

APPENDIX I. INTERSTITIAL WATER STUDIES ON SMALL CORE SAMPLES, DEEP SEA DRILLING PROJECT, LEG 12

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ABSTRACT

With the exception of Site 114, all interstitial waters in Leg 12 showed marked increases in calcium, which can be attributed to diagenetic dissolution and recrystallization of calcium carbonate, especially coccolith and foraminiferal tests. Magnesium loss may be due to either or both replacement of iron in clays or the dolomitization of calcium carbonate. The lowest sample from Site 113, on the mid-Labrador Sea Ridge, yielded only 250 mg/kg magnesium but 2.56 g/kg calcium in interstitial water from a clayey, siliceous quartz silt. Strontium values close to and exceeding 100 mg/kg were noted, especially in sites showing extensive carbonate recrystallization. Few significant deviations in chloride concentration from sea water levels were noted.

INTRODUCTION

Leg 12 sites consist largely of Pleistocene-Neogene marly sediments, often showing relatively high depositional rates (5-20 cm/1000 yrs). In the absence of significant or consistent changes in conservative properties of pore waters, attention focuses on large variations in calcium, magnesium, strontium, silica, potassium and sulfate. These are linked to diagenesis and water-sediment interactions.

Sodium analysis by atomic absorption has been improved by acquisition of a new instrument, and more closely approximates values obtained by difference between anions and cations (except sodium). Although agreement between cations and anions now frequently approaches the accuracy characterized by the work of O. V. Shishkina (who has published some 36 papers dealing with pore fluids in piston cores from various seas and oceans), the sodium values by difference are still more reliable than the directly determined ones. Alkalinity, as in previous legs, may be too low, especially in the case of higher values. This is apparently partly caused by loss of HCO_3 on storage in heat-sealed plastic pipes. In general, methods are similar to those employed in previous leg reports.

RESULTS AND DISCUSSION

The chemical analyses of major constituents in pore fluids are listed in Table 1, which also provides bulk water and pH data supplied from the preliminary shipboard logs. Note that bulk water is taken from physical properties measurements, possibly including GRAPE (a gamma ray attenuation method which has not always yielded reliable values in the past), and refers to strata near, but not identical to, the samples studied here. The pH is determined on waters squeezed on board ship, and may have been altered owing to the change in temperature from bottom conditions to shipboard levels, as well as effects in squeezing.

Finally, corrections to potassium, magnesium, calcium and silica, owing to the influence of change in temperature

from time of recovery at the sea floor to squeezing of the sediments at room conditions have not been applied (Sayles *et al.*, 1972, and references cited therein). In Leg 15 these corrections (Sayles *et al.*, 1972) varied as follows for different constituents, depending on lithology and other factors: Sodium—1%; Calcium—1-6%; Magnesium—1-7%; Strontium—0-19%; Potassium—12-24%; Silica—0-41%; Boron—7-61%. Warming leads to increases of the univalent cation and decreases of divalent cations. No observable effect of temperature was found for chloride and sulfate (less than 0.5 per cent). In spite of the magnitude of some of the effects, they are consistent for a given lithology, and will not negate the validity of the larger diagenetic effects referred to here.

A brief summary of the major variations in pore fluid chemistry follows here.

Site 111 (Orphan Knoll)

After remaining near or somewhat below sea water values, calcium increases to 0.60 g/kg in the lowest sample. This appears to be related to a change in lithology from clay to chalky ooze.

Site 112 (Labrador Sea)

Calcium increases throughout the section, probably due to dissolution of calcium carbonate; there is strong petrographic evidence of corrosion and dissolution of biogenic carbonate debris. Strontium begins to rise sharply toward the bottom of the section, suggesting that recrystallization processes—as discussed by Manheim and Sayles (1971)—must become extensive here.

