Bivalve Shells—Unique High-Resolution Archives of the Environmental Past

Lars Beierlein, Gernot Nehrke, Tamara Trofimova and Thomas Brey

Abstract Understanding the climate of the past is essential for anticipating future climate change. Palaeoclimatic archives are the key to the past, but few marine archives (including tropical corals) combine long recording times (decades to centuries) with high temporal resolution (decadal to intra-annual). In temperate and polar regions carbonate shells can perform the equivalent function as a proxy archive as corals do in the tropics. The bivalve *Arctica islandica* is a particularly unique bio-archive owing to its wide distribution throughout the North Atlantic and its extreme longevity (up to 500 years). This paper exemplifies how information at intra-annual and decadal scales is derived from *A. islandica* shells and combined into a detailed picture of past conditions. Oxygen isotope analysis ($\delta^{18}O$) provides information on the intra-annual temperature cycle while frequency analysis of shell growth records identifies decadal variability such as a distinct 5-year signal, which might be linked to the North Atlantic Oscillation.

Keywords Sclerochronology · *Arctica islandica* · Frequency analysis · Raman microscopy · Stable oxygen isotopes · Palaeoceanography · Intra-annual · Decadal

1 Introduction

Current predictions of future climate change (e.g., IPCC 2013) are based on global circulation models (GCM) to a large extent. Such models incorporate observational and instrumental data of the oceans, continents and atmosphere. Instrumental data are available for the last two centuries at best, but we need climate and

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environmental data prior to the instrumental era in order to improve and verify such climate models. Therefore, climate sciences rely on climate archives such as sediment cores and ice cores. Such archives contain "*proxies*", i.e. physical, chemical or biological properties that correlate to certain environmental parameters and hence allow reconstructions of such parameters at the time of the formation of the archive. The relationship between water temperature and $\delta^{18}O$ is thought to be the most important relationship between an environmental parameter and its proxy.

Accretionally growing hard parts of aquatic organisms (e.g., corals, fish and squid otoliths, coralline algae, bivalve shells) are being used as climate archives

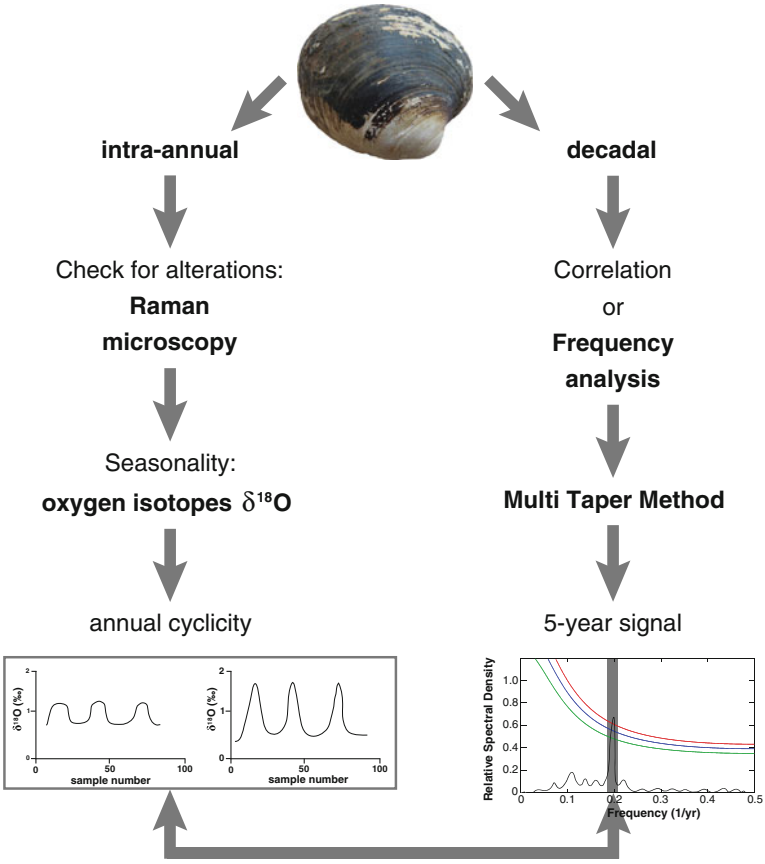

Fig. 1 Flow chart illustrating potential reconstruction techniques on various time-scales for bivalve shells. Geochemical analyses, such as $\delta^{18}O$ as a proxy for water temperatures, allow reconstructions on an intra-annual level. A test for preservation in fossil specimens—e.g., by using CRM—should be obligatory. The shell of *A. islandica* can additionally be used for a frequency analysis (e.g., Multi Taper Method) of the annual growth pattern, allowing the identification of decadal variabilities, such as a 5-year quasi-periodic signal

