## 19. GEOCHEMISTRY AND DIAGENESIS OF INTERSTITIAL FLUIDS AND ASSOCIATED CALCAREOUS OOZES, DEEP SEA DRILLING PROJECT, LEG 27, SITE 262, TIMOR TROUGH

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#### ABSTRACT

Detailed geochemical work was undertaken on pore water and sediment samples from a drill hole (Site 262) situated on the axis of the Timor Trough. The sediments comprise calcareous ooze with variable quantities of clay minerals. High-magnesian calcite is absent, though aragonite is present throughout the sequence. Dolomite rhombs are common, particularly in the lower half of the section, where they are believed to have formed diagenetically by the action of saline pore fluids on the calcareous ooze. Factors influencing the chemistry of the pore waters include:

1) The increasing carbonate content of the sediments with increasing depth has a relatively minor effect on the chemistry of the pore water.

2) The presence of large amounts of plant material in the sediments and the associated bacterial fermentation and sulfate reduction produce a solution rich in HCO<sub>3</sub> (and an abnormally high alkalinity) and a depletion of SO<sub>4</sub>. There is also a decrease in the  $Ca^{++}$  concentration, but the reasons for this are less apparent.

3) The influx of highly saline water in the lower half of the section is believed to emanate from evaporite deposits.

## INTRODUCTION

Continuous coring of pelagic calcareous sediments at Site 262 in the Timor Trough (Figure 1), at a water depth of 2315 meters, provided abundant core material for geochemical work, including onboard extraction of interstitial water. Material, 6 cm long, was taken from each core, at a vertical sampling interval of approximately 10 meters, compared to the normal sampling interval of approximately 50 meters. Because comparatively large amounts of sediment and water were available, it was also possible to undertake a wide range of analyses on the 45 samples obtained.

The drill hole intercepted a total of 442 meters of gray calcareous sediments. The sequence was composed of 414 meters of Quaternary and Pliocene planktonic ooze overlying 13 meters of Pliocene shallow marine foraminiferal dolomitic mud and 15 meters of Pliocene very shallow marine dolomitic shell calcarenite.

Thus, the sequence becomes progressively of shallower water origin with increasing depth down the hole. It is also evident that for the past 4-5 m.y. a comparatively rapid rate of deep-sea sedimentation (about 10cm/1000 y) has prevailed in the Timor Trough.

## ANALYTICAL PROCEDURES

After onboard extraction, using a modified hydraulic press, the interstitial water was stored in sealed plastic

tubes of about 10-20 ml in volume. A small quantity of water was used for onboard analysis, including the determination of pH by the flow-through and punch-in methods, alkalinity by potentiometric titration, and salinity by the refractive-index method using a Goldberg optical refractometer. All the onboard analyses and the methods used are standard for each leg of the Deep Sea Drilling Project.

The squeezed sediments were heat-sealed in plastic bags, and dried and ground to approximately 100 mesh before analysis. Chemical analyses on the water and sediment were subsequently undertaken at the Australian Mineral Development Laboratories, Adelaide; mineralogical analyses were carried out at the Bureau of Mineral Resources, Canberra.

#### **Onshore Water Analyses**

Immediately upon opening the vials, the samples were acidified with a known volume of 10% hydrochloric acid. Analyses were then undertaken as follows:

Ca, Mg, Sr, and Ba were determined by atomic absorption spectrometry using a nitrous oxide flame, a dilution ranging from 10-fold to 50-fold, and, where appropriate, an acid solution of KCl to suppress ionization. Fe, Mn, and Zn were determined directly by air-acetylene flame atomic absorption spectrometry using  $\times 20$  and  $\times 30$  scale expansions, and reading on a chart recorder; background corrections were made using a hydrogen lamp. Cu was determined by air-acetylene flame atomic absorption spectrometry after extraction, using methyl isobutyl ketone as the solvent and ammonium pyrrolidine thiocarbamate as the chelating agent (St. John, 1970). P<sub>2</sub>O<sub>5</sub> was determined colorimetrically after neutralizing with NaOH solution.

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Figure 1. Location of Site 262.

Absorbance was read at 880 nm in 2-cm cells against standards prepared in a similar matrix of NaCl. This method is fully described by Murphy and Riley (1962). Chloride was determined by titration against silver sulfate using an electrometric endpoint. Sulfate could not be determined by the classical precipitation method because of the small amount of material available so it was obtained by determining the amount of Ba (by atomic absorption spectrometry) precipitated from solution as BaSO4.

## **Onshore Sediment Analyses**

Mineralogical analyses were undertaken on a conventional Phillips X-ray-diffraction unit at standard settings. Preferred orientation effects were minimized by the use of a spinner. Calcined fluorite was used as an internal standard. Peak areas were determined using an electrically triggered planimeter. Peak positions were also measured, and the Goldsmith and Graf (1958) relation was used for the determination of carbonate mineralogy.

Various techniques were used for the chemical analyses. P<sub>2</sub>O<sub>5</sub> was determined spectrophotometrically using the molybdenum blue method. CO<sub>2</sub> was determined gravimetrically. All other elements were determined by atomic absorption spectroscopy on total solutions of the samples using mixed acids and HF.

To check the mineralogical significance of geochemical results, a number of samples were impregnated and thin sections cut.

## RESULTS

The results of pore water and sediment analysis of the 45 samples from Site 262 are given in Table 1. Tests of precision were undertaken on both pore water and sediment samples where sufficient material was available. In general, standards of reproducibility for pore water analyses are acceptable, including those for Mg ( $\pm 2.4\%$ ), Ca ( $\pm 2.2\%$ ), K ( $\pm 1.7\%$ ), Sr ( $\pm 2.6\%$ ), Li ( $\pm 3.5\%$ ), Cl<sup>-</sup>( $\pm 0.5\%$ ), and SO<sub>4</sub><sup>--</sup> ( $\pm 1.0\%$ ). Less satisfactory levels of precision were obtained for P<sub>2</sub>O<sub>5</sub> ( $\pm 34.0\%$ ), Fe ( $\pm 23.2\%$ ), Mn ( $\pm 19.1\%$ ), and Zn ( $\pm 26.7\%$ ).

Precision levels are generally good for the sediment analyses, including those for Ca ( $\pm 0.6\%$ ), Mg ( $\pm 1.9\%$ ), Sr ( $\pm 1.3\%$ ), Li (0%), Fe ( $\pm 1.5\%$ ), CO<sub>2</sub> ( $\pm 1.7\%$ ), Cu ( $\pm 2.8\%$ ), Mn ( $\pm 1.9\%$ ), and P<sub>2</sub>O<sub>5</sub> ( $\pm 3.8\%$ ). Acceptable levels were obtained for K ( $\pm 7.0\%$ ), Ba ( $\pm 8.7\%$ ), Zn ( $\pm 6.6\%$ ), and Cr ( $\pm 8.8\%$ ). Poor levels of precision were obtained for Pb ( $\pm 30\%$ ), Co ( $\pm 11.9\%$ ), and Ni ( $\pm 25.9\%$ ).

The degree of accuracy is more difficult to establish, and is rather less important to a relative study of this type, than the precision. Comparison of the Timor Sea surface-water analyses with those of standard seawater suggests that a reasonable level of accuracy was obtained.

