# 11. SHIPBOARD GEOCHEMICAL ANALYSIS, LEG 7, GLOMAR CHALLENGER

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Sediments collected on Leg 7 were sampled for geochemical analysis at sea. Some samples were analyzed for pH, Eh and salinity at sea; the remainder were delivered to shore-based laboratories for further work. This report summarizes the sampling and handling procedures used at sea and presents the results of the shipboard analyses. Handling procedures used were still in the development stage, and results should be used with caution. Results of shore-based geochemical analyses are presented elsewhere in this report.

#### SAMPLING PROCEDURES

Generally, samples for geochemical analysis were taken after the core had been split, and most sections were split after they had been standing at room temperature for many (8 or more) hours. Sections 1, 3, 4 and 5 of most cores taken from Hole 62.1 were stored at 4°C many days before they were processed. In a few cases, prior to splitting the core, the core liner was drilled and a needle inserted. A sample of interstitial gases were obtained in one or more vacuum containers. The containers were sealed and stored under refrigeration. As soon as possible after the sections were split, generally within 5 minutes, three or four 25 to 30-cubic centimeter samples for major elements, carbon dioxide, C-isotope and shipboard analyses were collected at 20 meter intervals at each site. One sample was stored, unsqueezed, for shore analysis. The remainder were squeezed as soon after sampling as possible. Four 25 to 30-cubic centimeter additional samples were collected for carbon dioxide and C-isotope analysis. All samples were sealed in glass bottles with polyseal caps and stored under refrigeration. Two samples (and, where carbon dioxide and C-isotope samples were collected, three samples) of 25 to 30 cubic centimeters of sediment were combined and squeezed to provide interstitial solutions (about 5 cubic centimeters) for analysis for major dissolved chemical species  $[0^{18}/0^{16}]$ , H/D] and shipboard analysis (about 2.5 cubic centimeters). The squeezed solutions and residue were stored at 4°C.

Four samples of 800 to 1000 grams of sediment were collected for trace element analysis (in concentrations of ppb). One-half of the working half over a 60 to 80 centimeter interval was removed, cleaned and placed in saran-coated mylar bags. Care was used to avoid contamination by hands, plastics or organic materials. After squeezing, the sediment residue was returned to the original mylar bag, the air was evacuated from the bag, and the sediment frozen at  $-20^{\circ}C\pm$ . The solutions were refrigerated at  $4^{\circ}C\pm$ .

# ANALYTICAL METHODS

Shipboard analyses of interstitial water samples were confined to measurements of pH, Eh and salinity. Salinities were measured using the Goldberg refractometer. Measurements of pH and Eh were made by electrochemical methods. The methodology is set forth in detail in the Shipboard Manual of the Deep Sea Drilling Project (revised July, 1968). Results of shipboard geochemical analyses are given in Table 1, and are summarized below.

#### RESULTS

# Site 61

Because of severe disturbance of the sediments during the coring operations, only one interstitial water sample was taken from this site. This one, from Section 2 of Core 1 of Hole 61.1, had a salinity of 34.7 per mille, pH of 7.53, and Eh of -300 millivolts.

#### Site 62

The salinity readings at Holes 62.0 and 62.1 are all in the range 34.1 to 34.7 per mille. This is the salinity of local sea water  $\pm$  0.3 per mille so that, given the error inherent in the instrument, no conclusions can be made except to say that the salinity of the interstitial water is similar to that of present-day sea water.

The pH and Eh readings for Hole 62.0 vary regularly with depth, and all the pH readings are less alkaline than that of local sea water (pH 8.4). The readings begin at 100 meters where the pH and Eh are 7.69 and -260 millivolts, respectively, then drop to 6.92 and -500 millivolts at 300 meters, only to rise again to 7.52 and -372 millivolts at 500 meters. Unfortunately, the results from Hole 62.1 which parallels Hole 62.0 are not as readily interpreted, and, in fact, are in conflict with those obtained from Hole 62.0. Data from Hole 62.1 consist of fifteen sets of values taken at approximately 40 meter intervals from 0 to 340 meters. The pH and Eh values are 7.38 and -310 millivolts, respectively, in the uppermost core and change irregularly with depth to values of 8.1 and +1.38 millivolts at 340 meters. Thus, at 300 meters, the values for pH and Eh in Hole 62.0 are 6.92 and -500 millivolts, respectively,

but the values in Hole 62.1 are 7.71 and +120 millivolts. Since these should come from approximately the same stratigraphic horizon, this is a serious conflict. The reason for this difference can probably be found in the fact that pore water left standing with the pH and Eh electrodes in it becomes progressively more basic with time, whereas the Eh becomes progressively more positive. While drilling Hole 62.0, the cutting and processing operation kept up with the drilling operation fairly well, so that the cores were split within 8 to 12 hours after coming on deck, but while drilling Hole 62.1, the cutting operation fell progressively behind. As a result, the values for the top of Hole 62.1 are in much closer agreement with the values from the corresponding horizons in Hole 62.0 than are the values from deeper levels in the two holes.

