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Freshwater unionid (Mollusca: Bivalvia) shells as environmental archives: Methodology and observations

by

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ABSTRACT

Multi-elemental analyses have been carried out on time-determined shell sections of the freshwater pearl mussel *Margaritifera margaritifera*. Fallout history of S and N could be indirectly followed in concentrations of these elements in shells. Concentrations of Fe, Co and Zn in shells seem to be correlated to acidification and its history. Aquatic chemistry and solubility characteristics are discussed.

INTRODUCTION

We have analyzed elemental concentrations in shells of the pearl mussel *Margaritifera margaritifera* from several Swedish rivers, one Norwegian river and one N Russian river. By using both recently collected shells and shells from museum collections, certain changes in environmental history, such as acidification, eutrophication and radioactivity, can be traced back 100-200 years (see also CARELL *et al.*, 1987).

STUDY AREA, MATERIAL AND METHODS

Twenty-three *Margaritifera* shells were analyzed. The material has been collected from seven Swedish rivers (Vramsån, S Sweden; Kasenbergaån and Slereboån, SW Sweden; Tansån, C Sweden; Vattenån and Bollstaån, NE Sweden; Pärlälven, N Sweden), one N Russian river (Kerjet), and one Norwegian river (Sörkedalselva, Oslo) (Figure 1). Ten shells, collected in the 1840s by A. W. Malm from the River Vramsån were obtained from the the Göteborg Natural History Museum and from the Swedish Museum of Natural History, Stockholm.

Elemental analyses were carried out mainly by instrumental neutron activation (INAA), but also by ICP-MS and specific methods (MUTVEI *et al.*, 1994). Shell growth rates and variations in elemental concentrations have been dealt with in the latter paper.

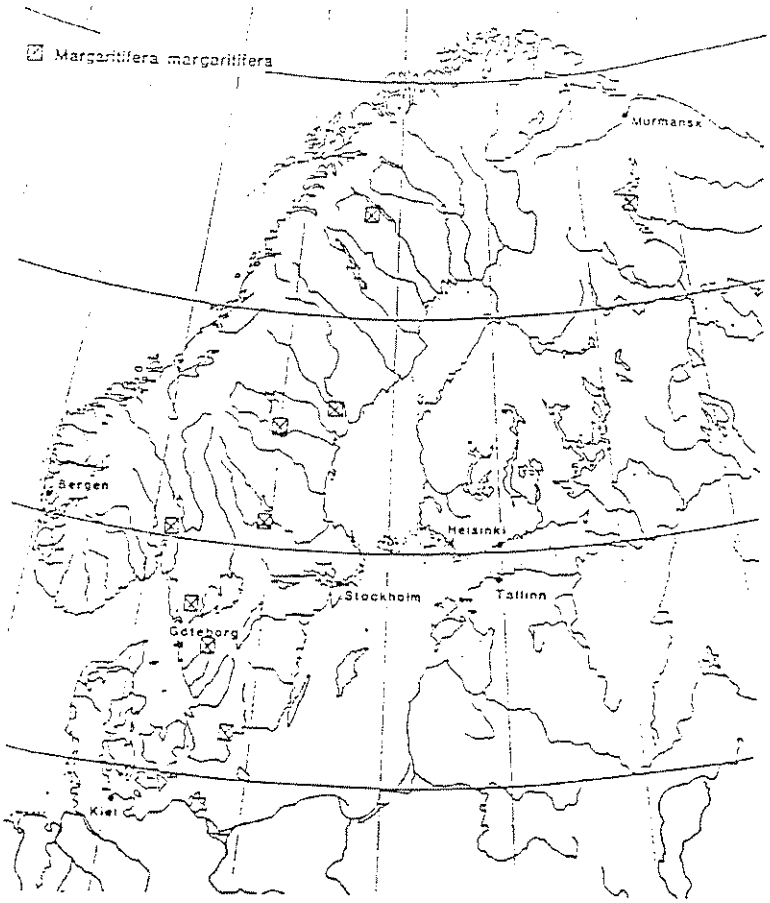

Figure 1 – Map of Scandinavia and NW Russia.

RESULTS

Total number of elements and their ranges in *Margaritifera* shells are shown in Table I. The elements are arranged according to their grouping in the periodic system (PS).

