

23. PRELIMINARY EVIDENCE FOR PLIOCENE CONVECTIVE FLUID FLOW THROUGH SEDIMENTS ON A RIDGE FLANK, HOLE 600C¹

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ABSTRACT

Strontium, magnesium, oxygen, and carbon isotope profiles of the carbonate fraction of Hole 600C sediments support the lithologic and petrographic observations of extensive CaCO₃ dissolution and recrystallization in the Pliocene basal section. Convective fluid flow through the sediments during the first 1 to 1.5 m.y. of the sedimentary history of these sediments may explain these observations.

INTRODUCTION

During Leg 92, three sites were drilled on 4.6-Ma crust, of which Site 600 is characterized by the highest heat flow. Three holes were drilled at Site 600. Drilling in Hole 600C recovered the thickest sediment record—11.8 m of Pliocene to Pleistocene clay-bearing to clayey nannofossil ooze and chalk. Basement was not reached in this hole.

The sediments in Hole 600C (18°55.70'S, 116°50.45'W) at a water depth of 3398 m are composed of various mixtures of two primary components: biogenic CaCO₃ and red brown to yellow brown semiopaque oxides (designated RSO by Leg 34 scientists; Quilty et al., 1976; Bass, 1976). The ratio of the amount of CaCO₃ to the amount of RSO decreases with increasing depth. Some basaltic glass, fragments of altered basalt, and traces of terrigenous material are present as well. A basaltic glass layer, highly altered to palagonite and poorly crystalline smectite, is present at 10.25 m sub-bottom.

According to Knüttel (this volume), the boundary between Pleistocene and Pliocene sediment is close to the top of Core 600C-1, Section 4, at about 4.5 m sub-bottom (see Fig. 1). A rather abrupt change in sediment color is observed in Section 600C-1-4 (35 cm) from brownish yellow (10 YR 6/6) to dark brown (7.5 YR 3/2 to 4/4). Chalk composes the basal 3 m of the recovered sediment column.

The heat flow at this site is 580 mW/m² (almost 14 heat flow units [HFU]) (Site 600 to 602 chapter, this volume); the theoretically expected value (Sclater et al., 1971) is significantly lower (~245 mW/m²). Interstitial water analyses by Gieskes (this volume) indicate only little down-hole change in Mg²⁺ concentration and a possible peak in dissolved Ca²⁺ at mid-depths in the sediment column. These results do not support the presence of recent convective fluid flow through the sediment column.

The sediments in Hole 600C were deposited above the lysocline (e.g., Berger and Winterer, 1974; van Andel et al., 1975; Broecker and Broecker, 1974; Berger et al.,

1976; Rea and Leinen, this volume). The preservation of planktonic foraminifers, however, is only moderate to good in younger samples and moderate to poor in the Pliocene section (Romine, this volume). Furthermore, the presence of at least a 3-m basal Pliocene chalk layer in such a thin and young calcareous section cannot easily be explained by well-documented rates of diagenetic reactions in pelagic calcareous oozes. Calcite dissolution and overgrowth were extensive in this section (Fig. 2).

METHODS

The weight percent of the CaCO₃ and insoluble residue fractions were determined by two methods: by CaCO₃ dissolution in an acetic acid Na-acetate buffer solution (pH 4.7) and by CO₂ coulometry (Table 1). The CO₂ coulometry results are more precise and are generally somewhat lower than the values from the dissolution method. The CO₂ coulometry data were used for all the chemical calculations presented in Table 1 and Figure 1.

Prior to CaCO₃ dissolution in the buffer solution, Sr²⁺ and Mg²⁺ were removed from ion-exchange and adsorbed sites by treatment with a 1M NH₄Cl solution for 15 min.; 1 g of sediment was immersed in 100 ml of 1M NH₄Cl solution. Silica analyses indicated that silicates were not attacked by the ion-exchange or the acetic acid Na-acetate buffer solutions. The ion-exchange pretreatment ensures that the Sr²⁺ and Mg²⁺ analyzed after complete carbonate digestion originated from the carbonate particles.

