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INTRODUCTION

Advances in mollusc sclerochronology and sclerochemistry: tools for understanding climate and environment

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Abstract This Special Issue of *Geo-Marine Letters* compiles papers on marine, estuarine and freshwater mollusc shells as recorders of environmental and climatic conditions. Considering that many past studies have differentiated geochemical investigations from sclerochronological investigations, we propose that the sub-discipline term "sclerochemistry" be used when geochemical investigations are undertaken. This issue starts with two review papers that discuss the importance of physiology or vital effects on both sclerochronology and sclerochemistry. Several sclerochemical calibration studies on modern specimens of both bivalves and gastropods are presented (including $\delta^{18}O$, Mg/Ca, Sr/Ca and Ba/Ca), which illustrate the usefulness and difficulties associated with using these proxies. Studies on fossil mollusc shells are also provided, with one study that uses Pliocene scallop shells to understand past ocean circulation and another that addresses the problem of diagenesis. Finally, a sclerochronological study of crystal prism width across the shell is presented. This Special Issue demonstrates that many elemental and isotopic proxies contained in mollusc shells are complex. In spite of these complexities, environmental and climatic conditions can be extracted for use in palaeoclimatic and palaeoenvironmental research.

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Introduction

With future climate change at the forefront of environmental policy making (IPCC 2007), studies of past climatic changes and their environmental effects are vital because they allow an understanding of the processes responsible for these changes. By using the past as a key to the future, we can better predict how the Earth will respond to certain environmental perturbations. Information about past climatic conditions and changes can be obtained through proxies; these are geochemical or physical signals recorded in biological or geological structures that reflect the environment in which they formed. Because they typically accrete or deposit sequentially through time, they can record a time series of environmental information. For example, environmental information has been obtained from tree rings, sclerosponges, speleothems, corals, fish otoliths, foraminifers, mammal teeth, laminated sediments, ice cores and mollusc shells.

The term sclerochronology was first applied to a radiographic study on corals by Buddemier et al. (1974, p. 196) and, more formally, by Hudson et al. (1976) in their paper on corals entitled "Sclerochronology: a tool for interpreting past environments". However, more recently at the 1st International Sclerochronology Conference, Jones et al. (2007) define sclerochronology as:

> "the study of physical and chemical variations in the accretionary hard tissues of organisms, and the temporal context in which they formed. Sclerochronology focuses primarily upon growth patterns reflecting annual, monthly, fortnightly, tidal, daily, and sub-daily increments of time entrained by a host of environmental and astronomical pacemakers. Familiar examples include daily banding in reef coral skeletons or annual

growth rings in mollusk shells. Sclerochronology is analogous to dendrochronology, the study of annual rings in trees, and equally seeks to deduce organismal life history traits as well as to reconstruct records of environmental and climatic change through space and time".

Many authors differentiate sclerochronological studies and geochemical studies; for example, Williams et al. (1982) state that they used "coordinated isotopic *and* sclerochronological (growth increment) studies", and Schöne et al. (2007) entitled their paper "Combined sclerochronologic and oxygen isotope analysis of gastropod shells …". Therefore, in line with the differentiation already used by dendrochronologists to separate studies of tree ring width increments (dendrochronology) from isotopic or chemical analyses across rings (dendrochemistry; e.g. Smith and Shortle 1996; Verheyden et al. 2005; Poussart et al. 2006), we propose to use *sclerochronology* for studies of the physical structure of the hard tissues of organisms, even when combined with geochemistry (e.g. growth-line periodicity), and that *sclerochemistry*, as a sub-discipline of sclerochronology, be used to describe solely geochemical (isotopic or elemental) studies of the hard tissues of organisms. Whether these terms and distinctions are adopted or not, it does provide an essential difference between the two approaches.

