LA-ICP-MS analysis of trace elements in biogenic minerals: time series recording of environmental changes

Background and objectives of the project

The objectives of the project were to improve our understanding of trace element behaviour in biogenic minerals *via* Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS) analysis. Indeed, it is well known that biogenic carbonates continuously record environmental conditions such as temperature, salinity and also pollutant level and thus represent potential archives of environmental changes that may have occurred during their lifetime. Focus was on carbonate secreting sponges from tropical seas and bivalves from coastal and deep-sea hydrothermal environments.

The Analytical Chemistry department (ANCH) at Vrije Universiteit Brussel (VUB) and...
the Geochemistry department of "Musée Royal d’Afrique Centrale" (MRAC, Tervuren, Belgium) had already optimised a high-resolution methodology, based on discrete point analysis, to study the variations of trace elements like e.g. Ba, Sr, Mg, Pb, U at very low concentrations (down to sub ppm levels). The aim of the project was to further develop this method and to check the potential of new types of biocarbonates from different marine environments with focus on short-(bivalves) and long-time (sclerosponge) environmental changes.

### Detailed description of results

#### Methodology

All trace element analyses were done by using a Fisons-VG Microprobe frequency quadrupled Nd-YAG (Neodymium doped Yttrium Aluminum Garnet) operating at 266 nm (ultraviolet wavelength), coupled with a Fisons-VG PlasmaQuad II+ mass spectrometer. The laser was operated in the Q-switched mode with a power of 2 mJ and a repetition rate of 10 Hz. The preablation time range was between 10 and 20 s depending on the substrate whereas, the acquisition times were all set at 20 s.

#### Sample preparation

The specimens were cut with a Labcut low speed diamond saw to obtain a 5-mm-thick slab perpendicular to the surface for the sclerosponge and a 5-mm-thick slab along the maximum growth axis for the molluscs (Fig. 1). The bivalves LA-ICP-MS analyses were made in the middle of the calcite layer and from the umbo towards the edge, approximately every 200 µm (Fig. 1). For sclerosponges, further details on methodology are given below, in B.

**Figure 1:** Methodology (A) *Isognomon ephippium* specimen sawed for LA-ICP-MS analyses and (B) scanning electron microscope picture of part of a slab analysed by LA-ICP-MS. Craters are about 30 µm in diameter and about 200 µm spaced.
LA-ICP-MS analysis

The most relevant elements analysed were $^{26}\text{Mg}$, $^{55}\text{Mn}$, $^{43}\text{Ca}$, $^{88}\text{Sr}$ and $^{138}\text{Ba}$. The instrumental instability and drift were corrected using $^{43}\text{Ca}$ as an internal standard. For quantification, the LA-ICP-MS data obtained on the samples must be compared with an external standard of known composition.

For the sclerosponge, the LA-ICP-MS data were compared to a "sclerosponge standard" cut out from the ancient part of the specimen with elemental composition established by ICP-MS measurements on eight acid dissolved micro-drilled samples. Accuracy of the LA-ICP-MS sclerosponge analyses was controlled by measuring trace element distribution in the aragonitic skeleton by inductively-coupled-plasma mass spectrometry (ICP-MS). Two series of 42 and 44 evenly spaced samples (approximately every 1.5 mm) were collected next to the LA-ICP-MS profile with a 1-mm-diameter drill parallel to the major growth direction of the sponge. Both analytical techniques gave very similar results confirming the validity of the methodology applied.

For the bivalves, analyses were calibrated using the NIST610 glass reference material as an external standard. However, the use of a non matrix-matched external standard (i.e. a glass standard for carbonate analysis) can lead to incoherent results due to matrix effects (Stix et al., 1995; Outridge et al., 1997; Vander Putten et al., 1999). In order to check whether the non-matrix matched standardisation produced accurate results, the concentrations determined with LA-ICP-MS were compared with ICP-OES and ICP-MS analyses of five successive samples taken from the calcite layer of each shell. These samples were prepared by carefully grinding the calcite surface layer of the shell part adjacent to the slab used for LA-ICP-MS with a 2 mm spherical drill (details in annex 4). The liquid results were compared with the average values of the corresponding series of laser ablation samples. Significant differences were observed between
LA-ICP-MS and ICP-OES/ICP-MS analysis on dissolved samples reflecting the difficulty of proper calibration in LA-ICP-MS in the absence of matrix matched standards. Consequently, mangrove bivalve LA-ICP-MS data are presented as a percentage of variation around the mean value (set to zero) of the transect for each profile. The black smoker data are however given in "ppm", what is valid for site by site comparison, but we must remember that they might not represent the exact trace element content.

