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► **To cite this version:**

Anne Lorrain, Yves-Marie Paulet, Laurent Chauvaud, Robert B. Dunbar, David A. Mucciarone, et al..  $\delta^{13}\text{C}$  variation in scallop shells: Increasing metabolic carbon contribution with body size?. *Geochimica et Cosmochimica Acta*, 2004, 68 (17), pp.3509-3519. 10.1016/j.gca.2004.01.025 . hal-00452417

**HAL Id: hal-00452417**

**<https://hal.science/hal-00452417>**

Submitted on 2 Feb 2010

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Submitted to *Geochimica et Cosmochimica Acta*, 10<sup>th</sup> September 2003

**Revised version submitted 12<sup>th</sup> January 2004**

**$\delta^{13}\text{C}$  variation in scallop shells:**

**Increasing metabolic carbon contribution with body size?**

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**Abstract** - We examined  $\delta^{13}\text{C}$  values of shallow and deep-water scallop shells as well as  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) from the Bay of Brest in western Brittany. Time series of shell calcite  $\delta^{13}\text{C}$  do not reflect seasonal variation in seawater  $\delta^{13}\text{C}$ , but rather show a consistent pattern of decreasing  $\delta^{13}\text{C}$  with age, suggesting a metabolic effect rather than direct environmental control. This  $\delta^{13}\text{C}$  trend reflects an increasing contribution of metabolic  $\text{CO}_2$  to skeletal carbonate throughout ontogeny, although this respired  $\text{CO}_2$  does not seem to be the major source of skeletal carbon (contribution of only 10% over the first year of life). We propose a model of this effect that depends on the availability of metabolic carbon relative to the carbon requirements for calcification. A ratio of "respired to precipitated carbon" is calculated, and represents the amount of metabolic carbon available for calcification. Interestingly, this ratio increases throughout ontogeny suggesting a real increase of metabolic carbon utilization into the skeleton relative to carbon from seawater DIC. This ratio allows us to separate two different populations of *Pecten maximus* of different water depth. It is therefore suggested that shell  $\delta^{13}\text{C}$  might be used to track differences in the metabolic activity of scallops from different populations.

Keywords: scallops; isotopes; carbon; metabolism; age

## 1. INTRODUCTION

The stable isotope geochemistry of biogenic  $\text{CaCO}_3$  has served as a source of paleoclimatic and paleoenvironmental information since the pioneering work of Urey and co-workers (Urey, 1947; Urey et al., 1951; Epstein et al., 1953). These early works demonstrated that the oxygen isotopic composition of biogenic carbonate ( $\delta^{18}\text{O}$ ) is governed by both the oxygen isotopic composition of the water in which precipitation occurs and the water temperature. The oxygen isotopic composition of different carbonate organisms has subsequently been used to reconstruct past seawater temperature in numerous environments (e.g., Krantz et al., 1987; Marshall, 1992; Hickson et al., 1999; Richardson, 2001; and many others).

Carbonate carbon isotopic composition ( $\delta^{13}\text{C}$ ) varies in a more complex fashion than  $\delta^{18}\text{O}$ , and the origin of its variability within the skeletons of aquatic organisms is still under debate (Fatherree et al., 1998). Early work suggested that skeletal carbonate originates directly from dissolved inorganic carbon (DIC) in seawater (e.g., Mook and Vogel, 1968; Killingley and Berger, 1979; Arthur et al., 1983).  $\delta^{13}\text{C}$  of carbonate skeletons was thought to be controlled by the isotopic composition of DIC and the pH of the water from which the carbonate precipitated (Romanek et al., 1992). As DIC  $\delta^{13}\text{C}$  is mainly influenced by the primary production and oxidation of organic matter (Kroopnick, 1985), the  $\delta^{13}\text{C}$  of carbonates was thought to reflect the state of these variables in the environment at the time of precipitation. More recently, Tanaka et al. (1986), McConnaughey et al. (1997), Furla et al. (2000) and others, have proposed that the process of calcification utilizes carbon from two reservoirs, seawater DIC and metabolic DIC, with the latter composed of respiratory  $\text{CO}_2$ . Thus, the "external source" of carbon is the dissolved inorganic carbon pool in the surrounding water, which in seawater has a mean  $\delta^{13}\text{C}$  value close to 1‰. The internal carbon

source, i.e., metabolically derived CO<sub>2</sub>, has a highly depleted <sup>13</sup>C isotopic signature relative to the external inorganic pool because organic matter consumed by organisms in the ocean is strongly enriched in <sup>12</sup>C (-20 to -26‰, Fontugne and Duplessy, 1981; Lorrain et al., 2002). The incorporation of such carbon would result in lower δ<sup>13</sup>C values, obscuring the signal derived from water δ<sup>13</sup>C<sub>DIC</sub>, and would therefore impact the interpretation of the carbonate isotopic record. McConnaughey et al. (1997) have moderated this idea, suggesting that in aquatic invertebrates, less than 10% of respired CO<sub>2</sub> is incorporated in the shell, resulting in only small decreases of shell δ<sup>13</sup>C (< 2‰) with respect to equilibrium values. If in corals, several mechanisms have been proposed to explain the incorporation of carbon derived from the metabolic processes of zooxanthellae and coral polyps into skeletal carbonate (McConnaughey, 1989; Swart et al., 1996; McConnaughey et al., 1997; Furla et al., 2000), few studies have developed a model for this so called "vital effect" in bivalve species (Klein et al., 1996).

