

## 18. INTERSTITIAL WATER STUDIES, LEG 65, DEEP SEA DRILLING PROJECT<sup>1</sup>

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### ABSTRACT

Studies of the chemical composition of interstitial waters obtained at Sites 482, 483, 484, and 485 on DSDP Leg 65 have revealed the following: (1) Early diagenetic processes in these rapidly deposited sediments led to large decreases in dissolved sulfate and concomitant increases in dissolved ammonia and bicarbonate (alkalinity). Associated with these processes of biodegradation of organic matter are carbonate-precipitation reactions leading to minima in dissolved calcium. (2) In Sites 482, 483, and 485 a flux of dissolved calcium from the basalts of Layer 2 into the sediments is implied. This flux is diffusive in nature, and in none of the sites, drilled on very young oceanic crust, is there any evidence for convective motion of pore fluids in the sediment column. (3) As a result of elevated temperatures in the sediments (caused by relatively high heat flow on young oceanic crust), silica diagenesis occurs at a relatively early stage. This diagenesis is associated with processes involving the alteration of volcanic matter in the sediments (low dissolved <sup>87</sup>Sr/<sup>86</sup>Sr), which results in decreases in dissolved silica, magnesium, and potassium, and increases in dissolved calcium, lithium, and strontium.

### INTRODUCTION

During Leg 65 of the Deep Sea Drilling Project (DSDP), a number of sites were drilled near the crest of the fast-spreading East Pacific Rise in the mouth of the Gulf of California (Fig. 1). In this area sediment accumulation rates are high, especially because of large inputs of detrital sediments from nearby continental sources. In such sediments, interstitial water concentration-depth profiles are often complex, as was demonstrated by studies at Site 474 of Leg 64, located in the same general area of the Gulf of California (Gieskes et al., in press). Interstitial water samples were collected at frequent depth intervals in these holes, to ensure that any complex features in the interstitial water chemistry could be described adequately.

It is of great interest to study interstitial waters in areas of very young oceanic crust, because upward or downward convection of water through the sediment column in such areas has often been invoked to explain anomalies in heat-flow observations (e.g., Anderson et al., 1979). Such convective movement of water should be noticeable in the distribution of the dissolved constituents. In addition, in sediments in areas of high heat flow, diagenetic processes might occur at more rapid rates and would again leave an imprint on the interstitial water chemistry.

The lithologies of the four drill sites of Leg 65 are presented in simplified form in Figure 2. Most of the sediments consist of hemipelagic clays and silts of terrigenous origin. Biogenic silica contents usually decrease with depth. At several sites (482, 483, 485), the sediments are intercalated with basalt flows or sills.

Of special interest are the four holes drilled in a sediment pond at Site 482. The drill holes are about 100 meters apart and lie along a line roughly perpendicular to the ridge axis (which lies 12 km to the west) and to the axis of the sediment pond, with Hole 482D being closest to the center of the pond (Fig. 3). The occurrence of dolomite at the upper basalt/sediment contact, especially in Holes 482C and D, has been interpreted as evidence of increased thermal influence toward the center of the pond (cf. site report, Site 482, this volume). Heat-flow measurements in Hole 482C indicated a heat flow of 12 heat flow units (i.e.,  $12 \times 10^{-6}$  cal cm<sup>-2</sup>s<sup>-1</sup>), yielding temperatures of about 80°C at the sediment/basalt interface and about 90 to 110°C at the bottom of the hole. Indirect measurements made in the hole with a downhole seismometer, however, indicated a temperature rise to 150°C after 42 days, implying upward advection of hydrothermal waters through a hot spring created by drilling (Duennebie and Blackinton, 1980; Duennebie et al., this volume). Interstitial waters were obtained in Holes 482A, B, C, and D.

Methods used were similar to those described for Leg 64 by Gieskes et al. (in press).

Shipboard data (on pH, alkalinity, chloride, salinity, calcium, and magnesium) as well as shore laboratory data are presented in Table 1 and also in Figures 4, 5, 6, and 7.

### DISCUSSION

In the following discussion we present briefly the data for each site, followed by a more general discussion of the interstitial water chemistry determined on Leg 65.

#### Site 482 (Fig. 4)

Because of the high rates of sedimentation, sulfate reduction is very important and vanishingly small sulfate concentrations are reached well within 15 meters of the

<sup>1</sup> Lewis, B. T. R., Robinson, P., et al., *Init Repts. DSDP, 65*: Washington (U.S. Govt. Printing Office).

