

### 33. $^{87}\text{Sr}/^{86}\text{Sr}$ RATIOS OF PLANKTONIC FORAMINIFERS AND INTERSTITIAL WATERS, DEEP SEA DRILLING PROJECT LEG 90, SITE 593<sup>1</sup>

Jennifer Hess and Jean-Guy Schilling, Graduate School of Oceanography, University of Rhode Island<sup>2</sup>

#### ABSTRACT

Detailed profiles of the Sr isotopic compositions of fossil planktonic foraminifers and interstitial waters have been measured from DSDP Site 593 to determine the Sr isotopic composition of seawater during the last 40 m.y. Foraminiferal recrystallization was assessed through scanning electron microscopy (SEM) and Sr/Ca ratios. Foraminifers were shown to be well preserved. Results document that the seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  has increased continuously but not uniformly, since the latest Eocene.

#### INTRODUCTION

The chemical and isotopic composition of seawater has varied significantly over the course of geologic time (see, e.g., Broecker, 1971; Shackleton and Kennett, 1975; Bender and Keigwin, 1979; Claypool et al., 1980; Burke et al., 1982; Graham et al., 1982; Delaney, 1983). Efforts to constrain the geological forcing functions responsible for these changes rely on paleochemical tracers. One such tracer, important in deciphering the long-term record of oceanic chemical changes, is the Sr isotopic composition of ancient seawater.

Because the chemistry of Sr is similar to that of Ca, high concentrations of Sr are substituted for Ca during biogenic carbonate precipitation. The isotopic composition of Sr incorporated into calcite records the contemporaneous seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, which in turn integrates the weighted fluxes and isotope compositions of the oceanic Sr sources. The long-term variations in the marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio arise from changes in the fluxes of Sr from the various isotopically different oceanic sources. These include deep-sea hydrothermal activity, continental erosion, and submarine sedimentary recycling (Peterman et al., 1970; Brass, 1976; Spooner, 1976; Albarède et al., 1981; Armstrong, 1971). Estimates of the mass fluxes for each of the source terms can be used to assess the relative contribution of each process in fixing the seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  and hence in regulating seawater chemistry.

We are determining the Cenozoic record of the marine  $^{87}\text{Sr}/^{86}\text{Sr}$  variations by measuring the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of well-preserved and well-dated fossil foraminifers from several DSDP cores of overlapping ages. Site 593 on the shallow Lord Howe Rise provides a complete, high-quality, carbonate-rich sequence from the latest Eocene to the present for use in our work. We report here the measurements of foraminiferal and interstitial water  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for Site 593. Because carbonate recrystallization

can obscure the true ancient seawater  $^{87}\text{Sr}/^{86}\text{Sr}$ , all samples were carefully checked for evidence of diagenetic alteration through the use of scanning electron microscopy (SEM) and Sr/Ca ratios.

#### ANALYTICAL METHODS

Sediment samples for Site 593 were collected by J. P. Kennett and the shipboard scientific party of DSDP Leg 90. Interstitial water samples were provided by P. A. Baker of Duke University from splits of his shipboard sampling. All Sr isotope analyses were done in the thermal ionization mass spectrometry laboratory at the University of Rhode Island.

Sample preparation is similar to procedures reported by other workers (Dasch and Biscaye, 1971; Brass, 1976; Elderfield, personal communication). Sediment samples were disaggregated in a hot Calgon solution, wet-sieved through a 63  $\mu\text{m}$  screen, and dried at 50°C. Whole foraminifer tests (mixed planktonic species, >150- $\mu\text{m}$  size fraction) were hand-picked from the sample, repeatedly cleaned ultrasonically to remove clay minerals trapped within the tests, and dried at 50°C. The cleaned tests were dissolved in 0.25 ml of 2 $\times$  quartz-distilled 2.5N HCl and loaded onto a Dowex 50W-8 $\times$ , 200-400 mesh cation exchange column. The Sr fraction was eluted with ultrapure 2.5N HCl, evaporated to dryness, and redissolved in 1  $\mu\text{l}$  of dilute phosphoric acid. This Sr-phosphoric acid solution was then loaded in a drop of tantalum oxide slurry on a single Re filament for isotopic analysis. Pore water samples were evaporated to dryness before going through the same procedure.

