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Chapter 21
Archaeology and Sclerochronology of Marine Bivalves

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Abstract In a rapidly changing world, maintenance of the good health of the marine environment requires a detailed understanding of its mechanisms of change, and the ability to detect early signals of a shift away from the equilibrium state that we assume characterized it before there was any significant human impact. Given that instrumental measurements of the oceans go back no further than a few decades, the only way in which we can assess the long-term baseline variability that characterizes the pre-perturbation equilibrium state of the marine environment is by the use of proxy records contained in stratified or layered natural archives such as corals, fish otoliths and bivalve mollusc shells.

In this chapter we will look at the ways in which the environmental signals recorded in the shells of bivalve molluscs can be used to shed light on marine variability both in the present and over past centuries and millennia, and specifically how they can be used to study marine climate, the marine environment and the economic and cultural history of the relationship between humans and the oceans.

The chapter is divided into two parts: section one describes the morphological, geochemical and crystallographic techniques that are used to obtain information from the shells, while section two covers the use of bivalve shells in a wide range of...
applications, including ecosystem services, environmental monitoring, archaeology, climate reconstruction, and climate modeling.

Abstract in Chinese  摘要: 在瞬息万变的世界中, 为了维护良好的海洋环境, 我们需要对其变化机制有一个详细的了解, 以便能够及时获取和辨识由人为影响造成的海洋生态平衡状态改变的早期信号。近几十年来, 我们评估海洋环境平衡扰动的长期基线变化的唯一途径是记录在珊瑚礁, 鱼耳石和贝类贝壳内不同年代的环境变化留下的信号。在本章中, 我们将着眼于研究当下和过去的数百乃至数千年中双壳贝类壳中记录的环境信号, 并基于这些信号来揭示长久以来海洋的变化情况, 包括如何利用这些信息来进行海洋气候研究, 海洋环境研究以及人类与海洋相互作用在经济与文化方面情况。

本章分为两部分: 第一部分描述如何通过形态学, 地球化学和晶体学技术从贝壳中获取信息; 第二部分介绍了双壳类贝壳在生态系统服务, 环境监测, 考古学, 气候状态重构和气候模拟等研究中的应用。

Keywords  Environmental monitoring · Mollusc · Archaeology · Marine climate · Ecosystems

关键词  环境监测 · 软体动物 · 考古学 · 海洋气候 · 生态系统

21.1  Physical and Geochemical Proxies

Everything that is known about past environmental and climatic conditions in the Earth’s history prior to the appearance of historical written records and the use of instrumental measurements is based on the identification and interpretation of proxies preserved in biological or geological structures. Proxies are measurable physical or chemical properties of biogenic or abiotic structures (e.g. shells, coral skeletons, trees, sediments, rocks) that can be interpreted as a signal of one or more environmental variables at the time during which the structures were formed. In addition, proxies enable monitoring of present day environmental conditions in locations where instrumental or historical observations are absent.

The major challenge when using bivalve shell material as a proxy archive (this is common to all proxy archives) is to establish the causal link between the wider environment in which the animal was living and the form, or configuration, with which the proxy manifests itself in the carbonate shell material. This is necessary in order to isolate the influence of the large-scale environment on the proxy from the effects of biomineralization or micro-environments. Complicating factors include vital effects, fractionation, multiple drivers in the environment, diagenesis, temporal lags, determination of the season of growth, and variable growth rates (throughout ontogeny and within each year) (Schöne 2008). While these sources of uncertainty can never be fully eliminated, they can be partially compensated through greater replication of chronologies in space (as the real environmental signal emerges from the background noise) and through mathematical modelling (Mueller et al. 2015; P. G. Butler et al.)

The main proxies used in bivalve sclerochronology are: variations in periodic shell growth (usually in the form of daily, tidally or annually deposited increments); stable oxygen, carbon and nitrogen isotopes and elemental composition of the shell; and changes in the shell crystal microstructure.

21.1.1 Shell Growth

Shell growth reflects the complex interactions of biological clocks and physiological processes with recurrent environmental pacemakers such as light/dark cycles, tidal exposure and diurnal or seasonal temperature variations. Interruption or reduction of shell growth results in the formation of distinct lines or bands (see Fig. 21.1), which delimit periodic growth increments at a range of temporal scales from sub-daily to annually.

Fig. 21.1 Annually-resolved growth increments imaged in the umbone (hinge) region of a specimen of *Glycymeris glycymeris*. Each increment (the wide lighter bands between the thin dark lines) consists of material laid down during the growth season (usually between 6 and 9 months). (Photo: Pedro Freitas)
While it is a challenging task to disentangle the signals of multiple environmental or climatic drivers in time-series of bivalve growth increments, growth increment series have been interpreted as a response to climate patterns in the Arctic (Ambrose et al. 2006) and north Atlantic (Reynolds et al. 2017, Swingedouw et al. 2015, Schöne et al. 2003), west African monsoon activity (Azzoug et al. 2012), sea surface temperature (Brocas et al. 2013; Reynolds et al. 2013; Black et al. 2009; Butler et al. 2010) and palaeo-productivity (Wanamaker et al. 2009; Witbaard 1996).

