

22. INTERSTITIAL WATER STUDIES, LEG 74¹

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ABSTRACT

Interstitial water studies from sites drilled during a transect of the Walvis Ridge indicate that concentration increases in calcium and decreases in magnesium toward and into the basement. These trends can be understood principally in terms of reactions taking place in Layer 2 of the oceanic crust. At Site 525, however, some removal of magnesium occurs within the sediment column. Concentration maxima of dissolved strontium clearly indicate that carbonate recrystallization occurs throughout the carbonate sediments, and studies of the Sr/Ca ratio in carbonates indicate that in chalks and limestones recrystallization is essentially complete. Predictions of dissolved strontium maxima generally fail; this can be understood as removal of strontium in basal sediments and/or basalts.

INTRODUCTION

The sites drilled across the southern Walvis Ridge during Leg 74 of the Deep Sea Drilling Project (Fig. 1) were at different water depths: Site 526 was at 1054 m and, of the transect sites; 525 was at 2467 m, 529 at 3035 m, 528 at 3800 m, and 527 at 4428 m. Among the major aims of the drilling program were the study of the nature of the basement of this aseismic ridge and of the paleoceanographic history of the southern Atlantic Ocean. The shipboard program included a very detailed sampling for interstitial waters. Shipboard analyses for dissolved calcium and magnesium indicated pronounced concentration depth gradients. For these reasons we decided on a more detailed analytical program in our laboratory, including both interstitial water analyses and analyses of the carbonates for their Mg and Sr contents.

Increases in dissolved calcium and decreases in dissolved magnesium with depth have often been interpreted as release of calcium and uptake of magnesium in reactions involving the alteration of volcanic matter dispersed in the sediments and/or the alteration of basalts in Layer 2 of the oceanic crust (Gieskes, 1981; Gieskes and Lawrence, 1981; Lawrence and Gieskes, 1981; McDuff, 1981). Dissolved strontium, in contrast, appears mostly affected by reactions involving carbonate recrystallization, though the ⁸⁷Sr/⁸⁶Sr isotopic ratio often shows a volcanic contribution to this ratio (Baker et al., 1982; Elderfield and Gieskes, 1982; Hawkesworth and Elderfield, 1978). In this report we will examine the concentration-depth gradients of various dissolved constituents of the interstitial waters and present preliminary interpretations. Work on the oxygen isotopic composition of the interstitial waters is in progress, as well as that on the isotopic composition of dissolved strontium.

METHODS AND RESULTS

Interstitial water constituents were analyzed using the methods described by Gieskes et al. (1982). Shipboard data (pH, alkalinity, salin-

ity, chloride, calcium, and magnesium) and shore laboratory data are presented in Table 1 and in Figures 2-7.

Sediments were washed with distilled water to remove sea salt, dried, powdered, and subsequently dissolved in acetic acid-sodium acetate buffer (pH ≈ 4.5). Sr and Mg analyses were carried out by atomic absorption spectrometry, whereas Ca was determined using complexometric EDTA titration. When clay contents are appreciable this methodology can yield exchangeable Mg (and perhaps some Sr), but when carbonate contents are >90%, the Mg/Ca and Sr/Ca ratios (see Fig. 8) should be representative of carbonates, although there may possibly be high Sr contents as a result of iron-manganese oxide coatings on carbonate debris (Turekian, 1964). Carbonate compositions are reported in Table 2 and in Figure 9. Liu and Schmitt (this volume) carried out Sr and Ca analyses of sediments obtained in Hole 525A. From these data, ratios of Sr/Ca in carbonates can be calculated. These indicate an average Sr/Ca of $\sim 14.9 \times 10^{-4}$ (atomic ratio), whereas our data yield an average of 18.0×10^{-4} . As we are at this stage not certain whether this difference is due to calibration errors, we will assume that the average initial ratio of deposited carbonates is $(16.5 \pm 1.5) \times 10^{-4}$. It should be noted, however, that the two sets of data do show the same features in Hole 525A, and below 300 m are generally in good agreement (Fig. 9).

DISCUSSION

Before making some general observations, we will discuss the interstitial water chemistry of each individual site.

Site 525 (Figs. 2 and 3)

Sedimentation rates at this site have been relatively slow (<10 m/m.y.) and for these reasons decreases in dissolved sulfate and increases in dissolved ammonia are small (Table 1). For similar reasons alkalinity changes are very small, no clear maximum occurs, and generally at all Leg 74 sites slight decreases in alkalinity occur with depth.

Changes in calcium and magnesium are gradual with depth, but, as can be observed from Figure 3, these changes are not linearly correlated with depth. Whereas the dissolved calcium profile is essentially linear with depth over the upper 300 m of Hole 525B (Fig. 3), that of magnesium shows curvature, indicating a sink for magnesium in this sediment section, probably in the upper 200 m. Though the deviation from linearity is small (~2 mM), the uptake reaction is significant and must be due either to uptake in carbonates during carbonate re-

¹ Moore, T. C., Jr., Rabinowitz, P. D., et al., *Init. Repts. DSDP, 74*: Washington (U.S. Govt. Printing Office).

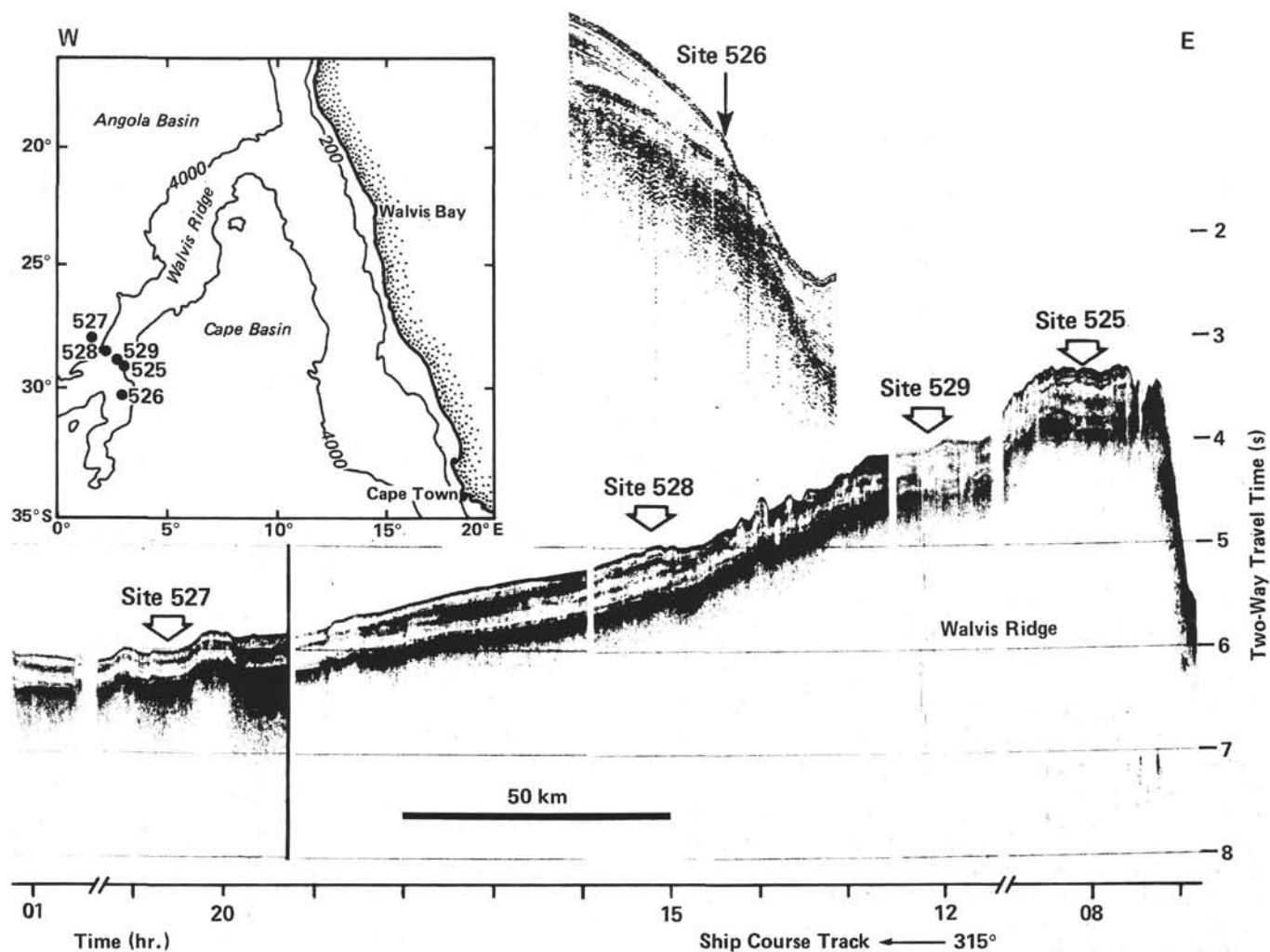


Figure 1. Map of the study area of the Leg 74 transect across Walvis Ridge.

