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10. Data Report: Dissolved Carbohydrates in Interstitial Waters from the Equatorial Pacific and Peru Margin, ODP Leg 201[1]

David J. Burdige[2]

ABSTRACT

Total dissolved carbohydrates (DCHOs) were determined in interstitial waters collected at open-ocean and Peru margin sites cored during Ocean Drilling Program Leg 201. Concentrations of DCHOs ranged from 0 to ~1500 µM and showed no consistent trends between open-ocean and Peru margin sites either in the magnitude or direction of downhole interstitial water gradients. In contrast, relative DCHO concentrations (normalized to dissolved organic carbon concentrations) were higher in open-ocean vs. margin sediments. These trends are consistent with results from more shallow estuarine and nearshore continental margin sediments and may be related to changes in the overall controls on sediment organic matter remineralization with decreasing remineralization rates.

INTRODUCTION

Total dissolved carbohydrates (DCHOs) in the interstitial waters of marine sediments have been determined in a limited number of coastal and continental margin sediments, with concentrations that generally range from ~10 to 400 µM C (see Burdige, 2002, for a review). In most cases DCHO concentrations increase with depth in shallow sediments (uppermost ~20–30 cm) and represent ~10%–40% of the total dissolved organic carbon (DOC). Relative DCHO concentrations also generally

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[2] Department of Ocean, Earth, and Atmospheric Sciences, Old Dominion University, 4600 Elkhorn, Norfolk VA 23529, USA. **dburdige@odu.edu**

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decrease with sediment depth, although the magnitude of these changes varies among the few sites that have been examined to date (see discussions in Burdige et al., 2000, for further details).

Concentrations of dissolved carbohydrates in sediment pore waters are apparently uncoupled from particulate (sediment) carbohydrate concentrations, and DCHO concentrations appear to be more strongly controlled by sediment remineralization processes (Burdige et al., 2000). Evidence to date also suggests that DCHOs may be preferentially found in the high molecular weight (HMW) interstitial water DOC pool, and therefore they likely represent some of the initial HMW intermediates produced and consumed during sediment organic matter remineralization (Arnosti and Holmer, 1999; Burdige et al., 2000).

During Leg 201, samples were collected for analysis of dissolved carbohydrates in the interstitial waters of these sediments. In one sense, studies of DCHOs in these sediments builds on past studies of dissolved carbohydrates in the pore waters of shallow-marine and estuarine sediments (e.g., Burdige et al., 2000). However, more importantly from the standpoint of the goals of Leg 201, this work will further the understanding of biogeochemical processes occurring in the deep marine biosphere.

METHODS AND MATERIALS

Total dissolved carbohydrates were analyzed in interstitial water samples collected from 30-cm-long whole-round sediment core sections. Interstitial waters were extracted aboard ship within hours of core retrieval. The outer edge of each sediment core section was first removed and the remaining sediment was then placed in a titanium sediment squeezer for interstitial water extraction. Extracted interstitial waters were filtered through a 0.45-µm filter (polysulfone) into acid-washed syringes. Aliquots for DCHO analyses were transferred to muffled (550°C) glass vials that were sealed with polytetrafluoroethylene (PTFE)-lined septa. Samples were stored at 4°C and transported to Old Dominion University (ODU) (Norfolk VA, USA) for shore-based analysis.

Total dissolved carbohydrates were determined spectrophotometrically using a modification of the 3-methyly-2-benzothiazolinone hydrazone hydrochloride (MBTH) procedure described by Pakulski and Benner (1992). In this technique, all dissolved carbohydrates in a water sample are first hydrolyzed to individual monosaccharides and then oxidized to alditols. The terminal glycol groups of the alditols are next oxidized to formaldehyde, which is finally determined spectrophotometrically with MBTH. Additional details about the analytical procedures used here can be found in Burdige et al. (2000).

All carbohydrate concentrations reported here were based on standard curves constructed from glucose standards that are hydrolyzed and analyzed along with samples, yielding total carbohydrate concentrations that are "glucose equivalent" concentrations. Glucose equivalent concentrations were multiplied by 6 to express concentrations on a per mole-carbon basis, since each glucose molecule contains 6 carbon atoms (see Pakulski and Benner, 1992, for additional details).

