STRONTIUM ISOTOPE GEOCHEMISTRY OF THE SCIOTO RIVER BASIN AND THE ^{87}Sr/^{86}Sr RATIOS OF THE UNDERLYING LITHOLOGIES[1,2]

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ABSTRACT

A survey has been made of the ^{87}Sr/^{86}Sr ratios and the rubidium and strontium concentrations in the different types of geologic materials underlying the Scioto River drainage basin in central Ohio. In the part of the basin north of the limit of maximum glaciation, these lithologies are mostly Paleozoic carbonate rocks and glacial deposits, as well as the soils that have developed on them. These materials have fairly low ^{87}Sr/^{86}Sr ratios of 0.708–0.715. South of the glacial limit, shales are abundant. These shales and the soils developed on them have much more radiogenic ratios of 0.703–0.745. Leaches of the shales and related soils, however, have ratios of only about 0.710–0.713. These data are in full accord with earlier published data and interpretations of the isotope geochemistry of strontium in the Scioto basin.

INTRODUCTION

Of the four stable isotopes of strontium, only ^{87}Sr is a radiogenic isotope produced by the radioactive decay of another isotope, ^{87}Rb. It follows that the abundance of ^{87}Sr in any geological material varies according to the Rb/Sr ratio and the age of that material. The abundance of ^{87}Sr is conveniently expressed as the isotopic ratio ^{87}Sr/^{86}Sr, and in nature, variations of 10 percent or more have been found in this ratio among different geological materials. Faure and Powell (1972) have recently reviewed the field of strontium isotope geochemistry.

Although most studies involving strontium isotopic ratios thus far have been concerned with the origin and genetic relations of igneous and metamorphic rocks, some recent studies have focused on the ^{87}Sr/^{86}Sr ratios in surface waters. Attempts have been made to correlate this ratio in the waters with provenance. Rocks of different chemistries and ages release strontium into surface waters by chemical weathering. The strontium released by different types of rock provides different ^{87}Sr/^{86}Sr ratios, so that determination of this ratio in a water sample should indicate the types of rock that water has traversed.

In Ohio, Eastin and Faure (1970) show that the Scioto and Olentangy Rivers have slightly different ^{87}Sr/^{86}Sr ratios and explain those differences both by the different lithologies in the two drainage basins and by different rates of discharge. Stueber, Pushkar, and Baldwin (1972) have analyzed surface and groundwater samples collected throughout Ohio and report a range of values of from 0.708 to 0.713. A striking correlation of those ratios with the local lithologies is evident; waters collected from areas underlain by Paleozoic carbonate rocks or by glacial overburden (which is composed largely of pulverized carbonate rocks in most areas) have ratios close to 0.708. Waters collected from areas south of the glacial boundary and underlain by clastic rocks have higher ratios. It is well established that sedimentary carbonate rocks of Paleozoic age have ^{87}Sr/^{86}Sr ratios close to 0.708 (Peterman, Hedge, and Tourtelot, 1970), so that a correlation between ^{87}Sr/^{86}Sr ratios in waters and in the local bedrock material has been shown.

The most recent study of ^{87}Sr/^{86}Sr ratios in waters is that of Curtis and Stueber (1973). In this study, 23 samples of water collected from the Scioto River and its

