34. INTERSTITIAL WATER STUDIES, LEG 79¹

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ABSTRACT

Interstitial water analyses of samples collected at Sites 544-547 of DSDP Leg 79 are presented. In Site 547 chloride concentrations increase to almost 80% of the halite saturation values. Gypsum occurrences in the sediments immediately overlying the halite deposit can be explained in terms of migration of Ca^{2+} and SO_4^{2-} from the underlying evaporites. At shallower depths sulfate concentrations decrease rapidly as a result of sulfate reduction processes. The same processes lead to the removal of calcium in the form of calcium carbonate. At Site 547, the chloride concentration depth profile suggests a maximum of dissolved chloride which may be the result of advective flow from nearby (~6 km) evaporite salt diapirs.

INTRODUCTION

Leg 79 of the Deep Sea Drilling Project visited the region of the Mazagan Plateau (Fig. 1) in April-May, 1981. Four sites were drilled and, in all, interstitial water samples were obtained from considerable depths in the sediment column. Drilling reached continental basement at Site 544 and a salt diapir at Site 546; Site 547 deeply penetrated Jurassic sediments. Site 545 was located just down slope of the Mazagan Escarpment. The sites drilled during Leg 79 are part of an extensive drilling program off North Africa, previously studied during DSDP Legs 14, 41, and 50.

In this report we present briefly both the interstitial water analyses carried out on board ship as well as in our laboratory. Site 546 is of special interest because it did reach halite/anhydrite-gypsum/sylvite salts at the base of the drill hole.

METHODS

Shipboard data include pH, alkalinity, calcium, magnesium, chloride, and salinity. To these we have added silica, ammonia, sulfate, strontium, potassium, and lithium. The methods used have been described by Gieskes (1974), Gieskes and Lawrence (1976) and Gieskes and Johnson (1981). The results are presented in Table 1. Additional shipboard data are given in Table 2.

DISCUSSION

Site 544 (Fig. 2)

Site 544 was drilled on a sialic basement high. The sediments of the upper 100 m have accumulated at rates between 8-15 m/m.y. A large hiatus separates the Miocene and Jurassic sediments at 103.8 m sub-bottom (see site chapter, this volume).

As a result of the relatively slow accumulation rate in the upper 100 m, only minor depletions in dissolved sulfate are observed accompanied by small increases in dissolved ammonia. Changes in dissolved calcium and magnesium are relatively small. A slight maximum in dissolved strontium is probably related to carbonate recrystallization processes occurring in the Miocene carbonate oozes (Baker et al., 1982).

In general, the interstitial water data from Site 544 indicate that diagenetic reactions occurring in the sediments leave only a minor imprint on the interstitial water composition.

Site 545 (Fig. 3)

The upper 100 m of Site 545 consist of rapidly accumulated Pleistocene foraminiferal-nannofossil oozes below which sediments occur that are characterized by much slower accumulation rates. A large hiatus occurs at 252 m (early Miocene/Cenomanian).

As a result of the recent rapid accumulation of Pleistocene sediments, a minimum in dissolved sulfate occurs together with maxima in dissolved ammonia and alkalinity. In addition, a slight minimum in dissolved calcium occurs at ~ 50 m as a result of calcium carbonate precipitation. Such observations are typical for sediment columns characterized by rapid sedimentation in recent times (Gieskes, 1975; 1981).

Increases with depth in dissolved calcium and decreases in magnesium level off between 200-250 m depth implying reactions involving these constituents in the upper sediment section. Dissolved strontium shows a welldefined maximum at ~ 250 m, i.e., at the base of the Miocene siliceous chalk section. This again can be understood in terms of carbonate recrystallization reactions. The magnesium and calcium profiles, however, are not necessarily related to carbonate diagenesis (Baker et al., 1982; Elderfield et al., 1982).

Changes in dissolved silica are related to the relative contributions of siliceous materials in the sediments; typically, Unit II contains relatively more opaline silica.

Site 546 (Fig. 4)

This site is of particular interest because it was drilled into a salt deposit consisting mainly of halite, with minor contributions of anhydrite and sylvite. Shipboard data indicated a steep increase in dissolved chloride values to

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Figure 1. Map of work area, Leg 79.

as high as 135 g/dm³ (~3.9 molar). McDuff et al. (1978) showed that in sites affected by evaporitic chloride deposits at depth, dissolved chloride gradients are conservative in nature. The slight curvature in the dissolved chloride profile is probably the result of the relatively rapid rate of accumulation (~22 m/m.y.) of the sediments of Unit I (McDuff, 1978). The conservative nature of the dissolved chloride gradient allows an examination of the remaining anion and cation gradients in the interstitial waters.

