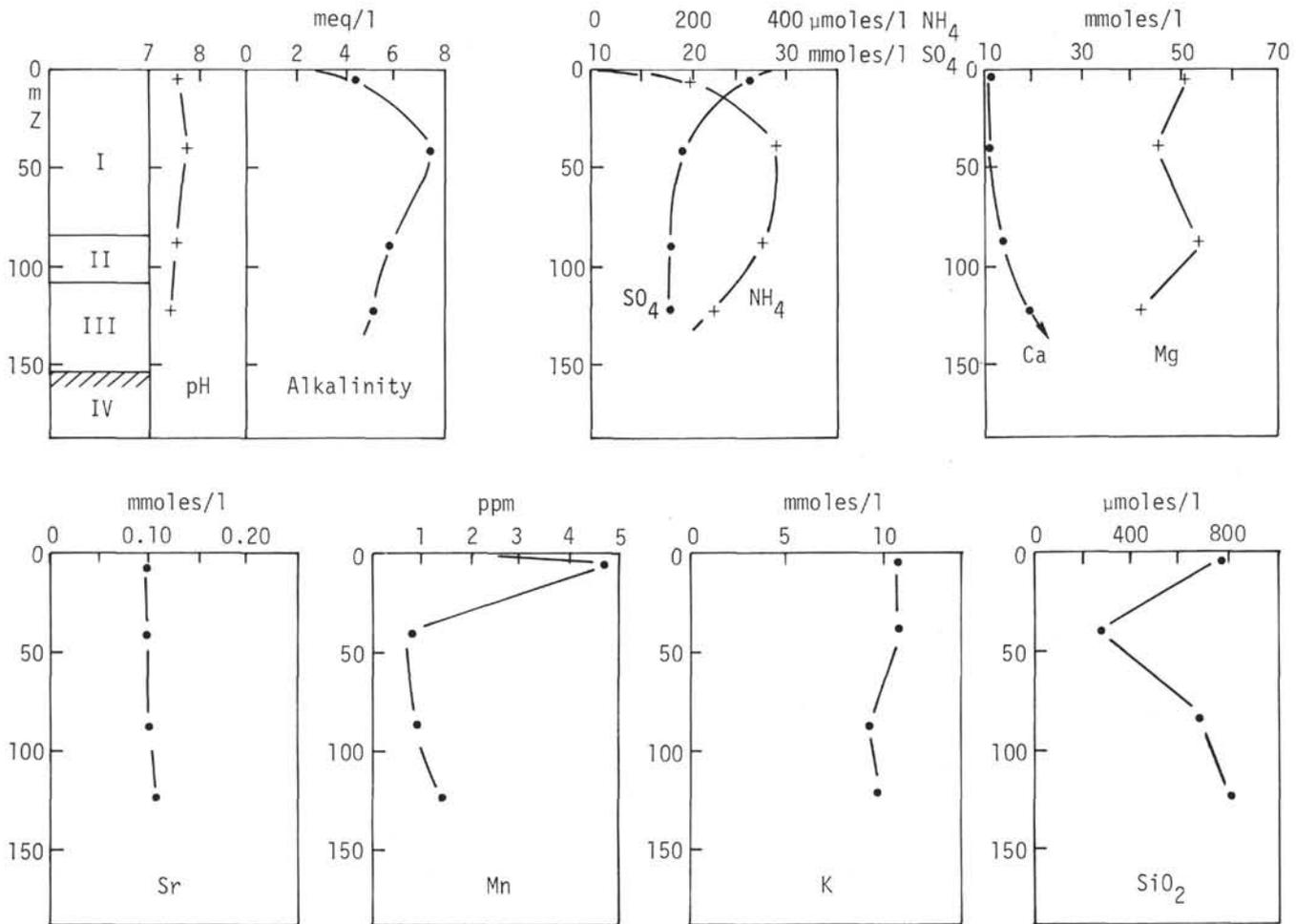


Figure 4. Interstitial water data, Site 342, (I): terrigenous mud and sandy mud with pebbles-Pleistocene; (II): mud and transitional siliceous ooze-Miocene; (III): transitional siliceous ooze-Miocene; (IV): basalt.

underlying these sediments are considerably weathered and are overlain by limestone and a basalt breccia with a chlorite/calcite cement.

Dissolved manganese again is highest in the surface sediments and shows a minimum in the alkalinity maximum and a maximum at about 150 meters. No clear reason for this concentration profile can be given, but perhaps the planned further analyses of the solid phases may throw light on this matter.

Dissolved silica typically reflects the presence of biogenous silica in these sediments, and values drop to under 200  $\mu\text{moles/l}$  below the siliceous Unit 3.

#### Site 342 (Figure 4)

This site was drilled in the vicinity of Site 338, but the Pleistocene section is somewhat thicker (80 m vs. 50 m). Shipboard reports suggest that between the lowermost sediments and the basalt there is a hiatus, probably of long duration. Pleistocene sedimentation rates are about 2-3 cm/1000 yr, and most of the sulfate reduction occurs in this section (Unit 1). Alkalinity values reach a maximum at about 50 meters, but they never drop below seawater values below this depth. Changes in  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{K}^{+}$  are very slight and do not indicate that much post-depositional alteration involving the in-

terstitial fluids has occurred in this site. Basalts are generally fresh, and little alteration has occurred.