Site 113 (Mid-Labrador Sea Ridge)

Calcium increases here appear related to coccolith dissolution as observed petrographically in the Pliocene-Pleistocene clays. However, the absence of strontium enrichments is quite unusual, for even a single cycle dissolution of enough coccolith calcite (assumed to contain 0.15

per cent strontium, according to data cited in Manheim and Sayles, 1971) to produce an excess of 2100 milligrams calcium (at 550 meters depth) would yield about 7 mg/kg extra strontium. Thus, it appears that either a low strontium carbonate is the source of calcium, or some phase is taking up strontium preferentially. No such uptake sites have been established to date. Phillipsite and chlorite were described from the lower sediments of the site, but we do not have data on the exchange or affinity of phillipsite for strontium to warrant a linkage between zeolites and the strange Ca-Sr relationships.

Site 114 (Reykjanes Ridge)

This site was largely free of carbonates and showed little enrichment in interstitial calcium. One may therefore assume that most carbonate was already lost prior to burial of the sediments. Appreciable sulfate deficiency and high alkalinity were noted at 207 meters.

Site 116 (Hatten-Rockall Basin)

The best set of samples was obtained from this deep site, and showed several distinctive features. The common antipathetic relationship between calcium (enrichment) and magnesium (depletion) observed in carbonate ooze-rich sediments was observed here (Figure 1). Moreover, a strong enrichment in strontium with depth was noted immediately below the sea floor and continued more gradually below 100 meters depth. A strong odor of hydrogen sulfide (H₂S) noted by the samplers at 216 meters was not reflected in unusually large deficiencies in sulfate at this depth, though a consistent decrease in sulfate with depth occurs in the site. Silica values are among the highest recorded in DSDP pore fluids, reaching nearly 40 mg/kg. However, we believe that a considerable part of the dissolved silica may be due to the higher temperature at which the recovered cores were equilibrated in the ship's laboratories. Dissolution of some of the siliceous organisms or other readily amorphous silica found abundantly by the petrologists may have occurred (see also Fanning and Pilson, 1971; Sayles *et al.*, 1972). In spite of the abundance of calcium carbonate in the core, the magnesium loss with depth cannot be entirely explained by the formation of magnesium-rich carbonates or dolomite because magnesium loss is roughly twice the calcium gain (mole/mole). The nearly perfect parallelism with sulfate (Figure 1) suggests that a reaction involving both magnesium and sulfate such as that proposed by Drever (1971), may be operative. Hydrogen sulfide, produced by bacterial reduction of sulfate, reacts with iron in chlorite or other clays to produce iron sulfides, accompanied by movement of soluble magnesium into the former iron positions. Finally, an unexplained increase in boron with depth occurs in this site.

Site 117 (West Slope of Rockall Basin)

A single sample of pore water is highly enriched in calcium, accompanied by strong depletions in both magnesium and potassium, and moderate depletion of Sodium.

Site 118 (Bay of Biscay, between French and Spanish Coasts)

Nearly all sulfate was lost from the interstitial waters, resulting in unusually high barium values (around 1 mg/kg). Possibly some calcium and alkalinity have been lost from these pore fluids by post-sampling precipitation of calcium carbonate as demonstrated by studies of Leg 15 samples (Gieskes, 1972). Strontium is very high for the two bottom-most samples, over 100 mg/kg and off scale for the instrumental procedure used in analysis. Follow up analysis has not been completed. The very high strontium, in the absence of increases in chloride which might suggest an evaporitic or other external source, would appear to call for extensive recrystallization of primary coccolith-foraminiferal carbonate to lower strontium varieties as previously discussed.

Site 119 (Cantabria Seamount)

Typical behavior of calcium (increases), magnesium (decreases) and strontium (strong increases) in biogenic carbonate sediments are noted here. Again, however, magnesium losses are more readily explained by the iron replacement, than a carbonate uptake model.

