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Variations of $^{87}Sr/^{86}Sr$ in Water from Streams Discharging into the Bothnian Bay, Baltic Sea

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The $^{87}Sr/^{86}Sr$ ratio in 53 water samples were analysed, 26 from streams in Sweden, 22 from streams in Finland and 5 from the Bothnian Bay itself. The brackish seawater of the bay had the isotope ratio 0.7095, while the stream-water samples varied from 0.7177 to 0.7366. The weighted average isotope ratio with respect to discharges was 0.7313, this high ratio reflecting the dominance of granitic Proterozoic rocks in the region.

For streams with an average discharge between 1-40 m^3/s the isotope ratio was within the interval 0.718-0.736, while those with discharges >150 m^3/s defined an interval of 0.728-0.735. The variations in isotope ratios are discussed with respect to bedrock geology of drainage basins, possible effects of seawater inundations and Postglacial uplift combined with the complex history of the Baltic Sea.

Introduction

The global geochemical cycle of strontium has often been studied with the help of the isotope ratio $^{87}Sr/^{86}Sr$, because the amount ^{87}Sr increases slowly due to the natural beta decay of ^{87}Rb (see for example Wadleigh *et al.* 1985), However, this ratio should also be a valuable tool in studies of many exogenic processes (Wickman and Åberg 1987, Åberg and Jacks 1985, Graustein and Armstrong 1983, Faure 1977) because of the great difference between the ratios of rainwater (0.709-0.710) and old granitic rocks (0.720 and greater). The aim of this study is to contribute background data for detailed studies of exogenic processes by studying the isotope ratio in stream waters of a restricted region. We selected the streams discharging into the Bothnian Bay, Baltic Sea.

The Bothnian Bay (Fig. 1), with an areal extent of 37,000 km^2, defines the northern end of the Baltic Sea and its drainage area covers most of the northern parts of Finland and Sweden (about 3-4$\times 10^5$km^2). The rocks of this region are dominated by Proterozoic bedrock (2.5-0.6 $\times$ 10^9 years) of more or less granitic composition. In Finland Archean ($>$2.5 $\times$ 10^9 years) rocks are also fairly important. Along the Swedish border towards Norway, within a zone 200-300 km from the coast, Ca-rich Caledonian rocks become dominant.

Sampling and Laboratory Techniques

The pre-sampling cleaning of the bottles, the sampling technique, the laboratory treatment of the samples and the mass spectrometric measurements are described in Wickman and Åberg (1987). Most of the samples were collected in September 1983 by one of us (F.E.W.) and consist of 25 samples from Sweden and 17 samples from Finland. An additional sample was taken in June 1985.

Dr. R. Löfvendahl has kindly supplied five additional water samples from Finland collected during August 1985 by him and Dr. P. W. Lahermo and five seawater samples from two stations in the Bothnian Bay collected in June 1983 during a cruise with R/V Strombus. His samples were handled like ours.

All sample localities are marked on the map in Fig. 1 and described in an Appendix that can be obtained from G. Åberg.

Results and Discussion

Results

All results of ^{87}Sr/^{86}Sr measurements are presented in Table 1 together with the date of collection and the discharge rate of the stream where applicable. The discharge values are averages of several decades, and have been supplied for Finland by Vesihallitus (National Board of Waters), Helsinki and for Sweden by Sveriges Meteorologiska och Hydrologiska Institut (Swedish Meteorological and Hydrological Institute), Norrköping. The isotope ratios were measured to five significant figures, but only four figures are used in the text. The values are therefore reproducible within ±0.0001 units.

The seawater values are constant within the limits of error and yield a value of 0.7095 which is slightly higher than the value for marine water, 0.7091. The difference probably reflects the effect of seawater mixing with stream water. Disregard-