For Sr and Ca determinations, foraminifers were hand-picked, cleaned ultrasonically, dried at 50°C, weighed, and then dissolved in dilute HCl for analysis. Sr and Ca concentrations were measured on these solutions by atomic absorption spectrometry. Ca was analyzed by flame techniques; Sr was analyzed by graphite furnace techniques.

#### RESULTS

Foraminiferal and interstitial water  $^{87}\text{Sr}/^{86}\text{Sr}$  are shown in Figure 1 and Tables 1 and 2, respectively. All Sr isotope values have been normalized to an  $^{86}\text{Sr}/^{88}\text{Sr}$  value of 0.1194 to correct for mass discrimination and an Eimer and Amend SrCO<sub>3</sub> standard  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.70800. Our laboratory value for this standard, covering the period of analysis, is  $0.708075 \pm 22 \times 10^{-6}$ , at the 95% confidence level (19 replicate analyses). Results of foraminiferal Sr/Ca ratio measurements and scanning electron microscopy examinations are given in Table 1.

At Site 593, the foraminiferal  $^{87}\text{Sr}/^{86}\text{Sr}$  is relatively constant to a depth of approximately 400 m (early middle Miocene), after which the ratio decreases rather linearly for the remainder of the section (early Miocene to

<sup>1</sup> Kennett, J. P., von der Borch, C. C., et al., *Init. Repts. DSDP*, 90: Washington (U.S. Govt. Printing Office).

<sup>2</sup> Address: Graduate School of Oceanography, University of Rhode Island, Kingston, RI 02881.

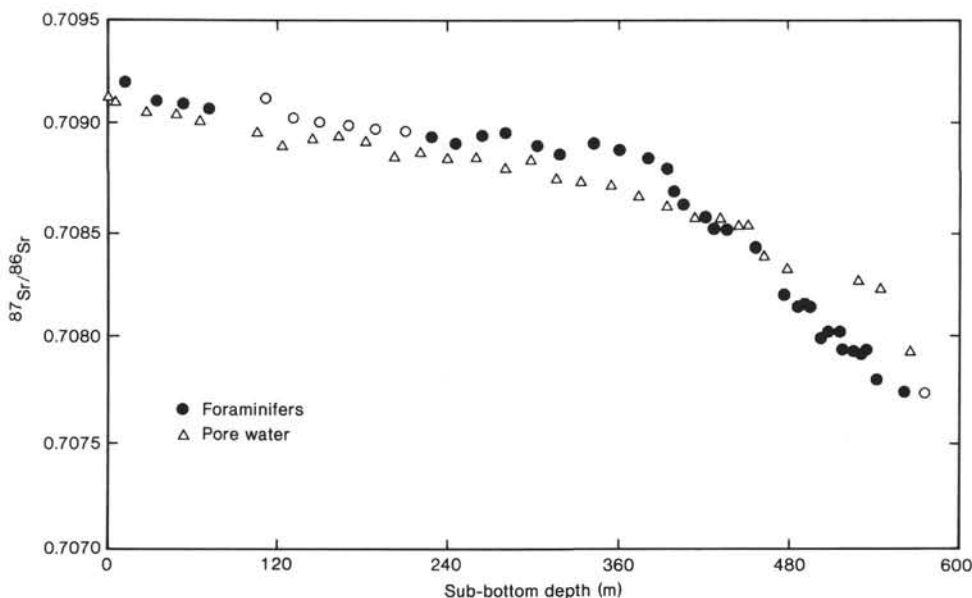


Figure 1. Foraminiferal and interstitial water  $^{87}\text{Sr}/^{86}\text{Sr}$  as a function of depth for Hole 593. Closed circles represent well-preserved foraminifer samples. Open circles indicate foraminifer samples that showed trace amounts of euhedral calcite crystals indicative of recrystallization when viewed under the SEM.

