Oregon State University | OSU | College of Earth, Ocean, and Atmospheric Sciences

Understanding the complex controls on biocalcification: A closer look at SIR and saturation state.

George G. Waldbusser
and several others

$$\Omega CaCO_3 = \frac{[Ca^{2+}][CO_3^{\ 2-}]}{K^*_{sp-CaCO_3}}$$

OR

$$SIR = \frac{[HCO_3^-]}{[H^+]}$$

What controls biocalcification?

Some Key Background

- Thermodynamics and Kinetics drive **abiotic** calcification
- Calcification is a surface controlled process
- CO_3^{2-} is not the only substrate (HCO_3^- and CO_2)
- H^+ is product of calcification
- Organisms are subject to multiple OA “Stressors”
- Ω and SIR do not have to be mutually exclusive

“The ability to hold two opposing thoughts in your mind…” -F. Scott Fitzgerald

Ratios and Absolutes of Carbonate Chemistry

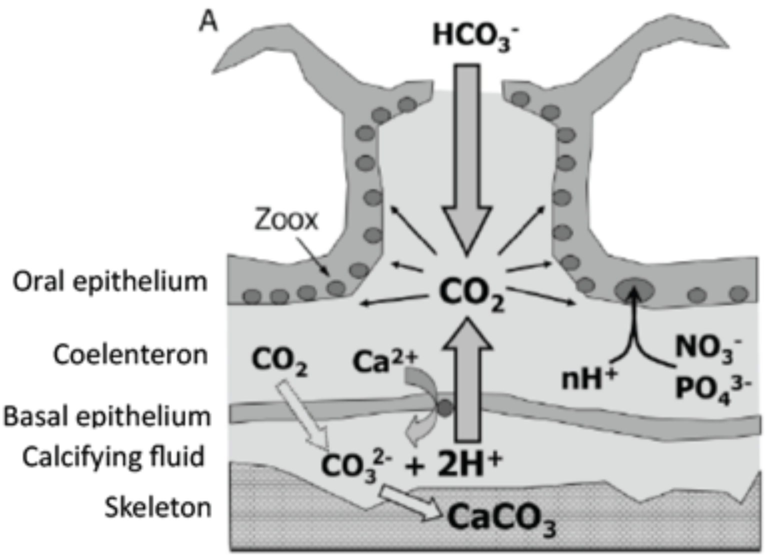
$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}^*}$$

$$SIR = \frac{[HCO_3^{\ -}]}{[H^+]}$$

$$[H^+] = \sqrt{(K_1 * K_2) * \frac{[CO_2^*]}{[CO_3^{2-}]}}$$

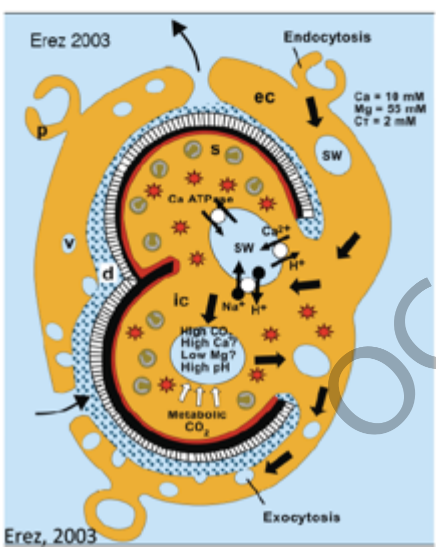
Modes of biocalcification: One way to Organize?

Modes of Biocalcification- Biologically Controlled

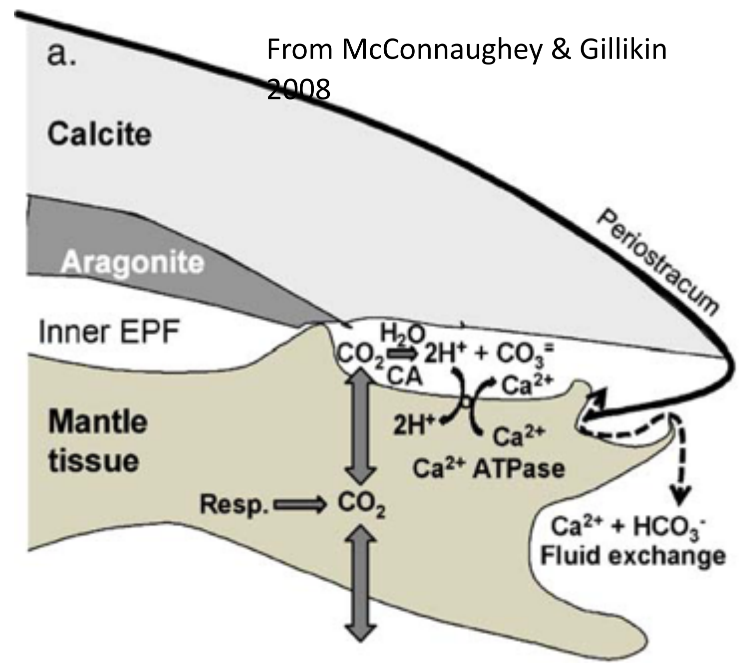


After Cohen and McConnaughey (2003)

Inter-Cellular (Corals)
Extra-Cellular (Mollusks)
Intra-Cellular (Forams)

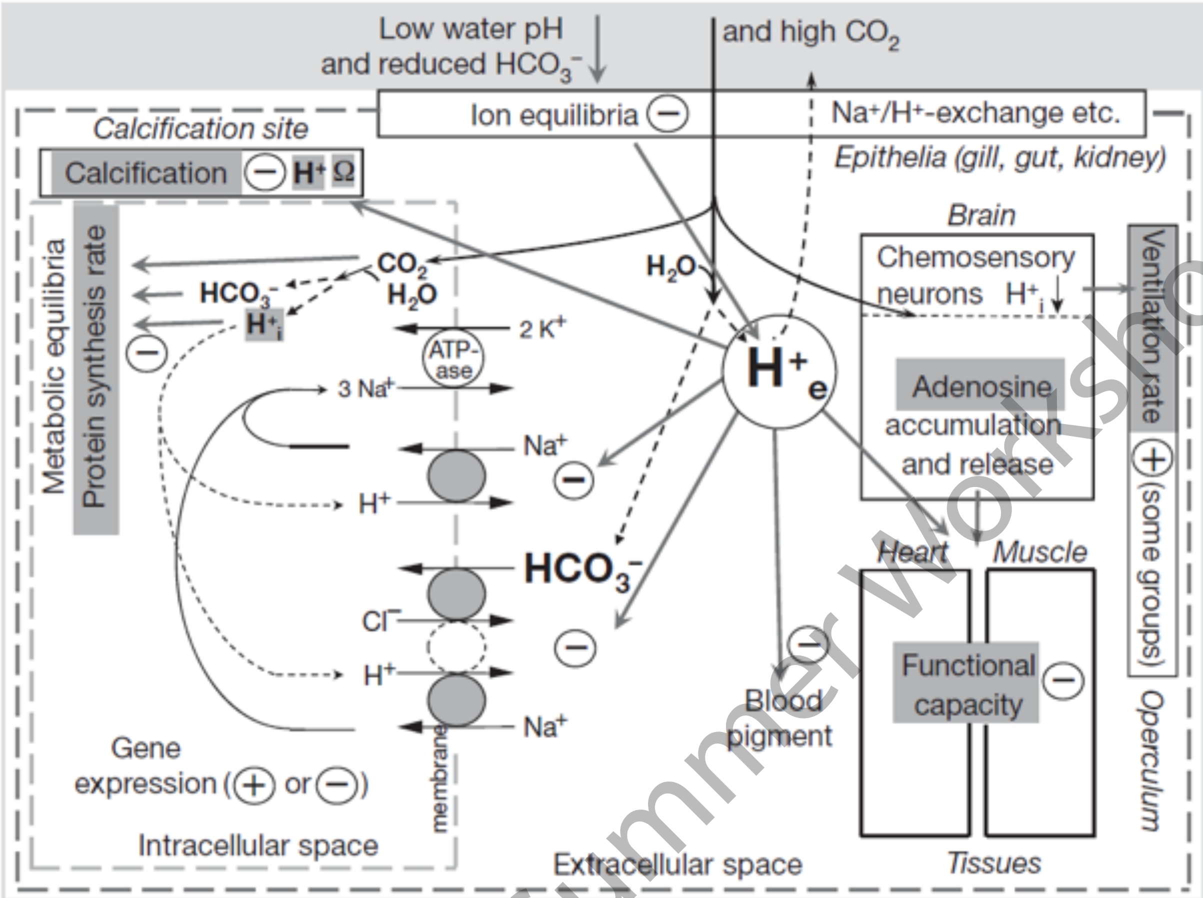


Would we expect one simple answer to what controls it?



From McConnaughey & Gillikin 2008

The Complicated Biology (pH effects on physiology)… (Portner 2008)

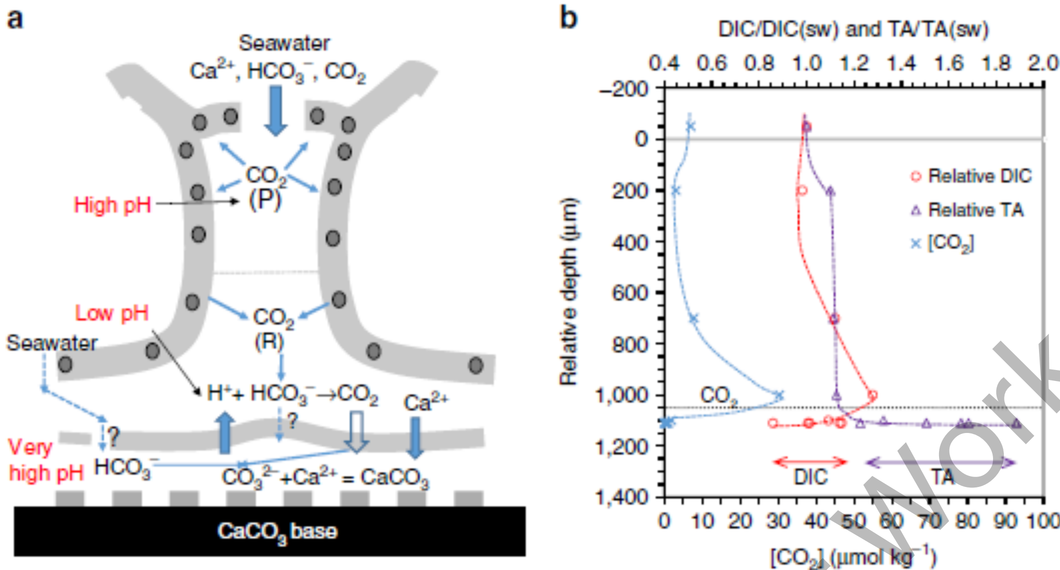


Nearly all animal cells regulate pH internally to a pH of 7.2-7.4

The 'blood' is regulated to differing degrees.