with increasing frequency, providing environmental information on daily to multi-centennial time-scales (Schöne et al. 2005b; Hallmann et al. 2009; Butler et al. 2010). For this purpose, analyses of the anatomical-morphological features of the skeletal hard parts—such as growth patterns and crystal structures—are commonly combined with geochemical analyses (e.g., stable isotopes, trace elements). Due to its wide distribution throughout the North Atlantic (Dahlgren et al. 2000) and its longevity (500 years and more, Butler et al. 2013), the bivalve *Arctica islandica* represents an exceptional bio-archive for northern temperate regions.

A. islandica forms annual growth rings (increments), which can be measured and used as a calendar (Jones 1980). However, when working with fossil specimens, the state of preservation is an essential aspect to consider prior to any kind of geochemical analysis (e.g., stable oxygen isotopes ($\delta^{18}O$) as a proxy for water temperature and salinity). Confocal Raman microscopy (CRM) is a non-destructive method, which allows a test for diagenetic alteration on the same sample that will later be used for the geochemical measurement.

The annual growth rate of bivalves mainly depends on ambient water temperature and food quality and availability (e.g., Witbaard et al. 1997) which vary on a regional scale, but may be affected by large-scale ocean-atmosphere phenomena, too (Schöne et al. 2003a), like the North Atlantic Oscillation (NAO). The frequency analysis of the growth record of just a single *A. islandica* shell can identify such decadal signals (several years to decades) in a time window corresponding to the animal's lifetime.

For demonstration purposes we combine the results from modern and fossil shell material to emphasise the unique character of the bio-archive *A. islandica*. We demonstrate its outstanding potential in terms of intra-annual (stable oxygen isotopes) as well as decadal (frequency analysis) climatic and environmental reconstructions and show how these can be combined to inform our understanding of climate in the past (Fig. 1).

2 Methods

2.1 Shell Origin and Laboratory Work

We use three *A. islandica* specimens of different geological age (see Table 1 for details) to demonstrate how sclerochronological analyses at intra-annual and decadal scale fit together. The CRM approach has been applied on Pliocene specimen AI-TjBe-01, which was removed from the biostratigraphically dated Tjörnes Bed formation, Iceland. Specimen AI-EgLo-02 has been found dead in beach deposits at the Lofoten, Norway, and used for the frequency analysis. Further, specimen

Table 1 Shell information

Shell ID	Length (mm)	Height (mm)	Width (mm)	Locality	Geological age	Ontogenetic age (years)	Applied method
Ai24568	86.7	82.0	23.2	Tromso, Norway	Modern	71	Oxygen isotope analysis
AI-EgLo-02	53.3	46.6	14.0	Lofoten, Norway	Found dead, beach deposit	45	Frequency analysis
AI-TjBe-01	57.2*	84.0	24.4*	Tjörnes, Iceland	Pliocene	Not determined	Raman microscopy

Information on shell morphology, shell origin, geological and ontogenetic ages as well as applied methods are given. Measurements marked with (*) for specimen AI-TjBe-01 give values for partly fragmented shell portions

Ai24568 has been live-collected in Tromsø, Norway in 2006 and used for the $\delta^{18}O$ approach.

In the laboratory, all specimens were cleaned using a paintbrush, deionized water and an ultrasonic bath. Afterwards, shells were externally strengthened with an epoxy resin and cut along the line of strongest growth (LSG, Fig. 2). The cut shell sections were glued onto glass slides and ground on sandpaper with varying grain sizes of 15, 10 and 5 µm respectively.

To improve the visibility of the individual growth increments, the thick-section intended for the frequency analysis (shell ID: AI-EgLo-02) was stained with Mutvei's solution (Schöne et al. 2005a). Digital images were taken under a stereomicroscope (Olympus, SZX12) attached to a CCD camera (Olympus) and

