CATENA vol. 17, p. 1–11 Cremlingen 1990

STRONTIUM ISOTOPES IN TREES AS AN INDICATOR FOR CALCIUM AVAILABILITY

G. **Åberg**, G. **Jacks**, T. **Wickman**, Stockholm
P.J. **Hamilton**, Glasgow

Summary

The increasing acidification and impoverishment of soil poses a great environmental problem today and in the future and is exemplified by the decreased availability of calcium in the soil pool. Unfortunately, budgeting the inputs and outputs of calcium in the soil-vegetation ecosystem is a very laborious task. Some of the fluxes are internal in the ecosystem and cannot be measured explicitely, like weathering of primary minerals. However, since strontium and calcium exhibit similar geochemical behaviour, it is possible to make an estimation of the calcium content in different media in the soil-vegetation eco-system using natural strontium isotopes. Preliminary analyses of water (precipitation, throughfall, runoff, soil-water), soil (mineral matter) and biological material (trees, musselshells) show that the use of the strontium isotope ratio $^{87}Sr/^{86}Sr$ is a powerful tool in estimating and understanding environmental changes.

ISSN 0341–8162
©1990 by CATENA VERLAG,
D–3302 Cremlingen-Destedt, W. Germany
0341–8162/90/5011851/US$ 2.00 + 0.25

1 Introduction

For many decades the $^{87}Sr/^{86}Sr$ ratio has been used as a petrogenetic tracer in granitic and gneissic rocks in the discussion about their source, to study element mobility in cracks and fissures, and the interaction between circulating fluids and their host rock. Proterozoic rocks, and soils derived from them, are enriched in ^{87}Sr, formed by radiogenic decay of ^{87}Rb. In old rocks, especially those rich in potassium, the ratio of $^{87}Sr/^{86}Sr$ is high, and spread out over a large interval, since rubidium follows potassium in the geologic processes. The rubidium-strontium method is common for the dating of rocks, especially Precambrian, due to the long half-life of ^{87}Rb. But the use of $^{87}Sr/^{86}Sr$ isotope ratios have also proved to be a powerful tool in establishing weathering rates in areas dominated by Proterozoic acid rocks such as Sweden (ÅBERG & JACKS 1985, 1987, ÅBERG et al. 1989, JACKS et al. 1989).

The aim of the present paper is to show the potential of using natural strontium isotope ratios for disciplines other than hardrock geology which are more or less directly connected to bedrock composition as mentioned above. We will focus our interest on trees as a medium that can be used as historical archives and thus be of use for extrapolating future trends. In addition we present a compilation of the ongoing research with strontium isotopes in the environment in Sweden.

Strontium is a common trace element in sea water with a concentration of ca. 8 ppm. The isotopic composition of strontium in the oceans ($^{87}Sr/^{86}Sr$ = 0.709) is a mixture of strontium from young volcanics (ca. 0.703), marine carbonates (ca. 0.708) and from older continental crust (ca. 720) (FAURE 1986). Comparing the residence time for strontium in the oceans, ca. $2 \cdot 10^7$ years, with the oceanwater mixing rate, ca. 10^3 years, the strontium isotopic composition in the oceans can be seen as constant. The strontium concentration of rainwater (which has the same isotopic composition as oceanwater) is ca. 1–2 ppb and streamwater in Sweden ca. 20–40 ppb (WICKMAN & ÅBERG 1987).

The strontium isotope method has also been used to show the annual variation in the $^{87}Sr/^{86}Sr$ ratio itself in source lakes from Central Sweden (WICKMAN & ÅBERG 1987). The ratios varied in a narrow range except during the spring thaw period when the ratio of the surface water was lowered by a contribution from melting snow. The variation in Sr isotope ratio, with respect to bedrock geology, suggested that a more important influence on the ratio is the mineralogic composition of the Quaternary deposits (mainly till).

