

## 28. INTERSTITIAL WATER STUDIES, DEEP SEA DRILLING PROJECT, LEG 75<sup>1</sup>

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### ABSTRACT

Interstitial water profiles obtained at Sites 530 and 532 of DSDP Leg 75 indicate complex concentration depth profiles resulting from diagenetic reactions taking place in the sediments. At both sites, large depletions in dissolved sulfate, resulting from bacterial sulfate reduction reactions, are accompanied by increased alkalinity values and also by increased dissolved ammonia concentrations. At Site 530, high sedimentation rates in the upper 200 m of the sediment column have led to a minimum in dissolved sulfate. Deep-seated reactions in basal sediments and/or basalts at this site cause downhole increases in dissolved calcium and decreases in dissolved magnesium. At Site 532, phosphate liberated by sulfate reduction has led to reaction with calcium ions to form authigenic Ca-phosphate minerals.

### INTRODUCTION

During Leg 75 of the Deep Sea Drilling Project (DSDP) two sites were drilled—Sites 530 and 532—which were sampled in great detail for interstitial waters. The drill sites are closely related to two sites occupied during Leg 40: Site 530 is 55 km NE of Site 363, at a water depth of 4629 m in the Angola Basin, and Site 532 is essentially a reoccupation of Site 362 of DSDP Leg 40.

Site 530 was piston cored to a depth of 180 m (Hole 530B) and rotary drilled to basement at 1103 m sub-bottom depth. Site 532 was piston cored to a depth of 300 m (Hole 532B); at this site a very detailed sampling program for interstitial waters was undertaken.

Both Sites 530 and 532 are characterized by very high sedimentation rates, especially in the younger sections, and this leads to complications in the interstitial water profiles as will be discussed.

### RESULTS

The shipboard data (pH, alkalinity, salinity, chloride, calcium, and magnesium) and the data obtained in our laboratory are presented in Table 1 and Figures 1, 2, and 3. Methods used were those described by Gieskes (1974), Gieskes and Lawrence (1976), and Gieskes and Johnson (1981).

### DISCUSSION

#### Site 530

The upper 100 m (Units 1a, 1b) were deposited at rates in excess of 65 m/m.y. and consist of diatom-nannofossil marls and debris-flow deposits. Sedimentation rates in the lower lying lithologic units were much less.

Hole 530B (Fig. 1) indicates that sulfate reduction is an important process in the upper section of the sedi-

ment column. This is evident from the rapid decrease in dissolved sulfate, the increase in dissolved ammonia (maximum of 3.25 mM at 80 m), and the increase in alkalinity (maximum of 25 meq/dm<sup>3</sup> at 80 m). Typically, the production of bicarbonate has led to the precipitation of calcium carbonate, thus causing the low concentrations of dissolved calcium in the upper 200 m. A rapid decrease in magnesium occurs which is not readily explained, but may be the result of processes involving the diagenesis of opaline silica (Kastner et al., 1977) or the formation of dolomite. Strontium concentrations increase rapidly below 40 m, probably as a result of carbonate diagenesis (Baker et al., 1982). Dissolved lithium appears to have a source in the lower lying sediments, i.e., in Unit 3 (Fig. 2). Data on dissolved silica indicate high concentrations, representative of those often found in siliceous sediments (Gieskes, 1981).

Holes 530 and 530A sampled the deeper section of Site 530, and the data indicate a well-established minimum in dissolved sulfate, located at about 200 m sub-bottom depth. This can be understood in terms of the higher sedimentation rates in the upper 200 m of the sediments, usually associated with increased levels of reactive organic carbon. With sedimentation rates of ~50 m/m.y. in the upper 200 m of the sediment column the communication length for diffusion is between 100–150 m, and thus nonsteady-state dissolved sulfate profiles, especially as a result of higher sulfate reduction rates in the upper sediment column, are to be expected (Gieskes et al., 1978; Gieskes, 1981). The sulfate minimum is accompanied by an ammonia maximum as well as an alkalinity maximum.

