

22. INTERSTITIAL WATER STUDIES, LEG 42A

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ABSTRACT

Interstitial water analyses of Sites 371, 372, 374, 375, 376, 377, and 378 are reported. Also, diffusion parameters have been measured in Sites 371, 372, 374, and 376. Diffusion model predictions of chloride gradients in Sites 371 and 374 agree very well with observed data. The diffusion model is subsequently used to investigate the nature of the major cation gradients in terms of diffusion and reaction. Site 374, especially, shows a complicated depth dependency in calcium and magnesium, implying substantial reactions in these sediments. Oxygen isotope data show little change with depth, although in Site 372 there is some sign of a slight enrichment with depth, possibly related to carbonate recrystallization processes.

INTRODUCTION

Studies of the interstitial waters collected during Leg 13 in the Mediterranean Sea showed that the presence of Messinian evaporites underlying the sediments exerts a strong influence on the chemical composition of the pore solution (Sayles et al., 1972) in addition to the effects of diagenetic processes observed in more typical sedimentary environments (Sayles and Manheim, 1975; Gieskes, 1975). This fact suggested that careful chemical study of interstitial waters obtained during Leg 42A could be of immense value in furthering our understanding of pore water phenomena, particularly regarding the relative effects of diffusion and reaction on pore water concentration profiles. The gradient of a non-reactive species such as chloride, established by dissolution of evaporitic phases underlying the sediment column, can serve as an ideal test for models of diffusive transport in sediments (McDuff and Gieskes, 1976). Deviation of pore water composition from this "conservative" distribution, determined by physical processes alone, can be used to identify locations of diagenetic reactions (Kastner and Gieskes, 1976) and to estimate rates of reaction. The extensive isotopic work performed on Leg 42A material provides further important constraints on the nature of the diagenetic processes. In addition, the chemistry of the pore waters can provide important clues to the composition of evaporitic phases underlying the sediments drilled (Manheim et al., 1974). The shipboard geochemical data verified the suitability of the samples from several sites for this sort of study. The contrasting profiles of calcium, magnesium, and chloride at Site 374 were indicative of an especially interesting interplay of diffusion and reaction.

This contribution is concerned mainly with the results of the analyses of chemical composition of the interstitial waters recovered from Leg 42A sites and of the measurements of physical properties (porosities, formation factors) of the bulk sediment. The discussion focuses on possible interpretations of the data from Sites 371, 372, and 374. Data from the other sites were too sparse to draw meaningful conclusions. We intend to perform further work in order to amplify the thoughts presented here.

METHODS

Interstitial waters were collected, using the routine shipboard squeezing techniques described by Manheim and Sayles (1974). Small amounts of the squeezed samples were used for shipboard measurements of salinity (refractometer), calcium, and magnesium (titrations described by Gieskes, 1974). For the analysis of alkalinity and pH, 5-10 ml samples were titrated with 0.1 N HCl, using the potentiometric technique described by Gieskes and Rogers (1973). These titrated samples were subsequently stored in sealed polyethylene vials for our shorebased analyses of other constituents (Na, K, Sr, SO₄, NH₄, Si). The analytical methods used for these species have been described by Gieskes (1974). We were interested in supplementing the shipboard interstitial water data at Site 374 in the interval between 360 and 390 meters, in which a sharp drop in the calcium concentration occurs. For this purpose we obtained small samples of sediment from the DSDP east coast core repository. These samples yielded as much as 2 ml of interstitial solution on which a fairly complete chemical analysis could be made. Previously we have shown in this laboratory, with stored cores from Legs 15 and 26, that interstitial

water data for major elements from samples squeezed immediately after recovery and samples squeezed after long-term storage agree quite well (after a minor adjustment for a slight chlorinity increase due to evaporation). On this basis, we consider the chemical analyses obtained from these stored samples representative of the original conditions.

Physical properties were measured at the DSDP core repository at Lamont in February, 1976. Formation factors were determined using a modification of the method described by Manheim and Waterman (1974). The principal change we made in this method was to use measurements on laboratory solutions of varying chloride and divalent/univalent compositions to provide the appropriate reference resistivity, rather than extracting pore solution for a direct measurement. Water contents were determined by wet weight/dry weight measurements, and porosities were calculated assuming a grain density of 2.6 g/cm^3 and a solution density appropriate to the composition.

Strontium interferes with the shipboard calcium titration, approximately 80% being recovered (Tsunogai et al., 1968). In addition, Gieskes and Lawrence (1976) note an artifact in the calcium determination dependent on the Mg/Ca ratio. The magnesium values, which are determined by difference, must also be corrected for strontium values. The shipboard data have been corrected for all these effects in the tables reported here.