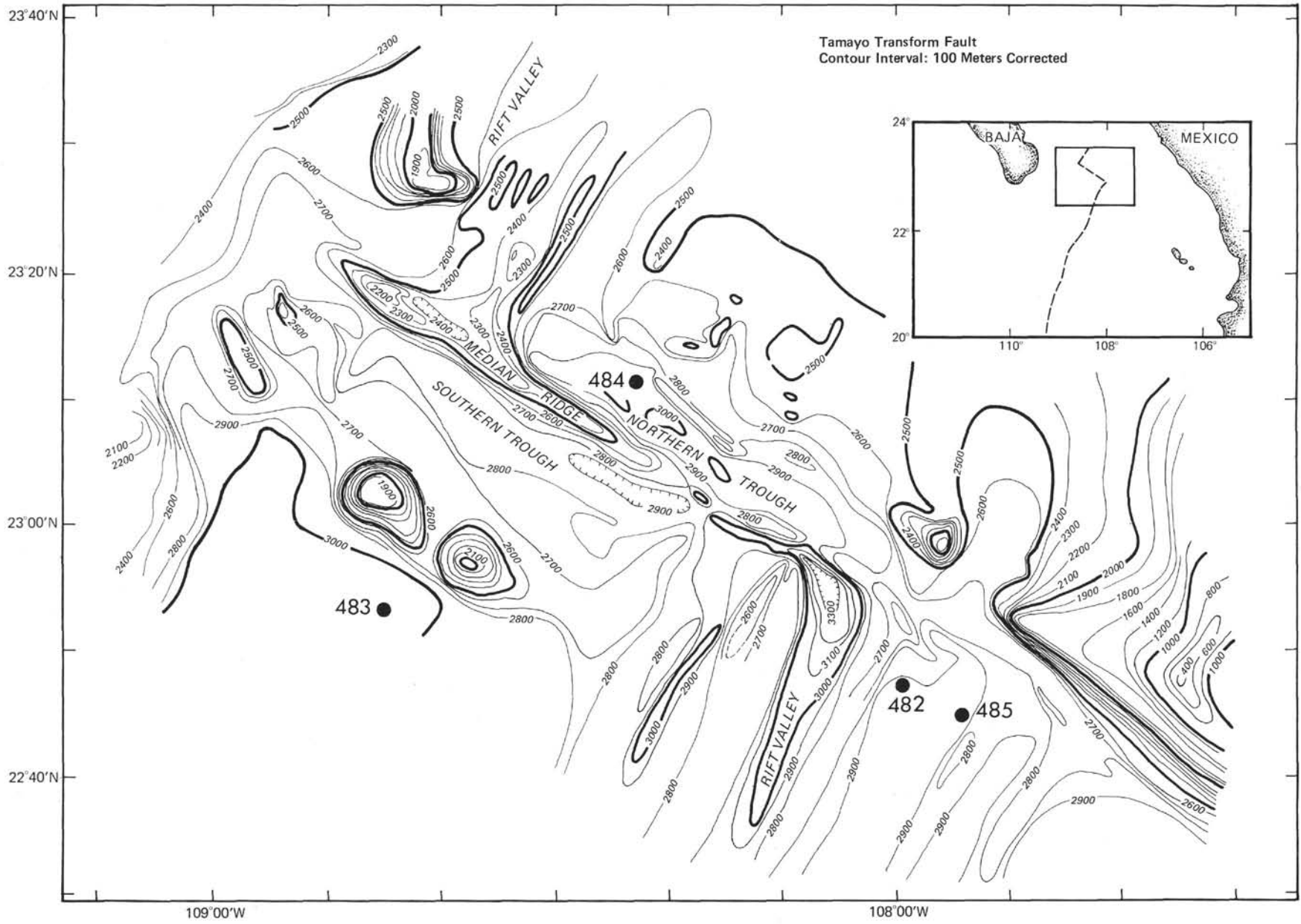


Figure 1. Map of Leg 65 drill sites.

sediment/water interface. Similarly, dissolved ammonia concentrations reach maximum values of 15 mM at about 50 meters depth, as at Site 474 of Leg 64 (Gieskes et al., in press). In all the drill holes of Site 482 concentration profiles of sulfate and ammonia are similar. For the various other constituents, however, each hole shows important differences. Thus, notwithstanding the close proximity of the drill holes, large lateral changes are noticed. The observations can best be explained in terms of reactions in the sediment column occurring at different rates. We shall address this problem in greater detail in a subsequent section.

The absence of a magnesium gradient above 40 meters, and the possible maximum in dissolved potassium at 40 meters may be related to ion exchange processes similar to those invoked to explain concentration anomalies at Site 474 of Leg 64 (Gieskes et al., in press).

#### Site 483 (Fig. 5)

Sedimentation rates in this hole have been much lower than at Site 482 and typically less drastic changes in alkalinity, dissolved sulfate, and ammonia are observed with depth. Indeed the minimum in dissolved sulfate shown in Figure 5 may be the result of increased sedimentation rates in the late Quaternary.

Data on dissolved calcium, magnesium, and potassium suggest that reactions involving basaltic material below Unit III are to a large extent responsible for the decreases in Mg and K and the increases in Ca observed with depth. Data for the pore water obtained from sediments sandwiched between the basalts appear to confirm this.

#### Site 484 (Fig. 6)

Site 484 is of interest because of the absence of significant gradients in calcium, magnesium, or potassium that could be linked to reactions occurring in basement. As is typical in rapidly deposited sediments, sulfate depletion is large, though a possible minimum occurs at about 35 meters sub-bottom depth. This minimum is accompanied by a maximum in alkalinity and ammonia. Associated with the large increase in alkalinity ( $\text{HCO}_3^-$ ) is a decrease in dissolved calcium as a result of carbonate precipitation reactions.

#### Site 485 (Fig. 7)

Site 485 is located east of Site 482 and is probably characterized by slower sedimentation rates than is Site 482. This is evident especially from the lower values of alkalinity and ammonia in their extrema. However, there are similarities in the distribution of calcium, magnesium, lithium, potassium, and silica between Sites 482 and 485.