Table 1. Interstitial water data, Leg 74.

| Sample (interval in cm) | Sub- bottom Depth (m) | pH | Alk (meq/dm ³) | S (g/kg) | Ca (mM) | Mg (mM) | Cl (g/kg) | Sr (μM) | Li (μM) | K (mM) | SO ₄ (mM) | NH ₄ (μM) | Si (μM) |
|----------------------------|--------------------------------|------|-------------------------------|-------------|------------|------------|--------------|------------|------------|-----------|-------------------------|-------------------------|------------|
| Hole 525 | | | | | | | | | | | | | |
| 1-1, 144-146 | 1 | 7.49 | 2.47 | 36.3 | 10.3 | 53.0 | 19.34 | 183.2 | 9.7 | 10.2 | 28.7 | 0 | 133.8 |
| 3-2, 140-150 | 45 | 7.30 | 2.81 | 35.2 | 12.3 | 51.7 | 19.75 | 415.2 | 37.5 | 9.9 | — | 0 | 96.3 |
| 5-4, 140-150 | 95 | 7.29 | 2.38 | 35.2 | 14.6 | 48.9 | 19.70 | 659.4 | 68.3 | 8.8 | — | 0 | 91.0 |
| 8-5, 140-150 | 182 | 7.25 | 2.16 | 35.2 | 17.6 | 46.3 | 19.65 | 713.8 | 66.1 | 8.2 | — | 0 | 119.8 |
| 11-5, 135-150 | 210 | 7.25 | 2.07 | 35.5 | 18.8 | 45.8 | 19.73 | 701.7 | 70.7 | 10.8 | — | 0 | 136.7 |
| 14-5, 135-150 | 239 | 7.20 | 2.12 | 36.3 | 19.8 | 45.1 | 19.89 | 665.4 | 79.8 | 7.3 | — | 0 | 212.0 |
| 19-3, 135-150 | 274 | 7.26 | 2.18 | 35.5 | 21.2 | 44.1 | 20.09 | 623.0 | 69.2 | 6.8 | — | 0 | 249.1 |
| 23-5, 135-150 | 315 | 7.16 | 2.21 | 35.5 | 22.4 | 44.6 | 20.08 | 647.2 | 79.1 | 6.6 | 26.2 | 0 | 278.0 |
| 26-2, 135-150 | 339 | 7.17 | 2.05 | 35.5 | 23.2 | 43.8 | 19.89 | 635.0 | 80.6 | 6.9 | — | 0 | 506.1 |
| 32-4, 135-150 | 389 | 7.16 | 1.86 | 36.8 | 24.1 | 43.3 | 20.01 | 623.0 | 76.7 | 8.2 | — | 0 | 434.6 |
| 35-6, 135-150 | 411 | 7.21 | 1.62 | 36.3 | 24.4 | 43.1 | 20.02 | 544.4 | 90.5 | 6.8 | — | 0 | 508.8 |
| 40-5, 140-150 | 456 | 7.22 | 1.27 | 36.0 | 27.0 | 41.2 | 20.06 | 544.4 | 92.0 | 6.5 | 21.3 | 42.4 | 311.6 |
| 45-5, 140-150 | 505 | 7.16 | 0.17 | 35.8 | 29.7 | 37.2 | 19.99 | 534.1 | 105.2 | 5.6 | — | 0 | 137.3 |
| 50-5, 140-150 | 550 | 7.50 | 0.27 | 37.1 | 33.5 | 35.9 | 20.33 | 504.5 | 103.8 | 5.1 | — | 14.6 | 104.0 |
| 60-5, 135-150 | 645 | — | — | 37.4 | 45.2 | 28.8 | 20.76 | 513.6 | 114.2 | 4.9 | — | 0 | 153.0 |
| Hole 525B | | | | | | | | | | | | | |
| 1-1, 140-150 | 1 | 7.44 | 2.61 | 35.2 | 10.5 | 53.1 | 19.31 | 91.6 | 8.2 | 10.7 | 26.2 | 0 | 145.5 |
| 3-1, 140-150 | 9 | 7.36 | 2.71 | 35.2 | 11.4 | 52.9 | 19.46 | 201.6 | 23.6 | 9.6 | — | 0 | 143.4 |
| 5-2, 133-143 | 18 | 7.35 | 2.64 | 36.3 | 11.6 | 51.6 | 19.44 | 302.0 | 27.0 | 10.9 | — | 0 | 142.6 |
| 7-2, 140-150 | 28 | 7.27 | 2.64 | 35.2 | 12.2 | 51.4 | 19.56 | 415.2 | 39.1 | 10.9 | — | 0 | 117.7 |
| 9-3, 111-121 | 38 | 7.29 | 2.61 | 36.3 | 12.5 | 50.8 | 19.46 | 470.2 | 43.7 | 11.2 | — | 0 | 105.9 |
| 11-2, 140-150 | 46 | 7.31 | 2.23 | 35.2 | 12.8 | 50.8 | 19.56 | 488.5 | 40.6 | 9.1 | — | 0 | 101.7 |
| 13-1, 140-150 | 54 | 7.27 | 2.51 | 35.2 | 13.2 | 50.3 | 19.49 | 549.5 | 46.8 | 9.1 | — | 0 | 103.8 |
| 15-1, 140-150 | 62 | 7.25 | 2.37 | 35.8 | 13.3 | 49.8 | 19.49 | 567.9 | 54.5 | 9.9 | — | 0 | 105.9 |
| 17-1, 140-150 | 71 | 7.24 | 2.23 | 35.2 | 13.7 | 49.7 | 19.51 | 586.2 | 54.5 | 10.7 | — | 0 | 107.0 |
| 19-2, 140-150 | 81 | 7.35 | 2.68 | 35.2 | 14.4 | 49.3 | 19.46 | 592.8 | 55.4 | 9.8 | — | 0 | 180.0 |
| 22-2, 140-150 | 94 | 7.28 | 2.18 | 35.2 | 14.5 | 48.8 | 19.56 | 598.4 | 57.5 | 9.1 | — | 0 | 102.7 |
| 24-2, 140-150 | 102 | 7.23 | 2.17 | 35.2 | 15.1 | 48.6 | 19.46 | 677.8 | 68.3 | 9.3 | — | 0 | 102.7 |

Table 1. (Continued.)

