

## 42. INTERSTITIAL WATER STUDIES, DEEP SEA DRILLING PROJECT LEG 60<sup>1</sup>

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### ABSTRACT

Interstitial water data obtained during Leg 60 show complex gradients at Site 453 in a sediment pond on the west side of the Mariana Trough. Concentrations of Ca, Mg, Sr, as well as of K and Li, suggest that slightly altered sea water penetrates below the sediments, most likely through brecciated igneous and metamorphic rocks, mainly gabbros, lying at the base of the pond. Interstitial water concentration gradients suggest that reactions involving igneous matter lead to increases in calcium and strontium in the pore fluids and to decreases in magnesium. Upward advection of water through the sediments does not appear to occur, so that the advected sea water most likely penetrates deeper into the breccias, perhaps leading to further hydrothermal activity elsewhere in this area.

Interstitial water gradients at Sites 458 (conservative) and 459 suggest that reactions in the sediments and underlying basalts are responsible for increases in dissolved calcium and decreases in magnesium and potassium.

### INTRODUCTION

The drilling program of the D/V *Glomar Challenger* during Leg 60 of DSDP concentrated on Site 452 on the Pacific plate, Sites 453 through 456 in the Mariana Trough, and Sites 456 through 461 between the active Mariana volcanic arc and the Mariana Trench axis.

The shipboard inorganic geochemistry program indicated no significant calcium and magnesium concentration changes at Site 452, 454, and 455 (no samples were taken at Site 457), and probably real changes (one or two depth levels only) in the concentrations at Site 460 and 461. However, Sites 453, 456, 458, and 459 did show very definite concentration changes, and we decided upon follow-up studies for these four sites.

In this report we present the data (Table 1) as well as some preliminary interpretations. Methods used were essentially the same as those described by Gieskes and Johnson (in press). In the case of Site 453, we decided to reinvestigate the nature of the calcium and magnesium gradients, because of their peculiar nature. For this, small samples of working half cores were obtained from the Scripps core locker and squeezed in our laboratory. This would, at the same time, provide an opportunity to test further our contention that such pore water sampling, months after the end of a DSDP Leg, still leads to valid data on pore water compositions.

### SITE 453—SPECIAL STUDIES

Gieskes (1976) and McDuff (1978) indicated that shorebased squeezes of stored sediment cores yielded significant data on pore water concentrations, providing adjustments were made for slight evaporations of the stored cores.

As we were particularly intrigued by the concentration reversals at Site 453 (Fig. 1), we obtained small samples (20–30 ml) from stored cores for pore water ex-

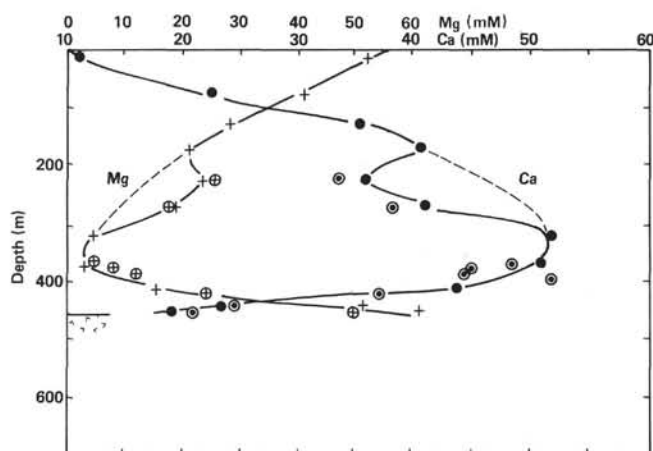


Figure 1. Calcium and magnesium gradients, Site 453. Shipboard and shore laboratory squeeze data. ● + = shipboard data; ⊗ ⊕ = shorebased squeezes.

traction in our laboratory. Most of these samples were obtained at a depth of more than 300 meters below the seafloor—that is, in the volcanic sandstone layers. This necessitated the use of a saw during the sampling procedure and caused slight fresh-water contamination of the samples (usually less than 10%). Only a few samples were obtained aboard ship in this manner, as indicated in Table 1.

