



# Nonlinear increase in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in the Oligocene to early Miocene and implications for climate-sensitive weathering

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**Abstract.** The  $^{87}\text{Sr}/^{86}\text{Sr}$  of marine carbonates provides a key constraint on the balance of continental weathering and hydrothermal Sr fluxes to the ocean, and mid-Oligocene to mid-Miocene features the most rapid rates of increase in the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the Cenozoic. Because previous records of the  $^{87}\text{Sr}/^{86}\text{Sr}$  increase with time were based on biostratigraphically defined age models in diverse locations, it was difficult to unambiguously distinguish m.y. scale variations in the rate of  $^{87}\text{Sr}/^{86}\text{Sr}$  change from variations in sedimentation rate. In this study, we produce the first  $^{87}\text{Sr}/^{86}\text{Sr}$  results from an Oligocene to early Miocene site with a precise age model derived orbital tuning of high resolution benthic  $\delta^{18}\text{O}$ , at the Equatorial Pacific Ocean Drilling Program (ODP) Site 1218. Our new dataset resolves transient decreases in  $^{87}\text{Sr}/^{86}\text{Sr}$ , as well as periods of relative stasis. These changes can be directly compared with the high resolution benthic  $\delta^{18}\text{O}$  in the same site. We find slowing of the rate of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase coincides with the onset of Antarctic ice expansion at the beginning of the Mid-Oligocene Glacial Interval, and a rapid steepening in the  $^{87}\text{Sr}/^{86}\text{Sr}$  increase coincides with the benthic  $\delta^{18}\text{O}$  evidence for rapid ice retreat. This pattern may reflect either northward shifts in the Intertropical Convergence Zone precipitation to areas of nonradiogenic bedrock, and/or lowered weathering fluxes from highly radiogenic glacial flours on Antarctic. We additionally generate the first  $^{87}\text{Sr}/^{86}\text{Sr}$  data from ODP Site 1168 and Integrated Ocean Drilling Program (IODP) Site 1406 during the Oligocene to early Miocene to improve the precision of age correlation of these Northern Hemisphere and Southern Hemisphere mid-latitude sites, and to better estimate the duration of early Miocene hiatus and condensed sedimentation.

## 1 Introduction

The mid-Oligocene through the mid-Miocene features the fastest rate of change in seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  of the Cenozoic, evidence of significant change in the balance of Sr sources to the ocean. Although the precise



35 causes of the Cenozoic  $^{87}\text{Sr}/^{86}\text{Sr}$  change remain under discussion, to first order the rise reflects an increase in the  
supply of dissolved Sr sourced from weathering of older rocks of higher  $^{87}\text{Sr}/^{86}\text{Sr}$ , which are found on continents,  
compared to the supply of dissolved Sr from rocks of lower  $^{87}\text{Sr}/^{86}\text{Sr}$  characterizing submarine volcanic  
40 weathering and subaerial weathering of young volcanic provinces (Palmer and Elderfield, 1985). This change in  
balance of sources can be accomplished by one or more processes including decrease in rate of hydrothermal  
weathering, increase in total continental weathering, or changes in the  $^{87}\text{Sr}/^{86}\text{Sr}$  of continental weathering flux due  
to either changes in the location of most intense weathering or changes in the composition and average age  
(Peucker-Ehrenbrink and Fiske, 2019) of rocks exposed to weathering.

Within the Oligocene-early Miocene period of rapid increase in  $^{87}\text{Sr}/^{86}\text{Sr}$ , some previous studies have  
suggested the potential for 1-3 million year timescale variations in the rate of increase (Oslick et al., 1994) and  
45 proposed that the liberation of Sr from silicate weathering may respond to changes in the production and exposure  
of glacially floured rock on Antarctica (Miller et al., 1991; Oslick et al., 1994; Zachos et al., 1999). However, the  
precision of estimates of the rate of change in  $^{87}\text{Sr}/^{86}\text{Sr}$  are limited by the precision of the independent age model  
in marine records. Where age model control points are of low resolution or low certainty, changes in  
sedimentation rate may cause apparent variations in the rate of change in  $^{87}\text{Sr}/^{86}\text{Sr}$ , so that changes in the rate of  
50  $^{87}\text{Sr}/^{86}\text{Sr}$  cannot be confidently inferred. To date, available  $^{87}\text{Sr}/^{86}\text{Sr}$  data for the Oligocene and early Miocene is  
derived from deep sea sediment cores featuring only biostratigraphically derived age models, whose precision is  
limited by the biostratigraphic sampling resolution as well as the potential for diachroneity among events.  
Precision on such age models can be limited by long distances between examined biostratigraphic points in the  
core and the potential for diachroneity in the first occurrence or last occurrence of taxa in diverse locations, and  
55 may feature uncertainties from 0.5 to 4 m.y. (Miller et al., 1988). Over the last decade, cyclostratigraphy has  
emerged as a powerful independent chronometer, and the success of continuous coring and splicing of deep ocean  
sediment cores has enabled the elaboration of precise independent age models based on orbital tuning of high  
resolution benthic  $\delta^{18}\text{O}$  records (Pälike et al., 2006; Liebrand et al., 2016; Westerhold et al., 2020; De  
Vleeschouwer et al., 2017).

60 In this study, we seek to apply the independent orbitally tuned Oligocene chronology for two purposes.  
First, we seek to evaluate the potential for dynamic changes in Sr sources by producing a  $^{87}\text{Sr}/^{86}\text{Sr}$  record from a  
site with an independent orbitally-resolved age model, Ocean Drilling Program (ODP) Site 1218 (Pälike et al.,  
2006; Westerhold et al., 2020). The very rapid rate of change in seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  also provides the opportunity  
for improved age correlation among distal sites (McArthur et al., 2020). Therefore, our second objective is to  
65 improve the fidelity of the age model for two further sites which currently lack an orbitally resolved age model,  
using existing reference curves and the Site 1218 record as an additional reference. For this objective, we focus  
on North Atlantic International Ocean Discovery Program Site 1406 and Southern Ocean ODP Site 1168, both  
emerging as important sites for Oligocene to early Miocene paleoceanographic studies (Scher et al., 2015; Hoem  
et al., 2022; Hoem et al., 2021; Guitián and Stoll, 2021; Kim and Zhang, 2022; Egger et al., 2018; Liu et al., 2018;  
70 Spray et al., 2019; Boyle et al., 2017). Site 1406 features a hiatus of poorly constrained duration in the early  
Miocene (Van Peer et al., 2017b; Norris et al., 2014). The Oligocene to Early Miocene Southern Ocean  
paleogeography produced strong provincialism in many marine taxa from Site 1168, so synchronicity with global  
biostratigraphic datums is uncertain. For paleoclimatic study, tuning to Site 1218 offers the advantage of



75 providing a precise link with the complete benthic  $\delta^{18}\text{O}$  record and therefore enabling direct correlation to the highest resolution paleoclimatic record available for this time interval.