| Sample (interval in cm) | Sub- bottom Depth (m) | pH | Alk (meq/dm ³) | S (g/kg) | Ca (mM) | Mg (mM) | Cl (g/kg) | Sr (μM) | Li (μM) | K (mM) | SO ₄ (mM) | NH ₄ (μM) | Si (μM) |
|----------------------------|--------------------------------|------|-------------------------------|-------------|------------|------------|--------------|------------|------------|-----------|-------------------------|-------------------------|------------|
| Hole 525B (Cont.) | | | | | | | | | | | | | |
| 26-2, 140-150 | 111 | 7.38 | 1.92 | 35.2 | 15.3 | 47.9 | 19.75 | 665.6 | 71.4 | 9.6 | 23.1 | 0 | 96.3 |
| 29-2, 140-150 | 124 | 7.35 | 1.97 | 35.2 | 15.9 | 47.2 | 19.61 | 776.5 | 75.2 | 9.7 | — | 0 | 180.0 |
| 31-2, 140-150 | 133 | 7.30 | 2.00 | 35.2 | 16.0 | 47.0 | 19.75 | 738.9 | 69.9 | 8.2 | — | 0 | 100.6 |
| 33-2, 140-150 | 142 | 7.32 | 2.01 | 35.2 | 16.7 | 46.5 | 19.73 | 714.4 | 62.2 | 8.8 | — | 0 | 101.7 |
| 35-1, 140-150 | 149 | 7.46 | 2.12 | 35.2 | 17.1 | 46.5 | 19.77 | 702.6 | 73.5 | 10.5 | — | 29.1 | 167.0 |
| 37-2, 140-150 | 160 | 7.34 | 2.23 | 35.2 | 17.3 | 46.4 | 19.70 | 696.1 | 68.3 | 6.3 | — | 64.2 | 118.8 |
| 39-2, 140-150 | 168 | 7.27 | 2.01 | 35.2 | 17.5 | 46.3 | 19.73 | 696.1 | 77.5 | 8.2 | — | 0 | 118.8 |
| 42-1, 140-150 | 175 | 7.48 | 1.38 | 35.2 | 17.7 | 46.1 | 19.77 | 684.1 | 76.7 | 8.3 | — | 0 | 129.6 |
| 45-3, 140-150 | 191 | 7.22 | 1.99 | 35.2 | 18.1 | 45.8 | 19.73 | 714.4 | 79.1 | 8.2 | — | 2.1 | 128.4 |
| 47-3, 140-150 | 201 | 7.28 | 2.03 | 35.2 | 18.6 | 45.6 | 19.71 | 714.4 | 77.5 | 8.2 | — | 0 | 138.0 |
| 49-3, 140-150 | 209 | 7.28 | 2.09 | 35.2 | 19.0 | 45.5 | 19.80 | 714.4 | 80.6 | 7.7 | 23.1 | 0 | 127.3 |
| 51-1, 140-150 | 274 | 7.24 | 2.09 | 35.5 | 21.4 | 44.3 | 20.09 | 667.6 | 79.1 | 7.7 | — | 0 | 262.2 |
| 53-2, 140-150 | 284 | 7.22 | 2.09 | 35.5 | 21.7 | 44.3 | 19.99 | 696.1 | 83.7 | 7.4 | — | 0 | 283.6 |
| Hole 526A | | | | | | | | | | | | | |
| 1-1, 143-150 | 29 | 7.26 | 2.61 | 35.2 | 10.9 | 52.5 | 19.20 | 177.5 | 19.2 | 13.7 | 25.4 | 0 | 154.4 |
| 6-2, 143-150 | 53 | 7.18 | 2.83 | 35.2 | 11.2 | 51.7 | 19.17 | — | — | — | — | 0 | 119.9 |
| 11-2, 140-150 | 75 | 7.20 | 2.57 | 34.9 | 11.3 | 51.8 | 19.27 | 240.1 | 22.5 | 10.1 | — | 0 | 113.4 |
| 16-2, 144-150 | 97 | 7.10 | 2.68 | 34.9 | 11.4 | 51.7 | 19.27 | 202.1 | 17.6 | 10.8 | — | 0 | 102.6 |
| 21-1, 140-150 | 119 | 7.26 | 2.73 | 35.2 | 11.4 | 51.6 | 19.34 | 185.4 | 16.2 | 9.8 | — | 0 | 94.8 |
| 26-2, 140-150 | 141 | 7.16 | 2.64 | 35.2 | 11.5 | 51.9 | 19.48 | 173.8 | 17.6 | 10.2 | — | 0 | 92.9 |
| 31-2, 140-150 | 163 | 7.25 | 2.64 | 35.2 | 11.5 | 52.2 | 19.69 | 156.7 | 17.8 | 9.5 | — | 0 | 94.8 |
| 36-2, 140-150 | 185 | 7.23 | 2.79 | 35.5 | 11.7 | 53.3 | 19.86 | — | — | — | — | 0 | 98.1 |
| 41-2, 143-150 | 207 | 7.23 | 2.70 | 35.5 | 11.7 | 52.8 | 19.69 | 130.7 | 11.4 | 9.7 | 25.4 | 0 | 121.0 |
| 45-2, 143-150 | 225 | 7.29 | 2.73 | 35.5 | 11.7 | 53.1 | 19.66 | 81.6 | 11.7 | 9.9 | — | 0 | 192.5 |
| Hole 527 | | | | | | | | | | | | | |
| 1-4, 144-150 | 6 | 7.27 | 2.40 | 35.2 | 10.6 | 52.6 | 19.44 | 143.0 | 16.1 | (19.7) | 24.4 | 0 | 162.0 |
| 3-2, 140-150 | 22 | 7.26 | 2.44 | 35.2 | 11.4 | 52.1 | 19.60 | 284.7 | 27.0 | 10.5 | — | 0 | 94.0 |
| 5-2, 140-150 | 40 | 7.25 | 2.39 | 35.2 | 12.6 | 51.1 | 19.53 | 361.5 | 34.5 | 10.2 | — | 0 | 80.3 |
| 12-4, 144-150 | 100 | 7.30 | 1.82 | 35.2 | 15.1 | 47.3 | 19.58 | 428.6 | 46.8 | 9.6 | — | 0 | 114.5 |
| 13-4, 140-150 | 110 | 7.28 | 1.86 | 35.2 | 15.6 | 46.4 | 19.53 | — | 42.6 | 9.7 | — | 0 | 280.8 |
| 16-3, 140-150 | 137 | 7.26 | 1.55 | 35.2 | 17.6 | 46.0 | 19.55 | 418.6 | 47.8 | 8.7 | — | 0 | 159.0 |
| 20-2, 140-150 | 173 | 7.18 | 1.51 | 35.2 | 18.8 | 45.3 | 19.56 | 400.4 | 60.0 | 9.5 | — | 90.1 | 241.7 |
| 23-1, 140-150 | 191 | 7.20 | 1.57 | 35.2 | 19.8 | 44.5 | 19.73 | 340.0 | 46.3 | 8.7 | — | 0 | 241.7 |
| 27-3, 140-150 | 232 | 7.23 | 1.48 | 35.2 | 21.8 | 42.5 | 19.72 | 309.7 | 49.3 | 9.5 | — | 0 | 241.7 |
| 32-4, 140-150 | 281 | 7.21 | 1.24 | 35.2 | 24.4 | 41.0 | 19.73 | 309.7 | 44.7 | 6.8 | — | 0 | 135.7 |
| 35-4, 140-150 | 309 | 7.18 | 1.17 | 36.3 | 25.4 | 40.3 | 19.73 | — | 54.0 | 6.3 | — | 0 | 134.6 |
| 38-4, 140-150 | 338 | 7.21 | 0.67 | 35.5 | 26.5 | 39.3 | 19.72 | 271.5 | 55.3 | 5.5 | — | 0 | 122.6 |
| 42-2, 135-140 | 362 | 7.16 | 0.20 | 35.2 | 54.4 | 15.0 | 19.73 | 225.0 | 54.0 | 1.9 | — | 0 | 196.1 |
| Hole 528 | | | | | | | | | | | | | |
| 1-1, 144-150 | 1 | 7.28 | 2.34 | 36.6 | 10.2 | 52.1 | 19.23 | 110.9 | 11.4 | 10.2 | 25.2 | 10.8 | 166.3 |
| 4-4, 140-150 | 147 | 7.19 | 1.66 | 35.2 | 18.8 | 44.4 | 19.56 | 598.4 | 57.5 | 7.4 | — | 0 | 134.8 |
| 9-5, 140-150 | 196 | 7.16 | 1.59 | 36.0 | 21.3 | 42.7 | 19.83 | 598.4 | 59.1 | 6.9 | — | 24.6 | 133.8 |
| 15-4, 140-150 | 251 | 2.10 | 1.60 | 35.8 | 23.3 | 41.4 | 19.80 | 567.9 | 59.1 | 6.6 | — | 0 | 196.9 |
| 20-2, 140-150 | 296 | 7.03 | 1.56 | 35.5 | 26.3 | 39.3 | 19.77 | 580.1 | 60.6 | (11.8) | — | 12.8 | 408.7 |
| 26-1, 140-150 | 351 | 7.04 | 1.43 | 35.5 | 28.4 | 36.6 | 19.83 | 362.9 | 69.2 | 6.3 | — | 67.8 | 519.4 |
| 32-3, 140-150 | 411 | 7.06 | 0.88 | 36.3 | 31.8 | 35.1 | 20.00 | 532.3 | 70.7 | 4.9 | — | 26.5 | 180.2 |
| 36-2, 140-150 | 452 | 7.14 | 0.14 | 36.0 | 33.4 | 33.1 | 20.00 | 514.2 | 76.7 | 4.9 | — | 0 | 81.6 |
| 39-11, 0-10 | 474 | 7.23 | — | 36.0 | 34.8 | 32.6 | 19.94 | 513.6 | 68.1 | 4.6 | — | 10.0 | 154.0 |
| 42-2, 51-66 | 503 | 7.15 | — | 36.3 | 56.3 | 12.5 | 19.94 | 485.0 | 60.9 | 2.8 | — | 2.0 | 115 |
| 43-1, 48-58 | 510 | 7.54 | 0.13 | 36.3 | 65.6 | 1.1 | 19.80 | 483.9 | 66.1 | 1.4 | — | 0 | 116.6 |
| 46-4, 135-150 | 542 | 7.83 | 0 | 37.1 | 76.5 | 1.2 | 20.11 | 527.3 | 71.5 | 1.6 | 22.3 | 31.5 | 92.4 |
| Hole 528A | | | | | | | | | | | | | |
| 2-1, 144-150 | 4 | 7.15 | 2.80 | 35.2 | 10.9 | 52.7 | 19.41 | 141.7 | 11.4 | 10.5 | — | 0 | 167.4 |
| 5-3, 144-150 | 21 | 7.22 | 2.53 | 35.2 | 12.0 | 52.1 | 19.61 | 326.6 | 23.9 | 10.5 | — | 0 | 96.1 |
| 17-1, 142-150 | 70 | 7.27 | 2.20 | 35.2 | 14.8 | 48.6 | 19.66 | 528.8 | 39.8 | 9.5 | — | 0 | 82.8 |
| 26-2, 143-150 | 111 | 7.28 | 2.65 | 35.2 | 17.0 | 47.1 | 19.66 | 603.4 | 49.2 | 8.9 | — | 0 | 97.0 |
| Hole 529 | | | | | | | | | | | | | |
| 1-4, 144-150 | 6 | 7.10 | 2.60 | 35.2 | 10.6 | 53.1 | 19.34 | 104.8 | 14.6 | 10.0 | 25.2 | 0 | 151.2 |
| 6-4, 140-150 | 52 | 7.17 | 2.30 | 35.2 | 12.4 | 50.9 | 19.81 | 240.4 | 23.9 | 9.4 | — | 0 | 109.1 |
| 11-5, 140-150 | 101 | 7.10 | 2.27 | 35.2 | 16.7 | 46.5 | 19.58 | 288.1 | 31.5 | 7.7 | — | 0 | 122.4 |
| 16-5, 140-150 | 149 | 7.10 | 1.89 | 35.2 | 19.8 | 43.8 | 19.72 | 369.8 | 47.2 | 8.9 | — | 0 | 172.8 |
| 21-5, 140-150 | 196 | 6.89 | 1.93 | 35.5 | 22.5 | 41.1 | 19.75 | — | — | — | 22.9 | 0 | 162.0 |
| 26-4, 140-150 | 242 | 6.93 | 1.85 | 35.5 | 25.9 | 38.0 | 19.94 | 443.7 | 51.8 | 6.6 | — | 0 | 436.3 |
| 31-2, 140-150 | 287 | 6.99 | 1.99 | 35.5 | 28.1 | 35.3 | 19.79 | 345.2 | 63.9 | 6.3 | — | 0 | 569.2 |
| 36-4, 139-150 | 337 | 6.92 | 0.23 | 35.5 | 31.8 | 29.7 | 19.91 | 532.3 | 67.6 | 6.5 | — | 0 | 439.9 |
| 42-4, 140-150 | 394 | — | — | 35.2 | 40.6 | 19.2 | 19.69 | — | — | — | — | — | — |

