# 20. INTERSTITIAL WATER CHEMISTRY: DEEP SEA DRILLING PROJECT, LEG 4<sup>1</sup>

B. J. Presley and I. R. Kaplan, Department of Geology and Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California

## **INTRODUCTION**

Interstitial water was removed from sediment on board the *Glomar Challenger* using either a gas operated squeezer similar to the one described by Presley *et al.* (1967) or, in the case of more highly indurated sediment, a hydraulic press of the type described by Manheim (1966). The water was forced into a disposable hypodermic syringe by the squeezer, and the syringe was then used to force the water through a 0.45-micron membrane filter and into polyethylene bottles for storage.

Twenty-two samples were collected from seven sites. In each case the samples, ranging in volume from 10 to 100 milliliters, were taken in duplicate; one set was quick-frozen and then reserved until analysis had begun, the other set was kept refrigerated at 4° C, except for the time required to air freight it to and from Lamont. The frozen samples were used for the silicon, phosphate, boron, and some of the sulfate analyses. All other work utilized the refrigerated samples. From 3 to 10 weeks elapsed between coring and the arrival of the refrigerated samples at UCLA. Analysis of these samples began immediately upon their arrival, and was completed in less than four weeks. The frozen samples were picked up from the ship in San Diego, 2 to 9 weeks after coring and were kept frozen until analyzed about four weeks later.

A very brief description of the sediments is included in Table 2, and a detailed description can be found elsewhere in this report. Eh and pH measurements were made on many of the water samples on board ship soon after squeezing.

The data has not been included here, since it is reported in full by Fred L. Sayles who took the measurements. The pH values given to the authors are so variable, and many of them are so low compared to other interstitial waters measured in this laboratory that their significance cannot be estimated at present.

# <sup>1</sup>Publication No. 842, Institute of Geophysics and Planetary Physics.

# **EXPERIMENTAL PROCEDURES**

The major cations were determined by atomic absorption spectroscopy after making necessary dilutions. For potassium and calcium, 100 milliliters of a 1 per cent lanthanum solution was added to 1 milliliter of each sample, both volumes measured with automatic pipettes. The lanthanum effectively buffers against interference from phosphate and other ions which can cause serious errors in the potassium and calcium determinations. This solution was further diluted for the sodium and magnesium analysis, by 1 + 100 and 1 + 9, respectively. Standards were prepared using the same lanthanum solution that was used for the samples. A sample of I.A.O.P. standard seawater of chlorinity 19.374 was also analyzed, giving values essentially the same as those listed by Culkin (1965).

The chloride was determined by Mohr titration and standardized with I.A.O.P. seawater. The bromide analysis used is a modification of the method of Balatre (1936) in which chloramine-T is used as an oxidizing agent in the presence of phenol red in an acetate buffer. The resultant color is measured spectrophotometrically and compared to standards in artificial seawater.

Dissolved sulfate was determined gravimetrically after precipitation as barium sulfate from an acidified aliquot of interstitial water.

Manganese, zinc and strontium were determined by atomic absorption spectrophotometry of undiluted interstitial water. Standards for manganese and zinc were made up in surface seawater, which was also used as a blank, since the concentration of these elements in seawater is negligible compared to that in interstitial water. Strontium-free artificial seawater gave a high blank, so the strontium values for the samples were obtained by assigning a value of 8 ppm to I.A.O.P. standard seawater against which measurements were made. A sample of seawater from near Hawaii, and one from the Scripps pier gave almost exactly the same absorbance as the I.A.O.P. water.

Lithium was determined by flame emission spectrography on samples which had been diluted 10 to 1 with distilled water. Artificial seawater could not be used to make up standards because of the high blank, so I.A.O.P. standard water was assigned a value of 170 ppb after it was observed to give readings essentially the same as seawater from near Hawaii and from the Scripps pier.

The boron procedure was modified from one given by Hayes and Metcalfe (1952), and involves developing a complex with curcumin in glacial acetic-concentrated sulfuric acid, then diluting to volume with ethanol. The resulting color is measured spectrophotometrically and compared to standards made from boric acid. Two milliliters of the same 10 to 1 solution used in the lithium determination was sufficient for the boron analysis. Standard seawater gave the expected concentration when it was used in the procedure.

Dissolved silica was determined essentially as outlined by Strickland and Parsons (1968) except that the molybdenum solution was made more dilute, and only 1 milliliter of sample was used instead of 25. The reduced silico-molybdate color was measured spectrophotometrically and compared to standards made from a commerical silicon standard.

Several samples were analyzed for phosphate using the ascorbic acid reduction method modified from Strickland and Parsons (1969). Two milliliters of sample were used in a final volume of 50 milliliters. The limit of detection when using only 2 milliliters of sample is about 1 ppm phosphate.

Iron, copper, nickel and zinc were determined by atomic absorption spectrophotometry after extraction into MIBK using APDC as a chelating agent (Brooks *et al.*, 1967). Only those samples for which more than 30 milliliters of water were available were extracted, hence the data for iron, copper and nickel are incomplete (Table 3). The values for zinc listed in Table 3 were obtained by direct aspiration of the water samples, and the extraction procedure was used as a check on these values. In all cases the agreement was remarkably good.

