Variations in the ^{87}Sr/^{86}Sr Ratio in Lake Waters from Central Sweden

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The ^{87}Sr/^{86}Sr ratios of lake waters from eastern Central Sweden, a region consisting mainly of 1.7-2.0 x 10^9 years old granitoid rocks are reported and discussed. The ratios range from 0.722-0.739, and are similar to lake and stream waters in geologically similar areas.

The annual variation of the isotope ratio in two small lakes varied in the range of 0.7323-0.7339 and 0.7313-0.7325 respectively, except at ice clearing in spring when the ratio of surface water was lowered by a contribution from melting snow. Small lateral differences also exist in Lake Mälaren, probably because its complex outline hinders complete mixing of its water.

The Sr isotopic ratio variations with respect to bedrock geology suggest that a more important influence on the ratio is the mineralogic composition of the Quaternary deposits (mainly till).

The great difference between the ratios of rain water (0.709-0.710) and those of rocks in old Precambrian platforms with granitic rocks (0.720 and greater) results in waters (ground, lake and river) with ratios around 0.720-0.740. This means that the ^{87}Sr/^{86}Sr ratio is an excellent tool in studies of hydrologic processes, such as mixing of waters and exchange reactions between water and mineral matter.

Introduction

For several decades the values of ^{87}Sr/^{86}Sr in granitic and gneissic rocks have been used as petrogenetic tracers in discussions of the origin of these rocks (see for example: Faure and Powell 1972 and Faure 1977). On the other hand, in studies of
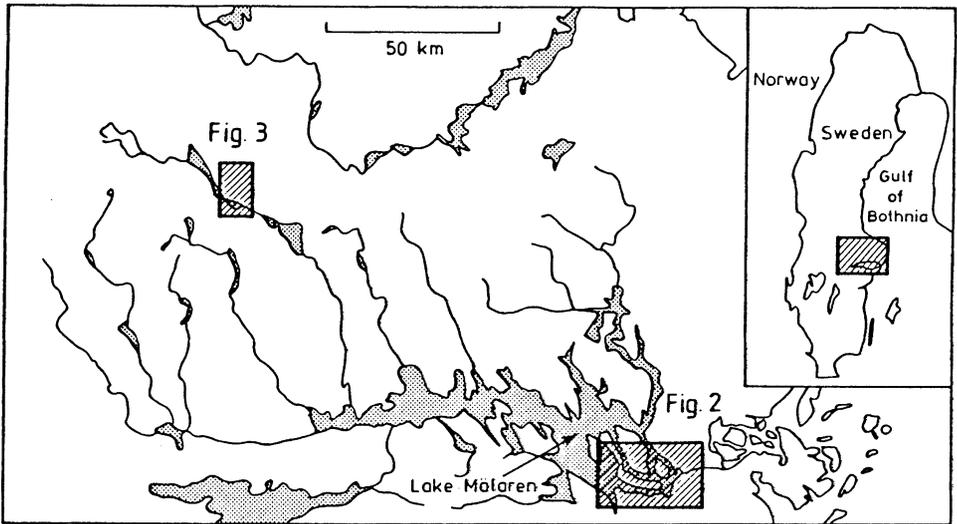
Fig. 1. Map of the eastern part of Central Sweden with Lake Mälaren. Locations of the two
sampling areas indicated.

exogenic processes values of this ratio in natural waters and other participating
materials are rarely utilized as arguments.

A possible reason for this neglect is probably the fact that large areas of the
continents are covered by marine carbonate rocks (Sr isotope ratios around 0.709-
0.710) or by young, basic igneous rocks (Sr ratios around 0.704-0.707). As these
ratios are close those of seawater and rainwater (ca. 0.709-0.710) no pronounced
effects should be expected from mixing or exchange of Sr isotopes between natural
waters and these kinds of bedrock.

However regions exist, particularly in the older parts of the continents, which
show much higher Sr ratios because of the presence of old granitic and gneissic
rocks with high Rb and low Sr contents. The production of radiogenic ^{87}Sr due to
the decay of ^{87}Rb can consequently change the ratio ^{87}Sr/^{86}Sr appreciably, often
giving ratios in the interval 0.8-1.0.