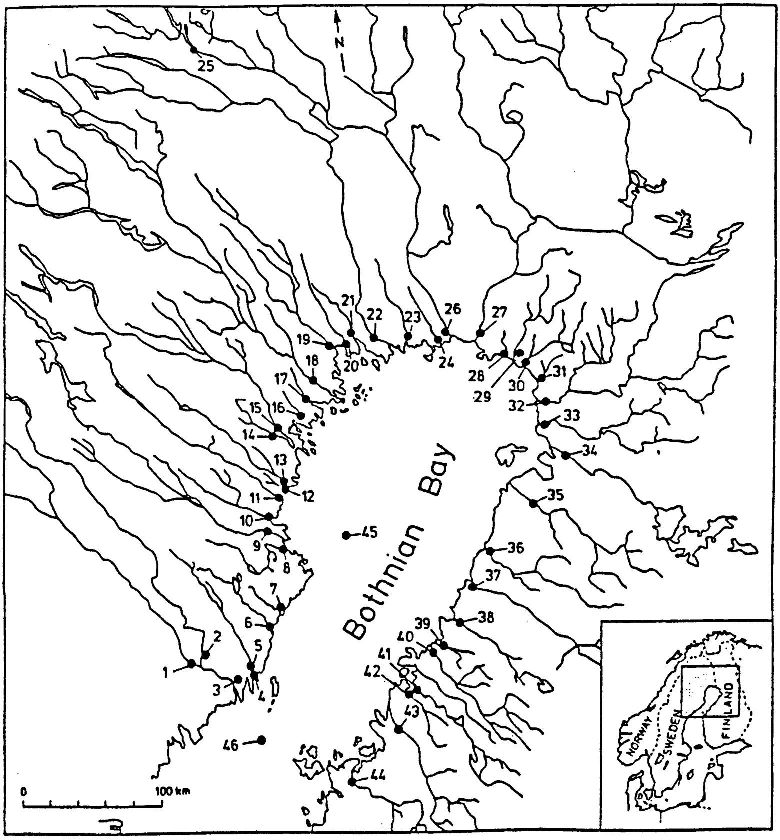

Fig. 1. Map of the Bothnian Bay area, northern Scandinavia, with sample locations indicated (see Table 1).

ing sample No. 4 which will be discussed below, the samples varied over an interval of 0.7177-0.7366, which is similar to that found for waters in the Bergslagen-Stockholm region, eastern Central Sweden (Wickman and Åberg 1987).

Bedrock and Mixing Effects

Contrasting rock compositions in river basins, especially when combined with large age differences, result in greatly differing isotope ratios for river waters. The study by Wadleigh et al.(1985) discussed the strontium isotope ratios of water from 39 major Canadian rivers with discharge rates similar to or larger than our largest streams. They primarily studied the global aspects of strontium geochemistry, especially the balance of Sr in the sea.

Two histograms in Fig. 2 show the distribution of isotope ratios. The Canadian rivers have drained an area with great variations in rock types and ages, which

Table 1 –Samples, sampling dates, discharge rates and Sr isotope ratios of streams discharging into the Bothnian Bay, Baltic Sea. * indicates estimated discharge rate. E4 is European road No.4; 8 and other numbers refer to the Finnish national road system. Translations: å,ån=brook or river, älv,älven=river, joki=river, L=Löfvendahl samples.

No	Stream Name, locality	Discharge m^3/s	Sampling Date	$\frac{^{87}Sr}{^{86}Sr}$
1	Umeälven, above junction with (2)	242	10.9.83	0.72371
2	Vindelälven, above junction with (1)	181	10.9.83	0.73664
3	Umeälven, Gimonäs	423	16.9.83	0.72822
4	Sävarån, Skeppsvik	12	11.9.83	0.71273
5	Sävarån, E4	12	24.6.85	0.73624
6	Rickeleån, Rickleby	18	11.9.83	0.73389
7	Flarkån, Hertsånger	5.5*	11.9.83	0.72406
8	Bureälven, E4	11*	11.9.83	0.73072
9	Skellefteälven, E4	158	11.9.83	0.73189
10	Kågeälven, Kåge	9.3	11.9.83	0.72089
11	Byskeälven, Byske	40	11.9.83	0.73467
12	Tåmeälven, E4	1.2*	11.9.83	0.72343
13	Åbyälven, E4	15*	11.9.83	0.73584
14	Lillpiteälven, Sjulnäs	6.3*	12.9.83	0.73173
15	Piteälven, Bölebyn	164	12.9.83	0.73344
16	Rosån, E4	2.0*	12.9.83	0.72056
17	Aleån, E4	6.*	12.9.83	0.72486
18	Luleälven, S. Sunderbyn	508	12.9.83	0.73416
19	Råneälven, Råneå	44	12.9.83	0.73064
20	Vitån, Jämthög	5.2*	12.9.83	0.72421
21	Töreälven, E4	4.4*	12.9.83	0.73404
22	Kalixälven, Månsbyn	286	12.9.83	0.73289
23	Sangisälven, E4	14	13.9.83	0.73511
24	Keräsjoki, E4	4.2*	13.9.83	0.72573
25	Torneälven, Jukkasjärvi	102	5.8.83	0.72396
26	Torneälven, Haparanda	371	13.9.83	0.72931
27	Kemijoki	538	14.9.83	0.73249
27L	Kemijoki	538	3.8.85	0.73429
28	Viantienjoki, E4	1.5	14.9.83	0.72380
29	Simojoki, Jokipää	38	14.9.83	0.73091
30	Kuivajoki, E4	16	14.9.83	0.72522
31	Olhavanjoki, E4	3.2	14.9.83	0.72380
32	Iijoki, water power station	173	14.9.83	0.73047
33	Kiiminjoki, at church	42	14.9.83	0.72806
34	Oulujoki, Madekoski	254	14.9.83	0.73261
34L	Oulujoki, Oulu	254	3.8.85	0.73352

