APPENDIX. INTERSTITIAL WATER STUDIES, LEG 661

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ABSTRACT

During Leg 66, a transect was drilled across the Middle America Trench off Mexico. In this report, interstitial water analyses for Sites 487 (on oceanic crust), 490, 491, and 492 (continental slope apron), and 493 (upper continental slope) are presented. All sites are characterized by high sedimentation rates, and as a result sulfate reduction and methane generation processes are very important. At Sites 490 through 492 decreases in chlorinity are evidence of the presence of gas hydrates. At Site 493 a sharp increase in dissolved calcium and the complete depletion of dissolved magnesium just above basement indicate that weathering of continental crust is still an ongoing process.

INTRODUCTION

During Deep Sea Drilling Project Leg 66, drilling was done at a series of sites across the Middle America Trench off Mexico (Fig. 1; Watkins, Moore, et al., 1982). A number of sites, particularly Sites 490, 491, and 492, were characterized by the occurrence of solid gas hydrates (Shipley and Didyk, 1982). Similar observations were made at Sites 496 and 497 of the more southern transect of DSDP Leg 67 (Hesse and Harrison, 1981: Harrison et al., 1982). These latter sites, as well as some additional shelf sites, were revisited during DSDP Leg 84, and again hydrates were found (Aubouin, von Huene, et al., this volume).

A typical observation at sites containing gas hydrates is that chlorinities decrease with depth, often coinciding with increases in the δ^{18} O of the interstitial waters (Harrison et al., 1982; Jenden and Gieskes, 1983). Whereas at Sites 496 and 497 gradual decreases in chloride concentrations with depth were observed, at other sites for example, Site 533 (Jenden and Gieskes, 1983) and Site 596 (Kvenvolden and McDonald, this volume), only minimal decreases in chloride have been observed. Harrison et al. (1982) concluded that the decrease with depth in chloride concentrations could be understood best in terms of the decomposition of hydrates during the interstitial water retrieval process. Apparently even the in situ interstitial water sampler employed during Leg 84 was not immune to these artifacts (Hesse et al., this volume).

During Leg 66, samples of interstitial waters were taken, but no shipboard analytical program was carried out. Because of the findings of Legs 67 and 84, however, we decided to carry out analyses of interstitial waters collected during Leg 66 in representative holes of the transect. For this purpose we chose Sites 487, 490, 491, 492, and 493 (Fig. 1).

METHODS

Samples collected on board ship and stored in polyethylene tubes were used in this study. Before opening the tubes, we shook them vigorously with the aim of suspending any calcium carbonate that may have precipitated from these samples during storage. This precipitation is particularly a concern when alkalinity values are well in excess of 20 meg \cdot dm⁻³ (Gieskes, 1973). After the sample was shaken, an aliquot of 10 cm3 was titrated for alkalinity using the method of Gieskes and Rogers (1973). This titrated aliquot was used subsequently for the determination of dissolved calcium, magnesium, sulfate, ammonia, and silica; we employed methods described previously by Gieskes (1973, 1974) and Gieskes and Lawrence (1976). It was assumed that any possible suspended carbonate would be redissolved during the alkalinity titration. Dissolved chloride was determined on a nonacidified aliquot by means of a Mohr titration (Gieskes, 1974). The data are presented in Table 1 and in Figures 2 through 7.

DISCUSSION

Site 487

The upper ~ 100 m of the Hole 487 sediment column are characterized by very high sedimentation rates (~ 125 m/m.y.), whereas the deeper sections show much reduced sedimentation rates ($\sim 7 \text{ m/m.y.}$ from 100-150 m; ~ 29 m/m.y. from 150-170 m). Organic carbon contents decrease gradually with depth and are low in unit II. Basalt basement was encountered at 171 m (Site 487 report; Watkins, Moore, et al., 1982).

As a result of the higher sedimentation rates in the upper 100 m, and because of the enhanced organic carbon contents (Site 487 report-Watkins, Moore, et al., 1982) in these sediments, sulfate reduction processes are very important in the upper 50 m. Below this depth dissolved sulfate returns to concentrations only slightly less than those of seawater. Such minima in dissolved sulfate are typical in sediment columns in which the upper section is characterized by high sedimentation rates and higher organic carbon contents (Gieskes, 1975, 1981; Gieskes et al., 1979). As a result of the sulfate reduction process, which is microbially mediated, maxima in ammonia and alkalinity are observed.

