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17. DATA REPORT: CARBONATE, ORGANIC CARBON, AND OPAL CONCENTRATIONS AND ORGANIC δ^{13} C VALUES OF SEDIMENTS FROM SITES 1075–1082 AND 1084, SOUTHWEST AFRICA MARGIN¹

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INTRODUCTION

One of the goals of Ocean Drilling Program (ODP) Leg 175 was to reconstruct the history of upwelling-induced biological productivity along the coast of Africa from the Congo River to the Cape of Good Hope. The amounts of inorganic and organic carbon that have accumulated in sediment are essential to this reconstruction, and these parameters were routinely measured during Leg 175 (Wefer, Berger, Richter, et al., 1998). We have augmented the shipboard data with carbon and opal measurements done on sediments from sites between 5°S and 25°S that represent different productivity regimes. Furthermore, we have determined the organic carbon stable isotope compositions of these same sediment samples.

METHODS

Sample Locations

Sediment samples were obtained from Pleistocene sequences at nine of the thirteen sites occupied during Leg 175. Sediments from Sites 1075, 1076, and 1077 in the Lower Congo Basin record varying histories of fluvial inputs, seasonal coastal upwelling, and excursions of the South Equatorial Countercurrent. Sediments from Sites 1078, 1079, and

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1080 on the Angola margin represent accumulation under low-productivity hemipelagic conditions that are influenced little by either fluvial contributions or coastal upwelling. Sediments from Site 1081 on the Walvis Ridge and Sites 1082 and 1084 in the Northern Cape Basin are influenced to different degrees by the elevated productivity associated with the Benguela Current. Samples were collected at a frequency of one per section meter at Sites 1075, 1076, 1077, 1080, and 1082 and one per core at Sites 1078, 1079, 1081, and 1084.

Samples were freeze-dried and then ground to a powder. Total carbon and organic carbon (TOC) concentrations were measured using a LECO CS-244 carbon/sulfur analyzer. Dried bulk sediment was first analyzed for total carbon and then digested with 2.4-N HCl to remove carbonates. The carbonate-free residue was washed thoroughly with distilled water, and then the residual carbon was measured. This value represents the TOC content of the sediment. The difference between the two carbon measurements gives the inorganic carbon content, which is reported as CaCO₃ concentration, assuming all of the inorganic carbon was present as calcite or aragonite. Precision of the analyses, based on duplicates of every tenth measurement and standards (pure calcium carbonate) for every fifth measurement, is $\pm 0.10\%$ and $\pm 0.02\%$ for total carbon and organic carbon, respectively.

Preparation of CO₂ gas for carbon isotopic analyses followed the routine procedures of Craig (1953). Carbonate-free sediment samples were combusted at ~850°C in the presence of Cu, CuO, and O₂ gas. Water was cryogenically removed by a dry ice and alcohol bath. The CO₂ was condensed using a liquid N₂ trap, and the noncondensable gases were pumped out. The volume of CO₂ was measured with a manometer that had been calibrated with a standard carbonate reagent. The CO₂ collected was then analyzed using a VG Sira 10 isotope ratio mass spectrometer at the National Sun Yat-Sen University, Taiwan. Results are reported in conventional δ values relative to the Peedee belemnite (PDB) standard. The analytical precision for the standards expressed as 1 σ is better than 0.06‰.

Biogenic opal concentrations were determined by a silica alkaline leaching procedure modified from Mortlock and Froelich (1989) by using different acid and base reagents. HCl was replaced by 0.5-M glacial acetic acid to prevent over-extraction of silicate (Murray et al., 1995). Instead of the 2-N Na₂CO₃ used by Mortlock and Froelich (1989), 0.5-N NaOH was employed as the basic leaching chemical for complete dissolution of opal. The values reported here as opal percent concentrations are calculated as opal = $2.4 \times Si_{opal}$ (Mortlock and Froelich, 1989) using dry sediment weights. The overall relative precision of opal determination is better than 1.5%.

