

36. MINOR ELEMENT AND STABLE ISOTOPIC COMPOSITION OF THE CARBONATE FINE FRACTION: SITE 709, INDIAN OCEAN

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ABSTRACT

Stable isotopic and minor element compositions were measured on the fine fraction of pelagic carbonate sediments from Ocean Drilling Program Site 709 in the central Indian Ocean. This section ranges in age from 47 Ma to the present. The observed compositional variations are the result of either paleoceanographic changes (past oceanic chemical or temperature variations) or diagenetic changes.

The CaCO₃ record is little affected by diagenesis. From previous work, carbonate content is known to be determined by the interplay of biological productivity, water column dissolution, and dilution. The carbon isotopic record is generally similar to previously published curves. A good correlation was observed between sea-level high stands and high ¹³C/¹²C ratios. This supports Shackleton's hypothesis that as the proportion of organic carbon buried in marine sediments becomes larger, oceanic-dissolved inorganic carbon becomes isotopically heavier. This proportion appears to be higher when sea level is higher and organic carbon is buried in more extensive shallow-shelf sediments.

The strontium content and oxygen isotopic composition of carbonate sediments are much more affected by burial diagenesis. Low strontium concentrations are invariably associated with high values of δ¹⁸O, probably indicating zones of greater carbonate recrystallization. Nevertheless, there is an inverse correlation between strontium concentration and sea level that is thought to be a result of high-strontium aragonitic sedimentation on shallow banks and shelves during high stands.

Iron and manganese concentrations and, to a lesser extent, magnesium and strontium concentrations and carbon isotopic ratios are affected by early diagenetic reactions. These reactions are best observed in a slumped interval of sediments that occurs between 13.0 and 17.5 Ma. As a result of microbial reduction of manganese and iron oxides and dissolved sulfate, it is hypothesized that small amounts of mixed-metal carbonate cements are precipitated. These have low carbon isotopic ratios and high concentrations of metals.

INTRODUCTION

A great deal of work in recent years has been carried out on the reconstruction of Cenozoic ocean temperature and composition from the isotopic and chemical compositions of marine carbonate sediments. Most often, these studies have been based upon the measurement of stable oxygen and carbon isotopic ratios in foraminifers or total carbonate compositions of bulk sediments. Other measurements have included various elemental concentrations in the carbonates (e.g., cadmium, lithium, barium, strontium, magnesium, iron, manganese, sodium, and rare earth elements) and various isotopic ratios (e.g., neodymium and strontium). For some of these parameters, the sources of secular variation are reasonably well understood (e.g., total carbonate, and strontium-, carbon-, and oxygen-isotopic ratios) and useful interpretations can be made from measured data. For many of the measurements, however, especially for many of the minor elements, virtually ad hoc decisions have been made, partly by necessity, as to what processes control their measured variations.

In this study we present minor element and stable isotopic measurements made on a large suite of carefully cleaned samples of the fine fraction of carbonate sediments from Site 709. We propose that the major processes controlling the concentrations of all of the reported elements and isotopes are (1) ancient ocean surface temperature at the time of carbonate precipitation, (2) ancient ocean chemical composition at the time of car-

bonate precipitation, and (3) near-surface or deeper burial diagenesis. All of these processes are important in some cases and, as will be seen, it is often very difficult to deduce the fractional role played by each. Each element or stable isotopic ratio responds differently to each of the forcing variables. For a variety of reasons, we think that a relative ranking of the presently reported parameters in terms of the fidelity of their recording of paleotemperature or paleochemistry (instead of diagenesis) is: CaCO₃ > δ¹³C > strontium > magnesium > iron > manganese > δ¹⁸O. That is, manganese concentrations in carbonates should be a lot more susceptible to diagenetic alteration than total carbonate variations. If minor elemental variations coincide with variations of total carbonate or δ¹³C, then we reason that they may be reflecting true paleoceanographic variations rather than postdepositional changes.

METHODS

Samples at Site 709 were collected with the hydraulic piston corer and the advanced hydraulic piston corer. A total of approximately 220 samples were used in this study. Approximately one g of each sample was treated for 30 min with 30 ml of 3% H₂O₂ in a water bath maintained at 55°C. This procedure disaggregated the samples and oxidized any organic carbon present in the samples. The samples were then wet sieved with deionized water and the fine fraction (<63 μm) was retained. Samples were centrifuged for 30 min and the supernatant liquid was decanted. A reductive cleaning step was performed next with a mixed reagent freshly prepared by combining 40 ml of 0.3 M sodium citrate and 5 ml of 1.0 M sodium bicarbonate. Samples were reacted for 30 min in a water bath at 55°C with 9 ml of mixed reagent plus 0.5 g of sodium dithionite. Samples were then centrifuged and the supernatant was decanted. The samples were rinsed three times with distilled water and centrifuged after each rinse. Finally, the samples were dried and precisely

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weighed subsamples of about 50 mg were dissolved in 50 ml of ammonium acetate-acetic acid (pH = 5.5) solution for about 10 min at room temperature. The samples were centrifuged for 30 min and the supernatant liquid was saved for analysis.

All elemental analyses were conducted with standard methods using a Perkin Elmer Model 5000 atomic absorption spectrophotometer. Replicate analyses indicate the following relative errors: 1.7% for CaCO₃, 2.2% for strontium, 3.4% for magnesium, 6.4% for manganese, and 24.4% for iron. Since typical instrumental errors are about 1%–2% for all elements, it is clear that sample heterogeneity is responsible for the large uncertainties in manganese and iron determinations. Uncertainties in CaCO₃ determinations are included in all the other elemental data.

Stable isotopic analyses were performed on fine-fraction samples that had been treated in exactly the same fashion as the samples for elemental analysis (except for the final dissolution step). Carbon and oxygen isotopic analyses were conducted with phosphoric acid dissolution using an automated on-line device reacting at 90°C for 10 min. Extracted CO₂ was analyzed on a MAT 251 stable isotope ratio mass spectrometer at the University of Miami. All results are reported relative to the PDB standard. External error, determined by analyses of 20 replicate samples, is ±0.026‰ for δ¹⁸O and ±0.016‰ for δ¹³C.

Sample ages were derived from nannofossil zonation and the ages for the zonal boundaries are presented in Shipboard Scientific Party (1988a, table 3). Within the zones, ages were determined by interpolation assuming constant sedimentation rates.

RESULTS AND DISCUSSION

All of the chemical and isotopic results from this study are presented in Table 1. The most relevant data are shown in Figures 1 through 7.

Carbonate Contents

Carbonate contents of the sediments are shown in Figure 1. The vast majority of samples have carbonate contents greater than 80%, making them suitable for this study. These data compare quite well with the carbonate determinations of bulk samples shown in Shipboard Scientific Party (1988b, p. 486, fig. 20). Major features include a carbonate low around 47 Ma, an increase in carbonate from 47 to 31 Ma, and two carbonate highs at 31 and 26 Ma with an intervening low at 29 Ma. There is a carbonate low at 20 Ma followed by a high centered at 18 Ma. This is followed by an interval of slumping between approximately 13.0 and 17.5 Ma (Shipboard Scientific Party, 1988b, p. 468); within this interval there are two discrete fluctuations of carbonate content. Each is associated with a slump block. The carbonate contents are thought to be repeats of the top of the underlying, non-slumped interval. Since 13 Ma, fluctuations have been somewhat smaller with a significant carbonate low showing up around 10 Ma (seen much better in the data of Shipboard Scientific Party, 1988b) and a carbonate high around 5 Ma. There appears to be some correlation between the overall sedimentation rate and the carbonate content (higher sedimentation rates are associated with higher carbonate contents), but the sedimentation rates are not very well constrained at this resolution.

Carbon Isotopes

Carbon isotopic data are shown in Figure 2. This record is similar to the carbon isotopic compositions of bulk carbonate sediments of the same age at Deep Sea Drilling Project (DSDP) Sites 525 and 528 reported by Shackleton and Hall (1984) and Shackleton (1987). The first-order features of both data sets are: high, positive values of δ¹³C from 47 to about 20 Ma, low or negative values at present, and a period of decrease of δ¹³C

from 10 Ma to the present. One notable feature, different from previously published curves is the 1.6‰ decrease in δ¹³C in the early Miocene. Because this decrease is coincident with large increases in iron, manganese, and magnesium, however, we think that it is produced by a diagenetic process that occurs during slumping (discussed below). It should be noted that the isotopic change is also coincident with a sharp decrease in the carbonate mass accumulation rate (Peterson and Backman, this volume) at neighboring (non-slumped) sites.

It is evident that there is also fine structure in the carbon isotopic record at Site 709. Before 20 Ma there are about five isotopic excursions, each lasting about 5 m.y. There are two major positive excursions in this period. These occur during the early Oligocene (about 32 Ma) and just after the Oligocene/Miocene boundary (about 23 Ma). There are three major negative excursions in the same period. They are centered at about 36 Ma (near the Eocene/Oligocene boundary), 30 Ma, and 26 Ma.

Shackleton (1987) interpreted the decrease in the δ¹³C of bulk carbonate sediments since the middle Miocene as a global oceanic signal reflecting a long-term decrease in the amount of organic carbon buried in sediments. Similarly, the positive excursions before 20 Ma may represent shorter time periods of globally increased burial of organic carbon. Vincent and Berger (1985) identified a positive carbon isotopic excursion of about 1 per mil lasting about 4 m.y. centered on 15.5 Ma (also observed by Shackleton, 1987). This shift was seen in both benthic and planktonic foraminifers and thus is considered to reflect a global oceanic change. Vincent and Berger (1985) suggested that this shift was produced by the increased burial of organic carbon beneath regions of high productivity. At Site 709 there is a positive isotopic excursion of about 1 per mil in about the same time interval, although because of the slumping in the 13–17.5 Ma interval at this site, the exact stratigraphic position of this isotopic peak is unknown.

One of the most obvious means of increasing the amount of carbon buried in marine sediments is to increase the area of shallow-water sedimentation by eustatic sea-level rise. Positive δ¹³C excursions, therefore, should be associated with high eustatic sea levels. This prediction seems to be borne out in applying the Cenozoic eustatic sea-level cycle chart of Haq et al. (1987) converted to the Leg 115 time scale. High sea-level stands occurred from 50 to 45 Ma, 42 to 40 Ma, 35 to 30 Ma, 24 to 23 Ma, and 17 to 14 Ma. Each of these intervals, including the excursion discussed by Vincent and Berger (1985), is also a time of higher δ¹³C.

These conclusions must be weighed carefully. Miller and Fairbanks (1985) found quite different timing of "global" carbon isotopic cycles in the Oligocene and Miocene epochs, and they concluded that these cycles were independent of eustatic sea-level changes. Shackleton (1987) concluded that the possible associations between δ¹³C events and sea level could not "be tested adequately until the sea-level record is better known and understood." Shackleton (1987) did not have available to him the chronology and sea-level cyclicity chart published by Haq et al. (1987). In fact, since the Paleocene, there does seem to be coincidence between sea-level highstands (Haq et al., 1987) and Shackleton's (1987) positive δ¹³C excursions.

