Estonian Journal of Earth Sciences, 2019, **68**, 1, 37–44 https://doi.org/10.3176/earth.2019.05

Sclerochronology-based geochemical studies of bivalve shells: potential vs reality

Michael Zuykov and Michael Schindler

Harquail School of Earth Sciences, Laurentian University, Sudbury, Ontario P3E 2C6, Canada; michael.zuykov@yahoo.com

Received 8 October 2018, accepted 3 February 2019, available online 28 February 2019

Abstract. Since the early 1980s, attempts to develop a method for the retrospective estimation of water chemistry have been increasingly discussed in terms of bivalve sclerochronology. Although the problem with the interpretation of chemical data from shell growth patterns remains unsolved and a method, or at least its concept, has never been proposed, the optimism about the potential of the bivalve shell as a possible tool in retrospective environmental monitoring has reached the apogee nowadays. Here, we provide a review of the changes in the conceptual framework of the bivalve sclerochronology during more than thirty-five years of studies in the field, together with the analysis of the meaning of the key term 'sclerochronology'. The new term, 'sclerochronochemistry' (*skleros* – hard, *chronos* – time, and *chemistry*), is proposed in order to fill a gap between sclerochronology and sclerochemistry.

Key words: sclerochronology, sclerochemistry, sclerochronochemistry, bivalve shell, aquatic pollution, environmental monitoring, Mussel Watch.

INTRODUCTION

The recent review papers by Binelli et al. (2015) and Beyer et al. (2017) provide an updated overview of ecotoxicological and pollution monitoring studies of the main freshwater and marine biomonitors, i.e., the zebra mussel (*Dreissena polymorpha* (Pallas)) and blue mussel (*Mytilus edulis* L.), respectively. These studies mentioned neither the term 'sclerochronology' nor 'sclerochemistry', because monitoring programmes (e.g., Mussel Watch) normally use only the soft tissues of bivalves.

In a more recent review, Butler et al. (2019, p. 431) 'have described and assessed some of the most notable proven applications of bivalve sclerochronology in ecosystem, environmental, cultural, and climate services'. They, in particular, noted (Ibid, p. 421):

> Bivalve shells can provide a tool for present and retrospective monitoring, establishing pre-impact environmental baselines, and allowing the reconstruction of marine and freshwater environments that range from estuaries to the deep-sea (e.g. Schöne and Krause 2016; Steinhardt et al. 2016; [refs: 3 papers]).

Therefore, we agree completely with Schöne & Krause (2016, p. 230) who noted: 'Mussel Watch community largely neglected the potential of bivalve shells in providing high-resolution, chronologically aligned archives of environmental variability.'

The main goal of this review is to answer the question – what if the problem is not merely the absence of communication between Mussel Watch and sclerochronology communities (as, in particular, noted by Schöne & Krause 2016), but because the potential remains unrealized and it has no clear strategy to be realized? For this purpose, we also demonstrate that the established practice in part of terminology within sclerochronology communities might inhibit the navigation in literature, paper preparation and lead to confusion among new researchers. Here we propose the new term, 'sclerochronochemistry' (*skleros* – hard, *chronos* – time, and *chemistry*), in order to fill a gap between two key terms, sclerochronology and sclerochemistry.

REMARKS ON TERMINOLOGY

Background

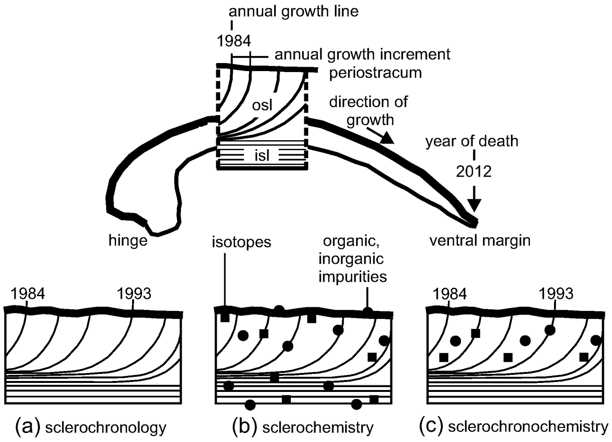
Analysis of variation in shell growth patterns (1) and measurement of elements/isotopes in shell section (2) represent independent scientific tasks. Described as (1) 'sclerochronology' (Buddemeier et al. 1974) and (2) ‘sclerochemistry’ (Gröcke & Gillikin 2008), these approaches require different equipment and methods, e.g., (for 1) optical or electron microscopy, and (for 2) laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) or micromill sampling together with ICP-MS/stable isotope ratio mass spectrometry. Here we highlight the sclerochronological approach because there are two different interpretations of the term ‘sclerochronology’ which are in obvious conceptual collision as noted below.