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Lithology Samples   Water Samples
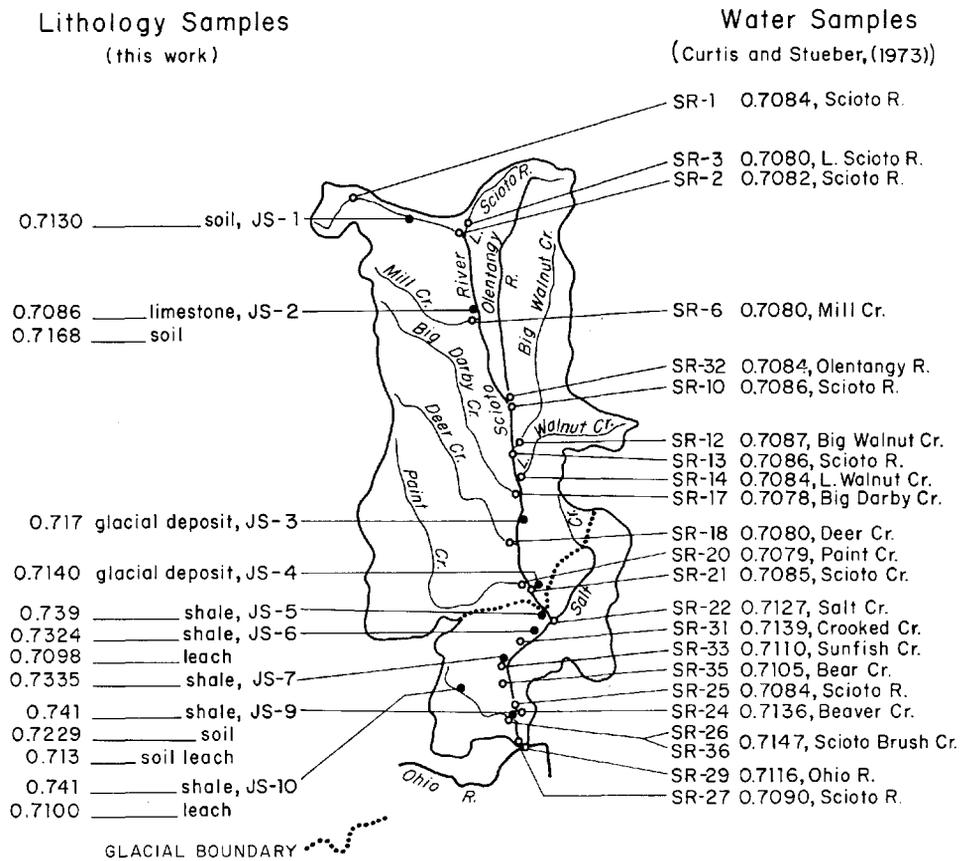   (this work)   (Curtis and Stueber, (1973))

FIGURE 1. Locations and ^{87}Sr/^{86}Sr ratios for rock, soil, till, and water samples.

tributaries in Ohio have been analyzed. Their data are included here in figure 1. Curtis and Stueber draw the following conclusions from their data:

1. The ^{87}Sr/^{86}Sr value of about 0.7084 that persists throughout the Scioto River is caused by the large amounts of strontium leached by the river in its upper parts. This portion of the drainage area is underlain by Paleozoic carbonate bedrocks and glacial till. Curtis and Stueber argue that Paleozoic carbonates are known to have ^{87}Sr/^{86}Sr ratios close to 0.708 and, because of their relatively high solubility, can supply large amounts of strontium to the river. In addition, the glacial till covering the surface of this area contains large amounts of pulverized carbonate and celestite, both of which are also readily soluble and both of which would also supply strontium with ^{87}Sr/^{86}Sr ratios close to 0.708. The downstream portion of the Scioto River basin is underlain by unglaciated Mississippian and Devonian shales, which may be expected to have significantly higher ratios, but any strontium from this source which enters the river is diluted beyond detection. This conclusion is supported by the measured concentrations of strontium in the water; the concentrations are very high in areas underlain by carbonate bedrock or till, but are less where the river flows on clastic rocks outside the glacial boundary.

2. The glacial boundary is a critical factor in determining the $^{87}Sr/^{86}Sr$ ratios of stream waters, as shown by the analyses of water from the tributaries of the Scioto River. Samples from those tributaries north of the boundary all have ratios close to 0.708. The tributaries south of the boundary have higher ratios.

The present study was conducted to complement the study of Curtis and Stueber. Samples of geologic material, both bedrock and glacial, underlying the Scioto River were analyzed so that their $^{87}Sr/^{86}Sr$ ratios could be compared with the ratios determined for the river water. In addition, leaches of several samples were made to determine $^{87}Sr/^{86}Sr$ ratios of the soluble strontium in these materials, so that these could also be compared.

ANALYTICAL PROCEDURES

A total of 11 samples was collected for this study (table 1). All samples were analyzed for $^{87}Sr/^{86}Sr$ ratios by mass spectrometry and for Rb and Sr concentra-

TABLE 1

Descriptions of Locations from which rock, glacial, and soil samples were taken

Sample no.	Description and location
JS–1	Soil on outwash, 2 mi W of Hepburn, Hardin Co.
JS–2	Dolomitic limestone, near Ohio 257, 6 mi SW of Delaware, Delaware Co.
JS–2A	Soil on outwash, same location as JS–2, along W bank of Scioto River
JS–3	Alluvium, near U.S. 23, 6 mi SW of Circleville, Pickaway Co.
JS–4	Outwash, near U.S. 35, 6 mi SE of Chillicothe, Ross Co.
JS–5	Shale, 1 mi N of Higby, Ross Co.
JS–6	Shale, near Ohio 335, Omega, Pike Co.
JS–6L	Experimental water leach of sample JS–6
JS–7	Shale, near Ohio 104, 0.25 mi S of Jasper, Pike Co.
JS–9	Shale, near Ohio 104, Rushtown, Scioto Co.
JS–9A	Soil, same location as JS–9
JS–9AL	Experimental water leach of sample JS–9A
JS–10	Shale, near Ohio 73, 6 mi E of Beaverport, Adams Co.
JS–10L	Experimental water leach of sample JS–10

