PALEOCEANOGRAPHY, VOL. 17, NO. 3, 1046, doi:10.1029/2001PA000745, 2002

Latest Eocene-earliest Miocene Sr isotopic reference section, Site 522, eastern South Atlantic

Timothy J. Reilly,[1] Kenneth G. Miller, and Mark D. Feigenson

Department of Geological Sciences, Rutgers, The State University of New Jersey, Piscataway, New Jersey, USA

Received 26 November 2001; revised 28 March 2002; accepted 7 May 2002; published 11 September 2002.

[1] We present a revised calibration of Sr isotopes to the geomagnetic polarity timescale (GPTS) using closely spaced (~0.15 m.y. resolution) samples from the classic uppermost Eocene through lowermost Miocene section at Site 522, eastern South Atlantic. The Sr isotopic data are fit with two linear segments with a sharp change in slope at circa 27.5 Ma from 0.000038/m.y. (27.5 to 34.4 Ma) to 0.000051/m.y. (23.8 to 27.5 Ma). Regression analysis indicates that stratigraphic resolution ranges from ±1 m.y. (for one analysis) to ±0.6 m.y. (for three analyses) for the younger interval and ±1.2 m.y. (for one analysis) to ±0.7 m.y. (for three analyses) for the older interval, representing an increase in resolution from previous studies of ±1–2 m.y. The paleoceanographic significance of this change in slope is unclear. It occurs during an interval of intermittent Antarctic glaciation, between the Oi2a and Oi2b glaciations. The subsequent interval from circa 27 to 24 Ma appears to be an interval of minimal glaciation. Thus this observation does not support previous suggestions that increases in rates of Sr isotopic change are directly associated with the frequency of Antarctic glaciations. Rather, the increase in slope may be related to increased weathering associated with the "mid-Oligocene" glaciation. *INDEX TERMS:* 1040 Geochemistry: Isotopic composition/chemistry; 1030 Geochemistry: Geochemical cycles (0330); 4267 Oceanography: General: Paleoceanography; 9604 Information Related to Geologic Time: Cenozoic; *KEYWORDS:* Sr isotopes, Oligocene, stratigraphy, glaciation

Citation: Reilly, T. J., K. G. Miller, and M. D. Feigenson, Latest Eocene-earliest Miocene Sr isotopic reference section, Site 522, eastern South Atlantic, *Paleoceanography*, *17*(3), 1046, doi:10.1029/2001PA000745, 2002.

1. Background

[2] Strontium-isotopic stratigraphy is a well-established relative dating technique applicable to unaltered marine carbonate throughout the Phanerozoic [*Burke et al.*, 1982]. Seawater $^{87}Sr/^{86}Sr$ is apparently uniform at any given time because the residence time of strontium (~2.5 m.y. [*Hodell et al.*, 1990]; ~5.1 m.y. [*Broecker and Peng*, 1982]) is much longer than oceanic mixing times (~1 k.y. [*Broecker and Peng*, 1982]). Seawater $^{87}Sr/^{86}Sr$ values have increased rapidly (relative to other intervals) since about 40 Ma [*Burke et al.*, 1982], providing moderate to high-resolution (typically ~0.3–1.0 m.y.) means of correlation. Thus Sr isotopic variations provide an excellent means of correlating "unknown" sections to the timescale, particularly difficult-to-correlate high-latitude and shallow-water sections [e.g., *Hess et al.*, 1986; *Miller et al.*, 1988; *McNeil and Miller*, 1990].

[3] Sr isotopic variations not only provide an excellent means of correlating sections of uncertain age to the timescale, but also record the balance of strontium inputs from continental weathering and hydrothermal flux and the buffering effect of the dissolution of marine carbonates (see *Elderfield* [1986] for review). Though changes in hydrothermal flux and carbonate weathering have contributed to an overall $^{87}Sr/^{86}Sr$ increase during the last 100 m.y., Sr isotopic variations were largely controlled by increases in either the riverine flux of radiogenic (continental) Sr or the $^{87}Sr/^{86}Sr$ values of riverine input [*Palmer and Elderfield*, 1985; *Hess et al.*, 1986; *Elderfield*, 1986; *Richter et al.*, 1992]. Sr isotopic variations were minimal in the Paleocene-middle Eocene, increased in the late Eocene, and again dramatically in the early Miocene (circa 22 Ma [e.g., *Hess et al.*, 1986]). This stepwise increase in the rates of Sr isotopic change has generally been attributed to increased continental weathering [e.g., *Richter et al.*, 1992], though increases in the ratio (due to weathering more radiogenic rocks) of the input cannot be precluded. The cause of this inferred increase in weathering is controversial. Most studies have attributed the change to increased input from the Tibetan-Himalayan plateau [*Raymo et al.*, 1988; *Raymo*, 1991; *Hodell et al.*, 1989, 1991; *Hodell and Woodruff*, 1994]. In contrast, *Miller et al.* [1991], *Oslick et al.* [1994], and *Zachos et al.* [1999] suggested that there was a relationship between late Eocene to Miocene $^{87}Sr/^{86}Sr$ changes and Antarctic glacial history inferred from $\delta^{18}O$ variations.

[4] Use of Sr isotopes for dating "unknown" sections or for understanding changes in seawater Sr evolution requires firm calibrations between age and empirically determined global Sr isotopic changes. Many Sr isotopic ages are calibrated by averaging results from several sections and fitting a linear or polynomial fit to the data [e.g., *Burke et al.*, 1982; *Hess et al.*, 1986; *Elderfield*, 1986]. *Miller et al.*

---

[1] Now at U.S. Geological Survey, Water Resources Division, West Trenton, New Jersey, USA.

0883-8305/02/2001PA000745$12.00

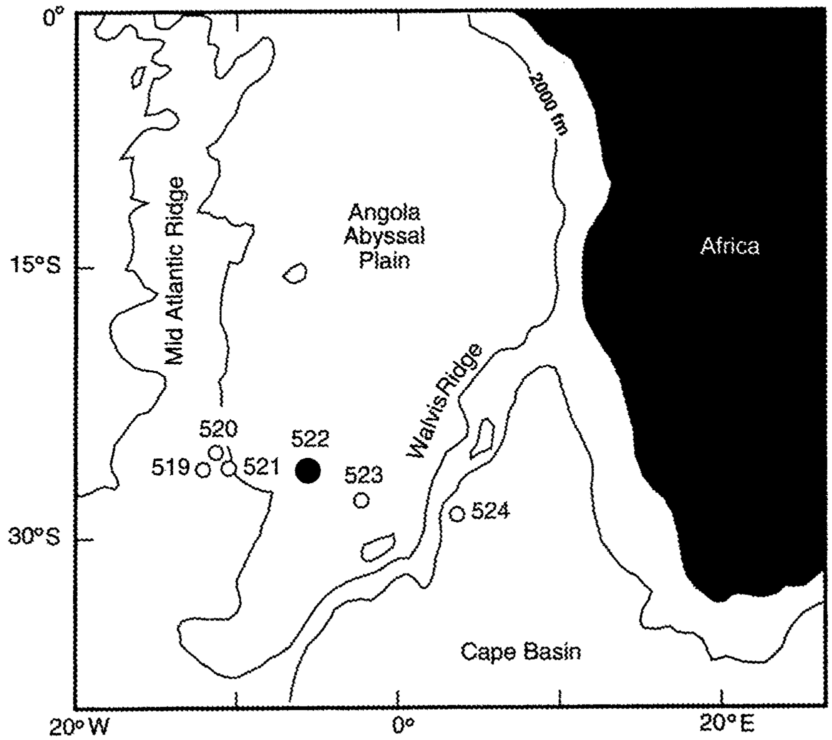

Figure 1. Site location map. Open circles indicate other sites from DSDP Leg 73. Map based on *Hsu et al.* [1984].