The extraction was effected into 5 milliliters of MIBK, resulting in at least a six-fold concentration (depending on the starting sample size); and, coupled with the enhancement of the signal due to the organic solvent, this resulted in a signal which was usually easy to measure. It was not possible, however, to do more than four metals on this volume of water.

Standards were prepared by spiking previously extracted seawater with incremental amounts of the metals, then extracting them as was done for the samples. This procedure corrects for possible incomplete extraction.

In general, the small sample size made replicate analysis impossible, however, chloride was measured in duplicate for all samples and only duplicate values differing by 0.05 milliliter or less of silver nitrate used were accepted. This corresponds to 0.18 g/l chloride. The precision of the other analytical procedures had been determined by replicate analysis on seawater or interstitial water during development or modification of the techniques used in this laboratory. These are given in Table 1 as relative standard deviations.

The accuracy of the major ion analysis can be judged from Table 4, where anions and cations are given as milliequivalents per liter. The sum of the positive and negative ions comes to within 1 per cent of being equal in over half the samples, if a normal seawater concentration of total dissolved carbonate species is assumed; and only two of the twenty-two samples are out of balance by more than 2 per cent. In both these samples the positive charge is too high, and it is very likely that total dissolved carbonate is higher than the normal seawater value of 3 meq/1. This would reduce the discrepancy. The values for all analysis on the I.A.O.P. standard seawater, except for chloride are the result of a single determination (as the other sample results are).

TABLE 1           Estimates of Precision of Analytical Procedures <sup>1</sup>										
Na	2.0%	Br	4.0%							
Mg	2.0%	В	7.0%							
Ca	2.5%	Si	8.0%							
K	2.5%	Fe	9.0%							
Sr	2.5%	Cu	5.0%							
Li	6.0%	Ni	9.0%							
Cl	0.8%	Mn	10.0%							
$SO_4$	3.0	Zn	10.0%							

<sup>1</sup>Based on replicated analyses of "average" interstitial water; given as coefficients of variation-standard derivation/mean.

## **RESULTS AND DISCUSSION**

The results obtained are presented in Tables 2, 3 and 4. The samples represent a variety of environmental conditions and range in age from Recent to Paleocene. Only preliminary shipboard lithological discriptions of the sediments were available when this report was written. Furthermore, samples from more than 3 depths were available for only two of the seven sites. The variety of environments and sediment types and the small number of samples available from each location makes it difficult to speculate on specific diagenetic processes which have affected the interstitial water. Nevertheless, certain trends are apparent, especially in those holes where the greatest number of depths were sampled.

TABLE 2	
Major Components of Interstitial	Water, JOIDES, Leg 4

Hole	Designation	UCLA No.	Depth (m)	Age Description	Na g/l	K mg/l	Ca mg/l	Mg mg/l	Sr mg/l	Cl g/l	SO <sub>4</sub> g/l	Br mg/l
Hole	Hole 23, 6° 08.75'S, 31° 02.6'W, water depth 5079 meters, foot of Continental Rise off Brazil											
3-2	(90-150 cm)	11	65	Miocene yellow-brown clay, Mn-Fe oxides	11.1	398	530	1216	10.5	19.82	2.59	64
4-4	(88-140 cm)	12	119	Miocene olive-green clay, turbi- dite	11.0	402	561	1205	11.9	20.09	2.56	65
Hole	Hole 24, 6° 16.2'S, 30° 55.2'W, water depth 5148 meters, foot of Continental Rise off Brazil											
4-2	(103-150 cm)	13	228	Paleocene brown claystone mot- tled with green	10.7	241	852	1001	33.4	19.77	1.79	64
Hole	26, 10° 55.53'N,	44° 02.57	'W, water	depth 5169 meters, Vema Fracture Z	one on N	lid-Atlar	tic Ridge	2.				
1-3	(81-130 cm)	14	100	Pleistocene gray silty clay, Mn pellets	11.0	331	275	1020	7.7	19.91	0.12	66
3-2	(100-150 cm)	15	230	Pleistocene olive-gray clay-clay- stone	10.9	269	280	881	8.1	19.86	0.00	71
5-1	(89-131 cm)	16	478	Pleistocene dark olive gray silty claystone	11.0	142	486	784	11.5	19.98	0.50	69
Hole	27A, 15° 51.39'N	, 56° 52.7	6'W, wate	r depth 5251 meters, area of rough b	asement	near Ant	iles					
1-5	(93-140 cm)	17	32	Pleistocene brown silty plastic clay	11.1	419	522	1185	6.9	20.05	2.53	64
2-3	(90-138 cm)	18	49	Pleistocene light brown to yellow brown clay, pyrite (?)	11.0	405	587	1155	7.1	20.27	2.43	64
Hole	Hole 27, 15° 51.39'N, 56° 52.76'W, water depth 5251 meters, area of rough basement near Antiles											
2-2	(95-150 cm)	19	143	Miocene light olive gray clay, red mottling	10.7	251	807	1092	7.1	19.88	1.82	67
3-2	(0-64 cm)	20	237	Miocene stiff green-gray clay	10.4	203	928	1030	12.1	19.80	1.16	65
4-3	(84-150 cm)	21	249	Miocene green-yellow mottled clay	10.4	220	960	1030	11.7	20.02	1.23	65