crystallization reactions, or to uptake in clay minerals during *in situ* alteration of volcanic material dispersed in the sediments. Elderfield et al. (1982) have suggested that, even in the very pure carbonate sections of Sites 288 and 289 of the Ontong-Java Plateau, alteration of

volcanic matter was responsible for ⁸⁷Sr/⁸⁶Sr ratios lower than those in contemporaneous seawaters. At present a program of analysis of this isotopic ratio is in progress with the specific aim of establishing a possible volcanic contribution to the interstitial water chemistry. Changes

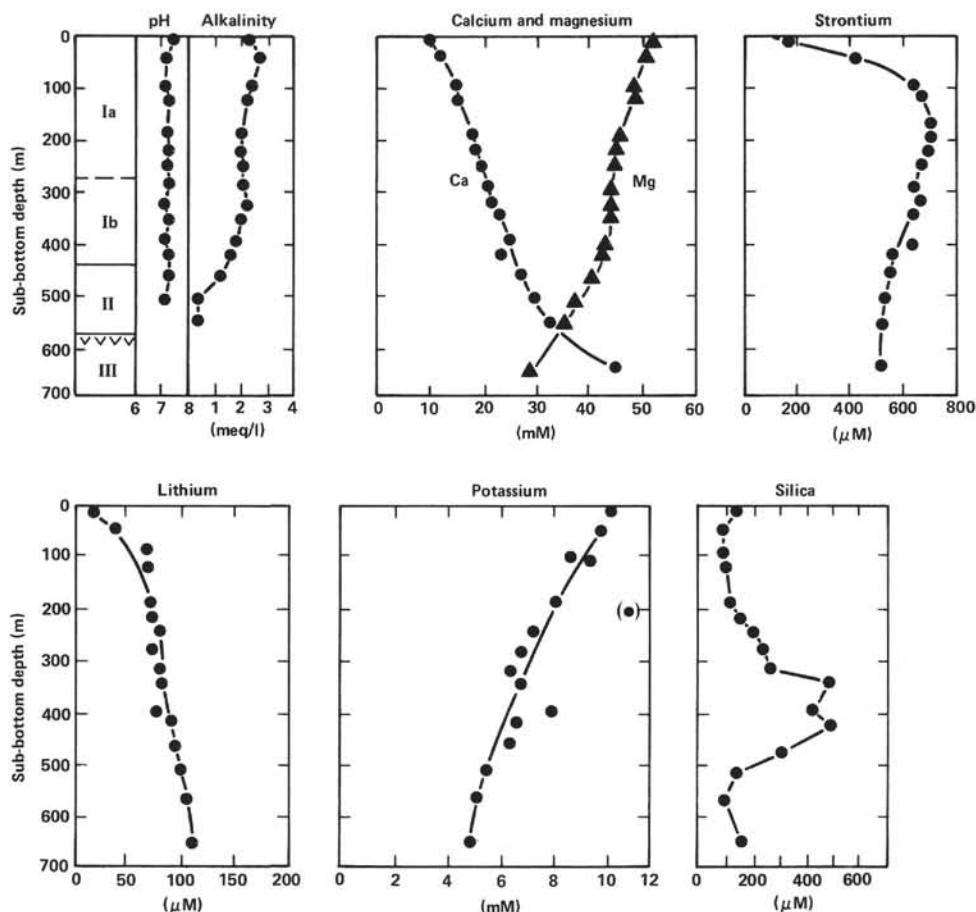


Figure 2. Interstitial water chemistry, Hole 525A. Lithology: Ia, Nannofossil and foraminifer-nannofossil ooze; Ib, nannofossil and foraminifer-nannofossil oozes and chalks, chert at base; II, cyclical nannofossil marly chalks and siltstone/sandstone of turbidite origin. III, basalt and interlayer sediment.

in the Mg/Ca ratio (Fig. 9) are small and variable and cannot be interpreted in terms of Mg uptake in carbonates during recrystallization.

The profile of dissolved strontium is typical for carbonate sites and can be understood best in terms of carbonate recrystallization (Baker et al., 1982). We shall return to the problem of carbonate recrystallization in a subsequent section.

The profiles of dissolved potassium and lithium indicate uptake of potassium in the sediments and release of lithium. At this stage, however, we are not able to define the sinks and sources for these elements.

Dissolved silica at all sites of Leg 74 follows closely the presence or absence of biogenic silica (Gieskes, 1981). At Site 525 this is clearly the case between 200 and 500 m sub-bottom depth.

Site 526 (Fig. 4)

This site, drilled at very shallow water depth (1054 m), is characterized by the absence of any significant concentration-depth gradients in dissolved calcium and magnesium. A possible slight decrease with depth in lithium occurs, and dissolved strontium shows a well-defined maximum.

The dissolved strontium maximum can be understood in terms of carbonate recrystallization. We shall return to this subject in a following section.

Site 527 (Fig. 5)

In Site 527 gradients in calcium and magnesium are linear with depth down to the contact between sediments and basalts. The lowermost sample was obtained from sediments intercalated by basalt layers and indicates a sharp drop in magnesium and a rise in calcium. The plot of calcium versus magnesium (Fig. 8) is linear throughout, which suggests that the source of calcium and the sink for magnesium are located in the basalts of Layer 2 and that the sharp break in the concentration-depth gradients is mainly due to enhanced resistance to diffusion in the poorly permeable basalt layers. For this concept to be true a decrease in the overall diffusion coefficient of about 20 times would be required.