#### Early Diagenetic Processes

All the sites of Leg 65 are characterized by rapidly accumulated sediments, with sedimentation rates at Site 482 being the highest (340–555 m/m.y.). Typically, the interstitial waters are characterized by large depletions in dissolved sulfate and large increases in dissolved ammonia and in alkalinity. As expected, data for Site 482

show the largest extrema, with almost complete sulfate depletion and a maximum in the ammonia concentration of 15 mM. In this site very little change occurs in dissolved magnesium in the upper 40 meters, which may well be related to the “production” of magnesium as a result of  $\text{NH}_4^+$  ion-exchange reactions with the solid phases (Gieskes et al., in press). Associated with the production of bicarbonate is a depletion in dissolved calcium as a result of carbonate precipitation reactions. Maxima in alkalinity can best be understood in terms of carbonate precipitation reactions in the deeper sediment sections as well as alkalinity consumption resulting from alteration reactions in the lower sediments and underlying basalts. Maxima in ammonia and minima in dissolved sulfate (Sites 483, 484) can be explained in terms of the increased importance of sulfate reduction in the upper, more rapidly accumulated sediments. In addition, ammonia may find a sink in clay minerals in the deeper sediment layers.

#### Exchange between Layers 1 (sediment) and 2 (basalts)

Increases in dissolved calcium and decreases in dissolved magnesium toward the base of the sediment column have often been explained in terms of exchange with the underlying basalts (McDuff, in press; Gieskes and Lawrence, in press). At this stage we do not possess data on the oxygen isotope composition of the pore fluids, but the gradients in dissolved calcium at Sites 482, 483, and 485 strongly suggest that alteration processes involving the basalts of Layer 2 affect the calcium and magnesium concentrations. Particularly relevant with regard to this problem are the continued increases in dissolved calcium in the intercalated sediments of Sites 483 and 485. Oxygen isotope data, to be determined in the future, will allow the quantitative estimation of such reactions (Lawrence et al., 1975, 1979). Such studies will be particularly relevant because of the very young age of the crust at these sites.

Of some interest is the apparent absence of a “basement signal” at Site 484. This site was drilled on top of a basement hill interpreted as a magnetic “diapir” (site chapter, Site 484, this volume). If the underlying basement unit were indeed serpentine, this might explain the absence of a basement-related calcium signal.

In none of the sites drilled during Leg 65 does any evidence exist of convective water circulation in the sediments. The shape of the gradients in the interstitial waters denies the importance of such convective processes. Thus, if hydrothermal circulation still occurs in Layer 2, as suggested by the downhole seismometer experiment of Duennebier and Blackinton (1980), the introduction of this circulating seawater must occur elsewhere, but not through the sediment column. These waters may be introduced through possible basement outcrops at the edges of sediment ponds in a manner suggested by Gieskes and Johnson (1981) for Site 453 in the Mariana Trough.

#### Diagenetic Reactions in the Sediments

One outstanding feature, both at Sites 482 and 485, is the observation of maxima in the concentrations of dis-