			. 1									
Hole	Designation	UCLA No.	Depth (m)	Age Description	Na g/l	K mg/l	Ca mg/l	Mg mg/l	Sr mg/l	Cl g/l	SO <sub>4</sub> g/l	Br mg/l
Hole 2	27, 15° 51.39'N,	56° 52.76	W, water	depth 5251 meters, area of rough ba	sement n	ear Antil	es					
5-2	(95-149 cm)	22	371	Oligocene green-gray calcareous silty clay	10.4	186	1550	835	16.0	20.39	0.82	69
Hole 2	8, 20° 35.19′N,	65° 37.33	'W, water	depth 5521 meters, outer ridge crest	of Puerto	o Rican 7	Trench					
2-3	(82-150 cm)	23	72	Unknown barren brown deep sea clay	10.7	371	760	1185	8.3	19.80	2.41	64
3-2	(89-150 cm)	24	171	Eocene calcareous gray-green stiff clay	11.0	390	959	1082	9.6	20.05	2.26	65
Hole 29, 14° 47.11'N, 69° 19.36'W, water depth 4247 meters, central Venezuelan Basin												
1-3	(90-150 cm)	25	4	Recent foraminiferal clay ooze	11.2	467	479	1210	8.7	20.30	2.70	65
4-3	(85-140 cm)	26	31	Pliocene olive clay ooze	11.4	450	508	1175	9.0	20.05	2.59	65
9-3	(80-136 cm)	29	139	Eocene radiolarian ooze	11.3	- 405	698	1155	6.9	20.14	2.56	66
Hole 2	9B, 14° 47.11′N	, 69° 19.3	6'W, wate	r depth 4247 meters, central Venezu	elan Basi	n						
2-2	(94-150 cm)	27	70	Miocene banded mica clay	10.9	378	603	1165	9.0	19.96	2.56	65
5-2	(99-150 cm)	28	100	Miocene white chalk	11.0	398	632	1155	8.2	20.16	2.53	65
Hole 3	0,12° 52.92′N,	63° 23.00	'W, water	depth 1218 meters, Aves Ridge in Ca	aribbean							
2-4	(90-150 cm)	30	64	Pleistocene fluid calcareous green clay	11.1	437	153	979	5.4	20.09	0.52	68
3-3	(90-150 cm)	31	11	Plio-Pleistocene fluid calcareous green clay	11.1	386	182	842	8.2	20.20	tr.	68
5-2	(90-156 cm)	32	66	Pliocene fluid calcareous green clay	11.3	340	268	689	10.0	20.16	0.00	73
		Sea w	ater (Culk	in, 1965, page 122)	11.1	397	424	1330	8.2	19.89	2.79	68

Sample Number	Depth (m)	Fe µg/l	Cu µg/1	Ni µg/1	Mn Mg/1	Zn µg/1	Li µg/1	Si Mg/1	B Mg/1
23-3-2	65	2.3	15.7	48.0	6.200	675	230	5.8	7.8
23-4-4	119	2.6	5.8	16.0	0.500	125	240	3.1	6.3
24-4-2	228	_	_		0.400	35	_		_
26-1-3	100	21.0	21.0	47.0	0.200	225	125	8.4	4.7
26-3-2	230	_	_	_	0.100	210	125	3.3	3.7
26-5-1	478			—	0.100	215	178	1.8	1.7
27A-1-5	32	3.2	7.3	15.0	2.900	150	140	2.3	3.2
27A-2-3	49	2.8	6.3	13.0	1.800	100	165	2.6	4.0
27-2-2	143	_	_	—	5.400	215	266	8.4	6.0
27-3-2	237	_	_	_	0.300	180	325	2.4	4.8
27-4-3	249	_	_	_ *	0.300	250	330	3.1	4.7
27-5-2	371	—	—	-	0.200	120	388	2.3	2.6
28-2-3	72	_	_	_	7.500	570	355	10.5	6.1
28-3-2	171	7.8	2.6	27.0	2.600	310	530	22.0	5.9
29-1-3	4	1.6	2.3	10.0	1.700	70	185	2.5	5.4
29-4-3	31	1.3	1.5	22.0	2.200	250	180	2.7	5.6
29B-2-2	70	1.5	3.1	36.0	6.500	225	200	4.7	6.2
29B-5-2	100	2.1	4.7	22.0	4.200	135	218	5.8	6.1
29-9-3	139	34.0	9.0	16.0	2.100	95	240	29.0	3.6
30-2-4	64	7.0	7.1	13.0	0.100	100	135	5.8	3.7
30-3-3	111	9.1	4.9	17.0	0.100	95	132	8.5	2.9
30-5-2	166	3.6	2.3	20.0	0.050	90	145	3.8	1.9
Std. Seawater	0	10.0	3.0	2.0	0.002	10	170	0-4.0	4.5

 TABLE 3

 Minor Components of Interstitial Water.
 JOIDES Leg 4

#### **Chloride and Bromide**

In only two of the twenty-two samples analyzed did the chloride concentration differ from that of average seawater by as much as 2 per cent. Furthermore, there was no tendency for chloride to become more enriched at depth in the hole, despite the fact that samples were from as deep as 478 meters and were as old as Paleocene.

The bromide concentration showed slightly more scatter than the chloride, but here too, all values are very close to those of average seawater, and there is little evidence of enrichment at depth.

It seems then that not only are chloride and bromide relatively inert to chemical changes occurring during diagenesis, but that concentration of pore water by ultrafiltration is not an important process in most environments, at least at the depths sampled here.

