



*Dissolution of  $\text{CaCO}_3$  in Shallow  
Water Carbonate Environments in the  
High  $\text{CO}_2$  World of the Anthropocene*

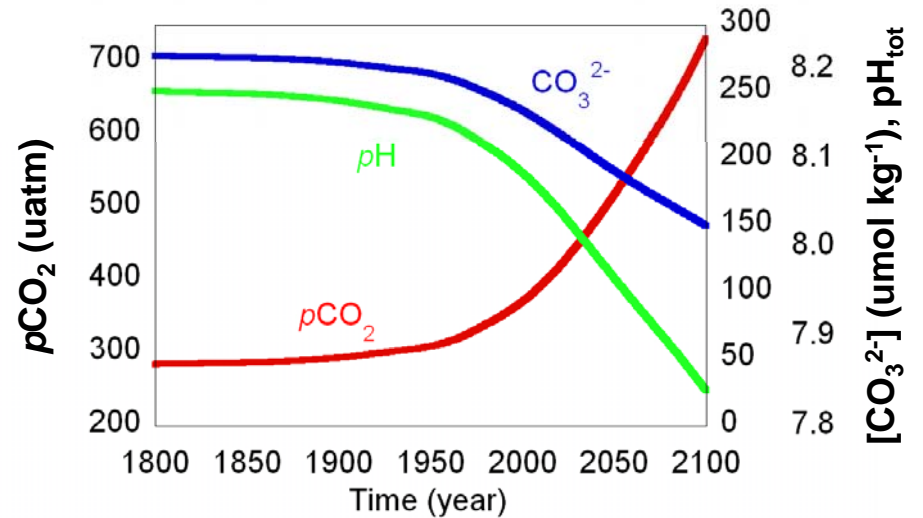
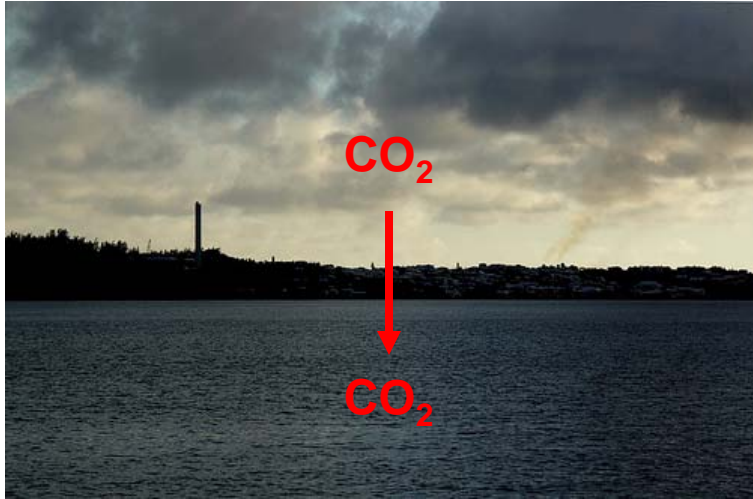
*Andreas J. Andersson  
Bermuda Institute of Ocean Sciences*

*Fred T. Mackenzie, Nicholas R. Bates, Ilsa  
B. Kuffner, Abraham Lerman, Paul L.  
Jokiel, Ku'ulei S. Rogers, Adrian Tan*



**BIOS**

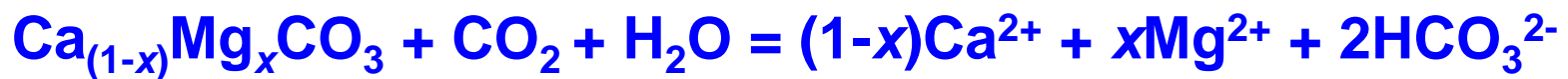
BERMUDA  
INSTITUTE  
OF OCEAN  
SCIENCES