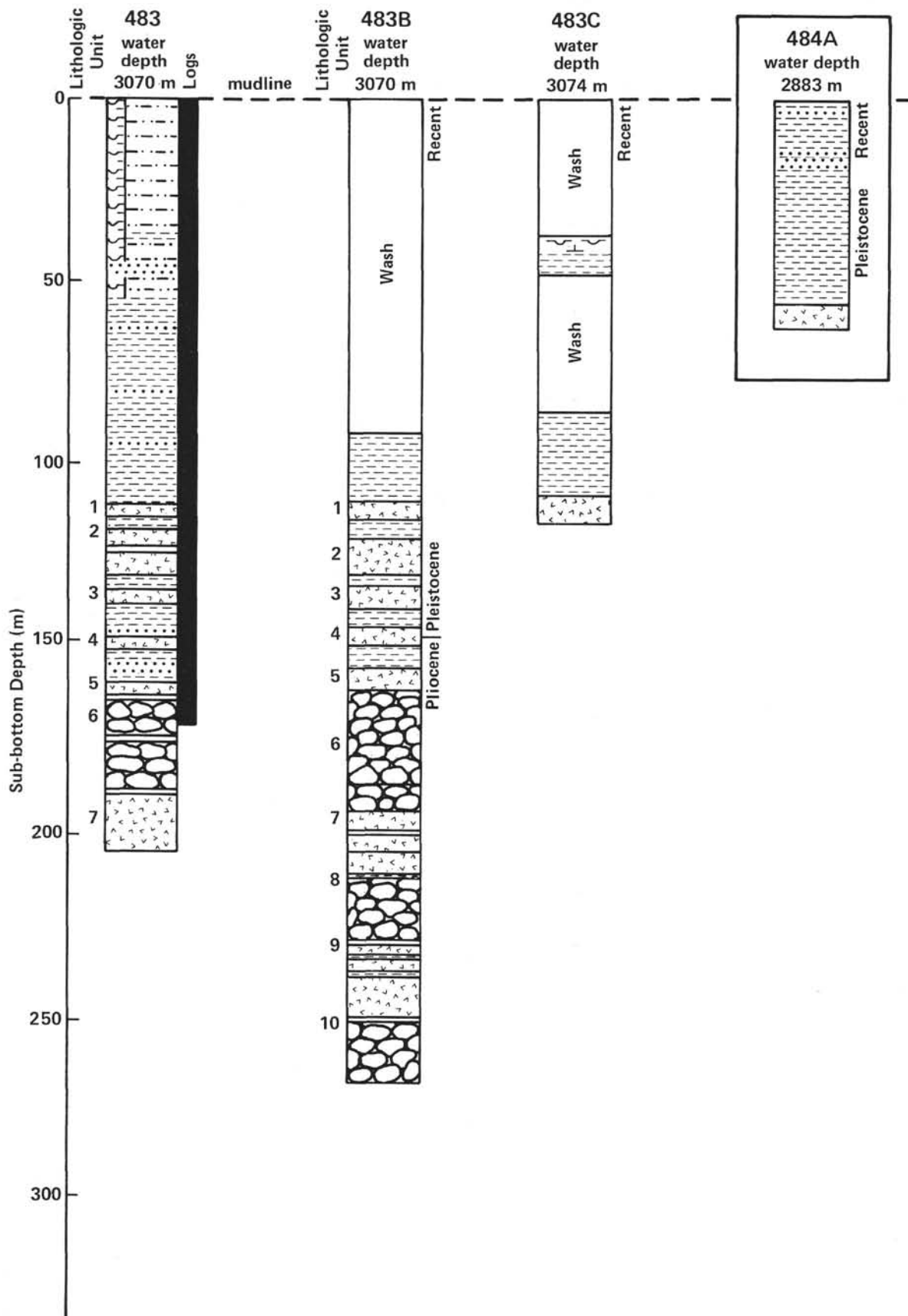


Figure 2. Simplified lithologic columns for holes drilled on Leg 65.

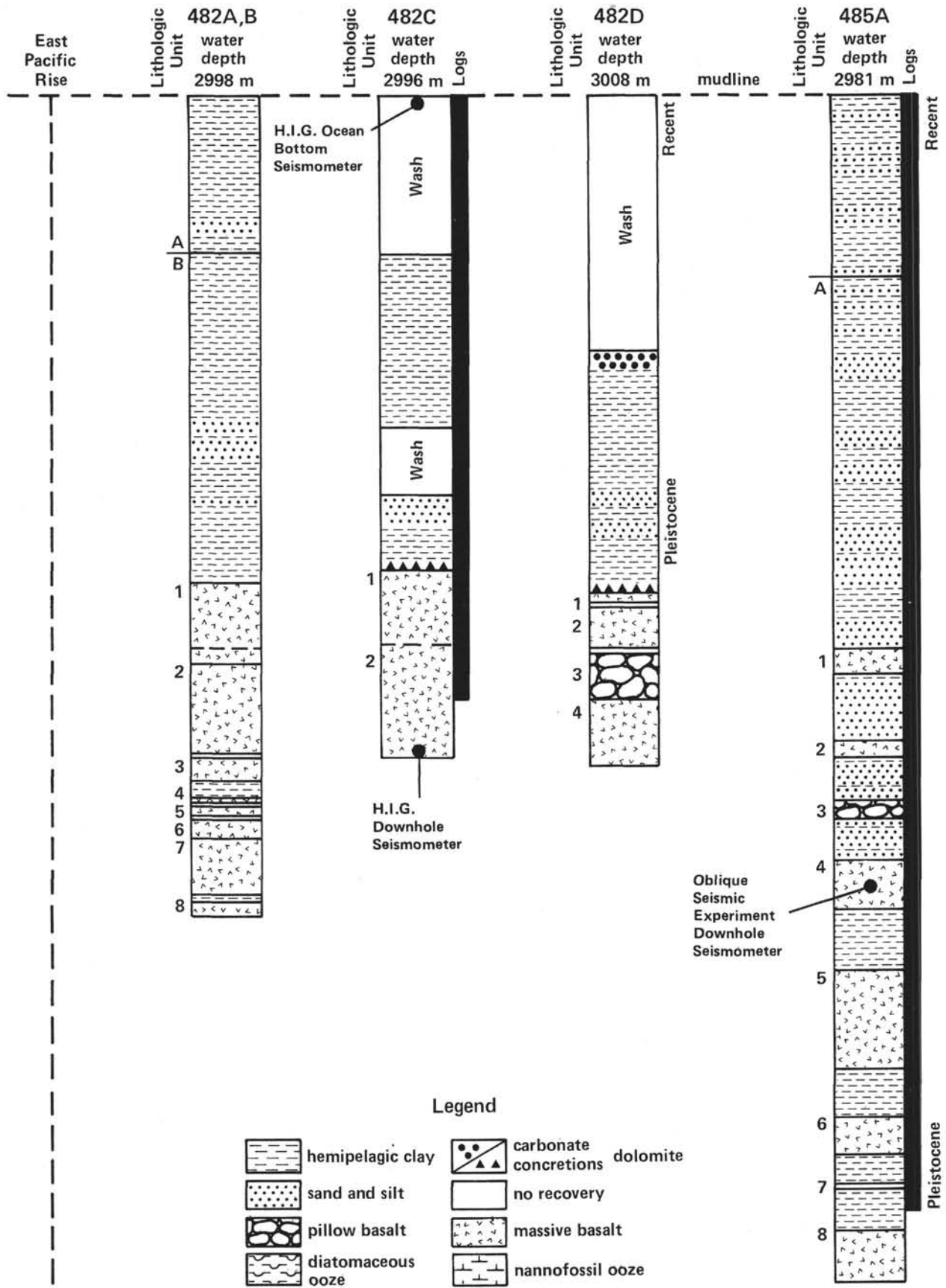


Figure 2. (Continued).