## Sulfate

Sulfate reduction had occurred in five of the seven sites sampled on Leg 4. At two sites, Hole 26 on the Vema Fracture Zone and Hole 30 on the Aves Ridge, sulfate had been completely removed at some depths. The sediment from Hole 26 is reported to consist of extremely organic-rich turbidites, which are very rapidly filling a deep trough on the fracture zone. Much of the organic matter appears to be the remains of terrigenous plants which have been carried into the trough by the turbidity flows. The Plio-Pleistocene sediments in Hole 30

Sample	C1 <sup>-</sup>	SO <sub>4</sub> =	(Sum)	К+	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	(Sum)	(Diff.)
23-3-2	559	54	613	10.2	26.4	100.0	483	619	+6
23-4-4	567	53	620	10.3	28.0	99.1	479	616	-4
24-4-2	558	37	595	6.2	42.5	82.3	465	596	+1
26-1-3	562	3	565	8.5	13.7	84.0	479	585	+20
26-3-2	560	0	560	6.8	13.9	72.5	474	567	+7
26-5-1	564	10	574	3.6	24.3	64.5	479	571	-3
27A-1-5	566	53	619	10.7	26.0	97.5	482	617	-2
27A-2-3	572	50	622	10.4	29.3	95.0	478	613	-9
27-2-2	561	38	609	6.4	40.3	89.8	465	602	-7
27-3-2	558	24	582	5.2	46.3	84.7	452	589	+7
27-4-3	565	26	591	5.6	47.9	84.7	452	591	0
27-5-2	575	17	592	4.7	77.3	68.7	452	603	+11
28-2-3	558	50	608	9.5	37.9	97.5	465	610	+2
28-3-2	566	47	613	10.0	47.9	89.1	478	625	+12
29-1-3	573	56	629	11.9	23.9	99.5	487	622	-7
29-4-3	566	54	620	11.5	25.3	96.7	496	629	+9
29B-4-3	563	53	616	9.6	30.1	95.8	474	610	-6
29B-5-2	569	53	622	10.2	31.5	95.0	478	615	-7
29-9-3	568	53	621	10.4	34.8	95.0	491	631	+10
30-2-4	567	11	578	11.1	7.6	80.5	483	582	+4
30-3-3	570	Trace	570	9.8	9.1	69.3	483	571	+1
30-5-2	569	0	569	8.7	13.2	56.7	492	570	+1
Std. Seawater	558	55	613	11.0	22.0	106.0	483	622	+9

TABLE 4 Major Components of Interstitial Water from JOIDES Leg 4 as Milliequivalents per Liter

reportedly consist in large part of the remains of calcareous marine organisms. The sedimentation rate is relatively high in this location too, due to the high organic productivity and the shallow water which results in little dissolution of carbonate. These processes cause organic matter to be rapidly buried, and interstitial water oxygen is depleted due to microbial activity. This leads to sulfate reduction and release of hydrogen.

There was reportedly no sulfide from these cores when they were collected, but it is not unusual to have sulfide produced then subsequently removed by reaction with iron and other heavy metals. Pyrite was reported to be replacing detrital organic matter at depth in Hole 26, giving evidence of this process.

## Sodium

Sodium rarely differed from its concentration in normal seawater by more than one per cent in six of the seven sites on Leg 4; and, the sodium to chloride ratios in samples also showed very small variations, with a single exception. The anomalous sodium values are those at the bottom of Hole 27. The sodium chloride ratio in this hole gradually decreased from 1 per cent less than the seawater value to 9 per cent at the deepest sample analyzed. The variation in the ratio is slightly larger than would be expected by the maximum analytical error and seems to be real. The calcium concentration increased to almost 4 times its seawater value in this hole, whereas, magnesium decreased markedly. These changes may be related to the apparent sodium decrease, probably by exchange reactions involving clays and/or carbonates.

### Potassium

Potassium is usually reported to be enriched in interstitial water relative to open ocean water due to leaching of feldspars and other detrital silicates. (Siever et al., 1965; Brooks et al., 1968). However, many scientists believed that degraded illites take up potassium from ocean water and from the well-ordered illite found in ancient sediments (for example, Krauskopf, 1967). This reaction, continued below the sediment-water interface, would tend to lower the potassium concentration in the interstitial water. If reactions of these types are occurring, and this would seem to be the usual circumstance, then it is difficult to predict what the interstitial water concentration should be. Even if dissolved potassium is in equilibrium with some solid phase, which is not at all certain considering the above, the exact phase would be difficult to determine; and, thermodynamic data for silicates is so scanty that any meaningful calculations would be almost impossible.

The potassium distribution is also confused because its concentration in the interstitial water may have been changed due to the temperature of squeezing. This has been commented on by Mangelsdorf *et al.* (1969); and, unpublished data of the authors show that potassium enrichments of 20 per cent or so are possible, depending on the sediment type, if the temperature is increased from 4° C to  $25^{\circ}$  C. The authors have no information on the *in situ* temperature when these cores were taken, or any information on how long the sediment remained at room temperature before squeezing. Because of this, it is impossible to estimate what effects, if any, were introduced by temperature changes.

There are interesting trends in the potassium concentration of the Leg 4 samples but, as would be expected from the comments above, it is not clear why the observed pattern occurs. For example, Hole 23 showed a uniform distribution of average seawater concentration down to 119 meters and into Miocene, yet in Hole 24 which was drilled only 10 kilometers away, the concentration at 228 meters in Paleocene clay is 60 per cent of the average seawater value.

