

Oligocene-Miocene strontium isotopes: Stratigraphic revisions and correlations to an inferred glacioeustatic record

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Abstract. This study tests and improves on previously published early and middle Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ marine correlations, presents Sr isotopic age correlations for this interval using the new timescale of *Cande and Kent* [1992], and evaluates Sr isotopic changes against an inferred glacioeustatic proxy. We generated a latest Oligocene to early late Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ isotope record from Ocean Drilling Program (ODP) Hole 747A; this site provides an excellent magnetostratigraphic record during most of this interval for independent age estimates, very good foraminiferal preservation, and excellent core recovery. Comparisons of new $^{87}\text{Sr}/^{86}\text{Sr}$ data from Hole 747A with previously published data from Deep Sea Drilling Project (DSDP) Sites 608 [Miller *et al.*, 1991a] and 588 [Hodell *et al.*, 1991] yield the following results: (1) confirmation and refinement of the early Miocene Sr isotope changes, (2) improved definition of the timing of the changes in slope of $^{87}\text{Sr}/^{86}\text{Sr}$ near 15.4 Ma and 22.8 Ma, (3) improved Sr isotopic age resolution for the middle Miocene with resolution as good as ± 0.7 m.y., and (4) identification of an inflection in the Sr isotope record at 28.0 Ma based on the combined records from DSDP Site 522 [Miller *et al.*, 1988] and ODP Hole 747A. We have been unable to determine the cause of middle Miocene offset between Site 588 and Hole 747A data, although we believe it may be attributed to problems in the age assignments for Hole 588A for the interval ~ 14 –11 Ma and Site 747 for the interval 11–8 Ma. Because Hole 747A results provide a better chronology than Site 588 for most of the Miocene and a better middle Miocene Sr isotope record than Site 608, we propose that Hole 747A serves as the best reference section for Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ variations from ca. 23 to 11 Ma. Using $^{87}\text{Sr}/^{86}\text{Sr}$ data from Sites 522, 608, and 747A, we relate late Eocene to early Miocene inflections in the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope record to oxygen isotope increases and decreases inferred to represent glacioeustatic events. The decreases (deglaciations) observed in the $\delta^{18}\text{O}$ record apparently lead the $^{87}\text{Sr}/^{86}\text{Sr}$ inflections by 1 to 1.5 m.y.

Introduction

Sr Isotopes and Global Change

The Sr isotope ratio in seawater is believed to be uniform at any given time, because the residence time is much longer than oceanic mixing times [Broecker and Peng, 1982]. Foraminifera (and other marine biogenic carbonates) record the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the seawater during the formation of their tests, thereby preserving the ratio in the sediment record, provided that diagenetic alteration has not occurred [Elderfield, 1986]. While the Sr isotope ratio in marine carbonates has increased and decreased throughout geologic history, $^{87}\text{Sr}/^{86}\text{Sr}$ has increased almost continuously since the late Eocene [Burke *et al.*, 1982].

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at a given time is a function of the amount of high $^{87}\text{Sr}/^{86}\text{Sr}$ terrigenous (felsic) detrital flux into the ocean relative to the low $^{87}\text{Sr}/^{86}\text{Sr}$ oceanic (mafic) crustal input, with the weathering of carbonates contributing as a buffering factor [Koepnick *et al.*, 1985, 1988; Elderfield, 1986]. The average $^{87}\text{Sr}/^{86}\text{Sr}$ value of felsic crustal sources is 0.718; mafic intrusives and volcanics (seafloor spreading and ocean/ocean active plate boundaries) average 0.703, and marine carbonate has a value of 0.708 [Elderfield, 1986]. Erosion of marine carbonates has less effect on the temporal variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, because this is limited to the range of average values for this type of material ($0.7067 < ^{87}\text{Sr}/^{86}\text{Sr} < 0.7091$ during the Phanerozoic eon [Burke *et al.*, 1982]).

Enhanced ^{87}Sr fluxes are believed to result from tectonic changes (e.g., increased uplift of continents or changes in seafloor spreading rates) or other mechanisms for increasing continental erosion (e.g., glaciation [Armstrong, 1971; Clemens *et al.*, 1993]), although the ability to distinguish quantitatively between these effects on the $^{87}\text{Sr}/^{86}\text{Sr}$ record has not yet been well established [Raymo *et al.*, 1988; Hodell *et al.*, 1989; Molnar and England, 1990]. Early efforts focused on tectonic controls of $^{87}\text{Sr}/^{86}\text{Sr}$ changes in marine carbonates. For example, Brass

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[1976] suggested that increases in seafloor spreading rates retard the rate of increase, or lower the $^{87}\text{Sr}/^{86}\text{Sr}$ value in marine carbonates, while increases in the weathering rate of continental crust-source rocks increase, or slow a decrease, in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

The $^{87}\text{Sr}/^{86}\text{Sr}$ record cannot be interpreted based strictly on plate-tectonic interactions and associated uplift. Other factors, such as extent and duration of epicontinental seas; topographic relief of land masses; extent, duration, and mineralogy of volcanic eruptions; and paleoclimatic variations (in particular, ice coverage and duration [DePaolo, 1986]) also complicate the interpretation of the $^{87}\text{Sr}/^{86}\text{Sr}$ record. For example, most recent studies have focused on the role of tectonic uplift, particularly of the Himalayas [Raymo *et al.*, 1988; Raymo, 1991; Hodell *et al.*, 1989, 1991; Hodell and Woodruff, this issue]; in contrast, Miller *et al.* [1991a] suggested that there was a relationship between late Eocene to Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ changes and Antarctic glacial history inferred from $\delta^{18}\text{O}$ variations.

The nature of Sr variations through time must be determined in order to evaluate mechanisms for changing oceanic Sr isotopic ratios. In particular, it is critical to evaluate the nature and timing of inflections in the rate of change of $^{87}\text{Sr}/^{86}\text{Sr}$. Such inflections evidently occurred in the early late Eocene [Hess *et al.*, 1986], near the end of the Oligocene [Hess *et al.*, 1989; Miller *et al.*, 1991a] and in the middle Miocene [Miller *et al.*, 1991a; Hodell *et al.*, 1991]. However, the timings of the inflections are poorly constrained, and age estimates differ among these studies by over 2 m.y. because of correlation problems. Our study resolves the timing of the latter two of these inflections. A fourth possible inflection in the Oligocene [Capo *et al.*, 1991] is discussed below. A possible link between the Sr isotope curve and the glacioeustatic record is also suggested, with the $^{87}\text{Sr}/^{86}\text{Sr}$ curve showing marked, sustained increases in slope beginning approximately 1 to 2 m.y. after sea level low stands interpreted from the global $\delta^{18}\text{O}$ record.

Sr Isotopes and Stratigraphy

Strontium isotope ratios provide a correlation technique for marine sediments for certain parts of the Phanerozoic, and high rates of change in $^{87}\text{Sr}/^{86}\text{Sr}$ enable good stratigraphic control for much of the late Eocene to Recent [Burke *et al.*, 1982; DePaolo and Ingram, 1985]. Sr isotope stratigraphy has greatly improved stratigraphic resolution where biostratigraphy is poor or lacking (e.g., the Arctic [McNeil and Miller, 1990] and the Oligocene [Hess *et al.*, 1986]). Changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio must be empirically calibrated to age. Age calibrations require a pristine chronology and diagenetically unaltered marine carbonate. Miller *et al.* [1988, 1991a] suggested that age calibrations should be developed using reference sections with good magnetostratigraphy that provide first-order correlations to the geomagnetic polarity timescale (GPTS). Age calibrations developed using biostratigraphic events alone have inherent errors of at least 0.5 m.y. because of diachronous and geographically restricted ranges and varying taxonomic and stratigraphic interpretations [Miller *et al.*, 1985; Miller and Kent, 1987; Hess *et al.*, 1989]. Miller *et al.* [1988, 1991a] argued that it is preferable to develop a reference section from a single site, because it avoids correlation problems between sections. However, most other studies [DePaolo and Ingram, 1985; Hess *et al.*, 1986; McKenzie *et al.*, 1988; Hodell *et al.*, 1991; Hodell and Woodruff, this issue] have developed composite records from different sites, because no single site contains a complete, unaltered Cenozoic section.

Miller *et al.* [1991a] developed a lower Miocene reference section at North Atlantic Site 608 that has a very good magnetostratigraphic record. The lower Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ record at Site 608 compares well with the lower Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ record at Site 588 [Hodell *et al.*, 1991]. However, the middle Miocene record at Site 608 shows considerable variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ data. Miller *et al.* [1991a] consequently suggested that middle Miocene Sr isotope age estimates developed using Site 608 as a reference section have large errors (± 2.3 m.y. or worse). In contrast, the middle Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ record at Site 588 shows considerably less variation [Hodell *et al.*, 1991]. Middle Miocene Sr isotope age estimates developed using Site 588 as a reference section have smaller errors ($\sim \pm 1.4$ m.y.) [Hodell *et al.*, 1991]. Differences between these studies remain unresolved, and we sought a section to resolve these discrepancies. Ocean Drilling Program (ODP) Hole 747A provides excellent magnetostratigraphic data, good carbonate preservation, and excellent core recovery for the upper Oligocene (~ 27 Ma) through upper Miocene (~ 9 Ma); therefore, it provides an excellent opportunity to test and refine previous Sr isotope studies for this interval.

Methods

Location and Drilling Summary

ODP Hole 747A was drilled on the central Kerguelen Plateau ($54^{\circ}48.68'\text{S}$, $76^{\circ}47.64'\text{E}$, at a present depth of 1962 m) (Figure 1). It is south of the present-day Polar Front, within the Antarctic Circumpolar Current. Hole 747A core recovery was nearly 100% throughout the lower to lower upper Miocene, with significant drilling disturbance and flow-in noted only in cores 5 and 7, sections 1-3, and flow-in occurring in core 9 [Schlich *et al.*, 1989].

Depths presented here for Hole 747A (Table 1) are corrected for core expansion which occurred aboard ship. The length of the recovered sediments for each core as shown in core photographs was considered the "expanded" length of the core (e.g., Core 7H = 9.89 m). The length of the core barrel (9.5 m) was divided by the "expanded" length to obtain an expansion factor (e.g., core 7H = 0.961). ODP depths (those presented by Schlich *et al.* [1989]) for the top of each core were accepted as fixed values (e.g., core 747A:7H top of core = 56.5 meters below seafloor (mbsf)). The initial sample depths or age control depths, as reported by Wright and Miller [1992], were multiplied by the expansion factor to determine a corrected depth.

Sr Isotopes

Samples were washed prior to stable isotope analyses by Wright and Miller [1992]. Samples for strontium isotope analysis were picked from either a greater than 150 μm or greater than 250 μm fraction, with the latter being utilized for samples where preservation quality was uncertain.

