

# THE ISOTOPIC COMPOSITION OF STRONTIUM IN FOSSILS FROM THE KENDRICK SHALE, KENTUCKY<sup>1, 2</sup>

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## ABSTRACT

Nine analyses of the isotopic composition of strontium in the carbonate shells of marine fossils from the Kendrick Shale (Lower Pennsylvanian) of Kentucky indicate an average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.7086 \pm 0.00035$  at the 95 percent confidence limit. This value is in satisfactory agreement with previous measurements by Peterman *et al.* (1970) and confirms that strontium in the oceans during Early Pennsylvanian time was anomalously enriched in radiogenic  $^{87}\text{Sr}$ , compared to that in earlier and later periods. The isotopic composition of strontium in skeletal calcium carbonate of cephalopods, gastropods, and brachiopods from the Kendrick Shale appears to be the same in spite of the different feeding habits of these animals.

## INTRODUCTION

The isotopic composition of strontium in rubidium-bearing rocks and minerals changes continuously as a function of time by the decay of naturally occurring  $^{87}\text{Rb}$  to stable  $^{87}\text{Sr}$ . The resulting increase in the isotopic abundance of  $^{87}\text{Sr}$  has been used to make age determinations of Rb-bearing rocks and minerals (see, for example, Faure and Powell, 1972; Hofmann and Faure, 1972; and Peters and Faure, 1972).

The isotopic composition of strontium dissolved in sea water has also attracted considerable attention, because it is believed to reflect the Rb-enrichment and age of the rocks which are exposed to weathering on the continents and in the ocean basins (Faure, *et al.*, 1965). A large number of isotope analyses of strontium in sea water has been reported in the literature, all of which indicate that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in sea water is a constant equal to 0.7091 (Faure and Powell, 1972). Consequently, strontium extracted from sea water is now being used by some investigators as an inter-laboratory isotope standard (Papanastassiou, *et al.*, 1970; Kaushal and Wetherill, 1969; Bogard, *et al.*, 1967).

If the isotopic composition of strontium in the oceans reflects the rubidium content and geologic age of the rocks now exposed to weathering on the continents and in the ocean basins, as proposed by Faure, *et al.* (1965), then the possibility exists that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the oceans has varied throughout geologic history in response to the changing composition and age of the rocks undergoing chemical weathering. This question has been investigated by Peterman, *et al.* (1970) by analysis of strontium in unreplaced calcium carbonate of marine fossils of Phanerozoic age. Their results indicate that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the oceans has varied systematically during Phanerozoic time and that strontium in the oceans appears to have been isotopically homogeneous.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of marine strontium during Phanerozoic time as reported by Peterman *et al.* (1970) is shown in Figure 1. It shows that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the oceans has varied systematically during the Paleozoic and Mesozoic eras, and that its present value is higher than at any time in the past. The increase in this ratio during Cretaceous and Tertiary time has been confirmed by Dasch and Biscaye (1971) using foraminifera from deep-ocean sediments. An interesting feature of the curve is the apparent existence of two short-term increases of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio during the Pennsylvanian and the Triassic periods. Armstrong

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(1971) suggested that these increases, as well as the high present-day value, correlate with the intensity of continental glaciation. He proposed that glaciation of Precambrian shield areas increases the input of radiogenic  $^{87}\text{Sr}$  into the oceans, thus causing the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio to increase.

The anomalously high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the Pennsylvanian oceans are based partly on isotope analyses of strontium from three fossils of the Kendrick Shale by Peterman *et al.* (1970). They analyzed *Linoproductus* sp., *Bellerophon* sp.,

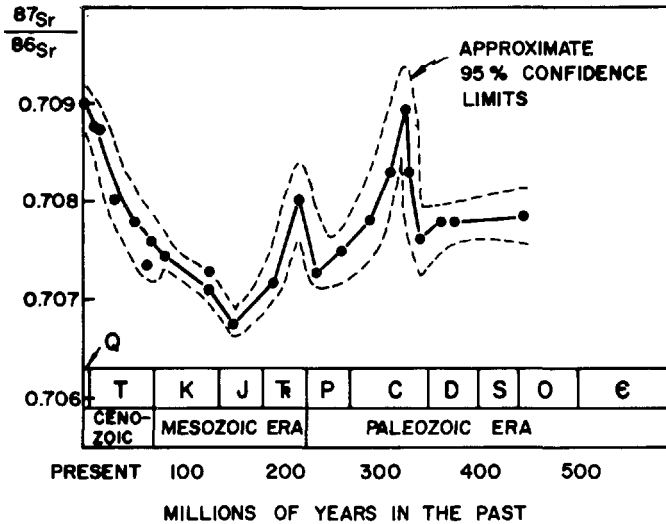


FIGURE 1. Variation of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the oceans during Phanerozoic time. Data from Peterman, *et al.* (1970).