Holes 27 and 29, from which the greatest number of samples were available, present even more of a contrast. Hole 29 in the Caribbean reached Eocene at 139 meters. Here potassium was enriched at the top of the core by about 10 per cent over seawater values, and dropped to near seawater values at the bottom of the core. Hole 27, located in the Atlantic just outside the Antilles Island Arc, reached Oligocene at 371 meters. Here the potassium concentration started at near seawater value, but dropped off with depth until less than half remained at the bottom of the hole.

Hole 26 on the Mid-Atlantic Ridge showed a decrease in potassium concentration with depth of about the same magnitude as was shown in Hole 27 and, whereas our deepest sample was from 478 meters depth, it is of Pleistocene Age.

It is not possible at this time to relate these variations in potassium concentration to sediment type, depth, age or any other variables that have been measured. However, it would seem from this group of samples that potassium uptake, probably by clays, prevents any significant buildup from weathering of silicates, except possibly near the sediment-water interface; and, there the temperature of squeezing could be the actual cause for enrichment. The general tendency to lose potassium with depth is shown in Figure 1.

#### Calcium

A decrease in calcium concentration in interstitial water from areas of sulfate reduction has been noted by several authors (for example, see Berner, 1966, or Presley and Kaplan, 1968). Presley and Kaplan were able to show that interstitial water from these areas is highly enriched in dissolved carbonate, which causes super-saturation with respect to calcite, and probable precipitation of some solid carbonate phase. This same process has no doubt been in operation in Holes 26 and 30, because in these holes low concentrations of both dissolved sulfate and calcium were found. Dissolved carbon dioxide was also high in Holes 26 and 30 (Fred Sayles personal communication) giving a picture identical to that in other areas of sulfate reduction.

In addition to the depletion in calcium which accompanied sulfate reduction in Holes 26 and 30, a second phenomenon can be seen in every hole sampled. That is an increase in calcium concentration with depth. The increase was especially dramatic in Hole 27, where the deepest sample contained almost four times as much calcium as is normal for seawater.

The shallowest sample available to the authors was from a range of few to many meters depth at every location; therefore, the complete distribution with depth is unknown, but regardless of whether the shallowest sample contained more or less calcium than seawater, deeper samples became progressively enriched in calcium at every site. This pattern is shown graphically in Figure 2.

#### Magnesium

The magnesium concentration in all samples is less than the value for average seawater, and in every case decreases with depth in the hole. This pattern is shown in Figure 3. The fact that calcium always increases with depth, while magnesium always decreases, strongly suggests that an "ion exchange" reaction of some type is responsible. One logical process of this kind would be



Figure 1. Potassium concentration in the interstitial water of Leg 4 sediments as a function of depth.



Figure 2. Calcium concentration in the interstitial water of Leg 4 sediments as a function of depth.



Figure 3. Magnesium concentration in the interstitial water of Leg 4 sediments as a function of depth.

the formation of dolomite from calcite by the traditional replacement reaction:

$$Mg^{2+} + 2 CaCO_3 = MgCa (CO_3)_2 + Ca^{2+}$$
 (1)

However, it can be seen from Table 4 that the increase in calcium on a molar basis is only very roughly compensated for by a decrease in magnesium. For example, in Hole 27, where the largest calcium increase occurred, only about three-fifths of the increase was balanced by a magnesium decrease, whereas in Hole 26 the magnesium decrease was twice the calcium increase.

Dolomite may have been formed in some places by replacement reaction (1) despite the lack of mass balance between magnesium lost and calcium gained by the pore water. Authigenic dolomite was reported to be present in some of the Leg 1 sediments (Leg 1 Preliminary Hole Summaries), but there was no report of dolomite in the Leg 4 Hole Summaries. These summaries were compiled on board ship from preliminary visual inspection of the sediment, and later more complete study will certainly add much information to that now available. When the final lithological descriptions are obtained a correlation between calcium and magnesium in the water and the presence or absence of dolomite may be revealed, but no correlation is possible at this time.

It should be noted that the amount of dolomite that can form from dissolved magnesium in interstitial water, even if all of it is utilized, is less than 1 per cent of the total sediment. Therefore, magnesium must be supplied by some solid phase, such as, high magnesium calcite, or a silicate, if much dolomite is to be produced. This magnesium would probably be transferred through the interstitial water, where a situation similar to that discussed for potassium would exist. That is, magnesium would be both added to and subtracted from the water at the same time, involving exchange with at least two different solid phases. An equilibrium between the water and a solid phase may not be maintained everywhere, rather the concentration in the water may be controlled by the kinetics of the various reactions that use or give up magnesium.

In summary, potassium, calcium, magnesium and, to a much lesser extent, sodium concentrations in interstitial water give evidence of reactions having occurred within the sediment column, otherwise their concentrations would be the same as that in seawater throughout all the cores. Furthermore, these reactions bring the interstitial water composition closer to that typical of formation waters, such as, oil well brines. Formation waters are generally impoverished in sulfate, magnesium and potassium and enriched in bicarbonate and calcium, relative to present-day seawater (White *et al.*, 1963). Many formation waters are also much more saline than seawater, but the samples so far analyzed show little or no tendency toward any increase in total salinity and thus no evidence of concentration by membrane filtration.

