

# Marine Dynamics and Biological Records: the *Adamussium colbecki* Multi-Proxy

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## Abstract

During the oceanographic expedition of the PNRA (National Antarctic Research Program) in the austral summer 2005-2006, the PolarDove project research group carried out an experiment to verify the feasibility of using the indigenous bivalve *Adamussium colbecki* (Smith, 1902) as an environmental-climate proxy, exploiting the connection between the mineralogical composition of molluscs' shell and the water masses characteristics (temperature, salinity, etc.) in which they grow [1]. In order to it, a mooring was installed near shore of Terra Nova Bay (Ross Sea), 145 m depth, equipped to measure the hydrodynamic parameters and with 2 cages, in which 60 living *A. colbecki* specimens stayed for 1 year. After the mooring recovery, some selected specimens shells were sampled to analyze the isotopic ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) and trace element composition. In this study we present the mooring logistic preparation, data analysis and multi-proxy methodology of the experiment. We discuss also preliminary interpretations of the  $\delta^{18}\text{O}$  signal as a temperature proxy, with particular attention at the shell growth rate impact [2]. Because of its longevity [3], wide circumpolar distribution [4] and availability of fossil fragments [5], the use of *A. colbecki* as proxy is a powerful mean to inferred climatic information at high temporal resolution about either known or less known Antarctic regions.

## 1 Introduction

Water masses dynamics in the Antarctic region is a key issue for the comprehension of the global thermo-haline circulation and variability, that play a crucial role on climate control. The two Antarctic basins, Weddel Sea and Ross Sea contribute mostly to the production and ex-

port of dense water, the Antarctic Bottom Water (AABW) that constitutes the ocean bottom water at global extent [6]. During the last years the PolarDove (Polar Deep Ocean Ventilation) project has focused on the study of the deep ventilation in the Ross Sea, connected to the HSSW (High Salinity Shelf Water) formation processes, that take place in the Terra Nova Bay region,

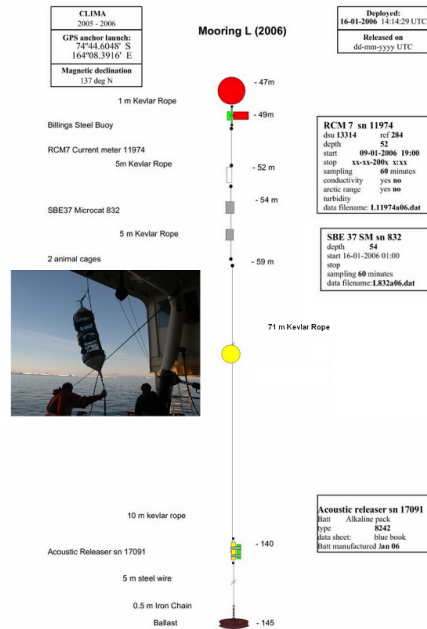
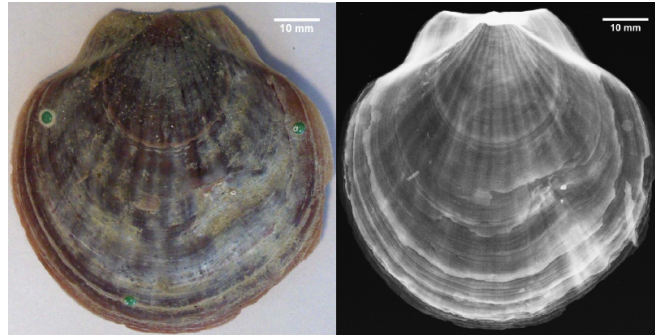


Figure 1: L mooring configuration with a photo of the *A. colbecki* bivalves cage deployment.

and to the HSSW northward flow that produces across the continental shelf slope the AABW new formation. The project deals with this issue with different approach, an experimental one, through the data analysis of the classical oceanographic instruments, a modelling approach and a multi-proxy approach. The last exploits the information recorded in the carbonatic matrix of animal species living in the water column. Since the 1950s [7] it's well-known the possibility to use biogenic carbonates as climate-environmental proxies, analyzing the isotopic (e.g.  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) and trace element (e.g. Mg/Ca, Sr/Ca) composition. This, indeed, depends on the environmental conditions (such as temperature, salinity, primary production...)