For more than 50 years, mollusc shells have been known archives of past environmental conditions (Davenport 1938; Epstein et al. 1953; Emiliani et al. 1964; Clark 1968). During mollusc growth, they sequentially deposit new layers of shell, and the physical structure and/or chemical composition of these layers may reflect the environmental conditions at the time they formed. Indeed, environmental data have been extracted from mollusc shell geochemistry (sclerochemistry) as well as from external or internal growth increments (sclerochronology). Molluscs are beneficial in that they can provide high-resolution seasonal records of environmental conditions and have a wide geographic distribution, whereas many other archives, such as scleractinian corals, are limited in their latitudinal extent. Although most molluscs typically live less than 10 years, some readily achieve 50 years (Peterson 1986) and there have been reports of bivalves (*Arctica islandica*) living up to 374 years (Schöne et al. 2005) or even longer. In addition, bivalve shells are often found in archaeological middens or as fossils, potentially allowing records of environmental conditions, such as seasonality, to be extended into not only historical records but also geologic time. However, it is becoming increasingly clear that the animals' physiology significantly impacts proxies recorded in the shell.

In 2005 a special issue on environmental records in accretionary hard parts of aquatic organisms including bivalved molluscs, fish, corals and coralline sponges was published (Schöne and Surge 2005). These papers have renewed the interest in the use of molluscs as recorders of past environmental conditions; in turn, this has led to workshops and conferences in 2007, such as a PAGES and SSHRC funded workshop, "Stable Isotopes in Archaeological Midden Shells: High-Resolution Paleoclimatic & Paleoenvironmental Archives", held between 10–13 July at the Parks Canada Discovery Centre in Hamilton, Canada (Fig. 1), and the 1st International Sclerochronology Conference between 17–21 July in St. Petersburg, Florida. During the discussions at the PAGES/SSHRC workshop, participants voted to initiate a Sclerochronology Listserv, which David Goodwin at Denison University volunteered to set up and administer (https://listserv.cc.denison.edu/wws/info/sclerochronology). The papers within this Special Issue derive mainly from the PAGES/SSHRC meeting and an open invitation through the Sclerochronology Listserv, and focus on mollusc shell sclerochronology and sclerochemistry (both elemental and isotopic studies) in marine, estuarine and freshwater molluscs.

To set the scene, two review papers that cover the topic of physiology are provided. *Schöne* presents an overall view of physiological effects on a range of geochemical proxies in molluscs. By taking a modelling approach with published and unpublished data, he looks at investigating periods of growth cessation, how long they are and what is influencing them. Subsequently by looking at variable growth rates, a greater understanding of the geochemical proxies can be obtained, thus eliminating this effects in our sclerochemical records. *McConnaughey and Gillikin*, however, deal specifically with carbon-isotope ratios in molluscs and how metabolic carbon can affect their distribution in the shell. With a process-orientated model, they determine the percentage of metabolically respired carbon versus dissolved inorganic carbon taken up into the shell. Very few isotope sclerochemical studies report carbon isotopes but, rather, only the oxygen isotope ratio. With this model and understanding of carbon isotopes in shells, it should be possible to determine ecosystem metabolism versus estuarine influences on shell geochemistry.

Two modern-based coordinated sclerochronological and sclerochemical studies follow. These are extremely important if one is to use archaeological and/or fossil mollusc shells to interpret environment and climate. *Andrus and Rich* conduct an oxygen-isotope study of *Rangia cuneata*, which inhabits an estuarine setting. Using oxygen isotopes, time-series seawater temperature data and various environmental assumptions, they produce a model–data comparison indicating that the microstructural increments of this species are controlled by tidal rhythms. *Mannino et al.* apply a similar approach but on the gastropod *Osilinus turbinatus* from the Mediterranean region. Several popula-

Fig. 1 Participants of the PAGES and SSHRC funded workshop "Stable Isotopes in Archaeological Midden Shells: High-Resolution Paleoclimatic & Paleoenvironmental Archives", 10–13 July 2007, Parks Canada Discovery Centre, Hamilton, Canada

tions of the gastropod were analyzed for oxygen isotopes, and compared against measured sea surface temperatures. Growth lines occur during the summer when temperatures reach a maximum. They report that the oxygen isotopes are recording the temperature all-year round and have minimal offsets, and thus can be used as a good climate indicator from archaeological sites in the Mediterranean.