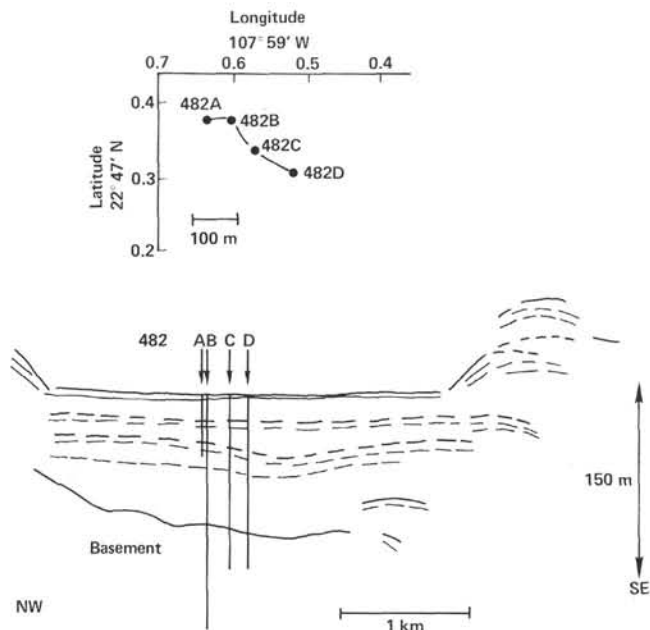


Figure 3. Relative location of drill holes in sediment pond at Site 482.

solved lithium and strontium. Similar observations were made at Site 474 of Leg 64 (Gieskes et al., in press). Detailed analyses of the strontium isotope composition at Site 482 (Fig. 4) indicate a substantial decrease in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the dissolved strontium with depth, which implies a large contribution of volcanic material to the dissolved strontium (Hawkesworth and Elderfield, 1978).

As at Site 474 (Gieskes et al., in press) the lithium and strontium maxima at Sites 482 and 485 appear to be associated with the level below which a rapid decrease in dissolved silica occurs. Although the sediments at Site 482 and 485 do not show strong signs of induration associated with the decrease in dissolved silica, this was certainly the case at Site 474. For these reasons we interpret the decrease in dissolved silica and the extrema in lithium, strontium, and  $^{87}\text{Sr}/^{86}\text{Sr}$  in terms of the occurrence of a diagenetic front involving the diagenesis of opaline silica and the associated alteration of volcanic materials. The reaction sequence would be very similar to that proposed by Kastner and Gieskes (1976) for Site 323 in the Bellingshausen Abyssal Plain. A further confirmation for this interpretation comes from the observed large decreases in dissolved magnesium and potassium (smectite and K-feldspar formation, respectively) and increases in dissolved calcium.

A comparison of the interstitial water profiles of Holes 482B, C, and D indicates that all these processes yield more pronounced signals toward the center of the sediment pond in which Site 482 was drilled. We interpret this in terms of increased reaction rates toward the center of the pond, perhaps associated with increased temperatures. This would imply increased heat flow near the pond's center. Unfortunately, no such measurements are available, but the greater abundance of dolomite in the basal sediments in Holes 482C and D

compared with 482B has been interpreted in terms of greater thermal influence, albeit presumably at an early stage of the sedimentation process. There is no doubt that as a result of the higher prevailing temperatures at the site, diagenesis of opaline silica is occurring at much faster rates, thus explaining the differences in depth and age of silicification fronts between Sites 323 (400 m,  $\sim 15 \times 10^6$  years,  $\sim 20\text{--}25^\circ\text{C}$ ), 474 (250 m,  $\sim 1 \times 10^6$  years,  $\sim 45\text{--}50^\circ\text{C}$ ), and 482 (75 m,  $< 0.5 \times 10^6$  years,  $\sim 50\text{--}60^\circ\text{C}$ ).

## CONCLUSIONS

Detailed studies of the chemical composition of interstitial waters recovered at Sites 482, 483, 484, and 485 in the mouth of the Gulf of California have revealed the following important information:

1) At all sites, as a result of relatively high organic carbon contents and rapid accumulation rates, sulfate reduction and coincident increases in alkalinity and dissolved ammonia are of great importance, leading to almost complete sulfate reduction at Sites 482 and 485, and to minima in dissolved sulfate at Sites 483 and 484. Associated with the increase in alkalinity ( $\text{HCO}_3^-$ ) are calcium-carbonate precipitation reactions leading to minima in the dissolved calcium concentration-depth profiles.

2) Though there is strong evidence of chemical exchange between the sediments and underlying basalts, such exchange occurs by diffusive transport. Even though all four sites were drilled on very young oceanic crust ( $< 1.2 \times 10^6$  years), no convection of fluids occurs through the sediment column.

3) Especially at Sites 482 and 485, there is strong evidence that reactions involving the transformation of biogenic silica and the alteration of volcanic material are responsible for maxima in dissolved lithium and strontium, changes in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, decreases in magnesium and potassium, and increases in calcium. At Site 482 the processes appear to occur at faster rates toward the center of the sediment pond in which the site was drilled, perhaps implying increased heat flow toward the center.

## ACKNOWLEDGMENTS

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Table 1. Interstitial water data, Leg 65.