tions by X-ray fluorescence. Included are at least one sample of each of the major lithologies in the Scioto basin: carbonate bedrock, shale bedrock, glacial till and outwash, and related soils. The sample localities are shown in figure 1.

One-half-gram representative fractions of the samples were digested in hydrofluoric acid in teflon beakers and converted to chlorides by repeat evaporations with hydrochloric acid. Strontium was separated by cation-exchange chromatography using 2N HCl and Bio-rad AG 50W–X8 resin. Samples (such as the shales) with high Rb/Sr ratios were leached with perchloric acid before conversion to chlorides and separation of strontium.

Leaching of samples was done by crushing approximately 200 g of sample material to approximately 100 mesh and putting this in polyethylene bottles containing approximately 5 liters of triple-distilled water. The bottles were then shaken in a Ro-Tap for periods of 30 to 49 hours, after which the water was filtered and passed through the cation-exchange columns as described by Stueber *et al.* (1972).

Mass spectrometry was carried out on two instruments: a 12-inch 90°-sector Nuclide Corporation mass spectrometer at Miami University, Oxford, Ohio, and a 6-inch 60°-sector instrument built and located in the Laboratory of Isotope Geochemistry at the University of Arizona in Tucson. Multiple rhenium filaments and expanded-scale recorders were used with both instruments.

Detailed descriptions of all the above procedures are given by Steele (1973). The X-ray-fluorescence analyses were done at the University of Arizona, using the technique described by Livingston and Fenton (1970).

RESULTS

The data obtained are presented in Table 2. As is the usual procedure, the analyzed ratios have been normalized to a $^{88}Sr/^{86}Sr$ ratio of 8.375. Analysis of the Eimer and Amend $SrCO_3$ interlaboratory standard gives $^{87}Sr/^{86}Sr$ ratios of 0.7079 for the Miami University instrument and 0.7080 for the University of

TABLE 2

Analyses of Scioto River basin samples

Sample	Total Rb ($\mu g/g$)	Total Sr ($\mu g/g$)	Rb/Sr	$^{87}Sr/^{86}Sr$*	S.D.
		Shale			
JS–5	57.9±0.8	37.5±0.3	1.72	0.739	0.001
JS–6	53.7±0.8	48.3±0.3	1.11	0.7324	0.0001
JS–7	24.3±0.3	26.3±0.2	0.93	0.7335	0.0004
JS–9	85.6±2.2	44.4±0.4	1.93	0.745	0.003
JS–10	120.5±1.4	76.4±0.4	1.59	0.741	0.001
		Limestone			
JS–2	———	95.5±0.8	———	0.7086	0.0006
		Glacial deposits			
JS–3	36.9±1.0	132.5±1.3	0.28	0.717	0.002
JS–4	37.5±1.0	159.5±1.5	0.24	0.7140	0.0009
		Soil above glacial boundary			
JS–1	84.9±3.6	285.0±0.8	0.30	0.7130	0.0005
JS–2A	69.0±2.0	131.8±0.7	0.52	0.7168	0.0005
		Soils below glacial boundary			
JS–9A	111.6±4.7	92.0±0.3	1.21	0.7299	0.0003
		Leaches of shale			
JS–6L	———	———	——	0.7098	0.0010
JS–10L	———	———	——	0.7100	0.0001
		Leach of soil below glacial boundary			
JS–9AL	———	———	——	0.713	0.001

*Normalized to $Sr^{88}/^{86}Sr = 8.375$. Ratios corrected to a value of 0.7080 for the Eimer and Amend $SrCO_3$ standard.

Arizona instrument. The normally accepted value for this standard is 0.7080. A blank determination yielded a negligible contamination level of 0.10 μg of strontium per analysis.

Most analyses of $^{87}Sr^{86}Sr$ ratios made today are reported to four significant figures. Several of the analyses in this study, however, are of poor quality and warrant only three significant figures. Limited access to the mass spectrometers prevented these analyses from being repeated.

