Mosher, D.C., Erbacher, J., and Malone, M.J. (Eds.)
Proceedings of the Ocean Drilling Program, Scientific Results Volume 207

7. DATA REPORT: STABLE ISOTOPIC RATIOS IN BULK CARBONATE FROM UPPER CAMPANIAN AND MAASTRICHTIAN SAMPLES (DEMERARA RISE, WESTERN TROPICAL NORTH ATLANTIC)[1]

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ABSTRACT

Stable isotopic values of 174 upper Campanian and Maastrichtian bulk carbonate samples from Demerara Rise, in the western tropical Atlantic (Ocean Drilling Program Leg 207, Sites 1257–1261), largely fall between 0‰ and 2‰ for $\delta^{13}C$ and between –2‰ and –3‰ for $\delta^{18}O$. The relatively low values and high scatter of $\delta^{13}C$ values observed suggest secondary calcite with a remineralized organic carbon component was present in most to all samples analyzed. Oxygen isotopic data exhibit less scatter and values closer to those expected for contemporary sea-surface conditions than do carbon data. However, trends in $\delta^{18}O$ data at any one section do not correlate among sites using shipboard age estimates. Regardless of whether subsequent age estimates modify correlation among holes, diagenetic concerns will remain a significant complication in any efforts to study isotopic trends during the late Campanian–Maastrichtian at these sites.

INTRODUCTION

Demerara Rise occupied a key paleogeographic position for examining paleoceanographic evolution during the late Campanian–Maastrichtian, a 5- to 10-m.y. interval of climate moderation at the end of

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[1] MacLeod, K.G., 2006. Data report: stable isotopic ratios in bulk carbonate from upper Campanian and Maastrichtian samples (Demerara Rise, western tropical North Atlantic). *In* Mosher, D.C., Erbacher, J., and Malone, M.J. (Eds.), *Proc. ODP, Sci. Results,* 207: College Station, TX (Ocean Drilling Program), 1–9. doi:10.2973/odp.proc.sr.207.110.2006

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Initial receipt: 21 October 2005
Acceptance: 5 February 2006
Web publication: 28 November 2006
Ms 207SR-110

~40 m.y. of Cretaceous greenhouse climate. Demerara Rise was located at tropical latitudes, and neither Maastrichtian tropical temperatures nor tropical temperature trends are well constrained (e.g., D'Hondt and Arthur, 1996; MacLeod and Huber, 2001; Pearson et al., 2001). Demerara Rise is also in the North Atlantic, which appears to have experienced regional warming (Wolfe and Upchurch, 1987; Corfield and Norris, 1996; Barrera and Savin, 1999; Frank and Arthur, 1999; MacLeod et al., 2005) at the same time as widespread and well-documented cooling at mid- to high latitudes (e.g., Douglas and Savin, 1975; Barrera et al., 1987; Spicer and Parrish, 1990; Huber and Watkins, 1992; Huber et al., 1995; Barrera and Savin, 1999; Francis and Poole, 2002; Lees, 2002). Finally, Demerara Rise is near the tropical Atlantic gateway, and changes in patterns of ocean circulation, including the nature of flow between the North and South Atlantic, have been invoked to explain Maastrichtian climate evolution (e.g., Barrera and Savin, 1999; Frank and Arthur, 1999; MacLeod and Huber, 2001; D'Hondt and Arthur, 2002; Frank et al., 2005; MacLeod et al., 2005).

The upper Campanian–Maastrichtian was recovered in multiple holes in each of the five sites drilled on Demerara Rise during Ocean Drilling Program (ODP) Leg 207. Unfortunately, foraminiferal preservation was variable throughout the interval. Test morphology is generally well preserved with hollow foraminifers found throughout, but sparry calcite is common within otherwise well-preserved specimens. In addition, well-formed, sand-sized "cockscomb" marcasite is present in many washes. That is, at least two diagenetic phases are common in these samples, and quality of isotopic preservation is a significant concern for any paleoceanographic study of samples from these cores. To provide initial constraints on the relative importance of primary paleoceanographic conditions and diagenetic overprinting in the Demerara record, bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ values were measured from upper Campanian and Maastrichtian samples. Values observed are not prohibitively unreasonable; however, scatter within trends in any section and lack of congruence in trends among correlative samples across sites argue that diagenetic overprinting will complicate any Campanian–Maastrichtian stable isotopic studies of Demerara Rise samples.