<u>Important features:</u>
- Calcification surfaces within body (extracellular)
- Everything linked through metabolism
- Regulation of internal acid-base chemistry is key

What happens inside: Measurements



Passive CO_2 diffusion for Carbonate supply

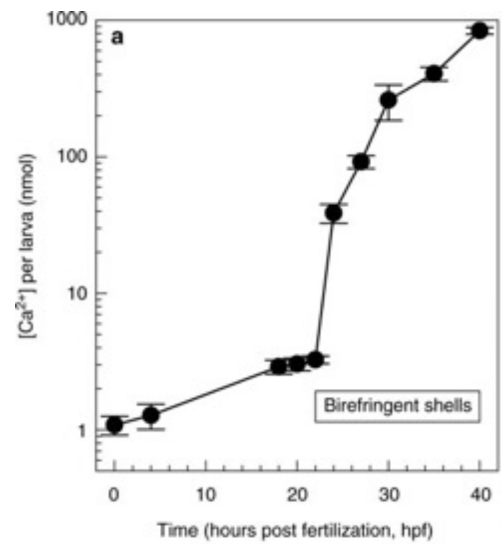
Maintain a low DIC concentration in calcifying fluid

easier to maintain higher pH (fewer protons to pump)

Cai et al. 2016

Ramesh et al. (2017) found that mussel larvae elevate pH and Ω at the site of calcification.

As acidification worsens the ability to alter calcification site chemistry decreases.



Crenshaw (1972) found despite low pH in the calcifying fluid of adult bivalves (~7.7), DIC concentrations were 2x seawater, thus Ω was above saturation.

A case for kinetics…

=

Fast or Slow Growers…

Limnol. Oceanogr., 59(3), 2014, 1081–1091

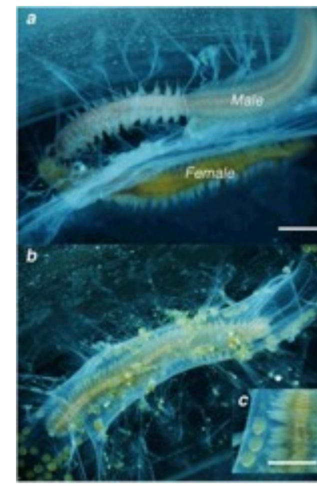
doi:10.4319/lo.2014.59.3.1081

Fast coral reef calcifiers are more sensitive to ocean acidification in short-term laboratory incubations

S. Comeau,* P. J. Edmunds, N. B. Spindel, and R. C. Carpenter

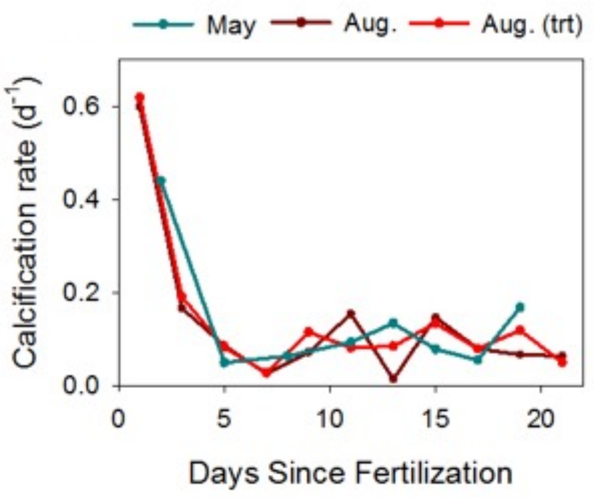
Department of Biology, California State University, Northridge, California

Current research on evolution and adaptation to OA is primarily focused on quantifying genetic variability of OA tolerant traits as an indicator of adaptive capacity into the expected future oceanic conditions[37,38,39,40]. Within this context, brooders may reach extinction far before their pelagic counterparts, as they typically hold lower genetic variability[24]. However, our evidence points to the opposite pattern. Lucey et al. 2015



While greater genetic variability should allow greater potential for adaptation to rapid environmental change, if the life history traits that provide for greater adaptive potential compromise fitness to a specific stressor, then you may be SOL.

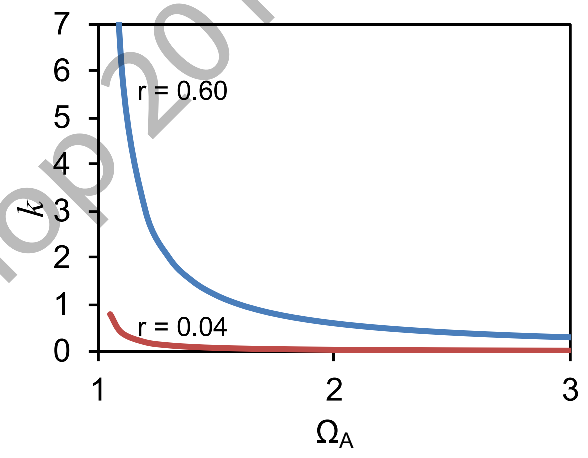
A Saturation State Sensitivity (it's all about Kinetics)



Brunner et al., 2016

$$r = k(\Omega - 1)^n$$

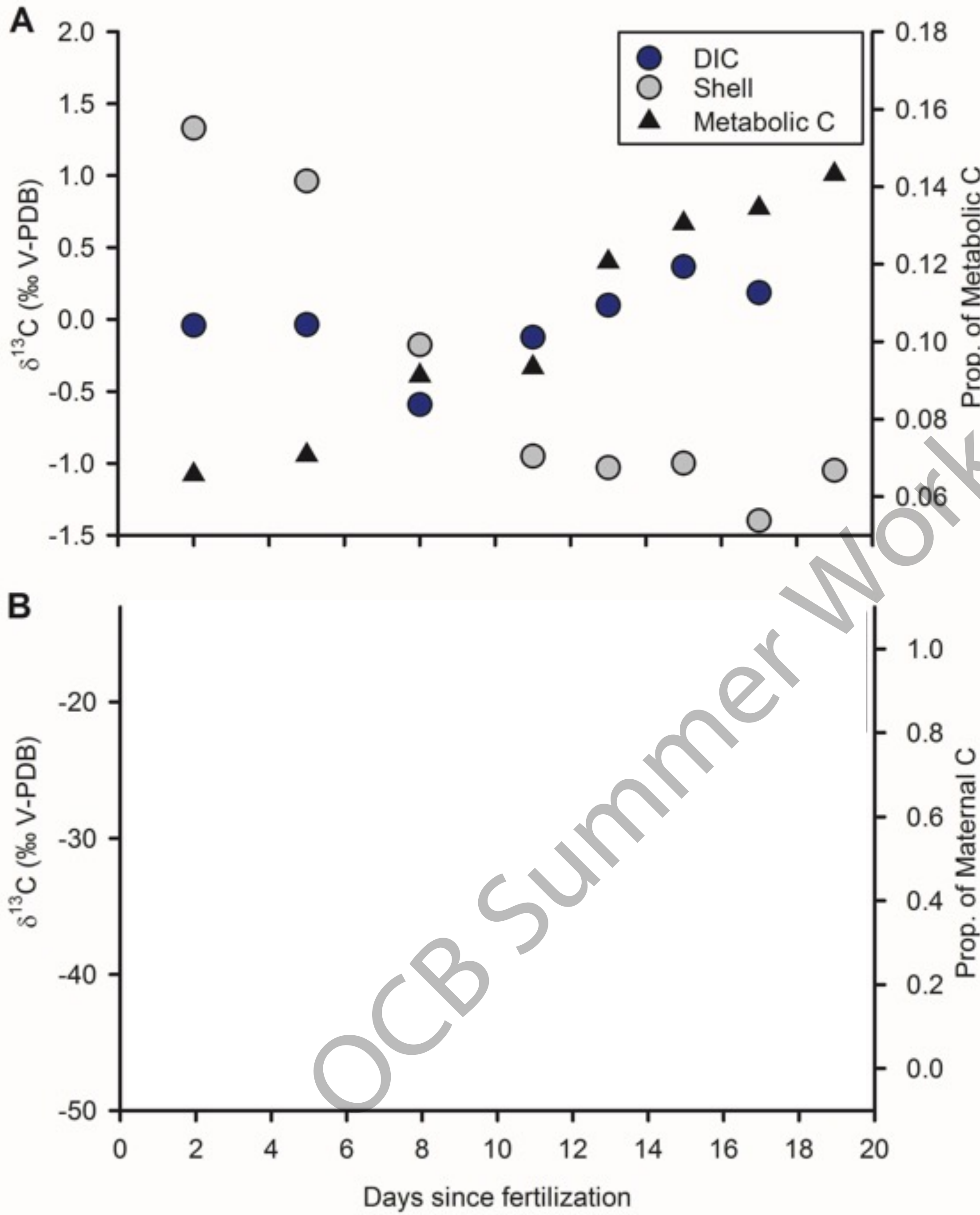
r = calcification rate
k = rate constant
Ω = saturation state
n = rate order (1)



Waldbusser et al., 2013

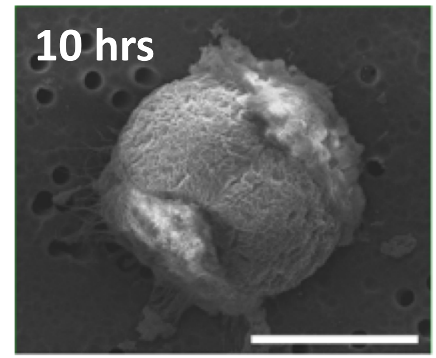
*This is clearly not the equation that defines the rate of **BIO**calcification, but it is a constraint on the system that biology must overcome.*