TABLE I

Elements and their ranges. M. margaritifera, *Swedish shells. Methods of analysis, elements found and their range. Periodic system: PS. INAA: Instr. Neutron Activation, CNAA: Chem. Neutr. Activ., ICP-MS: Inductively Coupled Plasma Mass Spectrometry, HW: Hot wire detector, EC: EC detector, AAS: Atomic Absorp. Spectrometry.*

Element	PS group	Main method(s) of analysis	Range µg/g (except Ca)
Ca	2	INAA	35.1-40 %
Na	1	"	1300-2500
K	1	CNAA	2-90
Rb	1	INAA	2-73 E-03
Cs	1	"	0.1-1.2 E-03
Mg	2	ICP-MS	5-94
Sr	2	INAA	155-590
Ba	2	"	17-99
Sc	3	"	0.1-32 E-03
La	3	"	0.9-38 E-03
Ce	3	"	2-20 E-03
Cr	6	"	0.3-84 E-03
Mn	7	ICP-MS, INAA	80-970
Fe	8	INAA	0.1-100
Co	9	"	0.1-150 E-03
Ni	10	ICP-MS	0.9-4.9
Cu	11	"	0.8-2.4
Ag	11	INAA	0.001-3.2
Au	11	"	0.03-31 E-03
Zn	12	"	0.02-1.5
Cd	12	"	0.07-0.2
Hg	12	"	0.6-22 E-03
Al	13	AAS	5-250
Sn	14	INAA	0.1-10
Pb	14	ICP-MS	0.04-2
N	15	HW	570-7100
P	15	CNAA	30-100
As	15	INAA	0.007-1.3
Sb	15	"	0.1-16 E-03
S	16	EC	26-290
Se	16	INAA	2-40 E-03
Br	17	"	0.02-1.6

Age-dependent elements

Na (PS group 1) shows a significant decrease with increasing age of the animal (Figure 2), both in recently collected shells and in shells collected in the 1840s. This decrease can therefore not have been caused by environmental changes but is age-dependent.

On the other hand, in the ocean quahog *Arctica islandica*, Fe and Co decreased and Se increased with increased age of the animal (WESTERMARK *et al.*, 1996).

Some non-metals

SULPHUR. This element shows considerable variations, ranging from tens to hundreds of µg/g. In general, high S concentrations in W Swedish localities decline towards the north (Figure 6).

Constant or nearly constant S levels, around 50-100 μg/g, were found in shells from the River Pärlälven, N Sweden, and the River Kerjet, N Russia, both situated close to the Arctic Circle.

Shells from the highly acidified River Slereboån, W Sweden, show a clear S maximum around 1960-1970 by μ-PIXE analysis (LINDH and MUTVEI, 1990). INAA analysis at low time-resolution confirm PIXE results in shells from the same locality (Figure 3). Measurements of S fallout (GRANAT, 1989) show linear correlation to the concentration in shells (Figure 4).

Shells from the River Bollstaån, N Sweden, show S and Mn minima in the 1950s (Figure 5). Similar results were obtained in shells from the River Vattenån, N Sweden, and the River Kasenbergaån, W Sweden. These three rivers are situated in districts of forest industries (sulphate and sulphite). The minimum S concentrations in shells may be correlated with reduced production rates in forest industries during the Second World War.

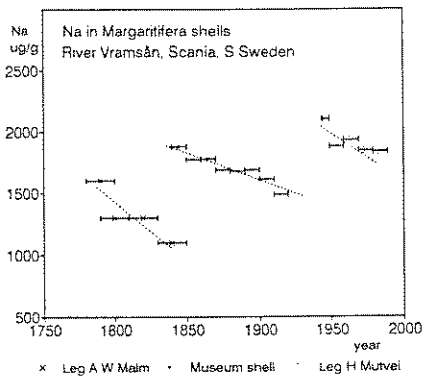

Figure 2 – Linear decrease of sodium concentrations with age in three shells, collected at different times.

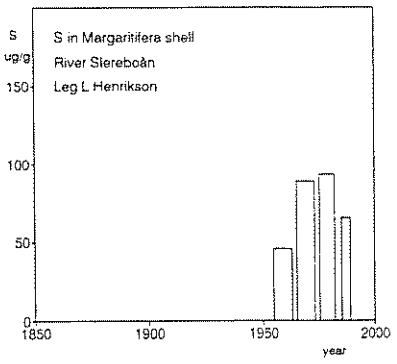

Figure 3 – Sulphur vs. time function in a shell from River Slereboån, W Sweden. Maximum load 1960-1980.

