

# Environmental and biological controls on elemental (Mg/Ca, Sr/Ca and Mn/Ca) ratios in shells of the king scallop *Pecten maximus*

Pedro S. Freitas<sup>a,b,\*</sup>, Leon J. Clarke<sup>a</sup>, Hilary Kennedy<sup>a</sup>,  
Christopher A. Richardson<sup>a</sup>, Fátima Abrantes<sup>b</sup>

<sup>a</sup> School of Ocean Sciences, University of Wales Bangor, Menai Bridge, Isle of Anglesey, LL59 5AB, UK

<sup>b</sup> Departamento de Geologia Marinha, INETI, Apartado 7586, 2721-866 Alfragide, Portugal

Received 23 September 2005; accepted in revised form 27 July 2006

## Abstract

The relationship between potential elemental proxies (Mg/Ca, Sr/Ca and Mn/Ca ratios) and environmental factors was investigated for the bivalve *Pecten maximus* in a detailed field study undertaken in the Menai Strait, Wales, U.K. An age model constructed for each shell by comparison of measured and predicted oxygen-isotope ratios allowed comparison on a calendar time scale of shell elemental data with environmental variables, as well as estimation of shell growth rates. The seasonal variation of shell Mn/Ca ratios followed a similar pattern to one previously described for dissolved Mn<sup>2+</sup> in the Menai Strait, although further calibration work is needed to validate such a relationship. Shell Sr/Ca ratios unexpectedly were found to co-vary most significantly with calcification temperature, whilst shell Mg/Ca ratios were the next most significant control. The temporal variation in the factors that control shell Sr/Ca ratios strongly suggest the former observation most likely to be the result of a secondary influence on shell Sr/Ca ratios by kinetic effects, the latter driven by seasonal variation in shell growth rate that is in turn influenced in part by seawater temperature. *P. maximus* shell Mg/Ca ratio to calcification temperature relationships exhibit an inverse correlation during autumn to early spring (October to March–April) and a positive correlation from late spring through summer (May–June to September). No clear explanation is evident for the former trend, but the similarity of the records from the three shells analysed indicate that it is a real signal and not a spurious observation. These observations confirm that application of the Mg/Ca proxy in *P. maximus* shells remains problematic, even for seasonal or absolute temperature reconstructions. For the range of calcification temperatures of 5–19 °C, our shell Mg/Ca ratios in *P. maximus* are approximately one-fourth those in inorganic calcite, half those in the bivalve *Pinna nobilis*, twice those in the bivalve *Mytilus trossulus*, and four to five times higher than Mg/Ca ratios in planktonic and benthonic foraminifera. Our findings further support observations that Mg/Ca ratios in bivalve shell calcite are an unreliable temperature proxy, as well as substantial taxon- and species-specific variation in Mg incorporation into bivalves and other calcifying organisms, with profound implications for the application of this geochemical proxy to the bivalve fossil record.

© 2006 Elsevier Inc. All rights reserved.

## 1. Introduction

Biominerals produced by marine and terrestrial aquatic organisms have long been recognized as extremely valuable archives from which environmental variability can be

reconstructed. Calcium carbonate skeletons produced by organisms such as foraminifera, ostracodes, corals and bivalves have the potential to contain within their isotope and elemental composition signatures that reflect the environment in which the organisms calcified (e.g. Lea et al., 1989; Wefer and Berger, 1991; Delaney et al., 1993; Druffel, 1997; Lea et al., 1999; Swart and Grottoli, 2003). Such a “proxy”-based approach is especially important when and where instrumental records of oceanographic and

\* Corresponding author.

E-mail addresses: [ospe03@bangor.ac.uk](mailto:ospe03@bangor.ac.uk), [pedro.freitas@ineti.pt](mailto:pedro.freitas@ineti.pt) (P.S. Freitas).

climatic parameters are absent. An ideal marine geochemical proxy will depend on a single oceanographic parameter, and will enable a perfect reconstruction of the variation of such a parameter in the past. Often multiple parameters can influence these proxies thereby confounding their use if individual parameter resolution proves impossible. Consequently, each new potential proxy needs to be rigorously calibrated and validated and its veracity confirmed. To complete such an exercise the role of environmental, and potentially biological, factors in controlling the proxy variation must be understood. During biomineralization organisms can exert strong controls over carbonate mineral precipitation that may result in different mineral properties (e.g., shape, size, crystallinity, isotope and trace-element composition) from that expected from inorganic precipitation (e.g. Weiner and Dove, 2003). Recognition of taxon- and species-specific factors, in addition to the influence of the ambient environmental conditions of interest, therefore is paramount when interpreting proxies, e.g. element/Ca ratios, in extant and ultimately extinct organisms.

### 1.1. Bivalve shell records

Marine bivalves are important palaeoenvironmental archives due to their incremental shell deposition, with the potential for high-temporal-resolution reconstructions of environmental conditions over a wide range of temporal scales, e.g. decades and even centuries (Jones, 1983; Weidman et al., 1994). Furthermore, marine bivalves occupy widely distributed habitats in the modern-day oceans, from coastal waters to hydrothermal environments, as well as being relatively common throughout the fossil record since the Cretaceous. Compared to other biogenic carbonate archives, most geochemical proxies in bivalves have yet to fulfil their potential, because of the limited number of calibration and validation studies so far completed. Importantly, an improved understanding of whether elemental geochemical proxies are applicable to different bivalve species is required, since it is also possible that species-specific effects could be evident.

### 1.2. Bivalve shell chemistry

Use of the stable oxygen-isotope composition ( $^{18}\text{O}/^{16}\text{O}$  ratios expressed as  $\delta^{18}\text{O}$  values) of biogenic carbonate archives as a proxy for seawater temperature and salinity, and for reconstructing ice-sheet volume, is one of the most powerful tools in palaeoceanographic studies. It is a common view that the  $\delta^{18}\text{O}$  value of marine mollusc shell carbonate is deposited at, or near, isotope equilibrium with the seawater solution from which precipitation occurs and hence reflects a combination of ambient temperature and the oxygen-isotope composition of the seawater medium ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ) (e.g. Epstein et al., 1953). As a consequence, bivalve shell  $\delta^{18}\text{O}$  records have been used to reconstruct both seawater temperatures (Klein et al., 1996a; Kennedy et al.,

2001; Elliot et al., 2003) and salinity changes (e.g. Ingram et al., 1996a; Mueller-Lupp et al., 2003). Nevertheless, deviations from oxygen-isotope equilibrium have been observed in some bivalve species with calcite shells (Mitchell et al., 1994), including the bivalve studied in the present work, the king scallop *Pecten maximus* (Owen et al., 2002a). More recently, *P. maximus* collected from the field (Chauvaud et al., 2005) has been shown to precipitate its calcite shell close to oxygen-isotope equilibrium. The occurrence of oxygen-isotope equilibrium in biogenic carbonates is a fundamental prerequisite for the investigation of the veracity of proxies, such as Mg/Ca and Sr/Ca ratios, when using the carbonate  $\delta^{18}\text{O}$  values for the estimation of calcification temperatures, as has been completed herein.

During the past two decades interest has grown rapidly in the use of the elemental composition (e.g. Mg, Sr, Mn and Ba) of biogenic carbonates for palaeo-reconstructions of environmental conditions. However, recent studies have increasingly confirmed that the use of the elemental composition of marine bivalve archives as palaeo-proxies is not a simple process and those factors controlling elemental incorporation are generally much less well understood than those that govern stable-isotope ratio composition (Lorens and Bender, 1977; Klein et al., 1996a,b; Stecher et al., 1996; Purton et al., 1999; Vander Putten et al., 2000; Lazareth et al., 2003; Takesue and van Geen, 2004; Chauvaud et al., 2005; Freitas et al., 2005; Gillikin et al., 2005a; Gillikin et al., 2005b; Lorrain et al., 2005; Gillikin et al., 2006). Mg/Ca and Sr/Ca ratios in calcite and aragonite biominerals, respectively, have been used as proxies of seawater temperature (e.g. Beck et al., 1992; Klein et al., 1996a; Elderfield and Ganssen, 2000; Lear et al., 2002). The growing importance of element/Ca ratio palaeothermometry has encouraged active research into the evaluation of additional biological (i.e. metabolic and growth rate) and environmental (e.g. temperature, salinity and carbonate ion concentration) factors that may influence non-equilibrium incorporation of Mg and Sr into biogenic carbonates. Such work largely has been developed for foraminifera (e.g. Lea et al., 1999; Erez, 2003; Russell et al., 2004), corals (e.g. de Villiers et al., 1995; Cohen et al., 2001) and to a lesser extent bivalves (Lorens and Bender, 1980; Klein et al., 1996a,b; Vander Putten et al., 2000; Freitas et al., 2005; Gillikin et al., 2005b; Lorrain et al., 2005). One outcome of these studies has been the identification of taxon- and species-specific differences in the incorporation of elements into carbonate skeletons. Previously, we have demonstrated that the large fan mussel *Pinna nobilis* exhibits higher Mg/Ca ratios than other biogenic calcites (Freitas et al., 2005). Comparison of the *P. nobilis* data to published values for the mussel *Mytilus trossulus* (cf. Klein et al., 1996a) further indicated that the Mg/Ca-temperature relationship in marine bivalves was strongly species specific (Freitas et al., 2005). Together with further evidence for metabolic and ontogenetic variability (Lorens and Bender, 1977; Freitas et al., 2005), such findings have fundamental implications for the use of the Mg/Ca

ratio proxy in bivalves as a means of reconstructing temperatures.

By comparison, the general absence of a relationship between Sr/Ca ratios in bivalve calcite shells and calcification temperature, indicates that Sr/Ca ratios in the calcite of the bivalve species studied to date appear to be controlled primarily by kinetic and metabolic effects (Klein et al., 1996b; Vander Putten et al., 2000; Freitas et al., 2005), although a possible secondary salinity influence also has been suggested (Klein et al., 1996b). Lorrain et al. (2005) have recently shown Sr/Ca ratios in *P. maximus* to be controlled by shell precipitation rates. Similarly, calcification rates were shown to control the Sr/Ca ratios of abiogenic calcite (Lorenz, 1981; Morse and Bender, 1990; Tesoriero and Pankow, 1996), as well as of biogenic calcites such as coccolith (Stoll and Schrag, 2000; Rickaby et al., 2002) and foraminiferal (Lea et al., 1999) calcite. A small temperature dependence for Sr/Ca ratios observed in some biogenic calcites has been attributed to a temperature influence on calcification (Lea et al., 1999), as well as to a correlation between temperature and growth rates (Stoll et al., 2002). Even in aragonite bivalves Sr/Ca ratios are not under a clear temperature control, but also are dependent on biological processes (Gillikin et al., 2005b) and/or shell growth rates (Takesue and van Geen, 2004).