[1988, 1991] and *Oslick et al.* [1994] promoted the idea of establishing Sr isotopic reference sections with the clearest ties to the geomagnetic polarity timescale (GPTS), establishing reference sections for upper Eocene to lowermost Miocene (eastern South Atlantic Site 522 [*Miller et al.*, 1988]) and Miocene strata (eastern North Atlantic Site 608 [*Miller et al.*, 1991]; Indian Ocean Site 747 [*Oslick et al.*, 1994]).

[5] Recent advances in cyclostratigraphy have resulted in an astronomical timescale (ATS) for upper middle to upper Miocene strata; Sr isotopic studies at Site 926 (Ceara Rise) allow direct calibration to the ATS [*Martin et al.*, 1999]. While astronomical timescales offer finer resolution, sections with clear magnetostratigraphy still provide an excellent opportunity to calibrate isotopic changes to the timescale because the GPTS is closely calibrated to the ATS. *Shackleton et al.* [2000] used cyclostratigraphy to suggest that the Oligocene/Miocene boundary, as calibrated to Chron C6Cn2, is significantly (~1 m.y.) younger than the GPTS of *Berggren et al.* [1995] (hereinafter referred to as BKSA95). Until this proposition is validated and its implications to the timescale are evaluated, we continue to use the GPTS for the late Eocene-early Miocene of BKSA95, with the Oligocene/Miocene boundary at 23.8 Ma.

[6] Deep Sea Drilling Project (DSDP) Site 522 (Figure 1) has figured prominently in our understanding of Oligocene oceanographic change, providing a classic section for magnetostratigraphic [*Tauxe et al.*, 1984; *Tauxe and Hartl*, 1997], oxygen isotopic [*Poore and Matthews*, 1984; *Miller et al.*, 1988; *Zachos et al.*, 1996], and Sr isotopic [*DePaolo and Ingram*, 1985; *Miller et al.*, 1988] changes. *Miller et al.* [1988] used Site 522 as a reference section for calibrating late Eocene to earliest Miocene Sr isotopic changes to the GPTS. However, *Mead and Hodell* [1995] suggested that Site 522 isotopic records suffer from diagenesis and that Ocean Drilling Program (ODP) Southern Ocean Site 689 provides a better calibration to the GPTS. They based the interpretation of diagenesis at Site 522 upon small (<0.000050) offsets between age calibrations derived from Sites 522 and 689. This difference could be attributed to interlaboratory calibration problems (i.e., a 0.000020 difference exists between University of Florida and other laboratories after correcting for differences in the NBS987 standard; see *Oslick et al.* [1994] and *Howarth and MacArthur* [1997] for discussion) and problems in age correlation, particularly at Site 689, where magnetostratigraphic correlations are ambiguous.

[7] Recent studies by *Pearson et al.* [2001] also raise the specter of diagenesis even in very shallowly buried sites (~100 m) such as Site 522 (~50–150 mbsf). Their study showed that planktonic foraminifers in some shallowly buried sites, by virtue of their open wall structure, suffered from ~50% diagenetic overprint for oxygen isotopes. One could argue that diagenetic overprinting of planktonic foraminiferal tests in shallow burials depth (i.e., reflecting bottom waters) would not affect $^{87}Sr/^{86}Sr$ because the ocean is well mixed with respect to Sr. Even if planktonic foraminifers are altered at Site 522, we analyzed benthic foraminifer, which, by virtue of their closed wall structure, are not as susceptible to shallow burial diagenesis [*Pearson et al.*, 2001]. In addition, Sr isotopic values are less generally less sensitive to burial diagenesis than $\delta^{18}O$