Sample aliquots comprised 250 to 500 planktonic foraminifera. Mixed species of planktonic foraminifera were chosen for analysis, because they are less susceptible to diagenesis than the sampling of bulk carbonates [Richter and DePaolo, 1988; Garrison, 1981]. Analyses of monospecific aliquots of Pliocene samples show no species effects on the $^{87}\text{Sr}/^{86}\text{Sr}$ values of fo-

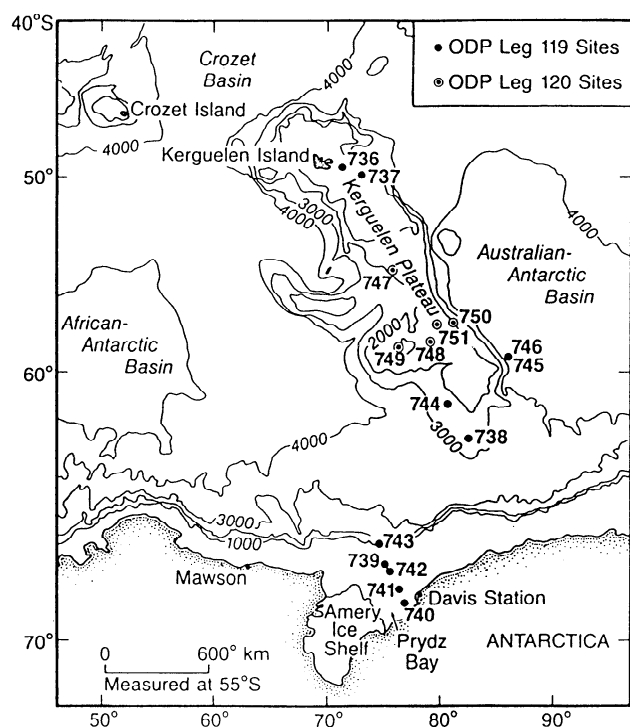


Figure 1. Map showing the location of Ocean Drilling Program (ODP) Site 747 on the Kerguelen Plateau. Other sites from Leg 119 and Leg 120 are also shown.

raminifera (*R. Poore et al.*, 1993, unpublished data). Although bulk carbonate sampling has been used successfully in other studies [e.g., *DePaolo and Ingram*, 1985; *DePaolo*, 1986], this method requires additional screening for diagenesis [*Richter and DePaolo*, 1988].

Samples were sonified for approximately 3 s and rewashed in double-distilled water. Strontium was separated out of the samples by standard ion exchange techniques [e.g., *Hart and Brooks*, 1974] utilizing the ion exchange columns at Rutgers University. Strontium isotope analyses were performed using a VG Sector mass spectrometer at Rutgers. For the development of the Sr age regressions presented, a total of 89 analyses were performed (Table 2), including 16 duplicates. One triplicate sample was analyzed, which was used to discard one of the previous two samples analyzed as a statistical outlier [*Draper and Smith*, 1981, p. 152]. Additionally, 11 Hole 747A and 10 Site 588 samples were reanalyzed at a later date when testing for an interlaboratory calibration problem (see discussion section, Table 3). Inclusion of these new data was determined to have no statistically significant effect on the regressions contained herein and thus are presented separately from the data provided in Table 2. The uppermost sample in the middle Miocene section was not used in developing regression equations. This sample has an abnormally high residual value relative to other data in various regression models computed (see below) and may also be discarded as an outlier [*Draper and Smith*, 1981]; it may have been affected by drilling disturbance and high bioturbation in this section of the core [*Schlich et al.*, 1989]. The final averaged data set for Hole 747A contains 72 data points (Figure 2).

Table 1. Magnetic Reversal and $\delta^{18}\text{O}$ Age Models for Ocean Drilling Program Site 747A

Depth, mbsf	Age ^a Ma	Age ^b Ma	Event
37.05	9.149	8.50	Mi7 = Base C4Ar1.n
46.26	10.40	9.60	Mi6
56.88	11.58	11.30	Mi5
60.82	11.852	11.55	Top C5A
64.66	13.094	13.01	Base C5AAn
66.80	13.263	13.20	Top C5AB
70.00	13.674	13.69	Base C5ABr = Top C5AC
72.80	14.164	14.20	Top C5AD
76.47	14.608	14.66	Base C5ADn = Top C5ADr
78.89	14.800	14.87	Top C5Bn1 = Base C5ADr
81.02	15.162	15.27	Base C5Bn.2n = Top C5Br
84.99	16.035	16.22	Top C5Cn.1n
90.92	16.755	16.98	Base C5Cn3 = Top C5Cr
93.09	17.310	17.57	Top C5Dn
94.50	17.650	18.14	Top C5Dr
99.78	18.317	18.56	Top C5En
107.30	19.083	19.35	Top C6n
115.08	20.546	20.88	Top C6An
120.51	21.787	21.90	Top C6AAn
123.20	22.599	22.57	Top C6Bn
125.83	23.357	23.27	Top C6Cn1
131.59	24.722	25.50	Top C7n.1n

Table is based on the magnetic interpretation of *Wright and Miller* [1992]; note that mbsf is meters below seafloor.

^a *Cande and Kent* [1992] geomagnetic polarity timescale (GPTS).

^b *Berggren et al.* [1985a, b] GPTS.

Table 2. Unaveraged Sr Isotope Data for Hole 747A

Sample	Age Ma ^a	Age Ma ^b	Depth mbsf	⁸⁷ Sr/ ⁸⁶ Sr	Internal Error
5-3,105-109	9.02	9.74	41.38	0.708992	0.000016
5-4,105-109	9.19	9.93	42.81	0.708950	0.000017
5-4,105-109	9.19	9.93	42.81	0.708948	0.000006
5-5,105-109	9.36	10.13	44.24	0.708929	0.000020
5-6,105-109	9.53	10.32	45.67	0.708934	0.000011
5-7,10-14	9.59	10.39	46.19	0.708917	0.000033
5-cc,10	9.70	10.47	46.89	0.708893	0.000040
6-1,105-109	9.88	10.59	48.00	0.708895	0.000005
6-2,105-109	10.11	10.75	49.42	0.708912	0.000006
6-3,105-109	10.33	10.91	50.82	0.708903	0.000007
6-3,105-109	10.33	10.91	50.82	0.708892	0.000007
6-4,105-109	10.55	11.06	52.22	0.708896	0.000009
6-5,105-109	10.78	11.22	53.62	0.708881	0.000027
6-6,105-109	11.00	11.37	55.02	0.708874	0.000021
6-cc,20	11.21	11.52	56.31	0.708864	0.000007
7-1,102-106	11.34	11.62	57.48	0.708903	0.000030
7-2,104-108	11.43	11.72	58.94	0.708894	0.000006
7-2,104-108	11.43	11.72	58.94	0.708890	0.000006
7-3,100-104	11.52	11.82	60.34	0.708891	0.000007
7-4,101-105	11.92	12.16	61.79	0.708868	0.000008
7-5,100-104	12.46	12.62	63.22	0.708877	0.000008
7-6,100-104	13.01	13.09	64.66	0.708875	0.000007
7-7,10-14	13.06	13.13	65.22	0.708845	0.000016
8-1,100-104	13.23	13.29	67.02	0.708849	0.000011
8-2,100-104	13.46	13.48	68.52	0.708841	0.000009
8-3,100-104	13.69	13.67	70.02	0.708826	0.000007
8-4,100-104	13.97	13.94	71.52	0.708822	0.000004
8-5,100-104	14.23	14.19	73.02	0.708826	0.000005
8-5,100-104	14.23	14.19	73.02	0.708807	0.000006
8-6,100-104	14.42	14.37	74.52	0.708807	0.000006
8-7,12-16	14.50	14.45	75.16	0.708813	0.000008
9-2,100-104	14.66	14.61	76.50	0.708782	0.000006
9-3,100-104	14.79	14.73	78.00	0.708785	0.000009
9-3,100-104	14.79	14.73	78.00	0.708808	0.000007
9-4,101-105	14.99	14.90	79.51	0.708790	0.000006
9-5,100-104	15.27	15.16	81.00	0.708798	0.000008
9-6,98-102	15.62	15.48	82.48	0.708803	0.000005
9-7,100-104	15.98	15.82	84.00	0.708817	0.000018
9-7,100-104	15.98	15.82	84.00	0.708801	0.000029
9-8,10-14	16.13	15.95	84.60	0.708768	0.000007
9-cc	16.20	16.02	84.90	0.708758	0.000005
10-1,100-104	16.35	16.16	86.01	0.708754	0.000027
10-2,100-104	16.54	16.34	87.49	0.708724	0.000014
10-3,100-104	16.73	16.52	88.98	0.708693	0.000015
10-3,100-104	16.73	16.52	88.98	0.708687	0.000018
10-4,100-104	16.92	16.70	90.46	0.708705	0.000006
10-5,100-104	17.26	17.02	91.95	0.708682	0.000016
10-6,100-104	17.71	17.39	93.43	0.708678	0.000007
10-7,10-14	17.95	17.54	94.03	0.708689	0.000004
11-1,100-104	18.22	17.77	95.47	0.708669	0.000005
11-2,102-106	18.33	17.96	96.91	0.708612	0.000020
11-3,100-104	18.44	18.13	98.32	0.708615	0.000006
11-3,100-104	18.44	18.13	98.32	0.708595	0.000006
11-4,100-104	18.56	18.31	99.74	0.708602	0.000020
11-4,100-104	18.56	18.31	99.74	0.708605	0.000021
11-5,101-105	18.71	18.46	101.18	0.708620	0.000009
11-6,101-105	18.86	18.60	102.60	0.708585	0.000012
11-7,10-14	18.92	18.66	103.16	0.708583	0.000004
12-1,100-104	19.11	18.84	104.97	0.708578	0.000053
12-2,100-104	19.26	18.99	106.39	0.708574	0.000005

Table 2. (continued)

Sample	Age Ma ^a	Age Ma ^b	Depth mbsf	⁸⁷ Sr/ ⁸⁶ Sr	Internal Error
12-2,100-104	19.26	18.99	106.39	0.708547	0.000006
12-3,100-104	19.45	19.18	107.82	0.708586	0.000030
12-3,100-104	19.45	19.18	107.82	0.708530	0.000040
12-3,100-104	19.45	19.18	107.82	0.708537	0.000020
12-4,100-104	19.72	19.45	109.24	0.708533	0.000007
12-5,100-104	20.02	19.72	110.67	0.708505	0.000006
12-5,100-104	20.02	19.72	110.67	0.708428	0.000021
12-6,100-104	20.29	19.99	112.09	0.708502	0.000006
12-6,100-104	20.29	19.99	112.09	0.708492	0.000007
12-7,10-14	20.41	20.09	112.66	0.708492	0.000008
12-7,10-14	20.41	20.09	112.66	0.708436	0.000030
13-1,101-105	20.77	20.44	114.51	0.708461	0.000005
13-2,101-105	21.05	20.76	115.98	0.708406	0.000013
13-2,101-105	21.05	20.76	115.98	0.708399	0.000020
13-3,101-105	21.32	21.09	117.44	0.708428	0.000006
13-4,101-105	21.60	21.42	118.91	0.708390	0.000006
13-5,100-104	21.88	21.76	120.37	0.708380	0.000006
13-6,100-104	22.22	22.19	121.84	0.708364	0.000027
13-7,10-14	22.37	22.37	122.43	0.708349	0.000008
14-1,102-106	22.78	22.83	124.01	0.708280	0.000017
14-2,102-106	23.18	23.25	125.46	0.708287	0.000008
14-3,102-106	23.68	23.62	126.91	0.708280	0.000007
14-4,102-106	24.26	23.96	128.37	0.708282	0.000007
14-5,101-105	24.81	24.30	129.81	0.708274	0.000018
14-5,101-105	24.81	24.30	129.81	0.708243	0.000020
14-6,101-105	25.39	24.64	131.27	0.708271	0.000019
14-7,12-16	25.62	24.78	131.86	0.708265	0.000009
15-1,100-104	26.24	25.17	133.48	0.708222	0.000010
15-2,100-104	26.78	25.51	134.93	0.708220	0.000015

Note that mbsf is meters below seafloor.