In Table 2 we present the concentration data for calcium and magnesium after correction for fresh-water contamination (normalization to  $19.38 \times 10^{-3}$  chlorinity). In Figure 1 the shipboard data and the data of Table 2 are plotted as a function of depth; in Figure 2 the calcium-magnesium correlation is presented.

Generally, the agreement between shipboard and shore laboratory data is excellent, and we submit that only the calcium data may have been slightly affected. We therefore conclude that the procedure of pore water retrieval using stored sediments is indeed valid, at least for the purpose of double-checking interstitial water concentrations observed from shipboard work.

<sup>1</sup> Initial Reports of the Deep Sea Drilling Project, Volume 60.

Table 1. Interstitial water data, Leg 60.

Sample (interval in cm)	Depth (m)	pH	Alk <sup>a</sup> (meq/l)	Cl <sup>a</sup> (10 <sup>-3</sup> )	S <sup>a</sup> (10 <sup>-3</sup> )	Ca <sup>a</sup> (mM)	Mg <sup>a</sup> (mM)	Sr (mM)	Mn (mM)	Li (μm)	K (mM)	Si (μM)	SO <sub>4</sub> (mM)	NH <sub>3</sub> <sup>b</sup> (mM)	Remarks
Hole 452															
1-5, 140-150	7.5	7.56	2.63	18.9	35.2	10.4	51.3								
Hole 452A															
1-4, 140-150	6.0	7.53	2.78	19.1	35.2	10.8	51.5								Stored two days then squeezed
3-4, 140-150	24.0	7.45	2.53	20.1	36.0	11.5	53.7								
Hole 453															
1-5, 142-150	7.5	7.65	2.70	19.2	35.2	11.1	52.4	0.094	0.254	24.1	10.2	393	30.2	0.07	
8-3, 140-150	70.5	8.36	2.40	19.5	35.8	22.2	41.3	0.115	0.098	24.6	8.9	308	29.5	0.09	
14-1, 140-150	124.5	8.39	1.31	19.5	35.8	35.5	28.4	0.134	0.022	27.9	6.3	295	29.8	0.11	
18-5, 140-150	168.5	8.27	0.88	19.5	35.8	40.6	21.5	0.144	0.049	32.5	4.8	190	29.8	0.10	
24-2, 140-150	221	7.93	1.45	19.5	36.3	35.8	23.9	0.135	0.084	38.5	6.3	761	29.1	0.10	
29-3, 140-150	270	8.04	0.93	20.5	36.3	40.9	19.1	0.134	0.025	42.6	5.9	659	30.5	0.09	
34-2, 142-150	316	7.68	0.68	20.0	36.0	52.0	4.9	0.141	0.056	46.3	(3.1)	288	(30.4)	—	
39-4, 140-150	366.5	8.18	0.55	20.5	35.5	51.1	3.4	0.108	0.047	43.8	5.3	220	29.6	0.09	
44-1, 140-150	409.5	8.16	1.96	20.2	35.5	42.9	15.6	0.109	0.090	32.6	5.6	640	28.8	0.06	
48-1, 4-14	446	8.04	2.58	18.4	34.1	17.1	54.3	0.100	0.051	15.3	4.1	—	—	—	Squeezed two days later
47-2, 57-90	439	7.61	1.95	17.3	32.4	19.4	42.9	0.093	0.037	20.6	5.6	299	28.5	0.11	
Hole 454															
3-3, 142-150	14.5	7.79	2.84	19.8	35.2	10.3	51.6								
Hole 454A															
1-4, 144-150	6.5	7.75	2.71	19.8	35.2	10.2	51.9								
Hole 455															
1-5, 144-150	7.5	7.64	2.60	19.1	35.2	10.7	52.4								
Hole 456															
2-4, 140-150	6.5	7.83	2.83	19.5	35.2	10.4	51.6	0.09	0.105	20.5	11.2	226	3.03	0.06	