The gradient in dissolved potassium indicates uptake of this constituent in the underlying basalts. In contrast, dissolved lithium clearly has a source in the sediment column.

Dissolved strontium again shows a maximum and its profile is clearly unrelated to that of dissolved calcium

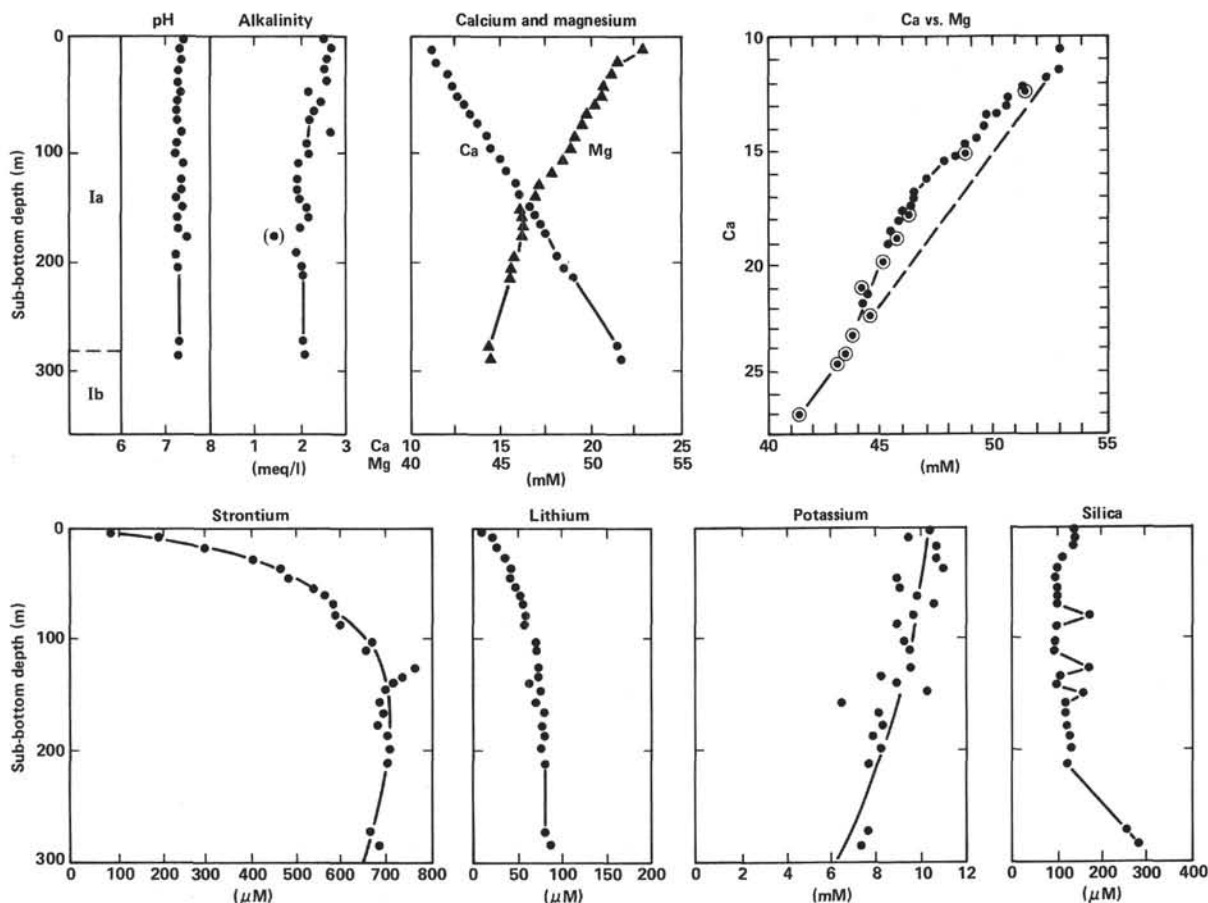


Figure 3. Interstitial water chemistry, Hole 525B. Lithology: Ia, Nannofossil and foraminifer-nannofossil ooze; Ib, nannofossil and foraminifer-nannofossil oozes and chalks.

and magnesium. We will return to the subject of carbonate recrystallization in a subsequent section.

Site 528 (Fig. 6)

As at Site 527, the concentration-gradients of calcium and magnesium are linear with depth and continue with a sharp break into the basement complex. If again the gradient in basement is continuous with that in the sediment column, the average diffusion coefficient in basement should be about 30 times lower than in the sediments.

The data for dissolved potassium imply sinks both in the sediments and in the underlying basalts. As usual, lithium has a source in the sediment column.

Dissolved strontium indicates a well-developed maximum at ~125 m and can be understood in terms of carbonate recrystallization.

Site 529 (Fig. 7)

Site 529 did not reach basement. Again gradients in calcium and magnesium are continuous with depth and changes in calcium and magnesium are linearly correlated. We postulate that both calcium and magnesium gradients are conservative in nature, that is, reactions at depths greater than 400 m are responsible for the observed concentration changes (McDuff and Gieskes, 1976; McDuff, 1978, 1981).

The dissolved potassium profile indicates possible uptake in the sediment column, particularly when the profile is compared with the shape of the calcium profile. Similar arguments can be made for lithium.

Dissolved strontium is produced throughout the sediment column. No maximum is observed for this constituent of the sediment.

Origin of Calcium and Magnesium Gradients

With the exception of Site 525, in which small deviations from a linear correlation between calcium and magnesium concentration changes were noted (Fig. 3), all remaining sites (no gradients were observed at Site 526) show linear correlations between calcium and magnesium (Fig. 8). At Sites 527 and 528 a ratio of $\Delta\text{Ca}/\Delta\text{Mg} = -1.16$ is observed, whereas at Site 529 one obtains a ratio of $\Delta\text{Ca}/\Delta\text{Mg} = -0.87$.

The linear correlations between ΔCa and ΔMg , with the additional observations that the concentration gradients continue into basement, strongly indicate that the major sinks and the major sources of magnesium and calcium, even at Site 525, are located in basalt basement. This interpretation is in agreement with previous estimates of the importance of reactions in Layer 2 to observed interstitial water compositions (McDuff and Gieskes, 1976; McDuff, 1978, 1981). At present a program of analyses of the interstitial water oxygen and hy-

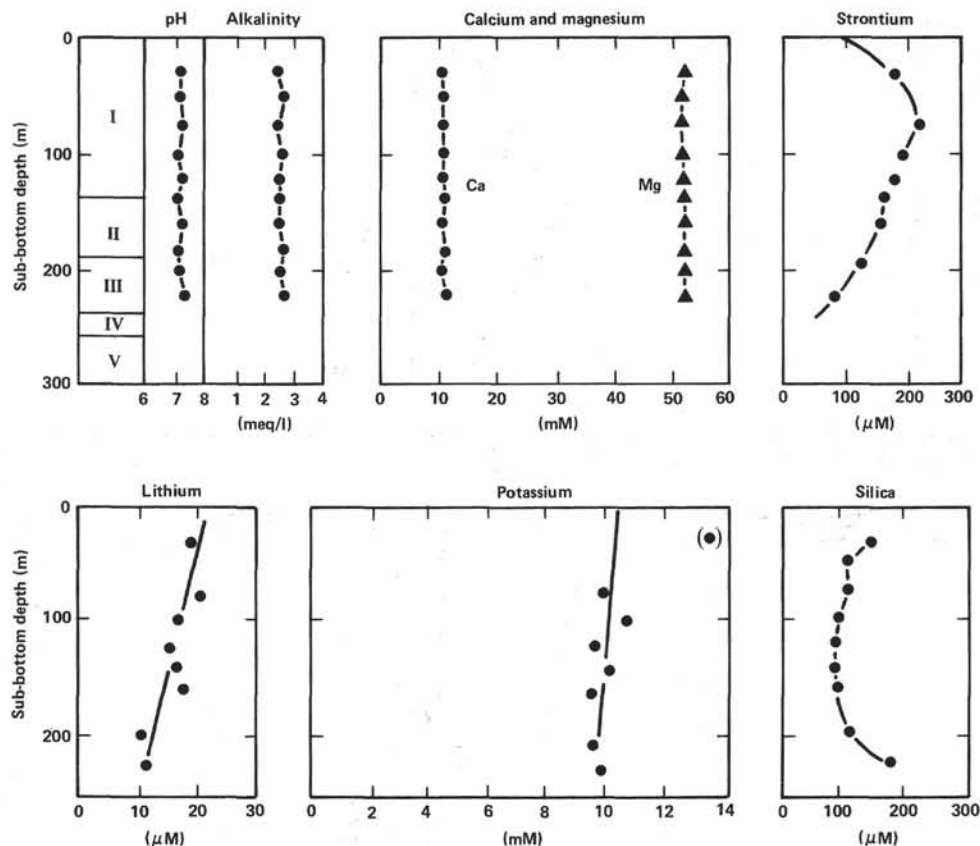


Figure 4. Interstitial water chemistry, Site 526. Lithology: I, White foraminifer and foraminifer-nannofossil ooze; II, nannofossil ooze with minor chalk layers; III, pink-gray foraminifer-nannofossil ooze; IV, white limestone with oncoliths; V, calcareous sand—very shallow water conditions.

drogen isotopic compositions ($\delta^{18}\text{O}$ and δD) is under way in an attempt to verify these observations and to estimate the extent of reaction in basement (Lawrence et al., 1975; Lawrence and Gieskes, 1981).

