High-resolution climate reconstruction for the Holocene based on growth chronologies of the bivalve *Arctica islandica* from the North Sea

Valérie Murielle Epplé

Dissertation for the doctorate degree
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Contents

Abstract

Until now, there has been no published documentation of North Sea year-to-year climate variability during the last 8000 to 10000 years. High-resolution instrumental time series of climatic and environmental data for the North Sea and the adjacent North Atlantic are only available for the last decades or a century at best. Long term paleoclimatic reconstructions in higher latitudes have been predominantly undertaken using land-based annually banded archives, such as trees, varves, glaciers, and speleothems. Marine sediment cores do not provide proxies with the necessary temporal resolution. A suitable long-term environmental archive with annual or even better resolution may be provided by $CaCO_3$-skeletons of long-lived marine invertebrates.

This study evaluates whether recent and subfossil shells of the long-lived bivalve *Arctica islandica* from the North Sea carry feasible information on Holocene climatic and oceanographic conditions. I compared modern shells of *Arctica islandica* from two very different habitats, a near-coastal shallow site ("German Bight") and a northerly, more central, deep site ("Fladen Ground"). From the latter, subfossil shells were analysed, also. This study demonstrates that *Arctica* from both sites provides suitable archives of marine environmental conditions in the form of (i) variations in annual shell growth rates and of (ii) its shell chemistry, both which allow for the reconstruction of local past climate conditions.

The attempt to identify a sole factor that controls shell growth of *Arctica islandica* in the southern North Sea failed. This is because high environmental variability of the dynamic and complex coastal hydrographic regime in time and space obscured possible relationships of this kind in the investigated 163-year growth chronology. Despite this failure, spectral density analysis of the 163-year chronology detected distinct 5- and 7-year periodicities which are within the range of frequencies reported for instrumental winter North Atlantic Oscillation (NAO) indices.

To evaluate whether the skeletal chemistry of the aragonitic shell of *Arctica islandica* provides climatic proxies, the trace elements Mg, Sr, Ca and Ba were analysed. The analyses were conducted by using the methods of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and electron microprobe. Within this study both methods were found to be suitable for analysing Mg/Ca and Sr/Ca ratios with high spatial/temporal resolution, whereas the electron microprobe was not suitable for Ba/Ca ratio measurements because of its higher analytical detection limit. A 144-year profile of trace element-to-calcium ratios in a specimen from the southern site exhibited distinct interannual variations. Characteristic Sr/Ca peaks were found at the “winter” growth lines. Shell Sr/Ca ratios were positively correlated to winter sea surface temperature, thus indicating their potential as a proxy for winter water temperature reconstructions. Ba/Ca was found to exhibit 1-2 sharp annual peaks which positively correlated to spring Elbe river discharge.

It was possible to reconstruct modern bottom water temperatures at the Fladen Ground based on shell-derived $\delta^{18}O$ with an acceptable accuracy of about +0.94°C, as indicated when calibrating against instrumental recordings. A subfossil shell from the early Holocene (9614 years B.P.) collected at the same site was used to reconstruct corresponding bottom water temperatures. The data indicated a larger interannual amplitude as well as significant lower annual minimum and annual average water temperatures for the subfossil shell. A comparison of annual growth rates of one modern and five subfossil shells that originated from periods between 11122 and 8406 years B.P. found significantly faster growth for the modern and the 8406 years B.P. shells and significantly slower growth for the individuals from the late Younger Dryas. This growth patterns coincides with the climatic conditions postulated for these time windows. Frequency spectra resembling modern NAO induced spectra were found in the long-lived shells from 9614 and 11101 years B.P. indicating the prevailing influence of the NAO already during the early Holocene and the end of the Younger Dryas in this area.

In summary, this study enhances our understanding of the relationships between environmental conditions and shell properties in *Arctica islandica* in the North Sea. We could demonstrate suitable proxies for: Winter water temperatures of the southern North Sea (Sr/Ca ratios), bottom water temperatures of the northern North Sea ($\delta^{18}O$) and spring Elbe river discharges of the southern North Sea (Ba/Ca ratios). The application of these proxies allows the reconstruction of past marine environmental conditions for both coastal and offshore sites in the North Sea.

Kurzfassung

Bis heute gibt es keine Studie, die Klimavariationen der letzten 8000 bis 10000 Jahre für die Nordsee in jährlicher Auflösung dokumentiert. Hochauflösende instrumentelle Klimaaufzeichnungen und Umweltdaten für die Nordsee und den angrenzenden Nordatlantik sind meist nur für die letzten Jahrzehnte oder für ein Jahrhundert vorhanden. Für die höheren Breitengrade waren Langzeit Paleoklimarekonstruktionen hauptsächlich mit Hilfe von terrestrischen, jährlich gebänderten Archiven, wie Bäumen, Varven, Gletschern und Stalagmiten möglich. Marine Sedimentkerne bieten keine Proxies mit der gewünschten zeitlichen Auflösung. Ein geeignetes und jährlich gebändertes Archiv mit langer Lebensdauer, welches die umgebenden Umweltveränderungen aufzeichnet ist das $CaCO_3$-Skelett von marinen Invertebraten.

Ziel dieser Studie war es herauszufinden, ob die Bivalve *Arctica islandica* aus der Nordsee als marines Archiv eingesetzt werden kann, welches Proxies zur Verfügung stellt, die Informationen in hochauflösender Form über die vergangenen ozeanographischen Bedingungen der Nordsee für das Holozän liefern. Um dieses Ziel zu erreichen habe ich rezente Schalen von *Arctica islandica* aus zwei ganz unterschiedlichen Habitaten untersucht, aus dem küstennahen Gebiet („Deutsche Bucht“) und einem nördlichen zentralen Gebiet mit großer Wassertiefe („Fladen Ground“). Des Weiteren habe ich auch subfossile Schalen von *Arctica* aus der nördlichen Nordsee untersucht. Die Ergebnisse dieser Studie demonstrieren den Gebrauch der Schale von *Arctica* als Archiv, welches Änderungen der umgebenden marinen Umwelt (i) in Form von jährlichen Wachstumsraten und (ii) der Chemie der Schale aufzeichnet. Weiter wurde gezeigt, daß es möglich ist vergangene lokale Umweltbedingungen zu rekonstruieren.

Der Versuch, einen signifikanten wachstumskontrollierenden Faktor von *Arctica islandica* aus der südlichen Nordsee zu finden, endete ohne Erfolg. Die großen Umweltschwankungen in Zeit und Raum und die komplexe dynamische Küstenhydrographie verdeckten eine Beziehung zwischen einem eindeutigen Faktor und der untersuchten 163 jährigen Wachstumschronologie. Neben diesem Ergebnis zeigte die Spektralanalyse der 163 jährigen Chronologie signifikante 5 und 7 Jahres Periodizitäten auf, welche für den Frequenzbereich des instrumentellen Winter Nord Atlantischen Oszillations- (NAO) Index berichtet werden.

Um einschätzen zu können, ob die Skelettchemie einer rezenten *Arctica islandica* Schale Proxies liefert, wurden die Spurenelemente Mg, Ca, Sr und Ba analysiert. Die Analyse wurde mit den Methoden der „laser ablation inductively coupled plasma mass spectrometry" (LA-ICP-MS) und der Elektronen Mikrosonde durchgeführt. In dieser Studie zeigte sich, daß beide Methoden geeignet sind, um Mg/Ca und Sr/Ca Verhältnisse in der aragonitischen Schale von *Arctica* in hoher räumlicher/zeitlicher Auflösung zu analysieren. Aufgrund der hohen analytischen Nachweisgrenze der Elektronen Mikrosonde war es nicht möglich die Spurenelementverhältnisse von Ba/Ca mit letzterer zu messen. Ein 144-Jahre Profil von Spurenelement/Kalzium (Calcium) Verhältnissen eines rezenten Exemplars aus dem südlichen Untersuchungsgebiet, zeigte klare saisonelle Elementschwankungen. Charakteristische Sr/Ca Spitzen wurden in den „Winter" Wachstumslinien gefunden. Die Schalen Sr/Ca Verhältnissen waren positiv mit den winterlichen Oberflächenwassertemperaturen korreliert und dies deutet ihr Potential als Proxy für die Rekonstruktion von Winterwassertemperatur an. Die Ba/Ca Verhältnisse zeigten 1-2 scharfe jährliche Spitzen, die positiv mit den Frühjahrsabflußraten der Elbe korrelierten und als Proxy, in diesem Fall für die Rekonstruktion von Elbeabflußraten angewendet werden können.

Es war möglich mit Hilfe des aus der Schale gewonnenen $\delta^{18}O$ eines rezenten Individuums aus dem Fladen Ground, Bodenwassertemperaturen zu rekonstruieren. Die Kalibrierung dieser Daten gegen instrumentelle Aufzeichnungen ergab eine akzeptable Genauigkeit von +0.94°C. Zusätzlich wurde eine subfossile Schale aus dem frühen Holozän der gleichen Lokation analysiert, um entsprechend Bodenwassertemperaturen zu rekonstruieren. Die Daten deuten auf eine größere saisonelle Amplitude und signifikant niedrigere jährliche minimale und mittlere Wassertemperaturen für die subfossile Schale hin. Ein Vergleich der jährlichen Wachstumsraten einer rezenten und fünf subfossilen Schalen, die aus der Zeitspanne zwischen 11122 und 8406 Jahren B.P. stammen, zeigte ein signifikant schnelleres Wachstum für die rezente und die Schalen von 8406 Jahren B.P. und ein signifikant langsameres Wachstum für die Individuen der späten jüngeren Dryas. Die Wachstumsmuster stimmen mit den klimatischen Bedingungen überein, die für diese Zeitfenster postuliert werden. In den Schalen der langlebigen Individuen von 9614 und 11101 Jahren B.P. wurden Frequenzspektren ähnlich den Spektren der gegenwärtigen NAO gefunden. Dies deutet darauf hin, daß die NAO bereits im frühen Holozän und am Ende der jüngeren Dryas vorherrschend war.

Zusammenfassend läßt sich sagen, daß diese Studie unser Wissen über die Beziehungen zwischen den Umweltbedingungen und den Schaleneigenschaften von *Arctica islandica* aus der Nordsee eingehend erweitert hat. Wir konnten geeignete Proxies für die folgenden Parameter aufzeigen: Winterwassertemperaturen der südlichen Nordsee (Sr/Ca Verhältnisse), Bodenwassertemperaturen der nördlichen Nordsee ($\delta^{18}O$) und Elbeabflußraten des Frühjahres der südlichen Nordsee (Ba/Ca Verhältnisse). Der Gebrauch dieser Proxies erlaubt die Rekonstruktion vergangener mariner Umweltbedingungen für die küstennahen und fernen Bereiche der Nordsee.

Introduction

Climate & Climate Variability

The term “climate” derived from “*klinein*”, the Greek word for bending, because summer and winter are the result of the ecliptic (bending of the earth’s axis relative to its path around the sun) (Latif, 2004). Climate is a broad composite of the average condition of a region, measured in terms of temperature, amount of precipitation, snow and ice cover, and winds (Ruddiman, 2001). Climate applies to longer-term changes (years and longer), rather than to the shorter fluctuations that last hours, days, or weeks and are referred to as weather. The principal driving force of the climate is the temporal and spatial variability of solar radiation reception on earth. On the one hand this depends on strength and variability of solar radiation by itself (e.g. modulated by the 11-year sunspot cycle), and on the other hand on the properties of the earth’s orbit around the sun, that is rotation, mainly eccentricity, notation, obliquity and precession. The latter causes the three Milankovitch cycles with the periodicities of 100000 years, 41000 years and 23000 years and triggers, for example, interglacial and glacial cycles. Additionally, volcanic eruptions can have distinct but short-term (up to decades) climatic effects. A very recent factor is referred to as “anthropogenic forcing”. This has mainly resulted in an increased release of green-house gases during the last 100 years that caused an increase of atmospheric concentrations of these gases (mainly CO_2) and a corresponding temperature rise (ICPP, 2001). All these factors combined control surface and deep-sea circulation of oceans, land vegetation, heat transfer in the atmosphere, air temperature and ice coverage. To predict future climatic development an understanding of natural climatic variability in the past is essential, especially in the light of the modern anthropogenic impact.

Today, the North Atlantic Oscillation (NAO) is the principal modulating force of northern European atmospheric variability (Hurrell, 1996). Its pronounced seasonal variation in position, intensity and shape reflects the strength of the westerlies across the Atlantic basin and accounts for probably a third of the interannual climate variability of northern Europe (Portis et al., 2001; Schulz et al., 2002). Existing instrumental data which reach back to the early nineteenth century provided index time series which reflect the NAO states (Hurrell, 1995; Jones et al., 2001). NAO indices for earlier periods have been statistically reconstructed using paleo-environmental data including e.g. tree-rings and ice-cores (Cullen et al., 2000).

Luterbacher et al. (2002) extended the existing winter NAO index reconstructions on a monthly / seasonal resolution back to 1500 B.P. using multiproxy composite data.

Northern Europe Holocene

The Holocene epoch, which includes the present, is a period of continuous climatic change. The documentation and understanding of this particular epoch has become more and more important due to concerns of future climate development, especially with respect to potential anthropogenic impact.

Since around 6500 B.P. man has inhabited and used the coastal area of the North Sea. After the development of larger salt marshes, settlements were founded and the wetland was used for cattle grazing, in some areas dating back to pre-Roman times. The building of dikes and the drainage of the lower wetlands in mid- and late Medieval times changed the natural landscape and a cultural landscape was formed (Meier, 2003). Today, 168 mio. people inhabit the neighbouring states of the catchment areas of the North Sea (Sterr, 2003). Apart from the importance of the coastal North Sea area as a settlement area, it provides the economic foundation for its residents. Instrumental recordings of sea surface temperature, salinity contents and river discharge volumes taken over slightly longer than the last century allow the calibration of proxy data derived from natural archives.

A special characteristic of the Holocene is the transition from the end of glacial times of the Pleistocene to the beginning of the Holocene. According to the Greenland ice cores, the Holocene began either around 11640 (GISP2) or 11550 (GRIP) calendar years B.P. The Swedish varv chronology also indicates a beginning of this geological period at 11525 calendar years B.P. (Johnsen et al., 1992; Alley et al., 1993; Andrén et al., 1999). On very long, multi-millennial time-scales, the main factors affecting Holocene climate change are related to orbital forcing (changes in obliquity, precession and solar radiation). It should be pointed out, however, that not all paleoclimatic variability seen in the Holocene can be ascribed to specific external forcing. The 8.2 cooling event, which covered the time between 8000 and 8400 B.P., resulted from proglacial lake drainage at the margins of the Laurentide Ice Sheet (Baldini et al., 2002). This rapid flooding of the North Atlantic with fresh water clearly had a strong local impact (cooling trend), unrelated to any external forcing.

The GRIP ice core record indicates a very rapidly rising temperature of about ~7°C within 50 years at the inception of the Holocene and a second warming of ~5°C at 9500 years B.P. (Johnsen et al., 1992). A drastic change of climatic conditions occurred in the northern water masses as summer insolation reached its maximum between 11000 and 9000 years B.P. In contrast, the orbitally driven changes, which are supposed to have triggered the Pleistocene - Holocene transition, were comparatively gradual.

In the early Holocene, precessional changes led to perihelion at the time of the northern hemisphere summer solstice (today it is closer to the winter solstice). This resulted in higher summer insolation in the Early Holocene at all latitudes of the northern hemisphere. July insolation has slowly decreased over the last 12.000 years B.P.. Kutzbach and Guetter (1986) found that during 9000 B.P. a 7% increase in solar radiation outside the atmosphere in low latitudes was associated with 11% higher net radiation at the surface due to a decrease in outgoing long-wave radiation. This effect allowed enhanced monsoonal circulation over large parts of the northern hemisphere which resulted in wetter conditions.

After this insolation maximum, a period of a so-called “climatic optimum” occurred and remained between 8000 and 5000 years B.P. In the second half of the Holocene the climatic conditions are characterized by a general cooling trend and these conditions are comparable to those at present.

The North Sea is a relatively shallow marginal sea of the North Atlantic with a wide opening in the north to the North Atlantic. The oceanic North Sea climate is determined by salinity and temperature of the North Sea, and these are mainly influenced by the northern gate to the North Atlantic. In the southwest, the North Atlantic has a small influence on the North Sea via the English Channel. The Baltic Sea is connected to the North Sea through the Great and Small Belts, as well as through the Kattegat/Skagerrak. The water depths of the North Sea differ in the north, east and south. The northern part exhibits varying depths of 50 – 200 m. Along the Norwegian coast down to the Skagerakk the glacially eroded Norwegian Trench reaches depths between 270 – 700 m. In contrast, the area of the Doggerbank and the southern coastline is very shallow. The complex oceanographic conditions are characterized by the inflow of Atlantic water masses, where salinity contents can reach >35 psu, and by the large freshwater inflow of the rivers and the Baltic Sea. The oceanographic-climatologic conditions, including temperature, salinity and circulation are strongly coupled to the NAO index.

The North Sea during the early Holocene

During the Holocene the sea-level of the North Sea rose continuously from ~65 m below the present-day position (Jelgersma, 1979; Eisma et al., 1981; Streif, 2002). At 8300 B.P. the southern North Sea became connected to the North Atlantic via the opening of the English Channel. Between 8600 and 7100 B.P. the sea-level rose from about 46 to 25 m below present-day level. Since 8500 B.P. the sea-level increased by about 30 - 35 cm per year from 25 m below the present-day level till it reached the sea-level position of today (Streif, 2002, 2003, 2004).

Climate Archives

Paleoclimatic changes in an environmental context are often preserved by archives, such as trees, glaciers, varves, marine sediments, corals and mollusc shells. These archives contain biotic or geochemical information which can serve as proxies for local environmental conditions. The most common proxies are annual growth rates (e.g. tree-rings, stalagmites, mollusc shells), oxygen isotope compositions of $CaCO_3$-skeletons (e.g. foraminiferas, corals and mollusc shells), and trace element/Ca ratios (e.g. sediment cores, varves, corals, mollusc shells). The proxy has to be translated, through calibration, into exact and validated information of past climatic conditions (Wefer et al., 1999).

Annually banded archives provide a very high temporal resolution of climatic conditions. As instrumental recordings are sparse, have only been available for about a century and are mostly sampled non-continuously, proxies are needed to resolve the full range of decadal-, multidecadal-, and centennial-scale natural climate variability. Direct calibrations of modern shell-derived proxy data against instrumental data are possible and can be used for accurate early Holocene marine environment reconstructions.

So far, high-resolution, long-term paleoclimatic reconstructions at higher latitudes were predominantly undertaken using terrestrial archives (and their proxies), such as ice cores and tree chronologies. Such data do not necessarily reflect the environmental conditions in the marine realm or may display possible land-sea interactions.

For this reason, mollusc shells became more attractive for retrospective environmental studies (Jones, 1981; Richardson et al., 1981; Krantz et al., 1984). Mollusc shells have several advantages with respect to paleo-environmental studies.

They occur worldwide in marine, brackish, and freshwater environments and their solid $CaCO_3$-shells conserve elemental as well as isotopic compositions. Most bivalve shells show distinct growth bands and many bivalves are long-living. New analytical techniques such as laser ablation inductively coupled plasma (see below) further enhance the suitability of mollusc shells.

The following methods are commonly applied in paleoclimatic studies of mollusc shells:

Sclerochronology, which can be seen as the marine counterpart to dendrochronology. ***Dendrochronology***, the measurement and interpretation of variable tree ring widths (Fritts, 1976; Luterbacher et al., 2002), is a widely accepted method to infer historical climatic changes. Commonly, annual shell growth bands are measured on acetate peels (method described by Ropes (1985)) of polished cross sections or the cross sections themselves (method described by Mutvei et al. (1994)). Each growth band can be assigned to a particular calendar year if sampling year and age of the mollusc are known. Correlation between standardized growth bands and instrumental data can indicate the growth-controlling environmental parameters and allow reconstructions of this parameter.

Oxygen isotope analysis is based on measurable variations in $^{18}O/^{16}O$ ratios of the shell carbonate and used for water temperature reconstructions (Epstein et al., 1953; Wefer and Berger, 1991; Schöne et al., 2004). Urey (1947) first suggested that variations in the temperature of the sea water from which $CaCO_3$ precipitated should lead to measurable variations in the $^{18}O/^{16}O$ ratio of the carbonate. Thus, molluscs can be expected to record the surrounding water temperature during growth. Carbonate powder samples are usually gained by micro drilling along shell cross sections with a micromill. To be able to reconstruct water temperatures from shell-derived $\delta^{18}O$, Epstein et al. (1951), Epstein and Lowenstam (1953) and Epstein and Mayeda (1953) established a calcite equation, which was later modified by Craig and Gordon (1965):

$$T\ (°C) = 16.9 - 4.2\ (\delta^{18}O_{calcite\ shell} - \delta^{18}O_{water}) + 0.13(\delta^{18}O_{calcite\ shell} - \delta^{18}O_{water})^2$$

where $\delta^{18}O_{calcite\ shell}$ represents the deviation of the calcite shell sample $^{18}O/^{16}O$ ratio from the Pee Dee belemnite (PDB) reference standard while $\delta^{18}O_{water}$ represents $^{18}O/^{16}O$ ratio of the water in which the shell grew, also relative to the PDB standard.