Sr²⁺ and Mg²⁺ were analyzed by atomic adsorption spectroscopy (accuracy: ±2%), Ca²⁺ by EGTA titration (±1%), and silica by molybdenum blue colorimetry (±2%). The results are summarized in Table 1 and Figure 3.

Several samples of the calcareous fraction were analyzed by a scanning electron microscope (SEM) with EDS attachment (Fig. 2).

Oxygen and carbon isotope ratios from samples reacted with 100% phosphoric acid (McCrea, 1950), were measured on a 6-cm V6 Micro-mass 602C mass spectrometer. The isotope analyses were corrected according to Craig (1957), and the results are reported as per mil relative to the PDB standard. The standard deviation is ±0.15 for both δ¹⁸O and δ¹³C. These results are presented in Table 2. In order to ensure that the observed increase in the δ¹⁸O and δ¹³C values with increasing depth is not due to higher ratios of benthic foraminifers to planktonic foraminifers plus coccoliths, the 38-to-0.45-μm carbonate fraction (which represents coccoliths) was analyzed separately in a few sediments (Table 2).

Oxygen isotope ratios of the pore fluids were carried out by the method of Epstein and Mayeda (1953). The isotope results are reported as δ¹⁸O‰ relative to standard mean ocean water (SMOW; Craig, 1961). The standard deviation is ±0.03.

RESULTS AND DISCUSSION

To understand the unexpectedly low degree of biogenic calcite preservation in these sediments, the chem-

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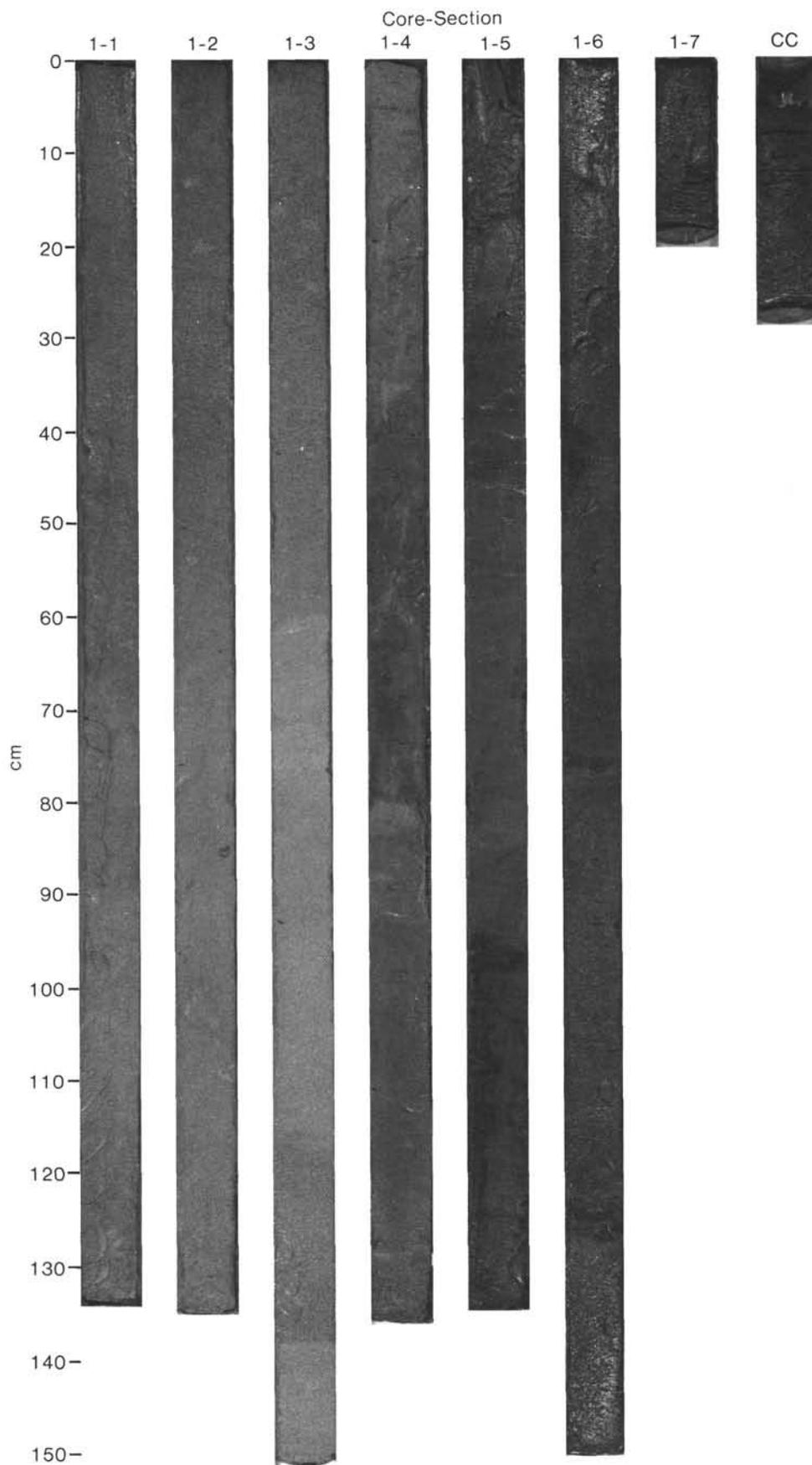