and a rugose coral, and obtained an average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.70897 \pm 0.00053$ . This is the highest value of this ratio obtained for any fossils of Phanerozoic age analyzed by Peterman *et al.* (1970), and is identical to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the modern oceans within experimental errors.

The objective of this study was to analyze additional material from the Kendrick Shale in order to confirm the important anomaly discovered by Peterman and his colleagues.

#### GEOLOGY OF THE KENDRICK SHALE

The Kendrick Shale is of Early Pennsylvanian (Late Morrow) age, and occurs in the lower part of the Breathitt Formation of the Pottsville Group (Jillson, 1931). The type section is located near the head of Cow Creek in Floyd County of Southeastern Kentucky, shown in Figure 2 and also on the geologic maps of Rice (1964, 1965). It is a dark-gray, sandy shale, and includes a fossiliferous section about 12 feet thick near its base. The samples used in this study were collected by C. H. Summerson from these fossiliferous beds exposed in Cow Creek.

The calcium carbonate shells and skeletons of the fossils in the Kendrick Shale have been unusually well preserved (Stehli, 1956) and still contain aragonite. Lowenstam (1964) reported  $(\text{Sr}/\text{Ca}) \times 10^3$  ratios of four species of gastropods from the Kendrick shale ranging from 4.4 to 6.3, which is significantly higher than those of Holocene marine gastropods which he also analyzed. We conclude from this that the calcium carbonate of the fossils in the Kendrick Shale has not completely recrystallized to calcite and that the shells probably have not lost appreciable amounts of strontium as a result of post-depositional alteration.

