A study of sclerochronology by laser ablation ICP-MS†‡

JAAS

Full Paper

Harry Toland,*[a] Bill Perkins,[a] Nick Pearce,[a] Fergus Keenan[b] and Melanie J. Leng[c]

[a]*IGES, University of Wales, Aberystwyth, Ceredigion, Wales, UK SY23 3DB*
[b]*VG Elemental, Ion Path, Road Three, Winsford, Cheshire, UK CW7 3BX*
[c]*NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham, UK NG12 5GG*

Received 13th March 2000, Accepted 9th May 2000
Published on the Web 9th June 2000

Sclerochronology is to shells what dendrochronology is to trees, *i.e.*, growth structures within some shells (in this case the bivalve mollusc *Arctica islandica* L., the Ocean Quahoc) resemble, in form and content, those growth structures in trees, which grow with an annual periodicity. By utilising laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), allied with stable isotope analysis to sample the growth structures within shells, environmental conditions (*e.g.*, ambient temperature, salinity, seasonality and productivity) prevalent at the time of shell genesis may be ascertained. A limiting factor in the retrieval of any data from biogenic carbonates such as these is the size of the repeated growth structures from which to extract information. In the case of *Arctica*, these can be as low as tens of μm. Micro-drilling techniques, such as those commonly used in isotope analyses, are constrained by the size of the drill bit used to collect the sample. LA-ICP-MS, with its ultra-high spatial resolution (10–20 μm ablation pits) and precision, delivers highly constrained analysis allowing accurate multi-element sampling of seasonal growth bands within shells. It may be feasible to use the elements strontium, magnesium and barium as records of inter-annual environmental conditions, thus removing the need to carry out stable isotope analyses in some instances, particularly where the size of the material to be sampled demands the high resolution of LA-ICP-MS.

Introduction

The rhythms of nature have been recognised and recorded for millennia. These rhythms are mirrored in the world around us. This study hopes to shed light on one of these phenomena, the recording of elemental and stable isotope signatures in the growth structures of bivalve molluscs. By interpreting these signatures correctly, it may be possible to reconstruct the environmental conditions that existed when these shells were formed.

Biogenic carbonates have been the subject of numerous studies in the past. Whether to ascertain pollutant levels (Price and Pearce;[1] Raith *et al.*;[2] Carell *et al.*;[3] Fuge *et al.*[4]), elemental signatures (Geffen *et al.*;[5] Feng;[6] Dodd and Crisp[7]), or organism age (Richardson *et al.*;[8] Jones[9]).

The marine bivalve, *Arctica islandica* L. has been studied extensively and the occurrence of annual growth increments within its shell are widely recognised (Thompson *et al.*;[10] Witbaard and Duineveld;[11] Jones and Quitmyer[12]). *Arctica* are found in temperate and boreal waters on both sides of the Atlantic and are limited by a temperature regime of 0–19 °C and a depth range from below the lowest low tide and ≈500 m (Nicol[13]). They have been reported to live for over 200 years (Ropes[14]). Within the aragonitic (one of the polymorphs of calcium carbonate, the other being calcite) shells of *Arctica*, seasonal growth is manifest in the appearance of successive light and dark layers or growth bands. The light coloured layers, which appear opaque to transmitted light, are generally laid down in periods of rapid growth from spring to early summer and are wider then the darker coloured layers, translucent to transmitted light, which are generally laid down from late summer to winter (Thomson *et al.*[15]).

Arctica is a filter feeder (Merrill *et al.*[16]) that feeds on algae (Yonge and Thompson[17]) extracted from the seawater along with minor and trace elements, which are incorporated into the $CaCO_3$ of the shells.

It is generally accepted that stable isotope composition of biogenic carbonates can serve as a proxy for ambient environmental conditions (temperature, productivity, salinity) (Krantz *et al.*;[18] Corfield[19]). In this study, sequential stable isotope analyses across growth bands in *Arctica* will be compared with levels of strontium, magnesium and barium obtained using LA-ICP-MS. The ultimate aim is to see if these elements record environmental conditions in a similar way to stable isotope data. The key to unlocking the information tied up in the shell of *Arctica* and other biogenic carbonates, is the resolution. Yearly growth bands within *Arctica* may be as small as tens of μm and as such demand ultra high resolution techniques in order to obtain meaningful data, *i.e.*, not merely an averaging of several months or indeed years of secreted material.

Materials and methods

Four live *Arctica* were collected on the 17th–22nd Feb. 1997 (labelled B1–B4) and four between 28th–14th April 1998 (B5–B8) from Borth sands near the centre of Cardigan Bay, Wales (grid. ref. SN 603 930; map available as Electronic Supplementary Information‡).

Cardigan Bay is a shallow embayment in the south-eastern Irish Sea, which receives Atlantic Ocean water from the south (Dickinson[20]). Temperature measurements collected by the Ministry of Agriculture Fisheries and Food from two stations within Cardigan Bay over a period of 12 years indicate that average yearly temperatures range from between 2 and 18 °C. The shells were collected immediately after storms; it is thought that the stormy conditions dislodged the shells from their habitat further out at sea. Living tissue was removed from the shells and the shells were washed and scrubbed thoroughly

†Presented at the 2000 Winter Conference on Plasma Spectrochemistry, Fort Lauderdale, FL, USA, January 10–15, 2000.
‡Electronic Supplementary Information available. See http://www.rsc.org/suppdata/ja/b0/b002041l

in de-ionised water to remove external contamination and dried in an oven at 45 °C for several hours to remove any trace of volatile organic matter.