Strontium

Strontium concentrations of ancient marine carbonate sediments were measured previously by many workers. It has been proposed that these concentrations were influenced by several factors, including leaching of strontium from noncarbonate sources during sample preparation, variations of the oceanic ratio of dissolved strontium-to-calcium (Sr/Ca) (e.g., Graham et al., 1982; Renard, 1986), variations of oceanic temperature (Kinsman, 1969), and diagenesis (e.g., Baker et al., 1982). We think

Table 1. Elemental and stable isotopic compositions of fine fraction samples from Site 709.

Core, section	Depth (mbsf)	Wt (mg)	CaCO ₃ (mg)	CaCO ₃ (wt%)	Sr (ppm)	Mn (ppm)	Fe (ppm)	Mg (ppm)	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Age (Ma)
115-709A-											
1H-1	0.98	49.8	44.77	89.90	1798	268	480	905	0.35	-0.20	0.11
1H-2	2.48	50.0	43.77	87.54	2011	217	605	685	0.13	-0.60	0.27
1H-3	3.98	50.8	44.77	88.13	2122	212	681	748	0.41	-0.02	0.37
1H-4	5.48	50.8	47.27	93.05	2084	159	635	497	1.09	-0.09	0.46
1H-6	8.48	50.0	43.39	86.79	2063	311	553	772	-0.22	-0.38	0.79
1H-7	9.88	50.9	41.02	80.58	2048	280	549	987	-0.39	-0.11	0.95
2H-1	11.08	49.9	39.64	79.44	2220	202	744	757	0.25	-0.50	1.08
2H-2	12.58	49.0	41.39	84.47	2029	387	640	858	0.61	-0.45	1.25
2H-3	14.08	50.9	44.14	86.72	1994	284	544	872	0.25	-0.25	1.42
2H-6	18.58	49.3	43.02	87.26	1953	372	802	872	0.22	-0.13	1.94
3H-1	20.68	49.7	41.64	83.79	2233	276	516	949	0.22	-0.03	2.14
3H-2	22.18	50.6	44.14	87.24	1710	204	510	770	0.32	0.09	2.28
3H-3	23.68	50.0	43.77	87.54	2011	366	765	982	0.48	-0.77	2.42
3H-4	25.18	50.8	40.64	80.00	1858	381	554	1316	-0.23	-0.32	2.56
3H-5	26.68	50.4	42.39	84.11	2076	295	401	1050	0.21	-0.58	2.70
3H-6	28.18	50.5	43.02	85.18	2080	321	337	872	0.40	-0.41	2.83
4H-1	30.38	50.0	30.63	61.28	2742	457	212	1290	0.28	-0.58	3.04
4H-2	31.88	50.0	32.64	65.28	2803	444	276	1103	0.31	-0.53	3.18
4H-3	33.38	51.0	33.01	64.73	2545	515	197	1091	0.34	-0.94	3.32
4H-4	34.88	49.8	42.77	83.86	1847	444	281	982	0.38	-0.29	3.46
4H-5	35.8	49.9	41.02	82.20	1792	414	219	1110	-0.16	-0.50	3.54
6H-1	49.68	50.0	44.14	88.29	1869	261	295	997	0.64	0.19	4.40
6H-1	49.68	50.1	43.77	87.36	1919	274	331	1017	0.64	0.19	4.40
6H-1	49.68	49.3	45.14	91.27	1783	255	354	964	0.64	0.19	4.40
6H-1	49.68	50.3	45.52	90.49	1812	253	286	956	0.64	0.19	4.40
6H-2	51.18	50.7	45.89	90.52	1830	240	490	904	0.00	0.04	4.49
6H-3	52.68	50.0	45.52	91.04	1845	242	319	923	0.54	0.17	4.58
6H-4	54.18	50.5	45.52	90.14	1692	297	406	1033	1.04	0.59	4.66
6H-5	55.68	51.0	45.14	88.52	1706	244	476	1008	0.21	-0.33	4.73
6H-6	57.18	50.7	45.14	89.04	1750	277	476	997	0.56	0.07	4.81
7H-1	59.28	49.7	43.77	88.06	1759	308	605	1040	0.82	0.27	4.91
7H-2	60.78	50.7	43.77	86.33	1805	286	583	1040	-0.01	-0.21	4.99
7H-3	62.28	50.9	44.77	87.95	1843	265	447	994	0.35	-0.15	5.17
7H-4	63.78	49.9	44.77	89.72	1843	279	380	905	0.56	0.04	5.14
7H-5	65.28	49.5	42.02	84.88	1880	297	345	952	0.81	0.15	5.22
7H-6	66.78	49.9	42.02	84.20	1999	286	535	940	-0.05	-0.40	5.30
8H-1	68.98	51.0	45.14	88.52	1861	266	354	853	0.80	0.31	5.41
8H-2	70.48	49.0	43.02	87.79	1953	291	395	872	0.62	-0.39	5.49
8H-3	71.98	50.6	46.14	91.19	1669	314	553	1084	0.66	0.69	5.56
8H-4	73.48	50.5	44.14	87.41	1869	272	510	997	0.30	0.03	5.64
8H-5	74.98	51.0	46.14	90.48	1550	271	347	1062	1.01	0.16	5.72
8H-6	75.48	50.0	43.02	86.03	1755	209	523	930	0.54	-0.30	5.74
9H-1	78.58	49.2	43.77	88.96	1634	286	388	1112	0.28	0.28	5.90
9H-2	80.08	50.9	42.77	84.02	1847	257	304	1040	0.61	0.23	5.98
9H-3	81.58	51.0	44.14	86.55	1824	227	272	952	1.04	0.20	6.06
9H-4	83.08	50.9	45.14	88.69	1673	244	410	1019	0.65	0.24	6.13
9H-5	84.58	50.0	43.02	86.03	1999	174	395	860	0.58	-0.30	6.21
9H-6	86.08	49.8	44.52	89.39	1696	225	573	1033	0.50	0.00	6.29
10H-1	88.28	50.9	42.02	82.55	1880	274	607	1047	0.92	-0.03	6.40
10H-2	89.78	50.0	38.27	76.53	2012	284	444	1084	0.78	-0.24	6.48
10H-3	91.28	50.2	42.02	83.70	1797	238	476	1095	0.93	0.03	6.61
10H-4	92.78	51.0	41.39	81.16	1776	302	290	1148	0.81	-0.44	6.77
10H-6	95.78	49.9	42.02	84.20	1916	238	309	976	0.99	-0.81	7.08
10H-7	96.9	50.8	44.52	87.63	1606	303	382	1123	0.77	0.16	7.20
11H-1	97.88	50.7	45.89	90.52	1722	240	436	654	1.09	0.00	7.30
11H-2	99.38	49.8	44.14	88.64	1620	249	419	1053	1.76	0.02	7.46
11H-3	100.88	50.4	43.77	86.84	1599	228	514	1142	0.74	-0.24	7.61
11H-4	102.38	50.0	42.77	85.54	1672	234	526	1076	0.86	0.00	7.77
11H-5	103.88	49.9	42.02	84.20	1749	262	345	1047	1.18	-0.09	7.93
11H-6	105.38	49.9	41.64	83.45	2113	324	516	672	0.99	0.04	8.08
12H-1	107.58	50.3	43.77	87.01	1634	354	297	1051	0.81	0.06	8.31
12H-2	109.08	50.7	43.39	85.59	1613	415	242	1060	1.02	-0.05	8.47
12H-4	112.08	50.5	42.77	84.69	1847	468	245	947	0.97	-0.10	8.77
12H-5	113.58	50.8	41.39	81.48	1691	664	314	1256	0.99	-0.09	9.08
12H-6	115.08	50.3	42.77	85.02	1882	736	281	1052	0.99	0.15	10.06
13H-1	117.18	49.8	42.01	84.37	1881	559	250	964	0.90	-0.23	10.93
13H-2	118.68	49.2	41.39	84.13	1945	568	193	930	1.41	0.01	11.11
13H-3	120.18	50.5	46.52	92.12	1773	645	226	946	1.29	0.47	11.28
13H-4	121.68	49.3	42.39	85.99	1651	720	283	1026	0.95	0.47	11.45
13H-5	123.18	50.5	45.14	89.39	1584	565	177	1063	0.93	0.61	11.62
13H-6	124.68	50.8	45.52	89.60	1768	593	351	1142	0.94	0.45	11.79
14H-1	126.78	50.5	44.14	87.41	1586	510	419	1155	1.56	0.19	12.03
14H-2	128.28	50.0	42.39	84.78	1486	330	342	1345	1.30	0.33	12.20
14H-3	129.78	49.0	42.39	86.51	1522	271	401	1321	1.62	0.23	12.37
14H-4	131.28	50.0	42.39	84.78	1522	201	377	1321	0.77	0.13	12.55
14H-5	132.78	50.0	43.39	86.79	1567	196	369	1129	0.54	-0.04	12.72

Table 1 (continued).