### Site 63

The salinity determinations at Site 63 were all at or near that of local sea water, that is, 34.4 per mille. The salinity varies irregularly with depth, and the total variation over the hole is only  $\pm 0.3$  per mille, which is close to the limit of resolution of the instrument.

The pH values are all more acidic than local sea water (that is, 8.3 to 8.4), ranging from 7.22 to 7.57, the average being 7.39. There is an irregular trend toward greater acidity with greater depth.

The Eh readings show values of about +150 millivolts in the first 60 meters of sediment. In the interval 100 to 270 meters, the values are (with one exception) around -325 millivolts.

#### Site 64

The interstitial water data for Site 64 consist of six sets of values for Eh, pH and salinity, from 0 to 460 meters. The material recovered from the hole below 460 meters was unsuitable for interstitial water sampling because it consisted of hard chalk. The salinity readings are all the same as local sea water (34.1 per mille), except for the value at 460 meters, which is 35.0.

The pH values show that the sediments become more acid as the depth increases. The pH values at the surface of the sediment have a pH of 7.82 and decrease, with one slight irregularity, to 7.23 at 460 meters. The pH of local surface sea water is 8.30.

The Eh readings showed with a value of -320 millivolts at the surface, and of +116 millivolts at 100 meters. From 100 meters to 460 meters, the Eh values become regularly more negative with depth, and the value of -330 millivolts at 460 meters is almost the same as the surface value.

# Site 65

The interstitial water data for Site 65 consist of seven sets of values for Eh, pH and salinity. These values are spaced evenly over the interval 20 to 150 meters. The salinity measurements are all the same as local sea water (34.4 per mille  $\pm$  0.3 per mille), except for the first sample, which had a salinity of 35.2 per mille.

The two pH values above 60 meters were 7.51 and 7.53, while the five samples below 60 meters had pH values of 7.69  $\pm$  0.01, except for one value which was 7.63. The pH of local sea water was 8.34.

The Eh was negative for all samples taken at Site 65. The values start at -242 millivolts, then irregularly become more negative to a depth of 125 meters, where the value is -513 millivolts. Below 125 meters, the values are about -325 millivolts.

## Site 66

The pH values ranged from 7.53 to 7.79, the higher value being from the pelagic clay section. All values are lower than local sea water (8.3 to 8.4). No vertical pattern is apparent.

The Eh values were negative for the radiolarian ooze and volcanic mud. The pelagic clay Eh was positive (+194).

Salinity measurements showed little deviation from local sea water (34.4 to 34.6 per mille), with one exception (35.2 per mille). No vertical pattern is evident.

### Site 67

Because of severe disturbance of the sediments during the coring operation, no interstitial water samples were taken.