METHODS

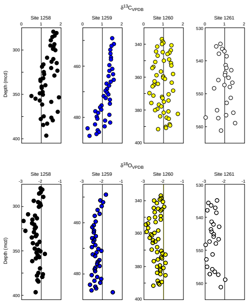
Bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ values were measured on total of 174 upper Campanian and Maastrichtian samples distributed among the five sites drilled during ODP Leg 207. Ages were estimated using shipboard foraminiferal and nannofossil datums (Erbacher, Mosher, Malone, et al., 2004). From each sample, ~75 µg of material was scraped from a clean, dried (<50°C) surface. This powder was loaded into a single reaction vessel and analyzed on a Kiel III carbonate device in line with a Finnegan Delta Plus isotope ratio mass spectrometer at the University of Missouri Biogeochemistry Isotope Laboratory. Results are reported in standard delta notation relative to the Vienna Peedee belemnite standard and were normalized to a nominal value of $\delta^{13}C$ = 1.95‰ and $\delta^{18}O$ = –2.20‰ for the National Bureau of Standards NBS-19 standard based on the average of multiple replicates of this standard run with the samples. Long-term precision for this standard (uncorrected) is <0.03‰ and <0.06‰ (1σ) for $\delta^{13}C$ and $\delta^{18}O$, respectively.

RESULTS

Values for $\delta^{13}C$ and $\delta^{18}O$ range between 0‰ and 2‰ (average = 1.1‰ ± 0.4‰, 1σ) for carbon and largely between –2‰ and –3‰ (average = –2.3‰ ± 0.3‰, 1σ) for oxygen (Table T1). For Sites 1258, 1259, 1260, and 1261, where stratigraphic coverage was good for some or all of the upper Campanian–Maastrichtian interval, $\delta^{13}C$ values show no apparent temporal trends with the exception of Site 1259 where $\delta^{13}C$ values <1‰ were only measured in lowest 15 m of section (Fig. F1). Site 1259 also exhibited the least amount of scatter in $\delta^{13}C$ values, whereas at the other three sites adjacent samples commonly differ by >1‰. The average $\delta^{13}C$ value is less than those values seen in correlative samples from Blake Nose (e.g., MacLeod et al., 2005), suggesting secondary calcite with a contribution from remineralized organic carbon was present in most, if not all, samples.

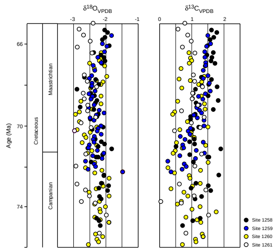
T1. Stable isotopic values of bulk samples, p. 8.

F1. Isotopic values vs. depth for bulk carbonate, p. 6.



Variation in $\delta^{18}O$ values among adjacent samples within each section is generally <0.5‰, and paleotemperatures calculated assuming an ice-free Earth are ~25°C (Erez and Luz, 1983; $\delta_w = -1‰$). This value is lower than expected for contemporary tropical sea-surface temperatures (e.g., Pearson et al., 2001), which is consistent with formation of secondary carbonate at the relatively shallow burial depths inferred for these samples. Assuming bottom water temperatures of ~10°C and an average geothermal temperature gradient, burial depths were shallow enough that diagenetic temperatures should not have exceeded surface water temperatures and alteration would have shifted values to cooler temperatures. At Sites 1258, 1259, and 1260, $\delta^{18}O$ values seem to decrease slightly in the middle portions of the record before increasing slightly toward the end of the Maastrichtian. The magnitude of any excursion, though, is small relative to between sample variation and apparent average diagenetic offsets. Further, when data from all four sections are projected onto a single age axis, the position of the minima do not correspond (Fig. F2).

F2. Isotopic data projected onto a common age axis, p. 7.



ACKNOWLEDGMENTS

Samples analyzed were provided by the Ocean Drilling Program (ODP). ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc. Funding was provided by the U.S. Science Support Program. Oliver Friedrich and Stuart Robinson are thanked for their helpful comments.