Dissolved calcium indicates a minimum (Fig. 2) as a result of carbonate precipitation processes in situ (Gieskes, 1975, 1981). The slight minimum in dissolved

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Figure 1. A. Location of Leg 66 sites. B. Schematic cross section (from Watkins, Moore, et al., 1982).

magnesium is probably the result of uptake in clay minerals. It is important to note that the underlying basement rocks have no influence on either the dissolved calcium or magnesium profiles. Dissolved silica reflects the presence of biogenic silica in these sediments. Changes in dissolved chloride are not significant at this site.

Sites 490 to 492

At Sites 490 through 492, all located on the landward side of the Trench (Fig. 1), drilling penetrated into sediments of the slope apron. Sedimentation rates in all three sites have been high (Site 490, $\sim 100 \text{ m/m.y.}$; Site 491, 25 m/m.y. in upper 75 m. > 1000 m/m.y. below 75 m; Site 492, 15 m/m.y. in upper 100 m, 30–40 m/m.y. below 100 m (Watkins, Moore, et al., 1982). As a result of both the high sedimentation rates and the high organic carbon contents of these sediments (Shipley and Didyk, 1982), sulfate reduction is completed at very shallow depths. Below these depths generation of methane and carbon dioxide are of great importance. The latter is reTable 1. Interstitial water data, Leg 66.

Sample (interval in cm)	Sub- bottom depth (m)	Alkalinity (meq · dm ^{- 3})	Ca (mM)	Mg (mM)	Cl (g·kg ¹)	SO4 (mM)	NH4 (μM)	Si (µM
Hole 487								
2-4, 110-146	6	15.9	6.7	63.0	19.38	18.1	1614	408
3-4, 140-150	16	34.1	4.5	50.5	19.70	2.75	2794	630
5-2, 140-150	32	33.1	3.1	48.7	19.44	2.73	2635	041 784
10-5, 140-150	84	13.7	5.2	48.3	19.83	9.44	1365	743
12-3, 140-150	100	12.9	5.0	49.2	19.77	-	1032	473
15-6, 140-150 18-6, 140-150	133	6.3	10.3	53.7	19.74	23.3	306	690 658
Hole 490								
1-3, 140-150	4	11.0	9.11	51.81	19.66	21.96	761	595
3-5, 140-150	26	56.7	0.69	53.63	19.97	0.0	5639	697
4-4, 140-150	34	68.1	0.90	58.10	19.57	1.72	7033	426
5-5, 140-150	45	69.7	0.76	60.08	19.64		7738	346
15-3, 140-150	137	119.8	2.64	58.08	18.49	2.23	16,180	163
18-5, 140-150	168	78.9	0.80	41.93	18.72		14,726	282
21-5, 140-150	197	91.0	0.43	48.04	18.92	7.80	14,130	418
25-3, 140-150	235	49.9	2 32	49.57	19.97		16,749	700
34-2, 140-150	305	32.9	1.19	35.54	20.55	8.18	10,248	604
40-5, 140-150	368	20.1	5.22	31.57	19.64	-	8452	389
54-3, 110-120 59-3, 140-150	488	16.4	6.15 14.8	34.13	20.16	4.85	6567 5404	546 493
Hole 491								
1-5, 140-150	7	19.8	7.36	46.88	19.47	5.95	2472	821
2-3, 140-150	14	20.0	6.43	44.60	18.75	2.45	2999	701
4-4, 140-150	31	35.3	2.74	39.51	19.05	-	9858	810
5-2, 140-150	39	33.7	1.43	39.73	18.79	-	11,540	761
7-5, 140-150	65	42.0	1.27	33.13	18.13	8.71	22,670	481
9-2, 140-150	117	30.0	4.15	25.67	15.32	0	28,323	503
19-3, 140-150	166	27.0	0.34	26.06	15.19		31,090	606
25-5, 140-150	217	37.1	0.99	32.37	16.37	0	31,734	718
30-5, 140-150	310	34.1	1.20	26.89	17.35	2.51	34,034	641
41-4, 140-150	367	38.7	2.68	26.16	14.76	-	32,882	692
48-5, 140-150 54-1, 140-150	435 488	8.1 9.9	5.87 4.81	37.03 32.86	17.94 17.84	17.89 4.55	22,979 23,022	657 553
Hole 492								
1-2, 140-150	3	8.8	9.45	51.50	19.38	22.48	1608	703
2-4, 140-150	9	18.2	7.13	48.94	19.47	12.16	8886	880
3-4, 140-150	19	16.2	4.57	43.47	19.05	9.12	2418	922
5-4, 140-150	38	20.0	5.59	43.93	19.16	0	3589	785
8-2, 140-150	63	16.0	6.82	39.46	18.13	-	4485	904
11-3, 140-150	93	10.3	6.45	38.78	17.80	0	9054	645
20-5, 140-150	182	14.0	18.66	34.66	17.02	0	10,601	731
23-5, 140-150	210	11.9	22.16	32.16	16.53	0	11,020	714
Hole 493								
1-3, 140-150	4	12.8	9.46	52.66	19.31	23.20	1412	578
3-1, 140-150	131	23.8	7.57	36.85	19.37	2.54	7710	550
5-3, 140-150	153	11.3	3.16	33.75	19.05		8835	838
7-2, 140-150	170	9.2	3.04	33.65	18.92	-	9390	834
11-2, 140-150	208	7.8	3.35	34.07	19.18	_	12,017	878
16-3, 86-96	257	4.9	7.31	37.61	19.11	-	2335	835
21-5, 140-150	308	8.8	13.14	31.33	20.72	0	20,108	654
31-5, 140-150	342	7.6	20.34	33.55	19.05	8.44	5795	819
36-3, 140-150	447	3.1	29.6	32.48	18.72		5658	183
41-2, 140-150	493	1.9	36.7	27.38	18.65	7.84	5445	119
46-4, 140-150 54-5, 140-150	620	1.6	136.3	1.17	17.55	4.35	2510	91
Hole 493A								
2-2, 143-150	5	26.0	2.32	52.57	20.16	_	2946	787
Hole 493B							-32605.0	16.574
1-2, 140-150	15	28.1	1.96	51.63	19.31	0	3426	797
2-4, 140-150	38	38.5	3.71	36.60	19.24	4.48	7411	723
5-2, 140-150	53	22.7	0.80	35.59	18.78	0	4734	738
7-2, 140-150	72	28.1	2.01	41.54	19.18	-	6418	739