$$\Omega = \frac{\{Ca^{2+}\}^{1-x} \{Mg^{2+}\}^x \{CO_3^{2-}\}}{K_{SP}}$$

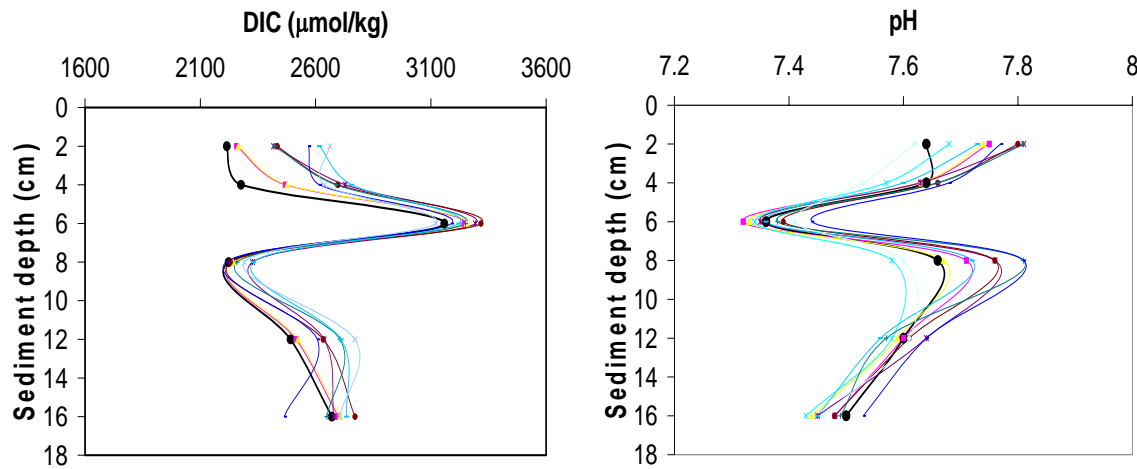
$\Omega > 1$  Supersaturated

$\Omega < 1$  Undersaturated

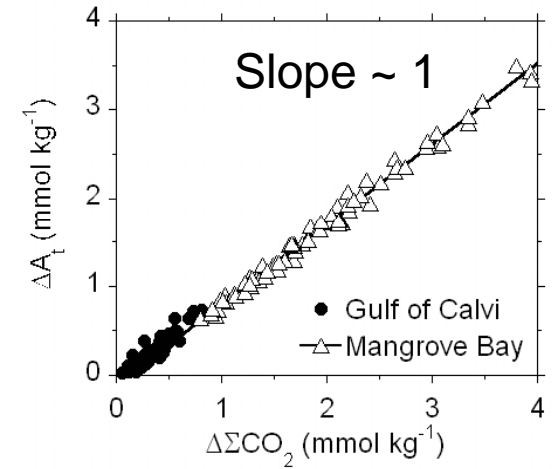


- Sink of CO<sub>2</sub>
- Produces alkalinity – increasing buffer capacity of the ocean
  - rate and amount of atm. CO<sub>2</sub> absorbed by the ocean
  - rate at which seawater chemistry is changing – buffering effect?
  - reef accretion – net accumulation or net loss?

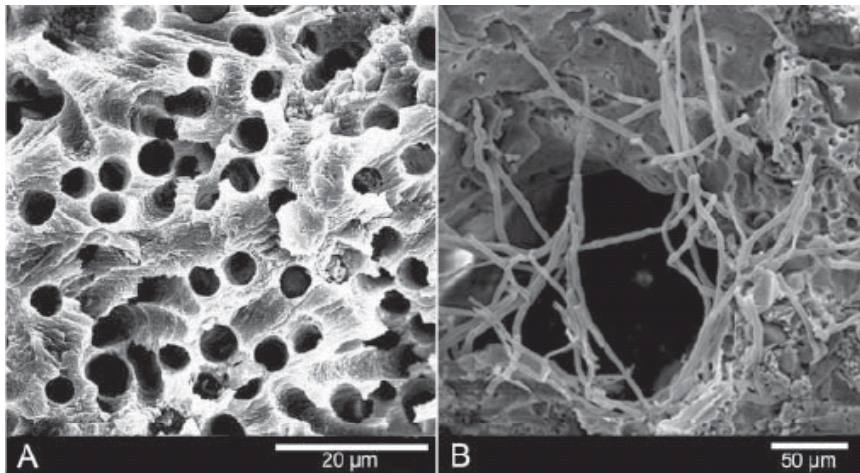
## Metabolic dissolution (e.g., microbial respiration)