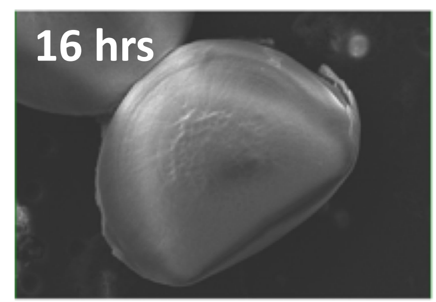
Birds fly in spite of gravity, but that doesn't mean it doesn't exist for them…



During PDI Shell Formation

1) Calcification "exposed"
2) Limited energy
3) Calcification rapid





Waldbusser et al. 2014. NCC

Waldbusser et al. 2013. GRL 40, 1–6

Experiments to understand what controls biocalcification (in bivalve larvae)…

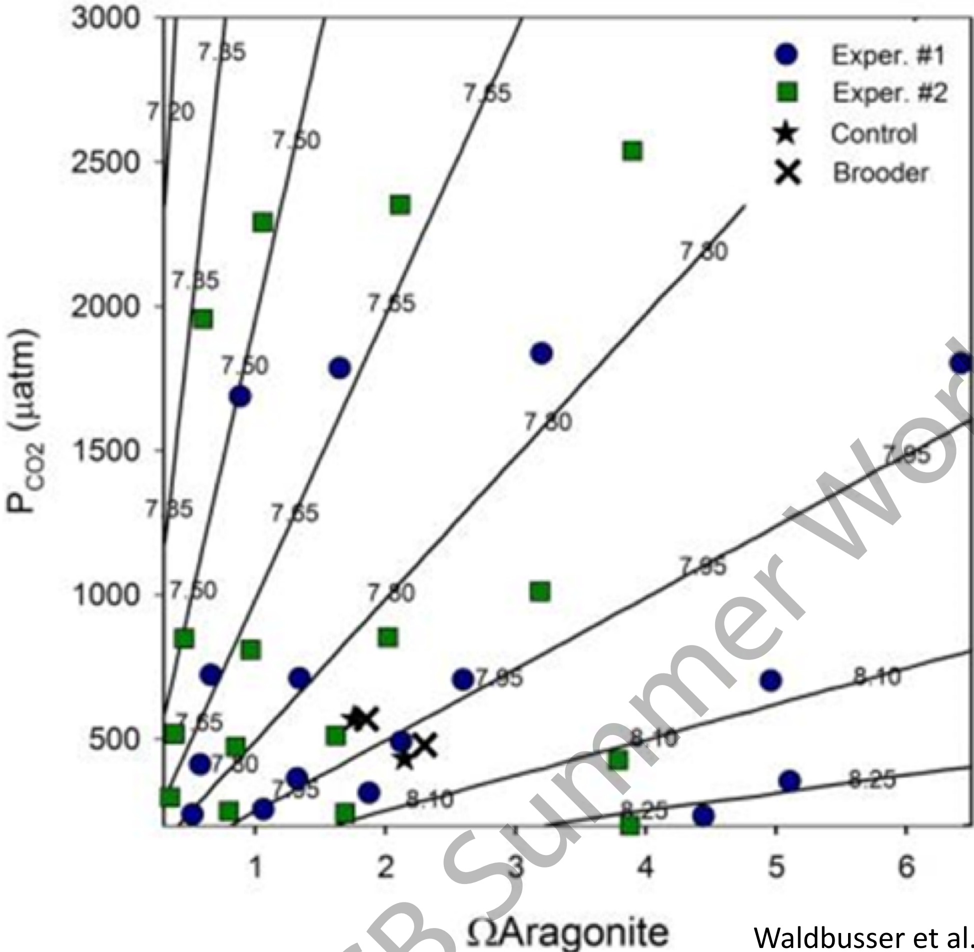
Gazeau et al. (2011) determined carbonate ion concentration was key variable, not Ω (by 2x Ca^{2+} at under-saturation).

Thompson et al. (2015) argued SIR not Ω was the key variable.

In these cases however, responses were correlated with Ω.

- Carbonate ion is an excellent scavenger of H^+ (this is the root of the OA thing)
- Stoichiometric considerations for carbonate formation (Nehrke et al. 2007)
- Proton diffusion coefficient is 2x most other simple cations
- In geologic time, carbonate chemistry parameters decouple

What Carbonate Chemistry Variable Matters to Developing Larvae?



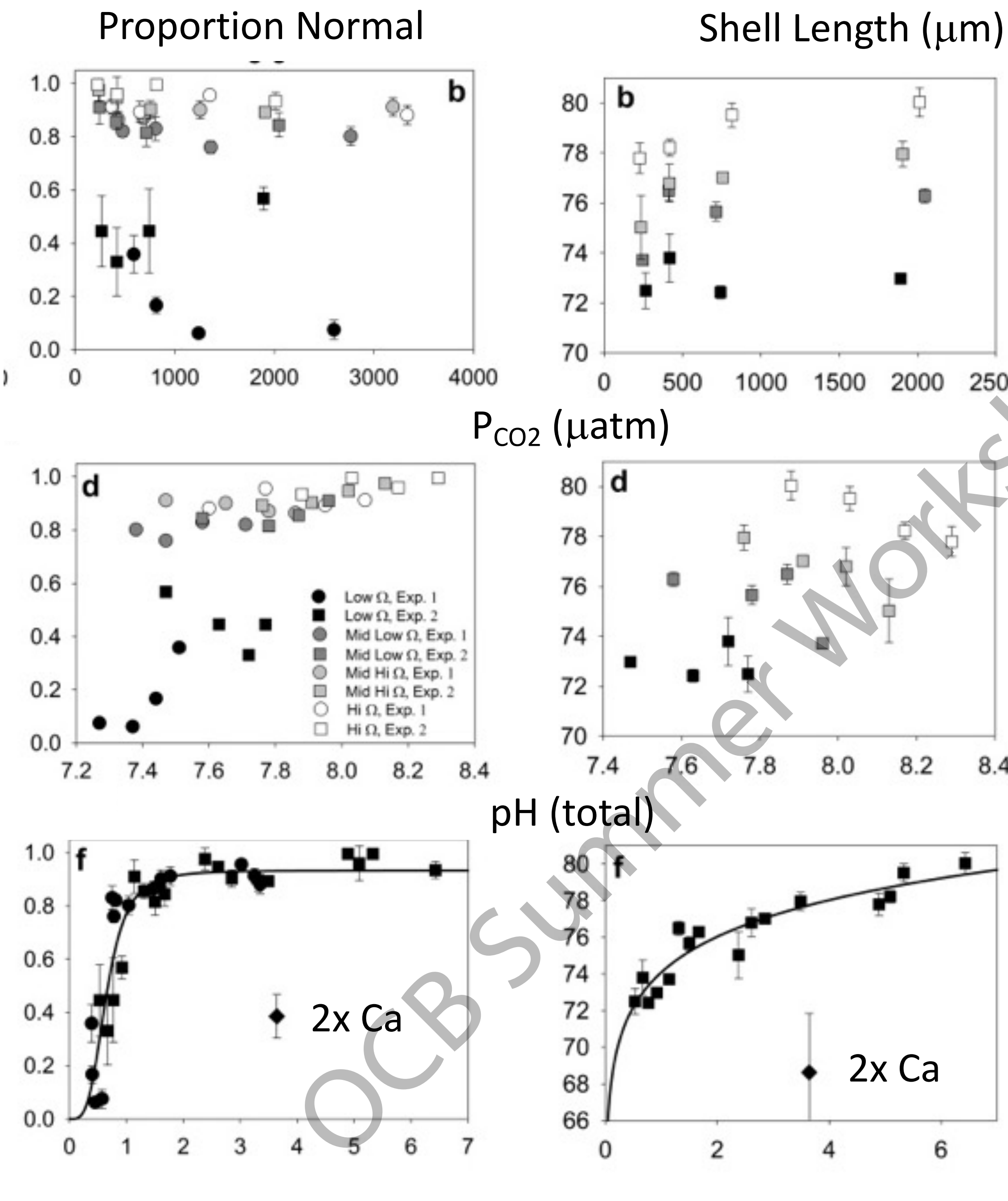
Waldbusser et al. 2015a,b, 2016

~600 to 6000 µmol kg^{-1} DIC

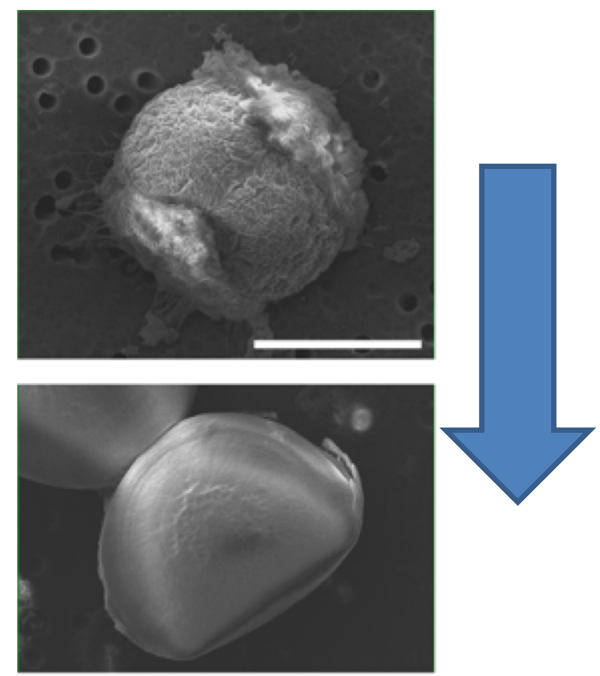
This approach:
Ability to partition mode of action
Chemistry on geologic scales

Measured:
Shell Development
Shell Length (or normal larvae)

Pacific Oysters The "canary in the coal mine"