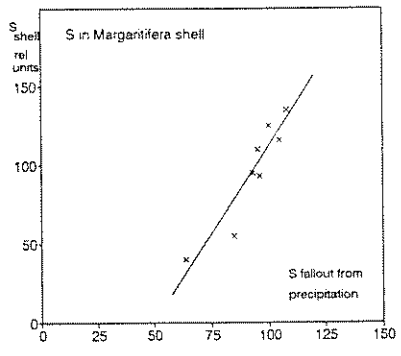

Figure 4 – Significant correlation between sulphur in shells and sulphate deposition per year 1950-1985, (data from L. Granat, Univ. of Stockholm).

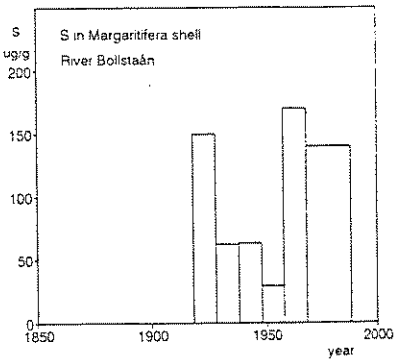

Figure 5 – Sulphur concentration in a shell from Bollstaån River, Västernorrland county, showing a minimum in 1950-60.

S fallout is generally assumed to form sulphuric acid. This causes lowering of pH and a higher solubility of Mn (DICKSON, 1980), increasing the uptake of this element into the shell.

The high level of S in W Sweden in 1960-1970 can be related to high acidification pressure by SOx, NOx and/or an increase in farming area. Changes in S concentrations along a south-north transect (Figure 6) are in reasonable agreement with changes in acidification loads (HALLBÄCKEN and POPOVIC, 1985; GRANAT, 1989; LANGNER *et al.*, 1992; FLEISCHER and KESSLER, 1993).

NITROGEN. The distribution pattern of this element is similar to that of S. Low levels at 1,000-1,400 μg/g were found in shells collected near the Arctic Circle (Figure 7). Around 1970-1980, the highest N levels occurred in W Sweden (e. g. the River Slereboån), correlating with the NOx fallout history (GRANAT 1989; WESTLING, 1992) (Figure 9).

N decrease in shells from the River Slereboån may be caused by liming of the source-lake in 1984, which resulted in higher pH and probably in denitrification of the river (Figure 8).

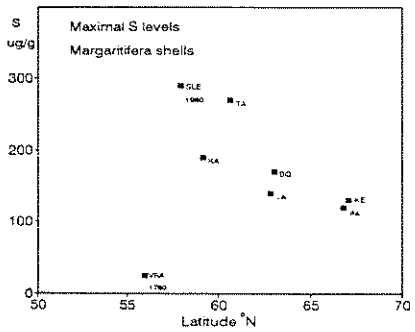

Figure 6 – Transect south-north of Scandinavia and Russia. *M.m.* localities studied using latitude as the coordinate. Maximum sulphur shell contents of the various localities show a decrease similar to that found by S-fallout and upper soil analysis.

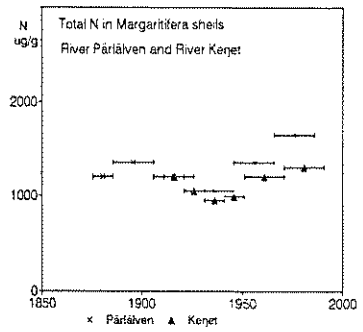

Figure 7 – N-concentrations vs. time in shells from rivers Kerjet and Pärlälven.

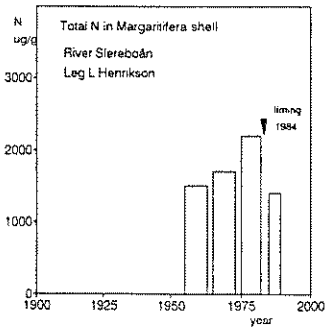

Figure 8 – Total N found in a shell from River Slereboån, S Sweden. Note the maximum level in later decades followed by a decrease after liming 1984.

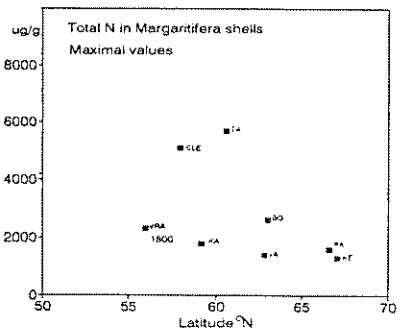

Figure 9 – Transect of Scandinavia and Russia showing concentrations of total N.

