# Coral Li/Ca in micro-structural domains as a temperature proxy

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## INTRODUCTION

Scleractinian corals secrete calcareous skeletons with minor and trace elements being incorporated as a function of the physical and/or chemical parameters in the ambient seawater in which they grew, although coral physiology has to varying degrees imprinted a 'vital effect' complicating paleo-climate reconstructions.

Trace element systematics in corals (e.g. Sr/Ca, U/Ca, Mg/Ca, B/Ca) is therefore potentially capable of providing reliable marine environmental records at high temporal resolution, such as records of water temperature, a critically physical attribute of the ocean in governing the climate system.

In order to decipher environmental from physiological effects we have utilised high sensitivity laser ablation ICP-MS to examine Li/Ca variations in the aragonite theca of living specimens of shallow (*Cladocora caespitosa*) and deep-water (*Lophelia pertusa*) corals at different temperature-depth regimes, together with samples cultured in temperature-controlled tanks. In addition, we analyzed the Li/Ca ratios in the aragonitic umbo of the bivalve *Mytilus galloprovincialis*. The aim was to rigorously test the temperature dependence of lithium, previously documented by Marriott et al. (2004) and Delaney et al. (1989), investigating the aragonitic portion of other marine biogenic carbonates.

The application of Li/Ca (Li/Mg) on specifically identified micro-structural domains will offer a unique opportunity to reconstruct changes in water T at different depth in the water column.

## MATERIALS AND ANALYTICAL METHODS

***Lophelia pertusa*** (cold-water coral): Recent samples were collected at different water depths (100 – 1000 m) from the North Atlantic and the Mediterranean, covering a large latitudinal transect (72°N to 7°S). This geographical range encompasses a wide variation of environmental settings, from eutrophic to oligotrophic, with temperature of 5.5 to 14°C and different seasonality.

***Cladocora caespitosa*** (high-latitude coral): Nubbins of the zooxanthellate coral were stained with Alizarin Red and maintained for 87 days in aquaria at 4 different temperatures (15, 18, 21 and 23°C; ± 0.2°C precision).

***Porites* sp.** (tropical coral): Coral core collected in Jarvis Island (South Pacific Ocean). Li/Ca ratios from Marriott et al. (2004), analyzed by MC-ICP-MS.

***Mytilus galloprovincialis*** (bivalve): Living samples were collected at 7m water depth in the North Adriatic Sea with SST ranges from 7.8 to 24.5°C.

**Li/Ca, Sr/Ca, Mg/Ca** and **U/Ca** ratios were analysed along the aragonite theca using a high efficiency laser ablation system (LambdaPhysik LPX 120i ArF excimer laser with a wavelength of 193 nm) connected to a Varian 820 MS. Laser was pulsed at 5 Hz with an energy of 50 MJ. The laser beam was masked using a rectangular slit 20 µm wide and 220 µm long, parallel to the outward growth axis of the wall in *L. pertusa*. A 137µm diameter spot was used for *C. caespitosa*, focusing the beam on the theca wall exposed by cross- sectioning the corallites. Surface contamination was removed by two pre-ablation scans using a 230 µm spot.
$\delta^{18}O$ and $\delta^{13}C$ were obtained by milling the thecal wall of *L. pertusa* at 100 µm resolution using a computer-controlled Micromill.

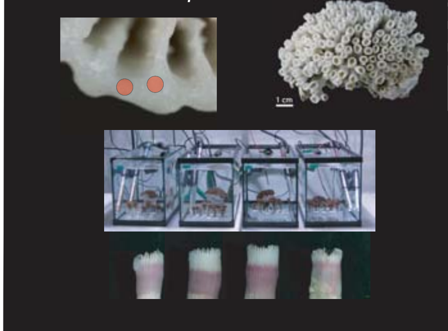



Fig. 1A, The *C. caespitosa* samples were cultured in 4 tanks at 15, 18, 21 and 23°C after being stained with Alizarin Red. Geochemical analyses were carried out on the centres of calcification and fibrous aragonite along the thecal wall (red dots)


Fig. 1B. The thecal wall of *L. pertusa* was investigated for trace elements (red lines) and stable isotopes (light red area) at fine-scale resolution.