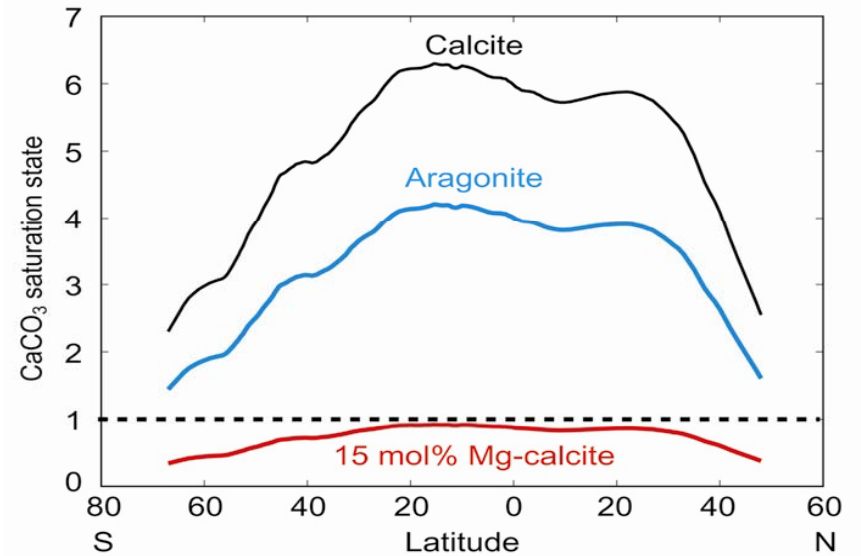
Mackenzie and Andersson 2008  
Moulin et al. 1985