To further insure against artifacts influencing the titration values due to the unusual composition of the samples, the calcium and magnesium values of some samples were spot-checked by atomic absorption spectrometry. Agreement of the two methods was satisfactory.

Oxygen isotope analyses of the interstitial waters were carried out in duplicate, using the CO_2 method of Epstein and Mayeda (1953).

RESULTS

The chemical data collected on pore waters are summarized in Table 1. In addition, data from Sites 371, 372, and 374 are presented in Figures 1-3.

Data on formation factors and porosities are tabulated in Table 2.

DISCUSSION

Before proceeding it is important to note that many of the samples show evidence of slight seawater contamination during drilling. This is most easily seen in the chloride profiles, which do not increase monotonically with depth as anticipated. This is also borne out by a regression of two species whose distributions are both controlled by diffusion—samples seemingly contaminated by the seawater end member fall on the regression line as expected.

DIFFUSIVE BEHAVIOR

A significant problem in interpreting interstitial water profiles is that of distinguishing between the

effects of diffusion and reaction. To do this, it is necessary to know how the diffusion coefficient varies as depth increases. Manheim and Waterman (1974) determined diffusion coefficients in DSDP cores using resistivity measurements. McDuff and Gieskes (1976) extended this approach by incorporating this type of measurement in a model for diffusive transport in deep-sea sediments. Gradients of chloride supported by dissolution of evaporites at Site 371 and 374 offer an ideal means of testing the validity of such a model.

Briefly, the equation for diffusion in one dimension can be expressed

$$p \frac{\partial c}{\partial t} = \frac{\partial}{\partial z} (pD_b \frac{\partial c}{\partial z}) - pu \frac{\partial c}{\partial z} = 0 \text{ at steady state}$$

where p is porosity, c is concentration, t is time, z is the vertical spatial coordinate relative to the sediment water interface, D_b is the bulk diffusion coefficient and u is the pore water velocity relative to the sediment water interface. The bulk diffusion coefficient is obtained from the diffusion coefficient in the pore water alone, D_p , and the formation factor, F , the ratio of the specific resistivity of the bulk sediment to that of the pore solution, by the relationship $D_b = D_p/pF$. The assumptions involved and the method of solution have been discussed in detail elsewhere (Imboden, 1975; McDuff and Gieskes, 1976).

Comparisons of the model calculations with the observed chloride data for Sites 371 and 374 are shown in Figure 4. Resistivities and porosities are those of Table 2, D_p is taken as $1.43 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ at 13°C (Li and Gregory, 1974) and temperature gradients as $7^\circ \text{C}/100$ meters at Site 371 (estimated) and $2.6^\circ \text{C}/100$ meters at Site 374 (Erickson and Von Herzen, this volume). The following conclusions can be drawn. At Site 371 the observed concentrations agree with the model. This is also the case at Site 374 to approximately the depth of 360 meters. Evaporitic salts are found in Core 11 (380 m) and below. One can conclude that the agreement of the observations with the model predictions shows that formation factor data can be reliably used to predict diffusive profiles in sediments.

One should note that the concentrations of chemical species whose distributions between two boundaries are controlled by diffusion and sedimentation will plot on a straight line. Further, the concentration of a species that is either produced or consumed between the boundaries, when plotted against that of a species controlled by physical processes alone, will show deviation from linearity (Craig, 1969). Consequently, at Sites 371 and 374, important information on the significance of chemical reaction can be gained by considering plots of various species versus chloride, since we have demonstrated that chloride is conservative.

Diagenesis

A general characteristic of Leg 42A sites is their rapid rate of sedimentation. In general, faster deposi-

