

# Effect of elevated pCO<sub>2</sub> on the boron isotopic composition and B/Ca ratio into the Mediterranean coral *Cladocora caespitosa*

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The Intergovernmental Panel on Climate Change (IPCC) predicts an increase in atmospheric CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) to levels of 490 to 1250 ppm in 2100, depending on the socio-economic scenario considered. Because one third of anthropogenic CO<sub>2</sub> emissions has been stored in the oceans, ocean pH has already declined by 0.1 unit compared with preindustrial values (Orr et al., 2005) and is predicted to decrease by another 0.4 units by the end of the century (Caldeira and Wickett, 2003). Seawater acidification will lead to a shift in inorganic carbon equilibria towards higher CO<sub>2</sub> and lower carbonate ion concentrations.

The carbonate ion is one of the building blocks of calcium carbonate (CaCO<sub>3</sub>) and changes in its ambient concentration can affect the ability of calcifying organisms to precipitate CaCO<sub>3</sub>. The Mediterranean sea is an interesting place to study global change and coral calcification because it is land-locked and acts like a miniature ocean, which reacts faster to environmental changes than the open ocean (Béthoux et al., 1990). It is one of the potential hot spots where critical pH values are reached first and should thus be regarded as a model system in studying changes of seawater chemistry and its effects on marine calcifiers.

In this study we have measured the boron isotopic composition and B/Ca ratio into the skeleton of the mediterranean coral *Cladocora caespitosa* (Picture 1).

Because boron isotopic signature in carbonates is controlled by pH, it may be used to better understand mechanisms of coral calcification, and the seawater chemistry at the site of calcification, which is difficult to obtain otherwise.

Corals should provide an ideal material for recording the paleo-pH of surface water. Their growth rates are high and they have high concentration of boron (5 times higher than in foraminifera). As with any promising new proxy, it is necessary to calibrate it, one goal of this study.

Why using boron isotopic composition as pH-recorder (Fig. 1)?

The distribution of the two major species of boron is pH-dependent

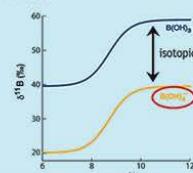
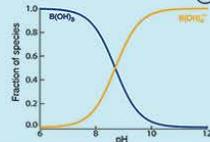
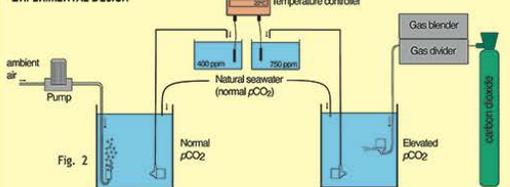


Fig. 1: Distribution of the two major species of boron (A), and boron isotopic composition of individual species (B) vs. seawater pH



Picture 1: *Cladocora caespitosa* is an endemic coral present throughout the whole Mediterranean (Zibrowius 1980; Peirano et al. 1998). Its vertical distribution range from 5 to 40 m depth and it is well adapted to turbid coastal environments with high sedimentation rates (Zibrowius 1974; Peirano et al. 2005).

## EXPERIMENTAL DESIGN



## CORAL COLLECTION and STAINING

Three colonies of *C. caespitosa* were collected in the Bay of Villefranche (43°41' N, 7°18' E) at 25 m depth, transported to the laboratory and divided into several nubbins. They were cleaned from epiphytes, associated fauna, and sediment, tagged on PVC supports and randomly assigned to one of the two treatments. These nubbins have been maintained during one year under the experimental conditions and have experienced the four seasons. During the whole experiment, no artificial food was supplied to the tanks, but corals were considered naturally fed because seawater supplied to the aquaria was not filtered.

At the beginning of the experiment, coral skeletons were stained with Alizarin (used as a chronological marker) (Picture 2A). At the end, corals were sacrificed, tissues were removed (NaOH) and the skeleton deposited during the experiment (i.e. after alizarine) was used for isotopic and trace element measurements (Picture 2B).

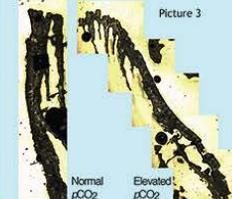
## BORON ISOTOPIC COMPOSITION

Samples were obtained using a conventional sampling method along a transect (Picture 3). Samples were mounted in epoxy and polished with diamond paste down to 1 µm. They were then ultrasonicated in double distilled water to avoid any contamination.

δ<sup>11</sup>B values were obtained using a CAMECA ims 1270 ion microprobe

### Results

No difference in δ<sup>11</sup>B between the treatments: 30.05 ± 1.51 ‰ vs. 29.33 ± 1.28 ‰ respectively for normal and elevated pCO<sub>2</sub>, corresponding to pH of 8.94 ± 0.11 and 8.89 ± 0.08 (Fig. 3).



