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ABSTRACT

Sites 417 and 418 show very similar concentration-depth gradients in sulfate (depletion), potassium (depletion), and strontium (increase) in the interstitial waters. Curvature in the sulfate profile suggests sulfate reduction throughout the sites, whereas almost linear gradients in strontium and potassium indicate reactions in the basal sediments and/or the underlying basalts. Strontium is probably due to carbonate recrystallization in the basal carbonates. No clear sink for potassium has been identified. Sites 417 and 418 mainly differ in gradients in calcium (417:larger increase) and magnesium (417:larger decrease), with linearly correlated concentration changes: $\Delta Ca/\Delta Mg = -1.43$ in Site 417 and -1.24 in Site 418. Differences in these gradients can be explained by slight differences in the nature of the underlying basalts, particularly with respect to their physical characteristics. Concentration changes in dissolved manganese indicate that reduction of manganese oxides is particularly active in sediments with higher biogenic silica contents.

INTRODUCTION

Studies of the composition of interstitial waters of DSDP cores, particularly of those obtained in areas of relatively slow sediment accumulation (< 2 cm/1000 yr), often reveal smooth concentration gradients in the major ionic constituents of sea water, particularly in dissolved calcium and magnesium. Concentration gradients in the latter two constituents have been interpreted in terms of alteration of basaltic rocks underlying the sediments, with the concentration gradients being a result of transport processes through the sediment column between the basalts and the overlying ocean. This interpretation is supported by oxygen isotope studies of the interstitial waters (Lawrence et al., 1975; McDuff and Gieskes, 1976; McDuff, 1978). When basalt alteration is mainly responsible for the observed calcium and magnesium gradients, the changes in calcium and magnesium will be linearly correlated because only transport processes are involved in the sediment column (McDuff, 1978). When substantial amounts of reactive volcanic components are present in the sediment column, concentration gradients may become more complex because of alteration reactions involving this material (Gieskes et al., 1975; Perry et al., 1975; Kastner and Gieskes, 1976; Anderson et al., 1976).

The shipboard data of Sites 417 and 418, drilled during Legs 51-53, indicated that small but distinct gradients occurred in calcium and magnesium and that these changes were linearly correlated. The basalts of Hole 417A are extensively weathered, presumably by direct interaction with sea water at relatively low temperatures. Thus, it is of interest to consider to what extent weathering processes are still occurring in these basalts.

METHODS

Samples were squeezed using the methods described by Manheim and Sayles (1974). Shipboard analyses consisted of alkalinity, pH, chloride, salinity, calcium, and magnesium. The remaining components (i.e., manganese, strontium, potassium, sulfate, silica, and ammonia) were determined using the analytical methods described by Gieskes (1974) and Gieskes and Lawrence (1976). Sulfate was determined by a polarographic method (Barnes et al., in press; Luther and Meyerson, 1975).

RESULTS

The data (including shipboard data) are presented in Table 1 and in Figures 1 and 2. Ammonia data did not appear reliable (long storage?) and therefore are not included in the figures.

DISCUSSION

Before comparing the results of Sites 417 and 418, we shall first consider the individual sites.

Site 417

Of interest in this site are the differences between Holes 417A and 417D. Basement in 417A (210 m) is substantially shallower than in 417D (345 m). The offset between the two holes is about 500 meters. Notwithstanding this depth difference, the gradients in Hole 417D below 210 meters appear continuous with those observed for Hole 417A. This implies that fluxes through the sediment column are similar in these holes. Dissolved strontium shows an almost linear gradient. We suggest that this gradient is essentially due to diffusive transport between the overlying ocean and the underlying basalts or basal carbonate sediments (Hole 417D). If strontium isotope data (Elderfield, in preparation) support the latter, the continuity of the gradient suggests that the difference in basement depth between Holes 417A and 417D does not severely interfere with the establishment of the overall vertical gradients in this site.