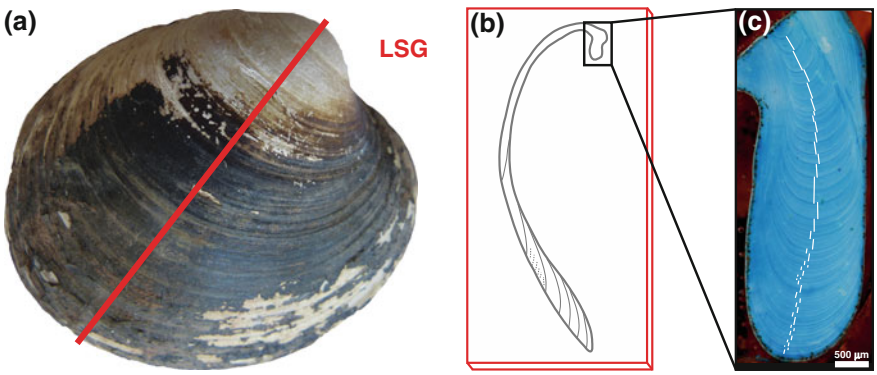

Fig. 2 Cutting axis and location of shell increments in *A. islandica*. **a** Right valve of an *A. islandica* specimen with line of strongest growth (LSG, equals cutting axis). **b** Graphical illustration of an *A. islandica* thick-section after cutting through the LSG (*red*). *Black box* indicates the umbonal area shown in **c**. **c** Magnification of the umbonal area, stained in Mutvei's solution and showing annual growth increments. Growth band widths are measured perpendicular to the increments, as indicated by the *white lines*

increment width was measured using the image processing software analySIS (Olympus, version 5.1).

2.2 State of Preservation

The shells of *A. islandica* consist of aragonite ($CaCO_3$), trace elements and organics (e.g., Schöne 2013). After burial and in terms of fossilisation, several factors such as heat and pressure at depth, as well as hydrothermal fluids, can cause alterations in the shell carbonate, e.g., recrystallization from pristine aragonite to the more stable $CaCO_3$ polymorph calcite (e.g., Bathurst 1964). In most cases the recrystallization process involves a dissolution and recrystallization process (*neomorphism*, e.g., Maliva 1998), which would replace the pristine stable oxygen isotope ratio within the carbonate and erase the associated environmental signal in the shell (e.g., Hendry et al. 1995).

Due to its high spatial resolution of a few hundred nm CRM provides an ideal tool for shell carbonate analysis. For our measurements on Pliocene specimen AI-TjBe-01 we used a WITec alpha 300 R instrument, equipped with a diode laser (excitation wavelength 532 nm) and a 20× Zeiss objective. Details on the measurements can be found in Nehrke et al. (2012).

2.3 Frequency Analysis

The growth record of shell AI-EgLo-02 was detrended using a cubic spline (JMP software, version 9.0.1 by SAS Institute Inc. 2007), and a standardized growth index (SGI) was calculated following Butler et al. (2010). The subsequent frequency analysis was conducted using kSpectra software (version 3.4 by SpectraWorks) with settings according to Ivany et al. (2011) and applying a Singular Spectrum Analysis (SSA) and the Multi Taper Method (MTM). Furthermore, we used wavelet transformation to examine whether quasi-periodic signals were stationary over time (http://ion.researchsystems.com/IONScript/wavelet/), following Torrence and Compo (1998). Growth records of specimens Ai24568 and AI-TjBe-01 have not been analysed.

2.4 Stable Oxygen Isotopes ($\delta^{18}O$)

During shell formation, *A. islandica* incorporates oxygen isotopes in equilibrium with the surrounding seawater (Weidman and Jones 1994). Since the incorporation of lighter oxygen isotopes is facilitated during higher temperatures (Grossman and Ku 1986), the oxygen isotope ratio $\delta^{18}O$ of most bivalve species provides

information on water temperatures (e.g., Schöne et al. 2005c) and salinity (e.g., Schöne et al. 2003b) at the moment of shell formation. In general, the modified temperature equation by Dettman et al. (1999) is used for *A. islandica*, which is based on the empirically determined relationship between temperature and $\delta^{18}O$ for aragonite by Grossman and Ku (1986).

Carbonate samples were milled by hand (Dettman and Lohmann 1995) using a 700 µm drill bit (Komet/Gebr. Brasseler GmbH & Co. KG) mounted onto an industrial high precision drill (Minimo C121, Minitor Co., Ltd.) and attached to a binocular microscope. Measurements were performed on a Thermo Finnigan MAT 253 isotope ratio mass spectrometer and calibrated against a NBS-19 standard with a precision error of 0.08 ‰ for oxygen. Shell-derived water temperatures have been compared to SST measurements reported online (http://www.seatemperature.org/europe/norway/tromso.htm).