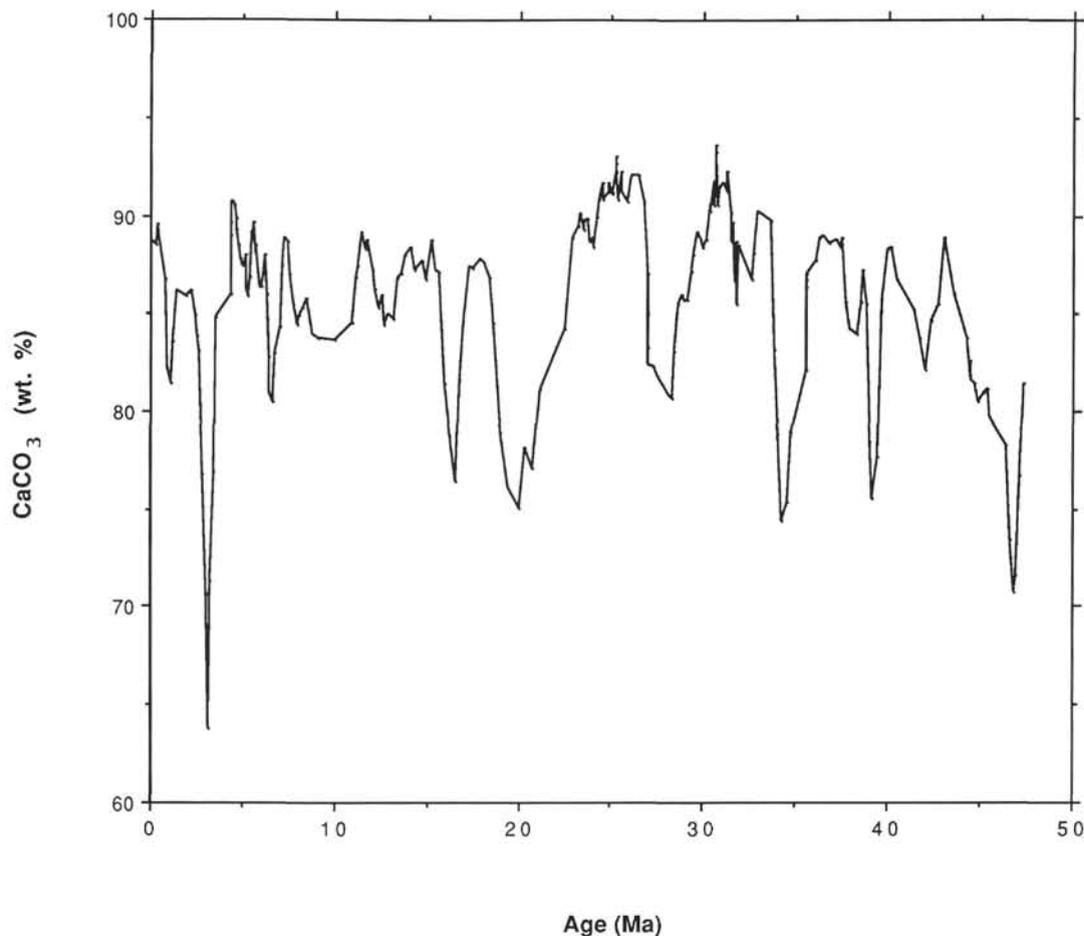
Core, section	Depth (mbsf)	Wt (mg)	CaCO ₃ (mg)	CaCO ₃ (wt%)	Sr (ppm)	Mn (ppm)	Fe (ppm)	Mg (ppm)	δ ¹³ C	δ ¹⁸ O	Age (Ma)
115-709A- (Cont.)											
14H-6	134.28	50.0	40.89	81.78	1492	220	257	1296	0.55	0.04	12.89
15H-1	136.48	49.8	43.02	86.38	1709	232	337	1069	0.55	0.33	13.14
15H-2	137.98	50.0	43.02	86.03	1709	291	279	976	0.37	-0.13	13.36
15H-3	139.48	49.2	43.39	88.20	1613	207	150	1037	0.64	-0.01	13.61
15H-4	140.98	50.8	44.14	86.90	1620	861	272	1405	1.48	-0.07	13.85
15H-5	142.48	50.0	44.52	89.04	1527	752	382	1269	1.56	-0.02	14.10
15H-6	143.98	49.9	44.52	89.21	1651	472	292	1269	1.34	-0.03	14.34
16H-1	146.18	49.6	41.39	83.45	1691	532	447	1474	1.20	-0.18	14.70
16H-2	147.68	49.8	45.14	90.65	1506	521	532	1174	0.90	-0.36	14.95
16H-3	149.18	49.9	43.02	86.21	1709	511	395	1104	0.94	-0.24	15.19
16H-4	150.68	50.0	44.77	89.54	1485	313	380	1195	0.76	-0.03	15.44
16H-5	152.18	50.5	43.39	85.93	1613	346	392	1210	0.45	0.08	15.68
16H-6	153.68	50.0	43.02	86.03	1627	349	395	1186	0.49	-0.04	15.93
17H-1	155.83	49.9	36.14	72.42	2089	789	664	1314	1.32	0.03	16.28
17H-2	157.33	50.0	38.89	77.78	1890	669	437	1234	1.01	-0.16	16.53
17H-3	158.83	50.2	39.64	78.97	1678	568	505	1337	0.75	0.42	16.77
17H-4	160.33	50.1	44.14	88.11	1461	498	419	1201	0.53	0.15	17.02
17H-5	161.83	50.0	43.39	86.79	1567	507	334	1152	0.66	0.13	17.26
17H-6	163.33	50.9	44.52	87.46	1887	494	505	977	1.05	-0.06	17.51
18H-1	165.58	51.0	44.77	87.78	1686	469	447	1061	0.67	0.06	17.88
18H-2	167.08	49.1	43.39	88.38	1740	323	300	1221	0.56	0.50	18.12
18H-3	168.58	50.1	43.39	86.61	1775	876	461	968	0.36	-0.06	18.37
18H-4	170.08	49.1	42.02	85.57	1797	940	190	1000	0.59	0.04	18.62
18H-5	171.58	49.0	39.89	81.41	1617	840	88	1203	0.52	0.19	19.02
18H-6	173.08	49.9	34.89	69.92	2049	946	530	1476	0.79	0.10	19.41
19H-1	175.28	49.6	38.27	77.15	1868	614	562	1228	0.84	0.04	19.99
19H-2	176.78	49.8	38.89	78.09	1980	476	437	1119	0.91	0.08	20.38
19H-3	178.28	50.0	39.64	79.28	2081	555	227	971	1.19	-0.15	20.78
19H-4	179.6	50.8	37.52	73.85	2146	453	27	986	1.22	-0.20	21.12
20H-1	184.88	50.4	45.52	90.31	2010	406	176	780	1.95	0.05	22.51
20H-2	186.38	49.8	44.14	88.64	1790	340	113	895	1.82	0.19	22.91
20H-3	187.88	49.9	43.77	87.71	1805	366	114	971	1.68	0.15	23.26
20H-4	189.38	50.5	46.52	92.12	1849	376	140	849	2.07	-0.02	23.50
20H-5	190.88	49.3	43.39	88.02	1694	403	150	1060	1.78	0.30	23.74
20H-6	192.38	49.7	44.52	89.57	1853	382	180	921	1.80	0.23	23.98
21H-1	194.48	49.5	44.14	89.18	1790	306	113	1008	1.31	0.05	24.32
21H-2	195.98	50.0	46.89	93.79	1951	266	139	864	2.31	0.28	24.56
21H-3	197.48	49.8	44.52	89.39	1774	247	236	1000	1.31	0.02	24.80
21H-4	198.98	50.3	45.52	90.49	1845	253	55	945	1.08	0.10	25.04
21H-5	200.48	49.8	46.52	93.41	1892	215	140	881	1.18	-0.16	25.28
21H-5	200.48	50.1	46.52	92.85	1924	215	140	915	1.18	-0.16	25.28
21H-5	200.48	50.0	45.89	91.79	1918	196	142	904	1.18	-0.16	25.28
21H-5	200.48	49.6	46.89	94.54	1877	192	75	863	1.18	-0.16	25.28
21H-6	201.98	49.7	44.77	90.08	1966	201	235	871	1.34	-0.08	25.54
115-709B-											
21X-1	188.18	50.9	46.14	90.66	1821	271	282	964	1.86	0.36	23.31
21X-2	189.68	49.3	44.14	89.54	1744	396	272	974	1.87	0.14	23.55
21X-3	191.18	50.2	44.77	89.18	1966	357	447	905	2.52	0.17	23.79
21X-4	192.68	49.2	43.02	87.43	1790	232	116	988	1.75	0.50	24.03
21X-5	194.18	50.5	44.77	88.65	1876	391	145	927	1.76	0.17	24.27
21X-6	195.68	50.0	46.89	93.79	1685	299	171	1034	1.69	0.66	24.51
22X-1	197.78	51.0	47.27	92.68	1862	243	106	899	2.03	0.31	24.84
22X-2	199.28	49.9	44.14	88.46	1869	283	113	940	1.56	0.05	25.08
22X-3	200.78	50.7	46.89	92.49	1759	192	277	981	1.26	-0.01	25.33
22X-4	202.28	50.8	46.52	91.57	1924	247	226	946	1.24	0.08	25.59
22X-5	203.78	50.9	45.52	89.43	1966	242	77	923	1.26	0.00	25.85
22X-6	205.28	50.4	45.89	91.06	1918	305	283	981	1.24	-0.14	26.11
23X-1	207.48	50.0	47.89	95.79	1942	115	52	793	1.20	-0.04	26.48
23X-2	208.98	50.9	45.51	89.43	1846	297	264	989	1.23	-0.15	26.74
23X-3	210.48	50.7	44.14	87.07	1948	261	147	986	1.32	0.04	27.00
23X-3	210.48	50.0	42.39	84.78	2029	271	307	1215	1.32	0.04	27.00
23X-3	210.48	50.5	42.02	83.20	2047	274	155	952	1.32	0.04	27.00
23X-3	210.48	50.9	41.64	81.81	2113	300	192	997	1.32	0.04	27.00
23X-4	211.98	49.8	41.02	82.36	2097	305	122	1109	1.19	-0.06	27.25
23X-5	213.48	50.8	42.02	82.71	2178	297	155	964	1.28	-0.04	27.51
24X-1	217.08	50.0	40.27	80.53	2222	372	323	981	1.55	0.10	28.13
24X-2	218.58	49.9	39.64	79.44	2258	290	265	933	1.44	0.20	28.31
24X-3	220.08	50.0	41.02	82.03	2011	268	122	865	1.61	0.13	28.47
24X-4	221.58	50.9	44.77	87.95	2044	313	290	860	1.41	-0.06	28.63
24X-5	223.08	50.2	43.39	86.44	1936	288	150	922	1.21	0.07	28.79
24X-6	224.58	49.8	41.64	83.62	2017	336	312	877	1.13	-0.09	28.95
25X-1	226.78	50.7	44.14	87.07	2186	306	272	770	1.50	-0.17	29.18
25X-2	228.28	50.2	43.39	86.44	1982	323	277	853	1.30	-0.17	29.33
25X-3	229.78	50.9	44.77	87.95	1966	335	78	771	1.01	-0.26	29.49

Table 1 (continued).