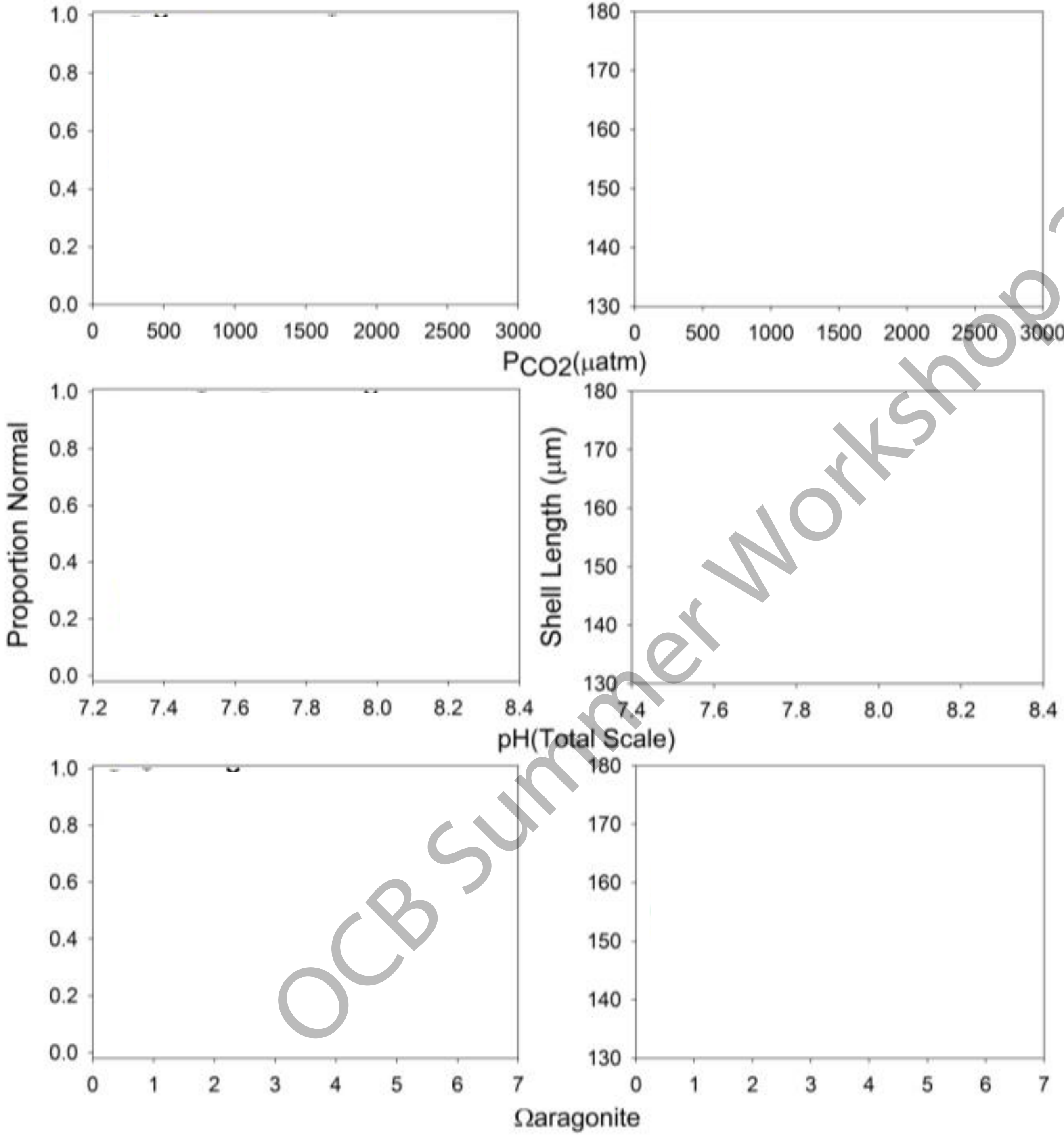


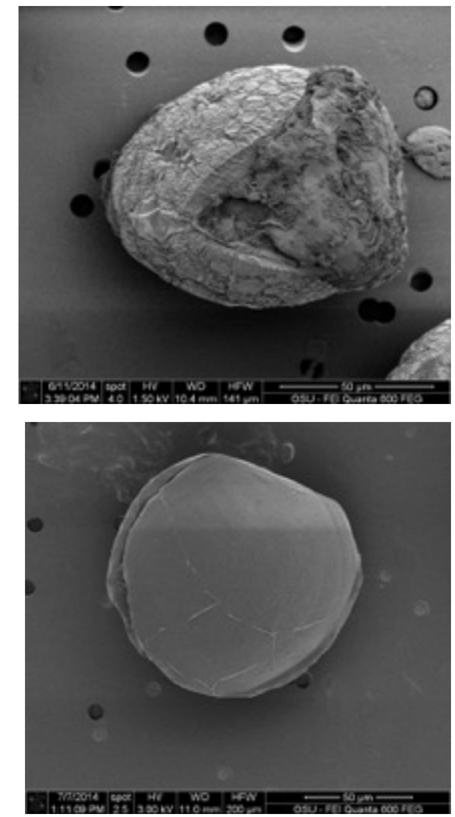
Waldbusser et al. 2015a



6 Hours

Olympia oyster larvae

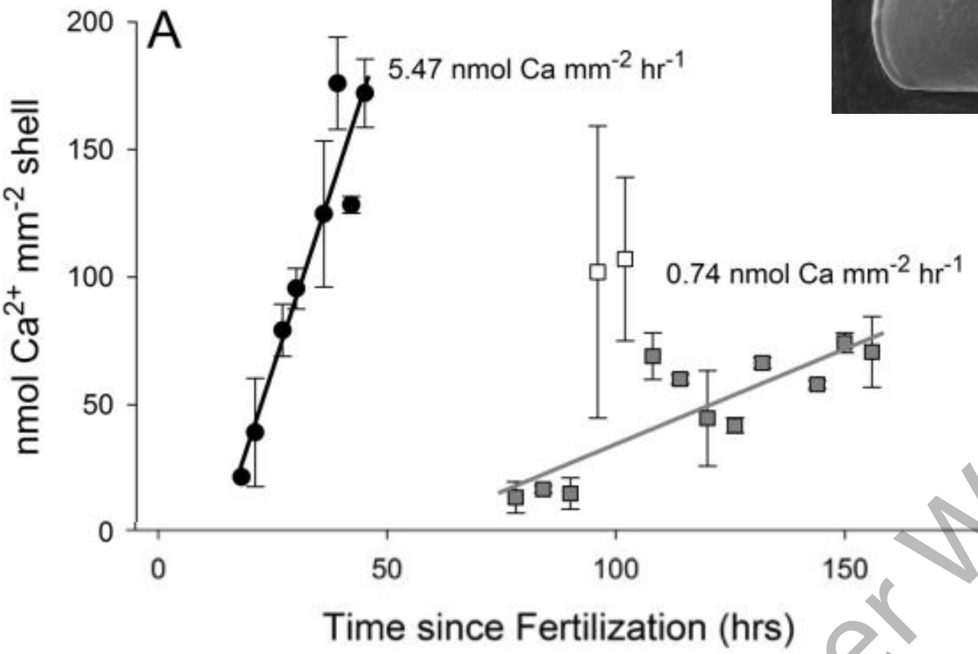


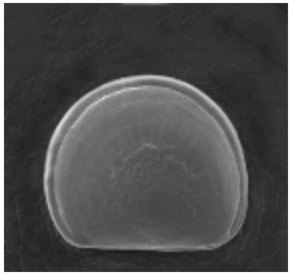


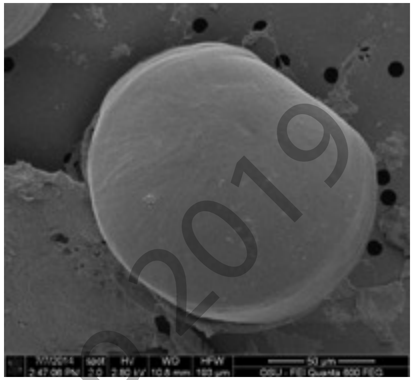
24 Hours

Waldbusser et al. 2016

Olympia Oysters







The Olympia Oyster grows far more slowly…

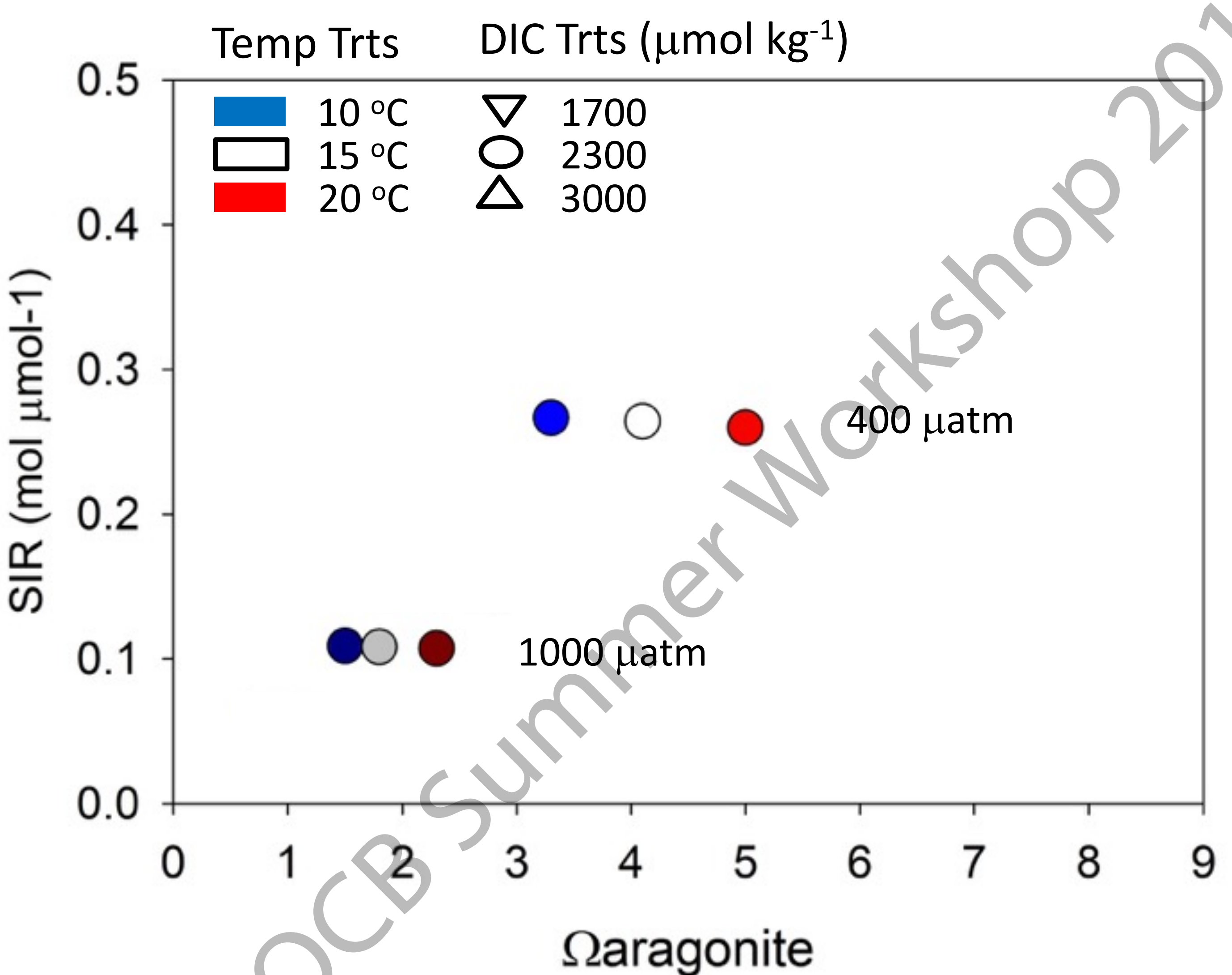
The slow shell movement!!!