In these regions rainwater will mix with groundwater and exchange Sr with
minerals producing waters with ^{87}Sr/^{86}Sr ratios much higher than the typical rain-
water value of 0.709. A striking example of this was given by Åberg and Jacks
(1985), who found that water from a fissure in Proterozoic granitic bedrock had
ratio of 0.782.

The ^{87}Sr/^{86}Sr ratio can be measured to five significant figures with present mass
spectrometers and the Sr-concentrations in water can be determined to within an
error of about one percent. It is therefore possible to study mixing and exchange
processes between different kinds of waters and also between water and solid

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phases, whenever they have different isotope ratios. The most favorable areas are those with rocks having high ratios, i.e. Proterozoic and Archean granitic areas. However, the sensitivity of the mass spectrometric method makes studies of the hydrologic cycle in areas of basalt and other basic rocks possible (0.704 versus 0.709 of rainwater), but the high Sr content of these rocks versus low content in rainwater makes the method less attractive.

This paper is a pilot study with the purpose of studying variations in the ^{87}Sr/^{86}Sr ratio of water from some lakes in an area of east Central Sweden (Fig. 1) where the bedrock consists predominantly of ca. 1.8-1.9 Ga (1 Ga= 10^9 years) old granites and gneisses. The unconsolidated cover rocks are mainly sediments from the last glaciation, consisting predominantly of till and, particularly in the Lake Mälaren area of glaciofluvial gravel, sand and clay. In the studied area the Sr concentrations are in the following ranges: rain and snow 1-2 ppb, groundwater, lake water etc. 20-40 ppb. For this reason we have not included other important variables such as cation and anion concentrations.

Sampling and Laboratory Procedures

Cleaning of the Sample Bottles
The 125 ml polyethylene (Nalgene) bottles used for collecting the water samples had to be specially cleaned in order to avoid contamination of the samples, as the lake waters contain only 10-100 ppb Sr. The bottles were rinsed in triple distilled water and then filled with 7 M HNO_3 for one week, rinsed a few times with triple distilled water and again filled with such water for one week. They were then rinsed again with triple distilled water and finally rinsed with sub-boiling two-bottle distilled water (DB-water).

Sampling
When sampling, the sealed bottles were opened and filled one decimeter below the water-air interface (if not stated otherwise). The bottles were immediately sealed and brought to the laboratory for storage in a refrigerator until they could be chemically treated. Analyses and handling was performed in a random order on the samples.

Laboratory Treatment
Sixty ml of water (the remaining fraction was stored for duplication runs or spiking) were evaporated to dryness in 100 ml test-tubes (Pyrex) in a semi-closed system, made by Tecator, Sweden. The vapors were exhausted with a special water suction system. The digestion system was placed in a clean-hood.

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Table 1 –^{87}Sr/^{86}Sr ratios in lake waters from Central Sweden

Söderbärke district			
Lake Stora Bjursjön (average for 1983)			0.73193
Lake Flaten (average for 1983)			0.73315
Lake Stora Gladtjärnen (July 1983)			0.72263
Lake Lilla Gladtjärnen (July 1983)			0.72224
Siljan Ring Structure			
Amtjärn Limestone Quarry (July 1983)			0.71019
Lake Mälaren			
Södra Björkfjärden Bay (Aug. 1983)			
Surface			0.72988
22 m depth			0.72957
City of Stockholm waterworks			
Norsborg-Lake Mälaren (23.XI.1982, 11 m depth)			0.72594
Norsborg-Lake Bornsjön (23.XI.1982, 9.5 m depth)			0.72845
Lovön-Lake Mälaren (23.XI.1982, 10 m depth)			0.72775
Tapwater (27.X.1983) Analysed	September	1984	0.72706
	January	1985	0.72711
	October	1985	0.72698
	Average		0.72705

When dry, the residue was picked up in 4 M HCl and transferred into quartz-beakers. A few drops of HClO$_4$ were then added to the sample to remove any organic matter, and the sample was again evaporated to dryness. It was then dissolved in 0.3 ml of 4 M HCl and passed through a preconditioned cation-exchange column placed in a clean-hood.