^a Berggren *et al.* [1985a, b] GPTS.

^b Cande and Kent [1992] GPTS.

We measured National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, (formerly National Bureau of Standards (NBS)), NIST-987 as 0.710255 ⁸⁷Sr/⁸⁶Sr (20 analyses, 1σ = ±0.000008, normalized to ⁸⁶Sr/⁸⁸Sr = 0.1194) during analysis of Hole 747A. Data from Deep Sea Drilling Project (DSDP) Sites 590B [DePaolo, 1986], 593 [Hess *et al.*, 1986], 522 [Miller *et al.*, 1988], 588 [Hodell *et al.*, 1991], and 608 [Miller *et al.*, 1991a] were all adjusted to this value for comparison. We report two values for Recent marine carbonates of 0.709186±6 and 0.709196±9 measured on the giant clam *Eniwetok-1* (EN-1), an informal Sr isotope standard; this allows conversion of the data to the δ_{seawater} notation of Hess *et al.* [1986].

There was no optical evidence for diagenetic alteration of the section sampled [Wright and Miller, 1992]. Benthic foraminiferal δ¹⁸O values from the same samples analyzed here are similar to δ¹⁸O records at other locations with different burial histories; this also argues against diagenesis [Wright and Miller, 1992].

Construction of Sr Isotope Age Calibrations

Sr isotope ratios were calibrated to age using the magnetostratigraphy for Hole 747A of Heider *et al.* [1992], as modified

by Wright and Miller [1992], and the reversal ages of the GPTS of Berggren *et al.* [1985a, b] and Cande and Kent [1992] (Figure 3). In addition, three middle Miocene δ¹⁸O zones identified at Hole 747A (Mi5, Mi6, and Mi7) [Wright and Miller, 1992] were used to establish age control where uncertainties in the magnetostratigraphic record occur (e.g., at the level of Zone Mi5 (Figure 2 and Table 1). Oxygen isotope events were identified at Hole 747A by correlation with DSDP Sites 563 and 608 [Wright and Miller, 1992]. Hole 747B was used to establish magnetostratigraphy for stable isotope correlations for the upper Miocene section. There is less than 1 m of offset from Hole 747A to Hole 747B for this section [Wright and Miller, 1992]. The magnetostratigraphic record in Hole 747A, in combination with the δ¹⁸O stratigraphy, permits accurate determination of sedimentation rates and ages for specific depths sampled within the core. However, the magnetostratigraphy of the section spanning the middle/upper Miocene boundary is uncertain (e.g. Wright and Miller, 1992).

Results

Sr Isotope Regressions

Hole 747A magnetostratigraphy was plotted with the unaveraged results for each Sr isotope analyses, together with previ-

Table 3. $^{87}\text{Sr}/^{86}\text{Sr}$ Analyses for Interlaboratory Calibration Test

Hole 747A Sample	Depth, mbsf	$^{87}\text{Sr}/^{86}\text{Sr}^a$	(Error x 10^{-6})	Δ^b
5-6, 105-109	45.67	0.708924	(08)	-0.000010
6-2, 105-109	49.42	0.708923	(06)	+0.000011
6-4, 105-109	52.22	0.708919	(08)	+0.000023
7-3, 100-104	60.34	0.708885	(08)	-0.000006
7-6, 100-104	64.66	0.708872	(08)	-0.000003
8-2, 100-104	68.52	0.708843	(25)	+0.000002
9-3, 100-104	78.00	0.708810	(08)	+0.000013
9-6, 98-102	82.48	0.708800	(08)	-0.000003
10-2, 100-104	87.49	0.708724	(07)	0.000000
10-7, 10-14	94.03	0.708703	(09)	+0.000014
11-1, 100-104	95.47	0.708664	(06)	-0.000005
Site 588 Sample	Depth, mbsf	$^{87}\text{Sr}/^{86}\text{Sr}^a$	(Error x 10^{-6})	Δ^c
<i>Hole 588</i>				
24-2	218.60	0.708930	(18)	+0.000007
24-7	226.10	0.708892	(16)	-0.000001
25-4	231.30	0.708872	(28)	+0.000004
<i>Hole 588A</i>				
1-4	240.90	0.708873	(31)	+0.000017
2-1	246.00	0.708855	(07)	+0.000009
3-3	254.00	0.708836	(28)	+0.000003
5-1	261.00	0.708840	(16)	+0.000002
5-3	264.00	0.708832	(31)	+0.000020
6-4	270.50	0.708848	(20)	+0.000028
8-1	276.00	0.708814	(14)	+0.000023

All analyses presented above were performed at Rutgers, using procedures described in the text.

^a NIST-987 $^{87}\text{Sr}/^{86}\text{Sr}$ at Rutgers is now measured as 0.710256, based on the average of 26 analyses taken during the period of this calibration test.

^b Change from previous analysis of sample (Table 2); change from average if previous analysis was duplicated.

^c Change from previous analysis of sample [Hodell *et al.*, 1991]; change from average if previous analysis was duplicated. To determine Δ value, 0.000021 was subtracted from measured values (this study) to adjust to NIST-987 = 0.710235 [Hodell *et al.*, 1991].

ously reported oxygen and carbon isotope data [Wright and Miller, 1992] (Figure 2). From 135 mbsf to 124 mbsf (uppermost Oligocene to lowermost Miocene) there is an increase of approximately 0.000070 in the Sr isotope values (Figure 2). From 124 to 85 mbsf (approximately the lower Miocene) there is a substantial (0.000490) increase in $^{87}\text{Sr}/^{86}\text{Sr}$, from 0.708300 to 0.708790. The middle Miocene section, from 85 mbsf to 41 mbsf shows a smaller increase (0.000150), from approximately 0.708800 to 0.708950 at the top of the sampled section.

Relationships between Sr isotope variations and age must be empirically determined, because the causes of changing $^{87}\text{Sr}/^{86}\text{Sr}$ through time are not well known. Independent age estimates were obtained for each $^{87}\text{Sr}/^{86}\text{Sr}$ sample by interpolating sedimentation rates between age-depth control points (see methods

section and Table 1). Our average sampling interval is 1.32 m, which corresponds to a sample resolution of 0.22 m.y. (based on the timescale of Cande and Kent [1992]), and thus we are unable to discern changes on a scale finer than about 0.5 m.y. The independent age estimates allow empirical evaluation of the nature of Sr isotopic changes on the million-year scale through the Miocene.

We plotted the data versus the GPTS of Berggren *et al.* [1985a, b] (herein after referred to as BKV85) to facilitate comparison with previous studies (Figure 3) [e.g., Hodell *et al.*, 1991; Richter and DePaolo, 1988; Miller *et al.*, 1991a]. Cande and Kent [1992] (herein after referred to as CK92) have recently revised the GPTS, making the first major revision to polarity durations since Heirtzler *et al.* [1968]. Although the largest changes between BKV85 and CK92 are in the Paleogene, there

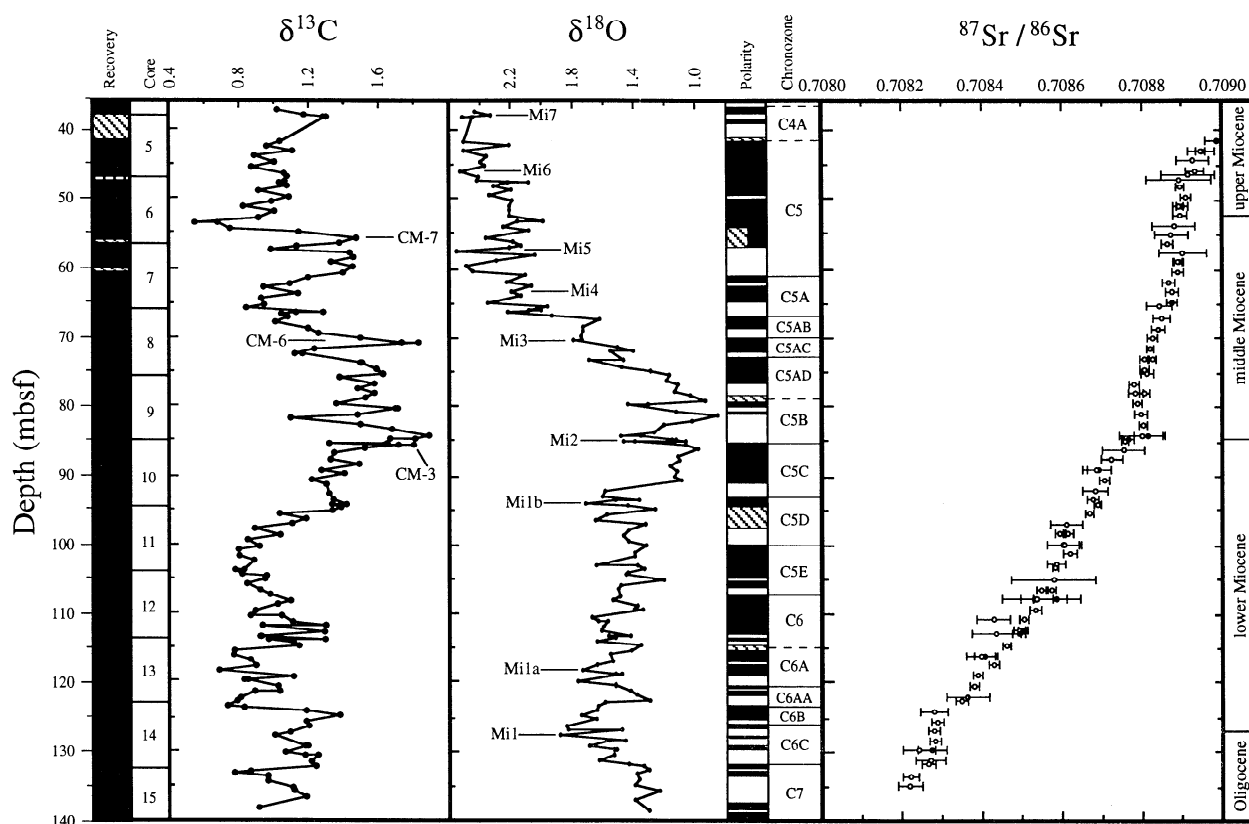


Figure 2. Sr, oxygen, and carbon isotopes versus depth. Magnetic interpretation, oxygen and carbon isotope data and $\delta^{18}\text{O}$ zonations are from *Wright and Miller* [1992]. Carbon isotope events are after *Woodruff and Savin* [1991]. All Sr analyses for Hole 747A are presented (unaveraged). Data are from Table 2. Error bars are plus or minus internal error of analyses. Black areas of polarity are normal, white are reversed, and hatched are uncertain polarities. Filled circles on Sr isotope plot are not used in averaged data set (41.38 and 107.82 meters below seafloor (mbsf)). Hatched intervals of recovery represent intervals of substantial drilling disturbance.