Beyond a palaeothermometry application, carbonate geochemistry has long promised, since the late 1920s, potential proxies that record seawater chemistry. The introduction of the concept of a non-thermodynamic partition coefficient (cf. Morse and Bender, 1990), is dependent on a simple consistent relationship being demonstrated between seawater and biogenic carbonate elemental compositions. For example, manganese carbonate ( $\text{MnCO}_3$ ) forms a solid solution with calcite (Pedersen and Price, 1982) and  $\text{Mn}^{2+}$  incorporation from seawater into inorganic calcite has been described to follow a first order relationship with dissolved  $\text{Mn}^{2+}$  concentration (Franklin and Morse, 1983). Mn/Ca records derived from biogenic carbonate archives thus potentially could provide a proxy for dissolved  $\text{Mn}^{2+}$  concentrations and thereby reflect those redox processes that control the concentration of this element in seawater. Little experimental work has been completed on those factors that influence Mn/Ca ratios in bivalve shells, but elevated shell Mn/Ca ratios in the bivalve *Mytilus edulis* have been suggested to be related both to seasonal changes in primary production (Vander Putten et al., 2000), and to increased riverine discharge events and associated phytoplankton blooms (Lazareth et al., 2003).

We contribute further to the development of this field by presenting geochemical data for the marine bivalve king scallop, *P. maximus*, grown in a field experiment during which measurements of contemporaneous environmental conditions also were taken. *P. maximus* is a non-sedentary bottom dweller that is found in coastal waters down to 200 m in the northeast Atlantic Ocean (Brand, 1991). It may grow to over 15 cm in length in approximately 10 years and possesses a calcite shell with foliated inner and outer

layers (Watabe, 1988) and a thin periostracum ( $<1 \mu\text{m}$ ) (Harper, 1997). In this study we have utilised the oxygen-isotope composition of field-deployed specimens of *P. maximus* (cf. Owen et al., 2002a) to investigate the potential of shell Mg/Ca ratios as a calcification temperature proxy and Sr/Ca ratios as a proxy for growth and/or shell precipitation rate. Where possible, we also assess these data with respect to other bivalve species, as well as with other major taxa, i.e. foraminifera and ostracodes. In an initial assessment of its veracity as a geochemical proxy, comparison of shell Mn/Ca ratios to seasonal changes of seawater dissolved manganese concentrations also has been made.

## 2. Methods

### 2.1. Field sampling and location

In a previous study, Owen et al. (2002a) deployed specimens of the bivalve *P. maximus* in the Menai Strait, north Wales, U.K. (Fig. 1), from the 27th September 1994 to the 25th September 1995, suspended 1 m below a moored raft. The animals were all less than 1 year old when deployed, obtained from one spat cohort and initially ranged from 1.8 to 2.1 cm in shell length. A clearly visible disturbance mark was formed in the shells when transferred from laboratory aquaria to the field and only shell material deposited after this check was analysed. For the duration of the field experiment, Owen et al. (2002a) recorded the following key seawater parameters: temperature, salinity, oxygen-isotope composition ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ) and pH, amongst others.



Fig. 1. Location of the field deployment site, Menai Strait, Wales, U.K.

## 2.2. Shell preparation and milling

Three *P. maximus* specimens that had not been used in the Owen et al. (2002a) study (labelled P21, P42 and P49) were used to derive coupled measurements of shell stable-isotope and elemental composition. The growth increment during the 1-year duration of field deployment was similar between all three specimens and to that of the specimens used by Owen et al. (2002a): 39.6 mm for P21, 39.7 mm for P42 and 42.2 mm for P49. Initially, any fouling of the shell surface was gently removed either directly or by washing and scrubbing with a soft brush. Powder samples were collected by milling the shell surface along the main axis of growth, from the deployment mark towards the shell margin. All sample distances were measured from the disturbance mark and samples were collected, at spacings ranging from 1 to 2 mm, using a 0.4 mm wide steel carbide burr (Minerva Dental Ltd.) attached to a hand-held dental drill. Accurate milling and shell measurements were completed under a binocular microscope fitted with an eyepiece graticule. Depth and width of milling were controlled carefully, with each sample taken from between the same pair of growth striae and laterally across three shell ridges (plicae). Milled powder samples then were split into separate aliquots for element and stable-isotope ratio determinations.

## 2.3. Stable-isotope and elemental ratio analysis

The analytical methodologies used in this study are exactly as described in detail in Freitas et al. (2005), since the samples in this study were measured at the same time. Stable-isotope-ratio data are reported in per mil (‰) deviations relative to VPDB and the overall analytical precision for  $\delta^{18}\text{O}$  measurements based on analyses of an internal laboratory standard run concurrently with all *P. maximus* samples is 0.05‰ (1 $\sigma$  standard deviation;  $n = 61$ ). Analysis of replicate shell samples of *P. maximus* yielded a sample precision of 0.06‰ (1 $\sigma$  standard deviation;  $n = 5$ ). Calibration for element ratio determinations was performed via an established ICP-AES intensity-ratio method (de Villiers et al., 2002), using synthetic standard solutions in the range 0–30 mmol/mol for Mg/Ca, 0–5 mmol/mol for Sr/Ca and 0–0.6 mmol/mol for Mn/Ca. Instrumental drift was monitored by running one of the intermediate calibration standards every 5–10 samples and data then were corrected accordingly. On the 3 days of analysis, analytical precision (expressed as relative standard deviation or RSD;  $n = 9$ , 9 and 6, respectively) was 0.52%, 0.86% and 1.13% for Mg/Ca (mean = 0.8%), 1.39%, 1.86% and 0.58% for Sr/Ca (mean = 1.3%) and 1.18%, 1.98% and 1.58% for Mn/Ca (mean = 1.6%). Analysis of replicate samples ( $n = 5$ ) from *P. maximus* yielded a sample precision of 3.5% for Mg/Ca, 2.0% for Sr/Ca and 7.1% for Mn/Ca, all expressed as RSD. For all samples Mn concentrations were above (2–36 times), but close to, the lower limit of detection of 0.01  $\mu\text{mol L}^{-1}$ , which likely explains the lower precision observed for the Mn/Ca ratios.

In order to assess the accuracy of our analytical procedures for Mg/Ca and Sr/Ca ratio determinations, we also analysed a set of solutions prepared by the Elderfield group at the University of Cambridge (Greaves, pers. comm., 2003; cf. de Villiers et al., 2002). The linearity of our intensity-ratio calibration lines, combined with the independent confirmation of the accuracy of our analytical procedure (Freitas et al., 2005), confirms the veracity of the *P. maximus* Mg/Ca and Sr/Ca ratios obtained in this study.

All geochemical data are reported in [electronic appendix 1](#).

## 2.4. Shell age models, shell growth rates and calcification temperatures

Chauvaud et al. (2005) demonstrated that *P. maximus* precipitate calcite close to oxygen-isotope equilibrium with seawater. Therefore, for our shell samples predicted  $\delta^{18}\text{O}_{\text{equil}}$  values (expressed relative to the VPDB standard) were calculated according to the equation of Chauvaud et al. (2005):

$$T \text{ (}^\circ\text{C)} = 14.84 - 3.75(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{H}_2\text{O}}) \quad (1)$$

using paired measurements of Menai Strait seawater temperature ( $T$ ) and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values (expressed relative to the VSMOW standard) taken every one to two weeks (cf. Owen et al., 2002a), concurrently with the field deployment of *P. maximus* (Fig. 2a).  $\delta^{18}\text{O}_{\text{equil}}$  is equivalent to  $\delta^{18}\text{O}_{\text{calcite}}$  in Eq. (1). Recent studies also have shown that aqueous carbonate-ion concentrations influence  $\delta^{18}\text{O}_{\text{equil}}$  (Kim and O'Neil, 1997; Spero et al., 1997; Bemis et al., 1998; Zeebe, 1999). For the dataset used in the present study, from field pH measurements, this effect would result in a negligible correction to  $\delta^{18}\text{O}_{\text{equil}}$  of  $0.03 \pm 0.05\text{‰}$  for the entire data set (cf. Owen et al., 2002a). Furthermore, uncertainty in the  $\delta^{18}\text{O}_{\text{equil}}$  values, derived from precisions of 0.05  $^\circ\text{C}$  for temperature measurements and 0.04‰ for  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  measurements (Owen, 1998), and using Eq. (1) is ca. 0.06‰ (1 $\sigma$ ).

Subsequently, we used the AnalySeries software package (Paillard et al., 1996), which is widely used in palaeoclimate studies for time-series and stratigraphic correlation, to assign calendar dates to each milled shell sample. The measured shell  $\delta^{18}\text{O}$  profile (Fig. 2b) from each specimen was matched to the predicted  $\delta^{18}\text{O}_{\text{equil}}$  (Fig. 2a) by comparing both absolute values and the shape of the profiles, with data plotted as days subsequent to September 27th 1994 (day 1), the day of initial shell deployment in the field (Fig. 2c). A correlation coefficient of 0.97 ( $r^2$ ) was obtained for each *P. maximus* specimen, providing a measure of the fit between the measured shell  $\delta^{18}\text{O}$  and the predicted  $\delta^{18}\text{O}_{\text{equil}}$ . The difference in the shape of the  $\delta^{18}\text{O}$  profiles in Figs. 2b and c is a result of each milled powder sample representing a time-integrated average of temperature and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  variation, with the degree of integration depending on shell growth rate and the amount of shell sampled. Consequently, we have calculated that the number of calendar days represented on average by each