RESULTS

Calcium Carbonate Concentrations

Concentrations of calcium carbonate are low in sediments from Sites 1075, 1076, and 1077 near the mouth of the Congo River (Fig. F1). Their maximum is 15.2 wt%, and most sediment samples contain <5 wt% CaCO₃ (Table T1), which generally agrees with the paucity of coccolith microfossils and the abundances of opaline and continental clastic material reported in these sediments (Wefer, Berger, Richter, et al.,

F1. CaCO₃ concentrations, p. 6.



1998). Sediments from Sites 1078, 1079, and 1080 on the Angola margin contain more $CaCO_3$ than those near the Congo River, probably because of diminished clastic dilution. Their concentrations typically fall between 10 and 20 wt% (Fig. F1). The highest calcium carbonate concentrations in our survey exist in sediments from Sites 1081, 1082, and 1084, where they vary between 13.2 and 80.9 wt% (Table T1). In particular, closely spaced and well-developed variations that are related to light–dark color changes and more gradual downhole increases and decreases in CaCO₃ concentration occur at Sites 1082 and 1084 in the Northern Cape Basin (Fig. F1).

Organic Carbon Concentrations

The organic carbon concentrations in sediments from the nine locations that we studied are generally higher than in most deep-sea sediments from the South Atlantic (~0.3 wt%) (Premuzic et al., 1982; Keswani et al., 1984). The concentrations are typically between 1 and 4 wt%, except for Sites 1081, 1082, and 1084, in which average values are >5 wt% (Table T1). In addition, the amount of variation is sometimes >5 wt% between adjoining samples at Sites 1082 and 1084 (Fig. F2).

Organic Carbon Isotopic Compositions

Organic carbon stable isotopic compositions ($\delta^{13}C_{org}$) differ among sediment samples of different age from the nine sites (Fig. F3). Dashed lines at –23‰ that are positioned between the typical $\delta^{13}C_{org}$ values of continental and tropical/temperate marine organic matter (about –26‰ and –20‰, respectively) (Sackett, 1989; Meyers, 1994) provide a reference for comparison. The $\delta^{13}C_{org}$ values (<–23‰ for most of the samples) at Sites 1076, 1078, and 1079 are notably more negative than at the other sites, which have values around –21‰ (Fig. F3). Of special interest is the sharp decrease in $\delta^{13}C_{org}$ values found in the uppermost samples at Sites 1075, 1076, and 1084 (Fig. F3). Of particular note, the 3.5‰ negative excursion at Site 1084 was confirmed by triplicate analyses.

Opal Concentrations

Concentrations of biogenic opal are relatively elevated in sediments from Sites 1075 and 1077 near the mouth of the Congo River than others (Fig. F4). Their maximum is 24.8 wt%, although most sediment samples contain between 15 and 20 wt% opal (Table T1). Concentrations are lower in sediments from Site 1076 (7%–11%), which is closer to the mouth of the river (Fig. F4). These patterns agree with the abundant but variable amounts of opaline and continental clastic material reported in the sediments of these three sites (Wefer, Berger, Richter, et al., 1998). Sediments from Sites 1078 and 1079 on the Angola margin contain low opal concentrations (2.4-5.5 wt%), whereas those at Site 1080 are relatively enriched in this biogenic sediment component. Values at this location in the southern Angola Basin are generally between 10 and 20 wt%, although one sediment sample (175-1080A-6H-4, 125-130 cm) contains 31.3 wt% opal (Table T1). The highest concentrations of opal in our survey exist in sediments from Sites 1082 and 1084, where they reach 36.0 wt% (Table T1). However, most of the sediments from these Northern Cape Basin locations, like those from Site 1081 on

F2. TOC concentrations, p. 7.







F4. Biogenic opal concentrations, p. 9.



the Walvis Ridge, contain <10 wt% opal (Fig. F4) because of their elevated concentrations of CaCO₃ (Fig. F1).

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Figure F1. CaCO₃ concentrations in sediment samples from the nine ODP sites studied in this survey.