DISCUSSION

Four main types of geologic materials were analyzed in this study: carbonate bedrock, shaly bedrock, glacial till and outwash, and soils. These four types include all the major lithologies in the Scioto Basin. Collecting sites of all the samples are shown in figure 1.

Peterman *et al.* have shown that the $^{87}Sr/^{86}Sr$ ratios for limestones of Ordovician to Mississippian ages are characterized by values close to 0.7078. The

carbonate sample analyzed in this study is a dolomitic limestone from the Devonian Columbus formation. Because of the very narrow range of $^{87}Sr/^{86}Sr$ ratios that have previously been found in carbonate rocks, only one sample was analyzed. The $^{87}Sr/^{86}Sr$ ratio measured was 0.7086, slightly higher than the value to be expected from the work of Peterman *et al.* (1970). This ratio is identical to the $^{87}Sr/^{86}Sr$ ratio found in the Scioto River water by Curtis and Stueber (1973). Concentrations of strontium as high as 8 mg/l have been reported by Curtis and Stueber for the upper part of the Scioto Basin where it is underlain by carbonate materials, so that large amounts of strontium with this ratio are evidently entering the river here.

The five samples of shale that were analyzed represent Mississippian and Devonian formations underlying the river basin south of the glacial boundary. Because shales have high Rb/Sr ratios, there is appreciable internal production of ^{87}Sr during their existence, and their $^{87}Sr/^{86}Sr$ ratios can reach high values. The ratios determined for the five shales analyzed are in the range 0.7324 to 0.7450 and are much higher than the ratios in the Scioto River water. However the strontium content of the shales is less than that of the carbonate rocks, and the silicate minerals in the shales themselves are much less soluble. Therefore any contribution to the river from these rocks seems to be completely masked by the large amounts of strontium derived from farther upstream. This is in full agreement with the conclusion of Curtis and Stueber (1973), that the $^{87}Sr/^{86}Sr$ ratio of the Scioto River is fixed by the upstream celestite and carbonate material and unaffected by the shales in the downstream part of the basin.

The $^{87}Sr/^{86}Sr$ ratios measured in the shales, however, are much higher even than the ratios from the tributaries that lie entirely below the glacial boundary and which contain very little carbonate material in their watershed. Such streams have $^{87}Sr/^{86}Sr$ ratios of 0.710 to 0.715 (fig. 1). Insight into this relationship is provided by the experimental leaching of two shale samples. Sample JS–6, having a $^{87}Sr/^{86}Sr$ ratio of 0.7324, yielded a leach with a ratio of 0.7098. Sample JS–10, with a ratio of 0.742, yielded a leach with a ratio of 0.7100.

It appears that there is a component in the shale that contains a $^{87}Sr/^{86}Sr$ ratio much lower than that for the shale as a whole and that this component contributes strontium to the leach much more readily than does the rest of the shale. Leaching experiments have also been conducted on shales by Bofinger, Compston, and Vernon (1968) and on granite by Dasch (1969). They have found that the soluble strontium has a lower $^{87}Sr/^{86}Sr$ ratio than does the total strontium in the original rock. In the present study the shales that were analyzed are quite limy and the easily leached component of the shale is most likely calcite ($CaCO_3$). The ratios analyzed in the leach are somewhat less than are those reported by Curtis and Stueber (1973) for the tributaries below the glacial boundary, although they are much closer to those values than are the ratios in the shales. It might be that as shales undergo progressive leaching they lose more and more of the easily leached calcite and release proportionately more and more strontium from silicate phases with high $^{87}Sr/^{86}Sr$ ratios.

The strontium in the southern tributaries with ratios up to 0.715 perhaps may be explained in this way. It would have been of interest to make and analyze successive leaches of a single shale sample, but time did not permit this. Another possibility is that rainwater may have been appreciably more acid through dissolution of atmospheric carbon dioxide and therefore may have been able to leach out more of the silicate strontium with high $^{87}Sr/^{86}Sr$ ratios than was the distilled water used in the experimental leaches.

Two samples of glacial material were analyzed. Both samples have $^{87}Sr/^{86}Sr$ ratios of approximately 0.715. By their nature, glacial deposits can be expected to have been transported, so that a variety of materials from different areas would become mixed. The major part of such deposits would probably be derived from the local Paleozoic carbonate bedrock, because this was the nearest and most

abundant material, but at least some of the till could have been derived from bedrock with high $^{87}Sr/^{86}Sr$ ratios. This rock could have been either local shales or other detrital rocks or even Precambrian gneisses and schists derived from Canada. The $^{87}Sr/^{86}Sr$ ratio of the deposits would have been controlled by the greater abundance of the carbonate materials and the generally higher concentrations of strontium in carbonates than in most silicate materials. Isotopic ratios close to 0.715 seem reasonable in view of these considerations.