It is also necessary to know the oxygen isotope composition of the surrounding water ($\delta^{18}O_{water}$). Where the shell consists entirely of aragonite, the equation of Grossman and Ku (1986) should be used:

$$T\ (°C) = 20.19 – 4.56\ (\delta^{18}O_{aragonite\ shell} - \delta^{18}O_{water}) + 0.19(\delta^{18}O_{aragonite\ shell} - \delta^{18}O_{water})^2$$

In this study, all oxygen isotope analyses were carried out using the Grossman and Ku (1986) formula.

LA-ICP-MS is a high sensitivity and high resolution tool for the analyses of minor and trace elements within the shell. In this study, all LA-ICP-MS measurements were carried out on a ThermoFinnigan Element2 double-focussing ICP-MS coupled to a Finnigan UV LaserProbe with a wavelength of 266 nm. The analytical conditions included a laser energy of 0.6 - 0.8 mJ, a pulse rate of 5 Hz and a beam diameter of 50 µm (30 µm for the thin section). Helium was used as sample gas in the ablation cell and Argon was subsequently added to the gas flow. The isotopes ^{25}Mg, ^{43}Ca, ^{88}Sr and ^{138}Ba were analyzed using 8 samples at each peak's flat top and a total dwell time of 160 ms per isotope. The NIST 610 glass standard reference material was used for external single-point calibration using the values of Pearce et al. (1997). This multi-element standard was analysed and a new calibration line established after every five samples (standard bracketing) to compensate for instrument drift.

The electron microprobe analyses major elements and highly concentrated trace elements with very high spatial resolution (<1µm). In this study, electron microprobe analyses of Ca, Mg and Sr were carried out on a CAMECA SX-100 at the Mineralogical Institute, University of Hannover, using a carbon-coated thin section. Analytical conditions included an accelerating voltage of 15 kV, a beam diameter of 5.5 µm, and beam currents of 40 nA for Ca and 100 nA for Mg and Sr. Counting times were 240 s on both peak and background for Mg, 180 s for Sr and 15 s for Ca.

The built-in PAP-procedure was applied for data reduction using Wollastonite, MgO and SrF_2 as calibration standards for Ca, Mg and Sr, respectively.

Ecology of Arctica islandica

Arctica islandica (*Cyprina islandica*, “ocean quahog”) is the only living species of the bivalve genus Arctica (Arcticidae, Veneroida, Heterodonta) which has its origin in the early Cretaceous (Nicol, 1951). It inhabits the boreal Atlantic and adjacent seas. The fossil family shows a great variety of species with a maximum in species diversity during the Mesozoic (Jaeschke and Duckheim, 1997).

The modern shell of this species is characterised by an almost circular shape and a dark brown periostracum (Fig. 1). In younger individuals the colours range from yellowish brown to mahogany. Shells can attain a maximum size of up to 118 mm (Thórarinsdottir and Jóhannesson, 1996). The two valves are nearly identical, except that the left hand valve has a large umbo or so-called “hinge tooth”.

Arctica islandica inhabits the entire continental shelf on both sides of the North Atlantic (Nicol, 1951; Weinberg, 1995). At the southern border of its distributional range, *Arctica* is restricted to deeper waters. *Arctica* is a marine suspension filter feeder. It lives just below the sediment surface with the ventral shell margin as well as their small siphons protruding into the water column to feed on phytoplankton and detritus. Adults tolerate temperatures between 0° and 19°C (Nicol, 1951; Merrill and Ropes, 1969). Adults are usually found at full salinities of 34 - 35 psu, but have been kept successfully at 22 psu for several weeks (Cargnelli et al., 1999) and can live permanently at salinities as low as 26 psu (Baltic, Mecklenburger Bight, (Zettler et al., 2001)). A special feature of this species is the high resistance to H_2S concentrations and oxygen deficiency of the surrounding water (Theede et al., 1969; von Oertzen and Schlungbaum, 1972). In times of anoxia, *Arctica* burrows itself into the sediment. During normal conditions, *Arctica* also exhibits sudden standstills/breaks, where it burrows itself into the sediment to remain there for days (Taylor, 1976). While burrowed, the valves are closed and heartbeat frequencies are very low. Within the class of the bivalves, *Arctica* has a remarkable generation structure. *Arctica* is among the longest-lived and slowest growing of marine bivalves (Murawski et al., 1982). The species has an exceptionally high life expectancy (>200 years). Adults are usually found in dense patches just below the surface of the sediment which ranges from medium- to fine- grained sand (Medcof and Caddy, 1971; Beal and Krause, 1989;

Figure 1. Young and old specimens of *Arctica islandica*.

Brey et al., 1990). In the northern part of their distributional range population densities of as high as 100 ind/m^2 were recorded (Zatsepin and Filatova, 1961; Thórarinsdottir and Einarsson, 1994) and in the northern North Sea maximum densities were found to range from 0.18 to 16 ind/m^2 (Witbaard et al., 1997). In the Baltic, *Arctica* populations of up to 13 ind/m^2 were recorded (Arntz and Weber, 1970). *Arctica* is found in water depths of 5 m (Thórarinsdottir and Jóhannesson, 1996) and as deep as >250 m (Nicol, 1951; Ropes, 1978).

Sexual maturity of this species is reached between 8 and 14 years. Only a few successful spawning periods within 80 to 100 years are necessary for the maintenance of the stock. Spawning takes place in late summer (Loosanoff, 1953; Mann, 1985; Fritz, 1991).

Arctica forms annual shell growth bands (Thompson et al., 1980). A shell growth band represents the annual growth period (the amount of calcium carbonate deposited during the year). The structure of the deposited shell material depends on the precipitation rate; therefore winter growth slows down or halts and results in a virtual growth "line" that separates adjacent growth bands (Merrill et al., 1961; Thompson et al., 1980). In the first 20 years daily growth rate and annual growth rate are comparatively rapid with up to 0.0024 mm per day (Brey et al., 1990). Growth can differ greatly between sites, so that individuals of similar size but from different locations can vary greatly in age.

Climate reconstruction based on shells of Arctica islandica

Longevity, the annually banded shell, and the distribution of *Arctica islandica* make it a prime candidate for North Atlantic paleo climatic reconstructions. Nevertheless only a few studies have explored this potential so far: Schöne et al. (2003) is of particular significance, as this study was able to reconstruct the winter NAO indices from growth band patterns of *Arctica islandica* sampled in the central North Sea. Bottom water temperatures have been reconstructed using oxygen isotope compositions of *Arctica islandica* inhabiting the east coast of America (Weidmann et al., 1994), Iceland (Buchardt and Simonarson, 2003), and the North Sea (Schöne et al., 2004).

The results of this study indicate whether it is possible to use the shell of *Arctica islandica* from the North Sea as an archive. This would provide proxies, such as variations in growth rates and geochemical shell properties that reflect seasonal and inter-annual variations of the physiological and chemical conditions during growth. The variations of modern shell growth rates and oxygen isotope values are compared to instrumental data in order to calibrate them and to create a multi-proxy archive of environmental variation. Additionally, past environmental conditions, such as bottom water temperature were reconstructed based on shell-derived proxy data.

The two investigated North Sea sites are (i) the German Bight and (ii) the Fladen Ground.

The German Bight (southern North Sea)

The German Bight is a shallow marginal sea (22 m average water depth) located at the south-eastern part of the North Sea (Sündermann et al., 1999) (Fig. 2). Here, tides, wind, fluvial freshwater inflows and density differences cause a complex flow regime characterised by dynamic gradients and by large annual oscillations in salinity and water temperature (Mittelstaedt et al., 1983). In the southern German Bight, sea surface salinity (SSS) ranges between < 25 psu in spring and up to 35 psu in late summer (Schott, 1966; Sündermann et al., 1999). This is predominantly due to the annual cycle in freshwater discharge of the rivers Elbe and Weser (Taylor and Stephens, 1980; Grabemann et al., 1983; Heyen and Dippner, 1998) which attain their maximum discharge values in March-April (Elbe: 718 m^3/s, Weser: 327 m^3/s (Lenhart et al., 1996)). Mean sea surface temperature (SST) varies between 2°C in February and >18 °C in August (Radach et al., 1995). Phytoplankton blooms occur in March/April and August (Reid et al., 1990; Edwards et al., 2001).

The Fladen Ground (northern North Sea)

The Fladen Ground is located about 100 miles north-east of Aberdeen (Scotland) (Fig. 2). The bottom consists of an irregular pattern of glacial depressions between 100 and 150 m deep (Basford and Eleftheriou, 1988). The area is located just south of the major water inflows from the Atlantic Ocean into the northern North Sea. The central and deeper parts of the area lie in the centre of a recently recognised, semi-permanent, topographically-steered cyclonic eddy formed by the “Fair Isle Current” and the “East Shetland Atlantic Inflow” Svendsen et al. (1991), Turrell (1992a) and Turrell (1992b). The Fladen Ground is thought to be characterized by fairly constant hydrographical conditions. In summer the area is thermally stratified with a thermocline between 30 and 70 m (McIntyre, 1961). This thermocline traps a bell of cold water in the central parts of the area, resulting in a seasonal temperature variation of the bottom water between 5.7°C (March) and 7.8°C (December) (Faubel et al., 1983). Year- to- year variation of the bottom temperature in summer are even smaller and cover the range between 5.9 -7.3°C

(Ellett and Blindheim, 1992). Salinity values are around 35‰ throughout the year. Bottom currents are known to be small (<0.25 m*s^{-1}).

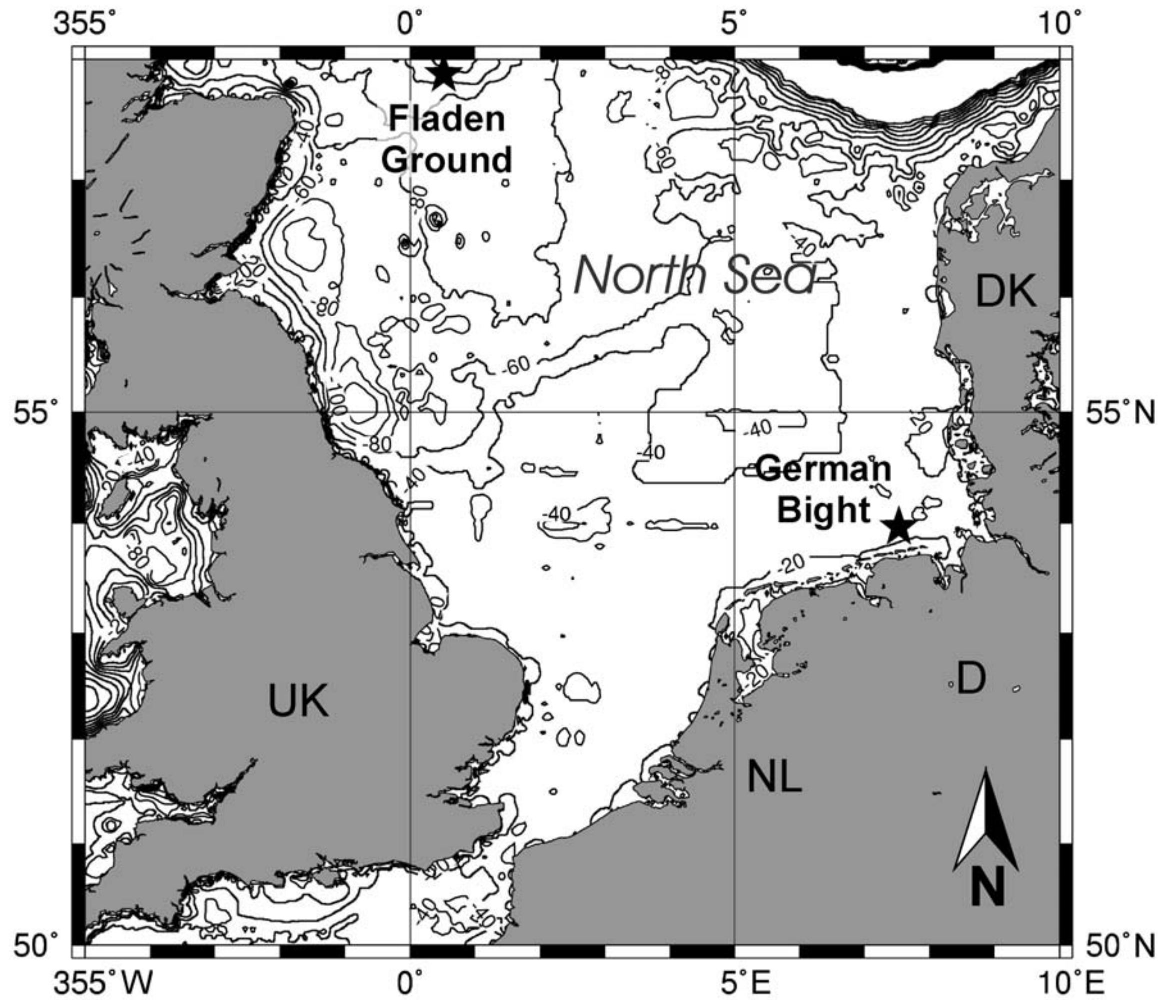

Figure 2. Overview of the sample locations in the North Sea (German Bight and Fladen Ground).

The tasks of this study are:

- to investigate whether *Arctica islandica* from the North Sea is a suitable archive providing proxies for the reconstruction of local marine paleo-environmental conditions during the Holocene,
- to obtain information of the annual growth controlling factors in modern *Arctica islandica* in the southern part of the North Sea - (the German Bight),
- to analyse whether *Arctica islandica* specimens from a near-shore location exhibit synchronous growth patters, as for example seen in off-shore areas,
- to assess the accuracy of the analytical method of the LA-ICP-MS and its suitability for measuring trace element profiles on a high spatial/temporal resolution,
- to improve our understanding of shell incorporated Mg/Ca, Sr/Ca and Ba/Ca ratios in modern *Arctica islandica* and to identify possible correlations between element/Ca ratio and environmental data, which could provide a new proxy,
- to compare the annual growth band patterns in modern and subfossil individuals collected in the northern North Sea,
- to investigate whether shell-derived $\delta^{18}O$ of *Arctica islandica* from the northern North Sea is a suitable proxy for water temperature reconstructions,
- to compare periodicities in modern and early Holocene shells of *Arctica islandica* and thus to identify impacts of the NAO on *Arctica islandica* shell growth.

Overview of research

This thesis comprises a study of modern and subfossil shells of *Arctica islandica* from two different sites in the North Sea and investigates their applicability as climatic archives providing proxies, which allow the reconstruction of past local marine environmental conditions. The results are presented in three chapters that represent separate publications.

Chapter 2: **Sclerochronological records from highly dynamic and variable environments - A lesson from the inner German Bight**, focuses on the suitability of *Arctica islandica* living in the dynamic near-shore habitat of the German Bight as a proxy for environmental parameters that may allow reconstruction of past environmental conditions from sclerochronological time series. The study shows that the annual growth rates of *Arctica* from the German Bight do not significantly correlate with any available environmental parameters and that synchrony between all investigated shells is very poor. It concludes that *Arctica islandica* from the German Bight does not record satisfying proxies of large-scale processes such as NOA owing to the strong environmental "noise" of the local system.

Chapter 3: **High-resolution trace element profiles in a mollusc shell of *Arctica islandica* obtained by LA-ICP-MS and electron microprobe**, compares different analytical methods including solution ICP-MS, LA-ICP-MS and electron microprobe based on analysed trace element ratios. The publication discusses the accuracy of the LA-ICP-MS analyses with calibration against the synthetic glass standard NIST 610 as the external and Ca as the internal standard. Furthermore, the study provides insight into the trace element distribution in the aragonitic shell of *Arctica islandica* from the German Bight for the last 144 years and the potential of Sr/Ca and Ba/Ca ratios as proxies for water temperature and river discharge reconstructions, respectively.

Chapter 4: **Holocene changes in bottom water temperature regime in the northern North Sea – evidence from *Arctica islandica* (Bivalvia) stable oxygen isotopes**, presents a study of oxygen isotope analyses obtained from modern and early Holocene shells of *Arctica islandica* from the Fladen Ground (northern North

Sea). Reconstructed average annual bottom water temperatures (based on shell $\delta^{18}O$) are in line with average annual instrumental water temperature recordings with a small average deviation of +0.94°C for the reconstructed water temperatures. Reconstructed bottom water temperatures of a shell from 9614 years B.P. of the same area indicated lower annual minimum and average water temperatures to those of today, and a larger interannual amplitude. Annual growth rates of all six shells indicated significantly faster growth of the modern and the 8406 years B.P. shells and significantly slower growth for the individuals from the late Younger Dryas. Furthermore, frequency spectra resembling modern NAO induced spectra were found in the long-lived shells from 9614 and 11101 years B.P. indicating the prevailing influence of the NAO already during the early Holocene, and the end of the Younger Dryas in this area.

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Sclerochronological records from highly dynamic and variable environments - A lesson from the inner German Bight

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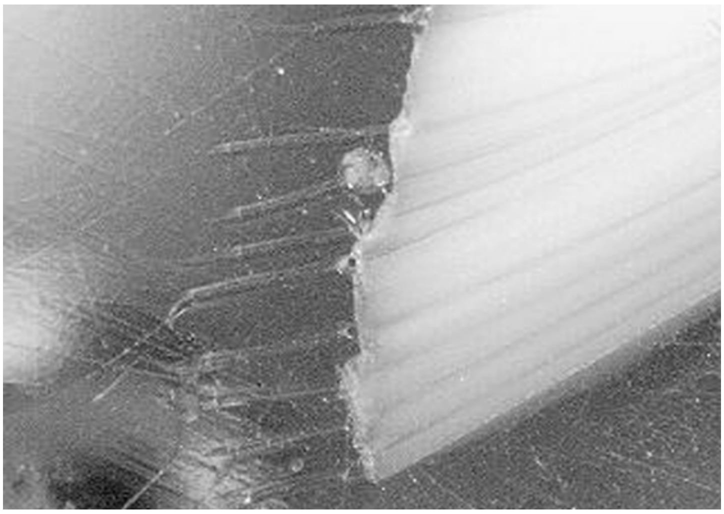

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Sclerochronological records from highly dynamic and variable environments - A lesson from the inner German Bight

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Abstract

Sclerochronological records of interannual shell growth variability were established for eight modern shells (26 to 163 years of age) of the bivalve *Arctica islandica* which were sampled at one site in the inner German Bight. The records indicate generally low synchrony between individuals. Spectral analysis of the 163-year master chronology detected distinct cyclic patterns with periodicities of 5- and 7-years. The master chronology correlated poorly to time series of environmental parameters over the last 90 years. High environmental variability in time and space of the dynamic and complex German Bight hydrographic system results in an extraordinary high “noise” level in the shell growth pattern of *Arctica islandica* compared to North Sea and Atlantic offshore sites.

Keywords: Arctica islandica, German Bight, sclerochronology, time series

Introduction

Holocene paleoclimatic reconstructions for the North Atlantic have been predominantly carried out using annually banded terrestrial proxies, such as tree-rings or ice-cores (Cook and Kariukstis, 1990; Luterbacher *et al.,* 2002; Davies and Tipping, 2004). The increment of such proxy is controlled by environmental parameters and thus a time series of the proxy reflects historic environmental conditions. Little is known about the influence of the terrestrial climate on the marine realm. So far, paleoclimatic marine conditions have been reconstructed mainly from oxygen isotope ratios obtained from the calcified annual density bands in tropical corals (Nozaki *et al.*, 1978). As these organisms are not present in boreal-cold waters, sclerochronological analysis of bivalves has become more attractive for retrospective environmental studies of the North Atlantic (Jones, 1981; Richardson *et al.*, 1981; Krantz *et al.*, 1984).

The bivalve *Arctica islandica* (Linnaeus, 1767) is a particularly useful marine “recorder”, owing to its longevity of > 200 years (Thompson *et al.*, 1980) and its occurrence in the entire North Atlantic (Nicol, 1951). First studies on *Arctica islandica* were carried out on the continental shelves along the US coast (Jones, 1983; Weidmann *et al.*, 1994; Marchitto *et al.*, 2000) and later in the Baltic (Brey *et al.*, 1990; Zettler *et al.*, 2001) and North Sea (Witbaard *et al.,* 1996; Schöne *et al.,* 2003). In the North Atlantic as well as in the North Sea *Arctica* deposits annual growth bands (Jones, 1983), which are synchronized within a population (Witbaard and Duineveld, 1990; Marchitto *et al.,* 2000). Shell growth is controlled by at least one environmental parameter. Knowing the functional relation between shell growth and this parameter allows the reconstruction of this parameter as well as of marine paleo-environmental conditions from shell growth time series. Depending on the study site and its hydrodynamics, the growth steering factors vary. Sea surface temperature (SST) is commonly found to be a dominant growth factor in *Arctica islandica* (Weidmann *et al.*, 1994; Witbaard *et al.*, 1997; Schöne *et al.*, 2003). Besides SST, food supply (Witbaard *et al.*, 2003) and sea surface salinity (SSS) (Zettler *et al.*, 2001) have been regarded as essential factors. Schöne *et al*. (2003) was able to reconstruct the winter North Atlantic Oscillation (NAO) from growth band patterns of *Arctica islandica* sampled in the central North Sea.