All acids and water used were of high purity. The ion-exchange columns, made from quartz-glass. were filled with 1 ml of Dowex AG 50WX12 100-200 mesh H-form resin. The chemistry work then followed the method of Birck and Allègre (1978). Four blank runs with 60 ml of DB-water gave a mean contamination of 0.31 ng Sr. The influence being c. 0.1 per mil.

Mass Spectrometry
The samples were, in random order, analyzed on a computer-controlled Finnegan MAT 261 mass spectrometer. The samples were loaded with HCl onto Re filaments on a magazine taking twelve samples and one Sr standard. The analytical error is 0.01-0.02 per cent, i.e. the error is not exceeding one digit in the fourth decimal. All samples were corrected for mass fractionation, ^{86}Sr/^{88}Sr=0.1194. Triplicate decompositions and runs of our internal standard (Stockholm tap water of 1983-10-27) gave a mean value of 0.7271 (Table 1).
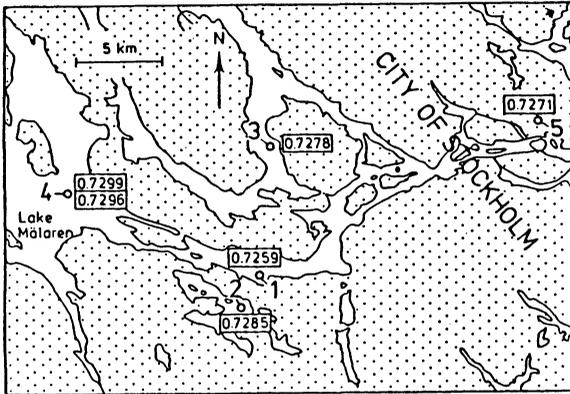
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Fig. 2.
The eastern part of Lake Mälaren.
Results are shown and sampling
points are as follows:
1 Norsborg-Lake Mälaren,
2 Norsborg-Lake Bornsjön,
3 Lovön-Lake Mälaren,
4 Södra Björkfjärden Bay,
5 Dept. of Geol., Stockholm Univ.

The ^{87}Sr/^{86}Sr Ratios of the Stockholm Tap Water and its Sources

The city of Stockholm obtains its drinking water from three water inlets, which are situated at the two water works at Lake Mälaren (Fig. 2): Norsborg, which is the main source for water to the southern part of the city, and Lovön, which mainly supplies the northern part. The third inlet, from Lake Bornsjön, is connected with Norsborg and supplies ca. 10 percent of the present consumption.

Lake Mälaren is a large (1,140 km^2, drainage area 2×10^4 km^2), elongated lake (E-W 117 km, N-S 0.5-50 km) with a complex outline and a great number of islands of all sizes. Its depth also varies considerably, from over 50 m to quite shallow. Stockholm is located at the eastern end of the lake with the outlet to the Baltic at the very center of the city. A great number of small streams feed into Lake Mälaren.

We have measured the Sr isotope ratios of Lake Mälaren water from five localities (Fig. 2; Table 1). The 22 m sample from Södra Björkfjärden was taken well below the summer thermocline. Another was taken 1 dm below the lake surface. The two quite close values indicate that the water in Södra Björkfjärden is well mixed at this time of the year.

The difference between the waters from Norsborg and Lovön is also small, 0.7259 and 0.7278, however this difference is quite a bit greater than our analytical uncertainty. Since the samples were taken the same day, the difference is most likely caused by the lake waters being to some extent separated from each other: Norsborg water is derived mainly from the west while Lovö water comes from the north and south.

The isotope ratio of the tap water in the Department of Geology (located in the inner city area) is a mixture of the three water sources in temporally variable proportions. The treatment with lime at the waterworks does not change the isotope ratio appreciably (limestone ratio = 0.7089).
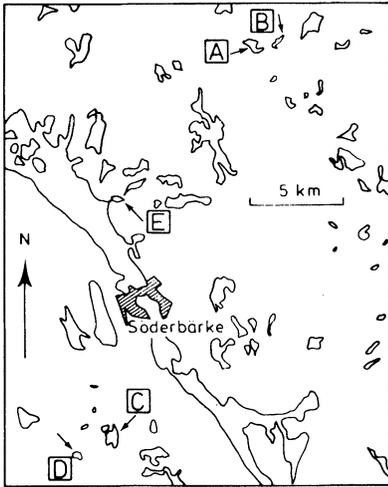
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Fig. 3. Söderbärke district. Lakes:
A Stora Gladtjärnen,
B Lilla Gladtjärnen,
C Stora Bjursjön,
D Flaten.
E Gladtjärnen Bay, Barken.