in which the mineralization occurs (isotopic equilibrium) and on merely biological effects, connected to the metabolism of the considered specie and specimen (kinetic and ontogenetic effects). The analysis of isotopic ratios and trace element composition has been applied with success to foraminifera, corals, ostracodes and molluscs [8, 9]. The Antarctic bivalve *Adamussium colbecki* (Smith, 1902) was selected as target specie to obtain high time resolution information about temperature and salinity of the water, in which it lives, from the isotopic and trace element analysis of its shell. The choice of the *A. colbecki* is due to its longevity [3], that allows to investigate a decadal time window, and to the wide geographic distribu-

Figure 2: Photo and mammography of one *A. colbecki*'s left shell.

Sample	H <sub>0</sub> (cm)	H <sub>1</sub> (cm)	ΔH (cm)	L <sub>0</sub> (cm)	L <sub>1</sub> (cm)	ΔL (cm)
B3	6.85	7.03	0.18	6.90	7.29	0.39
B9	7.20	7.42	0.22	7.20	7.32	0.12
G5	7.30	7.69	0.39	7.20	7.84	0.64
G19	7.55	7.79	0.24	7.60	7.98	0.38
V11	6.75	7.23	0.48	6.60	7.25	0.65
V14	6.80	7.00	0.20	6.80	7.00	0.20

Figure 3: Table with height (H) and length (L) of sampled specimens (see text for definition). 0 and 1 index refers to the deployment (January 2006) and to the recovery (January 2007) times respectively. ΔH (ΔL) are the differences between H1 (L1) and H0 (L0).

tion [4], that allows to infer information from other Antarctic regions, that are not monitored with traditional oceanographic instruments. Moreover, the possibility to recover some fossil fragments or individuals makes the multi-proxy approach a powerful tool to provide precious information for paleo-climatic models.

In this paper we will describe the methodology and the achievement of a first experiment carried out during the PNRA (National Research Program in Antarctica) oceanographic campaigns in the austral summer 2005-2006 and 2006-2007 in order to verify the feasibility to use the *A. colbecki*. Furthermore we deal with the issue of the isotopic equilibrium and the rel-

ative weight of kinetic and ontogenetic effects on the temperature- $\delta^{18}\text{O}$  relation. In the Ross Sea the *A. colbecki* experience extreme conditions, characterized by a temperature range of  $\sim 2^\circ\text{C}$ , but often, during winter season, with little excursions around the sea water freezing point. In these conditions the variations of  $\delta^{18}\text{O}$  signal are not only temperature dependent, but it's necessary to consider also the salinity variability. A contemporary measure of stable isotopes and trace element seems to be fundamental to fair estimate both the temperature and the salinity signals at high time resolution [10].

	Captivity	B3	B9	G5	G19	V11	V14
$\delta^{18}\text{O}$ ‰ (VPDB)	Mean	3.48	3.24	1.99	2.90	2.15	3.51
	St. Dev.	0.61	0.37	0.80	0.58	1.45	0.19
	Minimum	2.18	2.81	0.98	1.97	-0.68	3.33
	Maximum	4.30	4.07	3.62	3.83	3.86	3.98
$\delta^{13}\text{C}$ ‰ (VPDB)	Mean	1.19	1.46	-0.84	1.35	1.12	1.10
	St. Dev.	0.26	0.23	0.94	0.14	0.36	0.14
	Minimum	0.80	1.17	-1.93	1.12	0.57	0.96
	Maximum	1.46	1.81	1.31	1.63	1.57	1.42
	Previous Period						
$\delta^{18}\text{O}$ ‰ (VPDB)	Mean	4.25	3.47	3.30	3.69	2.25	3.38
	St. Dev.	0.65	0.49	0.55	0.27	1.10	0.36
	Minimum	2.83	2.47	2.09	3.05	-0.23	2.87
	Maximum	5.23	4.29	4.07	4.00	3.72	4.00
$\delta^{13}\text{C}$ ‰ (VPDB)	Mean	1.43	1.63	0.89	1.48	1.54	1.18
	St. Dev.	0.20	0.19	0.58	0.19	0.22	0.35
	Minimum	1.07	1.18	-0.82	0.97	1.06	0.71
	Maximum	1.86	1.92	1.46	1.84	1.90	1.95

Figure 4: Table containing mean, standard deviation, minimum and maximum values of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  measurements for each specimen for both the captivity and the previous period.

