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### **ACCEPTED MANUSCRIPT**

# Boron isotope sensitivity to seawater pH change in a species of *Neogoniolithon* coralline red alga

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The increase in atmospheric carbon dioxide (CO<sub>2</sub>) observed since the industrial revolution has reduced surface ocean pH by  $\sim 0.1$  pH units, with further change in the oceanic system predicted in the coming decades. Calcareous organisms can be negatively affected by extreme changes in seawater pH (pH<sub>sw</sub>) such as this due to the associated changes in the oceanic carbonate system. The boron isotopic composition ( $\delta^{11}$ B) of biogenic carbonates has been previously used to monitor pH at the calcification site (pH<sub>cf</sub>) in scleractinian corals, providing mechanistic insights into coral biomineralisation and the impact of variable pH<sub>sw</sub> on this process. Motivated by these investigations, this study examines the  $\delta^{11}B$  of the high-Mg calcite skeleton of the coralline red alga *Neogoniolithon* sp. to constrain pH<sub>cf</sub>, and investigates how this taxon's pH<sub>cf</sub> is impacted by ocean acidification.  $\delta^{11}$ B was measured in multiple algal replicates (n = 4 to 5) cultured at four different  $pCO_2$  scenarios – averaging (± 1 $\sigma$ ) 409 (± 6), 606 (± 7), 903 (± 12) and 2856 (± 54)  $\mu$ atm, corresponding to average pH<sub>sw</sub> (± 1 $\sigma$ ) of 8.19 (± 0.03), 8.05 (± 0.06), 7.91 (± 0.03) and 7.49 ( $\pm$  0.02) respectively. Results show that skeletal  $\delta^{11}B$  is elevated relative to the  $\delta^{11}B$  of seawater borate at all pH $_{sw}$  treatments by up to 18 ‰. Although substantial variability in  $\delta^{11}B$ exists between replicate samples cultured at a given pH<sub>sw</sub> (smallest range = 2.32 ‰ at pH<sub>sw</sub> 8.19, largest range = 6.08 %0 at pH<sub>sw</sub> 7.91), strong correlations are identified between  $\delta$ <sup>11</sup>B and  $pH_{sw}$  (R<sup>2</sup> = 0.72, p < 0.0001, n = 16) and between  $\delta^{11}B$  and B/Ca (R<sup>2</sup> = 0.72, p < 0.0001, n = 16). Assuming that skeletal  $\delta^{11}$ B reflects pH<sub>cf</sub> as previously observed for scleractinian corals, the average pH<sub>cf</sub> across all experiments was 1.20 pH units (0.79 to 1.56) higher than pH<sub>sw</sub>, with the

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