Core, section	Depth (mbsf)	Wt (mg)	CaCO ₃ (mg)	CaCO ₃ (wt%)	Sr (ppm)	Mn (ppm)	Fe (ppm)	Mg (ppm)	δ ¹³ C	δ ¹⁸ O	Age (Ma)
115-709B- (Cont.)											
25X-4	231.28	50.0	44.77	89.54	1999	279	268	804	1.26	-0.13	29.65
25X-5	232.78	51.0	45.89	89.99	2146	327	109	752	1.60	-0.29	29.81
25X-6	234.28	50.4	43.77	86.84	1885	343	183	891	1.11	-0.16	29.97
26X-1	236.48	50.4	44.52	88.33	1887	248	146	854	1.40	-0.06	30.20
26X-2	237.98	49.9	45.52	91.22	1615	253	176	923	0.86	0.22	30.37
26X-3	239.48	50.0	46.14	92.29	1669	271	141	878	1.21	0.06	30.54
26X-4	240.98	51.0	46.89	91.95	1791	245	224	832	1.38	0.38	30.70
26X-4	240.98	49.9	45.89	91.97	1754	272	261	795	1.38	0.38	30.70
26X-4	240.98	50.6	47.27	93.42	1745	264	190	772	1.38	0.38	30.70
26X-4	240.98	50.2	47.89	95.41	1681	240	251	773	1.38	0.38	30.70
27X-1	246.08	50.8	46.14	90.83	2059	142	76	715	1.41	-0.05	31.28
27X-2	247.58	49.5	44.77	90.44	1999	190	56	715	1.81	-0.11	31.45
27X-3	249.08	50.7	45.14	89.04	2027	188	266	764	1.89	0.23	31.62
27X-4	250.58	50.0	44.77	89.54	1921	123	78	804	1.53	0.01	31.78
27X-5	252.08	50.0	43.77	87.54	1919	206	297	845	1.96	-0.02	31.95
115-709C-											
26X-1	238.38	49.9	44.14	88.46	1790	283	147	816	1.18	0.09	30.41
26X-2	239.88	49.9	45.89	91.97	1798	251	54	774	1.33	0.01	30.58
26X-3	241.38	50.6	46.14	91.19	1821	217	76	726	1.49	0.04	30.75
26X-4	242.88	50.6	44.77	88.47	1720	246	112	648	1.71	0.55	30.92
26X-5	244.38	50.5	47.89	94.84	2099	209	167	606	1.91	-0.13	31.09
26X-6	245.88	50.3	46.14	91.74	1983	195	173	726	1.67	-0.25	31.26
27X-1	247.98	50.7	44.14	87.07	2152	227	113	759	1.87	0.05	31.49
27X-2	249.48	50.1	43.77	87.36	1919	195	240	777	1.80	0.07	31.66
27X-3	250.98	50.3	43.02	85.52	1953	256	116	802	1.85	0.01	31.83
28X-1	257.68	50.3	42.02	83.53	1880	381	190	1069	1.14	0.05	32.58
28X-2	259.18	50.6	46.14	91.19	1712	368	141	899	1.33	0.12	32.75
28X-3	260.68	49.9	44.77	89.72	1921	223	145	838	1.43	-0.12	32.92
29X-1	267.38	49.9	44.77	89.72	1876	335	112	893	1.28	-0.13	33.67
29X-2	268.88	50.2	45.14	89.93	1949	310	144	820	1.36	-0.25	33.86
29X-3	270.38	49.8	34.89	70.06	2107	502	72	1290	1.20	0.00	34.08
29X-4	271.88	50.0	38.27	76.53	1973	327	170	1202	1.22	0.12	34.30
29X-5	273.88	50.6	38.27	76.53	1921	327	131	1320	1.30	0.25	34.59
29X-6	274.88	50.0	36.51	73.03	1863	370	68	1452	1.53	0.58	34.74
30X-1	277.08	50.2	43.77	87.19	2090	286	57	674	1.26	-0.75	35.62
30X-1	277.08	50.4	43.39	86.10	2063	288	58	807	1.26	-0.75	35.62
30X-1	277.08	49.8	43.02	86.88	2080	267	116	732	1.26	-0.75	35.62
30X-1	277.08	50.0	43.02	86.03	2080	290	151	732	1.26	-0.75	35.62
30X-2	278.58	50.0	44.14	88.29	1461	249	204	1291	1.61	0.50	36.07
30X-3	280.08	50.8	45.14	88.86	1750	244	111	1086	2.10	0.46	36.31
30X-4	281.58	50.0	44.76	89.54	2000	257	179	385	1.28	-0.79	36.55
30X-5	283.08	50.5	44.76	88.65	1486	302	235	530	1.21	-0.26	36.77
31X-1	286.78	50.5	43.76	87.54	1348	263	80	1337	1.51	0.09	37.20
31X-2	288.28	50.0	45.14	90.29	1152	255	55	1495	1.89	0.28	37.38
31X-3	289.78	50.1	43.76	87.36	1348	251	240	1337	1.89	0.18	37.55
31X-4	291.28	50.3	44.77	89.00	1318	279	145	1340	1.78	-0.04	37.73
31X-5	292.78	50.5	40.64	80.48	1550	283	123	1156	1.63	-0.50	37.90
32X-1	296.38	50.0	41.64	83.28	1465	204	216	1189	1.66	-0.03	38.32
32X-2	297.88	50.6	44.14	88.00	1257	193	113	1201	1.69	0.31	38.50
32X-3	299.38	50.0	42.77	85.53	1344	234	117	1356	1.65	0.30	38.67
32X-4	300.88	50.0	44.14	88.29	1337	204	181	1155	1.57	0.00	38.85
32X-5	302.38	50.0	41.39	82.78	1305	157	157	1268	1.80	0.49	39.03
32X-6	303.88	49.9	32.14	64.41	1400	358	109	1633	1.70	-0.34	39.20
33X-1	306.08	49.8	39.64	79.60	1766	214	126	1022	2.06	-0.24	39.46
33X-2	307.58	50.3	44.77	89.00	1206	190	78	1094	1.76	-0.22	39.63
33X-3	309.88	49.8	44.14	88.64	1223	193	79	1303	1.58	0.22	40.00
33X-4	310.58	50.5	44.14	87.41	1144	193	57	1337	1.78	0.23	40.16
33X-5	312.08	50.0	44.51	89.04	1011	90	146	1499	1.85	0.74	40.51
34X-1	315.78	50.5	42.39	83.94	1062	153	118	1510	1.78	0.13	41.36
34X-2	317.28	50.0	41.39	82.78	1123	205	157	1570	1.74	0.22	41.70
34X-3	318.78	50.2	42.39	84.45	1062	177	153	1510	1.60	0.22	42.05
34X-4	320.18	50.0	39.64	79.28	996	189	88	1690	1.70	0.71	42.37
34X-5	321.78	50.0	45.14	90.29	676	122	76	1418	1.65	0.67	42.74
34X-6	323.28	49.9	43.39	86.96	749	196	115	1821	1.72	0.94	43.08
35X-1	325.38	50.0	44.77	89.54	849	145	112	?	1.60	0.17	43.57
35X-3	328.38	50.1	41.02	81.87	841	158	24	1621	1.77	0.16	44.26
35X-4	329.88	49.9	39.89	79.94	953	138	63	1579	1.76	0.33	44.51
35X-4	329.88	50.6	42.02	83.04	904	178	24	1535	1.76	0.33	44.51
35X-4	329.88	50.4	41.64	82.62	949	156	60	1537	1.76	0.33	44.51
35X-4	329.88	49.9	41.02	82.20	926	134	61	1548	1.76	0.33	44.51
35X-5	331.38	49.8	39.89	80.10	990	163	125	1529	1.81	0.25	44.70
35X-6	332.9	50.0	41.02	82.03	792	134	122	1682	1.64	0.47	44.89
36X-1	335.08	50.0	39.64	79.28	820	164	25	1766	1.71	0.52	45.17
36X-2	336.58	50.2	41.02	81.71	926	183	122	1646	1.79	0.31	45.36

Table 1 (continued).

Core, section	Depth (mbsf)	Wt (mg)	CaCO ₃ (mg)	CaCO ₃ (wt%)	Sr (ppm)	Mn (ppm)	Fe (ppm)	Mg (ppm)	δ ¹³ C	δ ¹⁸ O	Age (Ma)
115-709C- (Cont.)											
36X-3	338.08	49.8	41.02	82.36	792	183	61	1646	1.71	0.25	45.55
37X-1	344.88	49.9	37.52	75.18	920	227	93	1546	1.58	0.04	46.41
37X-2	346.38	50.3	38.89	77.32	836	219	64	1736	1.54	0.02	46.60
37X-3	347.88	50.8	34.39	67.69	874	218	29	1634	1.59	0.18	46.79
37X-4	349.38	50.0	33.64	67.28	1026	163	74	1680	1.66	0.34	46.98
37X-5	350.88	50.9	40.64	79.85	886	160	62	1513	1.55	0.33	47.18
37X-6	352.38	51.0	42.39	83.12	637	177	83	1757	1.48	0.60	47.37

Figure 1. Three-point moving average of CaCO₃ (wt%) in the fine fraction of sediments vs. age.

that we can rule out noncarbonate sources of strontium during leaching because of our sample cleaning procedures.

Changes in the Sr/Ca ratio of carbonate sediments can be ascribed either to changes in the distribution coefficient of strontium in calcite (D_c), thought to be primarily caused by temperature changes, or to the Sr/Ca ratio in seawater, $(\text{Sr}/\text{Ca})_{\text{sw}}$:

$$(\text{Sr}/\text{Ca}) = D_c (\text{Sr}/\text{Ca})_{\text{sw}}$$

Experimental work has shown that strontium uptake during nonbiogenic calcite growth is not strongly temperature dependent (Katz et al., 1972; Baker et al., 1982); however, there is conflicting evidence on the importance of temperature dependence on the strontium content of foraminiferal calcite. Delaney et al. (1985) found little correlation between seawater temperature and strontium concentrations in either core-top planktonic

foraminifers or in laboratory-cultured foraminifers. On the other hand, Cronblad and Malmgren (1981) observed large and consistent glacial/interglacial variations of strontium and magnesium in foraminifers from Pleistocene sediments near the Polar Front in the southern Indian Ocean. The positive correlation they observed between warm-water climatic indexes and strontium concentrations in planktonic foraminifers strongly suggests a temperature control on the strontium.

Graham et al. (1982) suggested that strontium concentration variations preserved in ancient sediments may reflect original variations in the Sr/Ca ratio in ancient seawater. On a much larger time scale, Renard (1986) attempted to correlate strontium and magnesium concentration changes in bulk pelagic carbonate sediments from many different localities and ascribed these changes to Sr/Ca and Mg/Ca secular variation in seawater. Recently, Boyle and Keigwin (1982) and Lea and Boyle

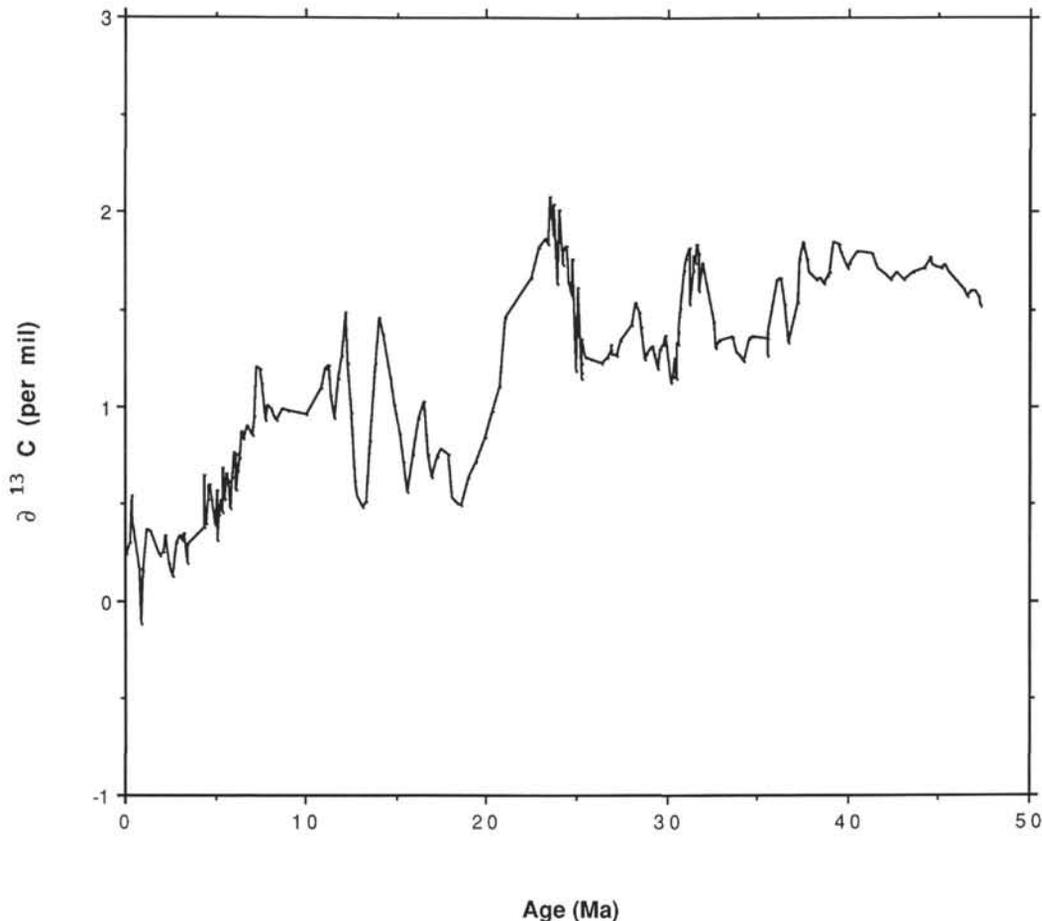


Figure 2. Three-point moving average of the carbon isotopic ratios in the carbonate fine fraction vs. age.