<u>An exaptation?</u>

A trait originally evolved for another purpose provides fitness in a way it wasn't originally intended.

Waldbusser et al. 2016

Still haven't disentangled SIR v. Omega....



Δ Temp

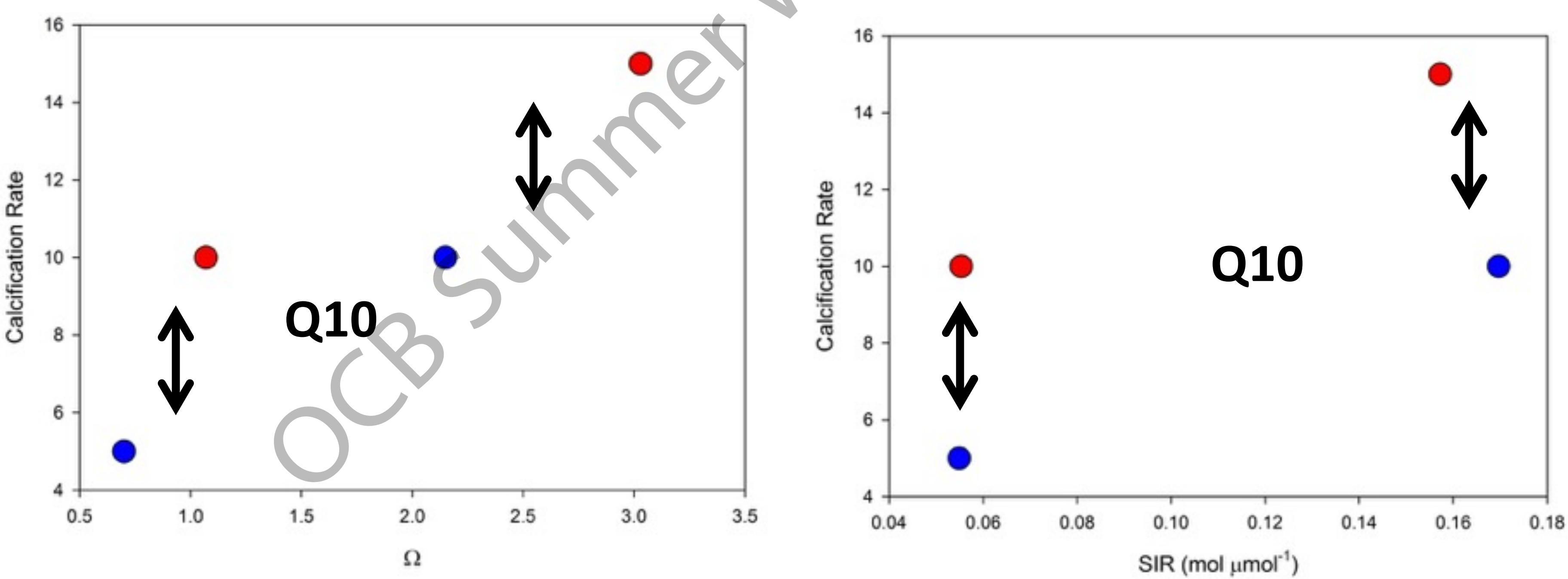
Δ PCO_2

Then use Q10 or Arrhenieus Equation to Correct Calcification Rates

What matters to biocalcification? Ω or SIR

An Empirical Approach (Waldbusser et al. in purgatory)

- Under constant temperature, salinity/DIC, and pressure Ω and SIR are perfectly correlated.
- What if there are experiments that alter T and/or DIC?
- What if some of those experiments had T treatments that were not harmful?
- What if we could account for positive thermal effects?



What controls biocalcification? Existing Studies…

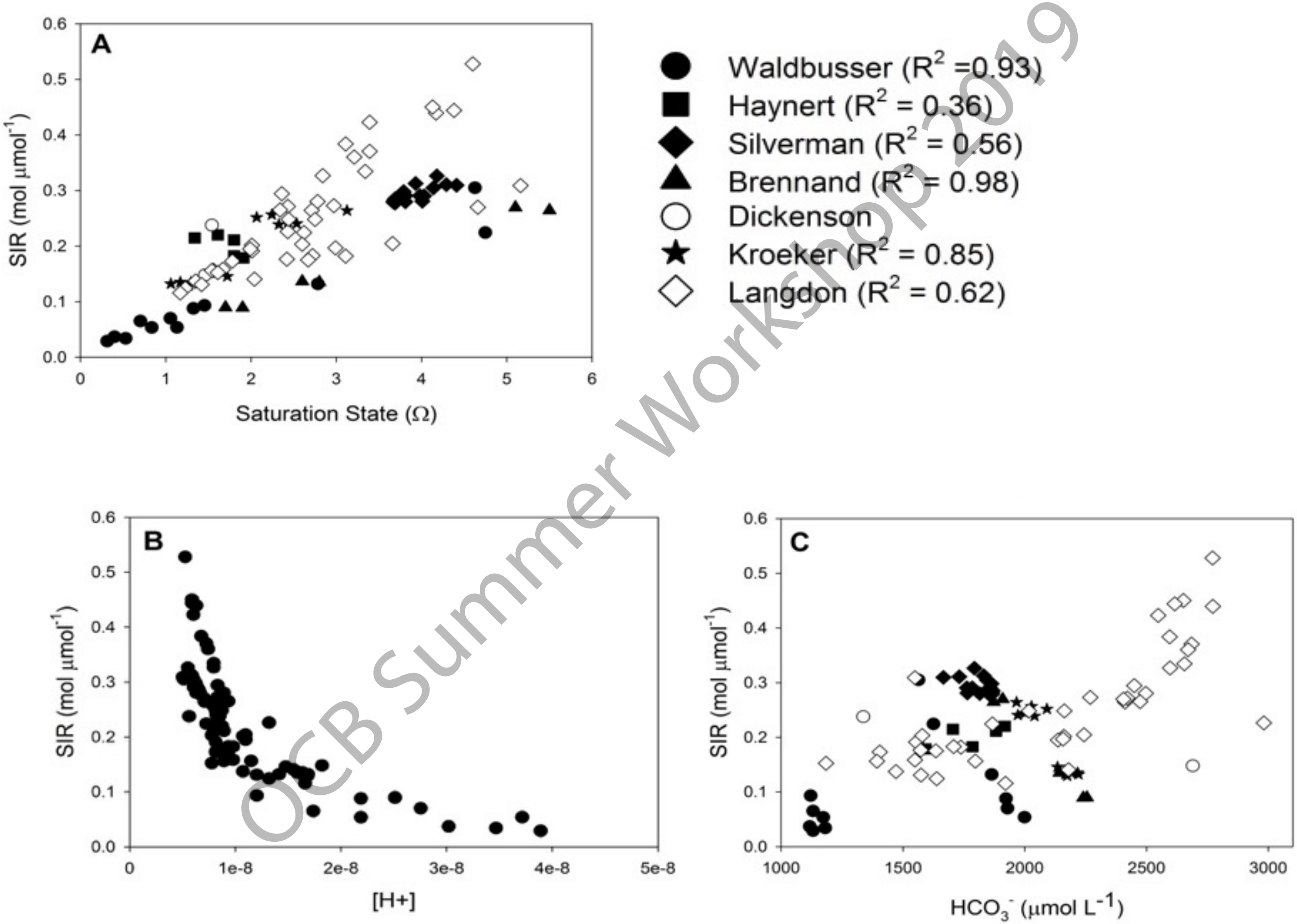
Criteria:

- Temperature and CO_2 treatments (or covariance)
- Fully constrained carbonate chemistry
- > 1 "non-harmful" temperature treatment
- Response of calcification or calcified structure growth
- Has to be rate measure to correct temperature effect

Queried Kroeker et al. (2013) database and literature search to find (as of 2016)… Seven Studies!