Carbonate Recrystallization

At all sites drilled during Leg 74 clear maxima are observed in dissolved strontium. This can be understood best in terms of carbonate recrystallization reactions.

Baker et al. (1982), in a study consisting mostly of Pacific Ocean carbonate sites, noted similar increases in dissolved strontium, but the maxima they observed were less pronounced; often strontium concentration showed a tendency to become constant after reaching a maximum. Baker et al. were able to calculate the maximum concentration from a knowledge of the initial Sr/Ca of the carbonate, the distribution coefficient of strontium, and the calcium concentration at the maximum. In Table 3 we report similar calculations, but agreement is generally not very good, probably because the maxima are well developed. Decreases in strontium at greater depths are probably the result of sinks for strontium in the basal volcanic sediments and/or the underlying basalts. This situation is similar to the profiles we observed at Site 253 on the Ninetyeast Ridge, where there is a sink for dissolved strontium in the volcanic sediments underlying the carbonate section (Elderfield and Gieskes, 1982).

In addition to information about the dissolved strontium maxima, Table 3 also provides the estimated depths of the carbonate ooze-chalk transitions. With as yet unexplained exceptions in the lower parts of Sites 525 and 528, predicted Sr/Ca ratios, particularly in the chalks, are in reasonable agreement with observed values. The downhole variability in Sr/Ca, however, is disturbing and makes these sites perhaps less attractive for studies of carbonate diagenesis than some of the sites studied by Baker et al. (1982). From Figure 9, especially in Sites 525 and 526, one does note increases in the Mg/Ca ratio in carbonates, when Sr/Ca ratios show appreciable decreases. We note that this observation is in agreement with previous observations (Matter et al., 1975; Renard, 1979), but predictions of Mg/Ca ratios are still tentative in the absence of precise information about distribution coefficients (Baker et al., 1982).

At present a study of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio of interstitial waters and carbonates is under way and may shed more light on the problem of carbonate diagenesis. This approach was successfully used for Site 289 on the Ontong-Java Plateau (Elderfield et al., 1982).

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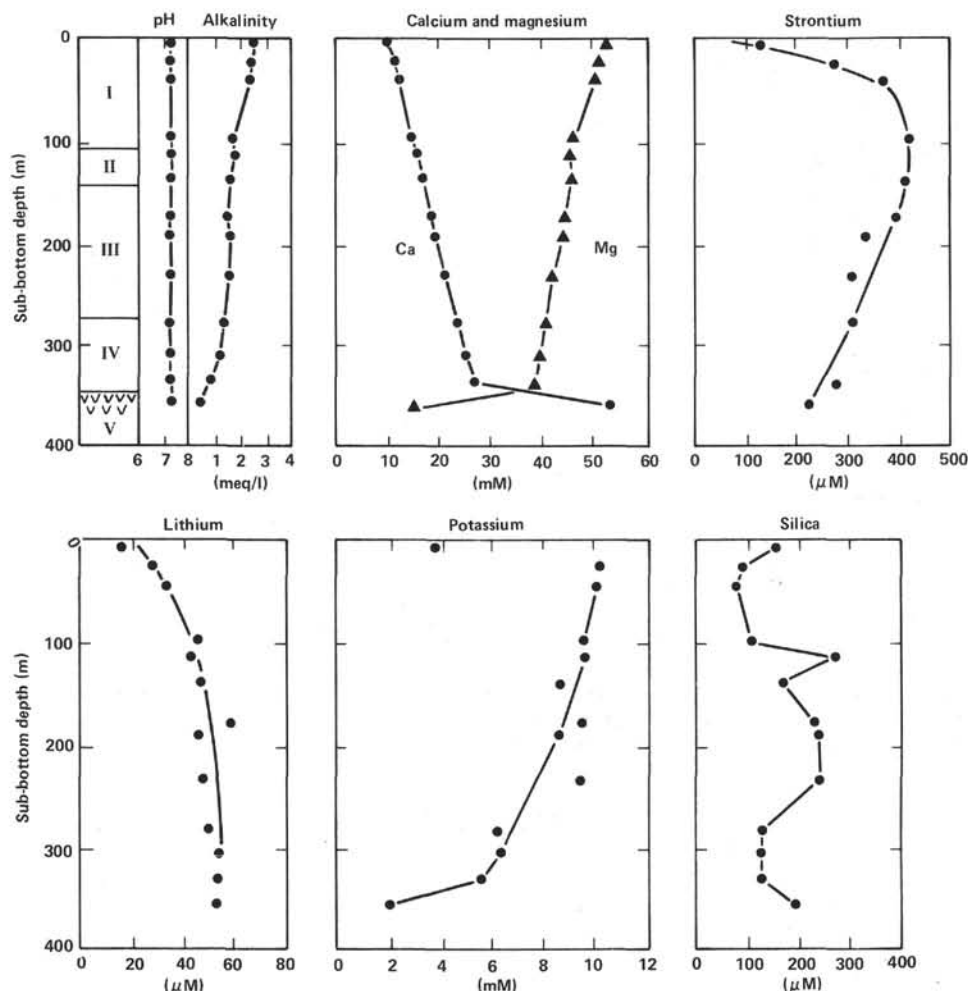


Figure 5. Interstitial water chemistry, Site 527. Lithology: I, White nannofossil and foraminifer-nannofossil ooze; II, brown marly nannofossil ooze and nannofossil clay; III, nannofossil oozes and chalks (increasing with depth); IV, red-brown nannofossil chalk and volcanogenic sediments; V, limestones and mudstones in basalts.

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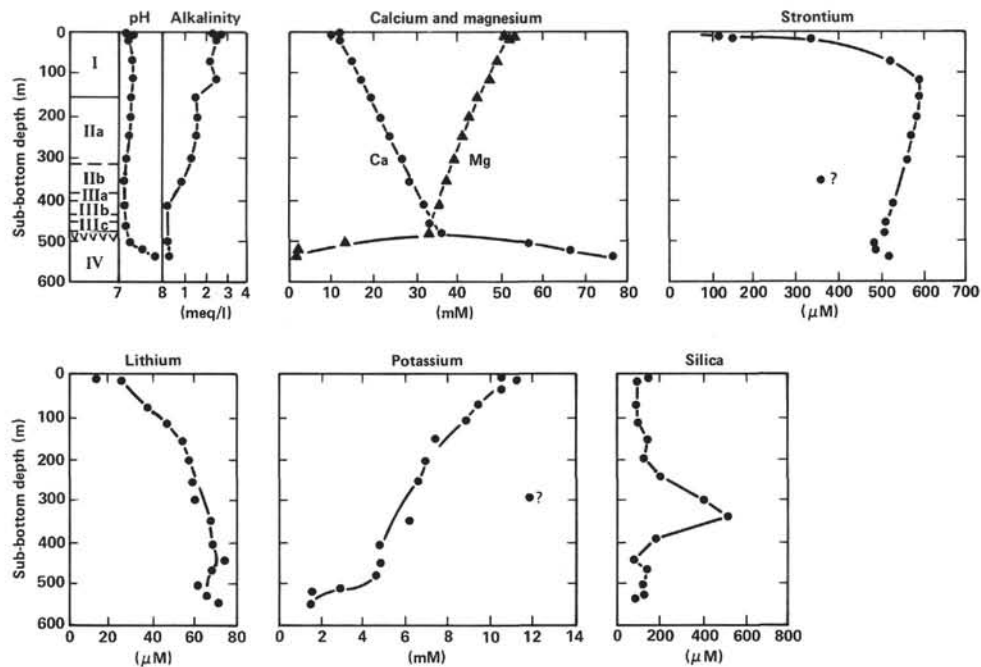


Figure 6. Interstitial water chemistry, Site 528. Lithology: I, White to pink-gray foraminifer-nannofossil ooze; II, pink nannofossil ooze and chalk (increasing with depth); III, chalks and volcanogenic sandstones; IV, basement with chalks and volcanogenic sediments.