## 2 Sites and Methods

### 2.1 Sediments

Ocean Drilling Program (ODP) Leg 199, Site Site 1218, equatorial Pacific ( $8^{\circ}53.378'\text{N}$ ,  $135^{\circ}22.00'\text{W}$ , 4.8-km water depth) features a detailed cyclostratigraphic age model from benthic  $\delta^{18}\text{O}$  originally spanning 22 to 25 Ma (Pälike et al., 2006). Subsequently, continuous tuning at precision of the 100 ky eccentricity cycle from 21.81 Ma through the lowermost Oligocene was generated on the GTS 2020 CENOGRID timescale (Westerhold et al., 2020). In Site 1218 we sought high resolution in the Middle Oligocene Glacial Interval (MOGI), previously hypothesized to feature inflection points in the  $^{87}\text{Sr}/^{86}\text{Sr}$  curve (Oslick et al., 1994). We targeted samples between 59.93 and 211.94 revised meter core depth (rmcd). Due to the modest carbonate content of Site 1218, not all targeted sample intervals contained sufficient foraminifera for analysis. We have picked  $>2$  mg of mixed species of planktonic or mixed species of benthic foraminifera, depending on the abundance in each sample. From some samples, populations of both benthic and planktic forams could be procured and we report the averaged  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for the two populations.

90 Integrated Ocean Drilling Program (IODP) Expedition 342 recovered Paleogene to Neogene sedimentary sequences in contourite drift deposits off the coast of Newfoundland in the Northwestern Atlantic. Here we focus on Site 1406 ( $40^{\circ}21.0'\text{N}$ ,  $51^{\circ}39.0'\text{W}$ ; 3814 mbsl) with samples dominantly from Hole A, but including a few samples from Holes B and C. Where exclusively data from Hole A are presented, we illustrate depth on CSF-A scale; where samples from all sites are plotted, we illustrate on the composite CCSF-A scale. Based on available biostratigraphy and previous age models (Norris et al., 2014) (Van Peer et al., 2017b), we sought samples spanning age range 17 to 30 Ma, represented by depths from 23.9 to 200 m on the CCSF-A depth scale. In the Southern Hemisphere, ODP Site 1168 was drilled offshore of the Australian plate at the western margin of Tasmania, at  $43^{\circ}36.57'\text{S}$  and  $139^{\circ}144'24.76'\text{E}$ , and 2463m water depth. This sequence is within a graben-developed basin with sediment accumulation since the latest Eocene (Exon et al., 2004). Based on available biostratigraphy (Stickley et al., 2004), we selected samples from Hole A, spanning the 16 to 27 Ma interval, representing sediments from 278 to 562 m depth on the CSF-A depth scale. Mixed planktonic foraminifera were picked for both sites 1406 and 1168.

### 2.2 Analytical

Strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) were measured on  $\sim 2$  mg of cleaned foraminifera carbonates. Foraminifera samples were crushed open under binocular inspection and the fragments were rinsed several times in MilliQ water, methanol and ultrasonicated to remove detrital contaminants (Pena et al., 2005). Each sample was treated individually to ensure that sufficient rinsing steps were applied. Cleaned fragments were dissolved in dilute double distilled nitric acid, and the resulting solution centrifuged at medium speed for 20 minutes to remove any potential detrital material left in the samples. The supernatant was transferred to clean Savillex-PFA beakers



110 and Sr was chemically separated from sample matrix and interfering Rb using Triskem Sr-Spec resin through  
column chromatography procedures at the LIRA ultra-clean laboratory (Universitat de Barcelona).

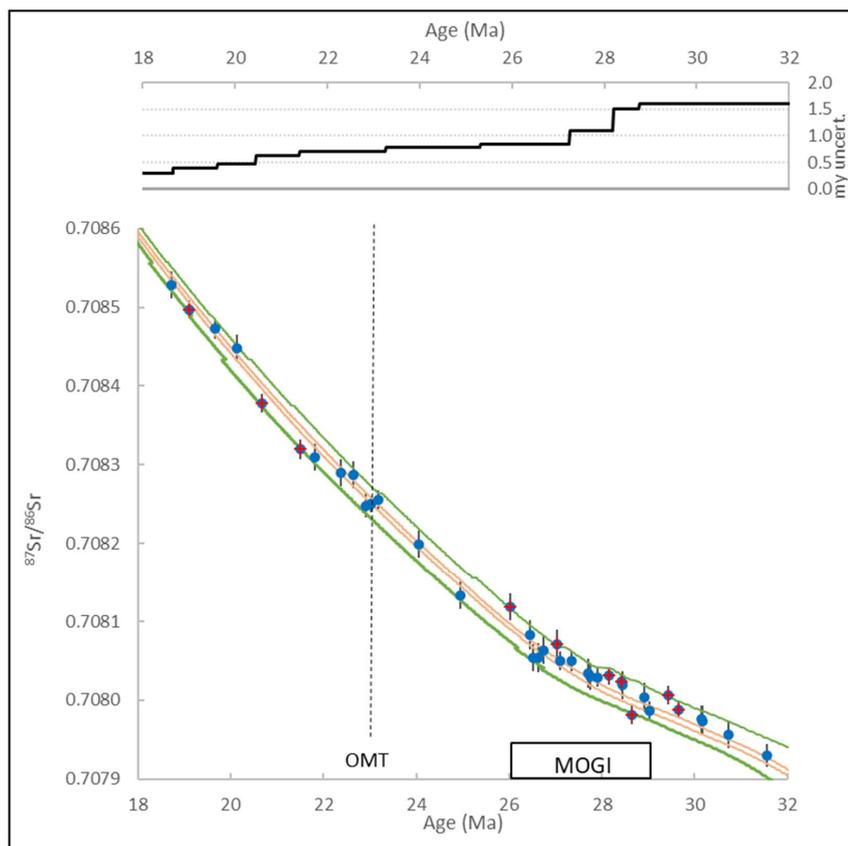
Following sample purification, Sr isotope ratios were determined by multicollector inductively coupled  
mass spectrometry on a Nu Instruments (Wrexham, UK) Plasma 3 MC-ICPMS at the University of Barcelona  
(CciT-UB). For the determination of the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios, the contribution of  $^{87}\text{Rb}$  to the  $^{87}\text{Sr}$  signal was  
115 corrected from the measurement of the  $^{85}\text{Rb}$  signal, assuming a  $^{87}\text{Sr}/^{85}\text{Sr}$  ratio of 0.38562. The  $^{86}\text{Kr}$  interference  
on  $^{86}\text{Sr}$ , caused by impurities in the argon gas, was also corrected by measuring the  $^{83}\text{Kr}$  signal, and assuming a  
 $^{83}\text{Kr}/^{86}\text{Kr}$  value of 0.66453.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized for instrumental mass bias to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ .  
Instrumental drift was corrected by sample-standard bracketing (SSB) using NBS987 = 0.710249 as the primary  
120 standard with matching standard and sample Sr concentrations. External analytical reproducibility during the  
session was  $\pm 0.000018$  ( $2\sigma$ ,  $n=19$ ). Procedural blanks are routinely measured at every analytical session. Typical  
procedural Sr blanks (including sample cleaning, purification and analysis) are  $369 \pm 264$  pg,  $n=12$ , 1SD. Blanks  
are systematically corrected for every measurement and the effect of the correction is in the sixth decimal place  
of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, well below the external reproducibility of the analytical method (5th decimal place).  
Values are normalized to SRM 987 using  $^{86}\text{Sr}/^{86}\text{Sr}$  of 0.1194 and  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.710249. This is identical to the  
125 normalization of (McArthur et al., 2020) using  $^{87}\text{Sr}/^{86}\text{Sr}$  0.709174 for modern marine-Sr (EN-1 and similar),  
equivalent to 0.710248 for SRM(NIST) 987.