Another study concerned the variations in Sr-ratio in water from streams discharging into the Bothnian Bay, Baltic Sea (ÅBERG & WICKMAN 1987). Water samples from 53 streams in Sweden and Finland were analysed. The weighted average isotope ratio with respect to discharge was high, reflecting the dominance of granitic Proterozoic rocks in the region. ÅBERG & WICKMAN (1987) also found that rivers with a higher discharge rate had their isotope ratios spread out over a smaller interval than those with a lower discharge rate. They suggested that rare rocks, which are of only local importance, have a much greater impact in a small drainage area.

A similar study was made by ÅBERG & JACKS (1987) who found a tendency for an inverse relationship between discharge for streams and Sr-ratios in an area in Central Sweden. They suggested that abundant rainwater with a low Sr-ratio will have a greater impact on the runoff value at high discharge. The residence time for the soilwater will also decrease with increased precipitation and thus limit the time for interaction with the soil minerals.

Results from Central Sweden (ÅBERG & JACKS 1985) yield $^{87}Sr/^{86}Sr$ ratios around 0.71 for precipitation. Throughfall (below the canopy), with ratios of the order of 0.72–0.73, is a mixture of atmospherically transported strontium caught by vegetation and strontium from the mineral soil. A similar observation was made by GRAUSTEIN & ARMSTRONG (1983). They found that the Sr in the forests is ultimately derived from two sources

(i) weathering, which is the chemical alteration and partial dissolution of the parent material of the soil, and

(ii) dust from remote areas transported through the atmosphere.

Further results of ÅBERG & JACKS (1985) from the same locality showed that shallow groundwater in a dug well and runoff water had ratios of around 0.73–0.74 and water from a fracture zone in a stream gave a value of 0.78. The rock in the fracture zone had a strontium value of 0.85.

Strontium, although not an interesting biogeochemical element, exhibits similar behaviour to calcium (WADLEIGH et al. 1985). Therefore it is possible to make an estimation of calcium release by weathering by assuming that calcium behaves like strontium (JACKS et al. 1989).

Within the "soil-water-vegetation" system, the cation fluxes can be readily characterized by nutrients like Ca^{2+} and Mg^{2+}, which are subject to considerable internal circulation within an ecosystem. There are two important inputs into this internal circulation: atmospheric deposition and weathering products. The losses are via runoff and harvest. In a steady-state ecosystem with constant composition of the exchange complex, inputs are equal to the losses.

Calcium is an essential nutrient for plant-life and is partly stored in the soil in exchangeable form. Exchangeable cations can neutralize acid deposition until their stores are depleted (PACES 1986). In a system in equilibrium, the mobilization of base cations by weathering matches the acid input. But calcium as an element is hard to relate to specific sources. That is, calcium in precipitation and throughfall and in runoff can be estimated by analyses. But as to how much of the calcium comes from the exchangeable storage in the topsoil or from the mineral soil by weathering is almost impossible to assertain. However, using strontium behaviour as a model for calcium has given a reasonable estimate of weathering rate in four out of five catchments (JACKS et al. 1989). In two of the five catchments there seems to be an ongoing loss of exchangeable calcium, where the loss by runoff occurs with sulphate being the dominant anion.

A calcium budget of inputs and losses over a few years' duration was calculated by ÅBERG et al. (1989) for an area in Central Sweden. They indicated that mineral weathering should be of the order of 8 kg Ca/ha·year to maintain the soil pool of exchangeable calcium constant. A major portion of the excess calcium-export, due to sulphur deposition, is taken from this soil pool, resulting in a gradual acidification of the soil (ÅBERG et al. 1989).

Strontium analyses were performed on samples from four localities spread out over Sweden (fig.1). The methodology of the sample collection and analytical work on the water and soil material has been presented in previous papers (WICKMAN & ÅBERG 1987, ÅBERG et al. 1989). For the tree samples, a two centimetre thick slice was sawed from the bole. After dating the different rings, samples were cut out with the help of a scalpel and ashed in an oven. The samples were dissolved in 4 M HCl, taken to dryness and then redissolved in 4 M HCl. After that they were treated by the same ion-exchange procedure as the water samples. The soil samples were analyzed on a Finnigan MAT 261 mass spectrometer at the Laboratory for Isotope Geology, Stockholm, and the water and tree samples on a Micromass 54 E mass spectrometer at Scottish Universities Research and Reactor Centre (SURRC), East Kilbride.