The ^{87}Sr/^{86}Sr Ratios in some "Unpolluted" Lakes in Central Sweden

Many cities and towns, including a sizeable fraction of the Swedish industry, are located around Lake Mälaren and in its drainage basin. Human activities have therefore polluted its lake water and for this reason we have also studied waters from lakes in an area where such pollution has been minimized.

Söderbärke district (Fig 3) represents such an area with low population density and low industrial activity. The bedrock is of Svecokarelian age (1.7.-2.0 Ga, Lundqvist 1979) and consists mainly of granitic and granodioritic intrusions. Metavolcanic rocks are also important in the district. Basic rocks occur only locally. All these rocks constitute the source for the Quaternary till and the small glaciofluvial deposits covering the bedrock.

In order to have some control on the effect of bedrock on the Sr isotope ratio we selected small source-lakes without habitation in their drainage areas. However, the Quaternary deposits complicate the picture because they represent a mixture of different proportions of the ice-transported rocks coming from the north to north-west of each lake. This means that generally rocks with granitic ^{87}Sr/^{86}Sr ratios (i.e. very high) have been mixed with the local rocks.

Stora Gladtjärnen and Lilla Gladtjärnen, Two Lakes in an Area with Basic Rocks

Two small lakes, Stora and Lilla Gladtjärnen (Fig. 3), were selected in order to find out to what extent the isotope ratios are controlled by the local bedrock. The bedrock around both lakes is gabbro and granodiorite, however a few km north of the lakes mica schists do occur. The silty till in the area therefore contains micaen-
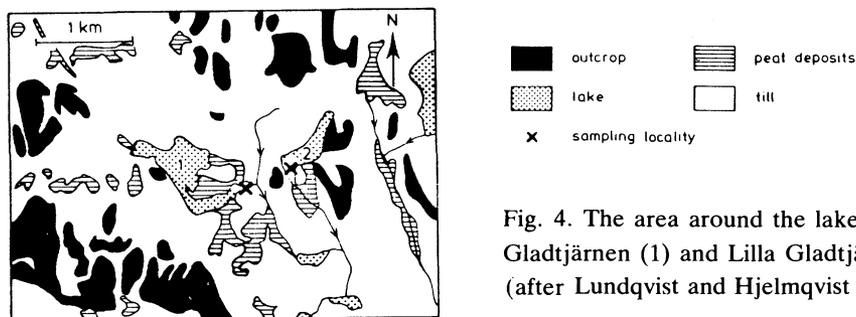
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Fig. 4. The area around the lakes Stora Gladtjärnen (1) and Lilla Gladtjärnen (2) (after Lundqvist and Hjelmqvist 1937).

riched (Rb-enriched) mica schists (Lundqvist and Hjelmqvist 1937; Strömberg 1983). The physical setting for the two lakes is presented in Table 2 and Fig. 4.

From Table 1 it is evident that the two isotopic ratios are almost similar, 0.7222 and 0.7226. Even if these ratios are low compared to those of water from Lake Mälaren, they are high compared to those found in gabbros, 0.704-0.705, or in rainwater, 0.709-0.710.

We also measured the Sr isotope ratio in water from a large pond formed by the excavation work within a limestone quarry at Amtjärn in the Siljan district (ca. 100 km NW of Söderbärke). The drainage basin of this pond is restricted to the quarry, and the rocks consist of marine Paleozoic limestones (ratio 0.7089) together with small amounts of shales with a high ratio, no Quaternary deposits. The pond water gave the isotope ratio 0.7102 (Table 1), which was consistent with rainwater in contact with the limestone and small amounts of shale.