The long-lived sclerosponge

Sclerosponges are sponges that secrete an aragonitic skeleton in which information on environmental conditions such as e.g. ambient water temperatures can be recorded. These sclerosponges have a very low growth rate, ranging from 100 to 300 µm/yr depending on the species, implying that even relatively small specimens can be several centuries old. We studied the *Ceratoporella nicholsoni* species that secretes a massive skeleton allowing high-resolution analysis like LA-ICP-MS.

The specimen studied (Fig. 2a) originates from the Bahamas (sampled 1985) and was obtained via the courtesy of Ph. Willenz (Royal Institute of Natural Sciences, Brussels). We assigned it a maximum age of 390 yr. based on a mean annual growth rate of 230 ± 45 µm/yr. obtained from *in situ* labelling of 10 specimens with calcein over a 10 yr. interval in Jamaica (Willenz and Hartman, 1999). The LA-ICP-MS ablation craters (Fig. 2b-c) were 30 µm or 50 µm in diameter, depending of instrumental settings, which means that, considering a mean annual growth rate of 230 µm/yr., the largest craters correspond to 3 months of skeletal accretion, whereas the smallest ones correspond to 1.5 months. The longest profile led to a time series extending from 1760 to 1983 with a measurement for every 1.6 yr. of growth. High resolution shorter profiles (one point analysis every 2.6 month), adjacent to the low resolution transect, confirmed the good reproducibility of the analysis whereas liquid analyses (dental-drill removal of CaCO₃ powders analysed by ICP-MS) allowed an external control on elemental concentrations obtained by LA-ICP-MS. The micro-drilled CaCO₃ samples for carbon isotope ratios determination were collected from a second slab of the *C. nicholsoni* studied, cut next to the one used for trace element determination.
Pb and $\delta^{13}$C results

It appears that sclerosponges record major global environmental changes in their skeleton, like atmospheric increase of lead and $\delta^{13}$C decrease (Fig. 3). This result yielded to a meeting presentation (Lazareth et al., 1999, cf. annexe 1) and a publication (Lazareth et al. 2000, cf. annexe 2).

Figure 3: Ceratoporella nicholsoni record of global environmental changes.

(A) $C. \text{nicholsoni}$ $\delta^{13}$C record compared with CO$_2$ content in ice-core air bubbles. Thick continuous line—$C. \text{nicholsoni}$ three-point running-average $\delta^{13}$C profile in $\delta$ notation relative to Vienna PDB standard; open diamonds—CO$_2$ records from Antarctic ice cores (data from Etheridge et al., 1998, Neftel et al., 1985, and Friedli et al., 1986).

(B) Evolution of Pb concentration in $C. \text{nicholsoni}$ from 1750 to 1990 compared...
with other Pb records. Solid line - *C. nicholsoni* three-point running-average LA-ICP-MS profile; open circles - Greenland snow Pb concentration, data from Murozumi et al. (1969); open triangle - Florida Keys *Montastrea annularis* (scleractinian coral) Pb/Ca ratio, data from Shen and Boyle (1987). Bar - analytical reproducibility of LA-ICP-MS analyses, $\pm 2\sigma$.

The $\delta^{13}C$ decrease observed over the past two centuries (analytical details in annex 2) is related to the increase of fossil-fuel burning and deforestation since pre-industrial time. Indeed, the resulting dramatic increase of atmospheric CO$_2$ has gone with a $^{13}C$ depletion (cf. review in Trabalka and Reichle [1986] and in Siegenthaler and Sarmiento [1993]). The *Ceratoporella nicholsoni* Pb profile is very similar to the one observed for Greenland snows (Murozumi et al., 1969) and for a Florida Keys coral (Shen and Boyle, 1987) (Fig. 3). In particular, it records the threefold input of anthropogenic Pb in the atmosphere after 1930. This observation has three major implications. First, it confirms the applied growth-rate value, at least for long-term measurements. Second, the similarity between our Pb profile and the one observed in Greenland snows shows that most of the Pb found in surface waters around the Bahama Islands has been derived from the atmosphere. Third, the coincidence between *C. nicholsoni* and the coral record from Shen and Boyle (1987) suggests that Pb could be incorporated in the carbonate skeleton of these two reef-building animals, belonging to distinct phyla, following a similar biological process.

