



Preface

Unraveling environmental histories from skeletal diaries – Advances in sclerochronology

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ABSTRACT

High-resolution proxy archives from aquatic settings are essential to better understand processes and mechanisms of global change. During the last decade, it has become increasingly evident that calcified tissues of bivalve mollusks and cold-water corals, in particular, can significantly increase our knowledge of seasonal to multi-decadal paleoclimate and paleoenvironmental variability in the extratropical oceans and coastal marine settings. Daily, tidal, fortnightly and annual growth patterns of periodically formed skeletal hard parts provide a means to place the proxy record in a precise temporal context. Their extreme longevity coupled with the running similarity between growth increment time-series of contemporaneous bivalves opens the possibility of constructing stacked chronologies covering centuries to millennia which provide information on decadal climate and environmental variability and magnitudes of climate variability through time. A current major research focus is on how to translate geochemical properties of the skeletons into quantifiable environmental proxy data and how to eliminate the adverse influence of vital effects on the proxy records.

This special issue presents the most recent advances in the field of sclerochronology, specifically calcified tissues of bivalve mollusks, cold-water corals and tropical shallow water corals. The majority of the contributions deal with the potential reconstruction of temperature, pH and productivity through the analysis of variable growth rates, Sr/Ca, Mg/Ca, Ba/Ca, U/Ca, Li/Ca, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{44/40}\text{Ca}$. Four papers present composite chronologies of two long-lived bivalve species and discuss inherent decadal climate variability, and one study demonstrates that sclerochronology can shed light on socioeconomic patterns of past human populations as well as resource use and resource management by people.

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1. Introduction

Proxy records of paleoenvironmental conditions are essential to understand climate and ecosystem dynamics prior to the instrumental era (ca. 1860 A.D.; Jones et al., 2001, 2009). To draw a more detailed picture of the past, however, requires seasonally to annually resolved, precisely chronologically aligned and, most importantly, quantifiable proxy data from various geographical settings (IPCC, 2007).

The majority of high-resolution (= annual to subannual) climate and environmental archives come from the terrestrial realm and largely capture atmospheric and/or continental conditions (e.g., tree-rings, speleothems, ice cores). By contrast, paleoenvironmental and paleoclimate records from marine settings are sparse and often have poor temporal resolution. However, well-constrained subannually

resolved archives for the marine environment do exist, i.e. in the form of sclerochronological¹ archives. Shallow-water corals have been used to reconstruct high-resolution paleoceanic records from around the tropics (Weber and Woodhead, 1970; Emiliani et al., 1978; Cobb et al., 2003). Shells of bivalve mollusks, fish otoliths, cold-water corals etc. are less utilized, but have significantly increased our knowledge of seasonal to interannual paleoclimate and paleoenvironmental variability in other portions of the oceans, in particular extratropical and coastal marine settings (Tripathi et al., 2001; Dutton et al., 2002; Black, 2009; Ivany and Runnegar, 2010; Wanamaker et al., 2012; Yan et al., 2012). The relevance of such data becomes evident when considering that the extratropical oceans play a major role in global heat exchange

¹ Sclerochronology is defined as the study of physicochemical variations in periodically growing hard tissues of organisms (Oschmann, 2009). Sclerochronology (Castanet et al., 1977), i.e. the study of physical and chemical variations in bones and teeth, should be considered as a sub-discipline of sclerochronology, because studies of skeletal parts (that form by accretion) of some vertebrates such fish otoliths have traditionally been already regarded as sclerochronology.

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(Manabe and Stouffer, 1999; Levitus et al., 2000; Visbeck, 2002), host major carbon sinks (Sabine et al., 2004) and govern quasi-decadal to multi-decadal climate variability (Rodwell et al., 1999; Sutton and Hodson, 2005; Keenlyside et al., 2008). Coastal marine settings are subject to extensive anthropogenic pollution, and humans have settled along the coasts for thousands of years and exploited shallow marine resources (see Andrus, 2011 for a review on archaeological-sclerochronology). More detailed information on the paleoenvironmental variability in these portions of the oceans is of paramount importance to understand evolutionary patterns and socioeconomic change, assess the human impact on these environments and establish well-constrained predictive numerical climate and ecosystem models. The increasing recognition of the importance of sclerochronological data for a set of different applications is reflected in the soaring number of publications in the field of sclerochronology.

