34. ^{87}Sr/^{86}Sr RATIOS OF THE BARREMIAN AND EARLY APTIAN SEAS[1]

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ABSTRACT

Study of 12 carbonate oozes from Deep Sea Drilling Project Hole 463, in the Mid-Pacific Mountains, suggests mean values of 0.70690 ± 0.00029 (2σ) and 0.70712 ± 0.00030 (relative to 0.71014 for the NBS 987 Sr isotope standard) as representing the Sr isotope composition of the Barremian and early Aptian seas, respectively. Two additional values of less than 0.7064 are the least radiogenic values known from the Phanerozoic and may be a consequence of the introduction of Sr depleted in the heavy isotope from massive submarine volcanic activity, which followed the initiation of the latest oceanic spreading episode in the Oxfordian.

INTRODUCTION

Knowledge of the isotopic composition of Sr in the oceans throughout geologic time is of general interest because it may be used indirectly as an age indicator of sedimentary rocks. The abundance of ^{87}Sr in rocks and minerals, conventionally expressed as the ^{87}Sr/^{86}Sr ratio, increases as a consequence of the natural decay of unstable radioactive ^{87}Rb to stable ^{87}Sr (Faure and Powell, 1972). The increase depends also on the Rb/Sr ratio: the higher the ratio, the greater is the ^{87}Sr/^{86}Sr ratio at any given time. The oceans have contained and still contain mixtures of Sr isotopes which have been released into solution during chemical weathering of continental and submarine rocks (Faure et al., 1965). The study of ^{87}Sr/^{86}Sr ratios in the oceans should therefore allow an estimation of this balance during geologic time. A previous study by Peterman et al. (1970) has shown that the ^{87}Sr/^{86}Sr ratio of marine carbonates, which incorporate Sr during their deposition, varied systematically but also irregularly during Phanerozoic time, probably as a result of changes in the balance between continental and submarine weathering. Further studies of the Phanerozoic (Dasch and Biscaye, 1971; Boger et al., 1973; Brass 1973; Veizer and Compston, 1974; Faure et al., 1978) confirmed these conclusions.

The purpose of the present study of 12 carbonate oozes from DSDP Hole 463, drilled on the Mid-Pacific Mountains was twofold:

1) to measure "in continuity" the Sr isotope composition of the Cretaceous ocean from the early Barremian to the early Aptian, and thus to contribute to a more complete knowledge of the ^{87}Sr/^{86}Sr variations with time; and

2) to compare the ^{87}Sr/^{86}Sr values for the early and late Barremian, to contribute to the placement of the boundary between them.

Sample locations in the core are given in Table 1. They are distributed over less than 200 meters of sediment, representing a time span of about 10 m.y.

ANALYTICAL PROCEDURE

After hand crushing in an agate mortar, 100 mg of each sample was gently leached in cold 1N hydrochloric acid. Sr was separated from other cations, and especially from Ca, by chromatography on cation-exchange resin (Dowex 50W × 12, 200–400 mesh) and analyzed on a single oxidized Ta filament in a solid-source mass spectrometer having a 30-cm radius and a 60° deviation angle. The errors of each individual measurement given in Table 1 are two standard deviations of the mean. The reproducibility of the mass spectrometer data, as established by duplicate analyses of routine samples and standard minerals, is better than 3×10^{-4}. Sr contamination by diluted hydrochloric acid and separation on the resin columns is about 2 to 3 ng for a sample of 100 mg. Additional information on the chemical procedures and the instrumental conditions are available in Clauer (1976a).

RESULTS

Prior to the present study, only three values of the ^{87}Sr/^{86}Sr ratio of Barremian and Aptian seas were available (Veizer and Compston, 1974). Collected in the

Table 1. Sr isotope data on carbonates from DSDP Hole 463 (21° 21.01′N; 174°40.07′E).

Sample (interval in cm)	Stratigraphic Position	Sub-bottom Depth (m)	^{87}Sr/^{86}Sr $\pm$ $2\sigma/\sqrt{N}$
463-70-1, 35–36	Lower Aptian	613.9	$0.70718 \pm 23 \times 10^{-5}$
71-2, 99–100	Lower Aptian	625.5	0.70708 ± 11
72-1, 43–44	Lower Aptian	633.0	0.70632 ± 15
73-1, 18–19	Lower Aptian	642.2	0.70710 ± 35
78-1, 72–73	Lower Aptian	690.2	0.70625 ± 15
79-1, 36–37	Upper Barremian	699.4	0.70719 ± 15
81-2, 45–46	Upper Barremian	712.5	0.70671 ± 23
83-1, 0–1	Upper Barremian	727.5	0.70676 ± 08
84-1, 19–20	Upper Barremian	737.2	0.70689 ± 22
89-1, 105–107	Upper Barremian	785.6	0.70689 ± 17
91,CC	Lower Barremian	803.5	0.70685 ± 43
92-1, 0–1	Lower Barremian	813.0	0.70701 ± 23

Note: Ratios corrected for the ^{86}Sr/^{88}Sr ratio of 0.1194 and adjusted to 0.71014 for the ^{87}Sr/^{86}Sr ratio of the NBS 987 standard; the individual error represents two standard deviations of the mean of N, which is the number of observations in each run.

High Tatra Mountains, near the boundary between Czechoslovakia and Poland, these samples have a mean $^{87}Sr/^{86}Sr$ ratio of 0.70717 ± 0.00070 (2σ, adjusted to a value of 0.7080 for the $^{87}Sr/^{86}Sr$ ratio of the Eimer and Amend standard). Ten new $^{87}Sr/^{86}Sr$ ratios obtained here on similar material for the same time span are slightly lower (Table 1; Fig. 1). Furthermore, two values from the Upper Barremian and Lower Aptian are the lowest ever observed for Phanerozoic time (cf. compilation of the known values in Clauer, 1976a).

