

APPENDIX IV. INTERSTITIAL WATER CHEMISTRY: DEEP SEA DRILLING PROJECT, LEGS 21 AND 22

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INTRODUCTION AND PROCEDURES

Leg 21 of the Deep Sea Drilling Project consisted of operations around Australia in some of the marginal basins of the Pacific. Leg 22 was also largely a southern hemisphere operation, but followed Ninetyeast Ridge to almost 10°N latitude before turning west to end in Colombo, Ceylon. These legs were conducted in late 1971 and early 1972, but the pore waters sent to Texas A&M were not analyzed until June 1973. This long storage could have adversely affected the pore water chemistry, especially for such constituents as silicon and ammonia, but we have no evidence that such is the case, and no unexpected values or trends that might be attributed to storage are evident. We intend to compare our data with that of the Woods Hole group when their report is received, and this should shed some light on storage effects that will be useful to future investigations.

The samples we received consisted of 2-3 ml aliquots of membrane-filtered water that had been heat sealed into short sections of polyethylene tubing. They were kept refrigerated at all times between collection and analysis, except for transit by air mail.

The analytical procedures used are essentially the same as those described in an earlier DSDP report (Presley, 1971). We have, as usual, analyzed all samples for major cations and are including the Leg 21 data in this report. The Woods Hole group is reporting major cation data on the Leg 22 samples, as they have on all previous legs; therefore, our data have been omitted from the report.

RESULTS AND DISCUSSION

All samples have, as usual, been analyzed for chloride. This analysis is done using only 0.1 ml of water, and only a few duplicates are run due to the small sample size and time requirements. Duplicates, or repeat runs on suspicious values, seldom disagree with the first value determined by more than 0.1 parts per thousand, thus the values given in Tables 1 and 2 are thought to be reliable for the purpose intended.

Samples from previous legs have almost always given Cl values within a few percent of that of present-day seawater, except where evaporite deposits are present, or where continental fresh water has had an influence. There have been, however, a few samples from several previous legs that were difficult to explain by either of these mechanisms. In some cases, where only a single isolated value is involved, sample contamination during coring or storage must be suspected. This might be true of Samples 206-11-3 and 218-15-1 in the present group. In other cases,

however, unmistakable trends with depth below the sea floor can be seen, and these must have considerable geochemical significance, although the values are difficult to explain at this time. An example of this is the low Cl values found on Legs 16 and 19 and the high values found in some of the present samples (see also the Woods Hole report, Chapter 31). In any case, some reevaluation of the chlorinity or salinity of all the DSDP pore waters should be made at some future date with a view towards explaining the anomalous values.

One aid in explaining salinity changes is the bromide concentration, as we have pointed out in previous leg reports. In the present group of samples, for example, the anomalous Cl value at Site 206 is matched almost exactly by an anomalous Br value so as to leave the Cl/Br ratio unchanged. At Site 218, on the other hand, the Br seems to be impoverished by about 20%. Thus, it is easy to explain Sample 203-11-3 as representing a simple dilution with fresh water, but it is not so easy to explain Sample 218-11-2, unless, of course, an error has been made in one of the measurements.

In the same way, the almost 13% chlorinity increase at Site 216 is accompanied by a corresponding Br increase so the ratio changes by only a little over 1%, but at Site 214 the Br increase is much larger than that of Cl so the ratio goes down by about 13%. A similar, but less clear-cut, case occurs at Site 210. The Br and Cl values can, then, aid in interpreting the geological history of a site with respect to influences by evaporite deposition and leaching.

The major cation concentrations at the Leg 21 sites show most of the phenomenon we have been observing on the DSDP samples since Leg 4. That is, either little change with depth of burial, or pronounced trends of decreasing Mg and K and increasing Ca. The factors which determine which trend occurs have still not been worked out. At Site 210 we also see a rather drastic decrease in Ca concentration in the Pleistocene sediments. This is undoubtedly due to an increase in carbonate alkalinity, as explained by Presley and Kaplan (1968), but the decrease may have been intensified by precipitation during storage as CO₂ was lost by outgassing. The Ca increases at Sites 204 and 210 are by more than 350%, but even more drastic increases were found in some of the Leg 22 samples (see also Chapter 31). These large changes in Ca concentration can only be due to rather extensive diagenetic changes in the solid phases of the sediment.