Figure F2. Total organic carbon (TOC) concentrations of in sediment samples from the nine ODP sites studied in this survey.

Figure F3. $\delta^{13}C_{org}$ values in sediment samples from the nine ODP sites studied in this survey. Dashed lines at -23% for each site provide a reference for comparison.





Figure F4. Biogenic opal concentrations in sediment samples from the nine ODP sites studied in this survey.

Table T1. Calcium carbonate, total organic carbon, and biogenic opal concentrations and $\delta^{13}C_{org}$ values for sediment samples from the nine ODP sites studied in this survey. (Continued on next two pages.)

Core, section, interval (cm)	Depth (mbsf)	CaCO ₃ (wt%)	TOC (wt%)	δ ¹³ C (‰ PDB)	Opal (wt%)
175 1075 4					
1/5-10/5A-	0.95	1 46	1 70	22.64	0 12
2H_1 137_140	2.87	1.40 2.45	3.17	-22.04	0.45 21 /0
2H-2, 137-140	4.37	2.93	3.27	-21.13	24.81
2H-3, 137-140	5.87	1.43	2.68	-21.13	24.40
2H-4, 137-140	7.37	1.35	2.98	-21.51	22.02
2H-5, 137-140	8.87	0.83	2.27	-21.62	16.91
2H-6, 137-140	10.37	2.41	1.67	-21.15	15.47
3H-1, 137-140	12.37	2.58	2.16	-22.09	14.30
3H-2, 137-140	13.87	1.93	1.62	-21.76	12.69
3H-3, 137-140	15.37	1.21	2.02	-22.09	12.57
3H-4, 137-140	16.87	0.48	2.09	-22.40	12.39
3H-5, 137-140	18.37	0.80	1.49	-22.69	6.94
3H-6, 137-140	19.87	3.41	2.54	-21.27	15.29
4H-1, 137-140	21.87	2.63	2.68	-21.15	17.85
4H-2, 137-140	23.37	2.22	1.85	-21.26	15.//
4H-3, 137-140	24.87	0.93	3.62	-21.56	19.37
411-4, 137-140	20.37	1.49	1.01	-21.69	12.00
4H-3, 137-140	27.07	0.54	2 72	-20.96	11.42
411-0, 137-140 5H-1 137-140	29.37	0.80	2.67	-21.90	18.07
5H-2 137-140	32.87	11 28	2.07	-21.76	20.20
5H-3, 137-140	34.37	0.81	1.62	-22.07	17.43
