

SURVEY OF $^{87}\text{Sr}/^{86}\text{Sr}$ RATIOS AND TOTAL STRONTIUM CONCENTRATIONS IN OHIO STREAM AND GROUND WATERS¹

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ABSTRACT

A total of 23 Ohio stream and ground waters has been sampled and analyzed for total Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios in an attempt to evaluate the potential usefulness of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a tracer of water provenance. Sampling stations were selected in order to provide a wide geographic distribution and a variety of contacted lithologies. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.7078 to 0.7130, with the higher ratios occurring in eastern and southern Ohio and the lower ratios to the north and west. This trend is apparently due in part to the change in the dominant lithology of the Paleozoic sediments across Ohio. In the east, clastic sediments predominate, whereas in the west, limestone becomes the major important component of the sedimentary sequence. Most limestones of Paleozoic age are known to have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of approximately 0.708, whereas shales have a range of higher values. The observed trend in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the water samples also appears to be related to the position of the glacial boundary. The widespread occurrence of easily soluble carbonate material in the glacial till north of the boundary has apparently had a strong effect on the strontium isotopic compositions of the local waters.

INTRODUCTION

Natural variations in the isotopic ratio $^{87}\text{Sr}/^{86}\text{Sr}$ have been investigated by geochemists for approximately the past ten years. The element strontium has four stable isotopes: ^{88}Sr , ^{87}Sr , ^{86}Sr , and ^{84}Sr . One of these, ^{87}Sr , is the daughter product of the radioactive decay of ^{87}Rb and its abundance has therefore increased throughout geologic time. The relative abundance of ^{87}Sr is conveniently expressed as the ratio $^{87}\text{Sr}/^{86}\text{Sr}$. This ratio increases in a rock at a rate which is proportional to its Rb/Sr ratio and the decay constant of ^{87}Rb . The present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in a rock depends upon these two factors and upon the geologic age of the rock. These relationships are presented graphically and as an equation in Figure 1.

In general, Rb-rich rocks such as shales have relatively high present $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, whereas Rb-poor rocks such as carbonates have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios today. These generalizations are illustrated by typical $^{87}\text{Sr}/^{86}\text{Sr}$ growth curves for shales and carbonates (fig. 1). Once such different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been produced in natural materials, they can be changed only by the addition of strontium having a different $^{87}\text{Sr}/^{86}\text{Sr}$ ratio or by the continued decay of ^{87}Rb . Present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be used as tracers of the source of certain materials. For example, all modern oceans contain dissolved strontium with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio very close to 0.7090 (Faure, *et al.*, 1965). Thus all materials formed today solely by precipitation from sea water, such as most carbonate rocks and evaporites, also have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7090. Continental rocks, on the other hand, have a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The average value for the sialic crust today is probably close to 0.725 (Faure and Hurley, 1963).

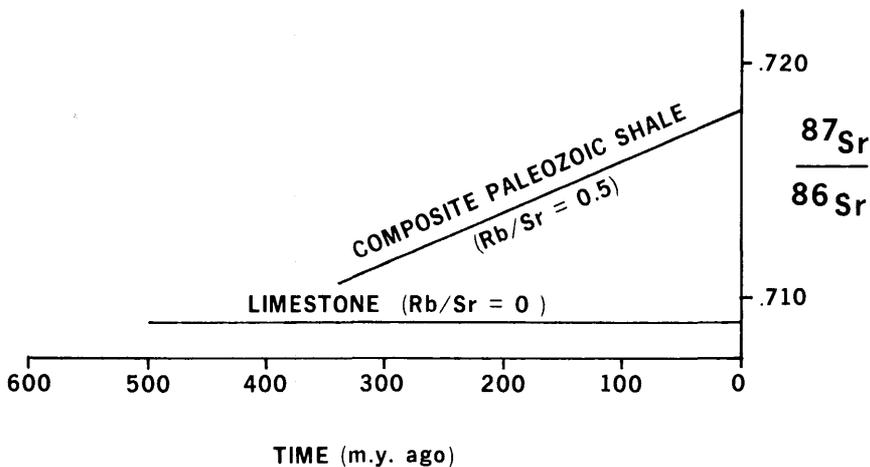
The use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in natural materials as a tracer should be applicable to surface and ground waters. In this case, the ratio may indicate the source of these waters or the rock types through which they subsequently migrated. Chemical weathering of a rock releases strontium into solution in the ground water, whose isotopic composition then reflects that of the rock. Strontium leached from

