

## 13. DATA REPORT: GEOCHEMISTRY OF MIOCENE SEDIMENTS, SITES 1006 AND 1007, LEEWARD MARGIN, GREAT BAHAMA BANK<sup>1</sup>

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### ABSTRACT

Total carbon and carbonate contents, quantitative carbonate mineralogy, trace metal concentrations, and stable isotope compositions were determined on a suite of samples from the Miocene sections at Sites 1006 and 1007. The Miocene section at Site 1007, located at the toe-of-slope, contains a relatively high proportion of bank-derived components and becomes fully lithified at a depth of ~300 meters below seafloor (mbsf). By contrast, Miocene sediments at Site 1006, situated in Neogene drift deposits in the Straits of Florida and composed primarily of pelagic carbonates, do not become fully lithified until a depth of ~675 mbsf. Diagenetic and compositional contrasts between Sites 1006 and 1007 are reflected in geochemical data derived from sediment samples from each site.

### INTRODUCTION

This report provides the results of geochemical analyses performed on Miocene sediments recovered during Ocean Drilling Program (ODP) Leg 166 at Sites 1006 and 1007. Sites 1006 and 1007 are the most distal of five sites along the Bahamas Transect drilled into prograding carbonate sequences along the western margin of the Great Bahama Bank (GBB). Site 1007 is located on the toe-of-slope of the western GBB in ~647 m of water. At Site 1007, a nearly complete 900-m-thick Miocene section consisting of a succession of bioturbated, periplatform limestone (e.g., Schlager and James, 1978) with interbeds of turbiditic packstone, grainstone, and floatstone (Eberli, Swart, Malone, et al., 1997) was recovered. Site 1006, the most distal site along the Bahamas Transect, was drilled ~30 km from the platform edge of the GBB in 658 m of water. Approximately 334 m of middle and upper Miocene sediments were recovered at this site, which is positioned in a nearly continuous sequence of Neogene drift sediments that onlap and interfinger with prograding bank slope deposits (Eberli, Swart, Malone, et al., 1997). Because of its more distal location, the Miocene section at Site 1006 has relatively few turbiditic deposits and a significantly higher pelagic component, and it consists primarily of nannofossil chalk and limestone.

The Miocene section at Site 1007, which contains a relatively high proportion of bank-derived components, has been affected by diagenesis. Sediments are fully lithified below ~300 meters below seafloor (mbsf) and exhibit burial compaction features including anastomosing solution seams at depths greater than ~1120 mbsf. By contrast, Miocene sediments at Site 1006, composed primarily of pelagic carbonates, do not become fully lithified until a depth of ~675 mbsf. It is well known that periplatform carbonates undergo accelerated rates of diagenesis relative to low-Mg calcite (LMC)-dominated pelagic counterparts, primarily because of the metastable nature of the platform-derived aragonite and high-Mg calcite (HMC) component in deep, cold seawater (e.g., Schlager and James, 1978; Mullins et al., 1985; Dix and Mullins, 1988, 1992; James and Choquette, 1990). However, to what extent the early onset of lithification in periplatform carbonates influences further alteration during burial is poorly known. In this regard, the suite of geochemical data derived from the sequences of pelagic and periplatform carbonates at Sites

1006 and 1007, respectively, provide a foundation for the examination of the influence of initial sediment composition on patterns and processes of burial diagenesis in fine-grained, shelf carbonates.

Bulk sediment samples (~10–20 cm<sup>3</sup>) were collected aboard the *JOIDES Resolution* during Leg 166. A representative range of lithologies from the Miocene sections at Sites 1006 and 1007 was chosen at semi-regular intervals on the basis of core descriptions and visual observations. Approximately one fourth of each bulk sample was powdered and dried in a 75°C oven; in cases where individual sediment samples were lithologically diverse, an equivalent amount of each lithology was prepared. Bulk powders were subsequently analyzed for total carbon and carbonate contents, carbonate mineralogy, trace metal contents, and carbon and oxygen isotope compositions. The selective removal and analysis of individual petrographic components in Site 1007 samples were commonly precluded by the dense cementation and the fine-grained nature of most lithologies. However, an absence of cement in intermittent clay-rich intervals at Site 1007 allowed for the disaggregation of selected samples and the isotopic analysis of individual petrographic components. These samples were disaggregated by soaking in a 5.25% sodium hypochlorite (NaOCl) solution for 24 hr and rinsing repeatedly in deionized water. Disaggregated samples were then washed with deionized water and oven dried at 50°C. Additional carbon and oxygen isotope analyses were performed on individual petrographic components from these separates, which were selected with the aid of a binocular microscope. Data for Holes 1006A and 1007C are reported in Tables 1 and 2, respectively.

### ANALYTICAL METHODS AND RESULTS

#### Carbon Coulometry

The coulometric titration technique measures all of the CO<sub>2</sub> that is liberated by acidifying and heating sediment samples in a closed system and back-titrating to a coulometric end point. To determine carbonate carbon concentrations, ~10 mg of sample was reacted with a 50% phosphoric acid solution in a heated reaction vessel. The percentage of carbonate in each sample reflects the amount of inorganic carbon (IC) liberated as CO<sub>2</sub> with the assumption that all inorganic carbon is present as calcium carbonate, such that CaCO<sub>3</sub> = IC × 8.332. No corrections were made for the presence of either siderite or dolomite. Total carbon (TC) concentrations reflect the amount of carbon released as CO<sub>2</sub> during combustion of a ~5-mg sample in oxygen at 1000°C. The amount of organic carbon (C<sub>org</sub>) was calculated as the

<sup>1</sup>Swart, P.K., Eberli, G.P., Malone, M.J., and Sarg, J.F. (Eds.), 2000. *Proc. ODP, Sci. Results*, 166: College Station TX (Ocean Drilling Program).