Our internal water standard (Stockholm tap water of 1983-10-27) gave a value of 0.72691 at East Kilbride (average of three decompositions), to be compared with a previous Stockholm mean value of 0.72705 (triplicate decompositions; WICKMAN & ÅBERG 1987). Another check of the complete analyti-

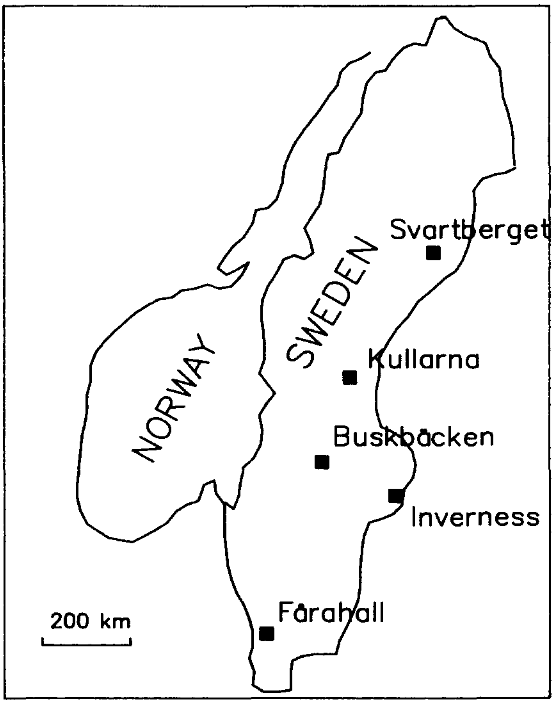

Fig. 1: *Map of Sweden showing the investigated localities.*

cal procedure was made by duplicate decompositions of four runoff water samples. The mass spectrometric runs at East Kilbride showed very small internal variations between the duplicates (tab.1).

Date	$^{87}Sr/^{86}Sr$
85-08-30	0.73860
Duplicate	0.73872
85-09-17	0.73817
Duplicate	0.73822
85-10-02	0.73896
Duplicate	0.73901
85-10-16	0.73808
Duplicate	0.73811

Tab. 1: *Sr ratios for runoff water from Svartberget.*

2 Results and discussion

Preliminary analyses of the $^{87}Sr/^{86}Sr$ ratio for the soil samples (HF-digested) shows weathering to be related to the size of the mineral grains. Smaller grains have a lower strontium ratio compared with larger grains (tab.2; samples KÖ-8). One explanation may be the greater surface to volume ratio of the smaller grains resulting in a stronger susceptibility to weathering. With time, the total effect will be an ongoing impoverishment of the soil and a diminishing contribution of strontium and other exchangeable cations to the groundwater and biological systems.

A preferential leaching can also be suggested for strontium on basis of the isotope results. That is, ^{87}Rb has an ion-radius of 1.48 Å and charge +1, while

Locality	Sample	Depth (m)	Size (mm)	^{87}Sr/^{86}Sr
Kullarna	KÖ-8	1.0–2.0	<0.125	0.75955
Kullarna	KÖ-8	1.0–2.0	0.250–0.125	0.76751
Kullarna	KÖ-8	1.0–2.0	1.0–0.25	0.77938
Kullarna	W 1-B	0.1–0.2	<0.125	0.75801
Kullarna	W 2-B	0.1–0.2	<0.125	0.75920
Kullarna	W 3-B	0.1–0.2	<0.125	0.75530
Kullarna	W 4-B	0.1–0.2	<0.125	0.75679
Kullarna	W 5-B	0.1–0.2	<0.125	0.75585
Svartberget	SB-1	1.0	<0.125	0.73933
Svartberget	SB-2	1.0	<0.125	0.74053
Svartberget	SB-4	1.0	<0.125	0.74262
Svartberget	SB-7	1.0	<0.125	0.73814
Svartberget	JC-3	1.0	<0.125	0.74094
Svartberget	KC-3	1.0	<0.125	0.73961