## Bioerosion (boring micro-organisms/flora)



## Environmental dissolution



Tribollet 2008

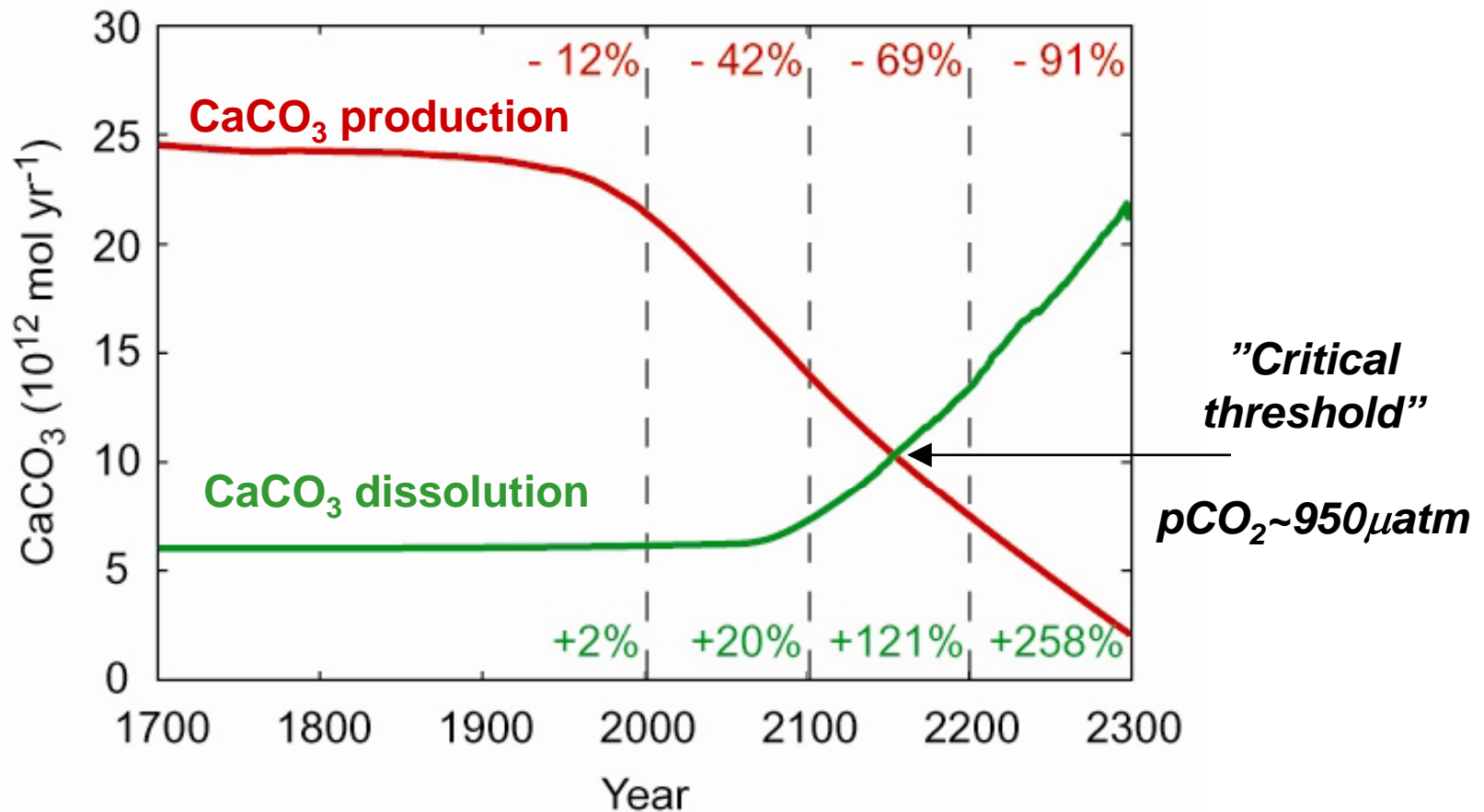
Andersson et al. 2005

# *Objective*

- Anthropogenic ocean acidification could push shallow water ocean environments to a state of net dissolution
  1. *Numerical simulations*
  2. *Field observations*
  3. *Mesocosm incubations*