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Table 1. Geochemical data, Hole 1006A.

Depth (mbsf)	Component	CaCO <sub>3</sub> (wt%)	C <sub>org</sub> (wt%)	Silt/clay (wt%)	δ <sup>18</sup> O	δ <sup>13</sup> C	Ba/Ca (×1000)	Fe/Ca (×1000)	Mg/Ca (×1000)	Mn/Ca (×1000)	Sr/Ca (×1000)
501.81	Whole rock	87.91	0.26	11.83	-0.74	1.84	0.736	1.319	8.589	0.368	14.724
501.81	<68-μm fraction				-1.05	1.82					
501.81	<68-μm fraction				-1.06	1.79					
501.81	<i>Cibicides</i> sp.				-1.16	1.53					
501.81	<i>Cibicides</i> sp.				-0.22	1.47					
501.81	Planktonics				-0.60	1.69					
502.10	Whole rock	88.22	0.29	11.48	-0.65	1.59	0.517	1.207	9.483	0.402	13.506
502.10	<68-μm fraction				-0.69	1.60					
502.10	<68-μm fraction				-0.63	1.71					
502.26	Whole rock	87.88	0.31	11.81	-1.22	1.56	0.571	0.931	9.309	0.300	15.315
502.26	Whole rock				-0.90	1.76					
502.26	<68-μm fraction				-1.23	1.97					
502.26	<68-μm fraction				-0.98	2.07					
502.26	<i>Cibicides</i> sp.				-0.50	1.69					
502.35	Whole rock	86.47	0.50	13.02	-1.09	1.61	0.764	1.210	10.191	0.255	14.650
502.35	<68-μm fraction				-0.59	2.09					
502.35	<68-μm fraction				-1.50	1.61					
502.35	Whole rock	84.63	0.43	14.95	-1.09	1.61					
502.35	<i>Cibicides</i> sp.				0.02	1.91					
502.52	Whole rock	88.42	0.19	11.40	-1.05	1.81	0.561	0.642	9.091	0.294	15.775
502.52	<68-μm fraction				-1.28	1.79					
502.52	<68-μm fraction				-1.13	1.96					
502.52	<i>Cibicides</i> sp.				-0.65	1.59					
502.83	Whole rock	80.92	0.28	18.79	-0.73	1.69	0.573	1.688	18.790	0.446	14.650
502.83	<68-μm fraction				-0.75	1.68					
502.83	<i>Cibicides</i> sp.				-0.69	1.77					
502.83	<i>Cibicides</i> sp.				-0.35	1.76					
502.83	Planktonics				-0.22	1.67					
503.04	Whole rock	78.03	0.52	21.45	-0.82	1.60	0.721	2.557	14.426	0.426	17.049
503.04	<68-μm fraction				-0.73	1.84					
503.04	<68-μm fraction				-0.67	1.79					
503.04	<i>Cibicides</i> sp.				-0.81	1.79					
503.25	Whole rock	83.16	0.31	16.53	-0.70	1.77	0.561	1.756	7.561	0.341	13.415
503.25	<68-μm fraction				-0.93	1.81					
503.25	<68-μm fraction				-1.00	1.75					
503.25	<i>Cibicides</i> sp.				-0.86	1.47					
503.25	<i>Cibicides</i> sp.				-0.44	1.72					
503.50	Whole rock	87.33	0.24	12.43	-0.56	1.77	0.856	1.150	9.358	0.348	14.973
503.50	<68-μm fraction				-0.81	1.78					
503.50	<i>Cibicides</i> sp.	87.33	0.24	12.43	-0.27	1.63					
503.50	<i>Cibicides</i> sp.				-0.65	1.53					
503.50	Planktonics				-0.97	2.28					
505.45	Whole rock				-0.80	2.04					
506.39	Whole rock	87.42	0.26	12.32	-0.21	1.65					
516.79	Whole rock	91.74	0.45	7.81	-0.81	1.93					
516.79	Whole rock	90.95	0.55	8.51							
517.03	Whole rock	92.31	-0.06	7.75	0.71	1.80					
517.03	Whole rock	91.91	-0.02	8.11							
529.84	Whole rock	87.83	0.03	12.14	0.03	1.77					
536.75	Whole rock	87.77	0.17	12.06	0.10	1.64					
550.43	Whole rock	90.24	0.08	9.69	0.41	1.41					
550.43	Whole rock	77.18	0.25	22.57	-0.52	1.17					
561.92	Whole rock	<90.30	-0.06	9.77	0.29	1.28					
562.67	Whole rock	80.63	0.60	18.78	-0.67	1.60					
569.72	Whole rock	84.11	0.28	15.61	-0.46	1.44					
569.79	Whole rock	85.99	-0.24	14.25	-0.18	1.39					
569.79	Whole rock	84.73	-0.09	15.36							
585.62	Whole rock	75.50	0.12	24.38	-0.99	1.46	0.684	0.494	10.266	0.380	14.068
586.02	Whole rock	69.30	1.62	29.09	-0.69	1.34	1.393	0.984	15.984	0.615	11.475
586.24	Whole rock	73.48	0.15	26.37	-0.67	1.29	0.808	0.943	15.152	0.572	10.774
597.12	Whole rock				-0.65	1.11					
710.43	Whole rock				-1.21	1.14					

Table 2. Geochemical data, Hole 1007C.