(1989) have convincingly shown that variations in seawater barium and cadmium concentrations are recorded by benthic foraminifers. Although neither strontium nor magnesium show very significant nonconservative behavior in modern-day seawater, past variations in their concentrations, relative to calcium concentrations, can be expected to be recorded by carbonate-producing organisms.

Graham et al. (1982) proposed two major mechanisms for changing oceanic Sr/Ca ratios: (1) variable hydrothermal input of calcium to the oceans at the ridge crests and (2) variable rates of strontium removal resulting from changes in the proportion of high-strontium aragonite vs. low-strontium calcite sedimentation. The ratio of aragonite to calcite should increase during high sea-level stands when more shallow carbonate banks are flooded. Graham et al. (1982) concluded that both processes played important roles in determining Cenozoic Sr/Ca ratios. Delaney and Boyle (1986) concluded that for the past 40 m.y. both Li/Ca and Sr/Ca ratios in foraminifers changed very little and that lack of variability in the Li/Ca ratio implied that there has been no significant variability in oceanic hydrothermal fluxes. They also concluded that over the past 100 m.y. there has been less than a factor of 2 decrease in hydrothermal chemical fluxes. On the other hand, Renard (1986) has reported numerous larger variations of Sr/Ca and Mg/Ca ratios in bulk pelagic carbonate samples and once again attributed these variations to both hydrothermal and sea-level variations.

Increased hydrothermal activity should bring about an increase in oceanic-dissolved strontium but a larger increase in oceanic-dissolved calcium; hence, the Sr/Ca ratio of seawater

should decrease (Palmer and Edmond, 1989). Likewise, increased hydrothermal activity is thought to cause global sea-level rise, in which case more aragonite sedimentation would be expected on shallow shelves and bank tops and the pelagic Sr/Ca of seawater should decrease.

Strontium concentration is a useful indicator of carbonate diagenesis because foraminifers and, especially, nannofossils precipitate calcite that is enriched in strontium relative to equilibrium calcite. During burial diagenesis, some of the biogenic calcite is dissolved and reprecipitated. In the process, strontium is released into the pore fluids (Baker et al., 1982) and diagenesis results in a lower concentration of strontium in older carbonate sediments.

The potential importance of diagenesis in determining the observed strontium concentrations (Fig. 3) can be evaluated with the pore-water strontium analyses for Site 709 reported by Swart and Burns (in this volume). From their data, we can estimate a present-day, near-surface, dissolved strontium gradient of about 4.2×10^{11} mol/cm⁴. Using Fick's Law and a diffusion coefficient in the sediments of about 3×10^{-6} cm²/s, we can calculate a diffusive flux of strontium out of sedimentary pore waters into the overlying seawater of 4.0×10^{-3} mol/cm²/m.y. Compare this to the rate of accumulation of strontium in the sediments (at 75% porosity, 90% CaCO₃, 2100 ppm Sr, 10 m/m.y. sedimentation rate): 1.94×10^{-2} mol/cm²/m.y. (note that this is cm² of pore water). Thus, about 20% of all the strontium that accumulates on the seafloor diffuses back into overlying seawater (and, at the very least, 20% of the carbonate has been recrystallized). However, as shown previously (Baker, 1985; Rich-

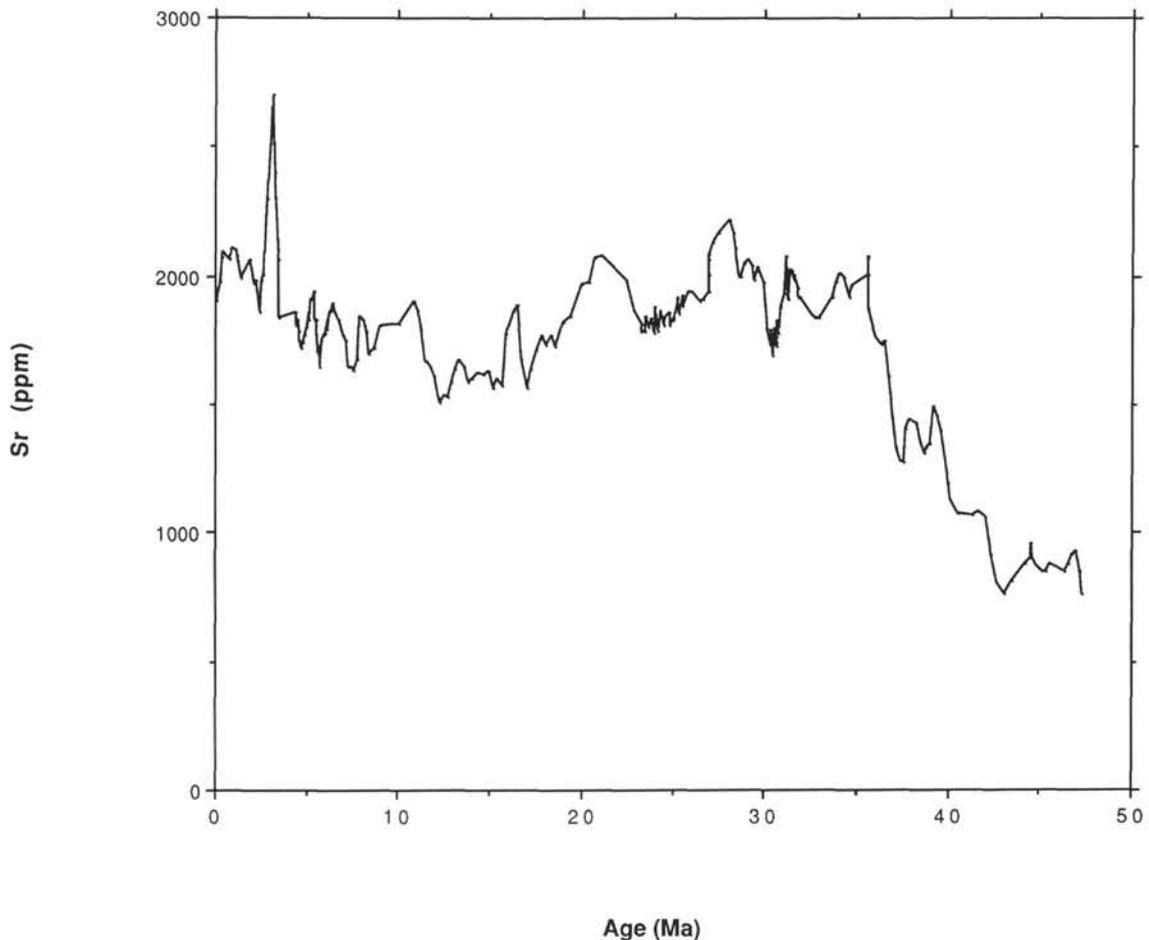


Figure 3. Three-point moving average of the strontium concentrations in the carbonate portion of the fine fraction vs. age.

ter and DePaolo, 1988), this number is probably closer to 50% recrystallized within about 10 m.y. of deposition. Almost all of this strontium is lost from the upper 100 m of sediment, since below this depth there is no observed pore-water strontium concentration gradient (Swart and Burns, this volume). If we assume that the present-day average strontium concentration in the carbonate fine fraction of 2100 ppm was typical of sediments for the last several million years, then these calculations give us the result that after about 7-m.y. (the age at 100 m below seafloor [mbsf]) of diagenesis there should be a decrease to about 1680 ppm. In fact, this is approximately the magnitude of concentration change observed in sediments from 7 Ma to the present.

The factor that seems most likely to change the dissolved strontium gradient out of the sediments and the resulting diagenetic strontium loss of ancient sediments is bottom-water (hence, pore-water) temperature. Temperature can affect the strontium distribution coefficient in calcite and the diffusion coefficient of strontium in sediments, but the most thermally activated process is the rate of calcite recrystallization. For example, assuming that a 10°C rise in bottom-water temperature can produce a doubling of the rate of calcite dissolution and reprecipitation, then we could expect roughly a doubling of the rate of strontium release to the pore waters and a doubling of the diffusive flux of strontium to overlying seawater. The net result should be lower strontium concentrations in the sediments during periods of higher bottom-water temperature.

There is a feedback mechanism to the above-mentioned process. At the present time, calcite produced during diagenesis be-

low 100 mbsf should have about 1160 ppm strontium (given the average Sr/Ca ratio of pore waters observed below 100 mbsf and a distribution coefficient of strontium in calcite of 0.04; Baker, 1985). Clearly, except in the Eocene, diagenetic calcite probably constitutes only about 50% of the total fine fraction (assuming for the moment an original strontium content of 2000 ppm). If rates of recrystallization are sufficiently accelerated, the Sr/Ca ratio of pore waters would be elevated, the diagenetic calcite would have a higher strontium content, and there would be a decreased loss of strontium from the sediments.

In summary, diagenesis has been demonstrably important in influencing the strontium content of the carbonate sediments at Site 709, but original variations of the strontium concentrations of the carbonate, caused by paleotemperature changes or changes in seawater Sr/Ca ratios, could persist. In the simple case where 50% of the biogenic calcite has been replaced by diagenetic calcite of a fixed composition, the original concentration variation would be halved by diagenesis. Accordingly, to crudely deconvolve the strontium curve shown in Figure 3, we should do the following:

1. Fix the modern-day ratio at the observed value.
2. Back to 7 Ma, adjust the observed values for linearly increasing amounts of diagenetic calcite to 50% calcite of 1160 ppm strontium by 7 Ma.
3. Before 7 Ma, any carbonate with greater than 1580 ppm originally had >2000 ppm and any carbonate with <1580 ppm originally had <2000 ppm. If we assume a 50% addition of diagenetic carbonate of 1160 ppm, then the following simple al-