## Model simulations: Shallow water Ocean Carbonate Model

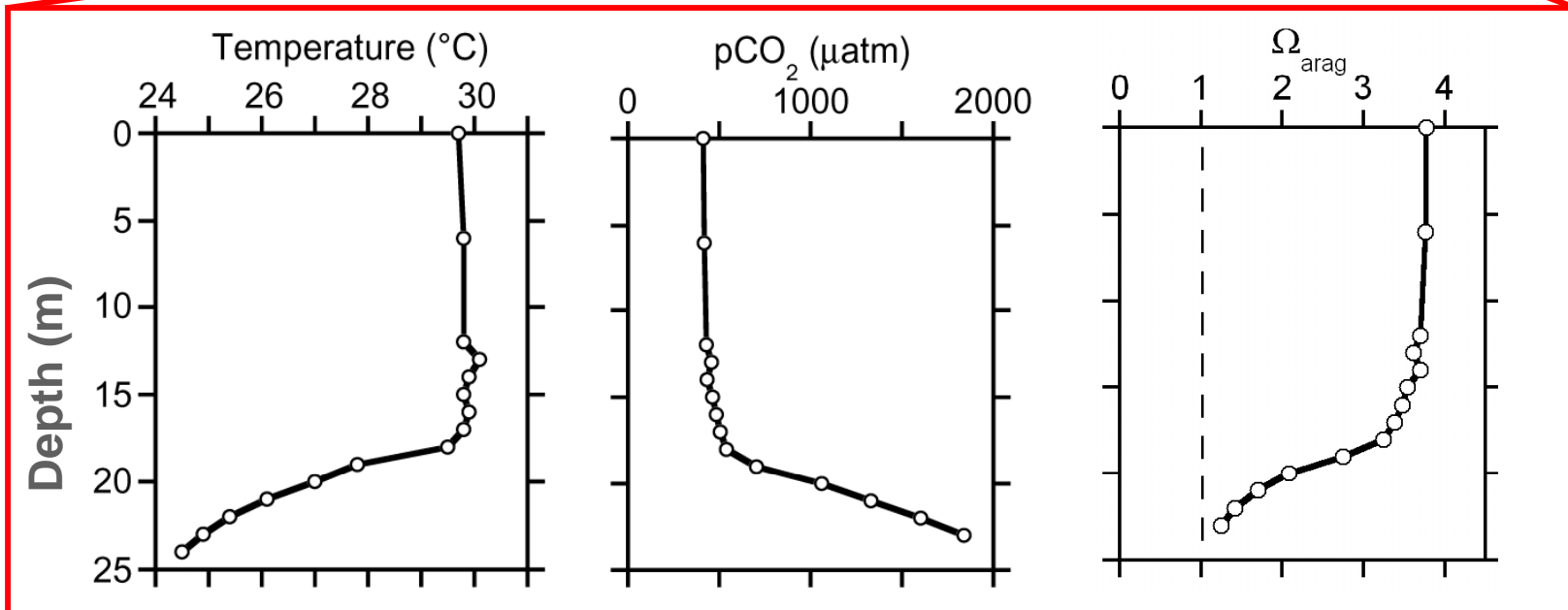
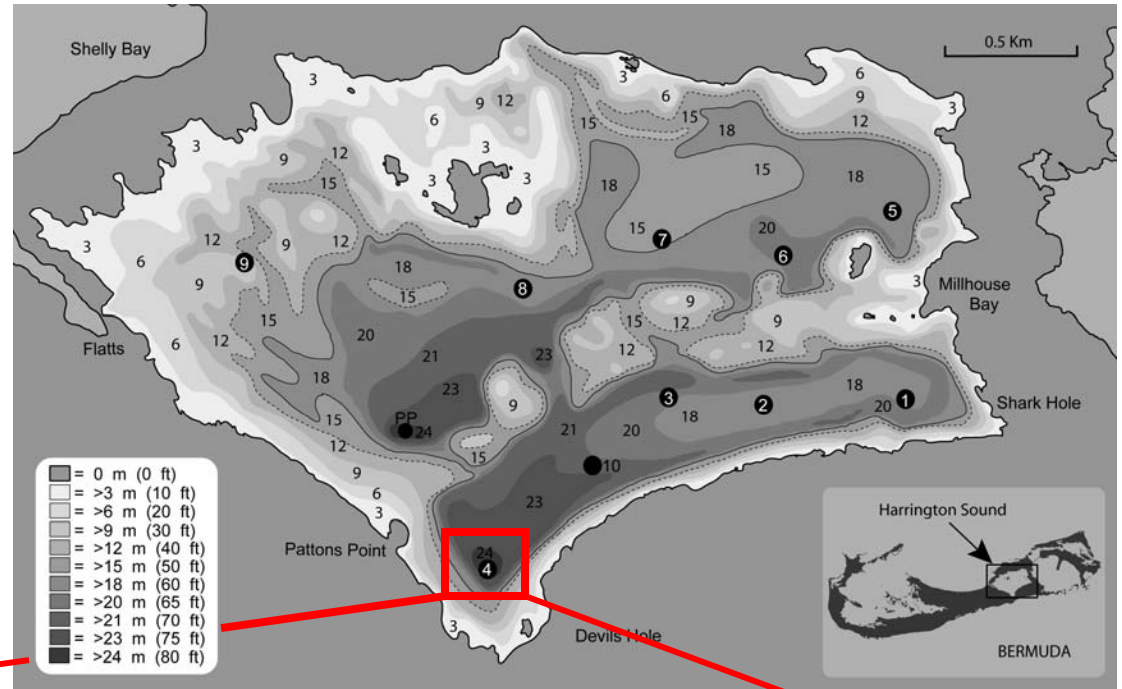
- process driven biogeochemical box model
- global coastal ocean
- IS92a CO<sub>2</sub> emission scenario - linearly extrapolated to year 2300