## 2 Materials and Methods

The experiment was set up in the Terra Nova Bay (Ross Sea), placing 2 cages at -59 m depth along the Kevlar wire of the mooring L (position: 74°44'.604 S, 164°08'.391 E; depth: 145 m), which was equipped with a current meter Aanderaa RCM 7 to measure the current speed and the temperature (sampling time: 60') and with a MicroCAT SBE probe to measure temperature, pressure and conductivity (sampling time: 20') (Figure 1). The instruments were installed on 16th January 2006 and were recovered on 31st January 2007. The current meter worked correctly during the period, whereas the probe worked very partially, inhibiting the data recover.

In the cages (Figure 1), specially made from molluscs breeding lanterns, were placed 60 *A. colbecki* specimens, previ-

ously collected near the Italian Mario Zucchelli Station and identified with numbered labels on the shell. During the yearlong deployment, 5 of the 60 initial individuals died. Before the deployment and after the recovery the maximum dimension along the dorso-ventral axis from umbo to the ventral margin (H) and the maximum dimension parallel to the hinge (L) were measured for each specimen's shell with a calibre (accuracy: 0.01 cm).

The shells of 6 specimens, whose we have also the mammography plates and that aren't damaged at the margin, are available to analyse the isotopic and trace metal composition. The shells were cleaned via ultrasonic baths in milliQ water and drying in oven at 50°C.

The central zone of the left valve [11] were sectioned by hand with a drill and were sampled through a micromill sampling sys-

tem (New Wave Research). The sampling occurred drilling in continuous from the shell ventral margin toward the umbo; for one step the sampled distance was 1/12 of the specimen's growth in captivity during the experiment. Step by step the photographs of the sampled shell were acquired in order to measure a posteriori the actual sampling distance. For each specimen we collected 36 samples to cover a time window of about 3 years. The samples' powder were sent to the geochemical laboratory IAMC-CNR of Naples (Italy) to proceed with the isotopic analysis of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ , using an automated, continuous-flow carbonate preparation GasBenchII device and a ThermoElectron Delta Plus XP mass spectrometer. The reference standards are the Carrara marble (internal) and the international NBS19 (external). Standard deviations of carbon and oxygen isotope measures were estimated to be 0.1 and 0.08‰. All values are reported using delta notation ( $\delta$ ) in parts per mil (‰) relative to the VPDB [Vienna Pee Dee belemnite] standard.

From one part of the shell, remained after the cut with the drill, we obtained a 500-700 $\mu\text{m}$  thick slice on glass slide by incorporating in epossidic resin. The slices were photographed at the stereoscope. 3 specimens were also photographed near the margin at the Scanning Electron Microscope.

### 3 Results

The Figure 2 shows a photo and a mammography plate of one *A. colbecki*'s left valve, before the micromill sampling. The table in Figure 3 reports the identification codes and the morphometric parameters of the 6 studied specimens. The differences  $\Delta\text{H}$  and  $\Delta\text{L}$  measure the spec-

imens' growth during the captivity in the H and L directions. The error associated to  $\Delta\text{H}$  and  $\Delta\text{L}$  is 0.02 cm by propagating the calibre error. We calculated from the Stereoscopic and SEM photographs the shell thickness, that is 150-600 $\mu\text{m}$  in the sampled part. The thickness is not uniform, but shows some discontinuities due to periodic slow down or break of the shell growth.

The table in Figure 4 reports the base statistics for each specimen, while the graphs in Figure 5 show the trend of measured  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  for B9 and V14 specimens. The origin coincides with the ventral margin. Both in the Figure 4 and in the Figure 5 we distinguish the captivity period from the previous one.

For the captivity and previous period we observed that B3, B9, G19 and V14 have  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  mean values comparable within one standard deviation; whereas G5 and V11 show a high  $\delta^{18}\text{O}$  variability and mean values lower than the other. In general the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  mean values are lower during the captivity than in the previous period.