The biology of the scallop *Pecten maximus* in the Bay of Brest is well understood in terms of growth rate, reproduction, and energy allocation (Paulet et al., 1988; Paulet et al., 1997; Chauvaud et al., 1998; Saout et al., 1999; Lorrain et al., 2000; Chauvaud et al., 2001; Lorrain et al., 2002). In particular, daily growth striae have been described for this species from a natural population that was sampled intensively (Chauvaud et al., 1998) allowing the estimation of daily growth rates by measuring the distance between successive striae during the period of growth. Daily striae formation was found to be limited to a growing season and a complete cessation of growth was observed during the winter (Chauvaud et al., 1998). For example, second year scallops have an annual period of daily growth, (i.e., the growth between the first and the second winter growth ring visible on the shell) which continues from the end of March through late November with growth rates between 50 and 300 μm d<sup>-1</sup> (Chauvaud et al., 1998; Lorrain et al., 2000).

In field (Owen et al., 2002a) and laboratory (Gruffydd, 1981) experimental conditions, striae are not produced daily as handling or manipulation of live specimens of *P. maximus* stresses the organisms and alters their growth pattern. We also never manage to reproduce this daily periodicity in numerous lab experiments (unpublished data).

Therefore, the daily pattern of striae in natural populations of *P. maximus* allows us to precisely date carbonate deposits along the shell growth axis, enabling a precise calibration of geochemical tracers during the growth period (see also Schöne et al., 2002), something that is often impossible to do with other species (Jones and Quitmyer, 1996; Price and Pearce, 1997; Hart and Blusztajn, 1998). In some studies, for example, the linear extension rate is assumed to be constant and approximate calendar dates are estimated by equal time-step interpolation, causing a potentially large mismatch between measured skeletal isotopic values and observed environmental parameters (Klein et al., 1996; Hickson et al., 1999; Vander Putten et al., 2000). In the case of *Pecten maximus*, using the daily growth band chronology, each individual geochemical value can be matched to the corresponding environmental parameter measured where the scallop lives, allowing accurate calibration.

The main goal of this study is to determine the factors that control  $\delta^{13}\text{C}$  in scallop calcite. Because of the possibility of non-equilibrium or "vital-effect" fractionation, we monitored the carbon isotopic composition of DIC in ambient seawater collected while the scallops were growing in the Bay of Brest during 2000. We also examine calcite  $\delta^{13}\text{C}$  variability among different individuals that grew contemporaneously. Using knowledge of the biology of this species, we investigate the effect of scallop metabolism on carbon isotopic variations in shell calcite. Finally, we extend our observations from juvenile and adult scallops collected at a shallow site (Bay of Brest) to explain isotopic observations derived from scallops collected from deeper locations on the continental shelf.

## 2. METHODS

Time series' of the carbon isotopic composition ( $\delta^{13}\text{C}$ ) of scallop shells were determined on six individuals of *Pecten maximus*: four from the Bay of Brest (shells A, B, C and N) and two from an offshore location situated on the continental shelf (shells I, J) at the western part of Brittany in the Iroise sea (France, Fig. 1). Specimens were collected by dredging at 30 m depth in the Bay of Brest (4°30'W, 48°20'N, A, B, C) in December 2000 by our group, and at 150 m depth on the continental shelf (47°55'N, 6°25'W, I, J) during 1998 by IFREMER (cruise PERCOL).

For shells A, B and C, the study was conducted using data from the scallop's second year. In the Bay of Brest, scallops in their second year grow from late March-early April to late November (Chauvaud et al., 1998) and during this period (between the first and the second winters), scallops exhibit the maximum number of annual days of growth, and thus accumulate the longest annual record (Chauvaud et al., 1998). Each year, the exact date of growth restart is calculated by counting and measuring daily increments from the edge to the first winter mark on juveniles sampled during the growth period. Dates are thus assigned to each striae by backdating from the collection date. Because we needed isotopic data spanning the full growth season, shells A, B and C were sampled after growth cessation (i.e., in December). The truncated growth rate series, measured on scallops from the same cohort that were sampled during summer 2000 have then been used to assign absolute calendar dates to the full year series' recorded by individuals A, B and C collected during the subsequent winter.

Older individuals were sampled, one in the Bay of Brest (shell N) and two at the deeper site on the continental shelf (shell I and J) to examine the effect of age on isotopic values. No absolute calendar assignation has been done for those shells because the aim was not to

compare day-by-day shell isotopic variations to environmental parameters for these individuals.