Note: - indicates no data.



Figure 2. Interstitial water composition, Site 487. Lithology: I. hemipelagic mud, silt, and clay-Quaternary; II. brown pelagic clay-Miocene and Pliocene; III. basalt.

flected in elevated levels of alkalinity (HCO $\frac{1}{3}$) at all three sites. In addition, the process of de-ammonification, which accompanies the bacterial processes of methane generation, leads to very high levels of dissolved ammonia. At Site 490, which is characterized by a continuous high sedimentation rate, increases in ammonia are up to 20 mM, and here dissolved magnesium indicates a maximum at ~90 m (Fig. 3). Moore and Gieskes (1980) and Gieskes et al. (1982) have shown that this maximum can be explained best in terms of ion exchange with the clay phases, that is, enhanced NH⁺₄ concentrations will lead to significant release of magnesium ions from exchange positions. At Sites 491 and 492 this process is not evident in the magnesium profiles (Figs. 4 and 5). This is of particular interest for Site 491, which shows a very large increase in dissolved ammonia in the upper 100 m. Sedimentation rates, however, are much lower in the upper 75 m at Site 491, thus allowing diffusive processes to smooth out any anomalies created by the ion exchange processes observed at Site 490. These observations demonstrate the complexity of the processes that need to be considered in any evaluation of concentration-depth profiles.

Calcium concentrations, especially in the upper sediment sections, are low as a result of calcium carbonate precipitation during the generation of HCO_3^- (alkalinity). In all three sites undocumented processes (uptake in clays? dolomitization of carbonates?) has led to depletions in dissolved magnesium.