Na Versus C1: Sodium concentrations were calculated by charge balance considerations. The data are plotted versus chloride concentrations in Figure 5. Linearity implies conservative behavior of dissolved sodium. In addition the data imply that mixing occurs between seawater and an almost pure sodium chloride brine. Increases in dissolved potassium are very small indicating a negligible influence of sylvite dissolution. The data in Figure 4 extrapolate to a chloride concentration at the sedimentsalt contact of about 150 g/dm³, equivalent to a solution of ~4.2 M NaCl.

Ca Versus C1: The plot of calcium versus chloride concentrations (Fig. 6) clearly indicates a nonlinear profile, whereas the calcium versus sulfate plot is linear. These correlations imply that calcium and sulfate at the base of the hole originate from gypsum (or anhydrite) dissolution, but both calcium and sulfate are removed in equivalent proportions from the interstitial waters in the sediment column above the salt deposit. We suggest that this removal of both sulfate and calcium can be understood in terms of sulfate reduction processes and concomitant carbonate precipitation.

Mg Versus C1: The plot of magnesium versus chloride (Fig. 6) is linear, implying a sink for magnesium in the sediments just above the salt deposits or in the salt deposit itself.

The observation that chloride concentrations estimated from extrapolation of the chloride concentration depth profile are about 150 g/dm³, whereas saturation concentrations would be ~190 g/dm³ or 5.37 M is of some interest. The extrapolated chloride concentrations are about 78% of the saturation values. Perhaps a much steeper gradient in chloride occurs, partly as a result of gypsum cementation of pore spaces, at the interface between the salt deposits and the overlying sediments.

The gypsum problem is of interest in these sediments. Gypsum solubility data in sodium chloride brines (Marshall and Slusher, 1966; Harvie and Weare, 1980) are presented in Figure 7. Data have been converted to the molarity scale using the density data of Danielson et al. (1980) for sodium chloride-seawater mixtures. Note that in an NaC1-saturated brine (~ 5.37 M) gypsum solubility is less than in a brine of 4.2 M. In the sediments just above the salt deposit, using extrapolated concentrations of $[Ca^{++}] \approx 40$ mM and $[SO_4^{-}] \approx 60$ mM, an ion product of $[Ca^{++}] [SO_4^{-}] = 0.0024 \text{ mol}^2/\text{dm}^6$ is obtained. Using the data of Marshall and Slusher (1966), given in Figure 7, one obtains a saturation solubility product of $0.0023 \text{ mol}^2/\text{dm}^6$ for a 4.2 M NaCl solution, that is, in very good agreement with the estimated *in situ*

Table 1. Interstitial water data, Leg 79.