Daily growth rate was determined for each scallop by measuring distances between successive daily growth striae using the image analysis method described in Chauvaud et al. (1998). Shell surfaces were cleaned using Milli-Q water and consecutive shell samples were collected from the outer calcitic layer of the flat valve (Roux et al., 1990) along the axis of maximum growth using a 300 $\mu$ m drill bit. Samples used for mass spectrometry weighed on average  $76\pm 15\mu$ g (N = 325) and represent 1 to 5 days of shell growth, depending on the growth rate. Calcite powder samples were acidified in 100% phosphoric acid at 70°C for 470s and analyzed using an automated Finnigan MAT Kiel III carbonate device coupled to a Finnigan MAT 252 Isotope Ratio Mass Spectrometer at Stanford University (California, USA). A total of 389 shell samples, 86 NBS-19 (National Institute of Standards and Technology, NIST SRM 8544) and 40 SLS-134 (Stanford Isotope Lab Standard) standards were analyzed. Replicate analyses of standards yielded  $\delta^{13}\text{C}$  standard deviations of 0.033‰ and 0.035‰ ( $\pm 1\sigma$ ) for NBS-19 and SLS-134, respectively. Additionally, 30 (7.7%) shell samples were replicated, yielding an average standard deviation of 0.04‰ for  $\delta^{13}\text{C}$ . The  $\delta^{18}\text{O}$  results from this study will be reported elsewhere.

For DIC  $\delta^{13}\text{C}$  determination, 48 bottom seawater samples were collected from the Bay of Brest between 23 January 2000 and 14 January 2001 using 5-liter NISKIN bottles. After collection, water samples were immediately poisoned with  $\text{HgCl}_2$  to stop biological activity and stored in glass-stoppered bottles until analysis. DIC  $\delta^{13}\text{C}$  samples were analyzed using a Fisons Optima mass spectrometer in the Laboratoire des Sciences de l'Environnement et du Climat (CNRS, Gif sur Yvette, France).  $\text{CO}_2$  was extracted by adding 2mL of 15N  $\text{H}_3\text{PO}_4$  to a 70mL seawater aliquot in a vacuum-tight system sparged with He gas (flow rate 80mL h<sup>-1</sup>)



according to Leboucher et al. (1999). Reproducibility of  $\delta^{13}\text{C}$  measurement was better than 0.15‰. All isotope data are expressed in conventional delta ( $\delta$ ) notation where:

$$\delta \text{ in } \text{‰} = (((\text{Ratio sample} - \text{Ratio reference}) / (\text{Ratio reference})) * 1000) \quad (1)$$

and where the isotope ratios of  $^{13}\text{C}/^{12}\text{C}$  are reported relative to the international VPDB (Vienna Pee Dee Belemnite) standard.

Biological data used in this paper are derived from the Bay of Brest scallop population survey conducted by the LEMAR laboratory (Laboratory of Marine Environmental Science in Brest). This study includes the sampling and dissection analysis of 20 scallops collected every two to four weeks since 1989. Shell heights and weights together with tissue dry weights from this long term survey are used in the present study. This data is used to fit shell height with shell and tissue weight (using power models), and to determine seasonal and annual variation of soft tissue weights.

Individual oxygen consumption was estimated using an equation relating dry body mass to basal oxygen consumption rate in *P. maximus* from the bay of Brest (Suprpto, 1986):

$$R = 0.703 \times W^{0.704} \quad (2)$$

where  $R$  is oxygen consumption expressed in  $\text{ml h}^{-1} \text{g}^{-1}$  and  $W$  the soft tissue dry weight of the individual. Although direct respirometer measurements are not available for scallops from the deeper offshore site, this same equation has been used for our work with specimens I and J.

### 3. RESULTS

#### 3.1 Allometric relationships

Metabolic rates were derived from biometric relationships between shell heights, weights, and soft tissue dry weights using more than two thousand individuals from the Bay of Brest

(data from 1989 to 2003). Results are presented in Fig. 2. These relationships are used in this study to estimate biological parameters from shell heights.

## 3.2 Bay of Brest

### 3.2.1. Scallop biology

Fig. 3A shows daily growth striae thickness for the three scallops from the 30m Bay of Brest site. After winter cessation, growth began again at the end of March, and the rate increased until July to an average rate of  $250\mu\text{m d}^{-1}$  and then decreased through November. All three scallops had the same general trend.

Fig. 4 shows daily growth results for shell N (age class 4). Four annual growth cycles corresponding to the years 1997 to 2000, are easily deciphered. During the first growth cycle, the daily maximum growth rate was  $\sim 300$  to  $330\mu\text{m d}^{-1}$  in summer, and then progressively decreased to  $\sim 130\mu\text{m d}^{-1}$  the last year of life (i.e., in 2000). Based on counts of daily deposits during each year of growth, the annual growth period (i.e., number of days with calcite accretion from spring through fall) decreases with age. For example, scallop N grew for more than two hundred and thirty days per year at the beginning of its life but only about one hundred days per year at the end.

### 3.2.2 Water

The carbon isotopic composition of DIC in Bay of Brest bottom water ranged between  $-0.21$  and  $1.42\text{‰}$  (Fig. 3B). We observe the classic seasonal cycle with low  $\delta^{13}\text{C}$  values during the winter and high  $\delta^{13}\text{C}$  values during the spring-summer. Enrichment in the spring and the summer may be attributed to preferential uptake of  $^{12}\text{C}$  within the photic zone by phytoplankton during bloom events (Hellings et al., 2000; Hellings et al., 2001). Lower  $\delta^{13}\text{C}$  values during the winter reflect the combined effects of autochthonous respiration and

increasing river input, which contains DIC enriched in  $^{12}\text{C}$  (Hellings et al., 2000; Hellings et al., 2001).