(i) The original definition by Buddemeier et al. (1974, p. 196) is as follows:

> We had originally hoped that seasonal variations in the amount of colony growth would prove to be correlated between colonies and with some environmental observations. This would not only help to explain external controls over the growth and distribution of corals, but would also permit their use as environmental recorders. Similar potentials have already been realized in the case of dendrochronology (Fritts 1971); an analogous approach to the study of growth patterns in calcareous exoskeletons or shells could be designated sclerochronology.

This definition well shows the possible application/potential of sclerochronology whereas the core of the term itself (i.e., object/content of study) was only outlined as ‘seasonal variations in the amount of colony growth’ and ‘growth patterns in calcareous exoskeletons or shells’. Therefore, the right way to understand precisely the authors’ position is to analyse the meaning of the term ‘dendrochronology’ as it was used in ‘Fritts (1971)’, i.e., in Fritts et al. (1971). That paper deals with a correlation of well-dated ring-width chronologies of trees from western North America and climatic and hydrologic parameters in the environment as shown in climatic maps. It is absolutely clear that chemical analyses of elements/isotopes in trees rings have not been performed by Fritts et al. (1971). Consequently, it becomes obvious that the sclerochronology (i.e., sclerochronology *s.s.*), as it was originally defined by Buddemeier et al. (1974), lacks a chemical aspect (Fig. 1a).

(ii) The common opinion in the sclerochronology communities, as summarized by Oschmann (2009, p. 1), is that ‘Sclerochronology is the study of physical and chemical variations in the accretionary hard tissues of organisms, and the temporal context in which they formed.’ This definition is not that of Oschmann, but reflects the established practice in the sclerochronology community where this point of view tends to dominate (e.g., Gröcke & Gillikin 2008; Andrus 2011; Helmle & Dodge 2011; Schöne & Gillikin 2013; Schöne & Krause 2016; Steinhardt et al. 2016).



(a) sclerochronology (b) sclerochemistry (c) sclerochronochemistry

Fig. 1. Schematic cross section of a bivalve shell with block schemes showing (a) sclerochronological, (b) sclerochemical and (c) sclerochronochemical approaches. Shell layers: outer shell layer (osl) and inner shell layer (isl).

According to all the authorities mentioned above, there is clearly sclerochronology *sensu stricto* and *sensu lato*. In addition, difficulty arises with the related term, ‘sclerochemistry’, defined by Gröcke & Gillikin (2008, p. 266) as ‘a sub-discipline of sclerochronology, be used to describe solely geochemical (isotopic or elemental) studies of the hard tissues of organisms’. Figure 1b illustrates that the measurement of elements/isotopes in shell (in section and on surfaces) without time-related aspect belongs to the competence of sclerochemistry.

Although this ‘terminological diversity’ has been repeatedly discussed (e.g., Gröcke & Gillikin 2008; Thomas 2015; Twaddle et al. 2016), no attempts have been made to revise it. The artificial nature of sclerochronology *s.l.* was noted by Twaddle et al. (2016, p. 360):

> While the term was originally coined by Buddemeier et al. (1974) and Hudson et al. (1976) in reference to the study of density bands in stony head coral, its definition has since broadened to encompass a variety of physical and geochemical techniques (Oschmann 2009).

Here, the authors have shown flexibility in the application of the terminology. In particular, Prendergast & Schöne (2017, pp. 33, 45) mentioned: ‘A sclerochronological approach can therefore be used to pre-screen limpet shell sections before geochemical sampling’, ‘A combined stable isotope and sclerochronology sampling approach has revealed that major growth lines coincide with the lowest $\delta^{18}O_{shell}$ values at all study sites’, whereas, in a paper issued simultaneously they have used sclerochronology *s.l.* (Prendergast et al. 2017, p. 2): ‘The study of the structure and chemistry of the incrementally deposited hard parts of organisms is known as sclerochronology.' Some authors consider sclerochronology *s.s.* and sclerochemistry as independent approaches, but avoided to use both terms together as evidenced by the following titles of papers: 'Sclerochronology and geochemical variation in limpet shells …' by Fenger et al. (2007), 'Combined sclerochronologic and oxygen isotope analysis of gastropod shells …' by Schöne et al. (2007), 'Bivalve sclerochronology and geochemistry' by Schöne & Surge (2012). Interestingly, Butler & Schöne (2017, p. 296) in their editorial/review paper on sclerochronology do not mention a prospective way (or ways) of shell characterization under the first appearance of the key term in the text: 'Sclerochronology (Hudson et al. 1976), the study of periodically layered archives (including mollusc shells, corals and fish otoliths), …'. Nevertheless, Hudson et al. (1976, p. 362) defined the term in a more clear manner, i.e., as 'sclerochronology *s.s.*': 'sclerochronology, the relatively new study of density bands in stony corals, …'.