10-2, 140-150	79.5	8.68	1.87	19.7	35.8	8.4	37.9	0.06	0.010	19.2	8.6	120	29.5	0.04	Sampled 8 hours later
14-1, 41-50	115	8.68	0.80	18.7	34.4	17.1	30.8	0.05	0.004	22.6	4.9	103	—	—	
Hole 456A															
1-4, 142-150	6.0	7.80	2.87	19.0	35.2	10.1	51.8	0.09	0.086	22.8	10.4	278	29.7	0.06	Probably affected by dist. H <sub>2</sub> O (by cutting)
3-2, 140-150	41	8.40	2.88	19.2	35.2	9.9	51.6	0.09	0.041	19.4	10.0	315	—	0.06	
8-1, 10-18	85.6	8.72	2.31	19.4	35.5	8.7	37.5	0.09	0.010	20.9	11.0	141	31.1	0.05	
10-4, 64-83	105	7.89	1.37	17.9	33.3	10.1	47.9	0.08	0.010	20.8	9.4	197	29.3	0.05	
Hole 458															
1-5, 140-150	7.5	7.67	2.35	19.2	35.2	10.5	50.9	0.10	0.00	23.5	12.0	329	—	0.04	
6-3, 144-150	52	7.56	1.53	19.5	35.5	20.1	44.2	0.14	0.082	23.8	11.4	508	—	0.04	
11-2, 103-117	97.5	7.58	1.47	19.8	35.5	26.6	39.9	0.21	0.041	33.6	10.1	616	—	0.04	24 hours after (cut by hand)
16-2, 0-8	144	8.12	1.46	19.7	35.8	35.4	31.5	0.17	0.078	27.4	9.8	611	—	0.04	
25-1, 140-150	229.5	7.35	0.90	19.7	36.3	52.4	24.6	0.25	0.012	45.6	7.0	704	—	0.04	
27-2, 40-48	249	7.90	1.65	15.9	30.0	40.5	13.4	0.18	(0.06)	10.2	6.1	255	—	—	24 hours (cut by saw)
Hole 459															
1-1, 42-150	1.5	7.69	2.78	19.3	35.2	10.4	52.1	0.078	0.000	29.4	10.3	368	27.9	0.07	
Hole 459B															
1-4, 144-150	6.0	7.61	2.58	19.4	35.2	10.9	49.7	0.086	0.000	18.8	10.7	403	29.0	0.08	
6-3, 142-150	50	7.70	1.37	19.8	35.5	19.1	46.0	0.13	(0.111)	29.0	9.8	321	28.0	0.07	
11-1, 140-150	94.5	8.12	0.96	19.9	35.8	24.2	32.4	0.13	0.044	27.8	8.9	510	26.8	0.09	
15-1, 144-150	132.5	8.14	0.92	19.9	35.8	26.3	28.4	0.15	0.055	26.8	9.9	592	25.3	0.11	
24-1, 140-150	218	7.72	0.83	20.0	36.0	36.0	19.8	0.20	0.094	32.8	7.6	750	25.9	0.09	
29-2, 140-150	267	8.43	0.54	20.0	36.3	41.6	11.9	0.21	0.039	40.5	7.1	528	26.3	0.10	
35-1, 140-150	322.5	8.63	0.63	20.2	36.6	46.6	8.3	0.23	0.034	44.3	6.2	564	26.2	0.12	
40-2, 140-150	371.5	8.63	1.21	20.5	37.1	51.6	6.3	0.26	0.031	45.6	6.2	567	26.5	0.12	
46-1, 140-150	427	7.63	0.60	20.7	37.4	54.3	6.3	0.23	0.061	51.7	4.7	923	26.2	0.11	
51-1, 140-150	474.5	7.69	0.80	20.5	37.4	59.4	5.1	0.31	0.035	52.8	3.7	822	27.9	0.11	
57-2, 16-24	532	7.40	0.72	19.9	36.0	63.5	1.3	0.16	0.008	21.5	1.1	358	27.8	0.02	
59-2, 70-80	551	7.55	0.51	20.2	36.8	60.2	2.1	0.13	0.003	18.4	1.0	435	27.2	0.08	½ working half
60-1, 14-28	558	7.60	0.92	18.4	33.8	57.3	3.2	0.13	0.003	20.0	0.9	185	25.5	0.07	
Hole 460															
1-4, 144-150	6.0	7.77	4.82	18.9	35.2	11.1	52.7								
Hole 460A															
1-4, 144-150	6.0	7.66	4.74	19.4	35.5	11.6	53.2								
5-2, 144-150	39.5	7.59	2.99	19.6	35.5	13.9	48.2								
Hole 461															
2-1, 144-150	3.0	8.11	2.60	19.0	34.6	12.6	48.2								