#### Site 343 (Figure 5)

This site has been discussed previously because of its pronounced sulfate minimum in the rapidly deposited Pleistocene section ( $>3$  cm/1000 yr). Values of alkalinity drop to below 1 meq/l below the Pleistocene alkalinity maximum, and this is probably related to the same processes that involve changes in  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ , and, to a minor extent,  $\text{K}^{+}$ . Again, small increases with depth in the chlorite concentration (4%-5%) appear real, indicating substantial alteration. Basalts in this hole are highly altered, and a sill overlies the deeper basalts, separated from them by a thin layer of sediment.

Dissolved manganese shows increases to over 7 ppm in the siliceous sediments. This is a common observation for all sites. Dissolved manganese maxima occur in the siliceous material. Subsequent investigations of the solids may reveal the causes of these observations.

#### Site 344 (Figure 6)

This site is the northernmost site of Leg 38. Pleistocene sedimentation rates have been high, but the un-

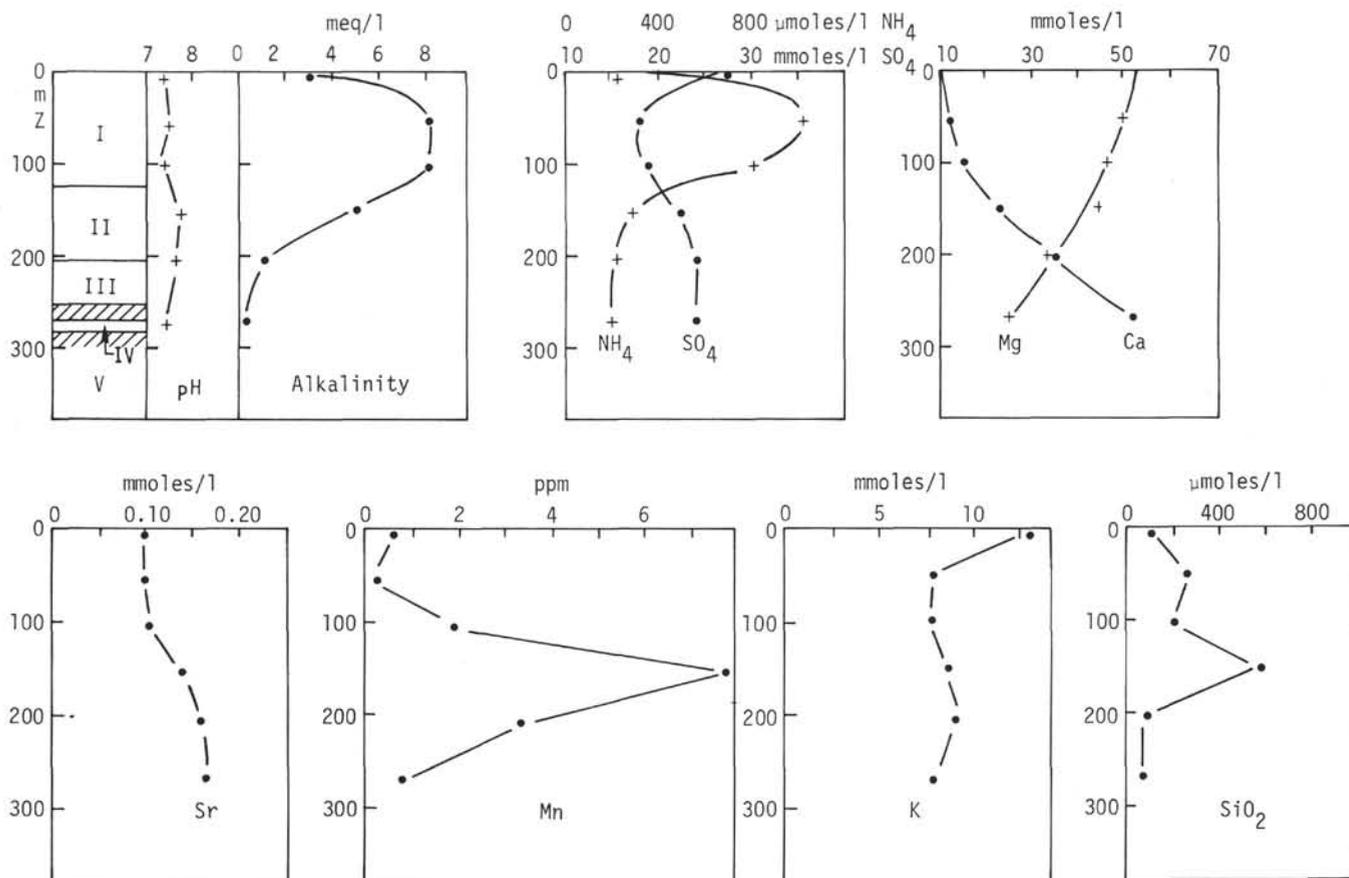


Figure 5. Interstitial water data, Site 343, (I): terrigenous mud and sandy mud with nanofossil ooze horizons—"Glacial"; (II): terrigenous layered mud, sandy mud, and transitional siliceous biogenic ooze; (III): terrigenous mud and clay; (IV): clay between basalts; (V): basalt.