So the main problem is that the implied agreement within sclerochronology communities about understanding and use of the term 'sclerochronology *s.l.*' is not sufficient to avoid confusion among new 'external users' of the sclerochronological approach. Moreover, they will need an overload of papers by extended remarks on terminology; this differentiation also plays critical importance for navigation in literature and in the framing of correct titles and key words for new papers. Simply, it is not clear why it is necessary to expand the concept of 'sclerochronology *s.l.*' and neglect the use of the terms 'sclerochronology *s.s.*' and 'sclerochemistry' although they have been successfully used for different tasks by many authors (e.g., Karney et al. 2011; Huck & Heimhofer 2015).

New term – 'sclerochronochemistry'

The term 'sclerochronochemistry' (*skleros* – hard, *chronos* – time, and *chemistry*) is proposed here for complex twin studies of the bivalve shell (and accretionary hard tissues of some other organisms, e.g., shells of gastropods, corals, fish otoliths): (1) characterization of growth history (i.e., sclerochronology *s.s.*), (2) identification and quantification of any impurities (i.e., organic, heavy metals, radionuclides, etc.) or isotopes (carbon, oxygen, nitrogen) in accordance with established successional growth patterns (Fig. 1c). The main scientific basis for sclerochronochemistry is that the behaviour and fate of impurities in the organism's microenvironment, e.g., incorporation into the shell, is under strong physiological (biological) control (e.g., Carroll & Romanek 2008; Schöne 2008; Wanamaker & Gillikin 2018). Accordingly, external and internal shell surfaces should be excluded from potential sampling zones of shell material when the sclerochronochemical approach is applied.

PROMISE – POTENTIAL – PARADIGM

The conceptual framework of bivalve sclerochronochemistry (= sclerochronology *s.l.*) is rife with promises and expectations about the use of bivalve shells as geochemical archives. This is illustrated in the pioneering papers on this topic:

> Use of hard parts of bivalves as recorders of environmental levels of metals is clearly promising, but before this can be done reliably further research must be carried out on the effects of major variables on the concentration of chemical elements in shell [refs]. (Carriker et al. 1982, p. 235)

> The present study indicates that shells of living mussels, together with museum or subfossil shell material may be used to date environmental changes caused by natural events and large-scale industrial, agricultural or nuclear contamination. (Carell et al. 1987, p. 2, abstract)

> The concentrations detected in the annual increments may therefore reveal environmental time sequences, i.e. constitute valuable archives of the present and past. Before a reliable method is established it is necessary to demonstrate that the bivalves behave as benign "samplers". (Ibid, p. 2)

Over thirty years later Schöne & Surge (2014, p. 21) pointed out that 'The potential [authors: potential No. 1] of bivalve sclerochronology [authors: sclerochronochemistry] in the fields of archeology and anthropology, evolution, retrospective environmental monitoring, and ecology is still waiting to be fully exploited'. More recently, Schöne & Krause (2016) reviewed the state of the art of bivalve sclerochronochemistry with respect to its application in the Mussel Watch monitoring programme. They suggested that:

> Mussel Watch could greatly benefit from the potential [authors: potential No. 2] of bivalve shells in providing high-resolution, temporally aligned archives of environmental variability. (Schöne & Krause 2016, p. 228, abstract)

> Bivalve sclerochronology provides an enormous potential [authors: potential No. 1] for adding a historical perspective to the Mussel Watch and the techniques outlined below should be strongly considered as an important complement to existing biomonitoring initiatives. (Ibid, p. 230)

Because potentials No. 1 and No. 2 are closely related, we have combined them into a single ‘potential’ hereafter. According to the *Oxford English Dictionary* (Stevenson & Brown 2007, p. 2303), the noun ‘potential’ means ‘That which is possible as opp. to actual; a possibility’; the electronic version of the *Oxford Dictionary* (https://en.oxforddictionaries.com) gives a longer version: ‘Latent qualities or abilities that may be developed and lead to future success or usefulness’. Hence, it allows us to propose that the ‘potential’, at least partly, has already been applied (i.e., been realized) in different science disciplines, in particular, in aquatic pollution studies. Consequently, after reading the review papers by Schöne & Krause (2016), Steinhardt et al. (2016) and Butler et al. (2019) which report on the ‘potential’, and some further optimism (*1*), bivalve sclerochronochemistry looks like a very attractive topic for new researchers to invest time and money.