### 3 Results

Our new data from Site 1218 on the Cenogrid age model (Figure 1, Table 1), reveal a similar long term  
amplitude and rate of rise in  $^{87}\text{Sr}/^{86}\text{Sr}$  as previously reported data on biostratigraphically constrained age models  
130 (McArthur et al., 2020). However, the new data reveal a 1 m.y. duration period of negligible  $^{87}\text{Sr}/^{86}\text{Sr}$  rise (27-28  
Ma) and local reversals in the overall trend of increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  during the Middle Oligocene Glacial Interval  
(MOGI) and at the Oligo-Miocene transition. The new data also reveal several intervals of especially abrupt  
increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  within and at the end of the MOGI.

135 In Site U1406, a prominent reversal in the  $^{87}\text{Sr}/^{86}\text{Sr}$  rise is observed between 48.7 and 45.4 m (Figure 2a,  
depths described on the CCSF-A scale). A significant jump in  $^{87}\text{Sr}/^{86}\text{Sr}$  suggests an appreciable hiatus between  
33.3 m and 34.7 m. The abrupt change in  $^{87}\text{Sr}/^{86}\text{Sr}$  between 176.2 and 170.1 may also indicate a hiatus or  
significantly condensed interval. In Site 1168 (Figure 2b), a prominent reversal in the  $^{87}\text{Sr}/^{86}\text{Sr}$  rise occurs between  
538.2 and 527.8 m CSF-A.

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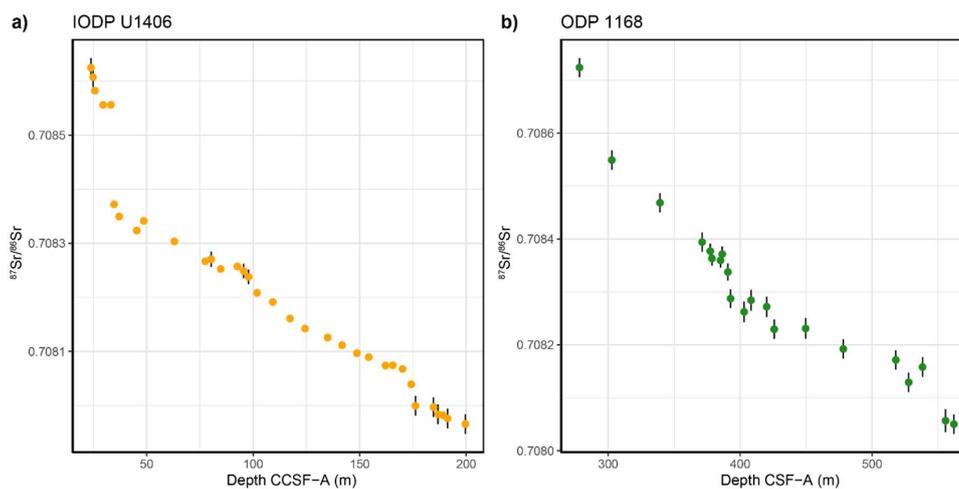
145 **Figure 1:**  $^{87}\text{Sr}/^{86}\text{Sr}$  results from Site 1218 (blue circles with  $2\sigma$  analytical uncertainty shown). The orange lines show the upper and lower bounds of the LOESS fit of biostratigraphically defined  $^{87}\text{Sr}/^{86}\text{Sr}$  (McArthur et al., 2020). Samples falling outside the biostratigraphically defined long term curve are highlighted in red. The green lines illustrate expanded age bounds for LOESS fit of biostratigraphically constrained age models (McArthur et al., 2020). Upper panel illustrates the width of the age uncertainty of the expanded bounds. The Middle Oligocene Glacial Interval (MOGI) from 29 to 26 Ma is labelled, as is the Oligocene-Miocene Transition (OMT).

## 4 Discussion

### 4.1 Variation in the rate of change of $^{87}\text{Sr}/^{86}\text{Sr}$ in Site 1218

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The steep long term Oligocene to early Miocene increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  is long recognized and variably attributed to exhumation of readily weathered radiogenic bedrock during the Himalayan orogeny (Krishnaswami et al., 1992; Raymo et al., 1988), or to accelerated weathering of radiogenic bedrock in Antarctica with the onset of its glaciation (Miller et al., 1991). The cause of this long term increase is beyond the scope of this study and  
155 our focus is on the variability in the rate of increase within the Oligocene to early Miocene.



160 **Figure 2:**  $^{87}\text{Sr}/^{86}\text{Sr}$  results from a) U1406 and b) 1168. Vertical error bars indicate  $2\sigma$  analytical uncertainty where it exceeds the size of the plotted symbol.

Significantly, the precise independent chronology of Site 1218 confirms that the long term Oligocene and early Miocene increase in  $^{87}\text{Sr}/^{86}\text{Sr}$  is punctuated by significant structure, including reversals, periods of negligible  $^{87}\text{Sr}/^{86}\text{Sr}$  increase, as well as more abrupt increases in  $^{87}\text{Sr}/^{86}\text{Sr}$ . Reversals beyond analytical uncertainty are also seen in published high resolution Mid-Oligocene  $^{87}\text{Sr}/^{86}\text{Sr}$  records from both ODP Site 522 (Reilly et al., 2002) and ODP Site 689B (Mead and Hodell, 1995), suggesting that they are a robust feature of the Oligocene ocean Sr cycle. The uncertainty in absolute chronology complicates the inference of m.y. scale periods of stasis or abrupt  $^{87}\text{Sr}/^{86}\text{Sr}$  increase in previously published records with biostratigraphic age models. To further evaluate how the rate of change of  $^{87}\text{Sr}/^{86}\text{Sr}$  deviates from a monotonic increase from 32 to 18 Ma, we generate a smoothed fit to the data based on local linear regression model (Figure 3). In the model, local regressions were based on 3 to 6 consecutive samples and age range of at least 0.25 Ma, with the exception of a single shorter span of only 0.18 Ma at 26 Ma. To estimate the rate of change, we illustrate the derivative of this smoothed fit, as well as the slope and its uncertainty for each linear segment (Figure 3b). This analysis illustrates periods of both more rapid increase as well as slowed or inverted  $^{87}\text{Sr}/^{86}\text{Sr}$  increase.