### 21.1.2 Stable Isotopes

The ability to use stable isotopes as geochemical proxies relies on the fractionation (i.e. the relative preference) between the lighter and heavier isotopes of an element during chemical reactions (e.g. carbonate precipitation or respiration) and the preservation of the resultant stable isotope ratio in the shell material. Stable isotope ratios of oxygen and carbon are commonly used in bivalve shells, while the use of stable isotope ratios of other elements (e.g. magnesium, boron, nitrogen, sulphur or strontium) is less common (e.g. Levin et al. 2015; Liu et al. 2015; Carmichael et al. 2008; Holmden and Hudson 2003), as is the use of clumped isotopes (Eagle et al. 2013).

#### 21.1.2.1 Stable Oxygen Isotopes

The stable oxygen isotope ratio ($\delta^{18}$O$_{\text{shell}}$) of shell carbonate depends on both the ambient temperature and the isotopic composition of the water, the latter being influenced by precipitation-evaporation dynamics and water mass mixing, thus being correlated (in marine environments) with salinity (Carmichael et al. 2008; Epstein et al. 1953; Urey 1947). Empirical palaeotemperature equations have been developed to reconstruct temperature from $\delta^{18}$O$_{\text{shell}}$ (e.g. Kim and O’Neil 1997; Grossman and Ku 1986), although these assume that $\delta^{18}$O$_{\text{water}}$ is known or can be estimated. Bivalves usually precipitate their shell calcite and aragonite in or close to oxygen isotopic equilibrium (e.g. Wefer and Berger 1991) and palaeotemperature equations have been produced for several bivalve species, including Pecten maximus (Chauvaud et al. 2005), Mytilus edulis (Wanamaker et al. 2007), Glycymeris glycymeris (Royer et al. 2013), Tridacna gigas (Aharon 1983) and Tridacna maxima (Duprey et al. 2015). The effect of seasonally variable growth rates must be taken into account, particularly in annually resolved records, since this causes variable time averaging and bias in $\delta^{18}$O$_{\text{shell}}$ records towards the season of highest growth and may inhibit the preservation of the full seasonal temperature amplitude (Schöne 2008; Goodwin et al. 2003).
21.1.2.2 Stable Carbon Isotopes

The stable carbon isotope composition of bivalve shell carbonate ($\delta^{13}C_{\text{shell}}$) has been proposed as a proxy for $\delta^{13}C$ of dissolved inorganic carbon ($\delta^{13}C_{\text{DIC}}$), and the processes that control it: salinity, the marine $\delta^{13}C$ Suess effect (Butler et al. 2009), and productivity and respiration (e.g. Schöne et al. 2011; Arthur et al. 1983; Killingley and Berger 1979; Mook and Vogel 1968). However, shell carbon does not originate only from DIC, but also includes a proportion of metabolic carbon with highly depleted $\delta^{13}C$ values and it can also be affected by kinetic isotopic disequilibrium (e.g. Gillikin et al. 2007; Kennedy et al. 2001; Mcconnuaughey et al. 1997; Klein et al. 1996; Tanaka et al. 1986). Nevertheless, $\delta^{13}C_{\text{shell}}$ can provide valuable information on environmental conditions in species with a stable metabolic influence or where the $\delta^{13}C_{\text{DIC}}$ signal is large enough to be preserved in $\delta^{13}C_{\text{shell}}$ (Butler et al. 2011; Schöne et al. 2011; Khim et al. 2003).

21.1.2.3 Stable Isotopes in the Shell Organic Matrix

Bivalve shells contain an organic matrix comprising up to 5% of the shell material (Marin et al. 2012), which can be analysed for $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ (e.g. Carmichael et al. 2008), albeit at a lower temporal resolution than is possible for the inorganic fraction. $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ in the organic matrix depend, as with bivalve soft tissues, on the isotopic composition of food sources and on fractionations associated with metabolic processes (Vander Zanden and Rasmussen 2001), providing information on primary consumer food sources, ecosystem trophic structure (Graniero et al. 2016; Ellis et al. 2014; Dreier et al. 2012; Versteegh et al. 2011; Mae et al. 2007; O’Donnell et al. 2003, 2007), and anthropogenic nitrogen inputs (Black et al. 2017; Kovacs et al. 2010; Watanabe et al. 2009; Carmichael et al. 2008).

21.1.3 Elemental Composition of Shell Carbonates

The elemental composition of bivalve shells (expressed as normalized E/Ca ratios) has – at least in theory – potential for palaeoceanographic reconstruction and environmental monitoring, this being related to the control of element incorporation by environmental variables such as temperature, or ambient element concentration. However, the complexities of bivalve shell biomineralization lead to strong physiological and kinetic effects related to metabolism, growth rates, ontogenetic age, shell mineralogy, crystal structure and the organic matrix (e.g. Freitas et al. 2008, 2009, 2016; Shirai et al. 2014; Lazareth et al. 2013; Schöne et al. 2013; Carré et al. 2006; Klein et al. 1996; Lorens and Bender 1977). Minor and trace elements can be incorporated in shell carbonate by various processes, including substitution of calcium in the carbonate crystal lattice (Soldati et al. 2016; Lingard et al. 1992); differential adsorption to heterogeneous crystal surfaces (Schöne et al. 2013); binding
to organics (Takesue et al. 2008); and co-precipitation as separate mineral phases (Fritz et al. 1990). As a result, the effective use of bivalve shell E/Ca ratios as environmental proxies has been limited, often to species-specific applications or applications restricted to particular environmental settings (e.g. Bougeois et al. 2014; Elliot et al. 2009).