Compared to offshore environments, less is known about the ecology of *Arctica* inhabiting dynamic estuary-like habitats such as the German Bight. This study analyses whether *Arctica islandica* living in the dynamic near shore habitat of the German Bight is a suitable proxy for environmental parameters that allows reconstruction of past environmental conditions from sclerochronological time series.

Study area

The German Bight (Fig. 1) is a shallow marginal sea (22 m average water depth) located at the south-eastern part of the North Sea (Sündermann *et al.*, 1999).

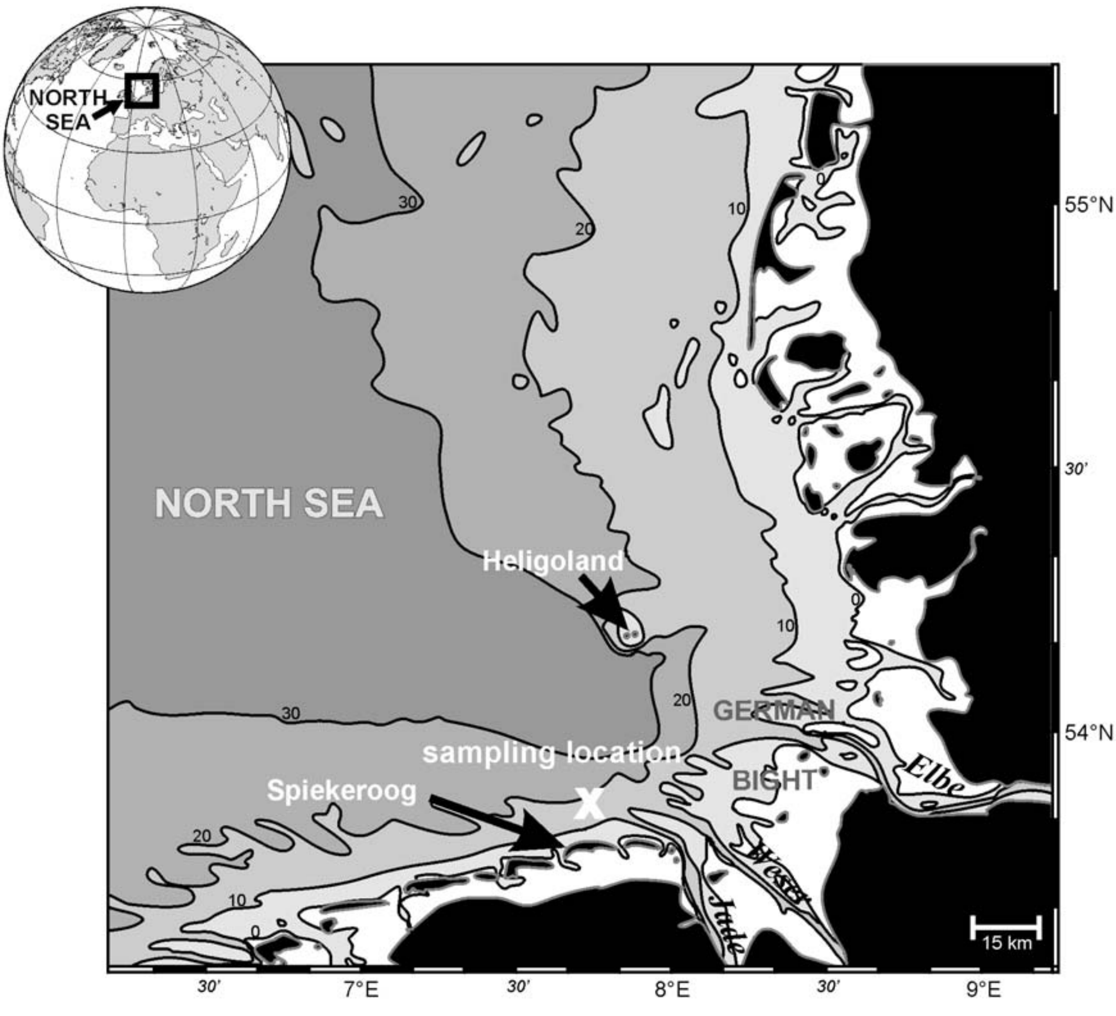

Figure 1. Bathymetric map of the German Bight showing the sample location of the bivalves.

Here, tides, wind, fluvial freshwater inflows and density differences cause a complex flow regime characterised by dynamic gradients and by large annual oscillations in salinity and water temperature. (Mittelstaedt *et al.*, 1983). In the southern German Bight, sea surface salinity (SSS) ranges between < 25 psu in spring and up to 35 psu in late summer (Schott, 1966; Sündermann *et al.*, 1999), predominantly owing to the annual cycle in freshwater discharge of the rivers Elbe and Weser (Taylor and Stephens, 1980; Grabemann *et al.,* 1983; Heyen and Dippner, 1998) which attain their maximum values in March-April (Elbe: 718 m^3/s, Weser: 327 m^3/s (Lenhart *et al.*, 1996). Mean sea surface temperature (SST) varies between 2°C in February and >18 °C in August (Radach *et al.*, 1995). Phytoplankton blooms occur in March/April and August (Reid *et al.,* 1990; Edwards *et al.,* 2001).

Material and methods

Shell samples

The eight shells of *Arctica islandica* used in this study were collected in May 2002 by a commercial fisherman with a beam trawl north of the East Friesian Island Spiekeroog in 15 to 20 m water depth along a transect of about 500 m length (Fig. 1).

Shell growth

In *Arctica islandica*, a shell growth band represents the annual growth period (the amount of calcium carbonate deposited during the year). Each growth band is delimited by a growth line deposited in the colder winter months when shell deposition slows down or ceases (Merrill *et al.*, 1961; Thompson *et al.*, 1980) (Fig. 2). Cross-sections and acetate peels were prepared of all left-hand valves following Ropes (Ropes, 1985), additionally these cross-sections were etched with glutaraldehyde/acetic acid (Mutvei *et al.*, 1994) after peel preparation to improve readability of the growth bands. In each shell section subsequent growth bands were identified and measured under a microscope. As all specimens were caught alive, it was possible to assign a particular calendar year to every growth band. Two different statistical methods were used to remove the ontogenetic trend of decreasing width of growth increment GI_i width with age i from the data. Standardized growth increments SGI were computed by (i) a seven year moving average filter (MAV)

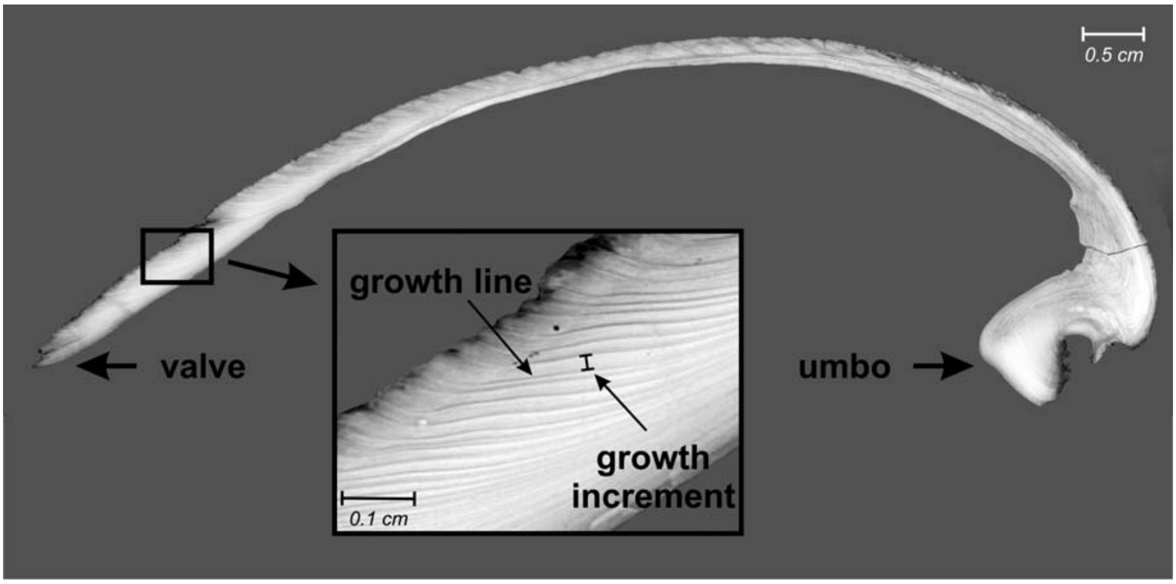

Figure 2. Cross-section of *Arctica islandica* from the German Bight with a shell length of 9.22 cm (from the outer shell to the umbo).

$$SGI_{MAV,i} = \frac{GI_i}{\sum_{i-3}^{i+3} \overline{GI_i}} \qquad (1)$$

and (ii) a simple exponent smoothing (SES) procedure:

$$SGI_{SES,i} = \frac{GI_i}{GI_{i,Predicted}} \qquad 2)$$

where $G_{i,Predicted}$ is the estimate of a simple exponential function fitted to the growth increment series. Detrending of growth increments GI resulted in a standardized time index series for each specimen which indicate whether or not the annual standardized growth increment SGI_{MAV} or SGI_{SES}, respectively, during a particular year was above or below lifetime average (mean = 0, S.D. = 1).

From the eight standardized index series, a 163-year master chronology was constructed by computing the average SGI_{MAV} and SGI_{SES} per calendar year.

Synchrony among the eight standardized time index series was analysed by the running similarity (“Gleichläufigkeit”) statistics using a white noise order of 1 (http://www.unifrankfurt.de/~grieser/dfg/node40.html). Running similarity was assessed by the index G

$$G(a,b,...,m) = \frac{1}{n-1}\sum_{i=1}^{n-1}\left|\sum_{k=1}^{m} G_{ak,i}\right| \quad (3a)$$

and

$$G_{a,i} = \begin{cases} \frac{1}{m} if \Delta_{a,i} > 0 \\ 0 \ if \Delta_{a,i} = 0 \\ -\frac{1}{m} if \Delta_{a,i} < 0 \end{cases} \quad (3b)$$

where $\Delta_{a,I}$ is the difference in SGI of two successive years ($\Delta_{a,I} = SGI_{i+1} - SGI_i$), *n* is the number of growth bands and *m* the number of shells compared. The running similarity index G ranges between 0 (perfect negative synchrony) and 1 (perfect positive synchrony).

A spectral density analysis (statistical package JMP, (SAS-Institute, 2002)) was applied to explore the 163-year master chronology for cyclic patterns.

Environmental data

Time series of environmental data assumed to be relevant for the investigation area were taken from published sources (Table 1). Unfortunately most data sets have gaps or cover a few years or decades at best.

Relations between environmental data and shell growth chronologies. Statistical relations between the *Arctica islandica* master chronology and environmental data time series were analysed by correlation and partial correlation and subsequent construction of a multiple linear model (Deutsch, 2003). Owing to the large gaps in the sea surface salinity (SSS) time series we decided to work with two data sets, one including SSS (55 years between 1908 and 1995) and one excluding SSS (83 years between 1908 and 2002).

Results

Shell growth chronologies

The age of the eight *Arctica islandica* specimens and hence the length of the shell chronologies ranged from 26 to 163 years covering the time span 2002 – 1840 (Fig. 3). Synchrony between the growth patterns of the eight shells was very poor, as indicated by running similarity values between 0.30 and 0.64 (maximum overlap) and between 0.42 and 0.69 (26 year overlap), respectively (Table 2). Spectral density analyses indicates significant periodic components ($P<0.05$) in the 163-year master chronology with distinct peaks at 5- and 7-years (Fig. 4).

Relations between environmental data and shell growth chronologies

Correlations between the master chronologies and environmental parameter time series are poor, as no significant relation could be detected (Tables 3 and 4). Owing to the poor correlation, we abstained from the construction of a multiple linear model.

Table 1. List of environmental data sets used in the present study, including time span, measurement location and source.

environmental parameter	time span	data resolution	recording location	data source
SST	1880-2001	monthly	Datafield: 188 and 37	GISST, Version 2.3b (http://badc.nerc.ac.uk-data-gisst)
SST	1873-1881	monthly	Heligoland Reed (Isle of Heligoland)	data provided by Federal Maritime and Hydrographical Agency, Hamburg, FRG (BSH)
	1883-1892			
	1908-1944			
	1960-1995			
SST + SSS	1924-1988	annual	LV Weser 53° 52 ‘N 07° 50 ‘E	light vessels (LV) positioned in the southern German Bight data provided by Federal Maritime and Hydrographical Agency, Hamburg, FRG (BSH)
			LV Amrumbank 54° 33 ‘N 07° 53 ‘E	
			LV Außeneider 54° 13 ‘N 07°18 ‘E	
			LV Borkumriff 53° 44 ‘N 06° 24 ‘E	
			LV Bremen 53° 47 ‘N 07° 08 ‘E	
			LV Elbe 1 54° 00 ‘N 08° 07 ‘E	
			LV Elbe 4 53° 56 ‘N 08° 40 ‘E	
			LV P11 / P8 54° 10 ‘N 06° 21 ‘E	
			LV P15 / P12 LV 54° 00 ‘N 07° 51 ‘E	
SSS	1873-1881	monthly	Heligoland Reed (Isle of Heligoland)	data provided by Federal Maritime and Hydrographical Agency, Hamburg, FRG (BSH)
	1883-1886			
	1888-1893			
	1907-1919			
	1927-1944			
	1960-1995			
Elbe river discharge	1908-2000	monthly	gauge in Neu Darchau	data provided by Local Waterways and Shipping Office, Lauenburg
Weser river discharge	1977-2000	monthly	gauge in Intschede	data provided by Local Waterways and Shipping Office, Verden
precipitation	1851-1997	annually	City of Emden	data available at Levitus (1994) (http://www.cdc.noaa.gov/cdc/data.nodc.woa94.html)
chlorophyll *a*	1975-1976	daily	East Friesian Isle of Norderney	data provided by J. E: E. van Beusekom from the Alfred-Wegener-Institut für Polar- und Meeresforschung, Bremerhaven, Germany
	1978-1982			
	1984-1992			
	1994-2000			
chlorophyll *a*	1966-2000		Heligoland Reed (Isle of Heligoland)	data published by Radach and Bohle-Carbonell (1990)
chlorophyll *a*	1997-2002	daily	54.097°N, 7.86°E (in front of the Isle of Spiekeroog)	SeaWiFS (http://daac.gsfc.nasa.gov/data/dataset/SeaWiFS)
chlorophyll *a*	1966-1970	hourly		data provided by Federal Maritime and Hydrographical Agency, Hamburg, FRG (BSH)
	1974-1980			
	1985-2000			
winter NAO index SL (Station Lisboa)	1864-2002	annually		data provided by Hurrell, (http://www.cgd.ucar.edu/~jhurrell/nao.html)
winter NAO index PC (principal component)	1899-2002	annually		data provided by Hurrell, (http://www.cgd.ucar.edu/~jhurrell/nao.html)

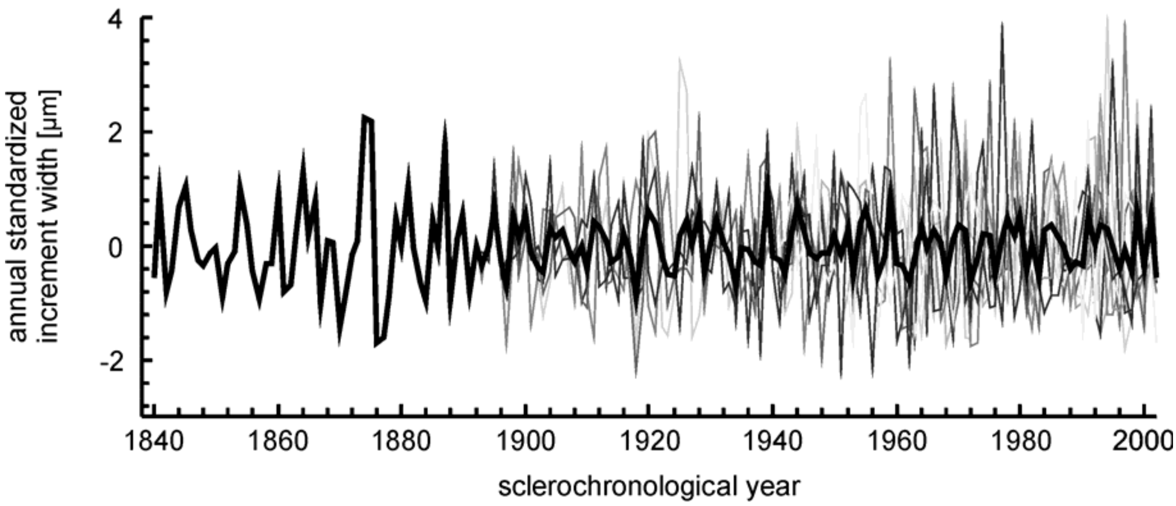

Figure 3. 163 year master chronology (black line) of *Arctica islandica***.** Grey lines indicate the eight standardized time index series the master chronology is based on.

Table 2. Pair wise calculation of running similarity ("Gleichlaeufigkeit") between the eight specimens for 26 years (1976 -2002) below the diagonal and for the period of maximum overlap, that is, lifetime of the younger specimen, above the diagonal (moving average standardization technique). Overall running similarity of all eight shells over 26 years is 0.50.

Spec	SL (cm) Age (y)	NSP 4	NSP 5	NSP 6	NSP 7	NSP 13	NSP 17	NSP 20	NSP 24
NSP 4	8.54 60		0.52	0.53	0.61	0.46	0.47	0.51	0.64
NSP 5	9.22 163	0.67		0.43	0.39	0.58	0.52	0.53	0.47
NSP 6	9.46 106	0.69	0.48		0.59	0.44	0.52	0.48	0.57
NSP 7	9.15 106	0.67	0.54	0.60		0.67	0.61	0.49	0.54
NSP 13	6.41 26	0.46	0.58	0.44	0.67		0.46	0.58	0.58
NSP 17	8.63 63	0.54	0.67	0.49	0.58	0.46		0.45	0.44
NSP 20	8.44 110	0.58	0.46	0.44	0.46	0.58	0.50		0.51
NSP 24	9.24 108	0.67	0.46	0.65	0.54	0.58	0.52	0.54	

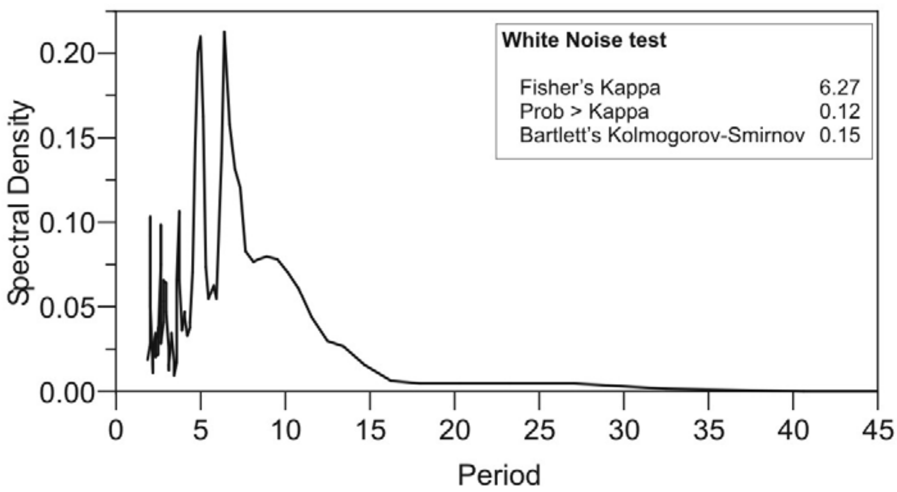

Figure 4. Spectral density analyses of the 163 year master chronology. The time series shows significant periodic components (P <0.05). Note peaks at 5- and 7-years.

Discussion

The eight specimens analysed here show a very low growth synchrony, as indicated by the running similarity values (Table 2, Fig. 3). This is in contrast to the findings of Thompson *et al.* (1980), Witbaard *et al.* (1996), Marchitto *et al.* (2000), Schöne *et al.* (2003) which all describe significant growth synchrony in *Arctica islandica* specimens from the same site or region. Thompson *et al.* (1980) noted that in the Georges Bank population of *Arctica islandica* synchrony decreases with increasing distance between sampling sites. This effect, however, was visible across distances > 5 km. Hence, it appears to be quite uncommon to observe such poor growth synchrony between specimens sampled along a rather short transect of about 500 m. All eight specimens were collected alive and simultaneously, and standard procedures were used for increment measurements and standardisation. Therefore we conclude that the poor synchrony results from the environmental conditions in the sampling area. Situated just north of the Wadden Sea and within the Elbe-Weser estuary, this subtidal area is part of a highly dynamic region with extreme fluctuations in salinity, turbidity, temperature and other parameters. Tides in this area range between 3.5 and 6.2 m (Lassen and Siefert, 1991). North of the East Friesian Island Norderney tidal currents up to > 1 m/s have been recorded (Umweltbundesamt, 1999). Tidal dynamics combine with wind driven currents and river runoff dynamics.