<sup>a</sup> Shipboard data.<sup>b</sup> NH<sub>4</sub> data <0.08 are not considered significant.

Table 2. Shorebased squeezes adjusted for evaporation<sup>a</sup> to  $Cl = 19.38 \times 10^{-3}$ , Site 453.

Core-Section-Interval (in cm)	Depth below Seafloor (m)	Ca (mM)	Mg (mM)
24-2	221	33.1	26.2
29-2	267	38.2	18.8
39-2, 30-32	365	45.6	5.3
40-3, 93-95	375	42.1	8.4
41-2, 17-20	385	41.8	12.1
42-2, 80-83	392	39.1	—
45-2, 110-116	420	34.9	24.4
47-2, 15-18	438	22.9	—
48-1	446	21.3	44.9

<sup>a</sup> Evaporation never higher than 15 percent.

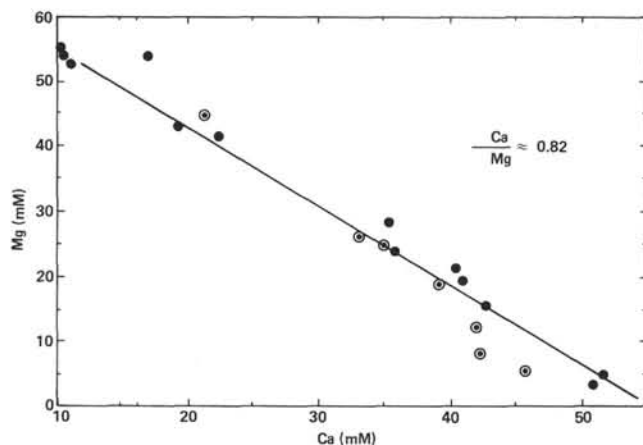


Figure 2. Calcium-magnesium correlation, Site 453. ● = shipboard data; ○ = shorebased data.

## DISCUSSION OF THE DATA

### Site 453

In Figure 3 the interstitial water data are presented. Notwithstanding the high sedimentation rates at this site—about 10 meters/million years, no appreciable sulfate reduction occurs (Table 1), mostly because of the low organic carbon contents of these volcanic turbidites.

We previously mentioned the observed reversals in calcium and magnesium concentrations between 200 and 300 meters. These also appear to be reflected in alkalinity, strontium, and perhaps potassium concentrations. Dissolved lithium data are rather smooth, with the main source located at the top of the volcanic sandstones—that is, just below 300 meters. Sediments at this site are fairly uniform in composition, with a somewhat more basaltic contribution to the base (Schmincke, this volume). At this point it is difficult to state with certainty whether the observed reversals are due to the presence of several reaction zones in the sediments or whether the samples have been affected by sea-water contamination in the sediments between 200 and 300 meters and below 350 meters. No coring problems have

been reported that would make the latter possibility likely.