are some important differences in the Miocene, particularly the late middle to early late Miocene (e.g., as great as 1 m.y. in the age estimates of Chron C5). We use the CK92 scale in Figure 3 (left) and report our regressions versus both timescales. There are minor differences between the CK92 scale and recent attempts to astronomically tune the late Miocene scale [*Shackleton et al.*, 1994], and the CK92 scale may be revised. However, we note that given the age resolution of this study, the late Miocene differences between CK92 and the astronomical timescale are minor (<0.3 m.y.) and that the CK92 scale should be the reference for the Miocene GPTS until a new generation of radiometric dates is obtained.

We compute relationships between age and $^{87}\text{Sr}/^{86}\text{Sr}$ using linear and higher-order regression analysis. In these regressions, $^{87}\text{Sr}/^{86}\text{Sr}$ values measured at each level are the dependent variable, while age estimates provided by magnetostratigraphy and isotopic chronology are the independent variable [*Draper and Smith*, 1981; *Miller et al.*, 1991a]. This is opposite to most previous attempts to regress age and Sr isotopes [e.g., *Hodell et al.*, 1991]; however, it is justified by *Draper and Smith* [1981]. They developed a regression model using ^{14}C data as the dependent variable (analogous to our $^{87}\text{Sr}/^{86}\text{Sr}$ measurements) and dendrochronology as the independent variable (analogous to our magnetostratigraphic estimates).

Higher-order (fourth- or fifth-order) polynomial regressions

provide excellent fits to the entire Sr isotope data set (Figure 3), although most previous studies have approximated the higher order regressions with linear regressions of shorter intervals (e.g., 5 to 10 m.y.) [*McKenzie et al.*, 1988; *Miller et al.*, 1988]. For example, the fifth-order polynomial regression provides a remarkably high correlation coefficient ($r = 0.991$) for the Miocene Hole 747A data presented here. However, the change between the early and middle Miocene may be approximated using two linear regressions. These linear regressions provide a fit to the data which is not significantly different from the higher-order regression. In the absence of a theoretical prediction, the simplest relationship that adequately fit the data should be used, in this case two linear regression models. Inflection points between the linear regressions were placed by first visually estimating the point and then refined by running various test regressions using different inflection points until the regressions with the best correlation coefficients and standard errors were obtained.

Two sets of linear regressions were obtained. Regression equations labeled (a) are derived using the CK92 timescale, and regression equations labeled (b) are derived using the BKV85 timescale. The regression equations obtained for the middle Miocene section of ODP 747A, based on 30 samples, are

$$(^{87}\text{Sr}/^{86}\text{Sr}) = -0.0000266x(\text{Age, Ma}) + 0.709194 \quad (1a)$$

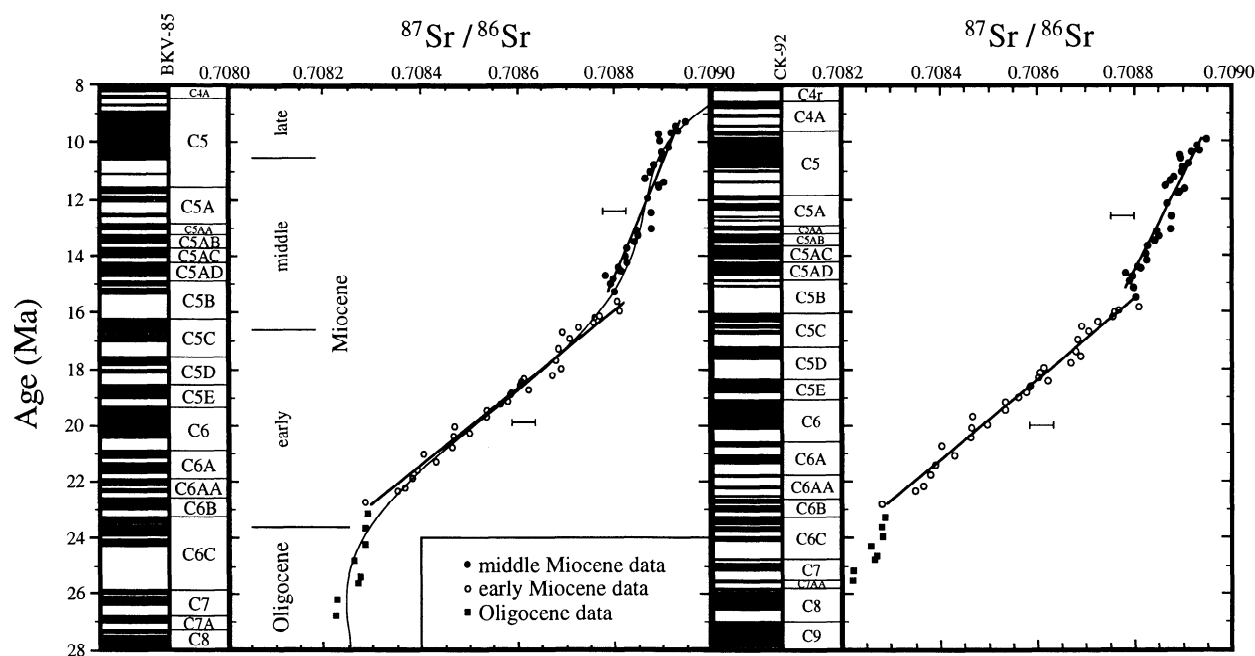


Figure 3. Averaged Sr isotopes versus age. (left panel) Magnetic timescale is from *Berggren et al.* [1985a, b]. Thin line is fifth-order polynomial regression of entire averaged data set for Hole 747A. Thick lines are linear regressions for early and middle Miocene regressions presented (equations (1b) and (3b)). Error bars are ± 0.000026 , representing estimated external error of analyses. (right panel) Magnetic timescale is from *Cande and Kent* [1992]. Thick lines are linear regressions for early and middle Miocene regressions presented (equations (1a) and (3a)). Error bars are ± 0.000026 , representing estimated external error of analyses.

$$(^{87}\text{Sr}/^{86}\text{Sr}) = -0.0000223x(\text{Age, Ma}) + 0.709135 \quad (1b)$$

We invert these equations to obtain an unknown age from a measured $^{87}\text{Sr}/^{86}\text{Sr}$ value:

$$(\text{Age, Ma}) = 26661.43 - (^{87}\text{Sr}/^{86}\text{Sr}) \times 37593.98 \quad (2a)$$

$$(\text{Age, Ma}) = 31799.78 - (^{87}\text{Sr}/^{86}\text{Sr}) \times 44843.05 \quad (2b)$$

Equation (1a) (CK92) has a correlation coefficient (r) of 0.957, a standard error (s) of 0.000014, and a slope of 0.000027/m.y. It is valid from 9.9 Ma (the youngest sample of our data set) to 15.2 Ma, corresponding to $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.708930 to 0.708789. Equation (1b) (BKV85) has a correlation coefficient (r) of 0.953, a standard error (s) of 0.000014, and a slope of 0.000022/m.y. It is valid from 9.2 Ma (the youngest sample of our data set) to 15.2 Ma, corresponding to $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.708930 to 0.708789.

The regressions were derived for the lower to lowermost middle Miocene section of ODP 747A based on 33 samples:

$$(^{87}\text{Sr}/^{86}\text{Sr}) = -0.0000683x(\text{Age, Ma}) + 0.709855 \quad (3a)$$

$$(^{87}\text{Sr}/^{86}\text{Sr}) = -0.0000692x(\text{Age, Ma}) + 0.709890 \quad (3b)$$

These are inverted to

$$(\text{Age, Ma}) = 10393.19 - (^{87}\text{Sr}/^{86}\text{Sr}) \times 14641.29 \quad (4a)$$

$$(\text{Age, Ma}) = 10258.53 - (^{87}\text{Sr}/^{86}\text{Sr}) \times 14450.87 \quad (4b)$$

Equation (3a) (CK92) has a correlation coefficient (r) of 0.991, a standard error (s) of 0.000019, and a slope of 0.000068/m.y. It is valid from 15.5 Ma to 22.8 Ma, corresponding to $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7087889 to 0.708305. Equation (3b) (BKV85) has a correlation coefficient (r) of 0.991, a standard error (s) of 0.000020, and a slope of 0.000069/m.y. It is valid from 15.6 Ma to 22.8 Ma, corresponding to $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7087889 to 0.708305.

Age Error Analysis

Errors in estimating the age of a sample are controlled by (1) the technical limitations of measuring the $^{87}\text{Sr}/^{86}\text{Sr}$ value (e.g., accuracy or sample reproducibility) and (2) the statistical reliability of the regression equations used to translate the Sr isotope value into an age. In practice, the technical limitations are described by the ability to reproduce Sr isotope measurements in two or more stratigraphically equivalent samples. This is a function of both the internal and external error of isotope measurements.

Average internal error (intran variability) at Rutgers was ± 0.000013 for the 89 Hole 747A samples analyzed. External error at Rutgers has previously been reported as ± 0.000026 (2σ) for NIST-987 [Miller et al., 1991]. Analyses of 20 samples of NIST-987 during Hole 747A data collection yielded a 1σ standard deviation of ± 0.000008 . The average internal error for these samples was ± 0.000016 . The average external error of the 17 geological duplicates analyzed from Hole 747A is ± 0.000020 , and this is probably a good estimate for external precision in this study. However, the variation in $^{87}\text{Sr}/^{86}\text{Sr}$ measurements between geologic duplicates ranged from as good as ± 0.000002 to

as poor as ± 0.000077 , and our external precision does not include errors in the regressions.

The differences between observed Sr isotope values and predicted values (residuals) illustrate the errors in regression equations (1a) (Figure 4a) and (3a) (Figure 4b). These residuals show no trends, indicating that the regression models adequately fit the data [Draper and Smith, 1981]. Residuals of 26 of 30 (equation (1a), 87%) (Figure 4a) and 26 of 33 analyses (equation (3a), 79%) (Figure 4b) fall within ± 0.000020 of the regressions. A more rigorous method of measuring errors in age prediction including those in the regression follows.