> *1.* In addition, the annual banding pattern in shells can provide an absolute chronometer of environmental variability and/or industrial effects. (Steinhardt et al. 2016, p. 1, abstract)
>
> The range of applications based on sclerochronology now offers a wide and increasing repertoire of techniques for monitoring natural and anthropogenic environmental variability and distinguishing between them, with applications to a broad range of commercial and regulatory users [Fig.]. (Ibid, p. 19)

With that said, the ‘potential’ represents the linguistic transformation of the promises and expectations which are based on a clear scientific base – i.e., bivalves incrementally and sequentially precipitate the calcium carbonate shell with elements derived from the ambient environment. Besides, for attempts of sclerochronology communities for over thirty-five years to develop a ‘method’ (retrospective estimation of water chemistry) on the basis of the ‘potential’, we can make already use of the category ‘paradigm’ that implies the ‘way of thinking’.

One of the factors that support the above-mentioned paradigm is the misleading contextualization that often is presented in introductory and concluding parts of papers on this topic. One such case, from a very recent paper, is the subject of our short analysis:

> Bio-mineralized carbonate skeletal materials such as mussel shells and corals have a long history of producing accurate, high resolution information about past water chemistry [refs: 5 papers]. Specifically, metal-calcium and oxygen isotope ratios are useful for reconstructing changes in both water chemistry and temperature in ocean systems [refs: 4 papers]. (Geeza et al. 2018)

The citation transmits a positive (or at least quite optimistic) message about the ‘potential’. In fact, scrutiny of the referred papers should be able to confirm these results, i.e., ‘producing accurate, high resolution information about past water chemistry’ with mussel shells. In attempts to confirm these findings, we checked all the papers mentioned above. Only two of them (Gillikin et al. 2006; Goodwin et al. 2013) dealt with bivalve shell and chemical elements, and considered the only barium/calcium ratios in two bivalves species collected from several sites in the San Francisco Bay (USA) and Oosterschelde estuary (The Netherlands). In this regard, Gillikin et al. (2006, p. 395) noted:

> Unlike corals and foraminifera, much of the bivalve data presented suggests that many of these elemental profiles (e.g., Sr, Mn, Pb, U), which often largely differ from expected concentrations based on inorganic and other biogenic carbonates, cannot be used as proxies of environmental conditions [refs]. There have been some promising reports of bivalve shell Mg/Ca ratios as a proxy of sea surface temperature (SST) [ref.], but other reports illustrate that this is not always the case, and is apparently strongly species specific [refs].

We use this example not because we are arguing against the ‘potential’, but because the specific context should be used properly both for the convenience of other scientists and to avoid confusing conceptual constructs when such simple logic, as applied above, is used.

REALITY

Metal detection in bivalves, i.e., in soft tissues and/or in a whole shell, is frequently applied in ecotoxicological research (for references see Zuykov et al. 2013). Further discussion should take due cognizance that metals which associated with the shell, came via three independent ‘channels’: by adsorption onto its external (1) and internal (2) surfaces and through incorporation into shell matrix during shell growth (3). The first is appropriate for all metals available in the ambient water, whereas the two others are only appropriate for bioavailable metals.

We agree with the view (Schöne & Krause 2016; Steinhardt et al. 2016) that the whole shell approach, i.e., whole-shell chemical analyses of multiple specimens collected at different times, is less suitable for time-related studies in comparison with a characterization of one shell (as the ‘potential’ offers). However, bivalve sclerochronochemistry considers one third (or even less) of all metals available for measurement in the shell

(Fig. 1). In this regard, elements (or isotopes) partitioning between shell parts/layers/microstructural units have been the focus of many studies and will not be further considered here (e.g., Koide et al. 1982; Carroll & Romanek 2008; Delong & Thorp 2009; Zuykov et al. 2009, 2012; Füllenbach et al. 2017).

Even if the heterogeneity between sampling sites provides a unique trace element signature in the shells or 'trace element fingerprints' (Ricardo et al. 2017) and the element concentrations generally exhibited similar trends for animals of one species in each particular sampling site (or in a laboratory aquarium), a method for retrospective estimation of water chemistry or at least its concept that would use a single bivalve shell has never been proposed. It agrees well with the note by Schöne & Krause (2016, p. 245): 'Despite significant advances in sclerochronology, it still remains extremely challenging to interpret the trace and minor element time-series obtained from (single) bivalve shells.'