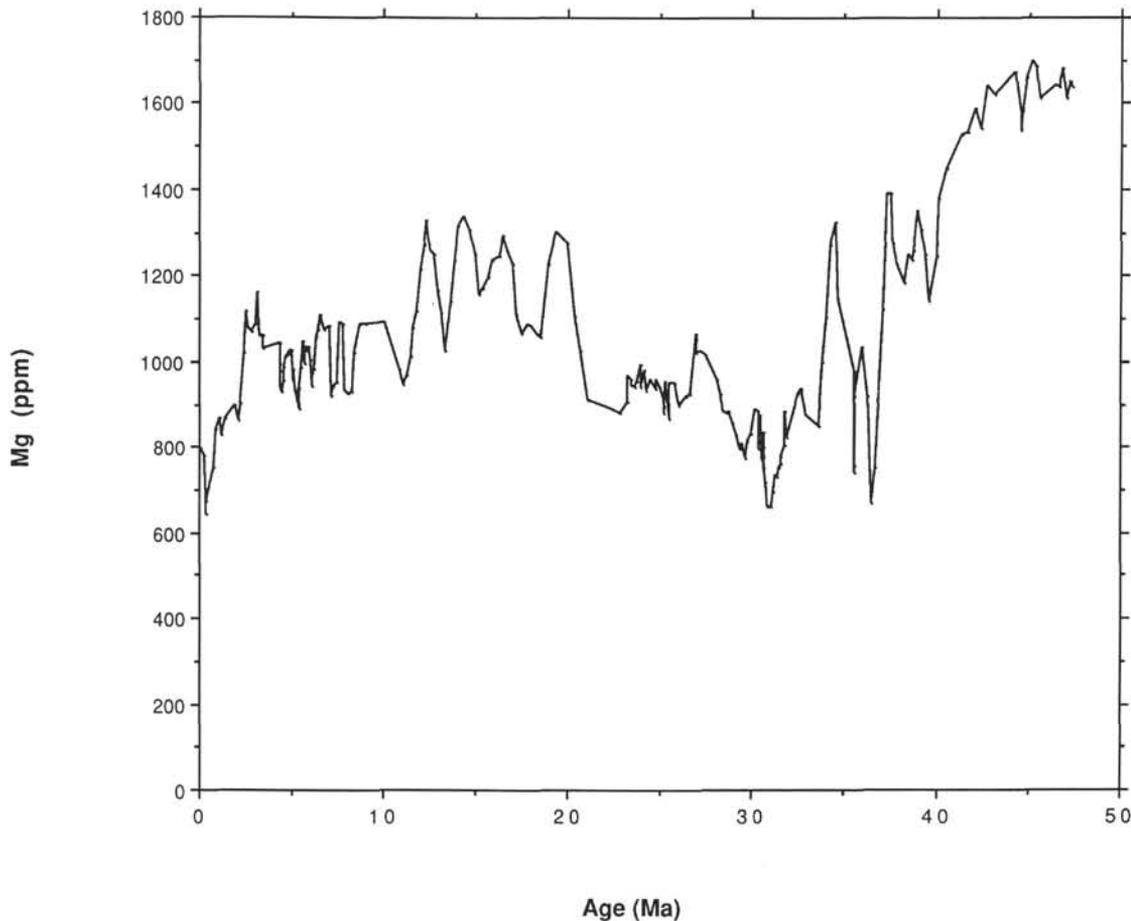


Figure 4. Three-point moving average of the magnesium concentrations in the carbonate portion of the fine fraction vs. age.

gorithm can be used to calculate the original strontium content of carbonate (Sr_i) from the present-day observed value (Sr):

$$2 \times Sr - 1160 = Sr_i \text{ (in ppm).}$$

4. Note that we have not accounted for any variation of rates of diagenetic strontium loss and we have assumed steady-state conditions in the pore waters throughout.

The deconvolved strontium concentration curve (Fig. 8) is quite similar to the results published by Graham et al. (1982) for Sr/Ca ratios of planktonic foraminifers. The most striking feature of both studies, also noted by Renard (1986) and apparent in Delaney and Boyle (1988), is the late Eocene strontium increase. This feature coincides with the late Eocene initiation of the rise in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater (Elderfield, 1986). It also coincides with the decrease in seafloor spreading rates (Pitman, 1978) and the lowering of sea level from middle Eocene highs (Haq et al., 1987).

Elsewhere, strontium concentrations display less dramatic variations, but there seems to be some correlation between high sea level stands and low strontium concentrations, and vice versa. For example, some of the lowest sea levels of the Neogene were thought to have occurred during the middle and late Miocene centered at about 10 Ma. A strontium peak also occurs at this time. Low sea levels in the late Oligocene coincide with high strontium concentrations. Low sea levels in the late Pliocene and Pleistocene coincide with high strontium concentrations.

This implies that sea level is important, but it does not distinguish between the hydrothermal and shallow-water aragonitic causes.

What fraction of the strontium concentration change can reasonably be explained by variations in the aragonite/calcite ratio? This question was originally addressed by Graham et al. (1982) and it is their model, with a minor adaptation, that we apply below to look again at this problem.

The oceanic mass balance for strontium can be written as:

$$dSr/dt = F_D + F_R - F_S,$$

where F is the flux of strontium to the ocean and subscripts D , R , and S represent the diagenetic, riverine, and carbonate sedimentation fluxes of strontium, respectively. The value, F_D , was discussed by Elderfield and Gieskes (1982). As noted by Graham et al. (1982), F_S is given by:

$$F_S = f_A F_A + (1 - f_A) F_C,$$

where F_A and F_C are the sedimentary fluxes of aragonite and calcite, respectively, and f_A is the fraction of aragonite.

Furthermore,

$$F_S = f_A D_A (Sr/Ca)_{sw} J + (1 - f_A) D_C (Sr/Ca)_{sw} J,$$

where J is the burial flux of carbonate sediments. We have assumed values of $D_A = 1.00$ and $D_C = 0.23$ from present-day

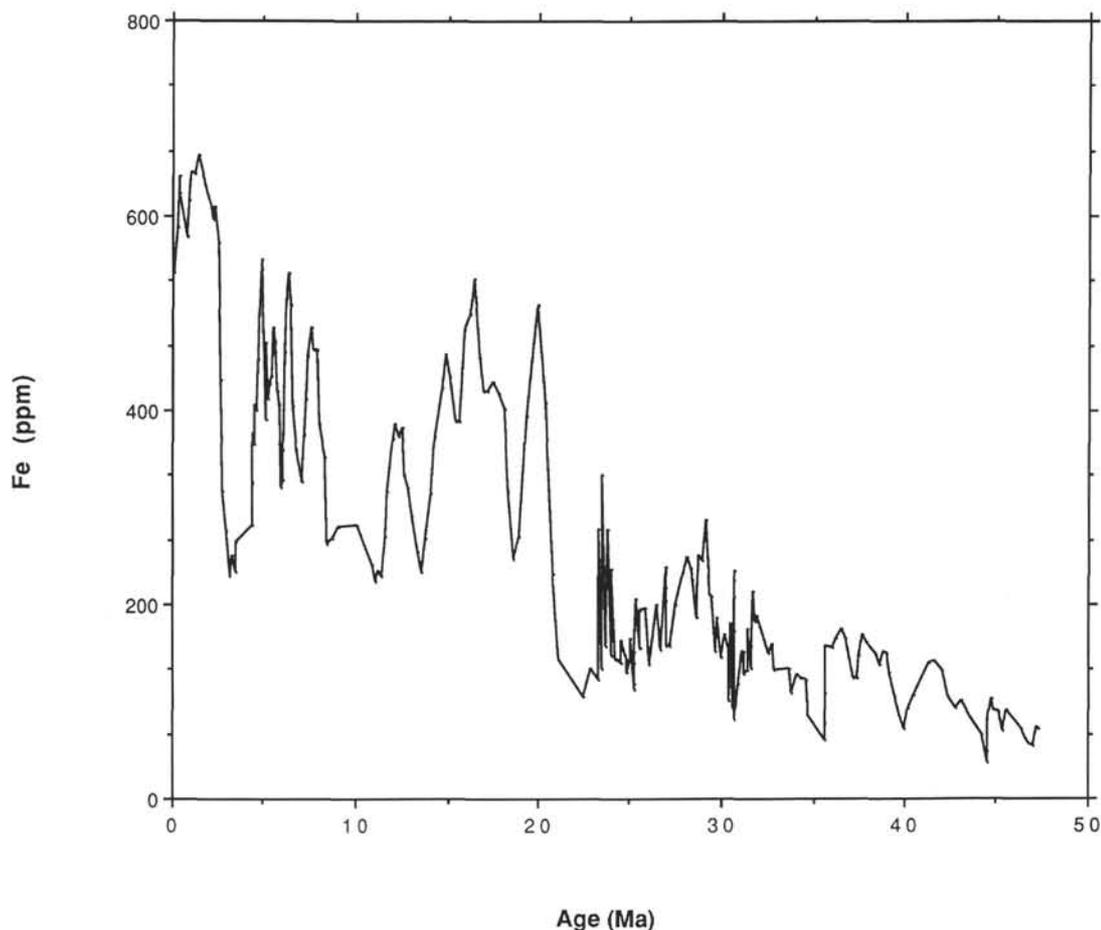


Figure 5. Three-point moving average of the iron concentrations in the carbonate portion of the fine fraction vs. age.

values of the Sr/Ca ratio of seawater, aragonitic benthic green algae and corals, and bulk pelagic carbonate sediments. Here we take

$$F_D = (0.2)D_C(\text{Sr}/\text{Ca})_{\text{sw}}J$$

because, as discussed above, about 20% of the strontium in modern carbonate sediments is returned to overlying seawater (and possibly higher in aragonitic sediments). Then, at steady state

$$F_R/J(\text{Sr}/\text{Ca})_{\text{sw}} = 0.77f_A + 0.184.$$

At the present time,

$$(F_D + F_R)/J = 0.0025,$$

which can be adjusted to make the present-day f_A come out at the most appropriate value. Substituting for F_D , we find that

$$F_R/J = 0.0021,$$

which is very close to the estimate of Delaney and Boyle (1988).

We can assume, for the sake of discussion, that this ratio (F_R/J) has been constant throughout time. This allows us to evaluate independently the importance of changes in f_A :

$$f_A = 0.00273/(\text{Sr}/\text{Ca})_{\text{sw}} - 0.239.$$

The results of this calculation are given in Table 2. One can see that late Eocene values of 1000 ppm strontium ($\text{Sr}/\text{Ca} = .00114$) imply that about 30% of the total CaCO_3 was deposited as high-strontium aragonite. During the late Oligocene sea-level low stand (around 28 Ma), the high values of Sr/Ca imply a value of $f_A = 0$ (i.e., there was no high-strontium aragonite; most shallow carbonate-producing banks must have been sub-aerially exposed). The model is adjusted to make modern values of high-strontium aragonite equal a reasonable value of total CaCO_3 sedimentation.

With regard to strontium concentration variations, we conclude the following. First, diagenesis is clearly of importance in decreasing the strontium concentrations of carbonate sediments. Nevertheless, real paleoceanographically controlled variations are preserved to some degree. The reasonable correlation between high sea-level stands and low strontium values suggests some kind of sea-level control, most likely through a shelf/basin fractionation mechanism. High sea-level stands resulted in larger fractions of aragonitic sediments and less strontium in seawater. As pointed out by Delaney and Boyle (1986), a similar shelf/basin fractionation mechanism can also account for the secular changes observed in the carbonate compensation depth (CCD). Variations in hydrothermal fluxes may also produce changes in the oceanic Sr/Ca ratio, but Delaney and Boyle (1986) concluded that these changes were insufficient to account for more than a fraction of the observed strontium variations. Paleotemperature changes deduced from the oxygen isotopic record are also probably insufficient to account for the observed variations of strontium.