Mean compositions for the upper and lower halves of the section at Site 262 are given in Tables 2 and 3. In addition, the vertical variation in major and trace element compositions of the pore water and the sediment is shown in Figures 2 and 3.

## DISCUSSION

## **Pore Waters**

Mean pore-water compositions for Site 262 are given in Table 2. Many of the values do not appear to differ significantly from values obtained from Leg 8 (Presley and Kaplan, 1971; Manheim and Sayles, 1971). However, there are some notable differences including salinity, alkalinity, chlorinity, Ba, and Fe which are considerably greater, and SO<sub>4</sub><sup>---</sup>, Ca, and Mn which are significantly less at Site 262 than in Pacific sediments obtained on Leg 8. It seems probable that the pore waters at Site 262 show marked enrichment in total dis-

			_								,	No.	-	_			_		_				
	1	2	3	4	5	6	7	8	9	10		12	13	14	15	16	17	18	19	20	21	22	23
Section	4	4	5	3	4	6	1	6	5	1	6	6	1	1	6	6	6	4	5	3	6	5	6
Depth (m)	3.50	9.50	18.96	27.00	38.00	50.50	\$2.50	69.50	77.50	81.00	98.00	107.50	109.50	120.44	136.00	145.50	156.44	161.50	173.94	180.44	193.00	201.00	212.00
Stratigraphic Unit	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	2
Pore Water													-							-			
pH(ft)	7.12	7.55	7.62	7.72	7.72	7.67	7.80	7.92	7.63	7.86	7.80	7.86	7.85	7.77	7.77	7.83	7.71	7.64	7.84	7.81	7.66	7.72	7.47
pH(pi)	7.12	7.50	7.40	7.48	7.62	7.40	7.55	7.48	7.52	7.65	7.90	7.64	7.64	7.53	7.54	7.61	7.46	7.47	7.52	-	-	-	-
Salinity ( <sup>0</sup> /00)	33.6	36.3	37.4	37.4	37.4	38.0	37.4	36.6	36.3	36.3	35.5	35.2	35.2	34.9	35.2	35.8	36.3	36.3	36.0	37.1	36.8	36.8	36.8
Alkalinity (meq/l)	22.48	73.22	87.39	90.32	87.19	92.86	82.21	76.93	65.59	63.64	53.37	50.64	45.36	36.27	47.07	50.44	52.59	48.19	49.95	51.22	46.92	39.59	28.05
SO <sub>4</sub> (ppm)	500	50	50	50	100	50	50	100	50	IS <sup>a</sup>	50	50	100	200	100	50	IS <sup>a</sup>	50	50	50	50	50	100
C1 (°/00)	19.4	19.6	19.6	19.9	19.9	19.9	19.9	19.8	20.0	ISa	20.0	20.0	20.0	19.9	20.2	20.3	20.5	20.8	21.0	21.1	21.6	21.7	21.9
P2O5 (ppm)	0.41	16.0	22.5	15.1	15.5	25.6	23.3	23.3	16.0	14.2	12.8	11.0	10.6	10.8	13.5	13.8	10.4	11.5	8.9	8.4	7.95	5.75	2.85
Mg (ppm)	1240	1470	1530	1500	1530	1560	1500	1340	1240	1270	1160	1130	1130	1180	1180	1190	1270	1270	1290	1340	1240	1250	1080
Ca (ppm)	156	40	35	28	32	26	230	35	40	40	40	40	38	62	38	35	38	46	32	28	32	59	62
K (ppm)	365	560	575	515	585	610	600	590	560	595	525	550	595	565	575	565	575	510	555	565	565	510	525
Sr (ppm)	8.2	3.6	3.1	2.6	2.6	2.0	1.8	2.8	3.6	3.6	4.1	4.2	3.9	4.4	4.1	4.1	4.2	- 4.8	3.9	3.9	4.6	7.4	8.9
Ba (ppm)	0.5	13.8	9.2	7.4	7.0	6.2	4.4	6.8	9.4	9.2	11.0	10.6	10.0	6.2	12.0	14.6	15.4	16.6	15.0	15.0	17.0	21.2	23.2
Li (ppm)	0.14	0.13	0.13	0.15	0.15	0.15	0.15	0.17	0.19	0.20	0.22	0.22	0.22	0.21	0.21	0.25	0.23	0.21	0.25	0.26	0.26	0.27	0.34
Cu (ppm)	0.01	0.01	0.01	0.05	0.01	0.03	0.01	0.03	0.13	0.07	0.05	0.04	0.03	0.09	0.04	0.07	0.04	0.04	0.04	0.04	0.02	0.06	0.03
Fe (ppm)	0.06	0.08	IS	0.24	0.24	0.22	0.21	IS	0.26	0.24	0.17	0.19	0.19	0.10	0.19	0.27	0.12	0.20	0.14	0.19	0.17	0.57	0.19
Mn (ppm)	0.60	0.009	0.09	0.05	0.05	0.06	0.05	0.05	0.06	0.07	0.06	0.05	0.07	0.09	0.08	0.07	0.08	0.06	0.05	0.05	0.06	0.24	0.09
Zn (ppm)	0.42	0.68	0.34	0.31	0.22	0.23	0.21	0.28	0.28	0.51	0.24	0.20	0.15	0.27	0.18	0.23	0.20	0.17	0.19	0.18	0.15	2.68	0.22
Sediment																							
Fe (%)	2.1	2.5	2.5	2.8	2.8	2.8	2.7	3.0	3.0	3.0	3.1	3.0	2.9	3.2	2.9	3.2	2.9	3.0	2.8	3.0	2.9	3.0	3.1
A12O3 (%)	7.9	8.9	8.6	9.5	9.4	9.0	8.7	9.5	9.6	10.3	9.7	10.6	11.1	11.2	10.6	11.1	9.7	10.2	10.6	10.7	9.5	10.3	9.6
CO2 (%)	21.2	15.1	13.8	12.5	13.9	15.4	15.3	14.3	13.3	12.1	12.4	11.3	12.0	12.3	14.0	11.9	13.2	13.2	13.3	14.9	13.4	13.6	14.4
Ca (%)	18.0	14.3	13.0	11.9	12.8	14.5	14.0	13.3	12.5	10.8	10.6	10.1	11.0	11.1	12.9	10.7	12.3	11.8	12.2	13.4	13.1	12.1	13.3
Mg (%)	1.5	1.25	1.15	1.2	1.15	1.2	1.15	1.2	1.25	1.15	1.25	1.3	1.2	1.2	1.15	1.25	1.15	1.3	1.2	1.3	1.2	1.35	1.2
K (%)	0.84	1.2	1.2	1.25	1.24	1.1	1.2	1.35	1.4	1.4	1.45	1.55	1.45	1.5	1.45	1.15	1.35	1.45	1.6	1.45	1.45	1.55	1.5
Sr (ppm)	1000	10800	700	600	700	850	850	800	750	600	550	500	550	550	650	450	650	650	600	650	700	650	650
Ba (ppm)	350	450	460	420	410	410	450	400	410	400	420	380	420	410	450	400	450	460	440	470	450	470	440
Li (ppm)	20	30	30	30	30	30	30	30	30	30	30	40	30	40	30	40	30	40	30	40	30	40	40
Cu (ppm)	40	45	45	45	45	45	40	45	45	45	50	50	45	45	45	45	45	45	45	40	45	45	45
Pb (ppm)	15	13	10	8	5	8	13	8	10	15	20	8	5	18	15	15	10	1	10	15	8	15	10
Zn (ppm)	75	65	80	85	85	85	90	90	90	90	85	90	90	95	90	90	90	95	95	95	95	100	95
Co (ppm)	5	13	3	8	5	10	8	8	8	10	8	10	15	10	10	10	13	4	8	4	10	8	0
NI (ppm)	30	40	40	40	35	35	35	40	40	40	40	45	45	45	40	40	35	30	35	40	35	40	45
Mn (ppm)	410	900	700	900	800	700	650	650	900	1000	1100	1100	800	1200	1200	1100	700	900	900	900	/50	750	/50
Cr (ppm)	65	15	85	70	105	80	85	75	70	85	90	90	70	65	60	90	70	65	15	90	15	95	1077
P <sub>2</sub> 0 <sub>5</sub> (ppm)	1168	1146	1237	1260	1260	1260	1283	1260	1260	1283	1283	1260	1260	1260	1260	1260	1168	1191	1260	1260	1146	1123	10//
Carbonate Compo	nents																						
Dolomite (%)	16.6	-		-	-	1	4.5	-	$\sim$	-	5.6	2.9	-		3.3	-	_	2.7	1.8	2.4	1.8	3.1	1.8
Calcite (%)	78.7	93.8	92.1	94.8	93.3	93.2	88.6	91.6	90.9	93.8	89.8	91.2	95.9	95.7	94.8	98.7	97.3	92.0	95.2	95.8	95.1	93.9	95.1
Aragonite (%)	4.7	6.2	7.9	5.2	6.7	6.8	6.8	8.4	9.1	6.2	4.6	5.9	4.1	4.3	2.0	1.3	2.7	5.3	3.0	1.8	3.1	3.1	3.0