The implication here seems to be that the method should be harmonized between any species of bivalves, marine and freshwater environments, different regions of the world, any contaminants detectable in shells, etc. The absence of reliable correlations and interpretations in wider environment is because of direct, indirect and/or cumulative influences of environmental and physiological (biological) factors, as well as they impact on the incorporation of elements into the shell in unpredictable ways (e.g., Vander Putten et al. 2000; Carroll & Romanek 2008; Schöne 2008; Shirai et al. 2008; Immenhauser et al. 2016; Piwoni-Piórewicz et al. 2017; Roger et al. 2017; Zhao et al. 2017; Kelemen et al. 2018; Wanamaker & Gillikin 2018).

In addition, bivalve sclerochronochemistry is a very complicated approach that requires both the high professional qualifications of researchers and high-resolution analytical equipment with multi-step sample preparation protocols and calibrations (Schöne et al. 2010; Marali et al. 2017). We agree with the view of Dunca et al. (2009, p. 4): 'However, in many cases, we are dealing with ambiguous results, whereby different techniques give different results and give rise to different interpretations of the same material.' Thus, due to natural variability and analytical uncertainties, the generation of controversial data and conclusions are to be expected and can even be considered an attribute of bivalve sclerochronochemistry.

With that said, we believe that nowadays, bivalve sclerochronochemistry could be applicable only in some sorts of archaeological, palaeoclimate and palaeoenvironmental studies (for references see Butler et al. 2019).

DIRECTION OF FURTHER STUDIES

As researchers working on aquatic pollution studies, we think that the further development of a method for retrospective environmental monitoring using bivalve shells needs to be continued as it might have a perspective. The recommended way found in the literature is in investigations of the mechanisms of incorporation of trace elements, heavy metals and other contaminants into the shell; it also includes receiving knowledge on elements partitioning between ambient water and shell (Holland et al. 2014). In particular, it is advised to continue focus on the influence of abiotic and biotic factors on the incorporation process (e.g., Schöne & Krause 2016; Steinhardt et al. 2016; Butler & Schöne 2017). However, these recommendations lack novelty and originality, i.e., they have been already known since the 1980s.

Because these studies are based mostly on data from laboratory controlled experiments (e.g., with isolation of individual factors), we need to emphasize that the multiple influences of multi-factors (as occuring in the field conditions) cannot yet be simulated in the laboratory. Hence, reactions of physiological mechanisms responsible for metal incorporation into the shell cannot be fully predicted; the same problem is also relevant for field observations including translocation experiments due to the influence of unique local biogeochemical conditions.

CONCLUSIONS

Analysis of literature on bivalve sclerochronology *s.l.* showed uncertainty in part of the misleading contextualization and the terminology, which scarcely contribute to a better realization of the 'potential'. The meaning of the term 'sclerochronology' as originally defined clearly suggests that its application is related exclusively to the study of growth patterns in 'calcareous exoskeletons or shells', whereas their chemical studies which lack the time-related aspect are managed by sclerochemistry. The new term, 'sclerochronochemistry', proposed here for time-related geochemical studies of bivalve shells, cannot lead to confusing conceptual constructions for those researchers who will use designation as 'sclerochronology *s.l.*' because all three approaches (sclerochronology, sclerochemistry and sclerochronochemistry) do not overlap. Following this logic, the term is applicable to those groups of animals where the term 'sclerochronology' has been used in its broad sense.

Currently, recommendations for further studies in the field of bivalve sclerochronochemistry lack any significant difference from those recounted in pioneering papers. It is clear, therefore, that without any new revolutionary ideas expected outcomes will only replicate the results discussed above. Likewise, optimistic expectations of the 'potential' of the bivalve shell in 'providing high-resolution, chronologically aligned archives of environmental variability' look overrated in comparison with existing data, i.e., it should be acknowledged that the 'potential' has a high uncertainty. Besides, bivalve sclerochronochemistry, in terms of metal detection, will always be less informative than a whole-shell chemical analysis.

It can be admitted that some peaks of some selected elements (e.g., metal-to-calcium ratios) detected in shells collected in polluted sites may be interpreted (with some confidence or not) as short-term anthropogenic pollution events over an interval of time. No doubt, these results can be used for comparative purposes in sclerochronology-based archaeological, palaeoclimate and palaeoenvironmental studies.

Acknowledgements. Financial support to M. Z. was provided by the Ontario Graduate Scholarship programme and The VETAC Mining and Environment Doctoral Bursary. M. S. was supported by a NSERC discovery grant. Kalle Kirsimäe and two anonymous reviewers provided critical and constructive comments, which greatly helped to improve the clarity of our discussion. The publication costs of this article were covered by the Estonian Academy of Sciences.

REFERENCES

Andrus, C. F. T. 2011. Shell midden sclerochronology. *Quaternary Science Reviews*, **30**, 2892–2905.