TABLE 1
Interstitial Water Data, Leg 42A

Section	Depth (m)	Na mmole/l	K mmole/l	Mg mmole/l	Ca mmole/l	Sr mmole/l	Cl mmole/l	SO ₄ mmole/l	Alk meq/l	pH	NH ₄ mmole/l	Si mmole/l
Site 371												
1-5	8	—	—	63.5	13.4	0.20	647	26.5	3.58	6.9	590	130
2-2	207	—	—	194.	208.	2.7	1670	7.9	0.63	6.0	1430	96
3-5	369	—	—	273.	317.	3.8	2210	5.6	0.57	8.2	970	130
4-5	407	—	—	456.	509.	4.4	2910	8.8	0.55	6.2	1180	75
5-5	464	—	—	653.	656.	5.9	3680	5.0	0.57	5.8	540	57
8-2 ^a	549	—	—	1280.	960.	14.9	4930	23.6	2.91	5.3	1490	51
Site 372												
1-3	120	—	—	77.6	33.5	0.60	866	33.5	2.37	6.8	1910	180
2-3	139	744	7.5	74.5	45.2	0.69	915	37.6	1.61	6.8	1680	190
3-2	148	745	8.4	75.6	49.9	0.68	924	40.2	1.36	6.9	1740	170
9-3	203	958	8.9	85.4	79.8	1.1	1230	34.1	1.13	6.8	3250	310
14-4	251	980	8.5	70.1	67.3	1.8	1230	18.0	0.75	7.1	3350	150
19-4	299	1010	7.3	57.7	74.1	2.4	1270	9.3	0.58	7.5	3540	150
24-5	348	1140	7.5	59.5	74.1	2.6	1400	7.5	0.76	6.9	3690	200
29-4	395	1380	7.8	63.0	93.7	2.7	1690	6.8	0.74	7.2	3930	420
33-5	471	1320	6.7	67.1	97.6	2.4	1650	5.0	0.86	7.0	4100	360
36-5	579	1480	7.5	67.7	111.	2.4	1840	5.9	0.88	7.0	2820	430
Site 374												
2-2	160	773	8.9	92.6	16.6	0.34	986	5.8	3.70	7.6	2100	210
4-3	255	986	14.0	527.	127.	1.4	2260	25.2	0.89	5.5	—	94
5-4	302	1020	31.0	1160.	253.	2.3	3850	13.3	0.41	4.9	1170	86
6-1	322	860	44.0	1030.	342.	2.1	3630	9.4	0.34	4.8	750	69
6-5	338	770	49.0	1060.	354.	2.1	3620	14.6	0.35	5.1	660	77
7-1	342	—	48.0	1340.	466.	2.3	4400	13.2	1.56	6.0	2300	100
7-3	345	632	44.0	1380.	472.	2.2	4350	16.3	~1.5	—	1710	100
7-4	346	726	44.0	1370.	480.	2.3	4450	11.2	1.72	5.6	1630	120
7-6	350	714	57.0	1360.	470.	2.2	4380	26.8	1.62	6.0	1740	100
8-2	356	686	48.0	1320.	431.	2.0	4170	34.2	2.03	6.0	1740	85
9-3	367	(539)	68.0	1600.	454.	2.0	4690	(13.2)	2.97	5.9	2340	52
11-2 (22 cm) ^b	378	—	—	1940.	300.	—	4740	26.4	—	—	—	—
11-2 (86 cm) ^b	381	—	—	2150.	286.	—	4620	(21.9)	—	—	—	—
12-1 ^b	383	—	—	2210.	176.	—	4730	41.6	—	—	—	—
12-2 ^b	385	—	—	2280.	87.0	—	4770	44.6	—	—	—	—
13-1	389	519	40.0	2140.	24.1	0.30	4790	47.2	3.42	5.6	2000	110
14-1	395	572	43.0	2250.	9.7	0.16	4950	90.0	4.86	5.3	1770	130
15-1	405	640	49.0	2250.	9.7	0.14	5020	95.8	4.90	5.3	1350	190
Site 375												
5-3	365	—	1.6	25.4	11.6	0.24	590	—	3.66	8.0	—	75
7-5	573	—	3.8	18.0	11.8	0.28	550	—	3.70	8.1	—	64
Site 376												
1-4	6	—	10.2	57.3	9.9	0.14	614	—	—	8.0	—	330
5-4	44	—	8.6	54.9	10.7	0.16	608	—	3.02	7.7	—	150
9-3	82	—	7.3	55.5	15.4	0.18	604	—	1.44	7.6	—	310
12-3	109	—	8.5	52.9	23.1	0.20	599	—	1.27	7.6	—	500
13-2	118	—	7.4	53.7	26.3	0.22	601	—	1.33	7.7	—	530
15-2	129	—	7.8	56.6	36.3	0.37	629	—	0.61	7.8	—	190
Site 377												
1-1	19	—	6.4	38.1	6.6	0.18	653	—	5.20	7.4	—	230
Site 378												
1-2	92	531	7.7	34.7	9.9	0.64	606	10.0	3.32	7.5	—	360
5-1	130	542	7.0	35.9	12.2	0.69	614	14.6	3.40	7.3	—	760
7-4	177	523	6.6	35.4	13.8	0.77	604	11.7	1.87	7.5	—	530
8-1	224	524	6.6	35.4	14.0	0.79	604	12.2	2.62	7.2	—	970
11-3	310	526	7.3	42.1	38.3	0.51	604	45.0	0.62	7.6	—	190
Site 378A												
1-2	51	557	8.5	36.0	6.8	0.33	616	15.7	4.13	7.5	—	360
3-5	300	536	8.5	41.6	38.3	0.50	616	44.2	0.63	7.7	—	150

Note: Values in parentheses are questionable.