5H-4, 137-140	35.87	9.36	1.88	-22.11	17.03
5H-5, 137-140	37.37	2.09	2.44	-22.21	18.38
5H-6, 137-140	38.87	0.86	3.52	-22.29	11.34
6H-1, 137-140	40.87	1.61	2.77	-21.97	17.95
6H-2, 137-140	42.37	2.45	2.01	-21.64	17.88
6H-3, 137-140	43.87	2.94	1.65	-22.11	15.67
6H-4, 137-140	45.37	0.63	1.99	-22.73	18.93
6H-5, 137-140	46.87	1.27	1.98	-22.90	12.05
6H-6, 137-140	48.37	3.00	2.25	-21.85	16.90
7H-1, 137-140	50.37	5.57	2.68	-21.57	20.81
7H-2, 137-140	51.87	2.06	2.02	-21.86	21.33
7H-3, 137-140	53.40	0.22	2.17	-21.89	16.51
7H-4, 137-140	54.94	1.58	3.16	-21.89	17.04
/H-5, 13/-140	56.44	0.46	2.70	-22.09	17.71
/H-6, 13/-140	57.94	0.76	2.13	-22.09	15.69
8H-3, 137-140	62.92	0.24	1.48	-25.03	/.59
1011-4, 127-130	03.04 99.22	2.20	2.58	-23.00	10.91
11H-7, 133-130	89.65	1 30	2.50	-21.80	20.06
11H-3 127-130	90.95	1.52	1.20	-22.05	20.00
11H-4, 139-142	92.47	0.18	1.72	-21.85	15.02
11H-5, 137-140	95.35	0.97	2.06	-21.68	15.60
11H-7, 137-140	96.75	0.56	2.85	-21.24	14.51
175 10764					
1/3-10/0A- 1H_1 137-1/0	1 37	0.03	1 98	24.16	7 69
1H-3 137-140	1.37	12.84	2.01	-24.10	7.09
2H-2 137-140	7.67	2.67	2.01	-23.02	11 72
3H-3, 137-140	18.67	1.38	1.90	-24.73	7.71
5H-3, 137-140	37.67	0.92	3.16	-23.60	8.47
6H-3, 137-140	47.17	0.37	2.25	-23.30	8.74
7H-3, 137-140	56.67	15.22	2.45	-23.16	7.56
8H-3, 137-140	66.17	0.30	2.35	-23.19	7.22
9H-3, 139-142	75.69	4.09	2.29	-22.35	7.45
10H-3, 127-130	85.07	0.39	1.86	-25.02	5.73
11H-3, 127-130	94.57	1.17	2.45	-23.92	10.47
17H-4, 0-3	150.75	0.18	1.86	-25.57	7.82
175-1077B-					
12H-2, 145-150	103.59	0.29	1.51	-23.25	11.12
12H-4, 142-147	106.70	1.06	2.00	-23.61	14.91
12H-6, 146-151	109.87	0.59	1.46	-21.78	15.42
13H-2, 129-134	112.69	3.10	1.75	-21.04	15.18