Figure 1. Photo of sediments recovered from Hole 600C.

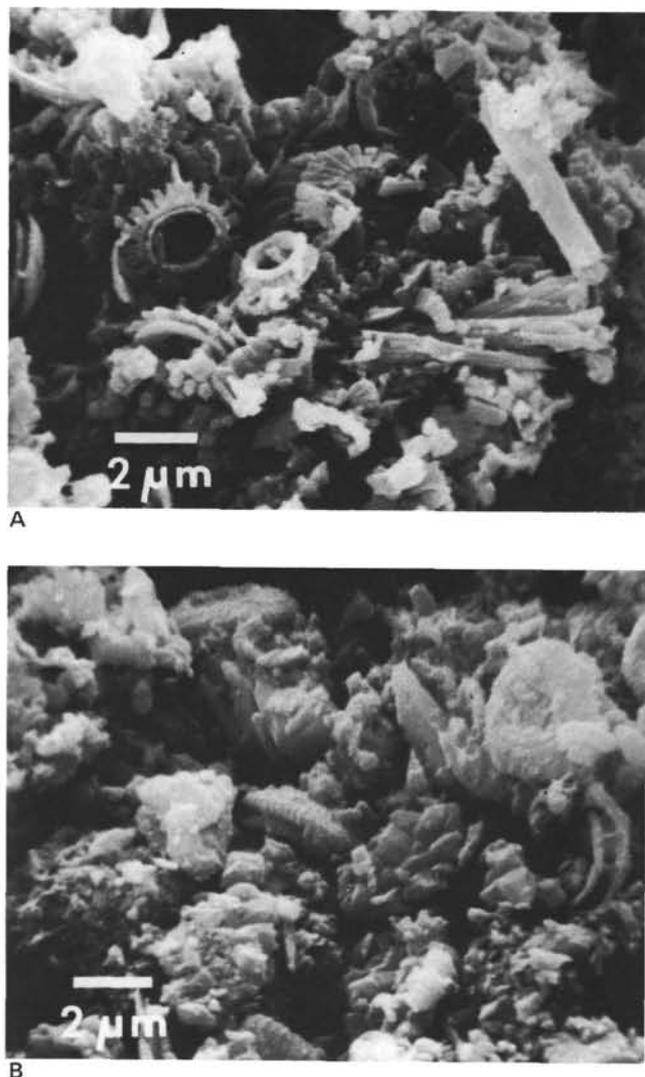


Figure 2. SEM photographs of calcareous ooze, Hole 600C. A. At 2.1 m depth. B. At 11.2 m depth. Note extensive overgrowth on coccoliths at 11.2 m, but not at 2.1 m.

istry of the calcareous fraction was analyzed in great detail. Submarine biogenic calcite recrystallization is manifested in changes in chemistry (including stable isotopes), and, often, mineralogy (e.g., Schlanger and Douglas, 1974; Baker et al., 1982; Killingley, 1983 and refs. therein).

Changes with increasing depth in percent CaCO_3 , Mg^{2+} and Sr^{2+} concentrations, and mole ratios of Mg/Ca , Sr/Ca , and Mg/Sr in the calcareous fractions are shown in Table 1 and Figure 3.