Table 3: Correlations and partial correlations between environmental data (NAO, SST, Elbe river discharge and precipitation) and master chronology of standardized growth increments SGI between 1908 and 2002 (n=83). Coefficients in the first column refer to SGI_{SES} and coefficients in the first row refer to SGI_{MAV}. No SSS data are available for this time span.

Correlation Matrix (*: significant at α = 0.05)

	Mean SGI_{MAV}	NAO (PC)	SST	Elbe discharge (Spring)	Elbe discharge (Summer)	Precipi-tation
Mean SGI_{SES}		0.0084	-0.0060	-0.1113	0.0880	0.0140
NAO (PC)	-0.0322		0.6498*	-0.0119	-0.4009*	-0.1613
SST	0.0575	0.6498*		-0.0138	-0.4073*	-0.0238
Elbe discharge (Spring)	-0.0357	-0.0119	-0.0138		0.3899*	0.3939*
Elbe discharge (Summer)	0.0232	-0.4009*	-0.4073*	0.3899*		0.2351*
Precipitation	0.0520	-0.1613	-0.0238	0.3939*	0.2351*	

Partial Correlation Matrix (*: significant at α = 0.05)

	Mean SGI_{MAV}	NAO (PC)	SST	Elbe discharge (Spring)	Elbe discharge (Summer)	Precipi-tation
Mean SGI_{SES}		0.0065	0.0081	-0.1820	0.1600	0.0632
NAO (PC)	-0.0669		0.5810*	0.1427	-0.1954	-0.1873
SST	0.1052	0.5810*		0.0461	-0.2374*	0.1240
Elbe discharge (Spring)	-0.0703	0.1427	0.0461		0.3838*	0.3507*
Elbe discharge (Summer)	0.0515	-0.1954	-0.2374*	0.3838*		0.0525
Precipitation	0.0528	-0.1873	0.1240	0.3507*	0.0525	

The Wadden Sea topography adds further spatial variability. The interaction of these factors may result in such small scale variability in environmental conditions (e.g. turbidity or food supply) that a strong random component is added to the growth pattern of each individual clam. The water temperature regime at shallow sites in the German Bight may be of particular significance. *Arctica islandica* is a temperate, cold water species (Cargnelli *et al.*, 1999). Its presumed temperature optimum for adults is about 6 - 16°C, whereas temperatures > 20 °C cause mortality (Merrill and Ropes, 1969). Water temperature in the German Bight can rise up to 18°C in summer, taking *Arctica islandica* close to its thermal limits. This may enhance the clam's sensitivity to other environmental stress or even induce growth reduction or cessation.

Table 4: Correlations and partial correlations between environmental data (NAO, SST, SSS, Elbe river discharge and precipitation) and master chronology of standardized growth increments SGI between 1908-1919,1927-1944 and 1960-1995 (n=63). Coefficients in the first column refer to SGI_{SES} and coefficients in the first row refer to SGI_{MAV}.

Correlation Matrix (*: significant at α = 0.05)

	Mean SGI_{MAV}	NAO (PC)	SST	SSS (Win-Spr)	SSS (Spr-Sum)	Elbe discharge (Spring)	Elbe discharge (Summer)	Precipi-tation
Mean SGI_{SES}		0.0212	-0.0118	0.0349*	0.0864	0.0870	-0.0530	0.0095
NAO (PC)	-0.0900		0.6953*	-0.2404	0.0809	-0.0440	-0.3906*	-0.0986
SST	-0.0328	0.6953*		-0.2153	-0.0410	-0.0449	-0.3843*	-0.0396
SSS (Win-Spr)	0.1624	-0.2404	-0.2153		0.5301*	-0.6127*	-0.3036*	-0.4107*
SSS (Spr-Sum)	-0.0034	0.0809	-0.0410	0.5301*		-0.5667*	-0.6421*	-0.3727*
Elbe discharge (Spring)	-0.0231	-0.0440	-0.0449	-0.6127*	-0.5667*		0.4872*	0.4746*
Elbe discharge (Summer)	0.0715	-0.3906*	-0.3843*	-0.3036*	-0.6421*	0.4872*		0.2044
Precipitation	-0.0231	-0.0986	-0.0396	-0.4107*	-0.3727*	0.4746*	0.2044	

Partial Correlation Matrix (*: significant at α = 0.05)

	Mean SGI_{MAV}	NAO (PC)	SST	SSS (Win-Spr)	SSS (Spr-Sum)	Elbe discharge (Spring)	Elbe discharge (Summer)	Precipi-tation
Mean SGI_{SES}		-0.0045	0.0213	0.1026	0.0866	-0.0712	0.1995	0.1035
NAO (PC)	-0.0116		0.5658*	-0.2554	0.0920	0.0196	-0.1538	-0.1453
SST	0.0840	0.5658*		-0.0814	-0.3112*	-0.0541	-0.3456*	-0.0542
SSS (Win-Spr)	0.2118	-0.2554	-0.0814		0.1960	-0.3844*	-0.0833	-0.2137
SSS (Spr-Sum)	0.0203	0.0920	-0.3112*	0.1960		-0.1311	-0.5715*	-0.1658
Elbe discharge (Spring)	0.0114	0.0196	-0.0541	-0.3844*			0.1962	0.2606
Elbe discharge (Summer)	0.1160	-0.1538	-0.3456*	-0.0833	-0.1311	0.1962		-0.2037
Precipitation	0.1455	-0.1453	-0.0542	-0.2137	-0.1658	0.2606	-0.2037	

We could not detect a correlation between our masterchonology and time series of environmental parameters relevant for the North Sea and German Bight (Tables 3 and 4). This is in contrast to studies from the central North Sea, where annual growth rate of *Arctica islandica* is clearly coupled to the winter NAO index (Schöne *et al.*, 2003). Again, the dynamics of the near shore German Bight may explain this failure. Although, the spectral analysis of the 163-year master chronology detected distinct 5- and 7-year periodicities. Local variability in time and space obscure the large scale superior parameters, thus preventing them to imprint a clear signal on the clam growth history, and keeping synchrony of growth between specimens low, as discussed above.

Conclusions

High spatial and temporal environmental variability at our near shore investigation site is assumed to be the major reason for the poor synchrony between specimens as well as between the master chronology and time series of superior environmental parameters. The only way to check whether *Arctica islandica* from the German Bight does record large scale superior parameters at all would be the analysis of many more individuals and of longer time series in order to cancel out the locally induced statistical noise. The spectral density analysis of the 163-year master chronology (Fig. 4) gives a hint that this may be a worthwhile approach, because the distinct 5- and 7-year periodicities detected are within the range of frequencies reported for instrumental and proxy NAO indices.

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High-resolution trace element profiles in a mollusc shell of *Arctica islandica* obtained by LA-ICP-MS and electron microprobe

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Submitted to Geochimica et Cosmochimica Acta, 8th of September 2004

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Abstract

A thin section covering three years and a cross-section covering 144-years of a modern *Arctica islandica* shell from the German Bight was analysed for trace element ratios of Mg/Ca, Sr/Ca and Ba/Ca by electron microprobe (EMP) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Both methods extract geochemical information at a high spatial and temporal resolution. Unfortunately, the LA-ICP-MS technique inherits calibration problems with respect to biogenic calcium carbonates. As the use of a synthetic glass standard (NIST 610) for calibration may introduce matrix effects, we compared the data yield from LA-ICP-MS with element analyses of solution ICP-MS. Sr/Ca ratio differences found to be within the analytical uncertainty. We obtained a minor deviation for Mg/Ca ratios (5%) and Ba/Ca ratios (8%) obtained by LA-ICP-MS. Trace element ratios of Mg/Ca measured by EMP and LA-ICP-MS along the thin section revealed nearly identical results. Sr/Ca ratios gained by LA-ICP-MS were 14% below the EMP measurements, which might be explained by possible matrix effects of the EMP caused by the calibration with SrF_2.

A comparison between element ratios and environmental parameters resulted in a positive correlation between Sr/Ca and winter sea surface temperature, as well as Ba/Ca and Elbe river discharge. The present application of LA-ICP-MS to the analysis of the *Arctica islandica* shell using NIST 610 as the external and ^{43}Ca as the

internal standard demonstrates a powerful and accurate analytical method measuring shell calcium carbonate. Furthermore, our data indicate the possible usage of Sr/Ca and Ba/Ca profiles of *Arctica islandica* as proxies for winter sea surface water temperatures and Elbe river runoff reconstructions.

1. INTRODUCTION

Mollusc shells are increasingly being used as archives of paleo-environmental conditions. The annually deposited shell calcium carbonate layers allow the construction of precisely dated growth chronologies that can cover decades or even centuries. The elemental concentrations of Mg, Sr, and Ba in mollusc shells have been shown to be driven by environmental parameters (Dodd, 1965). Sr has been pointed out to be an indicator for water temperature. Studies of Dodd (1965) showed cyclic annual variations in the Sr concentration in the aragonitic layer in *Mytilus edulis* and a negative correlation between Sr concentration and water temperature. Similar results were found by Palacios et al. (1994) and Thorn et al. (1995), who demonstrated a significant inverse relationship between Sr incorporation and water temperature in the aragonitic shell of *Mya arenaria*. Mg on the other hand is suggested to be a temperature indicator in purely calcitic shells or layers as seen in the calcitic shell of *Isognomon ephippium* were Mg mirrors sea surface temperature (Lazareth et al., 2003). Ba serves as an indicator for spring phytoplankton bloom intensities, as characterized by very sharp peaks within the growth bands (Stecher et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003). Although an ideal candidate, no annual or inter-annual high resolution analysis of trace elements across the internal growth bands have been assessed so far for the long-lived bivalve *Arctica islandica* (Linneaus, 1767). This purely aragonitic species (Bøggild, 1930) is known to form annual growth bands (Thompson et al., 1980) and to reach ages over 200 years.

The method of laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) has recently received much attention with respect to the rapid and sensitive multi-element analysis of minor and trace elements in solid materials. In particular, the high spatial resolution enables geochemical analyses of mollusc shell growth bands down to seasonal temporal resolution even in very narrow bands (Stecher et al., 1996; Vander Putten et al., 2000; Lazareth et al., 2003).

Although LA-ICP-MS is a powerful method to reveal variations in element concentrations, obtaining accurate quantitative data from biogenic carbonate can be problematic. Due to the lack of a commonly accepted homogeneous calcium carbonate standard, synthetic silicate glass standard reference materials (SRM) such as NIST 610 and NIST 612 are often used for calibration (Vander Putten et al., 2000; Lazareth et al., 2003). As these are not matrix-matched with the sample materials, there may be differences in the behaviour of the standard and sample during ablation and hence inaccurate measurements can result. Alternatively, pressed pellets of powdered shell carbonate were successfully used for calibration. In the study of Pearce et al. (1992), multi-element standards with the addition of Mg, Mn, Sr, Ba and Pb were prepared as pressed powders and fused glass discs. The calibration graphs resulted in acceptable values obtained using the pressed powders, but better accuracy was achieved with fused glass discs, which can be attributed to a combination of inhomogeneous grain size in the matrix and uneven distribution of the powder additions. Therefore, this approach means perfect matrix-matching, but has the disadvantage of heterogeneities of the calibrated standard on the µm scale.

The purposes of this study are 1) to assess the accuracy at LA-ICP-MS analyses of trace element ratios in the aragonitic shell of *Arctica islandica* using the synthetic glass standard NIST 610 as calibration standard, and 2) to investigate the potential of shell-derived Mg/Ca, Sr/Ca and Ba/Ca ratios as proxies for water temperature and primary production for use in paleoclimate reconstructions. To address the potential calibration problems, we analysed the powdered Japanese coral standard JCp-1 (Okai et al., 2001) and a house-standard (a powder of *Arctica islandica*) by both laser ablation and solution ICP-MS and compared the results. Furthermore, we compared a compositional profile of Mg/Ca, Sr/Ca and Ba/Ca analysed by electron microprobe (EMP) to that obtained by LA-ICP-MS.

2. STUDY AREA

The German Bight is a shallow marginal sea located at the south-eastern part of the North Sea (Sündermann et al., 1999) (Fig. 1). Here, tides, wind, freshwater fluvial

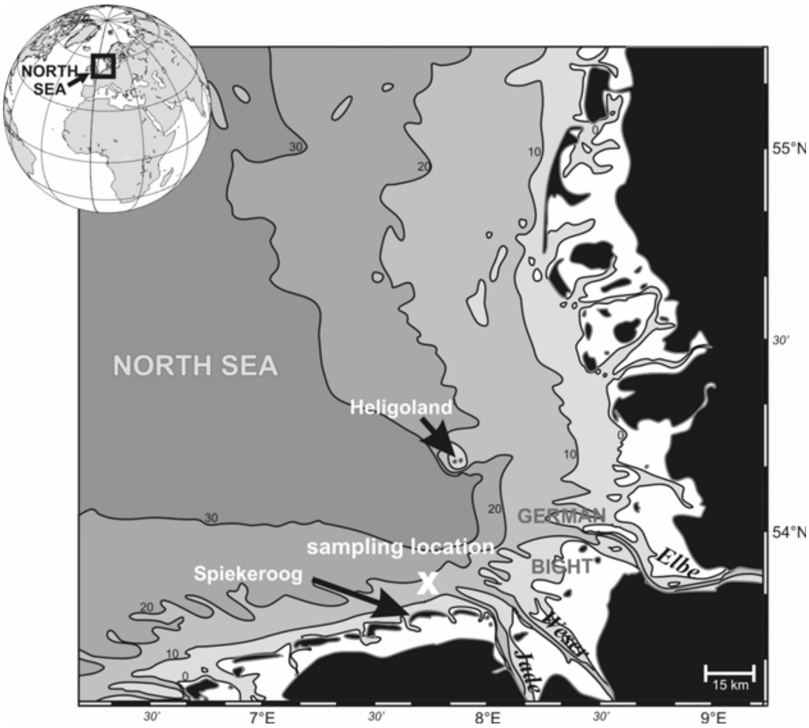

Figure 1. Bathymetric map of the German Bight showing the sample location.

inflows and density differences cause different flow systems. The wind-driven coastal current flows in an anti-clockwise direction, nonetheless wind driven currents can cause eddies which also move clockwise through the Bight (Mittelstaedt et al., 1983). Because the German Bight is a transitional region between fluvial freshwater and saline North Sea water, sea surface salinity (SSS) has been recorded to be less than 25 psu in the coastal waters during spring and rise up to 35 psu in late summer (Schott, 1966; Sündermann et al., 1999). Salinity in the southern part of the Bight is affected predominantly by discharge of the Elbe and Weser rivers (Taylor and Stephens, 1980; Grabemann et al., 1983; Heyen and Dippner, 1998). In terms of discharge volume, the Elbe river is the largest river with an average annual river runoff of 718 m^3/s, with a maximum in April. The recorded average runoff for the Weser river accounted 327 m^3/s with a maximum in March (Lenhart et al., 1996). Due to its small discharge volume of only 10.5-11 m^3/s (Dörjes et al., 1969) the Jade has no influence in this area. Mean sea surface temperature (SST) values vary from a minimum of 2°C in February to a maximum of >15 °C in August (Radach et al., 1995). Primary production of > 200 g/cm^2 per year can be found during the phytoplankton blooms in March/April and August (Reid et al., 1990; Edwards et al., 2001).

3. ANALYTICAL METHODS

3.1. Sample preparation

The specimen of *Arctica islandica* used in this study was collected in May 2002 by a commercial fisherman with a beam trawl north of the East Friesian Island Spiekeroog, Germany, in 15 to 20 m water depth. The left-hand valve of the shell was embedded in epoxy resin and a cross section was cut from the umbo to the ventral margin along the maximum of growth (Fig. 2). From the ground and polished cross section acetate peels were prepared according to the method described by Ropes (1985). In *Arctica islandica*, a shell growth band represents the annual growth period (the amount of calcium carbonate deposited during the year). Each growth band is delimited by a growth line deposited in the colder winter months when shell deposition slows down or ceases (Merrill et al., 1961; Thompson et al., 1980) (Fig. 2). From the acetate peel growth bands were identified and the annual growth rate was measured under a microscope. As the individual was caught alive, it was possible to assign a particular calendar year to every growth band. The entire shell comprised 163-years of growth, and the most recent 144-years of the shell (1858 to 2002) were studied for their trace elemental composition.

For comparing LA-ICP-MS with electron microprobe (EMP) analyses, a polished 80 µm thin section was prepared from a small part of the shell opposite to the cross section described above. Three years of growth including four growth lines were analyzed (1955 to 1957) (Fig. 2).

For comparing quantitative data obtained by LA-ICP-MS and solution ICP-MS analyses we used two biogenic carbonate powders, the coral standard JCp-1 (Okai et al., 2001) and a powder prepared from the periostracum-free outer shell of a *Arctica islandica* specimen. We will refer to the second powder as *Arctica* standard. One split of these powders was pressed at 10 tons to pellets for laser ablation, and another split was digested in HNO_3 for solution ICP-MS.

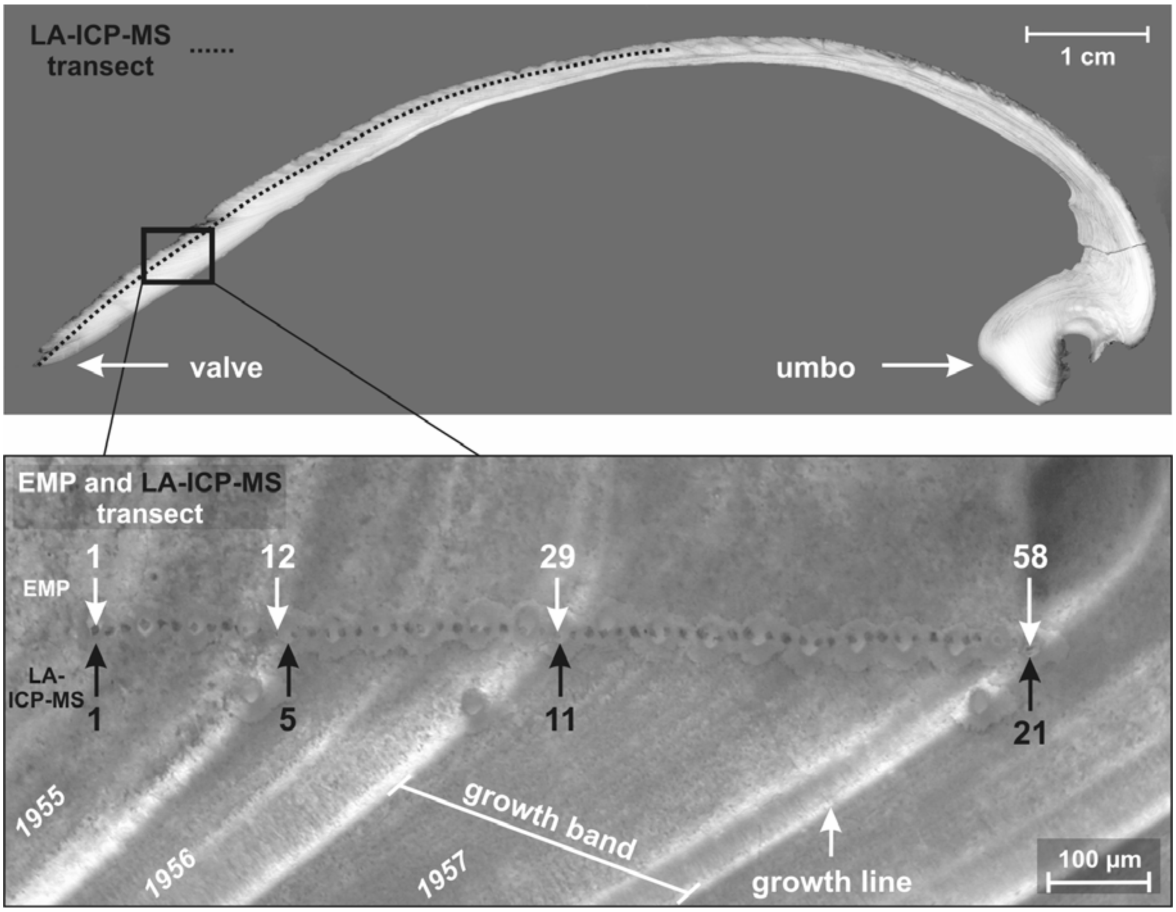

Figure 2. Cross-section of the analysed *Arctica islandica* specimen with the LA-ICP-MS transect for 144-years (above) and the EMP and LA-ICP-MS transect for the years 1955 to 1958 (below).