Beyer, J., Green, N. W., Brooks, S., Allan, I. J., Ruus, A., Gomes, T., Bråte, I. L. N. & Schøyen, M. 2017. Blue mussels (*Mytilus edulis* spp.) as sentinel organisms in coastal pollution monitoring: a review. *Marine Environmental Research*, **130**, 338–365.

Binelli, A., Della Torre, C., Magni, S. & Parolini, M. 2015. Does zebra mussel (*Dreissena polymorpha*) represent the freshwater counterpart of *Mytilus* in ecotoxicological studies? A critical review. *Environmental Pollution*, **196**, 386–403.

Buddemeier, R. W., Maragos, J. E. & Knutson, D. W. 1974. Radiographic studies of reef coral exoskeletons: rates and patterns of coral growth. *Journal of Experimental Marine Biology and Ecology*, **14**, 179–200.

Butler, P. G. & Schöne, B. R. 2017. New research in the methods and applications of sclerochronology. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **465**, 295–299.

Butler, P. G., Freitas, P. S., Burchell, M. & Chauvaud, L. 2019. Chapter 21: Archaeology and sclerochronology of marine bivalves. In *Goods and Services of Marine Bivalves* (Smaal, A. C., Ferreira, J. G., Grant, J., Petersen, J. K. & Strand, Ø., eds), pp. 413–444. Springer Open.

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.

Carriker, M. R., Swann, C. P. & Ewart, J. W. 1982. An exploratory study with the proton microprobe of the ontogenetic distribution of 16 elements in the shell of living oysters (*Crassostrea virginica*). *Marine Biology*, **69**, 235–246.

Carroll, M. & Romanek, C. S. 2008. Shell layer variation in trace element concentration for the freshwater bivalve *Elliptio complanata*. *Geo-Marine Letters*, **28**, 369–381.

Delong, M. D. & Thorp, J. H. 2009. Mollusc shell periostracum as an alternative to tissue in isotopic studies. *Limnology and Oceanography: Methods*, **7**, 436–441.

Dunca, E., Mutvei, H., Göransson, P., Mörth, C.-M., Schöne, B. R., Whitehouse, M. J., Elfman, M. & Baden, S. P. 2009. Using ocean quahog (*Arctica islandica*) shells to reconstruct palaeoenvironment in Öresund, Kattegat and Skagerrak, Sweden. *International Journal of Earth Sciences* (*Geologische Rundschau*), **98**, 3–17.

Fenger, T., Surge, D., Schöne, B. R. & Milner, N. 2007. Sclerochronology and geochemical variation in limpet shells (*Patella vulgata*): a new archive to reconstruct coastal sea surface temperature. *Geochemistry, Geophysics, Geosystems*, **8**, 1–17.

Fritts, H. C., Blasing, T. J., Hayden, B. P. & Kutzbach, J. E. 1971. Multivariate techniques for specifying tree-growth and climate relationships and for reconstructing anomalies in paleoclimate. *Journal of Applied Meteorology*, **10**, 845–864.

Füllenbach, C. S., Schöne, B. R., Shirai, K., Takahata, N., Ishida, A. & Sano, Y. 2017. Minute co-variations of Sr/Ca ratios and microstructures in the aragonitic shell of *Cerastoderma edule* (Bivalvia) – Are geochemical variations at the ultra-scale masking potential environmental signals? *Geochimica et Cosmochimica Acta*, **205**, 256–271.

Geeza, T. J., Gillikin, D. P., Goodwin, D. H., Evans, S. D., Watters, T. & Warner, N. R. 2018. Controls on magnesium, manganese, strontium, and barium concentrations recorded in freshwater mussel shells from Ohio. *Chemical Geology*, doi: 10.1016/j.chemgeo.2018.01.001

Gillikin, D. P., Dehairs, F., Lorrain, A., Steenmans, D., Baeyens, W. & André, L. 2006. Barium uptake into the shells of the common mussel (*Mytilus edulis*) and the potential for estuarine paleo-chemistry reconstruction. *Geochimica et Cosmochimica Acta*, **70**, 395–407.

Goodwin, D. H., Gillikin, D. P. & Roopnarine, P. D. 2013. Preliminary evaluation of potential stable isotope and trace element productivity proxies in the oyster *Crassostrea gigas*. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **373**, 88–97.

Gröcke, D. R. & Gillikin, D. P. 2008. Advances in mollusc sclerochronology and sclerochemistry: tools for understanding climate and environment. *Geo-Marine Letters*, **28**, 265–268.