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a shale has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio significantly higher than strontium leached from a marine limestone. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of water in a stream reflects the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and the relative proportions of the various ground-water components which contribute to the stream. By measuring the isotopic ratios and total strontium concentrations in a stream and the local ground waters, or in a stream and its tributaries, mixing models could be set up which place limits on the proportions of stream water derived from different sources.

In this study an attempt has been made to evaluate the potential usefulness of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a tracer in the study of stream and ground waters in the state of Ohio. In order to make practical application of this concept, it is neces-

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{today}} \approx \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{initial}} + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right) \lambda t$$



GROWTH OF ($^{87}\text{Sr}/^{86}\text{Sr}$) IN SEDIMENTARY ROCKS

FIGURE 1. Growth of $^{87}\text{Sr}/^{86}\text{Sr}$ in sedimentary rocks.

sary first to demonstrate that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in waters within a given area are significantly variable, and that such variations can be related to lithologic type of bedrock and overburden. This aspect of the overall concept has been investigated in the present study by making a reconnaissance of stream and ground waters throughout the state. The only previous work of this nature in Ohio was by Eastin and Faure (1970), who reported strontium isotopic analyses of water samples from the Olentangy and Scioto Rivers at Columbus.

Sample Collection

Collection stations were chosen so as to obtain water from several different lithologies and hydrologic environments characteristic of Ohio. The suite of samples, collected from both sides of the Pleistocene glacial boundary, represents both surface and ground waters from areas whose bedrock ranges from Upper Ordovician through Permian age. Nearly all the samples were collected during the dry summer months (July and August, 1970) in order to minimize the contribution of direct surface runoff to total stream discharge. At this time of year,

ground waters would have had a greater effect on the strontium isotopic composition of stream waters. Four of the water samples were collected in the spring of 1971, in order to gain further geographic coverage of the state. The possible effect of seasonal variation upon the isotopic compositions of these samples is thought to be insignificant.

All samples were collected and stored in polyethylene bottles. Each bottle was washed three times with the water to be collected before finally being filled. Waters for isotopic analysis were collected in 9.5-liter containers, whereas those for total strontium determinations were collected in 1-liter bottles.

ANALYTICAL PROCEDURES

Strontium Isotopic Analyses

The separation of dissolved strontium from the water samples was carried out by cation-exchange chromatography. Approximately one liter of a water sample was filtered into a reservoir fitted into the top of a glass-chromatography column, 2 cm in diameter and 30 cm in length, which contained 100–200 mesh analytical-grade cation-exchange resin. The filtered water was allowed to drain through the column. Tests using small amounts of a ^{89}Sr radioactive tracer indicated that all the dissolved strontium was sorbed within the top few mm of the resin column. The column was then eluted with 500 ml 2 N HCl, which moved the Sr to the vicinity of the bottom of the column. The next 400 ml of eluate, containing the Sr, were collected in a Vycor beaker and evaporated to dryness within a glass fume hood. The residue was treated with a few ml of high-purity nitric and perchloric acids in order to oxidize any resin that might have been released from the chromatography column. After evaporation to dryness, the Sr fraction was covered with parafilm and stored for mass-spectrometric analysis.

