35. STABLE-ISOTOPE AND PERCENTAGE-OF-CARBONATE DATA FOR UPPER CRETACEOUS/ LOWER TERTIARY SEDIMENTS FROM DEEP SEA DRILLING PROJECT SITE 524, CAPE BASIN, SOUTH ATLANTIC[1]

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INTRODUCTION

This paper presents a compilation of stable-isotope and percentage-of-carbonate data for the Upper Cretaceous/lower Tertiary hemipelagic sediments from DSDP Leg 73, Site 524. Although these data have never been previously published, they have already been utilized in several papers (Hsü et al., 1982 and in press; McKenzie et al., 1982; Perch-Nielsen et al., 1982; Hsü, this vol.). Rather than review the conclusions derived from these data, our intention herein is to present the data along with a discussion on methodology and refer the reader to previously published works for a discussion of the data's significance.

STRATIGRAPHY AT SITE 524

DSDP Site 524 was located at 29°29′S, 3°31′E at a water depth of 4796 m in the Cape Basin (Fig. 1). The hole was drilled into a submarine fan at the mouth of a submarine canyon cut into the Walvis Ridge. Lower Eocene sediments crop out here where younger sediments have not been deposited or have been eroded away. The uppermost Cretaceous and lower Tertiary sediments have been buried at such a shallow depth that there is little evidence of postdepositional changes that might have altered their isotopic compositions. Those sediments constitute a continuously deposited sequence from the Maestrichtian to the lower Eocene (Fig. 2). Volcaniclastic components derived from the nearby Walvis Ridge are present both in the turbidites and in hemipelagic sediments; these components account for the rapid sedimentation rate of about 30 m/m.y. for the Maestrichtian and Paleocene. Samples of hemipelagic sediments from this expanded sedimentary record permitted us to reconstruct the record of environmental and biostratigraphic changes during the critical period of the Cretaceous/Tertiary (C/T) transition (Hsu et al., 1982).

PERCENTAGE OF CARBONATE

Over 200 samples from Site 524 were analyzed for their calcium carbonate content by using a combustion-titration apparatus. The results are given, in wt.%, in

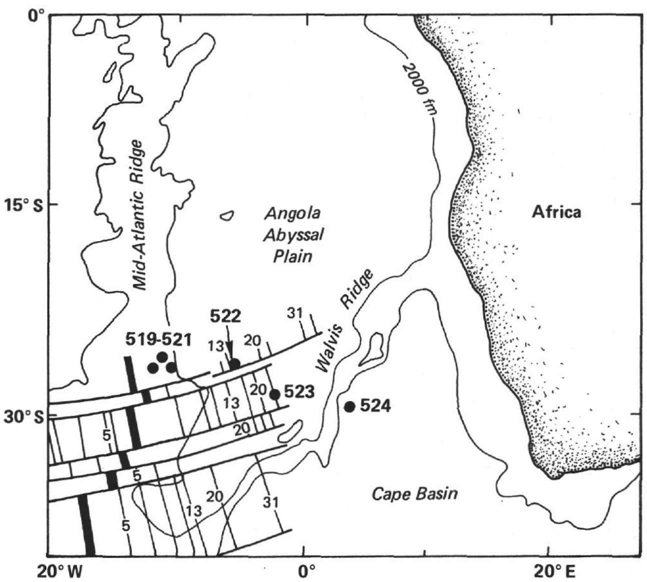

Figure 1. Location of Site 524. Numbers beside dots indicate drill sites, and numbers between lines indicate seafloor magnetic anomalies. The 2000-fm bathymetric contour is also shown.

Table 1. The lower Paleocene sediments are marly oozes with an average calcium carbonate content of about 40%. The uppermost Maestrichtian sediments are also marl oozes, with a carbonate content between 30 and 40%. However, as in every continuously deposited C/T transition known to us, there is a $CaCO_3$ anomaly at or near the boundary. A remarkable systematic trend is apparent in sediments from Core 20, Section 3: the $CaCO_3$ content rapidly decreases from 39% at 116 cm to 32% at 109 cm to 19% at 108 cm in the same core and reaches a minimum carbonate value of 2% for the C/T boundary clay at 104–105 cm. Above this, the $CaCO_3$ content increases to 10% to 25%, but it decreases dramatically again to about 1% in Samples 524-20-1, 124–126 cm and 148–150 cm, 2.5 m above the C/T boundary. It returns to normal values within the nannofossil zone NP2, some 350,000 yr. after the beginning of the Tertiary.

