UNIVERSITY OF SZEGED
DOCTORAL SCHOOL OF ENVIRONMENTAL SCIENCES

THESES OF DOCTORATE (PhD) DISSERTATION

Stable isotope variations of bivalve and gastropod shells: Climatic and environmental reconstruction in the watershed of Lake Balaton

Gabriella Schöll-Barna

SUPERVISORS:

Dr. Attila Demény
and
Dr. Pál Sümegi

SZEGED
2013

Introduction and aims

Lake Balaton is the largest shallow lake in Central-Europe with an average depth of 3 m. Due to its shallow depth, this lake is sensitive to climatic variations, which makes the lake appropriate for a detailed study of environmental changes as the water level can change considerably during periods characterized by intensive evaporation or precipitation.

Geochemical and palynological investigations of sedimentary sequences in and around Lake Balaton have shown that during the history of the lake, the water level varied along with climatic fluctuations, turning into marshland several times (Cserny et al., 1995; Cserny, 2002; Nagyné Bodor és Cserny, 1998). The large-scaled picture of the climate history of Lake Balaton evolved in the last decades as a result of combined climate reconstructions based on methods such as sedimentology (Cserny, 2002; Sümegi, 2007), Ca/Mg ratio of lacustrine carbonates (Tullner and Cserny) and pollen and macrofossil analyses (Jakab et al., 2005, Sümegi et al., 2008).

Studies have shown that the stable isotope compositions of mollusk shells provide a useful tool for the reconstruction of freshwater environmental changes (Schöne et al. 2004, Jones et al., 1989). To precipitate their skeletons ($CaCO_3$), molluscs take the necessary material from the ambient water, therefore the stable isotope compositions of shell carbonate reflect the composition of ambient water (Grossman and Ku, 1986, Dettman et al., 1999). The stable isotope composition of lake water depends on the variability of climatic parameters (precipitation, evaporation and inflow). Therefore the isotope signal preserved in shell carbonate can provide detailed information about the variability of these climatic parameters.

In my thesis I completed climatic reconstructions for Lake Balaton with the results of stable isotope compositions of bivalve and gastropod shells as a new aspect. This method is unique, because - beside the large scale reconstruction -, using sampling at higher resolution, seasonal changes can be also detected.

The aims of the dissertation were:

- to study the growth patterns of *Unio pictorum* shells in order to narrow the period represented by the stable isotope signal
- the interpretation of stable isotope composition of recent *Unio* shells from Lake Balaton.
- to investigate the impact of climatic parameters on stable isotope variability of lake water in order to better understand the climatic signals in $\delta^{18}O_{shell}$ record. Adaptation

of the isotope mass balance model (Gat and Levy, 1978) for Siófok basin of Lake Balaton.

- to study the impact of extreme wet and dry conditions on the stable isotope compositions of lake water and shell carbonate.
- application of the method on *Unio* shells derived from archaeological excavations to investigate past climate changes in the Late Copper Age (Balatonkeresztúr-Réti-dűlő and Balatonőszöd-Temetői-dűlő) and Bronze Age (Ordacsehi Bugaszeg and Kistöltés).
- analyses of stable isotope compositions *Pisidium* and *Valvata* shells from lacustrine core of Balatonederics I. to create a 10 kyr climate reconstruction and compare the results with reconstructions based on other method sedimentology and macrofossils.
- to interpret the stable isotope variation of *Valvata* gastropod shells from Sárkeszi I. core and to investigate the climatic and hydromorphological effects.

Material and Methods

In order to determine how climate conditions can be reflected by the stable C and O isotope compositions of *Unio* shells, lake-dwelling *Unio pictorum* shells were collected at Siófok, Balatonszéplak and Tihany from the Lake Balaton. In total 279 carbonate samples were taken from 6 shells for the stable isotope analyses. Beside the isotope composition of shells, the $\delta^{18}O$ of lake water, precipitation and river runoff (Zala and Nyugati-övcsatorna) were also measured to complete the existed $\delta^{18}O$ time series (by courtesy of Tibor Cserny) for the period of 2006-2010. An isotope mass balance model was constructed using these data as well as monthly averages of evaporating moisture $\delta^{18}O$. The latter input parameter could not be measured directly, therefore had to be calculated for the period 1999-2008 using the Craig and Gordon model (1965).