The cause for the relatively high values in the aforementioned lakes must therefore be sought in the till. Exchange reactions at the interface between mineral grains and groundwater change the isotope ratio. Large surfaces are needed for a real change of the ratio. The contact area in the bedrock, even if cracked, is negligible compared to the surface areas of the comminuted rocks and minerals in the till. The influence of gabbro and granodiorite on the isotope ratios in the lakes is therefore determined by their importance as constituents of the local till and not of the bedrock.

Table 2 – Physical geographic characteristics of the lakes studied.

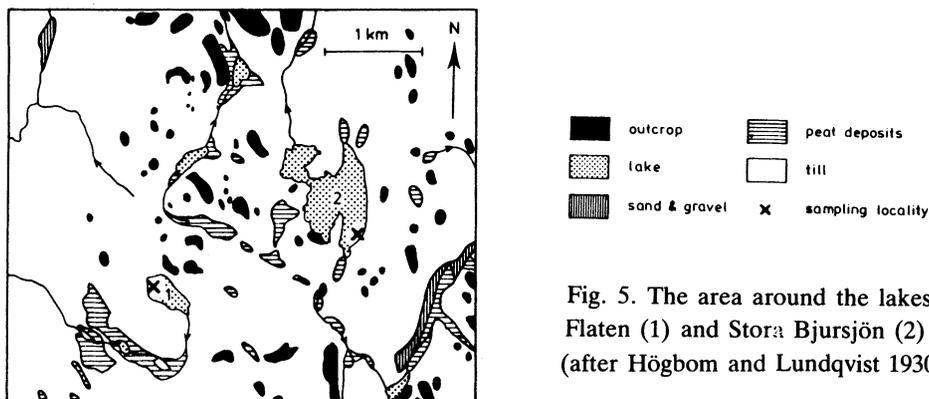| Name	Altitude	Area	Volume	Drainage
	(m) a.s.l.	(km^2)	in 10^5 m^3	area* (km^2)
Stora Gladtjärnen	179	0.32	25	1.6
Lilla Gladtjärnen	186	0.11	3	0.6
Stora Bjursjön	215	0.43	16	1.6
Flaten	271	0.11	3	0.3

* inclusive lake

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Fig. 5. The area around the lakes Flaten (1) and Stora Bjursjön (2) (after Högbom and Lundqvist 1930).

Stora Bjursjön and Flaten, Two Lakes in an Area with Granitic Rocks

We have also studied two small lakes, Stora Bjursjön and Flaten (Fig. 3), where the bedrock consists of granite and to a minor extent of granodiorite, about 5 km to the north metavolcanics occur (Strömberg 1983). The Quaternary deposits consist of sandy to silty till (Högbom and Lundqvist 1930). The lakes were sampled during a period of one year in order to study the seasonal variations in the isotope ratios. The lakes were covered by ice early in December 1982 and for both lakes, the day of clearing of ice was May 1, 1983. Data about the physical geography of the lakes are shown in Table 2 and Fig. 5.

The results of the measurements are presented in Table 3 and Fig. 6. The figure shows that the isotope ratios vary in a similar fashion for the two lakes. The sample in Stora Bjursjön from April 24 is not necessarily an exception because road conditions around Lake Flaten made sampling impossible that day. At a first glance it appears that the ratios are increasing during the year. This effect may be real but it is more likely an "optical illusion" caused by the increase of the ratios occurring between the first two and the last two sampling dates. When the value from April 24 is disregarded the means and standard deviations are: Lake Flaten 0.7332 ± 0.004 and Lake Stora Bjursjön 0.7319 ± 0.004 (Table 1).

Small simultaneous changes in the isotope ratios of the two lakes were observed in July and August. Since the isotope values were nearly constant most of the year and the distance between the lakes is only two km, it is natural to assume that a common cause for such seasonal variations is precipitation. Periods of more or less continuous rainy weather or episodic heavy rains (with the ratio 0.709-0.710) depress the ratio, while periods of dryness may increase the ratio. Additional studies are needed to separate and categorize these processes, because the effects depend on many factors such as dissolution and exchange rates of Sr from soil and till. The available data on the local weather in July-August 1983 does not contradict this interpretation.