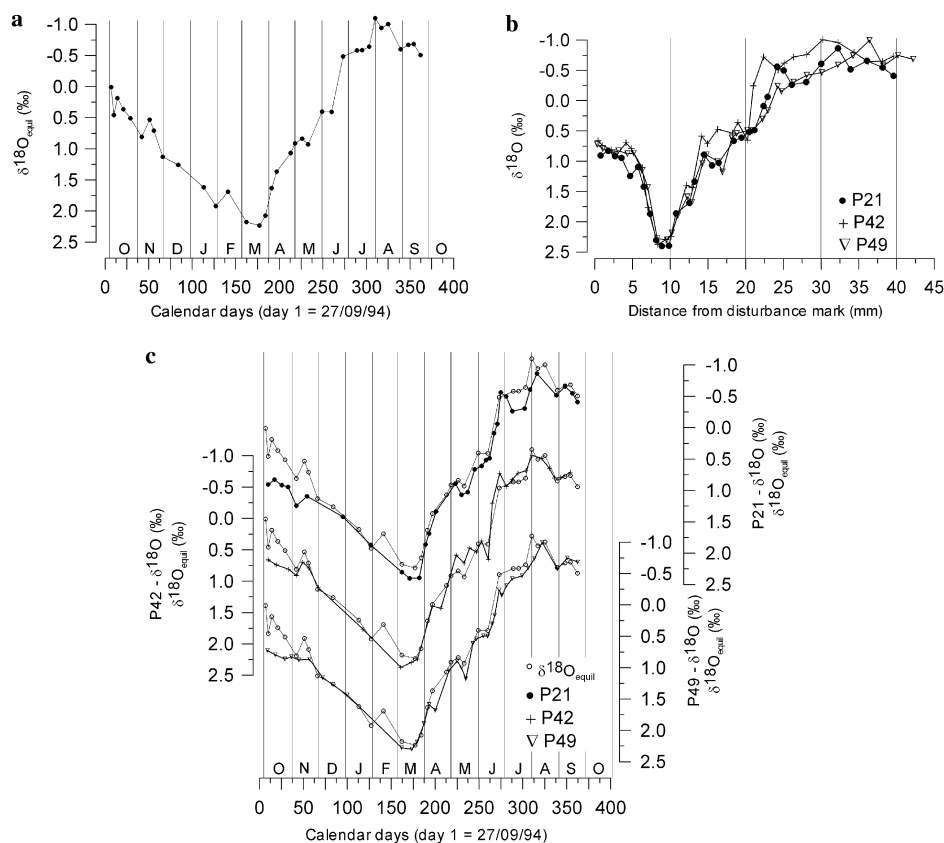


Fig. 2. (a) Predicted  $\delta^{18}\text{O}$  values for shell precipitated in isotope equilibrium (see Section 2.4 for approach used). (b) Measured *P. maximus* shell  $\delta^{18}\text{O}$  profiles from three specimens deployed in the Menai Strait. Distance is measured along the growth axis from the disturbance mark towards the shell margin. (c) Age model for each *P. maximus* shell developed by comparing the measured shell  $\delta^{18}\text{O}$  profiles with oxygen-isotope values predicted for calcite precipitated in equilibrium with seawater (open circles). Letters indicate calendar month.

milled sample varies from around 30 days from December to February–March, to between 5 and 10 days between March–April and October.

The advantages of obtaining an age model for each *P. maximus* specimen in this way are: (1) seasonal variation in the shell records can be defined; (2) Mn/Ca ratios recorded in the shell subsequently can be compared to seawater data on a calendar time scale; (3) daily shell growth rates can be estimated for each interval between two samples (assuming constant growth within each interval) by utilising distance and time differences between samples, and these growth rate estimates then compared to shell Sr/Ca ratios.

To investigate the potential of shell Mg/Ca ratios as a temperature proxy we compare Mg/Ca ratios directly to calcification temperatures determined from  $\delta^{18}\text{O}$  measurements made on the same milled shell sample. Calcification temperatures were calculated using Eq. (1) for each measured shell oxygen-isotope value and using the mean annual  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value of  $0.14 \pm 0.1\text{‰}$  ( $1\sigma$  standard deviation;  $n = 35$ ), such that errors associated with interpolation are avoided (see [electronic appendix 1](#)). The uncertainty in calcification temperatures obtained using Eq. (1) is ca.  $0.1\text{ °C}$  ( $1\sigma$ ) based on an analytical precision of  $0.04\text{‰}$  ( $1\sigma$ ) for shell  $\delta^{18}\text{O}$  values and an averaging error of  $0.1\text{‰}$  for the mean annual  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  value.

## 2.5. Statistical analysis

Two-sample *t*-tests have been used to determine statistically whether significant differences exist between the measured geochemical proxies and calculated calcification temperatures. Herein, probability levels less than 5% ( $p < 0.05$ ) are considered significantly different. Running correlations were used to discern smaller temporal scale variations in the relationship between any two parameters within shells. Correlation factors (*r*) and probability levels (*p*) thus obtained were plotted against time at the centre point of each integration window.

## 3. Results

### 3.1. Shell $\delta^{18}\text{O}$ profiles and calcification temperatures

Shell  $\delta^{18}\text{O}$  values, and hence calcification temperatures, showed a clear pattern in all three specimens (Fig. 2b). The highest shell  $\delta^{18}\text{O}$  values, corresponding to the lowest seawater temperatures that characterize the winter period, were recorded at approximately 8–10 mm from the disturbance mark in the three shells, whilst the lowest shell  $\delta^{18}\text{O}$  values, corresponding to the highest summer seawater temperatures, were recorded ca. 30–35 mm from the

deployment mark. One of the shells (P42) consistently exhibits more negative shell  $\delta^{18}\text{O}$  values and consequently higher calcification temperatures than the other two shells from 15 to 35 mm (Fig. 2b and c). Higher shell  $\delta^{18}\text{O}$  values than predicted equilibrium  $\delta^{18}\text{O}$  values were observed in the earliest half of the shell record during October–November 1994, and to a lesser extent in February–March and July 1995, normally by less than 0.2–0.3‰ although some shell samples in October 1994 are up to 0.6‰ higher (Fig. 2b). Derived calcification temperatures display similar absolute ranges in the three specimens (5.3–17.6 °C in P21, 5.4–18.1 °C in P42 and 5.7–18.1 °C in P49) and relate well to the measured seawater temperature range of 6.3–18.9 °C (cf. Owen et al., 2002a).

### 3.2. Shell growth rates

Estimated shell growth rates show a clear seasonal variation in all three specimens (Fig. 3 and electronic appendix 1), with the lowest rates (<20  $\mu\text{m}/\text{day}$ ) during winter (December–February) before generally increasing from the spring to the beginning of autumn (March–August) with a maximum growth rate of 350–400  $\mu\text{m}/\text{day}$ . These values are within the range of shell growth rates (0 to 350–400  $\mu\text{m}/\text{day}$ ) reported for *P. maximus* of similar age from non-manipulated populations (Chauvaud et al., 1998; Lorrain et al., 2000; Chauvaud et al., 2005; Lorrain et al., 2005), but higher than the ones (0 to ~250  $\mu\text{m}/\text{day}$ ) reported for *P. maximus* by Owen et al. (2002a). The fact that growth rates in our specimens are near identical to those of non-manipulated natural populations strongly supports our consideration that shell deposition in our specimens is characteristic of *P. maximus* normal growth patterns. Cessation of *P. maximus* shell growth during low winter seawater temperatures and during spring diatom or toxic dinoflagellate blooms, which leads to no shell record of environmental conditions, has been reported for *P. maximus* by several authors (Chauvaud et al., 1998; Owen, 1998; Lorrain et al., 2000; Owen et al., 2002a). *P. maximus* shells have been reported to stop growing at seawater temperatures below 9 °C (Dare and Deith, 1991), although growth at temperatures as low as 5–7 °C

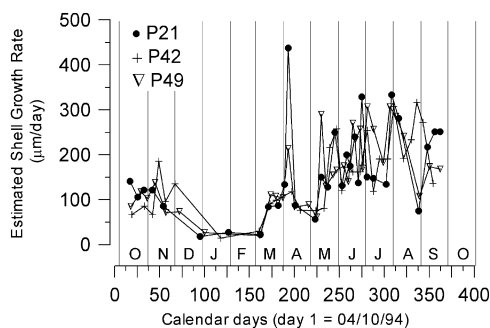


Fig. 3. Seasonal variation in shell growth rates estimated using the calendar dates derived from the  $\delta^{18}\text{O}$ -based age models and calculated assuming linear growth between adjacent samples.

(Laing, 2000; Owen et al., 2002b) also has been reported. We cannot identify any cessation in shell growth using the methodologies employed to sample our shells and to build the  $\delta^{18}\text{O}$ -based age models, but the overall similarity of profiles of measured and predicted  $\delta^{18}\text{O}$  values (Fig. 2c) suggests that our shells have recorded a seasonal cycle of ambient conditions, albeit with variable time averaging dependent on varying shell growth rates. One of the consequences of seasonally variable shell growth rates can be seen in the seasonal bias in the distribution of milled shell samples, i.e. although powder samples were collected at approximately regularly spaced intervals along the shell growth axis (Fig. 2b), when plotted on a temporal scale the density of geochemical data obviously is higher at times when shell growth rate is higher (Fig. 2c).

### 3.3. Shell Mn/Ca ratio profiles

A common pattern of shell Mn/Ca variation was observed in the three shells (Fig. 4a), with shell Mn/Ca ratios decreasing in the earlier part of the record to a minimum during the winter months (December–March), followed by an increase during spring (March–April) and broad but variable maxima that continued through the summer months. After July shell Mn/Ca ratios decrease to values similar to those in the earlier part of the record, during autumn–winter 1994. Differences between the three shells also were observed, as indicated by different winter minimum shell Mn/Ca ratios (0.014 mmol/mol in P21, 0.027 mmol/mol in P42 and 0.044 in P49) and summer maximum shell Mn/Ca ratios (0.112 mmol/mol in P21, 0.109 mmol/mol in P42 and 0.09 mmol/mol in P49). Mean Mn/Ca ratios are significantly different between P21 and the two other shells,

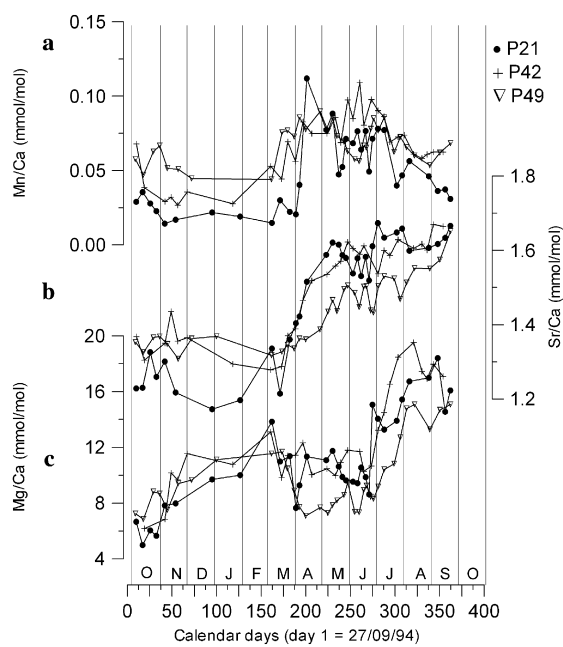


Fig. 4. Seasonal element/Ca profiles from *P. maximus* shells: (a) Mn/Ca, (b) Sr/Ca and (c) Mg/Ca ratios.

P42 and P49 ( $t$ -test,  $p = 0.003$  and  $p < 0.001$ , respectively), but not between the latter.

### 3.4. Shell Sr/Ca ratio profiles

Shell Sr/Ca ratios range from 1.2 to 1.7 mmol/mol in P21, 1.3–1.7 mmol/mol in P42 and 1.3–1.7 mmol/mol in P49 (Fig. 4b). Sr/Ca ratios in the three shells do not show a common pattern, albeit having lower values during the Autumn–Winter months (October to February), which then increase during the spring and summer months (March to September) in all three shells. There is, however, a period during which shells P21 and P42 show a similar pattern, i.e. a gradual increase in Sr/Ca ratios, from mid March until May. The Sr/Ca record of shell P49 is somewhat ‘flatter’ during the initial months, remaining relatively constant in magnitude up to March, after which values increase until the end of the record, albeit always with lower values than those observed in specimens P21 and P42. Differences at the level of individual shells were observed, with shell P21 having significantly lower mean Sr/Ca ratios than P42 and P49 in the earlier part of the record (October–March), when minimum shell Sr/Ca ratios occur ( $p < 0.005$  and  $p < 0.001$ , respectively), while shell P49 showed significantly lower mean Sr/Ca ratios than P21 and P42 from late March onwards ( $t$ -test,  $p < 0.001$  for both shells).