The left valve of each shell was selected and filled with resin and allowed to harden. This strengthened the valves, which facilitated cutting of the valves with a diamond tipped saw. The valves were then sectioned into 10 mm slices from the umbo (a boss or protuberance; the beak like prominence which represents the oldest part of a bivalve shell) to the most distal (farthest) point on the ventral (the youngest portion of the shell) margin; crossing all growth increments, these were labelled LB1–LB8 (views of unarticulated *Arctica* shell and sawn left value of *Arctica* shell are available as Electronic Supplementary Information‡). Finally, the sections were polished with different grades of carborundum powder and cleaned in an ultrasonic bath.

Acetate peels (Kennish *et al.*[21]) were prepared from these sections and labelled accordingly. The numbers of annual growth increments were counted for each whole section. *Arctica* grows throughout its life, although growth slows down after the onset of reproduction (Witbaard and Duineveld[11]), presenting decreasing widths of growth bands from which to obtain material.

Small sections from each of the larger shells sections were chosen for analysis. These were selected to satisfy several criteria, *i.e.*, growth bands were large enough to accommodate the drill bit used to obtain material for stable isotope analyses (0.5 mm); and different segments of shell were chosen to reflect different stages within the life of *Arctica* and thus different sets of years within the last century (the shells chosen were 80–120 years old).

One section from each of the shells, LB2, LB5, LB6 and LB7, was chosen for analysis.

Analytical techniques

LA-ICP-MS

Due to the sample size required for solution ICP-MS and the nature of the annual growth increments within *Arctica* (they can vary in size from mm to tens of μm), analysis by solution ICP-MS can result in homogeneity of elemental signatures from several years. Laser Ablation ICP-MS has a spatial resolution of $\geqslant 10$ μm and is therefore the ideal tool to extract material from within the yearly growth bands.

Analysis was carried out using the VG Microprobe II laser ablation system coupled to a VG PlasmaQuad 3 ICP-MS system (VG Elemental, Ion Path, Road Three, Winsford, Cheshire, UK; recently incorporated by Thermo Jarrell Ash, Franklin, MA, USA.).

The laser used was a frequency quadrupled Nd:YAG laser operating at 266 nm. The samples were mounted in a sealed chamber within the body of the laser, which in turn was mounted on an externally controlled *xyz* stage. The firing mechanism of the laser was computer interfaced and, with the addition of NT software, "point and click" control of laser parameters and commands supported the rapid acquisition of material. Real time images of the analyses were conveyed by an in-line CCD camera; it was also possible to store images of the analyses on hard disc (see Fig. 1).

Two types of laser analyses were used: raster and single spot. As the resolution of stable isotope analyses (0.5 mm drill holes, see below) dictates the area over which direct comparisons with laser derived elemental analyses is effective, the use of raster and single spot is justified. Raster laser patterns have a tendency to homogenise the signal over the area analysed. Each of the raster patterns was centred at the base of the stable isotope drill holes and had areas of $\approx 100\ \mu m \times 50\ \mu m$. Single spot analyses were employed where raster analyses were difficult because of stable isotope analyses drill hole characteristics (shearing *etc.*). Three single spot ablations were

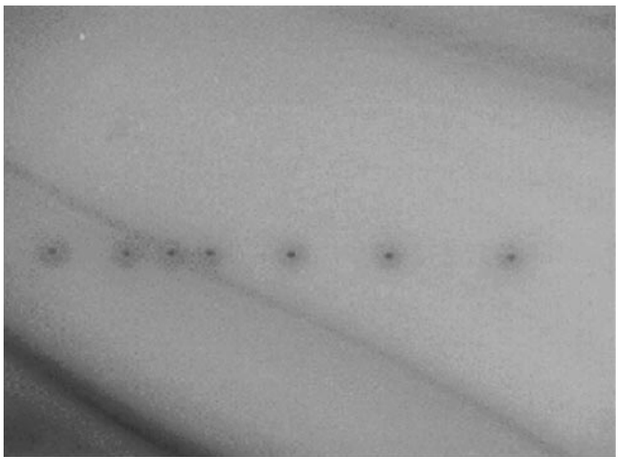

Fig. 1 Internal growth banding within the shell of *Arctica*, crossed by a trace of laser ablation pits. Ablations are ≈ 15 μm in diameter.

completed for each drill hole; each ablation pit was equidistant from the other and together sampled the same area, as would a raster pattern if this had been employed. The ablation pits had diameters ≈ 15 μm. Distance between each ablation was ≈ 50 μm. Average elemental data from all three ablation pits were used as final data. Although this method of laser ablation reduces the effective resolution of the technique, it facilitates the direct comparisons with stable isotope data from the same section of shell material. Laser power fluctuated between 1.0–1.3 mJ. Repetition rate was 10 Hz. The majority of ablations were performed at the bottom of each stable isotope analysis drill hole, however, in some cases, hole walls had sheared off and ablations were made immediately beside these holes.

The carrier gas used to transport the ejecta from the ablation chamber to the plasma of the ICP-MS was argon at a constant flow rate of $1\ l\ min^{-1}$.

The ICP-MS was optimised, using a piece of natural calcite ($CaCO_3$), to ^{88}Sr. The calibration standard was BCS CRM 393 prepared as a pressed limestone powder. Typical analytical precision based on the analysis of the standard was about $\pm 10\%$.