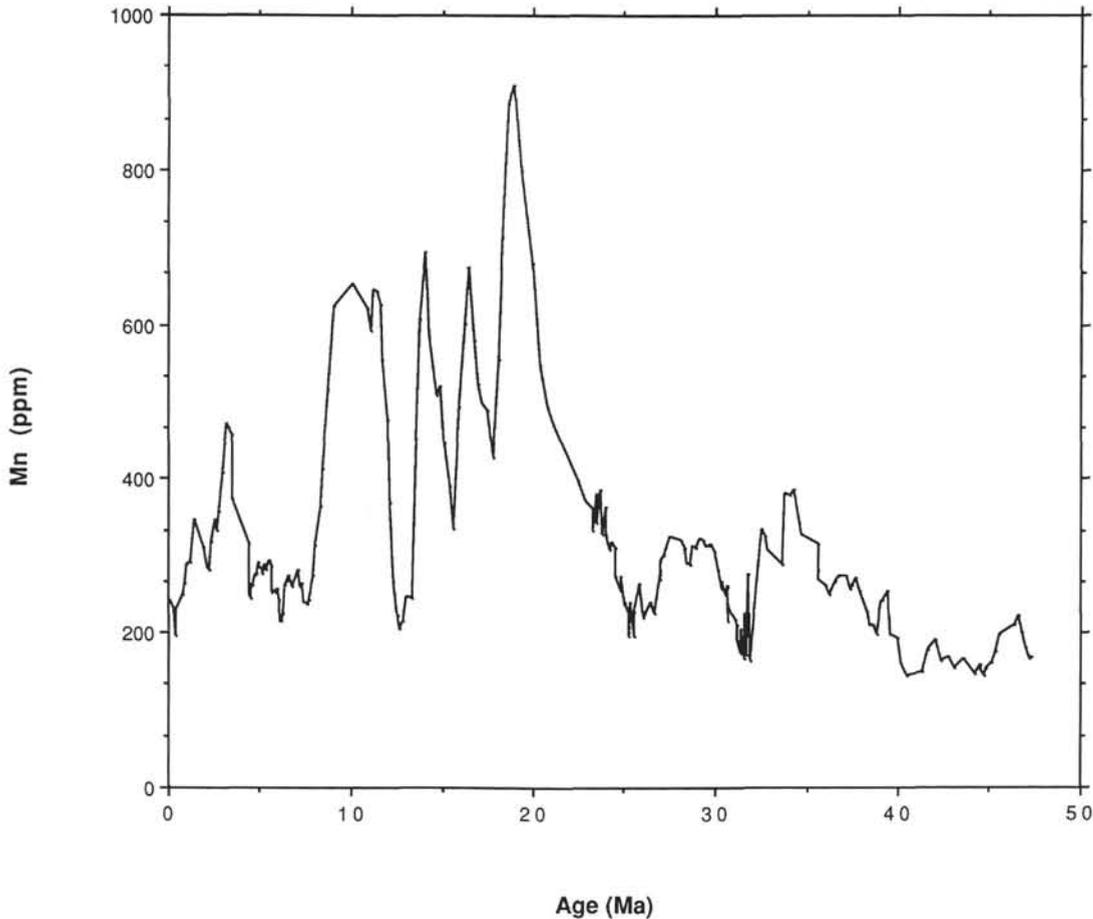


Figure 6. Three-point moving average of the manganese concentrations in the carbonate portion of the fine fraction vs. age.

Oxygen Isotopes

If it is correct, as deduced above, that diagenetic calcite constitutes about 50% of the carbonate sediments, then this should be reflected in the oxygen isotopic composition of the fine fraction. In Figure 9, the approach of the carbonate sediments to apparent oxygen isotopic equilibration with pore waters is illustrated. For the sake of these calculations it was assumed that (1) the $\delta^{18}\text{O}$ of pore waters was constant at 0.0‰ (SMOW) (near the present-day values measured by P. K. Swart, pers. comm., 1989), (2) the bottom-water temperature was 2°C, and (3) the average geothermal gradient at this site was about 35°C/km. The oxygen isotopic fractionation factor was calculated from the equation of O'Neil et al. (1969). From these calculations, we can safely conclude that the course of burial diagenesis throughout the history of Site 709 would have involved an increase in $\delta^{18}\text{O}$ of the carbonate sediments. This is particularly evident if we assume, following Savin (1977), that before 15 Ma the oceans were about 1‰ lower in $\delta^{18}\text{O}$ than at present (of course, the pore waters before 15 Ma also would have been isotopically lighter).

A comparison of the oxygen isotopic data (Fig. 7) with the strontium concentration data (Fig. 3) reveals an inverse correlation: almost invariably, lower strontium values are associated with higher oxygen isotopic compositions. This relationship is most clearly revealed in the Eocene chalks. Because similar coincident variations would be expected to result from temperature

changes (colder temperatures should result in heavier oxygen isotopic ratios and lower strontium concentrations) and diagenetic changes, it is not straightforward to differentiate between diagenetic and paleoclimatic causes for the observed relationship.

Magnesium

The Mg/Ca ratios in carbonate sediments respond to the same factors that influence Sr/Ca ratios, namely, the temperature of precipitation, the Mg/Ca ratio of ancient seawater, and diagenesis. Cronblad and Malmgren (1981) showed an apparent positive correlation between near-surface, ocean-water temperature and magnesium concentrations in planktonic foraminifers. The range of observed concentrations was from about 400 to 800 ppm. Temperature controls, therefore, should bring about a correlation between strontium and magnesium concentrations (which we did not observe). If sea-level changes can cause a secular variation of aragonite/calcite ratios, they should also bring about a similar variation of the ratio high-magnesium calcite/calcite. Because high-magnesium calcite is usually much less abundant in shallow-water carbonate sediments than aragonite, however, these variations would not be very effective in altering seawater Mg/Ca values. Hydrothermal input should have a strong influence on the seawater Mg/Ca ratio and in the same direction as the seawater Sr/Ca ratio. Because of the longer residence time of magnesium than strontium, however, maxima (or minima) in Mg/Ca ratios should follow the maxima (or minima) of Sr/Ca ratios by a few million years (e.g., Renard, 1986),

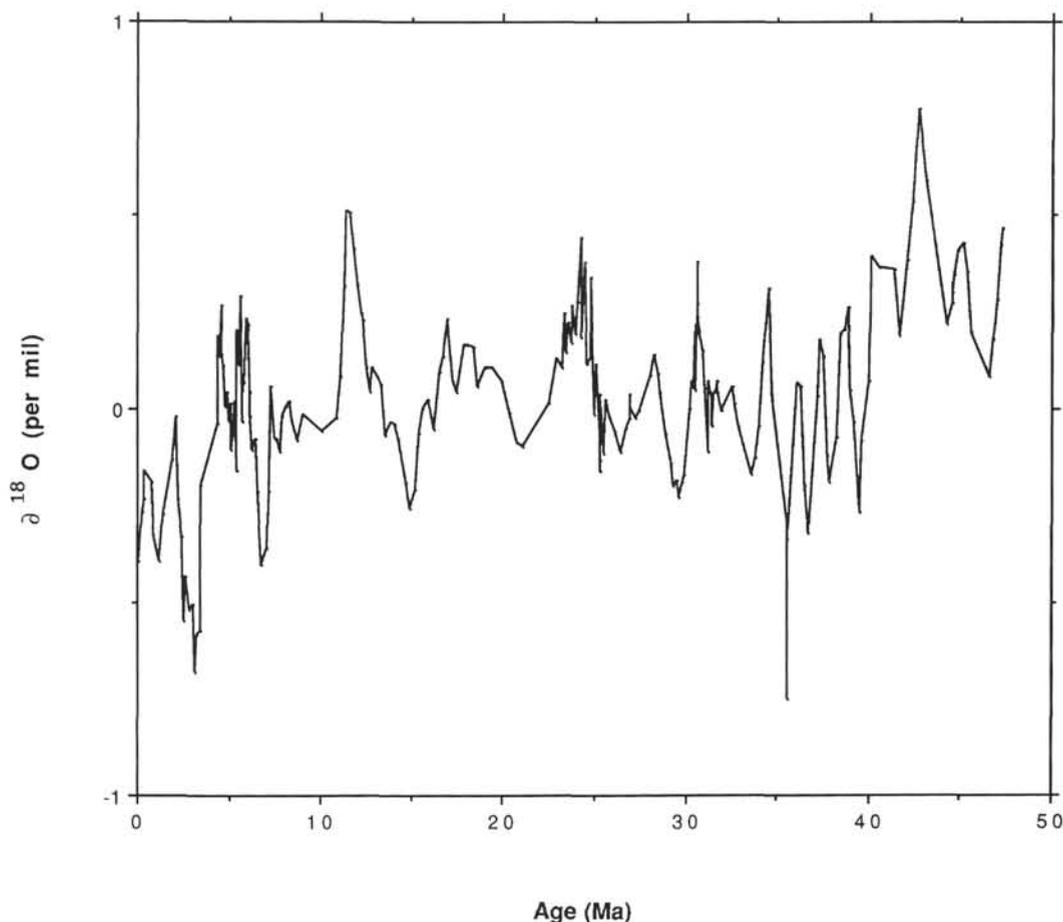


Figure 7. Three-point moving average of the oxygen isotopic ratios in the carbonate fine fraction vs. age.

and variations should generally be positively correlated. Finally, diagenesis should bring about an increase in the Mg/Ca and a decrease in the Sr/Ca ratio of pelagic carbonate sediments (e.g., Baker et al., 1982), thus producing an inverse correlation between strontium and magnesium concentrations.

In comparing Figures 3 and 4, we observe a tendency for strontium and magnesium to be inversely correlated. This is best observed at the top of the core (in the last 3 m.y.) where diagenetic recrystallization of calcite occurs at a maximum rate and near the bottom of the core (from about 35 to 47 Ma). We therefore think that a major portion of the changes observed in the Mg/Ca and Sr/Ca ratios of the carbonate fine fraction are of diagenetic origin. Nevertheless, as mentioned previously, diagenesis should not eliminate original variations; rather, it should only dampen their observed amplitudes.

Iron and Manganese

Iron (Fig. 5) and manganese (Fig. 6) are both transition metals with similar ionic radii and charges; thus, both would be expected to have similar distribution coefficients in calcite. Both elements display variable redox states in seawater and shallow pore waters. Manganese (II) is thought to be the dominant redox state of manganese in seawater (even though it is thermodynamically unstable), whereas iron (III) is thought to be dominant for iron (Bruland, 1983). Neither element is well mixed in seawater. Generally, manganese is more abundant than iron, particularly in surface waters (Bruland, 1983). Both iron and manganese are greatly enriched in pore waters as a result of microbial oxidation of organic carbon. Although low levels of

manganese and iron may be incorporated into biogenic calcite, it seems much more likely that diagenesis will play the greatest role in their incorporation into carbonate sediments. Because manganese is reduced more easily and rapidly than oxidized iron, pore-water maxima of these elements are attained at different sub-bottom depths (e.g., Froehlich et al., 1979). Manganese is also generally more abundant than iron in pore waters (Froehlich et al., 1979; Sawlan and Murray, 1983). At Site 709 there is good evidence for sulfate reduction in the pore waters (Swart and Burns, this volume) and pyrite precipitation in the sediments; hence, dissolved iron concentrations in the pore waters should only be high in the upper few meters of the sediment column.

From the above discussion, we conclude that it is most likely that iron and manganese concentrations in pelagic carbonate sediments are controlled by diagenetic processes. Their microbial reduction allows them to be solubilized and made available for incorporation into reprecipitated diagenetic calcite or perhaps into trace amounts of a mixed iron, manganese, magnesium, and calcium carbonate phase. Because of their slightly different redox chemistries, peak concentrations of these elements in the carbonate phase may be offset in terms of sub-bottom depth, and concentration peaks for both elements may not exactly coincide.