#### Strontium

The strontium concentration, as might be expected, follows fairly closely that of calcium. This is especially apparent in Hole 27, where more than a three-fold increase in calcium concentration was paralleled by a strontium increase of more than two-fold. In other places, such as Hole 29, the correlation is not as good, probably reflecting the difference in sediment type found at depth at the various drilling sites.

The strontium concentration in the only sample analyzed from Hole 24 was unusually high, 33 ppm. Here calcium was enriched over the seawater value by a factor of 2, and it seems likely that the phase which released calcium was rich in strontium.

#### Lithium

The lithium concentrations for the Leg 4 samples are given in Table 3, along with other minor elements which were determined. It can be seen that lithium shows a more consistent pattern than the other trace elements, because it increases in concentration with depth in every hole. This is shown graphically in Figure 4. Note that even when lithium was slightly depleted with respect to the normal seawater value at shallow depths, there was a gradual increase in concentration with depth and, in most cases, an enrichment over seawater at the bottom of the hole. The highest enrichment occurred at the bottom of Hole 28, where a concentration three times greater than the seawater value was found.

The increase in lithium concentration with depth may be an indication of either a leaching of "basement" rocks or some kind of volcanic emanations from below. Lithium has been reported to be concentrated in the residual fluids during magmatic crystallization (Goldschmidt, 1954); this, plus its high concentration in many "magmatic" waters (White *et al.*, 1963), makes the latter hypothesis attractive. The two sites which showed a low interstitial water lithium concentration also had the thickest sediments: Hole 26, which was drilled in a deep trough filled with turbidites; and, Hole 30, which was in a thick sequence of carbonate-rich sediments. This greater sediment thickness may have diluted any contribution of lithium from depth.

Moreover, the highest lithium concentration was found in Hole 28, where the sediments are reportedly thin and the Moho is unusually shallow (Leg 4, Hole Summaries). This area on the outer ridge of the Puerto



Figure 4. Lithium concentration in the interstitial water of Leg 4 sediments as a function of depth.

Rican Trench should be one of tension and normal faulting, according to present views of down-warping or over-thrusting associated with trench formation. Volcanic emanations from such an area may more readily escape upward and influence the sediments and interstitial water. Such a process may have contributed to the high lithium concentration in the Red Sea geothermal deeps (Brooks *et al.*, 1969).

Despite the attractiveness of the idea of volcanic contributions of lithium to interstitial water, a simple leaching of silicates containing lithium cannot be ruled out. Lithium forms few minerals of its own, but usually substitutes in the structure of more common minerals. If these minerals break down at depth in the sediment column during diagenesis, forming new minerals *in situ*, the lithium may be excluded, thereby increasing its concentration in the interstitial water.

#### Boron

The boron distribution proved to be somewhat irregular, but there was a general tendency for the shallow samples to be somewhat enriched relative to seawater. with a decrease to values significantly lower than seawater at depth. This is shown in Figure 5. Tageyeva (1965) found boron to be significantly enriched in interstitial water from Arctic Ocean sediments in cores 17 to 60 centimeters long. In the Caspian Sea sediments, Tageyeva (1958) found boron to be enriched in recent interstitial water, but impoverished in ancient pore water; this is in agreement with the trend found in the present samples. No other data on boron in interstitial water was available to the authors at this time, so it is not possible to speculate on whether or not the boron enrichment at the tops of cores noted by Tageyeva is a general phenomenon.

Goldschmidt (1954) has reported that the calcareous or siliceous hard parts of nearly all organisms investigated contained detectable amounts of boron, commonly 10 to 1000 ppm boric oxide. The leaching or organic remains would thus be one way to enrich interstitial water in boron.

Many authors have pointed out that sediments, especially marine shales, are enriched in boron relative to igneous rocks, for example, Goldschmidt (1954) and Turekian and Wedepohl (1961). The source of the excess boron (see Horn and Adams, 1966) and the controversy over using the boron content of shales to determine paleosalinity is not of concern here, since there seems to be little disagreement with the proposition that clays can take up boron during diagenesis. This process is probably the reason for the observed tendency toward lower boron concentrations in interstitial water.

# Silica

The dissolved silica concentration shows moderate variation, with most values somewhat higher than those typical of deep seawater (Armstrong, 1965). The measured values are lower than those obtained from short cores of near shore sediments by Emery and Rittenberg (1952) and are in general lower than values reported by Siever et al. (1965). Siever's samples were from a variety of deep sea and shallow water environments, and like the present samples showed considerable variation from place to place. However, Siever found a clustering of values between 20 and 50 ppm silicon dioxide. It should be noted that the values given in Table 3 are in milligrams per liter of silicon, and would have to be multiplied by 2.14 to give milligrams per liter silicon dioxide. When this is done most of these samples, like those of Siever, fall between saturation with respect to quartz (about 10 ppm) and saturation with respect to amorphous silica (about 120 ppm). The bottom sample from Hole 29 seems to be just saturated with respect to amorphous silica according to the solubility data of Siever (1962), which is not surprising since the sediment is reported to be radiolarian ooze. The concentration in all other water samples is lower, and there is no consistent clustering of values around any one concentration that would suggest an equilibrium with clays or other silicates. Rather, the concentration is probably controlled by kinetic factors with siliceous organisms and volcanic glass dissolving, and authigenic silicates forming. Equilibrium may be approached where the sediment is composed almost entirely of amorphous silica, or where it contains practically none. The usual circumstance, however, seems to be an intermediate condition.