Sample (Interval in cm)	Depth (m)	pН	Alk (meq/1)	°/00	C1 (mM)	SO4 (mM)	Na ^a (mM)	K (mM)	Ca (mM)	Mg (mM)	Sr (mM)	Mn (mM)	NH ₄ (μM)	SiO ₂ (µM)
Hole 417A														
1-4, 144-150 6-5, 144-150	8.5 56	7.5 7.3	2.85 2.28	34.9 36.3	554 571	27.5 27.3	468 490	10.2 9.3	11.0 13.6	55.9 50.7	0.12	0.0 0.129	323 90	119 150
11-5, 144-150 16-1, 0-6 21-3, 0-10	103.5 151 198.5	7.5 6.8 7.1	1.52 1.03 1.40	36.0 36.0 36.0	566 568 571	24.8 24.5 25.0	475 470 471	8.4 9.8 6.9	19.6 24.2 27.4	46.6 43.9 43.6	0.13 0.15 0.16	0.317 0.533 0.344	459 224 276	280 894 373
Hole 417B														
1-3, 144-150	4.5	7.5	3.12	36.0	554	-	27,	-	11.6	50.5	-	$\underline{\omega}$	-	12
Hole 417D								1.67						
1-3, 144-150 8-1, 138-145 12-3, 144-150 17-1, 144-150	4.5 212.5 252.2 305.9	7.5 6.8 6.9 7.4	2.65 1.14 1.28 1.17	37.4 36.3 36.0 36.8	557 574 563 574	28.1 	481 (469) 444 467	10.1 7.8 5.9 5.5	10.7 30.1 34.2 37.3	51.5 40.9 44.9 35.3	0.11 0.18 0.20 0.21	0.411 0.289 0.098	206 140 75 80	160 678 582 351
Hole 418A														
1-2, 140-150 6-2, 144-150	120.5 168	6.9 7.0	1.30 1.26	36.3 35.8	566 568	1	-	-	$\begin{array}{c} 14.0\\ 16.0\end{array}$	50.3 50.4	-	_		1
Hole 418B														
4-3, 138-150 9-7, 0-15 15-3, 144-146 27-1, 140-150 31-2, 0-10 33-1, 0-150 ^b 34-1, 34-35	32 75 130 250 294 309 319	7.2 7.1 6.9 7.8 7.5 8.4 7.4	2.68 1.64 1.36 2.97 2.55 1.06 2.15	35.5 36.3 36.3 36.3 36.3 36.3 36.3	566 580 577 588 577 586 577	28.5 27.2 25.3 23.4 23.2 21.0 22.5	489 506 490 495 483 488 488	10.5 10.9 8.0 6.7 6.9 7.1 7.9	11.3 12.8 14.1 20.8 21.2 23.5 25.5	50.2 51.4 50.7 45.6 45.1 42.8 41.3	0.11 0.12 0.15 0.18 0.19 0.20 0.21	0.149 0.320 0.346 0.086 0.034 0.013 0.007	75 160 130 195 50 225 (540)	161 565 281 227 487 123 110

TABLE 1 Interstitial Water Data, Legs 51-53

^aNa determined by difference.

^bInterval uncertain.

Dissolved calcium and magnesium show appreciable gradients for a site that has shown accumulation rates of less than 0.2 cm/1000 yr during the last 10 m.y. B.P. Calcium and magnesium concentration changes are linearly correlated with $\Delta Ca/\Delta Mg \approx -1.43$ (r² = 0.96).

Dissolved sulfate shows that sulfate reduction may occur throughout the sediment column.

Dissolved potassium values indicate that the main location of removal is either in the lowermost sediments or in the underlying basalts.