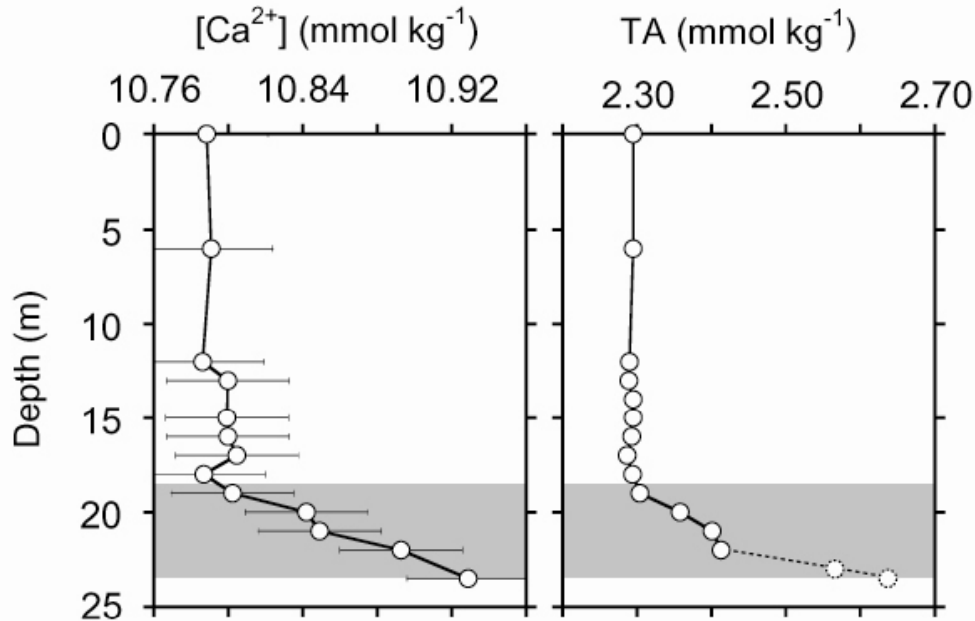
e.g. Andersson et al. 2003, 2005, 2006

# Devil's Hole, Bermuda – natural laboratory

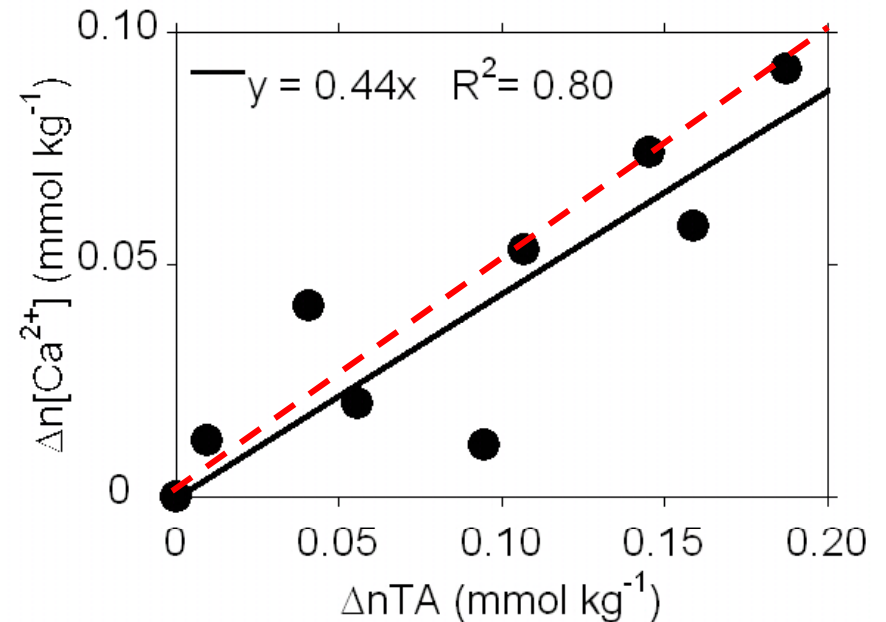
- ❑ Do  $\text{CaCO}_3$  minerals dissolve under elevated  $\text{CO}_2$ ?
- ❑ What carbonate phases are dissolving?
- ❑ What is the rate of dissolution?