No chemical gradients are apparent in the uppermost 4 to 4.5 m of the sediment column. An abrupt change in the chemistry of the carbonate is observed at and below this depth, which coincides with color change at 600C-1-4 (~35 cm) (Fig. 1). Sr^{2+} concentrations decrease from 1350–1400 to about 1000 ppm, and Mg^{2+} concentrations increase from 570 to about 2000 ppm. Sample 600C-2-2, 4–6 cm at 10.25 m (Table 1 and Fig. 3) is unusual. It is a basaltic glass layer and contains only 37 wt.% CaCO_3 . Both Sr^{2+} and Mg^{2+} increase in the associated recrystallized carbonate.

The glass is highly palagonitized and altered to smectite. It is intimately associated with the recrystallized CaCO_3 , the chemistry of which has been affected by the glass alteration.

These chemical trends indicate extensive calcite recrystallization and/or dolomite formation (e.g., Baker et al., 1982; Katz et al., 1972). However, no dolomite was detected by X-ray diffraction or by SEM analyses.

Extensive CaCO_3 dissolution and recrystallization is strongly supported by SEM analysis (Fig. 2) and oxygen and carbon isotope analyses of the carbonates (summarized in Table 2). Both the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the bulk carbonate fraction and of the coccolith fraction increase significantly with increasing depth. The observed heavy oxygen and carbon isotope values cannot be explained by variations in paleotemperatures (e.g., Douglas and Savin, 1973, 1975; Savin and Yeh, 1981; Berger et al., 1981). Instead, recrystallization of planktonic foraminifers and coccoliths at lower temperatures than surface water temperatures is responsible for the increases observed in the $\delta^{18}\text{O}$ values of the carbonate fraction. The $\delta^{18}\text{O}$ value of calcite precipitated from seawater at 2°C and a water $\delta^{18}\text{O}$ of -1‰ (SMOW) is 1.90‰ (PDB), and that at 2°C and a water $\delta^{18}\text{O}$ of 0‰ is 2.88‰ (O'Neil et al., 1969). As for the carbon isotopes, the $\delta^{13}\text{C}$ of ΣCO_2 of surface waters is higher than that of deep and bottom waters (Kroopnick et al., 1972). In Pacific Deep Water, the average ΣCO_2 value is low (2300 $\mu\text{mol}/\text{kg}$). Therefore, in a seawater- CaCO_3 system in which extensive CaCO_3 is being dissolved and reprecipitated, the $\delta^{13}\text{C}$ of the total carbonate (ΣCO_2) will be controlled by the solid (the CaCO_3). The fractionation of carbon isotopes between solid CaCO_3 and dissolved HCO_3^- , at 20°C, is $1.85 \pm 0.23\text{‰}$ (Emrich et al., 1970), and the temperature effect, up to 60°C, is small ($0.035 \pm 0.013\text{‰}/^\circ\text{C}$). Accordingly, during recrystallization at low to moderate temperatures, the $\delta^{13}\text{C}$ value of the inorganically precipitated calcite will increase.

No trend in the oxygen isotopes of three interstitial water samples from 1.4, 5.5, and 7.0 m was observed (Samples 600C-1-1, 135–150 cm; 600C-1-4, 135–150 cm; and 600C-1-5, 135–150 cm). The mean $\delta^{18}\text{O}$ value is $-0.05 \pm 0.03\text{‰}$ (SMOW). Similar $\delta^{18}\text{O}$ values were obtained for four interstitial water samples at the nearby lower heat flow site (601). No bottom water samples are available. The $\delta^{18}\text{O}$ values of bottom water samples from a GEOSECS S-N transect in the eastern Pacific Ocean vary between 0.00 and -0.08‰ (SMOW) (Craig, pers. comm., 1984). Most values lie between -0.04 and -0.08‰ . Craig and Gordon (1965) have shown that the oxygen isotope values of Pacific deep waters are extremely uniform. Hence, the mean pore water $\delta^{18}\text{O}$ value of -0.05‰ (SMOW) at this site, as well as at Site 601, represents present-day Pacific deep waters. Thus, the extensive CaCO_3 recrystallization reactions observed in these sediments are not presently reflected in the oxygen isotope composition of the pore waters.