RESULTS AND CONCLUSIONS

Concentrations of DCHOs ranged from 0 to ~1500 µM C in the interstitial waters at the seven sites studied (Table T1). Depth profiles showed no consistent trends (Figs. F1, F2). At some sites (1226, 1227, 1228, and, perhaps, 1231), DCHO concentrations decrease with depth, whereas at Site 1225 DCHO concentrations increase with depth. At the remaining sites (1229 and 1230) DCHO concentrations show minimal downhole gradients. Of equal importance, both the magnitude and direction of these downhole gradients showed no consistent trends between open-ocean (Sites 1225, 1226, and 1231) and Peru margin sites (1227, 1228, 1229 and 1230) (Figs. F1, F2).

Relative DCHO concentrations (i.e., as a fraction of the total DOC concentration in the interstitial waters) did, however, appear to vary consistently among the different sites (Fig. F3; DOC data from Smith, this volume). Although there is scatter in the data, at the open-ocean sites relative DCHO concentrations were ~0.8, suggesting that the DOC in these sediment interstitial waters is extremely carbohydrate rich. In contrast, relative DCHO concentrations were lower at the Peru margin sites (~0.3 at Sites 1227, 1228, and 1229 and ~0.1 at Site 1230). When compared with maximum interstitial water dissolved inorganic carbon (DIC) concentration at these sites (data from D'Hondt, Jørgensen, Miller, et al., 2003), relative DCHO concentrations decreased with increasing values of DIC_{max} (Fig. F4).

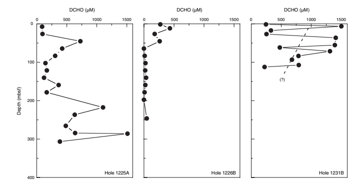
If we assume that values of DIC_{max} can be used as a first-order proxy for rates of sediment organic matter remineralization, the results in Figure F4 suggest that dissolved carbohydrates become an increasingly less important component of the interstitial water DOC pool as remineralization rates decrease. This trend is consistent with results from shallower estuarine and continental margin sediments (Burdige et al., 2000). In this study, these observations were interpreted as being related to changes in the overall controls on sediment organic matter remineralization, based on the assumption that dissolved carbohydrates are preferentially found in the pool of reactive HMW-DOC intermediates produced and consumed during sediment organic matter remineralization.

This explanation assumes that as rates of sediment organic matter remineralization decrease, that oxidative or hydrolytic processes affecting the initial HMW-DOC intermediates of sediment organic matter remineralization exert increasingly more control on remineralization. This, therefore, allows HMW-DOC intermediates to increase in the pore waters to a greater extent (also see related discussions in Burdige and Gardner, 1998). Conversely, as remineralization rates increase, fermentative or perhaps terminal respiratory processes exert increasingly more control on sediment organic matter remineralization (e.g., see Brüchert and Arnosti, 2003, and references therein).

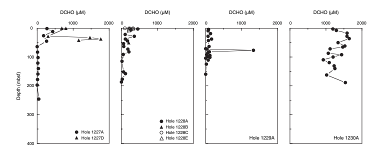
At the same time though, most DOC in sediment interstitial waters appears to be refractory low molecular weight material (Burdige and Gardner, 1998). Therefore, the high relative DCHO concentrations observed at the open-ocean sites could also suggest that some (or all) of these dissolved carbohydrates are refractory to microbial degradation, yet are still chemically recognized by the assay used here. Additional studies will be needed to more critically examine all of these suggestions.

T1. DCHO concentrations, p. 10.

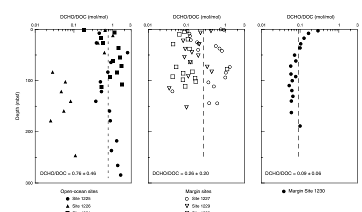
F1. DCHOs, open-ocean sites, p. 6.



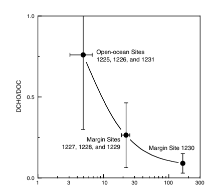
F2. DCHOs, Peru margin sites, p. 7.



F3. Relative DCHO concentrations, p. 8.



F4. Relative DCHO vs. DIC_{max}, p. 9.



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Pakulski, J.D., and Benner, R., 1992. An improved method for the hydrolysis and MBTH analysis of dissolved and particulate carbohydrates in seawater. *Mar. Chem.,* 40:143–160. **doi:10.1016/0304-4203(92)90020-B**

Figure F1. Downhole profiles of total dissolved carbohydrates (DCHOs) at the three open-ocean sites cored during Leg 201.