TABLE 1
Composition of Interstitial Waters and Associated Sediments from
Site 262, Timor Trough

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TABLE 1 – Continued

											Co	ore No.										
	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Section Depth (m) Stratigraphic Unit	6 221.5 2	5 229.5 2	5 239.0 2	4 247.0 2	3 255.0 2	5 267.5 2	5 277.0 2	6 288.0 2	6 297.5 2	6 307.0 2	4 313.5 2	6 326.0 2	6 335.5 2	6 345.0 3	5 353.0 3	5 362.5 3	5 372.0 3	6 383.0 3	5 391.0 3	2 396.0 3	3 407.0 3	6 421.0 4
Pore Water							_															
pH(ft) pH(pi) Salinity ( <sup>0</sup> /00)	7.47	7.61	8.04 	8.17 - 38.2	7.58	7.65	7.45	7.50 - 39.9	7.67	7.44	7.50 	7.75 42.6	7.70 	7.83 43.7	7.71 	7.38 47.3	7.73 	7.98 - 49.8	8.09 - 48.1	8.01 - 48.1	7.68 - 51.4	7.41 - 53.1
SO <sub>4</sub> (ppm) C1 ( $^{0}$ /oo) P <sub>2</sub> O <sub>5</sub> (ppm)	19.43 100 22.2 1.16	50 22.4 2.63	13.73 50 23.2 2.38	50 23.6 2.02	14.47 50 24.1 1.55	50 24.2 0.85	240 24.1 2.48	50 25.3 1.59	4.20 50 24.1 0.63	4.69 140 26.1 0.71	4.30 50 26.4 0.51	2.93 50 27.1 0.62	240 27.3 1.01	50 28.2 0.60	100 28.2 0.55	50 32.3 0.63	15 <sup>a</sup> 15 <sup>a</sup> 0.94	470 31.7 0.71	750 30.2 0.70	930 30.0 0.67	820 32.2 0.58	IS <sup>a</sup> 33.1 1.27
Mg (ppm) Ca (ppm) K (ppm)	995 102 535	1050 115 485	1020 56 605	920 42 750	955 132 570	830 155 540	860 241 460	845 245 485	830 259 485	815 285 505	860 306 480	800 303 485	880 355 460	800 353 435	920 423 430	890 538 405	990 518 415	965 628 430	1020 658 425	965 612 415	1020 810 415	1060 896 395
Sr (ppm) Ba (ppm) Li (ppm) Cu (ppm)	11.4 24.7 0.39 0.04	12.2 23.1 0.35 0.03	9.2 23.8 0.33 0.03	7.6 18.4 0.38 0.08	17.9 36.1 0.40 0.05	24.0 26.9 0.36 0.05	27.9 7.6 0.33 IS	37.5 27.8 0.33 0.09	37.5 14.0 0.26 0.22	47.0 19.4 0.28 0.12	54.5 10.4 0.27 0.05	68.0 10.4 0.28 IS	82.5 8.4 0.25 0.05	94.0 8.8 0.22 0.14	108 4.0 0.24 0.07	117 3.0 0.26 0.08	119 0.8 0.27 0.08	146 0.6 0.32 0.08	140 0.7 0.33 0.08	0.4 0.32 0.08	0.5 0.43 0.07	0.4 0.50 0.07
Fe (ppm) Mn (ppm) Zn (ppm) Sediment	0.10 0.10 0.21	0.09 0.17 0.22	0.03 0.05 0.88	0.12 0.07 0.24	0.20 0.07 0.24	0.38 0.41 0.16	0.20 0.04 0.35	0.38 0.04 0.31	0.12 0.03 0.14	0.49 0.03 0.27	0.21 0.04 0.27	0.14 0.04 0.17	0.13 0.04 0.23	0.13 0.04 0.47	0.19 0.02 0.33	0.36 0.03 0.40	0.30 0.03 0.40	0.30 0.04 0.35	0.30 0.04 0.35	0.26 0.04 0.30	0.21 0.05 0.29	0.20 0.05 0.29
Fe (%) A1 <sub>2</sub> O <sub>3</sub> (%) CO <sub>2</sub> (%)	2.8 10.2 15.4	2.9 9.6 15.3	2.7 9.3 17.0	2.4 8.6 21.3	1.8 5.7 26.6	1.9 6.4 25.7	1.5 5.3 29.6	1.5 5.1 29.2	2.0 7.2 23.4	1.3 4.9 30.1	1.15 4.3 31.3	2.1 6.9 24.2	1.55 5.4 27.0	2.2 6.7 24.9	0.70 2.1 38.8	0.80 2.3 35.4	0.80 2.7 35.3	0.80 2.1 37.5	1.05 3.6 31.0	0.75 2.1 37.5	0.95 2.7 35.0	0.15 0.1 42.9
Ca (%) Mg (%) K (%) Sr (ppm)	14.3 1.2 1.5 750	14.1 1.05 1.45 700	15.6 1.25 1.4 900	19.3 1.05 1.15 1050	23.6 1.0 0.88 1500	22.9 1.05 0.97 1500	27.7 1.1 0.73 2200	26.0 0.95 0.79 2300	21.9 1.4 1.1 1700	27.1 1.05 0.71 2200	28.0 1.3 0.63 2600	21.5 1.5 1.1 1400	24.3 2.1 0.78 1800	21.6 1.35 1.05 2100	32.7 1.25 0.25 1500	30.2 1.5 0.40 1800	30.2 1.4 0.39 1700	30.7 2.2 0.31 1400	26.5 1.4 0.58 2000	1.8 0.31 1600	28.6 2.2 0.44 1300	31.5 4.8 0.05 600
Ba (ppm) Li (ppm) Cu (ppm)	420 40 40	460 30 45	480 30 45	450 30 90	440 20 30	330 30 30	310 20 30	290 20 25	260 30 25	210 20 25	180 20 25	160 30 25	150 20 20	150 20 20	90 10 10	50 10 10	100 10 10	70 10 10	100 20 10	70 10 4	90 10 8	20 1 3
Zn (ppm) Co (ppm) Ni (ppm)	100 1 45	23 90 2 40	95 8 40	90 4 35	65 1 40	75 8 40	65 1 30	65 3 35	5 75 4 30	55 1 25	55 1 35	70 1 30	55 1 15	60 1 20	13 30 1 10	30 1 10	35 1 13	3 1 8	35 1 10	25 1 10	2 3 1 8	13 1 3
Mn (ppm) Cr (ppm) P <sub>2</sub> O <sub>5</sub> (ppm)	550 90 1146	600 90 •1054	700 75 1375	700 30 1352	340 55 1191	270 50 1489	190 50 1375	190 55 1420	190 75 1489	150 45 1558	120 50 1512	240 65 1260	110 50 1650	120 65 1260	70 35 1398	70 25 2016	65 80 1535	75 50 2635	95 60 1489	70 35 2268	85 50 2635	15 5 1604
Carbonate Compo	nents																					
Dolomite (%) Calcite (%) Aragonite (%)	98.4 1.6	97.6 2.4	1.2 95.1 3.7	97.1 2.9	5.5 86.0 8.5	4.1 90.9 4.9	6.9 81.7 11.5	5.3 82.8 11.9	10.1 80.9 9.0	6.6 93.9 9.5	11.9 74.1 14.0	19.8 73.8 6.3	31.3 59.5 9.2	8.6 74.6 16.8	11.6 85.8 2.6	20.3 74.8 4.8	15.8 78.9 5.4	36.9 61.9 1.2	14.4 78.4 7.2	22.5 74.1 3.5	23.1 74.4 3.5	63.6 36.1 0.3