Unit 3 (250–450 m) is characterized by red and green muds, with appreciable volcanic contributions. Dissolved silica values are low, indicating little contribution of biogenic silica. The profiles of dissolved lithium and potassium indicate a source for lithium, leading to a maximum in this zone, and a sink for potassium, perhaps as a result of uptake in clay minerals. No sink for magnesium is indicated by the dissolved magnesium profile.

<sup>1</sup> Hay, W. W., Sibuet, J.-C., et al., *Init. Repts. DSDP, 75*: Washington (U.S. Govt. Printing Office).

Table 1. Interstitial water analyses, Leg 75.

Sample (interval in cm)	Sub-bottom depth (m)	pH	Alk. (meq/dm <sup>3</sup> )	S (g/kg)	Ca (mM)	Mg (mM)	Cl (g/kg)	Sr (μM)	Li (μM)	K (mM)	So <sub>4</sub> (mM)	NH <sub>4</sub> (μM)	Si (μM)
Hole 530													
2-6, 140-150	124	7.54	16.32	33.0	5.50	39.7	23.49	166	88	10.7	5.0	1407	895
Hole 530A													
5-6, 140-150	172	7.77	12.40	33.0	7.39	38.3	19.55	254	161	10.0	4.5	1425	1227
10-6, 140-150	219	7.44	6.79	32.2	8.09	38.3	19.55	197	158	6.95	—	1113	495
15-5, 140-150	265	7.52	2.19	32.4	8.13	37.6	19.31	167	136	6.65	—	871.5	118
20-5, 140-150	313	6.81	3.26	33.0	13.41	37.7	19.41	234	136	6.60	8.9	582	82
25-6, 140-150	362	7.42	2.32	31.9	17.91	36.5	18.67	275	145	3.00	—	378	167
30-4, 140-150	406	6.81	1.96	33.0	23.61	29.8	19.11	320	160	2.90	17.1	370	125
35-4, 140-150	416	7.06	1.50	32.4	24.68	31.4	18.87	387	197	2.50	—	274	107
40-3, 140-150	500	7.58	1.46	34.1	21.77	36.2	19.78	387	133	4.20	20.4	252	781
50-3, 110-120	594	7.64	0.92	34.1	24.42	29.1	19.75	593	97	2.86	—	340	375
60-1, 140-150	687	7.25	0.22	34.1	32.89	16.5	19.61	725	90	2.55	18.5	250	122
89-5, 140-150	965	—	—	31.9	87.70	15.8	18.93	735	—	1.39	—	—	—
99-4, 140-150	1050	—	—	31.4	43.53	13.1	18.33	630	182	1.39	—	—	—
Hole 530B													
4-2, 143-150	14	7.65	12.53	35.2	6.93	52.4	19.46	96	48	10.72	20.9	1550	759
9-2, 143-150	35	7.47	19.95	34.4	6.74	46.6	19.46	81	53	8.46	8.4	2518	787
14-2, 140-150	57	7.57	23.38	33.3	5.63	41.2	19.46	124	57	11.34	7.4	3041	944
20-2, 140-150	83	7.35	24.02	33.6	4.88	40.3	19.69	178	69	9.07	—	3252	916
26-2, 140-150	106	7.41	20.82	32.7	5.69	38.5	19.39	186	69	9.70	3.8	3238	974
32-1, 140-150	124	7.64	14.81	32.4	5.12	37.1	19.63	177	98	8.20	3.5	2934	970
38-2, 140-150	149	7.48	10.56	32.2	5.33	31.3	19.29	170	120	10.0	3.6	2559	875
46-1, 140-150	172	7.47	10.66	32.2	6.35	35.6	19.49	170	142	7.41	4.5	2209	787
Hole 532													
3-4, 0-11	8	7.01	2.23	35.5	10.73	49.8	—	104	47	6.90	30.0	40	44
12-2, 140-150	51	7.52	13.22	34.4	9.00	41.1	—	134	70	7.17	15.0	2198	782
21-2, 140-150	90	7.20	19.35	32.7	7.06	36.9	—	195	123	6.83	7.2	3784	893
31-2, 140-150	130	7.27	19.88	32.2	8.31	27.8	—	234	163	10.29	2.9	4421	866
40-2, 143-150	164	6.93	19.81	32.4	6.65	27.9	—	298	208	8.87	3.9	5242	840
