

24. INTERSTITIAL WATER STUDIES, LEG 92¹

J. M. Gieskes, Scripps Institution of Oceanography,
and

J. Boulègue, Laboratoire de Géochimie et Métallogénie, Université de Paris²

ABSTRACT

Interstitial water studies along a DSDP drill hole transect along ~19°S toward the East Pacific Rise during DSDP Leg 92 have revealed only very small changes in major ionic constituents, with small increases in Ca²⁺ and slight decreases in Mg²⁺. Evidence from dissolved-nitrate profiles suggests that slight production occurs in the upper sediments, but little or no consumption of nitrate occurs at depth. An analysis of the distribution of Ca²⁺ and Mg²⁺ suggests that slow upward advection of water through the sediment column may occur (0.075 ± 0.05 cm/yr.).

INTRODUCTION

During Leg 92 a transect of sites was drilled along latitude ~19°S toward the crest of the East Pacific Rise (Fig. 1). A principal aim of this DSDP leg was to determine the importance of hydrothermal circulation at or near mid-ocean ridges, among which the advective movement of waters through the sediment column could be important as a result of the circulation of seawater through the upper layers of basaltic basement. Such circulation has often been invoked to explain anomalous heat flow patterns in the sediments, some of which have been observed at considerable distances from oceanic ridges (Anderson and Hobart, 1976; Anderson et al., 1977, 1979). McDuff (1978, 1981) observed that concentration gradients in major ionic constituents of interstitial waters are often absent in relatively young and/or thin sediment columns. He suggested that the absence of gradients might result from advective processes occurring in these sediments.

In order to investigate the possibility of the advective motion of interstitial water, a detailed investigation of the chemical composition of the interstitial water at the sites drilled for the Leg 92 transect was undertaken. Most of the data and methods are reported in the respective site chapters (this volume). In this report we wish to summarize our findings.

DATA QUALITY

Systematic errors may result from inaccuracies in the analytical methodologies and errors in the handling of the sediments during core retrieval and interstitial water extraction. Handling errors are usually small as a result of good core recovery with the hydraulic piston corer. These errors, especially for the principal constituents under consideration in this report, are relatively small, and we estimate them to be ±2% for Ca²⁺, ±2% for Mg²⁺, and ±6% for K⁺.

In addition to errors due to these factors, other errors do occur in the data, especially because most interstitial water samples are not obtained *in situ*. Most extractions were carried out as soon as possible after core retrieval, at temperatures of 23° ± 2°C. For the constituents for which temperature-of-squeezing artifacts are mainly determined by ion exchange processes (Sayles et al., 1973; Gieskes, 1973), such as Mg²⁺ and K⁺, this extraction temperature will lead to systematically low Mg²⁺ and high K⁺ values.

For the species involved in carbonate equilibria, however, the case is not as simple. For instance, our data clearly suggest that not only does a negative shift in Ca²⁺ occur as a result of ion exchange reactions, but also that a partially compensating shift occurs as a result of the enhanced temperatures at which samples are retrieved in the laboratory. The reasons for the latter are not clear, especially because calcium carbonate solubility increases with decreasing temperature and increasing pressure. The previous experience of one of us (Gieskes) has also indicated that samples obtained on board ship at simulated *in situ* temperatures (by centrifugation extraction) had much lower Ca²⁺ concentrations than true *in situ* samples. Often errors appear to cancel, and immediate extraction at temperatures of about 20°C leads to reasonable agreement with *in situ* results.

For dissolved-silica values, the differences between the results obtained during shipboard extractions at room temperature and those carried out *in situ* are often quite large (Gieskes, 1973, 1974; Sayles and Manheim, 1975). Dissolved-silica concentrations are also strongly dependent on local lithologies. For these reasons our data, with the exception of the *in situ* data, are of limited use for the present investigation.

RESULTS

Major Ion Constituents

Below we summarize the principal results, especially for Ca²⁺, Mg²⁺, and K⁺, for each site (Fig. 2). More detail is provided in each site chapter (this volume).