On the basis of paleoceanographic and the previously documented chemical, isotopic, and petrographic evidence, the extensive CaCO_3 recrystallization in the sediments of Hole 600C between 4–4.5 m and 11.8 m sub-

Table 1. Amount of the carbonate fraction (in wt.%) and Mg^{2+} and Sr^{2+} concentrations in the carbonate fraction, Hole 600C, Leg 92.

Core-Section (interval in cm)	Sub-bottom depth (m)	Carbonate (wt.%)		Insoluble residue ^b (wt.%)	Mg^{2+} in carbonate ^b (ppm)	Sr^{2+} in carbonate ^b (ppm)	Mg/Ca $\times 10^{-3}$	Sr/Ca $\times 10^{-3}$	Mg/Sr
		CO_2 coulometer ^a	Dissolution method						
1-1, 81-83	0.81-0.83	93.4	93	6.6	573	1431	2.39	1.65	1.44
1-2, 11-13	1.46-1.48	91.0	94	9.0	648	1353	2.66	1.54	1.73
1-2, 78-80	2.13-2.15	91.4	94	8.6	693	1344	2.87	1.54	1.86
1-3, 28-30	2.98-3.00	93.2	93	6.8	588	1444	2.48	1.69	1.47
1-3, 131-133	4.01-4.03	93.6	94	6.4	605	1383	2.48	1.57	1.58
1-4, 28-30	4.49-4.51	90.8	92	9.2	844	1179	3.50	1.34	2.58
1-4, 72-74	4.93-4.95	88.4	89	11.6	1012	1227	4.11	1.38	2.97
1-4, 118-120	5.39-5.41	85.7		14.3	847	1448	3.51	1.66	2.11
1-5, 32-34	5.89-5.91	84.0	83	16.0	929	1245	3.82	1.42	2.69
1-5, 72-74	6.29-6.31	81.9	82	18.1	1059	1267	4.31	1.43	3.01
1-5, 112-114	6.69-6.71	64.9	64	35.1	1426	1279	6.12	1.52	4.02
1-6, 28-30	7.20-7.22	68.5	71	31.6	1318	1250	5.52	1.45	3.80
1-6, 128-130	8.20-8.22	74.9	78	25.1	1171	1143	4.77	1.29	3.69
1-7, 8-10	8.50-8.52	78.7	81	21.4	1117	1086	4.72	1.27	3.71
1, CC, 14-16	8.76-8.78	77.4	81	22.6	1123	1143	4.59	1.30	3.54
2-1, 38-40	9.27-9.29	78.4	80	27.0	1655	1010	6.93	1.18	5.94
2-1, 81-83	9.70-9.72	74.8	73	25.2	2063	1078	8.82	1.28	6.90
2-2, 4-6	10.23-10.25	37.2		62.8	2071	1266	11.85	2.01	5.90
2-2, 74-76	10.93-10.95	71.5	77		1792	1086	7.55	1.27	5.95
2-2, 101-103	11.20-11.22	74.8	78	25.2	1819	1074	7.31	1.20	6.10

Note: Mg/Ca , Sr/Ca , and Mg/Sr are mole ratios.

^a Accuracy is $\pm 3\%$ of the values shown.

^b Calculated from CO_2 coulometer wt.% carbonate.