Goewert and Surge have adopted the above approach by analyzing the Pliocene scallop, *Chesapecten madisonius*, from Virginia in order to determine seasonality. Based on the presence of growth lines as markers of a season, they use oxygen isotopes to determine if these occurred in winter or summer. The results indicate that the growth lines occur during winter but not summer, which is common for molluscs from cold-temperate regions but not for warm-temperate faunas. They conclude that this may be the result of a change in the Labrador Current and/or the migration of warm-water temperate species following the Gulf Stream that, during cold intervals, would result in a reduction of shell growth. *Lu* uses an alternative approach to determine whether fossil mollusc shells preserve a pristine isotopic signature that can be used for palaeoenvironment and palaeoclimate reconstructions. The Miocene shells in Lu's study were evaluated for an array of elemental and isotopic signals to determine the degree to which there is any diagenetic alteration. Using modern seawater geochemical baselines, it was found that although these Miocene shells look pristine because their fabric had been maintained, they had undergone diagenetic alteration. This type of approach suggests that all future deep-time sclerochemical studies should incorporate a suite of geochemical investigations before using the data to reconstruct palaeo-seawater conditions.

The next two studies assess the potential of trace element proxies in estuarine bivalves. *Gillikin et al.* investigate the barium signal in calcite and aragonite bivalve shells (*Pecten maximus*, *Saxidomus giganteus*). They have previously shown that the background Ba/Ca signal is related to water Ba/Ca ratios in *Mytilus edulis* shells, but here focus on the episodic nature of the Ba/Ca peaks. The Ba/Ca peaks are highly reproducible between specimens, and do not seem to be related to phytoplankton blooms as has been previously proposed. Other possible causes such as dissolved Ba in ambient water, spawning, shell organic matter content and kinetic growth rate effects are discussed, but none provide satisfactory explanations for these Ba/Ca peaks. However, the background signal does seem to be related to water Ba concentrations in these species, providing further evidence that this is a useful proxy. *Wanamaker et al.* cultured juvenile mussels (*Mytilus edulis*) in different temperatures and salinities, and found that the shell Mg/Ca and Sr/Ca ratios were not well correlated with water temperature. However, when using shells grown in the lowest salinity, the relationships between shell elemental chemistry and water temperature improve moderately (R^2=0.75 and 0.82 for Sr/Ca and Mg/Ca respectively). This study highlights the difficulty with these proxies, but does give hope that they may be useful in some environmental settings.

The last two studies in this Special Issue deal with freshwater bivalves. *Carroll and Romanek* studied the sclerochemistry of five specimens of *Elliptio complanata* from four streams (i.e. 20 shells). They compared Mn, Cu, Sr and Ba of the inner and outer shell layers, and found that both record accurate environmental information. When comparing shell elemental concentrations to water concentrations, they found a strong correlation for Mn, Sr and Ba, but only after excluding five shells from a polluted stream. Their results suggest that sclerochemistry of shells from polluted streams do not accurately record stream geochemistry. This is one of the first studies to clearly illustrate that elemental concentrations in freshwater mussel shells can be used to obtain environmental information. Finally, *Vancolen and Verrecchia* investigated the detailed sclerochronology of *Unio tumidus* shells. Their study focuses on the distribution of the prism width inside the prismatic layer of the shell, which has implications for growth-line formation and proxy incorporation. They found that prism widths are randomly distributed and are not related to either growth lines or environmental parameters. Crystal morphology has been noted as being responsible for trace element incorporation into inorganic calcite; therefore, this study should be repeated on several species of molluscs to ascertain the influence of crystal morphology on sclerochemistry.

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