Diagenetic changes are also evident from the silicon measurements because there are, as usual, large differences in concentration at different depths at most sites. It is difficult to see how these concentration gradients can be

TABLE 1
Selected Major and Minor Constituents, Interstitial Water, Leg 21

Sample ^a	Depth ^b (m)	Age and Description of Sediment ^c	Cl (g/kg)	Br (mg/kg)	Cl/Br	Na (g/kg)	K (mg/kg)	Ca (mg/kg)	Mg (g/kg)	Si (mg/kg)	Mn (mg/kg)	Li (mg/kg)	NH ₃ (mg/kg)
203-1-2	2	Pleistocene; ashy CaCO ₃ ooze	19.8	67	294	10.9	423	416	1.37	11.3	2.79	0.18	0.7
203-3-6	117	Pleistocene; ashy CaCO ₃ ooze	19.8	68	289	11.3	409	425	1.36	12.3	7.37	0.20	<0.1
204-1-5	6	Quaternary; dark brown silty clay	20.1	68	296	11.2	433	444	1.34	15.4	<0.01	0.19	1.5
204-4-4	89	Eocene (?); dark brown clay, Fe ₂ O ₃	21.1	71	297	9.8	437	1470	0.97	6.8	0.02	0.18	<0.1
205-3-6	27	Late Miocene; Fe ₂ O ₃ clay, thin CaCO ₃ beds	20.2	68	295	11.1	451	498	1.32	10.9	<0.01	0.15	<0.1
205-10-2	86	Late Miocene; CaCO ₃ ooze, ash	20.1	69	289	11.0	438	745	1.05	14.3	3.42	0.07	2.3
205-20-2	181	Middle Miocene; vitric tuff, CaCO ₃	20.0	69	293	11.1	422	871	0.89	15.2	3.15	0.10	1.4
206-1-3	2	Pleistocene; CaCO ₃ ooze, glass shards	20.3	68	297	11.0	451	408	1.26	13.9	0.82	0.18	1.0
206-11-3	95	Pleistocene; CaCO ₃ ooze	16.6	57	289	9.2	367	369	0.93	21.3	0.04	0.13	5.2
206-24-6	219	Late Miocene; CaCO ₃ ooze, SiO ₂ beds	19.7	69	284	10.8	409	571	0.98	26.2	0.04	0.11	7.6
207-5-5	46	Pliocene; CaCO ₃ ooze, glass shards	20.1	70	287	10.8	421	454	1.31	7.6	0.05	0.23	1.0
207A-7-5	109	Miocene; CaCO ₃ ooze, SiO ₂ beds	20.0	69	288	10.7	387	782	1.24	8.6	0.02	0.33	1.6
207A-21-4	243	Eocene; CaCO ₃ ooze, SiO ₂ beds	20.0	70	284	10.8	370	571	1.13	25.5	0.07	0.50	3.0
208-4-6	44	Pliocene; CaCO ₃ ooze, pyrite	20.1	69	290	10.9	403	429	1.27	4.8	0.04	0.18	0.3
208-14-6	166	Miocene; CaCO ₃ ooze, pyrite	20.2	70	286	10.9	361	494	1.15	6.8	0.05	0.24	2.3
209-2-6	18	Pleistocene; CaCO ₃ ooze	19.8	70	284	10.7	409	444	1.24	4.8	0.32	0.22	1.7
209-6-6	54	Miocene; CaCO ₃ ooze	20.2	70	290	10.9	390	518	1.26	5.1	0.09	0.30	0.6
210-1-6	9	Pleistocene; silty clay, CaCO ₃ beds	19.5	68	287	10.7	438	327	1.11	9.0	3.60	0.11	7.6
210-10-4	87	Pleistocene; silty clay, CaCO ₃ beds	19.8	71	278	10.8	330	137	0.88	7.9	0.21	0.11	12.6
210-27-5	411	Miocene; silty clay, CaCO ₃ beds	20.2	75	269	—	116	1486	0.28	2.6	1.70	0.41	18.2
Average seawater			19.4	67	290	10.8	387	413	1.29	0.5	<0.01	0.17	<0.1

^aHole-core-section.

^bDepth below sea floor.

^cFrom preliminary hole summaries.