Helmle, K. P. & Dodge, R. E. 2011. Sclerochronology. In *Encyclopedia of Modern Coral Reefs* (Hopley, D., ed.), pp. 958–966. Springer, Netherlands.

Holland, H. A., Schöne, B. R., Marali, S. & Jochum, K. P. 2014. History of bioavailable lead and iron in the Greater North Sea and Iceland during the last millennium – A bivalve sclerochronological reconstruction. *Marine Pollution Bulletin*, **87**, 104–116.

Huck, S. & Heimhofer, U. 2015. Improving shallow-water carbonate chemostratigraphy by means of rudist bivalve sclerochemistry. *Geochemistry, Geophysics, Geosystems*, **16**, 3111–3128.

Hudson, J. H., Shinn, E. A., Halley, R. B. & Lidz, B. 1976. Sclerochronology: a tool for interpreting past environments. *Geology*, **4**, 361–364.

Immenhauser, A., Schöne, B. R., Hoffmann, R. & Niedermayr, A. 2016. Mollusc and brachiopod skeletal hard parts: intricate archives of their marine environment. *Sedimentology*, **63**, 1–59.

Karney, G. B., Butler, P. G., Scourse, J. D., Richardson, C. A., Lau, K. H., Czernuszka, J. T. & Grovenor, C. R. M. 2011. Identification of growth increments in the shell of the bivalve mollusk *Arctica islandica* using back-scattered electron imaging. *Journal of Microscopy*, **241**, 29–36.

Kelemen, Z., Gillikin, D. P. & Bouillon, S. 2018. Relationship between river water chemistry and shell chemistry of two tropical African freshwater bivalve species. *Chemical Geology*, doi: 10.1016/j.chemgeo.2018.04.026.

Koide, M., Lee, D. S. & Goldberg, E. D. 1982. Metal and transuranic records in mussel shells, byssal threads and tissue. *Estuarine, Coastal and Shelf Science*, **15**, 679–695.

Marali, S., Schöne, B. R., Mertz-Kraus, R., Griffin, S. M., Wanamaker, A. D., Butler, P. G., Holland, H. A. & Jochum, K. P. 2017. Reproducibility of trace element time-series (Na/Ca, Mg/Ca, Mn/Ca, Sr/Ca, and Ba/Ca) within and between specimens of the bivalve *Arctica islandica* – A LA-ICP-MS line scan study. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **484**, 109–128.

Oschmann, W. 2009. Sclerochronology: editorial. *International Journal of Earth Sciences* (*Geologische Rundschau*), **98**, 1–2.

Piwoni-Piórewicz, A., Kukliński, P., Strekopytov, S., Humphreys-Williams, E., Najorka, J. & Iglikowska, A. 2017. Size effect on the mineralogy and chemistry of *Mytilus trossulus* shells from the southern Baltic Sea: implications for environmental monitoring. *Environmental Monitoring and Assessment*, **189**: 197, 1–17.

Prendergast, A. L. & Schöne, B. R. 2017. Oxygen isotopes from limpet shells: implications for palaeothermometry and seasonal shellfish foraging studies in the Mediterranean. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **484**, 33–47.

Prendergast, A. L., Versteegh, E. A. A. & Schöne, B. R. 2017. New research on the development of high-resolution palaeoenvironmental proxies from geochemical properties of biogenic carbonates. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **484**, 1–6.

Ricardo, F., Pimentel, T., Génio, L. & Calado, R. 2017. Spatio-temporal variability of trace elements fingerprints in cockle (*Cerastoderma edule*) shells and its relevance for tracing geographic origin. *Scientific Reports*, **7**: 3475, 1–9.

Roger, L. M., George, A. D., Shaw, J., Hart, R. D., Roberts, M., Becker, T., McDonald, B. J. & Evans, N. J. 2017. Geochemical and microstructural characterisation of two species of cool-water bivalves (*Fulvia tenuicostata* and *Soletellina biradiata*) from Western Australia. *Biogeosciences*, **14**, 1721–1737.

Schöne, B. R. 2008. The curse of physiology – challenges and opportunities in the interpretation of geochemical data from mollusk shells. *Geo-Marine Letters*, **28**, 269–285.

Schöne, B. R. & Gillikin, D. P. 2013. Unraveling environmental histories from skeletal diaries – Advances in sclerochronology. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **373**, 1–5.

Schöne, B. R. & Krause, R. A. 2016. Retrospective environmental biomonitoring – Mussel Watch expanded. *Global and Planetary Change*, **144**, 228–251.

Schöne, B. R. & Surge, D. M. 2012. Part N, Revised, Vol. 1, Chapter 14: Bivalve sclerochronology and geochemistry. *Treatise Online*, 46, 1–24,.