The decrease of $CaCO_3$ could be due to a greater influx of noncarbonate detritus, to reduced production of calcareous plankton, and/or to increased seabottom dis-

[1] Hsü, K. J., LaBrecque, J. L., et al., *Init. Repts. DSDP*, 73: Washington (U.S. Govt. Printing Office).

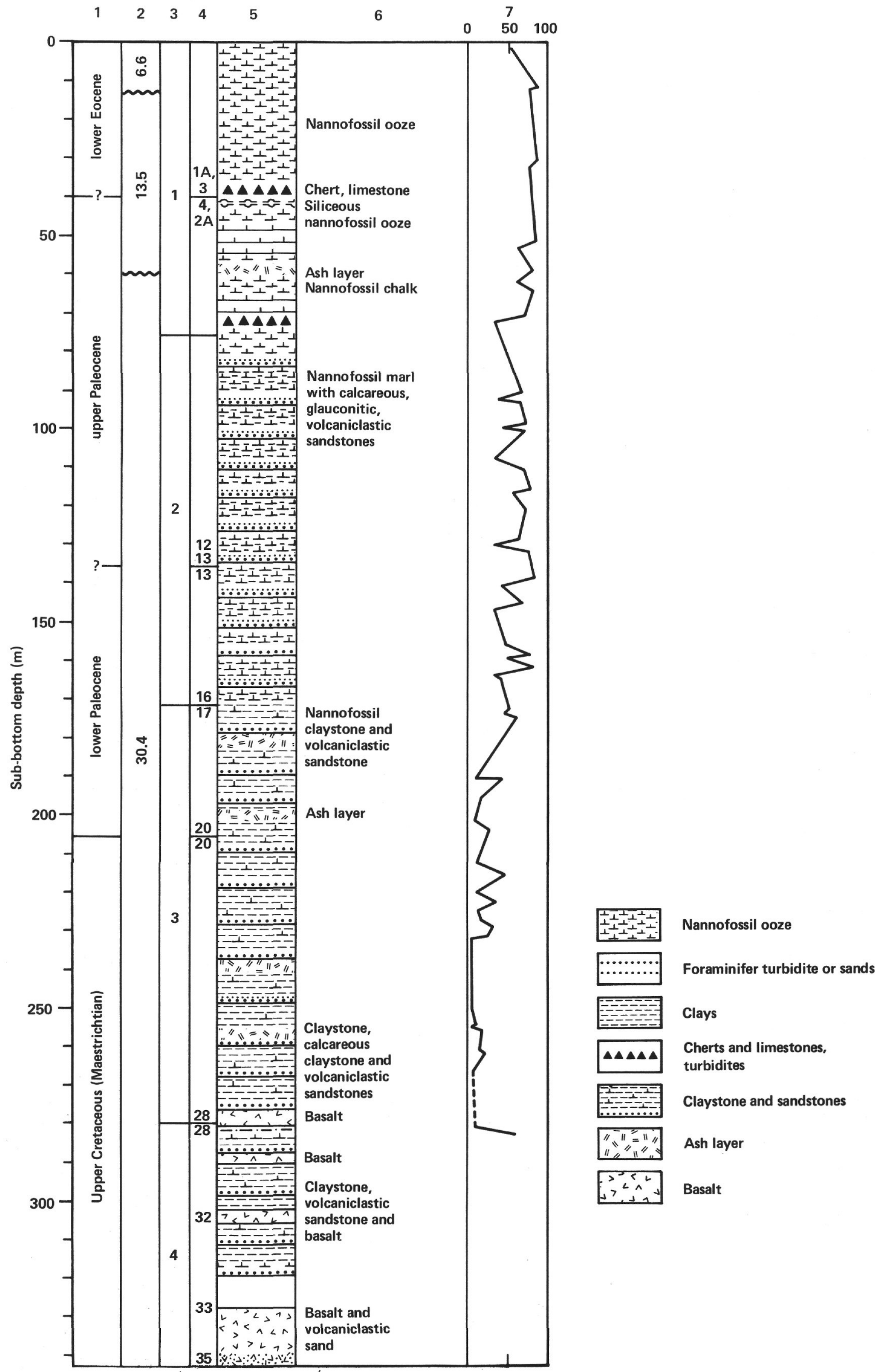

Figure 2. Sedimentary sequence at Site 524: (1) age, (2) sedimentation rate (m/m.y.), (3) lithologic unit, (4) core number, (5/6) lithology, (7) variation of $CaCO_3$ content (wt.%).

Table 1. Carbonate content of Site 524 samples.

Core-Section (interval in cm)	Carbonate content (wt.%)
2-1, 65–66	94.05
3-1, 46–47	89.37
3-3, 75–76	81.45
3-3, 105–106	88.76
4-1, 30–35	70.31
4-1, 108–109	88.78
4-2, 12–13	86.22
4-2, 137–138	76.76
4-3, 104–105	87.24
5-1, 19–21	80.71
5-2, 62–64	83.80
5-3, 130–132	82.28
5-4, 126–128	78.18
5-5, 103–105	86.44
6-1, 60–62	85.03
6-2, 90–91	83.62
6-2, 98–100	74.94
6-2, 131–133	63.93
6-3, 70–72	55.76
6-3, 100–101	52.56
7-1, 113–114	64.22
7-1, 133–135	60.01
7-2, 86–88	54.03
7-2, 106–107	53.62
8-1, 90–92	53.82
8-1, 130–131	57.96
8-2, 58–60	62.80
8-2, 106–108	74.37
8-3, 83–84	55.59
8-3, 118–120	73.39
8-4, 23–25	73.20
8-4, 60–61	74.08
8-5, 16–18	70.42
8-5, 47–48	77.96
8-6, 34–35	59.36
9-1, 63–65	76.05
9-1, 115–116	71.38
9-2, 115–116	73.07
9-2, 125–127	74.89