Data handling

Data was collected in counts per second (cps) in peak jumping mode and manipulated off line. To correct for instrument drift over the course of analyses, background gas concentration was recorded at the start and finish of each analysis run. These data were then drift corrected (see below) and the corrected data used as a means of blank subtraction. Similarly, a standard of known elemental concentration (BCS CRM 393) was analysed at the start and end of each analysis run and the results recorded and manipulated off-line. These data were also drift corrected and provided a means of quantification of the analytes of interest within the sample. To overcome differences in ablation yield, each analyte of interest was normalised to ^{44}Ca recorded coevally from the same ablation pit.

Instrument drift was corrected for by the addition of a gas drift formula such that:

$$\theta = A/(B - C)$$

where θ is the drift correction factor, A is the final gas minus the starting gas both in cps, B is the time equivalent time value of the final gas and C is the time equivalent time value of the starting gas. The time value is a decimal number substituted for the actual time of analysis. The decimal number is a value ranging from 0 (zero) to 0.99999999, representing the times from 0 : 00 : 00 (12 : 00 : 00 am) to 23 : 59 : 59 (11 : 59 : 59 pm).

The drift correction factor is then used in the gas blank formula, which corrects for instrument drift over the duration of the analyses while simultaneously removing any background

signal. This can be represented by:

$$\varepsilon = A - \{B + [\theta \times (A_1 - B_1)]\}$$

where ε is the gas-blanked analyte (in cps), A is the analyte in question prior to gas subtraction (in cps), B is the initial gas background (in cps), θ is the drift correction factor and A_1 and B_1 are the time values for A and B, respectively.

Quantitative computation of the concentration of the analyte in question is achieved with the following calculations:

$$\kappa = [\varepsilon/(A/B)]/\{C + [D \times (\varepsilon_1 - E)]\}$$

where κ is the concentration in parts per million (ppm) of the analyte within the shell, normalised to ^{44}Ca from within the same ablation pit with reference to a known standard (BCS CRM 393), ε is the gas-blanked analyte (in cps), A is the concentration of ^{44}Ca within the analyte (in cps), B is the total elemental concentration of Ca in the analyte and C is the ratio of the measured concentration of analyte within the standard normalised to ^{44}Ca within the standard to the actual concentration of analyte within the standard (in ppm). [In other words the ratio of ε of the analyte in question to ε of ^{44}C from the same ablation pit divided by the total concentration of ^{44}C within the shell (in % CaO) then all divided by the actual concentration of analyte within the standard (in ppm).] C is effectively the slope of the line between measured and actual concentration within the standard. D is the difference in slope between C_1 and C_2 such that C_1 and C_2 are initial standard concentration and final standard concentration, respectively. ε_1 is the time value for ε, while E is the time value for the first ablation of the standard.

Concentrations of analyte within the sample can now be reported quantitatively in ppm with a high degree of confidence.

Stable isotope analysis

After his prediction in 1931 that the vapour pressures of the isotopes of hydrogen should be different, Harold C. Urey working with Murphy and Brickwedde went on to confirm the existence of deuterium, the isotope of hydrogen. This led, over several intervening years, to the proposal that natural processes may fractionate the stable isotopes of oxygen recorded in the calcium carbonate of biogenic marine organisms. The extent of any fractionation is dependent on the temperature of the surrounding seawater (Urey[22]). Similar work has been undertaken for the isotopes of carbon with promising results that point to carbon isotopes as indicators of productivity within the oceans (Arthur *et al.*;[23] Krantz *et al.*[18]).

Samples were taken at intervals of 0.5–0.6 mm along the cross section between the umbo and the ventral edge (Fig. 2), using a 0.5 mm diameter drill bit. Approximately 0.2 mg of calcium carbonate was removed from each hole drilled. The powders were then transferred to the NIGL stable isotope laboratory in Keyworth, where stable isotope analysis was performed. 100 μg portions were analysed in a VG Isocarb+ Optima mass spectrometer system (VG Elemental, Ion Path, Road Three, Winsford, Cheshire, UK; recently incorporated by Thermo Jarrell Ash, Franklin, MA, USA) together with a similar sized sample of a laboratory calcite standard. Results are reported in the usual δ^{18}O and δ^{13}C notation, in per mille (‰) *versus* VPDB (Vienna Pee Dee Belemnite standard), based on calibration of the laboratory standard against NBS-19. Analytical precision (1σ), based on the laboratory standard is typically <0.07‰ for both δ^{18}O and δ^{13}C.

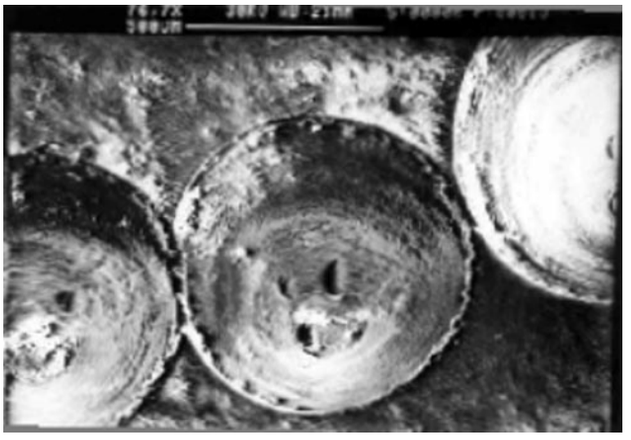

Fig. 2 SEM photograph of stable isotope drill holes with laser ablation pits at the base. Scale bar indicates that drill holes are ≈500 μm across.