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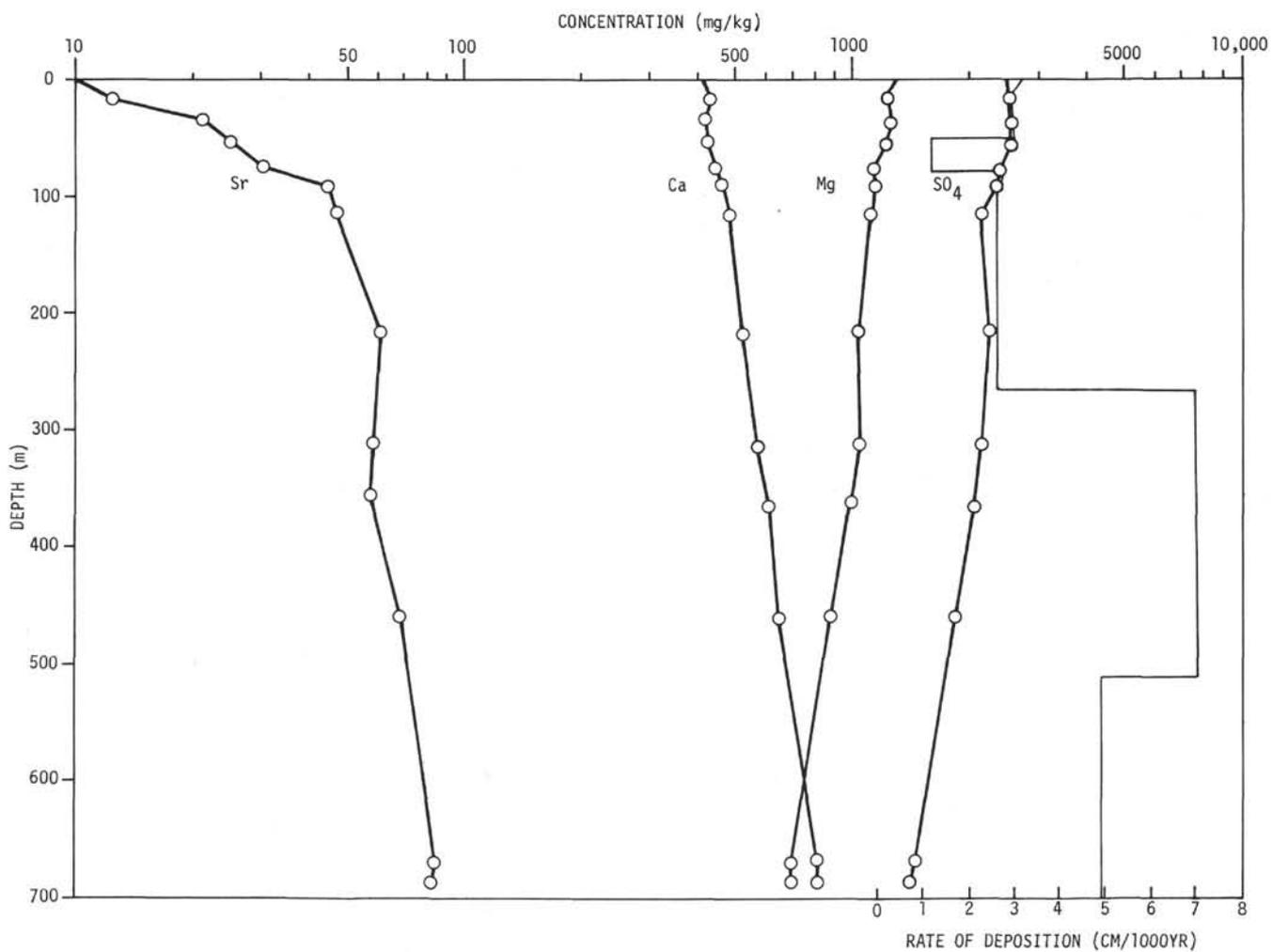


Figure 1. Plot of concentration in interstitial water vs. depth in Site 116 and 116A.

TABLE 1
Leg 12 Major Constituents of Pore Fluids. Values in g/kg, except as noted.