Site 597—Data for Mg²⁺ and K⁺ show both systematic offsets and trends with increasing depth. Perhaps a

¹ Leinen, M., Rea, D. K., et al., *Init. Repts. DSDP, 92*: Washington (U.S. Govt. Printing Office).

² Addresses: (Gieskes) Scripps Institution of Oceanography, La Jolla, CA 92093; (Boulègue) Université de Paris 6, Laboratoire de Géochimie et Métallogénie, 75230 Paris, France.

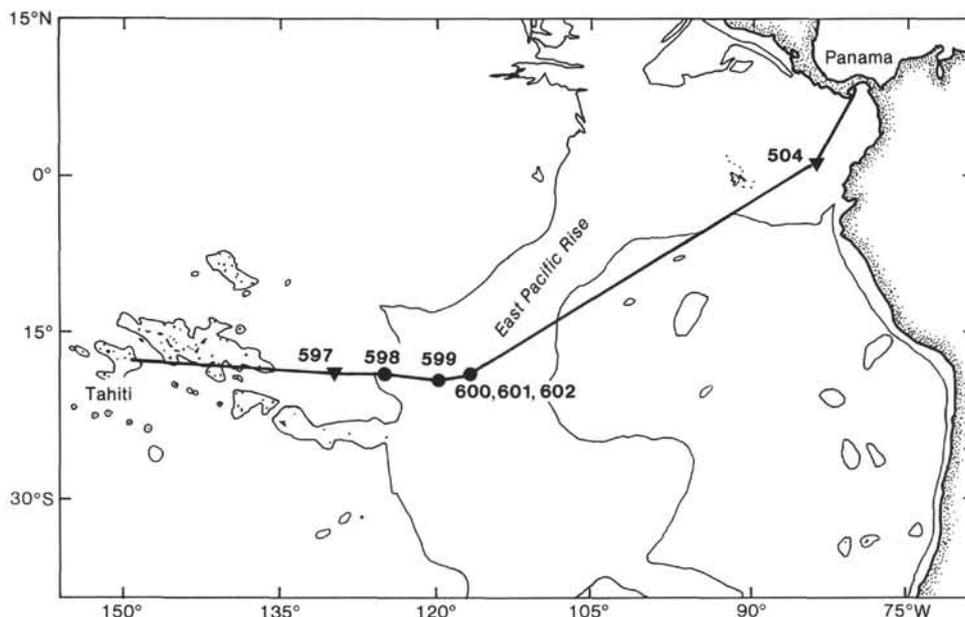


Figure 1. Track of Leg 92. Inverted triangle denotes re-entry site.

slightly enhanced content of clay and RSO (red brown to yellow brown semiopaque oxides) at the top and bottom of the hole leads to enhanced temperature artifacts. Thus, little or no downhole trend in Mg^{2+} and K^+ occurs, an observation also supported by the *in situ* data. The near-bottom gradient in Mg^{2+} is probably maximal and thus indicates a possible 5–6% depletion in Mg^{2+} at about 50 m.

The change in Ca^{2+} is quite systematic and implies a change of almost 1 mM at depth or a 10% increase in concentration. An equivalent decrease in Mg^{2+} would amount to a change of about 2% in Mg^{2+} concentration.

Site 598—Again a systematic (~5%) increase in Ca^{2+} is observed, with an associated possible decrease of magnesium of ~1 mM (or 2%).

Site 599—Concentration–depth profiles for Site 599 are very similar to those for Site 598; that is, small increases in Ca^{2+} appear to be associated with small decreases in Mg^{2+} .

Site 600—The profiles for Site 600 appear rather undefined but may indicate small downhole increases in Ca^{2+} and decreases in Mg^{2+} .

Site 601—Increases in Ca^{2+} are again accompanied by decreases in Mg^{2+} . The suggested profiles show some curvature, although this is minimal, not unlike the profiles for the upper 20 m of Sites 598 and 599.