Results

The analyses were taken from the periostracum (a dark organic covering on the outer surfaces of bivalves) edge of the shell section, crossing several of the annual increments (Fig. 3). This portion of the shell was chosen due to the biogenic characteristics of *Arctica*. Calcium carbonate is laid down at both the leading edge of the mantle, adding length to the shell, and within the mantle, adding thickness to the shell. This results in a layering effect, whereby a wide, prismatic-structured layer (the layer to be analysed) is sandwiched between a layer of thin cross-laminar structured, nacreous (crystals faces parallel to cleavage) aragonite ($CaCO_3$) and the dark coloured periostracum. The results are shown graphically in Figs. 4–7.

Each of the shell sections were analysed at different positions along their length. Different numbers of years were analysed for each section. Results will therefore reflect different suites of successive years of growth within Cardigan Bay. The *x*-axes in the graphs denote the number of analysis sites. Analyses increase sequentially from the older portion of the shell (the umbo region) to the younger (the ventral margin). The *y*-axes denote the elemental concentration in parts per million (ppm) and for the isotope analyses in per mille (‰) *versus* VPDB. The vertical lines within the graphs indicate the position of the start/end of successive growth increments within the shell section. Distances between the vertical lines equate to the size of any one growth increment within the shell (the equivalent of one year).

Fig. 8 records the average temperature for Cardigan Bay over the period from 1985–1997.

The values of δ^{18}O and δ^{13}C within the shells are indicative of open estuarine conditions (Aguirre *et al.*[24]) with a range of values from ≈0.5–3.5‰, for δ^{18}O and from ≈1.5–3.8‰ for δ^{13}C. These data are characterised by a series of peaks and troughs throughout, reflecting variations in temporal, spatial and ontogenetic (life-cycle history of the organism) conditions. The cycles have a sharply rising leading edge, coupled with a gradual fall towards the next lowest value. All, with the exception of LB2, exhibit a trend towards increasing values with age.

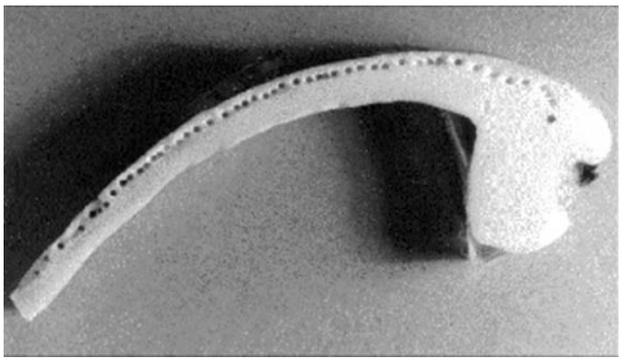

Fig. 3 Section of *Arctica* with a line of stable isotope analyses drill holes running along the upper edge of the shell, from the umbo (older part of shell) towards the ventral edge (younger part of shell). Drill holes are ≈500 μm. Section shown is ≈4 cm long.

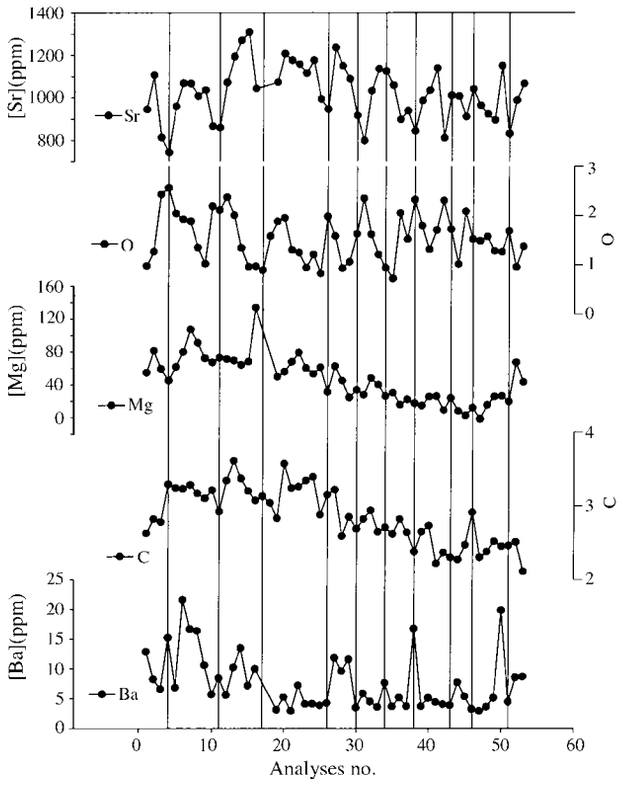

Fig. 4 Graph of Sr, Mg and Ba *versus* $\delta^{18}O$ and $\delta^{13}C$ within the shell LB2. Vertical lines represent the end of one year and beginning of the next.

The elemental signals also exhibit a cyclic variation, with sharply rising leading edges and gradually falling trailing edges. Sr concentrations range in value from ≈600–1300 ppm, Mg varies from ≈40–170 ppm and Ba has a range of ≈5–80 ppm.