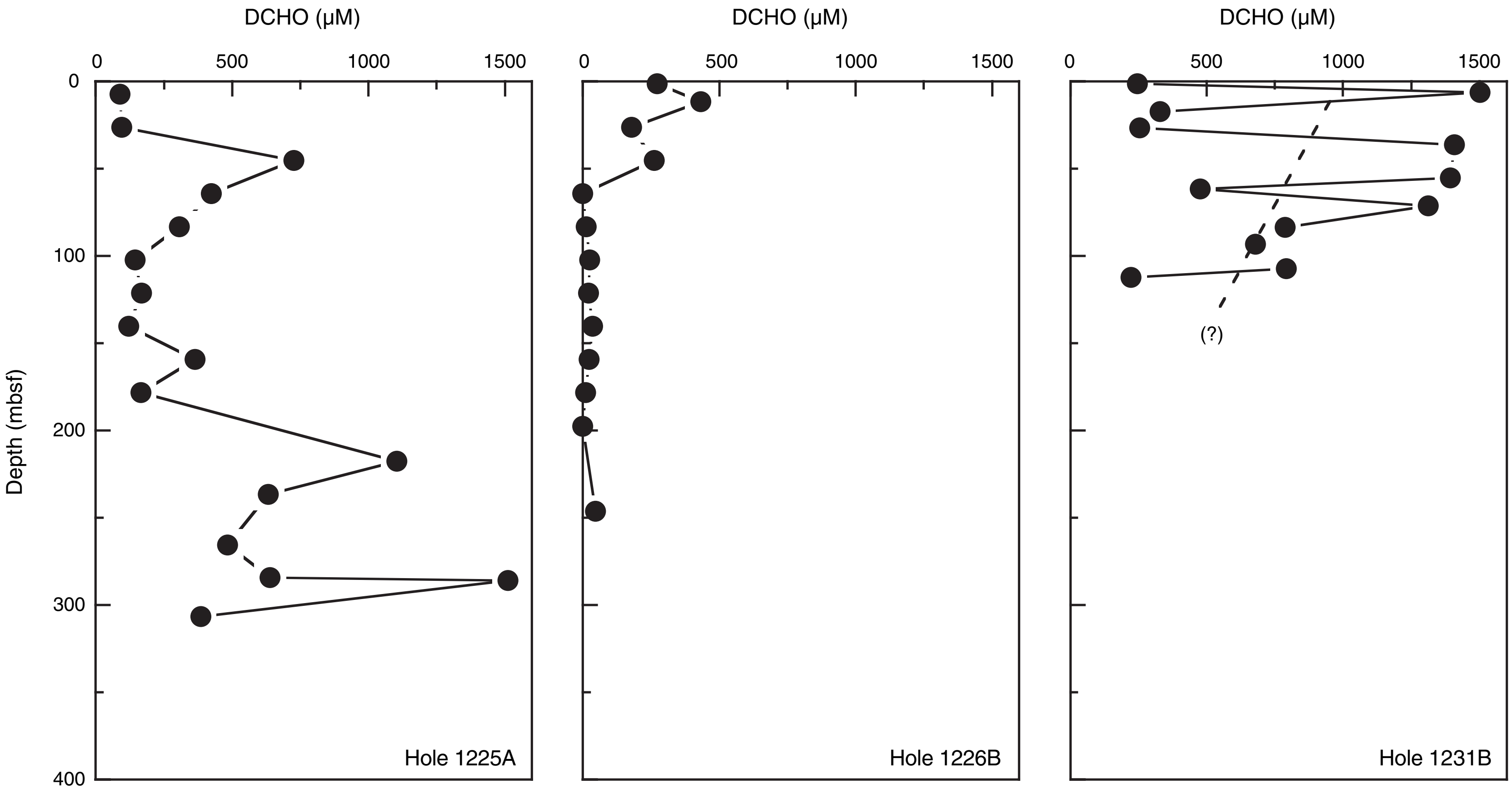

Figure F2. Downhole profiles of total dissolved carbohydrates (DCHOs) at the four Peru margin sites cored during Leg 201.