Dissolved Nitrate and Ammonia

Figure 3 presents composite profiles of dissolved nitrate, ammonia, and silica for Sites 597 to 601. Each hole has quite different dissolved-nitrate profiles; the distribution of nitrate is probably a strong function of *in situ* metabolic activity. As expected, this metabolic activity is highest in the upper sediment layers, and generally slight maxima are observed in the upper 10 m. The ammonia profiles, though showing variability, again indicate higher values in the near-surface sediments. In

our opinion, the various sites visited along the transect, even those in close proximity (such as Sites 600 and 601), have metabolic processes that do not occur at the same rate or to the same extent. These processes are probably related to small relative differences in the burial of reactive organic carbon.

At all sites the nitrate concentrations remain higher than the bottom-water concentrations, with the possible exception of Site 601, where the deepest values equal those of bottom waters.

Dissolved Silica

Dissolved-silica measurements obtained in this study were generally obtained at temperatures different from *in situ* temperatures (about 23°C vs. 2 to 6°C). Thus, with the exception of the silica concentrations obtained with the *in situ* probe, offsets from the real *in situ* concentration will occur (Gieskes, 1973; Sayles et al., 1973). Generally these differences tend to be constant, and in the present study they amount to about $90 \pm 10 \mu M$. The variation is easily seen in the composite of the silica data presented in Figure 3. Below we summarize the *in situ* data:

Site	Depth (m)	H_4SiO_4 (μM)
597	14.5	208
598	34.5	210
599	15.0	376
599	34.3	451
601	17.0	207

The *in situ* values at Sites 597, 598, and 601 are very close, but at Site 599 much higher concentrations are reached. Dissolved-silica concentrations usually are a strong function of local lithology, so that large concentration differences can occur over short intervals. This is

well demonstrated by the silica profile for Site 599, which shows a well developed maximum. Most of the silica profiles in Figure 3 yield concentrations of about 250 μM at a depth of 1.5 m, which would mean an *in situ* concentration of about 160 μM , or about 35 μM above bottom-water values. Below this depth, however, concentrations rise in a variable manner, mainly as a result of local changes in sediment lithology. These changes are probably not easily detected, although at Site 599 the changes are substantial.

DISCUSSION

The studies of interstitial water composition along a transect toward the East Pacific Rise at about 19°S (Sites 597 through 602) have revealed only very minor changes in the composition of major constituents. Although the *in situ* data are quite different from data obtained through shipboard extraction techniques, increases in Ca^{2+} of up to 10%, small decreases in Mg^{2+} (2 to 6%), and no significant changes in K^+ have been observed. In all cases sediment accumulation rates have been low ($\ll 10$ m/m.y.), so that diffusive communication with the overlying seawater has never been hampered. The question therefore arises as to whether the observed small changes in Ca^{2+} and Mg^{2+} are due to reactions in the sediments or changes in basement fluids.

Small changes in carbonate chemistry in the lower parts of Hole 600C (Kastner et al., this volume) have been explained in terms of carbonate diagenesis induced by advective flow of basement waters at low temperature and seawater-like composition. These changes appear to have taken place during the first few million years of the existence of the site. Little change in carbonate chemistry has been observed in the upper part of Hole 600C. Although we suggested in the site chapters that carbonate dissolution and/or recrystallization might explain the increases in Ca^{2+} as well as the curvature of the Ca^{2+} profiles, this idea remains speculation without more detailed chemical data on carbonates.

We have attempted to model the other extreme (that is, that all changes in Ca^{2+} and Mg^{2+} are due to the advection of basement waters from below). For these purposes we have considered a simple advection-diffusive equation (at steady state) assuming constant diffusion coefficients ($D \approx 2 \times 10^{-6}$ cm²/s; McDuff, 1981), constant upward advective flow velocity (w), and constant porosity:

$$0 = \frac{\delta}{\delta z} D \left(\frac{\delta c}{\delta z} \right) - w \left(\frac{\delta c}{\delta z} \right)$$

with both the depth coordinate and the upward fluid velocity positive upward. This equation has the simple solution (Craig, 1969):

$$(C - C_0) = (C_m - C_0)f(z)$$

where $f(z) = (e^{z/z^*} - 1)/(e^{z_m/z^*} - 1)$ and $z^* = D/w$. C_0 and C_m are boundary concentrations at the sediment/water interface and at the bottom of the sediment column, respectively. The parameter z^* can be evaluated

for fixed $D (= 2 \times 10^{-6}$ cm²/s) and variable w (10^{-10} – 10^{-8} cm/s).