Prehistoric shells of Late Copper and Bronze Ages are derived from the sites of Balatonkeresztúr-Réti-dűlő, Balatonőszöd-Temetői-dűlő, Ordacsehi-Bugaszeg and Ordacsehi-Kis-töltés which were processed between 2003 and 2004 within the framework of preventive excavations along the M7 highway. From the archaeological objects, 693 samples (32 *Unio* shells) were measured in order to reconstruct the past climate conditions that determined the life of the local ancient cultures.

Beside the reconstructions the climate parameters that prevailed in short time scales, longer-scaled changes of environmental conditions were studied using stable isotope compositions of bivalves (*Pisidium*) and gastropod (*Valvata*) shells from the Balatonederics I. and Sárkeszi I. cores. In total, 142 carbonate samples were measured for the large scaled reconstructions.

The shells used in the study (*Unio, Pisidium* and *Valvata* sp.) are aragonitic. Aragonitic shells are prone to alteration to calcite, which enhances fluid-carbonate isotope exchange (Pingitore, 1982). The possibility of aragonite-calcite conversion was checked for all specimens using cathodoluminescence (CL) microscopy. Cathodoluminescence analyses were conducted using a Reliotron-type cold-cathode equipment attached to a Nikon Eclipse E600 optical microscope with a Nikon Coolpix 4500 digital camera. Aragonite samples showed green luminescence, whereas calcite is indicated by orange CL colour. Only pure aragonite samples were used for further analyses.

Contaminations from the shell surfaces were mechanically removed and the smooth carbonate surfaces were treated with sodium hypochlorite. In case of recent and archaeological *Unio* shells, the carbonate samples (150-200 μg) were drilled equidistantly, using a 0.6 mm tip dental drill following the maximum width of the shell (i.e. highest growth rate). The cleaned and treated *Pisidium* and *Valvata* shells (derived from the cores) were dried and milled.

The stable oxygen and carbon isotope compositions of drilled and milled carbonate samples and the stable oxygen isotope composition of collected samples of lake-, river water and precipitation were measured using an automated GASBENCH II sample preparation device attached to a Thermo Finnigan Delta Plus XP mass spectrometer at the Institute for Geological and Geochemical Research. The stable isotope compositions are expressed as $\delta^{13}C$ and $\delta^{18}O$ values in ‰ relative to international standards,

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \cdot 1000 ,$$

where R is the $^{13}C/^{12}C$ or $^{18}O/^{16}O$ ratio (McKinney et al. 1950), and the standards are V-PDB and V-SMOW for carbonate and water samples respectively (Coplen 1996).

The stable isotope measurements were financially supported by the Hungarian Scientific Research Fund (OTKA-68343).

New scientific results

1. Based on comparisons of measured and calculated $\delta^{18}O$ data of recent shells, it is assumed that in Lake Balaton the growth cessation of *Unio pictorum* presumably happens below 12.7-13 ˚C. During summer, temporary pause of shell formation can occur caused by elevated water temperature (26-28 °C) (Schöll-Barna et al., 2012).

2. Using an isotope mass balance model, I tested the hypothesis that the $\delta^{18}O$-variability of lake water at Siófok basin can be described as a result of the combined effects of three main climatic parameters such as precipitation, evaporation and river runoff. Based on the modelled-measured $\delta^{18}O$ comparisons, moderate isotope stratification can be assumed during spring and autumn (Schöll-Barna, 2011).

3. I used the mass balance model to present the effect of precipitation and evaporation on shell $\delta^{18}O$. I determined the relationship between intra-shell $\delta^{18}O$-variability and precipitation amount (precipitation/evaporation ratio) which allows to make a quantified prediction of meteorological parameters affecting the oxygen isotope composition of shell carbonate (Schöll-Barna, 2011).