cont.

Table 1 – cont.

No	Stream Name, locality		Discharge m^3/s	Sampling Date	$\frac{^{87}Sr}{^{86}Sr}$
35	Siikajoki, 8		40	14.9.83	0.72537
36	Pyhäjoki, 8		30	14.9.83	0.71772
36L	Pyhäjoki		30	2.8.85	0.72226
37	Kalajoki, 8		27	14.9.83	0.72958
38	Lestijoki, Himanka		11.4	15.9.83	0.72710
39	Kälvianjoki		2.1	15.9.83	0.72500
40	Perho å, 8		19.4	15.9.83	0.72962
41	Esse å, 8		13.2	15.9.83	0.72883
41L	Esse å		13.2	2.8.83	0.73056
42	Purmo å, 8		6.9	15.9.83	0.72744
43	Lappo å, 8		32	15.9.83	0.72914
44L	Kyrönjoki, 7174		46	1.8.85	0.72924
45L	83-19,	3 m	–	16.6.83	0.70935
	$64^0\ 42^1$ N $22^0\ 09^1$ E	50 m	–	16.6.83	0.70951
		80 m	–	16.6.83	0.70947
		100 m	–	16.6.83	0.70948
46L	STA 83-53,	5 m	–	19.6.83	0.70951
	$63^0\ 30^1$ N $20^0\ 38^1$ E	35 m	–	19.6.83	0.70938

explains the large spread of their values. The values define three main groups. One with isotope ratios around 0.705 from the young basalt province on the Canadian west coast. The second group has ratios that range from about the rain-seawater value, 0.709 up to about 0.720, and correspond to drainage areas where many kinds of rocks like granitoids, limestones etc. are mixed. The third group contains waters with ratios from about 0.725 to 0.740 and these rivers come from old, Proterozoic-Archean granitic areas around Hudson Bay.

Even though we cannot draw a direct parallel between our study and that of Wadleigh et al.(1985) because areas with young basaltic composition are lacking in the Baltic Shield, the river Umeälven (Table 1, Nos. 1-3) and its main tributary Vindelälven, for example illustrate the considerable differences that can exist in the same river system. Just above their junction the two rivers have the ratios 0.7237 and 0.7366, respectively. The reason for this difference is not obvious from the bedrock geology of their drainage areas. An explanation therefore has to await a careful sampling study of the whole drainage system.

The value below their junction is 0.7282, that is surprisingly close to simple mixing of the two river waters, 0.7292, assuming the same Sr-concentration. The listed discharge values are probably the major source of error, because the mean