# *Is carbonate mineral dissolution occurring in Devil's Hole?*



Andersson et al. 2007  
Balzer and Wefer, 1981



- $Ca^{2+} : TA \sim 1:2$
- *Slope*  $< 0.5$
- *High production of Mg-calcites*  
– little mineralogical evidence  
in deep, fine grained sediments

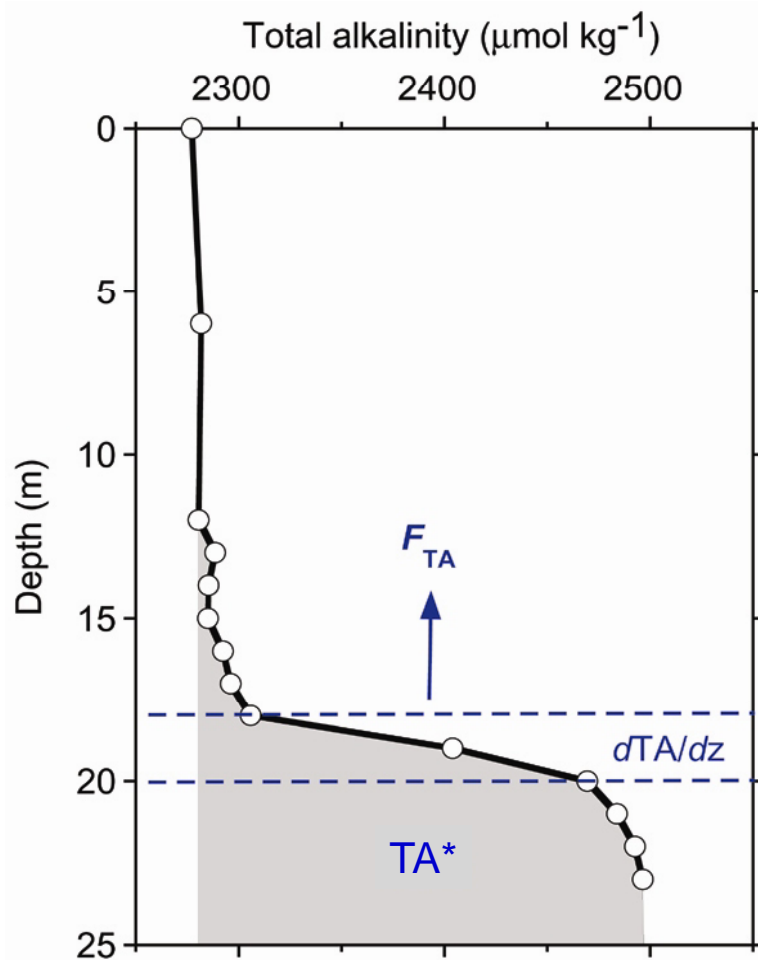
$\Rightarrow$  *Dissolution*

$\Rightarrow$  *Mg-calcite*

$\Rightarrow$  *Selective dissolution*

*Neumann 1965*

# What is the rate of dissolution of carbonate minerals in Devil's Hole?



$$R_{\text{Diss}} = \frac{\Delta TA^* + \bar{F}_{TA}}{2}$$