Sample (interval in cm)	Sub-bottom depth (m)	pH	Alk (meq/dm ³)	(g/kg ⁻¹)	Ca (mM)	Mg (mM)	Cl (g/dm ³)	Sr (µM)	Li (µM)	K (mM)	SO4 (mM)	NH4 (μM)	Si (µM)
Hole 544													
1-1, 144-150	2	7.29	2.87	35.7	10.7	51.3	20.06	80.4	43.6	12.4	29.2	20	208
Hole 544A													
2-4, 144-150	13	7.24	2.91	36.0	10.9	51.0	20.13	111.3	47.0	13.7	28.1	53	192
4-1, 144-150	27	7.22	2.54	35.8	11.9	48.7	20.03	135.4	48.5	13.0	26.5	64	145
8-2, 144-150	67	7.31	2.20	35.9	13.4	45.8	20.13	159.7	52.0	10.8	28.0	64	162
20-1, 144-150	158	7.34	2.54	36.0	14.3	48.7	20.31	86.3	46.9	13.7	28.1	61	327
Hole 545													
2-4, 144-150	14	7.24	5.96	35.3	8.0	51.7	19.75	76.5	52.1	11.8	24.9	302	237
8-3, 144-150	70	7.21	8.05	35.1	6.3	49.7	19.83	142.8	74.9	12.3	16.6	325	326
12-4, 144-150	109	7.25	4.70	34.2	9.9	45.1	19.75	232.9	86.9	11.2	17.6	708	191
19-3, 144-150	174	7.42	2.41	35.1	12.8	42.2	19.62	369.6	107.5	11.6		558	167
23-3, 144-150	212	7.15	2.97	35.1	15.1	40.6	19.86	402.7	106.5	11.3	19.4	474	614
27-3, 144-150	250	7.16	3.58	35.1	17.5	38.7	19.86	436.2	126.4	10.3		420	703
31-1, 144-150	285	7.78	4.98	33.0	18.4	41.5	18.75	442.4	129.9	7.3	20.5	227	274
34-1, 144-150	314	7.39	3.66	34.1	18.2	41.7	19.20	436.9	130.1	7.9		324	202
38-1, 140-150	353	7.24	3.74	34.9	19.0	39.7	19.75	449.5	131.9	10.2	24.4	300	277
42-5, 140-150	396	7.20	3.13	35.8	18.9	40.1	19.86	409.5	133.7	11.4		316	650
46-3, 140-150	431			35.2	19.2	40.4	19.86	360.0	117.2	9.8	24.3	207	725
Hole 546													
2-1, 144-150	4	7.22	4.12	39.7	10.3	52.1	22.87	100.2	54.6	12.1	27.01	316	204
6-3, 144-150	45	7.19	3.71	71.5	14.6	47.6	44.00	205.3	80.6	11.6	28.92	584	158
8-4, 144-150	65	7.03	3.13	92.4	15.2	46.6	57.6	272.1	90.5	12.4	32.09	609	142
10-4, 144-150	84	7.15	2.33	111.9	17.4	43.4	72.3	275.6	101.8	13.2		615	138
12-4, 140-150	103	7.11	1.74	138.6	21.1	38.7	90.9	286.2	102.9	13.1	37.96	637	120
14-3, 140-150	121	6.91	1.61	162.0	24.8	34.5	109.3	267.4	111.3	11.6		330	99
17-3, 120-130	149	6.79	1.22	198.0	33.9	27.6	137.2	145.4	105.8	16.0		323	87
18-1, 30-40	155	6.97	0.58	193.6	39.3	25.9	130.1	114.7	95.2	15.2	59.00	313	47
Hole 547A													
1-2, 144-150	54	7.41	7.10	35.2	5.4	50.3	20.10	141.5	65.3	10.3	16.48	1018	244
5-4, 144-150	114	7.23	4.99	35.2	9.9	45.9	20.24	258.6	85.3	8.9	20.41	805	197
9-3, 144-150	151	7.29	3.76	35.2	14.8	42.8	20.46	343.1	101.9	8.9		708	428
14-2, 140-150	197	7.20	2.81	35.5	17.9	40.6	20.66	407.8	113.2	8.7		626	621
20-5, 140-150	258	7.05	2.70	35.2	20.6	40.3	20.21	462.9	121.7	6.4	21.84	533	587
25-3, 140-150	302	7.20	2.47	36.3	21.1	40.2	21.09	510.8	131.8	7.3		538	677
30-3, 140-150	350	7.13	2.29	36.8	24.4	36.8	21.93	608.7	166.3	7.0	15.75	952	534
35-1, 140-150	395			36.3	25.3	35.5	21.93	652.8	5.2		745		
40-1, 110-120	433	7.46	1.49	35.8	26.6	35.9	20.88	713.8	175.3	3.8	17.68	711	137
45-2, 140-150	482	7.35	1.44	36.6	28.8	33.9	21.90	792.3	218.0	3.2	200222	724	112
50-2, 140-150	529	7.65	1.19	37.4	31.1	32.9	22.14	887.3	258.0	3.4	14.75	935	71

ion product. Above sub-bottom depths of 150 m, the interstitial waters become rapidly undersaturated with respect to gypsum.

The appearance of gypsum in the sediments above the salt diaper must be understood in terms of migration of calcium and sulfate out of the salt deposit. Although the concentration product of calcium and sulfate in the basal sediments exceeds the saturation concentration product in the pure halite brine, the thermodynamic activity product will be closely equal. This explains the apparent contradiction of a flux of calcium and sulfate ions off the salt deposit against an inferred concentration gradient. Diffusion is driven by chemical potential differences, caused by the rapid drop in the chloride concentration across the salt-sediment interface.

Site 547 (Fig. 8)

Again, in this site, the upper 100 m are characterized by rapidly deposited Pleistocene carbonate oozes. As in Site 545, a minimum in dissolved sulfate with concomitant maxima in ammonia and alkalinity are observed. Calcium and magnesium again show gradual changes with depth, with calcium showing a minimum at ~ 50 m. Dissolved strontium appears to have its principal source well below 500 m, as does dissolved lithium.