Depth (mbsf)	Component	CaCO <sub>3</sub> (wt%)	C <sub>org</sub> (wt%)	Silt/clay (wt%)	Dolomite (wt%)	Calcite (wt%)	Aragonite (wt%)	Quartz (wt%)	δ <sup>18</sup> O	δ <sup>13</sup> C	Ba/Ca (×1000)	Fe/Ca (×1000)	Mg/Ca (×1000)	Mn/Ca (×1000)	Sr/Ca (×1000)
351.14	Whole rock	95.42	0.06	4.52	0.00	74.50	25.50	0.00	0.39	2.13					
351.14	Whole rock	89.94	0.72	9.34											
360.39	Whole rock	89.01	0.67	10.32	0.00	76.80	23.20	0.00	1.17	2.75					
360.39	Whole rock	87.65	0.83	11.51											
362.06	Whole rock	98.79	0.34	0.87	0.00	100.00	0.00	0.00	2.00	2.68					
362.06	Whole rock	97.43	0.43	2.14											
372.91	Whole rock	95.57	0.15	4.28					2.11	2.52	1.492	0.222	24.762	0.159	9.524
381.03	Whole rock	95.11	0.30	4.59	9.70	90.30	0.00	0.00	2.10	2.51					
381.99	Whole rock	96.57	0.31	3.13	5.40	94.60	0.00	0.00	1.92	2.43					
381.99	Whole rock	95.37	0.45	4.18											
390.07	Whole rock	87.08	0.92	12.00	7.50	92.50	0.00	0.00	1.87	2.29					
399.90	Whole rock	95.60	-0.02	4.41	5.10	94.90	0.00	0.00	1.84	2.15					
399.90	Whole rock	95.20	-0.02	4.41	3.10	90.20	1.30	0.30							
408.13	Whole rock	95.41	-0.01	4.59	4.10	95.90	0.00	0.00	1.76	2.09					
410.74	Whole rock	95.43	0.71	3.86	0.00	100.00	0.00	0.00	1.81	2.00					
410.74	Whole rock	95.43	-0.02	4.59											
419.39	Whole rock	86.83	-0.05	13.23	5.50	73.10	21.40	0.00	0.67	1.88					
428.08	Whole rock	90.13	0.43	9.44					1.32	1.89	1.079	0.127	8.571	0.159	4.444

Table 2 (continued).