Multi-component analysis on the thecal wall of *L. pertusa* and *C. caespitosa*

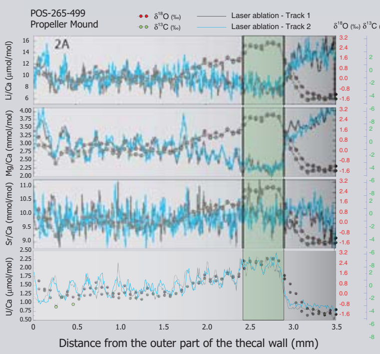
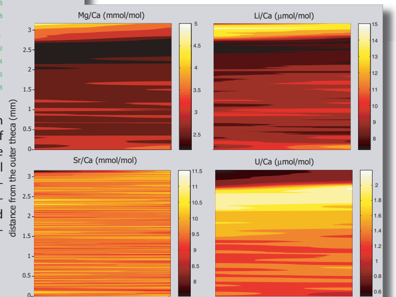



Fig. 2A. Li/Ca, Mg/Ca, U/Ca, Sr/Ca ratios and stable isotopic variation along the thecal wall of *L. pertusa* (Propeller Mound). The effects of the coral biology ("vital effect") on the geochemical composition are not uniform over the skeleton and are often correlated with skeletal micro-structural features, with the centers of calcification being enriched in Mg/Ca and Li/Ca and depleted in U/Ca, $\delta^{18}O$ and $\delta^{13}C$ compared to the fibrous aragonite. Sr/Ca, Li/Ca and Mg/Ca values used for the calibrations were obtained from the fibrous aragonite portion with $\delta^{18}O$ values closest to equilibrium (green area in Fig. 2A).



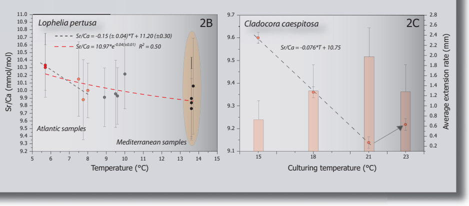

Mg/Ca, Li/Ca, Sr/Ca and U/Ca maps for the thecal wall of *L. pertusa*. The maps were obtained by gridding and countouring two parallel laser ablation tracks in Fig. 1B. Areas with low Mg/Ca and Li/Ca and high U/Ca ratios represent the coral microstructures selected for the calibratios.

### *Sr/Ca vs. Temperature*

Sr/Ca vs. Temperature calibrations

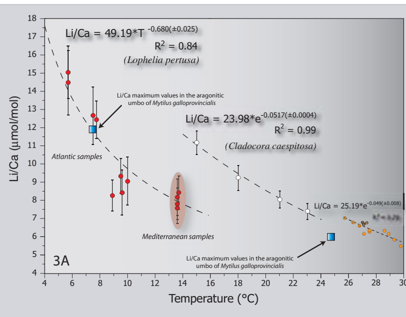
2B: The linear regression calculated using T values below 8°C is similar (within error) to the one obtained by Cohen et al. (2006) in the same T range. Considering all the values the calibration becomes exponential with decreasing temperature sensitivity.

2C: Sr/Ca ratios and Average extension rate between 15 and 18°C are negatively and positively correlated with T, respectively. Linear regression is similar to the one obtained by Montagna et al. (2007). At 23°C Sr/Ca is clearly affected by a growth-rate-related kinetic effect, complicating the T reconstruction.



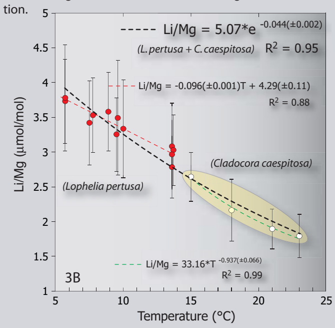

### *Li/Ca vs. Temperature*

3A. Li/Ca vs. Temperature relations for the scleractinian corals *L. pertusa* and *C. caespitosa*. The best fit is obtained using a weighted power and exponential function, respectively. Error bars represent 1SD of specific coral components (i.e. fibrous aragonite with $\delta^{18}O$ closest to equilibrium) and are larger than the analytical uncertainty. Also plotted values for *Mytilus galloprovincialis* (blue squares) and data ricalculated from Marriott et al. (2004) (orange hexagons). Li/Ca is controlled primarily by temperature, with the Li/Ca ratios decreasing with increasing water temperature, indicating a stronger sensitivity at lower temperatures.




### *Li/Mg vs. Temperature*

Temperature does not seem the only factor affecting the Li/Ca ratios in marine biogenic carbonate and other mechanisms, such as, for example, pH-induced calcification rate (i.e. changes in the carbonate ion concentration in the calcification pool that control the saturation state with respect to aragonite) might have an influence. Magnesium shows a diagonal relationship with Lithium, being an element of similar atomic and ionic radius, and it might be affected by similar (temperature-dependent) physiological processes. Therefore, we used the Mg/Ca ratios to correct the biological effects on Li/Ca and derive a multi-species Li/Mg vs. T equation.




3B. Weighted exponential fit (Li/Mg vs. Temperature) considering values for *L. pertusa* and *C. caespitosa*. Error bars represent the propagated SD for Li/Ca and Mg/Ca ratios.

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