Table T1 (continued).

Core, section, interval (cm)	Depth (mbsf)	CaCO ₃ (wt%)	TOC (wt%)	δ ¹³ C (‰ PDB)	Opal (wt%)
13H-3, 50-52	113.44	3.39	1.87	-21.13	15.36
13H-4, 126-128	115.66	1.68	2.05	-21.84	24.06
13H-6, 133-138	118.70	2.38	1.72	-21.90	21.23
14H-2, 117-122	121.17	0.71	1.26	-22.41	10.04
14H-4, 125-130 14H-6, 140-145	123.94	0.53	1.6/	-21.54	14.44
1411-0, 140-145	120.90	0.55	2.74	-21.04	17.71
175-1078A-					
1H-1, 132-135	1.32	20.01	2.98	-24.44	4.01
1H-1, 132-135 2H-3, 132-135	3.6Z 11.82	10.17	2.00	-24.39	3.00 2.07
3H-3, 132-135	21.32	16.53	2.00	-24.39	4.71
4H-3, 132-135	30.82	18.51	2.43	-25.11	4.58
5H-3, 122-125	40.25	14.41	1.62	-24.65	2.43
6H-3, 127-130	48.88	16.18	2.72	-22.57	4.38
7H-3, 127-130	59.29	16.51	2.83	-24.56	4.38
175-1079B-	5.07	17 77	2 20	22.55	2 41
2H-6 147-150	15 97	17.77	2.29	-23.33 -24 21	3.01 4.59
3H-6, 147-150	25.47	13.72	2.85	-24.48	4.54
4H-6, 147-150	34.97	22.47	2.64	-23.99	3.87
5H-6, 147-150	44.47	11.48	4.16	-24.23	3.98
6H-6, 147-150	53.97	12.31	2.42	-24.29	3.78
7H-2, 147-150	57.47	13.38	2.44	-24.29	4.64
8H-6, 147-150	/2.9/	17.33	2.46	-24.44	3.81
9H-5, 147-150 10H-6 138-141	00.97 91 38	4.17	4.10	-24.31 -23.94	4.22 4.36
11H-6, 39-42	99.89	6.48	2.25	-23.62	4.08
12H-7, 21-24	109.21	11.05	2.00	-24.54	3.82
13H-6, 98-101	117.98	7.30	2.54	-24.86	4.63
14H-5, 147-150	126.47	17.60	2.40	-24.38	5.54
175-1080A-					
1H-1, 135-140	1.35	10.16	2.33	-20.67	14.72
1H-2, 135-140 2H-1 135-140	2.85	7 86	2.08	-20.50 -20.60	0.04 15.00
2H-2, 135-140	6.15	8.57	2.89	-20.70	20.86
2H-3, 135-140	7.65	4.15	3.62	-21.01	20.18
2H-4, 135-140	9.15	4.50	2.81	-21.27	13.69
2H-5, 135-140	10.65	5.81	1.75	-21.48	16.64
2H-6, 135-140	12.15	6.97	1.70	-21.81	13.35
3H-1, 135-140	14.15	12.78	1.32	-21.86	10.88
3H-2, 135-140 3H-3, 135-140	15.70	1.27	1.39	-22.20	13.54
3H-4, 135-140	18.80	3.35	2.20	-21.82	12.16
3H-5, 135-140	20.35	4.01	1.76	-21.76	9.28
4H-3, 135-140	25.49	16.04	1.28	-21.31	8.21
4H-5, 135-140	27.15	5.85	1.95	-21.18	12.13
4H-7, 135-140	28.76	6.07	1.89	-21.22	8.41
4H-9, 140-145	30.56	3.88	2.26	-21.29	13.30
4H-11, 133-140	32.20	2.20	2.29	-20.45	17.29
5H-5, 115-120	37.25	2.54	1.54	-21.33	15.57
5H-6, 105-110	38.35	0.52	2.09	-21.37	20.72
5H-7, 105-110	39.55	5.24	1.92	-21.71	17.30
5H-9, 105-110	41.95	1.78	2.63	-20.79	18.26
6H-2, 125-130	42.99	2.35	3.14	-21.04	18.41
6H-4, 125-130	45.39	3.65	2.45	-21.14	31.34
0H-3, 123-130 6H_6 125 120	40./9 ⊿ହ 10	U.16 0.42	2.6/ 2.82	-20./4 _21.14	17.90 22.04
6H-7, 125-130	49.59	0.52	2.39	-21.73	19.07
175-1081A-					
2H-1, 137-140	2.37	37.08	5.37	-20.94	11.38
2H-3, 137-140	5.37	40.42	4.40	-21.34	14.61
3H-2, 127-130	13.27	36.63	4.64	-21.04	3.42
4∏-3, 12/-130 5H_3 127-130	24.27 33 77	44.89 28 56	5.40 5.35	-21.28 _21.14	3.90 3.56
6H-3, 127-130	43.27	17.40	7.55	-22.09	4.60
7H-3, 127-130	52.77	25.11	5.29	-21.25	12.47

Table T1 (continued).