derlying Pliocene sediments have been deposited at even faster rates (8-12 cm/1000 yr). Sulfate depletions are large and, similarly, dissolved ammonia reaches concentrations of well over 2000  $\mu\text{moles/l}$ , with a small decrease toward the bottom of the hole, below 250 meters. Increases in alkalinity are relatively small, and below 50 meters a gradual decrease from 6 meq/l to 1 meq/l is observed. Even the uppermost sample (3 m below the sediment-water interface, possibly somewhat deeper) shows a depletion in dissolved sulfate of 12 mmoles/l and an alkalinity of only 4 meq/l. The  $\text{Mg}^{++}$  concentration has already dropped by 10 mmoles/l. On the other hand,  $\text{Ca}^{++}$  concentrations start to change markedly from that of seawater only below 50 meters. It is not clear what process causes the observed changes. The small increases in alkalinity with the large increases in sulfate depletion imply the removal of  $\text{HCO}_3^-$  ions, presumably by calcium carbonate precipitation. At 3 meters (344-2-1, 145-150 cm) mmoles/l, the precipitation of which removed 20 meq/l in alkalinity. This presumed increase in  $\text{Ca}^{++}$ , of course, balances the decrease in  $\text{Mg}^{++}$ . This could imply the weathering of glacially derived debris, releasing  $\text{Ca}^{++}$ , which subsequently precipitates as  $\text{CaCO}_3$  and involves the uptake of  $\text{Mg}^{++}$  (into montmorillonite?). More detailed X-ray work may shed some light on this problem, but similar observations have been made in

Antarctic glacial sediments of the Ross Sea (Mann and Gieskes, 1974). Below 100 meters, this process is less important and the  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  gradients become almost linear. In the absence of a precise knowledge of the diffusional properties of these very rapidly deposited sediments (8-12 cm/1000 yr), it is not clear what processes are causing these gradients or whether they occur throughout the sediment section. Of interest is the  $\text{Sr}^{++}$  gradient, which is essentially linear throughout the sediment column. Presumably the source of this  $\text{Sr}^{++}$  is the same as for  $\text{Ca}^{++}$  in the deeper sediments, but this bears further investigation.

#### Site 345 (Figure 7)

Interstitial water sampling was halted about 160 meter above basement, so information is not complete at this site. Sedimentation rates in Unit 1 (Plio/Pleistocene) have been about 1.3 cm/1000 yr. A hiatus of about  $13 \times 10^6$  yr separates this unit from Unit 2, and sedimentation rates during the Miocene and Oligocene have been 2.1 cm/1000 yr, with somewhat higher rates during the Eocene.

Sulfate reduction occurs throughout this site, as is also evident from the dissolved ammonia distribution. Alkalinity data show a very weak maximum at the base of Unit 1, below which a gradual decrease occurs.

Decreases in dissolved  $\text{Mg}^{++}$  are large, and the shape of the concentration profile indicates reaction