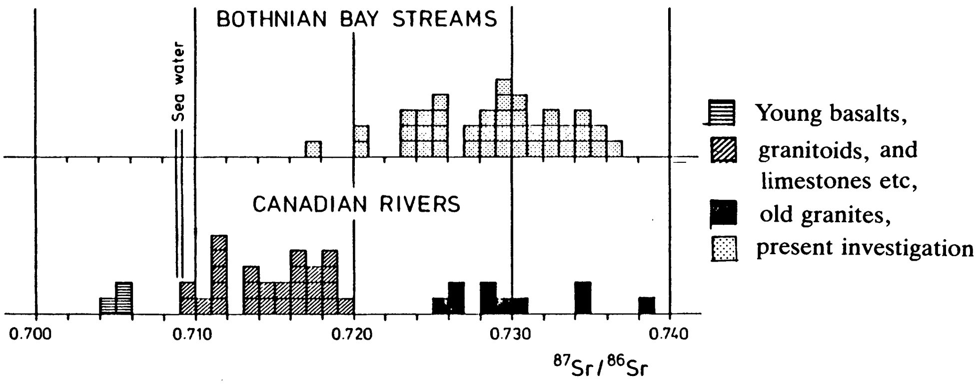

Fig. 2. Histogram compiling the results of Wadleigh *et al.* (1985).

values may differ considerably from the actual values at the time of sampling.

A similar difference exists between two samples (Nos. 25 and 26) from the river Torneälven. This river has several important tributaries joining downstream the sample locality at Jukkasjärvi. The upstream value is in this case lower than the value of the sample taken not far from the river's mouth, 0.7240 and 0.7293, respectively. These data suggest that one or several of the downstream tributaries must have ratios over 0.7300.

Inundation and the Boundary Zone between Stream Water and Seawater.

Almost all samples were taken near river mouths. Tide effects are negligible in the Bothanian Bay, however storms and periods of persistent wind direction temporarily change the sea level. Normal variations are less than a few decimeters, but exceptional values of more than one meter have been observed. Since the Bothnian Bay is partly encircled by a coastal plain, it is sometimes difficult to predict the size of the effects of brackish seawater inundation on a stream bed. The isotope ratio of river water is very sensitive to contamination by bay water because the Sr concentration in brackish water is much higher than in river water.

We were therefore careful to avoid sampling too close to the river mouth, but at the same time wanted samples taken sufficiently close that the water should represent water discharged into the Bothnian Bay. Sample No. 4, for example illustrates the difficulties in applying these principles. It was taken at a site where small pleasure-boats from the local archipelago are kept. The Sr ratio for this sample, 0.7127, is close to the Bothnian Bay water values, 0.7095, and suggests that the sampling locale was unsuitable. A new sample (No. 5) collected a few kilometers upstream gave the value 0.7362.

The Cases of Repeated Sampling

A comparison between our and Löfvendahl's samples shows that his samples con-

Table 2 –Differences between the isotope ratios in the samples collected by Löfvendahl (all higher) and ours. Positive distance value indicates that our sample was taken upstream of those of Löfvendahl.

River	Isotope ratio difference	Distance (km)
Kemijoki	0.0018	4
Oulukoki	0.0010	9
Pyhäjoki	0.0046	0
Esse å	0.0018	–1

sistently give higher values than ours. R. Löfvendahl and P. W. Lahermo were particularly careful to sample at locations where no inundation effects could have occurred. Table 2 furthermore demonstrates that such effects cannot be responsible for the differences because there is no relationship between isotope ratio and the upstream sample.

A possible clarification for these differences comes from our study in Bergslagen (Wickman and Åberg 1987) which indicated differences in the Sr isotopic ratio of the order of magnitude observed here. These differences depend on variations in the climatic conditions, that is to say periods of rainy weather or dryness. For larger rivers the water discharging at any moment is a mixture of water from the whole drainage area. As the transport time and the local weather conditions vary, it is evidently not significant to draw any conclusions from the weather at the sampling spot when the sample was taken. A study of this problem needs a whole drainage area which can be studied for a climatic season or more.

Isotope Ratio and Discharge

A graph showing the discharges against our isotope ratios is shown in Fig. 3. Two features are noteworthy. First, the general distribution of the points seems to be the same for both Finnish and Swedish streams. The isotope ratios overlap roughly in the same interval. Secondly, Fig. 3 also reveals that rivers with a discharge rate over 150 m^3/s have isotope ratios between 0.728-0.735, while streams with discharge rates between 1-40 m^3/s have their ratios spread out over the interval 0.718-0.736. Note however that there is also no difference between Finnish and Swedish streams in this respect.

Why do low isotope ratios only occur in streams with small discharge? There are certainly several possible causes. One, for example, is the occurrence of rocks with low isotope ratios, such as mafic rocks and limestones, in the drainage area. If they form a considerable part of the bedrock and thus of the unconsolidated deposits, a lower isotope ratio will result. The rule that in this region low ratios only exists for small streams, can therefore be interpreted as follows. The rocks mentioned are rather rare and of only local importance. That is in a small drainage area they may, by chance, be important, but for a large drainage area this situation is unlikely.