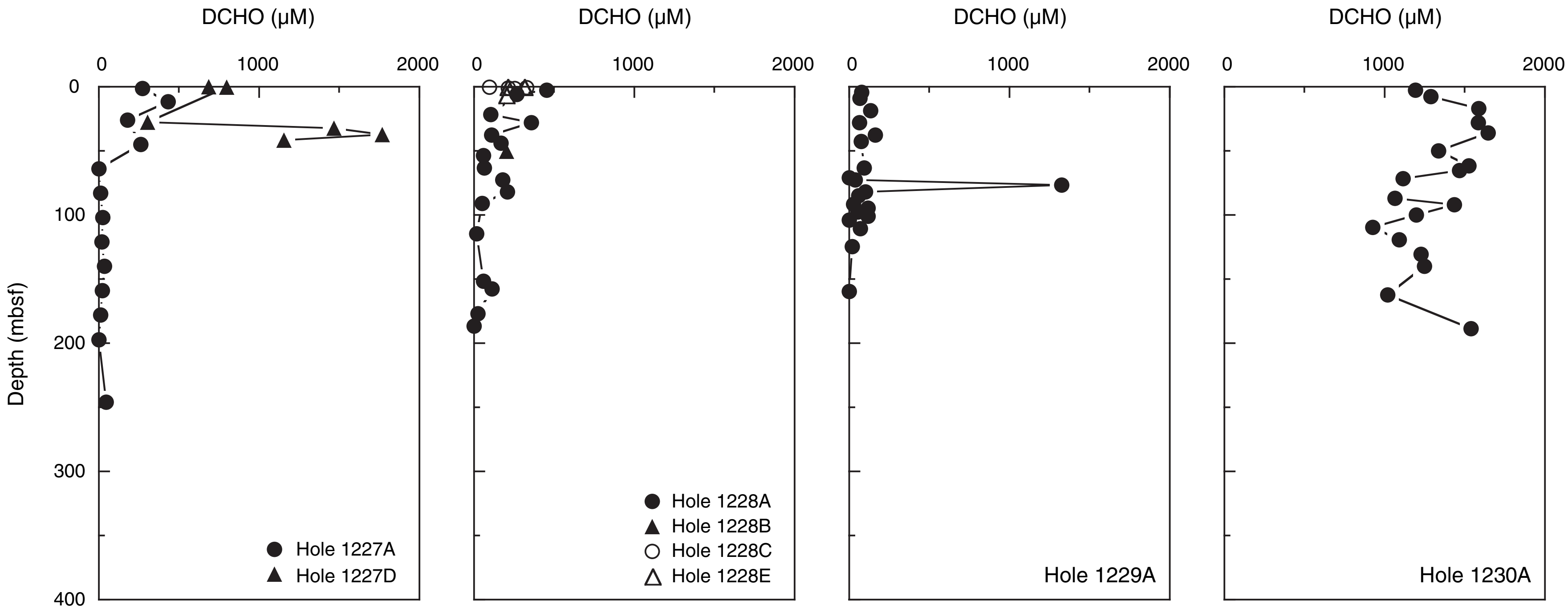

Figure F3. Downhole profiles of relative total dissolved carbohydrates (DCHO) concentrations (DCHO/dissolved organic carbon [DOC]) for all sites sampled during Leg 201. Note the apparent differences in relative DCHO concentrations at the open-ocean sites; Peru margin Sites 1227, 1228 and 1229; and Peru margin Site 1230. At Site 1226, DCHO and DOC data were not available for the same hole (DCHO data for Hole 1226B and DOC data for Hole 1226E). However, because the DOC data in Hole 1226E showed virtually no depth gradient (**Smith,** this volume), the DCHO data from Hole 1226B were normalized to an average DOC concentration for Hole 1226E. Also note that in a few instances values of DCHO/DOC were >1. Since DCHOs are a subset of the total DOC pool, this is physically impossible. At the present time, it is unclear as to whether these DCHO values are too high or the DOC values are too low.