Tab. 2: *Sr ratio for sieved soil samples.*

Locality	Depth (m)	Size (mm)	^{87}Sr/^{86}Sr
Buskbäcken	0.00–0.05	<0.125	0.7989
Buskbäcken	0.05–0.15	<0.125	0.8003
Buskbäcken	0.15–0.30	<0.125	0.7718
Buskbäcken	0.30–0.45	<0.125	0.7712
Buskbäcken	0.45–0.60	<0.125	0.7739
Buskbäcken	0.80	<0.125	0.7713*
Buskbäcken	1.00	<0.125	0.7703
Fårahall	0.00–0.06	<0.125	0.74439
Fårahall	0.06–0.10	<0.125	0.74177
Fårahall	0.10–0.20	<0.125	0.74293
Fårahall	0.20–0.30	<0.125	0.73710
Fårahall	0.40–0.50	<0.125	0.73664
Fårahall	0.50–0.70	<0.125	0.73620
Fårahall	0.70–1.00	<0.125	0.73608
Fårahall	1.00	<0.125	0.73535
Fårahall	1.00	<0.160	0.74081

* Pooled sample (eight localities)

Tab. 3: *Sr ratios for sieved soil samples.*

its daughter ^{87}Sr, formed by radioactive decay, has an ion-radius of 1.13 Å and charge +2. The strontium ion will thus leave its rubidium site more easily than a strontium ion more tightly bonded in the lattice.

In a depth profile the total soil samples show high strontium ratios in the uppermost layer which then decrease strongly at around 20 cm depth. After ca. 20 cm the values stabilize and this trend continues to groundwater level (tab.3). The last Fårahall sample (tab.3) having larger grain size also has a higher strontium ratio in accordance with the previous paragraph. However, within an area

Sample	Date	Depth (m)	$^{87}Sr/^{86}Sr$
W	85-10-27	0.05	0.74176
W		0.10	0.73849
W		0.30	0.73709
W		0.75	0.73742
W		1–2	0.73707
W	86-04-20	0.05	0.74112
W		0.10	0.73895
W		0.30	0.73782
W		0.75	0.73855
W		1–2	0.73242
SE	86-04-20	0.05	0.75445
SE		0.10	0.74020
SE		0.30	0.73163
SE		0.60	0.73163

Tab. 4: *Sr ratios for soil- and groundwater from Buskbäcken.*

Depth (cm)	Ca (ppm)	Sr (ppb)	$^{87}Sr/^{86}Sr$
-3–0	2.35	201	0.7346
0–5	1.03	28	0.7484
5–15	0.48	10	0.7497
15–30	0.57	12	0.7413
30–45	0.31	4	0.7325
Throughfall			0.7381
Throughfall			0.7345
Throughfall			0.7308
Throughfall			0.7282

Tab. 5: *Analytical results from NH_4Ac extracts of soil samples and of throughfall from Buskbäcken catchment.*

(some 100 m^2) at the same depth, the soil is quite homogeneous, having similar strontium ratios (tab.2). Samples W are taken from between 10–20 cm while samples SB-JC-KC are taken at about 100 cm depth. Lysimeter samples follow the same depth trend as the soil samples but have lower strontium ratios. The decrease in strontium ratios appear in the first 5 to 10 cm, contrasting with ca. 20 cm for the soil samples (tab.4).

The uppermost soil layer, -3 to 0 cm depth, consisting of humus (organic matter), is enriched in products that have passed up through the trees and then been deposited in the form of needles and twigs in the ground. Leaching of this soil layer with NH_4Ac gives a value similar to that of the throughfall (tab.5). Leaching of the next layer, the upper mineral soil (0–15 cm), yields a slightly higher strontium value (tab.5) than that recorded for the soil water (tab.4), and also a higher value than that of the previous humus-layer. Exchange sites in the mineral-soil layer consist of organic material that has been washed down from the humus-layer and mixed with inorganic material. The strontium is largely adsorbed onto organic matter on the mineral grains. In comparison to soil water, a stronger leaching agent like NH_4Ac removes more of the strontium that has been adsorbed onto the organic matter and mineral grains.