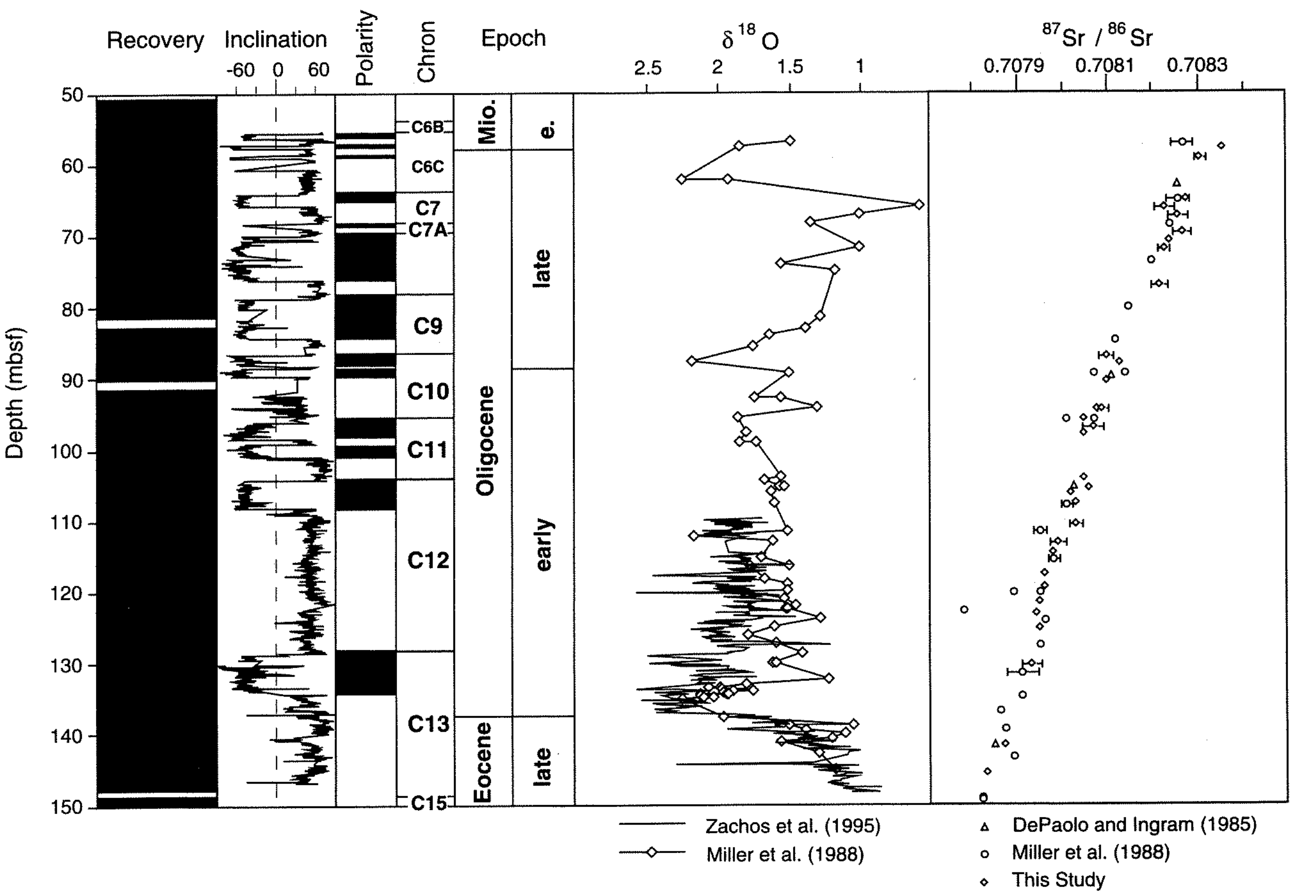

Figure 2. Uppermost Eocene to lowermost Miocene $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ records plotted against depth in m below seafloor (mbsf) and magnetostratigraphy at DSDP Site 522. Magnetostratigraphy modified after *Tauxe et al.* [1984] using data from *Tauxe and Hartl* [1997]. Oxygen isotopic data are indicated by diamonds [*Miller et al.*, 1988] and a line [*Zachos et al.*, 1996]. Strontium isotopic data are indicated by triangles [*DePaolo and Ingram*, 1985], circles [*Miller et al.*, 1988], and diamonds (this study). Chrons and epochs are from *Berggren et al.* [1995]. Error bars reflect the interrun variability of each analysis.

values. *Miller et al.* [1991] suggested that $\delta^{18}O$ potentially provides one means of screening deep-sea sections for Sr isotope diagenesis. Various studies have documented the fidelity of the benthic foraminiferal $\delta^{18}O$ records at Site 522 [*Poore and Matthews*, 1984; *Miller et al.*, 1988; *Zachos et al.*, 1996] and the Sr isotopic record from this site compares remarkably well with coeval sections [*DePaolo and Ingram*, 1985; *Miller et al.*, 1988; this study]. We thus conclude that diagenesis does not significantly affect the Site 522 benthic foraminiferal $^{87}Sr/^{86}Sr$ record.

[8] We revisited the Site 522 Sr isotopic record by quadrupling the original sample resolution study (from 0.68 m.y. to 0.17 m.y.) and recalibrating our age model to the new timescale [*Berggren et al.*, 1995]. We compare our Sr isotopic results with the Site 689 record of *Mead and Hodell* [1995] and the oxygen isotopic records of *Zachos et al.* [1996] and *Miller et al.* [1988].

2. Methods

[9] Samples for strontium isotope analysis were soaked in hydrogen peroxide and sodium metaphosphate, washed with sodium metaphosphate in tap water through a 63-μm sieve, and air-dried. Eighty to 100 benthic foraminifera were selected from each sample from the greater than 150 μm size fraction. The foraminifera from Site 522 were examined for signs of diagenesis and recrystallization. All samples used in this study were found to be well-preserved and exhibited no visible signs of diagenesis or recrystallization. In addition, benthic foraminiferal $\delta^{18}O$ values from the Oligocene at Site 522 are similar to $\delta^{18}O$ records at other locations with different burial histories (see *Miller et al.* [1988] for comparisons), arguing against significant diagenetic alternation.

[10] Samples for strontium isotope analysis were sonified for approximately three seconds and rinsed in double-distilled water. Standard ion exchange techniques developed by *Hart and Brooks* [1974] were used to isolate the strontium from the samples for analysis. Samples were analyzed using a VG Sector Mass Spectrometer at Rutgers, The State University of New Jersey where NBS 987 is routinely measured to be 0.710255 ($1\sigma = \pm 0.000008$, normalized to $^{86}Sr/^{88}Sr = 0.1194$; *Oslick et al.*, 1994). External precision (inter-run variability) for Sr isotopic analyses is on the order of ±0.000020 or better [*Oslick et al.*, 1994].

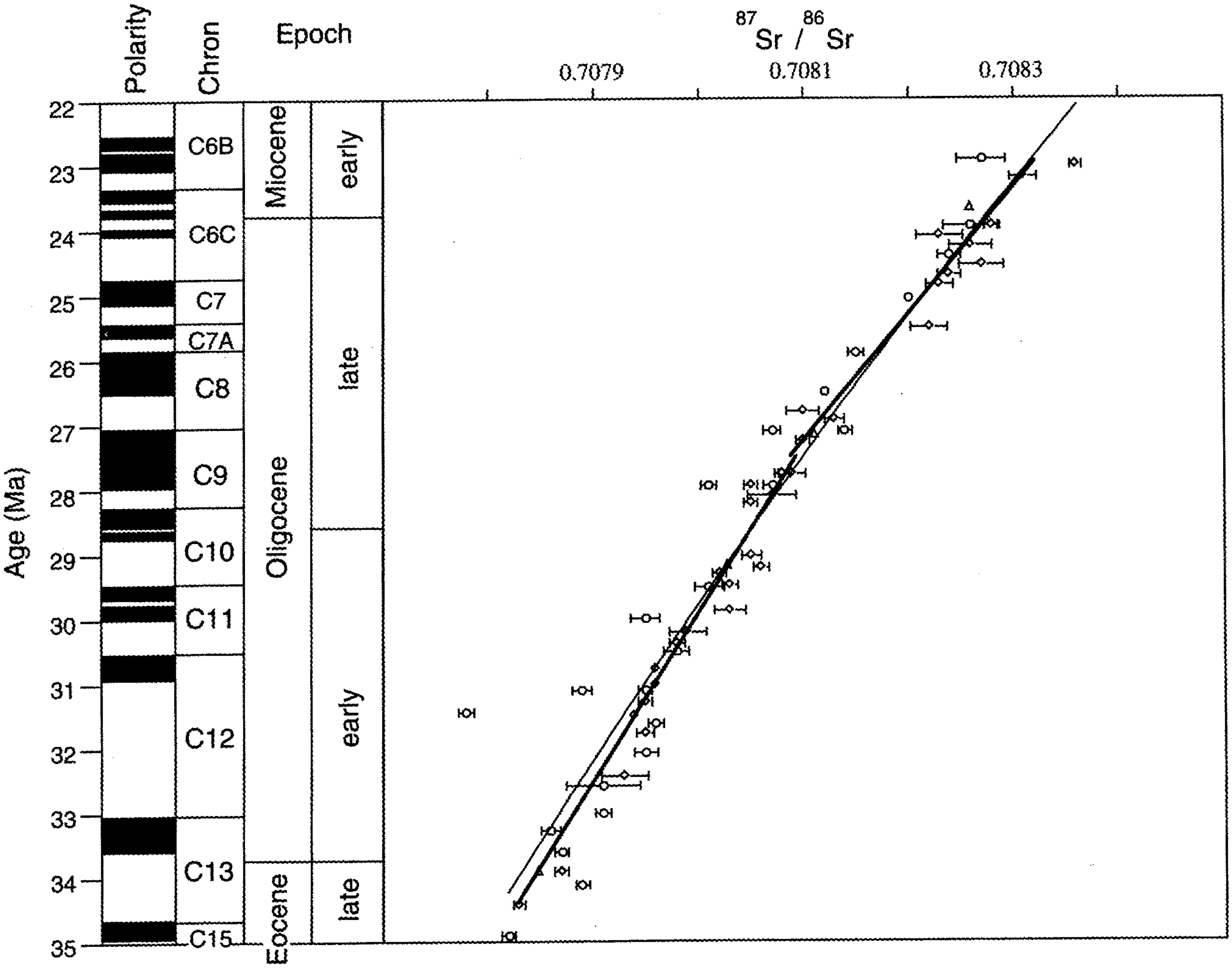

Figure 3. The $^{87}Sr/^{86}Sr$ data versus age for Site 522. Strontium data are indicated by triangles [*DePaolo and Ingram*, 1985], circles [*Miller et al.*, 1988], and diamonds (this study). The thin black line is the fifth-order polynomial used to constrain the timing of the change in the rate of $^{87}Sr/^{86}Sr$ decrease. The two thick lines are linear regressions drawn based on the data from *DePaolo and Ingram* [1985], *Miller et al.* [1988], and this study. Error bars reflect the interrun variability of each analysis.