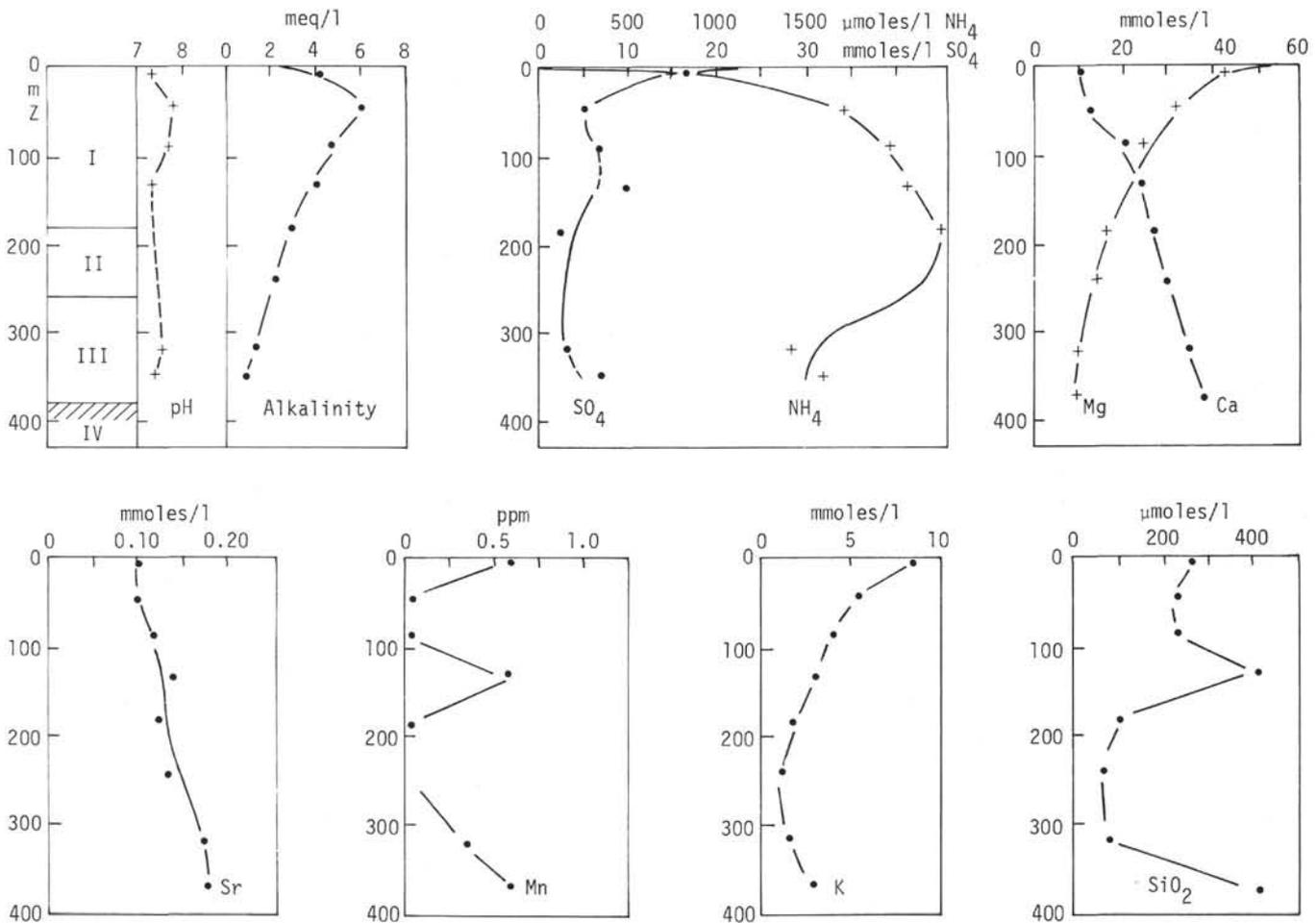


Figure 6. Interstitial water data, Site 344, (I): terrigenous muds, sandy muds, some ash, clays-Pliocene and Pleistocene, (II): sandy muds and diamictons-Pliocene (III): muds, sandy muds, mudstone, sandstone-lower Pliocene on Miocene; (IV): basalt.

throughout this site. Similarly, the profile of dissolved calcium suggests production and perhaps consumption of this component in the sediments. Again, one can only be definite about these conclusions when more information is available on the diffusional properties of these sediments. Dissolved strontium increases to about 550 meters and then an apparent reversal occurs. Again, reactions postulated above appear to be the best explanation for these observations. X-ray data indicate a sharp increase in montmorillonite in the sediments below Unit 1. Perhaps this is one of the end products of the postulated reactions, i.e., weathering of igneous material.

Chloride increases with depth appear real and amount to about 4%-5%. This again may be due to substantial changes in the solids, leading to uptake of water by clay minerals.

#### Site 348

This site is of great interest because of a rather drastic change in sedimentation pattern. Unit 3 is influenced by terrigenous contributions from Greenland, whereas Unit 2 has more biogenic and pelagic contributions as a result of the cut-off of terrigenous supplies because of the elevation of the Jan Mayen Ridge.

Sulfate decreases are significant in this hole, but the alkalinity distribution shows no maximum. In addition, between Unit 2 and Unit 3 there is a sharp "discontinuity" in the alkalinity distribution. Magnesium decreases are very large and concentrations drop to zero in Unit 3. Calcium concentrations increase gradually with depth, with clear evidence of production in the upper sediment column, as well as in the deeper parts.

X-ray evidence shows the presence of a clay fraction in Unit 3 consisting mostly of a mixed-layer clay, with a high content of montmorillonite (generally >70%). This is presumably the result of alteration of detrital igneous material in the sediments. Oxygen isotope depletions are among the largest yet measured in sedimentary pore fluids and suggest substantial alteration (Lawrence et al., 1975, 1976). Chloride increases are probably about 5%-7%, again suggesting substantial alteration reactions.

#### Site 350 (Figure 9)

Sedimentation rates are not well defined, but appear to have been 1.3 cm/1000 yr or less. Sulfate depletion is moderate and appears to have occurred throughout the site; this is also reflected in a gradual increase in am-