Depth (mbsf)	Component	CaCO <sub>3</sub> (wt%)	C <sub>org</sub> (wt%)	Silt/clay (wt%)	Dolomite (wt%)	Calcite (wt%)	Aragonite (wt%)	Quartz (wt%)	δ <sup>18</sup> O	δ <sup>13</sup> C	Ba/Ca (×1000)	Fe/Ca (×1000)	Mg/Ca (×1000)	Mn/Ca (×1000)	Sr/Ca (×1000)
429.11	Whole rock	95.79	0.07	4.15	0.00	100.00	0.00	0.00	1.57	1.96					
439.14	Whole rock	80.12	0.86	19.02	0.00	72.50	27.50	0.00	0.23	1.74					
441.23	Whole rock	88.61	0.29	11.11	0.00	100.00	0.00	0.00	1.15	1.62					
441.23	Whole rock								1.13	1.64					
446.50	Whole rock	85.77	0.92	13.31					-0.52	2.06	1.171	0.167	8.696	0.201	9.699
448.15	Whole rock	89.19	0.20	10.61	0.00	87.90	12.10	0.00	1.02	1.56					
457.92	Whole rock	80.94	0.21	18.85					0.26	1.68	1.233	0.205	14.726	0.274	6.849
461.41	Whole rock	90.20	0.17	9.63	9.80	90.20	0.00	0.00	1.20	1.68					
467.54	Whole rock	88.19	0.18	11.63					0.92	2.20	1.307	0.163	8.824	0.163	11.438
468.70	Whole rock	68.16	0.90	30.94	0.60	61.10	14.70	0.70	0.47	1.88					
472.24	Whole rock	96.79	0.29	2.92					1.18	1.58	1.023	0.114	8.523	0.170	6.250
476.67	Whole rock	92.68	0.12	7.20	0.00	100.00	0.00	0.00	0.96	1.40					
478.79	Whole rock	90.69	0.11	9.20	15.50	84.50	0.00	0.00	1.67	1.57					
482.34	Whole rock	99.28	0.10	0.62					1.49	1.26	0.949	0.136	11.111	0.136	7.046
486.39	Whole rock	88.22	0.53	11.25	14.40	66.50	16.30	2.80	1.46	1.59					
494.41	Whole rock	16.90	0.15	82.95					-0.10	1.56					
494.41	Whole rock	16.37	0.21	83.42											
498.80	Whole rock	95.06	0.09	4.86	4.60	91.60	0.00	3.80	1.09	1.58					
507.51	Whole rock	94.70	0.63	4.67					1.18	1.92	3.469	0.148	13.284	0.111	9.594
507.78	Whole rock	92.22	0.74	7.03	0.00	82.50	17.50	0.00	0.68	1.68					
508.14	Whole rock	95.21	0.50	4.29					0.74	1.69	2.435	0.052	11.140	0.104	8.549
542.70	Planktonics								0.25	2.27					
542.70	<63-μm fraction								0.03	1.73					
545.33	<i>Cibicides</i> sp.								0.20	1.83					
545.33	<63-μm fraction								-0.05	1.39					
545.33	Planktonics								0.02	2.14					
545.33	Cemented fragment								0.49	1.82					
547.47	<63-μm fraction								-1.01	0.85					
547.47	Planktonics								-1.15	2.35					
547.47	Cemented fragment								-0.50	1.93					
556.76	Whole rock	90.92	1.37	7.72					-0.28	2.36	3.311	0.066	9.603	0.099	15.232
557.13	Whole rock	96.01	0.41	3.58					0.83	2.66	2.488	0.100	12.687	0.100	10.448
559.04	Whole rock	89.65	0.89	9.46					0.54	2.21	3.155	0.126	19.243	0.158	14.196
622.95	Whole rock	92.87	1.66	5.48					-0.81	2.55	1.173	0.123	7.407	0.154	18.519
622.95	Whole rock	92.87	1.59	5.54											
625.43	Whole rock	96.88	0.35	2.77	0.00	100.00	0.00	0.00	0.76	2.66					
651.77	Whole rock	95.98	0.49	3.54					-0.26	2.63					
652.50	Whole rock	95.82	1.43	2.75	0.00	100.00	0.00	0.00	0.43	2.73					
691.02	Whole rock	97.88	0.50	1.62	0.00	100.00	0.00	0.00	-0.02	3.18					
692.49	Whole rock	97.34	0.57	2.09	0.00	85.10	14.90	0.00	0.14	3.19					
692.49	Whole rock	97.34	0.48	2.18											
737.40	Whole rock	96.83	0.31	2.86	0.00	100.00	0.00	0.00	0.04	2.95					
738.04	Whole rock	98.94	0.17	0.89	0.00	100.00	0.00	0.00	0.17	3.08					
764.37	Whole rock	97.73	0.29	1.98	7.20	92.80	0.00	0.00	0.24	3.08					
764.37	Whole rock	97.05	0.37	2.58											
764.98	Whole rock	97.69	0.15	2.16					-0.11	2.82	1.242	0.196	19.281	0.131	10.458
764.98	Whole rock								-0.01	2.88					
777.01	Whole rock	83.40	1.26	15.34					-1.07	1.70	1.268	0.211	12.324	0.211	8.451
777.01	Whole rock	83.40	1.39	15.21					-0.94	1.82					
777.12	Whole rock	91.70	0.40	7.90	0.00	100.00	0.00	0.00	-0.34	2.45					
787.20	Whole rock				0.00	71.30	28.70	0.00	-1.38	2.30					
787.85	Whole rock				0.00	100.00	0.00	0.00	0.51	3.02					
795.62	Whole rock				0.00	72.40	27.60	0.00	-0.73	2.75					
795.62	Whole rock				0.50	94.10	2.80	0.00							
802.50	Whole rock				0.00	100.00	0.00	0.00	0.67	3.25					
806.02	Whole rock				0.00	100.00	0.00	0.00	-0.33	2.92					
812.16	Whole rock				0.00	88.20	11.80	0.00	0.32	2.64					
822.13	Whole rock				0.00	100.00	0.00	0.00	0.38	2.82					
823.40	Whole rock				10.30	89.70	0.00	0.00	-0.01	2.74					
833.41	Whole rock				6.90	78.60	14.50	0.00	-0.73	2.57					
834.73	Whole rock				0.00	100.00	0.00	0.00	1.44	3.09					
841.90	Whole rock				0.00	100.00	0.00	0.00	0.03	2.95					
844.21	Whole rock				4.20	78.20	17.60	0.00	-0.07	2.73					
850.42	Whole rock	96.37	0.12	3.50	25.00	75.00	0.00	0.00	0.31	2.85					
850.42	Whole rock	94.52	0.35	5.13	25.00	75.00	0.00	0.00	0.44	2.89					
851.80	Whole rock	84.47	6.19	9.34	25.00	75.00	0.00	0.00	-0.89	2.13					
851.80	Whole rock	84.64	1.52	13.84	25.00	75.00	0.00	0.00	-1.23	2.30					
890.00	Whole rock	86.07	0.47	13.47					-0.91	2.50	1.443	0.302	5.034	0.201	5.369
890.00	Whole rock	85.55	0.53	13.93					-0.91	2.50	1.443	0.302	5.034	0.201	5.369
890.44	Whole rock	86.29	1.00	12.72	0.00	100.00	0.00	0.00	0.22	2.51					
890.44	Whole rock	85.37	1.11	13.52											
901.31	Whole rock	80.21	1.04	18.75	0.00	100.00	0.00	0.00	-1.53	2.18					
901.46	Whole rock	71.62	0.58	27.80					-0.92	2.30	1.156	0.188	6.250	0.156	5.625
901.46	Planktonics								-1.25	2.68					
901.46	Planktonics								-0.95	2.51					
901.46	Whole rock	96.70	0.03	3.27					-0.92	2.30	1.488	0.248	6.612	0.207	5.372
901.46	<63-μm fraction								-1.55	2.14					
901.46	<63-μm fraction								-0.88	2.43					
901.46	Planktonics								-0.97	2.78					
929.91	Whole rock	85.70	1.36	12.95	0.00	100.00	0.00	0.00	-0.85	1.78					
929.93	Planktonics								-0.99	1.64					
930.25	Whole rock	77.75	1.25	20.99					-1.08	1.60	1.621	0.553	9.091	0.237	5.929
930.25	Whole rock	77.75	1.31	20.93					-1.21	1.51					
930.34	Planktonics								-2.14	2.18					
930.43	Whole rock	95.07	0.10	4.83					0.40	1.94	1.131	0.149	5.952	0.208	5.952
930.43	Whole rock								0.64	2.21					
930.43	Cement								0.47	2.13					
930.43	Cement								0.58	2.08					
930.43	Planktonics			0.82	2.26										

Table 2 (continued).