### 3.2.3 Scallop shells

Shell calcite  $\delta^{13}\text{C}$  values in Bay of Brest juvenile scallops range between -0.2 and 1.1‰ (Fig. 3C).  $\delta^{13}\text{C}$  decreases steadily from growth restart in spring through the summer and autumn.  $\delta^{13}\text{C}$  values for shell A were higher than those of shells B and C, until the summer months. The seasonal shell  $\delta^{13}\text{C}$  signal does not parallel  $\delta^{13}\text{C}$  variations in seawater DIC. There is no discernible relationship between shell calcite  $\delta^{13}\text{C}$  and daily growth rate ( $p > 0.01$ ) for any of the three shells.

For the four year-old shell (shell N),  $\delta^{13}\text{C}$  values range from  $\sim -1$  to 1.5‰ and a pattern of decreasing  $\delta^{13}\text{C}$  with age is observed as well as some 0.2 to 0.5‰ oscillations, which could reflect seasonal cycles (Fig. 4). In 2000 (last year of growth),  $\delta^{13}\text{C}$  values range from  $\sim -1$  to -0.1‰, values much more negative than for the three juvenile scallops A, B, C growing during the same year. A significant but weak relationship ( $p < 0.01$ ,  $r^2 = 0.26$ ) exists between shell calcite  $\delta^{13}\text{C}$  and daily growth rate for shell N.

## 3.3 Offshore scallops

### 3.3.1 Scallop biology

As for the inshore scallops, growth cycles were observed and interpreted as annual cycles (Fig. 5). During the first growth cycle, the daily maximum growth rate was  $\sim 250$  to  $300\mu\text{m d}^{-1}$  in summer, and then progressively decreased. The annual growth period also decreases with age, but was shorter than that for inshore scallops. For example, scallop J grew for more than one hundred days per year at the beginning of its life but only about twenty

days per year at the end, which is approximately one hundred days less than shell N (shallow site) at the beginning of its life.

### 3.3.2 Scallop shells

$\delta^{13}\text{C}$  values ranged from 1.5 to 0.3‰ and the same pattern of decreasing  $\delta^{13}\text{C}$  with age was observed in both outer shelf shells (Fig. 5). These shells also contained several  $\delta^{13}\text{C}$  oscillations that could reveal some regular seasonal periodicity. In shell J, the  $\delta^{13}\text{C}$  values are stable during the first year of life. No correlation was found between growth rate and  $\delta^{13}\text{C}$  values for the two scallops ( $p > 0.1$ ).

## 4. DISCUSSION

Historically, the  $\delta^{13}\text{C}$  of mollusk carbonate has been thought to respond mainly to variability in ambient water  $\delta^{13}\text{C}_{\text{DIC}}$  values (e.g., Mook and Vogel, 1968; Killingley and Berger, 1979; Arthur et al., 1983). But our study, in agreement with many authors (e.g., Tanaka et al., 1987; McConnaughey et al., 1997; Hickson et al., 1999; Dettman et al., 1999), contradicts this premise. At the seasonal scale and over the entire lifetime of the organisms, we observe the same pattern of decreasing  $\delta^{13}\text{C}$  values in all six scallop shells, a pattern that is independent of the DIC  $\delta^{13}\text{C}$  signal. Variability in  $\delta^{13}\text{C}$  between the specimens (e.g., shell  $\delta^{13}\text{C}$  of scallop A is higher than that of shells B and C values for several months) suggests that a variable biological control exists. We suggest that variability in metabolic activity among the different scallops is responsible for this pattern. Heterogeneity in near-bottom seawater DIC  $\delta^{13}\text{C}$  may be an alternative explanation, but one that is unlikely given that all three scallops were recovered from a dredge haul that sampled the bottom over a distance of less than 500 m.

Theoretical equilibrium values are well established for the partitioning of  $^{13}\text{C}$  and  $^{12}\text{C}$  during inorganic calcite precipitation (Romanek et al., 1992). Expected calcite equilibrium  $\delta^{13}\text{C}$  values are about 1‰ greater than the  $\delta^{13}\text{C}_{\text{DIC}}$  of seawater.  $\delta^{13}\text{C}_{\text{DIC}}$  in the Bay of Brest is on average 0.8 ( $\pm 0.4$ )‰, so equilibrium calcite  $\delta^{13}\text{C}$  values at in situ temperatures should be  $\sim 1.8$ ‰. Observed  $\delta^{13}\text{C}$  values for juvenile Bay of Brest scallop calcite range from -0.2 to 1.1‰, significantly lower than predicted at isotopic equilibrium. Furthermore, shell  $\delta^{13}\text{C}$  values for the same year 2000 in the Bay of Brest are different for age class 1 and age class 4, i.e., lower for older scallops, confirming again that  $\delta^{13}\text{C}_{\text{DIC}}$  was not the unique contributor to shell  $\delta^{13}\text{C}$ .

Nonequilibrium incorporation of carbon in biogenic carbonates has been attributed to "vital effects" and even to habitat characteristics (Krantz et al., 1987; McConnaughey, 1989; Keller et al., 2002). Vital effects are usually separated into kinetic and metabolic isotope effects (e.g., McConnaughey et al., 1997; Heikoop et al., 2000) even if they are both mediated by biological processes and are often difficult to separate quantitatively. Kinetic effects are specifically related to shell growth rate, and to slower hydration and hydroxylation of  $\text{CO}_2$  by molecules bearing the heavy isotopes of carbon. Metabolic effects are related to production and incorporation of respiratory  $\text{CO}_2$  within the body of an organism (McConnaughey et al., 1997).