Sample (interval in cm)	Depth (m)	pH	Alkalinity (meq/l)	S (g/kg)	Cl (g/kg)	Ca (mM)	Mg (mM)	Sr ( $\mu$ M)	$^{87}Sr/^{86}Sr$	Mn ( $\mu$ M)	K (mM)	Li ( $\mu$ M)	SO <sub>4</sub> (mM)	NH <sub>4</sub> (mM)	Si ( $\mu$ M)
Hole 482															
1-2, 144-150	3	7.76	12.5	34.9	19.2	9.40	51.2	76	0.70921	15.5	10.9	23.4	19.5	0.67	504
Hole 482A															
1-3, 144-150	4.5	7.62	20.9	34.6	19.2	8.72	50.5	82	0.70914	13.4	12.8	25.5	12.3	1.68	630
2-4, 114-120	11.7	7.51	39.1	34.6	19.5	5.06	50.8	87	0.70921	0	12.1	24.2	1.0	4.17	661
3-1, 0-6	15.5	7.42	41.0	34.1	19.3	5.04	50.3	70	0.70915	0	8.9	15.9	1.5	3.40	518
4-4, 144-150	31	7.42	58.6	36.3	19.25	3.39	50.0	125		0	13.3	43.3	3.4	11.8	669
5-5, 146-150	42	7.29	64.1	36.0	19.5	3.69	50.8	157	0.70898	0	12.1	69.4	4.3	13.4	913
Hole 482B															
1-4, 144-150	50	7.32	65.8	36.0	19.6	4.97	49.2	141	0.70919	0	12.5	89	1.7	15.0	867
4-2, 144-150	75.5	7.31	41.2	35.5	19.4	7.57	50.5	116	0.70898	0	9.9	248	4.4	12.8	907
6-6, 96-105	100	7.15	37.3	34.1	19.3	11.8	31.0	157	0.70879	0	6.3	295	2.5	11.4	814
8-5, 0-6	110.5	7.11	19.7	33.8	19.4	19.0	27.1	157		0	2.7	—	2.6	5.6	465
10-5, 140-150	137	6.91	3.12	33.8	19.25	30.9	25.8	147	0.70836	0	4.3	168	—	0.80	—
Hole 482C															
6-3, 140-150	115.5	6.90	11.9	33.3	19.3	18.3	24.3	237	0.70733	0	7.7	215	2.9	4.3	392
7-6, 0-10	128	6.90	2.75	34.1	19.4	28.5	22.7	223		6.5	5.8	—	—	1.34	—
8-1, 140-150	131.5	7.24	1.71	34.9	19.2	37.8	23.7	123	0.70788	13.7	6.8	118	14.8?	0.98	118
Hole 482D															
1-4, 144-150	76.5	6.94	29.8	33.8	19.4	11.9	29.8	172	0.70838	0	10.7	430	2.8	11.5	973
2-5, 6-13	86	7.10	23.7	33.7	19.4	15.2	24.3	244	0.70808	0	5.5	480	2.2	9.5	568
3-5, 144-150	97	7.02	17.1	33.3	19.5	15.7	23.6	271	0.70784	0	4.6	444	1.7	7.4	363
5-1, 114-120	110	7.06	8.3	33.0	19.6	17.7	21.8	292	0.70726	0	3.7	280	—	3.7	240
7-2, 144-150	130.5	6.84	1.86	34.1	19.3	31.6	18.1	236	0.70745	5	4.5	180	—	1.64	—
Hole 483															
2-3, 0-6	4	7.44	7.95	34.9	19.0	9.48	50.7	83	—	34.4	—	18	23.2	1.03	666
3-3, 144-150	15	7.50	14.6	34.9	19.2	9.17	49.3	90	—	16.7	11.9	20	17.8	0.92	676
4-2, 144-150	23	7.38	16.9	34.6	19.3	8.35	47.3	86	—	4.2	11.5	19	12.2	1.49	719
5-3, 144-150	34	7.36	17.1	34.4	19.3	8.13	45.4	66	—	0	11.9	19	10.5	1.55	759
7-4, 144-150	55	7.37	14.6	34.1	19.4	10.71	42.9	57	—	26.4	9.9	40	9.4	1.44	793
9-5, 144-150	75	7.45	11.3	34.4	19.3	15.5	39.4	82	—	39.6	8.4	55	—	1.49	—
11-4, 144-150	93	7.49	6.65	34.6	19.4	20.6	37.0	90	—	31.2	6.8	59	14.3	0.50	234
13-1, 144-150	107	7.80	2.43	34.9	19.2	25.7	34.9	98	—	11.4	6.2	53	—	0.61	—
18-3, 144-150	155	7.77	0.57	35.5	19.5	50.5	13.4	133	—	14.8	4.8	49	23.3	0.25	119
Hole 484															
1-2, 144-150	3	7.61	6.84	34.9	19.1	9.68	50.6	66	—	35.0	13.6	23	27.5	0.75	591
Hole 484A															
1-4, 144-150	6	7.66	13.7	34.6	19.1	8.90	50.5	84	—	24.9	14.2	25	21.8	1.22	662
2-4, 144-150	14	7.55	28.6	35.2	19.3	6.34	51.1	87	—	0	13.7	22	7.4	2.31	706
3-4, 144-150	24	7.43	36.4	34.6	18.9	4.28	51.1	77	—	0	14.1	21	2.8	3.61	821
4-3, 144-150	31.5	7.51	38.0	34.9	19.3	3.85	48.6	86	—	0	13.5	24	3.9	3.67	751
5-4, 144-150	42.5	7.61	32.5	34.6	19.4	3.77	49.2	83	—	10.6	13.7	21	3.4	3.56	797
6-2, 144-150	49	7.57	27.2	34.9	19.4	4.13	50.9	72	—	0	12.5	23	6.8	3.19	703
Hole 485															
1-1, 144-150	1.5	7.53	3.38	34.9	19.1	10.10	50.7	82	—	25.8	12.7	27	29.1	0.41	498
2-2, 144-150	6	7.43	16.6	35.2	19.4	8.49	49.8	86	—	0	13.1	25	19.8	1.97	657
3-6, 144-150	21.5	7.44	19.7	34.6	19.4	7.03	49.7	75	—	0	12.5	25	8.3	3.12	737
4-2, 144-150	25	7.38	26.6	34.9	19.4	6.29	48.9	79	—	0	11.3	28	14.4	—	762
5-4, 144-150	37.5	7.12	28.5	34.1	19.5	4.70	43.9	94	—	0	9.8	29	2.6	5.61	816
Hole 485A															
1-5, 144-150	58	7.19	26.0	34.1	19.5	5.81	43.3	99	—	0	9.7	56	2.6	4.94	718
3-2, 144-150	72.5	7.11	26.8	33.8	19.4	6.59	41.8	93	—	0	8.3	—	2.6	—	916
5-3, 144-150	93	7.33	22.0	33.8	19.3	8.75	34.6	103	—	0	5.2	128	2.1	6.71	336
7-1, 144-150	109	7.16	18.1	33.3	19.4	9.91	30.9	100	—	0	4.2	175	3.3	5.73	406
9-1, 144-150	128	7.26	6.73	34.4	19.4	11.18	39.0	109	—	0	3.2	120	17.2?	4.32	261
11-2, 144-150	148.5	7.45	8.87	32.7	19.4	11.56	29.1	124	—	0	2.3	150	2.7	4.03	249
19-1, 144-150	189.5	7.49	2.61	34.4	19.3	21.0	33.7	197	—	0	3.2	120	—	2.36	—
22-5, 140-150	209	7.79	0.80	34.4	19.5	29.7	22.6	300	—	0	1.2	115	18.5	0.78	84
36-1, 140-150	290	—	—	36.3	19.4	48.4	26.4	197	—	4.3	2.1	—	22.4	0.75	129