Depth (mbsf)	Component	CaCO <sub>3</sub> (wt%)	C <sub>org</sub> (wt%)	Silt/clay (wt%)	Dolomite (wt%)	Calcite (wt%)	Aragonite (wt%)	Quartz (wt%)	δ <sup>18</sup> O	δ <sup>13</sup> C	Ba/Ca (×1000)	Fe/Ca (×1000)	Mg/Ca (×1000)	Mn/Ca (×1000)	Sr/Ca (×1000)
930.43	Planktonics								0.69	2.38					
957.60	Whole rock	78.54	0.62	20.84					-0.68	1.03	1.466	0.263	6.015	0.263	5.639
957.60	Whole rock								-0.79	1.13	1.466	0.263	6.015	0.263	5.639
960.96	Whole rock	89.79	0.11	10.10	5.00	95.00	0.00	0.00	-0.23	1.73					
968.23	Whole rock	77.50	1.13	21.28	5.30	91.00	0.00	3.70	-0.97	0.61					
969.07	Whole rock	92.68	0.27	7.05					-0.22	1.68	1.134	0.262	5.814	0.233	5.233
995.24	Whole rock	90.02	0.00	9.98					0.81	1.85	1.167	0.189	10.410	0.221	5.994
998.32	Whole rock	84.76	0.14	15.10					0.24	1.80	1.237	0.389	15.901	0.318	5.654
998.32	Whole rock	84.39	0.18	15.43					0.24	1.80	1.237	0.389	15.901	0.318	5.654
1033.86	Whole rock	80.33	1.07	18.59					-0.81	1.59	0.138	0.345	10.000	0.172	8.276
1033.86	Whole rock								-0.93	1.65					
1033.86	Whole rock	88.34	0.27	11.39					1.02	2.08	0.141	0.310	21.690	0.225	5.634
1033.86	Whole rock								0.88	1.98					
1050.57	Whole rock	69.50	0.76	29.74					0.04	1.05	4.762	0.913	8.333	0.397	6.349
1050.57	Whole rock	89.34	0.50	10.16					0.45	1.60	0.146	2.216	12.245	0.466	6.122
1050.76	Cement								0.32	1.42					
1050.76	<63-μm fraction								-1.15	0.43					
1050.76	<63-μm fraction								-0.23	0.97					
1050.76	Planktonics								-1.13	1.62					
1050.76	Planktonics								-0.48	1.58					
1050.76	Planktonics								-0.23	1.86					
1050.76	Cemented fragment								-0.91	1.33					
1055.90	Whole rock				6.70	93.30	0.00	0.00	0.38	1.68					
1057.31	Whole rock				3.60	96.40	0.00	0.00	0.40	1.71					
1058.74	Whole rock								0.21	1.76					
1066.71	Whole rock				7.80	87.60	0.00	4.60	-0.35	0.97					
1075.29	Whole rock				0.00	100.00	0.00	0.00	0.23	1.65					
1078.09	Whole rock								0.66	1.75					
1082.52	Whole rock				0.00	100.00	0.00	0.00	0.44	1.81					
1082.52	Whole rock				0.00	100.00	0.00	0.00	0.39	1.81					
1082.98	Whole rock				15.30	84.70	0.00	0.00	-0.07	1.68					
1091.17	Whole rock				4.40	95.60	0.00	0.00	0.39	1.75					
1093.74	Whole rock				5.30	94.70	0.00	0.00	0.24	1.63					
1110.79	<63-μm fraction								-0.17	1.31					
1110.79	Planktonics								-0.44	1.50					
1110.79	Cemented fragment								-0.06	1.48					
1112.39	Whole rock				4.50	95.50	0.00	0.00	-0.17	1.54					
1112.51	<63-μm fraction								-0.02	1.45					
1112.51	Planktonics								-1.17	1.83					
1112.51	Cemented fragment								-0.07	1.58					
1117.00	<63-μm fraction								0.19	1.50					
1117.00	Planktonics								-0.16	1.76					
1117.00	Cemented fragment								0.25	1.59					
1118.25	Whole rock								-0.25	1.56					
1118.37	<63-μm fraction								0.17	1.66					
1118.37	Planktonics								-0.36	1.57					
1118.37	Cemented fragment								0.19	1.49					
1119.66	Whole rock				3.90	93.70	0.00	0.00	0.50	1.79					
1120.66	Whole rock	86.16	0.42	13.42	4.00	96.00	0.00	0.00	0.61	1.64					
1120.66	Whole rock	86.16	0.42	13.42	4.00	96.00	0.00	0.00	0.44	1.58					
1121.38	Whole rock	69.34	0.34	30.32	0.00	95.20	0.00	4.80	-0.09	1.39					
1125.64	<63-μm fraction								0.87	1.60					
1125.64	Planktonics								0.47	1.32					
1125.64	Cemented fragment								0.98	1.70					
1157.41	Whole rock	66.35	0.23	33.43					0.83	1.72	5.430	0.000	15.385	0.226	6.787
1157.41	Whole rock	65.46	0.33	34.20					0.83	1.72					
1157.41	Whole rock	87.73	0.14	12.13					0.19	1.87	4.422	0.204	6.803	0.306	4.422
1157.65	<i>Cibicides</i> sp.								1.52	1.16					
1157.65	<63-μm fraction								0.01	1.65					
1157.65	Planktonics								0.70	1.67					
1157.65	Cemented fragment								0.99	1.34					
1157.65	Cement								-0.37	1.85					
1157.65	<63-μm fraction								0.06	1.74					
1157.65	Planktonics								-0.44	1.85					
1166.31	Whole rock	73.88	0.33	25.79					0.41	1.81	3.929	0.107	13.571	0.179	5.357
1166.31	Whole rock								0.14	1.71					
1166.31	Whole rock	86.90	0.29	12.81					0.25	1.98	2.764	0.075	6.784	0.201	3.769
1166.31	Whole rock	86.90	0.64	12.46					0.08	1.92					
1166.31	<63-μm fraction								0.33	1.74					
1166.31	<63-μm fraction								-0.11	1.88					
1166.31	Planktonics								0.17	1.80					
1166.31	Planktonics								-0.59	1.90					
1170.16	<63-μm fraction								0.05	1.72					
1170.16	Planktonics								-0.06	2.03					
1170.16	Cemented fragment								0.46	1.84					
1174.39	<63-μm fraction								0.32	1.48					
1174.39	Planktonics								0.65	1.49					
1174.39	Cemented fragment								0.80	1.68					
1197.24	Whole rock	97.43	0.14	2.43	0.00	100.00	0.00	0.00	0.93	2.13					
1198.74	Whole rock	95.14	0.09	4.77	5.20	94.80	0.00	0.00	0.95	2.16					
1208.24	Whole rock	97.34	0.00	2.65					0.86	2.14	0.961	0.120	8.709	0.090	1.652
1208.24	Whole rock								0.85	2.22					
1217.00	Whole rock	92.41	0.58	7.01					1.23	2.24	1.068	0.032	10.032	0.097	2.071
1218.22	Whole rock	95.70	0.29	4.01					1.39	2.35	0.952	0.140	9.524	0.084	1.681
1220.70	Whole rock	98.21	-0.11	1.90					0.93	2.15	1.018	0.120	7.784	0.090	2.036
1225.95	Whole rock	91.75	0.28	7.97					0.96	2.28	1.104	0.189	11.987	0.158	2.019
1226.51	Whole rock	97.71	0.18	2.11					1.39	2.35	0.935	0.142	8.782	0.142	1.615
1226.51	Whole rock								1.13	2.46					
1228.52	Whole rock	91.05	0.33	8.62					1.39	2.35	0.991	0.120	9.610	0.060	1.742