Core, section,	Depth	CaCO ₃	TOC	δ13C	Opal
interval (cm)	(mbsf)	(wt%)	(wt%)	(‰ PDB)	(wt%)
8H-3, 127-130	62.27	22.03	3.76	-21.79	8.44
9H-3, 127-130	71.77	13.23	4.34	-21.26	12.42
10H-3 127-130	81 27	34 51	3.05	_21 40	4 4 4
11H-3 127-130	90.77	20.10	4 36	21.10	1.11
1111-3, 127-130	100.77	29.19	4.30	-21.33	4.32
120-3, 127-130	100.27	38.40	4.55	-21.04	5.49
175-1082A-					
1H-1, 137-140	1.37	59.65	3.63	-22.61	4.61
1H-2 137-140	2.87	46.43	6.22	-23.13	2.38
1H-3 135-138	4 35	57.82	6.95	_23.46	3 36
111-5, 155-150	5.87	50.18	6.57	23.46	5.50
111-4, 157-140	3.67	30.18	4.01	-23.40	3.03
1Π -3, 130-133	7.30	43.04	4.01	-21.70	5.91
2H-1, 137-140	9.17	42.02	5.12	-22.06	4.68
2H-2, 137-140	10.67	47.85	6.15	-22.05	2.89
2H-3, 127-130	12.07	57.93	4.13	-22.17	3.87
2H-4, 127-130	13.47	53.85	6.48	-22.11	2.18
2H-5, 127-130	14.87	62.18	4.40	-22.21	2.00
2H-6, 124-127	16.24	42.95	3.97	-22.88	4.12
3H-1, 123-125	18.53	47.57	4.10	-22.42	11.35
3H-2, 123-125	19.93	58.09	2.96	-22.75	5.91
3H-3 119-122	21 29	43 64	6 37	_22 31	3 1 5
3H_A 123_125	27.22	18.01	5 77	22.51	3 54
211- 1 , 123-123	22.75	51 47	5.40	-22.44	2.54
$3\Pi - 3, 123 - 123$	24.15	51.47	3.40	-22.40	2.01
3H-7, 118-121	26.88	68.22	2.55	-22.12	2.28
4H-1, 123-125	28.03	48.77	8.31	-20.98	2.27
4H-2, 123-125	29.43	67.36	3.04	-22.30	1.21
4H-3, 119-122	30.79	65.76	3.32	-22.61	3.49
4H-4, 123-125	32.23	49.50	4.93	-22.26	1.65
4H-5, 123-125	33.63	62.49	3.49	-22.03	2.50
4H-6, 123-125	35.03	63.28	3.10	-21.69	2.53
5H-1, 123-125	37.53	64.70	3.84	-23.24	2.80
5H-2, 123-125	38.93	72.50	2.31	-22.97	4.54
5H-3 119-122	40.29	61 17	2 60	_21 12	3.05
5H_4 123_125	10.25	70.74	2.00	21.12	2.03
511-4, 123-125	42.12	70.74	2.02	-21.15	1.00
511-5, 125-125	43.13	70.38	2.20	-21.09	1.90
SH-0, 123-125	44.55	54.19	4.79	-22.22	2.00
6H-1, 123-125	47.03	55.76	4.80	-21.64	5.38
6H-2, 123-125	48.43	60.84	3.54	-21.35	3.04
6H-3, 123-125	49.83	35.73	5.97	-21.94	3.90
6H-4, 123-125	51.33	34.89	7.71	-22.31	4.41
6H-5, 123-125	52.73	55.97	4.22	-22.87	3.41
6H-6, 123-125	54.13	24.75	9.14	-22.51	3.37
7H-3, 129-132	59.59	37.44	6.08	-21.64	4.88
8H-4, 129-132	69.30	15.65	5.54	-22.43	36.03
9H-3, 109-112	78.39	27.42	5.48	-21 74	28.38
10H-4 109-112	88 33	35.63	4 41	_22.84	22 41
11H-3 114-117	97.44	46.07	7.08	21.55	5.82
1111-3, 114-117	107.44	40.07	7.08	-21.55	3.02
1211-4, 117-120	107.01	29.20	4.55	-21.34	50.00
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1H-1, 137-140	1.37	61.83	4.01	-23.53	6.94
1H-2, 0-3	1.50	59.82	4.30	-20.19	7.46
2H-2 137-140	5.87	27.80	6.23	-20.98	25.67
2112, 137 110	6.00	20.03	6 39	20.90	24.34
211-5, 0-5	10.27	15.09	4 91	-20.75	24.57
211-3, 137-140	10.57	10.90	4.01	-22.24	54.55
∠⊓-0, U-3	10.50	10.92	0.24	-22.10	
3H-3, 137-140	16.87	44.94	6.19	-21.69	9.25
4H-3, 137-140	26.37	60.93	4.35	-22.16	7.93
5H-3, 127-130	35.77	32.14	10.15	-22.17	7.89
6H-3, 127-130	45.17	20.80	7.30	-22.62	19.54
7H-4, 132-135	55.85	51.30	6.72	-22.03	7.84
8H-3, 127-130	64.27	57.85	3.69	-22.20	5.23
9H-3, 124-127	73.74	80.89	2.48	-22.50	3,50
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