9-3, 115–116	69.76
9-3, 137–139	71.36
9-4, 76–78	67.89
9-4, 104–105	72.70
9-5, 61–63	69.91
9-5, 115–116	65.54
10-1, 103–104	55.07
10-1, 115–117	58.66
10-2, 62–64	62.69
10-2, 143–144	63.85
10-3, 79–81	64.78
10-3, 141–143	68.19
10-4, 29–31	76.30

Table 1. (Continued).

Core-Section (interval in cm)	Carbonate content (wt.%)
10-4, 106–107	76.37
10-5, 41–43	78.81
11-1, 99–100	63.62
11-1, 119–121	74.42
11-2, 58–60	66.16
11-3, 10–12	57.48
11-4, 10–11	74.79
11-4, 55–57	68.16
11-5, 65–66	69.33
11-5, 77–79	68.25
12-1, 87–88	70.78
12-1, 90–92	66.35
12-2, 94–95	64.52
12-2, 98–100	59.76
12-3, 47–48	62.69
12-3, 91–92	60.35
12-4, 35–37	24.98
12-4, 124–125	59.69
12-5, 77–78	70.00
12-5, 120–122	69.58
12-6, 19–20	66.58
12-6, 24–26	75.42
13-1, 4–5	86.21
13-1, 50–52	70.90
13-1, 53–55	71.68
13-2, 27–29	74.13
13-3, 76–78	69.77
13-3, 148–150	74.78
14-4, 68–70	76.09
13-5, 53–55	99.31
14-1, 116–118	75.45
14-2, 109–110	63.42
14-2, 112–114	61.00
14-3, 43–45	63.56
15-1, 19–21	34.00
15-2, 106–108	47.74
15-3, 126–128	52.96
15-4, 72–73	57.98
15-5, 46–47	80.98
16-1, 68–70	47.83
16-2, 94–96	56.06
16-3, 107–109	44.22
16-3, 145–146	84.95
16-4, 113–115	58.21
16-5, 56–58	55.29
17-1, 97–99	41.75
17-1, 138–140	65.48
17-2, 55–57	56.07
17-3, 70–72	45.65
17-4, 82–84	57.42
17-5, 98–100	45.61
18-1, 68–70	43.55

Table 1. (Continued)..