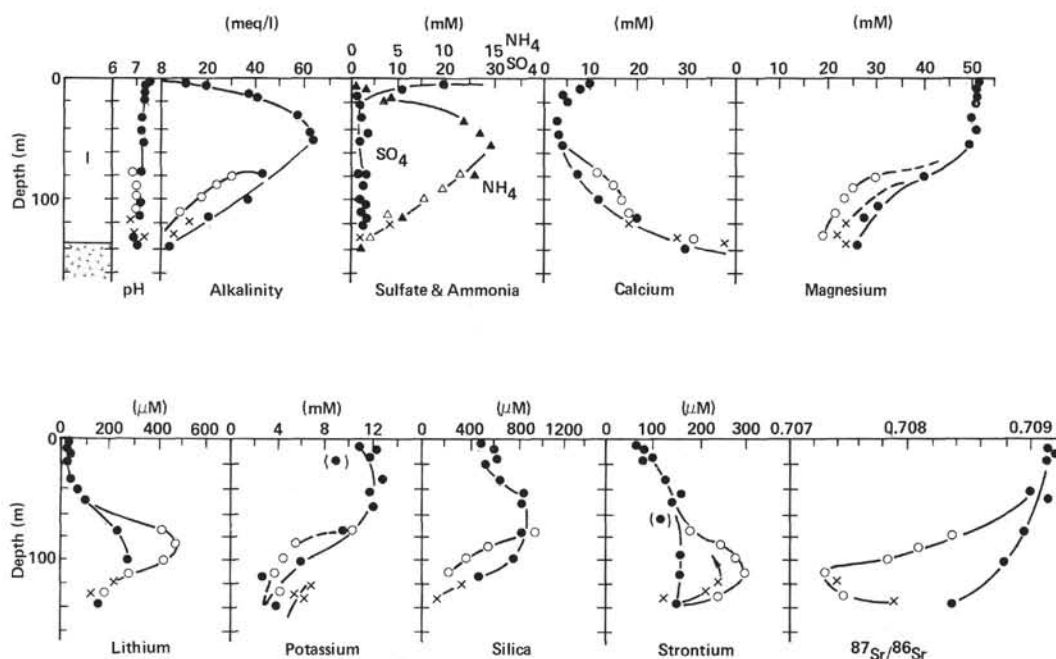


Figure 4. Interstitial water chemistry, Site 482. ● = 482, 482A, 482B; ○ = 482D; × = 482C. Lithology: I—Hemipelagic clays.

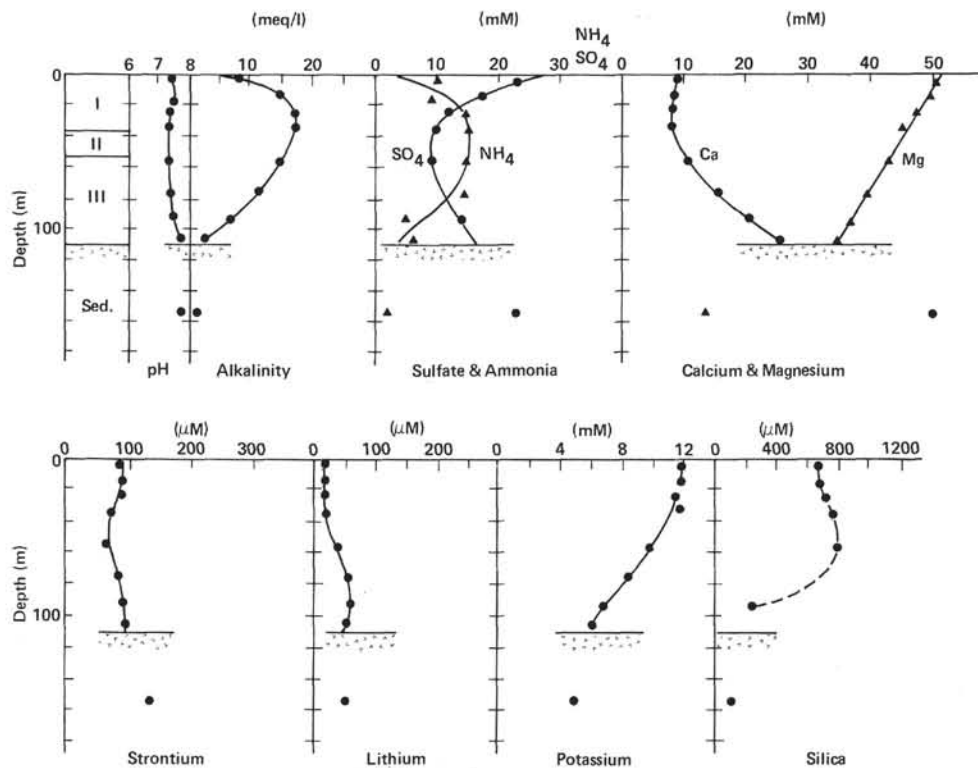


Figure 5. Interstitial water chemistry, Site 483. Lithology: I—siliceous detrital clays; II—transitional siliceous detrital clays; III—fine-grained clay and turbidite; minor siliceous component.