Calculated profiles for Ca^{2+} are presented in Figure 4 with boundary conditions $C_0 = 11$ mM and $C_m = 10.25$ mM. From this figure it can readily be seen that at upward velocities of 10^{-9} cm/s (~ 30 cm/1000 yr.) and higher, curvature becomes increasingly important (see also Crow and McDuff, 1981). For comparison we present actual Ca^{2+} profiles for Sites 598 and 599. These profiles indicate potential advective velocities of 10^{-9} – 4×10^{-9} cm/s, or 30 cm/1000 yr. – 120 cm/1000 yr. These advective velocities are generally much lower than those often invoked by heat flow measurements (Crow and McDuff, 1981). Indeed, with the diffusivity of heat being about 100 times that of salt, almost linear temperature profiles would be expected, even at fluid velocities of 10^{-8} cm/s. That is, z^* is 200 cm for Ca^{2+} diffusion, as opposed to 20.00 cm for heat diffusion.

The calculations above are intended as order-of-magnitude calculations, and changes in porosity with depth might slightly affect the results. Yet, if advection is of importance in these sediments, the advective flow is probably about 75 ± 50 cm/1000 yr. or 0.075 ± 0.05 cm/yr.

At these relatively slow advective velocities, maxima in NO_3^- and H_4SiO_4 can occur in the sediment column, so that the advection of water through the sediments itself is not precluded by the occurrence of these maxima. Especially for dissolved silica, with its rather high production term (see, for example, Lerman, 1977), maxima can be pronounced. At this stage, however, the profiles do not allow the detailed modeling of potential reaction rates.

It is of some interest to establish whether an advective flux of 0.075 cm/yr. has important geochemical implications in this area. Let us assume that basement waters are depleted by ~ 3 mM in Mg^{2+} and that advection occurs over a distance of 2000 km from the ridge axis and along 10,000 km of the East Pacific Rise. An advective flow of 0.075 cm/yr. then implies a flux of Mg into basement of 9×10^{10} moles/yr., which at a river flux of 5×10^{12} moles/yr. is about 2% of the river flux. This flux, therefore, is not significant when compared to the river flux or the flux into high-temperature alteration products in ridgecrest hydrothermal systems (Edmond et al., 1979). For Ca^{2+} , the implied fluxes are also less than 1% of the overall flux of Ca^{2+} into the ocean.

Kastner et al. (this volume) argued that carbonate diagenesis in the bottom of Hole 600C occurred under conditions of advective water flow. Other sites in the Leg 92 transect also show carbonate recrystallization in the deeper parts of the holes. We postulate that such reactions must have occurred under conditions of much more rigorous flow than was calculated in the above section.

CONCLUSIONS

Data on major ion constituents of interstitial waters of sediments recovered during Leg 92 show only minor increases in dissolved Ca^{2+} (< 1 mM), small decreases in Mg^{2+} (< 4 mM), and no significant changes in K^+ . Although reactions involving carbonates may cause the changes in Ca^{2+} and Mg^{2+} , an equally or more plausi-