Table 1. Foraminiferal  $^{87}\text{Sr}/^{86}\text{Sr}$ , Sr/Ca, and SEM examinations for Hole 593.

Sample Core-Section (interval in cm)	Sub-bottom depth (m)	Ratio $\pm 2\sigma \times 10^{-6}$	Sr/Ca Atom ratio ( $\times 1000$ )	SEM observations
2-6, 2-4	12.6	0.709205 $\pm$ 41	1.41	No recrystallization
4, CC	33.9	0.709117 $\pm$ 32	1.39	No recrystallization
6, CC	53.1	0.709105 $\pm$ 26	1.40	No recrystallization
8, CC	72.3	0.709080 $\pm$ 26	1.34	No recrystallization
12, CC	110.7	0.709064 $\pm$ 32	1.36	Minor recrystallization
14, CC	129.9	0.709035 $\pm$ 34	1.36	Minor recrystallization
16, CC	149.1	0.709020 $\pm$ 34	1.32	Minor recrystallization
18, CC	168.3	0.709003 $\pm$ 30	1.28	Minor recrystallization
20, CC	187.5	0.708988 $\pm$ 24	1.30	Minor recrystallization
22, CC	206.7	0.708974 $\pm$ 30	1.28	Minor recrystallization
24, CC	225.9	0.708949 $\pm$ 28	1.40	No recrystallization
26, CC	245.1	0.708917 $\pm$ 22	1.30	No recrystallization
28, CC	264.3	0.708961 $\pm$ 26	1.38	No recrystallization
30-5, 1-2	279.9	0.708969 $\pm$ 26	1.39	No recrystallization
32, CC	302.7	0.708910 $\pm$ 36	1.41	No recrystallization
34-5, 1-2	318.3	0.708868 $\pm$ 28	1.41	No recrystallization
36, CC	341.1	0.708911 $\pm$ 36	1.36	No recrystallization
38, CC	360.3	0.708876 $\pm$ 30	1.39	No recrystallization
40, CC	379.5	0.708848 $\pm$ 24	1.26	No recrystallization
42-3, 70-72	392.8	0.708802 $\pm$ 14	1.35	No recrystallization
42, CC	398.7	0.708698 $\pm$ 24	1.35	No recrystallization
44-1, 35-37	408.7	0.708637 $\pm$ 16	1.28	No recrystallization
44, CC	417.9	0.708557 $\pm$ 20	1.35	No recrystallization
46-1, 35-37	427.9	0.708515 $\pm$ 32	1.37	No recrystallization
46, CC	437.1	0.708515 $\pm$ 24	1.35	No recrystallization
48, CC	456.3	0.708446 $\pm$ 20	1.36	No recrystallization
50, CC	475.5	0.708211 $\pm$ 28	1.39	No recrystallization
52-2, 35-37	487.0	0.708161 $\pm$ 12	1.32	No recrystallization
52-4, 35-37	490.0	0.708159 $\pm$ 28	1.35	No recrystallization
52, CC	494.7	0.708145 $\pm$ 32	1.39	No recrystallization
53-3, 35-37	498.1	0.708003 $\pm$ 16	1.35	No recrystallization
54-1, 35-37	504.7	0.708027 $\pm$ 28	1.35	No recrystallization
54-2, 35-37	506.2	0.708038 $\pm$ 16	1.39	No recrystallization
54, CC	513.9	0.708030 $\pm$ 20	1.41	No recrystallization
55-2, 35-37	516.8	0.707959 $\pm$ 18	1.41	No recrystallization
56-2, 35-37	525.4	0.707932 $\pm$ 36	1.43	No recrystallization
56-5, 35-36	529.9	0.707911 $\pm$ 24	1.39	No recrystallization
56, CC	533.1	0.707945 $\pm$ 32	1.40	No recrystallization
57-6, 35-37	540.1	0.707809 $\pm$ 24	1.36	No recrystallization
58-2, 35-37	544.6	0.707816 $\pm$ 14	1.41	No recrystallization
60-2, 35-37	563.8	0.707752 $\pm$ 20	1.45	No recrystallization
60, CC	571.5	0.707747 $\pm$ 34	1.45	Minor recrystallization