According to McConnaughey (1989) and Klein et al. (1996), kinetic isotope effects result in depletion of skeletal  $^{13}\text{C}$ , with greater degrees of isotopic disequilibria in the portions of carbonate skeletons that are rapidly growing. Interestingly, just the opposite relationship is observed in our study, with the lowest  $\delta^{13}\text{C}$  values associated with the lowest growth rates. Furthermore, a significant correlation between daily growth increments and scallop  $\delta^{13}\text{C}$  variations has been found only for one shell, the five other shells presented no correlation between these two parameters. Results of  $\delta^{18}\text{O}$  will be reported in another paper showing that

shell  $\delta^{18}\text{O}$  values follow temperature close to equilibrium, and that no ontogenetic trend are observed, resulting in no correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values.

Therefore, kinetic isotope effects seem to be small, or if such effects exist, other processes overwhelm them. Owen et al. (2002b, c), working on the same species (i.e., *P. maximus*), also found that  $\delta^{13}\text{C}$  values were depleted relative to equilibrium. They explained this by a metabolic effect at low growth rates and combined kinetic and metabolic effects at high growth rates (Owen et al., 2002c). They also claimed that seasonal variations in shell growth rates were a governing factor influencing shell  $\delta^{13}\text{C}$ . However, if they demonstrated that there were  $\delta^{13}\text{C}$  differences between low growth rates ( $< 0.06\text{mm d}^{-1}$ ) and high growth rate portions of the shell, no relationship appears between growth rate and  $\delta^{13}\text{C}$  between  $0.1$  and  $0.24\text{mm d}^{-1}$  which corresponds to the major portion of the year (Fig. 4 in Owen et al., 2002c). We therefore believe that they have overestimated the effect of shell growth rate on shell  $\delta^{13}\text{C}$ . Furthermore, these authors worked with shells grown under different conditions: i) scallops were raised on boxes above the sediment, i.e., not in natural conditions as in our study; ii) one-year-old juvenile scallops were studied and their hypothesis was not compared with older scallops; iii) growth rates were measured once a month, and daily growth was estimated as a monthly average; and finally iv) isotopic measurements were made on shell material deposited during each month (e.g., producing a monthly average value). Our study used a substantially different approach. We analyzed the carbonate isotopic composition of individuals from natural populations of *P. maximus*, using several age classes and two locations (two different populations with juvenile and old scallops on one site). We determined precisely daily growth rates (see Chauvaud et al., 1998) and our isotopic sampling was conducted at a time interval of from  $\sim 1$  to 5 days, depending on the growth rate. This approach allowed the comparison of seawater isotopic composition, growth rate, and shell isotopic composition on a daily to weekly scale rather than at a monthly scale.

One other possible source of  $^{13}\text{C}$  depletion is incorporation of pore water DIC from the underlying sediments. Pore water DIC is enriched in  $^{12}\text{C}$  due to the oxidation of sedimentary organic matter. Incorporation of pore fluid DIC has been proposed to explain  $\delta^{13}\text{C}$  differences between bivalve species or in some instances when decreasing  $\delta^{13}\text{C}$  values with increasing age were observed (Krantz et al., 1987; Keller et al., 2002). Keller et al. (2002) hypothesized that decreasing  $\delta^{13}\text{C}$  in the shell of *Chamelea gallina* was due to the progressive deepening of the mollusk into the sediment with age. This source cannot explain the decreasing  $\delta^{13}\text{C}$  pattern with age that we see in our study as *P. maximus* lives right at the same depth relative to the sediment surface throughout its lifetime (Paulet, private communication). However, we cannot rule out that some of the DIC incorporated into the shell might be from  $^{13}\text{C}$ -depleted pore waters, as scallops typically scoop out a depression in the surface of the sediment. A pore water influence might explain the average depletion we observe with respect to the equilibrium, but not the general decrease in  $\delta^{13}\text{C}$  with age.

We now explore the possibility that a metabolic effect, implying the incorporation of  $^{13}\text{C}$ -depleted respiratory  $\text{CO}_2$  into the extrapallial fluid (EPF), and subsequently into the precipitated carbonate is causing the observed shell calcite  $\delta^{13}\text{C}$  pattern.  $\delta^{13}\text{C}$  variability among the scallop shells used in this study supports the notion that differences in metabolic rate rather than an environmental signal are controlling shell  $\delta^{13}\text{C}$ . Tanaka et al. (1986) found that 35 to 85% of the shell calcite carbon came from respiratory  $\text{CO}_2$  in the bivalves *Mytilus edulis* and *Mya arenaria*. They proposed a simple equation to approximate the percentage of this metabolically derived carbon, M:

$$M = 100 \times \frac{\delta^{13}\text{C}_{\text{DIC}} + \epsilon_{\text{cl-b}} - \delta^{13}\text{C}_{\text{calcite}}}{\delta^{13}\text{C}_{\text{DIC}} + \epsilon_{\text{cl-b}} - \delta^{13}\text{C}_{\text{meta}} - \epsilon_{\text{cl-CO}_2}}$$

