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Coccolith B/Ca ratios using SIMS ion probe analysis

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B/Ca ratios are proposed as a paleo-carbonate ion or paleo-pH proxy due to the preferential incorporation of borate ion into the calcite lattice, relative to boric acid which is the dominant species of B at lower pH. The relative importance of cellular regulation vs external pH on the carbonate B/Ca remains to be characterized for most organisms. Here we describe initial results of B/Ca analyses of coccoliths produced in laboratory culture under variable carbonate ion concentrations. Due to the impossibility of physically separating the micron-sized coccoliths from non-coccolith sediment material in quantities large enough for TIMS or ICP-MS analysis of B/Ca, eventual analysis of coccolith B/Ca from the fossil record will need to be conducted on individually picked coccoliths on the ion probe as is currently done for other trace element (eg. Sr/Ca) ratios. Hence, we employ the CAMECA IMS 1280 ion probe at the Northeast National Ion Microprobe Facility at Woods Hole Oceanographic Institution to measure B/Ca in coccoliths from cultures. We evaluated cleaning methods using a synthetic cleaning target (crushed marble) contaminated with noncalcifying algae. Cleaning is crucial for obtaining accurate B/Ca ratios and precluding sample charging. B/Ca ratios of different genera of modern coccoliths range from 5 to 25 umol/mol, 3 to 10fold lower than planktic foraminifera or abiogenic calcite precipitated in seawater in the same pH range. These low ratios suggest much more restricted uptake of B into the algae cell in the vesicle calcification used by coccolithophores, compared with the seawater vacuole calcification typical of foraminifera. Different coccolith species grown at the same pH exhibit different B/Ca ratios. One species, Coccolithus pelagicus, cultured at a range of pH conditions from 7.7 to 8.4, exhibits no significant change in B/Ca ratios across the range of pH. One explanation is pH homeostasis at the calcification site. In possible support of pH homeostasis, the degree of calcification of this species was insensitive to variable CO2 and pH conditions in published experiments. We will also present results from strains of Emiliania huxleyi grown at different pH, for which more acidic pH resulted in depressed calcification.