3 Results

3.1 State of Preservation

From the Raman scan it can be seen that the area of the fossil *A. islandica* shell (shell ID: AI-TjBe-01) marked in Fig. 3a consisted of both aragonite and calcite. An area scan of 520 × 500 µm (Fig. 3b), partly covering the potentially recrystallized shell portion, indicates the distribution of (pristine) aragonite and (recrystallized) calcite within the shell carbonate. Both polymorphs share carbonate-specific peaks at 155 and 1085 cm^{-1} in their Raman spectra (Fig. 3c). The aragonite-specific peak at ~206 cm^{-1} (blue line in Fig. 3c) is shifted towards ~280 cm^{-1} in (recrystallized) calcite (red line in Fig. 3c).

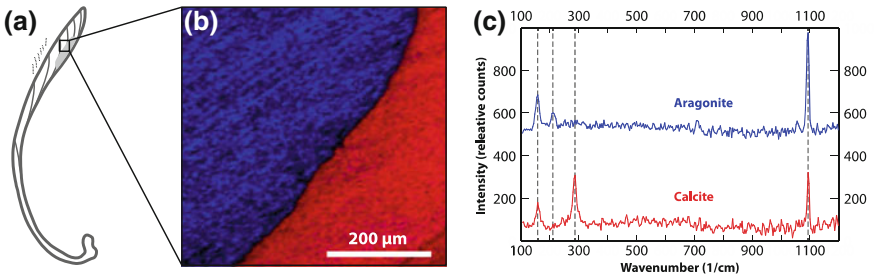

Fig. 3 State of preservation tested by confocal Raman microscopy. **a** Schematic illustration of a (fossil) *A. islandica* specimen. *Light grey colour* exemplary indicates area of potential recrystallization. **b** Areal CRM scan in specimen AI-TjBe-01 close to the altered shell portion and as indicated in **a**. Two different materials have been identified. **c** Raman spectra for two different polymorphs of calcium carbonate explaining colour coding in B. Intensity differences in liberation modes (peaks at ~206 cm^{-1} for aragonite and ~280 cm^{-1} for calcite) in single spot Raman spectra identify pristine aragonite (*blue*) and recrystallized calcite (*red*)

