MULTI-SPECIFIC CALIBRATION OF THE B ISOTOPE PROXY IN CALCAREOUS RED ALGAE FOR PH RECONSTRUCTION

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OBJECTIVES

- INVESTIGATING THE BORON SIGNAL IN NATURALLY OCCURRING **ACIDIFIED** MARINE ENVIRONMENTS
- PROPOSING A MULTI-SPECIFIC **CALIBRATION** OF $\delta^{11}B$ FOR PH RECONSTRUCTIONS
- DISCUSSING EVENTUAL VARIATIONS DUE TO POSSIBLE ALGAE-SPECIFIC AND CRYSTALLOGRAPHIC **CONTROL**

(A)

$$\delta^{11}B_{borate} = \left(\delta^{11}B_{CaCO3} - c\right)/m$$

(B)

$$pH = pK^{*}_{B} - \log\left(-\left(\delta^{11}B_{sw} - \delta^{11}B_{borate}\right) / \left(\delta^{11}B_{sw} - \alpha_{B3-B4}{}^{*}\,\delta^{11}B_{borate} - \varepsilon_{B3-B4}\right)\right)$$

Figure 1. Equations for pH reconstructions (B) given the $\delta^{11}B$ of the calcium carbonate ($CaCO_3$) and its linear regression with the $\delta^{11}B$ of borate in solution (A). The dissociation constant for the boric acid/borate equilibrium in seawater (pKB), the $\delta^{11}B$ of seawater (sw), and the aqueous boron isotope fractionation factor (α) have also to be known.

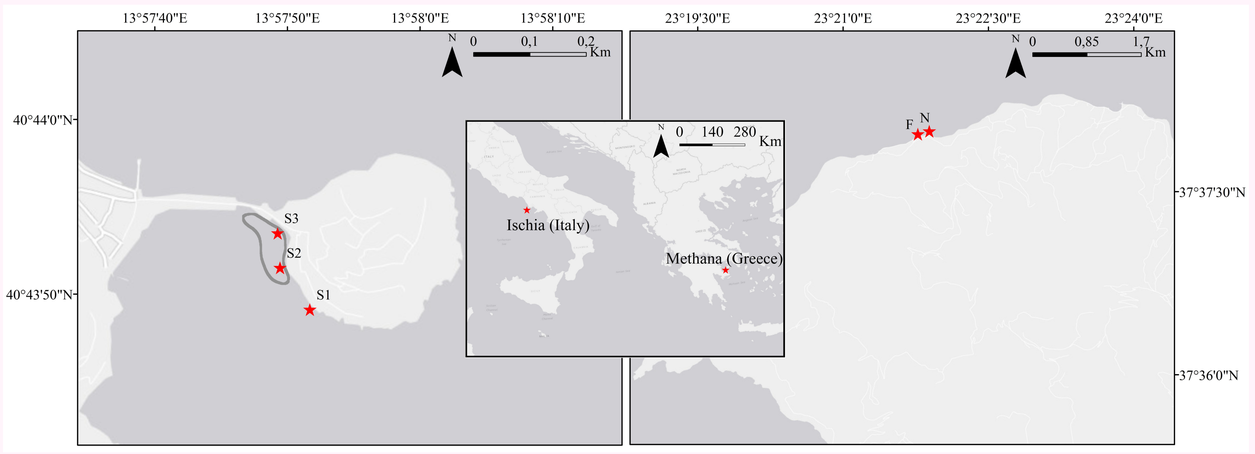

Figure 2. Sampling sites of *C. officinalis*, *Peyssonnelia* sp. (Ischia, on the left), and *Amphiroa* sp. (Methana, on the right). In Ischia, the venting area, including sites S3 and S2, is circled in grey. In Methana, the main venting site corresponds to site N. Site F is located 200 m westward from the vents. Service Layer Credits: Esri, HERE, Garmin, (c) OpenStreetMap contributors, and the GIS user community.