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  trend is variable for the different specimens in both considered periods (see Discussion). Moreover the statistical standard deviation is higher than the analytical error; that is the data variation is an actual variation in the signal recorded by the animal.

For 4 specimens  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are significantly ( $p < 0.001$ ) correlated with correlation coefficient higher than 0.82 for the captivity and/or the previous period.

Figure 6 represents our data for the captivity period on a ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) plane and compares them with the predicted ones for conditions of isotopic equilibrium mineralization. The vertical lines mark two  $\delta^{13}\text{C}$  extreme values for spring and summer,

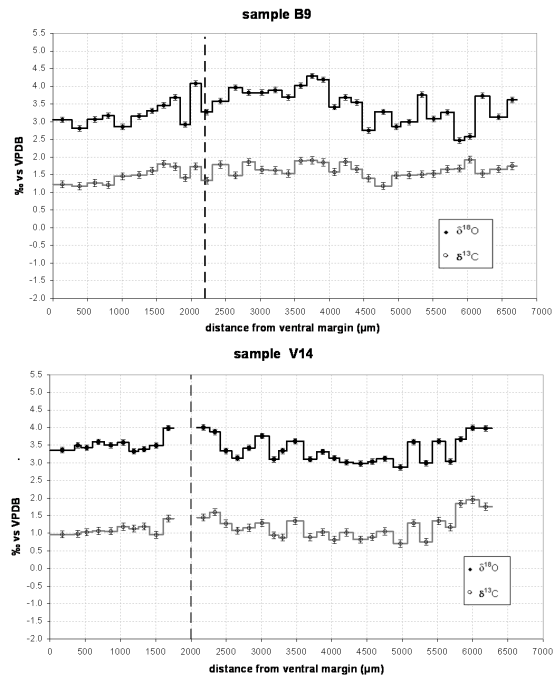


Figure 5: Sequences of measured  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  from the ventral margin (origin of the axes) toward the umbo for B9 and V14 specimens. The horizontal scale extends to the whole sampled region and it is different for B9 and V14. The sampling rate is about 1/12 of  $\Delta H$  and the error bars are equal to the analytical error (0.08 and 0.10 ‰ for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  respectively). The captivity ranges from the origin to the vertical dashed line.

such as reported by Barrera et al. [11] and calculated from water  $\delta^{13}\text{C}(\text{DIC})$ , pH and temperature near McMurdo Sound (Ross Sea). The horizontal lines delimit the  $\delta^{18}\text{O}$  interval, that is predicted from temperature data, measured at the mooring L, and based on the equation (\*) for the isotopic equilibrium mineralization, that was obtained by Kim and O'Neil and reported by King and Howard [12], in the following form:

$$(*) T(^{\circ}\text{C}) = 16.1 - 4.64 (\delta^{18}\text{O}_s - \delta^{18}\text{O}_w) + 0.09 (\delta^{18}\text{O}_s - \delta^{18}\text{O}_w);$$

$2\delta^{18}\text{O}_s$  is the measured  $\delta^{18}\text{O}$  of the sample and  $\delta^{18}\text{O}_w$  is the  $\delta^{18}\text{O}$  of the wa-

ter, where the mineralization of the sample occurred. Both are expressed as ‰ VPDB. In our case  $\delta^{18}\text{O}_w$  is equal to  $-0.38\text{‰}$  SMOW, that was converted in the VPDB scale by subtracting  $0.27\text{‰}$ . This  $\delta^{18}\text{O}_w$  value was measured from a water sample collected during the Italian 1987-1988 austral summer oceanographic campaign in a site nearby the mooring L at 50 m depth [13]. The most of the data stay within the predicted interval for  $\delta^{13}\text{C}$  and the  $\delta^{18}\text{O}$  data are centred in the interval calculated from the equation (\*). A better agreement would be possible, if we had

