

31.2. INTERSTITIAL WATER CHEMISTRY: DEEP SEA DRILLING PROJECT, LEG 13

B. J. Presley,¹ Chari Petrowski, and I. R. Kaplan, Department of Geology and Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California

INTRODUCTION AND PROCEDURES

Drilling during Leg 13 of the Deep Sea Drilling Project was confined almost exclusively to the Mediterranean Sea. This was the first time deep drilling had been conducted in a so-called small, or inland, ocean basin, and the sediments penetrated turned out to be extremely complex, both lithologically and stratigraphically. There was abundant evidence of erosional loss of sediment at some locations and equally clear indications of large scale faulting, bringing old rocks up over younger sediments. Almost every possible sediment and rock type was involved in this tectonic activity. For example, pelagic oozes, sapropels, evaporites, pebble conglomerates, detrital gypsum, nodular anhydrite, and sand layers were described in the cores which were squeezed for pore water. These were often interlayered and otherwise showed evidence of varying environmental conditions with time.

The interstitial water chemistry is, as would be expected, highly variable, both with depth and location. The mechanisms which lead to variability in interstitial water chemistry are poorly understood, even in areas of uniform lithology (see previous leg reports). Here lithologic changes and tectonic activity complicate the picture, making interpretation very difficult.

A total of eighteen samples, which had been collected at five drilling sites, were received at U.C.L.A. These had been forced through a 0.45 micron filter immediately after removal from the sediment and had been stored at 4°C in sealed plastic syringes. Analysis was started as soon as the samples were received, nevertheless this was as long as three months after collection.

The analytical procedures currently being used in our pore water program are essentially those described in some detail elsewhere (Presley, 1971; Presley and Claypool, 1971). These procedures have evolved as we have sought to get more and better data from the small samples provided by the Deep Sea Drilling Program. Therefore, the procedures used for Leg 13 may, in some instances, be modifications of those described in the references, but any changes are considered not sufficiently significant to warrant a separate description here.

RESULTS AND DISCUSSION

All data that we have obtained to date from the water samples is given in Table 1, except major cation concentrations which were omitted, as they are discussed in the report by Sayles *et al.* (this volume). The shipboard ΣCO_2 values which were given in our previous reports have been omitted here, because, as on previous legs, the laboratory and shipboard values show moderately good agreement, and the laboratory values are more reliable.

Chloride and bromide values have been close to those of average seawater in samples from previous legs, except in locations where the presence of evaporites was known or implied, and in a few locations that apparently were influenced by continental ground water. The Leg 13 samples show a sharp increase in both components with depth, and once again the change is clearly due to the presence of evaporite minerals. Gypsum and anhydrite were identified in the deepest sample analyzed at Site 125, and were reported about 60 meters below the deepest sample we obtained from Site 124. Chloride concentration at Site 124 was more than twice that at Site 125, however, and the Cl/Br ratio was much more abnormal there (507 compared to 306, when seawater gives 290). This can only be due to a difference in the history of the two evaporite sequences, one of which is in the Balearic Basin (124) and the other in the Ionian Basin (125).

Site 127 was also drilled in the Ionian Basin, and the interstitial water there was even more enriched in Cl than at Site 124, despite the fact that only Quaternary sediments were sampled. Here too the Br/Cl ratio is highly abnormal, but in an opposite sense to that at Site 124. That is, here Br is enriched relative to Cl, as would be expected in a very late stage evaporite deposit or a residual liquor. The bottom sample from Site 124, on the other hand, must have resulted from the leaching of relatively pure NaCl. The Cl/Br ratio at Site 125 differs from the seawater value by only 5 percent and it seems likely that no halite is associated with the anhydrite recovered at this site.

Lithium concentrations up to thirteen times those of seawater were measured in Leg 13 pore waters, and while the enrichments seem to be related to salinity increases, they are not due solely to such increases. At Site 127 for example, the Li/Cl ratio is near seawater value at 22 meters depth, considerably lower at the next two sampled depths (43 m and 52 m), and again near the seawater ratio at 108 meters and 233 meters. The ratio jumps sharply to more than three times that of seawater at 290 meters and the bottom sample at 336 meters has a ratio more than twice that of seawater. The Li/Cl ratio at depth at other sampled sites is also two to three times that of seawater. Thus, some mechanism of Li release to the pore water has been operating, as it has on many of the sites sampled on previous legs.