4. I completed the modelled period with studying years characterized by extreme conditions (2002–2003 dry and 2010 wet). I observed significant correlations between the shell oxygen isotope composition and meteorological parameters (precipitation amount, change in natural water budget etc.). Based on the results it has been established that the isotope compositions of shell carbonate reflect the climatic variations (Barna et al., 2007; Schöll-Barna, 2011; Schöll-Barna et al., 2012).

5. The stable isotope compositions of archaeological shells indicated that during the Late Copper Age the mild climate was interrupted by a short wet period around 5310 cal yr BP (related to transitional subphases between Boleráz and Early Classic subphases of Baden culture at the Balatonkeresztúr-Réti-dűlő site). The significant shifts to lower $\delta^{13}C$ and $\delta^{18}O$ values and large intra-shell amplitudes of *Unio* shells from suggested the effect of increased precipitation (Schöll-Barna et al., 2010, 2012).

6. Information on Bronze Age climate was based on stable isotope compositions of *Unio* shells from Ordacsehi–Bugaszeg and Kis-töltés sites. Based on a positive shift in $\delta^{13}C$ and $\delta^{18}O$ values in shell from early to Middle Bronze Age a dry climate can be assumed in the time of the Somogyvár-Vinkovci and Kisapostag culture, while the remarkable shift in $\delta^{18}O$ values indicate a considerable change during the Middle Bronze Age (related to Encrusted Pottery culture in Ordacsehi sites, 3668 ± 72 cal. BP). The strong isotopic change may have been caused by significant increase in precipitation that caused change in the local environment, but other (non-climatic factors, such as changes in fishery habits) should also be taken into account.

7. Based on the variability of the stable isotope compositions of *Pisidium* and *Valvata* shells from Balatonederics I. core, wet and dry periods during the last 15000 yr can be distinguished at a 100-200 year resolution.

8. Beside interpretation of stable isotope variability of *Pisidium* and *Valvata* shells from the Balatonederics I. core, the zoological approach of the stable isotope differences between the species and the $\delta^{18}O$-$\delta^{13}C$ correlation analyses provided new aspects of the results. Based on the diversity of isotope data of the two studied species (*Pisidium* bivalve and *Valvata* gastropod) due to their different habitat, periods characterized by shallow water level and elevated dissolution of organic material can be assumed. The representation of the $\delta^{18}O$-$\delta^{13}C$ correlations provided information about the past hydrological characteristic of the lake.

9. The variability of stable isotope composition of *Valvata* shells from the Sárkeszi I. core supported the fluvial-lacustrine hydrological change (confirmed by sedimentological observations of Sümegi P.). According to the stable isotope data, following the evolved lake, the environment formed by climatic effect. This supported by a good correlation between the isotope data of Sárkeszi I. and Balatonederics I. cores for the period.

References

Coplen, T.B. (1996): New guidelines for reporting stable hydrogen, carbon and oxygen isotope ratio data. Geochimica et Cosmochimica Acta 60: 3359-3360.

Craig, H., Gordon, L.I. (1965): Deuterium and oxygen-18 variations in the ocean and the marine atmosphere. In E. Tongiorgi (ed.): Stable Isotopes in Oceanographic Studies and Paleotemperatures. Lab. Geol. Nucl., Pisa pp. 1-122.

Cserny, T. (2002): A balatoni negyedidőszaki üledékek kutatási eredményei. Földtani Közlöny 132 különszám: 193-213.

Cserny, T., Hertelendi, E., Tarján, S. (1995): Results of isotope-geochemical studies in the sedimentological and environmental geologic investigations of Lake Balaton. Acta Geologica Hungarica 38: 355-376.

Dettman, D. L., Reische, A. K., Lohmann, K. C. (1999): Controls on the stable isotope composition of seasonal growthbands in aragonitic fresh-water bivalves (Unionidae). Geochimica et Cosmochimica Acta 63: 1049-1057.

Gat, J.R., Levy, Y. (1978): Isotope hydrology of inland sabkhas in the Bardawil area. Sinai. Limnology and Oceanography 23: 841-850.