Note: pH salinity, and alkalinity were determined onboard the D/V Glomar Challenger by J. Pine. All other chemical determinations were made by the Australian Mineral Development Laboratories; mineralogical determinations were made by the Bureau of Mineral Resources.

	Cores 1-23 <sup>a</sup>	Cores 24-45 <sup>b</sup>	Mean Value for DSDP Leg 8	Mean Value for Timor Sea Surface Water	Standard Seawater
pH	7.70	7.70	7.60	8.23	8
Salinity ( <sup>0</sup> /00)	36.3	42.8	35.2	34.6	35.0
Alkalinity (meq/1)	58.3	6.56	2.73	2.49	2
SO <sub>4</sub> ( <sup>0</sup> /00)	0.080	0.021	2.45	2.75	2.70
C1 <sup>-</sup> ( <sup>0</sup> /00)	21.1	26.9	19.6	19.9	19.4
P <sub>2</sub> O <sub>5</sub> (ppm)	12.6	1.1	8.1	0.26	0.17
Mg (ppm)	13.00	922	1120	1310	1298
Ca (ppm)	53	365	610	433	408
K (ppm)	559	483	390	391	388
Sr (ppm)	4.2	28.8	25.8	7.7	8.1
Ba (ppm)	11.0	12.3	0.09	0.19	0.03
Li (ppm)	0.20	0.32	0.19	0.1	0.17
Cu (ppm)	0.04	0.08	0.02	0.01	0.003
Fe (ppm)	0.20	0.22	0.09	0.08	0.01
Mn (ppm)	0.09	0.07	0.32	0.02	0.002
Zn (ppm)	0.37	0.31		0.07	0.01

TABLE 2 Average Composition of Interstitial Waters and Seawater

Note: Mean Leg 8 values calculated from Presley and Kaplan (1971) and Manheim and Sayles (1971). <sup>a</sup>Upper part of hole. <sup>b</sup>Lower part of hole.

		TABLE 3
Major an	d Trace	<b>Element Compositions of the Calcareous</b>
	Oozes in	DSDP. Site 262, Timor Trough

	Cores 1-23 <sup>a</sup>	Cores 24-45 <sup>b</sup>	Average Over Entire Site 262	Average Cenozoic Sediment on Leg 27 (excluding Site 262)
Fe (%)	3.0	1.5	2.2	2.32
A1 <sub>2</sub> O <sub>3</sub> (%)	9.9	5.2	7.6	7.27
CO <sub>2</sub> (%)	13.8	28.8	21.1	20.8
Ca (%)	12.6	25.0	21.0	18.7
Mg (%)	1.23	1.54	1.38	1.10
K (%)	1.35	0.77	1.07	1.15
Sr (ppm)	1105	1572	1333	1830
Ba (ppm)	432	222	329	500
Li (ppm)	33	20	-	30
Cu (ppm)	45	22	-	21
Pb (ppm)	11	7.5	9.3	12
Zn (ppm)	89	54	72	85
Co (ppm)	9	2	6	18
Ni (ppm)	39	24	32	75
Mn (ppm)	860	228	544	2600
Cr (ppm)	79	54	67	600
P <sub>2</sub> O <sub>5</sub> (ppm)	1227	1578	1403	1600
Dolomite (%)	2.0	14.5	8.3	-
Calcite (%)	93.2	79.1	86.2	<u> </u>
Aragonite (%)	4.8	4.4	5.5	-

<sup>a</sup>Upper part of hole. <sup>b</sup>Lower part of hole.





Figure 2. Vertical variation in the chemical composition of pore waters from Site 262.

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Figure 3. Vertical variation in the chemical and mineralogical composition of Site 262.

solved salts, PO, K, Ba, Fe, Mn, Zn, and  $HCO_3$  (as indicated by the alkalinity value) and significant depletion in SO<sub>4</sub> and Ca when compared with Timor Sea surface water.

Equally marked differences between the elemental composition of pore waters in the upper part of the hole and those in the lower part are also apparent from Table 2. It is clear from Figure 2 that these vertical changes are, in general, gradational and that many of them are interrelated, with, for instance, Sr varying sympathetically with Ca. Some of these interrelations will be discussed in some detail.

Using a computer program written by Mayo (personal communication), X - Y plots, the equation of the regression line, and correlation coefficients were obtained for all interelement associations. These interrelations are summarized in the form of a correlation matrix (Table 4), and it is clear from this that there are a number of associations. At the 99% confidence level the following components show a positive correlation with depth: salinity, Cl-, SO4--, Cu, Ca, Sr, and Li; a negative correlation is shown by alkalinity, P2O5, Mg, and K. Not surprisingly, most elements show a positive correlation with salinity, but Mg, K, and Ba are notable for their negative correlation. Many components show strong positive correlations with alkalinity, including P2O5, Mg, and K, but Cl, Ca, Sr, and Li all show a strong negative correlation. pH is notable for its paucity of significant correlations; only Mn and K show a correlation with pH at the 99% confidence level. Some of the more important components will now be considered in some detail.