#### **Transition Metals**

Normal seawater contains transition metals in the ppb range, so it is necessary to concentrate them in some way before they can be determined by most analytical techniques. The same is true, generally, for interstitial waters, but manganese and zinc are often enriched to the extent that they can be determined without preconcentration. Therefore, all interstitial waters received by UCLA from the deep sea drilling project have been analyzed for these two elements.

The zinc concentration was found to be uniformly much higher than seawater, and higher than values obtained on interstitial water from near-shore sediments in this laboratory (Brooks *et al.*, 1968). Little other data is available on heavy metals in interstitial water so comparisons are difficult, but Tageyeva (1965) reported values from Arctic Ocean sediments comparable to the ones found in the Leg 4 sediments. Of the samples analyzed by Tageyeva, however, iron concentrations were several times higher than zinc, a situation which the authors have never observed in analyzing a



Figure 5. Boron concentration in the interstitial water of Leg 4 sediments as a function of depth.

large number of interstitial waters from a variety of marine environments. This makes it difficult to evaluate the significance of the high zinc values. Perhaps the more complete breakdown of organic matter which occurs at the depths of the present samples does in fact enrich the interstitial water in zinc, but there is no obvious relationship between the zinc concentration and depth or organic content.

An item which appeared in the popular press (Ocean Industry, October, 1968) may have a bearing on the high zinc concentrations. It concerned a "popping" sound reported by the drill crew as the drill string was being raised from each hole. The sound was traced to a chipping off of small specks of the "zinc rich" plastic paint used on the drill pipe, apparently because high-pressure water became trapped under the paint at depth. It seems unlikely that paint on the outside of the drill pipe would affect sediment inside the core line, but more work will have to be done before there is assurance that the high zinc concentrations are real and not a result of contamination during the drilling operation.

Manganese showed far more variation in concentration than any other trace metal, in agreement with previous observations (Presely et al., 1967). Furthermore, there is no clear-cut correlation between dissolved manganese concentration and lithology or Eh-pH conditions. Very low manganese concentrations were found, however, in the apparently reducing sediments at Sites 25 and 30, where sulfate had been strongly depleted. This seems to be a general phenomenon in samples the authors have analyzed from other localities. The high concentration of dissolved carbonate resulting from sulfate reduction may prevent manganese concentrations from rising due to precipitation of manganese carbonate. Regardless of the mechanism, it is obvious that, despite popular opinion, reducing conditions alone to not lead to manganese dissolution. In fact, the opposite is usually true.

The manganese concentration data does not support a model of leaching of solids at depth and re-deposition as oxides at the surface (Lynn and Bonatti, 1965). In fact, the distribution in most holes is complex. In Hole 29, for example, the dissolved manganese concentration was high at 70 meter's depth in what was reported to be a Miocene-banded mica clay, and became progressively lower both below and above this layer. It is possible that manganese dissolution is occurring in this one layer, and diffusion is carrying it both up and down, but why should manganese dissolve mainly from one layer? Hole 23 also appears anomolous. Here green clay was reportedly overlain by brown clay, exactly the conditions postulated by Lynn and Bonatti to cause an upward migration of manganese, yet dissolved manganese showed a very strong concentration gradient of the opposite sense making upward migration impossible. The "manganese problem" has been discussed in some detail by Presley (1969), and the data presented here only reinforces the previous conclusions. That is, although manganese has been shown to be extremely mobile in the marine sedimentary environment, more work will have to be done before the reasons for and consequences of this mobility can be given.

Those Leg 4 samples for which at least 30 milliliters of water remained after the analyses discussed above were completed, were analyzed for iron, nickel, and copper by the trace element technique outlined in the procedures section of this report. It was not possible to do more than three elements on this small volume of water, but the signal-to-background ratio was good for these three, and the results (Table 3) are thought to be reliable.

The iron concentrations are somewhat higher than that of open seawater (the value given by Goldberg, 1965, is almost certainly too high for typical seawater), but they are comparable to values obtained by the authors in other interstitial water studies. The low values of iron make it unlikely that the drilling operation had contaminated the interstitial water with structural metals, and they add confidence to the data on copper, nickel and manganese. Too few analyses for iron, copper and nickel were made to reveal any trends with area or depth, but the one sample analyzed from Hole 26, where sulfate reduction had occurred, was enriched in all three of these metals. This confirms previous observations by the authors that interstitial water from reducing sediments is usually enriched in heavy metals, except for manganese, relative to water from oxidizing environments. However, Hole 30 was also an area of sulfate reduction, yet no particular enrichment in heavy metals occurred there. The actual reduction of sulfate in both of these holes had occurred at some previous time, since hydrogen sulfide was reported to be absent from the sediments when the cores were collected and the Eh was positive in almost every case (Fred Sayles, personal communication). Thus, changes occurring after sulfide production are complicating factors that effect the present heavy metal concentration in the interstitial water.

