

The 100,000 year cyclicity in seawater $^{87}\text{Sr}/^{86}\text{Sr}$: an enviro-analytical artifact?

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Introduction

Time-series analysis of single-species planktonic foraminifera has resulted in the apparent resolution of 100-kyr cyclicity in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and its covariation with changes in global ice volume over the past 450 kyrs (Dia *et al.* 1992; Clemens *et al.* 1993). Both records indicated ~ 0.000020 (20 ppm) variability between glacial- and interglacial-age seawater $^{87}\text{Sr}/^{86}\text{Sr}$. Although this variability is at or near analytical resolution at the 1s level, the persistence of the signal over several 100-kyr cycles and a strong in-phase covariation with global ice volume lent support to possible interpretation as an environmental signal driven by changes between glacial and interglacial climates.

We sought to further test the global nature of this signal by developing an independent high-resolution record based on benthic foraminifera from a North Atlantic site. These analyses also displayed a 100-kyr isotopic signal and an in-phase relationship with ice volume ($\delta^{18}\text{O}$). However,

improved analytical precision associated with these data allowed resolution of a systematic, positive relationship between instrumental fractionation and $^{87}\text{Sr}/^{86}\text{Sr}$ that accounts for the 20 ppm range of variability. Thus the 100-kyr cyclicity in the Sr isotopic composition of seawater from this site appears to stem from variations in instrumental fractionation (possibly of environmental origin) and is therefore an analytical artifact.

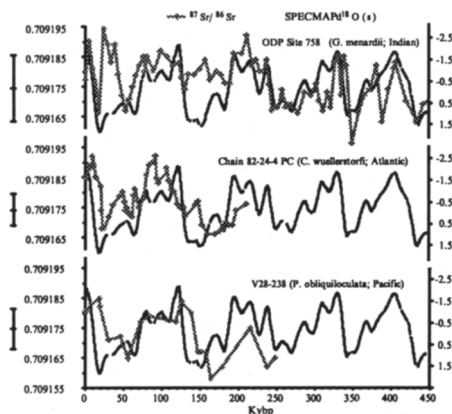


FIG. 1. Time series records of $^{87}\text{Sr}/^{86}\text{Sr}$ and planktonic $\delta^{18}\text{O}$ (global ice volume). Sr isotopic data are plotted relative to an NBS-987 value of 0.710257. Error bars for the Sr data represent 1 σ .

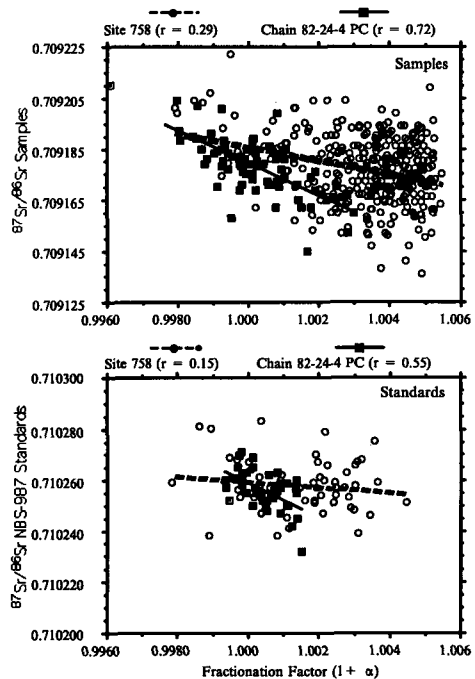


FIG. 2. Chain 82-24-4 PC and Site 758 $^{87}\text{Sr}/^{86}\text{Sr}$ vs. fractionation for both samples (upper) and standards (lower). Data are plotted relative to an NBS-987 value of 0.710257. α = fractionation per atomic mass unit. The large number of Site 758 data points in the upper plot reflect duplicate and triplicate analyses from raw sample as well as replicate runs of individual filaments.

