Biocalcification Responses to Ocean Acidification: the Interplay of Physicochemistry and Physiology

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- Aragonite is the favored CaCO₃ polymorph in today's oceans
- Skeletons made of a wide range of polymorphs; biominerals not simply precipitates from ambient seawater
- Evidence for calcifying space within which organisms manipulate saturation state
- Despite this control, as seawater Ω decreases, significant negative impact on the ability to calcify
- Why? Predictive capabilities requires mechanistic understanding (corals as an example)



CaCO₃ in marine skeletons and skeletal structures

Gorgonian nodules, Zoe Bond



High Mg-Calcite





Ascidian spicule, Joanna Aizenberg

ACC interior, calcite exterior.



Physicochemical constrains on mineralogy



Morse et al., Geology, 1997

Organisms Overcome Physicochemical Constraints

aragonitic corals in Antarctica



vaterite skeletons





Mineralization can be intracellular, intercellular or extracellular: growing skeleton is seldom exposed directly to external seawater

intracellular





Scleroblasts/vacuoles Leptogorgia (Watabe and Kingsley, 1989) Between utricles in *Halimeda* segment (Justin Ries, WHOI 2007; Torres and Baars, 1992)

Beneath tissue in corals
(Cohen and McConnaughey 2003)

extracellular











Mineralization by larval oyster in under-saturated seawater

Cohen and McCorkle, 2007



Ω~3

Ω~0.95

Ω~0.2

Mineralization occurs

•No dissolution

•Malformations indicate disruption of normal calcification process

Seawater is sequestered into calcifying compartment





Seawater saturation state is elevated by influx of Ca²⁺ ions and efflux of protons



Model (Cohen and McConnaughey 2003)

Data *(Al-Horani et al., 2003)*

Evidence consistent with localized Ca²⁺-ATPase activity at coral mineralization site

Zoccola et al., 2004



Also in: Coccolithophores (Klaveness, 1976); gorgonians (Kingsley and Watabe 1985)

In situ data consistent with highly supersaturated calcifying fluid ($\Omega_{aragonite}$ >20)



Spherulite and crystal morphology (aspect ratio) inversely proportional to fluid saturation state



Ω~4

Ω**~**17

Holcomb et al., in review

Crystal morphologies in coral dissepiment consistent with Ω ~20-30





Small changes in seawater saturation state elicit strong negative response in many calcifiers



Langdon and Atkinson JGR, 2005

Skeletal development in larval corals







Cohen, McCorkle, de Putron 2007

Systematic decrease in extent of skeletal development (1° and 2° septa, basal plate) in 8-day old corals with decreasing $\Omega_{\text{aragonite}}$



Ω=3.7

Ω**=2.4**

Ω=1

Ω**=0.2**

Cohen et al., (in review)



Observed and predicted sensitivity of larval coral calcification to changes in sw saturation state



Caldeira and Wickett, 2005

Systematic changes in crystal morphology of larval coral aragonite with changes in $\Omega_{\text{aragonite}}$





Aragonite spherulite and crystal morphology (1/aspect ratio) proportional to fluid saturation state

Using relationship established for experimental abiogenic aragonite, estimate Ω of calcifying fluid



Energetic cost associated with driving the Ca²⁺-H⁺ exchange sets the limit on how much the fluid saturation state is elevated



(Cohen and McConnaughey 2003)

- Biomineralization occurs in a controlled environment: seawater saturation state not equal to calcifying fluid saturation state
- Observed responses to changes in seawater saturation state occur via (poorly understood) biological processes associated with biomineralization
- In corals (and other organisms), energetic cost associated with raising fluid saturation state limits growth rate
- In many, but not all, organisms studied larval and adult stages - the response is negative in terms of survivability/viability