^aShipboard Ca, Mg in error

^bSqueezed from stored sediment

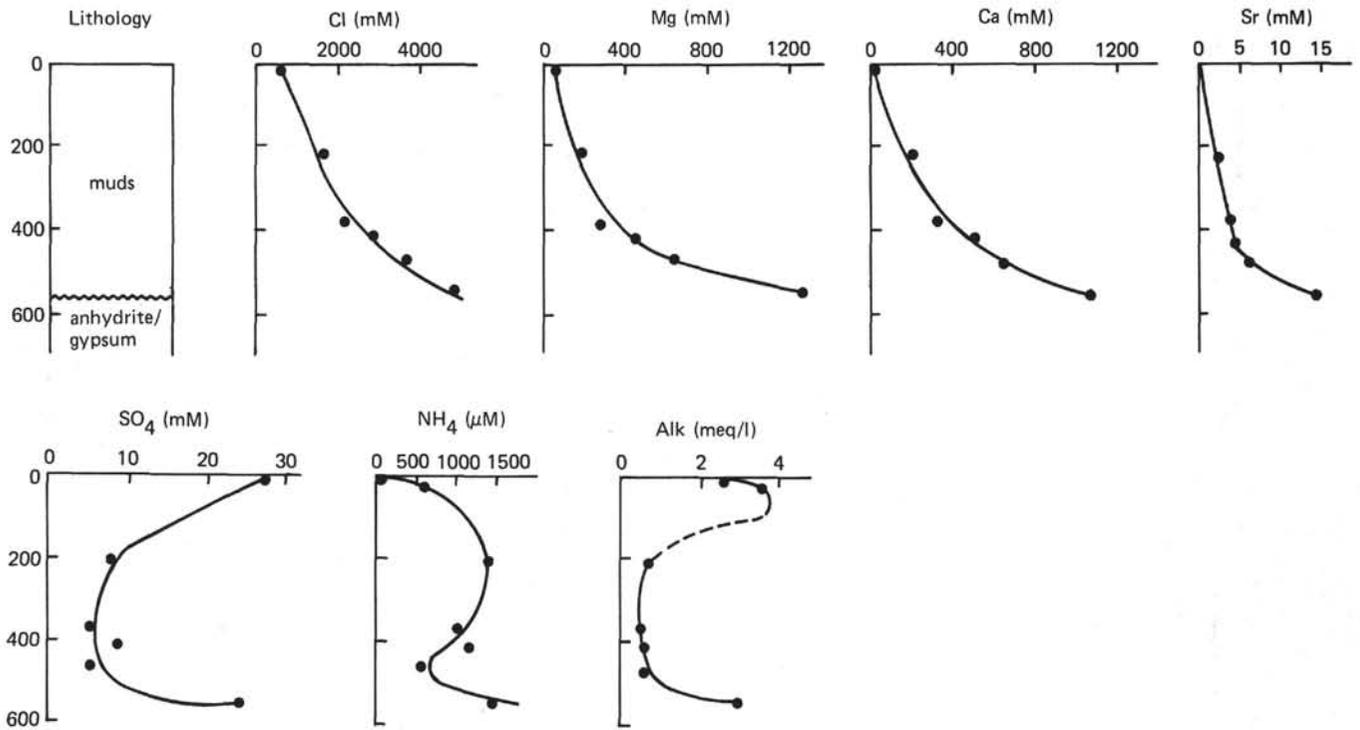


Figure 1. Interstitial water profiles, Site 371.