### 21.1.4 Microstructure

While shell microstructure has commonly been used in phylogenetic studies, only more recently has it been found that crystal fabrics at the micrometre scale might preserve information on environmental conditions at the time of shell formation: these include pH in *Mytilus edulis* shells (Milano et al. 2016; Hahn et al. 2014) and temperature in *Trachycardium procerum* (Perez-Huerta et al. 2013) and *Cerastoderma edule* shells (Milano et al. 2017; Nishida et al. 2012).

### 21.2 Goods and Services of Bivalve Sclerochronology

#### 21.2.1 Ecosystem Services

##### 21.2.1.1 Introduction

The marine system has been estimated to supply about two-thirds of all ecosystem services provided by the natural environment (Gesamp 2001). These include, but are not limited to, fisheries, aquaculture, carbon sequestration, water quality, energy production, aggregate extraction and biodiversity. However, the present day marine system is challenged by the combined impact of climate change and industrial scale fisheries, and the definition of a “natural” baseline ecosystem or any kind of ecosystem equilibrium is problematic and challenging. While regime shifts in response to natural climate variability undoubtedly occurred before the industrial era (Hare and Mantua 2000; Minobe 1997), these did not take place in the context of steep trends in ocean temperature, ocean $pCO_2$ and selective harvesting of key species (Rocha et al. 2015). To maintain ecosystem resilience under such conditions is a challenging task for ocean management, and a key part of the process will be to assess the degree of ecosystem variability that characterizes a resilient system (Steinhardt et al. 2016; Willis et al. 2010). It is this degree of variability that can be assessed with the help of biochronologies drawn from multiple sources (eg bivalve molluscs, fish otoliths, corals).

The term “ecosystem variability” in this context includes population dynamics of single species, predator-prey relationships, trophic chains and host-pathogen relationships. Indicators of ecosystem variability that can be identified in bivalve shell archives include growth rate, population dynamics, environmental DNA and stable
isotope ratios (see Sects. 21.2.1.1, 21.2.1.2, 21.2.1.3 and 21.2.1.4 below). Although these are inherently limited as ecosystem proxies, being based on single species, their usefulness can be substantially enhanced by comparing them directly with other precisely dated archives, such as tree rings, corals, coralline algae and fish otoliths (e.g. Black 2009; Black et al. 2009) or by characterizing bivalve growth patterns using mixed effects models (Mazloumi et al. 2017; Morrongiello et al. 2012). In this way it is possible to develop detailed timelines of ecosystem variability, including leads and lags at annual and seasonal resolutions between different ecosystems and different parts of the same ecosystem.

With the use of modern statistical techniques such as principal components analysis and mixed effects models to isolate the causes and effects of interacting environmental drivers on multiple proxy archives, it is now possible to reconstruct ecosystem dynamics over many centuries. Long chronologies can be used in tandem with shorter archival records and instrumental data (Black et al. 2014), so that the dynamics of ecosystem regime shifts can be modeled and extended back in time with the application of mixed effects models (Morrongiello and Thresher 2015) to the long proxy archive. The use of networks of bivalve chronologies can add a spatial element to the extended archive (Reynolds et al. 2017).

### 21.2.1.2 Bivalve Growth Rates

To a first approximation, variability in bivalve growth rates can be assumed to be a response to variations in food supply to the benthos (Witbaard 1996). However, this apparently straightforward assumption is complicated by predator-prey relationships in the upper part of the water column, so that food supply to the bottom-dwelling bivalves can sometimes be anticorrelated with primary production at the surface (Witbaard et al. 2003). A further level of complexity is introduced by the position of the bivalve population above or below the seasonal thermocline, so that more complex ecosystem variability in shallow surface waters appears to result in rather low growth synchrony between animals in the same population (Marali and Schöne 2015), or the reversal of the correlation between growth and seawater temperature (compare Mette et al. 2016, with Brocas et al. 2013, and Butler et al. 2010). Bivalve growth rates therefore seem to reflect an emergent outcome of a complex web of ecosystem relationships in the overlying water column. This complexity can be deconvolved using multivariate analysis techniques such as multiple linear regression (Mette et al. 2016), Bayesian hierarchical modeling (Helser et al. 2012), principle component analysis (Tao et al. 2015), or mixed effects models (Izzo et al. 2017).
21.2.1.3 Population Dynamics of Bivalve Fisheries

The use of long absolutely-dated chronologies adds enormous value to studies of population dynamics and the management of commercial bivalve fisheries (Ridgway et al. 2012; Harding et al. 2008; Kilada et al. 2007). The ability to determine precise dates of settlement over long time frames enables changes of population structure over time to be determined. These changes can be related to information about climate, regime shifts, hydrography and predator-prey relationships, allowing aspects of the underlying ecosystem variability to be inferred (Ridgway et al. 2012; Witbaard and Bergman 2003; Witbaard et al. 1997).

21.2.1.4 Environmental DNA

A number of recent studies have shown that ancient DNA (aDNA) can be recovered from fossil material (e.g. Pruefer et al. 2014; Orlando et al. 2013), raising the possibility that changes in environmental DNA over time could be reconstructed by extracting aDNA from precisely dated fossil shell material. Snippets of aDNA recovered from the organic fraction of the shell matrix may characterize not only the genome of the bivalve itself, but also other species in the environment (from both inside and outside the shell). Metagenomic analysis of modern and fossil shells (Der Sarkassian et al. 2017) has shown that the shell biominerals (depending on their condition) may contain a range of microbial DNA from the marine environment, as well as the DNA of the host organism itself and its pathogens. This work indicates that there is potential to use environmental DNA and ancient DNA in shells to monitor the evolutionary history of bivalve species, their associated microbial communities and their relationship with pathogens.