[11] In order to determine the relationship between Sr isotope ratio and age, Sr values must be correlated to an independently derived chronology. In this study, the Sr values were directly calibrated to the GPTS using the relatively clear magnetostratigraphy at Site 522 [*Tauxe et al.*, 1984; *Tauxe and Hartl*, 1997]. Independent age estimates were obtained by linearly interpolating sedimentation rates between the magnetochron boundaries revised by *Tauxe and Hartl* [1997]. The ages of the magnetochron boundaries were taken from the GPTS of *Berggren et al.* [1995]. The average Sr isotopic sampling interval is 1.59 m., corresponding to a sample resolution of approximately 0.15 m.y.

3. Results and Discussion

[12] Sr isotopic values generally increase upsection through the upper Eocene (Chronozone C15n, partim) through lowermost Miocene (Chronozone C6Br, partim) section at Site 522 (Figure 2). Sr isotopic values reported here agree well with those reported from Site 522 by *DePaolo and Ingram* [1985] and *Miller et al.* [1988] (Figure 2).

[13] Sr isotope values were plotted versus age to determine the evolution of seawater $^{87}Sr/^{86}Sr$ through time (Figure 3). As in previous studies that follow linear regression techniques developed for radiocarbon calibration [*Draper and Smith*, 1981], $^{87}Sr/^{86}Sr$ values measured at each depth are dependent variables and age estimates (based upon magnetochronology) are independent variables [*Miller et al.*, 1991; *Oslick et al.*, 1994]. To be consistent with previous illustrations [e.g., *Oslick et al.*, 1994], Sr isotope values were plotted with age on the abscissa even though age is the independent variable (Figure 2 and Table 1). A fifth-order polynomial was fit to the $^{87}Sr/^{86}Sr$ data assuming that age is the independent variable (Figure 3). Based on an inflection seen in the fifth-order fit, the data set was then broken into two groups, 23.8 to 27.5 Ma. (0.708320 to

Table 1. Sr Isotopic Data, Site 522

Section	Depth in Section, cm	Depth, mbsf	Age, Ma	$^{87}Sr/^{86}Sr$	Error	Reference
14-3	122	54.92	22.92	0.708269	0.000023	*Miller et al.* [1988]
14-cc	6	55.06	23.01	0.708362	0.000006	this study
15-1	28	55.38	23.21	0.708312	0.000013	this study
15-2	63	57.23	23.70	0.708260		*Depaolo and Ingram* [1985]
15-3	28	58.38	23.95	0.708277	0.000008	this study
15-3	30	58.40	23.95	0.708255	0.000026	*Miller et al.* [1988]
15-cc	5	59.45	24.11	0.708232	0.000023	this study
16-1	110	60.60	24.27	0.708265	0.000021	this study
16-2	61	61.61	24.41	0.708243	0.000011	*Miller et al.* [1988]
16-3	28	62.78	24.57	0.708273	0.000021	this study
16-cc	4	63.79	24.71	0.708241	0.000011	this study
17-1	84	64.74	24.86	0.708229	0.000013	this study
17-2	54	65.94	25.08	0.708200	0.000005	*Miller et al.* [1988]
17-cc	14	68.39	25.51	0.708225	0.000018	this study
18-2	73	70.53	25.92	0.708150	0.000007	*Miller et al.* [1988]
19-2	62	74.82	26.52	0.708119	0.000005	*Miller et al.* [1988]
19-cc	3	76.93	26.81	0.708100	0.000016	this study
20-1	54	77.84	26.95	0.708128	0.000009	this study
20-2	34	79.14	27.13	0.708070	0.000008	*Miller et al.* [1988]
20-2	34	79.14	27.13	0.708135	0.000006	*Miller et al.* [1988]
20-2	73	79.53	27.19	0.708112		*Depaolo and Ingram* [1985]
20-cc	15	80.10	27.28	0.708097	0.000006	this study
21-2	55	83.37	27.79	0.708084	0.000008	this study
21-2	59	83.41	27.79	0.708093	0.000013	this study
21-3	27	84.57	27.97	0.708052	0.000006	this study
21-3	27	84.57	27.97	0.708012	0.000007	*Miller et al.* [1988]
21-3	27	84.57	27.97	0.708073	0.000008	*Miller et al.* [1988]
21-cc	18	85.56	28.12	0.708071	0.000023	this study
22-1	58	86.28	28.24	0.708052	0.000006	this study
25-1	125	92.85	29.04	0.708045	0.000009	this study
25-2	126	94.03	29.22	0.708057	0.000008	this study
25-2	93	94.36	29.18	0.708028		*Depaolo and Ingram* [1985]
25-3	48	95.08	29.31	0.708024	0.000006	this study
26-1	103	96.63	29.50	0.708033	0.000007	this study
26-1	105	96.65	29.51	0.708010	0.000014	*Miller et al.* [1988]
26-3	104	99.64	29.88	0.708029	0.000015	this study
27-1	95	100.75	30.02	0.707945	0.000014	*Miller et al.* [1988]
27-2	94	102.23	30.21	0.707987	0.000017	this study
27-3	94	103.74	30.40	0.707976	0.000007	this study
28-1	62	104.82	30.53	0.707982	0.000012	*Miller et al.* [1988]
28-3	14	107.34	30.80	0.707959	0.000005	this study
29-1	87	109.47	31.03	0.707958	0.000005	this study
29-2	34	110.44	31.13	0.707891	0.000009	*Miller et al.* [1988]
29-2	34	110.44	31.13	0.707947	0.000006	*Miller et al.* [1988]
29-3	33	111.93	31.29	0.707949	0.000006	this study
29A-2	109	113.53	31.46	0.707784	0.000007	*Miller et al.* [1988]
30-1	108	114.08	31.52	0.707940	0.000005	this study
30-1	53	115.06	31.62	0.707964	0.000007	*Miller et al.* [1988]
30-2	56	116.51	31.78	0.707954	0.000008	this study
30-3	51	119.33	32.08	0.707949	0.000011	*Miller et al.* [1988]
32-1	76	122.56	32.43	0.707927	0.000023	this study
31-2	43	124.05	32.58	0.707909	0.000035	*Miller et al.* [1988]
32-2	75	128.12	33.02	0.707909	0.000008	*Miller et al.* [1988]
33-2	42	131.50	33.29	0.707856	0.000009	*Miller et al.* [1988]
34-2	30	135.62	33.62	0.707868	0.000006	*Miller et al.* [1988]
36-2	141	139.11	33.91	0.707870	0.000007	this study
35-2	42	139.32	33.93	0.707848		*Depaolo and Ingram* [1985]
36-3	12	142.10	34.14	0.707893	0.000006	*Miller et al.* [1988]
37-2	90	146.12	34.44	0.707825	0.000006	this study
38-2	92	150.09	34.90	0.707821	0.000006	*Miller et al.* [1988]