**Other results**

Some other results are promising but need supplementary work to be conclusive. Among them is the similarity between most of the trace element profiles obtained (Fig. 4) that might indicate similar process of incorporation into the sclerosponge skeleton.

![Similarity between Sr, Mg and Ba profiles in Ceratoporella nicholsoni. Data are 3 point running averages.](http://perso.wanadoo.fr/arnaga/LA-ICP-MS_report.htm (6 of 21)22.11.2004 19:06:42)

Moreover, some cyclic evolution arises from those profiles (Fig. 5). The assumed periodicity have different frequencies, the longest ones being around 40-45 yr., followed by some around 25 yr, the shortest being around 10 yr.. At this stage, we don't have enough data to be conclusive about these cycles, which can not be interpreted for the moment.
Finally, as it is well known that Mg incorporation in carbonate is mostly temperature related, we compared our longest Mg profile with a sea-surface temperature (SST) curve from Mann et al. (1998, obtained from direct and indirect records (Fig. 6).

The comparison between Mg and SST revealed 3 features which are (i) some quite direct correlation (black arrows on Fig. 6) (ii) some time-shifted peaks (arc on Fig. 5) which might result from the use of a constant growth rate rather than a variable one and (iii) break of relation after 1920 which might be related to the fact that SST might not be the sole controlling factor for Mg incorporation.

We demonstrated the efficiency of LA-ICP-MS to obtain trace element profiles in sclerosponges. This research confirms that sclerosponges with a massive aragonitic skeleton represent a new promising archive for paleoclimate proxies. These may be studied in the future to complement data obtained from scleractinian corals with the advantage of accesses longer time scales. However, it is clear that further investigation is necessary to fully understand the potential of sclerosponges for reconstructing marine environmental changes.

The mangrove bivalve *Isognomon ephippium*

The work done on these mangrove bivalves has been presented during an international meeting (Lazareth et al. 2000) and is now published (Lazareth *et al.*, 2003).
It has been demonstrated that the shell chemistry of various bivalves represents a record of environmental parameters (e.g., Dodd, 1965; Lorens and Bender, 1980; Klein et al., 1996a,b). For instance, variations in sea-surface temperature (SST) can lead to changes in the Mg content of bivalve shells (Dodd, 1965; Fuge et al., 1993; Klein et al., 1996a,b; Vander Putten et al., 2000), whereas phytoplankton blooms and freshwater discharge can be recorded by the shell as discrete Ba peaks (Stecher et al., 1996; Vander Putten et al., 2000). Because of their high growth rate, bivalve shells record these environmental changes on a seasonal scale that can be easily resolved using laser-ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS) (e.g., Fuge et al., 1993; Raith et al., 1996; Price and Pearce, 1997).

Here, we analysed *Isognomon ephippium* (Fig. 7), a common bivalve of the Kenyan mangroves, from three systems with distinct freshwater flow characteristics (Table 1): (i) the Tudor Estuary (T), adjacent to Mombasa city, (ii) Gazi (G) and (iii) Mida (M), two mangrove ecosystems, respectively 50 km south and about 100 km north-east of Mombasa, (Fig. 7).

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<tr>
<td>River Kombeni</td>
<td>++</td>
<td>/</td>
</tr>
<tr>
<td>River Tsalu</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Gazi</td>
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<tr>
<td>River Kidogoweni</td>
<td>++</td>
<td>+</td>
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<td>Mida</td>
<td>/</td>
<td>++</td>
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</table>

Table 1: Freshwater inputs characteristics of the three Kenyan sampling sites. ++ - major contribution; + normal contribution; / - no contribution.