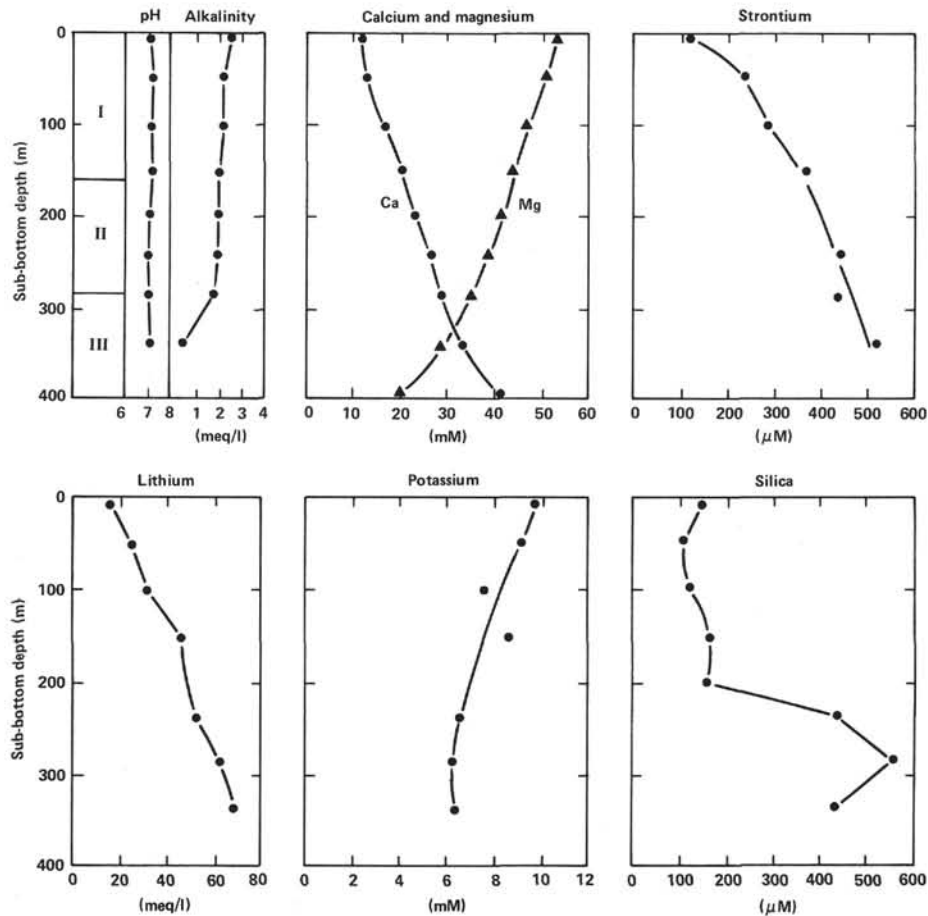


Figure 7. Interstitial water chemistry, Site 529. Lithology: I, White to pink-gray foraminifer-nannofossil ooze; II, pink nannofossil ooze and chalk (increasing with depth); III, foraminifer-nannofossil chalks.

Table 2. Carbonate compositions, Leg 74.

| Sample (interval in cm) | Depth (m) | CaCO ₃ (%) | Sr/Ca ($\times 10^{-4}$) | Mg/Ca ($\times 10^{-4}$) |
|----------------------------|--------------|--------------------------|-------------------------------|-------------------------------|
| Hole 525A | | | | |
| 3-2, 140-150 | 45 | 96.2 | 19.2 | 32 |
| 5-4, 140-150 | 95 | 99.1 | 18.0 | 56 |
| 6-4, 140-150 | 182 | 95.8 | 18.5 | 26 |
| 8-5, 140-150 | 210 | 91.9 | 19.8 | 39 |
| 11-5, 135-150 | 239 | 92.9 | 18.2 | 35 |
| 14-5, 135-150 | 274 | 96.4 | 18.1 | 31 |
| 19-3, 135-150 | 315 | 92.7 | 18.1 | 32 |
| 23-5, 135-150 | 339 | 96.8 | 8.8 | 51 |
| 26-2, 135-150 | 389 | 94.8 | 7.6 | 49 |
| 32-4, 135-150 | 411 | 92.7 | 11.6 | 44 |
| 35-6, 135-150 | 456 | 86.8 | 15.8 | 29 |
| 45-5, 140-150 ^a | 505 | 42.8 | 17.8 | (101) |
| 50-5, 140-150 ^a | 550 | 47.5 | 14.1 | (136) |
| 60-5, 135-150 ^a | 645 | 37.6 | 17.3 | (137) |
| Hole 525B | | | | |
| 1-1, 140-150 | 1 | 93.8 | 15.2 | 34 |
| 3-1, 140-150 | 9 | 91.1 | 16.7 | 30 |
| 5-2, 133-143 | 18 | 93.1 | 17.2 | 30.5 |
| 7-2, 140-150 | 28 | 94.6 | 16.2 | 32 |
| 9-3, 111-121 | 38 | 96.2 | 16.8 | 34 |
| 11-2, 140-150 | 46 | 93.5 | 17.3 | 28 |
| 13-2, 140-150 | 54 | 98.5 | 16.7 | 28 |
| 15-1, 140-150 | 62 | 90.7 | 17.7 | 31 |
| 17-1, 140-150 | 71 | 94.8 | 17.5 | 26 |
| 19-2, 140-150 | 81 | 97.2 | 17.8 | 22.5 |
| 22-2, 140-150 | 94 | 95.3 | 17.3 | 26 |
| 24-2, 140-150 | 102 | 96.6 | 18.9 | 29 |
| 26-2, 140-150 | 111 | 95.4 | 13.8 | 32 |
| 29-2, 140-150 | 124 | 93.1 | 15.0 | 32 |
| 31-2, 140-150 | 133 | 95.9 | 15.9 | 28 |
| 33-2, 140-150 | 142 | 95.2 | 17.0 | 27 |
| 35-1, 140-150 | 149 | 94.6 | 18.9 | 22 |
| 37-2, 140-150 | 160 | 93.8 | 17.7 | 28 |
| 39-2, 140-150 | 168 | 88.8 | 19.2 | 34 |
| 42-1, 140-150 | 175 | 94.0 | 17.3 | 33 |
| 45-3, 140-150 | 191 | 93.8 | 15.2 | 42 |
| 47-3, 140-150 | 201 | 93.1 | 17.9 | 40 |
| 49-3, 140-150 | 209 | 90.7 | 17.6 | 30 |
| 51-1, 135-150 | 274 | 92.9 | 15.1 | 31 |
| 53-2, 140-150 | 284 | 91.9 | 9.8 | 49 |
| Hole 526A | | | | |
| 1-1, 143-150 | 29 | 94.0 | 17.5 | 30 |
| 6-2, 143-150 | 53 | 86.0 | 17.6 | 30 |
| 11-2, 140-150 | 75 | 98.0 | 12.4 | 34 |
| 16-2, 140-150 | 97 | 93.8 | 15.3 | 35 |
| 21-2, 140-150 | 119 | 94.6 | 15.2 | 47 |
| 26-2, 140-150 | 141 | 86.8 | 20.1 | 35 |
| 31-2, 140-150 | 163 | 91.7 | 13.8 | 43 |
| 36-2, 140-150 | 185 | 92.9 | 11.7 | 54 |
| 41-2, 143-150 | 207 | 95.2 | 12.4 | 51 |
| 45-2, 143-150 | 225 | 95.4 | 3.4 | 129 |
| Hole 528 | | | | |
| 4-4, 140-150 | 147 | 86.4 | 18.1 | 44 |
| 9-5, 140-150 | 196 | 87.2 | 19.3 | 37 |
| 15-4, 140-150 | 251 | 85.2 | — | 28 |
| 20-2, 140-150 | 296 | 91.9 | 11.4 | 34 |
| 26-1, 140-150 | 351 | 79.0 | 13.7 | 30 |
| 32-3, 140-150 | 411 | 76.5 | 12.8 | 37 |
| 36-5, 140-150 | 452 | 71.6 | 17.1 | 44 |
| 39-1, 0-10 | 474 | 58.9 | 20.5 | 60 |
| 42-2, 51-66 ^a | 503 | 18.0 | — | 112 |
| 43-1, 48-58 ^a | 510 | 33.8 | — | 52 |
| 46-4, 135-140 ^a | 542 | 36.2 | — | 28 |

^a Unwashed sediment; low in carbonate; data in parentheses could be affected by exchangeable Mg.