The importance of litter fall for the strontium isotope ratio in the uppermost soil-layer can be shown when comparing two adjoining forests growing on similar soils. The strontium isotope ratio in lysimeter samples of the top layer from a matured forest area (tab.4; samples SE 1986) is found to be distinctly higher than that from a younger one (tab.4; samples W 1985, 1986). At a greater depth the inverse occurs. The internal circulation in the soil-vegetation system thus seems to be dependent on the extent of forestation. Larger and more matured forests will impoverish deeper soils of their cations and enrich the latter in the humus-layer through litter fall. Over a

Area	Tree	Sample	$^{87}Sr/^{86}Sr$
1	Spruce	Bark	0.71942
1	Pine	Bark	0.71926
1	Birch	Bark	0.72048
2	Spruce	Bark	0.72793
2	Pine	Bark	0.72785
2	Birch	Bark	0.73140
3	Spruce	Bark	0.72490
3	Pine	Bark	0.72360
3	Spruce	Outer wood	0.71634
3	Pine	Outer wood	0.71363
3	Spruce	Core wood	0.72781
3	Pine	Core wood	—

Tab. 6: *Sr ratios of bark and bole from spruce, pine and birch from Buskbäcken.*

forest generation, the biomass accumulation in stemwood and bark is considered to be a permanent loss from the catchment, since with timber harvesting these are removed from the catchment. In general forestry practice, branches with twigs and needles are left on the ground to decay.

In a test-project, bark of spruce, pine and birch from two areas were analyzed for strontium isotopes. In an additional area, bark, wood from the trunk's outermost growth-layer and wood from the core were analysed from both spruce and pine. The age of the trees was ca. 40 years. An advantage of analyses using tree material is the possibility to calculate the age of every specific ring, and that the transport system after some time is terminated and lignified. The system of the tree will thus be closed and its strontium isotope ratio frozen.

The bark from spruce and pine gave similar values within the two areas. The birch ratios were slightly biased towards higher values (tab.6). This deviation might be due to the deeper root system of the birch. In the third area, spruce and pine trees gave similar ratios for bark and the trunks outermost growth-layer (tab.6).

In an additional study, calcium was analyzed in tree-rings from pine from Inverness and Buskbäcken and spruce from Fårahall (fig.1). The pine from Buskbäcken and spruce from Fårahall represent two different regions in Sweden but the same time interval. The calcium uptake for these trees shows a similar trend. Starting at about 1000 ppm calcium in the 1940's (figs.2 & 3), there is a rapid decrease to 700–600 ppm. Then comes a slow decrease for about 25 years, followed by a rapid decrease to about 350–250 ppm in the 1980's. The pine from Inverness shows a similar decreasing trend (fig.4), starting at about 1000 ppm at the beginning of the 20th century and ending with ca. 300 ppm in the 1980's. This curve shows a maximum around 1943, and after that a similar trend to the trees from Buskbäcken and Fårahall. The analytical results from this tree, though, have a big scatter, probably because of analytical reasons.

The decrease in calcium content in the trees with time may have several explanations. One is that the tree when growing is impoverishing the soil and accumulating the nutrients in the trunkwood. Therefore the new wood has less calcium available to take up from the soil. Another explanation is that the ongoing acidification of the soil will transport cations like Ca^{2+} out of the ecosystem and impoverish the soil. In this case the input of cations from natural weathering cannot keep up with the export out of the soilpool. The decrease in calcium content over the years may also be

