

21. INTERSTITIAL WATER CHEMISTRY, DEEP SEA DRILLING PROJECT, LEG 1

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

A sediment squeezer similar to that described by Presley, *et al.* (1967) was placed on board the *Glomar Challenger* for the removal of interstitial water from sediment. The retrieved water samples were placed in cleaned polyethylene bottles and stored under refrigeration. On arrival at Lamont-Doherty Geological Observatory, these samples were forwarded to Los Angeles by mail and were analyzed within six weeks of their arrival.

Ten samples ranging in volume from 10 to 50 milliliters were obtained from Holes 2, 3, 4, 6, 6A, and 7. Unfortunately, neither pH nor Eh were measured on the water samples on board ship. The sediments from the various cores are described in detail elsewhere in this report.

EXPERIMENTAL

The major cations were analyzed by using atomic absorption spectroscopy after making the necessary dilutions. In the case of calcium and potassium, it was found necessary to add 1 per cent lanthanum oxide to each sample to prevent interference from phosphate and other ions. There was an insufficient volume of the waters for concentrating the trace metals elements by the technique of Brooks, *et al.* (1967), therefore, direct analysis was made by atomic absorption spectrometry without dilution of the waters. The conditions used for atomic absorption spectroscopy are given in Table 1. All samples were filtered through 0.45 millipore filters before analysis.

Dissolved sulfate was analyzed gravimetrically by precipitation as barium sulfate from an acidified aliquot of interstitial water.

Chloride and bromide were analyzed by Mr. G. Baker¹ through the courtesy of Dr. W. T. Holser. The chloride was analyzed by a potentiometric titration procedure using silver nitrate. Bromine was analyzed by a modification of the method described by Balatre (1936). This involved oxidizing the bromide with chloramine-T in the presence of phenol red and acetate buffer at pH5. The resultant color complex was measured by spectrophotometer at 595 millimicrons and compared directly to a standard calibration curve.

¹Chevron Oil Field Research Company, La Habra, California.

TABLE 1
Conditions for Atomic Absorption
Analysis of Cations

Element	Dilution Factor	Wave Length (Å)
Na	1:10,000	5890
K	1:100	7665
Mg	1:1000	2852
Ca	1:100	4227
Sr	Undiluted	4607
Mn	Undiluted	2801
Zn	Undiluted	2138

RESULTS AND DISCUSSION

The results obtained are presented in Table 2. Although they are too few to enable sweeping generalizations to be drawn, especially since they represent a variety of environments and depositional conditions not well known to the authors at the time of writing this report, some consistent trends are apparent.

Chloride-bromide ratios are good indicators of whether increase in concentration has occurred through simple concentration of sea water. All the measurements show that chloride is consistently more concentrated than in average present-day sea water (Goldberg, 1965). The bromide content is also higher in the analyzed samples than in average sea water. The chloride-bromide ratios are within 3 per cent of the ratio in sea water, with the exception of three samples from the Gulf of Mexico (Hole 2 and 3, UCLA Nos. 2, 4, and 5). Sample 2 is highly enriched in chloride over bromide, suggesting that the brine has been partially derived through the solution of halite in the cap rock, rather than concentration from a mother liquor. Halite is known to exclude bromine when it crystallizes. Sample 5 in Hole 3 near the Sigsbee Knolls also shows an enrichment of chloride over bromide. On the other hand, samples overlying this sediment layer are depleted in chloride relative to bromide. However, the data are too few for speculative interpretation.

TABLE 2
Interstitial Water Analyses

Sample Designation ^a	UCLA No.	Depth Below Sea Bed (m)	Age	Description	Na (g/l)	K (g/l)	Ca (g/l)	Mg (g/l)	Sr (mg/l)	Mn (mg/l)	Zn (mg/l)	Br (mg/l)	Cl (g/l)	SO ⁴ (g/l)
Hole 2 (23° 27.3'N, 92° 35.2'W, water depth 3572 m., Challenger Knoll, Gulf of Mexico)														
1-2 (0-65)	1	20	Pleist.	Calcareous mud	12.0	0.61	0.39	1.40	8.0	2.20	0.19	76.5	22.3	2.43
4-1 (30-90)	2	103	Pliocene	Cocc. ooze, H ₂ S	19.5	0.67	0.47	1.49	14.7	0.20	0.47	83.0	40.3	-
Hole 3 (23° 01.8'N, 92° 02.6'W, water depth 3746 m., abyssal plain, Gulf of Mexico)														
1-2 (0-72)	3	34	Pleist.	Calc. silt, clay	10.6	0.30	0.50	1.10	10.5	0.25	0.40	73.0	20.6	-
4-1 (33-100)	4	209	Pleist.	Cocc. ooze, clay	12.1	0.46	0.20	1.10	10.5	0.35	0.15	81.5	22.7	-
5-2 (102-150)	5	324	Pliocene	Cocc. ooze, clay	12.9	0.54	0.36	0.88	75.0	0.10	0.47	80.0	24.3	0.58
Hole 4 (24° 28.7'N, 73° 47.5'W, water depth 5320 m., E. of Bahama Island)														
1-4 (30-90)	6	6	Plio-Pleist.	Calcareenite	10.9	0.51	0.42	1.25	8.0	<0.02	0.15	70.5	20.4	2.47
Hole 6 (30° 50.4'N, 67° 38.9'W, water depth 5125 m, Bermuda Rise)														
1-1 (90-150)	7	43	Pliocene	Brown clay	11.1	0.46	0.54	1.25	8.5	8.70	0.39	71.0	20.6	2.32
2-2 (0-70)	8	153	Eocene	Gray-green clay	10.5	0.39	0.81	1.20	11.6	6.70	0.67	67.4	-	-
Hole 6A, (30° 50.4'N, 67° 38.9'W., water depth 5125 m, Bermuda Rise)														
1-2 (10-72)	9	15	Pleist.	Brown clay	10.8	0.51	0.48	1.23	8.0	1.10	0.26	70.0	20.6	2.58
Hole 7 (30° 08.0'N, 68° 17.8'W., water depth 5185 m., Bermuda Rise)														
1-3 (10-72)	10	3	Pleist.	Brown clay	10.6	0.52	0.44	1.25	8.0	0.02	0.13	71.5	20.3	2.47
Standard ocean water (Goldberg, 1965)					10.5	0.38	0.40	1.35	8.0	0.002	0.01	65.0	19.0	2.66