Although the statistical correlation between the isotope data and trace element data is low (average about −0.4 for Sr and $\delta^{18}O$) there is a strong visual inverse relationship between $\delta^{18}O$ and Sr, for all the shells analysed, with inflection points in one mirrored in the other. It is, however, clear that the majority of peaks and troughs are not in phase with the start/end of the yearly increments. This may imply a lead–lag relationship. $\delta^{18}O$, $\delta^{13}C$ and Sr values exhibit a sinusoidal tendency with minor fluctuations superimposed onto this major trend. Mg and Ba display similar characteristics to Sr, though Ba has pronounced erratic fluctuations.

Discussion

Patterns of elements and stable isotopes within *Arctica* suggest that *Arctica* is recording changing environmental conditions throughout its life span. The data are interpreted based on the following information: 1. *Arctica* live for up to 220 years (Ropes[14]); 2. *Arctica* exhibits yearly growth structures; 3. *Arctica* has a wide Boreo-Atlantic range; and 4. *Arctica* deposits its shell in isotopic equilibrium with respect to temperature and $\delta^{18}O$ of the surrounding water.

Arctica is primarily a filter feeder. It follows that a relatively large volume of seawater passes through the organism on a daily basis. The constituents abstracted for shell formation (Ca^{2+}, Mg^{2+}, Sr^{2+}, CO_3^{2-}) are either ingested as food or formed as metabolic products of respiration. The concentrations of trace elements incorporated in the shell vary according to the conditions that exist at the time of crystallisation. These conditions will reflect the ambient sea conditions at that time.

Fig. 8 records the average monthly temperatures from two stations in Wales, one in the north the other in the south. It may be assumed that similar temperatures have prevailed within the bay over the lifetime of the samples analysed in the present study.

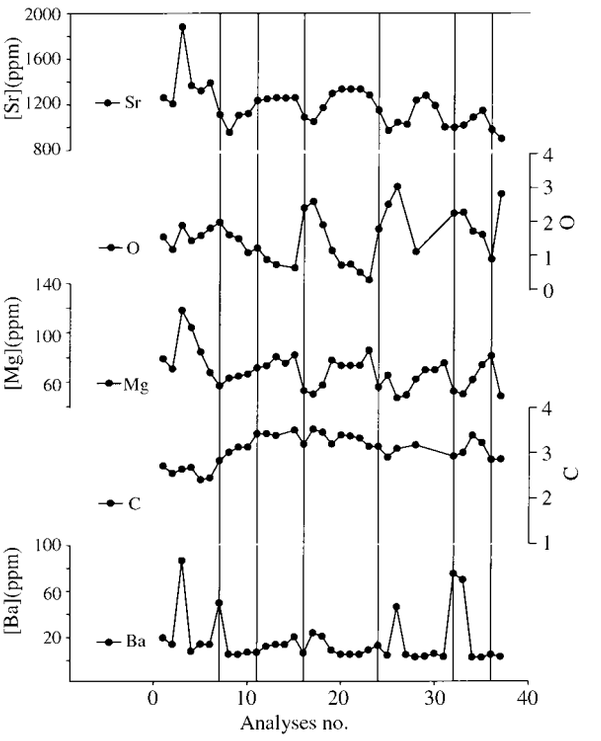

Fig. 5 Graph of Sr, Mg and Ba *versus* $\delta^{18}O$ and $\delta^{13}C$ within the shell LB5. Vertical lines represent the end of one year and beginning of the next.

In Figs. 4–7, each vertical line coincides with winter dark banding within the shell. Clearly, these winter growth lines are proximal (though somewhat out of phase) to the inflection points for each yearly cycle. The fact that we see elemental and isotopic repetition at these markers reinforces the principle that growth increments within *Arctica* are annual.

The growth increments fluctuate in size over the lifetime of the organism. This fluctuation demonstrates that growth is dependent on variables such as environmental conditions,

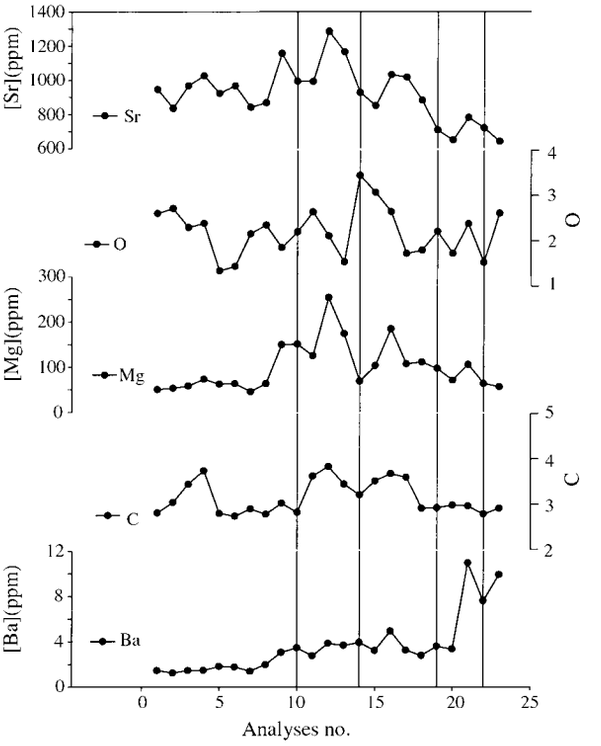

Fig. 6 Graph of Sr, Mg and Ba versus $\delta^{18}O$ and $\delta^{13}C$ within the shell LB6. Vertical lines represent the end of one year and beginning of the next.