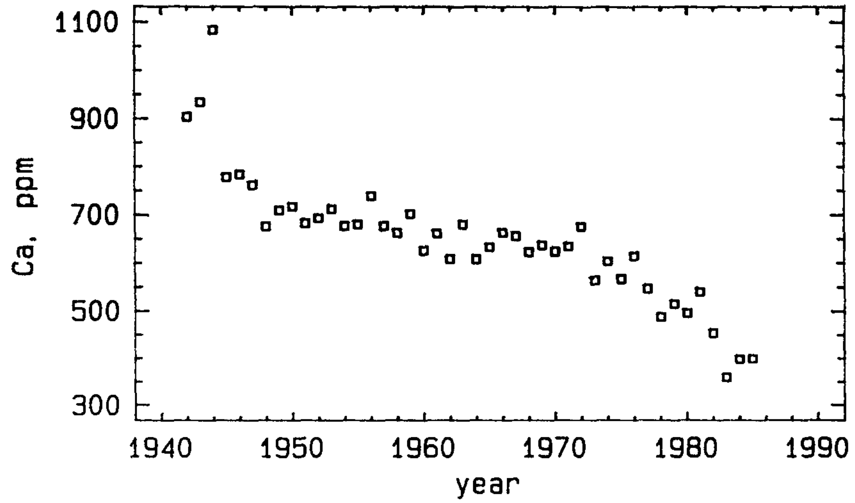

Fig. 2: *Calcium content versus time in pine tree-rings from Buskbäcken.*

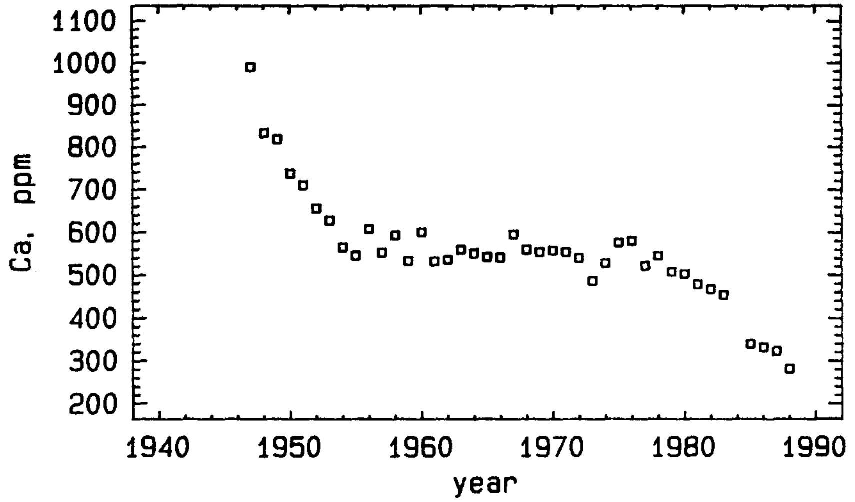

Fig. 3: *Calcium content versus time in spruce tree-rings from Fårahall.*

a combination of the two possibilities. Comparison of the three trees (figs.2–5) shows that, independent of region and soil properties, the calcium content of the younger trees decreases very rapidly to a level which the twice as old tree from Inverness has at the same date. The acidification explanation thus seems to be in better support.

Use of the strontium isotope ratios from the Buskbäcken spruce adds significant data for the interpretation. The decrease in $^{87}Sr/^{86}Sr$ ratio (tab.6) from 0.728 to 0.716 during 1942 (core wood)