### 3.5. Shell Mg/Ca ratio profiles

Shell Mg/Ca ratios range from 5.0 to 18.4 mmol/mol in P21, 6.2–19.5 in P42 and 6.8–15.1 mmol/mol in P49 (Fig. 4c). The striking feature of the measured shell Mg/Ca ratio profiles, which were expected to exhibit a seasonal temperature signal, is the absence of clear intra-annual variation like that observed for shell  $\delta^{18}\text{O}$  values. Shell Mg/Ca ratios initially increase in magnitude until early in March, the time when  $\delta^{18}\text{O}$  values reach a maximum and thus calcification temperatures a minimum. Mg/Ca values subsequently show a general decrease through to April and no consistent variation of Mg/Ca ratios in the three shells was observed from April–June. Shell Mg/Ca ratios increased, in the later part of the record, from July–September in all three specimens. Although the general pattern described above for the shell Mg/Ca profiles can be observed in all three shells, differences occur in both the shape of the profile and absolute Mg/Ca values at any given time during the calendar year.

## 4. Discussion

### 4.1. Shell Mn/Ca: A tracer of seasonal variation of dissolved $\text{Mn}^{2+}$ ?

Manganese is a redox-sensitive trace metal that is more soluble in its reduced (Mn II) than oxidised (Mn IV) form, the latter precipitating as oxyhydroxides. Dissolved

manganese ( $\text{Mn}^{2+}$ ) is delivered to the oceans by riverine input and is slowly removed from solution by oxidation to Mn IV, while reducing conditions in sediments and in particular situations in the water column can recycle  $\text{Mn}^{2+}$  back into solution.

Only a few studies have been undertaken on Mn/Ca ratios in biogenic calcites, with two investigations relating Mn/Ca in bivalve shells to environmental or biological variables. In the tropical mangrove bivalve *Isognomon ehippium* shell Mn/Ca ratios exhibited increases that were suggested to be related to increased monsoonal riverine discharge and associated phytoplankton blooms (Lazareth et al., 2003). Shell Mn/Ca ratios in the bivalve *M. edulis* from a field study in the Netherlands also were shown to follow a seasonal pattern, with high values during late spring, again considered to be related to seasonal variations in primary production (Vander Putten et al., 2000). In our *P. maximus* shells Mn/Ca ratios exhibit a pronounced seasonality, with minimum values during the winter months and higher, but variable, values in spring and throughout the summer (Figs. 4a and 5a). However, the increase in our *P. maximus* Mn/Ca ratios in March 1995 precedes that year’s initial spring bloom increase in chlorophyll *a* concentrations (Owen et al., 2002a) by approximately one month (cf. Fig. 5b), suggesting that seasonal variation in primary production is not the major factor determining the seasonal variation of our *P. maximus* shell Mn/Ca ratios.

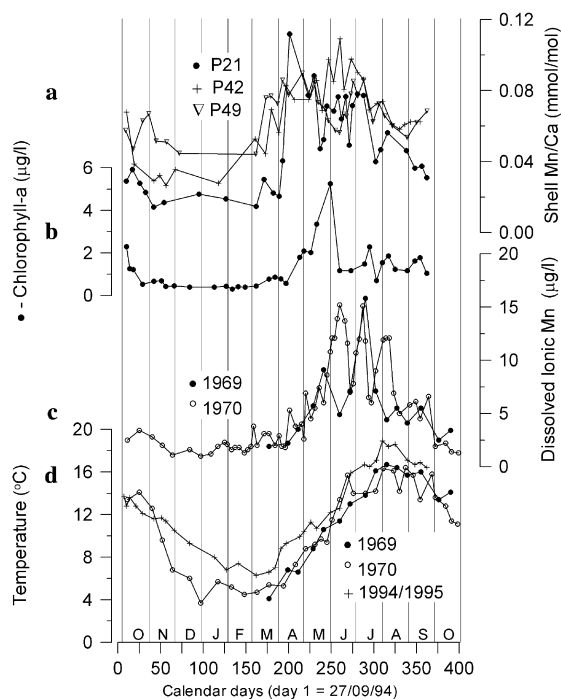


Fig. 5. (a) *Pecten maximus* shell Mn/Ca records for the years of 1994–1995. (b) Chlorophyll *a* concentration for the years 1994–1995. (c) Dissolved  $\text{Mn}^{2+}$  data for the Menai Straits for 1969–1970 (cf. Morris, 1974). (d) Seawater temperature for the years 1994–1995 and 1969–1970 (cf. Morris, 1974).

We consider that oxidation of  $\text{Mn}^{2+}$  and precipitation of  $\text{MnO}_2$  on the shell surface at times of high seawater  $\text{Mn}^{2+}$  concentrations (i.e. during spring and summer) cannot explain the shell Mn/Ca records observed. Such an oxide precipitation mechanism would affect all available shell surfaces at the moment of precipitation, thereby influencing shell Mn/Ca ratios for all previous growth, with no seasonal variation of shell Mn/Ca being recorded. Furthermore, we observed no significant correlations ( $p > 0.005$ ) between shell Mn/Ca ratios and shell growth rates or calcification temperature in any of our *P. maximus* shells, as has been described in inorganic calcite experimentally precipitated from seawater (Lorens, 1981; Mucci, 1988; Pingitore et al., 1988; Dromgoole and Walter, 1990).

Seawater dissolved or particulate Mn data does not exist for the Menai Strait during the 1994–1995 period that corresponds to the deployment of the *P. maximus* shells used in the present study. However, seasonal variation of both dissolved Mn II ( $\text{Mn}^{2+}$ ) (Morris, 1971, 1974) and particulate Mn (Morris, 1971) at the study site has been documented previously. During 1969 and 1970 (Fig. 5c)  $\text{Mn}^{2+}$  showed a pronounced seasonal variation, with low values throughout winter, before increasing during March–April until maximum values were attained during June or July, followed by a general decrease again to the minimum winter levels by November (Morris, 1974). Such large-scale seasonal variation of  $\text{Mn}^{2+}$  concentrations in the Menai Strait was not related to salinity and runoff variations, but was suggested to be closely associated to seawater temperature and redox changes in the sediments of the Menai Strait (Morris, 1974).

Seasonal variation of hydrographic conditions between 1994–1995 (this study) and 1969–1970 (Morris, 1974) were different (Fig. 5d). Seawater temperatures were generally higher during 1994–1995 relative to 1969 and 1970, and the duration of the period with the lowest winter temperatures was longer in 1969 and 1970 (Fig. 5d). The increase in our *P. maximus* shell Mn/Ca ratios in 1994–1995 and the increase in seawater  $\text{Mn}^{2+}$  concentrations in 1969 and 1970 both occurred at a time when seawater temperatures were increasing above ca. 7 °C. This temperature-change event occurred in March in our study, and in April in the Morris (1974) study (Fig. 5d). If seawater temperature influences  $\text{Mn}^{2+}$  concentrations in the Menai Strait as proposed by Morris (1974), then the temporal offset of one month between the increase in our shell Mn/Ca ratios and the previously documented increase in seawater  $\text{Mn}^{2+}$  concentrations likely derives from differences in seasonal variation of hydrographic conditions between the years 1994–1995 and 1969–1970. We suggest, therefore, that the intra-annual variation of shell Mn/Ca in *P. maximus* observed in our study shows a similar seasonal variation and most likely reflects the seasonal variation of seawater  $\text{Mn}^{2+}$  concentrations.

Bivalve shell Mn/Ca records therefore may provide a potential proxy for seawater dissolved  $\text{Mn}^{2+}$  concentrations. Future calibration work is needed in order to robust-

ly validate such a proxy and to test relationships to oceanographic parameters such as seawater temperature, phytoplankton primary production, and especially dissolved and particulate Mn concentrations. Furthermore, observed differences in the magnitude of shell Mn/Ca ratios between *P. maximus* specimens grown under the same conditions possibly suggest the presence of a biological influence, as well as ambient environmental control, on shell Mn/Ca ratios.

#### 4.2. Shell Sr/Ca ratios in *P. maximus* shells

Sr/Ca ratios in calcite minerals are not expected to exhibit a relationship with temperature since  $\text{SrCO}_3$  does not form a solid solution with calcite and is thought not to be thermodynamically controlled (Speer, 1983). A temperature dependence of Sr/Ca ratios has, however, been observed in foraminifera, albeit attributed to a kinetic influence (Lea et al., 1999). A large body of work exists describing potential controls on the Sr/Ca in inorganic calcite. It has been observed that Sr/Ca ratios increase with precipitation rate (Lorens, 1981; Mucci and Morse, 1983; Morse and Bender, 1990; Tesoriero and Pankow, 1996), with the Sr/Ca ratio of the solution from which precipitation occurs (Mucci and Morse, 1983; Pingitore and Eastman, 1986; Carpenter and Lohmann, 1992) and with increasing Mg concentration of the solution and solid mineral phases, since higher Mg concentrations increase mineral solubility and the incorporation of other elements by distorting the mineral lattice (Mucci and Morse, 1983; Ohde and Kitano, 1984; Morse and Bender, 1990; Carpenter and Lohmann, 1992). Mineral precipitation rates also currently are seen as a major control of biogenic Sr/Ca ratios in foraminifera (Lea et al., 1999), coccoliths (Stoll and Schrag, 2000; Rickaby et al., 2002) and bivalves, e.g. *Mytilus edulis* (Vander Putten et al., 2000) and *Pecten maximus* (Lorrain et al., 2005). Furthermore, in seawater, usually minor controls on Sr/Ca in bivalve shells have been shown to be due to variation in solution Sr/Ca (Lorens and Bender, 1980) and metabolic and/or salinity control (Klein et al., 1996b). A weak influence of salinity on Sr/Ca ratios also was observed in foraminiferal calcite (Lea et al., 1999). Even in bivalve aragonite, where a temperature control would be expected on Sr incorporation, strong biological and kinetic effects have been suggested to control Sr/Ca ratios (Lorens and Bender, 1980; Stecher et al., 1996; Purton et al., 1999; Takesue and van Geen, 2004; Gillikin et al., 2005b).