Miller *et al.* [1991a] showed how age errors can be statistically derived by utilizing the inverse regression statistics of Draper and Smith [1981, p. 49]. This method predicts the highest and lowest ages for a given confidence interval based on the statistical quality of the regression data and the slope of the regression. Miller *et al.* [1991a] presented equations for two situations. In the first case, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is a known value (i.e., it assumes that the number of analyses at a given stratigraphic level approaches infinity). This first formula provides a measure of the theoretical maximum resolution for a large number of analyses at a given level.

Age (upper, lower) =

$$\text{Age}_0 + (\text{Age}_0 - \overline{\text{Age}})g \pm \frac{ts}{b_1} \sqrt{\frac{(\text{Age}_0 - \overline{\text{Age}})^2}{\Sigma(\text{Age}_i - \overline{\text{Age}})^2} + \frac{1 - g}{n}} \quad (5)$$

(1 - g)

where Age_0 is the predicted age for the sample, Age_i is the independently estimated age (GPTS model age), $\overline{\text{Age}}$ is the mean age of regression (mean of all predicted ages) t is the Student's statistic, for a specific number of degrees of freedom and confidence interval, s is the standard error of estimate, b_1 is the slope of the regression, n is the number of analyses, and g (a constant for each regression equation) is $t^2/(b_1^2/(s^2/\Sigma(\text{Age}_i - \overline{\text{Age}})^2))$. In cases where the regression is well determined, such as the regressions presented above, g approximates zero [Draper and Smith, 1981, p. 49].

Miller *et al.* [1991a] also presented a modified version of this error-predicting equation which is valid for the situation where an individual $^{87}\text{Sr}/^{86}\text{Sr}$ value is not assumed to be the true value but a measure of the number of analyses at a given level (i.e., it is a dependent variable in a regression analysis). This equation is

$$\text{Age (upper, lower)} = \text{Age}_0 \pm \sqrt{\frac{(\text{Age}_0 - \overline{\text{Age}})^2}{\Sigma(\text{Age}_i - \overline{\text{Age}})^2} + \frac{1}{q} + \frac{1}{n}} \quad (6)$$

where q is the number of $^{87}\text{Sr}/^{86}\text{Sr}$ analyses at a given stratigraphic level. A summary of age error estimates produced by our two age models (BKV85 and CK92) and age error estimates reported for previous studies at other locations are presented in Table 2. For example, age errors for (equation) 1a (middle Miocene, CK92) for a single analysis are ± 1.17 m.y. at the 95% confidence interval and those for 2a (early Miocene, CK92) are ± 0.61 at the 95% confidence interval. As can be seen in the age error equation above, increasing the number of analyses at a given level substantially improves the resolution of the age esti-

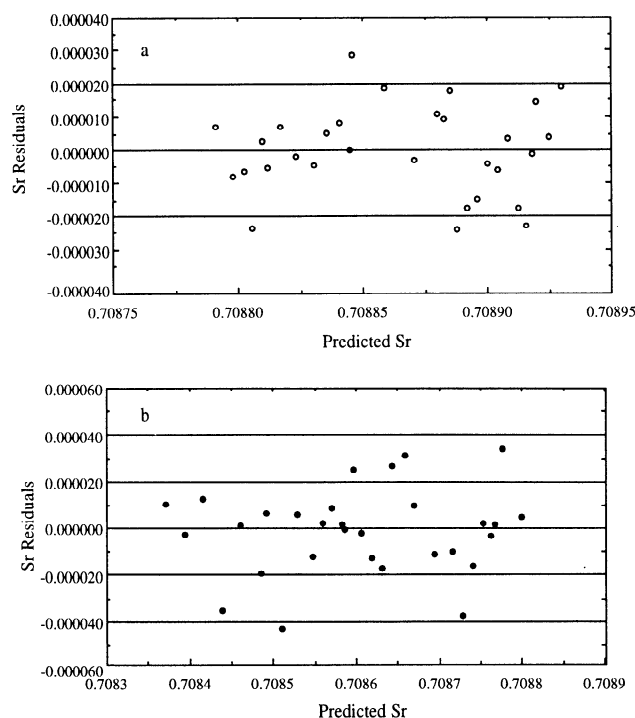


Figure 4. Plot of residual values for Hole 747A averaged Sr isotope data from CK92 regression for (a) the middle Miocene (equation (1a)) and (b) the early Miocene (equation (3a)).

mate (± 0.76 and ± 0.40 m.y. for three analyses each in the two cases specified above). Age error estimates resulting for various values of (q) and different confidence intervals are also provided (Table 4).

It should be noted here that the linear regressions obtained in this study may only represent a long-term average rate of change, because our stratigraphic resolution is limited by the sampling interval used (~ 1.3 m) and the interrun reproducibility of our analytical techniques. Several studies have indicated the presence of higher-order fluctuations in the Sr isotope curve on the tens of thousands of years scale [e.g., DePaolo, 1986; Hodell *et al.*, 1989; Dia *et al.*, 1992; Clemens *et al.*, 1993], as opposed to our hundreds of thousands of years scale observations. The cause of their higher-order fluctuations may be pulslike changes in the flux of high ^{87}Sr sources [Hodell *et al.*, 1989]. One interesting feature in common between Site 588 and Hole 747A is an apparent shift in the Sr records from the right side of the regression lines between approximately 15.3 Ma and 11.5 Ma to the left side of the regression lines between 11.5 and 9.5 Ma (Figure 5). Higher-resolution sampling for this interval may provide additional insight into any "hidden" structure in this interval.

Discussion

Comparison of Site 747 With Other Records

Comparisons of data from Hole 747A with Site 588 show good agreement between the two data sets for the early to earliest middle Miocene (to 16 Ma, Figure 5). Hodell *et al.* [1991] used BKV85 and reported an inflection point at 16.0 Ma from a period of higher slope in the early Miocene to a shallower slope from 16.0 to 8.0 Ma. Hole 747A has the same inflection point dated

Table 4. Summary of Oligocene and Early and Middle Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ Regression Statistics and Age Errors

Site	Age Range Ma	r	s	Slope per m.y.	Age Error (Ma)		
					95%	80%	3@95%
<i>Middle Miocene Regressions</i>							
747A ^a	9.9 - 15.2	0.957	0.000014	0.000027	±1.17	±0.74	±0.76
747A ^b	9.2 - 15.2	0.953	0.000014	0.000022	±1.42	±0.89	±0.92
588 ^c	8.0 - 15.4	0.960	0.000014	0.000021			
588	8.0 - 16.0	0.96	n/r	0.000022	±1.36	±0.8	n/r
<i>Lower Miocene Regressions</i>							
747A ^a	15.5 - 22.8	0.991	0.000019	0.000068	±0.61	±0.39	±0.40
747A ^b	15.6 - 22.8	0.991	0.000020	0.000069	±0.64	±0.41	±0.42
588 ^c	15.4 - 24.0	0.991	0.000023	0.000058			
588	16.0 - 24.0	0.99	n/r	0.000060	±0.74	±0.48	n/r
608	25.1 - 14.6	0.984	0.000034	0.000060	±1.2	±0.8	±0.7
<i>Oligocene Regressions, Sites 747A and 522 Combined</i>							
	23.2 - 28.0	0.959	0.000021	0.000051	±1.08	±0.67	±0.8
	29.5 - 34.8	0.924	0.000026	0.000037	±1.97	±1.18	±1.46

Here r is the correlation coefficient, s is the standard error, 95% and 80% are the confidence intervals, and 3@95% is the confidence interval for 3 independent samples at the same stratigraphic level; n/r indicates value not reported.

^a CK92 age model.

^b BKV85 age model.

^c Regressions calculated for this paper using *Hodell et al.* [1991] data. Age errors are assumed to be similar to those shown for the original regressions.

between 15.2 and 15.6 Ma using the BKV85 timescale (Figure 3). We initially reported that Hole 747A had a steeper slope during the middle Miocene than did the Site 588 data [*Oslick et al.*, 1992] based on data to ~11 Ma. Data for Hole 747A are now presented to 9.0 Ma (younger data cannot be obtained because of extreme drilling disturbance), which indicate a slope almost identical to that of Site 588 (Table 4 and Figure 5). However, the regressions at the two sites appear to be uniformly offset with respect to age for the middle to early late Miocene, with the Site 588 regression yielding ages ~ 1 m.y. younger than at Hole 747A. The cause of this offset is unknown, but could be attributed to interlaboratory calibration problems, diagenesis of one or both sections, or problems in correlating one or both sections.

We cannot attribute the middle Miocene differences to interlaboratory calibration problems. Two different standards (NIST-987 and EN-1) show identical offsets between the two laboratories. Analyses of Site 588 samples provided by D. Hodell (personal communication, 1993) yielded similar results to those obtained by *Hodell et al.* [1991] (Table 3). Recently repeated analyses of samples from Hole 747A at Rutgers yielded values identical to those used to establish the Sr age relationships presented in this paper (Table 3).

We cannot readily explain the difference as being due to diagenesis. We show that there is no offset between Sr isotope records for the lower Miocene at Site 588 and that at Hole 747A (Figure 5). The lower Miocene Sr isotope records at both sites compare well with other sites with vastly different burial depths

[*Hodell and Woodruff*, this issue]. However, we note that *Hodell and Woodruff* [this issue, figure 12] show an offset between Site 588 and 747 in the lower Miocene. This difference in offset between the studies led us to suspect problems in correlation.

We attribute differences between the middle Miocene at Sites 588 and 747 to problems in correlating Site 588 from 14-11 Ma and in correlating Site 747 from 11-8 Ma. Correlations of Site 588 from the upper middle Miocene (ca. 14-11 Ma) rely on magnetostratigraphy of Hole 588A. The magnetostratigraphic record at Hole 588A is based entirely on natural remanent magnetizations [*Barton & Bloemendal*, 1986] and thus may be suspect. In attempting to solve the problem of the middle Miocene offsets, we established a chronology for Hole 588A based entirely on biostratigraphic correlations. This resolved much of the offset between the records. We note that the correlations of the upper Miocene at Site 588 rely on the much better (i.e., cleaned to 200 Oe) magnetostratigraphic record of Hole 588 (from mid-Chronozone C5n2, younger than about 10.5 Ma, using CK92), while the correlations of C5n2 at Site 747 are uncertain. We believe that the Site 747 record better represents the interval 14-11 Ma, while Site 588 may better represent the interval younger than 10.5 Ma. The chronology of both records appears equivocal between 11 and 10.5 Ma, and future studies should address this interval.