3.2. LA- ICP-MS

All ICP-MS measurements were carried out on a ThermoFinnigan Element2 double-focussing ICP-MS at the Department of Geosciences, University of Bremen. The instrument was operated at low resolution (R = 300) to maximize sensitivity. For laser ablation, the instrument was coupled to a Finnigan UV LaserProbe with a wavelength of 266 nm. The analytical conditions included a laser energy of 0.6 – 0.8 mJ, a pulse rate of 5 Hz and a beam diameter of 50 µm (30 µm for the thin section). Helium was used as sample gas in the ablation cell and Argon was subsequently added to the gas flow (for details see Table 1). The isotopes ^{25}Mg, ^{43}Ca, ^{88}Sr and ^{138}Ba were analyzed using 8 samples at each peak's flat top and a total dwell time of 160 ms per isotope. The NIST 610 glass standard reference material was used for external single-point calibration using the values of (Pearce et al., 1997). This multi-element standard was analysed and a new calibration line established after every

Table 1. Ranges of ICP-MS, LA-ICP-MS and EMP operating conditions.

Solution ICP-MS	
Forward power	1200 W
Reflected power	5 W
Argon flow rates	
Carrier gas	1.02 l/min
Auxiliary gas	0.8 l/min
Cooling gas	16.0 l/min
Acquisition mode	analog modus for Mg, Sr and Ca; counting modus for Ba
Points/peak	12
Dwell time	10 ms
Acquisition time	2 min
LA-ICP-MS	
Forward power	1200 W
Reflected	002 W
Argon flow rates	
Carrier gas	0.8 l/min
Auxiliary gas	0.9 l/min
Cooling gas	15 l/min
Helium flow rates	
Sample gas (Helium)	0.4 l/min
Laser parameters	
Type:	UV laser
Wavelength:	266 nm
Beam size:	50 / 30 µm
Pulse nature:	Q - switched mode
Pulse duration:	~3 ns
Pulse repetition rate:	5 Hz
Preablation time:	20 s
Pulse energy:	0.6 – 0.8 mJ
EMP:	
Type:	CAMECA SX-100
Beam size:	5,5 µm
Beam energy:	15 keV 100 nA

five samples (standard bracketing) to compensate for instrument drift. One problem in using NIST 610 may arise from interferences by elements that are abundant in the standard but less so in the samples, where $^{27}Al^{16}O$ on ^{43}Ca may be particularly disturbing. We have investigated this problem by analysing an aliquot of digested NIST 610 glass by solution ICP-MS at low resolution, where these peaks overlap, as well as at medium resolution (R = 4000) where the peaks are separated. The results agreed well within error limits indicating that interferences on the isotopes of interest are neglectable.

At these conditions, the external precision (1 sigma) as determined by replicate analyses of pressed pellets of *Arctica* and JCp-1 powder is 5 - 8 % for Mg, 2 - 6 % for Sr and 21 - 28 % for Ba, where the high values for Ba were found to reflect powder heterogeneities rather than bad precision. As the signal intensities and blanks of Ba and Mg are of similar magnitude, we infer that the actual analytical precision of Ba resembles that of Mg. Accordingly, replicate analyses of NIST 610 yielded a precision of <5 % for Mg, Sr and Ba. For the comparison of LA-ICP-MS with solution ICP-MS data, the analyses of pressed pellets were carried out with increased beam size (up to 200 µm) and energy (up to 2 mJ).

For data reduction the software package GeoPro™ was used. ^{43}Ca was selected as internal standard with a fixed concentration of 38.5 wt% which is the average of our EMP measurements (see below). The blank duration prior to ablation was 10 - 25 s and the evaluated signal duration 15 - 30 s following a pre-ablation period of 5 -10 s.

3.3. Solution ICP-MS

Analyses by solution ICP-MS of the JCp-1 and *Arctica* standards serve as reference values for assessing the accuracy of data obtained by laser ablation. Elemental concentrations were determined on the isotopes ^{25}Mg, ^{43}Ca, ^{88}Sr and ^{138}Ba; ^{89}Y was used as internal standard. Since the compositions of both carbonate standards are different, we used separate calibrations based on two stock solutions. Each calibration includes one blank and four standards diluted from the respective stock solution. Stock solutions were prepared from mono-elemental standards. For the JCp-1 the stock solution contained 25 ppb Mg, 10 ppm Ca, 200 ppb Sr, and 150 ppt Ba. For the *Arctica* standard the concentrations in the stock solution were 20 ppb Mg, 10 ppm Ca, 40 ppb Sr and 1 ppb Ba.

198 mg of the JCp-1 powder were digested in 200 ml 2% sub-boiled HNO_3 and further diluted down to 3.79 ppm for Ca. 241 mg of the *Arctica* standard were digested in 100 ml HNO_3 and diluted down to 4.68 ppm for Ca.

3.4. Electron microprobe (EMP)

Electron microprobe analyses of Ca, Mg and Sr were carried out on a CAMECA SX-100 at the Mineralogical Institute, University of Hannover, using a carbon-coated thin section. Analytical conditions included an accelerating voltage of 15 kV, a beam diameter of 5.5 µm, and beam currents of 40 nA for Ca and 100 nA for Mg and Sr. Counting times were 240 s on both peak and background for Mg, 180 s for Sr and 15 s for Ca. The built-in PAP-procedure was applied for data reduction using Wollastonite, MgO and SrF_2 as calibration standards for Ca, Mg and Sr, respectively. The detection limits were 26 ppm for Mg and 79 ppm for Sr; Ba concentrations are below detection limit and could not be analysed. Internal precision as based on counting statistics (2 sigma) was 6 - 12 % for Mg and 2 - 5 % for Sr.

3.5. Environmental data

The measured annual growth rates were compared with instrumental sea surface temperature (SST) covering monthly data from 1880 to 2002 (http://badc.nerc.ac.uk/data/gisst), monthly sea surface salinity (SSS) measured between 1908 and 1995 with interruptions (data provided by the Federal Maritime and Hydrographical Agency, Hamburg, FRG (BSH)) recorded from a nearby location, and monthly river discharge volumes of the river Elbe covering the years 1908 to 2001 recorded at the gauge in Neu Darchau (data provided by the Local Waterways and Shipping Office, Lauenburg).

4. RESULTS

4.1. Solution ICP-MS analyses of carbonate powders

To assess the accuracy of the carbonate analyses by LA-ICP-MS calibrated against NIST 610 glass, powders of the JCp-1 and *Arctica* standards were analyzed by both LA-ICP-MS and solution ICP-MS as described above, where the latter serves as the reference data. The results are presented in Table 2. For JCp1, the data

Table 2. Comparison of Mg/Ca, Sr/Ca and Ba/Ca ratios in the Japanese coral carbonate standard JCp-1 and in the house standard of *Arctica* as analysed by solution ICP-MS and LA-ICP-MS.

	Mg ppm	Sr ppm	Ba ppm	Mg/Ca mmol/mol	Sr/Ca mmol/mol	Ba/Ca µmol/mol
JCp-1 coral reference material						
Reference value	965	7275	10	4.17	8.71	7.64
Solution ICP-MS	974	7327	9.2	4.20	8.77	7.01
Laser ablation ICP-MS	862	6299	7.9	3.72	7.54	6.01
Difference laser - solution (%)	-11.4	-14.0	-14.3	-11.4	-14.0	-14.3
Difference laser - reference (%)	-10.6	-13.4	-21.3	-10.6	-13.4	-21.3
Arctica NSP powder						
Solution ICP-MS	105	1190	10.6	0.451	1.41	8.01
Laser ablation ICP-MS	100	1191	9.7	0.429	1.42	7.37
Difference laser - solution (%)	-4.8	0.1	-8.0	-4.8	0.1	-8.0

reported by Okai et al. (2001) is well reproduced by solution ICP-MS, whereas the laser ablation data is too low by 11 % for Mg, 13 % for Sr and 21 % for Ba. For the *Arctica* standard, the laser ablation data matched the solution ICP-MS data perfectly for Sr and was too low by 5 % for Mg and 8 % for Ba (Table 2). The better accuracy of the *Arctica* laser ablation data as compared to the JCp-1 coral data can be explained by the high concentrations of Mg and Sr in the coral: they exceed those of the NIST 610 calibration standard two-fold and fifteen-fold, respectively, and are thus far outside the calibration range. In contrast, Mg and Sr concentrations in *Arctica* are below or near those of NIST 610. The accuracy for Ba is more difficult to quantify, however, because this element is highly concentrated in some individual powder grains and hence irregularly distributed within a pellet. This inhomogeneous distribution accounts for much of the scatter and the large variation during replicate analyses of the pressed pellets. In contrast, analysing Ba/Ca ratios with the solution ICP-MS method total Ba is measured, due to digestion of the pellet.

The combined data suggest that there are systematic errors of laser ablation data for Mg and Ba but not for Sr when analysing shells of *Arctica* calibrated against NIST 610. These errors may reflect different ablation behaviour of these elements in silicate glass and in the carbonate matrix, i.e., different fractionation of Mg, Sr and Ba relative to Ca during the ablation process. We note, however that these elements are all lithophile and show similar fractionation indices (Jackson, 2001). For the analysis of the *Arctica islandica* shell, the data of Table 2 suggest a systematic relative error of -5 % for Mg, -8% for Ba, and no systematic error for Sr.

4.2. High-resolution transect by electron microprobe (EMP) and LA-ICP-MS

Mg/Ca ratios obtained by 58 EMP measurements range from 0.26 to 2.87 mmol/mol (average 0.80 mmol/mol) exhibiting large variations along the whole transect (Fig. 3a). The variations show no apparent systematic errors and no correlation with growth patterns. In contrast, the Sr/Ca ratios gained by EMP range from 0.99 to 5.21 mmol/mol (average 1.7 mmol/mol) and show well-defined maxima at the growth lines, whereas Sr/Ca minimum were found within the growth bands (Fig. 3b). Sr/Ca ratios in the growth lines reach up to 5.21 mmol/mol in the peak, whereas the growth bands shows values between 0.99 and 2.16 mmol/mol with an average of 1.4 mmol/mol (Fig. 3b and Table 3).

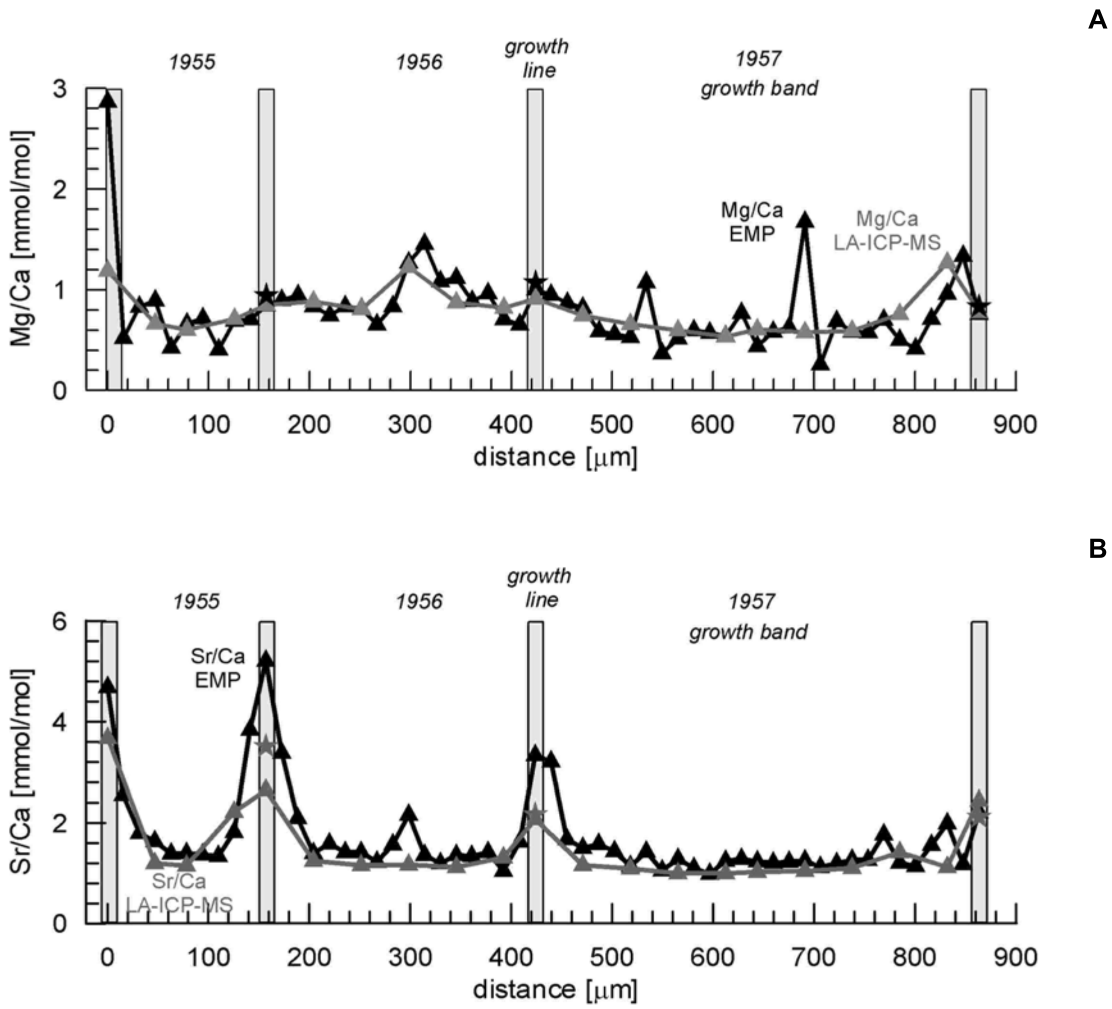

Figure 3a, b. High-resolution profile showing a) Mg/Ca and b) Sr/Ca for the years 1955 to 1958 as analysed by EMP (58 sample points, distance 15.8 µm, beam size: 5.5 µm and by LA-ICP-MS (21 sample points, distance 30 to 45 µm, beam diameter 30 µm). The stars indicate additional LA-ICP-MS measurements directly on the growth lines, whereby black stars represent Mg/Ca and grey stars Sr/Ca. The standard deviation accounts 0.21 mmol/mol for Mg/Ca for the LA-ICP-MS analyses and 0.39 mmol/mol for the EMP analyses. The standard deviation for Sr/Ca obtained by LA-ICP-MS is 0.28 mmol/mol and 0.26 mmol/mol for the EMP.

For a comparison of Mg/Ca and Sr/Ca ratios obtained by EMP and LA-ICP-MS on the thin section, a spacing of 30 µm was chosen for the laser to come closer to the spatial/temporal resolution of the EMP. The LA-ICP-MS transect was conducted along the EMP transect, whereby the laser ablation points were focussed directly onto every third EMP point (Fig. 2). Special attention was given to the exact measurement of the growth lines (Fig. 3a, b, 4). A total of 21 measurements were taken, plus three repeated measurements on each growth line as these were given special attention (the values are listed in Table 3).

Table 3. Mg/Ca and Sr/Ca ratios and their deviation (%) for three growth bands representing the years 1955 to 1958 using EMP and LA-ICP-MS.

sample point	year	EMP [mmol/mol] Mg/Ca	Sr/Ca		sample point	year	LA-ICP-MS [mmol/mol] Mg/Ca	dev %	Sr/Ca	dev %	Ba/Ca	
1	1955	2.87	4.69	g.l.	1	1955	1.19	-58%	3.68	-22%	0.009	g.l.
2	1955	0.52	2.55									
4	1955	0.89	1.64		2	1955	0.66	-26%	1.20	-27%	0.003	
6	1955	0.43	1.39									
7	1955	0.67	1.40		3	1955	0.60	-10%	1.16	-18%	0.003	
8	1955	0.72	1.37									
9	1955	0.41	1.34									
10	1955	0.69	1.82		4	1955	0.71	3%	2.22	22%	0.005	
11	1955	0.71	3.84									
12	1956	0.84	5.21	g.l.	5	1956	0.85	0%	2.65	-49%	0.006	g.l.
					5b	1956	0.94	12%	3.51	-33%	0.006	g.l.
13	1956	0.90	3.38									
14	1956	0.95	2.09									
15	1956	0.83	1.40		6	1956	0.89	6%	1.25	-11%	0.008	
16	1956	0.74	1.59									
17	1956	0.83	1.42									
18	1956	0.81	1.42		7	1956	0.81	0%	1.16	-18%	0.004	
19	1956	0.66	1.23									
20	1956	0.84	1.57									
21	1956	1.27	2.16		8	1956	1.23	-3%	1.17	-46%	0.004	
22	1956	1.46	1.36									
23	1956	1.09	1.21									
24	1956	1.12	1.36		9	1956	0.87	-22%	1.13	-17%	0.006	
25	1956	0.89	1.34									
26	1956	0.96	1.42									
27	1956	0.71	1.05		10	1956	0.82	16%	1.31	25%	0.006	
28	1956	0.66	1.63									
29	1957	1.01	3.34	g.l.	11	1957	0.91	-9%	2.08	-38%	0.011	g.l.
					11b	1957	1.07	6%	2.16	-35%	0.008	g.l.
30	1957	0.95	3.21									
31	1957	0.87	1.68									
32	1957	0.82	1.51		12	1957	0.74	-9%	1.16	-23%	0.020	
33	1957	0.59	1.58									
34	1957	0.56	1.44									
35	1957	0.53	1.14		13	1957	0.66	24%	1.09	-4%	0.007	
36	1957	1.07	1.43									
37	1957	0.37	1.06									
38	1957	0.52	1.29		14	1957	0.60	16%	0.99	-23%	0.003	
39	1957	0.60	1.11									
40	1957	0.58	0.99									
41	1957	0.54	1.25		15	1957	0.54	-1%	0.99	-20%	0.002	
42	1957	0.50	1.32									
43	1957	0.77	1.29									
44	1957	0.44	1.24		16	1957	0.61	38%	1.03	-17%	0.006	
45	1957	0.58	1.21									
46	1957	0.63	1.23									
47	1957	1.67	1.25		17	1957	0.58	-65%	1.05	-16%	0.005	
48	1957	0.26	1.13									
49	1957	0.69	1.20									
50	1957	0.58	1.27		18	1957	0.59	2%	1.11	-13%	0.004	
51	1957	0.58	1.27									
52	1957	0.70	1.77									
53	1957	0.50	1.21		19	1957	0.76	52%	1.42	17%	0.005	
54	1957	0.42	1.14									
55	1957	0.71	1.56									
56	1957	0.96	1.99		20	1957	1.27	32%	1.13	-43%	0.004	
57	1957	1.34	1.18									
58	1958	0.76	2.21	g.l.	21	1958	0.78	2%	2.44	11%	0.011	g.l.
					21b	1958	0.83	10%	2.12	-4%	0.006	g.l.

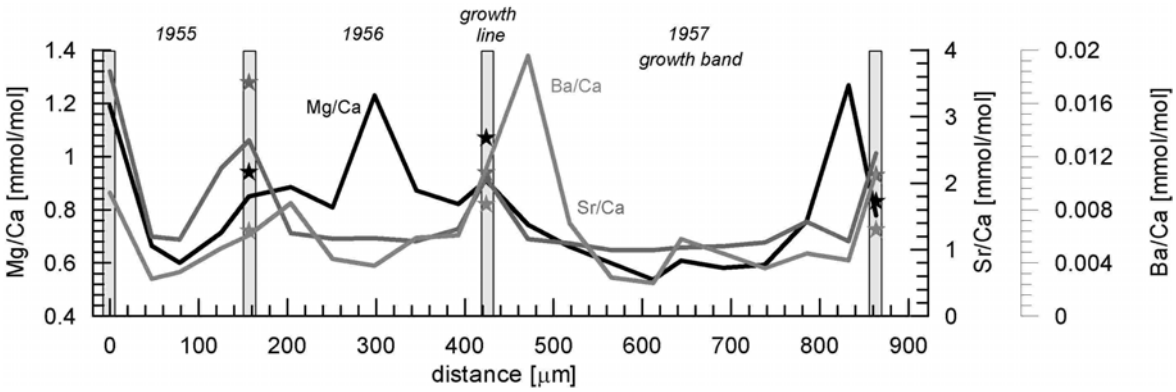

Figure 4. LA-ICP-MS generated profiles of Mg/Ca, Sr/Ca and Ba/Ca ratios. Stars indicate additional measurements directly on the growth lines in the vicinity of the profile (measurement point number 5b, 11b and 21b).