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Fig. 6. Variations in the $^{87}Sr/^{86}Sr$ ratio in the lakes Stora Bjursjön and Flaten during 1983 with sampling dates.
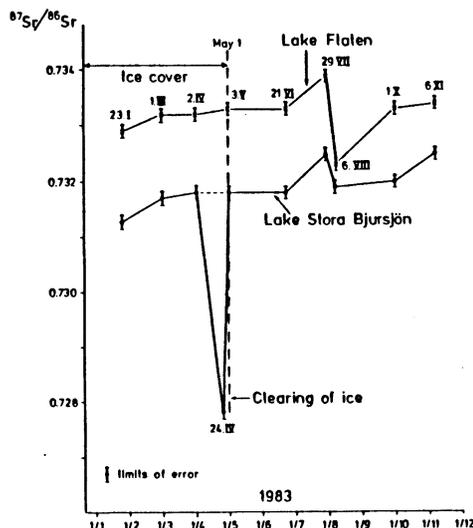
Table 3 – $^{87}Sr/^{86}Sr$ ratios of water from Lake Stora Bjursjön and Lake Flaten, two source-lakes near Söderbärke, Central Sweden in 1983.

Sampling date	Lake Stora Bjursjön	Lake Flaten
January 23	0.73131	0.73286
March 1	0.73170	0.73317
April 2	0.73180	0.73316
April 24	0.72782	
May 3	0.73180	0.73312
June 21	0.73182	0.73314
July 29	0.73250	0.73394
August 6	0.73193	0.73225
October 1	0.73201	0.73328
November 6	0.73246	0.73341

How much rainwater is needed in order to obtain the observed variations? When mixing two sources with different Sr concentrations and different isotope ratios the resulting isotope ratio is (see also Faure 1977 chapter 7)

$$r_3 = \frac{x c_1 r_1 (A+r_2) + (1-x) c_2 r_2 (A+r_1)}{x c_1 (A+r_2) + (1-x) c_2 (A+r_1)}$$

where x – fraction of source 1

c_1 and c_2 – Sr concentrations in ppb in sources 1 and 2,

r_1 and r_2 – $^{87}Sr/^{86}Sr$ ratios in sources 1 and 2,

and r_3 – in mixture

A – sum of the relative abundances of the nonradiogenic isotopes 84, 86 and 88, with the 86-value fixed to 1 ($A=9.430$).

The percentage of p_1 of water from source 1 in the mixture is then

$$p_1 = \frac{c_2 (A+r_1) (r_3-r_2)}{c_2 (A+r_1) (r_3-r_2) + c_1 (A+r_2) (r_1-r_3)} \times 100$$

The Sr concentrations in our samples are not exactly known, but in the present area rainwater contains 1-2 ppb Sr and groundwater, lakes etc. 20-40 ppb Sr. We therefore use the averages, $c_1 = 1.5$ and $c_2 = 30$ ppb, for estimates.

The April 24 value of Stora Bjursjön, $r_3 = 0.7278$, is the most interesting. The values on April 2 and May 3 are both 0.7318 ($= r_2$), and the rainwater value is
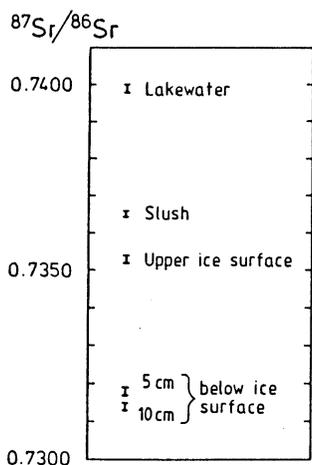
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$^{87}Sr/^{86}Sr$

Fig. 7.
Variations in the $^{87}Sr/^{86}Sr$ ratio of ice and water from the bay Gladtjärnen, Lake Barken, in April 1985. The ice is an upper layer floating on the black ice of the lake.

Table 4 – $^{87}Sr/^{86}Sr$ ratios of ice and water from Gladtjärnen, a sheltered bay of Lake Barken, Central Sweden, on April 1985.