Sample Designation	Depth (m)	Age	Description	Na ^a	Na ^b	K	Ca	Mg	Total Cations (meg/kg)	Cl	SO ₄	Alk. (meg/kg)	HCO ₃	Total Anions (meg/kg)	Sum	H ₂ O (‰) ^c	pH
Site 111 (50° 25.6' N, 46° 22.0' W, water depth 1811 m, Orphan Knoll)																	
<i>Surface ocean water</i>				10.0	10.0	0.37	0.41	1.26	569	18.10	2.69	3.1	0.19	569	33.0	-	-
111-1-4	4	Pleistocene	Light grayish brown silty clay; disturbed.			Apparently evaporated.											
111-2-5	100	Pleistocene	Gray silty clay; disturbed.	10.7	10.6	0.29	0.34	1.17	587	19.4	1.58	4.1	0.25	583	33.6	(11)	7.4
111A-1-5	111	Pleistocene	Gray clay with silty patches scattered throughout.	(10.6)	10.6	0.34	0.33	1.12	579	(19.2)	1.64	4.0	0.25	(579)	33.5	20	7.4
111A-5-4	140	Pliocene	Dark gray clay with black reduced horizons.	10.4	10.4	0.36	0.42	1.10	574	18.9	1.71	3.7	0.23	572	33.1	25	7.6
111A-7-4	158	Early Eocene	Gray clay lumps in a matrix of glauconitic sand.	10.5	10.5	0.37	0.42	1.21	587	18.9	2.37	4.3	0.26	586	34.0	45	7.5
111A-11-5	188	Maestrichtian	Grayish green chalky ooze; moderately mottled.	10.6	(10.6)	0.38	0.60	1.21	600	(19.5)	2.33	2.0	0.12	600	34.7	29	7.2
Site 112 (54° 01.0' N, 46° 36.2' W, water depth 3667 m, Labrador Sea)																	
112-1-6	35	Pleistocene	Gray sandy silt; disturbed.	10.8	10.8	0.41	0.46	1.22	604	19.5	2.53	2.5	0.15	605	35.1	-	7.3
112A-1-5	85	Pleistocene	Gray glacial silty clays; deformed and disturbed.	(10.5)	10.5	0.33	0.60	1.02	580	(19.1)	2.03	1.4	0.09	(580)	33.6	-	-
112-2-5	106	Pliocene	Gray glacial clay; disturbed by coring.	10.8	10.8	0.32	0.58	1.06	595	19.4	2.23	2.4	0.14	594	34.5	38	6.9
112-3-6	157	Miocene	Greenish gray marly clay.	11.0	10.9	0.40	0.70	0.87	596	19.6	1.81	0.6	0.04	591	34.3	-	6.9
112-4-2	203	Miocene	Greenish gray clay w/mottles and laminae of dark green gray and dusky red clay.	10.8	10.6	0.36	0.84	0.88	602	19.5	1.99	0.3	0.02	592	34.2	51	7.4
112-9-4	312	Oligocene	Gray marly clay.	10.6	10.4	0.31	1.15	0.82	594	19.4	1.85	1.9	0.12	587	34.1	-	7.4
112-12-0	384	Oligocene	Greenish gray very stiff nannoplankton marl.	10.2	10.2	0.23	1.34	0.86	588	19.5	1.70	2.2	0.13	587	34.0	40	-