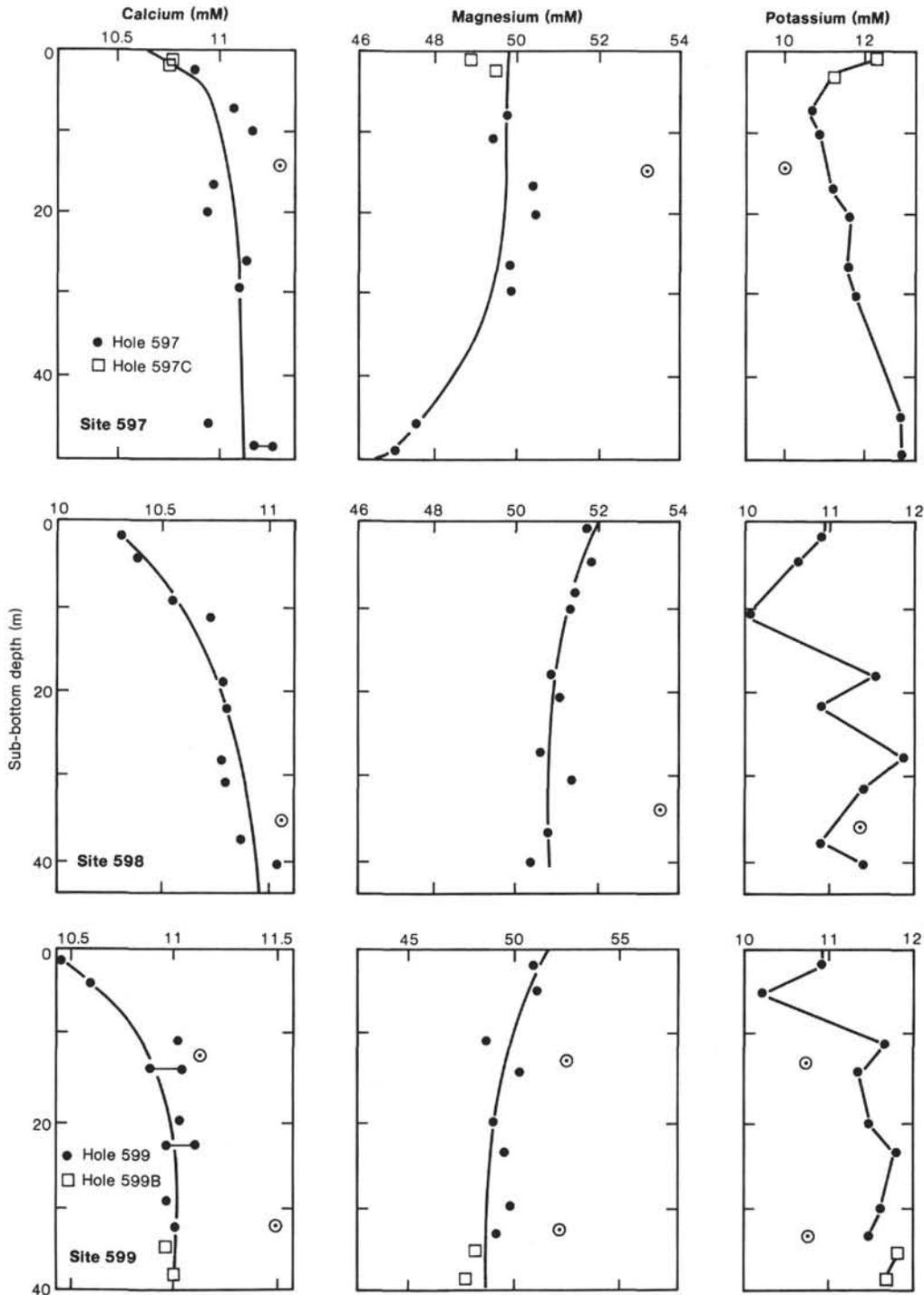


Figure 2. Ca^{2+} , Mg^{2+} , and K^{+} concentrations. Data in circles are *in situ* values.

ble explanation may be found in terms of the upward advection of fluid from underlying basement rocks at velocities of 0.075 ± 0.05 cm/yr. The geochemical fluxes implied by such advective processes imply only a few percent of the river fluxes of Ca^{2+} and Mg^{2+} and thus are not significant.

ACKNOWLEDGMENTS

This research was supported by NSF Grant OCE-82-18539 (JMG) and by the Conseil National de Recherches (JB).

We gratefully acknowledge the assistance of Mr. Jim Pine, the shipboard chemist, in our efforts in the chemistry laboratory of *Glomar Challenger*. The thoughtful review by Dr. R. E. McDuff was very much appreciated.

REFERENCES

Anderson, R. N., and Hobart, M. A., 1976. The relation between heat flow, sediment thickness, and age in the eastern Pacific. *J. Geophys. Res.*, 81:1968-1989.
 Anderson, R. N., Hobart, M. G., and Langseth, M. G., 1979. Geothermal convection through oceanic crust and sediments in the Indian Ocean. *Science*, 204:828.