Boron was depleted relative to chloride on all Leg 13 samples. The B/Cl ratio varied from about 1.5 to 4 times less than the seawater value, which is more of a variation than has been found on most previous legs. The one high salinity sample from the Gulf of Mexico (Leg 10) which we analyzed for B was depleted by a factor of 10, however, so perhaps this is a common phenomenon.

Silicon too showed considerable variation in concentration in these samples, but this would be expected with such diverse lithologies. There is little relationship between

¹Present address: Department of Oceanography, Texas A&M University, College Station, Texas.

TABLE I
Selected Major and Minor Elements, Interstitial Water, Deep Sea Drilling Project, Leg 13

Sample Number ^a	Depth ^b (m)	Age and Description of Sediments ^c	Cl g/Kg	Br mg/Kg	B mg/Kg	Si mg/Kg	NH ₃ mg/Kg	Mn µg/Kg	Li µg/Kg	ΣCO ₂ mM/Kg	δC ₁₃ PDB
121-1-3	64	Quaternary green marl ooze	21.4	83	2.4	12.0	43.0	100	245	9.6	-11.9
121-3-4	160	Quaternary green marl ooze	24.5	96	1.4	21.7	89.1	200	570	5.1	+0.9
121-4-4	253	Quaternary green marl ooze	28.0	115	2.1	9.7	73.6	200	700	2.6	-2.1
124-1 CC	128	Pleistocene nanno ooze/sand layers	37.1	98	3.4	4.4	24.5	600	635	2.4	-3.5
124-3 CC	307	Pliocene nanno ooze/sand layers	65.0	128	5.4	2.5	26.2	1000	1395	0.6	-5.3
125-1-4	6	Quaternary nanno ooze/sapropel	21.3	75	3.5	4.8	6.1	1000	240	2.5	-1.2
125-5-1	40	U. Pliocene nanno ooze/dolomite	22.4	77	3.4	4.1	8.3	200	275	2.0	-8.5
125-A-3 CC	53	M. Pliocene nanno ooze/dolomite	22.6	79	3.3	4.7	5.7	375	280	2.0	-2.6
125-A-6 CC	80	L. Pliocene marl ooze/anhydrite	23.7	82	3.3	4.9	8.4	350	320	2.7	-2.4
125-A-9 CC	102	L. Pliocene anhydrite/gypsum/pyrite	27.6	90	4.0	14.4	11.8	600	490	2.0	-9.4
126-1-6	43	Quaternary marl ooze/sand layers	21.7	77	3.2	4.9	21.7	375	215	5.1	-7.3
127-1-3	22	Quaternary marl ooze/pebbles	21.5	75	3.2	4.1	17.0	500	180	5.7	-11.5
127-3-5	43	Quaternary marl ooze/sand (disturbed)	22.2	78	3.4	4.3	35.8	550	170	5.7	-18.2
127A-3-4	52	Quaternary marl ooze	23.9	85	3.7	9.4	55.4	200	155	9.4	-21.1
127-6-5	108	Quaternary marl ooze/sand layers	36.0	122	3.0	14.2	135.0	375	315	9.7	+1.7
127-9 CC	233	Quaternary nanno ooze/silt	77.1	358	7.2	3.4	81.5	2000	695	1.3	-13.5
127-10 CC	290	Quaternary nanno ooze/silt	80.8	405	9.6	2.4	62.3	2000	2320	0.7	-10.7
127-12 CC	336	Quaternary nanno ooze	82.5	400	8.2	2.4	68.8	850	1685	0.7	-12.7
Average Sea Water			19.4	67	4.5	3.0	<0.1	2	170	2.5	0

^ahole, barrel, section.

^bdepth below sediment-water interface

^cfrom preliminary hole summaries.

the salinity and the Si concentration, except that the four highly saline samples (Cl < 65‰) all had low Si content.

Ammonia was highly enriched in all Leg 13 samples, as has been the case with biogenous sediments on previous legs. Once again the dissolved ammonia concentration is much higher than would be predicted from the dissolved CO₂ concentration, and increasingly so at greater depth. This is most likely the result of a loss of CO₂ by carbonate precipitation, rather than an anomaly in the C/N ratio released by organic matter.

The concentration of total dissolved carbonate species is higher than is typical for seawater at shallow depths, except for Site 125, but decreases sharply with depth. The carbon isotope ratios show the source of the added CO₂ to be organic matter (Presley and Kaplan, 1968), and the decrease in concentration is most likely due to carbonate precipitation.

Manganese concentrations show the wide variation that has characterized all of our pore water work, DSDP and otherwise. As usual there is no correlation between Mn and other measured parameters.

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31.2. INTERSTITIAL WATER CHEMISTRY

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