In order to obtain a preliminary indication on site differentiation, regarding trace element recording by the shells, we decided to compare the whole shell composition of specimens from the three sites. Subsequently, we made discrete point analyses via laser ablation inductively coupled plasma spectrometry (LA-ICP-MS) to get temporal information over the lifetime of the
Whole shell

One shell of five specimens from each site was analysed by ICP-OES, after removing of organic matter (through H$_2$O$_2$ treatment) and dissolution (HNO$_3$), for Mg, Mn, Sr and Ba (details in annex 4). The Mg shell contents show some variability between sites, whereas for Sr, the three sites give similar results with an overall mean of 771 ppm (Fig. 8a-b). For Mn and Ba on the other hand, the shells from the three sites show significant differences (one-way ANOVA). The Tudor shells show the highest concentrations for Mn and Ba followed by the Gazi shells which in turn are slightly richer in Mn and Ba than the shells from Mida (Fig. 8c-d). These lowest Ba and Mn content of the shells from Gazi and Mida could result from a poor nutrient availability of these sites.

Figure 8: Mg, Sr, Mn and Ba contents in the whole valve of *Isognomon ephippium* from Tudor, Gazi and Mida. Mean (ppm) ± 2σ indicated.

Trace element profiles

The LA-ICP-MS analysis were made in the remaining valve of one to two specimens from each site (T1 and T3 for Tudor, G4 for Gazi and M2 for Mida). Only most relevant data are presented here, but further details are given in annex 3-4.

Mg profiles: The Mg LA-ICP-MS profiles in the calcite shell layer of *Isognomon ephippium* are characterised by a sinusoidal-like pattern (Fig. 9).
It has been demonstrated that Mg variations in the shell of various types of bivalves show a positive correlation with seawater temperature (Dodd, 1965; Fuge et al., 1993; Klein et al., 1996a, b). Consequently, we decided to investigate more closely the Tudor Mg profiles (the full T1 profile and the second half of the T3 profile), to deduce a time-dependent Mg distribution for these shells. Therefore, a fitting was performed by arbitrarily forcing the Mg minima to coincide with the sea-surface temperature minima (SST), taking the date of collection as the reference time point. The fitting obtained between the Mg- and SST-profiles is very good (Fig. 10), pointing towards a dominant control of SST on Mg incorporation.

Sr profiles: The Sr patterns are more complicated than those of Mg. In the present study, the similarities between Mg and Sr in most shell profiles indicate that Sr incorporation might be Mg-dependent, and/or, to a certain extent, temperature dependent (Fig. 9). Nevertheless, the Sr profiles in T1 and in the second part of T3 are not perfectly in phase with Mg. For the Tudor (and Mida shells), some of the Sr maxima coincide with Ba peaks (arrows in Fig. 9-11). This might indicate that the factor(s) explaining the Ba peaks also have an influence, direct or indirect, on the incorporation of Sr.

Ba and Mn profiles: The Ba and Mn patterns in the calcite layer of the Tudor *Isognomon ephippium* are characterised by several narrow maxima (Fig. 11). These are regularly distributed...
The presence of Ba peaks has already been reported for *Mercenaria mercenaria* and *Spisula solidissima* (Stecher *et al.*, 1996) and for *Mytilus edulis* (Vander Putten *et al.*, 2000), in the latter case together with Mn peaks. In both cases, the Ba (Mn) peaks were related to periods of high phytoplankton productivity. In coastal tropical systems, like the Kenyan sites studied, the phytoplankton blooms are initiated essentially through an increase in nutrient inputs, linked with the monsoon regime. In addition to nutrients, freshwater is also enriched in barium relative to the open-ocean water (Broecker and Peng, 1982). As a result, freshwater inputs into tropical coastal systems not only cause phytoplankton blooms through increased nutrient supplies but also provide a significant input of barium that can be incorporated by phytoplankton, which can subsequently be ingested by filtering bivalves. The Tudor Ba profiles were thus compared with precipitation data, to which river outflows are, most probably, directly related. We used the Ba profiles calibrated against time via the Mg-SST fitting. Apparently, the sharp Ba (and Mn) maxima generally occur at the end of the rainy period associated with the Southeast monsoon (Fig. 12). Thus, a delay of a few weeks seems to occur between the increased run-off of freshwater carrying high contents of nutrients and dissolved Ba and the appearance of high Ba (Mn) concentrations in the shell. This can be explained by the fact that phytoplankton blooms in Kenyan coastal lagoons generally occur after the surge of rainfall, when turbidity has decreased again but nutrient contents are still favourable (M.H. Daro, personal communication). This also fits with the hypothesis that Ba is probably deposited in the shell as a result of enhanced ingestion of Ba/barite associated with the filtered particles and not via direct uptake of dissolved Ba. The Ba-Mn co-variation, indicates that (1) freshwater inputs also bring a large amount of Mn to the environment and (2) Mn incorporation occurs essentially via ingestion of enriched particulate
matter such as phytoplankton. The lack of a direct correlation between the magnitude of precipitation (and thus river runoff) and the amount of incorporated Ba (Mn) suggests, however, that the process is complex.