51-2, 140-150	211	7.92	19.47	33.0	9.57	24.7	—	351	267	10.60	3.9	5505	657
Hole 532B													
2-2, 140-150	8	7.61	3.76	34.9	10.82	54.2	18.83	104	50	11.24	31.0	328	512
4-2, 140-150	17	7.69	4.20	35.2	10.71	53.8	18.77	122	50	9.28	28.4	398	536
6-2, 140-150	25	7.46	4.96	35.2	10.22	53.7	19.92	124	51	8.27	31.0	510	565
8-2, 140-150	34	7.53	7.49	35.2	9.35	54.2	19.68	126	58	11.44	—	958	687
10-2, 140-150	43	7.49	9.96	35.2	8.08	52.2	19.41	129	59	10.61	24.3	1322	700
12-1, 140-150	52	7.34	12.34	35.2	7.28	50.8	19.78	130	59	10.64	23.3	1719	832
14-2, 140-150	61	7.52	13.55	34.3	7.06	46.9	19.98	134	79	9.84	—	2153	761
16-2, 140-150	69	7.48	14.68	33.8	5.02	44.0	19.88	147	81	12.62	13.1	2584	883
18-1, 140-150	78	7.49	16.34	34.1	4.89	43.8	19.41	151	89	10.97	—	2757	788
20-1, 140-150	87	7.52	18.98	33.3	5.00	40.8	19.34	173	82	11.15	8.3	3043	839
22-1, 140-150	96	7.51	18.61	33.0	4.94	36.7	19.14	184	118	9.07	—	3241	840
24-2, 140-150	105	7.38	17.93	33.0	5.04	35.1	19.41	184	124	11.04	4.9	2889	829
26-3, 140-150	113	7.54	15.20	32.4	5.20	32.3	19.21	195	132	11.75	—	4126	786
28-2, 140-150	121	7.52	18.64	32.7	5.24	32.2	18.97	198	139	11.13	7.3	4130	831
30-2, 143-150	129	7.39	18.20	33.0	4.98	31.7	19.17	196	138	10.0	9.4	4955	812
32-2, 140-150	138	7.45	20.46	33.0	6.28	30.9	19.17	235	129	10.02	—	4851	800
34-2, 140-150	146	7.63	18.98	33.0	5.12	31.8	19.34	237	177	11.81	7.3	4974	801
36-2, 143-150	154	7.67	18.83	32.4	6.00	30.9	19.14	274	188	10.87	—	5264	804
38-3, 0-006	162	7.7	17.80	32.2	5.77	33.7	20.12	272	196	10.86	9.4	5609	753
40-2, 140-150	170	7.67	18.13	31.9	6.24	29.1	19.54	284	216	11.47	—	5358	757
42-2, 140-150	177	7.31	11.06	31.9	5.41	24.6	19.51	219	234	15.17	6.7	5061	349
44-2, 140-150	184	7.54	18.65	32.2	6.31	30.9	19.34	279	203	11.42	—	5649	831
47-2, 140-150	196	7.68	17.42	32.4	6.94	28.3	19.34	302	265	8.49	9.3	6873	673
50-2, 140-150	208	7.48	13.84	32.2	7.18	24.4	19.44	274	279	12.14	—	5716	372
52-2, 140-150	216	7.74	17.30	32.2	7.20	27.8	19.21	320	288	10.63	9.3	6106	653
54-2, 140-150	224	7.67	17.86	32.4	7.59	28.4	19.37	366	274	10.40	—	5061	725
56-2, 140-150	232	7.82	16.01	32.7	7.43	27.7	19.68	366	274	10.82	9.2	6458	764
59-2, 140-150	243	7.65	15.51	32.2	7.18	27.0	19.51	375	292	10.86	—	6209	726
61-2, 140-150	251	7.48	12.24	32.2	5.57	26.0	19.41	325	294	8.05	8.9	6858	452
63-2, 140-150	258	7.55	12.39	32.2	6.98	26.4	19.17	365	297	9.45	—	6230	527
65-2, 140-150	264	7.69	13.70	32.4	7.71	26.8	19.61	377	295	8.24	8.9	6011	678
67-2, 140-150	271	7.66	11.98	32.2	5.63	26.2	19.44	376	312	8.95	—	6272	457
69-2, 140-150	279	7.59	9.70	32.2	4.94	26.2	19.88	364	291	—	6.7	6591	363
71-1, 140-150	285	7.57	10.41	31.9	5.57	25.9	19.14	316	285	10.55	—	5500	363
73-1, 140-150	290	7.84	12.56	34.1	7.28	28.4	19.27	304	254	8.90	7.8	3500	883