The strong control of precipitation rate on Sr/Ca led Lorrain et al. (2005) to estimate the total amount of shell precipitated, as an advance on using a linear measure of shell growth along the main growth axis, and showed that Sr/Ca ratios in *P. maximus* shells are better explained by the former rather than by the latter parameter. The total amount of shell calcite precipitated can be expressed by two parameters derived from strong morphometric relationships with shell height, one parameter being shell



weight (Daily Weight Increment) and the other shell surface area (Daily Surface Area Increment or DSAI) (Lorrain et al., 2005). The relationships described by Lorrain et al. (2005) may not be appropriate for all populations of *P. maximus*, since morphometric relationships likely vary from one population to another and we cannot assess such variation in our population. Indeed, shell weight estimated from shell height using the equation of Lorrain et al. (2005) overestimates the weights of our scallop specimens, most likely reflecting differences in shell thickness between the two scallop populations. By comparison, shell surface areas estimated from shell height (P21 = 31.4 cm<sup>2</sup>, P42 = 37.2 cm<sup>2</sup> and P49 = 38.4 cm<sup>2</sup>) are similar, albeit larger, to the shell surface area measured using digital imaging methods for our three specimens (P21 = 30.7 cm<sup>2</sup>, P42 = 36.5 cm<sup>2</sup> and P49 = 38.1 cm<sup>2</sup>,  $1\sigma = 0.5$ ) and so we have assumed that the equation of Lorrain et al. (2005) is applicable to our scallop specimens and have used it to estimate shell surface area ( $S = 0.802 \times H^{2.045}$ , with  $S$  in cm<sup>2</sup> and  $H$  in cm) and subsequently the amount of shell deposited, i.e. DSAI, for comparison to shell Sr/Ca ratios (see [electronic appendix 1](#)).

In our *P. maximus* shell Sr/Ca ratios are significantly correlated to calcification temperature, shell Mg/Ca ratios, shell growth rate (SGR) and DSAI, but not to salinity (Table 1). In contrast to the observations of Lorrain et al. (2005), calcification temperature and Mg/Ca appear to be the main factors controlling our shell Sr/Ca ratios ( $r^2 = 0.64$ ) and the addition of DSAI only accounts for an additional 1.5% of the data scatter for our specimens ( $r^2 = 0.65$ ) (Table 1). Lorrain et al. (2005) report *P. maximus* shell Mg/Ca ratios between 5 and 15 mmol/mol, while we observed shell Mg/Ca ratios as high as 19.5 mmol/mol, especially in the later part of the shell records after May–

June (Fig. 4c). It is possible, therefore, that the higher Mg/Ca ratios in our *P. maximus* specimens may impart a stronger control on shell Sr/Ca ratios in our specimens. A lower influence on shell Sr/Ca ratios by precipitation rate in our *P. maximus* specimens is suggested by weaker correlations of shell Sr/Ca to both SGR ( $r^2 = 0.29$ ,  $p < 0.001$ ) and DSAI ( $r^2 = 0.45$ ,  $p < 0.001$ ), compared to those of Lorrain et al. (2005) ( $r^2 = 0.52$  and  $r^2 = 0.74$ , respectively). Nevertheless, our data does confirm the observation of Lorrain et al. (2005) that shell Sr/Ca ratios are better explained by the amount of shell calcite deposited, i.e. DSAI, rather than by shell growth rates. We cannot discount, however, the possibility that any error associated with our using a morphometric relationship from a different scallop population, or the fact that daily growth rates were estimated from the  $\delta^{18}\text{O}$ -based age model assuming constant linear growth between consecutive samples, may explain the reduced significance of DSAI as a variable controlling shell Sr/Ca ratios observed in the present study.

An 11-point running correlation between Sr/Ca and Mg/Ca, calcification temperature, shell growth rate and DSAI further shows the existence of a temporal variation in the inter-relationships that control shell Sr/Ca ratios (Fig. 6). Calcification temperature, as well as SGR and DSAI, appear to control Sr/Ca ratios mainly in April and May (Fig. 6a–c), a period representing the spring marked increase of calcification temperatures and shell growth rates. This observation strongly suggest the co-variation of shell Sr/Ca with calcification temperature observed in our shells most likely is the result of a secondary influence on shell Sr/Ca ratios by kinetic effects, the latter driven by seasonal variation in shell carbonate precipitation that is in turn influenced in part by seawater temperature. On the other hand, Mg/Ca ratios appear to

Table 1

Regression statistics for linear relationships between *P. maximus* shell Sr/Ca ratios and possible dependent variables (following the format of Lorrain et al., 2005)

Variables		$r^2$	Overall $p$ -value	Additional variable $p$ -value
<i>Simple regression with Sr/Ca</i>				
Temperature		0.55	<0.001	
Mg/Ca		0.41	<0.001	
DSAI		0.45	<0.001	
SGR		0.29	<0.001	
Salinity		<0.01	0.742	
<i>Multiple regression with Sr/Ca</i>				
Variable 1	Variable 2			2nd
Temperature	Mg/Ca	0.64	<0.001	<0.001
	DSAI	0.59	<0.001	0.004
	SGR	0.58	<0.001	0.075
Variable 1	Variable 2	Variable 3		3rd
Temperature	Mg/Ca	DSAI	0.65	<0.001
		SGR	0.65	<0.001

Multiple regressions were completed using variables with the strongest correlation to Sr/Ca ratios as fixed variables 1 and 2.

$r^2$ , Correlation coefficient; Mg/Ca (mmol/mol); Calcification temperature (°C); DSAI, daily surface area increment (mm<sup>2</sup>/day); SGR, shell growth rate (µm/day).

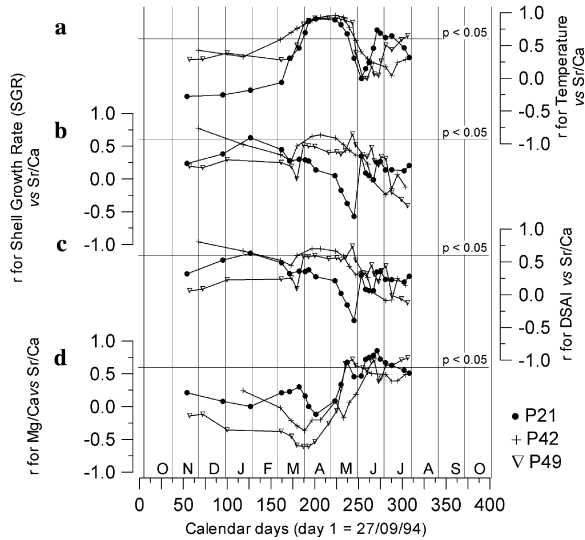


Fig. 6. An 11-point running correlation between Sr/Ca and: (a) calcification temperature, (b) shell growth rates (SGR), (c) daily surface area increment (DSAI), and (d) Mg/Ca ratios. Horizontal line defines  $p < 0.05$ .

be the dominant control on Sr/Ca ratios later in the shell records, from May to the end of the experimental period. These latter observations indicate that several factors influence shell Sr/Ca ratios through time, with calcification temperature and Mg/Ca being the main controls in these shells.

#### 4.3. *Pecten maximus* shell Mg/Ca relationship to calcification temperature

The incorporation of Mg into inorganic calcite experimentally precipitated from seawater exhibits a strong temperature dependence (Chilingar, 1962; Katz, 1973; Burton and Walter, 1987; Mucci, 1987; Oomori et al., 1987). Such temperature dependence also has been described in detail for biogenic calcites, in foraminifera (Nurnberg, 1995; Nurnberg et al., 1996a; Rosenthal et al., 1997; Lea et al., 1999; Elderfield and Ganssen, 2000), in ostracodes (Dwyer et al., 1995; Corregge and Deckker, 1997) and in coccoliths (Stoll et al., 2001). As a result, biogenic calcite Mg/Ca ratios are increasingly being used for temperature reconstructions. Several studies have shown, however, that factors other than temperature can influence the Mg content of both abiogenic and biogenic calcites. Solution Mg/Ca ratio is thought to exert a strong control on inorganic calcite Mg/Ca ratios (Berner, 1975; Mucci and Morse, 1983). In foraminiferal calcite, pH (Lea et al., 1999; Russell et al., 2004) and salinity (Nurnberg et al., 1996a,b; Lea et al., 1999) have been shown to exert small, but significant, influences on Mg/Ca ratios, the latter decreasing with an increase in pH and increasing with an increase in salinity.

In marine bivalves an unambiguous dependence of Mg/Ca ratios on temperature remains unproven. A temperature dependence of Mg/Ca ratios in bivalve calcite previously has been described for the mussel *M. trossulus* (Klein et al., 1996a), whereas the absence of a significant

correlation between Mg/Ca and calcification temperature was observed recently for the scallop *P. maximus* (Lorrain et al., 2005). Metabolic control on calcite Mg content has been proposed in a close relative of *M. trossulus*, the blue mussel *M. edulis* (Lorens and Bender, 1977), which may explain the observed breakdown in the relationship between Mg/Ca and temperature reported for the latter species (Vander Putten et al., 2000), as well as an apparent ontogenetic control of Mg/Ca ratios described in the fan mussel *Pinna nobilis* (Freitas et al., 2005).

The *P. maximus* specimens investigated in this study do not show a clear seasonal pattern in Mg/Ca ratios. Nevertheless, we observed a significant, albeit weak, correlation ( $r^2 = 0.30$ ,  $p < 0.001$ ), between Mg/Ca ratios and calcification temperature in our *P. maximus* shells. All three shells showed an increase in Mg/Ca ratios from October 1994 until March 1995 (Fig. 4c), during which time oxygen-isotope ratios increased (Fig. 2c) and seawater temperatures decreased (Fig. 5d). Interestingly, shell Mg/Ca ratios during October 1994 were significantly lower ( $t$ -test,  $p < 0.001$ ,  $DF = 23$ ) than during late May–early June 1995 (Fig. 4c), whilst seawater temperatures were similar ( $t$ -test,  $p = 0.580$ ,  $DF = 25$ ) (Fig. 2c). Considering the expected positive relationship between calcification temperature and shell Mg/Ca ratios an 11-point running correlation was applied in order to determine at what time of year, if any, such a relationship occurred (Fig. 7). As a result of this exercise, the relationship between *P. maximus* shell Mg/Ca ratios and calcification temperatures can be divided into two segments: an inverse correlation from October to March–April and a positive correlation from May–June to September. We have no explanation for the significant inverse correlation observed between Mg/Ca ratios and calcification temperature in the early part of the shell records (Fig. 7), although based on the similarity of the shell records from the three *P. maximus* shells analysed we do believe that the documented increase in shell Mg/Ca ratios during winter to be a real geochemical signal and not a spurious observation.

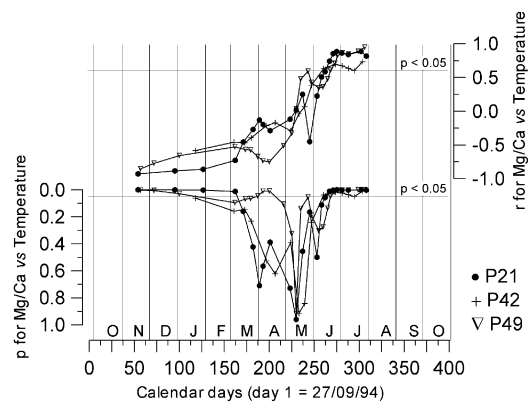


Fig. 7. An 11-point running correlation between *P. maximus* shell Mg/Ca ratios and calcification temperatures, applied to determine the temporal variation in the significance of the Mg/Ca–calcification temperature relationship. Horizontal line defines the point from which  $p < 0.05$ .