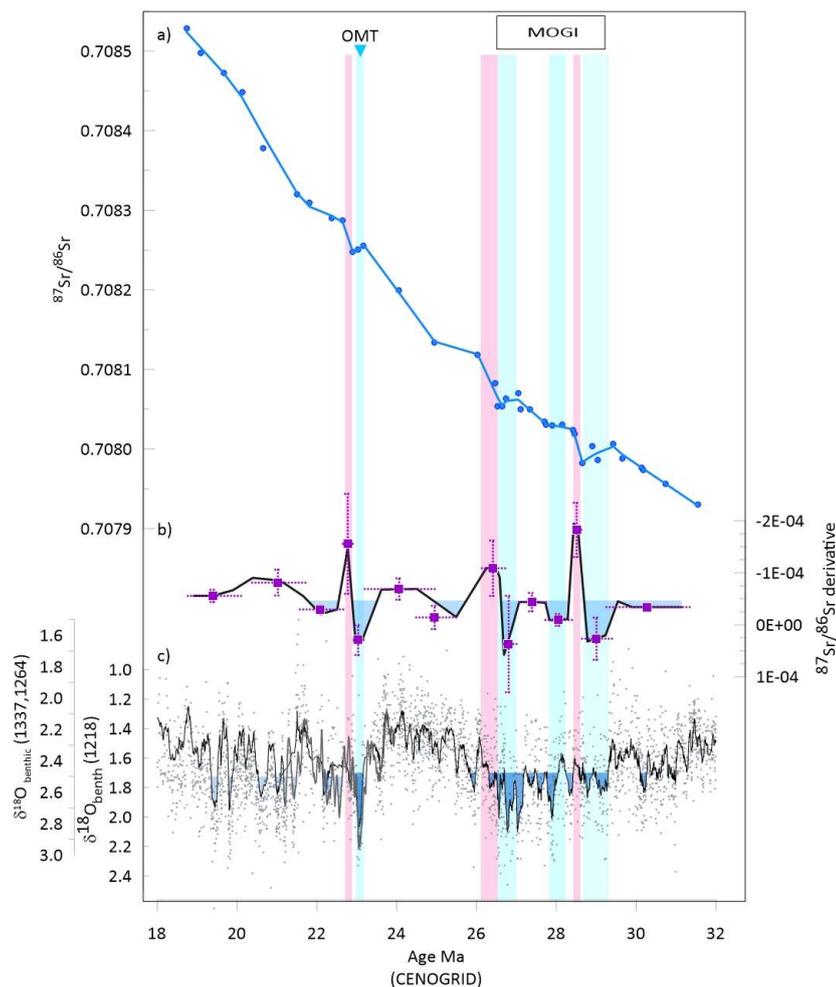
In Site 1218, appreciably lower rates of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase (or even  $^{87}\text{Sr}/^{86}\text{Sr}$  decrease) occur centered at 29 Ma and 26.8 Ma during the MOGI, and at 23 Ma during the OMT (Figure 3). Each of these periods is followed by a large acceleration of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase. Our new data provide the most precise comparison between  $^{87}\text{Sr}/^{86}\text{Sr}$  and the benthic  $\delta^{18}\text{O}$  record of deep sea temperature and ice volume because the records derive from the same deep sea sediment archive (without correlation uncertainty) and the benthic  $\delta^{18}\text{O}$  record is very high resolution, without aliasing which can occur in records sampled at resolution comparable or greater than periods of orbital variation. The earliest reduction in the rate of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase which we resolve (centered at 29 Ma) coincides with the onset of heavier average benthic  $\delta^{18}\text{O}$  demarcating the Mid-Oligocene Glacial interval (MOGI), and the recovery of rapid  $^{87}\text{Sr}/^{86}\text{Sr}$  increase coincides with a shift towards more negative benthic  $\delta^{18}\text{O}$  (ice volume decrease and/or warming). The return to more intense glaciation from 28 to 26.8 Ma yields a pronounced slowing



of the rates of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase. The subsequent acceleration of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase at 26.5 Ma coincides with the  
185 onset of the negative shift in benthic  $\delta^{18}\text{O}$  marking the end of the MOGI with ice volume decrease and/ or  
warming. The reduction of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase (or  $^{87}\text{Sr}/^{86}\text{Sr}$  decrease) at the OMT coincides with an intense glacial  
phase, and subsequently a consequent acceleration of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase at the end of the glacial phase. This event  
may coincide with the post-OMT acceleration previously defined as 22.4 Ma on the Cande and Kent (Cande and  
Kent, 1992) timescale (Oslick et al., 1994). We are unable to evaluate if there are similar  $<0.5$  Ma variations in  
190 the rate of  $^{87}\text{Sr}/^{86}\text{Sr}$  change between 26 and 23 Ma as our sample resolution is not high enough in this interval.  
The main changes in slope are significant at the 68% CI (1s) level, but an increase in the sample resolution and  
number of data points would be needed to confidently distinguish many of these differences at the 95% CI (2s)  
level.

Variations in the isotopic composition of Sr inputs on timescales of  $10^5$  yr are not expected to reflect  
195 changes in ocean crustal production rate and hydrothermal flux, nor significant changes in the composition of  
bedrock exposed on continents. Therefore, such changes are suggestive of change in either the intensity of  
continental weathering relative to hydrothermal sources or changes in the locus of most intense continental  
weathering among continental sources of contrasting  $^{87}\text{Sr}/^{86}\text{Sr}$ . For example, a short term relative increase in  
weathering intensity in areas underlain by younger average bedrock compared to older average bedrock would  
200 lead to a decreased  $^{87}\text{Sr}/^{86}\text{Sr}$  of the riverine Sr flux and the marine reservoir. Alternatively, a short term decrease  
in the intensity of weathering and thereby in the continental Sr flux (higher  $^{87}\text{Sr}/^{86}\text{Sr}$  than the hydrothermal flux)  
could also lead to a decreased marine  $^{87}\text{Sr}/^{86}\text{Sr}$ . In either case, the long residence time of Sr in the ocean would  
result in lags between onset of elevated fluxes and peak response in ocean chemistry and would cause significant  
attenuation of the time-varying input signal.

The coincidence of periods of slowed  $^{87}\text{Sr}/^{86}\text{Sr}$  and the onset of glacial advance on Antarctica evidenced  
205 in benthic  $\delta^{18}\text{O}$  suggests a climate control on the variations in the continental Sr flux on  $10^5$  yr timescales from  
one or both of these mechanisms. Changes in the location of intense rainfall, such as shift in the polar front or  
Intertropical Convergence Zone (ITCZ), could alter the locus of most intense weathering. Potentially, episodes  
of Antarctic glacial expansion could cause an equatorward movement of the SH westerlies and associated rainfall  
210 band, or could cause a mean ITCZ shift toward the northern Hemisphere. However, climatically-driven changes  
in the position of main heavy rainfall belts such as ITCZ is usually limited to  $< 10$  degrees latitude and may be  
longitudinally variable (Atwood et al., 2020). A movement of precipitation belts would have a significant  
consequence on global riverine  $^{87}\text{Sr}/^{86}\text{Sr}$  only in cases of fortuitous distribution of bedrock of widely different  
ages on similar if a northward shift of the mean ITCZ significantly increased the Sr flux from this region, the  
215 marine  $^{87}\text{Sr}/^{86}\text{Sr}$  could experience a transient decrease length scale as movement of rainfall. One potential such  
configuration could be the exposure of highly weatherable nonradiogenic rocks of the Deccan volcanic series of  
India and the Ethiopian Traps, located just north of the equator in the late Oligocene (Kent and Muttoni, 2013).