21.2.1.5 Stable Isotope Ratios

The position of an animal in the surrounding food web is a useful indicator of predator-prey interactions or trophic chains, and one that can be approached through the analysis of stable isotope ratios of carbon and nitrogen in the organic fraction of the shell (e.g. Gillikin et al. 2017). Stable isotopes can also indicate disruption of the ecosystem as a result of anthropogenic inputs such as agricultural runoff or wastewater input (Versteegh et al. 2011). For more information on the use of stable isotopes in the shell organic matrix, see Sect. 21.1.2.3.
21.2.2 Environmental Services

21.2.2.1 Introduction

Reliable monitoring of past and present environmental conditions is essential if we are to accurately assess the impacts of anthropogenic and natural changes on the marine environment. 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; Fortunato 2014; Richardson 2001; Jones 1983). While the soft tissues of bivalves are commonly used in monitoring projects such as the well-known Mussel Watch program (Schöne and Krause 2016), the use of bivalve shells presents several distinct advantages: (1) shells are usually not affected by post-deposition alterations, while soft tissue decomposes rapidly; (2) there is potential to obtain both high-resolution (circa-daily to annual) records with accurately-dated banded shell material, and lower resolution time-averaged records from whole shells or fractions of shells; (3) temporal snapshots can be obtained from individual specimens; (4) where the bivalves are sufficiently long-lived, the proxy record can be extended into the past beyond the lifetime of single individuals through replicated cross-matched chronologies (see Sect. 21.2.4.1.); (5) shells can provide proxy records for times and locations where instrumental networks and records are absent. However, the use of shells for environmental monitoring and reconstruction is still limited, due to analytical limitations (e.g. stable isotopes in the organic matrix), unknown pathways of incorporation into the shell (e.g. hydrocarbons and other organic pollutants), significant inter-shell variation, or the complex control of most proxies by multiple environmental and biological variables. Consequently, most studies of bivalve shell environmental proxies have focused on the evaluation and validation of environmental and physiological controls for individual species at specific sites. Nevertheless, with the added value provided by crossdating and replication, bivalve shells can provide baseline monitoring and reconstruction services for a range of environmental characteristics (see Schöne and Krause 2016 and Steinhardt et al. 2016 for recent reviews), including contamination events, temperature, salinity and river discharge.

21.2.2.2 Pollution Events

Minor and trace elements, due to their role in biogeochemical processes and their potentially hazardous impact on the environment, have been of particular interest in studies of the capacity of bivalve shells to record natural and anthropogenic changes in ambient chemistry, including pollution events. Most studies have compared whole shells or fractions of shells from contaminated and non-contaminated sites (see Schöne and Krause 2016 for a recent review). Elevated levels of metals (e.g. Mn, Fe, Cu, Zn, Cd, Pb and U) in the shells of several species (e.g. Arctica
islandica, Crassostrea gigas, Crassostrea virginica, Ensis siliqua, Modiolus modiolus, Mercenaria mercenaria, Mya arenaria, Mya truncata, Mytilus edulis, Mytilus californianus, Mytilus galloprovincialis, Perna perna, Perna viridis and Pinctada imbricata,) have been interpreted as an indication of elevated metal levels in the ambient seawater or sediment (Cariou et al. 2017; Holland et al. 2014; Krause-Nehring et al. 2012; Dunca et al. 2009; Klunder et al. 2008; Protasowicki et al. 2008; Bellotto and Miekeley 2007; Macfarlane et al. 2006; Pearce and Mann 2006; Gillikin et al. 2005a; Liehr et al. 2005; Nicholson and Szefer 2003; Yap et al. 2003; Richardson 2001; Almeida et al. 1998; Puente et al. 1996; Raith et al. 1996; Pitts and Wallace 1994; Fuge et al. 1993; Bourgoin 1990; Koide et al. 1982; Bourgoin and Risk 1987; Chow et al. 1976). However, most of this research is based on snapshots in time, and it rarely involves the use of a truly sclerochronological approach to produce time-series of metal levels in shells (e.g. Vander Putten et al. 2000; Price and Pearce 1997; Carriker et al. 1980). Recent studies have produced decadal to centennial records of environmental heavy metal variability using long-lived species, such as Pb and Fe in Arctica islandica (Holland et al. 2014; Krause-Nehring et al. 2012) or Pb in Mercenaria mercenaria (Gillikin et al. 2005b). Metal levels in the shells of freshwater bivalves (e.g. Mn, Co, Ni, Cu, Zn, Cd, and Pb) have also been demonstrated to record contamination from industrial or mining activities (Markich et al. 2002; Schettler and Pearce 1996; Anderson 1977) or even, using Na shell content, contamination from road-salt (O’Neil and Gillikin 2014). Elemental proxies have also been proposed as archives of changes in pelagic primary production, e.g. Mo/Ca (Barats et al. 2010; Thébault et al. 2009a), Ba/Ca (Barats et al. 2009) or Li/Ca (Thébault and Chauvaud 2013; Thébault et al. 2009b). However, in general, trace element ratios to calcium (Mg/Ca, Sr/Ca, Li/Ca, Mn/Ca and Ba/Ca) are more difficult to interpret in bivalves and seem to be very sensitive to vital effects, especially growth rate (Carré et al. 2006; Gillikin et al. 2005c; Takesue and Van Geen 2004). In addition to minor and trace elements, other proxies in bivalve shells have been used to record anthropogenic contamination. For instance, the δ15N composition of the shell organic matrix can provide information on nitrogen anthropogenic wastewater inputs to estuarine ecosystems (e.g. Gillikin et al. 2017; Kovacs et al. 2010; Watanabe et al. 2009; Carmichael et al. 2008).