Hole	Core	Section	Interval From Top (cm)	pН	Eh	°C	ΔN	Salinity	Comments
61.1	1	2	66-76	7.53	-300	24	63	34.7	A deep hard core showing little evidence of disturbance or drilling fluid intrusion.
62.0	1	2	89-100	7.69	-260	24	63	34.7	Core is a nannofossil-chalk ooze. It is stiff but disturbed, showing little signs of drilling fluid intrusion.
62.0	2	2	36-47	7.48	-350	23	63	34.7	From a nannofossil-chalk ooze, showing little signs of drilling fluid intrusion and disturbance.
62.0	3	2	90-100	6.92	-500	23	62	34.1	From a very hard dry undisturbed nannofossil-chalk ooze.
62.0	3	3	69-140						From a relatively undisturbed hard dry nannofossil-chalk ooze that showed little sign of drilling fluid intrusion.
62.0	4	4	30-40	7.50	-346	24	62	34.1	From a nannofossil-chalk ooze that is hard and dry and relatively undisturbed, with little drilling fluid intrusion.
62.0	5	3	30-40	7.52	-372	23	62	34.1	From a very hard dry undisturbed nannofossil-chalk ooze. Drilling fluid intrusion unlikely.
62.1	1	3	30-41	7.38	-310	24	62	34.1	From an undisturbed soft nannofossil-chalk ooze show- ing no sign of drilling fluid intrusion.
62.1	2	4	40-50	7.35	-426	24	62	34.1	From an undisturbed soft nannofossil-chalk ooze that shows no sign of drilling fluid intrusion.
62.1	4	6	39-48	7.63	+145	23	62	34.1	From a soft but relatively undisturbed nannofossil-chalk ooze. Sampling was delayed four days due to operational necessities.
62.1	6	5	30-38	7.27	-356	25	62	34.1	From a soft, very disturbed nannofossil-chalk ooze that has possibly suffered drilling fluid intrusion.
62.1	8	5	40-51	7.24	-586	24	62	34.1	From a soft but not mushy nannofossil-chalk ooze. The core was not too disturbed, but drilling fluid intrusion is a possibility.
62.1	12	2							From a disturbed nannofossil-chalk ooze that possibly had drilling fluid intrusion.
62.1	14	5	73-80	7.46	+146	24	63	34.7	From a mushy disturbed nannofossil-chalk ooze that probably has drilling fluid in it. The core had hard and soft sections. The sample was mostly from a hard section.

TABLE 1 Interstitial Water Analysis: Shipboard

Hole	Core	Section	Interval From Top (cm)	<i>p</i> H	Eh	Temp °C	ΔN	Salinity	Comments
62.1	16	5	49-59	7.26	+165	24	62.5	34.4	From a firm undisturbed nannofossil-chalk ooze that is unlikely to have drilling fluid in it.
62.1	18	2	40-50	7.56	+159	24	63	34.7	From a moderately disturbed, firm, relatively dry nannofossil-chalk ooze drilling fluid intrusion is unlikely.
62.1	20	5	40-47	7.43	+150	24	63	34.7	From a disturbed but firm nannofossil-chalk ooze. Drilling fluid intrusion unlikely.
62.1	24	5	40-48	7.51	-185	24	62	34.1	From a moderately disturbed nannofossil-chalk ooze that had alternating hard and soft sections. Sample mostly from a hard section.
62.1	26	2	132-140	7.49	+130	24	63	34.7	From a moderately disturbed nannofossil-chalk ooze. Sample taken in a hard section.
62.1	28	5	39-50	7.41	+89	24	63	34.7	From a hard nannofossil-chalk ooze that had alternating hard and soft layers. This may indicate drilling fluid intrusion.
62.1	30	2	40-50	7.47	+102	24	63	34.7	From a hard nannofossil-chalk ooze. Probably has little drilling fluid intrusion.
62.1	34	5	40-50	7.96	+139	2	63	34.7	From a hard dry undisturbed nannofossil-chalk ooze.
62.1	36	2	122-132	8.10	+138	23	62.5	34.3	From a hard dry nannofossil-chalk ooze. There is some chance of drilling fluid intrusion, but the sampled inter- val was pretty compact.
63.0	1	5	40-50	7.57	+147	25	62	34.1	From a soft pelagic clay which may have drilling fluid in it.
63.0	2	3	40-50	7.41	+163	24	62.5	34.4	From a firm nannofossil-chalk ooze that shows no sign of drilling fluid intrusion.
63.0	3	2	80-91	7.28	-242	23	63	34.7	From a very firm nannofossil-chalk ooze that shows no sign of drilling fluid intrusion.
63.0	4	2	80-90	7.41	-457		62.5	34.4	From a hard dry nannofossil-chalk ooze that is unlikely to contain drilling fluid.
63.1	5	2	60-70	7.34	-332	24	62.5	34.4	From a hard but disturbed nannofossil-chalk ooze.
63.1	7	2	79-90	7.22	-336	23	63	34.7	From a firm light-brown chalk ooze that was only slightly disturbed. No signs of drilling fluid intrusion.