# Anions Cl<sup>-</sup>, SO<sub>4</sub><sup>--</sup>, HCO<sub>3</sub><sup>-</sup> (Alkalinity), and $PO_4^{---}$ (P<sub>2</sub>O<sub>5</sub>)

These four anions make up the dominant anionic components in ocean waters and pore waters of essentially oceanic origin. However, in pore waters from Site 262, the relative proportions, as well as the absolute amounts, deviate markedly from those in seawater and most other pore waters in deep-ocean sediments.

Chlorinity and salinity gradually increase down the hole, attaining a maximum of 33.1% Cl, equivalent to a salinity increase of about 50% above normal seawater. In previous DSDP drilling, salinities of this order have been encountered only in areas underlain by evaporites, such as the Red Sea (Leg 23). It therefore seems reasonable to postulate that the high Timor Trough salinities possibly result from the influx of brines, emanating from evaporite deposits which may underlie the Timor Trough. There is no direct evidence of such evaporites, although the shallow-water aspects of sediments at the bottom of the hole suggest that such deposits are certainly possible.

The sulfate content of the pore waters also increases down the hole and there is a 99% probability that SO<sub>4</sub><sup>--</sup> correlates positively with Cl<sup>-</sup>, which is the normal relationship. Despite the high salinities, the SO<sub>4</sub><sup>--</sup> content of the waters is abnormally low (Table 2) compared with seawater and most other pore waters, implying that SO<sub>4</sub><sup>--</sup> is being extracted from the system. This will occur readily at high salinities (greater than about 39<sup>0</sup>/<sub>00</sub> total dissolved salts) when gypsum precipitates out.

1.000 Ba 0.274 1.000 FI 0.472 -0.519 1.000 S -0.308 1.000 0.402 K 1.000 - 0.774 - 0.965Matrix of Correlation Coefficients for Major Cations and Anions in Pore Fluids from DSDP, Site 262 0.571 -0.501 Ca 0.539 0.491 0.555 000.1 0.625 -0.160 Mg 0.042 0.055 0.031 0.120 0.083 0.012 Zn 0.149 -0.240 0.079 -0.173 1.000 0.228 0.069 Mn 0.135 0.422 0.154 0.223 0.164 0.237 1.000 0.000 Fe 0.374 -0.276 0.383 0.383 0.240 -0.261 -0.006 -0.565 0.245 Ca P205  $\begin{array}{c} 1.000\\ -0.400\\ -0.400\\ -0.124\\ -0.126\\ 0.866\\ 0.866\\ 0.866\\ 0.620\\ 0.620\\ 0.629\\ 0.629\\ 0.598\\ -0.598\\ 0.621\\ 0.715\\ -0.715\\ \end{array}$ -0.132  $\begin{array}{c} 1.000\\ -0.332\\ 0.096\\ 0.083\\ 0.096\\ 0.096\\ 0.096\\ 0.091\\ 0.602\\ 0.602\\ 0.602\\ 0.610\\ 0$ SO4  $\begin{array}{c} 1.000\\ 0.470\\ 0.708\\ 0.413\\ 0.413\\ 0.413\\ 0.413\\ 0.413\\ 0.413\\ 0.271\\ 0.271\\ 0.249\\ 0.249\\ 0.260\\ 0.950\\ 0.950\\ 0.960\\ 0.960\\ 0.960\\ 0.9337\\ -0.3337\end{array}$ 5  $\begin{array}{c} 1.000\\ -0.017\\ 0.171\\ 0.161\\ 0.161\\ 0.036\\ -0.086\\ -0.026\\ 0.041\\ 0.044\\ 0.048\\ 0.048\\ 0.048\\ 0.048\\ 0.048\\ 0.064\\ 0.066\\$ Hd  $\begin{array}{c} 1.000\\ 0.101\\ 0.797\\ 0.957\\ 0.957\\ 0.957\\ 0.957\\ 0.957\\ 0.973\\ 0.003\\ 0.003\\ 0.647\\ 0.647\\ 0.647\\ 0.647\\ 0.697\\ -0.731\\ 0.034\\ 0.034\end{array}$ Alk  $\begin{array}{c} -0.531\\ 0.353\\ 0.257\\ 0.257\\ 0.257\\ 0.257\\ 0.257\\ 0.258\\ 0.968\\ 0.968\\ 0.968\\ 0.964\\ 0.545\\ 0.545\\ 0.545\\ 0.545\end{array}$ 1.0000.6030.0340.9600.524Sal Depth 0.0560.9290.3860.3860.28250.24880.241880.241880.241880.241880.2618300.268300.83300.83300.8430.8430.76380.8430.8430.8430.84380.81.000 0.832 0.902 Depth Sal Alk PH CI CI CI CI CI CI CI CI CI SSO4 SA Ba Ba

TABLE

Note: Coefficients of  $\pm 0.378$  or more have a 99% confidence level and are considered to be statistically significant.

$$Ca^{++} + SO_{4}^{--} \rightleftharpoons CaSO_{4}$$
 (1)

The positive correlation between Ca and SO<sub>4</sub> at a greater than 99% confidence level supports the validity of this reaction. However, the situation is rather more complex as SO<sub>4</sub><sup>--</sup> is apparently being withdrawn from the system in the upper half of the hole at salinities which would normally be insufficient for precipitation of CaSO<sub>4</sub>. This suggests that some other mechanism may be involved. Sulfate-reducing bacteria may be present in the sediments producing reactions such as:

$$SO_4^{--} + 2C \rightleftharpoons S^{--} + 2CO_2$$
 (2)

$$SO_4^{--} + CH_4 \rightleftharpoons HS^- + HCO_3^- + H_2O$$
 (3)

Both equations only approximate the natural reactions because of the highly complex nature of the organic material (see Berner, 1971, p. 114-137), but are useful as simplistic models of the true systems. The abundance of pyrite in the sediments, the high alkalinity values, and the large quantities of  $CO_2$  and  $CH_4$  encountered during drilling all lend support to the importance of Equations 2 and 3.

Alternative equations for the decomposition of carbohydrates and protein in the anaerobic calcareous sediments in the presence of sulfate-reducing bacteria are given by Berner (1966).

$$2CH_2O + SO_4^{--} + CaCO_3 \rightleftharpoons Ca^{++}$$
$$+ HS^- + 3HCO_3^{-}$$
(4)

 $4CH_2NH_2COOH + 4H_2O + 3SO_{4^{--}} + CaCO_3$   $\Rightarrow 3HS^- + Ca^{--} + 9HCO_3 + 4NH_4^+$ (5)

In the lower half of the hole, below a depth of about 280 meters, salinities may become sufficiently high for the reaction represented by Equation 1 to become of major importance. Above this depth, sulfate reduction is probably the dominant mechanism for the extraction of sulfate.