Core-Section (interval in cm)	Carbonate content (wt.%)
18-1, 118–120	26.69
18-2, 115–117	41.57
18-3, 76–78	40.76
18-4, 118–120	26.69
18-5, 61–63	39.50
19-1, 53–54	49.34
19-1, 99–100	41.14
19-1, 120–122	58.85
19-2, 33–35	24.62
19-3, 13–14	40.31
19-3, 90–92	16.89
19-3, 135–136	38.69
19-4, 3–5	17.41
19-4, 61–62	17.05
19-4, 78–79	4.32
20-1, 26–28	5.19
20-1, 60–62	47.23
20-1, 62–64	15.50
20-1, 80–81	19.67
20-1, 98–99	19.41
20-1, 120–121	1.02
20-1, 124–126	1.12
20-1, 126–127	2.08
20-1, 144–145	0.57
20-1, 148–150	0.96
20-2, 14–15	12.00
20-2, 42–43	11.58
20-2, 52–54	9.97
20-2, 61–62	12.33
20-2, 67–69	18.02
20-2, 89–90	10.02
20-2, 98–99	3.29
20-2, 100–102	11.58
20-2, 110–112	25.27
20-2, 130–132	7.45
20-2, 135–136	10.00
20-2, 148–150	12.87
20-3, 10–11	13.67
20-3, 33–34	19.58
20-3, 50–51	20.25
20-3, 66–68	25.25
20-3, 71–72	21.25
20-3, 106–107	0.13
20-3, 80–82	10.87
20-3, 87–88	13.83
20-3, 98–100	11.25
20-3, 104–105	1.67
20-3, 107–109	18.58
20-3, 109–110	31.67
20-3, 115–117	38.71
20-3, 148–150	38.00
20-4, 18–20	36.69

Table 1. (Continued).

Core-Section (interval in cm)	Carbonate content (wt.%)
21-1, 115–117	12.61
21-2, 145–147	6.44
21-3, 48–50	12.67
21-4, 105–107	10.42
21-5, 123–125	23.00
22-1, 101–103	6.91
22-2, 46–48	28.31
22-3, 117–119	39.43
22-4, 122–124	27.10
22-5, 103–105	7.13
23-1, 102–104	26.14
23-2, 27–29	27.25
23-2, 31–33	26.18
23-3, 112–114	15.52
23-4, 128–130	25.35
23-5, 133–135	6.06
24-1, 106–108	11.30
24-3, 134–136	1.58
24-4, 140–142	24.12
24-5, 80–82	13.90
24-6, 23–25	35.03
25-1, 65–66	13.50
25-2, 110–112	20.61
25-2, 123–124	21.04
25-3, 44–46	17.46
25-4, 77–79	19.25
25-5, 135–137	30.28
25-6, 85–87	20.39
26-1, 108–110	5.62
26-1, 144–145	12.81
26-2, 54–56	14.49
26-2, 141–142	23.78
26-4, 95–97	6.06
26-4, 138–139	20.64
26-5, 85–87	11.29
26-6, 95–97	32.47
27-1, 41–43	32.75
27-2, 71–73	14.91
27-3, 48–50	28.94
27-4, 72–74	18.67
28-1, 59–60	46.90
28-1, 98–100	36.04
28-2, 125–127	26.82
28-3, 58–60	28.16
28-3, 120–122	31.66
28-4, 46–47	29.04
28-4, 75–77	27.60
28-5, 76–78	23.23
29-1, 20–22	21.99
29-1, 99–100	49.49
32-1, 33–35	7.83
32-2, 1–2	14.46

solution. Extensive dissolution of planktonic foraminifers in the latest Cretaceous sediments at Site 524 and at many other localities throughout the world indicates that carbonate dissolution markedly increased at the end of the Cretaceous. The data favor the hypothesis that the calcite compensation depth (CCD) rapidly became more shallow (Worsley, 1974). However, the CCD may have soon deepened again during the earliest Tertiary, because the earliest Tertiary foraminiferal tests show little evidence of dissolution.