220 **Figure 3. a)** Measured Site 1218  $^{87}\text{Sr}/^{86}\text{Sr}$  (symbols) and the smoothed fit from local linear regression (blue line). **b)** the  
derivative of the smoothed fit (black line) and the slope of each linear segment (purple square), together with  
the uncertainty on the slope (vertical error bar, 68% confidence interval) and the age range of the local linear fit (horizontal bar).  
Shading indicates sectors in which  $^{87}\text{Sr}/^{86}\text{Sr}$  rises more slowly than the average rate over 32 to 18 Ma. **c)** Benthic  $\delta^{18}\text{O}$   
225 measurements (gray points) and lines showing 20 point running mean. From Site 1218 (black line from 21.46 to 32 Ma)  
(Pälike et al., 2006) and from the Cenozoic reference splice derived from U1337 (Holbourn et al., 2015) and ODP Site  
1264 (Westerhold et al., 2020) both scaled as in (Westerhold et al., 2020), as gray line from 21.2 to 24 Ma when  
overlapping with 1219 record, and black line from 18 to 21.2 Ma. All data are plotted on the orbitally tuned  
CENOGRID timescale (Westerhold et al., 2020). Blue shading highlights intervals with benthic  $\delta^{18}\text{O}$  more positive  
than 1.7 ‰ in Site 1218 and 2.5 ‰ in Cenozoic reference splice 1264 and U1337. The Middle Oligocene Glacial Interval  
230 (MOGI) from 29 to 26 Ma is labelled, as is the Oligocene-Miocene Transition (OMT). Vertical blue and pink lines  
highlight intervals of slower and more rapid rate of change in  $^{87}\text{Sr}/^{86}\text{Sr}$ , respectively.

It has also been proposed that glaciation can affect the weatherability of bedrock. Generally, highest  
riverine dissolved Sr fluxes are produced from reactive young volcanic rock, as well as soluble carbonates, but  
the mechanical flouring of less reactive rock types by glacial erosion can significantly increase their weatherability  
235 and Sr contribution to the ocean. It has been suggested that weathering intensity of the Antarctic craton may have  
evolved over the late Eocene through Oligocene, as glacial flouring of Antarctic bedrock increased the  
weatherability of this continental Sr source (Miller et al., 1991; Oslick et al., 1994), contributing to the rise in



ocean  $^{87}\text{Sr}/^{86}\text{Sr}$ . Intermittent glaciation, characterized by significant changes in the spatial extent of ice coverage, may alternately generate highly weatherable fine grained silicates in a subglacial weathering-limited environment (low continental Sr fluxes) and then expose them to subaerial conditions of enhanced chemical weathering (high continental Sr flux). On previous biostratigraphic age models, apparent accelerations in the rate of  $^{87}\text{Sr}/^{86}\text{Sr}$  increase at 32, 28, 22.4, 19.5, and 16.5 Ma (on the Cande and Kent timescale) occur 1 m.y after deglaciation midpoint inferred from benthic  $\delta^{18}\text{O}$  maxima in ODP 747 (Oslick et al., 1994). This was interpreted to result from the deglacial exposure which may have contributed to a transient increase in flux of radiogenic Sr to the ocean.

East Antarctica is inferred to be underlain dominantly by Proterozoic and Archean bedrock (Kirkham et al., 1995). Exposed bedrock in East Antarctica is dominated by Archean and Proterozoic metamorphic rocks, with Paleozoic igneous and sedimentary rocks additionally exposed in the Transantarctic mountains (Licht and Hemming, 2017). Although the Sr isotopic composition of bedrock in Antarctica can be measured directly only in current exposures in the Transantarctic mountains and coastal areas, crustal rocks at the perimeters of major ice sheets may represent a major source of the sediment arriving at the margin and therefore weatherable during retreat (Farmer et al., 2003). Because erosion rates are highest at the perimeter of Antarctic ice sheet (Jamieson et al., 2010), the mapped bedrock in coastal areas may provide a reasonable representation of the source of sediment arriving to the glacial margin and weatherable during retreat. Additionally, the fine grained component of LGM tills exposed in the Ross Sea embayment provide constraints on modern underlying composition of present erosion (Farmer et al., 2006). Present till composition includes very radiogenic compositions up to 0.740 attributed to erosion of the Neoproterozoic Beardsmore Formation, and compositions in the range of 0.720 to 0.735 typical of 500 Ma Granite Harbor Intusive rocks exposed in southern part of Transantarctic Mountains and the Wilson terrane Proterozoic gneisses (Farmer et al., 2006). However, a caveat is that the currently exposed bedrock may be older than that exposed in the Oligocene due to denudation, and younger, less radiogenic bedrocks may have contributed more to glacial flouring in the Oligocene, making global fluxes less sensitive to the Antarctic weathering regime.

#### 4.2 Sr isotope constraints on age models of Site U1406 and Site 1168

Previous approaches for Sr isotope stratigraphy for the Cenozoic have inferred a continuous rise in  $^{87}\text{Sr}/^{86}\text{Sr}$ . The data from Site 1218 suggest several intervals with a negligible rate of rise and/or reversals. In the interval from 28 to 30 Ma, 5 of our 9 samples feature  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios whose analytical 95% CI fall outside of the bounds of the reference  $^{87}\text{Sr}/^{86}\text{Sr}$  curve of that age generated from biostratigraphically constrained age models (McArthur et al., 2020). For these intervals, particularly during the MOGI, age assignments from Sr isotope stratigraphy have a higher uncertainty than previously inferred. In the interval from 28 to 30 Ma, the deviation between the CENOGRID age and the reference curve ranges from 1.1 Ma older than the reference curve to 0.7 Ma younger, a significantly wider uncertainty than the +/- 120 to 180 ky uncertainty predicted for the reference curve. In the early Miocene, between 21.7 and 19.4 Ma, a number of our Site 1218 CENOGRID ages also deviate from the ages from the reference curve, by 0.18 to 0.42 Ma younger, a greater uncertainty than the +/- 70 to 50 ky reported for the reference curve. Consequently, in deriving ages for Site U1406 and Site 1168 on the CENOGRID scale from  $^{87}\text{Sr}/^{86}\text{Sr}$ , we expand the bounds of the age uncertainties from (McArthur et al., 2020) to encompass the Site 1218 data (Figure 1, green bounds). The width of the resulting age uncertainty therefore ranges from 300 ky in the early Miocene to 1.6 My in the early-mid Oligocene.