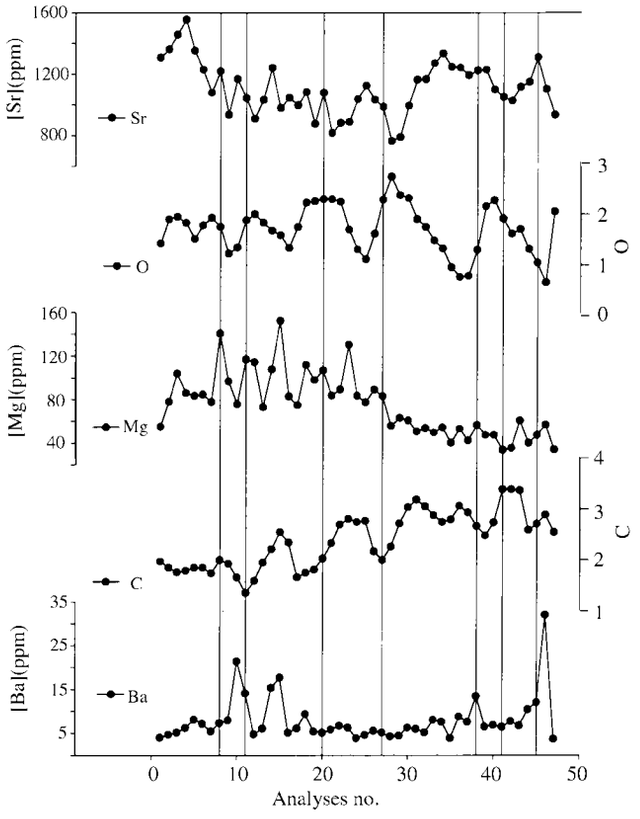

Fig. 7 Graph of Sr, Mg and Ba versus $\delta^{18}O$ and $\delta^{13}C$ within the shell LB7. Vertical lines represent the end of one year and beginning of the next.

spawning, disturbance, pollution and ontogenetic differences (Lutz *et al.*[25]), and not simply an aging effect. While it is typical for greater growth potential to be realised when the organism is in its younger stages, it is not an absolute rule and relatively larger growth increments do occur sporadically in later life, dependent on conditions (Geary *et al.*[26]). However, the commencement, duration and cessation of each cycle may be temperature dependent. Each growth increment exhibits a cyclic variation in elements and isotopes. Superimposed upon these major cycles are minor variations. The variations may be caused by influences other than temperature fluctuations, such as salinity differences, brought about by freshwater surges (Aguirre *et al.*[24]), by the cessation of food intake with the onset of spawning, or by the practice of *Arctica* of burying itself up to several cm beneath the sediment surface and assuming an anaerobic metabolism. The cycles have relatively steep angles of rise and shallow angles of fall. The isotopic signals peaks and troughs are also out of phase with the elemental signals peaks and troughs; this may be due to mismatching rates of elemental and isotopic incorporation within the aragonite, brought about by seasonally adjusted temperatures.

Figs. 4–7 show $\delta^{18}O$ values over a number of years, within sections of individual *Arctica* shells. As discussed above, $\delta^{18}O$ levels can be directly related to temperature. It has been well documented that $\delta^{18}O$ values have an inverse relationship with

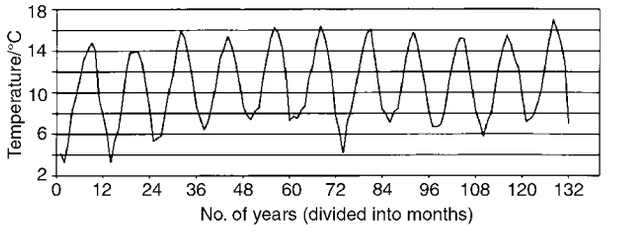

Fig. 8 Temperature in °C from two stations in Wales, Skomer in the South and Moelfre in the North, over the period 1985–1997.

temperature in biogenic carbonates. The $\delta^{18}O$ variation of $\approx 3‰$ is within the expected range for shell carbonate. Using the formula from Grossman and Ku,[27] for estimating the ambient seawater temperature from derived $\delta^{18}O$ values within aragonite, with modifications by Weidman *et al.*[28] included when calculating bottom water temperatures, a temperature scale can be applied to the $\delta^{18}O$ data:

$$T(^{\circ}C) = 20.86 - 4.69(\delta^{18}O_{sample} - \delta^{18}O_{seawater})$$

where $\delta^{18}O_{sample}$ is the $\delta^{18}O$ in the sample, $\delta^{18}O_{seawater}$ is the $\delta^{18}O$ of seawater [assumed to be 0.08‰ (Craig[29])].

It is possible to calculate the temperature of ambient seawater at the time of biogenesis by using the highest and the lowest values for $\delta^{18}O$ for each shell: LB2 temperature range = 8.48–17.11 °C; LB5 temperature range = 6.27–19.21 °C; LB6 temperature range = 4.35–14.2 °C; and LB7 temperature range = 7.68–17.43 °C.

These are estimates of highest summer temperature and lowest winter temperature for each shell between the first and last year analysed. These temperatures compare well with the measured range of sea surface temperatures for the area of study (see Fig. 8).