The strontium-isotopic compositions were determined on a solid-source mass spectrometer with a 12-inch radius of curvature, using double rhenium filaments. The strontium fraction separated from the water sample was dissolved in a few drops of dilute nitric acid and was evaporated onto one of the two rhenium filaments, both of which had been precleaned by heating in the mass spectrometer. After inserting the double-filament source into the mass spectrometer and obtaining a suitable vacuum, a stable strontium-ion beam was produced by evaporation and ionization of the strontium salt. After acceleration by an electric field of 3000 volts, the ion beam was resolved into its characteristic mass components by magnetic scanning. A typical analysis consisted of three charts, obtained with the aid of an expanded-scale circuit, each chart representing 20 scans across the mass range 86 to 88. The presence of isobaric contamination at mass 87 was checked by scanning the spectrum at mass 85 for the presence of ^{85}Rb . Peak heights were read from the charts, and the average $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{88}\text{Sr}/^{86}\text{Sr}$ ratios were calculated for each chart. Mass-fractionation corrections were applied by normalizing the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to a $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.375. The normalized $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the three charts were averaged and this value is reported for each analyzed sample in Table 1.

The accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ analyses was evaluated by analyzing the interlaboratory Eimer and Amend SrCO_3 standard. Our results (Table 2) are in good agreement with those reported by other laboratories, which fall within the range of from 0.7075 to 0.7085. The reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is indicated by duplicate analyses, including chemical processing, of two water samples (Table 3). It is clear that measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios which differ by one part in 700 or more are significant beyond the limits of experimental uncertainty.

The extent of strontium contamination during chemical processing and mass-spectrometric analysis was evaluated through a blank determination. The result (0.15 μg Sr) is negligible in terms of the total quantity of strontium processed in any water analysis.

TABLE 1
 $^{87}\text{Sr}/^{86}\text{Sr}$ Ratios and Total Strontium Concentrations of
 Ohio Water Samples.

Sample No.	Sample Location	$^{87}\text{Sr}/^{86}\text{Sr}^*$	Sr (mg/l)
SrCk-4	Little Hocking River Washington Co.	0.7130	0.17
SrCk-5	Little Miami River Greene Co.	0.7094	1.37
SrCk-7	Nettle Creek Champaign Co.	0.7089	1.70
SrCk-10	Mad River Logan Co.	0.7085	0.52
SrCk-11	Scioto River Hardin Co.	0.7087	12.35
SrCk-12	Grand River Ashtabula Co.	0.7117	0.13
SrCk-13	Tiffin River Defiance Co.	0.7091	0.40
SrCk-16	Lake St. Marys Mercer Co.	0.7090	0.41
SrCk-18	Killbuck Creek Wayne Co.	0.7100	0.21
SrCk-19	Sippo Creek Stark Co.	0.7093	0.10
SrC-1	Cumberland pond Muskingum Co.	0.7115	1.92
SrL-1	West Union spring Adams Co.	0.7129	0.13
SrL-2	Yellow Springs Greene Co.	0.7094	0.16
SrL-3	St. Paris spring Champaign Co.	0.7078	0.08
SrL-4	Blue Hole spring Erie Co.	0.7082	8.37
SrD-2	Becker spring Washington Co.	0.7130	0.04
SrS-3	Sinking Springs Highland Co.	0.7129	0.07
SrSH-1	Mineral Springs Adams Co.	0.7125	0.20
Srg-5	Austinburg spring Ashtabula Co.	0.7118	0.12
SrD-1	Veto well water Washington Co.	0.7130	0.31
SrS-4	Prattsville well water Vinton Co.	0.7111	0.51
SrSh-3	Ashley well water Delaware Co.	0.7088	9.84
Srg-1	Oxford well water Butler Co.	0.7084	0.22

*Normalized to $^{88}\text{Sr}/^{86}\text{Sr}=8.375$.

