Isotopes
2002

The shell chemistry of *Unio crassus batavus* as tool for reconstructing the evolution of the Rhine-Meuse delta and its use as indicator for river water composition.

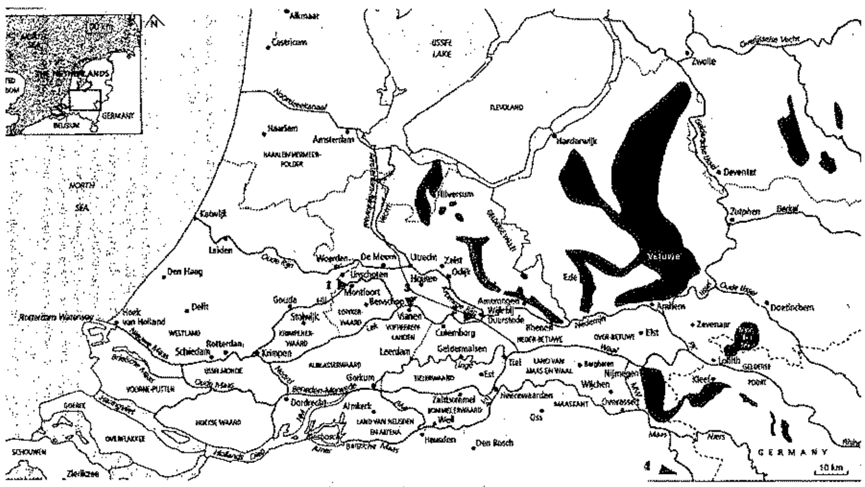

Figure 1: Recent morphology of the Rhine – Meuse delta (Berendsen et al., 2001) 1 = Montfoort, 2 = Wijk bij Duurstede, 3 = Vianen, 4 = Bergen.

During a six-month research several freshwater molluscan shells have been sampled and analysed on their isotopic signature. Using a micro-mill autosampler, shell sections have been drilled with a distance in between samples of approximately 100 µm. Dependant on growth rate this corresponds to a resolution of a week to months. Oxygen- and carbon isotopes have been measured on a Finnigan MAT 252 mass-spectrometer to determine the isotopic signal of the biogenic carbonate and to what extend this is influenced by temperature and environmental parameters.

The stable oxygen isotope profiles of the individual shells are studied for their use for distinction between Rhine and Meuse water, and moreover the determination of age and growth rate. The $\delta^{13}C$ profile reveals changes in metabolism and maturity. In the following a selection of the major findings will be presented.

Isotopic signals in the rivers of the Rhine-Meuse delta.

The rivers of this delta have a seasonal variation in the stable oxygen isotopic ratio, as can be seen in figure 2. There is a strong difference between the Rhine and Meuse. Both average isotopic ratio as well as the timing of the maximum value for $\delta^{18}O$ are characteristic for these two rivers.

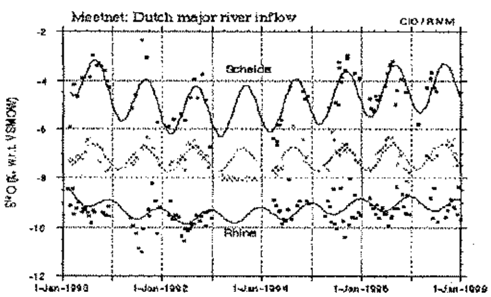

Figure 2: $\delta^{18}O$ for the Rhine, Meuse and Schelde (sampled near the Dutch border) in the period 1990-1997. (CIO/RIVM)

The Rhine river water has an average isotopic ratio of approximately –9 °/₀₀ with its maximum during winter, whereas the Meuse river water reaches its peak value for $\delta^{18}O$ during summer and has an average of approximately $\delta^{18}O$ of -7°/₀₀. The difference in average $\delta^{18}O$ value is a result of the difference in the source of their river water, which are the Swiss Alps for the Rhine and rainwater from France and the Ardennes for the Meuse. As a general rule there is a decrease in $\delta^{18}O$ of the source area with increasing distance from the sea. The causes for seasonal variation are also different for both rivers. The major events occur during the summer when for the Rhine the meltwater from the Swiss Alps lowers the $\delta^{18}O$ of the river water and for the Meuse the river water becomes more enriched in ^{18}O (higher $\delta^{18}O$) as a result of evaporation. This significant difference between the isotopic signals of the two rivers makes it possible to distinguish between Rhine and Meuse molluscs.