TABLE 1 - Continued

Sample Designation	Depth (m)	Age	Description	Na ^a	Na ^b	K	Ca	Mg	Total Cations (meg/kg)	Cl	SO ₄	Alk. (meg/kg)	HCO ₃	Total Anions (meg/kg)	Sum	H ₂ O (‰) ^c	pH
Site 113 (56° 47.4' N, 48° 19.9' W, water depth, 3629 m, Mid-Labrador Sea Ridge)																	
<i>Surface ocean water</i>				10.4	10.7	0.38	0.41	1.22	583	19.1	2.68	3.4	0.21	597	34.7	—	—
113-1-4	55	Pleistocene	Gray silty clay; disturbed by coring.	10.6	10.5	0.40	0.59	1.16	597	19.3	2.26	2.6	0.16	594	34.4	45	7.5
113-2-3	102	Pleistocene	Gray silty clay; disturbed by coring.	10.8	10.8	0.33	0.86	0.85	592	19.5	1.97	1.2	0.08	592	34.3	33	7.5
113-4-2	206	Pleistocene (?)	Gray silty clay; extensive distortion and flowage resulting from coring.	10.7	10.6	0.28	1.12	0.72	588	19.6	1.48	2.0	0.12	585	33.9	34	8.2
113-7-1	550	Pliocene	Gray clay and radiolarian ooze clasts in a matrix of wet silty quartz sand.	10.0	10.0	0.26	2.56	0.25	590	19.6	1.65	1.0	0.06	588	34.2	—	7.2
Site 114 (59° 56.0' N, 26° 48' W, water depth 1937 m, Reykjanes Ridge)																	
114-2-6	207	Pleistocene	Greenish gray clay slightly mottled greenish black; firm.	10.7	10.7	0.39	0.14	0.93	559	18.9	0.74	11.4	0.69	560	32.5	41	—
114-5-5	506	Pliocene	Gray alternating layers of watery glauconitic silty sand and indurated silty sand.	10.9	10.9	0.37	0.36	1.04	587	19.4	1.78	4.7	0.29	588	34.1	—	—
Site 116 (58° 54.4' N, 21° 07.0' W, water depth 2893 m, Hatton-Rockall Basin)																	
116A-2-5	15	Pleistocene	Gray and olive gray foraminiferal-nannofossil marl mud.	10.7	10.7	0.43	0.44	1.25	601	19.3	2.54	3.0	0.18	600	34.8	46	7.5
116A-4-6	34	Pleistocene	Creamy white and pale brown foraminiferal ooze, disturbed by coring.	10.8	10.8	0.43	0.42	1.26	606	19.4	2.57	3.6	0.22	604	35.1	29	7.5
116A-6-6	52	Pleistocene	Gray and white nannofossil ooze; disturbed by coring.	10.8	10.8	0.43	0.42	1.23	603	19.4	2.55	3.9	0.24	604	35.1	42	7.5

TABLE 1 - Continued

Sample Designation	Depth (m)	Age	Description	Na ^a	Na ^b	K	Ca	Mg	Total Cations (meg/kg)	Cl	SO ₄	Alk. (meg/kg)	HCO ₃	Total Anions. (meg/kg)	Sum	H ₂ O (°/∞) ^c	pH
116-1-4	75	Pliocene	Light gray to white foraminiferal-nannofossil ooze; disturbed by coring.	10.7	10.7	0.42	0.44	1.14	592	19.1	2.36	3.9	0.24	590	34.4	37	7.5
116A-10-6	88	Pliocene	White and light gray nannofossil ooze.	10.8	10.8	0.41	0.46	1.15	598	19.4	2.35	4.5	0.27	600	34.8	33	7.5
116-2-5	115	Pliocene	Very light gray-white foraminiferal-nannofossil ooze; disturbed.	10.7	10.7	0.39	0.48	1.12	592	19.3	2.16	3.5	0.21	592	34.4	33	7.4
116-4-6	216	Late Miocene	Gray to white foraminiferal-nannofossil ooze; strong odor of H ₂ S.	10.9	10.9	0.40	0.52	1.06	598	19.4	2.22	4.4	0.27	597	34.8	30	7.4
116-6-4	313	Middle Miocene	Bluish white foraminiferal-nannofossil ooze; moderately mottled; disturbed.	(11.4)	10.9	0.38	0.57	1.06	(621)	19.6	2.15	4.4	0.27	601	34.8	30	7.3
116-7-3	362	Middle Miocene	Bluish white foraminiferal-nannofossil ooze; slight mottling, varicolored.	10.8	10.9	0.37	0.61	1.00	592	19.4	2.07	3.9	0.24	594	34.5	29	7.3
116-9-2	460	Middle Miocene	Bluish white foraminiferal-nannofossil ooze; gray and yellowish gray mottling.	11.0	10.9	0.34	0.65	0.88	592	19.5	1.83	3.5	0.21	590	34.4	30	7.3
116-15-6	669	Early Miocene	Bluish white, foraminiferal-nannofossil ooze; slightly mottled.	11.1	11.0	0.29	0.81	0.70	589	19.7	1.44	2.4	0.14	588	34.2	31	7.3
116-17-5	686	Early Miocene	Bluish white, foraminiferal-nannofossil ooze.	11.0	11.0	0.28	0.82	0.70	584	19.6	1.40	2.2	0.14	585	34.0	29	7.3
Site 117 (57° 19.5' N, 15° 23.0' W, water depth 1048 m, west slope of Rockall Bank)																	
117A-3-6	229	Early Eocene	Olive gray, dense clay; burrowed.	9.6	9.6	0.20	2.18	0.67	587	19.1	2.27	1.0	0.06	585	34.0	51	7.5
Site 118 (45° 02.9' N, 9° 00.5' W, water depth 4901 m, Bay of Biscaye)																	
118-1-6	102	Pleistocene	Gray nannofossil ooze; highly deformed.	10.5	10.5	0.34	0.25	0.88	551	19.0	0.41	8.5	0.52	552	31.9	36	7.6