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Figure F1. Plots of isotopic values vs. depth for bulk carbonate from upper Campanian–Maastrichtian samples of Sites 1258,1259, 1260, and 1261. Carbon and oxygen data are plotted at the same scale in all plots. Note similar values are observed at all sites (including the few analyses for Site 1257; see Table T1, p. 8). Relatively low values and high scatter in $\delta^{13}C$ data may indicate a significant contribution from remineralized organic matter in secondary calcite in most samples. Relative lack of scatter in $\delta^{18}O$ values may result from diagenetic temperatures that did not differ too greatly from primary values. There is also a minimum in $\delta^{18}O$ values the upper half sections from Sites 1258, 1259, and 1260. VPDB = Vienna Peedee belemnite.

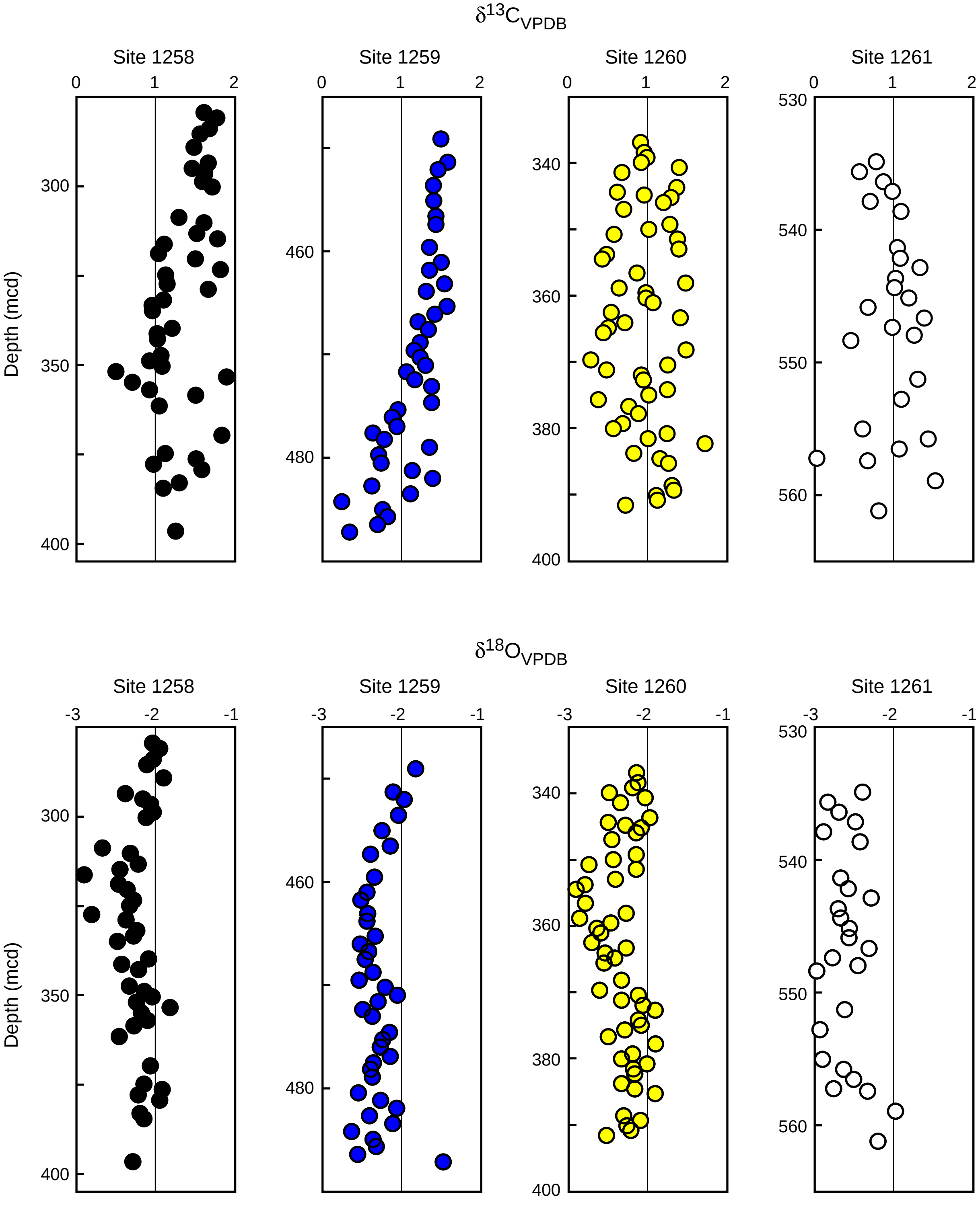

Figure F2. Isotopic data from Figure F1, p. 6, projected onto a common age axis. Age estimates are based on shipboard data (Erbacher, Mosher, and Malone, et al., 2004). Similarity in average δ^{13}C and δ^{18}O values among holes and difference in scatter between data carbon and oxygen data is again apparent. However, minima in the δ^{18}O curves at Sites 1258, 1259, and 1260 do not correlate using these age models suggesting either the trends do not reflect regional paleoceanographic variation or the age models lack precision. VPDB = Vienna Peedee belemnite.

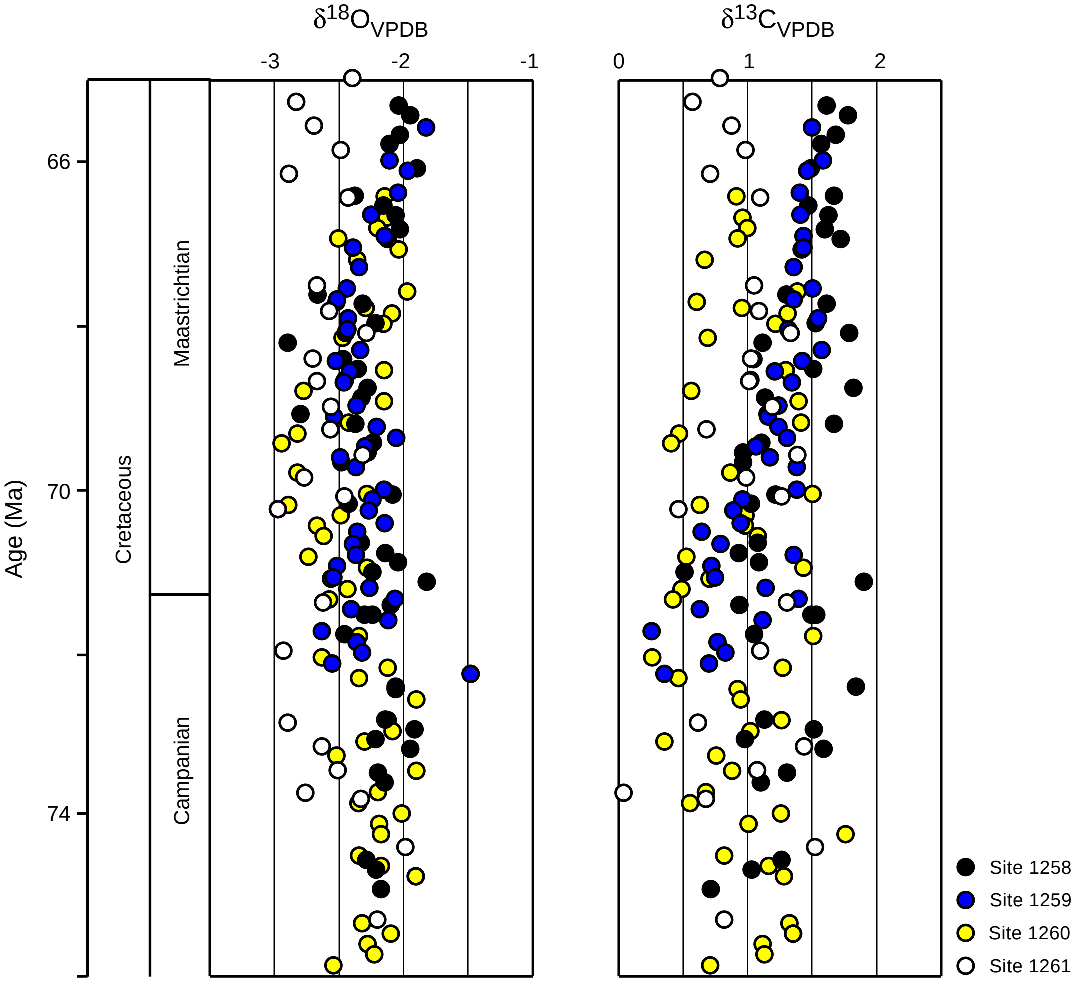

Table T1. Stable isotopic values of bulk samples from Holes 1257A, 1258A, 1259A, 1260A, 1261A, and 1261B. (See table notes. Continued on next page.)