The Molluscs

For this study the Unio crassus batavus has been used.
Unioninae have rather thick shells especially in comparison with the Anodontinae. They have a maximum length and height of 70 mm and 40 mm respectively. They can reach an age of 15 years. Unionidae are very sensitive to pollution and fluctuations in waterchemistry (such as oxygen level) and only a salinity of up to 0.5°/₀₀ is tolerated. *Unio crassus batavus* has been collected in the past from several rivers in the Netherlands e.g. the Rhine, the Meuse and the Lek and is known to prefer streaming waters and coarse sandy sediments. Their major advantage for this research is their relative high growth rate and the fact that they life relatively long.

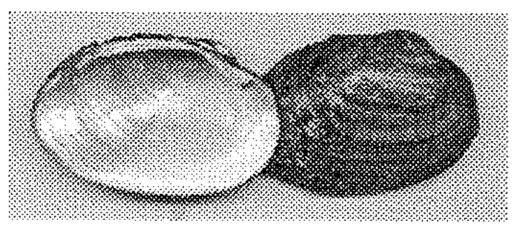

Figure 3: *Unio crassus batavus*

Major findings.

Stable oxygen isotopes.

From the results of the oxygen isotope measurement several characteristics of the $\delta^{18}O$ pattern in the mollusk shells are recognized. The major ones are the average $\delta^{18}O$ value and the seasonal variation of $\delta^{18}O$ and its dependence on river water chemistry, temperature and growth rate. The average value for $\delta^{18}O$ of the shell material from the mollusks corresponds to the average oxygen isotopic ratio of the river water in which the bivalves grew. For the Rhine specimens the $\delta^{18}O$ values have an average of – 9.1 ‰ and the bivalve collected from the Meuse showed an isotopic signal with an average of approximately – 6.5 ‰.
The results for two specimens are presented in figure 4 (a Rhine and a Meuse specimen).

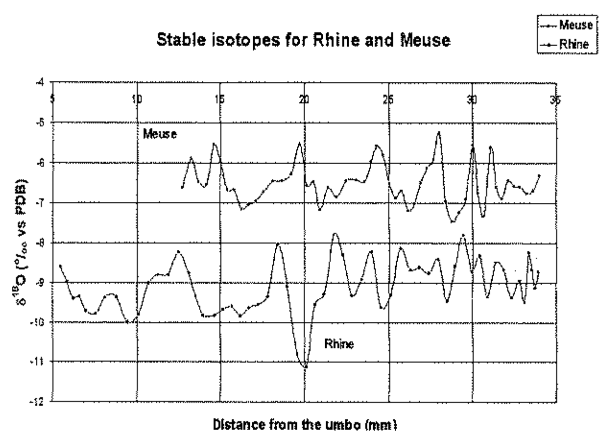

Figure 4: Combined plot of the aragonitic $\delta^{18}O$ for the molluscs from the Meuse (Bergen) and Rhine (Vianen). For the Meuse the x-axis gives correct values. For the Rhine specimen the real distances were divided by 2 to make a better fit. Note that these shells have not been precipitated simultaneously and have different growth rates.

Here it is evident that the mollusks from Rhine and Meuse have a distinct oxygen isotopic ratio. The average $\delta^{18}O$ for the Rhine specimen is significantly more negative than the average value measured in the specimen from the Meuse. This is also shown in figure 5, where the average $\delta^{18}O$ values for all specimens are presented.