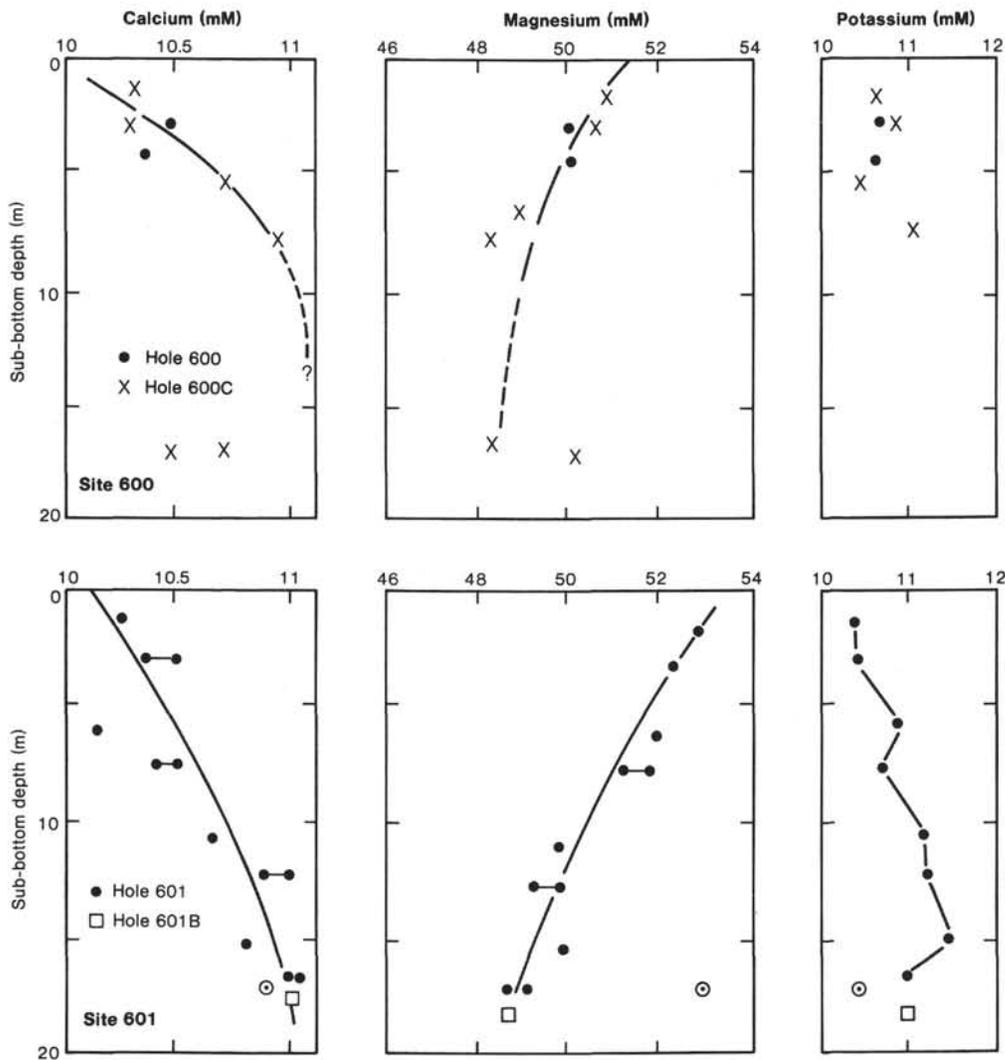


Figure 2 (continued).