Most important are the observations just above basement, where many of the pore water concentrations return to sea-water values. These data can be interpreted in various ways:

1) Only reactions in the sediment column at about 200 meter and 300 meter depths have caused the deviations from sea-water concentrations. This appears highly unlikely because diffusion processes would have led to increases in dissolved calcium and decreases in dissolved magnesium in the lower 50–100 meters during the lifetime of this site.

2) Sea-water contamination during drilling may have replaced pore waters to a greater or lesser extent in the sandstones below 300 meters. This possibility is unlikely, especially because a smooth gradient toward basement would be highly unlikely under such circumstances.

3) Brines of geothermal origin and of an unusual nature—low in Ca, K, Li and high in Mg and  $SO_4$ —are advected from below through the basalts. Brines of this nature have so far not been described in the literature. Indeed, most geothermal brines typically show depletions in Mg and  $SO_4$  and increases in Li, K, and Ca (Edmond et al., 1979). There is little doubt that basement is complex at this site, indicating the possibility that serpentinization and low-grade greenschist and perhaps amphibolite facies metamorphism have occurred. Yet, whether hydrothermal fluids of almost exact sea-water composition would result from these processes is questionable.

4) Sea-water penetrates through the porous brecciated rocks at the base of the pond, with these layers acting as an aquifer. It should be remembered that Site 453 is located in a sediment pond with 450 meters of sediments, but that sediment thicknesses at the edges of this pond are much less. Although we do not know what rocks may be exposed at the edges and walls of the basin, they may well be deep-seated, arc-related plutonic rocks of fairly high metamorphic grade. Thus, sea-water may penetrate the metamorphic breccia layer and then advect through this “aquifer” below the sediments. It should be noted that Site 453 is in an area of high, variable heat flow, supporting the contention that hydrothermal processes are still active in this area (Uyeda and Horai, this volume). Thus the upper and lower parts of the sediment column are bounded by “sea water.” The slightly depleted concentrations of K and Li relative to sea water in the lower sediment column may be related to alteration reactions of basalt, which is known to react relatively rapidly to remove K and Li at low temperature.

In our opinion, the last explanation is the most satisfactory and also the most exciting one. We realize that this explanation is as difficult to prove to be correct as any of the other suggestions. Studies of oxygen, deuterium, and strontium isotopes may be helpful here, but again are not likely to yield unambiguous results. The concentration gradients in the sediments suggest