0.708087) and 27.5 to 34.4 Ma (0.708093 to 0.707829). A linear regression was then fit to each subset.

$$23.8 \text{ to } 27.5\,\text{Ma}.\ ^{87}Sr/^{86}Sr = 0.7094816 - 5.07 \times 10^{-5} * (\text{Age, Ma}) \qquad (1)$$

$$27.5 \text{ to } 34.4\text{Ma}.\ ^{87}Sr/^{86}Sr = 0.7091378 - 3.80 \times 10^{-5} * (\text{Age, Ma}) \qquad (2)$$

Both data subsets fit extremely well to their respective regression lines (23.8 to 27.5 Ma, $r^2 = 0.954$ and 27.5 to 34.4 Ma, $r^2 = 0.954$). Equations to estimate the age of a

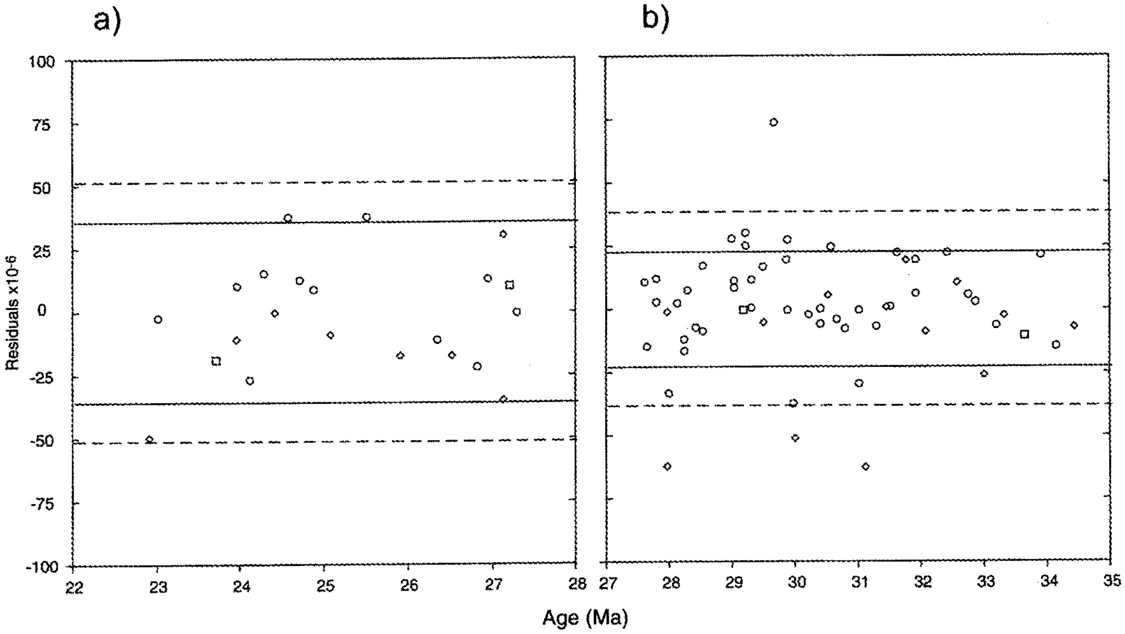

Figure 4. Plot of residual values for $^{87}Sr/^{86}Sr$ values from Site 522 linear regressions. Residual values are indicated by triangles [*DePaolo and Ingram*, 1985], circles [*Miller et al.*, 1988], and diamonds (this study). The solid lines approximate the 95% confidence interval for three independent analyses, and the dashed lines approximate the 95% confidence interval for one analysis.

sample based upon its Sr value were derived from the equations of the best fit lines by inverting equations 1 and 2:

$$23.8 \text{ to } 27.5 \text{ Ma. Age (Ma)} = \left[\left({}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}\right) - 0.7094816 \;/ -5.07 \times 10^{-5}\right] \quad (3)$$

$$27.5 \text{ to } 34.4 \text{ Ma. Age (Ma)} = \left[\left({}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}\right) - 0.7091378 \;/ -3.80 \times 10^{-5}\right] \quad (4)$$

[14] Residuals for each regression were calculated (Figures 4a and 4b). The lack of trends in the residuals document that the regressions provide a valid fit to the data (Figures 4a and 4b).

[15] Error analysis was conducted using calculated standard errors and 95% confidence intervals with single and multiple data point sets. *Miller et al.* [1991] presented a modified version of the *Draper and Smith* [1981] error-predicting equation that is valid for the situation where an individual $^{87}Sr/^{86}Sr$ 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

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

[16] Where Age_0 is the predicted age, s is the standard error, t is Student's statistic, b_1 is the slope, $\overline{\text{Age}}$ is the mean age of the regression, n is the number of measurements in the regression, and q = number of $^{87}Sr/^{86}Sr$ analyses at a given stratigraphic level. Based on equations 1, 2, and 5, stratigraphic resolution between 23.8 and 27.5 Ma is ±1 m.y. (for 1 analysis at the 95% confidence interval) to ±0.6 m.y. (for 3 analyses at the 95% confidence interval); stratigraphic resolution between 27.5 and 34.4 Ma is ±1.2 m.y. (for 1 analysis at the 95% confidence interval) to ±0.7 m.y. (for 3 analyses at the 95% confidence interval). This represents improved resolution versus previous statistical estimates for this interval (e.g., based on the coarse sampling at Site 522, *Miller et al.* [1988] and *Oslick et al.* [1994] estimated resolution of about 2 m.y.)

[17] In order to test the validity of our proposed Sr isotopic standard section, we compared results from Site 522 with the published $^{87}Sr/^{86}Sr$ record for Site 689 [*Mead and Hodell*, 1995] (Figure 5) using a revised age model for Site 689 (Table 2). After remodeling their data using the BKSA95 timescale and accounting for differences in standard measurement, regressions from both sites are similar between 34.4 Ma and circa 26 Ma. Site 689 suffers from a late Oligocene hiatus that precludes detection of the change in slope noted here (see below; Figure 5). Thus much of the purported differences between Sites 522 and 689 can be explained by problems in age correlation (Figure 5). The slight discrepancy between the two regressions is either due to problems of inter-laboratory calibration or the sometime cryptic paleomagnetic data from Site 689.