- Anderson, R. N., Langseth, M. G., and Sclater, J. G., 1977. The mechanisms of heat transfer through the floor of the Indian Ocean. *J. Geophys. Res.*, 82:3391-3409.
- Craig, H., 1969. Abyssal carbon and radiocarbon in the Pacific. *J. Geophys. Res.*, 74:5491-5506.
- Crow, J., and McDuff, R. E., 1981. Comparison of geochemical and geophysical estimates of convective flow through marine sediments. In Crow, J. (Ed.), *Mechanisms of Heat Transport through the Floor of the Equatorial Pacific Ocean* [Ph.D. dissert.]. Woods Hole Oceanographic Institution (WHOI-81-47), pp. 200-232.
- Edmond, J. M., Measures, C., McDuff, R. E., Chan, L. H., Collier, R., Grant, B., Gordon, L. I., and Corliss, J. B., 1979. Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: the Galapagos data. *Earth Planet. Sci. Lett.*, 46:1-18.
- Gieskes, J. M., 1973. Interstitial water studies, Leg 15: alkalinity, pH, Mg, Ca, Si, PO₄, and NH₄. In Heezen, B. C., MacGregor, I. D., et al., *Init. Repts. DSDP*, 20: Washington (U.S. Govt. Printing Office), 813-829.
- _____, 1974. Interstitial water studies, Leg 25. In Simpson, E. S. W., Schlich, R., et al., *Init. Repts. DSDP*, 25: Washington (U.S. Govt. Printing Office), 361-394.
- Lerman, A., 1977. Migrational processes and chemical reactions in interstitial waters. In Goldberg, E. D. (Ed.), *The Sea* (Vol. 6): New York (Wiley-Interscience), 695-738.
- McDuff, R. E., 1978. Conservative behavior of calcium and magnesium in the interstitial waters of marine sediments: identification and interpretation [Ph.D. dissert.]. University of California, San Diego.
- _____, 1981. Major cation gradients in DSDP interstitial waters: the role of diffusive exchange between seawater and the upper oceanic crust. *Geochim. Cosmochim. Acta*, 45:1705-1713.
- Sayles, F. L., and Manheim, F. T., 1975. Interstitial solutions and diagenesis in deeply buried marine sediments: results from the Deep Sea Drilling Project. *Geochim. Cosmochim. Acta*, 39:103-127.
- Sayles, F. L., Manheim, F. T., and Waterman, L. S., 1973. Interstitial water studies on small core samples, Leg 15. In Heezen, B. C., MacGregor, I. D., et al., *Init. Repts. DSDP*, 20: Washington (U.S. Govt. Printing Office), 783-804.