It is evident from Equations 2-5 that in a closed system an increase in the activity of sulfate-reducing bacteria will lead to a decrease in the amount of  $SO_4^{--}$  and a consequent increase in the amount of  $HCO_3^{-}$  in solution. This should result in a negative correlation between sulfate and alkalinity, and this is indeed the case at the 98% confidence level (Table 4).

Alkalinity results primarily from the generation of  $CO_2$  which then goes into solution. At the *pH* levels encountered at Site 262, bicarbonate is the dominant ion (Garrells and Christ, 1965; Krauskopf, 1967) and the reaction may be represented by:

$$H_2O + CO_2 \rightleftharpoons H^- + HCO_3^-$$
(6)

Maximum alkalinity of 93 meg/l occurs at a depth 50 meters below the sediment-water interface. This is considerably in excess of any alkalinity previously recorded from the Deep Sea Drilling Project. A high rate of sedimentation (about 10 cm/1000 y) in the Timor Trough is probably instrumental in ensuring that abundant organic material is buried before any extensive oxidation takes place. Alkalinity may reasonably be taken as an indicator of biological activity in general and sulfate reduction in particular (Presley and Kaplan, 1968; Berner et al., 1970). The abundance of organic material and pyrite suggests that conditions are strongly anaerobic within the sediment. Consequently, oxygenation of organic carbon is unlikely to be an important mechanism. Berner (1971) points out that microbiological fermentation reactions can produce CO<sub>2</sub> in an anaerobic environment, using the oxygen present in the organic matter. A simplified version of the reaction involving carbohydrate is

$$C_6 H_{12} O_6 \rightleftharpoons 3 CO_2 + 3 CH_4 \tag{7}$$

It is impossible to evaluate the relative importance of the biologically induced processes of fermentation and sulfate reduction in the determination of alkalinity. However, if alkalinity is an indicator of biological activity it is puzzling that the maximum value occurs at a depth of 50 meters and not just below the sedimentwater interface. The probable explanation for this is that the peak at 50 meters indicative of an ancient peak in biological activity. This would require that the system be closed. Alternatively, present-day biological activity might conceivably extend much farther below the sediment-water interface than is generally acknowledged.

J. Gieskes (personal communication) has suggested that the first alkalinity peak may be a sulfate-reduction peak, whereas the second peak is due to the dominance of fermentation processes.

The relationship between alkalinity and pH is of some interest, because Gardner (1973) has postulated a theoretical pH-alkalinity relation in calcareous sediments which involves an asymptotic association, with the correlation curve lying parallel to the alkalinity axis at a pH of about 6.6 (Figure 4). In the Timor Trough system, the asymptote in fact lies at a pH of 7.4 and 7.8 (Figure 4). This is similar to the Florida Bay results of Berner (1966) who places the limit at 7.3 to 7.7. It is probable that the development of  $NH_{4^+}$  and other ions which are not generally considered in theoretical systems are responsible for much of the deviation noted between the theoretical and the natural system.

Although  $P_2O_5$  (primarily in the form of  $PO_4^{---}$ ) makes a contribution to alkalinity, Gieskes and Rogers (1973) have shown that this contribution is negligible in most natural systems. Despite this, there is a strong positive correlation between alkalinity and  $P_2O_5$  (Table 4).  $P_2O_5$  also shows a significant positive correlation with Mg and K. This is perhaps a secondary correlation owing to the Mg and K content being dependent on alkalinity rather than from any tendency for these components to be  $PO_4^{---}$  dependent, although it is not

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clear why Mg and K should be alkalinity dependent. A possible explanation for the P<sub>2</sub>O<sub>5</sub>—alkalinity correlation is that the nutrient role of the phosphate radical is of some importance, so that abundant nutrients produce an increase in biological activity which, in turn, results in a high alkalinity value. Alternatively, alkalinity may itself have a direct influence on phosphate solubility.

## Ca, Mg, K, Sr, Ba, Li

These alkaline earth metals are commonly associated in aqueous systems, but at Site 262 the interrelations of these ions in pure waters appear to be fairly complex. All these cations will show a straight-line correlation with salinity if precipitation of components does not take place. Thus, Ca, Sr, and Li all show a strongly positive correlation with salinity (see Figures 5a and 5b). Mg, K, and Ba, on the other hand, all show a negative correlation with salinity (Figure 5c). The complex nature of these relationships is demonstrated by the Mgsalinity plot (Figure 5d). The regression line indicates a negative correlation, but this oversimplifies the true picture as there are two distinct trends. At low salinities, Mg varies from 800 to 1600 ppm without any sympathetic change in salinity. This near-horizontal trend is confined to the upper half of the section at Site 262. The second trend is a strongly positive correlation between salinity and Mg content. Samples lying on this positive correlation line are located in the lower half of the hole. The implication of these two divergent trends is that there are two sources of pore water: The first is oceanic water which has been incorporated and subsequently modified in situ in the interstices of the calcareous ooze in the upper half of the hole. The second, found in the lower half of the hole, is derived from (or at least modified by) the influx of saline brines possibly emanating from inferred underlying evaporite deposits.



Figure 5. Interrelations of various ions with salinity in Site 262 pore waters. Solid correlation lines have been calculated; dashed lines are approximate.

This twofold sources of interstitial fluids is also reflected in the Mg-Ca plot (Figure 6), with totally different regression lines in the upper and lower halves of the drill hole. The regression line in the lower half of the hole conforms to the more normal Mg-Ca positive correlation, whereas the negative trend in the upper half of the hole suggests either that Ca is being removed or Mg is being added to the system. Figure 7 shows that there is no marked change in salinity in the upper half of the hole associated with the change in the Mg/Ca ratio. Table 1 confirms that the high Mg/Ca values result primarily from low Ca concentrations. The correlation matrix (Table 4) indicates that the abundance of Mg solution may be controlled in part by the alkalinity of the solution. Figure 6a shows the good positive correlation (confidence level greater than 99%) that exists between alkalinity and Mg. The Ca-alkalinity plots (Figure 6b) shows a very different form, with the correlation line approximating an asymptotic curve.

The deficiency of Ca in the interstitial waters of the Timor Trough calcareous sediments is perhaps somewhat surprising. However, Berner (1966) found a similar feature in calcareous Florida sediments. He concluded that excess dissolved HCO<sub>3</sub><sup>-</sup> was the prime



Figure 6. Interrelations of various components in Site 262 pore waters. Solid correlation lines have been calculated; dashed lines are approximate.

cause of the deficiency, but suggested that Ca may also be extracted by the precipitation of calcium phosphate. The alternative explanation does not appear to be tenable for the Timor Trough sediments as there is no sympathetic depletion of phosphate in solution. Gardner (1973) offers the further alternative that in the presence of Fe<sub>2</sub>O<sub>3</sub>, sulfate reduction causes the precipitation of CaCO<sub>3</sub> and a consequent loss of Ca<sup>++</sup> from solution. Although the Fe<sub>2</sub>O<sub>3</sub> content of the sediments at Site 262 was not determined, comparison of the total Fe content (Table 1) with the pyrite content as determined by X-ray diffraction (Zemmels and Cook, this volume) suggests that Fe<sub>2</sub>O<sub>3</sub> is probably abundant.