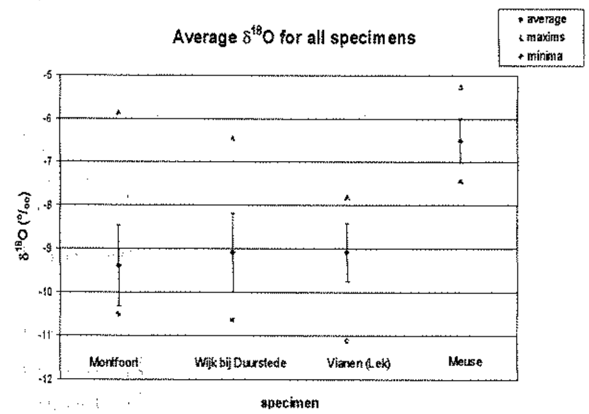

Figure 5: The average values for $\delta^{18}O$ of all specimens. The error bars give represent the SD. The maximum $\delta^{18}O$ is given by the red triangle and the green dots represent the minima.

The seasonal variation of $\delta^{18}O$ through the shell is evident and gives a lot of information about both the environment and the animal. A high growth rate, during a certain period, makes it possible to collect more samples from that part of the shell. Therefore, when the isotopic signal of the shell shows a large amount of samples with approximately equal $\delta^{18}O$ values, it can be concluded that the mollusk experienced a period of relative high growth rate, and thus excreted during the (warmer) summer period.

Consequentially, the sharp excursions result from measurements on shell material precipitated in the (colder) winter period. Using these features, the isotopic signal can be used to determine the number of years the animal has lived and the rate of growth during different years or periods of their life.
Because the seasons can be located in the isotopic pattern, it is also possible to compare the $\delta^{18}O$ signal from the shell with the $\delta^{18}O$ signal measured in river water. This has been done for both a Rhine and a Meuse specimen. In contrast to the results for the Rhine specimen the results for the $\delta^{18}O$ from the mollusk from the Meuse did not correlate with the water data. As shown in figure 6, the $\delta^{18}O$ signals for water (solid blue line) and shell (green diamonds) are exactly half a cycle out of phase. The cause for this disagreement is temperature. The well-known dependence of $\delta^{18}O$ in $CaCO_3$ on the temperature brings about the simultaneous variations in $\delta^{18}O$ in the biogenic carbonates for both rivers. The effect of temperature is so much greater than the seasonal fluctuation in the water, that both rivers have similar patterns of seasonal variations in their shell material. The bleu crosses in figure 6 illustrate this major temperature effect. These data points are calculated values for $\delta^{18}O$ with known $\delta^{18}O$ values for the water and temperature using:

$$T = 20.6 - 4.34\,(\delta O_{ar} - \delta_{W}) \qquad (1)$$

(Grossman and Ku, 1986)

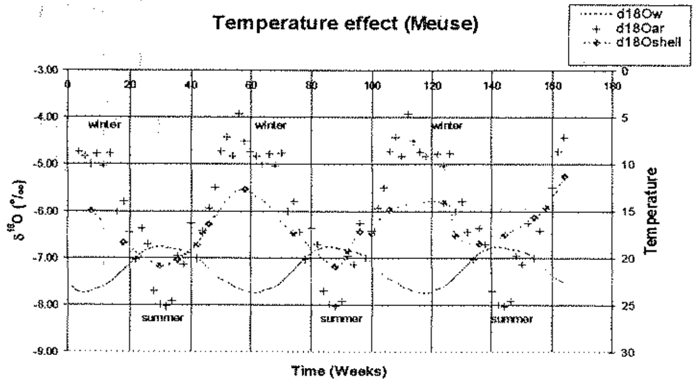

Figure 6: Temperature effect for biogenic carbonate form the Meuse. All values versus PDB. The values for $\delta^{18}O$ of river water have been measured by CIO and RIVM, and for the water temperature data from one year of temperature measurements near Eijsden is used (RIZA, waterbase). The plotted $\delta^{18}O$ for shell are the data from *Unio crassus batavus* from Vianen. Measured $\delta^{18}O$ values for the biogenic carbonate are stretched horizontally to fit in the graph.

Trace elements.

In addition to the stable isotopes also some trace elements (Ba, Mn, Fe, Mg and Sr) have been measured on all four specimens. The elements that showed the most significant patterns are Ba, Mn and Sr. The distribution of Ba in the shell has no seasonal variation. The relative high concentrations of Ba during winter periods are probably a result of increases in the Ba concentrations in the river water due to dissolution of barite from the sediment or an increased uptake of Ba by other organisms during the summer. The partition coefficient for barium is similar for the Rhine and Meuse– while the average values for Ba/Ca in the water are different for the two rivers - and has a value of approximately 0.1. This indicates a primary control of ambient water composition on the Ba content of the molluscan shells.