In contrast to corals, however, it still remains extremely challenging to translate the majority of physicochemical properties of many other sclerochronological records into climatologically or environmentally meaningful quantities. This challenge pertains in particular to bivalves and cold-water corals. Since most trace and minor element concentrations are influenced by kinetic or vital effects, the only well-accepted way to reconstruct, for example, temperatures from bivalve shells is through oxygen isotopes. In the case of cold-water corals, even oxygen isotope values are strongly affected by vital effects (e.g., Adkins et al., 2003).

Almost all bivalve species form their shells in oxygen isotopic equilibrium with the ambient water (e.g., Epstein et al., 1953; Wefer and Berger, 1991; Lécuyer et al., 2004), which potentially enables accurate $\delta^{18}\text{O}_{\text{shell}}$ -derived temperature estimates (e.g., Chauvaud et al., 2005). However, $\delta^{18}\text{O}$ is a dual proxy because it simultaneously records changes of temperature and the oxygen isotopic signature of the ambient water (Urey, 1948). To reconstruct precise water temperatures from the $\delta^{18}\text{O}_{\text{shell}}$ data, the $\delta^{18}\text{O}$ value (or salinity) of the water must be known, which is rarely the case for ancient environments. Therefore, an essential and pressing question remains unanswered: How can we obtain quantifiable paleotemperature data from bivalve shells? Likewise, this applies to other environmental and climate quantities that are recorded in many sclerochronological archives in the form of geochemical variations.

2. Sclerochronology proxy archives

One unifying characteristic of sclerochronological archives is a periodically changing rate of growth. This is most likely controlled and maintained by endogenous timekeeping mechanisms, so-called biological clocks (Pittendrigh and Bruce, 1957; Palmer, 1974; Rensing et al., 2001), which are constantly reset by environmental triggers such as light, tides, food etc. (Richardson et al., 1979; Block and Wallace, 1982; Williams and Pilditch, 1997). Regular changes in the rate of skeletal formation result in the formation of growth lines (i.e. time intervals of slow growth) and growth increments (i.e. time intervals of faster growth). By using daily, tidal, fortnightly or annual growth patterns, each portion of the skeleton can be placed in a precise temporal context. The notion that growth patterns may be used to estimate the age of organisms goes back to Aristotle (384–324 B.C.). In *History of the Animals* (Book V.XV) he states: 'The purpura [snail in the Mediterranean Sea] lives about six years, and every year its growth is clearly observable from the intervals in the shell of the spiral' (translated by Peck, 1970). Somewhat more recent ages estimations have been conducted by Pulteney (1781) and von Hessling (1859). Based on annual increment counts, Pulteney (1781) concluded that "50 or 60 years are imagined to be a moderate computation" for the life span of *Margaritifera margaritifera*, whereas von Hessling (1859) suggested that a lifespan of 200 years is "problematic", but 70 to 80 years are reasonable. The ontogenetic age of coastal marine bivalves was studied by Weymouth (1922) in cross-sections of *Tivela stultorum*.

Since the growth rate of invertebrates is largely controlled by external energy input, specifically temperature and food availability, the relative changes in skeletal growth of these organisms can also provide valuable information on changes of these environmental variables (e.g., Kennish and Olsson, 1975). Furthermore, numerous environmental data can be archived in the form of stable isotope ratios and trace/minor elements, i.e. environmental proxies. Sclerochronological proxy archives have been extensively explored for decades. Numerous research papers, books (Rosenberg and Runcorn, 1975; Rhoads and Lutz, 1980) and theme issues (Schöne and Surge, 2005; Gröcke and Gillikin, 2008; Oschmann, 2009; Wanamaker et al., 2011) deal with organisms that form skeletal hard parts by incremental growth.