A similar theme of annually adjusted $\delta^{13}C$ values appears within the shells. Previous investigators have shown that the main control of $\delta^{13}C$ within the water column may be the biogenic incorporation of C by pelagic organisms at the sea surface and subsequent dissolution of the test with depth. It is therefore feasible to establish a relationship between $\delta^{13}C$ values and primary production (Arthur *et al.*;[23] Krantz *et al.*[18]). The lighter, more abundant carbon isotope ^{12}C is preferentially incorporated, at the ocean atmosphere interface, into the biogenic skeletons of diatoms and foraminifera. The relationship between $\delta^{13}C$ and primary production is characteristically inverse, with high productivity at the surface, mirrored by high dissolution rates at depths and subsequent introduction by oxidation of isotopically light carbon. This increases the ratio of ^{12}C to ^{13}C, thus decreasing $\delta^{13}C$ values. Most of the surface waters in the central ocean basin have $\delta^{13}C$ values of $\approx 2.2‰$. This figure decreases with increasing depth, due to the constant downward flux of skeletal and organic detritus and subsequent dissolution and oxidation. Bivalves may or may not have $\delta^{13}C$ in equilibrium with the ambient seawater, although it is generally thought that the $\delta^{13}C$ value of the shell may reflect that of the surrounding water. The higher $\delta^{13}C$ values typically indicate periods of reduced primary production, while lower $\delta^{13}C$ values indicate a period of increased primary production.

Figs. 4–7 show a definite cyclicity; the majority of growth increments (1 year) characterised by early to mid-year increases in $\delta^{13}C$ values perhaps reflecting annual algal blooms within Cardigan Bay, or periods of increased metabolic activity. The variation of $\delta^{13}C$ within years, while pronounced, is generally relatively small. The overall trend of $\delta^{13}C$ values is increasing upward, indicating decreasing productivity, with the exception of LB2, which decreases with age. This is surprising since most organisms have high metabolic rates as juveniles, but could be due to availability of food (more food towards the latter years), or to a change in the metabolic rate/efficiency of the individual.

Variation of strontium within biogenic carbonates has been linked to temperature, salinity, kinetic controls, metabolic controls, ontogenetic effects and calcification rate, (Rosenberg and Hughes;[30] Brand and Morrison;[31] Stecher *et al.*;[32] Klein *et al.*[33]). The present study suggests that strontium, within *Arctica*, may vary in response to seasonal changes.

The Sr profiles produced by the analysis varies cyclically by about ± 400 ppm around a mean of between 1000 and 1200 ppm for most of these shells, in the early years analysed. In most cases the magnitude of this variation falls as the organism gets older, probably indicating that either growth exerts an influence on Sr incorporation, or mantle metabolism

is biasing Sr incorporation (Stecher *et al.*[32]). In general the signal within each growth increment is characterised by a mid year maxima, with beginning and end of year minima. Ostensibly this mirrors seasonally adjusted temperatures, with relatively cold winter water warming from the spring through summer then cooling again as autumn comes and winter returns.

The association of Mg concentrations with temperature has been well established in bivalves (Brand and Morrison;[31] Klein *et al.*[34]), although there are "probable exceptions" (Clarke and Wheeler[35]), and it has been recognised that salinity, growth rate, mineralogy and temperature can also effect Mg concentrations (Zolotarev[36]).

The present study area (Cardigan Bay) has a relatively constant salinity regime and therefore should not adversely influence the constituents of any biogenic carbonates precipitated within it. Magnesium concentration within *Arctica* varies around relatively constant means of $\approx$80–100 ppm, for each sample. The fluctuations around the mean Mg value are also relatively constant. The changes in signal amplitude appear to be abrupt yet cyclical. Seasonality may be the key to understanding Mg concentrations within biogenic minerals. Individual inputs to the system may change from season to season, increasing/decreasing the concentration of Mg within the system, but the overall variation around the mean remains constant.

Barium has been shown to be an effective tracer for regions of the oceans with high primary productivity. In a previous study, correlations have been drawn between Ba and primary production in molluscs (Stecher *et al.*[32]). It has been postulated that increased Ba/Ca ratios in *Mercenaria mercenaria* represent sudden influxes of barite to the sea floor from phytoplankton blooms above (Bishop;[37] Stroobants *et al.*[38]). Applying this hypothesis to the Ba data from the present study, it seems likely that a relatively large amount of Ba was incorporated into the shell of *Arctica* within some years, while within others very little was incorporated, which may indicate a relatively large phytoplankton bloom during that time. The signal, with its sharp rises and falls, may be tracking phytoplankton production with ephemeral and short lived 'superblooms' forming irregularly, overriding usual background levels of Ba production. The majority of Ba activity within the shells seems to occur after the start and before the end of most years, corresponding to the time of year when optimum bloom conditions exist (Brasier[39]).

Conclusion

Arctica islandica, L., the Ocean Quahoc, is the oldest living example of an ancient genus, which has its roots in the Cretaceous. Because of this and the fact that *Arctica*, like many other bivalve molluscs, precipitates its shell with an annual periodicity in equilibrium with the surrounding seawater, it is an excellent chronicler of ambient environmental conditions. The advent of high spatial resolution LA-ICP-MS now makes it possible to extract elemental information from the smallest of growth increments. Elemental analysis by LA-ICP-MS when allied with the proven technique of stable isotope palaeothemometry, allows interpretation of the relationships between element concentration and temperature. The following observations were made in this study:

1. Sr exhibited an inverse relationship with $\delta^{18}O$ and therefore may prove to be a reliable indicator of ambient sea temperature; 2. Mg concentrations, although only weakly allied with $\delta^{18}O$ may prove to be a reliable indicator of ambient conditions, once the origin and degree of other environmental factors becomes better understood; 3. the results obtained for Ba concentration within the shells, suggest that this element may be applied as an effective proxy for primary production within molluscan carbonate; 4. spatial resolution is excellent while precision is kept high; and 5. sample preparation time is relatively quick, as is analysis time.