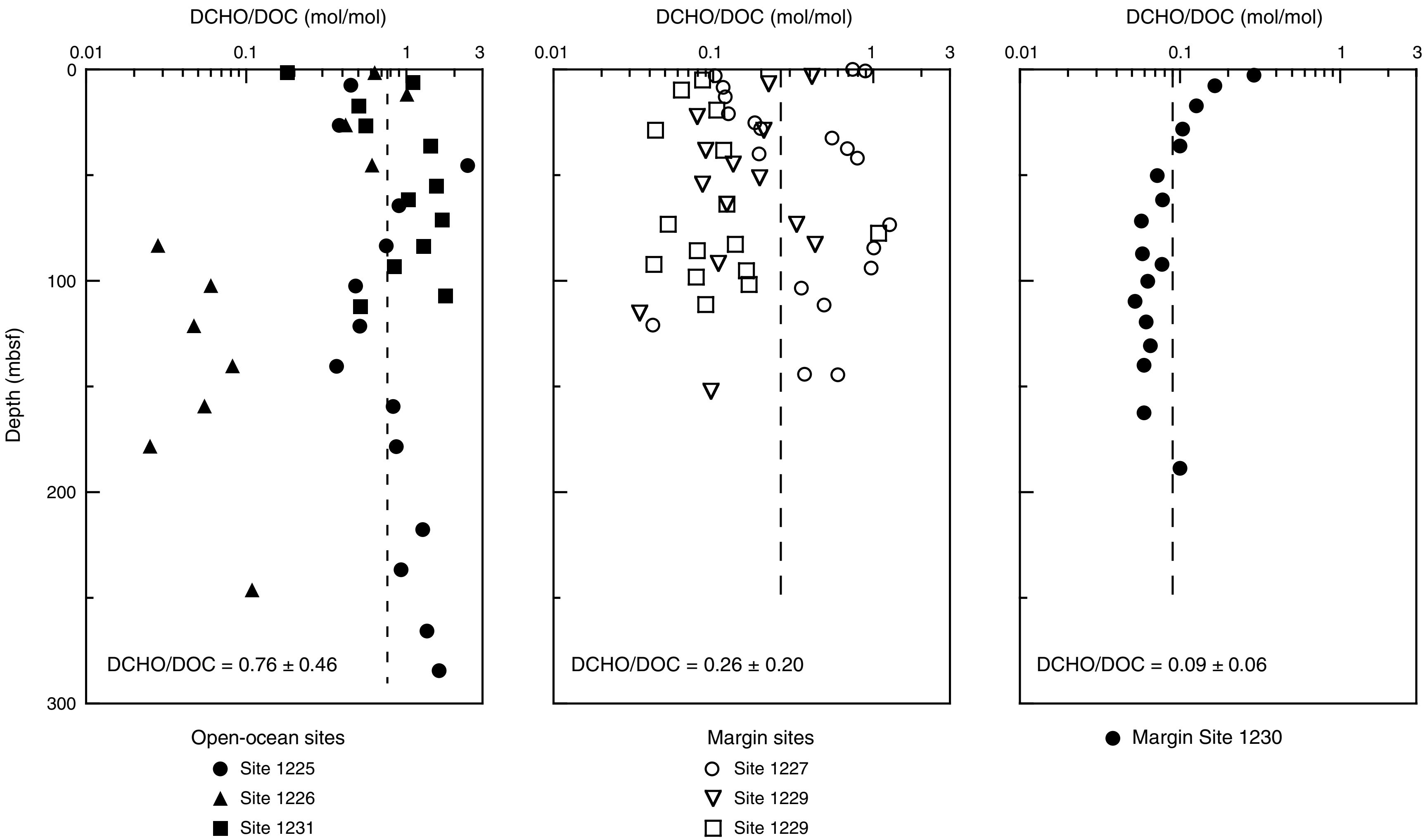

Figure F4. Relative total dissolved carbohydrates (DCHO) concentrations (DCHO/dissolved organic carbon [DOC]) vs. maximum concentrations of interstitial water dissolved inorganic carbon (DIC_{max}) at the open-ocean and Peru margin sites. Note the strong inverse relationship.