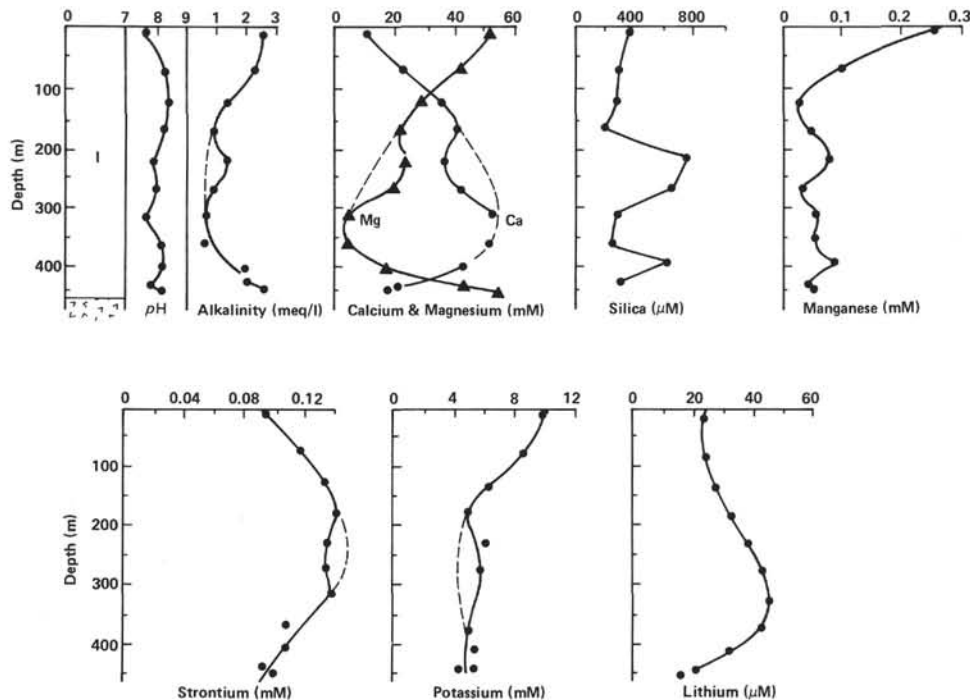


Figure 3. Interstitial water data, Site 453. Lithology: I = volcaniclastic turbidites—sandstones below 300 meters.

that no upward advection occurs in the sediments. In the deeper parts of Layer 2, hydrothermal alteration was observed and this activity may still be an ongoing process, fed by the advected water through the upper basalt layers.

In Figure 2, the calcium and magnesium data are plotted in a correlation plot; it is apparent that a good linear correlation exists, with  $\Delta\text{Ca}/\Delta\text{Mg} = 0.82$ . These changes are most likely related to reactions of volcanic matter leading to the uptake of Mg and release of Ca. We plan a study of the oxygen isotopic composition of the interstitial waters (Lawrence et al., 1975; Gieskes and Lawrence, in press) and of the strontium isotope composition of dissolved Sr (Hawkesworth and Elderfield, 1978) in order to support this opinion and to calculate the amount of alteration that has occurred in these sediments.

#### Holes 456, and 456A

Interstitial water data for these two holes are presented in Figure 4. Hole 456 has a heat flow of 3.2 heat flow units (HFU), whereas the heat flow in Hole 456A is much lower (1.3 HFU). Sedimentation rates at this site have been very high with an average of 100 meters/1 million years. Notwithstanding these high sedimentation rates, no sulfate reduction is observed (Table 1).

In general, Hole 456 shows larger changes in concentration with depth than Hole 456A. The reversal in magnesium in Hole 456A is somewhat puzzling. It is unfortunate that no closer sampling was undertaken in these holes. Generally, however, it appears that in the hole with slightly higher heat flow (Hole 456) reaction rates

may be enhanced and hence result in observable concentration gradients.

#### Sites 458 and 459

Sedimentation rates at Site 458 have been much slower than at Site 459, with both sites showing large sedimentation hiatus in the upper 100 meters (see site reports). At both sites, increases in calcium and decreases in magnesium are observed (Figs. 5 and 6). These profiles appear conservative at Site 458; that is, reactions in underlying basalts appear chiefly responsible for the observed concentration changes. At Site 459, however, the nature of the calcium and magnesium gradients suggests that in addition to possible reactions in the underlying basalts, reactions in the sediments must also contribute to the concentration changes. Although measurements of formation factors (McDuff and Gieskes, 1976) would be useful to confirm this, the typically non-linear correlation between calcium and magnesium requires this interpretation. Comparison of the concentration depth profiles of Ca and Mg with those of K at Sites 458 and 459 also emphasizes this point, the K profiles probably representing the most conservative profiles.

We are convinced that the observed "reversal" in Ca and Mg just above basement at these two sites are related to fresh water contamination during the cutting of the cores (see Remarks in Table 1). Correction to the appropriate chlorinities indicates that the data agree with the smooth trends established for the data. This, therefore, casts doubt on the interpretation of Desprairies (this volume) that these reversals are related to the oc-