The copper concentration was found to be similar to that of other interstitial water the authors have analyzed, and shows no trend which would suggest specific diagenetic processes. The nickel concentration is higher than that of most other interstitial water analyzed by a factor of 2 or 3, and is higher than the iron concentration in all but one sample. This enrichment of nickel relative to iron was observed in the East Pacific Rise cores (Presley *et al.*, 1967), but has not been observed in any near-shore environments. The authors have no explanation for this observation, but it is probably related to the fact that it is more difficult to precipitate nickel by oxidation than iron. In summary, zinc is the only transition element whose concentration in the Leg 4 samples is significantly different from those in the piston core samples which were analyzed by the authors. The high zinc concentrations found in the deep samples may be due to a more complete breakdown of organic matter at depth, but until more work is done, contamination during sampling or handling cannot be ruled out.

Manganese concentration is highly variable, and some samples show a concentration slightly higher than those from piston core samples previously analyzed. Here, as in the other areas studied, it seems that localized processes must be responsible, but it is not possible at this time to say whether such processes are biological, volcanic or sedimentary.

Iron and copper concentrations are similar to those found in previous studies; and, nickel concentration is similar to that of other deep-sea samples, but higher than that of near-shore samples.

#### REFERENCES

- Armstrong, F. A. J., 1965. Silicon. In Chemical Oceanography. J. P. Riley and G. Skirrow (Eds.) (Academic Press). 1, 409.
- Baltre, P., 1936. Colorimetric determination of small quantities of bormide in the presence of a large excess of chloride. J. Pharm. Chim. (Ser. 2) 24, 409.
- Berner, R. A., 1966. Chemical diagenesis of some modern carbonate sediments. Am. J. Sci. 264, 1.
- Brooks, R. R., Kaplan, I. R. and Peterson, M. N. A., 1969. Trace element compositions of Red Sea Geothermal brine and interstitial water. In Hot Brines and Recent Heavy Metal Deposits in the Red Sea. E. T. Degens and David A. Ross (Eds.) New York (Springer-Verlag), 180.
- Brooks, R. R., Presley, B. J. and Kaplan, I. R., 1967. APDC-MIBK extraction system for the determination of trace metals in saline waters by atomicabsorption spectrophotometry. *Talenta*. 14, 809.
- , 1968. Trace elements in the interstitial waters of marine sediments. *Geochim. Cosmochim. Acta.* **32**, 397.
- Culkin, F., 1965. The major constituents of seawater. In Chemical Oceanography. J. P. Riley and G. Skirrow (Eds.). (Academic Press). 1, 121.
- Emery, K. O. and Rittenberg, S. C., 1952. Early diagenesis of California basin sediments in relation to origin of oil. Bull. Am. Assoc. Petrol. Geologists. 36, 735.

- Goldschmidt, V. M., 1954. Geochemistry. (Oxford University Press).
- Hays, M. R. and Metcalf, J., 1962. The boron-curcumin complex in the determination of trace elements of boron. Analyst. 87, 956.
- Horn, M. K. and Adams, J. A. S., 1966. Computerderived geochemical balances and element abundances. *Geochim. Cosmochim. Acta.* 30, 279.
- Krauskopf, K. B., 1957. Introduction to geochemistry. McGraw-Hill.
- Lynn, D. C. and Bonatti, E., 1965. Mobility of manganese in diagenesis of deep-sea sediments. *Marine Geol.* 3, 457.
- Mangelsdorf, P. C., Wilson, T. R. S. and Daniell, E., 1969. Potassium enrichments in interstitial waters of recent marine sediments. *Science*. **165**, 171.
- Manheim, F. T., 1966. A hydraulic squeezer for obtaining interstitial waters from consolidated and unconsolidated sediments. U. S. Geol. Surv. Profess. Papers 550-6. 256.
- Presley, B. J., Brooks, R. R. and Kaplan, I. R., 1967. Manganese and related elements in the interstitial water of marine sediments. *Science*. 158, 906.
- Presley, B. J., Brooks, R. R. and Kappel, H. M., 1967. A simple squeezer for removing interstitial water from ocean sediments. J. Marine Res. 25, 355.
- Presley, B. J. and Kaplan, I. R., 1968. Changes in dissolved sulfate, calcium and carbonate from interstitial water of nearshore sediments. *Geochim. Cosmochim. Acta.* 32, 1037.
- Presley, B. J., 1969. Chemistry of Interstitial Water from Marine Sediments." (Ph.D. Thesis, UCLA).
- Siever, R., Beck, K. C. and Brener, R. A., 1965. Composition of interstitial waters of modern sediments. J. Geol. 73, 39.
- Siever, R., 1962. Silica solubility, O C 200 C, and the diagenesis of siliceous sediments. J. Geol. 70, 127.
- Strickland, J. D. H. and Parsons, T. R., 1968. A practical handbook of seawater analysis. *Fisheries Res. Board of Canada. Bull.* 167.
- Tagayeva N. V. 1958. The geochemistry of the clay sediments of the Caspian Sea. Proc. Acad. Sci. USSR English Transl. 121, 77.
- , 1965. Interstitial waters of Arctic Ocean sediments. Proc. Acad. Sci. USSR English Transl. 163, 207.
- Turekian, K. K. and Wedepohl K. N., 1961. Distribution of the elements in some major units of the earth's crust. Bull. Geol. Soc. Am. 72, 175.
- White, D. E., Hem, J. D. and Waring, G. A., 1963. Data of geochemistry Chapter F. U. S. Geol. Surv. Profess. Paper 440-F. F1-F67.