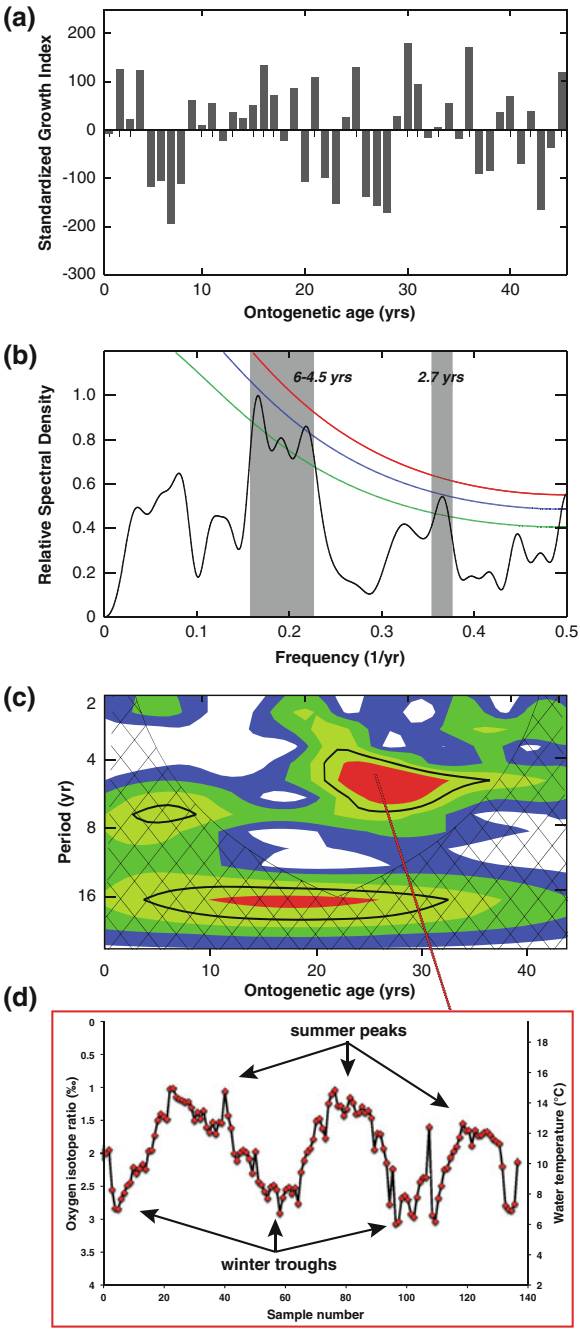

Fig. 4 Frequency analysis on *A. islandica* growth pattern. **a** Standardized growth index (SGI) giving relative information on positive (above 0) or negative (below 0) deviations from average shell growth. **b** Multi Taper Method (MTM) applied to the SGI shown in **a**. *Red*, *blue* and *green lines* represent significance levels of 99, 95 and 90 %, respectively. The significant (95 %) signal at the frequency of 0.197 (1/year) corresponds to a 5-year signal (combined SSA and MTM analysis). **c** Wavelet transformation giving information on the stationarity of quasi-periodic signals identified by SSA and MTM. The strength of the 5-year quasi-periodic signal varies over time, being more prominent from ontogenetic year 20 onwards. **d** Results for the $\delta^{18}O$ analysis in three ontogenetic years throughout the pronounced phase of the 5-year signal, as indicated in **c**. $\delta^{18}O$ values have been translated into water temperatures according to Dettman et al. (1999) assuming a $\delta^{18}O_{seawater}$ value of 0 ‰. *Arrows* indicate summer peaks and winter troughs

3.2 Frequency Analysis

The frequency analysis of the SGI (Fig. 4a) in specimen AI-EgLo-02 indicates a significant (95 % level) 5-year signal (Fig. 4b). Additionally, a signal at 2.7 years was significant at the 90 ‰ level. The wavelet transformation shows the variability of the indicated signals over time. Strength of the 5-year signal varies distinctly over time and is most prominent between ontogenetic years 20 and 30 (Fig. 4c).

3.3 Stable Oxygen Isotopes ($\delta^{18}O$)

Oxygen isotope ratios of three consecutively sampled ontogenetic years in modern *A. islandica* specimen Ai24568 show three distinct sinusoidal patterns (summer peaks and winter troughs) with amplitudes of about 2 ‰ each (Fig. 4d). Assuming a constant modern $\delta^{18}O_{seawater}$ ratio of 0 ‰ during shell formation, the measurements translate into water temperatures between 15 and 6 °C (Fig. 4d).

4 Discussion and Conclusions

When working on fossil shell material, the state of preservation must be evaluated prior to geochemical analysis (e.g., stable oxygen isotopes) to avoid serious errors and bias. Here, CRM represents a powerful, time-effective and non-destructive tool for the examination of shell carbonate polymorphs (Fig. 3).

In *A. islandica* shells it is possible to check the growth record for decadal variability throughout the life of the animal. In specimen AI-EgLo-02 (Lofoten, Norway) frequency analysis identified a significant 5-year signal, which, however, is not stationary over time (Fig. 4a–c). Since the date of death is unknown, a direct correlation to observational or instrumental time-series is not feasible. This would, however, be an essential step to unambiguously link our 5-year signal to the NAO (cf., Wunsch 1999). A number of studies have shown indeed *A. islandica* shell growth patterns to correlate with known ocean-atmosphere oscillations such as NAO (Schöne et al. 2003a; Wanamaker et al. 2009). Nevertheless, further investigations of additional shell material as well as of local forcing mechanisms are required.

$\delta^{18}O$ derived water temperatures (6–15 °C, Fig. 4d) in specimen Ai24568 correspond well to SST measurements (2.8–13.7 °C) for Tromsø, Norway. However, our temperature reconstruction does not account for seasonal changes in salinity and assumes a global average $\delta^{18}O_{seawater}$ value of 0 ‰, which would need verification by on-site measurements. Further, an assumed growing season from February/March to September (Schöne et al. 2004) in *A. islandica* might explain truncated winter minimum temperatures.

Conclusively, for demonstrating purposes, we combined the results from the frequency and $\delta^{18}O$ analyses from two different shell specimens to give an exemplary perspective on the potential of *A. islandica* as a recorder of the environmental past. Accordingly, if *A. islandica* growth increment series can be synchronized with the external forcing signal (e.g., NAO) intra-annual analysis techniques (such as $\delta^{18}O$) can be used to analyse whether intra-annual patterns differ between weak and strong phases of shell growth oscillation. In our example, $\delta^{18}O$ analysis allowed to link a seasonal water temperature amplitude of about 9 °C to the most prominent phase of the 5-year periodic signal (Fig. 4c, d). The high temporal resolution combined with an exceptional longevity distinguish *A. islandica* shells from all other marine archives and show the great potential and uniqueness of *A. islandica* for climatic and environmental reconstructions on various time-scales.

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