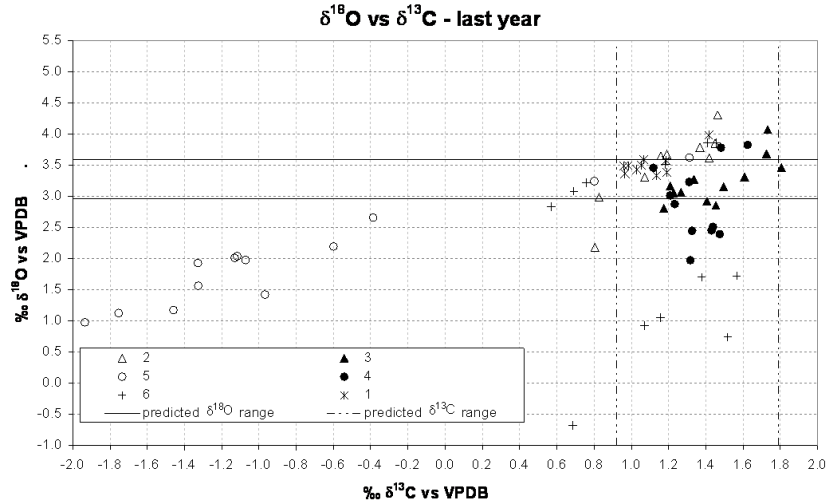


Figure 6: Scatter plot of ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) pairs for the captivity period. The vertical dashed lines indicate extreme values for  $\delta^{13}\text{C}(\text{DIC})$  in spring and summer as discussed inside the text, while the horizontal lines represent the extreme predicted values for  $\delta^{18}\text{O}$ , based on the (\*) equation and for  $\delta^{18}\text{O}$  equal to  $-0.38$  ‰ SMOW.

also a measure of  $\delta^{18}\text{O}$  for winter conditions. The G5 and V11 data don't lie in the predicted zone; they already show some differences in the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  mean values and they are the specimens with the higher growth rate.

#### 4 Discussion

The low specimens' mortality and the growth rate survey argue the success in the experiment achievement. Based on the Von Bertalanffy's equation parameters [14] and on the data in Figure 3, we established an age between 10 and 12 years for the individuals in January 2006. The growth rates are comparable with those revealed in the literature [15, 16].

Absolutely the  $\delta^{18}\text{O}$  values are compatible with the ones measured both by Heil-

mayer et al. [14] and by Barrera et al. [11]. The former reported values between 3.04‰ and 3.92‰ for 2 specimens and the latter between 3.65‰ and 4.75‰ for one specimen. Furthermore Barrera et al. [11] measured  $\delta^{13}\text{C}$  values varying in the range 0.09-2.50‰, that are compatible with our data with the exception of G5 specimen. The lower mean values in the captivity period in comparison with the previous are due to the different conditions which the animals experienced and are also due to a decrease of the stable isotopic ratios on the shell from the umbo to the ventral margin. This trend was already pointed out by Richardson [1] and is the result of the sum of kinetic effects and the signal integration during the life time, because of the growth bands overlapping in the shell formation. The correlations between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$

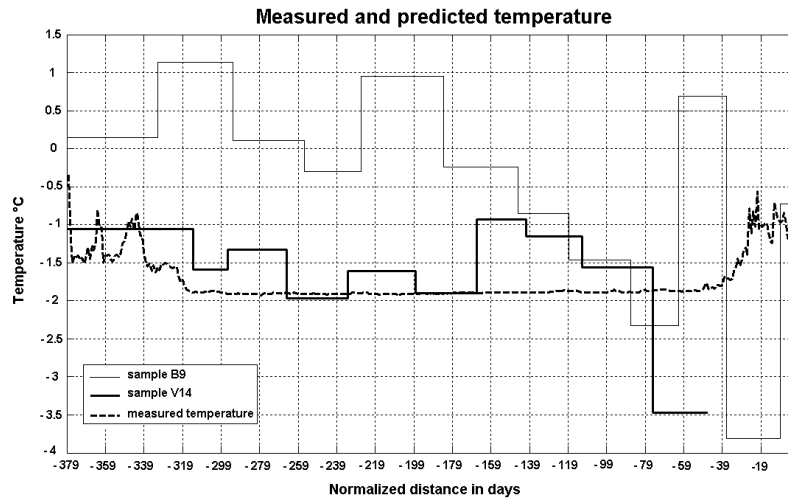


Figure 7: Trend of the mooring L measured temperature (daily averaged) and the predicted temperature from B9 and V14's  $\delta^{18}\text{O}$  data, using (\*) equation for  $\delta^{18}\text{O}_w = -0.38\text{‰ SMOW}$ .