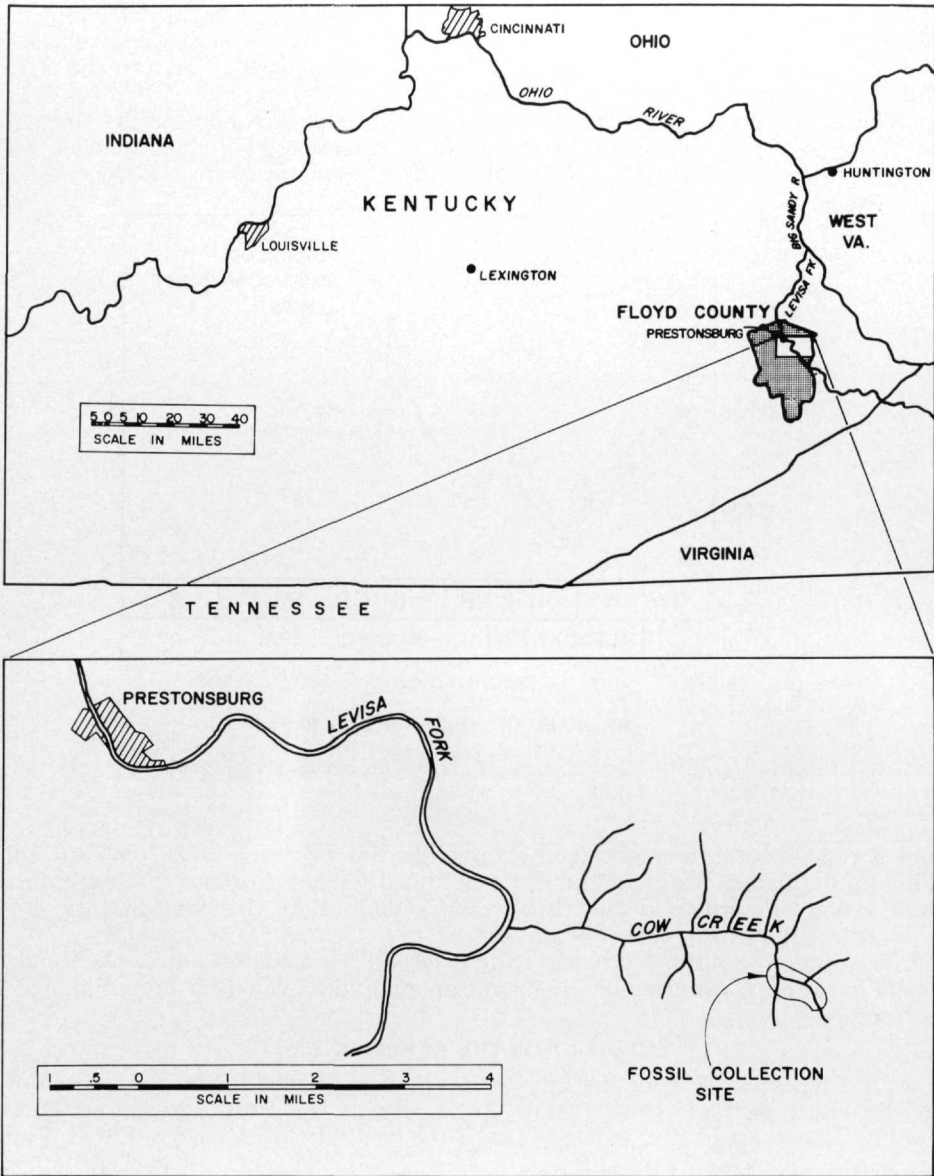


FIGURE 2. Location of fossiliferous exposures of the Kendrick Shale in Floyd County, Kentucky.

ANALYTICAL PROCEDURES

Several large specimens of fossiliferous rock were collected from exposures in Cow Creek. Shells of brachiopods, gastropods, and cephalopods were removed by breaking the surrounding rock matrix. The individual specimens were then crushed in an agate mortar and fragments of the shells hand picked from the crushed material. These fragments were ground to a fine powder in an agate mortar and homogenized. Aliquots weighing approximately 0.2g were weighed

out and dissolved in about 30 ml of 0.1N hydrochloric acid distilled in a Vycor glass distillation-apparatus. The dissolution was accomplished in less than five minutes and the resulting solutions were then centrifuged to remove insoluble residues. The liquid fraction was decanted and evaporated to dryness in Vycor evaporating dishes. The residue was then dissolved in double-distilled and demineralized water and placed on a cation-exchange column (Dowex 50, X-8, 200-400 mesh, cation-exchange resin) for separation of strontium. The eluant was 2.25 N Vycor-distilled hydrochloric acid. The insoluble residue was dried and weighed to determine the silicate content of the samples. The isotope analyses were made on a Nuclide Corp. Model 6-60-S solid-source, single-filament, mass spectrometer using pre-cleaned tantalum filaments. The accuracy and reproducibility of the isotope analyses was monitored by replicate analyses of the Eimer and Amend  $\text{SrCO}_3$  isotope standard and all measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were corrected for fractionation to a standard value of 0.1194 for the  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio.

The mineral composition of the shells was determined by x-ray diffraction using Cu, K-alpha, Ni-filtered x-radiation. Diffraction patterns were recorded on a strip chart between  $2\theta$  values of 25 and 35°. The approximate abundance of aragonite ( $2\theta=33.1^\circ$ ) relative to calcite ( $2\theta=29.4^\circ$ ) was determined by a calibration curve obtained by analyses of mixtures of calcite and aragonite in known proportions by weight. All of the measurements are compiled in Table 1.

TABLE 1  
*Analytical results for fossil shells from the Kendrick Shale*

Sample	Fossil	Insoluble Residue %	Aragonite %	$\frac{^{86}\text{Sr}}{^{88}\text{Sr}}$	$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{corr.}}$
	Cephalopods				
369a <sup>1</sup>	<i>Pseudorhynchoceras</i> sp.	73	100	0.1194	0.7087
369b	"	n.d. <sup>2</sup>	43	0.1184	0.7085
378	<i>Gastrioceras</i> sp.	47	56	0.1178	0.7082
	Gastropods				
370	<i>Trepostoma depressa</i>	55	51	0.1188	0.7087
371	<i>Sphaerodoma</i> sp.	n.d.	88	0.1173	0.7083
	Brachiopods				
373	<i>Chonetes</i> sp.	61	0	0.1197	0.7080
375	<i>Linoproductus</i> sp.	47	0	0.1173	0.7089
				0.1182	0.7094

<sup>1</sup>a and b are different individuals

<sup>2</sup>n.d.—not determined.