Hole 747A data allow for better placement of the middle Miocene inflection point in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve near 15.4 Ma and a better chronology than Site 588. The high-quality magneto-

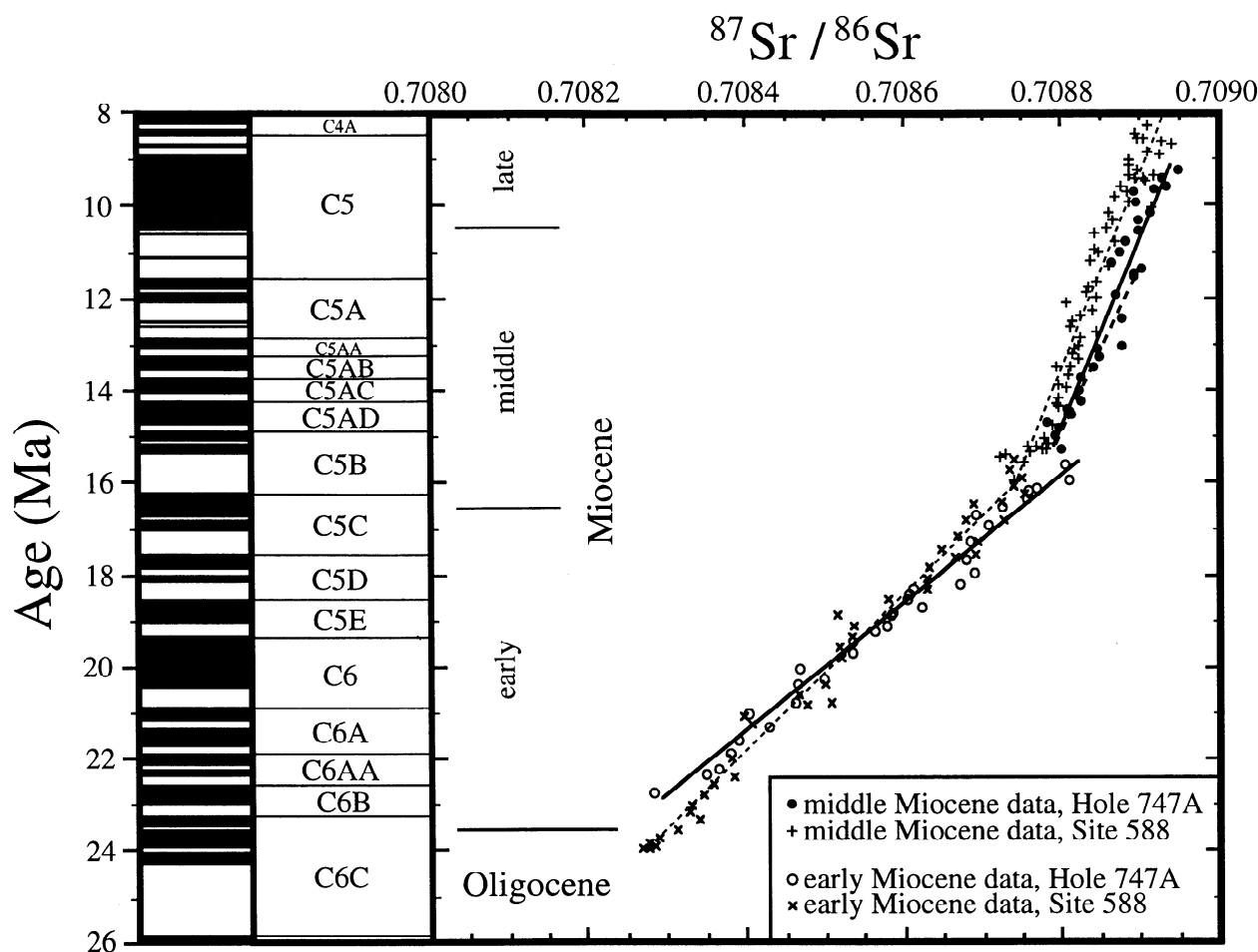


Figure 5. Comparison of Hole 747A and Site 588 data. Magnetic timescale is from *Berggren et al.* [1985a, b]. Heavy solid lines are linear regressions presented in this paper for Hole 747A. Thin dashed lines are linear regressions for Site 588 [*Hodell et al.*, 1991]. Heavy dashed line is the middle Miocene regression for 747A from 15.2 to 11.2 Ma [*Oslick et al.*, 1992]. All data corrected to NIST-987 = 0.710255.

stratigraphic record of Hole 747A [*Schlich et al.*, 1989, pp. 114–115] (also see discussion below) provides an excellent independent age estimate against which the $^{87}\text{Sr}/^{86}\text{Sr}$ regressions can be firmly established (Table 1). *Hodell et al.* [1991] placed the inflection at 16.0 Ma, while *Miller et al.* [1991a] placed it at approximately 14.6 Ma at Site 608. However, *Miller et al.* [1991a] acknowledged that scatter (poor resolution) in the middle Miocene Site 608 data makes the placement of the inflection difficult. *Hodell et al.*'s [1991] placement of the inflection at 16.0 Ma partly relies on biostratigraphy; as noted above there are problems with the middle Miocene chronology of this site. However, *Hodell et al.* [1991] also used $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ events, identified by *Woodruff and Savin* [1991] at 15.3 and 15.5 Ma respectively, to aid in constructing their age model for Site 588, and this part of the record should correlate with Site 747. We believe that it does (Figure 5) and that the differences in the timing of the inflection can be resolved.

Further statistical analysis of data from *Hodell et al.* [1991] shows that there is no difference in their Miocene regressions if the inflection point for Site 588 Sr isotopic data is placed at 15.3 Ma (Table 4). This brings the inflection point of the 588 data almost exactly in line with the 15.2 Ma inflection that we iden-

tify at Hole 747A. There appears to be a short interval of zero slope in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve from approximately 15.5 to 15.2 Ma at both sites (Figure 5), which may limit our ability to define an absolute inflection point. The early Miocene regression has little significant difference in quality from that of Site 588 other than that the data have a slightly tighter fit to the regression, which yields better statistical stratigraphic resolution. However, the regression for Hole 747A better defines the upper inflection at ~15.4 Ma.

At Site 289 *Hodell and Woodruff* [this issue] interpret an inflection in the Sr curve at 19.0 Ma (CK92). Site 289 has a slope of approximately 60 ppm/m.y. from 22.5 to 19.0 Ma and a slope of about 80 ppm/m.y. from 19.0 to 16.0 Ma. This inflection is not seen at Site 747A. The most likely cause of this disagreement is because of age differences between the two sites, although other effects (e.g., diagenesis) cannot be discounted.

Globally recognized carbon isotope events may also be used for correlation between sites. Although not used for age control datums, three $\delta^{13}\text{C}$ maxima, identified by *Woodruff and Savin* [1991], have been identified at Site 747A (Figure 2) using $\delta^{13}\text{C}$ data from *Wright and Miller* [1992]. These are CM-7 at 55.0 mbsf, 11.3 Ma (CK92); CM-6 at 70.0 mbsf, 13.7 Ma (CK92);

and CM-3 at 84.9 mbsf, 16.0 Ma (CK92). The ages for these events agree well with results from *Hodell and Woodruff* [this issue].

The Hole 747A magnetostratigraphic record has the least ambiguous age control of all middle Miocene $^{87}\text{Sr}/^{86}\text{Sr}$ records published to date. For the lower Miocene section, Hole 747A again provides an excellent magnetostratigraphic record [*Schlich et al.*, 1989]. Hole 747A shows possible evidence for a hiatus only during Chron C5AA, based on the suggestion of a concatenation of Chronozones C5A and C5AA [*Wright and Miller*, 1992].

The Site 747 record provides a firm estimate of the age of the change in slope near the Oligocene/Miocene boundary. This inflection was reported as near ca. 25 Ma by *Miller et al.* [1991a] based on Site 608, younger than ca. 22 Ma by *Miller et al.* [1988], and ca. 26 Ma by *Hess et al.* [1989]; all three studies used *Berggren et al.* [1985a, b], in which the Oligocene/Miocene boundary is 23.7 Ma. *Capo et al.* [1991] reported a change in Sr isotope slope in the late Oligocene from Apennine sections; they dated this change directly using radioisotopes as ca. 26 Ma, although Sr isotope data near this proposed inflection are sparse in these sections. At Site 747, there is a distinct increase in the rate of change near the top of Chronozone C6Bn (Figure 2); this change occurred at ca. 22.8 Ma (using CK92 (earliest Miocene) and 22.8 Ma using BKV85) (Figure 6). A corresponding increase in the rate of change is also seen at Site 608 at ca. 23 Ma (using CK92 (near the base of Chronozone C6Bn)) (inset on Figure 6). Minor age differences between the two records can be ascribed to uncertainties in this part of the Site 608 magnetostratigraphic record due to a probable unconformity in Chronozones C6A-C6 and a hiatus of ~1-2 m.y. (from ~22-20 Ma on the CK92 timescale) (inset Figure 6).

The Site 747 record compares favorably with Oligocene Sr isotope data from Site 522 [*Miller et al.*, 1988] in the interval of overlap (ca. 26-24 Ma using CK92) (Figure 6). However, the Site 522 age-Sr isotopic relationships shown here (Figure 6) differ from those reported by *Miller et al.* [1988]. We recalibrated the Site 522 record to the CK92 timescale in order to evaluate the changes in slope in the Oligocene. For example, it is not clear if the change reported near 26 Ma by *Capo et al.* [1991] corresponded to the change we reported from the base of the Miocene at Site 747 or if it was an older event, that is, one not detected in the Site 522 because of timescale problems [*Capo et al.*, 1991]. We also stacked the Site 522 and 747 record, fit a fifth-order polynomial to the data (Figure 6), and showed that the Oligocene Sr isotopic record may be approximated by two linear segments (using the CK92 timescale):

$$(^{87}\text{Sr}/^{86}\text{Sr}) = -0.0000514x(\text{Age, Ma}) + 0.709501 \quad (7)$$

$$(^{87}\text{Sr}/^{86}\text{Sr}) = -0.0000366x(\text{Age, Ma}) + 0.709096 \quad (8)$$

We invert these equations to obtain an unknown age from a measured $^{87}\text{Sr}/^{86}\text{Sr}$ value:

$$(\text{Age, Ma}) = 13803.52 - (^{87}\text{Sr}/^{86}\text{Sr}) \times 19455.25 \quad (9)$$

$$(\text{Age, Ma}) = 19374.21 - (^{87}\text{Sr}/^{86}\text{Sr}) \times 27322.40 \quad (10)$$

Equation (7), based on 16 samples, has a correlation coefficient (r) of 0.959, a standard error (s) of 0.000021, and a slope of

0.000051/m.y. It is valid from 23.2 Ma to 28.0 Ma and $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.708304 to 0.708065. Equation (8), based on 13 samples, has a correlation coefficient (r) of 0.924, a standard error (s) of 0.000026, and a slope of 0.000037/m.y. It is valid from 29.5 Ma to 34.8 Ma and $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.708015 to 0.70780. Detailed analysis of age errors related to these regressions are presented (Table 4).