STABLE-ISOTOPE ANALYSES

Methodology

Stable-isotope analyses were carried out on the carbonate components of the Site 524 sediments. Because the size of each sample was so small and foraminiferal tests were so rare, bulk samples were used to determine the general trends in the carbon and oxygen isotopic stratigraphy. Since larger foraminiferal tests were rare in all samples, the bulk samples should give an approximation of the isotopic composition of the calcareous nannoplanktons and, hence, the near-surface waters. Whenever it was possible to separate size fractions, a coarse fraction (>28 μm) and a fine fraction (<28 μm) of the calcareous sediment were also measured. The finer fraction comprises predominantly nannoplanktons and should be even more representative of surface-water conditions. The stable-isotope values for the bulk sediments and coarse and fine fractions are given in Table 2. The data show that the isotope variations with depth are similar for the bulk and fine fractions. In Table 3, the isotope ratios for *Gavelinella beccariiformis* (picked by

Table 2. Stable-isotope data (‰) for bulk and fine and coarse fractions of sediments from Site 524.

Core-Section (interval in cm)	Sub-bottom depth (m)	Bulk sample		Fine fraction		Coarse fraction	
		δ^{13}C PDB	δ^{18}O PDB	δ^{13}C PDB	δ^{18}O PDB	δ^{13}C PDB	δ^{18}O PDB
5-2, 130–131	59.80	+3.37	−0.41				
5-4, 100–102	62.55	+3.33	−0.27				
5-6, 11–12	64.61	+2.60	−0.10				
14-3, 110–111	146.60	+1.98	+0.06	+2.13	+0.45	+1.60	−0.30
15-2, 52–53	154.02	+1.36	+0.55	+1.46	+0.80	+1.13	−0.16
16-3, 112–113	165.62	+1.41	−0.12	+1.62	+0.11	+1.35	−0.52
17-2, 50–52	173.00	+1.84	−0.43	+2.11	+0.44	+1.43	−1.32
18-2, 133–134	183.33	+1.60	+0.17	+1.31	−0.40	+1.61	−0.40
19-1, 53–54	190.53	+1.70	−0.28				
19-1, 99–100	190.99	+1.90	−0.19				
19-1, 120–122	191.20	+1.78	−0.15				
19-2, 33–35	191.83	+1.69	+0.93				
19-2, 81–82	192.31	+2.02	−0.60	+2.10	+0.62	+1.69	−0.45
19-3, 13–14	193.13	+1.80	+0.17				
19-3, 90–92	193.90	+1.55	−0.40				
19-3, 135–136	194.35	+1.69	+0.09				
19-4, 3–5	194.35	+1.37	−1.87				
19-4, 61–62	195.11	+0.83	−1.69				
19-4, 78–79	195.28	+0.86	−1.28				
20-1, 26–28	199.76	+0.87	−0.24				
20-1, 60–62	200.10	+0.58	−1.37				
20-1, 62–64	200.12	+0.68	−1.22	+0.87	−0.50	+1.00	−0.54
20-1, 80–81	200.30	+0.70	−0.54				
20-1, 98–99	200.48	+0.75	−0.25				
20-1, 100–102	200.50	—	—	+0.87	−0.50	+1.00	−0.54
20-1, 124–126	200.74	−2.90	−2.79				
20-1, 148–156	200.98	−5.76	−5.58				
20-2, 5–7	201.05	−7.56	−6.56				
20-2, 14–15	201.14	+0.34	−0.99				
20-2, 40–42	201.40	+0.80	−1.44	−0.44	−2.42	+0.52	−1.90