Data

Three records have now been produced which bear upon the issue of 100-kyr cyclicity in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 1). The Sr isotopic record from Indian Ocean Site 758 was generated using the planktonic foraminifera *Globorotalia menardii* and analyzed in static multicollection mode using an exponential mass fractionation correction (Clemens *et al.* 1993). The record from North Atlantic core Chain 82-24 was generated using the benthic foraminifera *Cibicides wuellerstorfi* and analyzed in dynamic multicollection mode using a linear mass fractionation correction (this work). The record from Pacific core V28-238 was generated using the planktonic foraminifera *Pulleniatina obliquiloculata* and analyzed in dynamic multicollection mode using a power-law mass fractionation correction (Dia *et al.* 1992). Despite these significant analytical differences and the low signal-to-noise ratio inherent in attempting to measure such small variations, all three records show a similar relationship with planktonic ^{18}O whereby interglacial-age $^{87}\text{Sr}/^{86}\text{Sr}$ is ~ 20 ppm greater than glacial-age $^{87}\text{Sr}/^{86}\text{Sr}$. This first-order reproducibility in three ocean basins (two laboratories) indicates an environmental origin for the 100-kyr cyclicity associated with these data. Here we present evidence from the new Chain 82-24 data that this cyclical nature derives from incomplete correction for instrumental fractionation and not from changes in seawater $^{87}\text{Sr}/^{86}\text{Sr}$.

Of the three approaches to correction for instrumental mass fractionation, the power and exponential laws are more precise than the linear law (Russell *et al.* 1978; Wasserburg *et al.* 1981). Reduction of the Chain data by linear law, coupled with the higher analytical precision resulted in resolution of a positive linear relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and instrumental fractionation in both the geological samples and standards (Figure 2). A similar relationship is also detectable in the Site 758 samples, although poorly resolved (the variability in $^{87}\text{Sr}/^{86}\text{Sr}$ attributable to fractionation effects is less than the analytical scatter). We attribute this to the somewhat larger analytical uncertainties associated with the static multicollection data coupled with the more precise exponential fractionation correction. When corrected for the systematic relationship between fractionation and $^{87}\text{Sr}/^{86}\text{Sr}$, the Chain 82-24 record no longer shows resolvable evidence of glacial-interglacial cyclicity. Similar systematics may apply to the V28-238 data, possibly accounting for the inability to subsequently reproduce the full amplitude of the originally

reported signal (Henderson *et al.*, 1993).

Discussion

Chain 82-24 results indicate that the reported 100-kyr cyclicity in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is an analytical artifact related to instrumental fractionation associated with the thermal ionization process. The signals we measured reflect the inability of the fractionation corrections to completely remove fractionation or related effects at the level of measurement precision. The similarity among all $^{87}\text{Sr}/^{86}\text{Sr}$ records with respect to the 20 ppm glacial-interglacial amplitude suggests that similar systematics apply to all three regardless of the mass-fractionation correction used.

At this point, we are uncertain as to why the observed fractionation effects show a correlation to glacial-interglacial cycles. Perhaps the most likely explanation is that the amount of Sr loaded for a given analysis varied systematically with glacial-interglacial cycles. Despite having processed the same number of individual foraminifera for the time-series analysis of each core, differences in the mass of Sr loaded could arise from (1) glacial-interglacial differences in partitioning of Sr between seawater and foraminiferal calcite or in the concentration of Sr in ocean waters or (2) from glacial-interglacial differences in the mass or dissolution state of the foraminifera. We consider the latter less likely in light of the similar responses from different species (with different sensitivities to dissolution) and different oceans (with out-of-phase carbonate dissolution patterns). Other possible explanations include interfering elements, that vary with glacial-interglacial cyclicity, that may not have been quantitatively removed in ion-exchange chemistry (e.g., Ba).

References

- Clemens, S. C., Farrell, J.W. and Gromet, L. P. (1993) *Nature*, **363**, 607–10.
 Dia, A. N., Cohen, A. S., O'Nions, R. K. and Shackleton, N. J. (1992) *Nature*, **356**, 786–8.
 Henderson, G. M., O'Nions, R. K. and Shackleton, N. J. (1993) *Eos Trans. AGU*, **74**, 176.
 Russell, W. A., Papanastassiou, D. A. and Tombrello, T. A. (1978) *Geochim. Cosmochim. Acta*, **42**, 1075–90.
 Wasserburg, G. J., Jacobsen, S. B., DePaolo, D. J., McCullock, M. T. and Wen, T. (1981) *Geochimica et Cosmochimica Acta*, **49**, 1875–86.