These distribution coefficients are calculated using the following equation.

$$(Me/Ca)_{CaCO_3} = D * (Me/Ca)_{solution} \qquad (2)$$

Another element that showed a good correlation with river water is manganese. This element also has approximately similar partition coefficients for both rivers, which is 0.54 and 0.49 for Rhine and Meuse respectively. In addition to the major influence of the river water chemistry on Mn incorporation in the shell material there is also a secondary pattern that can be recognized in the Mn profile for the mollusk from the Meuse. Here the Mn has a strong variation through the year that correlates with the oxygen level in the river.

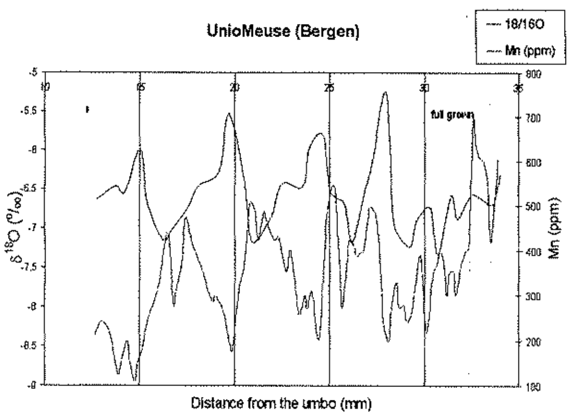

Figure 7: The $\delta^{18}O$ and Mn profile for the Unio crassus batavus from the Meuse.

This points out to a geochemical process involving the dissolution of Mn-oxides during periods of low oxigen levels resulting in a local increase in Mn. Oxygen levels in the Meuse are low during the summer and for the biogenic carbonates the Mn concentration is high during this period.

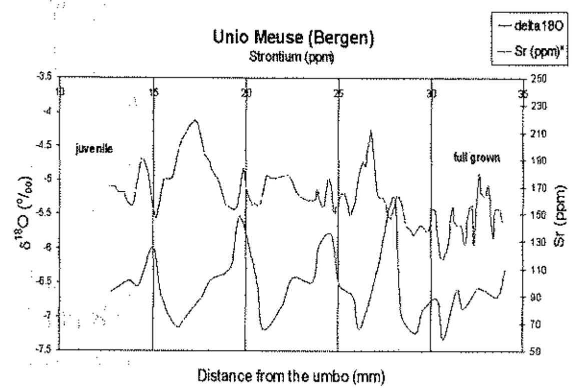

Figure 8: The Sr and $\delta^{18}O$ profile for Unio crassus batavus from the Meuse.

The major feature for Sr incorporation that is recognized during this study is the correlation with growth rate. This is most visible in the Sr profile of the mollusk from the Meuse (figure 8). Periods of high growth rates coincide with high levels of Sr in the $CaCO_3$, especially during the first year of the life of the mollusk, when the animal experiences the highest growth rate.

Conclusion

The $\delta^{18}O$ profile of the shell of *Unio crassus batavus* shows a clear seasonal variation, which is primarily influenced by water composition and temperature. The relationship between $\delta^{18}O$ of the aragonite and temperature as described by Grossman and Ku (1986) gives a very good approximation.
Maximum and minimum $\delta^{18}O$ values of both rivers are in phase but their average isotopic ratio shows an evident distinction between mollusc from the Rhine or the Meuse. Analysis of the stable oxygen isotope provides information on age and growth rate of the aragonite. For the trace elements Ba, Mn and Sr give the most information. Ba and Mn seem to correlate with the water composition and show a distribution coefficient of approx. 0.1 and 0.5 respectivelly. In addition the results also revealed a correlation between Mn incorporation and oxygen level of the river water. Low oxygen level seems to result in an elevated amount of Mn in the mollusk shell. For Sr it is evident that there is a large influence of growth rate on the coprecipitation of this element into the $CaCO_3$ lattice.

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