Dissolved manganese clearly shows that production occurs in the sediment column with a maximum occurring at approximately 150 to 160 meters. This maximum coincides with the occurrence of siliceous (Eocene) sediments, also reflected in high dissolved silica values. Similar maxima in dissolved Mn were found to coincide with high dissolved silica in sites drilled during Leg 38 (Gieskes et al., 1978). This can best be understood in terms of bacterial reduction of organic carbon in the siliceous sediments, which in turn mediates the reduction of manganese oxides. Donnelly (this volume) finds fairly high manganese concentrations in the solids above 240 meters, with highest values occurring from 195 to 240 meters and at about 115 meters. His manganese concentrations for the radiolarian clays from 130 to 160 meters are relatively low, but reduction processes may be of importance here. This mobilization of manganese in siliceous sediments may be responsible for the low MnO values in the sediments below 240 meters (Donnelly, this volume).

Gradients above and below the Mn⁺⁺ maximum appear diffusional in nature with sinks in the surface sediments (or sea water) and in the basal sediments or basalts.

Site 418

Observations in this site are similar in nature to those of Site 417, except for the much smaller gradients in calcium and magnesium. Calcium and magnesium are linearly correlated with $\Delta Ca/\Delta Mg = -1.43$ (r² = 0.996, omitting Mg⁺⁺at 30 m).

The maximum in dissolved manganese is less pronounced but centers around 90 to 100 meters, i.e., in Sub-unit 4A (radiolarian clay and ooze). Dissolved silica does not reflect this maximum, as no sample was actually taken in this unit; furthermore, dissolved silica reflects, as always, the local lithology and is much less influenced by diffusion processes. This can be understood in terms of the highly reactive nature of silica, so that local reactions dominate its concentration profile.

Dissolved sulfate, potassium, and strontium all show gradients very similar to those of Site 417. Sedimentation rates at Sites 417 and 418 have also been very similar, and we submit that reactions occurring at similar rates are responsible for these gradients.

NATURE OF CALCIUM, MAGNESIUM, AND STRONTIUM GRADIENTS IN SITES 417 AND 418

The major difference between these two sites is in the gradients in Ca^{++} and Mg^{++} . As previously indicated,



Figure 1. Interstitial water data, Holes 417A and 417D. 1 = Nannofossil clay; 2 = Pelagic clay; 3 = Zeolitic clay; 4 = Radiolarian clay and ooze; 5 = Clay; 6 = Organic claystone and chalk; 7 = Cyclic radiolarian claystone; 8 = Chalk; 9 = Basalt.

calcium and magnesium (particularly when linearly correlated) often have been interpreted in terms of basalt alteration. We expect to obtain some oxygen isotope data on the interstitial waters of these two sites in order to check on this hypothesis.

In Figure 3, we present correlations between concentrations of dissolved strontium and dissolved calcium for Sites 417 and 418. The slopes are Δ Sr/ Δ Ca = 28 × 10⁴ (Site 417) and 48 × 10⁴ (Site 418). It is important to note that concentration depth gradients of strontium are identical in both sites, thus yielding similar fluxes. We interpret this in terms of strontium released to the interstitial waters during carbonate recrystallization reactions in the basal carbonates. Differences in Δ Sr/ Δ Ca indicate that calcium is released by different reactions, most probably during alteration of the underlying basalts. Studies of the strontium isotopes of the interstitial waters (in progress) will be relevant here.

In view of the above considerations, we feel confident that the gradients in calcium and magnesium are due to reactions in the basalts, with an uptake of magnesium (smectites?) and a release of calcium. McDuff (1978) suggests that gradients in calcium and magnesium in sediments above reactive basalts may be regulated by the physical nature of the underlying basalts, inasmuch as pillow basalts are probably more open to diffusion into or out of the basalts than massive flows. To a large extent, the upper 50 meters of basalts in Hole 418A constitute such massive flows, whereas Holes 417A and 417D typically have pillow lavas in the upper 50 meters of basalts. Thus, one would expect a less-pronounced gradient in calcium and magnesium in Site 418. In addition, the slope $\Delta Ca/\Delta Mg$ in Site 418 would be smaller than in Site 417 (McDuff, 1978), as is indeed the case.