PHOSPHORUS. As indicated by μ-PIXE analysis, (LINDH and MUTVEI, 1990), P gradually decreases in shells from the River Sörkedalselva, Oslo, Norway. This was also found in shells from the River Vramsån, S Sweden. These two rivers are surrounded by farming areas upstream. It is possible that P is fixed in deep soil horizons under the influence of acid rain (HULTBERG, 1985), therefore decreasing P levels. In shells from the River Vramsån, it was possible to obtain a dose-response relation between P in the river and in the shells (Figure 10).

Other non-metals recorded in shells are: Br, Se, As, Sb, and occasionally Te.

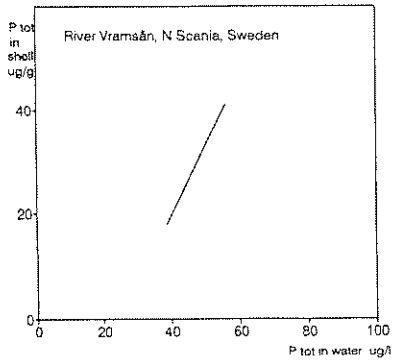

Figure 10 – P in Vransån River, S Sweden, vs. shell.

Metals which are unaffected or little affected by pH

CA, SR, BA. Ca concentration in shells is more or less constant. It decreases somewhat in connection with N increase, probably indicating higher glycoprotein levels in shells (e. g. in the River Slereboån).

Sr and Ba levels in shells are practically constant. However, μ-PIXE analysis show a marked Sr decrease (LINDH and MUTVEI, 1990) in a shell from the acidified River Slereboån after liming the source-lake in 1984. The decrease of Sr level was 30-40%, and this was confirmed by INAA analysis at low time-resolution. This element may have been depressed by high concentrations of Ca in the river after liming.

Elements affected by pH changes

FE, CO and ZN show special types of concentration curves in *Margaritifera* shells, particularly from highly acidified rivers in W Sweden. These curves are characterized by a more or less deep minima on the time axis (Figure 11). In some cases also lanthanides show similar curves. On the other hand, in shells from rivers at the Arctic Circle (Pärlälven, Kerjet, and rivers on the Kola Peninsula), these types of concentration curves are absent or indistinctly developed (Figure 12).

It is assumed here that the curves in question are formed in connection with acidification of the river system, owing to concentration changes of elements in the water. Effects of solubility-constrained elemental concentrations and their pH dependence were described by STUMM and MORGAN (1981). Solubility of Fe is dependent on a solid phase, being thermo-dynamically in equilibrium with the water phase. A clear minimum of the solubility occurs at a certain pH. Complexing agents, such as humic acids, may

shift the pH of the solubility minimum point, but these effects may not change the slopes of the curve. Co and lanthanides may follow Fe, due to co-precipitation (STUMM and MORGAN, 1981; STUMM, 1992).

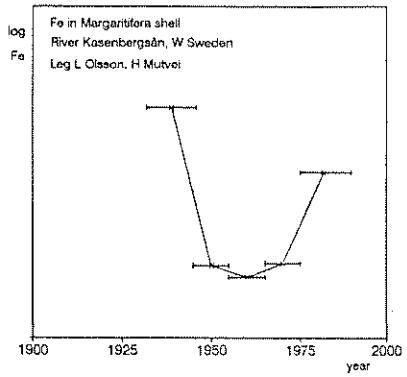

Figure 11 – Fe time function in shell.

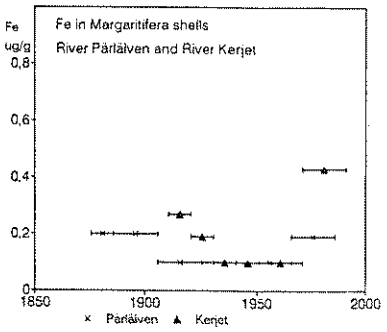

Figure 12 – Fe in shells from Rivers Pärlälven and Kerjet (Russia).