INTRODUCTION

Boron isotopes ($\delta^{11}B$) in marine carbonates are used as **pH-proxy** (Fig. 1), assuming that B incorporation occurs in isotopic equilibrium with seawater borate, which is enriched in ^{11}B as pH increases [1 2]. Still, there is large uncertainty on the mechanisms controlling **B incorporation** [3 4]. Moreover, literature data on $\delta^{11}B$ in calcareous red algae are sparse [5], and there is no clear calibration to use for pH reconstructions.

MATERIALS AND METHODS

$\delta^{11}B$ in the algae were measured by Multi Collector Inductively-Coupled Plasma Mass Spectrometry (MC-ICP-MS) on calcareous red algae grown at 1 m depth close to CO_2 seeps off the coasts of Ischia (Italy), and Methana (Greece) (Fig. 2), characterized by a broad range of natural pH in seawater (from 6.80 ± 0.43 to 8.08 ± 0.07 units). $\delta^{11}B$ in solution borate was calculated in MATLAB using 10000 Monte Carlo simulations randomly varying pH, temperature and salinity within their uncertainties. Environmental data were extracted from CMEMS products (Marine Copernicus Service Information), or provided by literature.

RESULTS

The $\delta^{11}B$ values in the algae analysed ranged from 22.23 ‰ to 26.59, calibrated over a range of $\delta^{11}B$ in aqueous borate extending from 12.68‰ to 18.05‰. Calcitic algae grown in the same site as aragonitic ones registered higher values of $\delta^{11}B$ (Figs. 5, 6). Evidence of up-regulation of calcification was observed in all taxa tested, revealing a common trend of internal pH elevation. The calculated **multi-species calibration**[6] (Fig. 4) used literature data of boron isotopes in cultured coralline algae combined with our new data on wild-grown specimens, widening the range of pH considered for $\delta^{11}B$ calibrations so far.

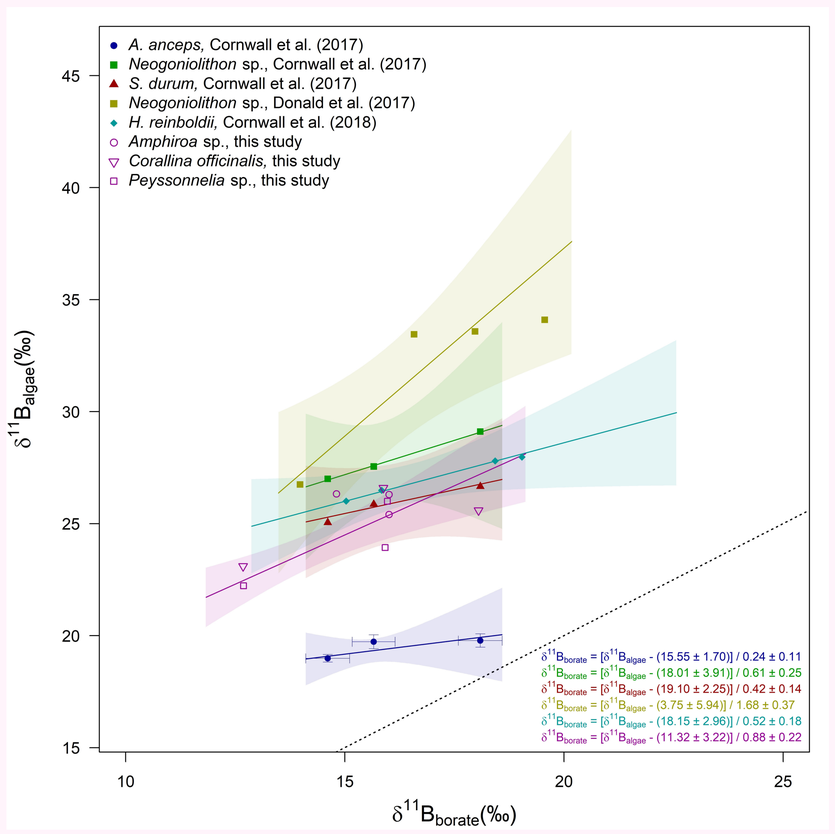

Figure 3. Calibration data showing MC-ICP-MS measurements of $\delta^{11}B$ in the algae versus solution borate $\delta^{11}B$ for published calcareous red algal cultures [8 9 10] and wild-grown algae [6]. Shaded polygons show 0.90 confidence intervals, considering standard errors of replicate measurements in the algal $\delta^{11}B$ and one standard deviation of 10000 Monte Carlo simulations in the $\delta^{11}B$ of borate. Uncertainties for points other than *A. anceps* are shown in Fig. 4. Note that all the calibrations plot above the 1:1 line (dotted line).