[18] We date a major inflection in the Sr isotopic record as circa 27.5 Ma (Chron C9n, planktonic foraminiferal ZoneP21b), where the slope changes from 0.000038/m.y. in the earlier Oligocene to 0.000051/m.y. (Figures 3 and 5) *Oslick et al.* [1994] used sparser data at Site 522 to suggest

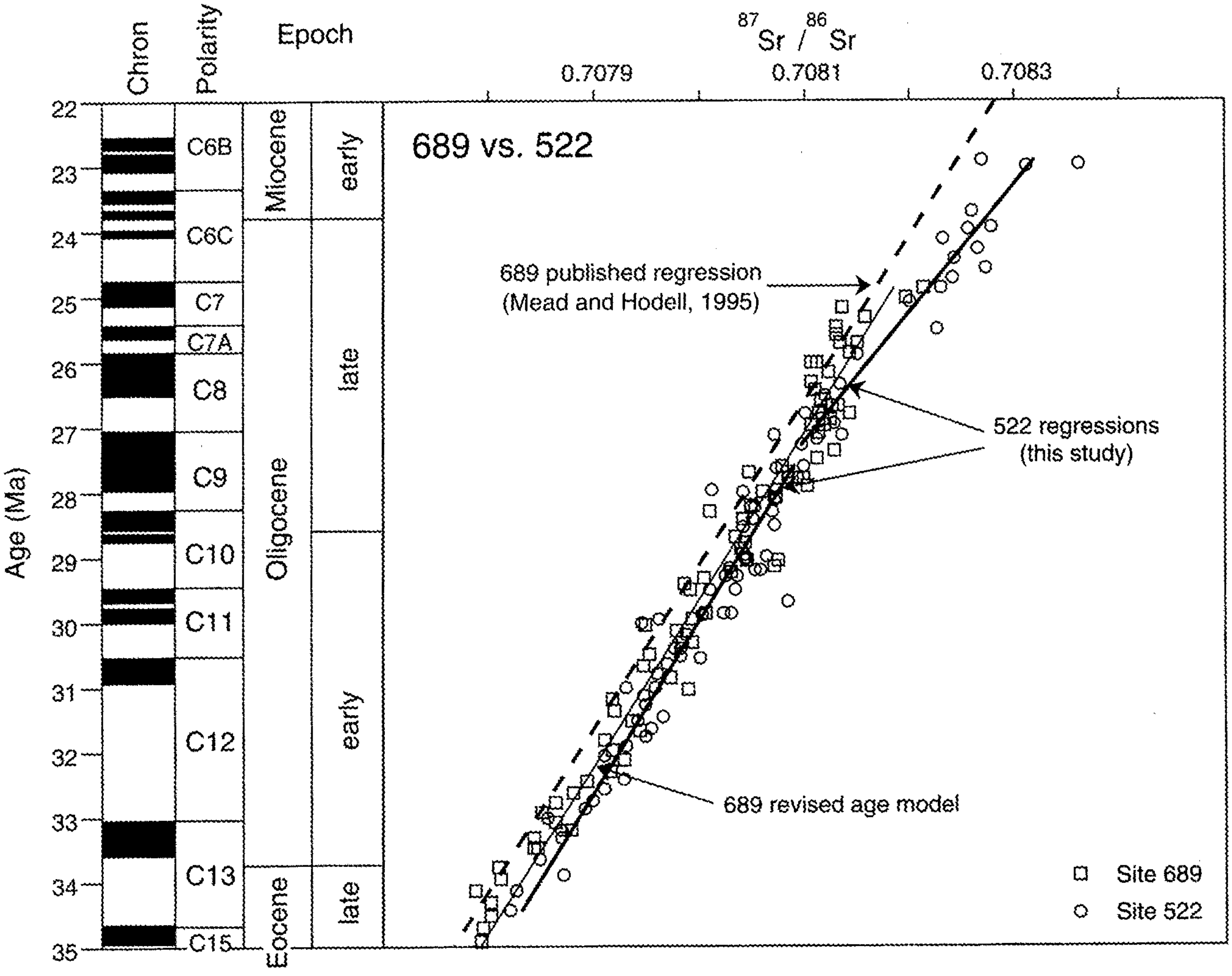

Figure 5. The ^{87}Sr/^{86}Sr data versus age for Sites 522 and 689. Strontium data are indicated by squares [*Mead and Hodell*, 1995] and circles (this study). The dashed line represents the regression published by *Mead and Hodell* [1995]. The thin line represents the Site 689 ^{87}Sr/^{86}Sr data from *Mead and Hodell* [1995] fit to a revised age model (see text). The two thick solid lines are linear regressions drawn based on the data from *DePaolo and Ingram* [1985], *Miller et al.* [1988], and this study.

an inflection at circa 28 Ma, while *Capo et al.* [1991] reported an inflection at circa 26 Ma based on studies of Apennine sections, though Sr isotope data near this proposed inflection are sparse in these sections. Our data set delineates this inflection well at circa 27.5 Ma and allows us to evaluate the relationship between changes in slope of seawater ^{87}Sr/^{86}Sr and glaciations (Figure 6).

[19] *Miller et al.* [1991] and *Oslick et al.* [1994] suggested that the tempo of Sr isotopic changes during the late Eocene through early Miocene was controlled by the frequency of Antarctic glaciations, with intervals of high ^{87}Sr/^{86}Sr increases associated with more numerous glaciations. To evaluate this hypothesis, we compared the ^{87}Sr/^{86}Sr results of this study to the oxygen isotope record of Site 522 [*Zachos et al.*, 1996; *Miller et al.*, 1988]. The increase in the slope occurs during an interval of intermittent Antarctic glaciation, between the Oi2a and Oi2b glaciations (Figure 6). The increase in rate does not correlate with any m.y.-scale oxygen isotopic event and the time interval subsequent to the Sr isotopic change circa 27 to 24 Ma is an interval of minimal glaciation. Thus our observations do not support previous suggestions that intervals with high rates of ^{87}Sr/^{86}Sr increase are associated with more numerous Antarctic glaciations.

[20] Nevertheless, it is possible that the rate of increase of ^{87}Sr/^{86}Sr during the Oligocene was related to changes in the tempo of Antarctic glaciations. The increase in slope at 27.5

Table 2. Age Model Interpolation Points, Site 689

Depth, mbsf	Age, Ma	Chron
67.11	24.835	top C7n.2n
75.97	26.554	base C8n.2n
79.46	27.027	top C9n
91.93	28.745	base C10n.2n
103.37	30.098	base C11n.2n
106.87	30.939	base C12n
116.71	33.058	top C13n
119.69	33.545 Ma	base C13n