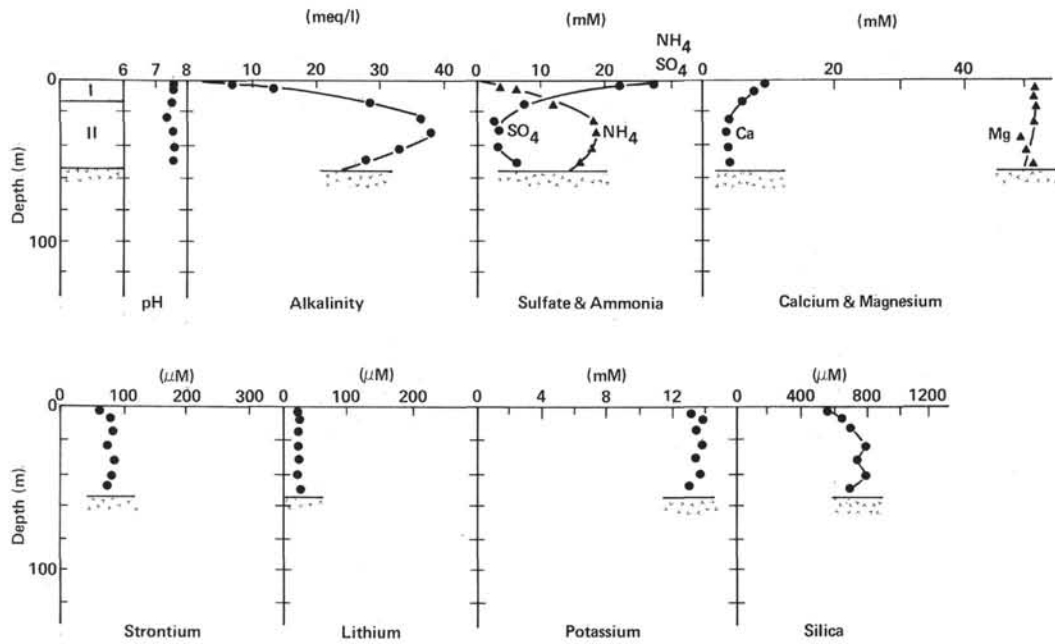


Figure 6. Interstitial water chemistry, Site 484. Lithology: I—siliceous clay; II—hemipelagic siliceous clay.

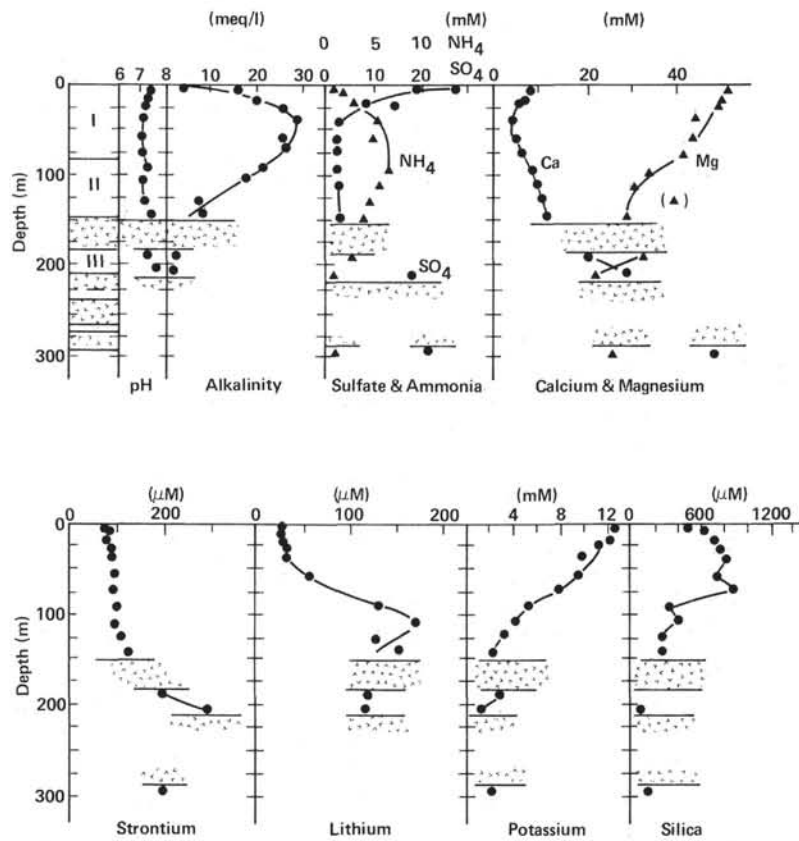


Figure 7. Interstitial water chemistry, Site 485. Lithology: I—hemipelagic siliceous clay; II—hemipelagic clay and silt; III—sediments and basaltic flows or sills.