#### RESULTS AND DISCUSSION

The insoluble-residue content of the samples ranges from 73 to 47 percent and consists primarily of the shale matrix in which the shells were embedded. An x-ray diffraction pattern of the shale failed to indicate the presence of either calcite or aragonite. The strontium in this shale has a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7231 and is therefore clearly enriched in radiogenic  $^{87}\text{Sr}$  compared to the strontium in the fossil shells. Consequently, it is possible that some of this radiogenic  $^{87}\text{Sr}$  may have been removed from the shale component during the dissolution of the samples in dilute hydrochloric acid. However, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the fossil shells in Table 1 do not correlate with the insoluble residue contents of the samples, indicating that this is a negligible source of error in this case.

The aragonite concentrations of the cephalopod and gastropod shells range from 43 to 100 percent. The brachiopod shells consist of calcite. The mineralogy

of the cephalopod and gastropod shells suggests partial recrystallization of aragonite to calcite, accompanied by possible alteration of the isotope composition of strontium in the shells. However, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the shells appear to be independent of the aragonite content, which indicates that any recrystallization of aragonite to calcite has not measurably affected the isotopic composition of the strontium in the shells.

The validity of the measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the fossil shells therefore depends primarily on the accuracy and precision of the mass spectrometric measurements, as indicated by our replicate analyses of the Eimer and Amend strontium isotope standard. These measurements are compiled in Table 2. The average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, corrected for fractionation, is  $0.7081 \pm 0.00038$  at the 95 percent confidence limit. Peterman *et al.* (1970) adjusted their data to a different isotope standard (United Mining and Chemical Corp., Lot B-857), but reported a value for the Eimer and Amend standard which agrees with ours within the uncertainty of the measurements. The reproducibility of our measurements is  $\pm 0.0010$  at the 95 percent confidence limit, as indicated by the standard deviation of the corrected  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in Table 2.

TABLE 2  
Results of isotope analyses of the Eimer and Amend strontium  
isotope standard (Lot No. 492327)

Date	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{88}\text{Sr}/^{88}\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{corr.}}$
4/8/1970	0.7121	0.1180	0.7079
6/14/1970	0.7119	0.1178	0.7072
7/22/1970	0.7135	0.1177	0.7083
8/12/1970	0.7117	0.1183	0.7084
6/10/1971	0.7107	0.1188	0.7088
7/8/1971	0.7081	0.1194	0.7081
7/22/1971	0.7103	0.1186	0.7078
8/13/1971	0.7113	0.1185	0.7087
8/31/1971	0.7106	0.1184	0.7078
Averages	0.7111	0.1184	0.7081
Std. Dev.	$\pm 0.0015$	$\pm 0.0005$	$\pm 0.0005$

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the fossil shells from the Kendrick Shale range from 0.7080 to 0.7094. The average of nine analyses of seven samples is  $0.7086 \pm 0.00035$  at the 95 percent confidence limit. Peterman *et al.* (1970) obtained an average of  $0.70897 \pm 0.00053$  from four analyses of three fossils from the Kendrick Shale. Our value agrees, within the analytical errors at the 95 percent confidence limit, with the result of Peterman *et al.* (1970).

The cephalopods have an average  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7085, the gastropods 0.7087, and the brachiopods 0.7088. These values are not statistically different from each other and we conclude that we have not detected any systematic differences in the isotopic composition of strontium in the shells of these animals. However, we suggest that mollusks which extract nutrients from organic-rich sediment may also extract radiogenic  $^{87}\text{Sr}$  from the sediment and may therefore deposit calcium carbonate having a higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio than that of the water in which they live. The shale matrix in which the fossils from the Kendrick Shale are embedded has a Rb/Sr ratio of 0.940 (Rb = 190 ppm, Sr = 206 ppm). Assuming an age of 325 million years (Early Pennsylvanian) and using the present  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio to 0.7231, we calculate that the strontium in the sediment at the time of deposition of the Kendrick Shale had a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of about 0.709. This value

is so similar to that of the water that the predicted enrichment in radiogenic  $^{87}\text{Sr}$  of sediment-ingesting animals is unlikely to be detectable in this case. However, the effect may be observable under more favorable conditions, where the sediment is strongly enriched in radiogenic  $^{87}\text{Sr}$  relative to the water, as for example in lakes and streams in Precambrian Shield areas.