Core, section, interval	Depth		$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB}$ (‰)
	(mbsf)	(mcd)		
207-1257A-				
17X-3, 8–8	143.74	149.21	1.47	–1.98
17X-3, 17–17	143.83	149.30	1.18	–1.70
17X-3, 30–30	143.96	149.43	1.10	–1.44
17X-3, 45–45	144.11	149.58	1.31	–1.86
17X-3, 60–60	144.26	149.73	1.18	–1.66
17X-3, 69–69	144.35	149.82	0.97	–1.35
17X-3, 86–86	144.52	149.99	1.43	–1.71
17X-3, 102–102	144.68	150.15	1.26	–1.46
18X-1, 45–50	150.75	156.55	1.20	–1.61
207-1258A-				
28R-2, 69–70	257.09	279.54	1.61	–2.03
28R-3, 70–71	258.60	281.05	1.77	–1.94
28R-5, 70–71	261.60	284.05	1.68	–2.02
28R-6, 70–71	263.10	285.55	1.56	–2.11
29R-2, 70–71	266.80	289.25	1.49	–1.89
29R-5, 70–71	271.12	293.57	1.66	–2.38
29R-6, 70–71	272.62	295.07	1.46	–2.15
29R-7, 70–71	274.12	296.57	1.62	–2.06
30R-2, 70–71	276.40	298.77	1.60	–2.02
30R-3, 70–71	277.90	300.27	1.72	–2.12
31R-2, 70–71	286.10	308.84	1.29	–2.67
31R-3, 70–71	287.60	310.34	1.61	–2.32
31R-5, 70–71	290.60	313.34	1.52	–2.22
31R-6, 70–71	292.10	314.84	1.78	–2.45
31R-7, 70–71	293.60	316.34	1.11	–2.90
32R-2, 70–70.5	295.70	318.91	1.04	–2.46
32R-3, 70–70.5	297.20	320.41	1.50	–2.35
32R-5, 69–69.5	300.19	323.40	1.82	–2.27
32R-6, 69–69.5	301.69	324.90	1.13	–2.32
33R-2, 70–71	305.30	327.41	1.15	–2.80
33R-3, 70–71	306.80	328.91	1.67	–2.37
33R-5, 70–71	309.80	331.91	1.10	–2.23
33R-6, 70–71	311.30	333.41	0.96	–2.27
33R-7, 70–71	312.80	334.91	0.96	–2.48
34R-2, 70–71	315.00	339.89	1.21	–2.08
34R-3, 70–71	316.50	341.39	1.02	–2.42
40R-3, 70–71	318.00	342.89	1.02	–2.21
35R-2, 67–70	324.57	347.44	1.07	–2.33
35R-3, 70–71	326.10	348.97	0.93	–2.14
35R-4, 69–71	327.59	350.46	1.08	–2.04
35R-5, 71–72	329.11	351.98	0.50	–2.24
35R-6, 70–71	330.60	353.47	1.90	–1.81
40R-5, 70–71	332.11	354.98	0.71	–2.17
36R-2, 70–71	334.20	357.07	0.93	–2.10
36R-3, 70–71	335.70	358.57	1.51	–2.27
36R-5, 70–71	338.70	361.57	1.05	–2.46
37R-4, 69–70	346.89	369.76	1.84	–2.06
38R-1, 70–70	352.00	374.87	1.12	–2.14
38R-2, 70–70	353.50	376.37	1.51	–1.91
38R-3, 70–70	355.00	377.87	0.97	–2.21
38R-4, 70–70	356.50	379.37	1.58	–1.95
39R-2, 70–70	362.33	383.07	1.30	–2.19
39R-3, 70–70	363.83	384.57	1.10	–2.14
40R-2, 70–71	372.70	396.63	1.25	–2.28
207-1259A-				
48R-1, 27–28	449.07	449.08	1.49	–1.82
48R-2, 104–105	451.34	451.35	1.58	–2.10
48R-3, 27–28	452.07	452.08	1.46	–1.96
48R-4, 27–28	453.57	453.58	1.40	–2.04
48R-5, 27–28	455.07	455.08	1.40	–2.25
48R-6, 27–28	456.57	456.58	1.43	–2.14
48R-6, 104–105	457.34	457.35	1.43	–2.39
49R-1, 31–32	458.71	459.57	1.35	–2.34
49R-2, 27–28	460.17	461.03	1.50	–2.44
49R-2, 104–105	460.94	461.80	1.35	–2.51