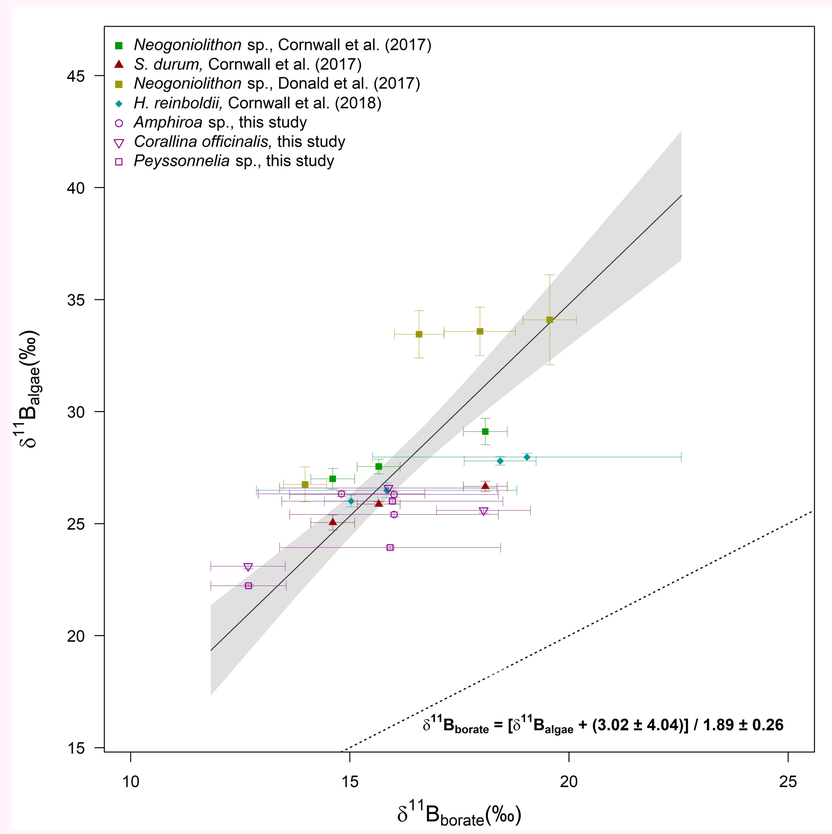

Figure 4. Multi-specific calibration proposed in this study grouping all published MC-ICP-MS measurements of calcareous red algae. The shaded polygon shows 0.90 confidence intervals, considering standard errors of replicate measurements in the $\delta^{11}B$ of the algae and one standard deviation of 10000 Monte Carlo simulations in the $\delta^{11}B$ of solution borate. Note that all the points plot above the 1:1 line (dotted line).

DISCUSSION

The general enrichment in ^{11}B in calcite had already been suggested to indicate a **crystallographic control** over B incorporation compared to aragonite[7]. Indeed, we observed higher $\delta^{11}B$ values in calcites (Figs. 3, 4). Values of $\delta^{11}B$ higher than in solution borate could be attributed to the up-regulation of the calcifying fluid pH exerted by the algae, as suggested by experiments on cultured corallines showing a species-specific control over the calcifying fluid pH[8], elevated up to 1 unit above the seawater pH. These results provide new insights into boron incorporation in calcareous red algae and the application of boron isotopes for pH reconstructions. The proposed multi-specific calibration could be particularly useful when experimental calibration is not possible, such as in the fossil record and in the case of ambiguous identifications.

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