The abnormally low values and the slight differences with results obtained by Veizer and Compston (1974) on contemporaneous carbonates emphasize two types of questions: (1) what are the reasons for the irregular temporal variations of the $^{87}Sr/^{86}Sr$ ratios in the past oceans, and (2) how representative are samples from one area compared to the entire ocean at a given period of the Earth's evolution?

Possible Causes of Irregular Variations

According to Peterman et al. (1970), variations of the $^{87}Sr/^{86}Sr$ ratios of the past oceans may be directly related to the types of rocks exposed to weathering on the continents. Spooner (1976) suggested that the $^{87}Sr/^{86}Sr$ ratio could be the result of a balance between Sr released from the continents (enriched in ^{87}Sr), and Sr from weathering of submarine basalts (depleted in ^{87}Sr). He even proposed a quantitative model to support his hypothesis. In a comment on Spooner's contribution, Brass and Turekian (1977), referring to earlier studies of Brass (1973, 1976), tried to minimize the influence of mantle Sr. They argued that marine Sr can vary between the same limits proposed by Spooner (1976) simply by varying the amount of weathered continental carbonates compared to weathered continental rocks enriched in ^{87}Sr. It should be noted that submarine weathering of volcano-sedimentary material produces clays and zeolites containing Sr depleted in ^{87}Sr (Hoffert et al., 1978). Moreover, Sr in smectites of hydrothermal origin is also depleted in ^{87}Sr (Clauer, 1979). Faure et al. (1978) also proposed a model allow-

ing a fair estimation of the part of marine Sr derived from old sialic rocks, young volcanic rocks, marine carbonates, and evaporitic rocks.

Clauer (1976a) remarked that during the Phanerozoic the $^{87}Sr/^{86}Sr$ ratios of the oceans were systematically high after the Cadomian (Pan-African), Caledonian, Hercynian, and Alpine orogenies, and that the lowest values occurred at the beginning of the latest sea-floor-spreading episode during the Oxfordian. He suggested an interpretation in terms of orogenic evolution and sea-floor spreading. Thus, as a consequence of orogenic activities, old sialic rocks are again exposed to weathering on the continents, whereas during sea-floor spreading basic volcanic rocks as well as hydrothermal fluids (Francheteau et al., 1979) are injected along the oceanic ridges. This hypothesis was later quantified by Brevart and Allegre (1978).

Representativeness of Samples

The long residence time of the Sr in the ocean (Goldberg, 1965) certainly is in favor of its complete isotopic homogenization in the world ocean at a given moment. Nevertheless, the presently observed variations occurred within 10 m.y. They could be due either to diagenetic recrystallization of carbonates, which may increase the $^{87}Sr/^{86}Sr$ ratios (Veizer and Compston, 1976; Tremba et al., 1975), or to peculiar geographic locations of the samples. Indeed, if samples are representative of a closed sea—like the Mediterranean, which evolved to an evaporitic basin during the Messinian—the ratios of the carbonates are influenced by the drainage basin (Clauer, 1976b). On the other hand, if carbonates precipitate close to spreading centers, their Sr ratios may be modified and depleted in the ^{87}Sr.

In the Lower Aptian of this study, important variations occur within 65 meters of sediment between Cores 78 and 71 (Table 1; Fig. 1). They underline the possibility of rapid chemical changes in the ocean inputs and show that the smooth variations of the $^{87}Sr/^{86}Sr$ ratio of the oceans proposed by Faure and Powell (1972) and Hart and Staudigel (1978) are not justified. The ratio in the oceans may change as quickly as in non-marine environments (Neat et al., 1979). Moreover, the model proposed by Hart and Staudigel (1978) to explain the different initial $^{87}Sr/^{86}Sr$ ratios of vein smectites and vein calcites in basaltic crusts becomes again debatable.

The two deepest samples (Cores 91 and 92) have a mean $^{87}Sr/^{86}Sr$ ratio of 0.70693 ± 0.00030, which is not significantly different from the mean of 0.70685 ± 0.00012 for the four Upper Barremian samples taken directly above (Cores 81, 83, 84, and 89). It is not possible to differentiate between Lower and Upper Barremian solely on the basis of the $^{87}Sr/^{86}Sr$ ratio. However, the close values of the ratios suggest a strong chemical continuity over almost the entire set of Barremian samples.
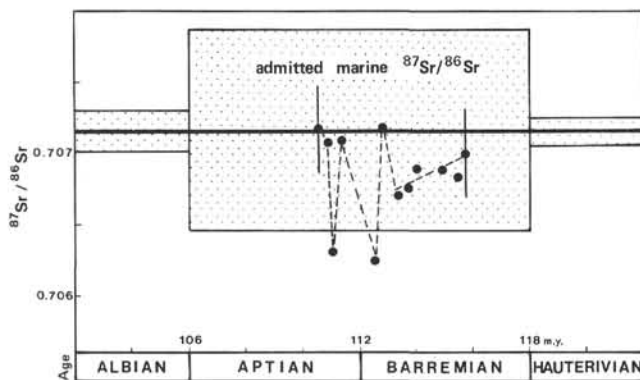
Figure 1. $^{87}Sr/^{86}Sr$ ratios of the Barremian and early Aptian oceans. The admitted $^{87}Sr/^{86}Sr$ ratios are values (with their errors) known from the literature. The two vertical bars at the oldest and youngest sample give the reproducibility of the mass-spectrometer data Boundary ages from Harland et al. (1964).

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