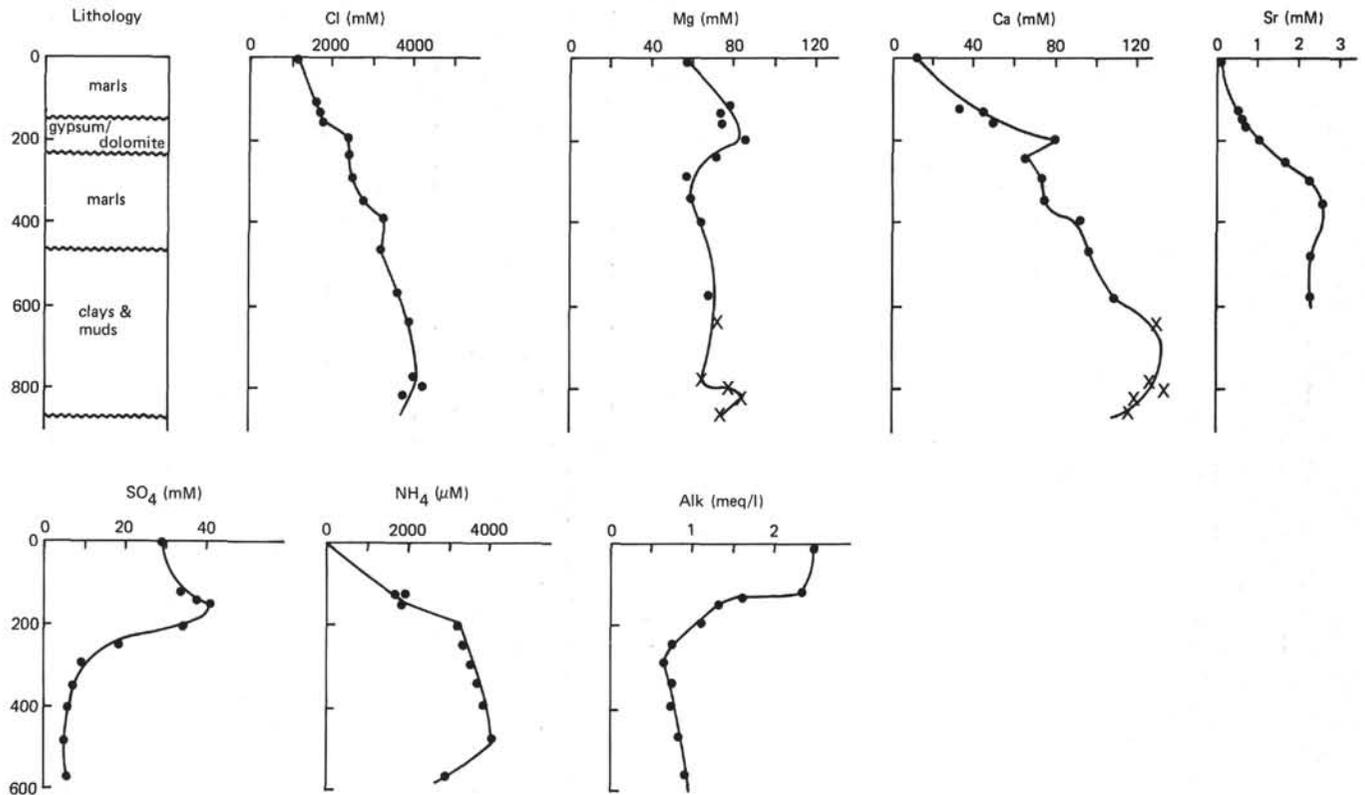


Figure 2. Interstitial water profiles, Site 372. The symbol ● denotes values from Table 1, and X denotes uncorrected ship-board values (see text).

tion, whether or not accompanied by high organic content, leads to depletion of dissolved sulfate and enrichment of dissolved ammonia (Gieskes, 1974; Gieskes and Lawrence, 1976). This is because diffusion

away from the zone of reaction is not as fast as the rate of sedimentation, and thus the sediments are not in communication with the overlying water. These considerations are apparent in the dissolved ammonia data.