Celestite ($SrSO_4$) has been reported in some of the glacial tills of the Scioto Basin (Feulner and Hubble, 1960), although it does not appear to have been present in any of the samples analyzed in this study. This material was presumably derived from Paleozoic deposits of celestite in northern Ohio. Because celestite, like carbonates, is derived from seawater, it would also have a $^{87}Sr/^{86}Sr$ ratio of about 0.708. However, because strontium is an essential constituent in celestite, rather than an impurity as in calcite, celestite-bearing tills would be expected to have very high concentrations of strontium characterized by $^{87}Sr/^{86}Sr$ ratios close to 0.708. Such tills would be very important in controlling the $^{87}Sr/^{86}Sr$ ratio of the Scioto River, as was noted by Curtis and Stueber (1973).

Three samples of soil were analyzed in this study. Two samples were collected above the glacial boundary; one of these samples came from the same site as the carbonate sample described earlier. Both soils have $^{87}Sr/^{86}Sr$ ratios close to 0.715, the same value as was obtained from the glacial till and outwash. This value is consistent with the formation of the soil from glacial till deposited over carbonate bedrock.

The $^{87}Sr/^{86}Sr$ ratios of about 0.715 for the glacial deposits and soils seem to have little effect on the ratio found in the Scioto River water. These ratios are only slightly higher than that of the river water, whereas the difference between the ratios for shale occurring below the glacial boundary and that of the river water is very large.

The third soil sample to be analyzed was collected below the glacial boundary and from the same site as one of the shale samples. The $^{87}Sr/^{86}Sr$ ratio of the soil is 0.7299, a value that approaches the ratios in some of the analyzed shales. However, that ratio is markedly lower than the ratio of 0.7450 obtained in the shale sample, which came from approximately 100 yards away and 10 feet higher stratigraphically; this shale is believed to be essentially the same as the bedrock underlying the soil.

Two observations may be made concerning this ratio from the soil. The glacial boundary may have the same effect on $^{87}Sr/^{86}Sr$ ratios in soils as it does in river waters: soils with high $^{87}Sr/^{86}Sr$ ratios are restricted to areas underlain by shales lying south of the glacial boundary. Many of the soils to the north of this boundary are developed from tills and, at least in the Scioto drainage basin, inherit the carbonate-dominated $^{87}Sr/^{86}Sr$ ratio from them. The second observation is that the genetic relationship between the soil and the underlying shale does not appear to be a simple one. If the soil developed from the shale by chemical weathering, the work of Dasch (1969) and of Bofinger et al. (1968) would suggest that the soil should contain the residual nonleachable strontium from the shale and should therefore have a higher $^{87}Sr/^{86}Sr$ ratio than does the shale. If the soil developed from the shale without any mineralogically controlled fractionation, the ratios in the soil and the shale should be identical. Because the soil has a lower ratio than the shale in this case, neither of these explanations can be valid. In addition, the effect of the high $^{87}Sr/^{86}Sr$ ratio in this soil on the $^{87}Sr/^{86}Sr$ ratio of the river is essentially the same as the effect of the shale, as shown by leaching experiments—both release into the river soluble strontium with a $^{87}Sr/^{86}Sr$ ratio of about 0.71.

The relationship between the $^{87}Sr/^{86}Sr$ ratios and the strontium concentrations in waters of the different parts of the Scioto River basin and in the underlying lithologies has been plotted graphically (figs. 2 and 3). In these figures, the $^{87}Sr/$

[86]Sr ratios and concentrations of strontium for several tributaries of the Scioto River have been plotted against a factor, called the lithologic factor, derived from the measured extents of the exposed and subsurface geologic materials in the drainage area of each tributary. The areas underlain by each of the three kinds of geologic materials—carbonates, glacial till, and shales—were measured with a
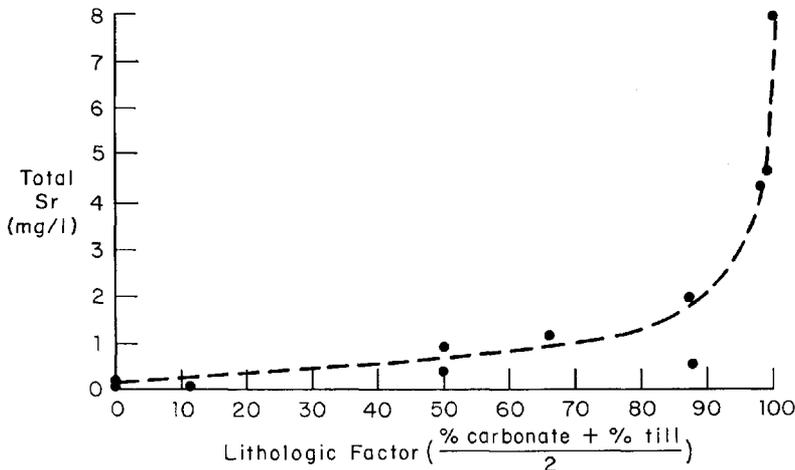