TABLE 2
 Analyses of Eimer & Amend SrCO_3 Standard

Date	$^{87}\text{Sr}/^{86}\text{Sr}$
11/25/70	0.7082
12/5/70	0.7081
1/7/71	0.7085
3/8/71	0.7080

TABLE 3
Duplicate Analyses of Water Samples

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$
SrSh-1	0.7125
	0.7121
SrL-4	0.7084
	0.7080

Total Strontium Analyses

The procedure used to determine the concentrations of elemental strontium in the water samples was that described by Fishman and Downs (1966), employing atomic absorption spectrophotometry. The analyses were carried out on a Perkin-Elmer Model 303 unit. Results are presented in Table 1.

As a test of the accuracy and reproducibility of the total strontium determinations, the U.S.G.S. standard water reference sample number 26 was run with each set of water samples analyzed. The values obtained (Table 4) compare favorably with the accepted value of 0.844 mg Sr/liter, and all are within the standard deviation of 0.151 mg/liter determined by 20 independent laboratory analyses.

TABLE 4
*Total Strontium Analyses of the U.S.G.S.
Standard Water Reference
Sample Number 26*

Date	Sr (mg/l)
8/5/70	0.820
8/20/70	0.868
8/21/70	0.868
8/25/70	0.890
2/27/71	0.862

DISCUSSION OF RESULTS

The common surface lithologies in Ohio are Paleozoic carbonates, sandstones, and shales, as well as glacial till composed primarily of pulverized bedrock. General knowledge of the strontium-isotopic compositions of shales and carbonates is sufficient to permit the prediction that significant differences in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exist in these lithologies in Ohio today. Marine carbonate rocks have very low Rb/Sr ratios; therefore, their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have increased imperceptibly since deposition and reflect the strontium-isotopic composition of the ocean at the time of their deposition. For Paleozoic carbonates, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio should be in the range of from 0.7073 to 0.7090 (Peterman, *et al.*, 1970). Shales, on the other hand, consist of detrital Rb-bearing minerals, and hence should be enriched today in radiogenic ^{87}Sr . Composites of Paleozoic shales have yielded $^{87}\text{Sr}/^{86}\text{Sr}$ values of about 0.718 (Faure and Hurley, 1963). Thus the potential exists for significant differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Ohio waters.

Twenty-three $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been determined for a total of 11 surface waters, eight spring waters, and four well-water samples (Table 1). The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.7078 to 0.7130, a variability which is significant far beyond the limits of experimental error. Many of the samples contain ^{87}Sr

which is more radiogenic than that which would be contributed by leaching of marine carbonate rocks alone.

A geologic map of Ohio is shown in Figure 2. Clastic sediments are a dominant component of the Paleozoic sedimentary rocks in the east (Stout, 1947). The Pennsylvanian and Permian formations of this area are dominantly shales, with minor amounts of coal, sandstones, and conglomerates. The Mississippian