In addition to these greater uncertainties, stratigraphic constraints prohibit reversals in ages where there is no independent evidence for reworking or sediment disturbance. Our Site 1218 data indicate that reversals in  $^{87}\text{Sr}/^{86}\text{Sr}$  are certain within the time interval of 29-26 Ma, and likely at the OMT. Thus, in estimating ages for 1168 and U1406 based on  $^{87}\text{Sr}/^{86}\text{Sr}$ , we assign an initial age based on (McArthur et al 2020) but adjust the age to preserve stratigraphic relationships (eg no age reversals in our age assignments). The detailed age models are shown in Tables 2 and Table 3.

#### 4.2.1. Site U1406

Because of the slow rate of the Site U1406  $^{87}\text{Sr}/^{86}\text{Sr}$  change and reversals during the MOGI, the U1406  $^{87}\text{Sr}/^{86}\text{Sr}$  cannot precisely pinpoint the duration of the hiatus or condensed interval between 153 and 149 m (CSF-A) (Figure 4). The condensed interval could contain 2 m.y. (28.45 to 26.58 Ma) or < 1 m.y. (27.3 to 26.58). On the other hand, the early Miocene condensed interval between 27 and 25 m (CSF-A) is constrained to represent 2 m.y. The Site 1406  $^{87}\text{Sr}/^{86}\text{Sr}$  data indicate that the uppermost 25 m of sediment in U1406, difficult to date due to sparse biostratigraphic markers, was likely deposited between 18.5 and 17.6 Ma. Sustained high sedimentation rates are confirmed between 21 and 26 Ma.

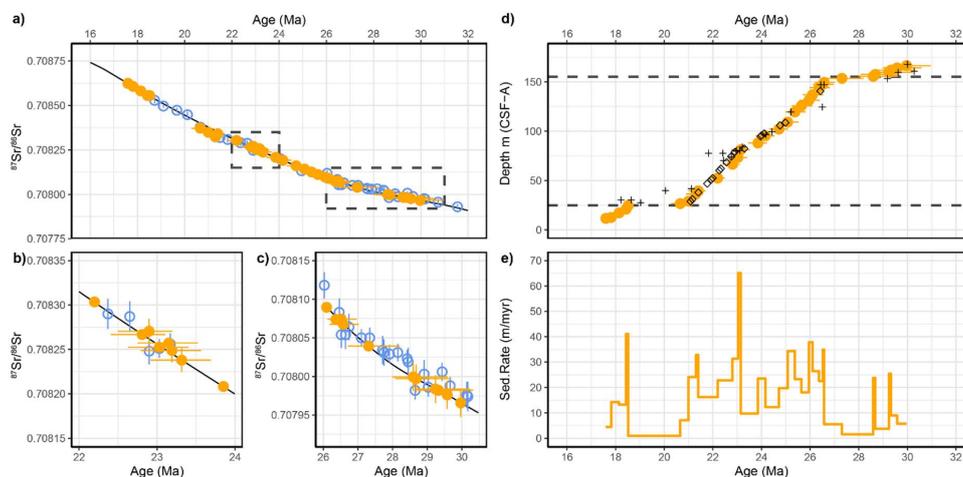


Figure 4. a) Site U1406  $^{87}\text{Sr}/^{86}\text{Sr}$  data (orange) vs age (CENOGRID scale) assigned here; also shown are the Site 1218 new data (blue) and the GTS LOESS curve (McArthur et al., 2020). b. and c. show insets. For Site U1406, horizontal lines indicate the uncertainty in the age assignments. d) Age depth plot for U1406A on the CSF-A scale. Orange circles denote the ages from  $^{87}\text{Sr}/^{86}\text{Sr}$  compared to previous biostratigraphy tiepoints (crosses; (Norris et al., 2014)) and magnetostratigraphy (open diamonds) (Van Peer et al., 2017a). Horizontal dashed lines delimit the strongly condensed intervals; e) the inferred sedimentation rate.

#### 4.2.2. Site 1168

This first  $^{87}\text{Sr}/^{86}\text{Sr}$  stratigraphy for Site 1168 implies significant differences in inferred ages compared to existing biostratigraphy, including significantly higher sedimentation rates in the early Miocene (20.5 to 18.5 Ma), but comparably slower sedimentation rates between 21.6 and 22.5 Ma just after the OMT (Figure 5). This is slightly earlier than the early Miocene hiatus found in many deep sea sedimentary records between 19 to 20 Ma; however, in other deep sea records the precise timing of early Miocene depositional gaps is not yet resolved and could coincide with the condensed interval in 1168 (Sibert and Rubin, 2021). Age assignments remain less precise



305 in the middle Miocene (25 to 27 Ma) due to the low rate of change and reversals in  $^{87}\text{Sr}/^{86}\text{Sr}$  during this time interval, as well as the current low  $^{87}\text{Sr}/^{86}\text{Sr}$  sample coverage.

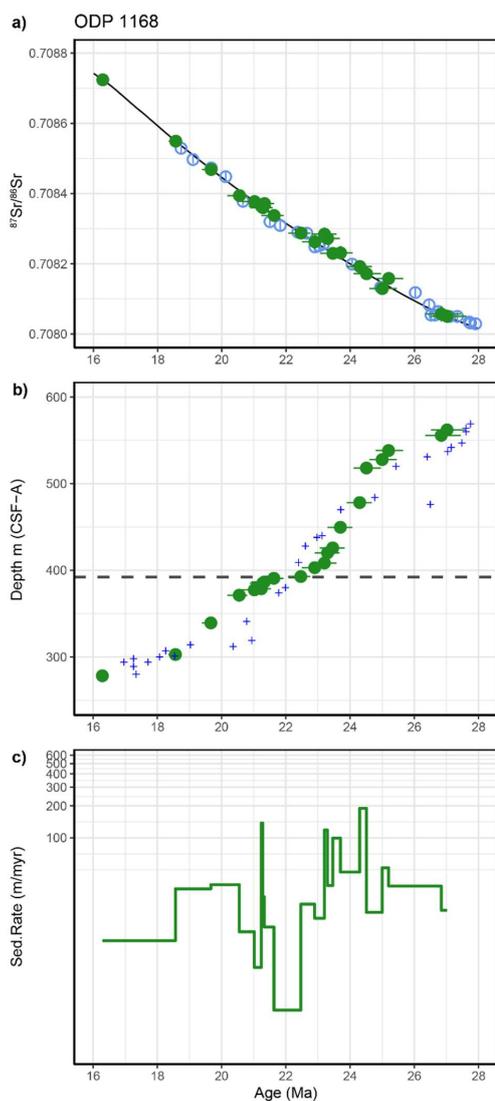


Figure 5: a) Site 1168  $^{87}\text{Sr}/^{86}\text{Sr}$  data (green) vs age (CENOGRID scale) assigned here; also shown are the Site 1218 new data (blue open symbols) and the GTS LOESS curve (McArthur et al., 2020) b). Age depth plot for Site 1168. Green diamonds denote the ages from  $^{87}\text{Sr}/^{86}\text{Sr}$  compared to previous biostratigraphy derived tie points (crosses). c) Sedimentation rate implied by the  $^{87}\text{Sr}/^{86}\text{Sr}$  age model. The horizontal dashed line in b) highlights the period of significantly slowed sedimentation of the Early Miocene.