20-2, 42–43	201.42	+0.50	−1.61				
20-2, 52–54	201.52	+0.57	−1.00				
20-2, 61–62	201.61	+0.63	−0.89				
20-2, 67–69	201.67	+0.83	−0.43				
20-2, 89–90	201.89	+0.62	+0.02				
20-2, 98–100	201.98	+0.53	−0.96	−1.92	−3.64	−1.92	−3.09
20-2, 105–106	202.05	+0.59	−1.22				
20-2, 110–112	202.10	+0.48	−1.37				
20-2, 130–132	202.30	−0.16	−2.13				
20-2, 135–136	202.35	+0.38	−2.12				
20-2, 148–150	202.48	+0.50	−1.95				
20-3, 10–11	202.60	+0.99	−1.77				
20-3, 14–16	202.64	+0.97	−0.59	+0.29	−2.31	+0.69	−1.16
20-3, 33–34	202.83	+1.38	−1.31				
20-3, 36–38	202.86	+1.36	−0.60	+1.21	−1.81	+1.03	−1.72
20-3, 50–51	203.00	+1.41	−1.36				
20-3, 52–54	203.02	+1.41	−0.35				
20-3, 60–62	203.10	+1.35	−1.64				
20-3, 66–68	203.16	+1.20	−1.87	+0.95	−2.20	+1.07	−1.82
20-3, 71–72	203.21	+1.56	−1.50				
20-3, 80–82	203.30	+1.09	−0.80				
20-3, 87–88	203.37	+1.77	−1.24				
20-3, 93–95	203.43	+2.10	−1.26	+1.54	−1.08	+1.39	−0.93
20-3, 98–100	203.48	+2.07	−1.38	+1.86	−1.49	+1.23	−1.49
20-3, 104–105	203.54	−0.61	+0.42				
20-3, 106–107	203.56	+0.83	−0.19				
20-3, 107–109	203.57	+2.78	−1.17	+1.24	−2.33		
20-3, 109–110	203.59	+1.93	−1.20				
20-3, 115–117	203.65	+2.56	−0.77				
20-3, 122–124	203.72	+2.72	−0.24	+2.65	+0.19	+1.89	−0.75
20-3, 136–138	203.86	+2.69	−0.73				
20-3, 148–150	203.98	+2.62	−1.03	+2.23	−1.24		
20-4, 18–20	204.18	+1.68	−1.10				
20-4, 43–45	204.43	+2.67	−0.72				
21-1, 115–117	210.15	+2.23	−0.49				
21-2, 145–147	211.95	+1.40	−1.10				
21-4, 24–25	213.74	+2.28	−1.05	+2.48	−1.14	+2.22	−1.08
22-3, 89–90	222.39	+2.00	−0.97	+1.53	−2.01		
23-2, 31–33	229.81	+1.95	−1.08				
24-3, 113–114	241.63			+1.66	−2.17		
25-5, 132–183	254.32	+2.21	−1.53				
26-2, 141–142	259.41	+1.98	−1.27				
26-4, 138–139	262.38	+2.11	−1.24				
27-1, 74–75	266.74	+2.50	−1.68				
27-3, 114–115	270.14	+2.13	−1.32				
28-1, 59–60	279.09	+2.42	−1.76				
29-1, 99–100[a]	285.99	+0.36	−6.79				

[a] Limestone.

Table 3. Stable-isotope data (‰) for *Gavelinella beccariiformis* from Site 524.

Core-Section (interval in cm)	$\delta^{13}C$ PDB	$\delta^{18}O$ PDB
16-3, 7–9	+1.12	−0.95
17-1, 99–101	+0.86	−0.89
17-5, 111–113	+0.54	−0.94
18-2, 43–45	+1.53	−0.17
18-6, 6–8	+1.33	−0.27
19-2, 35–37	+1.12	−0.41
19-4, 20–22	+1.06	−0.14
20-1, 57–59	+0.78	−1.86
20-3, 9–11	+1.15	−1.39
20-3, 67–69	+1.03	−0.85
20-3, 118–120	+1.21	−0.43
20-4, 22–24	+1.20	−0.84
21-5, 19–21	+0.68	−0.99
22-4, 27–29	+0.54	−0.57
23-2, 69–71	+0.52	−1.70

R. Wright) are presented. This benthic species occurs on both sides of the C/T boundary and is sufficiently abundant to be picked and analyzed.