where  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{meta}}$  are the values of the  $\delta^{13}\text{C}$  of dissolved inorganic carbon in seawater and the  $\delta^{13}\text{C}$  of respired  $\text{CO}_2$ , respectively;  $\epsilon_{\text{cl-b}}$  is the enrichment factor between

calcite and bicarbonate (1‰ in Romanek et al., 1992);  $\epsilon_{\text{cl-CO}_2}$  is the enrichment factor between calcite and aqueous  $\text{CO}_2$  ( $\epsilon_{\text{cl-CO}_2} = 11.98 - 0.12 \times T^\circ\text{C}$  in Romanek et al., 1992).  $\delta^{13}\text{C}_{\text{meta}}$  was estimated in their study to be the same as the  $\delta^{13}\text{C}$  value of the clam tissue. Using this mass balance approach, and taking into account the observed variations in  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{13}\text{C}_{\text{calcite}}$  and  $\epsilon_{\text{cl-CO}_2}$ , we find that 10 to 30% of the carbon within the scallop skeleton originates from metabolic  $\text{CO}_2$ , with whole shells averages of 19, 23, and 22% for shells A, B and C, respectively. However, McConnaughey et al. (1997) explained that the Tanaka et al. equation was in error because of the added isotope fractionation factor, which leads to overestimated values. These authors have proposed another equation to account for metabolic  $\text{CO}_2$  contribution:

$$M (\delta^{13}\text{C}_{\text{meta}}) + (1-M) \delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{shell}} - \epsilon_{\text{cl-b}}$$

Using this equation, we found that a maximum of 10% of metabolic  $\text{CO}_2$  was incorporated into the shells (8, 10 and 10% for shells A, B and C, respectively) which is in agreement with the general findings of McConnaughey et al. (1997): the metabolic respiratory  $\text{CO}_2$  represents only a small portion of the carbon incorporated into shell carbonate. They modeled the effect of gas exchange physiology on the skeletal incorporation of respired  $\text{CO}_2$  and suggested that aquatic invertebrates appeared to passively absorb (and subsequently lose) about 10 times more  $\text{CO}_2$  from the environment than they generated through respiration. Ambient  $\text{CO}_2$  therefore dilutes respired  $\text{CO}_2$  and prevents it from contributing much to the skeleton (McConnaughey, 2003)

However, working with *Mytilus trossolus*, Klein et al. (1996) found that the percentage of respiratory carbon was high enough to obscure the seawater  $\delta^{13}\text{C}_{\text{DIC}}$  signal. Therefore, even if the incorporation of metabolic  $\text{CO}_2$  in *P. maximus* represents a small contribution to total carbon, it could still explain the trend toward more depleted values observed during ontogeny. Several authors have already reported a pattern of decreasing  $\delta^{13}\text{C}$  in bivalve shells (Jones et



al., 1983; Krantz et al., 1987; Schein et al., 1991; Roux et al., 1990; Elliot et al., 2003). If we consider that two carbon pools (seawater DIC and respired CO<sub>2</sub>) can be incorporated into the skeleton, then decreasing shell calcite δ<sup>13</sup>C can be explained by the increasing utilization of <sup>13</sup>C-depleted respiratory CO<sub>2</sub> through ontogeny. Although increased utilization of respiratory CO<sub>2</sub> has been previously suggested to explain this pattern (Krantz et al., 1987; Keller et al., 2002), the underlying biology is not yet known. Krantz et al. (1987) hypothesized that the onset of sexual maturity and physiological changes related to gametogenesis combined with slower growth rates could explain trends towards lower shell δ<sup>13</sup>C values; but they did not propose a precise mechanism. The key question is what age-varying physiological parameter can explain an increasing contribution by respiratory CO<sub>2</sub> to the centers of calcification?

Klein et al. (1996) found significantly different δ<sup>13</sup>C values in calcite sampled within the same daily growth striae in *Mytilus trossolus*, and more specifically, higher skeletal δ<sup>13</sup>C values near the ventral margin than on lateral margins. Based on the work of Rosenberg et al. (1988, 1989), they proposed that different mantle metabolic activities in areas of different shell curvature influenced the δ<sup>13</sup>C composition of extrapallial fluid (EPF), and thus calcite δ<sup>13</sup>C in the vicinity. EPF in mollusks is the fluid located between the mantle and the shell in which calcification takes place (Klein et al., 1996). According to this study, calcite secreted from this fluid along the ventral margin of the shell, where metabolic activity is relatively low, receives more seawater DIC, whereas high mantle metabolic activity along lateral margins promote greater incorporation of metabolically derived CO<sub>2</sub>. Klein et al. (1996) suggested that carbon may be a limiting resource for calcification. Consequently, competition for carbon from different sources may occur. When metabolic activity is low, the amount of respiratory carbon in the EPF is low and mussels take carbon preferentially from seawater. Metabolic carbon availability therefore controls shell δ<sup>13</sup>C variations to a greater degree than the availability of seawater DIC. Using Rosenberg et al's (1988, 1989) proposition, Klein et

al. (1996) also proposed that shell growth rate is inversely proportional to mantle metabolic activity, as growth rates are lower at lateral margins. If we extend this idea to the scale of an individual mollusk's lifetime, this theory suggests that the diminution of growth rates through ontogenesis leads to increased availability of respiratory CO<sub>2</sub> in the EPF, and thus to an increase of respiratory carbon uptake by the skeleton. However, by comparing two different mussels, sampling each along the maximum growth axis, they also found that skeletal  $\delta^{13}\text{C}$  and growth rates were not correlated, and concluded that growth rate has minimal influence on shell  $\delta^{13}\text{C}$ . It appears that the concept of EPF composition, itself controlled by mantle metabolic activity, as a controller of shell  $\delta^{13}\text{C}$ , is valuable within a single growth band but not across many bands along the axis of maximum shell growth.