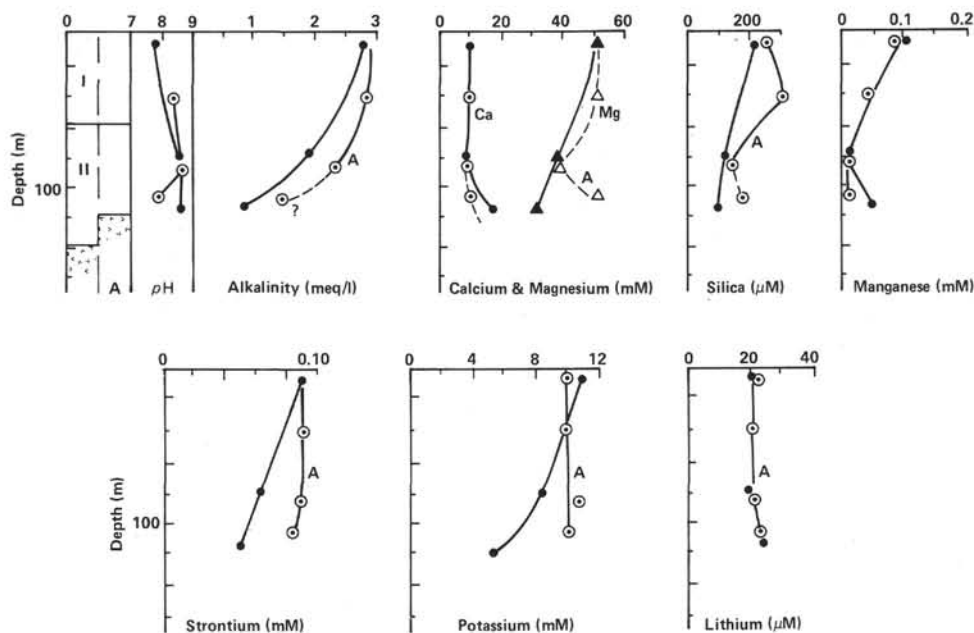


Figure 4. Interstitial water data, Holes 456 and 456A. Lithology: I = vitric muds and nannofossil oozes; II = vitric mudstones and nannofossil chinks.

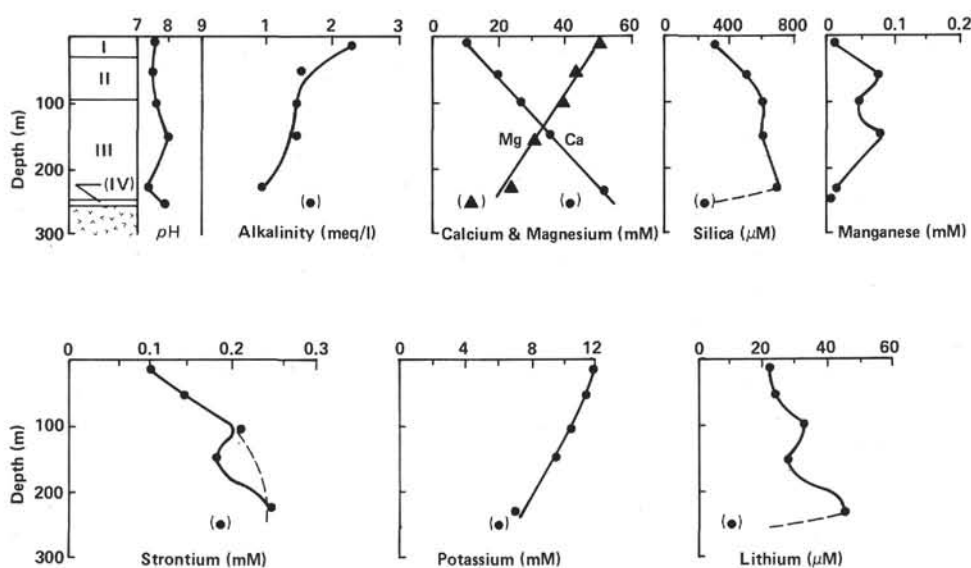


Figure 5. Interstitial water data, Site 458. Lithology: I = Siliceous-nannofossil-foraminifer-vitric muds and ash; II = nannofossil ooze-vitric-nannofossil ooze; siliceous-nannofossil ooze; III = vitric-siliceous-chalks; mudstones; IV = laminated vitric siltstones and sandstones.

currence of palygorskite in these cores. It is more likely that palygorskite formation, both in the sediments and in basalts (Natland and Mahoney, this volume) occurred during a much earlier stage in the history of these sites.