Schöne, B. R. & Surge, D. 2014. Bivalve shells: ultra high-resolution paleoclimate archives. *Past Global Changes Magazine*, **22**, 20–21.

Schöne, B. R., Rodland, D. L., Wehrmann, A., Heidel, B., Oschmann, W., Zhang, Z., Fiebig, J. & Beck, L. 2007. Combined sclerochronologic and oxygen isotope analysis of gastropod shells (*Gibbula cineraria*, North Sea): life-history traits and utility as a high-resolution environmental archive for kelp forests. *Marine Biology*, **150**, 1237–1252.

Schöne, B. R., Zhang, Z., Jacob, D., Gillikin, D. P., Tütken, T., Garbe-Schönberg, D., McConnaughey, T. & Soldati, A. 2010. Effect of organic matrices on the determination of the trace element chemistry (Mg, Sr, Mg/Ca, Sr/Ca) of aragonitic bivalve shells (*Arctica islandica*) – Comparison of ICP-OES and LA-ICP-MS data. *Geochemical Journal*, **44**, 23–37.

Shirai, K., Takahata, N., Yamamoto, H., Omata, T., Sasaki, T. & Sano, Y. 2008. Novel analytical approach to bivalve shell biogeochemistry: a case study of hydrothermal mussel shell. *Geochemical Journal*, **42**, 413–420.

Steinhardt, J., Butler, P. G., Carroll, M. L. & Hartley, J. 2016. The application of long-lived bivalve sclerochronology in environmental baseline monitoring. *Frontiers in Marine Science*, **3**: 176, 1–26.

Stevenson, A. & Brown, L. 2007. *Shorter Oxford English Dictionary on Historical Principles*. Oxford University Press, Oxford, 3742 pp.

Thomas, K. D. 2015. Molluscs emergent, Part I: themes and trends in the scientific investigation of mollusc shells as resources for archaeological research. *Journal of Archaeological Science*, **56**, 133–140.

Twaddle, R. W., Ulm, S., Hinton, J., Wurster, C. M. & Bird, M. I. 2016. Sclerochronological analysis of archaeological mollusk assemblages: methods, applications and future prospects. *Archaeological and Anthropological Sciences*, **8**, 359–379.

Vander Putten, E., Dehairs, F., Keppens, E. & Baeyens, W. 2000. High resolution distribution of trace elements in the calcite shell layer of modern *Mytilus edulis*:

environmental and biological controls. *Geochimica et Cosmochimica Acta*, **64**, 997–1011.

Wanamaker, A. D. & Gillikin, D. P. 2018. Strontium, magnesium, and barium uptake in aragonitic shells of *Arctica islandica*: insights from a temperature controlled experiment. *Chemical Geology*, doi: 10.1016/j.chemgeo.2018.02.012

Zhao, L., Schöne, B. R. & Mertz-Kraus, R. 2017. Controls on strontium and barium incorporation into freshwater bivalve shells (*Corbicula fluminea*). *Palaeogeography, Palaeoclimatology, Palaeoecology*, **465**, 386–394.

Zuykov, M. A., Pelletier, E., Rouleau, C., Popov, L., Fowler, S. W. & Orlova, M. 2009. Autoradiographic study of 241Am distribution in the shell of the freshwater zebra mussel *Dreissena polymorpha* exposed under laboratory conditions. *Microchimica Acta*, **167**, 173–178.

Zuykov, M., Pelletier, E., St-Louis, R., Checa, A. & Demers, S. 2012. Biosorption of thorium on the external shell surface of bivalve mollusks: the role of shell surface microtopography. *Chemosphere*, **86**, 680–683.

Zuykov, M., Pelletier, E. & Harper, D. A. T. 2013. Bivalve mollusks in metal pollution studies: from bioaccumulation to biomonitoring. *Chemosphere*, **93**, 201–208.

Karbikodade sklerokronoloogilis-geokeemilised uuringud: võimalused ja tegelik olukord

Michael Zuykov ja Michael Schindler

Karbikodade kasvukihtide uuringutes (sklerokronoloogias) on alates 1980. aastatest pööratud laialdast tähelepanu võimalusele selgitada nende abil muutusi (paleo-) keskkonna keemilises seisundis. Käesolevas ülevaateartiklis on analüüsitud sklerokronoloogia valdkonna uuringute rõhuasetuste ja uurimisülesannete muutumist viimase 35 aasta jooksul ja tehtud ettepanek võtta kasutusele uus mõiste *sklerokronokeemia*, millega piiritleda uuringuid, mis jäävad sklerokronoloogia ning sklerokeemia piirialadele.