21.2.2.3 Temperature, Salinity and the Stable Oxygen Isotope Proxy

Bivalve δ18O_{shell} values obtained at daily, annual or decadal resolutions reflect a wide range of habitats and species from deep-sea oysters Neoplyncnodonte zibrowii (Wisshak et al. 2009) to coastal (or estuarine) and freshwater bivalves, such as mussels (e.g. Unionidae (Dettman et al. 1999), Mytilus trossulus (Klein et al. 1996), Pinna nobilis (Kennedy et al. 2001), scallops (Pecten maximus – Chauvaud et al. 2005) and oysters (Crassostrea gigas – Ullmann et al. 2010); the geographical spread ranges from tropical (e.g. Tridacna gigas (Elliot et al. 2009), Hippopus hippopus (Aubert et al. 2009), Comptopallium radula (Thébault et al. 2007)) and temperate waters (e.g. Glycymeris glycymeris – Royer et al. 2013) to sub-polar (e.g.
Arctica islandica – Schöne et al. 2004, Marsh et al. 1999) and polar waters (Carroll et al. 2009; Tada et al. 2006; Simstich et al. 2005)(e.g. Astarte borealis (Simstich et al. 2005) Lernula elliptica (Tada et al. 2006), Serripes groenlandicus (Carroll et al. 2009)). They also perform an important analytical function, since diurnal or seasonal variation in $\delta^{18}O_{\text{shell}}$ effectively validates the periodicity of the growth patterns (e.g. Schöne and Giere 2005; Goodwin et al. 2001; Brey and Mackensen 1997; Jones and Quitmyer 1996; Witbaard et al. 1994; Krantz et al. 1984).

However, the most powerful application of $\delta^{18}O_{\text{shell}}$ has been to provide information about the oceanographic and climatic processes that control seawater temperature and salinity. For instance, bivalve $\delta^{18}O_{\text{shell}}$ has been used to determine changes in: seasonality (e.g. Beierlein et al. 2015; Wanamaker et al. 2011; Schöne and Fiebig 2009; Schöne et al. 2005b); ocean circulation and atmospheric forcing dynamics (e.g. Reynolds et al. 2017; Wanamaker et al. 2008); shelf and coastal seas hydrography, reflecting changes in circulation (e.g. Torres et al. 2011), river discharge (e.g. Muller-Lupp and Bauch 2005; Simstich et al. 2005; Dettman et al. 2004; Schöne et al. 2003; Surge et al. 2003; Khim et al. 2003; Mueller-Lupp et al. 2003; Ekwurzel et al. 2001) or glacial ice-melt runoff (e.g. Versteegh et al. 2012; Tada et al. 2006; Ekwurzel et al. 2001; Azetsu-Scott and Tan 1997); ENSO variability (e.g. Welsh et al. 2011; Carré et al. 2005); West African Monsoon variability (e.g. Azzoug et al. 2012); and coastal upwelling (e.g. Jolivet et al. 2015). However, within-shell trends in isotopic amplitudes and averages may also reflect decreases in growth rate rather than environmental fluctuations. Therefore, particular care should be taken when interpreting inter-annual isotope profiles from long-lived species (Goodwin et al. 2003).

In addition to $\delta^{18}O_{\text{shell}}$, other proxies have been proposed to record changes in salinity and river discharge of coastal and estuarine waters, e.g. Sr isotopes (Widerlund and Andersson 2006) and Ba/Ca ratios (Poulain et al. 2015; Carroll et al. 2009; Gillikin et al. 2006, 2008).

### 21.2.3 Cultural Services

#### 21.2.3.1 Introduction

Human interactions with the intertidal zone, including shellfish collection and in particular harvesting of bivalves have been part of human, and some non-human, cultures for over a hundred thousand years. Bivalve shells have become an increasingly valuable resource for archaeological studies of food habits, patterns of seasonal site occupation, migration, tool use, ornamentation, and the dating of archaeological sites (Thomas 2015a, b; Andrus 2011; Andrus and Crowe 2000; Claassen 1998). Interdisciplinary approaches, combining archaeology, biology and geochemistry have significantly contributed to increased understanding and interpretations of the long-term contributions of bivalves to human culture. The
application of bivalve sclerochronology in archaeology is expanding the range of questions archaeologists can ask about past human-environmental interactions.