Note: Dash = data not available.

Below Unit 3 the profile of dissolved calcium indicates a source of calcium in the deeper section of the sediment column, perhaps in the carbonate layers or in the underlying basement. For dissolved magnesium the situation is less clear, with possible uptake both in the sediments (dolomitization?) and in the underlying basalts. Dissolved strontium has a significant source in

Unit 5, which is characterized by calcareous sediments and limestones. At great depth dissolved strontium values again decrease.

In general the dissolved constituents of the interstitial waters recovered from Site 530 sediments indicate a complex set of reactions reflecting the variable lithological features of the sediments. Biogenic sulfate reduc-

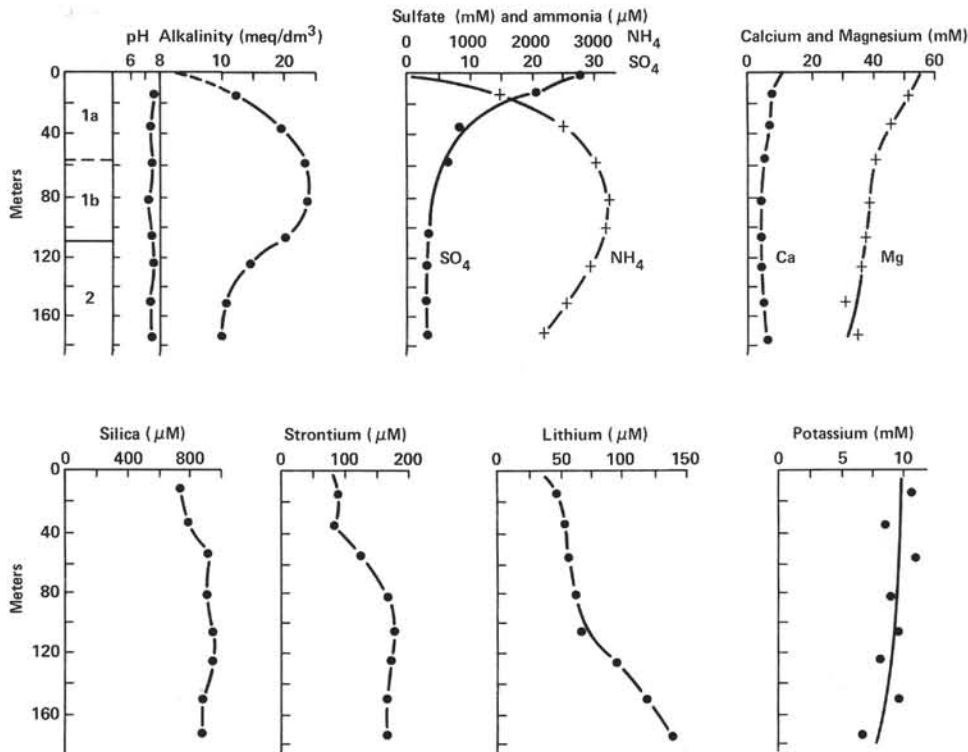


Figure 1. Interstitial water data, Hole 530B. Unit 1a: Diatom-nannofossil marl and ooze; debris-flow deposits— $\sim 65$  m/m.y. Unit 1b: Diatom ooze and debris-flow deposits— $\sim 65$  m/m.y. Unit 2: Nannofossil clay, marl, and ooze; debris-flow deposits— $\sim 20$  m/m.y.

tion processes in the upper sediment column cause complex nonsteady state profiles in dissolved sulfate, ammonia, alkalinity, and calcium.