Sr and Ca are closely associated and show a strong positive correlation (Figure 6d). However, there are evidently other factors controlling Sr solubility in addition to Ca, for the Ca/Sr ratio in normal seawater is approximately 56, whereas at Site 262 Ca/Sr ranges from 5 to 20. This indicates that despite the marked absolute decrease in the amount of Sr in these pore waters compared with the abundance of Sr in normal oceanic waters, there is an enrichment when compared with Ca abundance. Figure 7b suggests that the Ca/Sr ratio may be partly controlled by Mg; as the concentration of Mg increase so the relative abundance of Sr decreases compared to Ca. The reason for this apparent association is not known.

#### Cu, Fe, Mn, Zn

All the transition group elements tend to behave in a similar fashion in that they show a marked increase in concentration in the pore waters compared to the concentrations encountered in surface seawater (Table 2). However, there are few clear correlations between these transition elements or with most of the other porewater components. This is evident from the low correlation coefficients in Table 4.

Fe and Zn vary sympathetically but show no other significant correlations. Copper, on the other hand, does show significant positive correlations with depth, salinity, and chlorinity, and negative correlations with alkalinity,  $P_2O_5$ , and Mg. Mn correlates negatively with *p*H. Overall, however, Cu, Fe, Mn, and Zn show few definite patterns in these pore waters, and no definite conclusions can be reached regarding the mechanism controlling their concentration.

#### Sediments

## Mineralogy

X-ray diffraction analyses by the writer and by Cook, Zemmels, and Matti (this volume) indicate that the sediments at Site 262 are composed predominantly of calcite and clay minerals, with various amounts of aragonite, dolomite, quartz, and feldspar, and traces of pyrite and zeolites. There is a marked increase in the proportion of calcareous components with depth. There are also marked mineralogical changes in the calcareous fraction, with the proportion of dolomite increasing with depth. The proportion of aragonite in the carbonate fraction remains fairly constant throughout.

#### INTERSTITIAL FLUIDS AND ASSOCIATED CALCAREOUS OOZES

Using the method of Goldsmith and Graf (1958), it is possible to determine the amount of Mg substituting in the calcite lattice. There is a slight increase in the amount of substitution of Mg in the lattice with increasing depth, but throughout the calcite is of the low-magnesian variety ranging from Ca1.00 Mg0.00 CO3 to Cao.97 Mg0.03 CO3. The dolomite-type remains fairly constant and is an Mg-deficient form, ranging from Cao.60 Mg0.40 CO3 to Cao.54 Mg0.46 CO3. There does not appear to be any regular variation in the dolomite composition. The complete lack of any high-Mg calcite, even in the upper part of the hole where there is negligible dolomite, is somewhat surprising since the calcite is of biogenic origin. It is possible that the metastable high-magnesian calcite has reverted to lowmagnesian calcite and dolomite. If this has in fact taken place, then the lack of a significant decrease in the abundance of metastable aragonite is rather puzzling.

#### Chemistry

The major and trace-element composition of the Site 262 calcareous oozes is summarized in Table 1. It is apparent from this that there are some marked differences in the elemental composition of sediments in the upper half of the hole and those in the lower half. For example, the Ca composition of the total sediment in the upper half of the hole averages 12.6% compared with 25.0% in the lower half. On the other hand, the Mg content of the total sediment only shows a small variation (1.23% to 1.54%) despite an increase in the dolomite component of the calcareous fraction from 2.0% to 14.5%. The vertical variations in both elemental and mineralogical compositions are summarized in Figure 3.

Despite these vertical changes, the average inorganic composition of the Site 262 oozes is very similar to the average composition of Leg 27 Cenozoic calcareous oozes (Table 3), and there is, in turn, nothing to indicate that these differ from normal oceanic calcareous oozes. Consequently, none of the unusual features of the porewater composition can be explained on the basis of inorganic sediment composition. The fundamental abnormal feature is believed to be the abundance of organic plant material (producing organic carbon values of 1% and more) which has been incorporated in the sediment as a result of the close proximity of the Timor Trough to land and the extremely rapid rate of sedimentation. The organic carbon is available as a biological nutrient. This ultimately results in the high alkalinities encountered in the sediments and is also responsible for the abundant pyrite; it may also play a role in the modification of carbonate mineralogy.

#### Noncalcareous Components

Elements thought to fall into this category include Al, Fe, Co, Ni, Cr, Pb, Cu, Mn, Zn, Li, and Ba. All appear to be interrelated and commonly show positive correlations with each other (and negative correlations with the calcareous components—see Table 5). Some elements (such as Al and Fe) are essential lattice components of the clay minerals, whereas others such as



Figure 7. Variation of the Mg/Ca ratio in pore waters with salinity and with position at Site 262. Variation of the Ca/Sr ratio with Mg in Site 262 pore waters.

Cu and Zn may be adsorbed on the clay particle surface. Some elements such as Mn may be present as finely divided metallic oxides or complex oxides or hydroxides. There is a marked difference in the Co, Ni, Mn, and Cr content of the calcareous oozes at Site 262 and those of the other Leg 27 Sites. Mn averages 544 ppm, whereas in the other Cenozoic oozes of Leg 27 it averages 2600 ppm. The low values at Site 262 may be a reflection of the comparatively shallow water depth, i.e., abyssal zone waters may be richer in Mn. Alternatively, it may be a product of the high rate of sedimentation in the Timor Trough which results in the dilution of any chemical sediments.

Revelle (1944) first suggested that Ba is associated with carbonate in deep-sea sediments. Goldberg and Arrhenius (1958) subsequently suggested that the Ba content of deep-sea sediments is a function of the organic production of the euphotic zone, which is in turn partly dependent on latitude. Brongersma-Sanders (1967) showed that Ba becomes concentrated to a considerable degree in some diatom skeletons. In the Timor Trough sediments at Site 262, Ba correlates positively (at the 99% confidence level) with Al<sub>2</sub>O<sub>3</sub>, Fe, and all the other noncalcareous components (see Table 5) and shows a negative correlation with the calcareous components. There is, therefore, no evidence from these analyses that Ba content is related to CaCO<sub>33</sub>. It could conceivably be related to the abundance of siliceous organisms, but its strongest associations appear to be with terrigenous components such as clay minerals (as indicated by the Ba-Al<sub>2</sub>O<sub>3</sub> association) or with (?) inorganically precipitated oxides such as MnO (as indicated by the Ba-Mn association).

## **Calcareous** Components

Elements thought to fall into this category include Ca, Mg, C (expressed as CO<sub>2</sub>), Sr, and P (as P<sub>2</sub>O<sub>5</sub>). All show good positive correlations with each other and negative correlations with the noncalcareous group of elements (Al<sub>2</sub>O<sub>3</sub>, etc.—see Table 5). Calcareous components show a marked increase in abundance with increasing depth. The positive correlation between P<sub>2</sub>O<sub>5</sub> and Ca suggests that much of the P<sub>2</sub>O<sub>5</sub> may be of biogenic origin and is incorporated in the skeletons of microfossils.