We propose a simpler model, which we illustrate with our scallop data, wherein the availability of metabolic carbon relative to the carbon requirements for calcification during mollusk growth, accounts for the observed variability in shell  $\delta^{13}\text{C}$ . First, we consider that the availability of metabolic CO<sub>2</sub> is directly linked to respiratory activity (Respiratory quotient = 1 which means that respiration consumes O<sub>2</sub> and produces CO<sub>2</sub> with a 1:1 stoichiometry), which in turn depends on the whole soft body mass of the scallop with a coefficient that is species specific (see Peters (1983) and Reiss (1989) for reviews). Using the regression function that relates shell height to soft tissue dry weight (Fig. 1A) and our shell growth data, we estimate the soft tissue dry weight day-by-day for each scallop. Then using the relation between soft tissue dry weight and oxygen consumption (Suprpto, 1986; Fig.6A), we estimate daily respiration by a scallop throughout ontogeny (Fig. 7A, 8A). Secondly, a carbon "demand" associated with calcitic shell growth was calculated from the daily growth rate converted to  $\mu\text{mol C d}^{-1}$  (Fig. 6B, 7B). The scallop shell is considered to be pure calcium carbonate. From these two relationships, we defined a "metabolic carbon availability" index as the ratio of respired to precipitated carbon (Fig. 6C, 7C). We

hypothesize that the higher the index, the more metabolic carbon is available to be incorporated into the shell.

On Fig. 6, time series' of these different parameters are shown for shells A, B and C. While daily oxygen consumption (and therefore available respiratory carbon) increases with age (Fig. 6A), daily carbon precipitation rate increases through August and then decreases (Fig. 6B). The resulting "metabolic carbon availability" index therefore increases progressively over the year, mainly as a result of the increase in soft tissue biomass. These results suggest that increasing amounts of metabolic carbon are therefore incorporated into the shells as they age, explaining the observed decreasing  $\delta^{13}\text{C}$  pattern. Furthermore, shell A has the lowest "metabolic carbon availability" index, suggesting that less metabolic carbon is incorporated into the skeleton and indeed, this scallop exhibits the highest  $\delta^{13}\text{C}$  values through August. After August, shell  $\delta^{13}\text{C}$  values of the three specimens are similar, in agreement with their similar "metabolic carbon availability" index. This isotopic and body mass difference between individuals, as well as the coherence of these observations with our proposed model, is a strong argument for our proposition.

Fig. 7 shows that scallop N, the oldest scallop from the Bay of Brest (age class 4), exhibits the same general pattern with age, associated with an increase in "metabolic carbon availability" index that can explain the observed shell  $\delta^{13}\text{C}$  trends through ontogeny. Fig. 8 shows similar results for scallops I and J collected at 150 m on the continental shelf, confirming that our "metabolic carbon availability" index can explain the observed shell  $\delta^{13}\text{C}$  trends for scallops of different ages from different locations.

Although this model explains the general decreasing  $\delta^{13}\text{C}$  trends we have observed, there are some features that it doesn't explain. For example, the observed apparent seasonal variations in  $\delta^{13}\text{C}$  in older scallops are less well-explained. Furthermore, in juvenile scallops from the Bay of Brest (Fig. 6C), the largest decrease of the shell  $\delta^{13}\text{C}$  values occurs during

spring at a time when the "metabolic carbon availability" index did not increase. We note that the respiration rates we input to our model are only approximations. The validity of employing the same equation derived by Suprpto (1986) to calculate this parameter during the entire period of scallop growth has not yet been tested. Further study is needed to assess whether different respiration equations are required for each season or for each metabolic window established for scallops in the Bay of Brest (Lorrain et al., 2002).

We recognize that elucidation of the mechanism underlying carbon isotope vital effects in mollusks is a complex and long-standing goal. The transfer of carbon between the extrapallial fluid and the centers of calcification are not necessarily as straightforward and linear as we have suggested in this study. For example, the ratio of metabolic CO<sub>2</sub> availability to carbonate precipitation rate trends towards infinity when growth rate approaches zero, suggesting the likelihood of a non-linear carbon isotopic response under these conditions. In addition, Zeebe (1999) proposed that pH variations might account for some portion of  $\delta^{13}\text{C}$  variance in foraminiferal calcite. It therefore seems possible that changes in EPF pH could also account for shell  $\delta^{13}\text{C}$  variations. Temperature very likely plays a role as well since respiration is known to vary with this parameter seasonally and at different locations. Those caveats could explain why our model is not able to assess seasonal details and we therefore believe that at present, our model can only be used to predict general trends in mollusk shell  $\delta^{13}\text{C}$ .