The whole shell Ba and Mn contents of the *Isognomon ephippium* studied are directly correlated to the hydrodynamic properties and nutrient inputs of the sites. The strong correlation between Mg in Tudor shells and sea-surface temperatures confirms the dominant control of SST on Mg incorporation. Although Sr profiles are often close to the Mg ones, some similarities with the Ba profiles underlines the complexity of Sr incorporation into the shell. The peaked profiles of Ba reflect the phytoplankton bloom successions as governed by monsoon regime. The similarity between Ba and Mn confirms that incorporation of Mn is for a large part also governed by productivity.

This study highlights the potential of *Isognomon ephippium* as environmental recorder. However, it appears that further investigations, on a larger population associated with a site survey, are necessary to improve interpretation of data and to extend to fossil equivalents which might thus be witnesses of ancient hydrodynamic/productivity characteristics.

The black smoker mussel *Bathymodiolus sp.*

In the following we present preliminary results on the shell chemistry of *Bathymodiolus sp.* (black smoker mussel), the third biocarbonate investigated. *Bathymodiolus sp.* specimens were collected during the AMORES programme (MAST-3, CE), in 1997, in three hydrothermal vent fields, Menez Gwen (MG), Lucky Strike (LS) and Rainbow (R) (*Table 2, Fig. 13*), from the Mid-Atlantic Ridge (MAR). These mussels represent potential records of the hydrothermal activity, through trace element variations in their shell.

<table>
<thead>
<tr>
<th>Menez Gwen (MG)</th>
<th>Depth</th>
<th>Bathymodiolus Samples</th>
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<tr>
<td>N37°50</td>
<td>800</td>
<td>MG2</td>
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<tr>
<th>Lucky Strike (LS)</th>
<th>Depth</th>
<th>Bathymodiolus Samples</th>
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<td>N37°17</td>
<td>1700</td>
<td>LS-003 (Eiffel Tower)</td>
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<tr>
<td></td>
<td></td>
<td>LS1-M5 (Bairro Alto)</td>
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<tr>
<td></td>
<td></td>
<td>LS1-M9 (Bairro Alto)</td>
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Mean trace element contents

Since most shells were covered with a Fe-Mn oxy-hydroxide crust, we first checked whether or not the calcite layer was contaminated from this crust. Therefore, we realised transversal profiles in the shell, from the exterior to the interior (Fig. 14a). The results clearly demonstrate that no contamination arise as the trace element contents in the calcite layer are almost constant, but also that little chemical differences exist between the two layers of the shell (Fig. 14b). Thus, the trace element profiles in the calcite layer of the *Bathymodiolus* sp. studied represent a record of environmental changes (± physiological effects) during the life-time of the mussels.

The mean content of some trace elements in the calcite layer (mean of all LA-ICP-MS analyses, shell by shell) reflects the fluid chemistry of the sites. Indeed, the Cu and Co contents of the *Bathymodiolus* sp. shells increase in the order MG, LS and R, as observed for the Cu and Co fluid
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contents (VonDamme, 1990; Douville et al., submitted). The same trend occurred for the shell Ce content, thus suggesting an increase in the Ce hydrothermal fluid content from MG to R (no fluid data) (Fig. 15).

Figure 15: Mean content of Cu, Co and Ce (ppm, mean of all crater) of the Bathymodiolus sp. studied. Yellow: MG2; dark and light blue: LS samples; green: R9M7.

For other elements, such as Ba and Mn for which the relative fluid contents are in the order R>LS>MG (Von Damme, 1990; Douville et al., submitted), the direct relation between shell and fluid composition is only apparent for the MG and LS specimens (Fig. 16).

Figure 16: Mean content of Ba and Ce (ppm, mean of all crater) of the Bathymodiolus sp. studied. Yellow: MG2; dark and light blue: LS samples; green: R9M7.