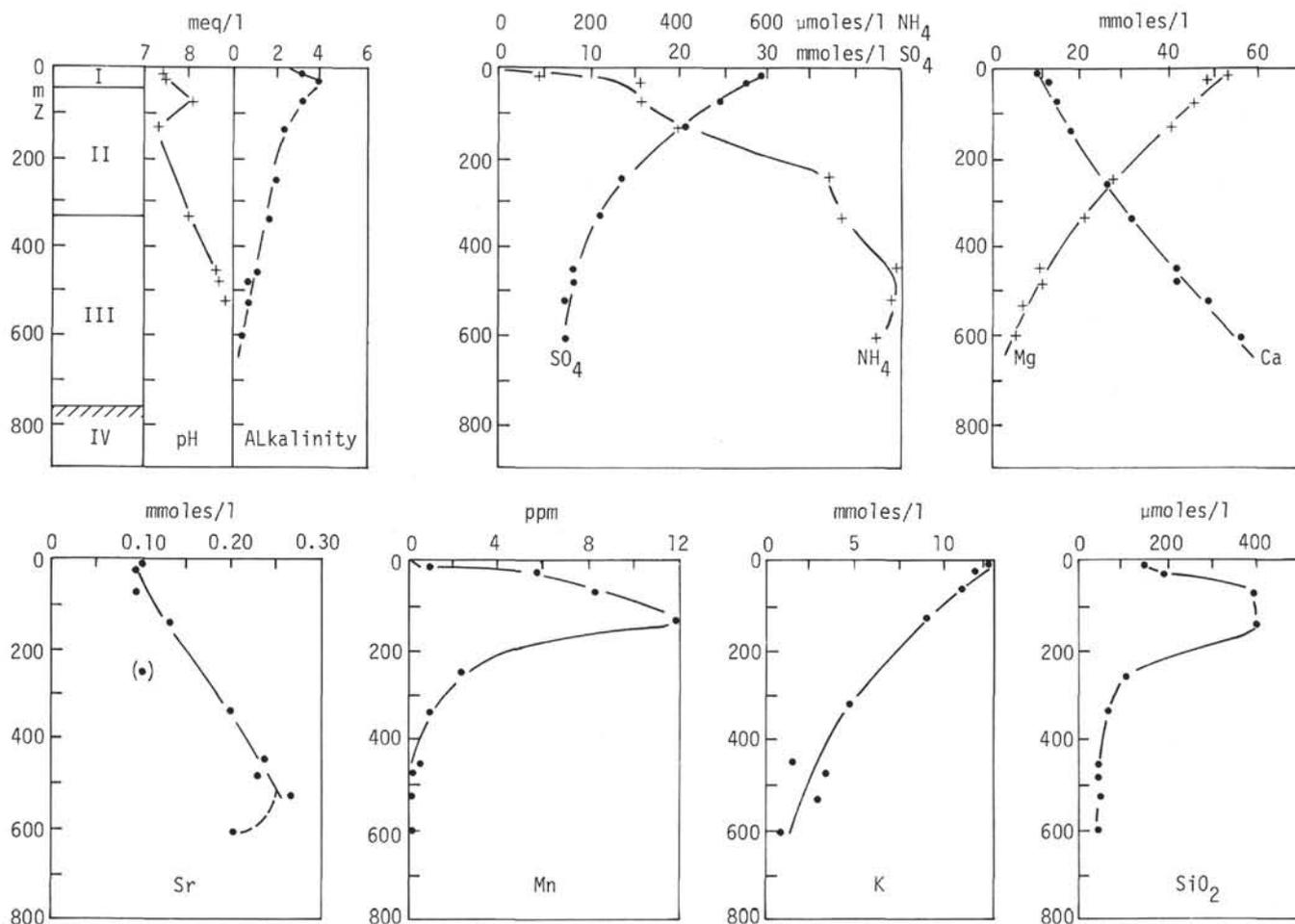


Figure 7. Interstitial water data, Site 345, (I): muds, sandy muds, foraminiferal oozes—"Glacial"; (II): clays, muds, transitional siliceous sediments, foraminiferal ooze to 160 meters mud(stone) and clay(stone) to 331 meters-Oligocene and lower Miocene; (III): mudstone with mud, sandy mud, calcareous sandy mud, sandstone, limestone to 762 meters-Oligocene and upper Eocene; (IV): basalt breccia.

monia. Depletions in  $Mg^{++}$  and  $K^{+}$  are relatively small, and alkalinity decreases throughout the site. Dissolved  $Ca^{++}$  increases throughout the site, and a linear increase of dissolved  $Sr^{++}$  with depth is observed.

Toward the bottom of the site, limestones are common, i.e., in Unit 3. No data are available on the stable  $C^{13}/C^{12}$  isotope ratio of these limestones, which should give an important clue to the origin of the carbon dioxide necessary for the precipitation of this material. Alteration must be substantial, as chloride concentrations increase significantly. Thus, a source of  $Ca^{++}$  is readily available for the precipitation of carbonate, but the source of carbonate ions is less clear. The presence of pyrite in these sediments, however, suggests that sulfate reduction processes have been important. These processes could account for much of the carbonate ions. Conglomerates and calcite veins in sediments recovered during Leg 35 (Anderson and Lawrence, 1976) typically showed  $\delta C^{13}$  values of  $-20\text{‰}$  (PDB), indicating a biogenic source of the carbonate.

The increase in dissolved  $Sr^{++}$  is large. If this  $Sr^{++}$  was the result of dissolution of calcareous fossils

( $Sr/Ca \cong 20 \times 10^4$ , atomic ratio), an increase in  $Ca^{++}$  of about 175 mmoles/l should have occurred. If this was so, 80% of this  $Ca^{++}$  must have reprecipitated as authigenic calcite. A complete chemical analysis of the limestones may, therefore, be most relevant, not only with regard to the provenance of the carbon dioxide but also with regard to  $Sr^{++}$  contents. Any significant uptake of  $Sr^{++}$  would imply even larger amounts of  $Sr^{++}$  (and hence  $Ca^{++}$ ) release by carbonate dissolution.

In general, it is a common observation at all sites of Leg 38 reaching basaltic basement that calcium concentrations increase with depth, whereas magnesium, potassium, and, perhaps, sodium decrease in concentration. In view of the large changes in oxygen isotope ratios of the pore waters at Sites 336 and 348, and because of the persistent small increase in chloride concentration with depth in many of the sites, we postulate that substantial diagenetic changes must occur in these sediments long after burial. The shapes of the concentration profiles cannot be used to delineate reaction zones in these sediments in the absence of more information on their diffusional permeability. We plan,