Of the factors besides temperature thought to control Mg/Ca ratios in biogenic calcite, it is not clear which could explain the high Mg/Ca ratios in the early part of our *P. maximus* shell records. The influence of metabolic activity on bivalve element/Ca ratios remains unclear. The models proposed for a metabolic control of Mg/Ca (Lorens and Bender, 1977) and Sr/Ca ratios in bivalve calcite (Klein et al., 1996b) and aragonite (Gillikin et al., 2005b) are based on the preferential transport of Ca and/or an exclusion of Mg or Sr from the precipitating solution, which in bivalves is the extra-pallial fluid (EPF). In these models lower Mg/Ca ratios are assumed to occur at times of higher metabolic activity, but such models cannot explain higher Mg/Ca ratios during lower metabolic activity since the effect is evident only at elevated metabolic rates. In foraminifera, pH has been described as a secondary factor controlling Mg/Ca ratios, responsible for a ~6% decrease of Mg/Ca per 0.1 pH unit increase (Lea et al., 1999), although the effect of the EPF pH on Mg/Ca ratios of bivalve calcite still is unknown. Bivalve EPF pH and chemical composition is thought to be under a tight metabolic control that is closely associated with shell deposition (Wada and Fujinuki, 1974). EPF pH has been found to range between 7.4 and 8.3 depending on bivalve species and the extent of valve opening, increasing with open valves (Crenshaw, 1972). It is, however, unrealistic to expect a sustained period of low EPF pH, since such a value would imply long periods of closed valves, at times of low temperatures and reduced metabolic activity and shell growth, in order to explain the high Mg/Ca ratios in the early part of the shell records. Salinity showed no clear seasonal pattern in the Menai Strait over the period of the experiment (Owen, 1998), with non-periodic variations of low magnitude (32.3–33.9), and was closely correlated with  $\delta^{18}\text{O}_{\text{water}}$  (Owen et al., 2002a). The ~4% increase in Mg/Ca ratios per salinity unit increase observed for foraminifera (Lea et al., 1999), if valid in bivalves, cannot explain the winter change in our Mg/Ca shell records of up to an 100% increase compared to October–November values. Shell Mg/Ca ratios were, however, significantly, albeit weakly, correlated with salinity ( $r = 0.364$ ,  $p < 0.001$ ) suggesting a weak influence of salinity on shell Mg/Ca ratios, most likely from variations in seawater absolute concentrations of  $\text{Mg}^{2+}$  (Zhong and Mucci, 1989), which varied by up to 5%.

Our recognition of the absence of a consistent positive relationship between *P. maximus* shell Mg/Ca ratios and measured  $\delta^{18}\text{O}$  values, and hence also calcification temperatures, an observation also reported previously by Lorrain et al. (2005), indicates that this geochemical proxy cannot be applied to *P. maximus*, and potentially other bivalve species, for the determination of absolute and even seasonal temperature changes.

#### 4.4. Variation of Mg/Ca composition in bivalve shell calcite

Partition coefficients ( $D_x$ ) are a means of quantifying the partition of an element between solution and solid phases,

i.e. for magnesium:  $D_{\text{Mg}} = \text{Mg/Ca}_{\text{calcite}}/\text{Mg/Ca}_{\text{seawater}}$ . Some of the reported values for  $D_{\text{Mg}}$  of inorganic calcite precipitated from seawater under chemical equilibrium at 25 °C and 1 atm are as follows: 0.0123 (Mucci and Morse, 1983); 0.0172 (Mucci, 1987); and 0.019 (Oomori et al.). Oomori et al. (1987) provide one of the best and most extensive datasets with a good temperature control and as such we prefer to use their values in our study. It has long been recognized that biogenic calcites usually contain lower Mg than those minerals precipitated inorganically, although bivalves exhibit higher  $D_{\text{Mg}}$  than both benthonic and planktonic foraminifera (Fig. 8 and Freitas et al., 2005).

Assuming a modern seawater Mg/Ca molar ratio of 5.13 (Morse and Bender, 1990), the range of partition coefficients we determine for the *P. maximus* shells investigated herein, across the range of calcification temperatures in

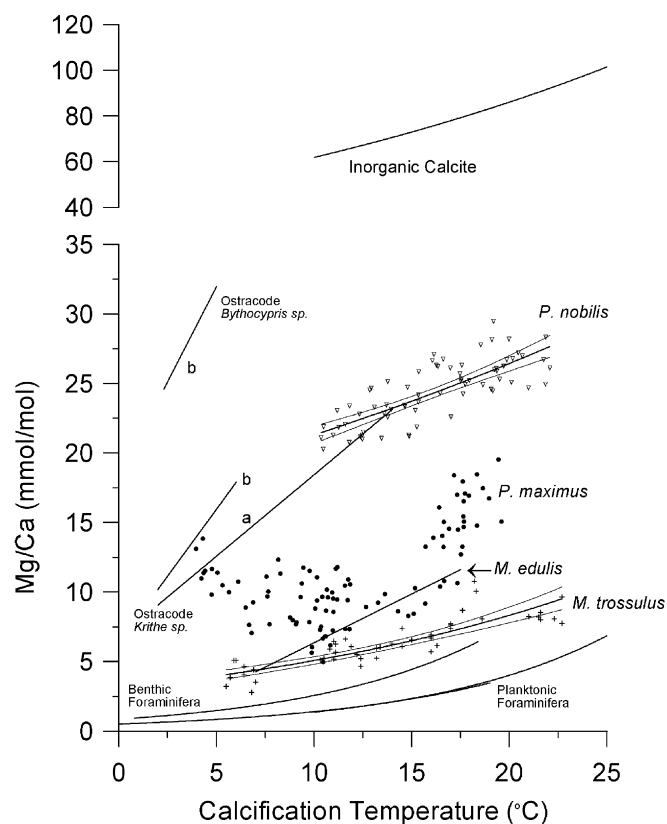


Fig. 8. Comparison of derived Mg/Ca to calcification temperature relationships in biogenic calcite in the bivalves *P. maximus*, *P. nobilis*, *M. trossulus* and *M. edulis*, as well as planktonic and benthonic foraminifera, ostracodes and inorganic equilibrium calcite. The 95% confidence intervals to the curve fits are shown for two of the bivalve data sets. An exponential calibration was applied to the *M. trossulus* data from Klein et al. (1996a,b) although a linear fit originally was used by the authors. *P. maximus* (this study); *P. nobilis* (Freitas et al., 2005); *M. trossulus* (Klein et al., 1996a); *M. edulis* (Mg/Ca data from laser ablation ICP-MS, Vander Putten et al., 2000); planktonic foraminifera, mixed species (grey curve) (Elderfield and Ganssen, 2000) and for *G. bulloides* (black curve) (Mashiotta et al., 1999); benthonic foraminifera, *Cibicides* spp. (Lear et al., 2002); Ostracodes (a, Dwyer et al., 1995; b, Corregge and Deckker, 1997); inorganic precipitation (Oomori et al., 1987).

our study (5–19 °C), is between 0.0010 and 0.0038. Comparison of  $D_{\text{Mg}}$  values for *P. maximus* shells to those of inorganic and other biogenic calcites results in several important observations and conclusions: (1)  $D_{\text{Mg}}$  values for *P. maximus* shells are lower than reported values for inorganic calcite, a similar observation to other biogenic calcites; (2)  $D_{\text{Mg}}$  values for *P. maximus* shells are higher than the ones reported for planktonic and benthonic foraminifera calcite, like those published for two other bivalve species; (3)  $D_{\text{Mg}}$  values for *P. maximus* shells are intermediate to those for other bivalves, i.e. higher than those in *M. trossulus* ( $0.0005 < D_{\text{Mg}} < 0.0021$ , Klein et al., 1996a) and *M. edulis* ( $0.0008 < D_{\text{Mg}} < 0.0023$ , Vander Putten et al., 2000), but lower than ones in *P. nobilis* ( $0.004 < D_{\text{Mg}} < 0.006$ , Freitas et al., 2005).

Clearly, there is significant taxonomic, and even bivalve species-specific, variability of Mg incorporation into biogenic carbonate archives. Shell Mg/Ca ratios in four bivalve species, thus far investigated, vary by up to a factor of four for the same range of temperatures. Bivalve shell deposition occurs from the EPF present in the extra-pallial space (EPS), an enclosed environment situated between the mantle, a thin organ that completely encloses the other soft-parts of the animal and the inner shell surface (e.g., Wilbur and Saleuddin, 1983). Ions in the EPF are derived both from the external seawater medium and the animal tissues (e.g. Nair and Robinson, 1998), reaching the EPF after diffusion or active transport across the mantle epithelium or diffusion through the periostracum (Crenshaw, 1980; Wilbur and Saleuddin, 1983; Wheeler, 1992), the latter a thin layer of organic material, mainly sclerotized protein, that acts as the initial substratum for shell deposition and seals the extra-pallial space isolating it from the external environment (Watabe, 1988). Since solution Mg/Ca is thought to exert a strong control on inorganic calcite Mg content (Berner, 1975; Mucci and Morse, 1983), control of the chemical composition of the EPF most likely is a fundamental factor in determining Mg/Ca ratios in bivalve shell calcite. The factors that control the chemical composition of the EPF include the thickness of the periostracum and the organism's metabolic activity, both of which differ between species.

Our work demonstrates that even within one taxon, i.e. marine bivalves, species-specific differences in the partitioning of Mg into calcite do occur. In *P. Maximus* shells temperature exerts only a weak control on shell calcite Mg/Ca ratios and other factors must have a significant role in the incorporation of Mg into the shell calcite of this organism. The question remains if robust palaeo-temperature reconstructions can ever be made systematically using the Mg/Ca geochemical proxy in bivalve shell carbonates. Therefore, an assessment of the influence of bivalve physiology and calcification mechanisms is required in order to understand the large variability of Mg/Ca ratios in bivalve calcite.