The earliest evidence of the intentional gathering of bivalves by humans is found at Terra Amata, France (Claassen 1998; Stein 1992). Bivalves were used as a staple and supplementary food source, and empty shells were used for tools and ornamentation by humans and even by our non-human ancestors (Duncan and Ghys 2018). Some of the earliest evidence for understanding human cognition and symbolism comes from the preservation of shell artefacts. Individuals were crafting marine shells into beads to be worn as ornamentation in Israel and Algeria 75,000 years ago (Vanhaeren et al. 2006), and as far back as 82,000 years ago, shell beads decorated with red ochre were left behind in human occupied caves in North Africa (Bouzouggar et al. 2007). Our extinct cousins, the Neanderthals, crafted adornments from the shells of the marine bivalves *Pecten, Glycymeris, Spondylus* and *Acanthocardia* at Cueva de los Avoines, Iberia, in the Middle Palaeolithic 50,000 years ago (Zilhao et al. 2010). Freshwater shells first appear in the archaeological record in southern Egypt 24,000 years ago. In hunter-fisher-gatherer societies, both past and present, shell tools are used as part of everyday tasks and shells have been valued as ornamentation and symbolic objects; in many early communities, thousands of shell disc beads were used to adorn the dead to prepare them for the afterlife and commemorate their status within society; for example, burials dating between 4000–3500 Cal. BP from the Salish Sea in British Columbia in Canada contain individuals who were buried with up to 350, 000 individual stone and shell beads (Coupland et al. 2017).

### 21.2.3.2 Shell Middens

The most abundant bivalve remains in the archaeological record appear in the context of shell middens and shell mounds (Roksandic et al. 2014) (Fig. 21.2). Cumulative everyday acts of bivalve collection over decades, centuries or millennia resulted in the formation of shell middens that can be found along almost all of the world’s coastlines. Shell middens are deposits that consist primarily of shell, although their micro-constituents can vary with site formation, duration of occupation, population size and purpose (Alvarez et al. 2011; Claassen 1998; Stein 1992). The size and shape vary, from small mounds of finely crushed shells, to extended mounds stretching over tens of kilometres of coastline and over 10 m in height (or depth). For example, modern-day shell middens, and archaeological shell middens from the Saloum Deltal in Senegal are over 15 m in height (Hardy et al. 2016). Shell middens are frequently regarded as homogenous ‘garbage heaps’ that can represent periods of shell acquisition and disposal that range from a few days of intensive harvesting to continuous harvesting over millennia. In other contexts, they can take the form of monumental architecture, such as those in the south-eastern United States, specifically the shell rings in Georgia and South Carolina (Marquardt 2010; Thompson and Andrus 2011). Our understanding of variability in the nature and extent of shell middens and mounds has been enriched by work on notable shell
Fig. 21.2 (top) Shell midden excavation in progress from the Salish Sea, southern British Columbia. (Photo: Terence Clark); (bottom) Intact sediment block from a shell midden embedded with fiberglass resin, north Calvert Island, British Columbia, Canada. (Photo: Meghan Burchell)
midden regions including the Jomon middens of Japan (e.g. Habu et al. 2011), Sambaquis of Brazil (Okumara and Eggers 2014), the Pacific Northwest Coast (Moss 2011), as well as the kitchen middens (“køkkenmøddinger”) on the coasts of Scandinavia (Anderson 2008), to name just a few studies among many.

21.2.3.3 Bivalves as a Food Source

Contemporary studies of indigenous populations attest to the importance of shellfish, particularly bivalves, as a food source, especially on the coasts of Australia, Chile, Papua New Guinea, Mozambique and South Africa (Bird and Bird 1997; Kyle et al. 1997), and demonstrate that bivalve gathering is not always a random activity, but is often governed by social and environmental circumstance. Bivalves in cultural contexts go beyond being simply a food source – their shape, colours, and sounds have influenced human cultural activities for millennia, and shells still hold a prominent place in many origin myths and rituals within indigenous societies today. Through the analysis of bivalves in various contexts, interpretations about long-term human environmental interactions and human interaction with the supernatural world can be interpreted.

Collection of oysters and limpets is first recorded at the open-air site of Terra Amata in France, and further evidence suggest gathering of bivalves began elsewhere in Europe as long ago as 450,000 years (Bailey and Milner 2008). The intensification of gathering of bivalves and other marine molluscs as a food source has been observed at approximately 9000 years ago at Cantabria, northern Spain (Waselkov 1987); overall, the increased visibility of bivalve collection has been associated with human population growth, economic intensification, and changes in sea level (Bailey and Craighead 2003).

Bivalves and other intertidal resources have, for the most part, been considered an insignificant, or ‘fall back’ resource at coastal sites, especially when compared to other food sources such as fish or marine and terrestrial mammals (Eerkens et al. 2016; Erlandson 2001). In previous archaeological studies, the presence of bivalves has often been little more than acknowledged (Fitzhugh 1995); however, as new methods emerge for studying the season and intensity of gathering, archaeologists are becoming better able to understand the role of bivalves in coastal economies of the past, especially regarding seasonal patterns of resource acquisition and by proxy, site occupation.