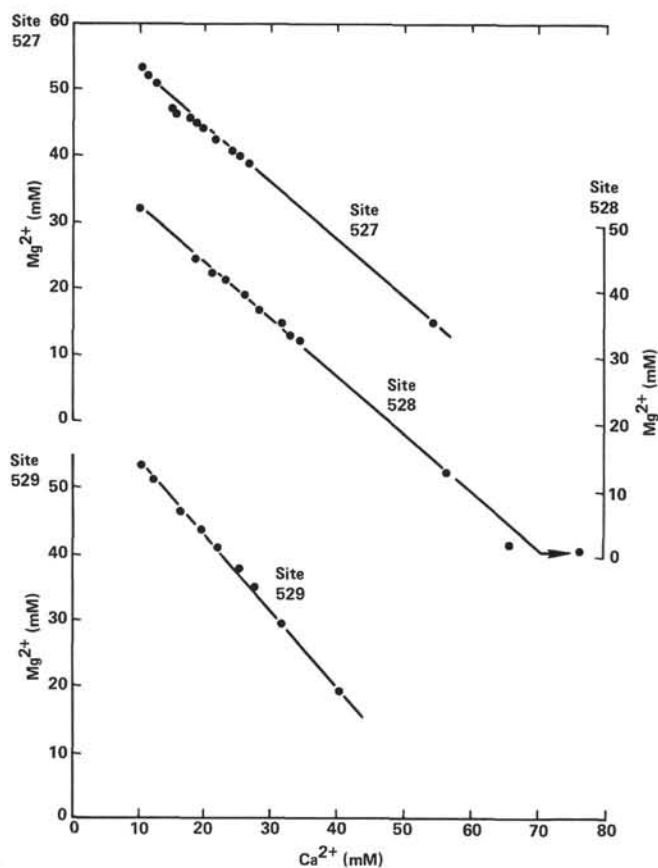


Figure 8. Mg-Ca correlations, Sites 527, 528 and 529.

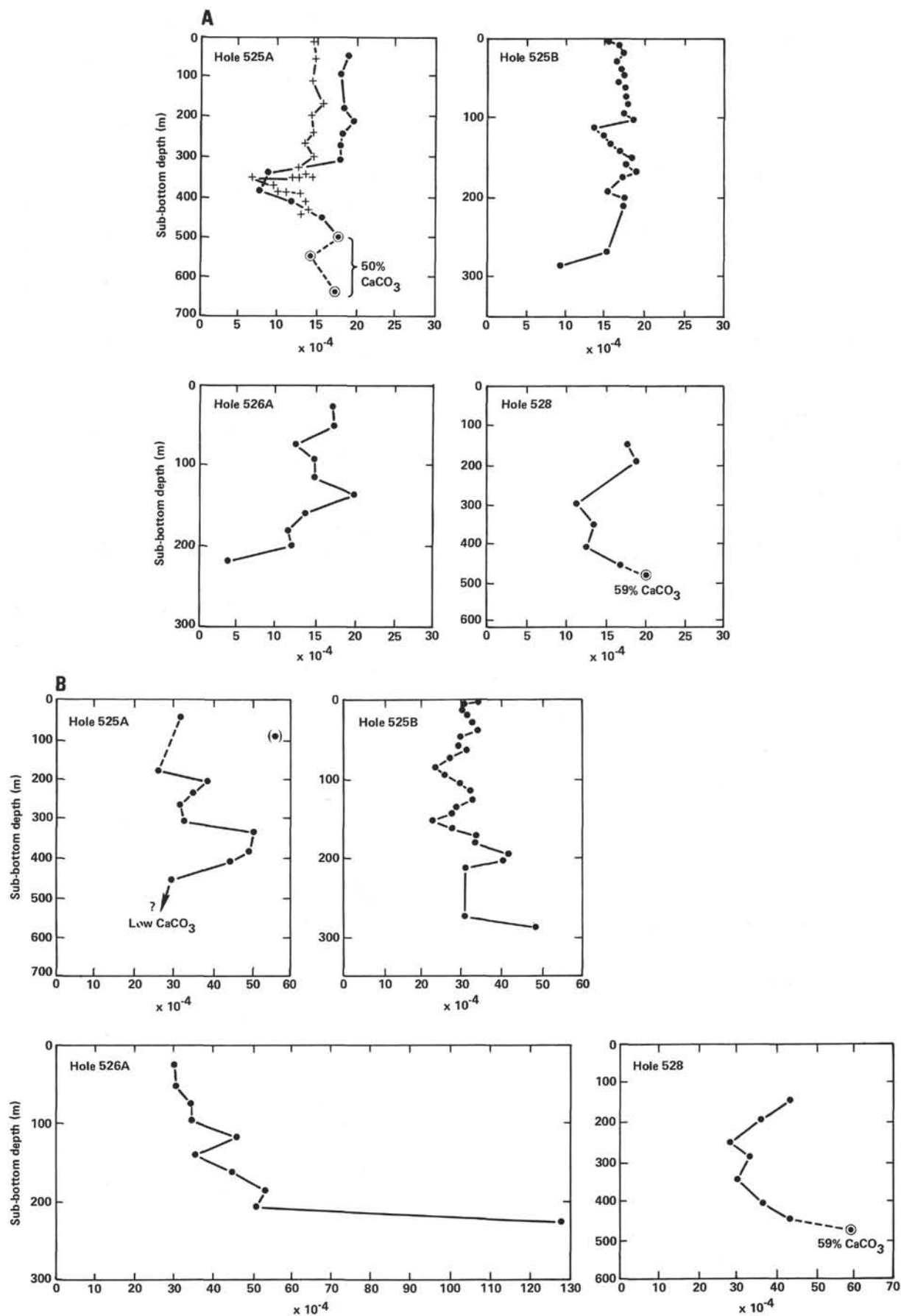


Figure 9. A. Sr/Ca ratios in carbonates of Sites 525, 526, and 528. B. Mg/Ca ratios in carbonates of Sites 525, 526, and 528.

Table 3. Strontium geochemistry of carbonates, Leg 74.

| Site | Sr Maximum | | | Ooze-chalk Transition (m) | | | Sr/Ca (atomic) $\times 10^{-4}$ | |
|------|----------------------|---------------------------------|-------------------------|---------------------------|-------|----------|--|--|
| | Sub-bottom Depth (m) | Concentration (μM) | | Start | Large | Complete | | |
| | | Observed | Calculated ^a | | | | | |
| 525 | 175 | 730 | 740 \pm 70 | 260 | — | 400 | 270 m | Observed: 8–15 Calculated ^b : 12.9 |
| | | | | | | | 400 m | Observed: 11.5 Calculated: 9.0 |
| | | | | | | | 500 m | Observed: 14 Calculated: 7.0 |
| 526 | 80 | 250 | 480 \pm 35 | 190 | — | 225 | Decrease in observed Sr/Ca below 70 m | |
| | | | | | | | 225 m | Observed: 3.4 Calculated: 3.5 |
| 527 | 110 | 400 | 660 \pm 60 | 160 | — | 240 | No information | |
| 528 | 125 | 600 | 750 \pm 70 | 160 | 200 | 350 | 300 m | Observed: > 11.5 Calculated: 10.0 |

^a Assumed $(\text{Sr}/\text{Ca})_{\text{initial}} = (16.5 \pm 1.5) \times 10^{-4}$ $\text{Sr}_{\text{max}}^{2+} = (\text{Sr}/\text{Ca})_{\text{initial}} \cdot (\text{Ca}^{2+})/0.039$; cf. Baker et al. (1982).

^b $(\text{Sr}/\text{Ca})_{\text{calculated}} = K_{\text{Sr}}(\text{Sr}^{2+}/\text{Ca}^{2+})$. K_{Sr} from Baker et al. (1982).