We date this inflection as ca. 28 Ma (Figure 6), slightly older than the inflection reported by *Capo et al.* [1991] (ca. 26 Ma), and ascribe the differences to closer sampling at Site 522 than the Apennine sections. This inflection was not apparent in the age regression of *Miller et al.* [1988] which presented the Site 522 data because of the timescale used [*Berggren et al.*, 1985b]; use of the CK92 timescale compresses the late Eocene-early Oligocene (~7 m.y. versus 10 m.y. on CK92 versus *Berggren et al.* [1985b]) slightly more than the late Oligocene (5 m.y. versus ~6 m.y.). Although additional data are needed to refine the Site 522 regressions, we have argued previously that Site 522 provides the best magnetochronology and a well preserved reference section for the Oligocene [*Miller et al.*, 1988].

A comparison of the Hole 747A Miocene data with earlier studies from DSDP Sites 593 [*Hess et al.*, 1986], 590B [*DePaolo*, 1986], and 608 [*Miller et al.*, 1991a] (Figure 7) illustrates the problems with age control that impaired previous Sr isotope work for the Miocene. Site 593 used biostratigraphy for primary age control, which resulted in large age offsets relative to the other sites. Site 590B also used biostratigraphic datum levels for age control but compares well with Hole 747A. The major deficiency in the 590B data set is the sparse sampling interval. Site 608 agrees well with Hole 747A for the early Miocene regression, deviating only in the middle Miocene section because of high scatter in the middle Miocene data at Site 608 [*Miller et al.*, 1991a].

Comparison of the Sr Isotope Record to the Inferred Glacioeustatic Record

Miller et al. [1991a] presented a speculative scenario relating the late Eocene to Miocene Sr isotopic changes to glaciations and deglaciations of the Antarctic craton. They suggested that Oligocene-early Miocene glaciations were intermittent, alternately covering and exposing the east Antarctic craton. As a result, each glaciation/deglaciation caused increases in the flux of silic weathering products and the mean steady state, which cumulatively resulted in the apparent monotonic (but actually logarithmic) $^{87}\text{Sr}/^{86}\text{Sr}$ increases. They explained the higher rate of change of $^{87}\text{Sr}/^{86}\text{Sr}$ during the early Miocene by an increase in the frequency of glaciations relative to the Oligocene and the lower rate of change in the middle Miocene by the development of a permanent ice cap in east Antarctica [e.g., *Shackleton and Kennett*, 1975; *Savin et al.*, 1975]. As a result of this permanent ice sheet, subsequent glaciations increased the volume, but not the area, of the east Antarctic ice cap and therefore did not significantly change the amount of silic weathering products or oceanic Sr isotopic composition. *Hodell et al.* [1990] suggested that glaciation alone can only explain 25% of the Sr isotope increase for the last 2.5 m.y.; *Hodell et al.* [1991], *Raymo et al.* [1988], and *Raymo* [1991] attributed the bulk of the late Neogene $^{87}\text{Sr}/^{86}\text{Sr}$ increase to mountain uplift.

Our recalibration of the Sr isotope versus age relationship provides empirical calibrations that can be used to evaluate

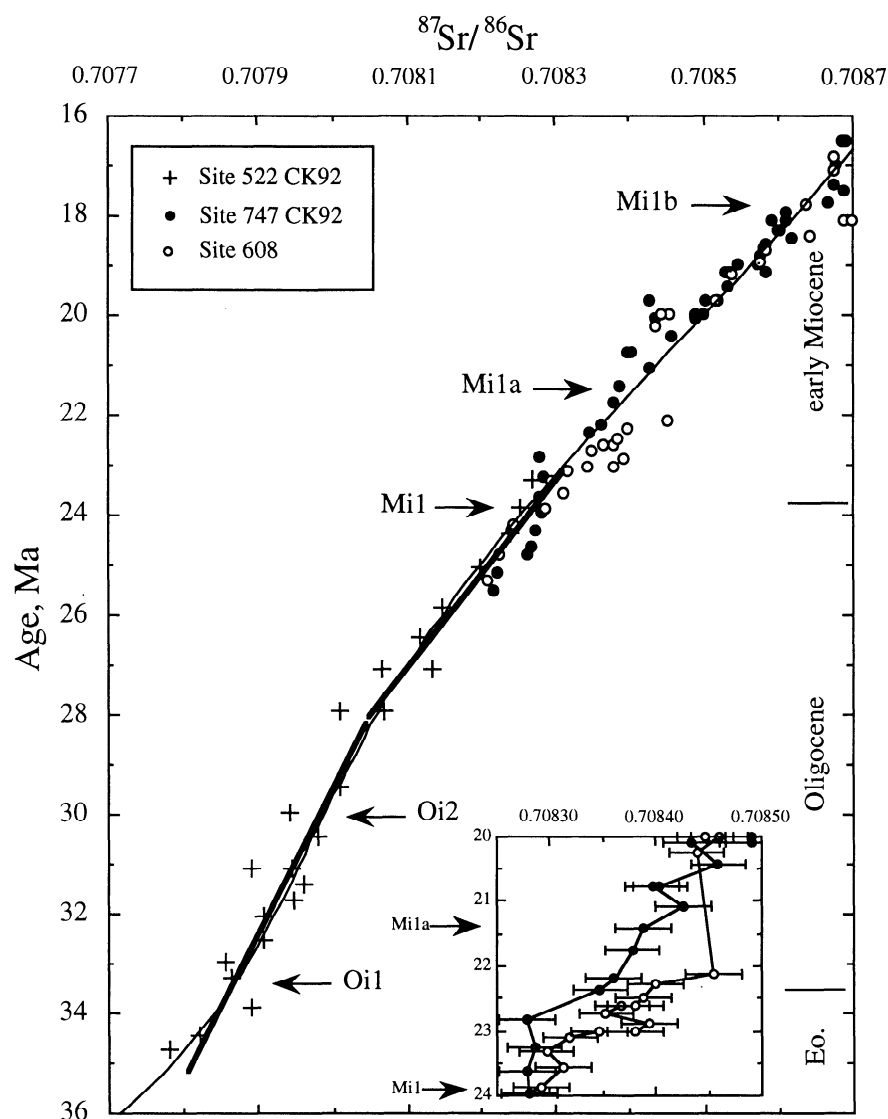


Figure 6. Age versus Sr isotopes for Deep Sea Drilling Project (DSDP) Sites 608 (averaged data), 522, and ODP Hole 747A (unaveraged data). Thin line is fifth-order regression for combined Sites 522 and 747A data. Thick lines are linear regression lines for 23.2 to 28.0 Ma and 29.5 to 34.8 Ma regressions (equations (7) and (8)). All data are calibrated to the geomagnetic polarity timescale (GPTS) of *Cande and Kent* [1992] and normalized to NIST-987 = 0.710255. Oxygen isotope event significance is discussed in text.

mechanisms for varying oceanic Sr isotopic values. We provide a direct calibration between the $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ records (Figure 8). We find that Oligocene through early Miocene increases in Sr isotopes are empirically linked to the oxygen isotope record, lagging the oxygen isotope decreases (measured from the middle point of deglaciations) of *Miller et al.* [1991b] and *Wright and Miller* [1992] by 0.9 to 1.4 m.y. (Figures 6 and 8, and Table 5). Relating the timing of ice growth events ($\delta^{18}\text{O}$ maxima) and $^{87}\text{Sr}/^{86}\text{Sr}$ increases does not produce as consistent time lags (Table 5). Six inflections toward increased $^{87}\text{Sr}/^{86}\text{Sr}$ are correlated with global $\delta^{18}\text{O}$ events.

1. The earliest Oligocene $\delta^{18}\text{O}$ event (Oi1 in Figure 6) (33.5–33.2 Ma using CK92) represents the first definitive glaciation/deglaciation in Antarctica [*Miller et al.*, 1991a]. This event may be associated with a slight increase in Sr isotope slope, al-

though additional data from this interval are needed to show this.

2. The deglaciation following the "middle" Oligocene $\delta^{18}\text{O}$ event (Oi2 in Figure 6) (30.1–29.0 Ma using CK92) that represents an inferred glacioeustatic episode [*Miller et al.*, 1991b] occurred 1.0 m.y. prior to the change in Sr isotope slope at 28 Ma.

3. A $\delta^{18}\text{O}$ decrease near the Oligocene/Miocene boundary (following Mi1 in Figures 6 and 8) (23.9 Ma using CK92) occurred 1.2 m.y. prior to the change in Sr isotope slope defined at Site 747. The high amplitude of the $\delta^{18}\text{O}$ in benthic and subtropical planktonic foraminifera indicates that this is a large (>50 m) glacioeustatic event [*Miller et al.*, 1991b].

4. A $\delta^{18}\text{O}$ decrease occurred (following Mi1a in Figures 6 and 8) (21.4 Ma using CK92) about 1.4 m.y. prior to an inflection in the Site 747 data (Figure 7 inset). We previously suggested that this oxygen isotope event may reflect a glaciocustatic lowering