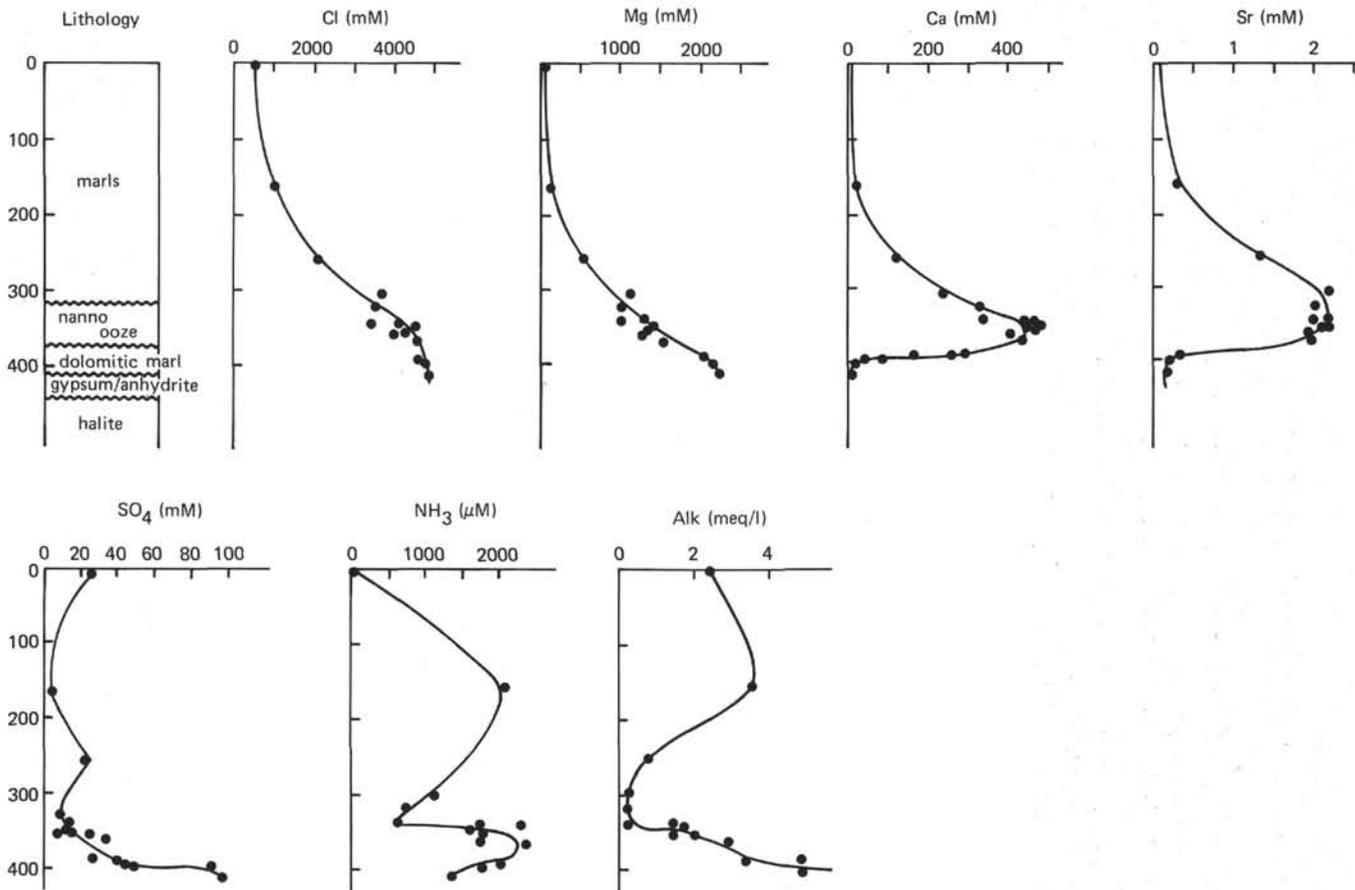


Figure 3. Interstitial water profiles, Site 374.

However, sulfate profiles are clearly influenced by a second process, dissolution of gypsum and/or anhydrite. Thus, the sulfate profiles are best understood in terms of reduction of sulfate oxidizing organic matter in addition to release of sulfate from evaporite phases. Thus at Sites 371 and 374 sulfate values are low until gypsum is reached at great depth, and at Site 372 sulfate shows a maximum due to the occurrence of gypsum in Cores 5-9.

The remaining components will be considered site by site.

Site 371

The divalent cations show an interesting contrast. Calcium plots linearly against chloride and therefore is conservative in the sediment column (Figure 5). Its probable source is calcium chloride salts in the region of the deepest sediments drilled. Perhaps a careful search would reveal this type of solid in the deepest sediments cored. Magnesium and strontium, however, show substantial depletion with respect to conservative behavior and thus are being removed in the sediment column. The depletion of alkalinity, despite clear evidence of sulfate reduction, is probably related to these removal processes, perhaps formation of magnesian calcite or dolomite. However, the magnitude of the deviation is too great for this to be the only process

acting. Some other as yet unidentified reaction must be operative.

Site 374

As was discussed earlier, the distribution of chloride is controlled mainly by physical processes between 0 and 360 meters. Below this, there must be a chloride source. The lack of enrichment of sodium demonstrates that it is not from the halite found in Core 22 and presumably deeper. This is also borne out by the relative constancy of chloride below 360 meters. Indeed, the resistivity measurement in Core 374-17, Section 4 indicates the presence of an impermeable layer. We would suggest that this source is a chloride salt located in or below Core 11.

Site 372

Sodium and chloride are linearly correlated, suggesting that they are both supplied by dissolution of evaporites located much below the deepest sediments drilled. However, because of insufficient data on the porosity minimum in the gypsum layers in Cores 5-9, we were unable to apply a diffusion model to verify this.

The alkaline earths do not correlate with chloride but, instead, follow a complicated curve, suggesting involvement in a variety of diagenetic reactions pro-