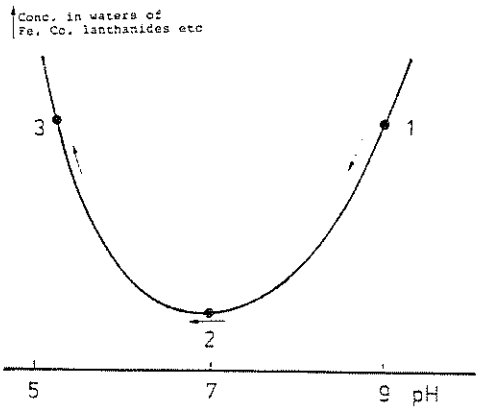

Figure 13 – A model of solubility-constrained elemental pH-dependence.

At a modest acidification rate, the solubility of Fe begins to decrease. With continuing acidification, Fe solubility reaches a minimum level and begins then to increase again, forming a cradle curve (Figure 13). This kind of curves may be used to elucidate pH levels and their changes in the past (see MUTVEI *et al.*, 1996).

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REFERENCES

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**, 1: 1-10.

DICKSON W., 1980. — Properties of acidified waters. — Proc. Int. Conf. Ecol. Impact Acid Precip., Norway, SNSF project: 75-83.

FLEISCHER S., KESSLER E., 1993. — eds of issue on acid water research, — *Ambio,* **22**, 5.

GRANAT L., 1989. — Luft- och nederbörds-kemiska stationsnätet inom PMK. Rapport från verksamheten 1989. — National Swedish Environment Protection Board. Report 3789. (In Swedish with a summary in English, see esp. fig 16).

HALLBÄCKEN L., POPOVIC B., 1985. — Markkemiska effekter av skog-smark-skalkning (Effects of forest liming on soil chemistry) in Swedish with a summary in English — Nat. Swe. Env. Prot. Board, SNV, Report 1880. (see esp. sec. 5.23).

HULTBERG H., 1985. — Changes in fish populations and water chemistry in Lake Gårdsjön and neighbouring lakes during the last century. — *Ecol. Bull.,* **37**: 64-72. (see esp. fig 9).

LANGNER J., RODHE H., CRUTZEN P. J., ZIMMERMAN P., 1992. — Anthropogenic influence on the distribution of tropospheric sulphate aerosol. — *Nature,* **359**: 712-715.

LINDH U., MUTVEI H., 1990. — Musselskal som miljökemiska arkiv – element-kartering av hög tidsupplösning (Mussel shells as ecochemical archives – element mapping of high temporal reolution) (In Swedish) — Nat. Swe. Env. Prot. Board, final report January, Contract 53 124 17-8, 53 132 37-9, 53 124 18-6: 1-14 (mimeographed).

MUTVEI H., WESTERMARK T., DUNCA E., CARELL B., FORBERG S., BIGNERT A., 1994. — Methods for the study of environmental changes using the structural and chemical information in molluscan shells. — *In:* Past and Present Biomineralization Processes. Considerations about the Carbonate Cycle. IUCN-COE Workshop, Monaco, November 1993. Doumenge F. (ed.), *Bulletin de l'Institut océanographique, Monaco*, n° spécial **13**: 163-189.

MUTVEI H., DUNCA E., TIMM H., SLEPUKHINA T., 1996. — Structure and growth rates of bivalve shells as indicators of environmental changes and pollution. — *In*: Biomineralization 93. Proceedings of the Seventh International Biomineralization Symposium. Monaco, November 1993. Allemand D., Cuif J.-P., (eds.), *Bulletin de l'Institut océanographique, Monaco*, n° spécial **14**, 4: 65-72.

STUMM W., MORGAN J. J., 1981. — Aquatic Chemistry — John Wiley N.Y. 2nd ed, 780 p.

STUMM W., 1992. — Chemistry of the solid-water interface — John Wiley N.Y., 428 p.

WESTERMARK T., CARELL B., MUTVEI H., FORBERG S., KULAKOWSKI E., 1996. — Elemental content in shells of ocean quahog *Arctica islandica* L.

(Mollusca: Bivalvia) from NW Europe as marine environmental archives — *In*: Biomineralization 93. Proceedings of the Seventh International Biomineralization Symposium. Monaco, November 1993. Allemand D., Cuif J.-P., (eds.), *Bulletin de l'Institut océanographique, Monaco*, n° spécial **14**, 4: 105-111.

WESTLING O., 1992. — Deposition och effekter av luftföroreningar i S. och M. Sverige. (Deposition and effects of air pollutants in S. and M. Sweden). — In Swedish with a summary in English-IVL report B 1079. (Swedish Environmental Research Institute, S-360 30 Lammhult, Sweden).