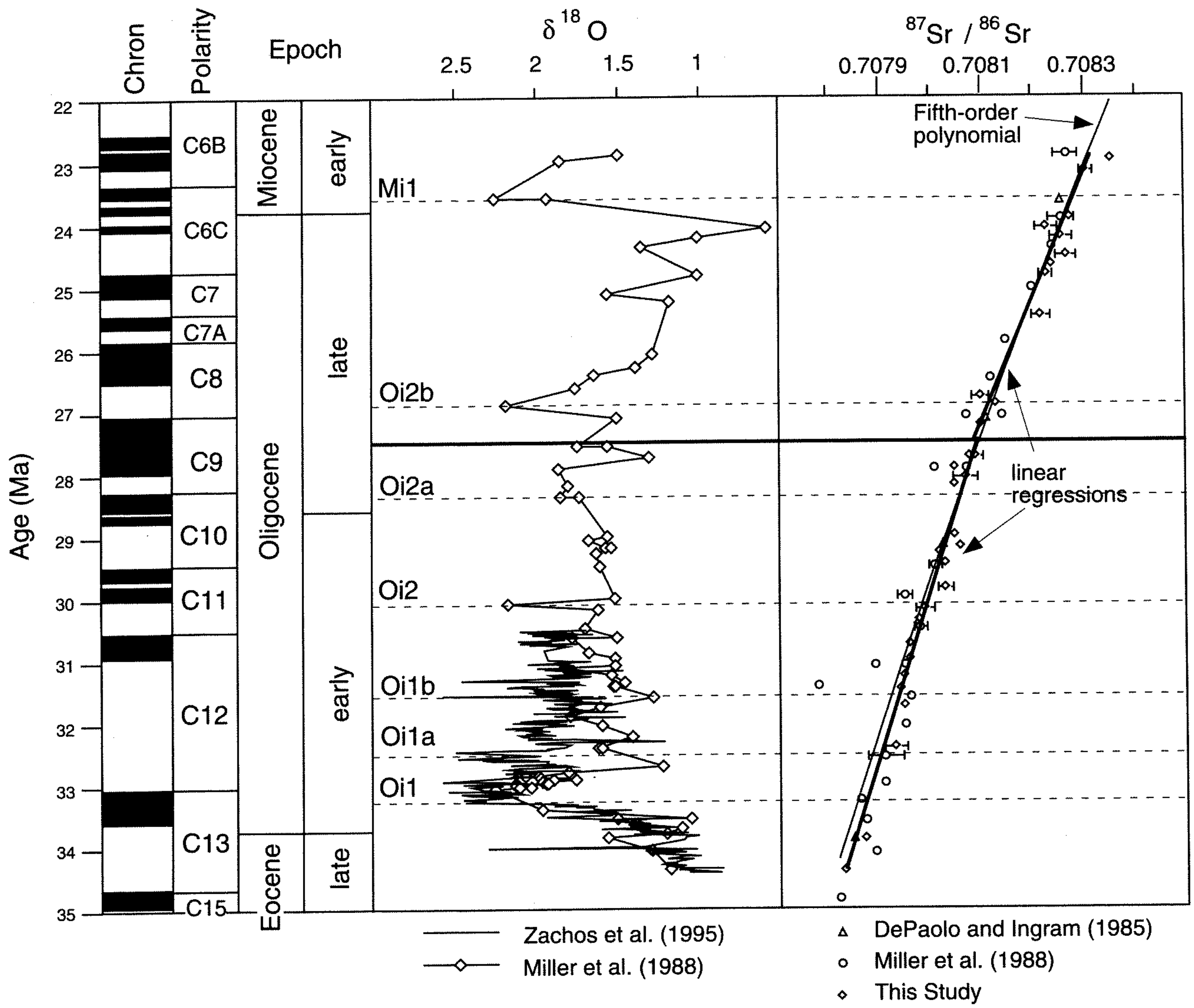

Figure 6. The $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ data versus age for Site 522. The thick horizontal line indicates the circa 27.5 Ma increase in the rate of Sr isotopic change. Oxygen data are indicated by diamonds [*Miller et al.*, 1988] and a line [*Zachos et al.*, 1996]. Horizontal dashed lines indicate oxygen isotope zones. Strontium data are indicated by triangles [*DePaolo and Ingram*, 1985], circles [*Miller et al.*, 1988], and diamonds (this study). The thin line is the fifth-order polynomial; the two thick lines are linear regressions drawn based on the data from *DePaolo and Ingram* [1985], *Miller et al.* [1988], and this study.

Ma occurred during "mid-Oligocene" glaciations (Oi2, Oi2a, Oi2b) and was followed by a period of lower/minimal ice volume. We suggest that flouring of Antarctic cratonic rocks during the mid-Oligocene and subsequent exposure during the late Oligocene deglaciation(s) resulted in greater delivery of radiogenic Sr to the oceans. Thus we agree with *Capo et al.* [1991] that the change of slope in the late Oligocene may reflect major "mid" Oligocene glaciations and glacioeustatic events. Subsequent on again/off again glaciations during the early Miocene resulted in even higher rates of delivery and $^{87}Sr/^{86}Sr$ increase [*Miller et al.*, 1991; *Oslick et al.*, 1991].

[21] While it is possible to explain the change in slope at 27.5 Ma by a decrease in hydrothermal flux, there are no empirical data to support such a decrease. It may also be possible to attribute the change to increased input from other continental weathering sources (e.g., the Himalayas). However, most studies have suggested that Himalayan inputs increased at circa 40 Ma and 21 Ma [e.g., *Raymo*, 1991; *Richter et al.*, 1992], while northern hemisphere glacial inputs increased at circa 2.5 Ma [*Capo and DePaolo*, 1990]. We conclude that while the cause(s) of Sr isotopic variations during the past 40 m.y. are still poorly understood, Sr isotopes provide an important correlation tool for this interval, particularly for challenging Oligocene correlations.

[22] Though Site 522 is firmly tied to the GPTS, it currently lacks an astronomical timescale. Though cyclostratigraphy may yield a more reliable chronology and *Weedon et al.* [1997] have provided a preliminary Oligo-

cene astronomical scale, there is no Oligocene section with a complete astronomical timescale. Thus stratigraphers must rely on referencing Sr isotopic variations to the GPTS of *Berggren et al.* [1995]. Because Sr isotopes provide a relative dating tool, the chronology of Sr isotopic variations obtained from direct correlation with the GPTS at Site 522 can be adjusted to a new astronomical time when it becomes available. We conclude that Site 522 still provides the best reference section with well-constrained error estimates for using Sr isotopic variations for correlations.

4. Conclusions

1. We present a closely sampled (0.15 m.y.) record of latest Eocene to earliest Miocene $^{87}Sr/^{86}Sr$ changes that is directly tied to the GPTS of BKSA95. Comparisons with Site 689 validate our conclusion that Site 522 still provides the best Sr isotopic reference section for the latest Eocene to earliest Miocene.

2. Regression analysis indicates that our revised Sr isotopic standard section provides stratigraphic resolution for "unknown" samples of ±1 m.y. (for 1 analysis) to ±0.6 m.y. (for 3 analyses) from 23.8 to 27.5 Ma and ±1.2 m.y. (for 1 analysis) to ±0.7 m.y. (for 3 analyses) for 27.5 to 34.4 Ma.

3. An increase in the rate of $^{87}Sr/^{86}Sr$ increase occurred at circa 27.5 Ma. The cause of this increase is unknown, though we speculate that this increase might be related to increased delivery of radiogenic Sr in an interval of minimal glaciation following several large mid-Oligocene glaciations.

[23] **Acknowledgments.** We thank M.E. Katz and two anonymous reviewers for comments and J.D. Wright for discussions. Most of the Sr isotope data collection and some sections of this paper were developed as part of an undergraduate research project at Rutgers University. Supported by NSF grant EAR99-09179. Samples were supplied by the ODP.

References

Berggren, W. A., D. V. Kent, C. C. Swisher, and M. P. Aubry, A revised Cenozoic geochronology and chronostratigraphy, in *Geological Time Scales and Global Stratigraphic Correlations*, edited by W. A. Berggren et al., *Spec. Publ. SEPM Soc. Sediment. Geol.*, *54*, 129–212, 1995.

Broecker, W. S., and T. H. Peng, *Tracers in the Sea*, 690 pp., Lamont-Doherty Earth Obs., Palisades, N.Y., 1982.