21.2.3.4 Bivalve Sclerochronology and Seasonality of Human Occupation

Seasonality plays a critical role in hunter-fisher-gatherer societies, particularly in temperate locations, since it influences the availability of food resources and structures the organization of activities and the timing of events. Seasonal changes are therefore integrated into all social, economic and settlement activities. Seasonal subsistence practices are scheduled to optimize the acquisition of resources that
vary in quantity, availability and abundance. The importance of seasonality also varies by location and is enhanced in areas with a ‘hungry season’, where food resources need to be stored to ensure a supply throughout the year (De Garine and Harrison 1988). Bivalves have been identified as a seasonally critical food source and a required source of carbohydrates and proteins during ‘lean seasons’. In response to seasonal changes, hunter-gatherers can practice resource management, including season-specific bivalve harvesting (Smith and Wishnie 2000) and drying and storage of their meat (Henshilwood et al. 1994). Using stable oxygen isotope analysis of shell carbonate, archaeologists are able to identify the season, or seasons of bivalve collection (Jew et al. 2013; Hallmann et al. 2009; Deith 1986; Killingley 1981; Shackleton 1973) and interpret long- and short-term settlement patterns (Prendergast and Schöne 2017; Burchell et al. 2013). Seasonality can also be determined through the analysis of sub-annual and annual growth patterns by measuring the distance between seasonally deposited lines (Carré et al. 2009; Milner 2001; Lightfoot et al. 1993). However, the methods used to identify seasonality are contingent on species, shell growth and locality. Some bivalves produce multiple ‘annual lines’ in their shells, and with these species, seasonality can only be resolved with high-resolution stable oxygen isotope analysis. This has been a critical advance in understanding how hunter-fisher-gatherers co-ordinated movements between sites and developed permanently settled villages. For example, by combining season-of-harvest determined from stable oxygen isotope analysis of the bivalve Saxidomus gigantea with sclerochronology, radiocarbon dating and ancillary lines of archaeological evidence, year-round occupation of the village site at Namu for at least 4500 years has been confirmed (Burchell et al. 2013; Cannon and Burchell 2017), predating previous ideas about when hunter-fisher-gatherers established permanent villages on the Pacific Northwest Coast of North America.

21.2.3.5 Bivalve Sclerochronology and Accurate Radiocarbon Dating

The marine radiocarbon reservoir effect (i.e. the uncertainty in radiocarbon dating of marine samples because the measured radiocarbon has spent an unknown period in the marine system before being taken up into the sample) is a longstanding challenge for archaeology in coastal sites, that can be usefully approached using bivalve sclerochronology. If the regional marine reservoir can be independently determined by radiocarbon analysis of an absolutely dated bivalve chronology (Wanamaker et al. 2012; Butler et al. 2009), a more accurate radiocarbon calibration can be applied to midden shells from the same region. Conversely, if there is an independent assessment of the date of occupation, radiocarbon dating of midden shells can be used to determine the regional marine reservoir (Ascough et al. 2006). It is also possible to further constrain radiocarbon dating of coastal sites by the construction of crossmatched floating chronologies using shells found at different levels in middens (Helama and Hood 2011).
21.2.4 Climate Services

21.2.4.1 Introduction

The key characteristics that make this archive so powerful are: (a) that the animals deposit periodic (daily, fortnightly or annual) well-defined increments in the shell; (b) that growth is synchronous within populations; (c) that individuals of certain species can live for hundreds of years (Arctica islandica (Butler et al. 2013, Schöne et al. 2005a) and Glycymeris glycymeris (Reynolds et al. 2013)); (d) that most species precipitate calcium carbonate in isotopic equilibrium with seawater; (e) that natural or anthropogenic deposits of bivalve shells are widespread and are found at all latitudes. Synchronous growth patterns provide prima facie evidence that the shells are recording a common environmental signal, while annual banding allows the precise calendar year of each band to be determined (as long as the year of the most recent band is known). In addition, where species have extended lifespans, the years of fossil shells can be precisely determined by comparing their banding patterns with those from live collected shells. In this way, crossdated and replicated timelines (chronologies) of shell material can be built that go back much further in time than the lifetimes of any live collected shell. For example, specimens of A. islandica off the north coast of Iceland regularly live for more than 300 years (Schöne et al. 2005a), and one specimen collected there in 2006 is (at 507 years; Fig. 21.3) the longest-lived non colonial animal known to science whose age can be precisely determined (Butler et al. 2013).

While the multicentennial length of long chronologies adds value to proxy-based reconstructions derived from them, these are only available for certain regions (in particular the temperate and boreal North Atlantic Ocean). In low latitudes, bivalves with much shorter lifespans can be used to reconstruct paleoclimate, albeit in shorter and less precisely dated windows. These include studies of seasonality in the Eocene in central Asia (Bougeois et al. 2014) and in the Miocene in the Amazon (Kaandorp et al. 2005; Vonhof et al. 1998), ENSO variability in the eastern (Carré et al. 2014) and western (Driscoll et al. 2014) tropical Pacific, and Holocene climate variability in the southwest Pacific (Duprey et al. 2012, 2014).

21.2.4.2 The Use of Proxy Archives in Climate Modelling

With the atmospheric concentration of CO₂ passing the 400 ppm threshold in 2016 and unlikely to fall back below it for the foreseeable future (Betts et al. 2016) and emissions continuing to increase at a rate equivalent to business as usual (Boden et al. 2015), the need for climate scientists to generate useful projections to inform mitigation and adaptation policy is more acute than ever. Impacts of climate change on the marine system include species range shifts, loss of ecosystems and biodiversity and impacts on coastal livelihoods (IPCC 2014). Accurate projections of regional change in the short to medium term (which are of most interest to policymakers) require sufficiently high resolution in climate models, and this in turn
depends on access to similarly high resolution instrumental and proxy data for assimilation (Fang and Li 2016; Phipps et al. 2013). Suitable methods are already being used for modeling of terrestrial systems using proxies from tree-rings (Breitenmoser et al. 2014; Loader et al. 2013) and speleothems (Baker et al. 2012) and for tropical marine systems using proxies from corals (Evans et al. 1998), and more recently it has been demonstrated that reconstructions of marine climate using bivalve shells can provide high resolution real world data for the temperate and boreal oceans that can be used to test and constrain coupled climate models (Pyrina et al. 2017; Emile-Geay et al. 2016; Swingedouw et al. 2015).