Shells of bivalve mollusks have gained particular interest, because they combine a number of requirements for being perfect climate and environmental recorders. Aside from providing subseasonally resolved environmental data and forming daily, tidal, fortnightly and annual growth patterns, some species reach extraordinary lifespans ranging from 200 to over 500 years (Thompson et al., 1980; Zolotarev, 1980; Mutvei et al., 1996; Schöne et al., 2005; Wanamaker et al., 2008). Based on similar growth patterns, annual increment chronologies of contemporaneous specimens can be combined to form longer, composite chronologies – very much like tree ring chronologies – covering centuries to millennia and many generations of bivalves (e.g., Jones et al., 1989; Marchitto et al., 2000; Schöne et al., 2004; Black et al., 2008; Butler et al., 2010). The remarkably broad biogeographic distribution of bivalves enables cross-calibration with other environmental and climate archives. They inhabit shallow water seas and the deep sea, occur in fully marine, brackish and freshwater environments from the polar regions to the equator.

3. The 2nd International Sclerochronology Conference and contents of this special issue

From July 24th to 28th 2010, the 2nd International Sclerochronology Conference (ISC2010) was held at the University of Mainz, Germany (Schöne and Nunn, 2010). In more than 125 contributions, participants from fifteen countries presented the most recent results of their research on skeletal hard parts, mainly invertebrates, and provided evidence that sclerochronology has come of age. ISC2010 aimed at integrating traditional sclerochronological research with the expertise from neighboring disciplines and sub-disciplines such as archaeology, anthropology, skeletochronology, biomineralization and paleoclimate modeling. This goal has been reached.

This special issue represents an outgrowth of ISC2010. As during ICS2010 (Fig. 1), the majority of the selected contributions of this special volume focus on proxy evaluation and optimization, specifically, proxies for temperature, ocean productivity and pH (DeLong et al., 2013-this issue; Gillikin and Dehairs, 2013-this issue; Marali et al., 2013-this issue; Hatch et al., 2013-this issue; Goodwin et al., 2013-this issue; Thébault and Chauvaud, 2013-this issue; Hippler et al., 2013-this issue; Mouchi et al., 2013-this issue; Lazareth et al., 2013-this issue; Schöne et al., 2013-this issue). Other papers demonstrate that sclerochronological records can provide valuable information on extratropical ocean dynamics covering decades and centuries to more than the past millennium (Brocas et al., 2013-this issue; Butler et al., 2013-this issue; Royer et al., 2013-this issue; Lohmann and Schöne, 2013-this issue) and resource use of human populations during the last ca. 7500 years (Hallmann et al., 2013-this issue).

One paper in this issue covers warm-water coral skeleton geochemistry. Many studies that use coral skeletons to reconstruct past oceanic conditions rely on only one geochemical record. However, DeLong et al. (2013-this issue) highlight the need for replicate geochemical records to increase the robustness of the chronology and Sr/Ca-based temperature estimates. Within the same tropical shallow-water coral colony (*Porites lutea*), Sr/Ca ratios can vary among contemporaneously deposited sections and over- or underestimate actual water temperatures

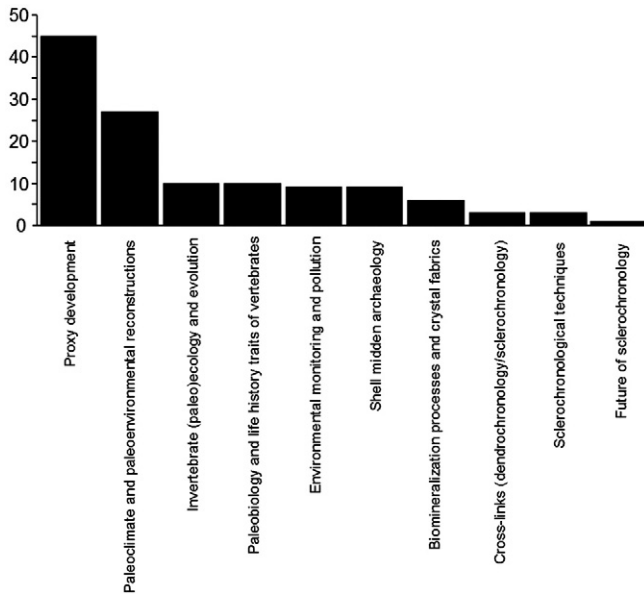


Fig. 1. Number of papers presented in the different sessions of ISC 2010.

by well over 2 °C. These differences are related to the coral architecture and suboptimal sampling strategies. Coral $\delta^{18}\text{O}$ values are less variable than Sr/Ca ratios in this coral species as long as growth rates remained above 6 mm/year.