Grossman, E.L., Ku, T.L. (1986): Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects. Chemical Geolology (Isotope Geoscience Section) 59: 59-74.

Jakab, G., Sümegi, P., Szántó, Zs. (2005): Késő-glaciális és holocén vízszintingadozások a Szigligeti öbölben (Balaton) makrofosszília vizsgálatok eredményei alapján. Földtani Közlöny 135(3): 405-431.

Jones, D.S., Arthur, M.A., Allard, D.J. (1989): Sclerochronological record of temperature and growth from shells of *Mercenaria mercenaria* from Narragansett Bay, Rhode Island. Marine Biology 102: 225-234.

McKinney, C.R., McCrea, J.M., Epstein, S., Allen, H.A., Urey, H.C. (1950): Improvements in Mass Spectrometers for the Measurement of small differences in isotope abundance ratios. Review of Scentific Instruments 21: 724-730.

Nagyné Bodor, E., Cserny, T. (1998): A balatoni öblök vízborítottságának összehasonlító fejlődéstörténete a palynológiai vizsgálatok eredményei alapján. Hidrológiai Közlöny 78(5-6): 360-363.

Pingitore, N.E. (1982): The role of diffusion during carbonate diagenesis. Journal of Sedimentary Petrology 52:27-39.

Schöne, B.R., Dunca, E., Mutvei, H., Norlund, U. (2004): A 217-year record of summer air temperature reconstructed from freshwater pearl mussels (*M. margarifitera*, Sweden). Quaternary Science Reviews 23(16-17): 1803-1816.

Sümegi, P. (2007): Üledékgyűjtő medencék környezettörténeti vizsgálata. In: Magyarország negyedidőszak végi környezettörténete. MTA doktori értekezés. Szeged-Budapest, pp. 373-389. (in hungarian)

Sümegi, P., Gulyás, S., Jakab, G. (2008): Holocene Paleoclimatic and paleohydrological changes in Lake Balaton as inferred from a complex quantitative environmental historical study of a lacustrine sequence of the Szigliget embayment. Documenta Praehistorica 35: 33-43.

Tullner, T., Cserny, T. (2003): New aspects of lake-level changes, Lake Balaton, Hungary. Acta Geologica Hungarica 46(2): 215-238.

Publications

List of publications concerning the topic of the dissertation

Schöll-Barna, G., Demény, A., Serlegi, G., Fábián, Sz., Sümegi, P., Fórizs, I., Bajnóczi, B. 2012. Climatic variability in the Late Copper Age: Stable isotope fluctuation of prehistoric Unio pictorum (Unionidae) shells from Lake Balaton (Hungary). Journal of Paleolimnology 47: 87-100.
$IF_{(2012)}$: 1,898

Schöll-Barna, G. (2011). An isotope mass balance model for the correlation of freshwater bivalve shell (Unio pictorum) carbonate $\delta^{18}O$ to climatic conditions and water $\delta^{18}O$ Lake Balaton (Hungary). Journal of Limnology. 70(2): 272-282.
$IF_{(2011)}$: 1,207

Schöll-Barna, G., Demény, A., Serlegi, G., Fábián, Sz., Sümegi, P., Fórizs, I., Cserny, T. (2010): Seasonal fluctuations in the Copper Age: stable isotope record of molluscan shells (Balaton region, Hungary). In: André L, Dehairs F, Mas R, Planchon F, Versteegh E (ed.): Bivalves Biomineralisation Archival Potential and Proxy Incorporation. The Royal Flemish Academy of Belgium for Science and the Arts. pp. 59-63.

Schöll-Barna G. (2012): A lelőhely kagylóhéjainak stabilizotóp-geokémiai elemzése In: Horváth T (ed.) Balatonőszöd–Temetői dűlő őskori településrészei: a középső rézkori, késő rézkori és kora bronzkori települések Budapest: MTA BTK Régészeti Intézete, 2012. pp. 365-370. (ISBN:978-615-5254-00-0)

Barna G., Fórizs I. (2007): A Balaton stabil-izotóp-hidrológiai karakterisztikája. Térbeli eloszlás és a párolgási izotóp-effektus. Hidrológiai Közlöny. 87. 2. pp 35-51.