## 5 Conclusions

The  $^{87}\text{Sr}/^{86}\text{Sr}$  record from the cyclostratigraphically dated Site 1218 provides the opportunity to assess ~1 m.y. variations in the Sr flux to the ocean during a period of dynamic Antarctic cryosphere evolution. Our dataset resolves relationships between the locus and/or intensity of continental weathering and phases of Antarctic glaciation. Overall, the data suggest that the major changes in mid-Oligocene high latitude climate – particularly the onset and end of the MOGI – do exhibit a close coupling between seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  and benthic  $\delta^{18}\text{O}$ . During periods of expanded ice coverage on Antarctica such as the MOGI, then, our data are consistent with either northward shifts in the ITCZ precipitation to areas of nonradiogenic bedrock, and/or lowered weathering fluxes from highly radiogenic glacial flours on Antarctic. Future, higher resolution sampling is required to further evaluate the significance of such changes. Additionally, the new  $^{87}\text{Sr}/^{86}\text{Sr}$  record from sites 1168 and U1406 improve the precision of age correlation of these Northern Hemisphere and

340 Southern Hemisphere mid-latitude sites with each other and with high resolution benthic  $\delta^{18}\text{O}$  records aligned to the CENOGRID chronology.



### Competing interests

345 The contact author has declared that none of the authors has any competing interests.

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350 Discovery Program for providing the samples used in this study.

### Author contributions

The study was conceived by HMS. Samples were selected by HMS with advice from HP. Foraminifera were prepared by JG, IHA, and TT. Sr isotope analyses were completed by LP. Interpretation was completed by HMS and figures were prepared by HMS and PG. The manuscript was written by HMS with input from all authors.  
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Table 1. ODP identifiers, CENOGRID age, and <sup>87</sup>Sr/<sup>86</sup>Sr data for Site 1218.

Lab ID	Exp	Site	Hole	Core	Core Type	Section	Section Half	Top Interval (cm)	Bottom Interval (cm)	depth (mcd, m)	age CENOGRID (Ma)	<sup>87</sup> Sr/ <sup>86</sup> Sr	Internal SE (2σ)
B2	199	1218	B	7	H	1	W	125	130	59.93	18.73	0.708529	1.71E-05
B3	199	1218	B	7	H	3	W	75	80	62.43	19.10	0.708497	1.13E-05
A1	199	1218	A	7	H	3	W	50	55	67.29	19.67	0.708473	1.21E-05
A2	199	1218	A	7	H	5	W	50	55	70.29	20.12	0.708448	1.71E-05
B4	199	1218	B	8	H	3	W	100	105	73.29	20.66	0.708378	1.17E-05
B5	199	1218	B	9	H	3	W	32	37	82.07	21.50	0.708320	1.21E-05
B6	199	1218	B	9	H	5	W	105	110	85.45	21.82	0.708309	1.71E-05
A4	199	1218	A	9	H	4	W	82	87	90.32	22.37	0.708290	1.71E-05
A5	199	1218	A	9	H	6	W	20	25	92.67	22.65	0.708287	1.71E-05
B7	199	1218	B	10	H	3	W	82	87	94.54	22.90	0.708248	1.50E-05
B8	199	1218	B	10	H	4	W	87	92	96.12	23.03	0.708251	1.06E-05
B9	199	1218	B	10	H	5	W	141	146	98.17	23.17	0.708256	1.19E-05
B11	199	1218	B	11	H	3	W	147	150	107.26	24.06	0.708199	1.71E-05
B12	199	1218	B	12	H	3	W	107	112	118.18	24.95	0.708133	1.71E-05
B13	199	1218	B	13	H	6	W	17	22	131.57	26.03	0.708118	1.71E-05
1218A 14H1 15-25cm	199	1218	A	14	H	1	W	15	25	138.00	26.46	0.708083	1.82E-05
A9	199	1218	A	14	H	1	W	100	105	138.73	26.52	0.708054	1.71E-05
1218A 14H2 115cm	199	1219	A	15	H	2	W	115	117	140.27	26.64	0.708054	1.84E-05
A10	199	1218	A	14	H	3	W	80	85	141.59	26.74	0.708064	1.71E-05
1218B 15H1 35cm	199	1218	B	15	H	1	W	35	38		27.04	0.708070	1.86E-05
B14	199	1218	B	15	H	2	W	30	35	147.04	27.10	0.708050	1.13E-05
B15	199	1218	B	15	H	4	W	80	85	150.56	27.34	0.708050	1.33E-05
1218B 16H1 25cm	199	1218	B	16	H	1	W	25	26.5	156.17	27.71	0.708034	1.82E-05
B16	199	1218	B	16	H	1	W	70	75	156.63	27.75	0.708031	1.71E-05
B17	199	1218	B	16	H	2	W	107	112	158.55	27.91	0.708029	1.21E-05
B18	199	1218	B	16	H	5	W	60	65	162.03	28.15	0.708031	1.13E-05
C1	199	1218	C	10	H	2	W	100	105	164.77	28.42	0.708023	1.13E-05
1218C 10H3 5cm	199	1218	C	10	H	3	W	5	7	165.25	28.45	0.708019	1.82E-05
B19	199	1218	B	17	H	3	W	120	125	170.40	28.65	0.707982	1.21E-05
1218C 11H1 115cm	199	1218	C	11	H	1	W	115	117	173.77	28.91	0.708003	1.84E-05
C2	199	1218	C	11	H	2	W	130	135	175.45	29.03	0.707986	1.21E-05
B20	199	1218	B	18	H	5	W	10	15	182.15	29.43	0.708006	1.21E-05
A11	199	1218	A	18	H	4	W	37	45	185.68	29.66	0.707988	1.12E-05
A12	199	1218	A	19	H	2	W	67	75	192.20	30.14	0.707976	1.71E-05
1218C 12H6 85cm	199	1218	C	12	X	6	W	85	87	191.63	30.17	0.707974	1.91E-05
B21	199	1218	B	20	X	3	W	117	122	199.97	30.73	0.707956	1.71E-05
B23	199	1218	B	21	X	4	W	12	17	211.94	31.55	0.707930	1.50E-05