21.2.4.3 Marine Climate of the North Atlantic Ocean

Arctica islandica is a particularly important proxy in this respect because of its distribution in the shelf seas surrounding the North Atlantic Ocean (Schöne 2013; Dahlgren et al. 2000). The North Atlantic is a highly sensitive sentinel of change in the climate system. Heat is transferred from the tropical to the boreal latitudes in the Gulf Stream/North Atlantic Current system. As the water gives up its heat by evaporation at high latitudes in the Labrador and Nordic Seas it becomes dense and sinks, a mechanism (the Atlantic Meridional Overturning Circulation (AMOC)) that plays an important part in driving the global ocean circulation system. Model experiments
indicate that the AMOC will weaken during the twenty-first century (Liu et al. 2017; Weaver et al. 2012), and there are some indications that this is already happening (Rahmstorf et al. 2015).

Recent research using the 1357-year A. islandica time series for the North Icelandic Shelf (NIS) (Butler et al. 2013) illustrate some of the climate services that can be obtained from this proxy. By measuring the radiocarbon age of shell material that has been independently dated using sclerochronology, it is possible to determine the radiocarbon age of the water mass in which the shell was deposited (i.e. the length of time since the water was last ventilated at the ocean surface). In the case of the NIS, this has enabled researchers to map changes in the relative strength of water masses with Arctic and Atlantic origins and gain a unique insight into the mechanisms driving the marine system in the North Atlantic (including the AMOC) during the past millennium (Wanamaker et al. 2012).

The NIS A. islandica series has also been used to validate models of the response of the ocean to large volcanic eruptions. For example, the modeled effect of a particular class of large tropical eruption on bidecadal North Atlantic Ocean circulation variability appears to be mirrored in growth variations in A. islandica from the NIS (Swingedouw et al. 2015).

Most recently, the first 1000-year annually-resolved stable oxygen isotope (δ¹⁸O) series for the marine environment has been obtained by sampling carbonate from individual increments in shells used in the NIS A. islandica chronology (Reynolds et al. 2017). By comparing the shell record with tree ring records, the researchers demonstrated a significant change in the lead-lag relationship between the marine and atmospheric systems. Before the industrial period (AD 1000–1800), changes in the marine system (forced by solar and volcanic variability and internal dynamics of ocean circulation) led changes in Northern hemisphere surface air temperatures (SATs), whereas after ~1800 the relationship was reversed, with changes in SATs leading changes in marine variability. This suggests that the climate effect of rapid increases in atmospheric greenhouse gases has masked the effects of natural external forcing and internal variability.

### 21.2.4.4 History of Carbon Cycling

The ocean currently acts as a buffer against rapidly increasing concentrations of CO₂ in the atmosphere, taking up between 26% and 34% of the net anthropogenic emissions (Sabine et al. 2004). Because CO₂ derived from fossil fuels is depleted in the heavy isotope ^13^C, measurement of the stable carbon isotope ratio (δ^13^C) in dated marine shells from different parts of the ocean can be used to determine spatio-temporal variability in the activity of the ocean as a sink for atmospheric CO₂. The temporal trend in atmospheric δ^¹³^C (~¹³^C Suess effect (Francey et al. 1999)) is an indicator of the increasing presence in the atmosphere of CO₂ derived from fossil fuels. The coeval trend in oceanic dissolved inorganic carbon (δ^¹³^C_DIC), which can be determined from time series of δ^¹³^C measured in absolutely dated bivalve shell material (Schöne et al. 2011; Butler et al. 2009), varies according to water depth and
the age of the local water mass, and indicates the spatial distribution of the rate at which the ocean has been acting as a sink for excess atmospheric CO$_2$.

In addition, radiocarbon in the shell can be used in water mass detection, since the age of the ambient water can be determined by measuring radiocarbon in shells of known age (Scourse et al. 2012; Wanamaker et al. 2012; Fontugne et al. 2004; Ingram and Southon 1996; Southon et al. 1995), and is also related to sea-air CO$_2$ exchange (Carré et al. 2016).

21.3 Conclusion

During their lifetimes, bivalve molluscs deposit carbonate material to form their shells. This material constitutes a physical archive, which may be time-delimited (usually with daily, tidal or annual periodicity) by well-defined banding patterns in the shells. This archive contains multiple morphological, structural and geochemical records which can be related to the environment in which the shell material was deposited, and which can be analysed as well-ordered and periodically-constrained time series by reference to the banding patterns. The ubiquity and durability of the shells enhances the power of the archives, so that the records contained within them can be used as environmental proxies for a wide range (both in space and in time) of marine and coastal settings.

In this paper, we have described and assessed some of the most notable proven applications of bivalve sclerochronology in ecosystem, environmental, cultural, and climate services. However, it has been necessary to address a vast amount of research in a limited number of words, and the examples described here do not by any means constitute an exhaustive selection. With analytical techniques continually being refined and updated, and new ones being developed (e.g. clumped isotopes and Raman spectroscopy), there is very significant potential in the coming decades for new applications and improved reliability of existing applications. For as long as human society values the environment within which it is constrained to exist, it will find useful tools in the insights into past environments provided by the shells of animals that actually lived in those settings.

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