FIGURE 2. Lithologic effects on total Sr of stream water.

planimeter for each tributary. These three areas were first calculated as percentages and then the sum of the carbonate and glacial-till percentages was divided by two. A value of zero for this parameter indicates that the area is underlain entirely by shale with no glacial cover; a value of 100 indicates that the area is underlain entirely by till and/or carbonates.

As is evident from the figures (figs. 2 and 3), strontium concentrations increase and $^{87}Sr/^{86}Sr$ ratios decrease as the lithologic parameter increases. This entirely supports the conclusion of Curtis and Stueber (1973) that the carbonate-rich rocks in the upper part of the Scioto River release large quantities of strontium with low $^{87}Sr/^{86}Sr$ ratios. These large quantities of strontium completely mask the influx of strontium with higher $^{87}Sr/^{86}Sr$ ratios that occurs in the lower part
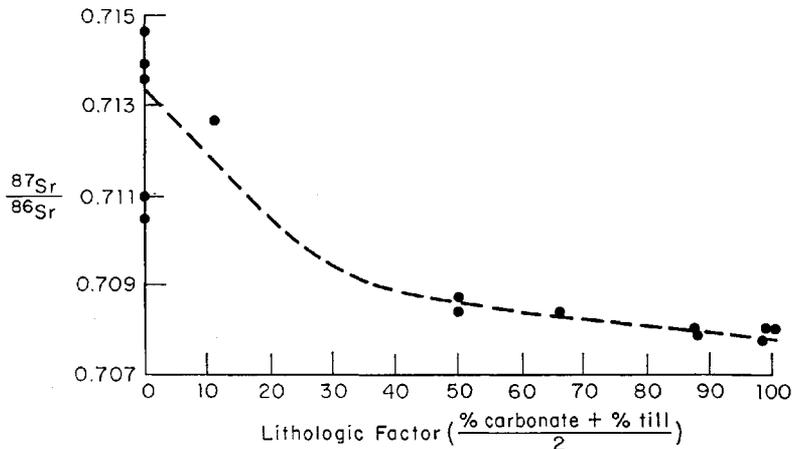

FIGURE 3. Lithologic effects on $^{87}Sr/^{86}Sr$ ratios of stream water.

of the river, below the glacial boundary. The $^{87}Sr/^{86}Sr$ ratio throughout the river is thus dominated by the strontium which enters it in its upper parts.

CONCLUSION

The following four conclusions can be drawn from this study.

1. Strontium-bearing carbonate minerals in the bedrock, glacial deposits (till and outwash), and soil underlying the northern part of the Scioto River basin have essentially the same $^{87}Sr/^{86}Sr$ ratio as does the Scioto River. The occurrences of celestite in the till reported by Feulner and Hubble (1960) very likely have the same ratio. Therefore they appear to be major sources of the strontium in the river, as was indicated by Curtis and Stueber (1973).

2. The shales and soil underlying the river basin to the south of the glacial boundary have very high $^{87}Sr/^{86}Sr$ ratios, but these ratios do not affect the ratio in the Scioto River because of the overwhelming amount of carbonate strontium contributed to the river from the carbonate materials in the upper parts of the basin.

3. The $^{87}Sr/^{86}Sr$ ratios in the shales and soils south of the glacial boundary are much higher than in the waters of tributaries draining such materials below the glacial boundary. However, leaching experiments show that the soluble strontium released by these materials has $^{87}Sr/^{86}Sr$ ratios that are only slightly different from the ratios in these tributaries.

4. Soils and glacial deposits above the glacial boundary have $^{87}Sr/^{86}Sr$ ratios somewhat higher than those of the carbonate bedrock. However, this does not appear to be sufficient to raise the $^{87}Sr/^{86}Sr$ ratios in the local streams above the normal carbonate values.

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