Note: Errors are 2 standard errors of the mean  $^{87}\text{Sr}/^{86}\text{Sr}$  in  $10^{-6}$  and represent in-run precision.

Table 2. Pore-water  $^{87}\text{Sr}/^{86}\text{Sr}$  for Hole 593.

Core-Section	Depth (m)	Ratio $\pm 2\sigma \times 10^{-6}$
Surface seawater		0.709131 $\pm$ 20
1-4	4.8	0.709115 $\pm$ 36
4-3	28.0	0.709063 $\pm$ 22
6-3	47.3	0.709050 $\pm$ 28
8-1	63.5	0.709032 $\pm$ 24
12-3	104.9	0.708967 $\pm$ 18
14-3	124.1	0.708907 $\pm$ 30
16-3	143.3	0.708939 $\pm$ 28
18-3	163.5	0.708952 $\pm$ 22
20-3	181.7	0.708927 $\pm$ 28
22-3	200.9	0.708858 $\pm$ 30
24-3	220.1	0.708883 $\pm$ 32
26-3	239.3	0.708849 $\pm$ 18
28-3	258.5	0.708864 $\pm$ 18
30-3	277.7	0.708806 $\pm$ 20
32-2	296.9	0.708842 $\pm$ 24
34-2	314.6	0.708762 $\pm$ 20
36-2	333.8	0.708745 $\pm$ 18
38-3	354.5	0.708721 $\pm$ 26
40-3	373.7	0.708665 $\pm$ 24
42-3	392.9	0.708629 $\pm$ 14
44-3	412.1	0.708564 $\pm$ 24
46-3	431.3	0.708557 $\pm$ 14
47-3	440.9	0.708532 $\pm$ 14
48-3	450.5	0.708533 $\pm$ 22
50-3	469.7	0.708392 $\pm$ 26
54-2	506.6	0.708345 $\pm$ 14
56-3	527.3	0.708275 $\pm$ 22
58-1	543.5	0.708244 $\pm$ 18
60-3	565.7	0.707945 $\pm$ 18

Note: Errors are 2 standard errors of the mean  $^{87}\text{Sr}/^{86}\text{Sr}$  in  $10^{-6}$  and represent in-run precision.

latest Eocene). This observation is consistent with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured at other DSDP sites and from other marine samples (Burke et al., 1982; Hess et al., 1984, and unpubl. data; DePaolo and Ingram, 1985; Palmer and Elderfield, in press). Pore-water  $^{87}\text{Sr}/^{86}\text{Sr}$  displays roughly the same pattern as do the foraminifers. The

pore-water Sr isotope ratios are fairly constant but consistently lower than the foraminiferal  $^{87}\text{Sr}/^{86}\text{Sr}$  to about 400 m, at which point the pore-water  $^{87}\text{Sr}/^{86}\text{Sr}$  decreases along with the foraminiferal  $^{87}\text{Sr}/^{86}\text{Sr}$ , but with consistently higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios than the foraminiferal ratios. The crossover point between the two curves is be-

tween 400 and 440 m, close to the ooze/chalk transition at 462 m.