However, although the overall trace element contents of the calcite shell layer reflect the distinct fluid chemistry of the sites, the quantitative aspects are not respected. As an example, the Cu fluid content at Rainbow is globally five times that of Lucky Strike and 100 times that of Menez Gwen whereas the Rainbow Bathymodiolus sp. shell contains only one or two times more Cu than the shells from the other sites. This might indicate the effectiveness of the detoxification processes of these hydrothermal bivalves (Rousse et al., 1999).

Trace element profiles
The trace element contents along the shells show variations (Fig. 17-18) with different patterns depending on the site. This might be related to changes in the intensity of the hydrothermal activity and/or in the fluid chemistry but also to mussel movements.

Figure 17: Bathymodiolus sp. Mn (ppm) profiles.

Figure 18: Bathymodiolus sp. Pb (ppm) profiles.

For the specimens from Menez Gwen and Rainbow, Ba and Ce profiles are very similar (Fig. 19), which might indicate a same hydrothermal control on these two elements at these two sites.

Menez Gwen Rainbow
Moreover, for the Rainbow *Bathymodiolus* sp. shell, most of the trace elements follow the same trend, with a significant peak between 30 and 35 mm from umbo, even if some of them (*e.g.* U and Mo) are close to zero in other parts of the shell (Fig. 20). This might also be interpreted as reflecting chemical changes in the surrounding mixed seawater / hydrothermal fluid environment.

Finally, the Sr evolution is close to a cyclic one for all the *Bathymodiolus* sp. shells (Fig. 21a) and the Sr cycles from two different sites (Eiffel Tower and Bairro Alto) within the Lucky Strike system seem to be quite concordant (Fig. 21b). Finally, each cycle represents, at a first approximation, between 1.5 and 2.7 cm of shell accretion, depending of specimen and site, what is comparable to the estimated mean growth rate of such bivalves (~ 2 cm; Comtet, 1998). Thus, the Sr signature seems to be governed by an annual environmental signal.

**Stable isotopes**

The stable isotope ratios were determined in the *Bathymodiolus* sp. LS1-M5 (Bairro Alto, Lucky Strike) which presented two quite similar Sr cycles with a nice amplitude (Fig. 21b). Analyses were done at the Department of Earth Sciences at the Vrije Universiteit Amsterdam under the guidance of H.B. Vonhof. Very small amounts of calcite powder (approximately 20 - 50 µg each, representing 4 laser ablation craters on average) were obtained by using the Merchantek microdrill system (Fig. 22). The $\delta^{18}$O and $\delta^{13}$C ratios of the microdrilled CaCO$_3$ samples were determined on a Finnigan 252 mass spectrometer, equipped with an automated carbonate extraction line (called Kiel device). Samples were digested in concentrated orthophosphoric acid at a temperature of 80°C. The data are reported vs VPDB (Vienna Pee Dee Belemnite) with a reproducibility (1 sd), determined by replicate analysis of NBS-19, within 0.09 ‰ for $\delta^{18}$O and $\delta^{13}$C.
The $\delta^{13}\text{C}$ ratios range between $+3.46$ and $+4.14\%$ and the $\delta^{18}\text{O}$ between $+2.18$ and $+3.30\%$. Signals are mostly anticorrelated (Fig. 23). It appears that the Sr profile is close to both the $\delta^{13}\text{C}$ profile (correlated) and the $\delta^{18}\text{O}$ one (anticorrelated) (Fig. 24).

Figure 22: Microdrilling system. (A) Beginning and (B) ending of the sampling operation.

Figure 23: Stable isotope ratios, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, in the calcite layer of the shell of a *Bathymodiolus sp.* (LS1M5) from the Bairro Alto site of the Lucky Strike field (MAR). The bars represent the extension of each microsampling.
Mollusc shells are generally precipitated in $^{18}\text{O}/^{16}\text{O}$ isotopic equilibrium with the external medium. Moreover, the oxygen isotope fractionation between shell calcite and the surrounding water is temperature related as described by Epstein et al. (1953).