Picture 3

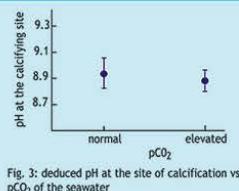
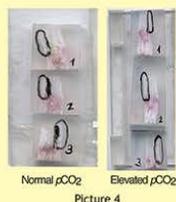


Fig. 3: deduced pH at the site of calcification vs. pCO<sub>2</sub> of the seawater

Despite a difference in the seawater pH (8.1 at normal and 7.9 at elevated pCO<sub>2</sub>), the pH calculated from the δ<sup>11</sup>B is the same for the two experimental conditions. The calcification rate measured during this study was not affected by an increase of CO<sub>2</sub> (Metapala et al. in prep), that can explain the lack of difference in δ<sup>11</sup>B between treatments. Another explanation is the huge standard deviation of the values. The alkaline pH measured here at the site of calcification imply a high control of the animal independently of seawater pH, questioning the use of δ<sup>11</sup>B as a pH proxy.

## B/Ca RATIOS

<sup>11</sup>B/<sup>10</sup>B ratios were analysed following the analytical method by Montagna et al. (2006, 2007). We used a high sensitivity pulsed laser ablation system, coupled with a Varian 820 ICP-MS. Before acquisition, surface contamination was removed by pre-ablating the coral surface twice, with a 230 µm diameter spot. The NIST glass standard 612 and a Porites pressed powder disc were analysed before and after each run on the samples, together with the acquisition of the background (gas blank) for 60s, allowing correction for long-term machine drift during analysis. The precision for B/Ca, calculated as the RSD (1σ/norm) of 60s acquisition on the Porites standard, was ~6%. The boron concentrations for the samples of *Cladocora caespitosa* were obtained analyzing different portions of the "fresh" thecal wall precipitated during the experiment (Picture 4).



Picture 4

Results of B/Ca did not show any difference between the treatments: 0.926 ± 0.06 vs. 0.929 ± 0.08 mmol/mol for normal and elevated pCO<sub>2</sub> respectively (Fig. 4). The long-period variations of B/Ca ratios observed for both the corallites are primarily controlled by the 9°C temperature change during the experiment. A similar relationship has been found by Montagna et al., (2007) studying the same species in the North Adriatic Sea. However, since borate is thought to be the B species incorporated into carbonates and its concentration in seawater is pH dependent, different B/Ca ratios were expected between treatments. The results are similar within error, indicating that the pH is not the primary factor controlling the B/Ca ratios in *C. caespitosa* and other factors, such as temperature, are probably more important.

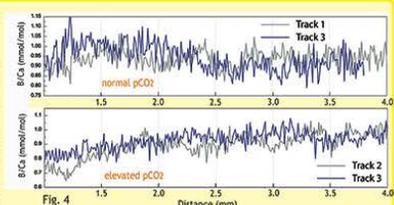


Fig. 4

Table 1: comparison of the δ<sup>11</sup>B data with other literature values.

Reference	Species	δ <sup>11</sup> B (‰ SD)	seawater pH
Vengosh et al. (1991)	Porites (tropical)	30.5	
	Fungia (tropical)	30.2	
	Sclerophyllia poritiformis (tropical)	31.0	
Hemming & Hanson (1992)	Porites (tropical)	29.3 ± 0.6	
	Porites (tropical)	29.8 ± 0.5	
	Alveolaria (tropical)	24.3	
Gallardet & Allegre (1995)	Acropora (tropical)	25.9 ± 1.0	
	Porites (tropical)	26.6 ± 0.3	8.2
Reynaud et al. (2004)	Acropora (tropical) - culture	25.9 ± 0.1	7.98
Honish et al. (2004)	Porites cylindrica (tropical) - culture	21.7	7.82
	Porites (tropical)	24.9	8.06
	Acropora mullis (tropical) - culture	21.1	7.82
Dorell et al. (2006)	Porites (tropical)	25.9	8.06
	Porites (tropical)	24.5	8.26
	Porites (tropical)	24.7	
Xiao et al. (2006)	Acropora corallopora (tropical)	26.3 ± 0.3	8.07
	Sclerophyllia poritiformis (tropical)	29.4 ± 0.1	8.11
	Porites poritiformis (tropical)	28.4 ± 0.1	8.08
Hemming et al. (2007)	Porites (tropical)	25.9	7.98
	Porites (tropical)	24.5	8.06
Colinvaux (unpublished data)	Porites (tropical)	25.7 ± 1.7 (GCM)	8.1
This study	Cladocora caespitosa (Mediterranean)	30.0 ± 1.5	8.1
	Cladocora caespitosa (Mediterranean)	29.3 ± 1.3	7.9

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