## ACKNOWLEDGMENTS

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## REFERENCES CITED

- Armstrong, R. L. 1971. Glacial erosion and the variable isotopic composition of strontium in sea water. *Nature* 230: 132-133.
- Bogard, D. D., D. S. Burnett, P. Eberhardt, and G. J. Wasserburg. 1967. Rb $^{87}$ -Sr $^{87}$  isochron and K $^{40}$ -Ar $^{40}$  ages of the Norton County chondrite. *Earth Planet. Sci. Letters* 3: 179-189.
- Dasch, E. J., and P. E. Biscaye. 1971. Isotopic composition of strontium in Cretaceous-to-Recent, pelagic foraminifera. *Earth Planet. Sci. Letters* 11: 201-204.
- Faure, G., and J. L. Powell. 1972. Strontium isotope geology. Springer Verlag New York, Inc., 188 p.
- Faure, G., P. M. Hurley, and J. L. Powell. 1965. The isotopic composition of strontium in surface water from the north Atlantic Ocean. *Geochim. Cosmochim. Acta* 29: 209-220.
- Hofmann, C. M., G. Faure, and A. Janssens. 1972. Age determination of a granite gneiss from the Precambrian basement of Scioto County. *Ohio J. Sci.* 72: 49-53.
- Jillson, W. R. 1931. The paleontology of Kentucky. *Kentucky Geol. Surv. Bull.* 36: 298-301.
- Kaushal, S. K., and G. W. Wetherill. 1969. Rb $^{87}$ -Sr $^{87}$  age of bronzite (H group) chondrites. *J. Geophys. Res.* 74: 2717-2726.
- Lowenstam, H. A. 1964. Sr/Ca ratio of skeletal aragonites from Recent marine biota of Palau and from fossil gastropods, p. 114-131. In H. Craig, S. L. Miller, and G. J. Wasserburg, Eds., *Isotopic and cosmic chemistry*, North-Holland Publishing Co., Amsterdam, 553 p.
- Papanastassiou, D. A., G. J. Wasserburg, and D. S. Burnett. 1970. Rb-Sr ages of lunar rocks from the Sea of Tranquility. *Earth Planet. Sci. Letters* 8: 1-9.
- Peterman, Z. E., C. E. Hedge, and H. A. Tourtelot. 1970. Isotopic composition of strontium in sea water throughout Phanerozoic time. *Geochim. Cosmochim. Acta* 34: 105-120.
- Peters, R. L., and G. Faure. 1972. Age determination of a glacial erratic in Columbus, Ohio. *Ohio J. Sci.* 72: 87-90.
- Rice, Charles. 1964. Geology of the Lancer Quadrangle, Kentucky. Map GQ-347. U.S. Geol. Surv., Washington, D.C.
- . 1965. Geology of the Harold Quadrangle, Floyd County, Kentucky. Map GQ-441. U.S. Geol. Surv., Washington, D.C.
- Stehli, F. G. 1956. Shell mineralogy in Paleozoic invertebrates. *Science* 123: 1031-1032.

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**Structural Geology.** *M. King Hubbert.* Hafner Publishing Company, New York. 1972. iv+329 p. \$12.00.

King Hubbert is a remarkable man who is well known to geologists for his important contributions in the areas of structural geology, ground-water flow, and energy resources. He has few peers as a student of the mechanics of deformations in the solid earth, and he is the most frequently cited contributor in my own courses in structural geology. This book brings together his most significant works in structural geology.

The book contains papers published by Hubbert and his colleagues between 1928 and 1961, along with a new 19-page introduction. The topics treated are: (1) direction of stresses producing strains, (2) theory of geologic scale models, (3) strength of the earth (can Texas be quarried?), (4) mechanical basis for geologic structures (sand-box experiment), (5) stress distributions and faulting (by W. Hafner), (6) mechanics of hydraulic fracturing, (7) role of fluid pressure in overthrusting (beer-can experiment), and (8) three discussions of the last paper.

The Introduction is a fascinating account of Hubbert's career as he progressed from one problem to the next. His early friendship with Nadai stimulated his interest in scale models and the use of the Mohr diagram. Lost-circulation problems in drilling oil wells led to his studies of fluid pressure, first in connection with inducing fractures in reservoir rocks, and eventually with overthrust faulting.

The publishers deserve thanks for making available this collection of classical papers. Librarians will welcome the volume to divert traffic from the heavily thumbed originals in their periodicals. I am delighted to have a copy for my personal library and will recommend it to geology students. It provides a lot of insight for the price.

CAMPBELL CRADDOCK