difference between TC and IC:  $C_{org} \text{ (wt\%)} = TC \text{ (wt\%)} - IC \text{ (wt\%)}$ . Reported silt/clay concentrations were calculated as the amount of insoluble residue during acidification that cannot be attributed to organic carbon:  $Silt/clay \text{ (wt\%)} = 100 - [CaCO_3 \text{ (wt\%)} + C_{org} \text{ (wt\%)}]$ . The precision of these acidification and combustion methods is better than 0.5% and was monitored by multiple analyses of a pure carbonate laboratory standard. The precision of the  $C_{org}$  determinations is defined by the combined precision of the TC and IC methods and is generally not better than 1.5%–2%.

With minor exceptions, carbonate contents at Site 1006 fall within a narrow range between 80 and 90 wt% (Fig. 1). Within the upper and middle Miocene sections at Site 1007, carbonate contents generally range between 80 and 100 wt% (Fig. 1). Contents within the lower Miocene section at this site are more variable and range between ~60 and 100 wt% (Fig. 1). Within the section at Site 1007 are occasional 2- to 5-cm-thick intervals characterized by exceptionally low carbonate contents (as low as 18 wt%; Eberli, Swart, Malone, et al., 1997) and, in some cases, concentrations of organic carbon that exceed 1.0 wt%. Variations in carbonate, clay/silt, and organic carbon concentrations correspond to decimeter- to meter-scale cyclic color changes that characterize the Miocene sections recovered during Leg 166 (Eberli, Swart, Malone, et al., 1997). In general, lighter intervals have higher carbonate and lower siliciclastic and organic carbon contents, whereas darker intervals are characterized by lower carbonate and higher clay/silt and organic carbon concentrations. Such compositional contrasts between light and dark intervals are more pronounced at Site 1007 than at Site 1006.

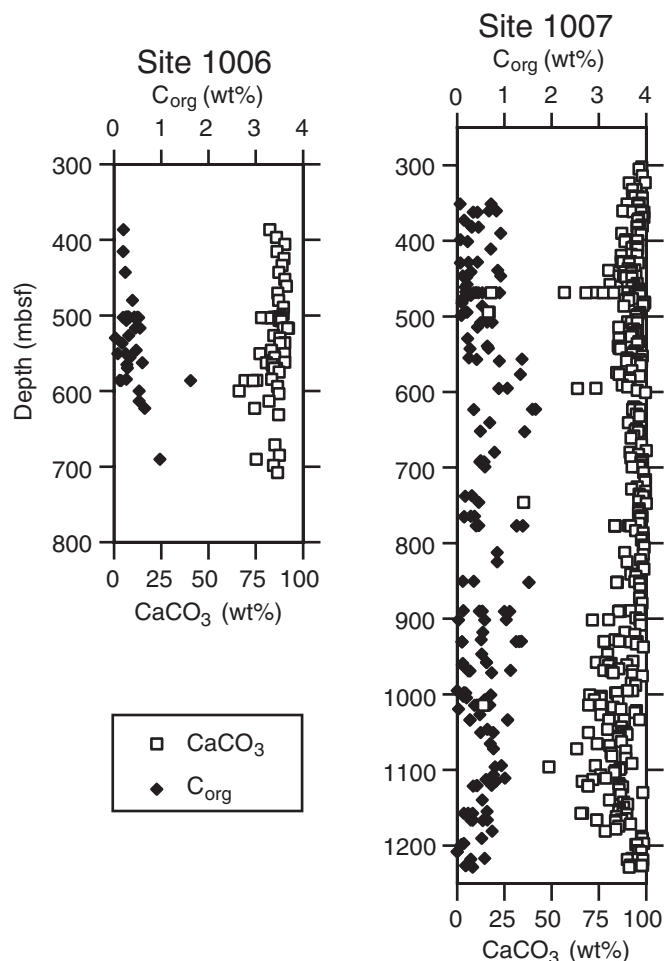


Figure 1. Downcore variation in inorganic ( $CaCO_3$ ) and organic ( $C_{org}$ ) carbon concentrations at Sites 1006 and 1007.