Date of Initial Receipt: 29 October 1984
Date of Acceptance: 10 March 1985

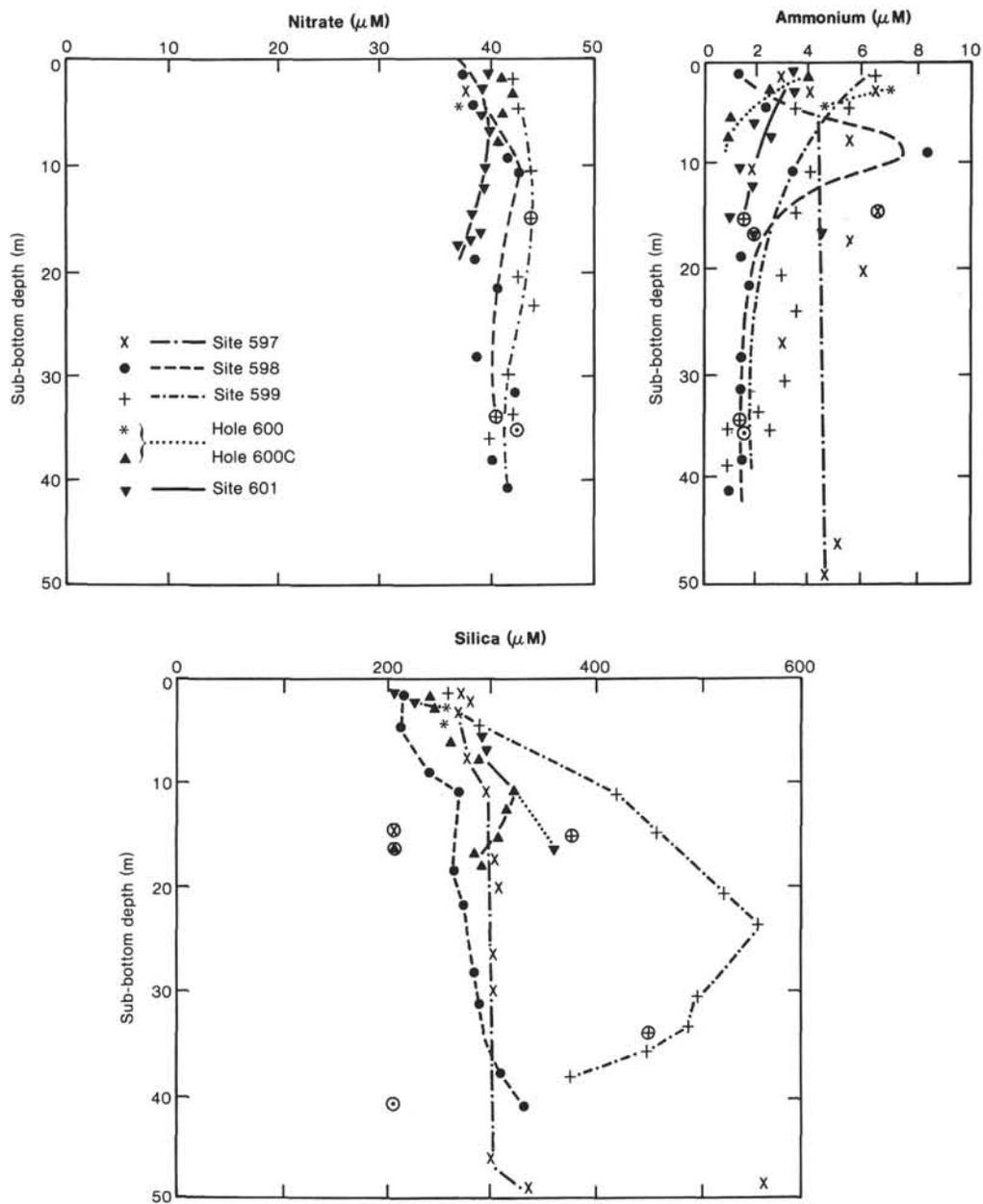


Figure 3. Composite profiles of dissolved nitrate, dissolved ammonium, and dissolved silica. Data in circles are *in situ* concentrations.

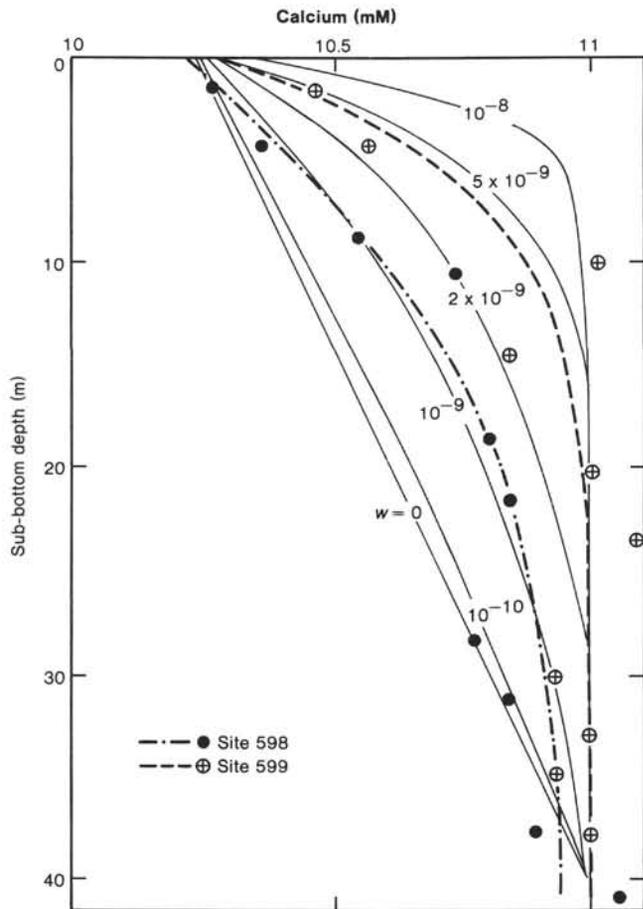


Figure 4. Calculated concentration profiles for Ca^{2+} using simple advection diffusion model (see text).