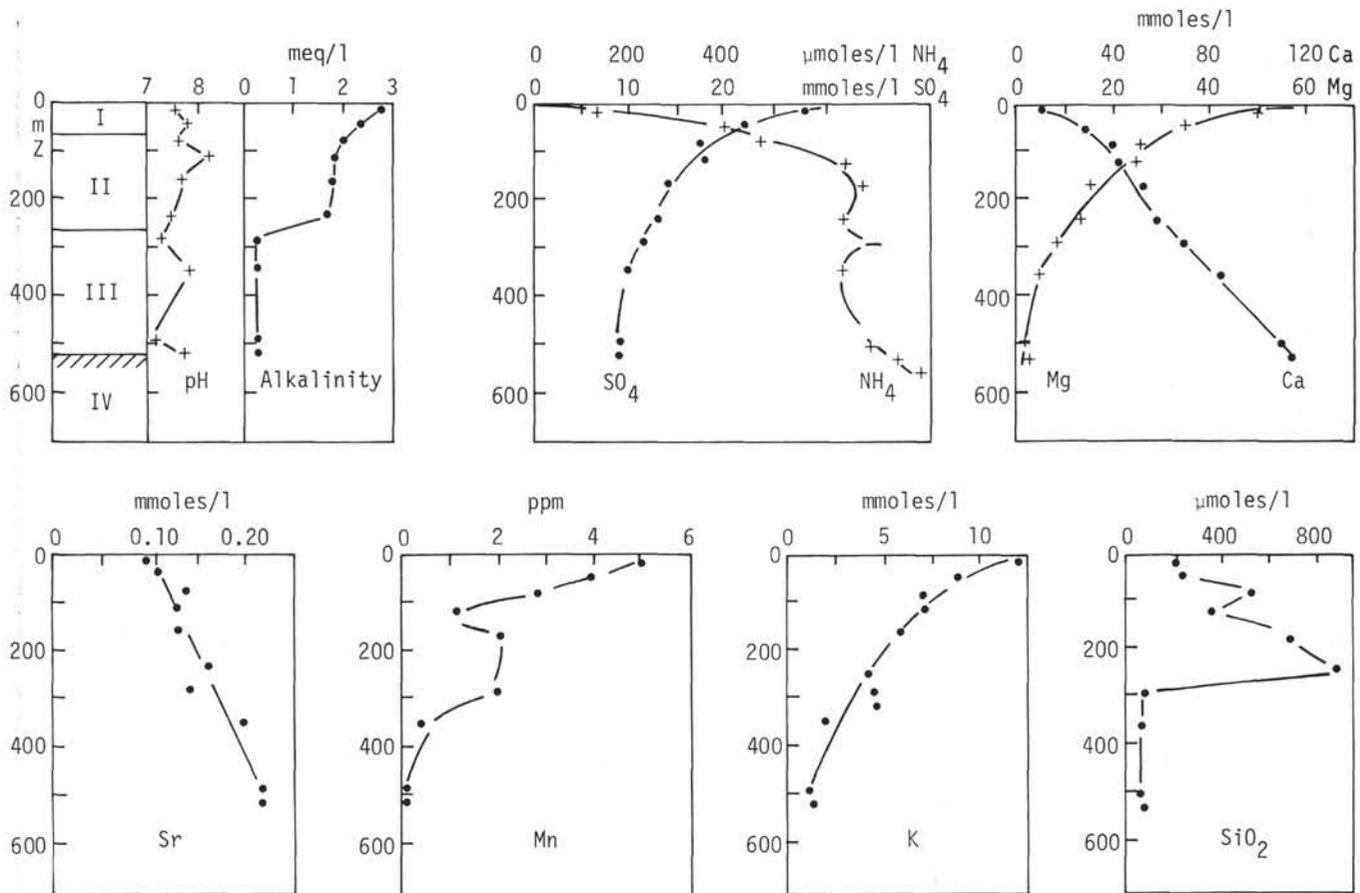


Figure 8. Interstitial water data, Site 348, (I): sandy mud, mud and clay, volcanic ash-“Glacial”; (II): transitional biogenic siliceous clay, mud, nannofossil and siliceous nannofossil ooze-Pliocene, Miocene; (III): terrigenous mud/mudstone, clay, claystone, sandy mudstone-Miocene, Oligocene; (IV): basalt.

however, to remedy this situation in the near future by carrying out measurements of the formation factors of these sediments (c.f., Gieskes and Lawrence, 1976).

We are of the opinion that the reactions involve, most probably, the alteration of basalt, volcanic ash, and/or igneous components of terrigenous debris. Such reactions imply both the consumption of protons in the weathering of plagioclase and related minerals and the production of protons by the formation of clay minerals and other authigenic products. Thus, relatively minor changes in alkalinity will occur, as is observed in most of these sites. In fact, at all sites it is a common observation that both alkalinity and the total CO<sub>2</sub> content of the interstitial waters decrease with depth. The latter can be attributed in large part to the precipitation of calcium carbonate due to the large increases in calcium concentrations. Additional bicarbonate for this precipitation is provided by the bacterial sulfate reduction processes that occur in all these sediments. The existence of the observed concentration gradients suggests that we are not dealing with a closed system. For instance, concentration gradients in magnesium imply that the alteration reactions that cause precipitation of magnesium ions (presumably as smectites) do not derive all their magnesium from the system but gain some magnesium by diffusional supply from higher sediment layers or the overlying ocean. O<sup>18</sup> depletions

correlate very well with Mg<sup>++</sup> concentrations (Figure 11). This may be an indication of the involvement of the Mg<sup>++</sup> exchange and oxygen isotope exchange in the same reaction. Further studies on the oxygen isotope budget of these sediments (Lawrence et al., 1975, 1976) may help to set limitations on the amount of alteration involved.