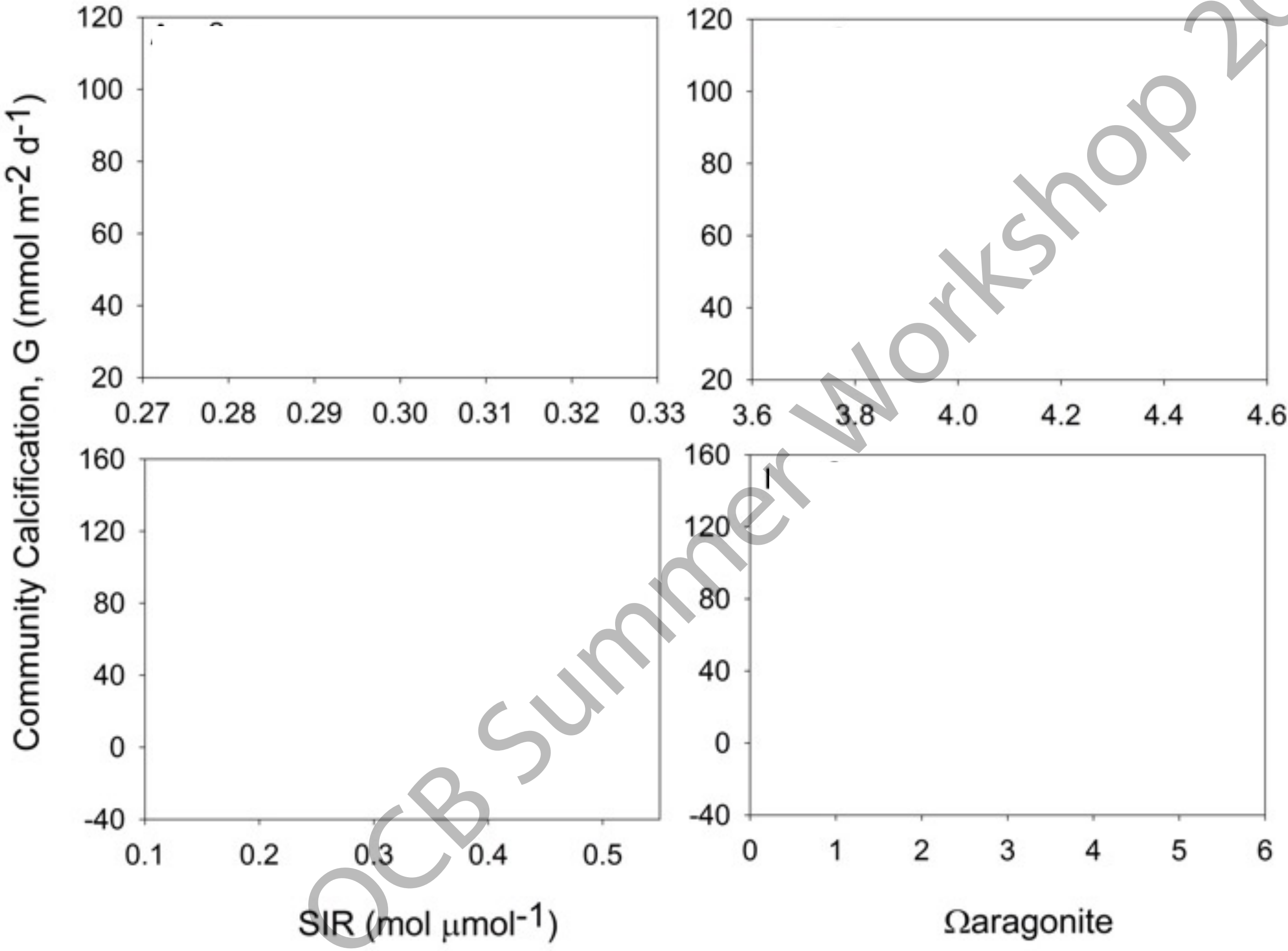
Forams	Haynert & Schoenfeld 2014
Clams	Dickenson et al. 2013
Oysters	Waldbusser et al. 2011
Mussels	Kroeker et al. 2014
Coral Reef	Silverman et al. 2007
Corals	Langdon et al. 2000*
Urchins	Brennand et al. 2010

What controls biocalcification? Existing Studies…



What controls biocalcification? Existing Studies…

Coral Reef Systems

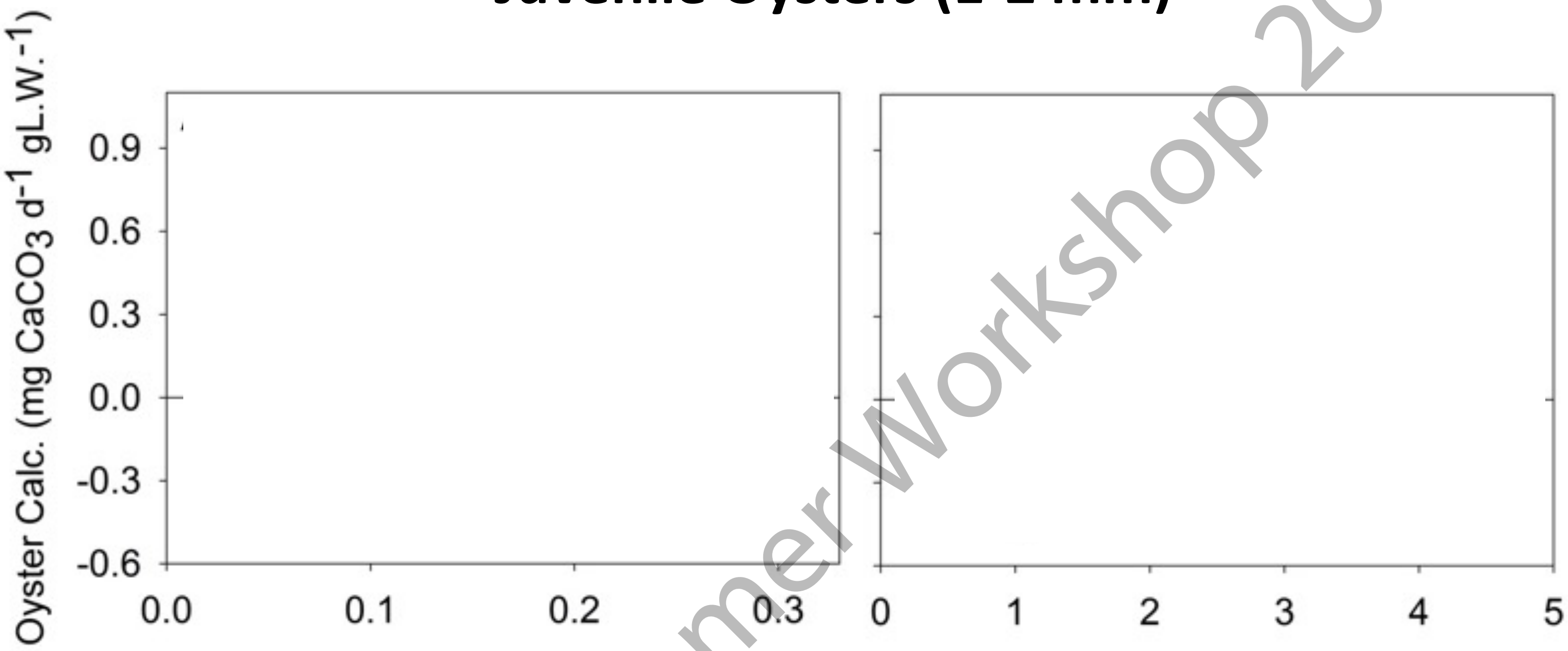


Silverman et al. 2007
Field Measurements

Langdon et al. 2007
Biosphere Expts.
Conditions varied by
controlled additions

What controls biocalcification? Existing Studies…

Juvenile Oysters (1-2 mm)



SIR (mol μmol-1)

ΩCalcite

Waldbusser et al. 2011

What controls biocalcification? Existing Studies…

Taxon	SIR R^2	Ω R^2	Study
Forams	Negative	Positive	Haynert & Schoenfeld 2014
Clams	n/a	n/a	Dickenson et al. 2013
Oysters	0.64, 0.47	0.97, 0.96	Waldbusser et al. 2011
Mussels	0.63	0.76	Kroeker et al. 2014
Coral Reef	0.47	0.84	Silverman et al. 2007
Corals	0.65	0.75	Langdon et al. 2000
Urchins	0.87	0.93	Brennand et al. 2010

Kwiatkowski et al. 2016- nigh time dissolution drives tidepool response to acidification

- Ω is a better predictor of calcification rate than SIR
- They don't have to be mutually exclusive
- OA is a multi-stressor that operates differentially across taxon and life history stage, but integrates on the organism
- Ω will always explain dissolution
- They don't have to be mutually exclusive!

What controls biocalcification? Ω or SIR?

The answer to any ‘this’ or ‘that’ question?

YES

Hypothesis + Antithesis = (Hopefully) Synthesis!
-Georg Wilhelm Friedrich Hegel

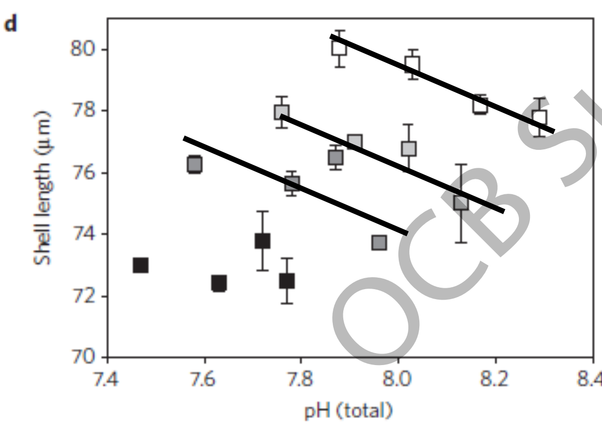
So what to do next? Take Homes…

- No one really likes a centrist…
- Do we want to rely on existing studies and re-analyses to make this argument?
- Probably from a global carbon perspective corals and bivalves are not entirely critical, but locally very important.
- Most variance in SIR is due to $[H^+]$, so maybe its just pH?
- OA has multiple modes of action (in mussel larvae pH affects respiration rate, Ω shell development and growth)
- There can always be something that alters biological rate processes, temperature, pollutants, etc.