TABLE 1 – Continued

Sample Designation	Depth (m)	Age	Description	Na ^a	Na ^b	K	Ca	Mg	Total Cations (meg/kg)	Cl	SO ₄	Alk. (meg/kg)	HCO ₃	Total Anions (meg/kg)	Sum	H ₂ O (‰) ^c	pH
118-3-3	301	Pliocene	Olive gray, light gray and white clay.	10.7	10.7	0.32	0.29	0.84	557	19.5	0.12	2.4	0.14	555	31.9	42	8.0
118-5-3	402	Upper Miocene	Varicolored gray firm clay with nannofossil ooze.	10.8	10.8	0.34	0.38	0.84	567	19.9	0.15	4.3	0.26	567	32.9	44	7.6
118-6-1	449	Upper Miocene	Light gray sandstone.	10.8	10.8	0.33	0.54	0.83	573	19.8	0.26	9.0	0.55	573	33.1	–	7.4
Site 119 (45° 02.3' N, 7° 58.8' W, water depth 4447, Cantabria Seamount)																	
<i>Surface ocean water</i>				10.9	10.9	0.39	0.43	1.32	614	19.6	2.77	3.3	0.20	614	35.6	38	–
119-2-2	51	Pleistocene	Olive gray silty clay; soft; disturbed by flow-in	10.7	10.8	0.43	0.36	1.26	508	19.3	2.35	6.6	0.40	601	34.9	–	7.5
119-4-2	150	Late Miocene	Light olive gray nannofossil clay.	10.7	10.7	0.39	0.51	1.16	506	19.4	2.16	4.0	0.25	596	34.6	–	7.5
119-6-3	243	Early Miocene	Light olive gray and olive gray dense clay.	10.5	10.6	0.32	0.84	1.07	505	19.4	2.09	5.7	0.35	597	34.6	–	7.2
119-10-2	277	Miocene/Oligocene	Yellowish gray and light olive gray, firm nannofossil clay	10.6	10.6	0.29	0.88	1.08	601	19.6	2.09	5.7	0.35	603	34.9	30	7.0
119-16-4	333	Oligocene	Light gray, hard uniform nannofossil clay.	10.6	10.6	0.30	0.86	1.06	599	19.7	1.83	5.1	0.31	590	34.7	–	–
119-18-2	349	Early Oligocene	Pale yellow, dense nannofossil clay; pale blue mottling.	10.4	10.5	0.29	0.97	1.04	594	19.5	2.02	5.4	0.33	596	34.6	–	7.2
119-20-3	368	Middle Eocene	Gray brown dense clay.	10.6	10.6	0.28	0.97	1.05	603	19.8	1.98	4.0	0.24	604	34.9	–	–

^{a,b}Na^a refers to analytically determined value, whereas, Na^b is determined by difference between anions and cations (excluding Na). H₂O values are obtained from shipboard logs reported under physical properties; they are given here for orientational purposes only and do not necessarily correspond to actual samples studied here. The pH is determined on squeezed effluent. Sum utilizes the Na by difference values, which are usually somewhat more precise than the directly determined values. NH₄ and other omitted ions usually do not contribute significantly to summations.

^c HCO₃ calculated assuming all alkalinity is present as bicarbonate ion.