^a Core-section (interval)

TABLE 3
Concentration of Elements Relative to Chloride

UCLA No.	Cl/Na	Cl/K ($\times 10$)	Cl/Mg	Cl/Ca ($\times 10$)	Cl/Sr ($\times 10^3$)	Cl/Br ($\times 10^2$)
1	1.86	3.65	15.9	5.71	2.78	2.91
2	2.07	6.02	27.1	8.58	2.74	4.86
3	1.94	6.87	18.7	4.12	1.96	2.83
4	1.88	4.94	20.7	11.37	2.16	2.79
5	1.88	4.50	27.6	6.75	0.32	3.04
6	1.87	4.00	16.3	4.86	2.55	2.90
7	1.86	4.48	16.5	3.82	2.43	2.90
9	1.91	4.04	16.8	4.30	2.58	2.94
10	1.91	3.91	16.2	4.62	2.54	2.84
S.W.*	1.81	5.00	14.1	4.75	2.38	2.92

*Goldberg, 1965

Sodium shows a general enrichment over its concentration in present-day sea water, although the chloride-sodium ratio (Table 3) shows that sodium is depleted relative to chloride. The most noticeable enrichment of chloride relative to sodium occurs in the brine of the Sigsbee Knoll, Sample 2.

Magnesium shows a depletion in all samples analyzed, with the exception of samples from Hole 2 on the Sigsbee Knoll. The high value of magnesium in Sample 2 may be indicative of an enrichment due to the solution of a salt phase enriched in the alkali metals. By contrast, the greatest depletion of magnesium is found in the core from Hole 3 close to the Sigsbee Knoll.

Calcium generally shows quite large variations. In some samples, as in Hole 3 in the Gulf of Mexico, it is depleted, whereas, in the Caribbean cores calcium is enriched. The greatest enrichment appears to be in the core from Hole 6 (Sample 8) where strontium is also enriched, bromide is depleted and potassium is unchanged. Since this sample came from a turbidite deposit, it may indicate a specific diagenetic reaction leading to solution of calcium and strontium and depletion of bromide.

Strontium does not show wide variations in concentration. The greatest anomaly occurs in Sample 5 from Hole 3. The measured value of 75ppm indicates an almost tenfold increase in strontium over its concentration in sea water; in contrast, magnesium shows the lowest concentration. One may speculate that reactions are occurring in this sediment column leading to the dolomitization and exclusion of strontium. The calcium content in this core shows relatively large variations

indicating that equilibrium reactions leading to solution and concentration are taking place.

Manganese and zinc are highly enriched over their concentration in sea water. In only one sample (Sample 6, from Hole 4) is the concentration of manganese below the detection limit. The greatest manganese concentration is in the cores from Hole 6 south of Bermuda, where values of 8.7 and 6.7 ppm are measured. In these cores, zinc attains values of 390 and 675 ppb, respectively. The latter value is obtained in Sample 8, which also shows the high calcium anomaly, suggesting that zinc and calcium contents may be related to the same controlling factors. The relatively large differences in concentration of manganese and zinc between cores from adjacent Holes 6, 6A, and 7, once more demonstrates the non-uniform character in trace metal concentration and the importance of local processes.

In all samples, sulfate shows a slight depletion in concentration compared to average sea water. In Sample 5, for example, marked depletion of 0.58 g/l is observed; and, Manheim and Sayles (1969) report sulfate depletion in all samples from the core taken in Hole 3. There is no report of sulfide generation in these samples, indicating that sulfate reduction has taken place at an earlier time. It is probable that the extent of sulfate reduction is limited by the amount of available organic matter.

REFERENCES

- Balatre, P., 1936, Colorimetric determination of small quantities of bromine in the presence of a large excess of chlorine. *J. Pharmacie et Chimie*, Ser. 2, 24, 409.

- Brooks, R. R., Presley, B. J. and Kaplan, I. R., 1967. The APDC-MIBK extraction system for the determination of trace elements in Saline waters by atomic absorption spectroscopy. *Talanta*. **14**, 809.
- Goldberg, E. D., 1965. Minor elements in sea water. In *Chemical Oceanography*. J. P. Riley and G. Skirrow (Eds.). London (Academic Press). **1**, 163.
- Manheim, F. T. and Sayles, F. L., 1969. Interstitial water studies on small core samples. This volume, Chapter 20.
- Presley, B. J., Brooks, R. R. and Kappel, H. M., 1967. A simple squeezer for removal of interstitial water from ocean sediments. *J. Marine Res.* **25**, 355.