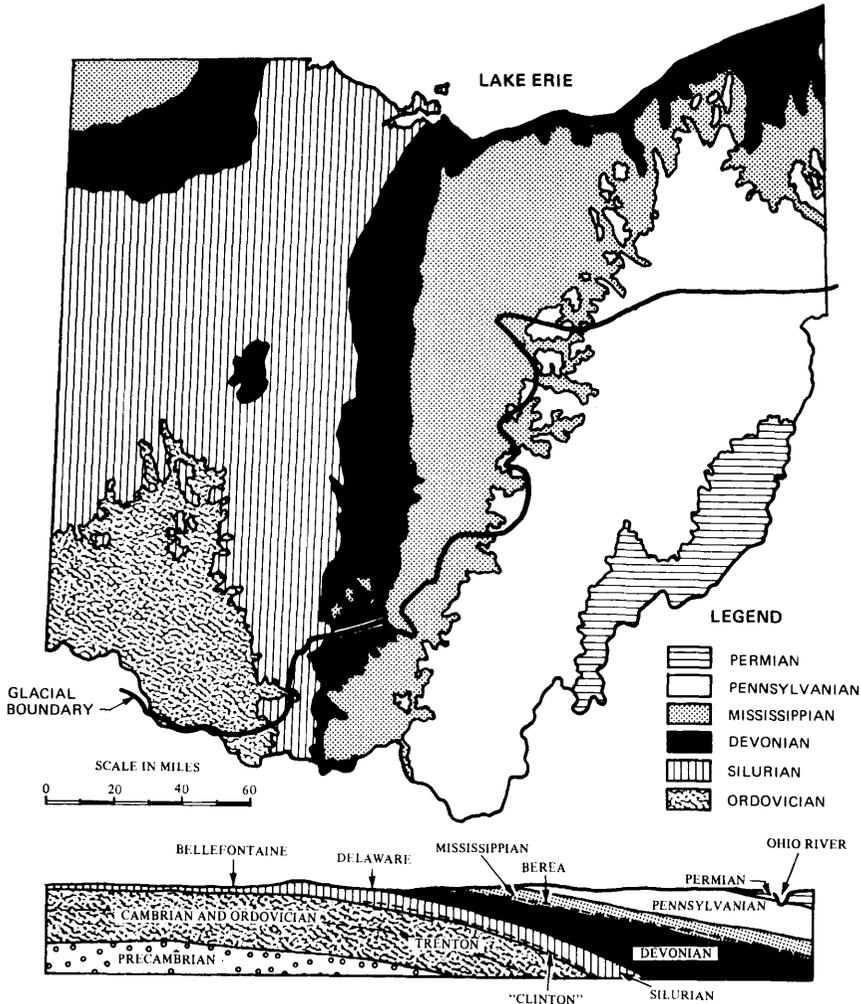


FIGURE 2. Geologic Map of Ohio.

formations are comprised of coal, sandstones, and shales. The Devonian consists of shale grading into dolostone near the base. The Silurian is nearly all carbonate material, and the Ordovician consists of calcareous shales with thin interbedded limestones (Stout, 1947).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios determined in this study and the averages of the values reported by Eastin and Faure (1970) for the Olentangy and Scioto Rivers at Columbus have been plotted on a map of Ohio (fig. 3). High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios occur in the east and south, where clastic sediments predominate, whereas low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are found in the north and west, especially where Silurian car-

bonate rocks are exposed. Relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from water samples from the eastern and southern areas are probably not as high as the $^{37}\text{Sr}/^{86}\text{Sr}$ ratios in the Paleozoic shales found in these areas, but leaching of these shales by the waters certainly must contribute significantly to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed in the waters, since these ratios are considerably higher than those which would be observed if the waters had acquired their strontium from carbonate material