## Carbonate Mineralogy

Quantitative carbonate mineralogy was determined by X-ray diffraction using the methods outlined in Eberli, Swart, Malone, et al. (1997). Analytical precision is within 5% of the actual weight percent, with a standard deviation of ~3%. The carbonate mineralogy at Sites 1006 and 1007 is dominated by LMC with lesser amounts of aragonite and dolomite (Fig. 2). Aragonite contents at Site 1006 are relatively uniform and range from 15 to 35 wt% between 450 and 550 mbsf and to <15 wt% at deeper depths. At Site 1007, aragonite contents in the Miocene section are generally <10 wt%, with spikes as high as 40 wt%. No aragonite was detected below ~1000 mbsf at Site 1007. Elevated aragonite contents at Site 1007 correspond to lower carbonate contents and increased concentrations of acid-insoluble residues (e.g., clays and silts). Aragonite concentrations at Site 1006 are relatively uniform and show little correlation with clay, silt, and organic matter contents. Dolomite contents at Site 1006 are consistently below ~5 wt%. At Site 1007, dolomite contents range to slightly higher concentrations (average 10 wt%) with occasional spikes as high as 40 wt%.

## Trace Metal Geochemistry

Concentrations of Ca, Ba, Fe, Mg, Mn, and Sr in the carbonate fraction of selected samples over a 100-m interval at Site 1006 and throughout the core at Site 1007 were determined using inductively coupled plasma-atomic emission spectrometry. In preparation for analysis, ~25 mg of sample was reacted in a buffered (pH = 4.4), ~6% acetic acid solution. The insoluble, noncarbonate fraction was subsequently removed by filtration and dried overnight in a 50°C oven. The amount of carbonate in each sample was calculated as the difference between the dry weights of the original sample and the filtered,

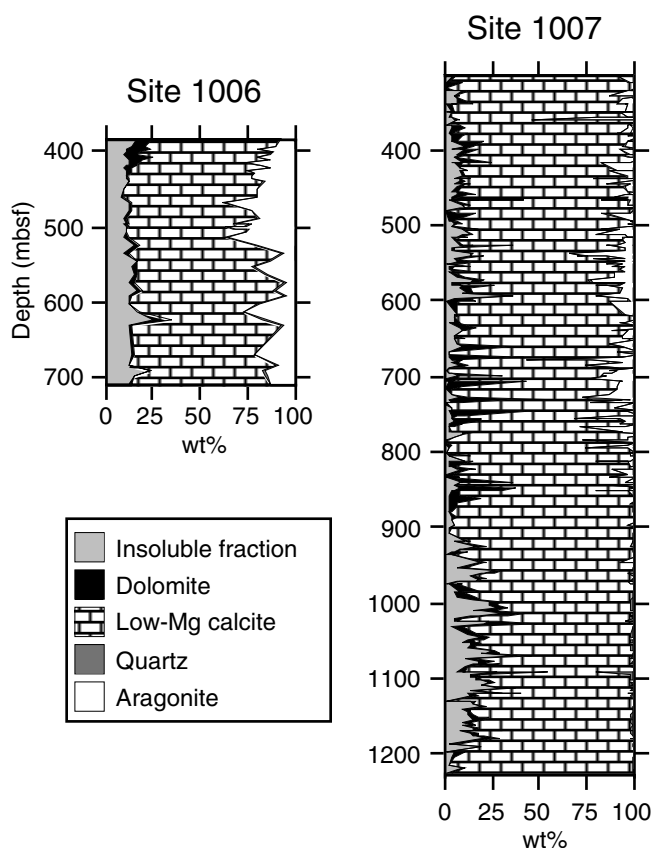


Figure 2. Downcore variation in mineralogy at Sites 1006 and 1007.

insoluble fraction. To avoid any uncertainties associated with weighing small samples, trace metal (TM) concentrations described below and listed in Tables 1 and 2 are reported relative to the major element, Ca:  $(TM/Ca) \times 1000$ . Analytical precision, determined using gravimetric standards, was  $\pm 2\%$  for Ca,  $\pm 3\%$  for Mg, Sr and Ba,  $\pm 4\%$  for Mn and  $\pm 5\%$  for Fe.

Sr concentrations at Site 1006 average  $14.3 \pm 1.7$  (Table 1). Sr contents are generally lower at Site 1007 (average =  $6.7 \pm 3.8$ ), but exhibit an increase to concentrations as high as 15.2 in the interval spanning ~500–800 mbsf (Fig. 3). Mg concentrations at Sites 1006 and 1007 are virtually identical and, on average, range between 10 and 11 (Table 1; Fig. 3). Ba concentrations at Site 1006 are uniform and average  $0.7 \pm 0.2$  (Table 1). Concentrations of Ba at Site 1007 generally range between 1 and 1.5, but exhibit two downcore increases (Fig. 3). Between 500 and 600 mbsf, contents increase to 4, and between ~1050 and 1200 mbsf, concentrations increase to as high as 5.4 (Fig. 3). Fe and Mn concentrations at Site 1006 are quite variable and, on average, slightly higher than those at Site 1007 (Table 1).