TABLE 2
Leg 12 Minor Constituents. Values in mg/kg^a

Sample Designation	Depth (m)	Age	B	Sr	Ba	Si (col.)	Si (spec.)
Holes 111 and 111A							
<i>Surface ocean water</i>			<3	6.0	<0.3	0.4	<4
111-1-4	4	Pleistocene	<3	3.3	<0.3	4.5	≤4
111-2-5	100	Pleistocene	4	9.2	<0.3	5.7	6
111A-1-5	111	Pleistocene	<3	3.4	<0.3	4.2	≤4
111A-5-4	140	Pliocene	<3	9.4	<0.3	9.1	8
111A-7-4	158	Early Eocene	3	9.1	<0.3	7.4	7
111A-11-5	188	Maestrichtian	<3	10.9	<0.3	10.3	10
Holes 112 and 112A							
112-1-6	35	Pleistocene	4	9.0	<0.3	12.7	15
112A-1-5	85	Pleistocene	<3	4.9	<0.3	4.9	≤4
112A-3-3	101	Pliocene	3	11.0	<0.3	9.7	9
112A-2-5	106	Pliocene	4	11.0	<0.3	6.8	7
112A-3-6	157	Miocene	<3	10.5	<0.3	3.4	4
112-4-2	203	Miocene	5	13.3	<0.3	17.6	16
112-9-4	312	Oligocene	<3	18.0	<0.3	25.6	25
112-12-0	384	Oligocene	<3	21.0	<0.3	10.7	12
Hole 113							
<i>Surface ocean water</i>			4	8.2	<0.3	0.1	<4
113-1-4	55	Pleistocene	3.5	9.1	<0.3	13.8	14
113-2-3	102	Pleistocene	3.0	9.0	<0.3	6.6	6
113-4-2	206	Pleistocene (?)	<3.0	8.4	<0.3	15.4	10
113-7-1	550	Pliocene	≤3.0	8.3	<0.3	4.6	5
Hole 114							
114-2-6	207	Pleistocene	5.5	6.4	<0.3	9.0	17
114-5-5	506	Pliocene	4.6	13.2	<0.3	13.7	20
Holes 116 and 116A							
116A-2-5	15	Pleistocene	4.2	12.3	≤0.3	8.8	10
116A-4-6	34	Pleistocene	5.0	21.0	≤0.3	12.6	13
116A-6-6	52	Pleistocene	4.0	25.0	≤0.3	15.2	16
116-1-4	75	Pliocene	7.0	30.0	≤0.3	17.3	16
116A-10-6	88	Pliocene	6.0	44.0	≤0.3	14.5	19
116-2-5	115	Pliocene	6.0	47.0	≤0.3	18.7	19
116-4-6	216	Late Miocene	9.0	61.0	≤0.3	5.1	26
116-6-4	313	Middle Miocene	9.0	58.0	≤0.3	11.0	29
116-7-3	362	Middle Miocene	11.0	57.0	≤0.3	24.8	29
116-9-2	460	Middle Miocene	13.0	69.0	≤0.3	35.0	38
116-15-6	669	Early Miocene	21.0	85.0	≤0.3	—	38
116-17-5	686	Early Miocene	23.0	82.0	≤0.3	34.3	38
Hole 117A							
117A-3-6	229	Early Eocene	≤2	39.0	≤0.3	16.9	≤5
Hole 118							
118-1-6	102	Pleistocene	4	11.2	1.8	9.5	9
118-3-3	301	Pliocene	<3	48.0	0.7	3.7	4
118-5-3	402	Upper Miocene	5	100.0	1.3	5.3	6
118-6-1	449	Upper Miocene	5	100.0	0.8	22.0	24
Hole 119							
<i>Surface ocean water</i>			4	8.2	<0.3	—	≤4
119-2-2	51	Pleistocene	7	10.7	<0.3	5.5	6
119-4-2	150	Late Miocene	6	34.0	<0.3	5.7	8
119-6-3	243	Early Miocene	5	56.0	<0.3	23.9	26
119-10-2	277	Miocene/Oligocene	5	59.0	<0.3	24.8	25
119-16-4	333	Oligocene	6	50.0	<0.3	11.7	18
119-18-2	349	Early Oligocene	7	82.0	<0.3	21.1	24
119-20-3	368	Middle Eocene	8	69.0	<0.3	16.5	17

^aSi (col) and Si (spec) refer to colorimetric and spectrometric determinations. The former determines orthosilicate, whereas the latter determines total silicate in solution.