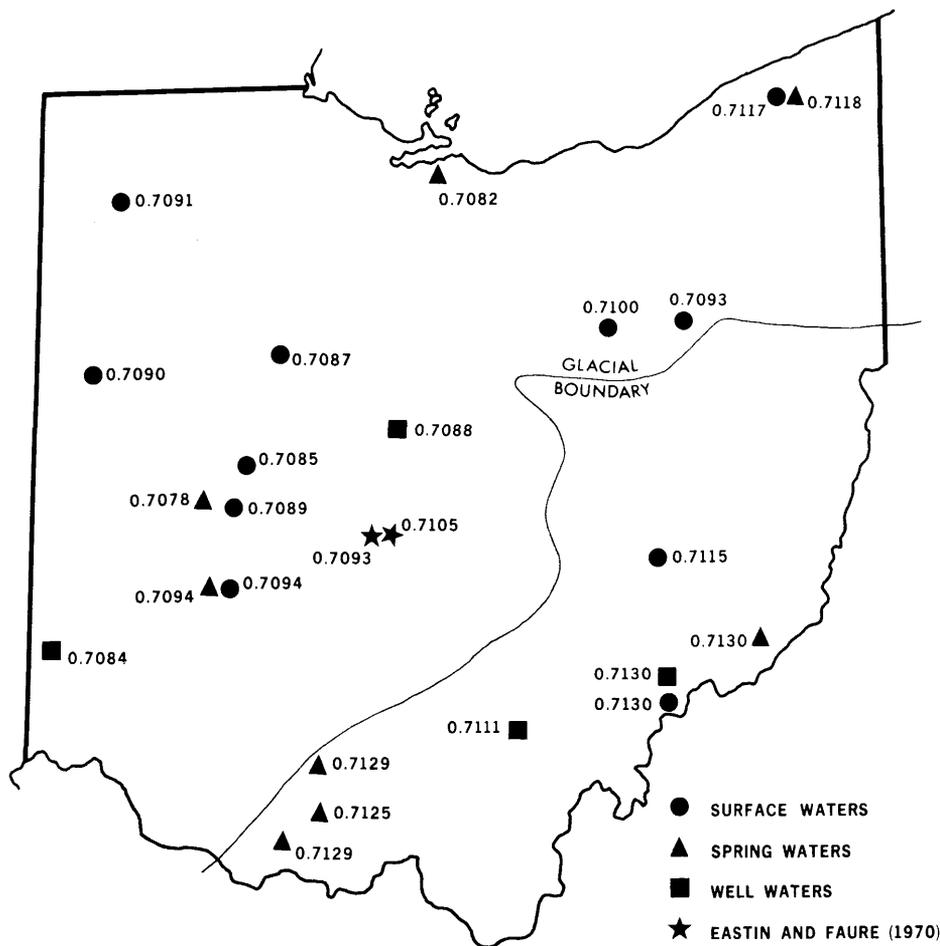


FIGURE 3. Map of Ohio showing water-sample locations, modes of occurrence, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

alone. The late Silurian rocks and glacial deposits of northwestern Ohio are known to contain important amounts of the mineral celestite (strontium sulfate), described by Feulner and Hubble (1960). Leaching of this mineral by the waters undoubtedly contributes a major portion of the strontium dissolved in the waters. The celestite is associated with limestone and with evaporite deposits of gypsum and rock salt, so that its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was probably inherited from the Paleozoic oceans and should therefore be about 0.708 (Peterman, *et al.*, 1970).

The data show a consistency in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters within limited regions in various parts of the state. In Washington County near the eastern Ohio border, water samples obtained from a stream, from a spring, and from a well all

yield $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7130 (fig. 3). Three samples of spring water from south-central Ohio have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios which are indistinguishable within the limits of experimental error. A stream-water sample and a spring-water sample from Ashtabula County in the northeast corner of the state are also in good agreement.

Though the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the waters seem to be controlled by the bedrock lithologies in the sampling areas, the presence of glacial till also seems to have an effect upon the observed values. In all but one case (Ashtabula County), relatively low ratios are found in waters from localities north of the glacial boundary where the bedrock is predominantly clastic and presumably has a significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than those observed in the waters (figs. 2 and 3). North and west of the glacial boundary, the glaciers incorporated carbonate bedrock into the till and transported it farther to the south and east. The presence of this carbonate material in the local till (overlying clastic bedrock) probably has a strong influence on the isotopic composition of the strontium dissolved in local surface and ground waters.

The weathering of more radiogenic Precambrian material in the till, presumably transported into the state from the north by the glaciers, has had no apparent effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the water samples.

SUMMARY AND CONCLUSIONS

This study demonstrates that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in surface and ground waters throughout the state of Ohio show a significant variability. The samples represent a wide geographic area and a variety of lithologies. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.7078 to 0.7130, with the higher ratios occurring in eastern and southern Ohio and the lower ratios to the north and west. We believe that this trend can be related to two controlling factors: the change in the dominant bedrock lithology from clastic sediments in the east to carbonates in the west, and the widespread occurrence of easily soluble carbonate material in the till north of the glacial boundary.

The study represents the initial phase of an attempt to use the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a tracer of stream- and ground-water provenance. We feel that the demonstrated variability of this parameter, and its apparent dependence on bedrock and overburden in the sampling areas, are sufficiently encouraging to warrant further study of the application of the overall concept.

ACKNOWLEDGMENTS

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