Dissolved strontium increases are relatively large and are probably related to carbonate recrystallization processes.

Dissolved manganese and lithium indicate that increases in these constituents are principally due to reac-

tions in the sediment column, probably associated with reactions involving the transformation of biogenic silica. Kling (this volume) reports few datable radiolarians older than Pliocene at these sites.

#### Sites 460 and 461

At these sites slight increases in calcium and decreases in magnesium have been observed with depth (Table 1), but only one or two depth levels have been sampled.



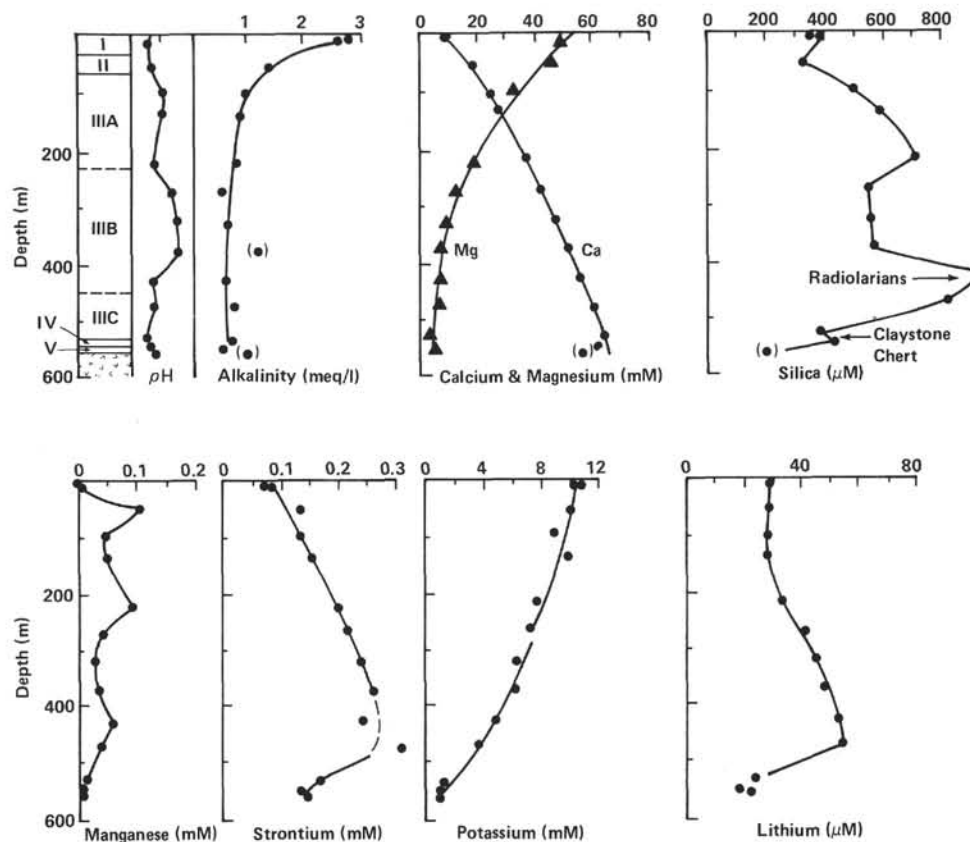


Figure 6. Interstitial water data, Site 459. Lithology: I = siliceous vitric mud and nannofossil-vitric ooze; II = hiatus; vitric muds, ash and nannofossil vitric muds; IIIA = turbidites in vitric chalks and mudstones; IIIB = mudstones and claystones; IIIC = vitric chalks and limestones; IV = claystone; V = claystones and cherts.

This does not allow much interpretation of the data but for the observation that such changes are compatible with observations made at Sites 458 and 459.

#### ACKNOWLEDGMENTS

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