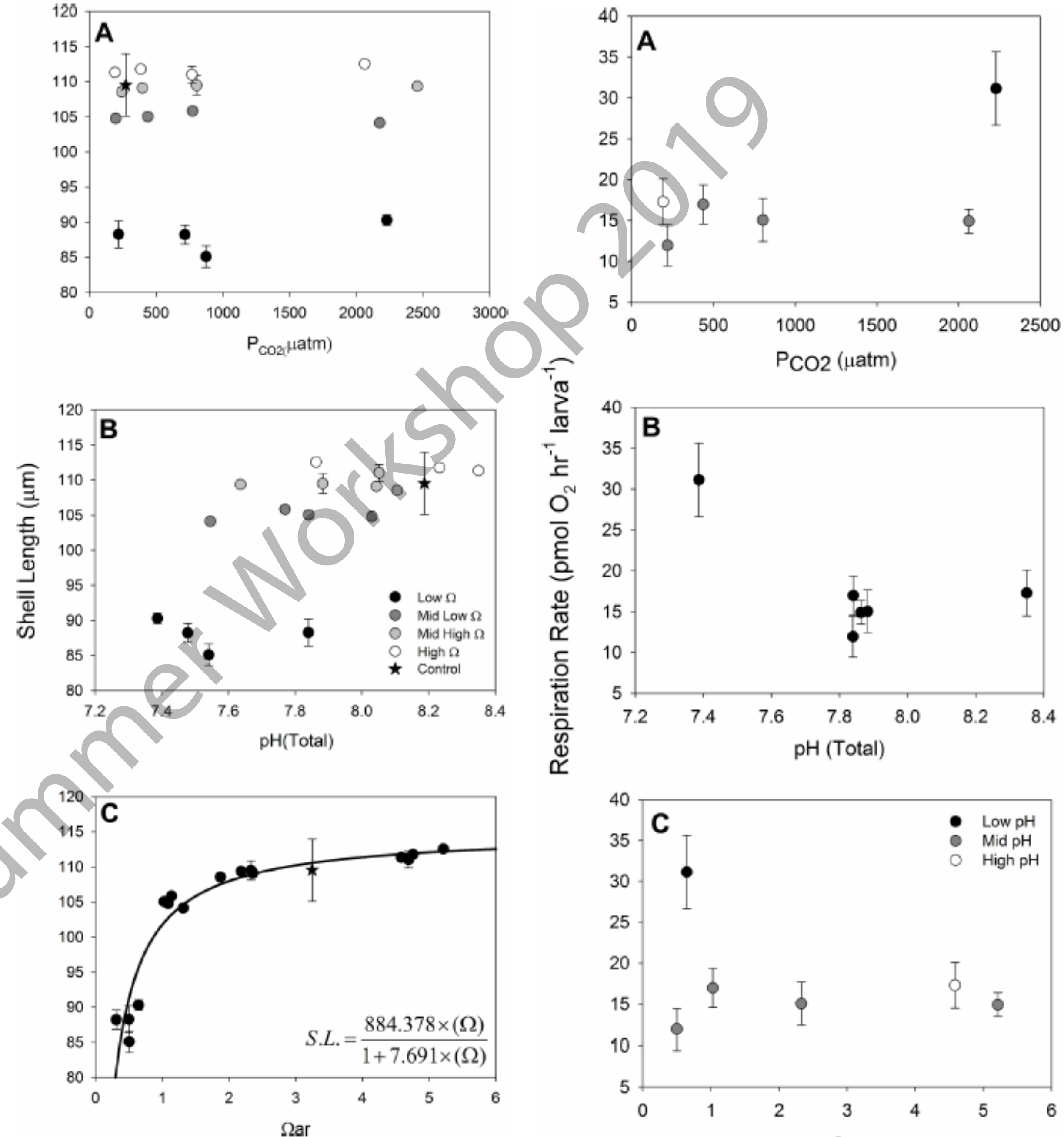
OA is a Multi-Stressor!

There are multiple modes of action on bivalve larvae (and probably lots of other critters).

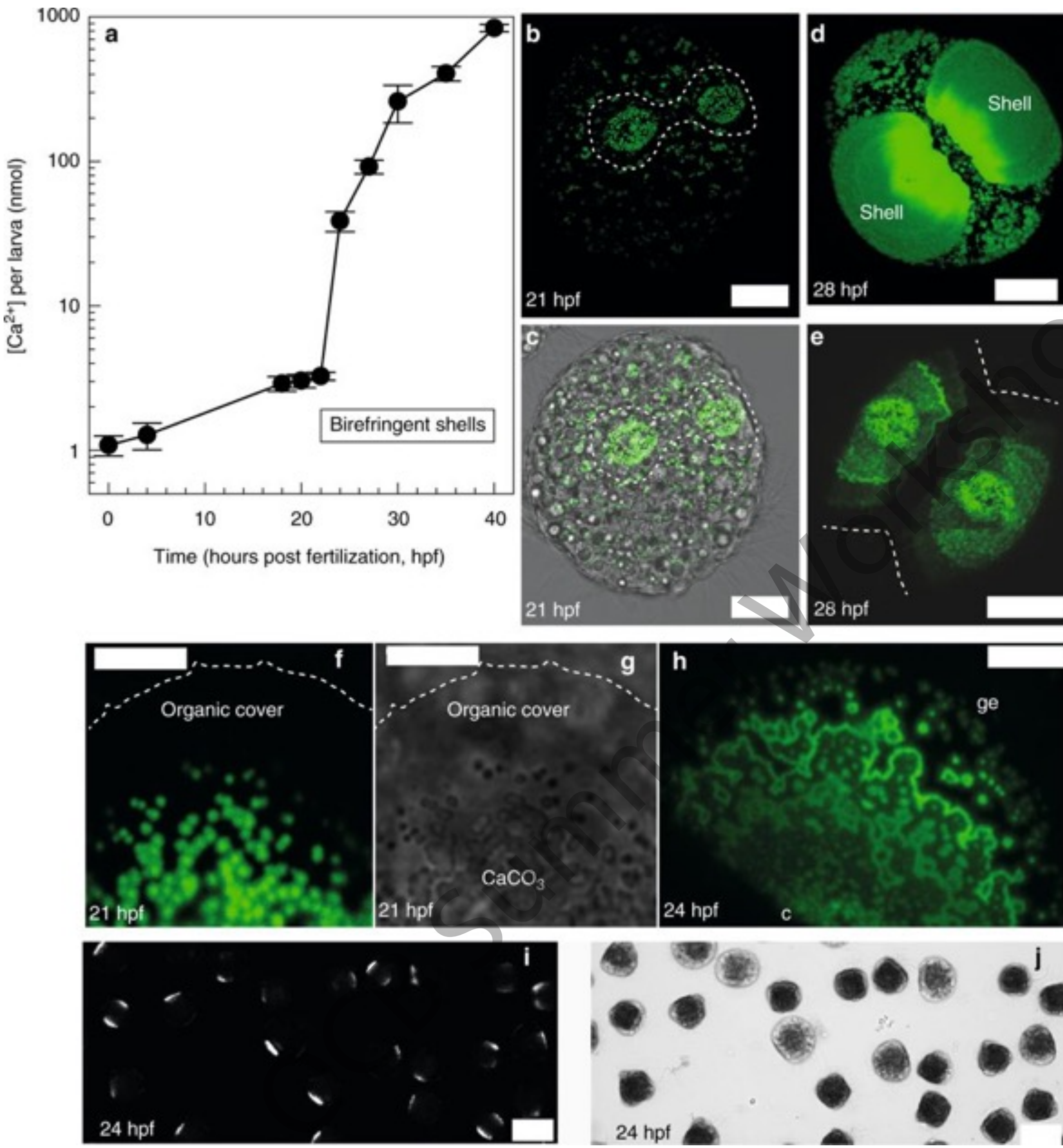
Nor do SIR and Ω effects have to be mutually exclusive!



Waldbusser et al. 2015 Nature CC **C. gigas**

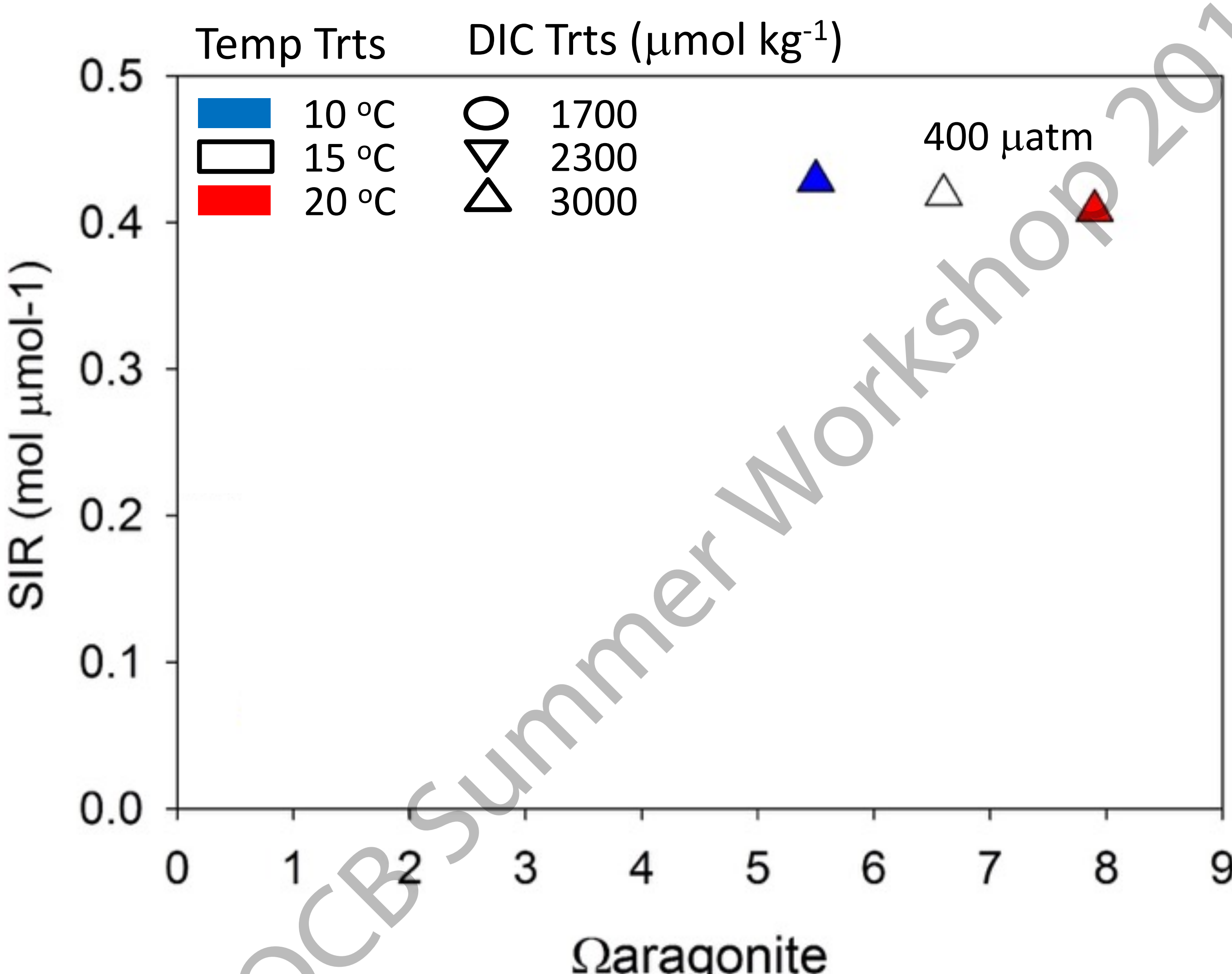


Waldbusser et al. 2015 PlosONE ***Mytilus californianus***



Ramesh et al. 2017

What controls biocalcification? Can we use this temp effect?