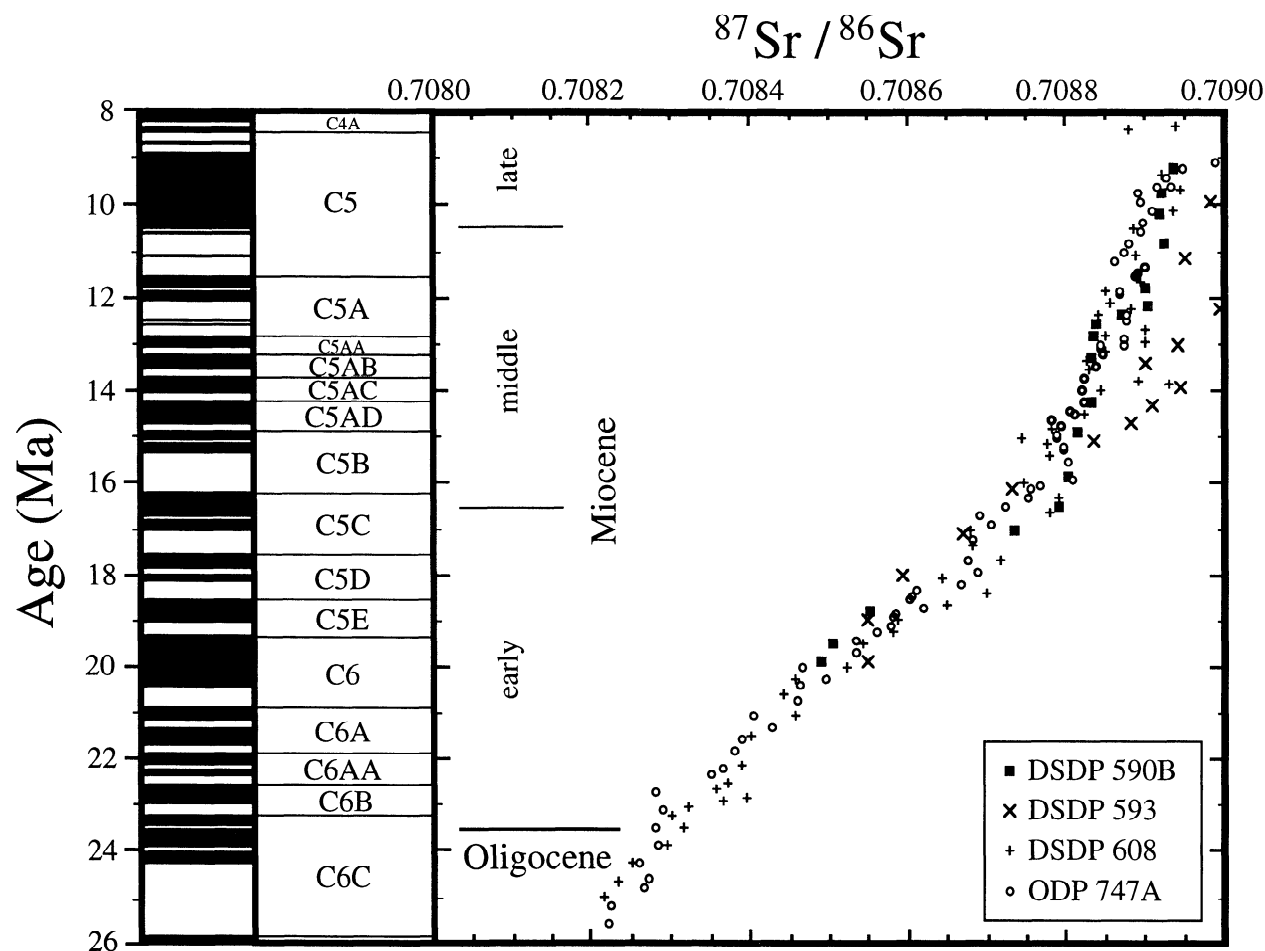


Figure 7. Comparison of Hole 747A Sr data and Sr data from DSDP Sites 590B [DePaolo, 1986], 593 [Hess et al., 1986], and 608 [Miller et al., 1991]. Magnetic timescale is from Berggren et al. [1985a, b]. All data corrected to NIST-987 = 0.710255.

of sea level [Miller et al., 1991b; Wright and Miller, 1992].

5. A $\delta^{18}\text{O}$ decrease (following Mi1b in Figures 6 and 8) (17.8 Ma using CK92) occurred about 0.9 m.y. prior to an inflection at ca. 16.5 Ma in the Site 747 data. We previously suggested that this oxygen isotope event may reflect a glacioeustatic lowering of sea level [Miller et al., 1991b; Wright and Miller, 1992].

6. The $\delta^{18}\text{O}$ decrease (following Mi2 in Figure 8) (15.2 Ma using CK92) occurred about 0.9 m.y. prior to an increase in Sr isotopes. This increase in Sr follows a plateau in the Sr curve which is documented both at Sites 747A and 588 [Hodell and Woodruff, this issue].

Subsequent $\delta^{18}\text{O}$ fluctuations (Mi3-Mi7) are associated with lower rates of increase in the Sr isotope record attributed to the development of a permanent ice sheet on Antarctica (see earlier). The Sr isotope changes may be related to these inferred glacioeustatic events; however, the small amplitude of the signal prevents us from determining if there was a relationship between the two.

We suggest that both mountain uplift and ice volume fluctuations contributed to the Neogene Sr isotopic signal. We speculate that tectonic processes may have controlled the long term trends in the Sr record (e.g., the high rate of change from 22.8 to 15.4 Ma) while on-off glaciations superimposed shorter-term

variations. Ice volume fluctuations are a more likely explanation than Himalaya/Tibetan plateau uplift for late Paleogene increases in the Sr isotope record, because much of the evidence for the timing of initiation of rapid Himalayan uplift indicates ages younger than ~22 Ma [Harrison et al., 1992; Hodges et al., 1992]. Although significant uplift events may have occurred earlier, no reasonably constrained ages for such events have been published. We acknowledge that 10^4 - to 10^5 -year variations may have occurred in the Sr isotopic record [e.g., Dia et al., 1992; Clemens et al., 1993]. As discussed by Clemens et al., these high-frequency variations in the Sr record cannot be readily explained using our current understanding of strontium reservoirs and exchange mechanisms.

A lag of the Sr isotope record to the $\delta^{18}\text{O}$ decreases is expected if the two are causally related for two reasons. First, with a long residence time, (~2.5 m.y. [Hodell et al., 1990], 4.0 m.y. [Hodell et al., 1989] and 5.1 m.y. [Broecker and Peng, 1982]), the response of the oceanic reservoir to transient inputs should lag by ~1.25 to 2.5 m.y. The data and analysis presented here are consistent with the shorter residence time estimates. Second, the maximum rate of input of silicic weathering products from the Antarctic craton should be associated with deglaciations, not with glaciations. This is consistent with our analysis showing a

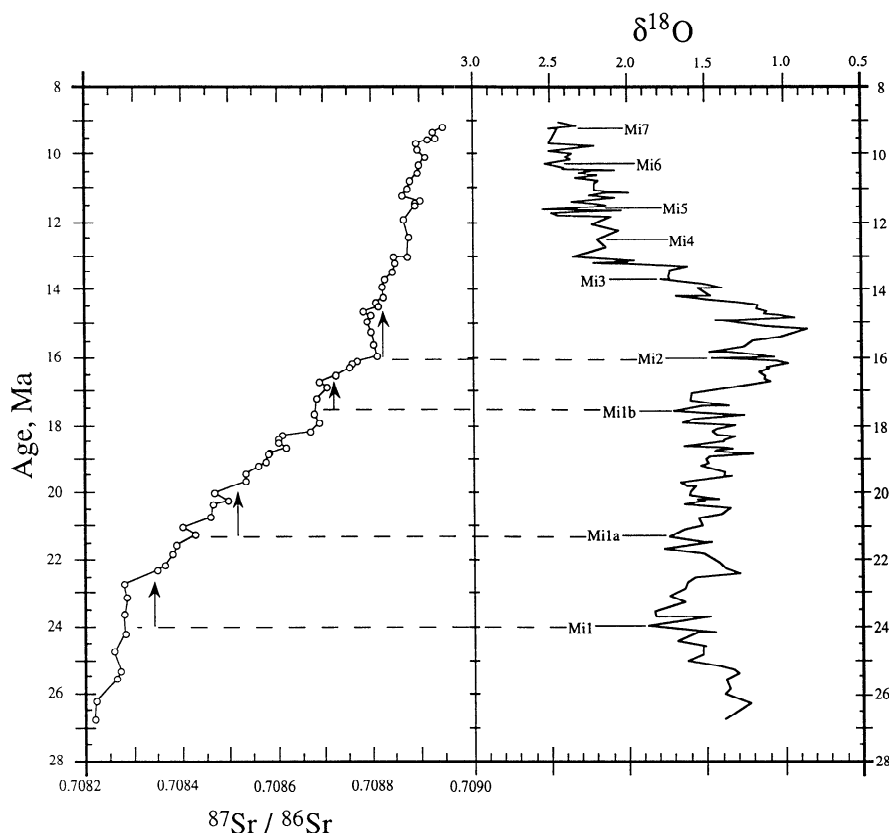


Figure 8. Age versus Sr isotopes and $\delta^{18}\text{O}$ record for Hole 747A. Data calibrated to GPTS of *Cande and Kent* [1992]. Benthic foraminifera oxygen isotope data is from *Wright and Miller*, [1992], with ages adjusted for this study. Arrows from $\delta^{18}\text{O}$ event levels to Sr isotope curve represent approximate response lag time discussed in text.

more constant lag period from the time of deglaciation to Sr increase than from maximum glaciation to Sr increases.

Our scenario relating oxygen isotope decreases as a glacio-eustatic proxy with Sr isotope changes is speculative. While an empirical relationship between Sr and $\delta^{18}\text{O}$ has been shown, singular causality by ice growth may not be the correct interpretation. Other mechanisms which induce a lowering of atmospheric $p\text{CO}_2$ including enhanced chemical erosion due to uplift, or enhanced CO_2 storage in biological or sedimentary reservoirs, may be the ultimate cause of the glaciation and therefore the increase in $^{87}\text{Sr}/^{86}\text{Sr}$ of the oceans. It is clear that Sr isotope studies are

approaching a new degree of stratigraphic and analytical resolution that will allow testing of such relationships. For example, as analytical precision approaches 0.000020 and sampling approaches better than 100 k.yr., it is possible to consider point by point changes in the Sr isotope record (Figure 6, inset and Figure 8). *DePaolo* [1986] attempted this, justifying it with an analytical precision of 0.000010; however, his sampling interval was still relatively coarse. With continued advances in precision and speed of analysis, future studies will be able to more rigorously evaluate paleoceanographic relationships and the Sr isotopic record.

Table 5. Lag Times for $^{87}\text{Sr}/^{86}\text{Sr}$ Increases Following Glacioeustatic Events

Ice Event	Glaciation Age Ma	Deglaciation Age* Ma	$^{87}\text{Sr}/^{86}\text{Sr}$ increase Age Ma	Lag Time Glaciation Sr Increase, m.y.	Lag Time Deglaciation Sr Increase, m.y.
Oi1	33.5	33.2	32.0	1.5	1.2
Oi2	30.1	29.0	28.0	2.1	1.0
Mi1	23.9	23.6	22.4	1.5	1.2
Mi1a	21.4	20.8	19.5	2.0	1.4
Mi1b	17.8	17.4	16.5	1.3	0.9
Mi2	16.0	15.5	14.6	1.4	0.9

* Midpoint of deglaciation.

Conclusions

The excellent magnetic record from ODP Hole 747A combined with its well-preserved foraminiferal sediments provide a Sr isotope reference section that is superior to previously published sections for the middle to lower upper Miocene (ca. 15-9 Ma). Previous sites analyzed for this section have been plagued by either poor age control over at least some portion of the curve or problems with analytical results not directly traceable to a geologic cause (middle Miocene at Site 608). We show that Sr isotopic age estimates for the middle Miocene may be as good as ± 1.2 m.y. for a single analysis to ± 0.7 for 3 analyses at a given level at the 95 % confidence level. We have also (1) confirmed the validity of previously published early Miocene to earliest middle Miocene Sr isotope regressions and provided late Eocene to late middle Miocene Sr isotopic correlations to the new GPTS of *Cande and Kent* [1992]; (2) provided relatively precise age estimates for changes in the rate of Sr isotopic change in the late Oligocene (ca. 28 Ma), earliest Miocene (ca. 23 Ma), and middle Miocene (ca. 15 Ma); and (3) compared the Sr isotopic changes with an inferred ice volume record, concluding that the inflections in the Sr isotopic record lag deglaciations by 1-1.5 m.y.

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