In cold-water corals, kinetic and vital effects exert a much stronger influence on light stable isotopes than in tropical shallow water corals, hampering the reconstruction of meaningful environmental conditions. Marali et al. (2013-this issue) studied these effects in solitary scleractinian species from the Azores. They report that when the 'Lines technique' of Smith et al. (2000) is utilized, $\delta^{18}\text{O}$ values of *Desmophyllum cristagalli* and *Caryophyllia cyathus* provided useful estimates of ambient water temperature.

Reconstruction of environmental variables based on geochemical properties of bivalve shells is still more challenging than in the case of corals. Typically, element/calcium ratios of bivalve shells remain well below those of the ambient water, suggesting vital effects play a major role in the incorporation of elements in shells. Moreover, contemporaneously deposited shell portions of *Arctica islandica* and *Protothaca thaca* exhibit a considerable geochemical heterogeneity (Schöne et al., 2013-this issue; Lazareth et al., 2013-this issue). In particular, magnesium levels can vary considerably in different portions of these aragonitic shells (e.g., by more than 60% within the outer shell layer of *A. islandica*; Schöne et al., 2013-this issue), while strontium and barium are less severely affected. Lazareth et al. (2013-this issue) attribute this finding to differences in the mantle epithelium and early diagenesis, while Schöne et al. (2013-this issue) observed a strong correlation of the chemical variability to crystal fabrics. Near major growth lines (irregular simple prismatic crystal fabrics), Sr/Ca and Mg/Ca values seem to approach values typical for seawater, suggesting shell formation at thermodynamic equilibrium (Schöne et al., 2013-this issue). Yet, both studies come to the same conclusion regarding the optimal sampling strategy and recommend geochemical analyses being completed at a precisely defined distance from the outer shell surface and always within the same type of crystal fabrics.

Ontogenetic age may be another important factor influencing the trace and minor element levels in bivalve shells. The importance of vital effects on elemental impurities seems to change through ontogeny (Gillikin and Dehairs, 2013-this issue; Mouchi et al., 2013-this issue). While U/Ca values exhibit strong seasonal cycles over the first six annual increments of *Saxidomus gigantea* from Puget Sound (Washington) and Kodiak Island (Alaska, USA), uranium levels fell

below the detection limit for the next four to sixteen years, suggesting strong vital effects (Gillikin and Dehairs, 2013-this issue). Gillikin and Dehairs (2013-this issue) also found indications of diagenetic alteration of the shell geochemistry: U/Ca ratios decreased toward the inside of the shell, and along contemporaneously deposited shell portions, suggesting uptake of uranium after the shell had formed. While the factors controlling U incorporation into shells is not clear, the authors conclude that U/Ca may not reflect environmental variability and does not function as a paleo-pH proxy.

Likewise, slower growing adult shell portions of *Crassostrea gigas* and *Ostrea edulis* are likely more severely affected by vital effects than shell portions formed during early ontogeny. Mouchi et al. (2013-this issue) found a good agreement between water temperature and Mg/Ca ratios of the first six annual increments of oysters grown under controlled conditions. For this reason, these authors provided a paleothermometry equation based on three of the four juvenile *C. gigas* shells in their study.

Since many previous attempts have been unsuccessful in using element/Ca ratios of aragonitic bivalves for temperature reconstructions, Hippler et al. (2013-this issue) pursued another approach and evaluated the potential use of calcium isotope ratios of *Arctica islandica*. Shell $\delta^{44}/^{40}\text{Ca}$ values of the ocean quahog are positively but non-linearly related to ambient temperature. The relationship is nearly linear only between 1° and 15 °C, and agrees with previous findings for many other inorganic and biogenic carbonates. The authors concluded that vital effects limit the use of $\delta^{44}/^{40}\text{Ca}$ as a temperature proxy in this species.