## 5. Summary

We present new shell element/Ca ratio data for a 1-year field deployment of the king scallop *P. maximus*, in which we have used the stable oxygen-isotope record as a template on which to base our interpretations of seasonal elemental ratio records. The intra-annual variation of shell Mn/Ca in *P. maximus* shells showed a similar seasonal variation to, and may reflect the intra-annual variation of, seawater dissolved  $\text{Mn}^{2+}$ . Future calibration work is, however, required to robustly validate shell Mn/Ca as a potential proxy for seawater dissolved manganese concentrations, as well as to determine the extent of any biological controls on shell Mn/Ca ratios. Shell Sr/Ca ratios have been shown to be controlled mainly by calcification temperature and shell Mg content in this study, whereas Lorrain et al. (2005) found that precipitation rate was the main control of Sr/Ca ratios in *P. maximus*. Shell Mg/Ca ratios in our *P. maximus* specimens have been found to be only weakly correlated to temperature, and most likely were controlled by other as yet unidentified factors. Our findings further support significant taxon- and species-specific differences in the controls of Mg/Ca ratios of calcifying organisms and marine bivalves in particular. Shell Mg/Ca ratios in different bivalve species are found to vary by up to a factor of four for the same range of calcification temperatures. As a consequence of these observations, our results further indicate that Mg/Ca ratios in bivalve calcite are an unreliable temperature proxy, with profound implications for the application of this geochemical proxy to the bivalve fossil record.

## Acknowledgments

The authors thank Paul Kennedy at the School of Ocean Sciences for his help and technical support for stable-isotope-ratio analyses and Richard Owen for supplying the scallop shells. Access to the U.K. Natural Environment Research Council ICP-AES Facility at Royal Holloway University of London, award No. ICP/196/1201, as well as the technical assistance of Sarah James and Jacqui Duffet, is acknowledged gratefully. This research was partially funded by Fundação para a Ciência e Tecnologia (FCT), Portugal, through a scholarship to Pedro Freitas, Contract No. SFRH/BD/10370/2002. We thank Andrew Johnson, two anonymous reviewers and the associate editor David Lea, for their comments that substantially improved an earlier version of this manuscript.

Associate editor: David W. Lea

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2006.07.029.

## References

- Beck, J., Edwards, R., Ito, E., Taylor, F., Recy, J., Rougerie, F., Joannot, P., Henin, C., 1992. Sea surface temperature from skeletal Sr/Ca ratios. *Science* **257**, 644–647.
- Bemis, B., Spero, H., Bijma, J., Lea, D., 1998. Reevaluation of the isotopic composition of planktonic foraminifera: experimental results and revised paleotemperature equations. *Paleoceanography* **13** (2), 150–160.
- Berner, R., 1975. The role of magnesium on the crystal growth of calcite and aragonite in seawater. *Geochim. Cosmochim. Acta* **39**, 489–504.
- Brand, A., 1991. Scallop ecology: distributions and behaviour. In: Shumway, S. (Ed.), *Scallops: Biology, Ecology and Aquaculture*. Elsevier, Amsterdam, pp. 517–584.
- Burton, E., Walter, L., 1987. Relative precipitation rates of aragonite and Mg calcite from seawater: temperature or carbonate ion control? *Geology* **15**, 111–114.
- Carpenter, S., Lohmann, K., 1992. Sr/Mg ratios of modern marine calcite: empirical indicators of ocean chemistry and precipitation rate. *Geochim. Cosmochim. Acta* **56**, 1837–1849.
- Chauvaud, L., Lorrain, A., Dunbar, R., Paulet, Y.M., Thouzeau, G., Jean, F., Guarini, J., Mucciarone, D., 2005. Shell of the Great Scallop *Pecten maximus* as a high-frequency archive of paleoenvironmental changes. *Geochem. Geophys. Geosyst.* **6** (8).
- Chauvaud, L., Thouzeau, G., Paulet, Y.M., 1998. Effects of environmental factors on the daily growth rate of *Pecten maximus* juveniles in the Bay of Brest, (France). *J. Exp. Mar. Biol. Ecol.* **227**, 83–111.
- Chilingar, G.V., 1962. Dependence on temperature of Ca/Mg ratio of skeletal structures of organisms and direct chemical precipitates out of seawater. *Bull. South. Calif. Acad. Sci.* **61** (1), 45–61.
- Cohen, A., Layne, G., Hart, S., Lobel, P., 2001. Kinetic control of skeletal Sr/Ca in a symbiotic coral: Implications for the paleotemperature proxy. *Paleoceanography* **16** (1), 20–26.
- Correge, T., Deckker, P., 1997. Faunal and geochemical evidence for changes in intermediate water temperature and salinity in the western Coral Sea (northeast Australia) during the Late Quaternary. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **313**, 183–205.
- Crenshaw, M., 1972. The inorganic composition of molluscan extrapallial fluid. *Biol. Bull.* **143**, 505–512.
- Crenshaw, M., 1980. Mechanisms of shell formation and dissolution. In: Rhoads, D., Lutz, R. (Eds.), *Skeletal Growth of Aquatic Organisms*. Plenum Press, pp. 115–132.
- Dare, P., Deith, M., 1991. Problems with reconstructing sea-water temperature records from oxygen stable isotopic profiles in shells of the Scallop *Pecten maximus*. *8th International Pectinid Workshop*.
- de Villiers, S., Greaves, M., Elderfield, H., 2002. An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES. *Geochem. Geophys. Geosyst.* **3**. doi:10.1029/2001GC000169.
- de Villiers, S., Nelson, B., Chivas, A., 1995. Biological controls on coral Sr/Ca and  $\delta^{18}\text{O}$  reconstructions of sea surface temperatures. *Science* **269**, 1247–1249.
- Delaney, M.L., Linn, L.J., Druffel, E.R.M., 1993. Seasonal cycles of manganese and cadmium in coral from the Galapagos Islands. *Geochim. Cosmochim. Acta* **57** (2), 347–354.
- Dromgoole, E., Walter, L., 1990. Iron and manganese incorporation into calcite: effects of growth kinetics, temperature and solution chemistry. *Chem. Geol.* **81**, 311–336.
- Druffel, E., 1997. Geochemistry of corals: Proxies of past ocean chemistry, ocean circulation, and climate. *Proc. Natl. Acad. Sci. USA* **94**, 8354–8361.
- Dwyer, G., Cronin, T., Baker, P., Raymo, M., Buzas, J., Correge, T., 1995. North Atlantic deepwater temperature change during late Pliocene and late Quaternary climatic cycles. *Science* **270**, 1347–1351.
- Elderfield, H., Ganssen, G., 2000. Past temperature and  $\delta^{18}\text{O}$  of surface ocean waters inferred from foraminiferal Mg/Ca ratios. *Nature* **405**, 442–445.
- Elliot, M., deMenocal, P., Linsley, B., Howe, S., 2003. Environmental controls on the stable isotopic composition of *Mercenaria mercenaria*: potential application to paleoenvironmental studies. *Geochem. Geophys. Geosyst.* **4** (7), 1056. doi:10.1029/2002GC000425.
- Epstein, S., Buchsbaum, R., Lowenstam, H., Urey, H., 1953. Revised carbonate-water isotopic temperature scale. *Bull. Geol. Soc. Am.* **64**, 1315–1326.
- Erez, J., 2003. The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies. In: Dove, P., DeYoreo, J., Weiner, S. (Eds.), *Biomineralization, Reviews in Mineralogy and Geochemistry*, vol. 54. Mineralogical Society of America, pp. 115–149.
- Franklin, M., Morse, J., 1983. The interaction of manganese (II) with the surface of calcite in dilute solutions and seawater. *Mar. Chem.* **12**, 241–254.
- Freitas, P., Clarke, L., Kennedy, H., Richardson, C.A., Abrantes, F., 2005. Mg/Ca, Sr/Ca and stable-isotope ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) ratio profiles from the fan mussel *Pinna nobilis*: seasonal records and temperature relationships. *Geochem. Geophys. Geosyst.* **6** (4), Q04D14. doi:10.1029/2004GC000872.
- Gillikin, D., Dehairs, F., Baeyens, W., Navez, J., Lorrain, A., Andre, L., 2005a. Inter- and intra-annual variations of Pb/Ca ratios in clam shells (*Mercenaria mercenaria*): a record of anthropogenic lead pollution. *Mar. Poll. Bull.* **50**, 1530–1540.
- Gillikin, D., Lorrain, A., Navez, J., Taylor, J., Andre, L., Keppens, E., Baeyens, W., Dehairs, F., 2005b. Strong biological controls on Sr/Ca ratios in aragonitic marine bivalve shells. *Geochem. Geophys. Geosyst.* **6** (5), Q05009. doi:10.1029/2004GC000874.
- Gillikin, D., Dehairs, F., Lorrain, A., Steenmans, D., Baeyens, W., Andre, L., 2006. Barium uptake into the shell of the common mussel (*Mytilus edulis*) and the potential for paleo-chemistry reconstruction. *Geochim. Cosmochim. Acta* **70**, 395–407.
- Harper, E., 1997. The molluscan periostracum: an important constraint in bivalve evolution. *Palaeontology* **40**, 71–97.
- Ingram, L., Ingle, J., Conrad, M., 1996a. Stable isotope record of late Holocene salinity and river discharge in San Francisco Bay, California. *Earth Planet. Sci. Lett.* **141**, 237–247.
- Jones, D., 1983. Sclerochronology: reading the record of the molluscan shells. *Am. Sci.* **71** (4), 384–391.
- Katz, A., 1973. The interaction of magnesium with calcite during crystal growth at 25–90 °C and one atmosphere. *Geochim. Cosmochim. Acta* **37**, 1563–1586.
- Kennedy, H., Richardson, C., Duarte, C., Kennedy, D.P., 2001. Oxygen and carbon stable isotopic profiles of the fan mussel, *Pinna nobilis*, and reconstruction of sea surface temperatures in the Mediterranean. *Mar. Biol.* **139**, 1115–1124.
- Kim, S.-T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* **61** (16), 3461–3475.
- Klein, R., Lohmann, K., Thayer, C., 1996a. Bivalve skeletons record sea-surface temperatures and  $\delta^{18}\text{O}$  via Mg/Ca and  $^{18}\text{O}/^{16}\text{O}$  ratios. *Geology* **24** (5), 415–418.
- Klein, R., Lohmann, K., Thayer, C., 1996b. Sr/Ca and  $^{13}\text{C}/^{12}\text{C}$  ratios in skeletal calcite of *Mytilus trossulus*: covariation with metabolic rate, salinity and carbon isotopic composition of seawater. *Geochim. Cosmochim. Acta* **60** (21), 4207–4221.
- Laing, I., 2000. Effect of temperature and ration on growth and condition of king scallop (*Pecten maximus*) spat. *Aquaculture* **183**, 325–334.
- Lazareth, C.E., Vander Putten, E., Andre, L., Dehairs, F., 2003. High-resolution trace element profiles in shells of the mangrove bivalve *Isognomon ephippium*: a record of environmental spatio-temporal variations? *Estuarine Coastal Shelf Sci.* **57** (5-6), 1103–1114.
- Lea, D.W., Mashiota, T., Spero, H., 1999. Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. *Geochim. Cosmochim. Acta* **63** (16), 2369–2379.
- Lea, D.W., Shen, G., Boyle, E., 1989. Coralline barium records temporal variability in equatorial upwelling. *Nature* **340**, 373–376.