TABLE 1 – Continued

TABLE 1	-Continued

Hole	Core	Section	Interval From Top (cm)	pН	Eh	Temp °C	ΔN	Salinity	Comments
63.1	7	3	80-150						From a light-brown chalk ooze that was only slightly disturbed. The sample was quite firm, so there is little chance of drilling fluid intrustion.
63.1	9	2	82-90	7.27	-350	24	62.5	34.4	From a hard brown chalk ooze. Sample was from hard undisturbed section, so is unlikely to have drilling fluid in it.
63.1	11	5	39-44	7.47	-305	24	62	34.1	From a chalk ooze that had hard chunks and soft greatly disturbed sediments. The sample was entirely from one of the hard chunks.
63.1	13	3	32-35	7.36	+172	25	62	34.1	From a chalk ooze that had hard chunks and soft, greatly disturbed sediments. The sample was entirely from one of the hard chunks.
63.2	2	3	30-38	7.58	+132	24	62.5	34.4	From a soft disturbed greenish marl ooze that may have drilling fluid in it.
64.0	1	3	119-127	7.82	-320	24	62	34.1	From a relatively undisturbed but very soft nannofossil- chalk ooze.
64.0	2	2	108-119	7.72	+116	25	62	34.1	Little or no drilling fluid intrusion. Little disturbance of a foraminiferal-nannofossil chalk ooze.
64.0	3	4	80-90	7.46	-130	25	62	34.1	From a soft but relatively undisturbed nannofossil- foraminiferal chalk ooze.
64.0	4	5	120-130	7.49	-220	25	62	34.1	From a firm nannofossil-chalk ooze that was slightly disturbed. Drilling fluid intrusion unlikely.
64.1	1	6	0-7	7.41	-330	25			From a broken up nannofossil chalk that may have drilling fluid in it.
64.1	2	5	72-150						From a hard nannofossil chalk that was broken up during drilling, so that it probably contains drilling fluid.
64.1	3	5	141-150	7.23	-327	25	64	35.2	From a badly deformed area that probably has drilling fluid in it. The core had hard blocks of chalk with soft disturbed mud. The sample was from the mud.
65.0	3	4		7.51	-242	25	64	35.2	From a soft radiolarian ooze that was disturbed but showed little sign of drilling fluid intrusion.

Hole	Core	Section	Interval From Top (cm)	pН	Eh	°C	ΔN	Salinity	Comments
65.0	7	6	0-10	7.52	-309	25	62	34.1	From a soft disturbed radiolarian ooze that showed little sign of drilling fluid.
65.0	9	2	25-45 75-92 105-150						From a firm radiolarian ooze.
65.0	9	2	25-45 75-95 105-150						From a disturbed radiolarian ooze that probably does not have drilling fluid in it.
65.0	9	6	90-150						From a firm radiolarian ooze which probably does not contain drilling fluid.
65.0	9	6	0-10	7.70	-362	24.1	62.5	34.4	From a soft radiolarian ooze that may have drilling fluid in it.
65.0	11	5	0-11	7.68	-350	24	63	34.7	From a disturbed radiolarian ooze that probably has some drilling fluid in it.
65.0	13	6	0-11	7.63	-513	25	62	34.1	From a radiolarian ooze that was disturbed, so it may contain drilling fluid.
65.0	16	5	140-150	7.69	-321	25	62.5	34.1	From a deformed radiolarian ooze that may contain drilling fluid.
65.1	4	5	0-10	7.69	-333	25	62.5	34.4	From a deformed radiolarian ooze that may contain drilling fluid.
66.0	2	2	139-150	7.65	-185	21.5	63	34.7	From a radiolarian ooze with some calcareous bedding.
66.0	3	5	139-150	7.53	-300	21.6	63	34.7	From an olive brown radiolarian ooze which may con- tain drill fluid.
66.0	6	2	66-150						From a fine-grained brown pelagic clay.
66.0	6	3	150	7.79	+194	23	62.5	34.4	From a stiff fine-grained pelagic clay. Probably no drill fluid.
66.0	7	3	139-150			24.1			From a grayish-brown pelagic clay.
66.0	7	4	65-150						From a grayish-brown pelagic clay.
66.0	9	3		7.66	-282	22	63	34.7	From a dark volcanic mud.
66.1	2	4		7.58	-380	22.2	62.5	34.4	From a radiolarian ooze which probably does not con- tain drill fluid.

TABLE 1 – Continued

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Hole	Core	Section	Interval From Top (cm)	pН	Eh	°C	ΔΝ	Salinity	Comments
66.1	6	5	0-10	7.59	279	23.2	64	35.2	From a radiolarian ooze which may contain drill fluid.
66.1	7	3	0-70						From a firm, relatively undisturbed radiolarian ooze.