### Site 532

Site 532 was essentially a reoccupation of Site 362 on the Walvis Ridge. Only the upper 300 m of this site were sampled, but very detailed sampling allowed a detailed determination of the interstitial water profiles. Sedimentation rates have varied between 40 and 50 m/m.y., and the sediments consist mostly of nannofossil marls (Fig. 3).

The alkalinity profile shows a broad maximum of  $\sim 20$  meq/dm<sup>3</sup> between 80–200 m. Dissolved sulfate shows a minimum located at the base of Unit 1b (diatom-nannofossil marl). This minimum is not reflected in the dissolved ammonia profile. Methane gas levels (not reported here) only become significant below 120 m, i.e., below the sulfate minimum. Dissolved ammonia has its main source at  $\sim 250$  m, with high production in the methane zones (120–250 m). Alkalinity increases, causing authigenic apatite (c.f., site summary) and calcium carbonate precipitation and consequently a decrease in dissolved calcium. Dissolved magnesium appears to have a sink in Unit 1b. Perhaps the decrease in magnesium is the result of partial dolomitization of carbonates in the low sulfate zone at  $\sim 100$  m. Both dissolved lithium and dissolved strontium have sources at  $\sim 280$  m. However, the nature of these sources remains unclear, though carbonate recrystallization reactions are the most likely source of dissolved strontium. The

data for dissolved potassium show little trend and are too scattered to suggest any possible significant variability downhole. Data on dissolved chloride are not precise enough to confirm the gradual downhole increase in dissolved chloride that characterized Site 362, particularly below a depth of  $\sim 300$  m (Sotelo and Gieskes, 1978). Agreement between alkalinity, dissolved calcium, and dissolved magnesium profiles obtained in Site 362 (Sotelo and Gieskes, 1978) and in Site 532 is very good.

### ACKNOWLEDGMENTS

We appreciate the efforts by the shipboard chemist, Mr. Ken Thompson. The manuscript has been reviewed by Drs. R. E. McDuff and G. Klinkhammer, whose criticisms are appreciated. This work was supported by NSF Grant OCE-8023966 to JMG.

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Date of Initial Receipt: October 6, 1982