- Lear, C., Rosenthal, Y., Slowey, N., 2002. Benthic foraminiferal Mg/Ca-paleothermometry: a revised core-top calibration. *Geochim. Cosmochim. Acta* **66** (19), 3375–3387.
- Lorens, R., 1981. Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. *Geochim. Cosmochim. Acta* **45**, 553–561.
- Lorens, R., Bender, M., 1977. Physiological exclusion of magnesium from *Mytilus edulis* calcite. *Nature* **269**, 793–794.
- Lorens, R., Bender, M., 1980. The impact of solution chemistry on *Mytilus edulis* calcite and aragonite. *Geochim. Cosmochim. Acta* **44**, 1265–1278.
- Lorrain, A., Gillikin, D., Paulet, Y.M., Chavaud, L., Lemerrier, A., Navez, J., Andre, L., 2005. Strong kinetic effects on Sr/Ca ratios in the calcitic bivalve *Pecten maximus*. *Geology* **33**, 965–968.
- Lorrain, A., Paulet, Y.M., Chauvaud, L., Savoye, N., Nezan, E., Guerin, L., 2000. Growth anomalies in *Pecten maximus* from coastal waters (Bay of Brest, France): relationship with diatom blooms. *J. Mar. Biol. Ass. UK* **80**, 667–673.
- Mashiotta, T., Lea, D., Spero, H., 1999. Glacial-interglacial changes in Subantarctic sea surface temperature and  $\delta^{18}\text{O}$ -water using foraminiferal Mg. *Earth Planet. Sci. Lett.* **170**, 417–432.
- Mitchell, L., Fallick, A., Curry, G., 1994. Stable carbon and oxygen isotope composition of mollusc shells from Britain and New Zealand. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **111**, 207–216.
- Morris, A., 1971. Trace metal variations in sea water of the Menai Straits caused by a bloom of *Phaeocystis*. *Nature* **233**, 427–428.
- Morris, A., 1974. Seasonal variation of dissolved metals in inshore waters of the Menai Straits. *Mar. Poll. Bull.*, 54–59.
- Morse, J., Bender, M., 1990. Partition coefficients in calcite: examination of factors influencing the validity of experimental results and their application to natural systems. *Chem. Geol.* **82**, 265–277.
- Mucci, A., 1987. Influence of temperature on the precipitation of magnesian calcite overgrowths precipitated from seawater. *Geochim. Cosmochim. Acta* **51**, 1977–1984.
- Mucci, A., 1988. Manganese uptake during calcite precipitation from seawater: conditions leading to the formation of pseudokutnahorite. *Geochim. Cosmochim. Acta* **52**, 1859–1868.
- Mucci, A., Morse, J., 1983. The incorporation of  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  into calcite overgrowths: influences of growth rate and solution composition. *Geochim. Cosmochim. Acta* **47**, 217–233.
- Mueller-Lupp, T., Erlenkeuser, H., Bauch, H.A., 2003. Seasonal and interannual variability of Siberian river discharge in the Laptev Sea inferred from stable isotopes in modern bivalves. *Boreas* **32** (2), 292–303.
- Nair, P., Robinson, W., 1998. Calcium speciation and exchange between blood and extrapallial fluid of the quahog *Mercenaria mercenaria* (L.). *Biol. Bull.* **195** (1), 43–51.
- Nurnberg, D., 1995. Magnesium in tests of *Neogloboquadrina pachyderma* sinistral from high Northern and Southern latitudes. *J. Foram. Res.* **25**, 350–368.
- Nurnberg, D., Bijma, J., Hemleben, C., 1996a. Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochim. Cosmochim. Acta* **60**, 803–814.
- Nurnberg, D., Bijma, J., Hemleben, C., 1996b. Erratum: assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochim. Cosmochim. Acta* **60**, 2483–2484.
- Ohde, S., Kitano, Y., 1984. Coprecipitation of strontium with marine Ca–Mg carbonates. *Geochem. J.* **18**, 143–146.
- Oomori, T., Kaneshima, H., Maezato, Y., Kitano, Y., 1987. Distribution coefficient of  $\text{Mg}^{2+}$  ions between calcite and solution at 10–50 °C. *Marine Chem.* **20** (4), 327–336.
- Owen, R., 1998. Partitioning of stable isotopes between scallop shell calcite and sea water and factors influencing shell growth and microgrowth patterns. Ph.D., University of Wales Bangor.
- Owen, R., Kennedy, H., Richardson, C., 2002a. Isotopic partitioning between scallop shell calcite and seawater: Effect of shell growth rate. *Geochim. Cosmochim. Acta* **66** (10), 1727–1737.
- Owen, R., Richardson, C., Kennedy, H., 2002b. The influence of shell growth rate on striae deposition in the scallop *Pecten maximus*. *J. Mar. Biol. Ass. UK* **82** (4), 621–623.
- Paillard, D., Labeyrie, L., Yiou, P., 1996. Macintosh program performs time-series analysis. *EOS Trans. AGU* **77** (39), 379.
- Pedersen, T.F., Price, N.B., 1982. The geochemistry of manganese carbonate in Panama Basin sediments. *Geochim. Cosmochim. Acta* **46** (1), 59–68.
- Pingitore, J., Nicholas, E., Eastman, M., Sandidge, M., Oden, K., Freiha, B., 1988. The coprecipitation of manganese (II) with calcite: an experimental study. *Mar. Chem.* **25**, 107–120.
- Pingitore, N., Eastman, M., 1986. The coprecipitation of  $\text{Sr}^{2+}$  with calcite at 25 °C and 1 atm. *Geochim. Cosmochim. Acta* **50**, 2195–2203.
- Purton, L.M.A., Shields, G.A., Brasier, M.D., Grime, G.W., 1999. Metabolism controls Sr/Ca ratios in fossil aragonitic mollusks. *Geology* **27** (12), 1083–1086.
- Rickaby, R., Schrag, D., Zondervan, I., Riebell, U., 2002. Growth-rate dependence of Sr incorporation during calcification of *Emiliana huxleyi*. *Glob. Biogeochem. Cycles* **16** (1), art. no. 1006 mar 2002.
- Rosenthal, Y., Boyle, E., Slowey, N., 1997. Temperature control on the incorporation of magnesium, strontium, fluorine and cadmium into benthic foraminiferal shells from Little Bahamas Bank: prospects for thermocline paleoceanography. *Geochim. Cosmochim. Acta* **61** (17), 3633–3643.
- Russell, A., Honisch, B., Spero, H., Lea, D., 2004. Effects of seawater carbonate ion concentration and temperature on shell U, Mg and Sr in cultured planktonic foraminifera. *Geochim. Cosmochim. Acta* **68** (21), 4347–4361.
- Speer, J., 1983. Crystal chemistry and phase relations of orthorhombic carbonates. In: R. Reeder (Ed.), *Carbonates: Mineralogy and Chemistry*, vol. 11, Rev. Mineral., Mineralogical Society of America, pp. 145–190.
- Spero, H., Bijma, J., Lea, D., Bemis, B., 1997. Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. *Nature* **390**, 497–500.
- Stecher, H., Krantz, D., Lord III, C., Luter III, G., Bock, K., 1996. Profiles of strontium and barium in *Mercenaria mercenaria* and *Spisula solidissima* shells. *Geochim. Cosmochim. Acta* **60** (18), 3445–3456.
- Stoll, H., Ruiz Encinar, J., Garcia Alonso, J.I., Rosenthal, Y., Klaas, C., Probert, I., 2001. A first look at paleotemperatures prospects from Mg in coccolith carbonate: Cleaning techniques and culture measurements. *Geochem. Geophys. Geosyst.* **2**, 2000GC000144.
- Stoll, H., Schrag, D., 2000. Coccolith Sr/Ca as a new indicator of coccolithophorid calcification and growth rate. *Geochem. Geophys. Geosyst.* **1**. doi:10.1029/2000GC000144.
- Stoll, H.M., Klaas, C.M., Probert, I., Ruiz Encinar, J., Garcia Alonso, J.I., 2002. Calcification rate and temperature effects on Sr partitioning in coccoliths of multiple species of coccolithophorids in culture. *Glob. Planet. Change* **34** (3–4), 153–171.
- Swart, P.K., Grottoli, A., 2003. Proxy indicators of climate in coral skeletons: a perspective. *Coral Reefs* **22**, 313–315.
- Takesue, R., van Geen, A., 2004. Mg/Ca, Sr/Ca and stable isotopes in modern and holocene *Protothaca staminea* shells from a northern California coastal upwelling region. *Geochim. Cosmochim. Acta* **68** (19), 3845–3861.
- Tesoriero, A., Pankow, J., 1996. Solid solution partitioning of  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Cd}^{2+}$  to calcite. *Geochim. Cosmochim. Acta* **60**, 1053–1063.
- Vander Putten, E., Dehairs, F., Keppens, E., Baeyens, W., 2000. High resolution distribution of trace elements in the calcite shell layer of modern *Mytilus edulis*: environmental and biological controls. *Geochim. Cosmochim. Acta* **64** (6), 997–1011.
- Wada, K., Fujinuki, T., 1974. Biomineralization in bivalve mollusca with emphasis on the chemical composition of extrapallial fluid. In: Watabe, N., Wilbur, K. (Eds.), *The Mechanisms of Mineralization in the Invertebrates and Plants*, vol. 5. University of South Carolina Press, pp. 175–188.

- Watabe, N., 1988. Shell structure. In: Trueman, E.R., Clarke, M.R. (Eds.), *The Mollusca*, vol. 11. Academic Press, New York, pp. 69–74.
- Wefer, G., Berger, W., 1991. Isotope palaeontology: growth and composition of extant calcareous species. *Mar. Geol.* **100**, 207–248.
- Weidman, C., Jones, G., Kyger, 1994. The long-lived mollusk *Artica islandica* – a new paleoceanographic tool for the reconstruction of bottom temperatures for the continental shelves of the northern North Atlantic Ocean. *J. Geophys. Res.* **99** (C9), 18305–18314.
- Weiner, S., Dove, P., 2003. Overview of biomineralization processes and the problem of the vital effects. In: Dove, P., De Yoreo, J., Weiner, S. (Eds.), *Biomineralization, Reviews in Mineralogy and Geochemistry*, vol. 54. Mineralogical Society of America, pp. 1–29.
- Wheeler, A., 1992. Mechanisms of molluscan shell formation. In: Bonucci, E. (Ed.), *Calcification in Biological Systems*. CRC Press, Boca Raton, FL, pp. 179–216.
- Wilbur, D., Saleuddin, A., 1983. Shell formation. In: Saleuddin, A., Wilbur, K. (Eds.), *The Mollusca*, vol. 4. Academic Press, New York, pp. 236–287.
- Zeebe, R., 1999. An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes. *Geochim. Cosmochim. Acta* **63** (13/14), 2001–2007.
- Zhong, S., Mucci, A., 1989. Calcite and aragonite precipitation from seawater solutions of various salinities: precipitation rates and overgrowth compositions. *Chem. Geol.* **78**, 283–299.