As a result of the comparison the trace element/Ca ratios obtained by LA-ICP-MS yielded a nearly identical average Mg/Ca ratio of 0.81 mmol/mol., whereby the measured values ranged between 0.54 and 1.27 mmol/mol. Small fluctuations in Mg/Ca were only detected within the EMP analyses, due to its higher spatial/temporal resolution. The average Sr/Ca ratios gained by LA-ICP-MS were lower and range between 0.99 and 3.68 mmol/mol (average 1.63 mmol/mol). The Sr/Ca peaks were also seen in the growth lines (g.l.) (Fig. 3b, 4 and Table 3) reach values of up to 3.68 mmol/mol and lower values in the growth bands Sr/Ca varies between 0.99 and 2.22 mmol/mol (average 1.21 mmol/mol). Focussing only on the average Sr/Ca ratios analysed within the growth bands, to exclude the high Sr/Ca peaks of the growth lines, a 14% lower average Sr/Ca ratio was found for the LA-ICP-MS analyses. Ba/Ca ratios, which were only analysed by LA-ICP-MS, range between 0.0025 and 0.0196 mmol/mol with an average of 0.0064 mmol/mol (Fig. 4).

4.3. Element profiles of the 144-year shell cross-section

Mg/Ca, Sr/Ca and Ba/Ca were determined by LA-ICP-MS along a profile on the outer part of the shell along the axis of maximum growth, starting at the ventral margin (Fig. 2). A regular spacing of about 50 µm was chosen allowing up to 12 spots per band in the younger (mostly wider) growth bands. With increasing age the growth bands become very narrow and limit the analyses to 1 - 2 measurements per increment (including an annual growth band and growth line). A total of 728 measurements covering 144-years were taken.

The profiles are shown in Fig. 5, in which the data points of every year were regularly distributed over the whole year. Measured element ratios range from 0.02 to

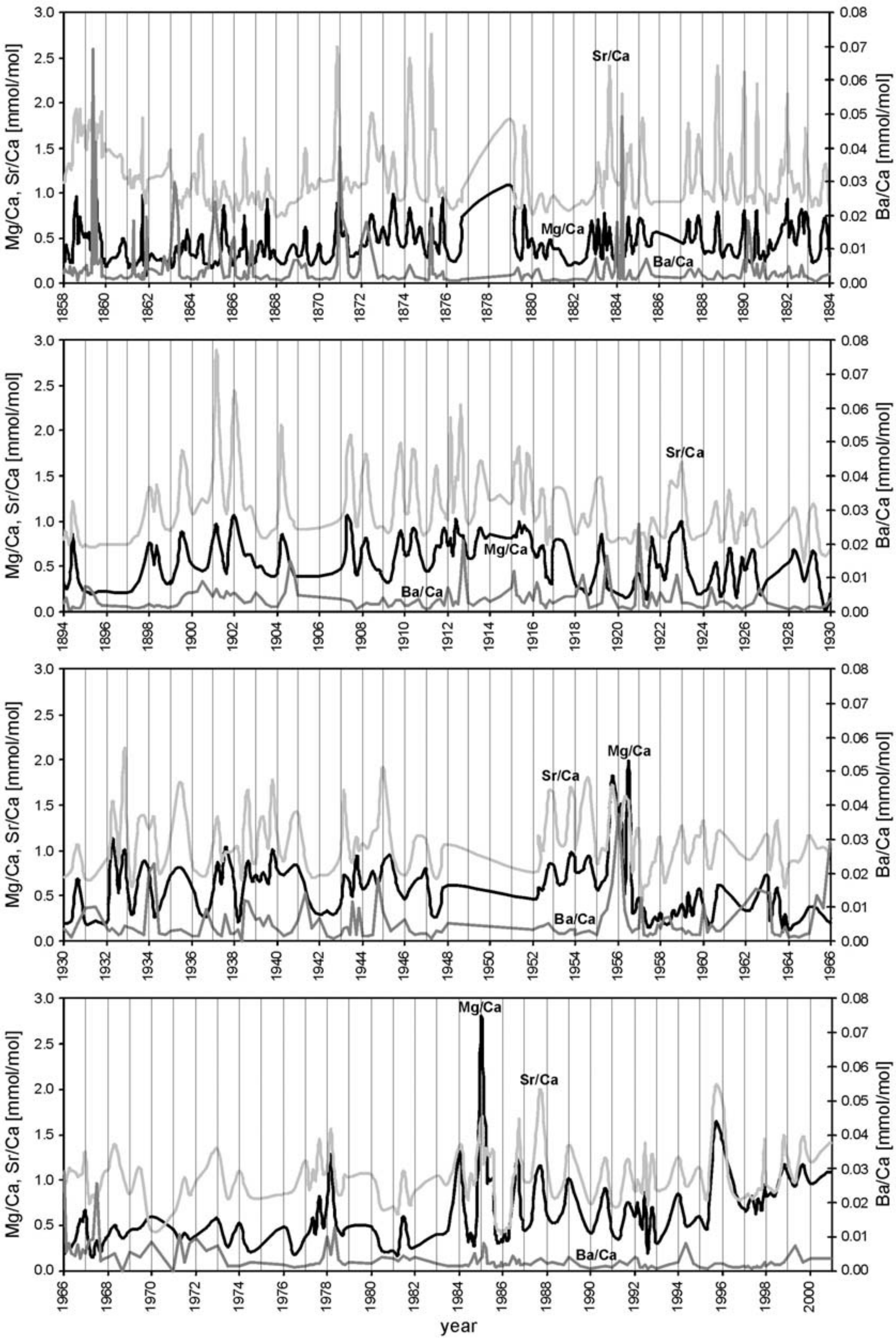

Figure 5. Profiles of Mg/Ca, Sr/Ca and Ba/Ca shell inbuilt ratios for the years 1858 to 2001 obtained by LA-ICP-MS in which the measurement points per year were regularly distributed over the whole year.

2.79 mmol/mol for Mg/Ca (average 0.52 mmol/mol), 0.41 to 2.89 mmol/mol for Sr/Ca (average 1.12 mmol/mol), and 0.001 to 0.069 mmol/mol for Ba/Ca (average 0.004 mmol/mol). Remarkably, there is a pronounced increase of the annual average Mg/Ca during the last decade, whereas Sr/Ca and Ba/Ca do not show a similar trend. The Mg/Ca profile shows high peak variability, with one or more peaks within the growth bands as e.g. in the years 1883 and 1884, but a system in these variations is not readily apparent. The Sr/Ca profile shows a clear seasonality with peaks at the growth lines. The Ba/Ca profile exhibits in many years one or two sharp peaks throughout the growth band, as seen e.g. in the years 1890 and 1943. These peaks, however, do not coincide with those of Mg/Ca and Sr/Ca (Fig. 5). The comparison of Mg/Ca, Sr/Ca and Ba/Ca with environmental data indicates a positive correlation between Sr/Ca and winter SST (Pearson correlation coefficient $r = 0.24$, number of data points $n = 96$, level of significance $p = 0.04$) (Fig. 6), and Ba/Ca and spring Elbe river discharge ($r = 0.26$, $n = 96$, $p = 0.04$) (Fig. 7). Mg/Ca shows no relationship with any environmental parameter on annual or seasonal time scales.

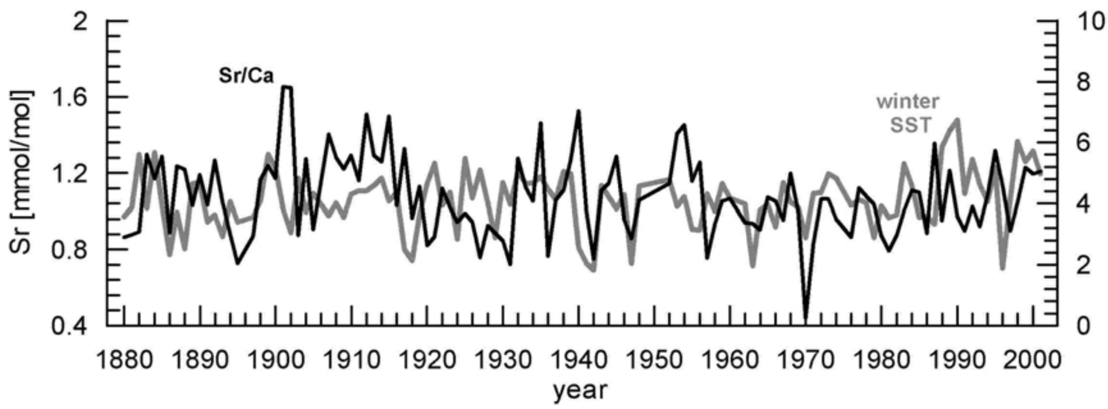

Figure 6. Annual mean Sr/Ca ratios obtained by LA-ICP-MS plotted against winter sea surface water temperature (SST) for the time period between 1880 to 2001.

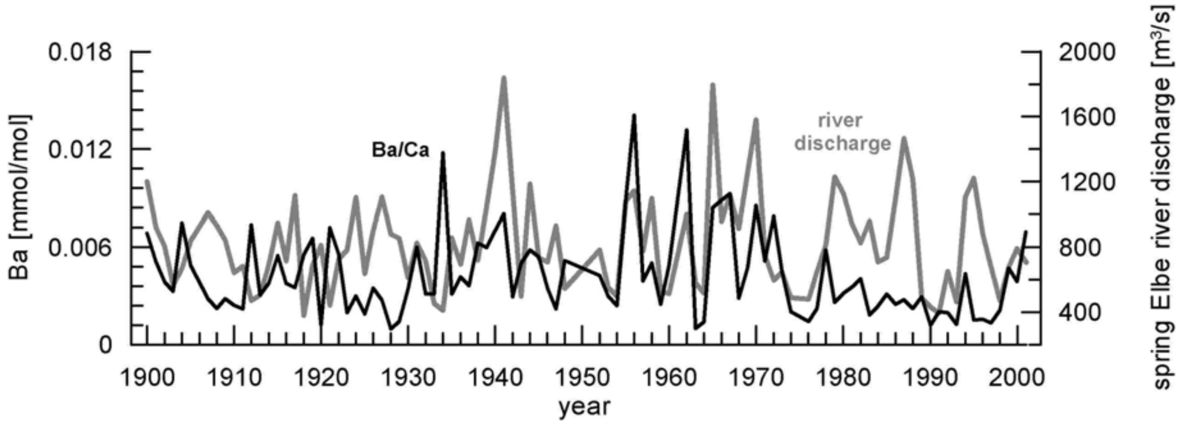

Figure 7. Annual mean Ba/Ca ratios obtained by LA-ICP-MS plotted against spring Elbe river discharge volumes for the years 1900 to 2001.

4.4. Shell chronology and environmental parameters

The investigated *Arctica* shell age accounted for 163 years and covered the years 1839 - 2002, which was reconstructed from the annual growth bands measured along the outer part of the acetate peel. The growth chronology shows a moderate but significant negative correlation with spring/early summer SST ($r = -0.34$, $n = 122$, $p = 0.05$). There is also weak positive correlation with high spring/early summer SSS ($r = 0.2$, $n = 79$, $p = 0.02$) (Fig. 8).

5. DISCUSSION

5.1. Accuracy and suitability of LA-ICP-MS and EMP data

A direct comparison of the LA-ICP-MS and the EMP transects (Fig. 3a, b) is difficult, due to the different spatial resolution and the different sample volumes analysed by both methods. The laser with an ablation diameter of 30 - 50 µm and an ablation depth of ~70 µm compared to the 5.5 µm beam size and ~2 µm penetration depth of the EMP, probes a volume of 50.000 – 140.000 µm^3 instead of the much smaller volume of ~50 µm^3 of the EMP. As demonstrated in Fig. 9, analysing a growth line with the LA-ICP-MS, bordering material is always integrated into the analyses reducing the Sr/Ca ratios.

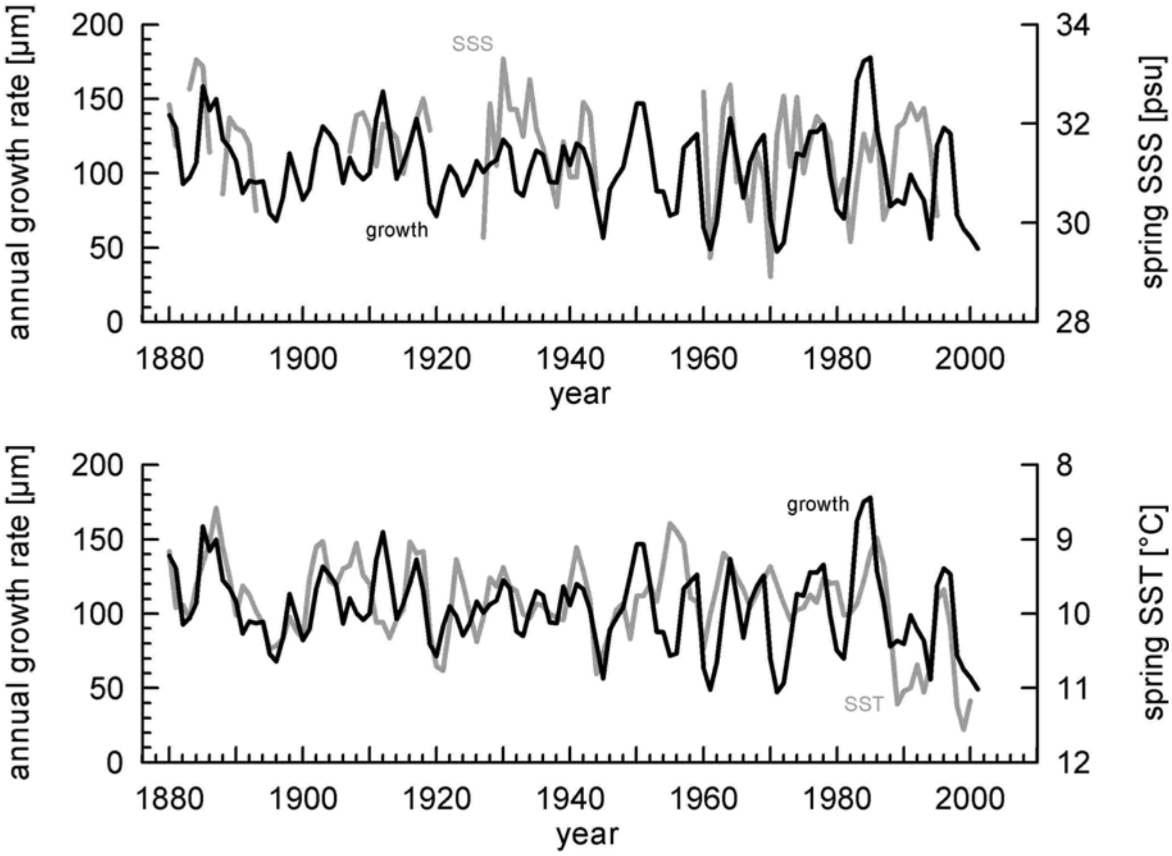

Fig. 8: Annual mean Ba/Ca ratios obtained by LA-ICP-MS plotted against spring Elbe river discharge volumes for the years 1900 to 2001.

The average Mg/Ca ratios obtained by LA-ICP-MS and EMP for the high-resolution transect (Fig. 3a) are nearly identical (0.80 and 0.81 mmol/mol, respectively) reflecting a good accuracy for the LA-ICP-MS analyses. The expected systematic error of -5% for the LA-ICP-MS data (as discussed above) is not apparent in this transect, probably because it is within the analytical precision of both methods and possibly there may be a similar bias of the EMP data as well. Such a systematic error could arise from the applied correction procedure since the matrix of the Wollastonite calibration standard ($Ca_2Si_2O_6$) and the sample are strongly different. The higher Mg/Ca fluctuation within the EMP analyses (standard deviation of 0.39 mmol/mol) compared to the LA-ICP-MS analyses (standard deviation of 0.21 mmol/mol) is caused by the high heterogeneity of Mg within the shell and the different sample volume. The average Sr/Ca ratio determined within the growth bands by LA-ICP-MS occurred to be 14 % lower than the average Sr/Ca ratios obtained by EMP (Fig. 3a, b). This is somehow surprising as we have shown above that the LA-ICP-MS data for Sr/Ca in *Arctica* should have no systematic error

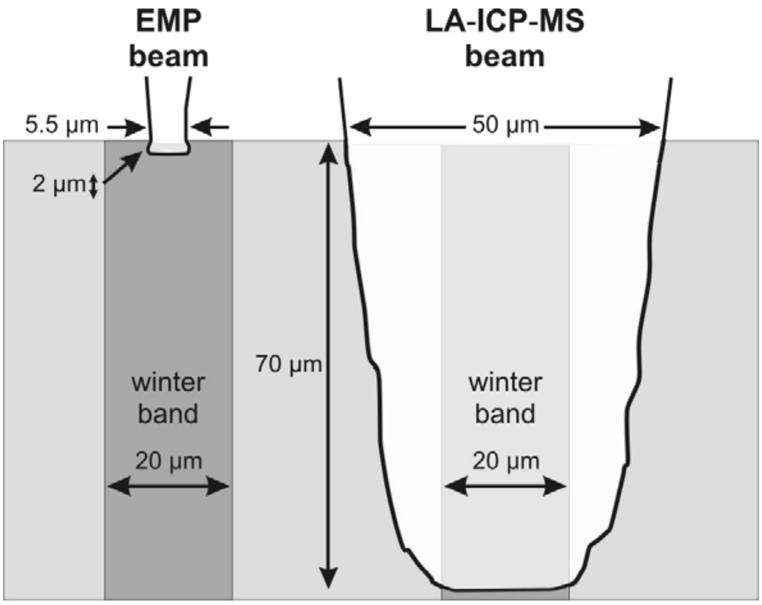

Figure 9. Schematic overview of the EMP current (left), its beam size of 5.5 µm and its ablation depth of 2 µm and the LA-ICP-MS laser beam of ~50 µm (right) and its ablation depth of ~70 µm in relation to a growth line of the shell.

(Table 2). This discrepancy might be explained by the different bulk compositions of the calibration standard SrF_2 and the carbonate analysed, similar to Mg/Ca. Alternatively, there may be indeed a systematic error in our LA-ICP-MS data not apparent from our determinations of accuracy above. Either way, we point out that the EMP and LA-ICP-MS data for Sr/Ca within the growth bands still overlap within the analytical precision. The variations of Sr/Ca within the growth bands as expressed by 1 sigma standard deviation, which is 0.28 mmol/mol for the LA-ICP-MS analyses and 0.26 mmol/mol EMP analyses, respectively. These results indicate that the distribution of Sr/Ca is relatively homogenous within the growth bands. In contrast, the LA-ICP-MS Sr/Ca ratios of the growth lines are lower than the EMP measurements. The Ba/Ca ratios of the thin section exhibited a similar high heterogeneity as seen in the 144-year chronology.

5.2. Application of shell inbuilt trace element ratios as proxies

Considering the single shell chronology of *Arctica islandica* and the positive correlations between annual growth rate and high spring/early summer SSS and cooler spring/early summer SST, it becomes evident that the main growth period and growth band deposition for this particular specimen is during spring and early summer (Fig. 8).

With respect to the Mg/Ca profiles obtained by LA-ICP-MS and EMP analyses, neither a trend related to growth band or growth line deposition nor a correlation with any environmental parameter appeared. Contrary to our findings, studies of the calcitic shell of *Mytilus edulis* and its inbuilt Mg/Ca ratios showed a relationship between Mg/Ca ratios and water temperature (Vander Putten et al., 2000; Richardson et al., 2004). The higher concentration of Mg in calcite as compared with aragonite has been explained on the basis of the easier substitution of the relatively small Mg ion for the larger calcium ion in the calcite lattice, which is isostructural with $MgCO_3$ (Dodd, 1967). The higher concentration of Sr observed in aragonite has been explained on a similar basis, aragonite being isostructural with $SrCO_3$. Shells of *Arctica islandica* are entirely aragonitic and results on aragonitic shells are emphasized in the further discussion. The Sr/Ca profile gained by our analyses showed a strong coincidence with seasonal changes. Sr/Ca peaks occurred in the growth lines, which are deposited during the winter months (Fig. 3b). On the other hand Sr/Ca ratios within the growth band, which is presumably formed during spring/early summer (considering the correlations between annual growth band and spring/early summer SSS and SST) (Fig. 8) are much lower than in the growth lines. The element profile trends for Mg/Ca and Sr/Ca illustrated in Fig. 3b is also visible in the 144-year chronology (Fig. 5), although the spatial and therefore temporal resolution is smaller. As expected the Mg/Ca variations did not show a correlation with any environmental parameter. However, a slight increase of the Mg/Ca ratio appeared in the last decade, probably explained by changes in the surrounding environment, such as increased pollution. A positive correlation appeared between Sr/Ca ratios and winter SST for the 144-year chronology (Fig. 6). Similar to the high-resolution transect, the Sr/Ca ratios show peaks around the beginning of every year. It should be considered that we measured along a transect using a beam diameter of 50 µm and a constant sample distance of 50 µm excluding the growth lines, which were not positioned directly on the transect. Nonetheless, it is still possible to record the element inter-annual variations in this chronology (Fig. 5). Similar results for the aragonitic shell *Mya arenaria* are demonstrated by (Palacios et al., 1994). They found a negative correlation between SST and Sr concentrations with Sr maxima corresponding to late winter and Sr minima in summer. Mineralogical control of Sr enrichment as a first order effect is well documented for molluscs (Dodd, 1965; Mann, 1992). The growth band accumulation in the warmer spring/summer months is associated with periods of fast growth and the growth line formation therefore with low growth, respectively. Detailed experimental studies conducted by Kalish (1989) indicate that temperature does not directly affect the Sr content of fish otoliths (aragonitic), but that its effect are mediated by physiological changes, associated in turn with the chemistry of the internal milieu. Whatever the nature of the intimate mechanisms affecting discrimination against Sr in biogenic carbonates might be, the cyclical signal in the Sr/Ca ratio in this particular *Arctica* specimen could be used as a proxy for winter SST reconstructions.