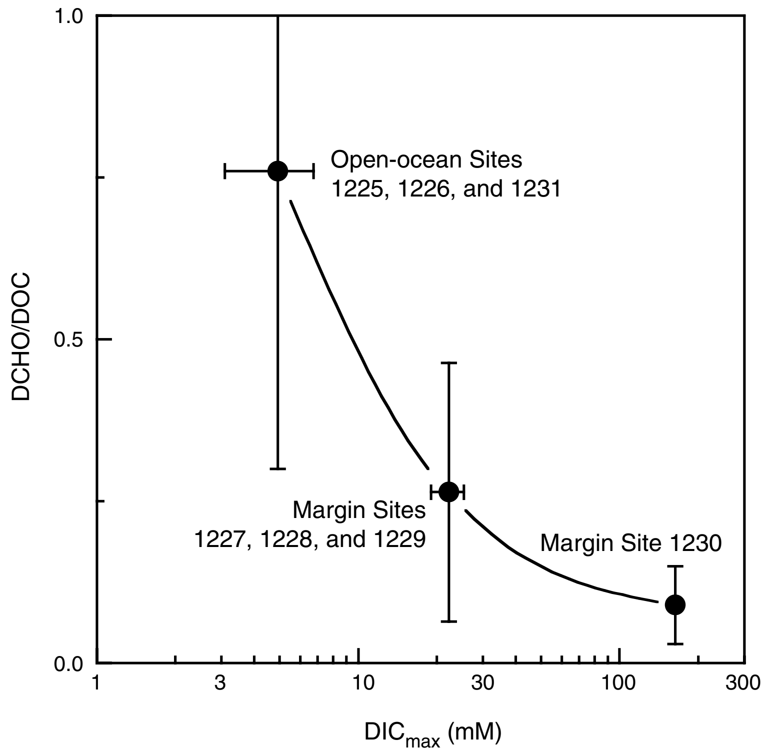

Table T1. Concentrations of total dissolved carbohydrates in interstitial waters.

Hole	Depth (mbsf)	DCHO (μM)
1225A	7.3	89.9
	26.3	95.6
	45.3	726.6
	64.3	424.2
	83.3	307.8
	102.3	145.1
	121.3	168.9
	140.3	120.9
	159.3	363.7
	178.3	165.2
	217.8	1104.3
	236.8	633.2
	265.59	484.2
	284.42	639.6
	286.07	1511.7
	306.7	385.1
1226B	1.3	271.7
	11.67	431.8
	26.2	178.9
	45.2	262.2
	64.2	0
	83.2	12.1
	102.2	25.9
	121.2	20.2
	140.2	35.2
	159.2	23.6
	178.2	10.7
	197.5	0
	246.2	46.7
1227A	2.85	108.7
	8.45	104.9
	12.95	122.2
	20.95	149.8
	25.26	205.9
	39.95	235.3
	73.45	1414.6
	84.45	875
	93.95	813
	103.45	274
	111.45	341.5
	120.95	29
	144.3	435.1
	144.45	438.3
1227D	0	685.3
	0.6	797
	27.85	305.9
	32.35	1468.5
	37.35	1767.8
	41.85	1154.6
1228A	2.76	453.5
	6.25	267.3
	21.75	106.4
	28.25	358.1
	37.75	109
	44.25	167.5
	53.75	58.4
	63.25	64.8
	72.75	180.1
	82.25	208.4
	91.25	51
	114.75	16.1
	151.75	59.9
	157.69	113.8
	177.25	25.6
	186.75	0
1228B	50.6	203.61
1228C	0.45	96.93
	0.75	328
	1.2	214.29
	1.35	253.12
1228E	0	209.98
	0.12	313.93
	6.35	200.96
1229A	4.31	76.9
	9.25	66
	18.75	133.3
	28.25	64.7
	37.75	162.3
	42.9	74.3
	63.25	93.5
	71.25	0
	72.75	36.7
	76.85	1325
	82.25	103
	85.25	60.5
	91.75	26
	94.75	117.6
	97.75	54
	101.25	117.5
1230A	2.85	1191.2
	7.65	1287.4
	17.15	1587
	28.15	1583.3
	36.15	1645
	50.23	1337.3
	61.65	1525.9
	65.35	1466.4
	71.65	1116
	87.15	1064.8
	92.15	1436.2
	100.15	1198.1
	109.65	927.1
	119.47	1089.9
	130.65	1228.3
	140.1	1249.3
1231B	1.35	247.3
	6.25	1502.7
	17.25	329
	26.75	255.8
	36.25	1409.3
	55.25	1394.8
	61.75	476.2
	71.25	1312.7
	83.75	787.4
	93.25	679.2
	107.25	792.5
	112.25	223

Note: DCHO = total dissolved carbohydrate.