in B3, B9 and G5 for the captivity period may be considered an indicator of presence of kinetic effects, that are consequence of an incomplete isotopic fractionation of the  $\text{CO}_2$  during the mineralization, as suggested by the McConnaughey's model [17] for the biogenic carbonates. According to the same model the biogenetic effects and, in particular, the incorporation of  $\text{CO}_2$  derived from the respiration, should be the reason of the low  $\delta^{13}\text{C}$  value, that we revealed for the G5 specimen. In Owen et al. [2] a similar shift in the ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) plane for the G5 and V11 specimens occurs for higher growth rate shells and is ascribed to a sum of kinetic and variable metabolic effects. In fact G5 and V11 are the specimens with the highest growth rate in our specific dataset. In Figure 7 we report in detail the comparison between the measured temperature (daily mean in  $^{\circ}\text{C}$ ) and the predicted one (from (\*) equation). The  $\delta^{18}\text{O}$  signal is

uniformly normalized for the captivity period (379 days), by supposing an uniform growth of the individuals during the year. The graph reports the trend for B9 and V14 specimens. The latter, which has a low growth rate and doesn't show  $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$  correlation during the captivity, has the better agreement between measured and predicted temperature.

In general, our data overestimate the temperature. Klein et al. [10] highlighted similar results with differences of  $\sim 10^{\circ}\text{C}$ , that were due to the salinity variations. The classical isotopic equilibrium equations, like (\*), don't take into account these variations. Indeed, the salinity impact is expressed by the  $\delta^{18}\text{O}_w$  term, that generally is forced to be constant and equal to a seasonal mean value [9]. To deal with this question a second experimental phase has been planned, in which the trace metal composition on the shell will be mea-



sured along the dorso-ventral axis via laser ablation and mass spectrometry (ICP-MS) technique. E.g. for other biogenic carbonates Mg/Ca and Sr/Ca ratios were already used as temperature proxies, unaffected by salinity variations [10]. The measure of trace element composition would allow an independent evaluation of the temperature and to estimate separately the salinity and temperature contribution to the  $\delta^{18}\text{O}$ . Moreover, it is impossible to superimpose directly the measured and predicted temperature trends by scaling uniformly the captivity period, but it would be necessary to take into account the seasonal growth rate of each specimen. Though there aren't direct field measures, we reasonably suppose that there is a slow down or a break in the growth of *A. colbecki* in the winter, based on the thickness discontinuities and on the observations for growth rate in laboratory experiments [16]. In such a case, our data would be compared only with summer temperatures and this would partially justify the temperature overestimation. The comparison is also affected by the  $\Delta H$  error, that causes a  $\sim 30$  days uncertainty for the dates in the Figure 7.

## 5 Conclusions

The experiment succeed in the technical achievement and demonstrated the feasibility of using the living *A. colbecki* specimens as target for similar experiments and perspective developments, because of the low mortality of the individuals during the experiment.

The stable isotopes analysis showed that the mean  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are in the range predicted for the isotopic equilibrium, according to the equation of Kim

and O'Neil, for the low shell growth rate individuals. Conversely, in our dataset the individuals with higher shell growth rate differ from the equilibrium because of kinetic and variable metabolic effects [2]. A direct comparison between measured and predicted temperature showed that the temperature alone is not enough to take into account  $\delta^{18}\text{O}$  evolution. This result is in agreement with the hypothesis that the salinity contribute to  $\delta^{18}\text{O}$  signal isn't negligible. In our particular conditions *A. colbecki* experience temperature range of about  $2^\circ\text{C}$ , often near the freezing point and salinity of the new formed HSSW could play a crucial role in the recorded signal. This question is under study by carrying out some measures of the shell trace element composition via laser ablation and ICP-MS technique.

This study highlighted the critical issue of matching the sequences measured on the shells and the time series revealed by the instruments. This is due to the uncertainty on the time life of the shell when mineralization occurred, especially in case of slowing down or breaking of the shell growth in the winter season.

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