The manganese data (Fig. 6) may be the best means for assessing the nature of the slumping process described by D. Rio and H. Okada (Shipboard Scientific Party, 1988b, p. 468). They determined that the interval between Sections 115-709C-15H-4 (136 mbsf) and 115-709C-18H-3 (164 mbsf) was disturbed. Al-

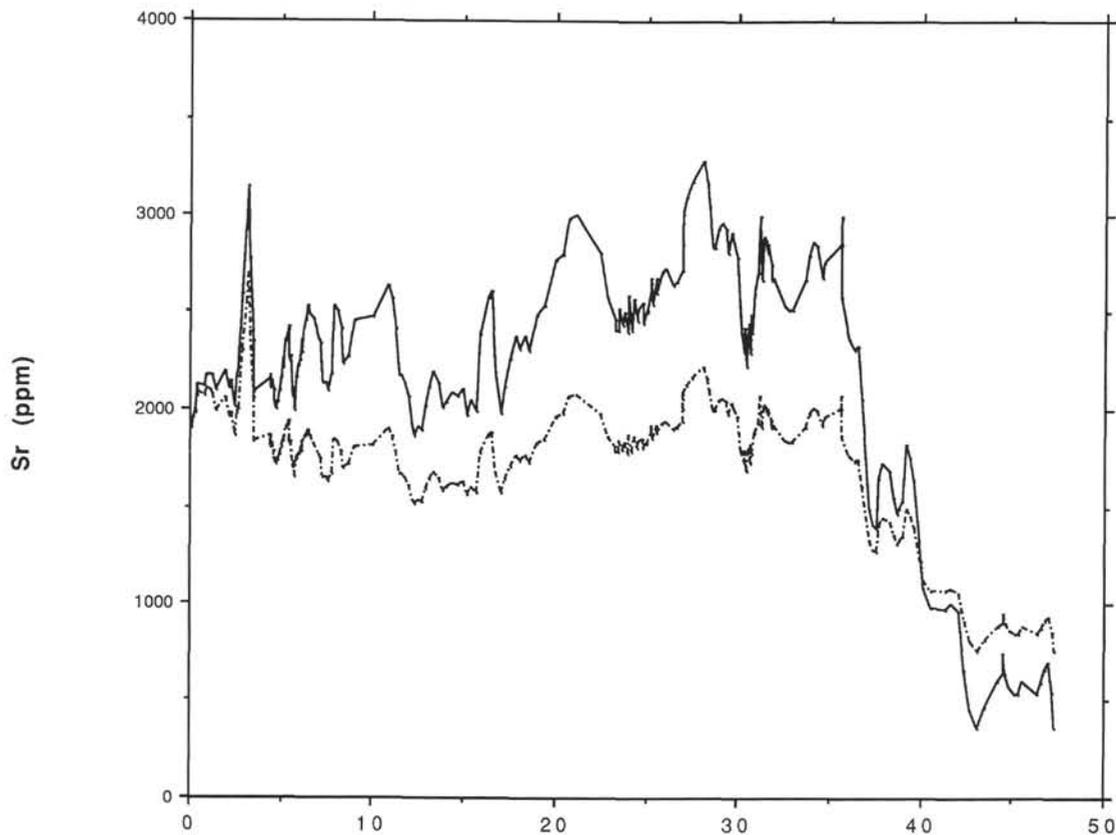


Figure 8. Three-point moving average of the deconvoluted strontium values (line) and strontium three-point moving average (dashed line) vs. age.

Table 2. The aragonitic fraction of the total carbonate sedimentation calculated to be necessary to explain the observed Sr/Ca ratio of pelagic carbonate sediments.

$(\text{Sr}/\text{Ca})_{\text{sw}}$	(Sr/Ca)	f_A
0.0030	0.00069	0.67
0.0050	0.00115	0.31
0.0080	0.00184	0.10
0.0087	0.00200	0.07
0.0100	0.00230	0.03
0.0110	0.00250	0.01

Note: $(\text{Sr}/\text{Ca})_{\text{sw}}$ = the ratio in seawater (0.0087 is the modern-day value); Sr/Ca = the ratio observed in pelagic carbonate sediments; and f_A = the fraction of aragonite of the carbonate sediments.

though the whole interval was stratigraphically disordered, they concluded that individual nannofossil assemblages were coherent. Thus, reworking must have resulted from discrete slump blocks. S. Robinson (pers. comm., 1989; Shipboard Scientific Party, 1988b) used magnetic susceptibility to correlate between

Holes 709A and 709C. From his work, we can place the top of the slumped interval in Hole 709A at about 135 mbsf. Presumably, the bottom of this interval in 709A is at about 163 mbsf. This depth interval corresponds to a time interval from about 13.0 to 17.5 Ma.

We interpret the large increase in manganese concentration (Fig. 6) at 19.0 Ma and subsequent decrease at 18.1 Ma as the top of the intact sedimentary record. This corresponds closely, but not perfectly, with a large iron concentration peak and, importantly, with a sharp decrease in the $^{13}\text{C}/^{12}\text{C}$ ratio. The rapid burial of this sediment by several meters of slumped sediment created an effective barrier to the diffusion of dissolved oxygen into the pore waters and rapidly accelerated the rates of manganese and iron reduction and, possibly, of sulfate reduction. The two following manganese cycles (with peaks at 13.8 and 16.3 Ma in Fig. 6) are interpreted as repeated sequences with similar diagenetic histories. If the enhanced concentrations of manganese, iron, and magnesium actually indicate the precipitation of one or two separate mixed carbonate mineral phases during early diagenesis, these phases would be expected to have very low carbon isotopic compositions. The presence of small amounts of such minerals could explain the associated decreases of $\delta^{13}\text{C}$ over the same depth interval. Two phases are proposed because iron and manganese correlate very closely over the slumped interval, but they do not correlate closely with magnesium and strontium. Small amounts of dolomite were identified in smear slides of sediments from the slumped interval and near the base of the hole from 44.5 Ma to the core bottom.

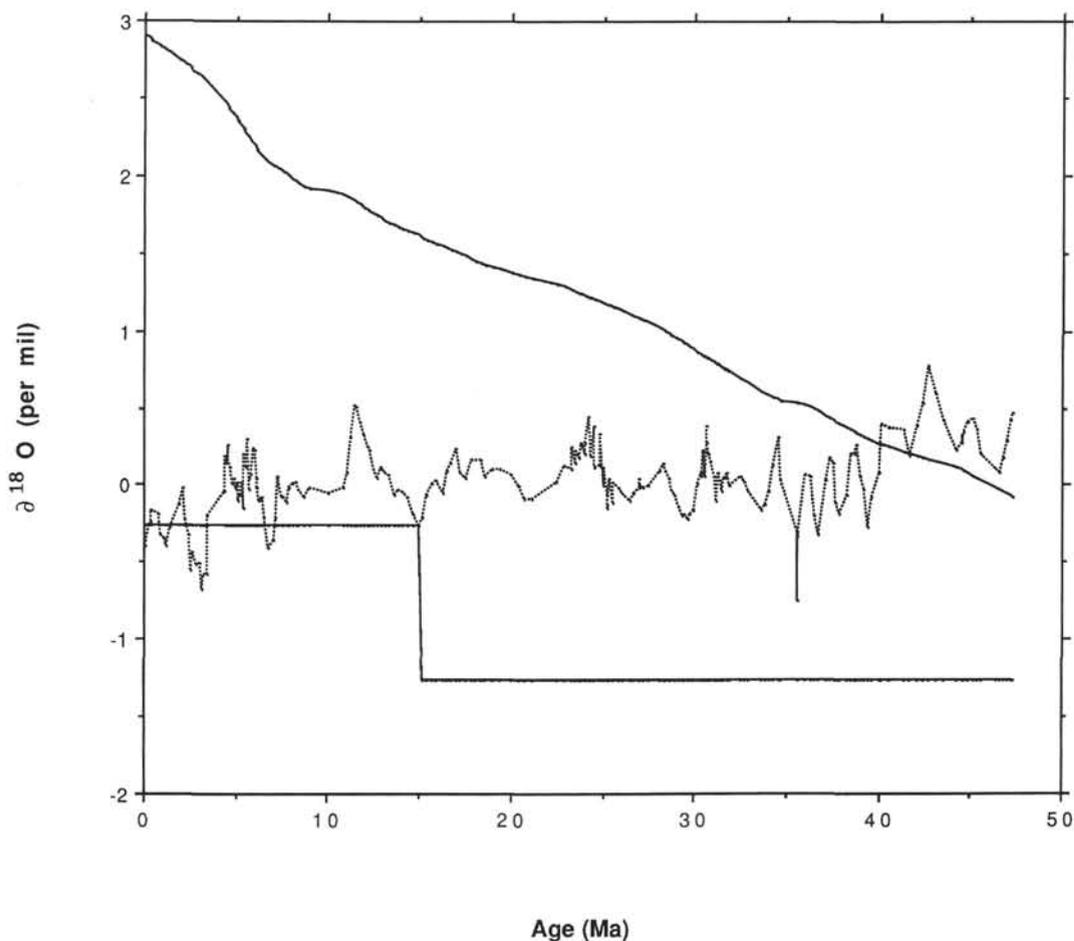


Figure 9. Oxygen isotopic composition of calcite in equilibrium with present-day pore waters, three-point moving average of the oxygen isotopic composition of the carbonate fine fraction (dotted line), and presumed initial isotopic composition of the fine fraction vs. age. See text for further details.

CONCLUSIONS

A quantitative evaluation of the mechanisms involved in producing minor element concentration variations in deep-sea carbonate sediments is not yet possible. Such determinations will require a careful comparison of several sets of chemical data measured on deep-sea carbonate sediments from different oceans and in different environmental settings. Nevertheless, we can draw some useful conclusions from the present study.

A correlation is observed between high sea-level stands and high values of $\delta^{13}\text{C}$. It is suggested that this supports the hypothesis proposed by Shackleton (1987) that $\delta^{13}\text{C}$ is controlled by the fraction of organic carbon that is buried: more organic carbon is buried during high stands and oceanic-dissolved inorganic carbon becomes isotopically heavier. Carbon isotopic changes mirror the long-term (Eocene to Present) decrease in sea level resulting from slower rates of seafloor spreading. Superimposed on this long-term change are several shorter term variations.

There appears to be some correlation between high sea-level stands and high CaCO_3 contents in the sediment (this relationship is discussed more thoroughly elsewhere in this volume). This relationship implies a shelf-basin fractionation mechanism for carbonate accumulation: more carbonate is deposited on the shelves during high stands and the CCD rises.

Because much of the shelf carbonate is aragonite, more strontium is buried during sea-level highstands and oceanic Sr/Ca ra-

tios decrease. As a result, we observed an inverse relationship between sea level and strontium concentration.

Diagenesis plays an important role in many of the observed parameters. Burial diagenesis clearly affects strontium and magnesium concentrations and undoubtedly oxygen isotopic ratios as well. Microbially mediated oxidation of organic carbon in the slumped sediments causes early diagenetic reactions such as reduction of iron and manganese oxides, sulfate reduction, and probably precipitation of mixed carbonate minerals. This causes large variations of iron, manganese, magnesium, and carbon isotopic ratios within the slumped interval.

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