Δ Temp

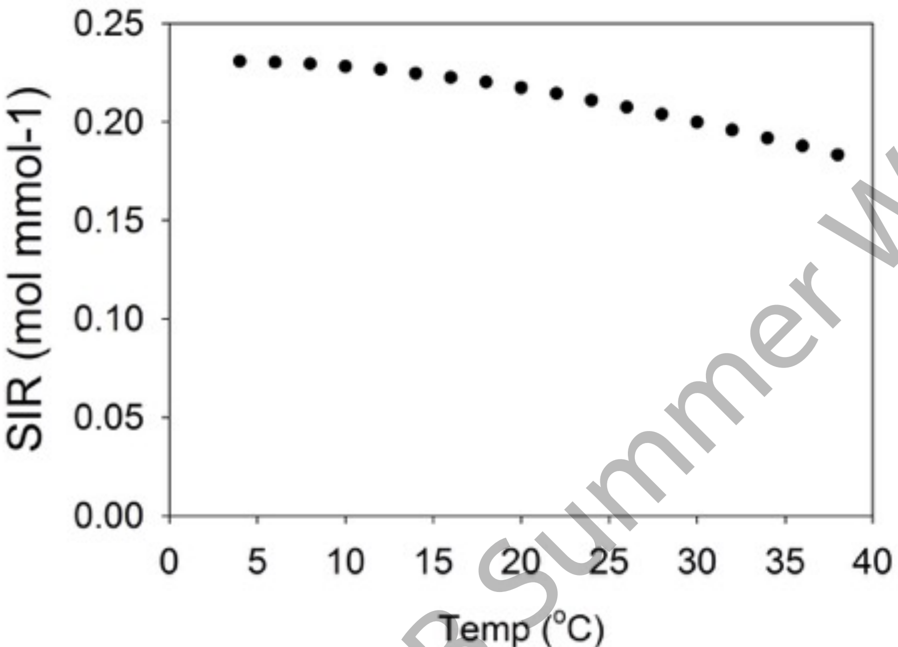
Δ PCO_2

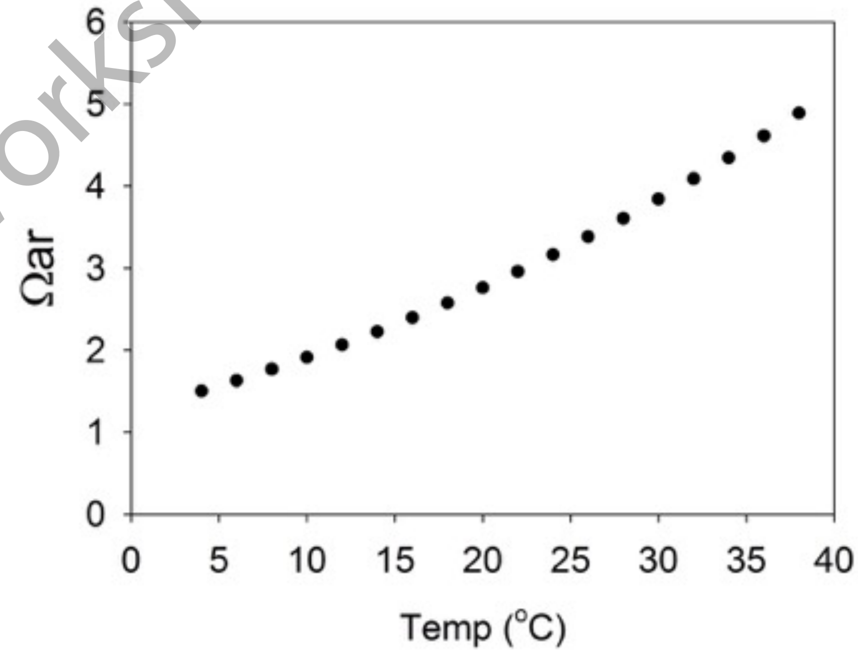
Δ DIC

Then use Q10 or Arrhenieus Equation to Correct Calcification Rates

What controls biocalcification?

TA = 2300 μmol kg^{-1}
PCO2 = 400 μatm
pH ~ 8.05
ΔT from 2-38 ^oC

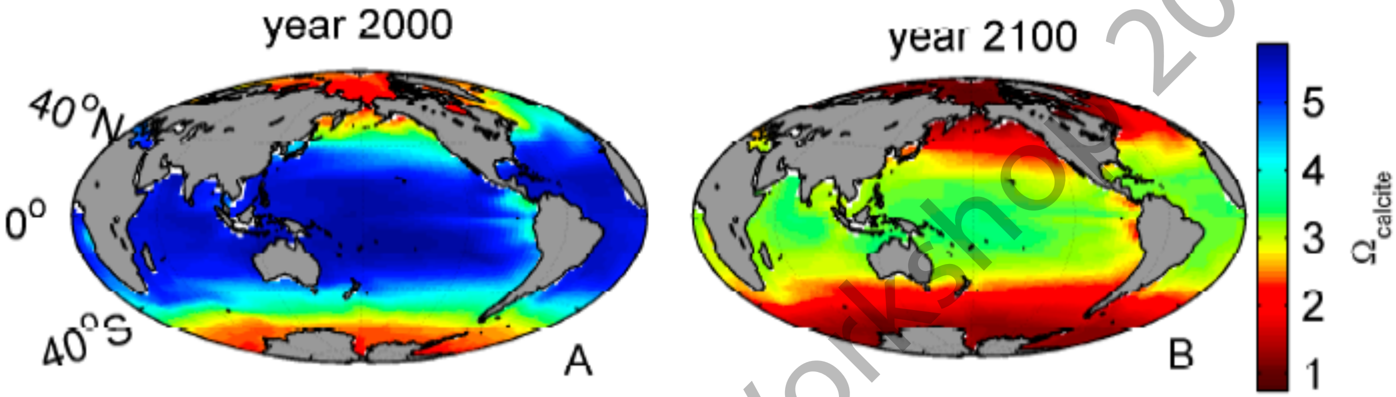




Talk Outline

What controls biocalcification? Why Bother?

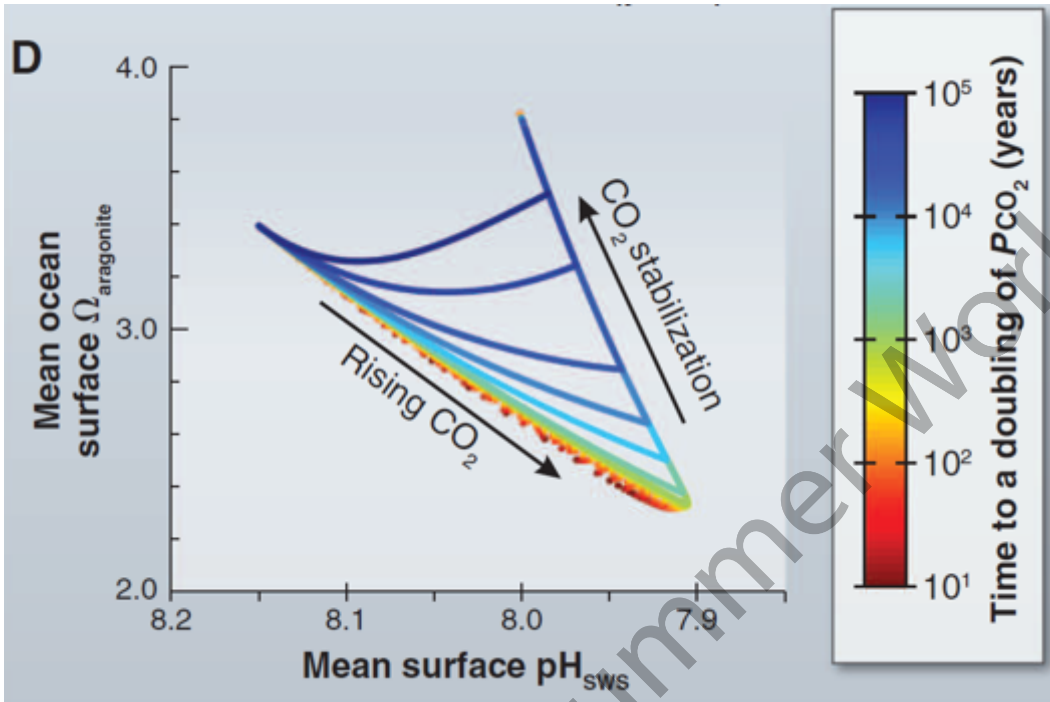
Ω



(Bach 2015)

What controls biocalcification? Why Bother?

1) Current Rates of PCO_2 Change are Unprecedented (Zeebe et al. 2016)



Hönisch et al. 2012

2) Decoupling of Carbonate System Parameters happens in Coastal Zones, and the Ocean Seasonally (Waldbusser and Salibury 2014, Fassbender et al. 2016)

3) Formation of $CaCO_3$ is largely biological, thus ocean acidification not only threatens corals and oysters, but the global $CaCO_3$ Cycle.

4) SIR and Ω will change differentially across the globe (Bach 2015)