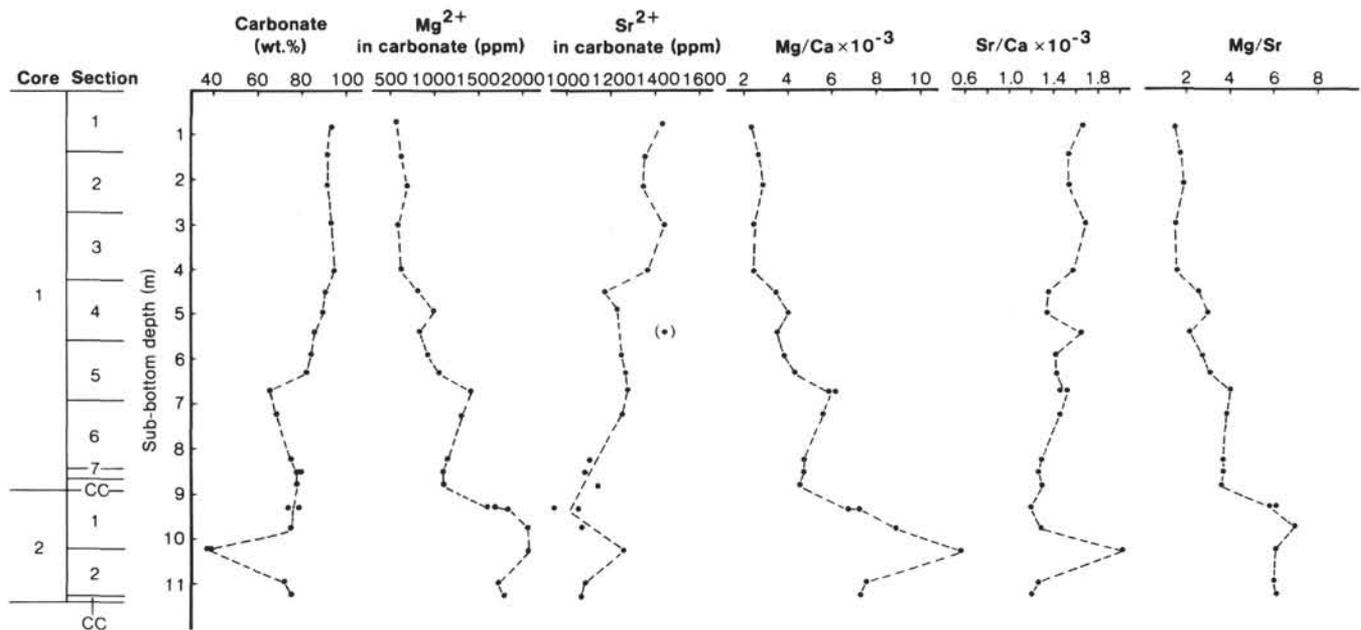


Figure 3. $CaCO_3$ (wt.%); Mg^{2+} and Sr^{2+} concentrations (ppm); and Mg/Ca , Sr/Ca , and Mg/Sr (mole ratios) in carbonate fraction of the sediments, Hole 600C.

bottom depth, but not in the uppermost 4 to 4.5 m, suggests that during the period when this recrystallization did occur, extensive convective fluid flow must have occurred through only the bottom 7.5 m of the sediment column. This convective fluid flow seems to have ceased rather abruptly in the late Pliocene. According to Knützel (this volume), the sediments are approximately 3 to 3.5 Ma at this depth. The crustal age at this site is 4.6 Ma (Rea, this volume). Hence, the convective fluid flow through the sediments continued for 1 to 1.5 m.y.

Therefore, it is not surprising that the interstitial water profiles do not show significant chemical and isotope gradients. For an oxygen diffusion coefficient (D) of $3 \times 10^{-6} \text{ cm}^2/\text{s}$ and sedimentation rates of 7 to 14 m/m.y., the communication depth after 1 m.y. is 134 m; for $D = 6 \times 10^{-6} \text{ cm}^2/\text{s}$, the communication depth is 189 m; and for $D = 9 \times 10^{-6} \text{ cm}^2/\text{s}$ it is 232 m. Diffusive processes since then have eradicated any changes in interstitial water composition, thus leaving a composition similar to present-day bottom water.

Table 2. Oxygen and carbon isotopes of carbonates (‰ PDB), Hole 600C.

Core-Section (interval in cm)	Sub-bottom depth (m)	Bulk carbonate		38–0.45 μm carbonate fraction	
		$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
1-2, 11–13	1.46–1.48	0.19	0.53		
1-2, 78–80	2.13–2.15	0.31	0.54	0.41	0.38
1-7, 8–10	8.50–8.52	1.74	1.29	1.98	0.99
2-1, 38–40	9.27–9.29	2.26	1.69		
2-2, 74–76	10.93–10.95	1.96	1.58		
202, 101–103	11.20–11.22	2.12	1.60	2.41	1.55

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