Of some interest is the consistent increase of dissolved strontium with depth. This strontium can have two possible sources: the postulated weathering of igneous material or the dissolution of biogenic calcareous material. If the latter is indeed the case, the dissolved calcium concentration increases may have two underlying causes: weathering of igneous material and dissolution of fossil shells. Carbonate ions released in the latter process must then reprecipitate elsewhere in the sediments, probably with the calcium ions derived from igneous material. Observations made by Kastner (1976) would be consistent with this mechanism. We intend to study the strontium geochemistry in these sediments in more detail, in order to unravel some of these questions. Stable isotope studies will be particularly helpful here.

#### Other Sites (Table 1)

Among the sites where drilling did not reach basaltic basement, three sites, 339, 340, and 341, were located

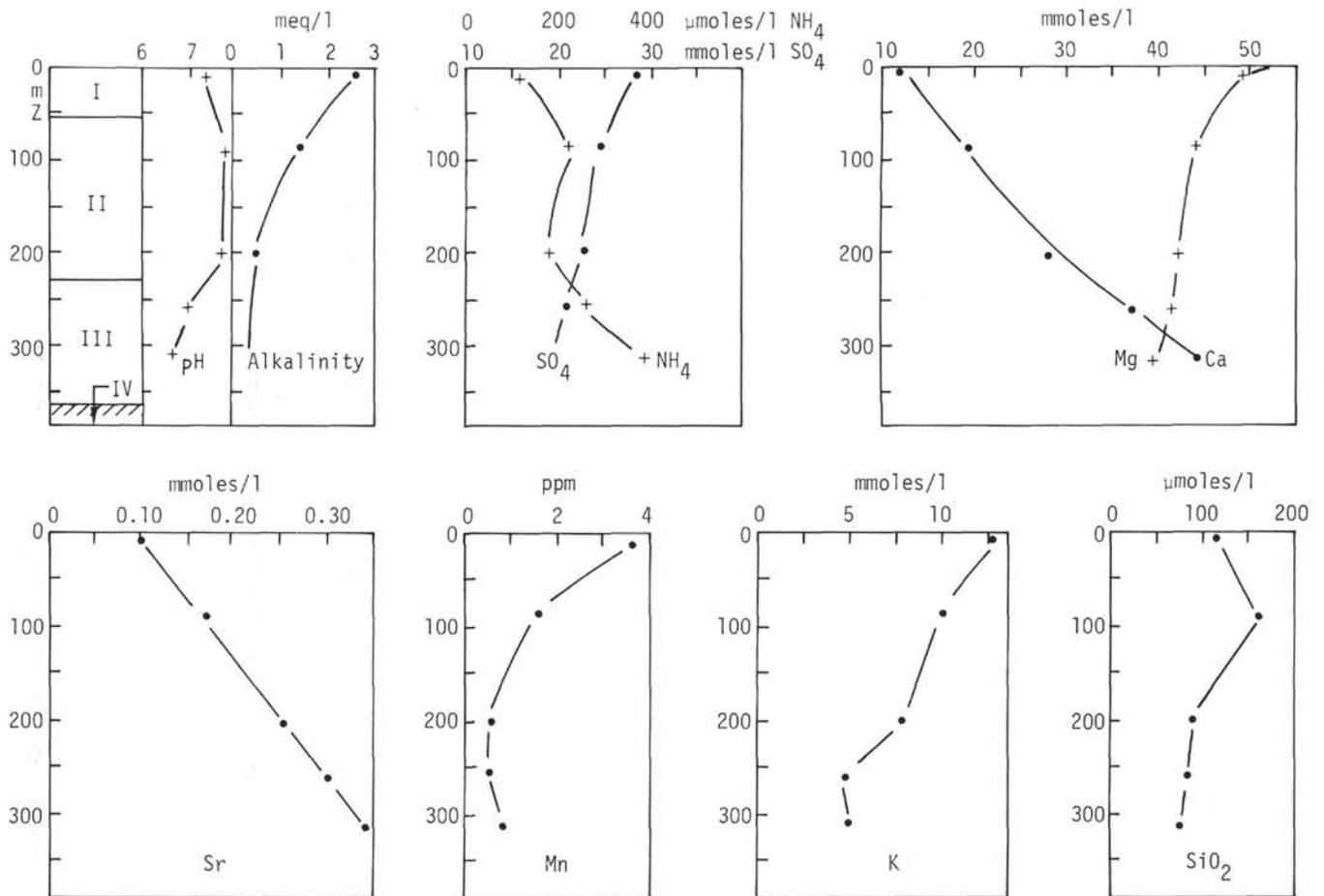


Figure 9. Interstitial water data, Site 350; (I): Sandy mud, some foraminiferal ooze—"Glacial"; (II): Clay/claystone, mud/mudstone-Miocene, Oligocene; (III): Mudstone, claystone, breccia-Oligocene, Eocene; (IV): Basalt.

on the Inner Vøring Plateau. Notwithstanding the fact that Site 340 is only slightly offset from Site 339, there are vast differences in the interstitial water chemistry. Whereas the "Glacial" sediments of Site 339 cover about 80 meters, the thickness of this layer is only 10 meters at Site 340. Sulfate depletion at Site 339 is extensive. In addition, there is strong evidence from the low salinities and the low chlorinities that fresh waters enter from deeper layers. This is equally true for Site 341. Such evidence is absent at Site 340, but here, as for dissolved sulfate, diffusional replenishment from the overlying ocean waters may annihilate any depletions. Fresh water input has been reported before (Sayles and Manheim, 1975; Gieskes, 1974; Mann and Gieskes, 1975) and is probably due to advection from sources on land. Sayles and Manheim (1975) suggest another possibility in the expulsion of water from clay minerals during deep burial. In general, however, freshening of interstitial waters has been observed only at sites not far distant from a continent. Thus, fresh water intrusions from deeper strata probably have their origins in deep aquifers connecting the Vøring Plateau to the Norwegian mainland.