Sr values are fairly normal, in general, except Core 2 (Table 1) which appears to be anomalously high. A strongly positive correlation is evident between Sr and Ca, but there is a weakly negative trend between Sr and Mg. This may be a reflection of the loss of Sr as a result of the dolomitization of calcite, i.e., replacement of Ca by Mg. There are marked variations in the Ca/Mg ratio which might reasonably be expected to correlate with

				Matrix of (	Correlation	1 Coefficie	nts for Ma	T/ or and Tra	ABLE 5 ce Elemen	its in Calca	reous Sed	ments fro	n DSDP, S	ite 262				
	Depth	A1203	co <sub>2</sub>	Co	Ni	Cr	Pb	$P_2O_5$	Cu	Fe	Mn	Zn	Mg	Ca	К	Sr	Li	Ba
Depth	1.000								ж									
A1203	-0.799	1.000																
C02	0.849	-0.985	1.000															
Co	-0.704	0.704	-0.727	1.000														
Ni	-0.712	0.873	-0.858	0.683	1.000													
5	-0.638	0.750	-0.780	0.438	0.656	1.000												
Pb	-0.312	0.371	-0.368	0.170	0.317	0.478	1.000											
P205	0.618	-0.715	0.706	-0.488	-0.712	-0.538	-0.423	1.000										
Cu	-0.873	0.956	-0.964	0.730	0.896	0.712	0.335	-0.737	1.000									
Fe	-0.796	0.987	-0.986	0.703	0.862	0.765	0.380	-0.700	0.951	1.000								
Mn	-0.808	0.903	-0.910	0.755	0.777	0.629	0.365	-0.578	0.897	0.900	1.000							
Zn	-0.742	0.967	-0.942	0.633	0.901	0.717	0.313	-0.733	0.946	0.958	0.822	1.000						
Mg	0.438	-0.543	0.527	-0.339	-0.614	-0.519	-0.246	0.447	-0.544	-0.526	-0.389	-0.583	1.000					
Ca	0.846	-0.974	0.992	-0.734	-0.825	-0.764	-0.377	0.686	-0.951	-0.979	-0.928	-0.918	0.434	1.000				
К	-0.709	0.971	-0.960	0.653	0.877	0.744	0.353	-0.706	0.925	0.969	0.852	0.960	-0.541	-0.946	1.000			
Sr	0.669	-0.706	0.731	-0.639	-0.508	-0.509	-0.335	0.410	-0.696	-0.723	-0.816	-0.620	-0.020	0.797	-0.659	1.000		
Li	-0.648	0.918	-0.894	0.574	0.856	0.704	0.313	-0.697	0.860	0.912	0.813	0.917	-0.453	-0.885	0.913	-0.637	1.000	
Ba	-0.806	0.910	-0.907	0.713	0.892	0.664	0.304	-0.725	0.952	0.902	0.838	0.931	-0.562	-0.888	0.890	-0.664	0.830	1.000
Note: C	oefficients	of ±0.378	or more h	iave a 99%	confidenc	e level and	l are consid	lered to be	statistical	ly signific.	ant.							

the abundance of dolomite if the dolomite has, in fact been formed by the dolomitization of calcite, but such a trend is not clearly defined (Figure 8). This may be partly because a significant amount of the Mg present in the sediments is associated not with dolomite (or magnesian calcite) but with the clay minerals. Additional possible mechanisms include direct precipitation of dolomite from solution rather than forming by the diagenetic dolomitization of calcite. Alternatively, some of the dolomite may be allochthonous, derived from an older formation which is presently being eroded, but the Mg-deficient nature of the dolomite suggests that the dolomite is comparatively young.

If the trends of calcareous components in the sediments are compared with the trends of these same elements in the pore waters, correlations are, in general, either completely lacking, or, at best, poorly defined. This is probably the result of most of the cations and anions in solution being derived from the original seawater rather than from the adjacent sediments.

However, there is a well-defined positive correlation between the concentration of Mg in the pore water and the abundance of dolomite in the sediments. The Mg/Ca ratio does not appear to have any great importance in the dolomitization process in this particular environment. This is unlike the supratidal environment where the Mg/Ca ratio is of some importance (Muller et al., 1972; Cook, 1973).

Ca concentration in the interstitial waters shows a poorly defined positive trend with Ca concentration in the sediments, but alkalinity appears to have a much greater influence. Sr and  $P_2O_5$  in solution show no obvious correlation with the Sr and  $P_2O_5$  content of the sediments. The transition metals in pore waters and sediment also fail to show any sympathetic trends.

## SUMMARY AND CONCLUSIONS

The sediments of Site 262 are similar in composition to most other deep-sea calcareous oozes. The only exception to this is that Mn, Ni, Co, and Cr are somewhat impoverished. This may result from the comparative shallowness of the oozes at Site 262 or, alternatively, is a consequence of the rapid rate of terrigenous and biogenic sedimentation which dilutes chemical sedimentation. The dominant trend in the sediments is one of increasing abundance of carbonate with increasing depth. This has a marked effect on the major- and trace-element geochemistry of the sediments, yet has little influence on the geochemistry of the pore fluids. By contrast, the organic-matter content of the sediments is believed to have a very marked effect on the chemistry of the pore waters. The organic matter present in the sediments is used by bacteria in sulfate reduction and fermentation reactions and the net effect of this is to produce abnormally high alkalinities in the pore waters. A sympathetic association between alkalinity and the Mg, K, and P2O<sub>5</sub> content of the pore waters is apparent, but the reason for these interrelations is not understood. Other associated effects include the loss of SO<sub>4</sub><sup>--</sup> from solution (by sulfate reduction) and also a decrease in Ca<sup>++</sup> which may be related to the presence of Fe<sub>2</sub>O<sub>3</sub> in the sediments (Gardner, 1973). The bacterial processes also result in the formation of pyrite in the sediments.



Figure 8. Plot showing lack of any clear correlations between the Ca/Mg ratio and the abundance of dolomite in the sediments.

A further geochemical trend of some importance is that of increasing salinity with increasing depth. This has a marked effect on both the anionic and cationic composition of the pore waters. It is also believed to have some effect on the sediment composition and particularly the abundance of dolomite, as dolomite also shows a marked increase in abundance with increasing depth. There is also a poorly defined trend of increasing substitution of Mg in the calcite lattice with increasing depth, but the complete absence of high-magnesian calcite is a puzzling feature, particularly as metastable aragonite is present throughout the hole.

In conclusion, there are three basic geochemical trends with increasing depth at Site 262. These may be generalized as (1) decreasing alkalinity, which is primarily a reflection of decreasing bacterial activity with depth; (2) increasing salinity; and (3) increasing abundance of carbonates in the sediment.

A summary of the three trends is shown in Figure 9. Elements which are dependent primarily on one of these factors such as  $P_2O_5$  and alkalinity (or bacterial activity) has a trend parallel to that factor. An element which is dependent on more than one factor, such as Mg, has a considerably more complex distribution pattern. Bacterial activity is thought to have a particularly marked effect on the pore-water composition in the upper half of the hole, whereas the effects of hypersalinity are dominant in the lower half. Both these features have a significant effect on the diagenetic changes taking place in the sediments.

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Figure 9. Summary of the three basic geochemical trends at Site 262.

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