Goodwin et al. (2013-this issue), Hatch et al. (2013-this issue) and Thébault and Chauvaud (2013-this issue) investigated potential proxies for primary productivity and nutrient levels. Whereas $\delta^{13}\text{C}$ values in shells of *Crassostrea gigas* seem to reflect phytoplankton abundance, Ba/Ca likely does not provide a useful proxy of ocean productivity. According to Goodwin et al. (2013-this issue), Ba/Ca peaks occur nearly contemporaneously with elevated nutrient levels during freshwater discharges. However, the Ba/Ca levels are unrelated to the nutrient levels and freshwater discharge volume. Hatch et al. (2013-this issue) present a high-resolution Ba/Ca study of the intertidal bivalve *Donax gouldii*. Their findings suggest that a nine to three day lag exists between Ba/Ca levels in the shell and higher Chl *a* and nutrient concentrations, respectively. Whereas diatom abundance was unrelated to Ba/Ca in the shells (Hatch et al., 2013-this issue), Li/Ca ratios of *Pecten maximus* may serve as a new proxy for diatom blooms. Thébault and Chauvaud (2013-this issue) found a significant correlation between Li/Ca levels and the timing and magnitude of diatom blooms in the Bay of Brest. This new tool is important for studying the effect of global change on phytoplankton dynamics, e.g. the recent shift toward non-siliceous taxa.

Four papers of this special issue focus on variations in shell growth as a proxy for water temperature and food availability as well as decadal climate variability. In two independent studies, Royer et al. (2013-this issue) and Brocas et al. (2013-this issue) found a strong coupling between annual shell growth of *Glycymeris glycymeris* and ambient water temperature. In addition to being from different localities (northwest of France, Royer et al., 2013-this issue; Irish Sea, Brocas et al., 2013-this issue), the two studies also approached their calibrations differently. Brocas et al. (2013, this issue) compared variations in annual shell growth to instrumental records, whereas Royer et al. (2013-this issue) computed water temperatures from stable oxygen isotope ratios of the shells. In the Irish Sea, annual shell growth also gave a weak signal of the North Atlantic Oscillation (Brocas et al., 2013-this issue), which was not observed in specimens of the Bay of Brest and Chausey Islands (Royer et al., 2013-this issue). Both studies illustrate the potential of *G. glycymeris* as a climate archive.

Annual shell growth of *Arctica islandica* from north Iceland (Butler et al., 2013-this issue) and northeast Iceland (Lohmann and Schöne, 2013-this issue) is apparently controlled by a more complex set of environmental variables. Although statistically highly significant,

temperature exerts only a weak control over shell growth (~4% of shell growth is explained by temperature variation; Butler et al., 2013-this issue). Food availability and circulation patterns likely played a more important role (Butler et al., 2013-this issue; Lohmann and Schöne, 2013-this issue). Both composite chronologies, the 1357-year time-series of Butler et al. (2013-this issue) and the 509-year chronology of Lohmann and Schöne (2013-this issue) reflect quasi- and multidecadal variability typical for the North Atlantic climate. During cold intervals in the 16th and 18th century, i.e. during time of climate re-organization, the inter-annual climate oscillations were more pronounced and sea ice export from northern latitudes was stronger (Lohmann and Schöne, 2013-this issue).

The final paper of this special issue, by Hallmann et al. (2013-this issue) exemplifies how sclerochronology can be applied in archaeology. Stable oxygen isotope values from shells of *Saxidomus gigantea* from archaeological shell middens of northern British Columbia confirm the persistence of wet climate conditions during the mid Holocene, specifically wet summers. In conjunction with seasonal $\delta^{18}\text{O}$ values, growth pattern analysis indicated that the people living in this region maintained a year-round shellfish harvest irrespective of significant climate changes during the Holocene.

This compendium provides excellent examples of how current sclerochronological research is linked to a plethora of disciplines – from climate science to archeology. We hope it spurs an intensified scientific interaction between neighboring disciplines and a continued interest in sclerochronology.

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