The Ba/Ca profile of the 144-year shell chronology with its characteristic sharp annual peaks shows a positive relationship with spring river discharge volumes of the Elbe river (Fig. 7). We suggest, that river runoff mirrors the phytoplankton bloom intensity, controlled by the amount of induced nutrients via river discharge. Increased nutrients are likely to enhance algal and phytoplankton growth providing enriched organic material deposits for the benthos. The findings might also provide a possibility to use the annual Ba deposits of *Arctica* out of this area as a proxy for past Elbe river run offs. In the study of Stecher et al. (1996) Ba appeared to be incorporated episodically into the aragonitic shell of *Mercenaria mercenaria*, with extreme changes occurring primarily in spring. The annual skeletal Ba maxima coincidence with algal biomass and presumably reflect elevated concentrations of particulate Ba associated with the phytoplankton bloom. Similar results were also found by Vander Putten et al. (2000), where the annual Ba/Ca cycles of the calcitic *Mytilus edulis* shells are dominated by a single narrow peak, which is systematically located in spring and related to primary production. Element composition of shells is the result of depositional and diagenetic processes. With respect to shell element incorporation, the metabolic control, ontogenetic effect and calcification rate plays an important role.

6. CONCLUSIONS

This investigation demonstrates the good accuracy and the great potential of the LA-ICP-MS analyses to study high spatial/temporal variations of Mg/Ca, Sr/Ca and Ba/Ca in shells of *Arctica islandica* when calibration with ^{43}Ca as the internal against NIST 610 as the external standard. The comparison of the measured element/Ca ratios obtained by LA-ICP-MS, solution ICP-MS and EMP resulted in a good accuracy for Mg/Ca analysed by LA-ICP-MS, solution ICP-MS and EMP. Whereas, the spatial/temporal resolution of the EMP analyses was much higher compared to the LA-ICP-MS analyses, the higher spatial/temporal resolution enabled to detect even smallest Mg/Ca variations. The Sr/Ca values determined by LA-ICP-MS and solution ICP-MS were nearly identical, whereby the Sr/Ca values measured by EMP are 14% higher than the LA-ICP-MS analyses. This discrepancy might be explained by the different bulk compositions of the calibration standard SrF_2 and the carbonate analysed. Ba/Ca ratios gained by LA-ICP-MS are -8% lower compared to those obtained by solution ICP-MS, which is possibly caused by the inhomogeneous distribution of the element within the pellet.

In spite of shell derived trace elements used as proxies for high temporal resolution climatic reconstructions, the clear cyclical signal of the Sr/Ca peaks in the shell growth lines can be applied to reconstruct winter sea surface temperatures. The annual peaks of Ba/Ca provide excellent markers for past spring phytoplankton blooms / Elbe river discharges of the inner German Bight. The Mg/Ca ratio did not show a relationship with any environmental parameter. To validate the results and to reach entire certainty, it is necessary to analyse a larger number of *Arctica* shells from this area.

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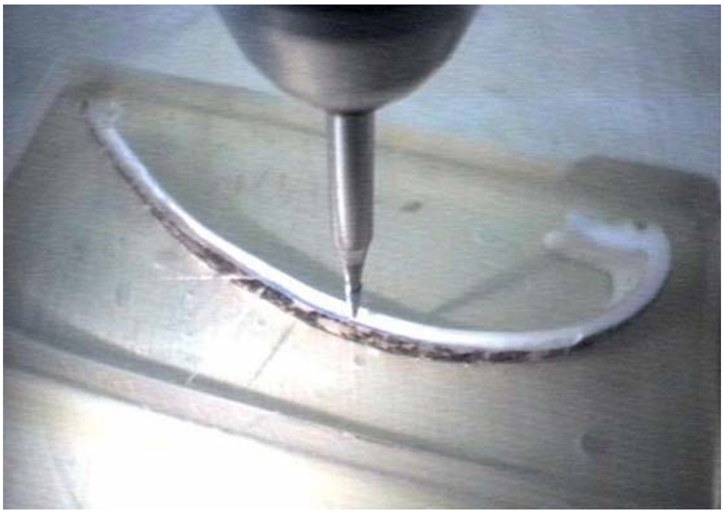
Holocene changes in bottom water temperature regime in the northern North Sea – evidence from *Arctica islandica* (Bivalvia) stable oxygen isotopes

Valérie M. Epplé, Thomas Brey, Rob Witbaard



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Holocene changes in bottom water temperature regime in the northern North Sea – evidence from *Arctica islandica* (Bivalvia) stable oxygen isotopes

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Abstract

Shell growth and oxygen isotope analyses were carried out with modern and early Holocene/late Younger Dryas (calendar age: 8406, 8406, 9614, 11101, 11122 years B.P.) shells of *Arctica islandica* from the Fladen Ground (northern North Sea). Reconstructed average annual bottom water temperature (based on modern shell $\delta^{18}O$ values covering a 9-year transect), 7.96°C, is in line with average annual instrumental water temperature, 7.02°C, with a deviation of +0.94°C. Reconstructed bottom water temperatures of a subfossil shell dated 9614 years B.P. indicate a larger interannual amplitude, 3.3°C to 10.1°C compared to 6.8°C to 9.3°C today. Annual minimum as well as annual average water temperatures are significantly higher in the modern shell. A comparison of annual growth rates of all six shells indicated significantly faster growth of the modern and the 8406 years B.P. shells and significantly slower growth for the individuals from the late Younger Dryas. This growth pattern coincides with the climatic conditions postulated for this time windows. Frequency spectra resembling modern North Atlantic Oscillation (NAO) induced spectra were found in the long-lived shells from 9614 and 11101 years B.P. indicating the prevailing influence of the NAO already during the early Holocene and the end of the Younger Dryas in this area.

Keywords: Arctica islandica, oxygen isotopes, Fladen Ground, early Holocene

1. Introduction

The Holocene epoch, which includes the present, is a period of permanent environmental change, the understanding of which becomes increasingly urgent in view of growing concerns for future climate development, especially with regard to growing anthropogenic impact during the last two hundred years.

The Holocene began between 11525 and 11640 calendar years B.P., according to the Swedish varv chronology and the Greenland ice cores GRIP and GISP2 (Anderson, 1959; Johnsen et al., 1992; Alley et al., 1993). The GRIP ice core record indicates a very rapidly temperature rising at the inception of the Holocene of about ~7°C and an additional temperature increase of ~5°C at 9500 B.P. (Koç and Jansen, 2002). A period of a so-called "climatic optimum" occurred and remained between 8000 and 5000 years B.P. (Koç et al., 1993; Koç et al., 1996). After 5000 years B.P. the climatic conditions are characterized by a general cooling trend (Imbrie et al., 1992; deMenocal et al., 2000). These naturally induced climate variabilities are followed by the most recent climate period, the so-called "modern optimum" (Schönwiese, 1988), which began in the 20th century. Temperature rising during the last one hundred years is assumed to be related to the anthropogenic induced increase in green-house gas concentration (ICPP, 2001).

High-resolution instrumental time series of climatic and environmental data for the North Sea are only available for the last decades or a century at best. Long term high-resolution paleoclimatic reconstructions in higher latitudes predominantly depend on land-based proxies, such as ice cores, dendrochronology and varv chronologies. Such data do not necessarily reflect marine environmental conditions or display possible land-sea interactions. Boreal early Holocene water temperature data derived from marine proxies on an annual resolution are almost non-existent. Therefore, the interest in sclerochronological analysis of mollusc shells for retrospective environmental studies increased steadily, as periodic accretion of skeletal calcium carbonate and its stable isotopic composition provide sources of information on seasonal variation in temperature (Marchitto et al., 2000; Schöne et al., 2004) albeit mollusc shells are still not used routinely in climatic studies.

The bivalve *Arctica islandica* (Linneaus, 1767) is a very suitable candidate for paleo bottom water temperature reconstructions due to its annual growth band formation (Jones, 1981) and its life span of over 200 years (Ropes et al., 1984;

Schöne et al., 2003). Reduced or sometimes ceased growth during winter results in the formation of a distinct shell growth pattern consisting of one wide growth band per year seemingly separated from the adjacent bands by narrow growth lines (Merrill et al., 1961; Thompson et al., 1980; Jones, 1981). Bottom water temperatures reconstructed from on modern *Arctica islandica* shell oxygen isotopic composition and calibrated against instrumental data provided a precision of about 1.2°C (Weidmann et al., 1994; Schöne et al., 2004). Fossil *Arctica ovata* (Tripati et al., 2001) from the Arctic Ocean and *Arctica islandica* from Iceland (Buchardt and Simonarson, 2003) were used for paleo water temperature reconstructions based on shell derived oxygen isotope compositions. Bottom water temperature reconstructions for the early Holocene have not been conducted for the North Sea. The Fladen Ground, which is situated in the northern part of the North Sea provides an excellent location for early Holocene marine environmental reconstructions. Nowadays, as well as during the entire Holocene the major inflow gate from the North Atlantic into the North Sea is positioned just north of the Fladen Ground. Until today, studies conducted on *Arctica* from the Fladen Ground concentrated on annual shell growth (Witbaard et al., 1997; Witbaard et al., 2003) and not on shell chemistry.

This study aims at the following questions:

Is *Arctica islandica* a suitable tool for the reconstruction of Fladen Ground bottom water temperature, i.e. are temperatures inferred from modern shell $\delta^{18}O$ in line with instrumental temperature records? Furthermore, what does $\delta^{18}O$ of subfossil shells tell us about early Holocene bottom water temperatures at Fladen Ground? And finally, how is the shell growth rate of *Arctica islandica* related to temperature at the Fladen Ground from early to recent Holocene?

2. Material & Methods

2.1. Shell material

Shells of *Arctica islandica* were collected in July 2000 (Witbaard, 2000) on the Fladen Ground (59°22.5’N 0°35’E) from a depth of 140 m (Fig. 1). Five subfossil shells (code FL1 to FL5) and one modem shell (code M1, caught alive) were used for sclerochronological analysis (Table 1).

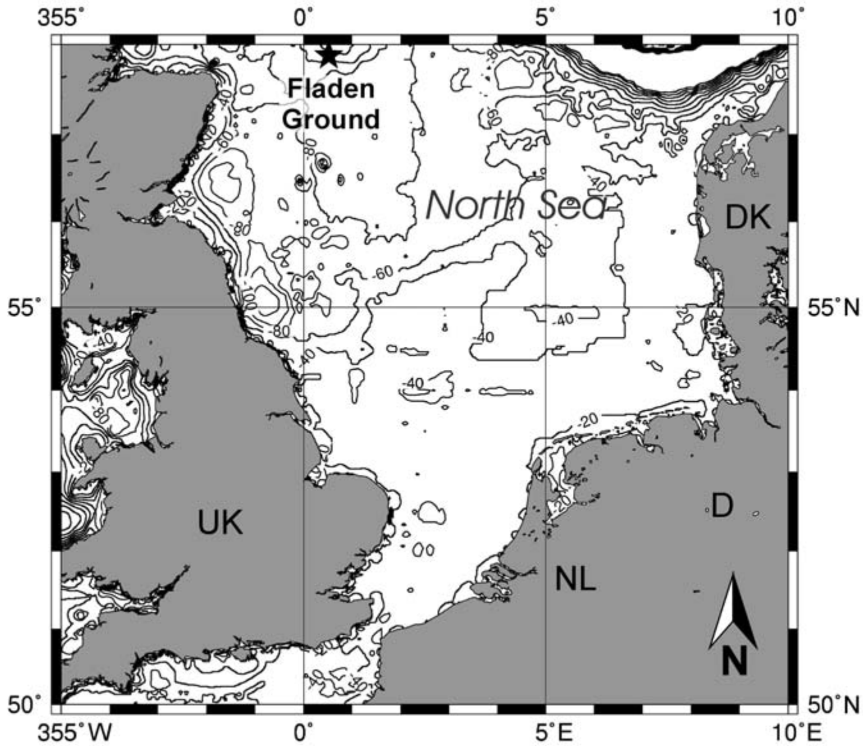

Fig. 1: Bathymetric map of the Fladen Ground (northern North Sea) showing the sample location (59°22.5'N 0°35'E) of the modern and early holocene shells of *Arctica islandica*.

Table 1. Calibrated ^{14}C age and the calculated calendar years B.P. of the five subfossil shells of *Arctica islandica* from the Fladen Ground.

sample	radiocarbon age	Δ *R*	calibrated age	calibrated age ranges	shell age (counted years)	shell length
modern shell M1	calendar year 2000				29	4.00 cm
subfossil shell FL1	8070 ± 50 BP	91± 30	8406 BP	8576 - 8328 BP	47	6.27 cm
subfossil shell FL2	8070 ± 60 BP	91± 30	8406 BP	8576 - 8328 BP	57	6.55 cm
subfossil shell FL3	9090 ± 55 BP	91± 30	9614 BP	9922 - 9116 BP	134	7.04 cm
subfossil shell FL4	10210 ± 60 BP	91± 30	11101 BP	11602 - 10533 BP	178	7.05 cm
subfossil shell FL5	10270 ± 60 BP	91± 30	11122 BP	11607 - 10645 BP	31	4.26 cm

2.2. Radiocarbon dating

For ^{14}C radio carbon dating (Libby, 1946) the absolute ratio of ^{14}C to ^{12}C in a >10 mg shell sample was determined by an Accelerator Mass Spectrometer (AMS). From the derived values, a radiocarbon age was calculated assuming a constant time independent atmospheric ^{14}C in the past. The radiocarbon ages are referred to as before present (B.P.). In the next step, the ^{14}C age B.P. was converted into more precise calendar age estimates using the CALIB 4.3 calibration program (http://radiocarbon.pa.qub.ac.uk/calib/), which is based on dendrochronological calibrations (Stuiver et al., 1998). A ΔR value of 121 years was used to correct for regional differences in reservoir age, based on *Patella vulgaris* from the Fair Isle (Harkness, 1983).

2.3. Shell preparation

In the shell of *Arctica islandica*, one growth increment represents one annual growth period (Fig. 2). Cross-sections and acetate peels were prepared from resin embedded left-hand valves following Ropes (1985). In each shell section subsequent growth bands were identified and measured under a microscope. As the modern specimen was caught alive, it was possible to assign a particular calendar year to every growth increment covering the time span 1972 - 2000. Accordingly, all age related growth discrepancies can be eliminated. For more details see Marchitto et al. (2000), Schöne et al. (2003) and Epplé et al., submitted (2004).

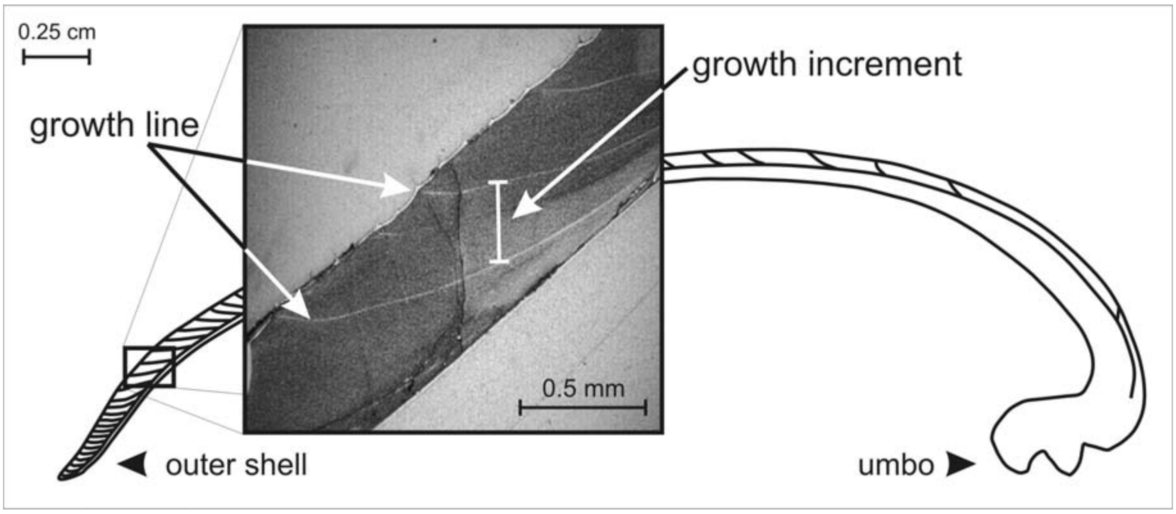

Fig. 2: *Arctica islandica* shell cut scheme and clipping of an example shell cut showing growth increments.

2.4. Spectral density analyses

Periodicities are a typical feature in climatic time series, e.g. the North Atlantic Oscillation (NAO) 7.8 year periodicity (Felis et al., 2004), which can be reflected in corresponding proxy time series, too, e.g. Schöne et al. (2003). A spectral density analysis (statistical package JMP, (SAS-Institute, 2002)) was applied to the detrended shell chronologies of the two most long-lived specimens FL4 (11101 years B.P., 178 years of age) and FL3 (9614 years B.P., 128 years of age) in order to identify cyclic patterns. Detrending was carried out by standard techniques (Fritts, 1976; Cook and Kariukstis, 1990) using a seven year moving average filter (Epplé et al., submitted 2004).

2.5. Comparison of growth performance between shells

To analyse whether the six specimens (FL1 to FL5, and M1) differed in growth performance during the first 29 years of life (= maximum age of specimen M1), annual growth increments $GI_{x,i}$ (specimen x, year i) were transformed into relative growth increments $RGI_{x,i}$ for each age i separately by

$$RGI_{x,i} = (GI_{x,i} - MI_i)) / SD_i$$

where

$$MI_i = \left(\sum_{x=1}^{6} GI_{x,i} \right) / 6$$

and SD_i is the corresponding Standard Deviation. Growth performance was then compared across the 29 years by a multiple paired t-test using year as the grouping parameter as well as by a one-way ANOVA.

2.6. Bottom water temperature reconstruction

Stable oxygen isotopes were used to reconstruct modern and early Holocene bottom water temperatures at the Fladen Ground. *Arctica islandica* is known to precipitate its shell in oxygen isotopic near-equilibrium with the ambient water (Weidmann et al., 1994). Salinity at the Fladen Ground is close to 35 psu throughout the year and hence does not affect oxygen isotope ratio $\delta^{18}O$.

In the modern shell M1 (29 years of age) 129 carbonate powder samples (ca. 20 µg) were drilled with a micro drill along a transect covering the first 25 growth increments. The last four increments were to narrow to be sampled adequately. In the fossil shell FL3 (134 years of age) embedding medium penetrated into the shell through the porous surface. In order to avoid sample contamination with resin, only the first 9 increments were sampled with a micromill (Dettman and Lohmann, 1995) resulting in 113 subsequent samples of about 25 µg each.

Oxygen isotope analyses were performed on a Kiel I carbonate device coupled to a Finnigan MAT 251 gas isotope ratio mass spectrometer. Isotope ratios are reported as parts per mil (‰) in the usual δ-notation relative to the V-PDB standard. The analytical standard deviation is about ±0.07‰ (= ±0.33°C) V-PDB (Isotope Laboratory University of Bremen). Water temperature was reconstructed from $\delta^{18}O$ using the formula of Grossman and Ku (1986):

$$T = 21.8 - 4.69(\delta^{18}O_{aragonite} - \delta^{18}O_{water})$$

where $\delta^{18}O_{aragonite}$ and $\delta^{18}O_{water}$ are reported relative to V-PDB and VSMOW. Early Holocene $\delta^{18}O_{water}$ had to be corrected for changes in oxygen isotope composition prior to temperature reconstruction. According to Fairbanks (1989), $\delta^{18}O_{water}$ increased by 0.011‰ with each meter of sea-level rise during the Holocene. Early Holocene sea-level of the North Sea was ~53 m below the present-day level (Streif, 2002), i.e. $\delta^{18}O$ values from early Holocene shell must be corrected by -0.58 ‰.

2.7. Instrumental data

Bottom water temperature time series (1973 - 1983) at the Fladen Ground were constructed from instrumental data available from ICES (http://www.ices.dk/ocean/, data files 18137079 and 18138089). Data refer to the positions 59°12`N 359°1.2'E and 57°58.2`N 357°10.2'E (91 km and 259 km distance from shell sampling site, respectively). Measurements were made at irregular time intervals and varying depths. Time series of monthly mean water temperature for the depth of 80 - 90 m and 120 - 150 m were computed from corresponding data. Upon this time series we fitted a spline and from this spline we used the respective predictions of the monthly means. A corresponding monthly mean sea surface water temperature series was taken from the GISST2.3 SST data set (data field 181) (http://badc.nerc.ac.uk/data/gisst/). The ICES and GISST data cover the years 1973 - 1981.