49R-3, 104–105	462.27	463.13	1.54	–2.43
49R-4, 27–28	463.00	463.86	1.31	–2.43
49R-5, 27–28	464.44	465.30	1.57	–2.33
49R-5, 104–105	465.21	466.07	1.42	–2.52
49R-6, 27–28	465.92	466.78	1.21	–2.41
49R-6, 104–105	466.69	467.55	1.34	–2.46
50R-1, 26–27	468.26	468.79	1.23	–2.36
50R-1, 103–105	469.03	469.56	1.15	–2.53
50R-2, 24–25	469.74	470.27	1.23	–2.21
50R-2, 100–101	470.50	471.03	1.30	–2.05
50R-3, 29–30	471.11	471.64	1.06	–2.29
50R-3, 105–106	471.87	472.40	1.17	–2.49
50R-4, 22–23	472.54	473.07	1.38	–2.37
50R-5, 39–40	474.08	474.61	1.38	–2.15
50R-5, 108–109	474.77	475.30	0.95	–2.24
50R-6, 33–34	475.51	476.04	0.88	–2.27
50R-7, 37–38	476.40	476.93	0.94	–2.14
50R-7, 99–100	477.02	477.55	0.63	–2.36
51R-1, 26–27	477.86	478.19	0.78	–2.39
51R-1, 102–104	478.62	478.95	1.35	–2.37
51R-2, 24–25	479.34	479.67	0.71	–2.51
51R-2, 104–105	480.14	480.47	0.74	–2.54
51R-3, 26–27	480.86	481.19	1.13	–2.26
51R-3, 104–105	481.64	481.97	1.39	–2.06
51R-4, 26–27	482.36	482.69	0.62	–2.40
51R-4, 103–105	483.13	483.46	1.11	–2.11
51R-5, 27–28	483.87	484.20	0.24	–2.63
51R-5, 103–104	484.63	484.96	0.76	–2.36
51R-6, 27–28	485.34	485.67	0.82	–2.32
51R-6, 103–104	486.10	486.43	0.69	–2.55
51R-7, 27–28	486.84	487.17	0.34	–1.47
2070-1260A-				
37R-1, 27–28	336.67	336.92	0.90	–2.14
37R-2, 27–28	338.17	338.42	0.95	–2.13
37R-2, 104–105	338.94	339.19	0.99	–2.20
37R-3, 27–28	339.67	339.92	0.91	–2.51
37R-3, 104–105	340.44	340.69	1.41	–2.03
37R-4, 27–28	341.17	341.42	0.66	–2.36
37R-5, 104–105	343.44	343.69	1.38	–1.97
37R-6, 27–28	344.17	344.42	0.60	–2.52
37R-6, 69–70	344.59	344.84	0.95	–2.29
37R-7, 27–28	344.98	345.23	1.30	–2.09
37R-7, 104–105	345.75	346.00	1.21	–2.15
38R-1, 26–27	346.26	347.00	0.68	–2.47
38R-2, 103–104	348.53	349.27	1.29	–2.15
38R-3, 26–27	349.26	350.00	1.01	–2.45
38R-3, 102–103	350.02	350.76	0.56	–2.77
38R-4, 26–27	350.76	351.50	1.39	–2.15
38R-5, 26–27	352.26	353.00	1.41	–2.42
38R-5, 104–105	353.04	353.78	0.46	–2.82
38R-6, 26–27	353.76	354.50	0.40	–2.94
39R-1, 25–25	355.85	356.59	0.86	–2.82
39R-2, 26–26	357.36	358.10	1.50	–2.28
39R-2, 103–104	358.13	358.87	0.62	–2.89
39R-3, 26–26	358.86	359.60	0.98	–2.48
39R-3, 103–103	359.63	360.37	0.97	–2.67
39R-4, 26–26	360.36	361.10	1.07	–2.62
39R-5, 23–23	361.83	362.57	0.52	–2.74
39R-5, 103–103	362.63	363.37	1.43	–2.28
39R-6, 29–29	363.39	364.13	0.70	–2.56
39R-6, 104–104	364.14	364.88	0.48	–2.43
39R-7, 26–26	364.86	365.60	0.41	–2.58
40R-1, 26–27	365.56	368.22	1.50	–2.34
40R-2, 26–27	367.06	369.72	0.25	–2.63
40R-2, 103–104	367.83	370.49	1.26	–2.12
40R-3, 26–27	368.56	371.22	0.46	–2.34
40R-3, 103–104	369.33	371.99	0.91	–2.06