Barna G., Cserny T., Fórizs I. (2007): Balatoni kagylóhéjak (*Unio pictorum* Linné) stabilizotópos vizsgálata. Hidrológiai Közlöny. 87. 6. pp 17-19.

Bajnóczi, B., **Schöll-Barna, G.**, Kalicz, N., Siklósi, Zs., Hourmouziadis, G., Ifantidis, F., Kyparissi-Apostolika, A., Pappa, M., Veropoulidou, R., Ziota, C. (2013): Tracing the source of Late Neolithic Spondylus shell ornaments by stable isotope geochemistry and cathodoluminescence microscopy. Journal of Archaeological Science 40:(2) pp. 874-882. (2013)
$IF_{(2012)}$: 1.914

Demény, A., **Schöll-Barna, G.,** Sümegi, P., Sipos, P., Balázs, B.R. (2011): Sedimentary change vs. climate signals in bivalve shell and bulk rock compositions in a Late Pleistocene to Early Holocene fluvial section at Körösladány, SE-Hungary. Central European Geology 54(1-2): 167-173.

Demény, A., **Schöll-Barna, G.**, Sümegi, P., Sipos, P., Fórizs, I., Balázs, B.R., Bajnóczi, B., Cook, G. Stable isotope composition of bivalve shells and bulk sediments in a 5-20 ky fluvial section at Körösladány, SE-Hungary: Sedimentary changes vs. climate signals. Central European Geology. In press

Demény, A., **Schöll-Barna, G.**, Siklósy, Z., Bondár, M., Sümegi, P., Serlegi, G., Fábián, Sz., Fórizs, I. (2010): Az elmúlt ötezer év éghajlatváltozási eseményei a Kárpát medencében és társadalmi hatásaik. Klíma-21 Füzetek. 59. pp. 82-95.

Kalicz, N., Siklósi, Zs., **Schöll-Barna, G.**, Bajnóczi, B. (2010): Aszódi-Papi-földek késő neolit lelőhelyen feltárt kagylóékszerek származási helyének meghatározása stabilizotóp-geokémiai módszerrel In: Kreiter Attila, Pető Ákos, Tugya Beáta (ed.) Környezet – Ember – Kultúra: Az alkalmazott természettudományok és a régészet párbeszéde [Environment – Human – Culture: Dialogue between applied sciences and archaeology] Budapest: Magyar Nemzeti Múzeum Nemzeti Örökségvédelmi Központ, 2010. p. 45. (ISBN:978-963-88584-8-1)

Serlegi G, Fábián Sz, Daróczi-Szabó M, **Schöll-Barna G.**, Demény, A. (2012): Éghajlati és környezeti változások a késő rézkor folyamán a Dunántúlon In: Kreiter Attila, Pető Ákos, Tugya Beáta (ed.) Környezet – Ember – Kultúra: Az alkalmazott természettudományok és a régészet párbeszéde [Environment – Human – Culture: Dialogue between applied sciences and archaeology] Budapest: Magyar Nemzeti Múzeum Nemzeti Örökségvédelmi Központ, 2012. pp. 139-150. (ISBN:978-963-88584-8-1)

Demény, A., Bajnóczi, B., Kele, S., Fórizs, I., **Barna, G.**, Siklósy, Z. (2009): Stable isotope analysis of carbonatic ornaments from the Late Copper age cemetery at Budakalász In: Bondár M, Raczky P (ed.) The Copper Age cemetery of Budakalász Budapest: Pytheas, 2009. pp. 437-447. (ISBN:978-963-9746-72-5)

Demény, A., **Schöll-Barna, G.**, Fórizs, I., Osán, J., Sümegi, P., Bajnóczi, B. Stable isotope composition and trace element concentrations in freshwater bivalve shells (*Unio* sp.) as indicators of environmental changes at Tiszapüspöki, Eastern-Hungary. Under review.

Additionally 1 popular science publication and 15 conference abstracts.