Site 341 shows, again, large sulfate depletions, and dissolved ammonia values are well above 2.5 mmol/l. Magnesium depletions at both Site 339 and Site 341 are substantial; the cause of this is not immediately clear.

Sites 346 and 349, on the Jan Mayen Ridge, did not reach basement, but interstitial water chemistry data suggest that processes responsible for compositional changes in the surrounding sites are also responsible for the observed changes at these sites.

#### ACKNOWLEDGMENTS

We wish to acknowledge the efforts of the shipboard chemist, Mr. Don Cameron, in accurately determining alkalinity, pH, calcium, and magnesium. His work led to our decision to follow this up with a more detailed study. This work was supported by grants from the U.S. National Science Foundation: DES-72-0140 (J.M.G.) and OCE-75-02968 (J.R.L.).

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TABLE 2  
Oxygen Isotope Composition of  
Interstitial Waters

Core-Section	Depth (m)	$\delta O^{18}$ (SMOW)
<b>Site 336</b>		
5-5	43	+0.5
11-4	117.5	-0.1
22-5	242.5	-1.6
30-4	336	-3.1
35-5	429.5	-3.5
<b>Site 348</b>		
4-2	40.5	-0.9 $\pm$ 0.1
12-5	168.5	-4.9 $\pm$ 0.1
16-5	235	-5.7 $\pm$ 0.4
24-5	349	-7.7 $\pm$ 0.1
29-5	491.5	-8.3 $\pm$ 0.1

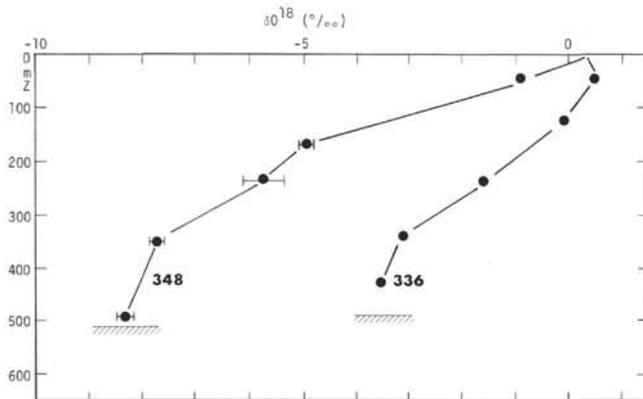


Figure 10. Oxygen isotope composition of interstitial waters, Sites 336 and 348.

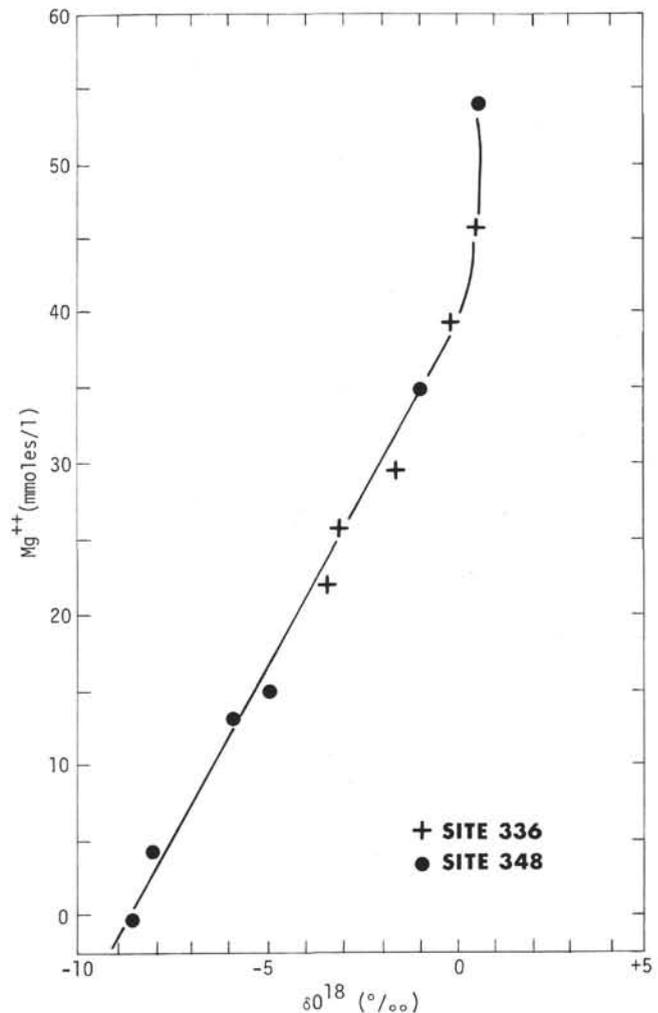


Figure 11.  $Mg^{++}-\delta O^{18}$  correlation, Sites 336 and 348.

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