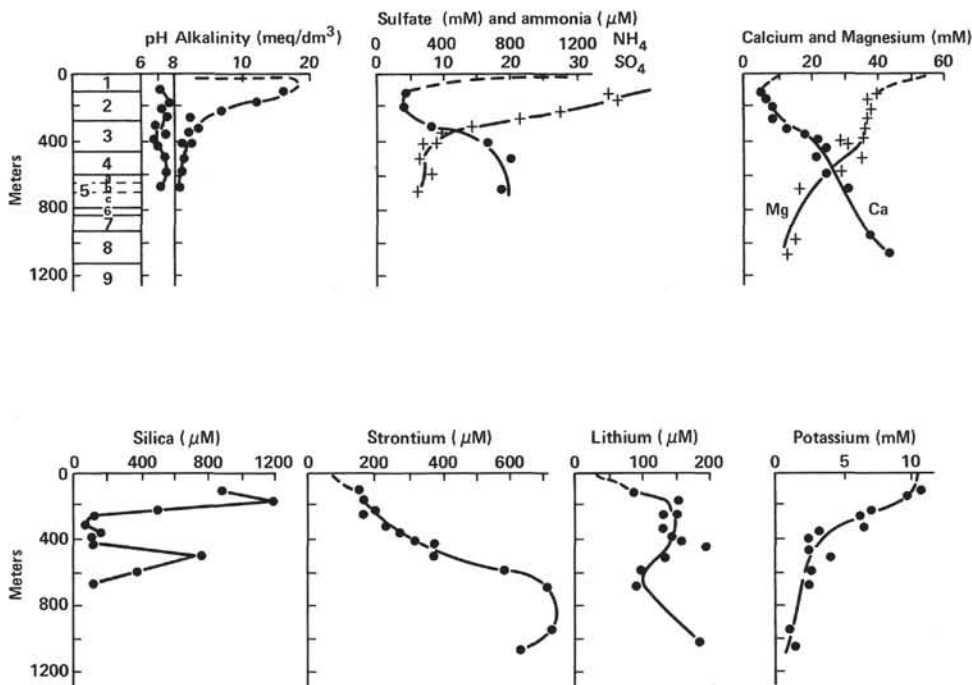


Figure 2. Interstitial water data, Hole 530A. Unit 1: Diatom-nannofossil oozes, marls, and debris-flow deposits—~ 65 m/m.y. Unit 2: Nannofossil clay, marl, and ooze; debris-flow deposits—~ 20 m/m.y. Unit 3: Red and green mud—~ 9 m/m.y.; Unit 4: Multicolored mudstone, marlstone, chalk, and clastic limestone—~ 5 m/m.y. Unit 5a: Mudstone, marlstone, limestone—~ 15 m/m.y. Unit 5b: Mudstone, marlstone, limestone, and siliciclastic sandstone—~ 38 m/m.y. Unit 5c: Mudstone, marlstone, calcareous siliclastic sandstone—~ 11 m/m.y. Unit 6: Glauconitic sandstone—~ 20 m/m.y. Unit 7: Claystone, siltstone, sandstone—~ 31 m/m.y. Unit 8: Claystone, marlstone, black shales—~ 9 m/m.y. Unit 9: Basalt.

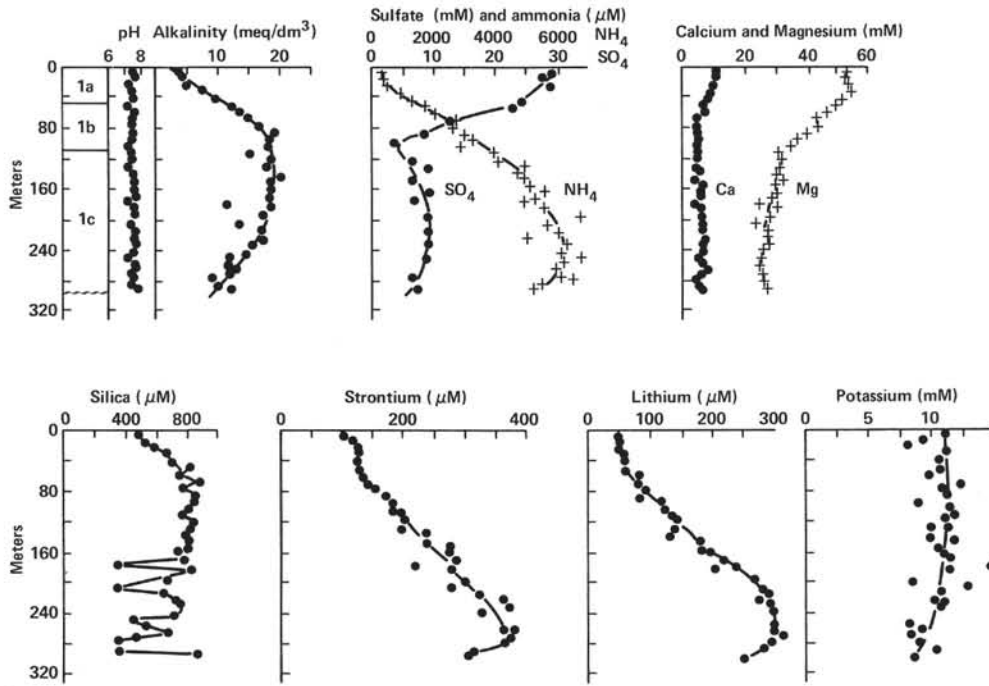


Figure 3. Interstitial water chemistry, Site 532. Unit 1a: Foram-nannofossil marl and ooze—~41 m/m.y.  
 Unit 1b: Diatom-nannofossil marl—~52 m/m.y. Unit 1c: Nannofossil marl—~40 m/m.y.