Table T1 (continued).

Core, section, interval	Depth		$\delta^{13}C_{VPDB}$	$\delta^{18}O_{VPDB}$
	(mbsf)	(mcd)	(‰)	(‰)
40R-4, 26–27	370.06	372.72	0.94	–1.90
40R-5, 26–27	371.56	374.22	1.26	–2.12
40R-5, 103–104	372.33	374.99	1.01	–2.08
40R-6, 26–27	373.06	375.72	0.35	–2.30
40R-7, 26–27.5	374.06	376.72	0.75	–2.52
41R-1, 27–28	375.17	377.83	0.87	–1.90
41R-2, 27–28	376.67	379.33	0.67	–2.20
41R-2, 104–105	377.44	380.10	0.54	–2.35
41R-3, 27–28	378.17	380.83	1.25	–2.01
41R-3, 104–105	378.94	381.60	1.00	–2.19
41R-4, 27–28	379.67	382.33	1.75	–2.17
41R-5, 27–28	381.17	383.83	0.81	–2.34
41R-5, 104–105	381.94	384.60	1.16	–2.17
41R-6, 27–28	382.67	385.33	1.28	–1.90
42R-1, 104–105	385.54	388.66	1.32	–2.32
42R-2, 27–28	386.27	389.39	1.35	–2.09
42R-2, 104–105	387.04	390.16	1.11	–2.27
42R-3, 27–28	387.77	390.89	1.12	–2.22
42R-3, 104–105	388.54	391.66	0.70	–2.54
207-1261A-				
40R-3, 27–28	557.43	557.43	0.67	–2.33
40R-4, 27–28	558.93	558.93	1.52	–1.98
40R-5, 104–105	561.20	561.20	0.81	–2.20
207-1261B-				
2R-1, 30–30	530.30	534.90	0.78	–2.39
2R-1, 105–105	531.05	535.65	0.56	–2.83
2R-2, 30–30	531.80	536.40	0.87	–2.69
2R-2, 105–105	532.55	537.15	0.98	–2.49
2R-3, 30–30	533.30	537.90	0.70	–2.89
2R-3, 105–105	534.05	538.65	1.09	–2.43
3R-1, 30–30	539.90	541.38	1.04	–2.67
3R-1, 110–110	540.70	542.18	1.08	–2.58
3R-2, 30–30	541.40	542.88	1.33	–2.28
3R-2, 110–110	542.20	543.68	1.02	–2.70
3R-3, 30–30	542.90	544.38	1.01	–2.67
3R-3, 110–110	543.70	545.18	1.19	–2.56
3R-4, 30–30	544.40	545.88	0.67	–2.57
3R-4, 110–110	545.20	546.68	1.38	–2.32
3R-5, 30–30	545.90	547.38	0.98	–2.77
3R-5, 90–90	546.50	547.98	1.26	–2.46
3R-6, 30–30	546.90	548.38	0.46	–2.97
4R-1, 105–105	550.25	551.29	1.30	–2.62
4R-2, 105–105	551.75	552.79	1.09	–2.93
4R-4, 30–30	554.00	555.04	0.60	–2.90
4R-4, 105–105	554.75	555.79	1.43	–2.63
4R-5, 30–30	555.50	556.54	1.07	–2.51
4R-5, 100–100	556.20	557.24	0.03	–2.76

Notes: Isotopic values are reported in δ-notation relative to the Vienna Peedee belemnite (VPDB) standard. External precision is <0.03‰ for $\delta^{13}C$ and <0.06‰ for $\delta^{18}O$ (1σ).