Lakewater	0.73880
	0.73889
	0.73886
	0.73875
	0.73904
Average	0.73887

Secondary ice layer
(12 cm thick)
above the black ice

Slush on the ice surface	0.73646
Surface ice, 0-2 cm	0.73527
Ice, ca. 5 cm depth	0.73175
Ice, ca. 10 cm depth	0.73143

taken as 0.7095 (r_1). From these values the p_1 value is found to be 81 percent, that is on April 24 4/5 of the surface layer consists of rainwater but is mixed with the rest of the lake water in less than nine days.

This result is most easily interpreted in terms of the climatic changes taking place between December and end of April in and on the lake. The water forming the ice in December (black ice) is lake water (ca. 0.732). Snow and rain (both ca. 0.710) precipitate on the ice cover during the winter months. When spring arrives cracks and areas of open water form in the ice and during the final stages before ice break up the snow on the ice is soaked by lake water and melting snow water from the frozen ground surrounding the lake. Therefore, samples taken a few days before ice clearing will be mixtures, the proportions of the different waters will depend on many local and fortuitous factors.

This interpretation was tested by taking a series of samples in April 1985 from a sheltered bay of Lake Barken (Fig. 3). The results are presented in Table 4 and Fig. 7.

Five water samples were taken, one every second day, water depth 60 cm. Their isotope ratios were very close to each other (ave. 0.7389). The lake was covered by a ca. 10 cm thick layer of snow, about one week old. Under this layer was a few cm of recrystallized, older snow. The next layer consisted of a ca. 12 cm thick ice layer floating on a thin water layer above the surface of the ca. 35 cm thick crystal-clear black ice. The upper surface of the "12 cm ice" was covered by a layer of slush. The

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snow layer samples were lost by mishap.

The slush and ice samples show a systematic decrease of isotope ratios with depth. This ice is a mixture of snow-water and lake water, but a detailed discussion is not possible since the history of the ice-snow situation on the lake during the winter is not known. However, it is evident that the results are consistent with the given interpretation of the "April 24" effect in Lake Stora Bjursjön.

For the "10 cm sample" (0.7314) the isotope ratio corresponds to 25 percent snow-water, using the same assumptions as above.

A calculation similar to the one given above but using $r_2 = 0.7389$ (Barken lake water) and $r_3 = 0.7314$ ("10 cm" sample) or $r_3 = 0.7365$ (slush) gives the rainwater content of the samples as 87 and 64 percent, respectively. The results are consistent with the interpretation given above.

The means (m) and standard deviations (σ) of the isotope ratios in water from Lake Flaten and Lake Stora Bjursjön define an addition of 26-27 percent rainwater in order to change the ratio from m to m-σ, and of 41-42 percent rainwater from $m+\sigma$ to m-σ. An interpretation must await much more detailed work.

Final Remarks and Conclusions

Disregarding the Amtjärn value (0.7102) the range of the lake Sr isotope ratios is 0.7390-0.7222 with a median value of 0.7306. No mean has been calculated since the samples do not represent an unbiased sampling. However, the interval corresponds fairly well to that observed for water from streams feeding into the Bothnian Bay of the Baltic Sea (Åberg and Wickman 1987).

The observed $^{87}Sr/^{86}Sr$ ratios in lake waters are determined by the composition of the mixture of rock types present in the Quaternary deposits, mainly till. The influence of the local bedrocks is only shown to the extent that they dominate the local drainage basin. The observed limited variations (ca. 0.017) are therefore an expression of the fact that granitoid, Proterozoic rocks are so common in this part of Central Sweden, and that mafic rocks and limestones are only minor constituents. Only very special conditions, like those in Amtjärn, can result in exceptional isotope ratios.

The results of this study and an additional one on $^{87}Sr/^{86}Sr$ ratios in Bothnian Bay streams (Åberg and Wickman 1987) show that it is possible to find areas characterized by waters having much higher isotope ratios than those of rainwater. The $^{87}Sr/^{86}Sr$ ratio therefore must be an excellent tool for hydrologic studies of exogenic processes taking place in old Precambrian shield areas.

A necessary condition for detailed studies is, of course, a control of the isotope ratio and Sr content of rain, snow and water participating in the processes. Hence, with careful planning and suitable sampling techniques it will be possible to study many kinds of hydrologic problems in practically all kinds of climatic environments.

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Acknowledgements

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