## DISCUSSION

The measured foraminiferal  $^{87}\text{Sr}/^{86}\text{Sr}$  accurately records the  $^{87}\text{Sr}/^{86}\text{Sr}$  of contemporaneous seawater only if the foraminifera are pristine or the effects of diagenetic alteration are minimal. Two criteria were used to screen for diagenetic alteration: scanning electron microscopy and Sr/Ca ratios. Physical evidence for recrystallization was evident in scanning electron micrographs by the presence of large, blocky, euhedral calcite crystals, cementation, or overgrowth. Seven foraminiferal samples from Site 593, indicated by the open circles in Figure 1, showed trace amounts of euhedral calcite crystals indicative of recrystallization. All other samples were free of any physical evidence of recrystallization (Table 1).

Diagenesis also affects the foraminiferal Sr/Ca ratio. Lorens (1981) showed that the magnitude of the calcite distribution coefficient for Sr is dependent on the rate of carbonate precipitation. At slower growth rates, the Sr distribution coefficient is lower. Because inorganic recrystallization rates are much slower than biogenic calcite precipitation rates, the foraminiferal Sr/Ca is lowered during diagenetic alteration. Sr/Ca ratios for the foraminiferal samples are given in Table 1. Comparison of the measured Sr/Ca ratio to the Sr/Ca age curve determined from well-preserved fossil foraminifera (Graham et al., 1982; Delaney, 1983) provide a second check on sample alteration. Samples with Sr/Ca ratios that were low relative to contemporaneous samples were suspected of being recrystallized. For Site 593, all Sr/Ca ratios were comparable to values on the Sr/Ca age curve.

As a final check on the integrity of our ancient seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  determinations, we measured the  $^{87}\text{Sr}/^{86}\text{Sr}$  of contemporaneous pore-water samples. If the foraminifera had recrystallized in some way that was not detected by our screening criteria, their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio would be influenced by the interstitial water  $^{87}\text{Sr}/^{86}\text{Sr}$  with which they equilibrated. As pore-water  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are affected by diffusion and advection as well as alteration of sedimentary volcanic matter and continental debris (Elderfield et al., 1982; Elderfield and Gieskes, 1982), the  $^{87}\text{Sr}/^{86}\text{Sr}$  of pore waters may differ from that of sedimentary biogenic calcite. Pore-water  $^{87}\text{Sr}/^{86}\text{Sr}$  are shown in Figure 1 and Table 2. Pore-water Sr isotope ratios are nearly identical to foraminiferal  $^{87}\text{Sr}/^{86}\text{Sr}$ . Thus, even if the samples were partially recrystallized, the influence on the foraminiferal Sr isotope composition would be minimal.

With the exception of seven slightly altered foraminiferal samples (open circles, Fig. 1), our analyses found no evidence for foraminiferal recrystallization. Therefore, we interpret our measured foraminiferal  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios as representative of ancient seawater  $^{87}\text{Sr}/^{86}\text{Sr}$ . The fact that our measurements for Site 593 agree well with  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from other DSDP sites supports this conclusion. On the other hand, on the basis of pore-water  $\text{Sr}^{+2}$  concentration increases with depth, Baker (this volume) calculated an initial bulk carbonate recrystallization rate of 10%/m.y. for Site 593. Since most of the carbonate

at Site 593 is composed of calcareous nannofossils, which may be more susceptible to alteration than most foraminifera, it is probable that this fine fraction provides most of  $\text{Sr}^{+2}$  excess to the pore water. A detailed study of the Sr isotopic composition of fine-fraction carbonates is planned to test this hypothesis.

## CONCLUSIONS

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of seawater, as reflected by the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of fossil foraminifera, has increased from the latest Eocene to the present. The rise was extremely rapid from the late Eocene to the early Miocene and very gradual from the middle Miocene to the present. This trend is consistent with Sr isotopic measurements from other DSDP cores. SEM examinations and Sr/Ca ratios showed that planktonic foraminifera (<150- $\mu\text{m}$  size fraction) were well preserved.

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