TABLE 2
Selected Major and Minor Constituents, Interstitial Water, Leg 22

Sample ^a	Depth ^b (m)	Age and Description of Sediment ^c	Cl (g/kg)	Br (mg/kg)	Cl/Br	Si (mg/kg)	Mn (mg/kg)	Li (μ g/kg)	NH ₃ (mg/kg)
211-1-3	5	Quaternary; clay-rich rad ooze, ash	19.4	67	289	19.4	15.5	187	<0.1
211-5-5	141	Pliocene; clay-rich rad ooze	20.0	71	281	22.9	5.9	170	7.4
212-2-3	14	Pliocene; interbedded nanno ooze and clay	20.1	69	290	5.4	0.5	230	0.5
212-8-3	131	Miocene; nanno ooze and chalk	20.0	71	283	5.5	0.9	295	5.0
212-11-3	198	Miocene; nanno ooze and chalk	20.3	72	282	8.0	0.6	370	3.2
212-15-3	293	Miocene; zeolitic claystone	19.5	69	280	7.6	1.7	408	4.4
213-2-5	17	Pliocene; clay-bearing SiO ₂ ooze	20.0	69	291	22.9	13.3	230	<0.1
213-5-5	45	Pliocene; clay-bearing SiO ₂ ooze	19.8	69	288	23.4	13.4	253	<0.1
213-9-6	85	Miocene; zeolitic clay, Mn-Fe oxide	19.8	69	286	21.8	12.0	253	8.3
213-13-6	123	Eocene; zeolitic clay, Mn-Fe oxide	19.6	69	285	5.2	0.1	227	<0.1
213-16-4	148	Paleocene; nanno ooze, Mn-Fe oxide	20.1	72	280	4.1	0.1	190	<0.1
214-1-5	8	Pleistocene; CaCO ₃ ooze	19.9	69	289	15.9	0.1	167	0.2
214-9-5	84	Pliocene; CaCO ₃ ooze	19.9	70	284	19.3	0.1	92	1.5
214-19-5	179	Miocene; CaCO ₃ ooze	20.1	73	276	21.9	0.2	92	3.6
214-31-5	293	Eocene; CaCO ₃ ooze	20.4	80	255	10.5	0.6	159	5.1
215-1-5	8	Quaternary; SiO ₂ ooze	20.0	70	285	21.5	6.8	171	<0.1
215-8-3	69	Miocene; rad-bearing clay	20.0	71	283	20.6	5.5	195	0.8
215-10-2	86	Eocene; clay-rich nanno ooze	19.6	69	284	20.8	<0.1	167	0.4
215-17-1	150	Paleocene; as above with Fe ₂ O ₃	19.6	69	283	9.6	—	—	—
216-1-6	9	Pleistocene; CaCO ₃ ooze, ash	19.6	68	289	15.1	0.4	162	0.4
216-5-5	166	Miocene; CaCO ₃ ooze	20.4	73	279	26.5	0.2	136	1.5
216-14-3	149	Oligocene; Nanno chalk	20.2	75	281	27.4	0.2	180	3.3
216-25-4	354	Cretaceous; chalk, ash, feldspar, clay	22.1	77	285	2.9	0.4	204	6.7
217-1-6	9	Quaternary; CaCO ₃ ooze with clay	19.6	69	286	19.7	1.9	161	<0.1
217-4-4	122	Miocene; CaCO ₃ ooze, SiO ₂ ooze, clay	20.3	71	286	25.0	0.2	513	2.3
217-9-6	315	Oligocene; clay-bearing nanno chalk	21.6	77	281	33.1	0.4	750	4.1
218-2-4	10	Pleistocene; nanno-bearing clayey silt	19.9	69	289	16.1	1.9	105	7.1
218-5-2	73	Pleistocene; nanno-bearing clayey silt	20.2	72	280	12.3	0.7	117	8.5
218-8-3	189	Pleistocene; nanno-bearing silty clay	20.2	70	288	11.8	0.3	137	21.8
218-11-2	301	Pliocene; CaCO ₃ ooze, silt and clay	20.2	71	285	4.6	0.6	405	11.7
218-15-1	450	Miocene; sandy silt, calcite, heavies	11.8	34	351	2.1	0.1	57	10.2
218-21-3	540	Miocene; laminated sandy silt	20.8	72	287	4.2	0.3	128	18.8
218-25-2	690	Miocene; silt and chalk	20.9	73	286	3.3	0.5	158	18.6
Average seawater			19.4	67	290	0.5	<0.01	170	<0.1

^aHole-core-section

^bDepth below sea floor.

^cFrom preliminary hole summaries.

maintained unless continuous reactions are occurring.

Manganese concentrations also show their usual wide variation, with the upper samples at Site 213 being among the highest yet found during the DSDP, yet many samples are near or below our detection limit. There is again no obvious relationship to lithology. Some of the samples where Fe-Mn oxides were conspicuous in the solids gave high dissolved Mn, but some gave low values.

Lithium concentrations have increased sharply with depth at many sites on previous legs, and this is shown well at Site 217. We still have no explanation for the phenomenon, however, nor any explanation for the low Li values found at a few locations.

Ammonia would seem to be more likely to change with the long storage these samples were subjected to than the other components, yet there is no indication this has happened. The high values were found at Sites 210 and 218, locations where the Ca data indicate active biological

activity. Sulfate concentrations would offer the best confirmation of this supposition, but we have no sulfate data at this time.

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