TABLE 2
Physical Properties, Leg 42A

Section	R _b (ohm cm _b)	R _p (ohm cm _p)	F (cm _b cm _p ⁻¹)	Water Content	Porosity
Site 371					
1-3	58.6	25.9	2.3	0.41	0.65
1-5	67.7	25.9	2.6	0.34	0.57
2-2	53.0	10.5	5.1	0.25	0.47
2-3	47.3	10.5	4.5	0.23	0.44
3-2	48.9	8.5	5.8	0.24	0.45
3-5	56.2	8.5	6.6	0.22	0.43
4-4	47.3	7.5	6.4	0.18	0.37
5-4	53.0	6.5	8.2	0.16	0.34
8-2	3230	5.5	608.	0.04	0.09
Site 372					
1-2	69.3	19.4	3.6	0.30	0.53
2-4	74.2	18.2	4.1	0.28	0.50
3-2	71.7	18.0	4.0	0.28	0.51
3-3	80.6	18.0	4.5	0.27	0.50
4-1	97.8	18.0	5.5	0.23	0.44
8-2	—	—	—	0.16	0.33
9-4	102.	13.9	7.3	0.23	0.44
11-2	76.6	13.9	5.5	0.25	0.46
18-6	94.6	13.7	6.9	0.25	0.47
27-4	134.	11.3	11.9	0.15	0.31
32-5	138.	10.3	13.3	0.16	0.33
34-4	104.	9.9	10.4	0.22	0.42
37-3	111.	8.9	12.5	0.16	0.33
39-3	126.	9.5	13.3	0.17	0.35
41-2	122.	8.7	14.1	0.17	0.35
44-4	122.	8.7	14.0	0.17	0.35
Site 374					
2-2	80.6	16.4	4.9	0.29	0.52
5-2	36.6	6.3	5.8	0.25	0.46
6-4	39.0	6.7	5.9	0.24	0.45
7-5	37.4	5.9	6.4	0.21	0.42
9-3	41.6	5.5	7.5	0.20	0.39
11-1	44.1	5.7	7.9	0.20	0.39
13-1	61.0	5.5	11.1	0.24	0.45
13-3	48.9	5.5	8.9	0.25	0.47
14-2	67.7	5.5	12.6	0.19	0.38
17-1	>3300	—	—	—	—
Site 376					
1-3	66.9	26.9	2.5	0.37	0.61
3-3	89.5	27.1	3.3	0.34	0.58
5-5	85.5	27.1	3.2	0.34	0.57
9-4	130.	27.3	4.8	0.22	0.42
12-4	130.	27.5	4.7	0.26	0.48
16-1	155.	26.5	5.9	0.25	0.47

Note: All measurements are at $4 \pm 1^\circ\text{C}$ and are corrected for the appropriate cell constant. Water contents are from wet weight/dry weight measurements. Porosities are calculated assuming grain density of 2.6 g cm^{-3} .

ceeding at different rates. The gypsum and dolomite layers in Cores 5-9 appear to serve as sources for calcium and magnesium, presumably due to dissolution of sulfates and/or associated dolomite. Below this horizon, there appears to be a sink for magnesium which is perhaps located in the carbonates and related to the depletion of alkalinity. Dissolved strontium exhibits a maximum at 350 meters which may be related to carbonate recrystallization processes. We cannot preclude the possibility of some supply of

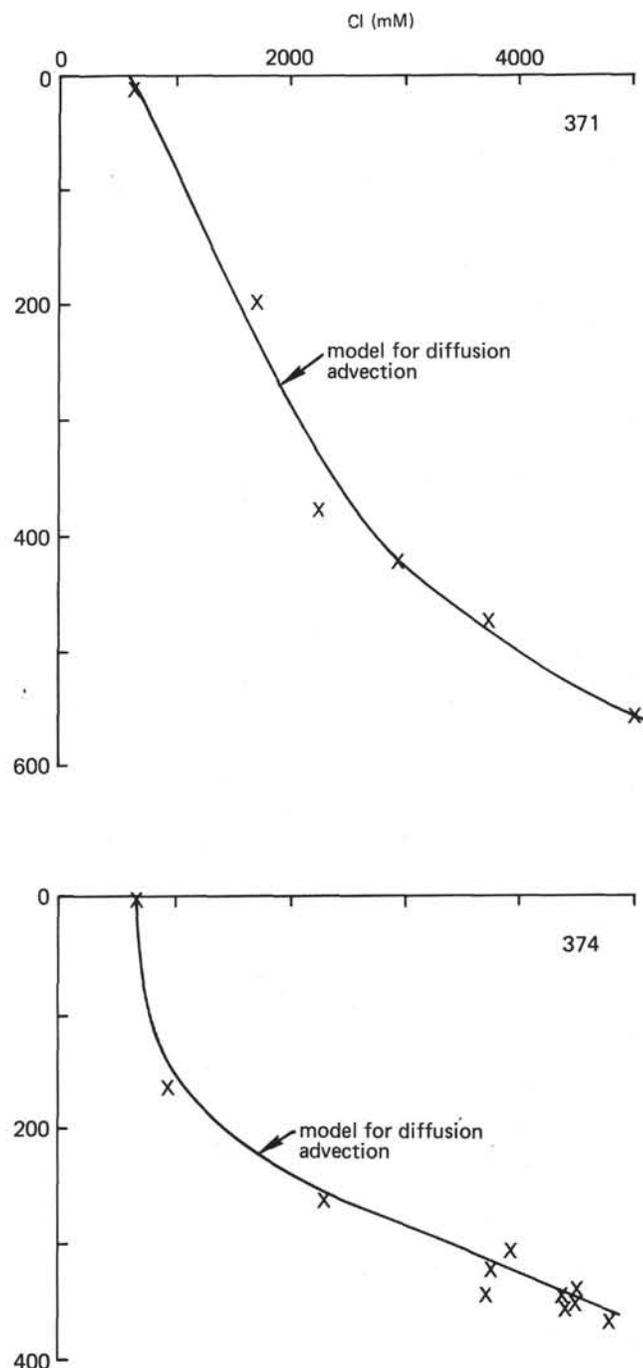


Figure 4. Comparison of profile calculated with model for diffusion and advection and observed chloride values, Sites 371 and 374. Conditions as stated in text.

calcium and magnesium from evaporites at the same location as the source of sodium and chloride.