$$T = 16.5 - 4.3 (\delta^{18}\text{O}_\text{c} - \delta^{18}\text{O}_\text{w}) + 0.14 (\delta^{18}\text{O}_\text{c} - \delta^{18}\text{O}_\text{w})^2$$

with $c$: carbonate; $w$: water and $\delta^{18}\text{O}$ the oxygen ratio of the sample compared to an appropriate isotopic reference standard ($\delta^{18}\text{O} = \frac{1000R_s - R_{std}}{R_{std}}$ where $R_s$ and $R_{std}$ are the $^{18}\text{O}/^{16}\text{O}$-ratios of the sample and the standard). $\delta^{18}\text{O}_w$ is generally given relative to the SMOW standard whereas the $\delta^{18}\text{O}_c$ are given relative to PDB standard. To convert $\delta^{18}\text{O}_w$ values from SMOW to
PDB scale, 0.26 ‰ are subtracted from all $\delta^{18}O_w$ values (Coplen et al., 1983). To calculate the possible maximum range of temperature witnessed by the Bairro Alto Bathymodiolus sp., we used as $\delta^{18}O_w$ (i) the Mean Ocean Water oxygen isotope ratio value ($\delta^{18}O_w = 0$ ‰), as if the mussel lived in a pure deep-seawater environment and (ii) the mean $\delta^{18}O_w$ of Lucky Strike fluid endmember ($\delta^{18}O_w = 1.17$ ‰; Jean-Baptiste et al., 1997), as if the mussel lived in a pure hydrothermal fluid environment (without any mixing with seawater). The maximum range obtained (Table 3) include mean discrete temperature data obtained at Bairro Alto site in location where Bathymodiolus sp. were observed (Desbruyères et al., submitted).

<table>
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<th>Min.</th>
<th>Max.</th>
<th>Mean ± 1 sd</th>
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<td>6.85</td>
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<tr>
<td>pure hydrothermal fluid environ.</td>
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<td>11.27</td>
<td>9.2 ± 1.0</td>
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<th>Bairro Alto (LS) temperature measurements (°C)</th>
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<tr>
<td>mussels + shrimps</td>
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<td>3.4</td>
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<tr>
<td>mussels</td>
<td>6.7</td>
<td>1.8</td>
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Table 3: Calculated and measured water temperature data for the Bairro Alto site (Lucky Strike, MAR).

The $\delta^{18}O$ of the calcite layer of the Bathymodiolus sp. seems to be a good temperature proxy and might thus be used to reconstruct temperature changes of the mussel's environment. The temperature variations in such deep-sea hydrothermal environment are most probably related to variable inputs of hydrothermal fluids but we might also consider a seasonal-like control on this temperature as indicated by the Sr cycle pattern. Indeed, the close relationship between Sr and $\delta^{18}O$ ratios of the shell (Fig. 24) might indicate a major temperature control on Sr incorporation. However, a physiological and/or a primary productivity control must not be excluded as indicated by the $\delta^{13}C$ - Sr similarity (Perrier et al., 1994; Halley et Roulier, 1999; Vander Putten, 2000).

The chemistry of the Bathymodiolus sp. shells from three hydrothermal field of the Mid-Atlantic Ridge seems to reflect the relative chemical differences of the hydrothermal fluids emitted in each site. The trace element variations observed might be interpreted as changes in the surrounding mixed see-water / hydrothermal fluid environment. The (annual?) Sr cycles observed might be related to a (seasonal?) temperature control as showed by its similarities with the $\delta^{18}O$ signature. The temperature calculated from the $\delta^{18}O$ data are in agreement with those measured.
on the site. This confirm the validity of Bathymodiolus sp. $\delta^{18}$O ratios as temperature proxy. The $\delta^{18}$O of water samples taken close to the mussel sampling sites will be soon completed and will be used to further validate the $\delta^{18}$O-T°C pair. This study showed the great potential of the Bathymodiolus sp. shell as recorder of hydrothermal vent characteristics.

References


LA-ICP-MS analysis of trace elements in biogenic minerals: time series recording of environmental changes


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[1] *Monthly averaged values of sea surface temperature were obtained from the web site "http://ingrid.ldgo.columbia.edu/SOURCES/IGOSS/.ncmc/.monthly/.sst/" as blended from ship, buoy and bias-corrected satellite data (Reynolds and Smith, 1994).*

[2] *Precipitation data from the web site "http://ingrid.ldgo.columbia.edu/SOURCES/.NOAA/.NCEP/.CAMS_OPI/.mean/.prcp/" (as blended from data of NOAA, National Centers for Environmental Prediction, Climate Prediction Center) for a geographical setting (41.25E 3.75S) encompassing the Mombasa area with its coastal waters and for a time-period including the life-time of the bivalves studied (1990-1998).*