The traditional phosphoric acid method (McCrea, 1950) was used, and the bulk, coarse-fraction, and fine-fraction samples were reacted at 25°C, while the foraminifer samples were reacted on a microline at 50°C. The released CO_2 gas was analyzed for its isotopic composition using a V.G. Micromass 903, a triple collecting mass spectrometer. The isotopic results are expressed as per mil deviations from the PDB isotopic standard as $\delta = [(R_{sample}/R_{standard})^{-1}] \times 10^3$, where R is $^{13}C/^{12}C$ or $^{18}O/^{16}O$. The precision of the measurements (the standard deviation of the mean calculated for replicate analyses) is ±0.02 ‰ for $\delta^{13}C$ and ±0.04 ‰ for $\delta^{18}O$. Samples chosen for stable-isotope analysis were taken from the pelagic sediments intercalated within the turbidite sequence.

Carbon Isotopes

Two remarkable carbon-13 anomalies are visible in the data. The first occurs at the C/T boundary, where only bulk analysis was performed because of the very low carbonate content. Sample 524-20-3, 104–105 cm, exactly at the boundary, has a $\delta^{13}C$ value of −0.6 ‰, which is significantly depleted in carbon-13 relative to the average Cretaceous value for bulk samples of +2.4 ‰. Sample 524-20-3, 106–107 cm is also relatively depleted in carbon-13 (+0.8 ‰), but the low value may be due to bioturbation and the mixing of the isotopically light carbonate into the sediment underlying the boundary clay. The $\delta^{13}C$ value of Sample 524-20-3, 98–100 cm, which is 5 cm above the boundary, is again more positive (+2.1 ‰). From this point, the carbonate content of the sediments shows a steady, linear decrease in $\delta^{13}C$ in both the bulk and fine fractions, reaching a second minimum (−0.16 ‰) at approximately 1 m (Sample 524-20-2, 130–132 cm) above the C/T boundary. A third minimum exists at 2.5 m above the C/T boundary, but the extremely negative values of both the carbon- and oxygen-isotope values suggest that this anomaly results from diagenetic alteration. Afterwards, the $\delta^{13}C$ ratio becomes gradually enriched in carbon-13 and approaches a Cretaceous-like value of +2.0 ‰ 11 m above the C/T boundary (Sample 524-19-2, 81–82 cm).

The $\delta^{13}C$ ratio of *Gavelinella beccariiformis* remains basically constant throughout this period of carbon-13 oscillation (Table 3). This indicates that the changes in carbon-13 ratio were surface-water phenomena and were not felt in the deep bottom waters. Since the carbonate samples and especially their fine fractions are made up almost exclusively of nannofossils, the signals represent changes in the isotopic composition of nannoplankton skeletons and reflect a change of the isotopic composition of dissolved carbonate in the surface water of the ocean.

Oxygen Isotopes

The changes in the composition of oxygen isotopes across the C/T boundary are less systematic than the carbon oscillations, but nevertheless they seem real. Cretaceous bulk samples from Cores 20 to 23 yielded $\delta^{18}O$ values ranging from −0.2 to −1.2 ‰. For the boundary clay (Sample 524-20-3, 104–105 cm), the $\delta^{18}O$ value is +0.4 ‰, which may represent a temperature minimum at the C/T boundary. However, the $\delta^{18}O$ ratio 5 cm above the boundary (in Sample 524-20-3, 98–100 cm) returns to Cretaceous values, and afterwards it shows a fluctuating but often decreasing value. A minimal $\delta^{18}O$ anomaly is registered by the value of −3.6 ‰ in the fine fraction of Sample 524-20-2, 98–100 cm, about 1.5 m above the boundary, and could represent a maximum temperature increase. The oscillating oxygen-18 values may signify varying degrees of contamination or isotopic disequilibrium, or they may be a true manifestation of temperature oscillations after the boundary event. The oxygen-isotope compositions of the bulk sediments, the fine fraction, and *Gavelinella beccariiformis* show the same trend. The synchronous decrease in the $\delta^{18}O$ of the fine fraction and benthic foraminifers could signify that the early Tertiary oceans became temporarily warmer throughout, while, during the same period, only the surface waters showed a decrease in the $\delta^{13}C$ content of the dissolved bicarbonate.

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