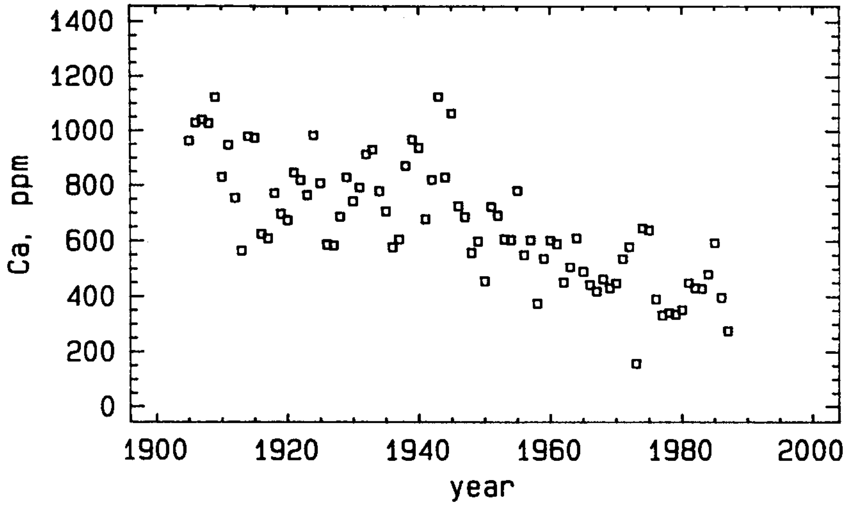

Fig. 4: *Calcium content versus time in pine tree-rings from Inverness.*

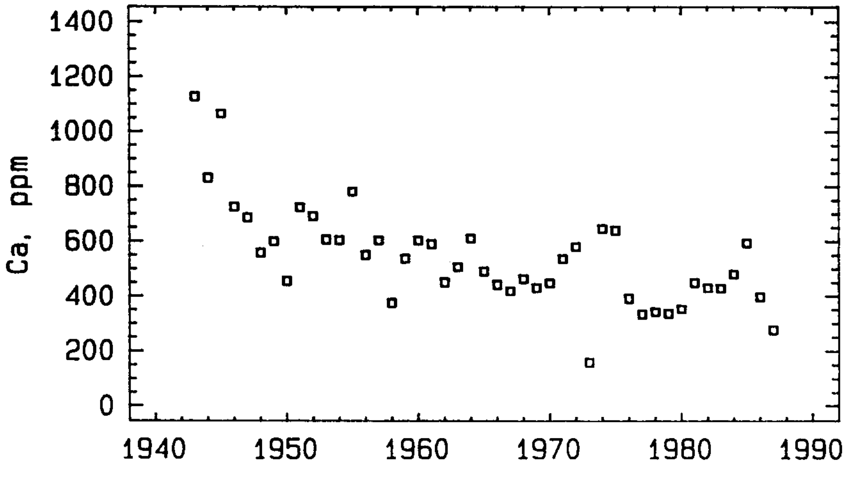

Fig. 5: *Calcium content versus time in pine tree-rings from Inverness (with focus on the years in between 1943 and 1987).*

to 1985 (outer wood) is independent of the amount of strontium the tree is able to take up from the soil, but shows the composition of the strontium entering the tree. The contribution of rainwater (Sr ratio ca. 0.71) to the soil can be seen as constant over the years (RODHE & GRANAT 1984). Thus, to change the composition and lower the ratio of the strontium entering the tree, contribution of strontium from the soil pool has to decrease. This happens if the export of cations from the soil pool out of the ecosystem is greater than the input from natural weathering. As a result, the ratio of strontium in the soil water taken up by the tree, is biased towards that of rainwater.

Unpublished $^{87}Sr/^{86}Sr$ isotope results of ÅBERG & MUTVEI for the freshwater pearl mussel *Margaritifera* in Central Sweden (50 kilometers north of the investigated locality) support the above acidification hypothesis. *Margaritifera* has a long life-span of over 100 years, making it a good environmental archive. Analyses of three samples, from 1915 to 1930, 1930 to 1945 and 1945 to 1985, showed a constant decrease in strontium isotope ratios, well outside the error limits, which is the same trend as found for the trees.

CARELL et al. (1987) used *Margaritifera* shells from the same locality for a study of environmental changes by means of element analyses and radioactivity. They analysed 30 elements with proton microprobe and neutron activation analysis. The results showed seasonal variations as well as changes over longer periods. Elements like gold, silver, iron and cobalt clearly decrease in amount with time. The reason, according to CARELL et al. (1987) is that increasing acidity might suppress the chemical/biological availability of gold and silver and also the uptake of iron and cobalt. They also reported an increase in manganese and sulphur, which supports an "ongoing acidification" hypothesis.

3 Conclusions

Since calcium and strontium exhibit similar geochemical behaviour, the results of strontium isotope analysis of trees show that there is an ongoing impoverishment of the soil in Sweden. Except for the losses to trees (which are partly returned to the soil again), the main loss is due to acidification; as is also shown by ÅBERG et al. (1989) and JACKS et al. (1989).