Magnesium is conservative to 360 meters and then shows marked enrichment relative to chloride; there seems to be a significant source below 360 meters. Calcium, on the other hand, shows production above 360 meters but then drops markedly to close to seawater values. We have verified that this change occurs smoothly; it is not possible that the gypsum layers in Core 11 Section 2 are acting as a diffusive

barrier. This is evident in the profiles of Ca^{+2} , Mg^{+2} , SO_4^{-2} , and Alk. In addition, there was no sign of a high formation factor in this interval. In this region, SO_4 is greatly enriched, presumably due to gypsum dissolution, so that calcium is being added. Thus we require a sink not only for the calcium diffusing in, due to the sharp gradient, but also for the calcium derived from the gypsum. Alkalinity could be produced by sulfate reduction; however, an anomalously high ammonia value would have to be observed if this were serving to precipitate calcium in addition to supporting the sharp alkalinity gradient. However, the gradients are indicative of such large fluxes that study of the solids should lead to positive identification of the responsible phases. In any case, the high magnesium concentration, coupled with some enhancement of PO_4 due to SO_4

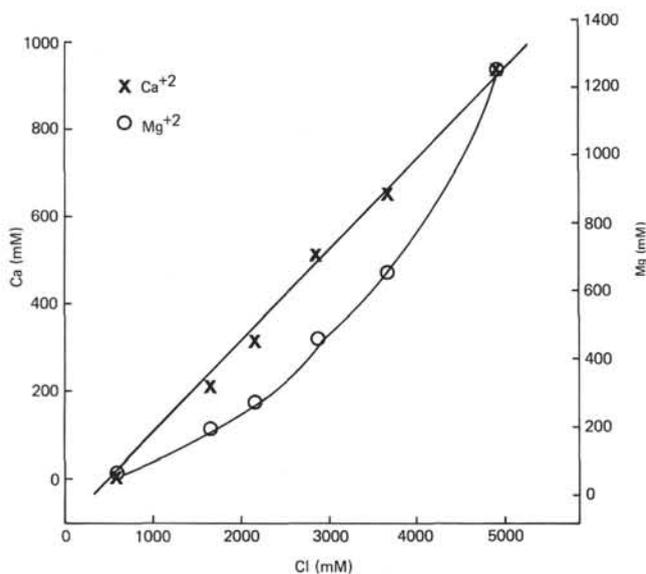


Figure 5. Calcium and magnesium versus chloride, Site 371. The linearity of calcium profile is indicative of conservative behavior, while the deviation of magnesium profile indicates removal of magnesium in the sediment column.

reduction (reflected in alkalinity), could perhaps lead to the occurrence of the Mg-phosphate balls. We plan some PO_4 measurements in the near future to follow this up.

OXYGEN ISOTOPE DATA

Analyses of the $^{18}\text{O}/^{16}\text{O}$ ratio of the interstitial waters (Table 3) show a very slight decrease with respect to present-day Mediterranean bottom water ($\delta^{18}\text{O} = +1.0$ to $+1.5$). Sites 371 and 374 show very slight decreases, whereas the interstitial waters of Site 372 are slightly enriched in O^{18} . Apparently the underlying evaporites have little or no influence on the oxygen isotope composition of the pore fluids.

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TABLE 3
Oxygen Isotope Analyses of
Interstitial Waters

Section	Depth (m)	δO^{18} (SMOW)
Site 371		
1-5	8	$+1.1 \pm 0.1$
2-2	207	$+0.3 \pm 0.4$
3-5	369	$+0.3 \pm 0.4$
5-5	464	$+0.7^a$
8-2	549	-0.5 ± 0.5
Site 372		
3-2	148	$+1.6 \pm 0.2$
19-4	299	$+2.6 \pm 0.2$
33-5	471	$+2.5 \pm 0.3$
38-3	649	$+3.0 \pm 0.2$
44-5	841	$+2.3 \pm 0.2$
Site 374		
2-2	160	$+1.3^a$
4-3	255	$+1.1^a$
5-4	302	$+0.9^a$
7-2	344	$+0.8^a$
13-3	390	$+0.9^a$

^aNo duplicates available.

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