Despite the caveats above, general trends in scallop calcite  $\delta^{13}\text{C}$  are explained by our "metabolic carbon availability" index. Additionally, when we use this model and plot shell  $\delta^{13}\text{C}$  versus the ratio of respiratory CO<sub>2</sub> availability to carbonate precipitation rate, we see the separation of two different populations of *P. maximus* (Fig. 9). Indeed, two different slopes can be established for inshore and offshore scallops. Thus, even if the shell  $\delta^{13}\text{C}$  cannot be used to reconstruct  $\delta^{13}\text{C}_{\text{DIC}}$  variations, it may allow discrimination of different populations

with different rates of metabolism and/or calcification. Further studies on populations from Norway to Spain will be used to test this idea.

## 5. CONCLUSIONS

The carbon isotopic composition of scallop calcite cannot readily be used as an isotopic tracer of paleoproductivity as shell  $\delta^{13}\text{C}$  does not directly respond to seawater DIC  $\delta^{13}\text{C}$ . As has been shown previously for other carbonate-producing organisms, scallop shell  $\delta^{13}\text{C}$  deviation from equilibrium can be explained by the mixing of two end member carbon pools with differing isotopic compositions: an external source (seawater DIC) and an internal source (metabolic  $\text{CO}_2$ ). This metabolic  $\text{CO}_2$  contributes an estimated maximum of 10% to total skeletal carbon, as calculated with an isotopic mixing equation. However, we show that a consistent decrease in shell  $\delta^{13}\text{C}$  with age, observed in both juvenile and older scallops, is caused by an increasing contribution of metabolic carbon to the skeleton during ontogeny. Increased utilization of metabolic carbon to satisfy the carbon requirements for calcification is suggested by the observed increase in the ratio of respiratory  $\text{CO}_2$  availability to calcite precipitation rate during aging.

If this model is valid, the  $\delta^{13}\text{C}$  of skeletal calcite may be a useful tracer of scallop metabolism (via the amount of metabolically derived carbon that ends up in the scallop's shell) in different environments and could provide an alternative method for estimating scallop metabolism in parallel with biological analyses. In addition, seawater DIC  $\delta^{13}\text{C}$  could be reconstructed from the shell  $\delta^{13}\text{C}$  signal if such a metabolic contribution could be removed from the signal. Further work is needed to assess precisely the metabolic carbon contribution to the precipitated calcium carbonate in the scallop shell.

*Acknowledgements.* This study was supported by the French Ministry of Research's Actions Concertées Incitatives Program (ACI PECTEN) and the INERIS Erika Program. We thank Spyros Fifas (IFREMER Brest) who provided us with scallops from the continental shelf and Monique Briand and Robert Marc for great help in map and figures confection. We also thank Jennifer Guarini for English corrections; and Ted McConnaughey and David Dettman for constructive comments that greatly improve the quality of the original manuscript.

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Figure captions:

Fig.1. Sampling stations in the Bay of Brest (shells A, B, C) and in an offshore location situated on the continental shelf (shells I, J) at 150 meters depth in the western part of Brittany (France).

Fig. 2. Biometric relationships between: A. Soft tissue dry weights (g) and shell height (mm) and B. Shell weight (g) and shell height (mm).

Fig. 3. Bay of Brest results in 2000: (A) Daily growth increments ( $\mu\text{m d}^{-1}$ ) for the three scallops A, B and C; (B)  $\delta^{13}\text{C}_{\text{DIC}}$  values (‰; (C) shells  $\delta^{13}\text{C}$  values (‰) in the three scallops A, B and C.

Fig. 4. Daily growth increments ( $\mu\text{m d}^{-1}$ ) and shell  $\delta^{13}\text{C}$  values (‰) for the scallop N (age class 4) from the Bay of Brest sampled at 30m in September 2000. Black arrows represent the winter growth cessations.

Fig. 5. Daily growth increments ( $\mu\text{m d}^{-1}$ ) and shells  $\delta^{13}\text{C}$  values (‰) for the scallops I (A) and J (B) from the continental shelf sampled at 150m in June 1998. Black arrows represent the winter growth cessations.

Fig. 6. A) Daily oxygen consumption ( $\mu\text{mol d}^{-1}$ ), B) Daily carbon precipitation ( $\mu\text{mol d}^{-1}$ ) and C) Respired to precipitated carbon ratio (i.e., "metabolic carbon availability" index) and  $\delta^{13}\text{C}$  values for shells A, B and C from the Bay of Brest during the year 2000.

Fig. 7. A) Daily oxygen consumption ( $\mu\text{mol d}^{-1}$ ), B) Daily carbon precipitation ( $\mu\text{mol d}^{-1}$ ) and C) Respired to precipitated carbon ratio and  $\delta^{13}\text{C}$  values for shell N from the Bay of Brest.

Fig. 8. A) Daily oxygen consumption ( $\mu\text{mol d}^{-1}$ ), B) Daily carbon precipitation ( $\mu\text{mol d}^{-1}$ ) and C) Respired to precipitated carbon ratio and  $\delta^{13}\text{C}$  values for shells I (right) and J (left).

Fig. 9.  $\delta^{13}\text{C}$  values versus respired to precipitated carbon ratio for all the shells (A, B, C, I, J and N).



