3. The Fladen Ground study area

3.1. At present

The Fladen Ground is located about 100 miles north-east of Aberdeen (Scotland) (Fig. 1). The bottom consists of an irregular pattern of glacial depressions between 100 and 150 meter depth (Basford and Eleftheriou, 1988). The area is located just south of the major water inflows from the Atlantic Ocean into the northern North Sea. The central and deeper parts are situated in the centre of a semi-permanent, topographically steered cyclonic eddy formed by the “Fair Isle Current” and the “East Shetland Atlantic Inflow” (Svendsen et al., 1991; Turrell, 1992a; Turrell, 1992b).

The variation in bottom water temperature throughout the year is 1 to 2°C and varies between 5.7 and 7.8°C (Faubel et al., 1983). Bottom water salinity is constantly around 35‰ (Faubel et al., 1983) and bottom currents are supposed to be <0.25 m s^{-1} (McIntyre, 1961; Lenz, 1982). During summer the water is thermally stratified with a thermocline between 30 and 70 m (McIntyre, 1961).

3.2. Early Holocene

At the beginning of the Holocene 10000 years B.P. the coastline of northeast England was just east of the present coastline and the North Sea comprised the area of the Norwegian Trough and a western embayment extending south to the latitude of Flamborough Head (Peltier, 1994). Around 9.000 years B.P. the coastline of northeast England was nearly identical with the present coastline (Shennan et al., 1999).

During the Holocene the sea-level of the North Sea rose continuously from ~65 m below the present-day position at 10000 years B.P. up to the present sea-level (Jelgersma, 1979; Eisma et al., 1981; Streif, 2002). Between 8600 and 7100 years B.P. the sea-level rose from about 46 to 25 m below present-day level. Since 8500 years B.P. the sea-level increased from 25 m below to the present-day of about 30 - 35 cm per year to the sea-level of to (Streif, 2002).

Unfortunately, there are no continuously high-resolution climatic data covering the complete time period between 11122 years B.P. and 2000 A.D. for this area. Koç and Jansen (1994) and Koç and Jansen (2002), who investigated the summer sea surface temperatures based on the Nordic Seas sediment core HM79-6/4 for the time window between 11500 and 4000 ^{14}C dated age B.P. found temperatures of ~1°C at the end of the Younger Dryas. A temperature rise up to ~14°C occurred between 10000 and 9500 ^{14}C dated age B.P. with a slight temperate increase between 9800 and 9500 ^{14}C dated age B.P.- (The Preboreal Oscillation). During 9000 and 11000 B.P. the summer insolation in the Nordic Seas including the present area reached its maximum (Koç et al., 1993; Andruleit and Baumann, 1998). After this insolation maximum, a period of so-called “climatic optimum” occurred and remained between 8000 and 5000 years B.P.. A coupled model including the atmosphere-ocean circulation and the orbital forcing covering the time between 7000 years B.P. and 1900 A.D. indicates much warmer summer sea surface temperatures and colder winter sea surface temperatures between 5000 and 7000 years B.P. than for the time between 4500 years B.P. and 1800 years A.D. (Lorenz and Lohmann, 2004). Most likely, the situation was quite similar around 8000 and 9000 years B.P. (Lohmann, pers. communication 2004).

4. Results

4.1. Subfossil shell age and individual shell age

The radiocarbon dating of the five fossil shells of *Arctica islandica* from the Fladen Ground yielded in calibrated ages of 8406 years B.P for individual FL1 and FL2 , 9614 years B.P. for FL3, 11101 years B.P. for specimen FL4 and 11122 years B.P. for shell FL5 (Table 1). Individual age as determined from the number of shell growth bands differed distinctly among the six specimens. It amounted to 29 years in the modern shell M1, 47 years in shell FL1, 57 years in shell FL2, 134 years in shell FL3, 178 years in shell FL4 and 31 years in shell FL5 (Table 1).

4.2. Instrumental and reconstructed bottom water temperatures

The shell $\delta^{18}O$ based reconstructed annual bottom water temperature for the years 1973 to 1981, where at least 10 carbonate samples were obtained from each growth increment (except year 1981) indicate an average mean water temperature of 7.97°C. Annual temperatures range between 6.78°C and 9.34°C (Fig. 3).

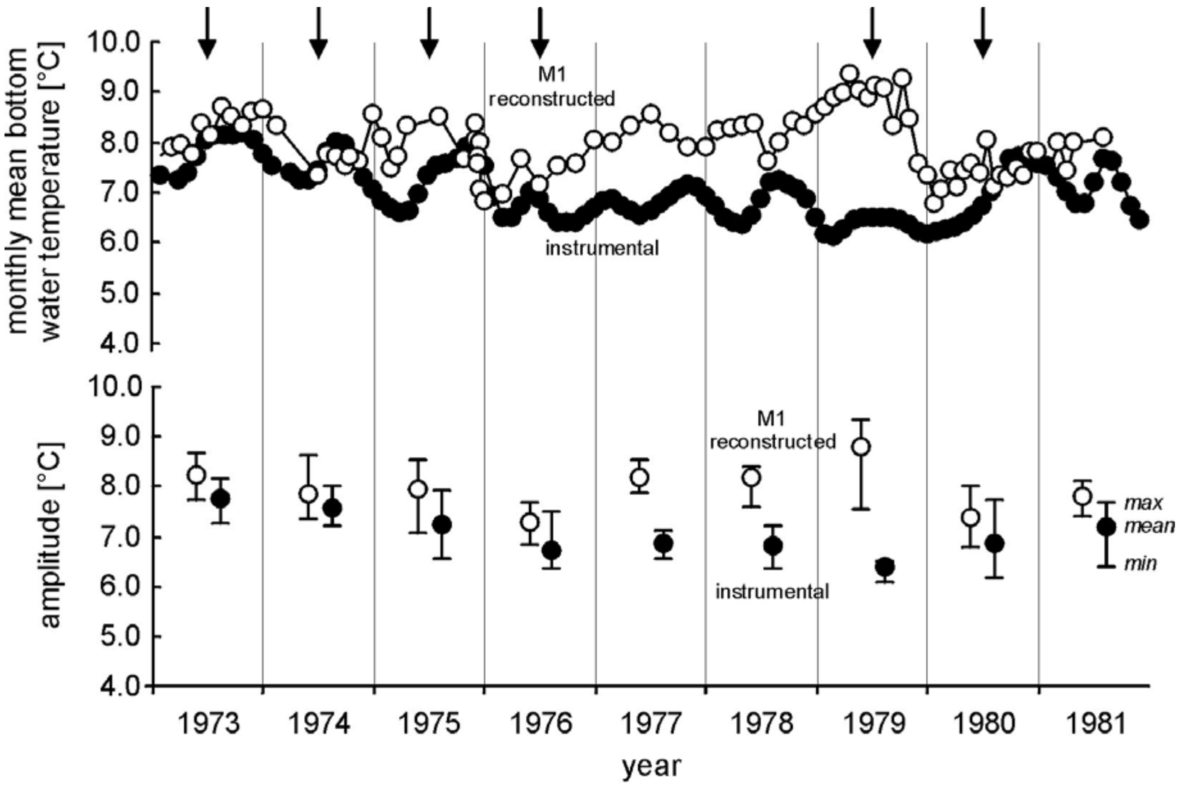

Fig. 3: Monthly mean bottom water temperatures at 140 m (instrumental and reconstructed from shell M1). Please note that the exact position in time of each reconstructed temperature value within the year is not known. Arrows indicate the years, where a good agreement between instrumental and reconstructed oscillation occurred. In the lower part of the figure the corresponding annual means and ranges are shown.

Instrumental and reconstructed bottom water temperatures for the period 1973 to 1981 are shown in Fig. 3. The comparison of the two data series is hampered to a certain extend, because the exact position in time of each reconstructed temperature value within each year is not known due to seasonality in shell growth. Nevertheless, Fig. 3 indicates reasonable coincidence between the two data series: (i) the pattern of oscillation peaks and troughs is similar except for the years 1977 and 1978; (ii) the annual temperature ranges are similar except in 1979 and 1980, and (ii) based on mean annual values, the average deviation of reconstructed from instrumental data is +0.94°C only.

4.3. Comparison of modern and early Holocene temperature regime

The 9-year bottom water temperature profile reconstructed from the subfossil shell FL3 (9614 years B.P.) as well as the corresponding annual means and ranges are shown in Fig. 4 Compared to modern temperatures as reconstructed from shell M1, annual minimum temperature (7.35°C versus 5.12°C, P = 0.002) and annual mean temperature (7.94°C versus 7.02°C, P = 0.001) are significantly lower in early Holocene, whereas annual maxima do not differ significantly (8.44°C versus 8.36°C, P = 0.811).

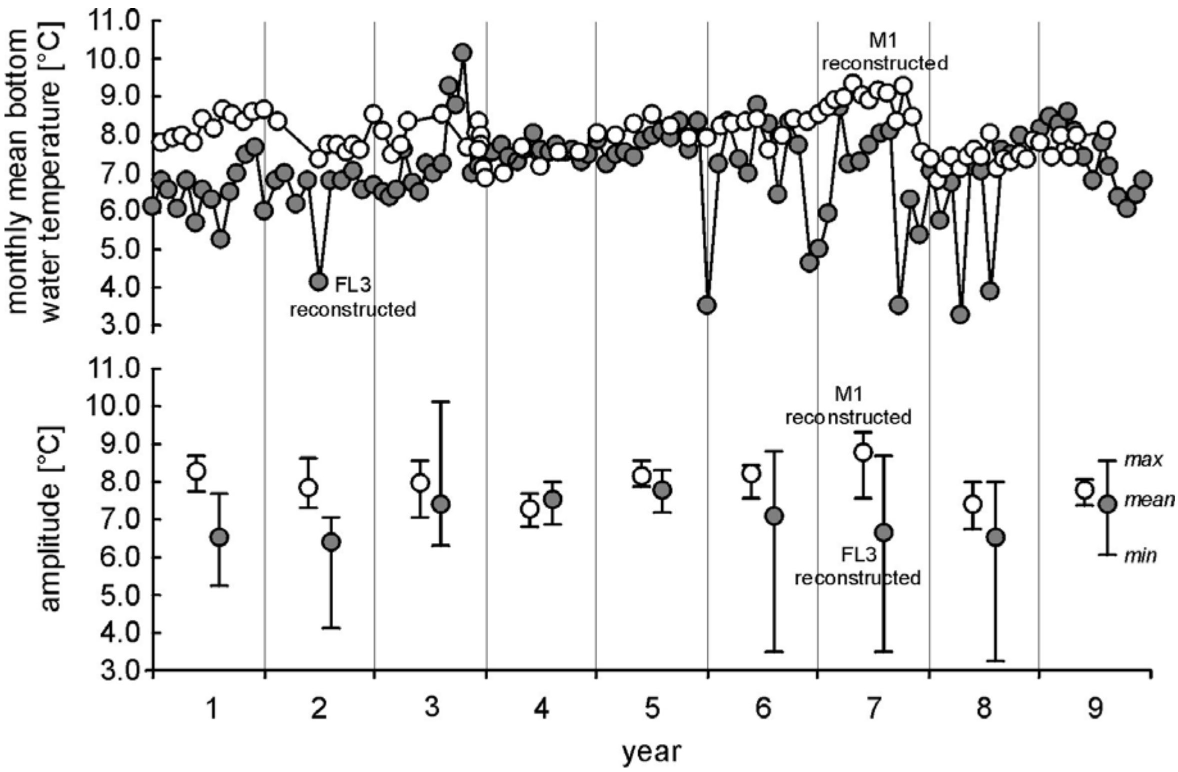

Fig. 4: Monthly mean reconstructed bottom water temperatures at 140 m (obtained by the modern shell M1) and at 87 m (gained by the subfossil shell FL3 from 9614 years B.P.). In the lower part of the figure the corresponding annual means and ranges are shown.

4.4. Differences in growth performance

Both the multiple paired t-test and the one-way ANOVA identified the sample pattern of differences in growth between the six specimens (Table 1). Specimens M1 (modern), FL1 and FL2 (both 8406 years B.P.) represent a homogeneous group of significantly highest growth, whereas specimens FL5 (11122 years B.P.) and especially FL4 (11101 years B.P.) show significantly poor growth. The individual FL3 (9614 years B.P.) showed an average growth rate (Table 2).

Table 2: Comparison of growth performance of the six specimens across the first 29 years of life with a multiple paired t-test of the relative growth increments *RGI* and year as the grouping parameter. Table shows mean *RGI* values and P-values for pair wise comparisons between specimens. Bold figures indicate significant differences at P <= 0.05. A one-way ANOVA provided identical results albeit slightly different levels of significance.

	FL1	FL2	FL3	FL4	FL5	M1
Mean *RGI*	0.651	0.211	-0.092	-0.941	-0.247	0.417
FL1		0.058	0.014	0.001	0.001	0.126
FL2			0.382	0.001	0.111	0.840
FL3				0.001	0.214	0.244
FL4					0.005	0.001
FL5						0.026

4.5. Shell growth chronologies and growth patterns

Spectral density analysis of the shell growth chronologies of the specimen FL4 (11101 years B.P., 178 years of age) and FL3 (9614 years B.P., 128 years of age) indicated a periodicity with a frequency of 5.5 years in both shells and an additional 8-9 year signal in shell FL4 (11101 years B.P.) (Fig. 5).

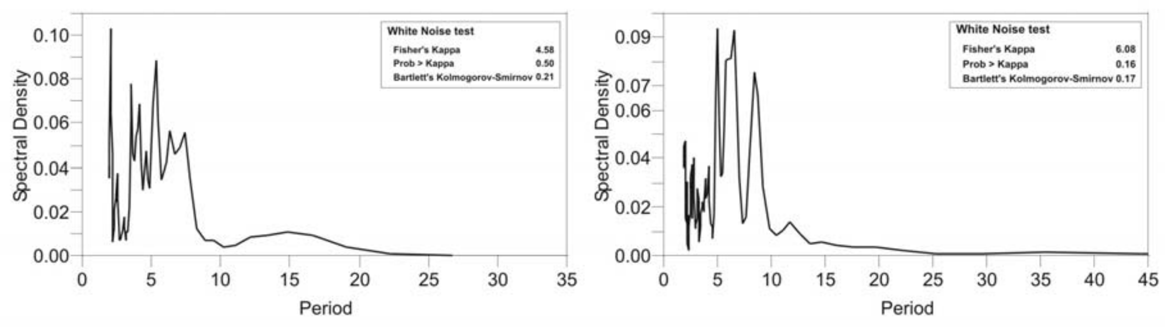

Fig. 5: Spectral density analyses of the two holoce individuals FL3 (134 years of age) from 9614 years B.P. and FL4 (178 years age) from 11101 years B.P.. The spectral analysis reviled in peaks between 5.5 years for both individuals and a additional peak between 8 - 9 years for specimen FL4.

5. Discussion

5.1. Is Arctica islandica a suitable tool for temperature reconstructions?

During the years 1973 - 1981 reconstructed (shell-derived $\delta^{18}O$) and instrumental temperature time series from the Fladen Ground coincide reasonably well except in the years 1977 to 1979 where partially both time series appear to be out of phase and partially reconstructed data are distinctly above instrumental data (Fig. 3). This difference may, on the one hand, be related to methodical shortcomings in $\delta^{18}O$ analysis such as the general analytical error (±0.07‰, i.e. ±0.33°C) or insufficient temporal resolution, especially in those parts of the shell that correspond to low or ceased growth during winter. On the other hand, the instrumental time series is based on a data compilation scattered in time (discontinuous recordings), in depth (120 to 150 m) and in space (two stations, both several miles off our sampling location) and thus may be biased to an unknown extend with respect to the conditions at our sampling location. Despite these difficulties, mean annual bottom water temperatures reconstructed from *Arctica islandica* deviate from instrumental data by +0.94°C only, which is in line with previous findings (Weidmann et al., 1994; Schöne et al., 2004).

5.2. What do subfossil shells tell us about early Holocene environmental conditions?

The 9-year temperature profile reconstructed from the shell of specimen FL3 (9614 years B.P.) indicates a higher seasonal amplitude compared with today with significantly lower annual minima, i.e. cooler winter and slightly warmer summer water temperatures. This is in good agreement with the predictions of the coupled atmosphere-ocean circulation model ECHO-G (Lorenz and Lohmann, 2004; Lohmann, 2004 pers. comm.).

Differences in growth between the six specimens analysed here (Table 2) correspond well to known differences in environmental conditions during their life time. The fastest growth was found in the modern shell M1 and the shells FL1 and FL2 from 8406 years B.P., which falls in the climate optimum (Koç and Jansen, 1994). The slower growth observed in specimen FL3 coincides with the lower average reconstructed temperature compared to specimen M1. This reconstructed temperature, in turn, confirms that 9614 years B.P. is situated within the colder Preboreal Oscillation (Koç and Jansen, 2002). Lowest growth is exhibited by the two shells FL4, FL5 (>11100 B.P.) from the late Younger Dryas, a time of very low water temperatures of ~1.5 °C (Koç and Jansen, 2002).

Growth chronologies of many modern biogenic carbonates from the Northern hemisphere such as corals (Felis et al., 2004) reflect the influence of the Arctic Oscillation/North Atlantic Oscillation (AO/NAO) on climatic conditions. Such NAO periodicities have also been found in modern *Arctica islandica* from the southern and central North Sea by spectral analysis (Schöne et al., 2003; Epplé et al., submitted 2004). Regarding *Arctica islandica* from the Fladen Ground, Witbaard et al. (2003) concluded that the annual shell growth is coupled to copepod abundance which, on the other hand, is statistically linked to the winter NAO index. The spectra of our subfossil long-term shell chronologies from the early Holocene (9614 years B.P.) and the late Younger Dryas (11101 years B.P.) exhibited peaks at 5.5 and 8 - 9 years, indicating the presence of a NAO-like oscillation pattern (Fig. 5). These findings indicate that Northern hemisphere climate has been controlled by AO/NAO already 9000 and 11000 years B.P. ago.

Our study covers only a few narrow windows of time in the Holocene history of the North Sea area. It represents, however, a significant contribution towards the establishment of a complete Holocene chronology based on *Arctica islandica* shells from the Fladen Ground, a task currently explored by various working groups in Europe.

6. Conclusions

- *Arctica islandica* shell $\delta^{18}O$ is a suitable proxy for water temperature reconstructions. Average deviation of annual means from instrumental data is +0.94°C only.
- The comparison between the annual reconstructed water temperature range of the specimen from 9614 years B.P. and the modern shell indicate significant higher minimum and average annual water temperatures for the modern shell.
- Shell growth rates were exhibited in accordance to predicted environmental conditions, whereas the modern shell and the individuals from 8406 years B.P. showed significantly high growth rates, albeit the growth of the shells from the late Younger Dryas (>11100 years B.P.) found to be significantly poor.
- Spectral analyses revealed NAO-type peaks at 5.5 years for the specimens from 9614 years B.P. and from 11102 years B.P.. An additional peak at 8-9 years was found in the individual from 11102 years B.P..

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Conclusions

Modern and early Holocene specimens of *Arctica islandica* from two different sites of the North Sea were investigated in detail for biotic and geochemical proxies suitable for paleoclimatic marine environmental reconstructions.

The major conclusions of this study are:

- Specimens of *Arctica islandica* from the German Bight can reach ages up to 163 years,
- growth chronologies of modern shells from the German Bight exhibited an overall low synchronology,
- high environmental variability in time and space of the dynamic German Bight hydrography system obscured the identification of the significant shell growth controlling factor,
- the analytical methods of LA-ICP-MS and electron microprobe are both suitable to analyse Mg/Ca and Sr/Ca ratios on a high spatial/temporal resolution in the aragonitic shell of *Arctica islandica*,
- Sr/Ca ratios in the shell of *Arctica islandica* from the German Bight can be used as proxies for winter water temperature reconstructions,
- Ba/Ca ratios in the shell of *Arctica islandica* from the German Bight can be used as proxies for spring Elbe river discharge volumes,
- Mg/Ca ratios in the shell of *Arctica islandica* from the German Bight did not show a relationship with any environmental parameter,
- shell-derived $\delta^{18}O$ of *Arctica islandica* from the Fladen Ground is a suitable proxy for bottom water temperature reconstructions with a deviation of +0.94°C,
- the comparison between the annual reconstructed water temperature range of the specimen from 9614 years B.P. and the modern shell indicate significant higher minimum and average annual water temperatures for the modern shell,
- shell growth rates were exhibited in accordance to predicted environmental conditions, whereas the modern shell and the individuals from 8406 years B.P. showed significantly high growth rates, albeit the growth of the shells

from the late Younger Dryas (>11100 years B.P.) found to be significantly poor,

- spectral analyses revealed NAO-type peaks at 5.5 years for the specimens from 9614 years B.P. and from 11102 years B.P.. An additional peak at 8-9 years was found in the individual from 11102 years B.P..