Of importance are the chloride decreases with depth when consideration is given to the cation concentration changes in calcium and magnesium observed at these sites. If chloride decreases are large and if these decreases are the result of artifacts caused by hydrate decomposition, then actual concentration changes in calcium and magnesium may be less severe as observed. For instance, Sample 491-41-4, 140-150 cm indicates a chloride depletion of $\sim 25\%$, whereas the magnesium depletion is $\sim 50\%$. However, it is difficult to assess the artifact in the magnesium depletion estimate, especially because changes in the sodium concentration may have affected exchangeable calcium and magnesium concentrations. Hesse et al. (this volume) have tried to assess similar effects at Leg 84 sites.

An important observation in the chloride-depth profiles of the sites drilled during Leg 66 is that chloride decreases with depth are not gradual, but show large variations with depth. The well developed chloride minimum at Site 490 coincides with the depth from which solid hydrates have been recovered (Shipley and Didyk, 1982). Below 250 m at Site 490 chlorinities are relatively normal, although hydrates have been recovered from nearby horizons. Chlorinities at Site 491 show substantial depletions throughout the site, particularly below about 90 m, that is, in the rapidly deposited lower sediment section. Dissolved ammonia values are in excess of 30 mM. The variability in dissolved chloride with depth can be understood best in terms of variable hydrate contents. At Site 492 chlorinity decreases are relatively gradual, and we postulate that methane-hydrate formation is continuous with depth, as is also evident from the continuous rise in dissolved ammonia.

With the exception of Site 492, chlorinity variations are extremely variable at the three sites studied on the slope apron (Sites 490, 491, 492; see Fig. 1). Shipley and Didyk (1982) suggest that hydrates occur mainly in restricted zones consisting of porous volcanic ash or sand layers. Similar variability in chlorinity has been observed at Site 533 (Jenden and Gieskes, 1983). The hydrate decomposition hypothesis (Harrison et al., 1982; Hesse et al., this volume) suggests that the observed decreases in chlorinity are caused by the dilution effect on pore waters as a result of hydrate thawing after recovery. The variability in dissolved chloride can thus best be understood in terms of an uneven distribution of hydrates in these sediments. This contrasts with the situation at sites drilled during Legs 67 and 84 (Sites 496, 497, and 568) in which gradual, reasonably smooth chloride gradients



Figure 3. Interstitial water composition, Site 490. Lithology: I. muddy silt, mud-Quaternary; II. muddy siltstone-Pliocene, lowermost Quaternary; III. muddy siltstone, chalk and ash beds-Pliocene, Miocene. (Data in parentheses may be uncertain.)



Figure 4. Interstitial water composition, Site 491. Lithology: I. olive green mud and silt—Quaternary and upper Pliocene; II. muddy silt and muddy siltstone—lower Pliocene; III. muddy silt, siltstone, pebbly sands—early Pliocene.



Figure 5. Interstitial water composition, Site 492. Lithology: I. muddy silt and siltstone-Quaternary to upper Miocene.

were observed, suggesting a gradual increase of hydrates throughout the sediment column sampled (Harrison et al., 1982; Hesse et al., this volume).

Site 493

Drilling at this site occurred at a shallow water depth of 645 m and bottomed in continental diorite basement. Average sedimentation rates have been ~ 45 m/m.y.

As a result of high sedimentation rates and high organic carbon contents, sulfate reduction is complete at ~20 to 30 m sub-bottom depth, and below this depth generation of methane and ethane is observed (Site 493 report, Watkins, Moore, et al., 1982). Typically, maxima occur in alkalinity in the upper 50 m but at ~ 300 m a very sharp maximum in ammonia occurs (Figs. 6 and 7) that is, at the base of the zone of almost zero dissolved sulfate. Chlorinity data, however, do not suggest large depletions with depth, although a small gradual decrease with depth is observed. Gas hydrate formation in this site—if any—must be of minor importance.

Below 400 m, large increases in dissolved calcium and the complete disappearance of magnesium at the base of the sediment section indicate that alteration reactions involving the diorite basement leave an imprint of the interstitial waters.

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Figure 6. Interstitial water composition, Hole 493. Lithology: I. muddy silt—Quaternary; II. muddy silt, siltstone, mudstone—Pliocene and late Miocene; III. muddy siltstone to sandstone—early Miocene; IV. diorite.



Figure 7. Interstitial water composition, Holes 493A and B. Lithology: I. muddy silt-Quaternary; II: muddy silt, siltstone, mudstone-Pliocene and late Miocene.