### Stable Isotope Geochemistry

Carbon and oxygen isotope analyses were performed in stable isotope facilities at the University of Michigan (UM) and Pennsylvania State University (PSU). At UM, samples were reacted with anhydrous phosphoric acid at  $73^\circ\text{C}$  in individual reaction vessels of an on-line, automated Kiel-type device coupled to a Finnigan-MAT 251 mass spectrometer; whereas at PSU, samples were reacted at  $90^\circ\text{C}$  in an automated carbonate device (common acid bath) coupled to a Finnigan-MAT 252 mass spectrometer. Duplicate sample analyses reveal no laboratory-dependent trends in measured compositions. Carbon and oxygen isotope ratios are reported in parts per thousand (‰) relative to the Vienna Pee Dee belemnite standard (Tables 1, 2). Precision is better than  $0.05\text{‰}$  for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values and was monitored through multiple analyses of National Bureau of Standards 19 and other powdered calcite standards. A comparison of isotopic data

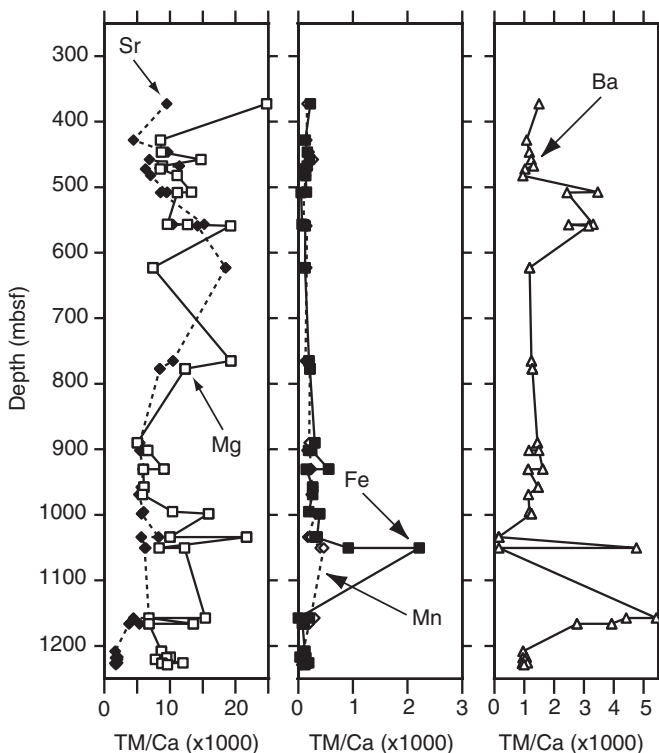


Figure 3. Downcore variation in Mg, Sr, Fe, Mn, and Ba concentrations in the carbonate fraction at Site 1007. TM = trace metals.

from upper Miocene sections at Sites 1006 and 1007 reveals that whereas  $\delta^{13}\text{C}$  values from both sites are virtually indistinguishable,  $\delta^{18}\text{O}$  values of whole-rock samples from Site 1006 are generally more negative than values of whole-rock samples of equivalent age from Site 1007 (Fig. 4).

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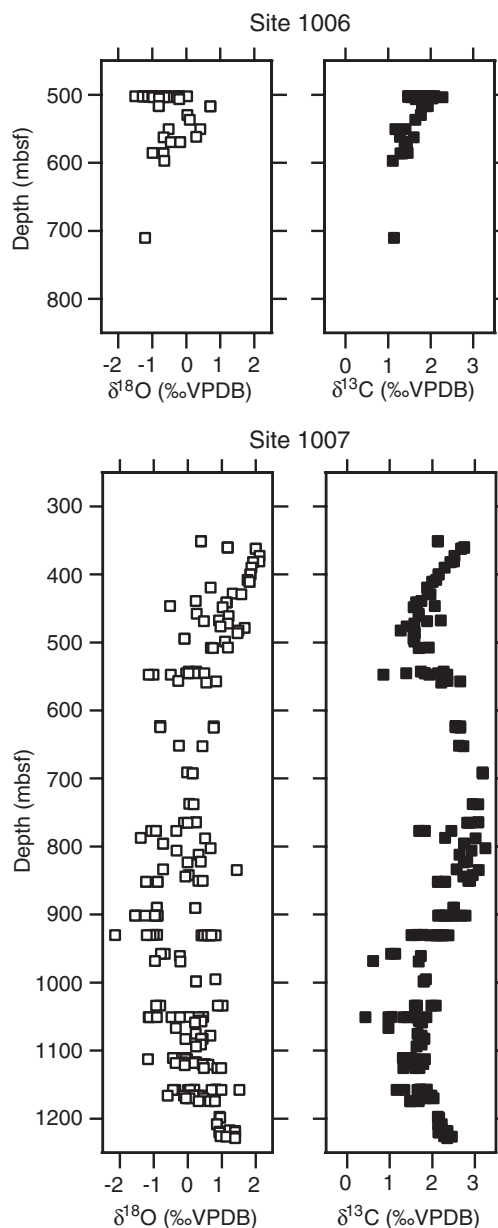


Figure 4. Downcore variation in  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of samples from Sites 1006 and 1007. VPDB = Vienna Pee Dee belemnite standard.

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