LA-ICP-MS and the apparent suitability of elemental signatures as proxies for environmental conditions warrant further study and interpretation.

References

1 G. D. Price and N. J. G. Pearce, *Marine Pollut. Bull.*, 1997, **34**, 1025.
2 A. Raith, W. T. Perkins, N. J. G. Pearce and T. E. Jeffries, *Fresenius' J. Anal. Chem.*, 1996, **355**, 789.
3 B. Carell, E. Dunca, U. Gardenfors, E. Kulakowski, U. Lindh, H. Mutvei, J. Nystrom, A. Seire, T. Slepukhina, H. Timm, T. Westermark and V. Ziuganov, *Annal Chim.*, 1995, **85**, 353.
4 R. Fuge, T. J. Palmer, N. J. G. Pearce and W. T. Perkins, *Appl. Geochem.*, 1993, 111.
5 A. J. Geffen, N. J. G. Pearce and W. T. Perkins, *Mar. Ecol. Progr. Series*, 1998, **165**, 235.
6 L. Feng, *Advances in X-ray analysis: proceedings of the annual conference on application of X-ray analysis*, 1994, **37**, 213.
7 J. R. Dodd and E. L. Crisp, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 1982, **38**, 45.
8 C. A. Richardson, S. A. Collis, K. Ekaratne, P. Dare and D. Key, *Ices J. Mar. Sci.*, 1993, **50**, 493.
9 D. S. Jones, *J. Palaeontol.*, 1981, **55**, 1076.
10 I. Thompson, D. S. Jones and D. Dreibelbis, *Mar. Biol.*, 1980, **57**, 25.
11 R. Witbaard and G. C. A. Duineveld, *Basteria*, 1990, **54**, 63.
12 D. S. Jones and I. R. Quitmyer, *Palaios*, 1996, **11**, 340.
13 D. Nicol, *J. Washington Acad. Sci.*, 1951, **41**, 102.
14 J. W. Ropes, *Nautilus*, 1985, **99**, 53.
15 I. Thompson, D. S. Jones and D. Dreibelbis, *Mar. Biol.*, 1980, **57**, 25.
16 A. S. Merrill, in *The encyclopaedia of marine resources*, ed. F. E. Firth, Van Nostrand Reinhold Co., New York, 1969, 125.
17 C. M. Yonge and T. E. Thompson, *Living marine molluscs*, Collins, London, 1976, 1–288.
18 D. E. Krantz, D. F. Williams and D. S. Jones, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 1987, **58**, 249.
19 R. M. Corfield, *Geological Society special publication*, 1995, **83**, 27.
20 R. R. Dickinson, *Aquat. Environ. Monit. Rep.*, MAFF Direct. Fisheries Research, Lowestoft, 1987, 17.
21 M. J. Kennish, R. A. Lutz and D. C. Rhoads, in *Skeletal growth of aquatic organisms*, ed. D. C. Rhoads and R. A. Lutz, 1980.
22 H. C. Urey, *J. Chem. Soc.*, 1947, **1**, 562.
23 M. A. Arthur, D. F. Williams and D. S. Jones, *Geology*, 1983, **11**, 655.
24 M. L. Aguirre, M. J. Leng and B. Spiro, *Holocene*, 1998, **8**, 613.
25 R. A. Lutz, R. Mann, J. G. Goodsell and M. Castagna, *J. Mar. Biol. Assoc. UK*, 1982, **62**, 745.
26 D. H. Geary, T. A. Brieske and B. E. Bemis, *Palaios*, 1992, **7**, 77.
27 E. L. Grossman and T. L. Ku, *Chem. Geol.*, 1986, **59**, 59.
28 C. R. Weidman and G. A. Jones, *J. Geophys. Res.*, 1994, **99**, C9, 18,305.
29 H. Craig, in *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, Spoleto, 1965, 1–24.
30 G. D. Rosenberg and W. W. Hughes, *Lethaia*, 1991, **24**, 83.
31 U. Brand and J. O. Morrison, *Geosci., Canada*, 1987, **14**, 85.
32 H. A. Stecher, D. E. Krantz, C. J. Lord and G. W. Luther, *Geochim. Cosmochim. Acta*, 1996, **60**, 3445.
33 R. T. Klein, K. C. Lohmann and C. W. Thayer, *Geol.*, 1996, **24**, 415.
34 R. T. Klein, K. C. Lohmann and C. W. Thayer, *Geochim. Cosmochim. Acta*, 1996, **60**, 4207.
35 F. W. Clarke and W. C. Wheeler, United States Geological Survey, Professional Paper, 1922, **124**, 1–62.
36 V. N. Zolotarev, *Geochem. Inter*, 1974, **11**, 347.
37 J. K. B. Bishop, *Nature*, 1988, **332**, 341.
38 N. Stroobants, F. Dehairs, L. Goeyens, N. Vanderheijden and R. van Grieken, *Mar. Chem.*, 1991, **35**, 411.
39 M. D. Brasier, *Geological Society special publication*, 1995, **83**, 113.