Burke, W. H., R. E. Denison, E. A. Hetherington, R. B. Koepnick, H. F. Nelson, and J. B. Otto, Variations in seawater $^{87}Sr/^{86}Sr$ ratio during Phanerozoic time, *Geology*, *10*, 516–519, 1982.

Capo, R. C., and D. J. Depaolo, Seawater strontium isotopic variations from 2.5 million years to the present, *Science*, *249*, 51–55, 1990.

Capo, R., A. Montanari, and D. J. DePaolo, Flexure of the strontium isotopic curve in the upper Oligocene of the pelagic sequence at Gubbio: Signature of a major eustatic event?, *Geol. Soc. Am. Abstr. Programs*, *178*, A178, 1991.

DePaolo, D. J., and B. L. Ingram, High-resolution stratigraphy with strontium isotopes, *Science*, *227*, 938–940, 1985.

Draper, N. R., and H. Smith, *Applied Regression Analysis*, 709 pp., John Wiley, New York, 1981.

Elderfield, H., Strontium isotope stratigraphy, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *57*, 71–90, 1986.

Hart, S. R., and C. Brooks, Clinopyroxene-matrix partitioning of K, Rb, Cs, and Ba, *Geochim. Cosmochim. Acta*, *38*, 1799–1806, 1974.

Hess, J., M. L. Bender, and J.-G. Schilling, Evolution of the ratio of strontium-87 to strontium-86 in seawater from Cretaceous to Present, *Science*, *231*, 979–984, 1986.

Hodell, D. A., and F. Woodruff, Variations in the strontium isotopic ratio of seawater during the Miocene: Stratigraphic and geochemical implications, *Paleoceanography*, *9*, 405–426, 1994.

Hodell, D. A., P. A. Mueller, J. A. McKenzie, and G. A. Mead, Strontium isotope stratigraphy and geochemistry of the late Neogene ocean, *Earth Planet. Sci. Lett.*, *92*, 165–178, 1989.

Hodell, D. A., G. A. Mead, and P. Mueller, Variations in the strontium isotopic composition of seawater (8 Ma to present): Implications for chemical weathering rates and dissolved fluxes to the oceans, *Chem. Geol.*, *80*, 291–307, 1990.

Hodell, D. A., P. A. Mueller, and J. R. Garrido, Variations in the strontium isotopic composition of seawater during the Neogene, *Geology*, *19*, 24–27, 1991.

Howarth, R. J., and J. M. MacArthur, Statistics for strontium isotope stratigraphy; a robust LOWESS fit to marine Sr-isotopic curve for 0-206 Ma, with look-up table for derivation of numeric age, *J. Geol.*, *105*, 441–456, 1997.

Hsu, K. J., et al., *Initial Reports of the Deep Sea Drilling Project*, vol. 73, 798 pp., U.S. Gov. Print. Off., Washington, D.C., 1984.

Martin, E. E., N. J. Shackleton, J. C. Zachos, and B. P. Flower, Orbitally-tuned Sr isotope chemostratigraphy for the late middle to late Miocene, *Paleoceanography*, *14*, 74–83, 1999.

Mead, G. A., and D. A. Hodell, Controls on the $^{87}Sr/^{86}Sr$ composition of seawater from the middle Eocene to Oligocene: Hole 689B, Maud Rise, Antarctica, *Paleoceanography*, *10*, 327–346, 1995.

McNeil, D. H., and K. G. Miller, High-latitude application of $^{87}Sr/^{86}Sr$: Correlation of Nuwok Beds on North Slope, Alaska to standard Oligocene chronostratigraphy, *Geology*, *18*, 415–418, 1990.

Miller, K. G., M. D. Feigenson, D. V. Kent, and R. K. Olsson, Oligocene stable isotope ($^{87}Sr/^{86}Sr$, $\delta^{18}O$, $\delta^{13}C$) standard section, Deep Sea Drilling Project Site 522, *Paleoceanography*, *3*, 223–233, 1988.

Miller, K. G., M. D. Feigenson, J. D. Wright, and B. M. Clement, Miocene isotope reference section, Deep Sea Drilling Project Site 608: An evaluation of isotopic and biostratigraphic resolution, *Paleoceanography*, *6*, 33–52, 1991.

Oslick, J. S., K. G. Miller, M. D. Feigenson, and J. D. Wright, Oligocene-Miocene strontium isotopes: Stratigraphic revisions and correlations to an inferred glacioeustatic record, *Paleoceanography*, *9*, 427–443, 1994.

Palmer, M. R., and H. Elderfield, Sr isotope composition of sea water over the past 75 Myr, *Nature*, *314*, 526–528, 1985.

Pearson, P. N., P. W. Ditchfield, J. Singanao, K. G. Harcourt-Brown, C. J. Nicholas, R. K. Olsson, N. J. Shackleton, and M. A. Hall, Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs, *Nature*, *413*, 481–487, 2001.

Poore, R. Z., and R. K. Matthews, Late Eocene-Oligocene oxygen and carbon isotope record from South Atlantic Ocean DSDP Site 522, *Initial Rep. Deep Sea Drill. Proj.*, *73*, 725–736, 1984.

Raymo, M. E., Geochemical evidence supporting T. C. Chamberlin's theory of glaciation, *Geology*, *19*, 344–347, 1991.

Raymo, M. E., W. F. Ruddiman, and P. N. Froelich, Influence of late Cenozoic mountain building on ocean geochemical cycles, *Geology*, *16*, 649–653, 1988.

Richter, F. M., D. B. Rowley, and D. J. DePaolo, Sr isotope evolution of seawater: The role of tectonics, *Earth Planet. Sci. Lett.*, *109*, 11–23, 1992.

Shackleton, N. J., M. A. Hall, I. Raffi, L. Tauxe, and J. Zachos, Astronomical calibration age for the Oligocene-Miocene boundary, *Geology*, *28*, 447–450, 2000.

Tauxe, L. P., and P. Hartl, 11 million years of Oligocene geomagnetic field behavior, *Geophys. J. Int.*, *128*, 217–229, 1997.

Tauxe, L., P. Tucker, N. P. Peterson, and J. L. LaBreque, Magnetostratigraphy of Leg 73 sediments, *Initial Rep. Deep Sea Drill. Proj.*, *73*, 609–612, 1984.

Weedon, G. P., N. J. Shackleton, and P. N. Pearson, The Oligocene time scale and cyclostratigraphy on the Ceara Rise, western equatorial Atlantic, *Proc. Ocean Drill. Program Sci. Res.*, *154*, 101–114, 1997.

Zachos, J. C., T. M. Quinn, and S. Salamy, High resolution (10^4 yr) deep-sea foraminiferal stable isotope records of the earliest Oligocene climate transition, *Paleoceanography*, *11*, 251–256, 1996.

Zachos, J. C., B. N. Opdyke, T. M. Quinn, C. E. Jones, and A. N. Halliday, Early Cenozoic glaciation, Antarctic weathering, seawater $^{87}Sr/^{86}Sr$: Is there a link?, *Chem. Geol.*, *161*, 165–180, 1999.

M. D. Feigenson and K. G. Miller, Department of Geological Sciences, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA.

T. J. Reilly, U.S. Geological Survey, Water Resources Division, 810 Bear Tavern Road, Suite 206, West Trenton, NJ 08628, USA. (tjreilly@usgs.gov)