The strontium results also show that the compositional trend for water and soil is similar despite location of the test area. The spread and variation in the $^{87}Sr/^{86}Sr$ ratios thus makes strontium isotopes a powerful tool when it comes to detecting trends of base cation depletion in the soil vegetation system. There is obviously a great potential in combining different parameters like soil, water, biological material and isotopes for the study of environmental changes over a period of years, especially when taking the increasing acidification into account.

Since sampling of the past is a difficult task in many disciplines, trees have many advantages as environmental archives because they preserve information over periods of time. Trees which may be up to a few hundred years old, such as oak, could also be used as historical archives, as well as (subject to conditions of storage), wood from museum collections in order to study environmental changes.

Acknowledgement

We wish to thank P. Collopy, who kindly corrected the English and made some valuable suggestions for the improvement of the manuscript. The study was mainly supported by the Royal Society of London (Surface Waters Acidification Programme) and in part by The Swedish Council for Forestry and Agricultural Research.

References

ÅBERG, G. & JACKS, G. (1985): Estimation of weathering rate by ^{87}Sr/^{86}Sr ratios. Geol. Fören. Stock. Förh. **107**, 289–290.

ÅBERG, G. & JACKS, G. (1987): ^{87}Sr/^{86}Sr as a tool in studies of weathering rates. Proc. "Geochemistry of the Earth Surface and Processes of Mineral formation". Ed. Y. Tardy. Granada, Spain, March 1986, 67–76.

ÅBERG, G., JACKS, G. & HAMILTON, P.J. (1989): Weathering rates and ^{87}Sr/^{86}Sr ratios: An isotopic approach. Journal of Hydrology **109**, 65–78.

ÅBERG, G. & WICKMAN, F.E. (1987): Variations of ^{87}Sr/^{86}Sr in water from streams discharging into the Bothnian Bay, Baltic Sea. Nordic Hydrology **18**, 33–42.

CARELL, B., FORBERG, S., GRUNDELIUS, E., HENRIKSON, L., JOHNELS, A., LINDH, U., MUTVEI, H., OLSSON, M., SVÄRDSTRÖM, K. & WESTERMARK, T. (1987): Can mussel shells reveal environmental history? Ambio **16**, 2–10.

FAURE, G. (1986): Principles of isotope geology. 2nd edition. 589 pp. John Wiley & Sons, New York.

GRAUSTEIN, W.C. & ARMSTRONG, R.L. (1983): The use of strontium-87/strontium-86 ratios to measure atmosphere transport into forested watersheds. Science **219**, 289–292.

JACKS, G., ÅBERG, G. & HAMILTON, P.J. (1989): Calcium budgets for catchments as interpreted by strontium isotopes. Nordic Hydrology **90**, 85–96.

PACES, G. (1986): Weathering rates of gneiss and depletion of exchangeable cations in soils under environmental acidification. J. Geol. Soc. London **143**, 673–677.

RODHE, H. & GRANAT, L. (1984): Sulfate in European Precipitation 1955–1982. Atmospheric Environment **18**, 2627–2633.

WADLEIGH, M.A., VEIZER, J. & BROOKS, C. (1985): Strontium and its isotopes in Canadian rivers: Fluxes and global implications. Geochim. Cosmochim. Acta **49**, 1727–1736.

WICKMAN, F.E. & ÅBERG, G. (1987): Variations in the ^{87}Sr/^{86}Sr ratio in lake waters from Central Sweden. Nordic Hydrology **18**, 21–32.

Addresses of authors:
G. Åberg, G. Jacks, T. Wickman
Department of Land and Water Resources
Royal Institute of Technology
S-100 44 Stockholm, Sweden
P.J. Hamilton
SURRC, East Kilbride
Glasgow G75 OQU, Scotland
Present addresses:
G. Åberg
Central Board of National Antiquities
Box 5405
S-114 85 Stockholm, Sweden
P.J. Hamilton
CSIRO
P.O. Box 136
North Ryde, NSW 2113
Australia