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Figure 2. Interstitial water data, Hole 418B. 1 = Nannofossil clay; 2 = Pelagic clay; 3 = Zeolitic clay; 4A = Radiolarian clay and ooze; zeolitic clay; 4B = Clay; 4C = Zeolitic clay; 5 = Multicolor clay; 6 = Organic clay and chalk; 7 = Cyclic radiolarian clay; 8 = Black clay and chalk; 9 = Basalt.

REFERENCES

- Anderson, T.F., Donnelly, T.W., Drever, J.I., Eslinger, E., Gieskes, J.M., Kastner, M., Lawrence, J.R., and Perry, E.A., 1976. Geochemistry and diagenesis of deep sea sediments: Leg 35, DSDP, *Nature*, v. 473, p. 261.
- Barnes, R.O., Gieskes, J.M., Horvath, J., and Akiyama, W., in press. Interstitial water studies, Leg 47A, B. In Ryan, W.B.F., et al., Initial Reports of the Deep Sea Drilling Project, v. 47, Part 2: Washington (U.S. Government Printing Office).
- Gieskes, J.M., Horvath, J., and Akiyama, W., in press. Interstitial water studies, Leg 47A, B. In Ryan, W.B.F., et al., Initial Reports of the Deep Sea Drilling Project, v. 47, Part 2: Washington (U.S. Government Printing Office).
- Gieskes, J.M., 1974. Interstitial water studies, Leg 25. In Simpson, E.S.W., Schlich, R., et al., Initial Reports of the Deep Sea Drilling Project, v. 25: Washington (U.S. Government Printing Office), p. 361.
- Gieskes, J.M., Kastner, M., and Warner, T.B., 1975. Evidence for extensive diagenesis, Madagascar Basin, Deep Sea Drilling Site 245, Geochim. Cosmochim. Acta, v. 39, p. 1385.
- Gieskes, J.M. and Lawrence, J.R., 1976. Interstitial water studies, Leg 35. In Hollister, C.D., Craddock, C., et al., Initial Reports of

the Deep Sea Drilling Project, v. 35: Washington (U.S. Government Printing Office), p. 407.

- Gieskes, J.M., Lawrence, J.R., and Galleisky, G., 1978. Interstitial water studies, Leg 38. In Supplement to volumes 38, 39, 40, and 41, Initial Reports of the Deep Sea Drilling Project: Washington (U.S. Government Printing Office), p. 121-134.
- Kastner, M. and Gieskes, J.M., 1976. Interstitial water profiles and sites of diagenetic reactions, Leg 35, Bellingshausen Abyssal Plain, *Earth Planet. Sci. Lett.*, v. 33, p. 11.
- Lawrence, J.R., Gieskes, J.M., and Broecker, W.S., 1975. Oxygen isotope and cation composition of DSDP pore waters and the alteration of Layer II basalts, *Earth Planet. Sci. Lett.*, v. 27, p. 1.
- Luther, G.W. and Meyerson, A.L., 1975. Polarographic analysis of sulfate ion in seawater, Anal. Chem., v. 47, p. 2058.
- Manheim, F.T. and Sayles, F.L., 1974. Composition and origin of interstitial waters on marine sediments, based on deep sea drill cores. *In* Goldberg, E.D. (Ed.), *The Sea*: New York (Wiley Interscience), v. 5, p. 895.
- McDuff, R.E., 1978. Conservative behavior of calcium and magnesium in the interstitial waters of marine sediments: identification and interpretation, Ph.D. thesis, University of California, San Diego.



Figure 3. Sr-Ca correlations, Holes 417A, 417D, and 418B.

McDuff, R.E. and Gieskes, J.M., 1976. Calcium and magnesium profiles in DSDP interstitial waters: diffusion or reaction?, *Earth Planet. Sci. Lett.*, v. 33, p. 1.