The concentration depth profile of dissolved chloride is intriguing (Fig. 9). The existence of a chloride increase with depth is beyond doubt. The data in the lower part of the hole, however, suggest that there may be a maximum in chloride between 800–900 m sub-bottom depth. If this observation is correct, then, the profile implies advection or diffusion of chloride through the sediments in a manner similar to that described by Gieskes et al. (1980) for Sites 415 and 416, located to the west of the region of diapiric structures (Fig. 1). Site 547 is located at about 6 km from the zone of diapiric structures, therefore the lateral transport of chloride is likely to be advective.

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Sample (interval in cm)	Sub-bottom depth (m)	S (g/kg)	Ca (mM)	Mg (mM)	C1 (g/dm ³)
Hole 544A					
12-2, 11-13	104	36.3	15.0	48.5	20.34
17-1, 26-27	139	37.1	17.1	50.7	20.69
19-1, 45-46	150	36.1			
21-1, 147-150	167	36.4	14.5	50.0	20.48
Hole 545					
56-3, 140-150	526	36.0	13.3	50.6	19.90
Hole 546					
4-3, 92-96	25	57.5			
6-6, 140-150	49	78.4			
in situ	50	78.1	13.9	49.3	51.77
7,CC	59	85.3			
8,CC	68.5	97.9			
9,00	78	105.0			
10.CC	87.5	110.6			
11.CC	97.0	126			
12.CC	106.5	139.7			
13.00	116.0	151 3			
14.CC	125.5	161.7			
15.CC	135.0	152.9			
16 CC	144 5	177 2			
17 CC	154.0	174 9			
18,CC	163.5	216.7			
Hole 547A					
55-1, 140-150	575	37.3	31.4	30.4	21.89
60-4, 140-150	627	38.4	33.4	29.9	22.35
66-2, 140-150	681	40.8	122220		0.000.000.000
70-2, 136-150	719	41.2	37.2	29.3	24.23
Hole 547B					
2-3, 140-150	738	40.7	37.8	30.0	23.74
5-6, 140-150	771	41.2	40.2	31.0	24.17
11.CC	819	42.9	48.8	34.7	24.23
25-1, 10-10	933	44.0		17/27/2	
26-3, 135-150	946	44.3	58.5	29.6	23.56
27-1, 140-150	952	45.1	2012	2710	20100
28-3, 140-150	964	46.8			25.39
30-3 0-10	980	44 7	57 9	32 8	23 46
33-3, 0-10	200	/	21.1	54.0	40,40

Table 2. Shipboard data on interstitial waters, Leg 79.

^a Data suspect because of seawater contamination.

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Figure 2. Interstitial water chemistry, Site 544. Lithology: I. Clayey foraminiferal nannofossil oozes and chalks; II. Glauconitic nannofossil chalk and nanno-bearing claystone; III. Limestone; IV. Sandy mudstone and muddy sand-stone.



Figure 3. Interstitial water chemistry, Site 545. Lithology: IA. Clayey foraminiferal nannofossil ooze; IB. Clayey nannofossil ooze with breccia layers (carbonate platform rocks, Jurassic); II. Radiolarian-nannofossil chalk; IIIA. Nannofossil-bearing clay/claystone; IIIB. Nannofossil claystone and chalks; IIIC. Nannofossil claystone and chalks; clayey nannofossil chalk.



Figure 4. Interstitial water chemistry, Site 546. Lithology: I. Clayey foraminiferal nannofossil ooze; II. Clayey nannofossil ooze and red clay; gypsum-rich layers from 147-149 m; gypsiferous clay from 149-156.5 m; III. Halite with rare anhydrite and sylvite. (Note: *in situ* data in circles).



Figure 5. Plot of chloride versus sodium of Site 546 interstitial waters.



Figure 6. Correlation plots Ca versus Cl, Mg versus Cl, and Ca versus SO₄ for Site 546.



Figure 7. Gypsum solubility in sodium chloride, concentrations in molarities (data from Marshall and Slusher, 1966; Harvie and Weare, 1980). Note range of NaC1 concentrations at bottom of hole (\sim 4.2 M) to saturated NaCl (\sim 5.37 M).



Figure 8. Interstitial water chemistry, Site 547. Lithology: I. Clayey foraminiferal nannofossil ooze; IIA. Nannofossil ooze; IIB. Clayey nannofossil ooze and chalk; III. Conglomerate beds in nannofossil chalk, IVA. Nannofossil chalk, radiolarians, and porcellanites; IVB. Debris flows in nannofossil chalk; V. Nannofossil-bearing claystone and mudstone.



Figure 9. Ca, Mg, and C1 in Site 547, note possible maximum in dissolved chloride.