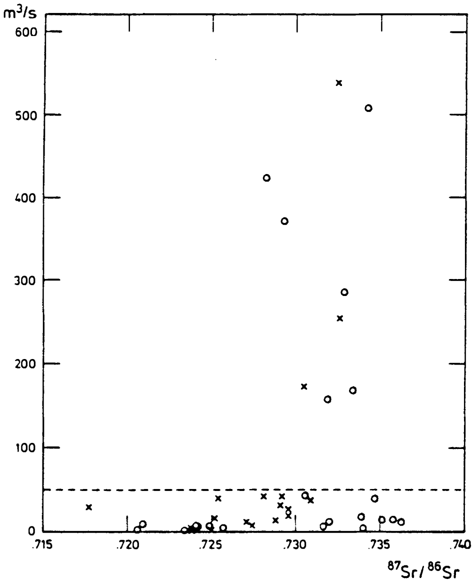

Fig. 3.
Diagram comparing discharge rates with Sr isotope ratios for the investigated rivers. The O:s in the diagram represent Swedish data and the X:s represent Finnish ones.

We have probably such an example in No. 10. In the Kåge Valley, about 15 km upstream from our sample, there is an area with Proterozoic limestone deposits, which have been exploited commercially for a long time.

Possible Effects of the Postglacial Uplift on the $^{87}Sr/^{86}Sr$ Ratio of Stream Water

The complex Postglacial history of the Baltic Sea and the rapid postglacial uplift in the present region may also have an effect on the isotope ratios of some stream waters. The contemporary uplift in the region of the Gulf of Bothnia is ca. 8-10 mm per year but this rate was considerably higher earlier. The present salinity is a few permil but earlier it was greater and passed through a maximum about 4000 years ago during the Littorina Sea stage of the Baltic Sea. At that time, the sea level around the Gulf of Bothnia was about 100-120 m above the present one.

As the topographic gradient is quite small in many of the present coastal areas, large areas will be affected by the uplift in a few centuries. When the bottom sediments rise above the sea level, their pore water Sr as well as their absorbed Sr will approximate the isotope ratio of seawater. This Sr is more easily lost than the Sr in solid solution in the mineral grains and will therefore be removed more readily from the system. The rate of this "cleaning" process depends on many factors such as the porosity of the sediment, the salinity of the pore water, and the adsorbtion properties of the sediment.

The Sr content of ordinary rain-derived ground water in this region is only 10-100 ppb while the present salinity in the bay waters corresponds to a Sr content of 300-700 ppb. The Sr-concentration during the Littorina Sea stage was perhaps 10 times as high. It appears that high concentrations of Sr with low ^{87}Sr/^{86}Sr isotopic ratios could change the Sr isotopic ratios of stream water during a certain period of time, even if it cannot be estimated presently because of lack of pertinent data.

Since the "cleaning" process is a time dependent process, it is evident that the most noticeable effects should be close to the coast and decrease inland with increasing altitude for the same kind of sediment. In other words, the greatest effects on the isotope ratio should be expected in streams with small near-coastal drainage areas.

Average Isotope Ratios

The weighted average isotope ratios of our Finnish and Swedish stream waters using the discharges as listed give 0.7308 for Finland, with a total discharge of 1,248 m^3/s and 0.7315 for Sweden and 2,108 m^3/s. The total average of our samples from the two countries is 0.7313 and 3,356 m^3/s.

The major rivers, if we define them as the nine with a discharge over 100 m^3/s, have a total discharge of 2,875 m^3/s or 85 percent of the total listed discharge. Corresponding average isotope ratio is 0.7317.

Conclusions

The ^{87}Sr/^{86}Sr ratios in water from about 50 rivers around the Bothnian Bay varies from 0.7177 to 0.7366. These high ratios reflect the importance of granitic, Proterozoic rocks in the region. The variability of the ratios in such areas opens up a method to study the mixing processes of waters in river networks with the help of Sr-isotope ratios. In order to make full use of the method in a complex river network it is necessary to study the variations over the network for a longer period of time and to include other important hydrochemical and meteorological variables.

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