365 Table 2.  $^{87}\text{Sr}/^{86}\text{Sr}$  data for Site U1406 and the assigned ages and age uncertainties.

Site	Hole	Core	Core Type	Section	Section Half	Top Interval (cm)	Bottom Interval (cm)	Depth CSF-A (m)	Depth CSF-A (m)	$^{87}\text{Sr}/^{86}\text{Sr}$	Internal SE (2 $\sigma$ )	midpoint age assigned (Ma)	lower age (Ma)	upper age (Ma)
1406	A	2	H	4	w	89	93	11.61	23.9	0.708625	0.000018	17.60	17.45	17.75
1406	A	2	H	5	w	36	40	12.58	24.9	0.708607	0.000018	17.82	17.67	17.97
1406	A	3	H	2	w	5	8	17.14	25.7	0.708582	0.000004	18.14	17.99	18.29
1406	A	3	H	4	w	89	92	20.98	29.6	0.708556	0.000004	18.43	18.28	18.58
1406	A	3	H	7	w	8	12	24.68	33.3	0.708556	0.000004	18.52	18.30	18.70
1406	A	4	h	1	w	139	143	26.61	34.7	0.708372	0.000004	20.66	20.29	20.91
1406	A	4	H	3	w	81	85	29.03	37.2	0.708350	0.000004	21.00	20.60	21.30
1406	A	5	H	2	w	6	9	36.27	45.4	0.708323	0.000003	21.30	20.90	21.60
1406	A	5	H	4	w	33	37	39.55	48.7	0.708341	0.000004	21.40	21.00	21.70
1406	A	6	H	6	w	74	80	52.47	63.0	0.708303	0.000004	22.20	21.80	22.50
1406	A	8	H	3	w	16	22	66.39	77.6	0.708267	0.000003	22.81	22.41	23.11
1406	C	8	H	1	w	80	84		80.3	0.708271	0.000014	22.90	22.50	23.20
1406	A	9	H	1	w	62	68	73.35	84.8	0.708252	0.000005	23.03	22.63	23.41
1406	A	9	H	6	w	91	95	81.16	92.6	0.708257	0.000004	23.15	22.75	23.53
1406	B	10	H	3	w	140	144		95.6	0.708249	0.000013	23.19	22.79	23.57
1406	B	10	H	5	w	70	74		97.9	0.708238	0.000013	23.32	22.92	23.69
1406	A	10	H	4	w	127	133	88.00	101.8	0.708208	0.000004	23.85	23.45	24.23
1406	A	11	H	3	w	53	59	95.26	109.2	0.708191	0.000004	24.16	23.76	24.54
1406	A	12	H	1	w	90	94	102.12	117.3	0.708161	0.000006	24.72	24.32	25.09
1406	A	12	H	6	w	44	48	109.16	124.4	0.708142	0.000007	25.07	24.67	25.52
1406	A	13	H	7	w	21	25	119.45	135.0	0.708126	0.000004	25.37	24.97	25.82
1406	A	14	H	4	w	97	103	125.70	141.8	0.708112	0.000007	25.64	25.24	26.09
1406	A	15	H	2	w	6	10	131.28	148.7	0.708097	0.000003	25.95	25.55	26.40
1406	A	15	H	5	w	103	107	136.81	154.3	0.708090	0.000004	26.10	25.70	26.55
1406	A	16	H	4	w	26	30	143.98	162.1	0.708074	0.000004	26.37	25.97	26.82
1406	A	16	H	6	w	66	70	147.38	165.5	0.708074	0.000005	26.52	26.12	26.97
1406	A	17	H	1	w	128	132	149.40	170.1	0.708068	0.000005	26.58	26.18	27.03
1406	A	17	H	4	w	86	90	153.48	174.2	0.708039	0.000003	27.31	26.71	28.21
1406	A	17	H	5	w	136	140	155.48	176.2	0.707999	0.000018	28.59	27.99	29.59
1406	A	18	H	1	w	19	23	157.51	184.7	0.707997	0.000018	28.68	28.08	29.68
1406	A	18	H	2	w	94	98	159.60	186.8	0.707984	0.000018	29.24	28.64	30.24
1406	A	18	H	4	w	20	24	161.86	189	0.707982	0.000004	29.33	28.73	30.33
1406	A	18	H	5	w	96	100	164.12	191	0.707976	0.000018	29.58	28.98	30.58
1406	A	19	H	2	w	15	19	166.37	200	0.707966	0.000018	29.97	29.37	30.97



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**Table 3.**  $^{87}\text{Sr}/^{86}\text{Sr}$  data for Site 1168 and the assigned ages and age uncertainties.

Site	Hole	Core	Core Type	Section	Section Half	Top Interval (cm)	Bottom Interval (cm)	Depth CSF-A (m)	$^{87}\text{Sr}/^{86}\text{Sr}$	Internal SE (2 $\sigma$ )	central age (Ma)	min age (Ma)	max age (Ma)
1168	A	30	X	5	W	2	8	278.25	0.708724	1.82E-05	<b>16.29</b>	16.14	16.44
1168	A	33	X	2	W	52	58	302.75	0.7085492	1.82E-05	<b>18.57</b>	18.35	18.74
1168	A	37	X	1	W	43	49	339.26	0.7084685	1.82E-05	<b>19.67</b>	19.39	19.87
1168	A	40	X	3	W	59.5	64.5	371.22	0.7083942	1.82E-05	<b>20.55</b>	20.18	20.80
1168	A	41	X	1	W	5	7.5	377.36	0.7083771	1.41E-05	<b>21.02</b>	20.62	21.32
1168	A	41	X	1	W	135	138	378.66	0.7083633	1.35E-05	<b>21.24</b>	20.84	21.54
1168	A	41	X	6	W	34	36.5	385.15	0.7083596	1.35E-05	<b>21.28</b>	20.88	21.58
1168	A	41	X	7	W	34	47.5	386.46	0.7083715	1.41E-05	<b>21.33</b>	20.93	21.63
1168	A	42	X	3	W	45	25.5	390.78	0.7083377	1.62E-05	<b>21.63</b>	21.23	21.93
1168	A	42	X	4	W	137	139	392.78	0.7082875	1.76E-05	<b>22.47</b>	22.07	22.77
1168	A	43	X	5	W	55	57	403.06	0.7082624	1.95E-05	<b>22.90</b>	22.50	23.28
1168	A	44	X	2	W	69	71	408.3	0.7082843	1.95E-05	<b>23.20</b>	22.80	23.58
1168	A	45	X	3	W	143	145	420.14	0.708272	1.92E-05	<b>23.30</b>	22.90	23.68
1168	A	46	X	1	W	49	55	425.82	0.7082296	1.82E-05	<b>23.46</b>	23.06	23.84
1168	A	48	X	4	W	65	67.5	449.65	0.708231	1.95E-05	<b>23.70</b>	23.30	24.08
1168	A	51	X	4	W	38	42	478.2	0.7081923	1.82E-05	<b>24.30</b>	23.90	24.68
1168	A	55	X	5	W	33	39	518.06	0.7081716	1.82E-05	<b>24.51</b>	24.11	24.96
1168	A	56	X	5	W	37	43	527.8	0.7081292	1.82E-05	<b>25.00</b>	24.60	25.45
1168	A	57	X	5	W	113	117	538.25	0.7081581	1.86E-05	<b>25.20</b>	24.80	25.65
1168	A	59	X	4	W	83	87	555.75	0.7080568	2.19E-05	<b>26.84</b>	26.34	27.44
1168	A	60	X	2	W	57	61	562.09	0.7080503	1.84E-05	<b>27.02</b>	26.52	27.62

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