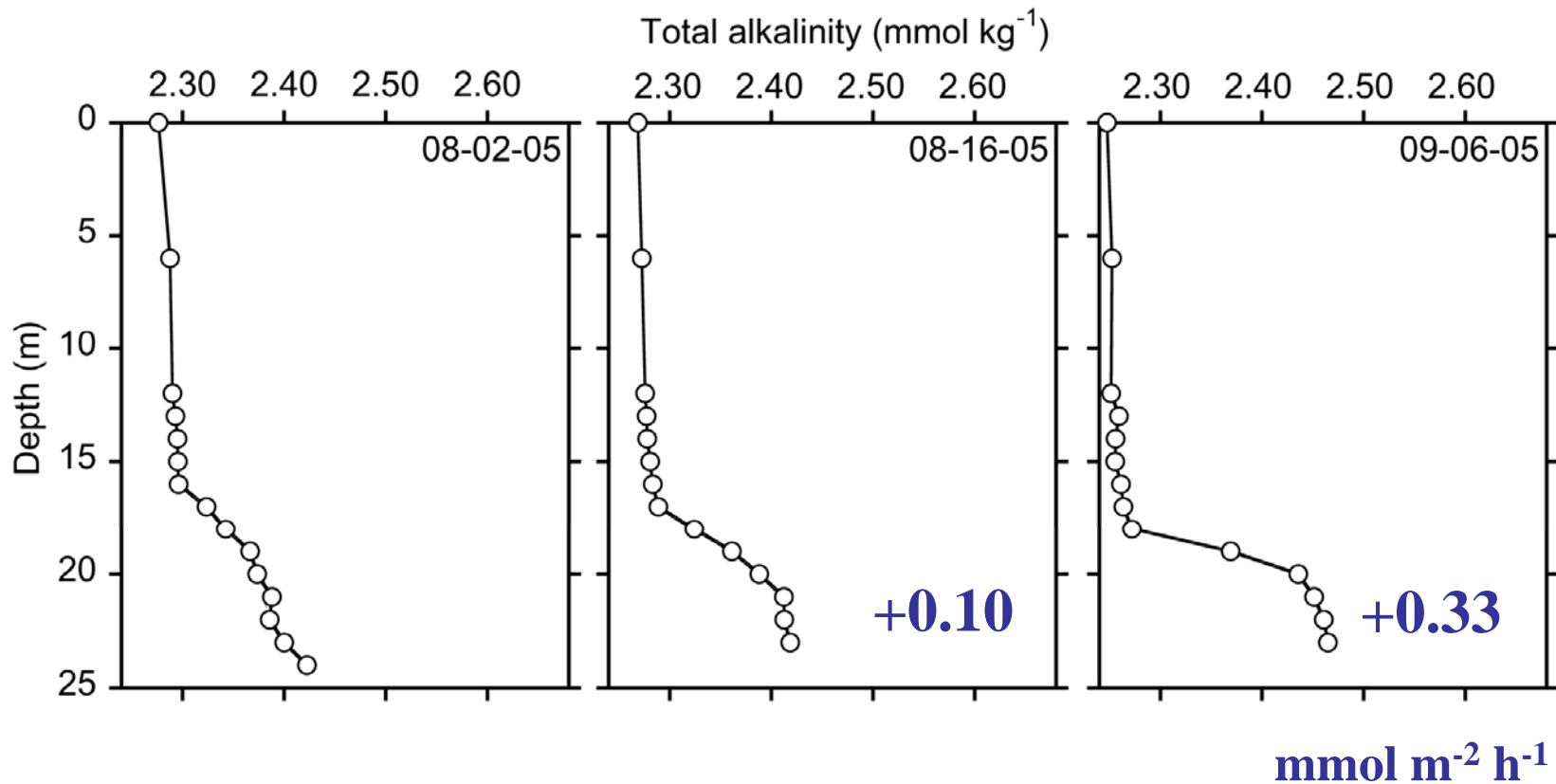
- **Excess alkalinity ( $TA^*$ )**
  - Integrate subthermocline section ( $\Sigma TA$ )
  - Preformed alkalinity ( $TA^0$ )

$$\Rightarrow TA^* = \Sigma TA - TA^0$$

- **Vertical alkalinity flux ( $F_{TA}$ )**
  - Fick's first law of diffusion
  - $F_{TA} = -D \times dTA/dz$
  - $D = 2 \text{ to } 6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  (Brown, 1980; heat budget)

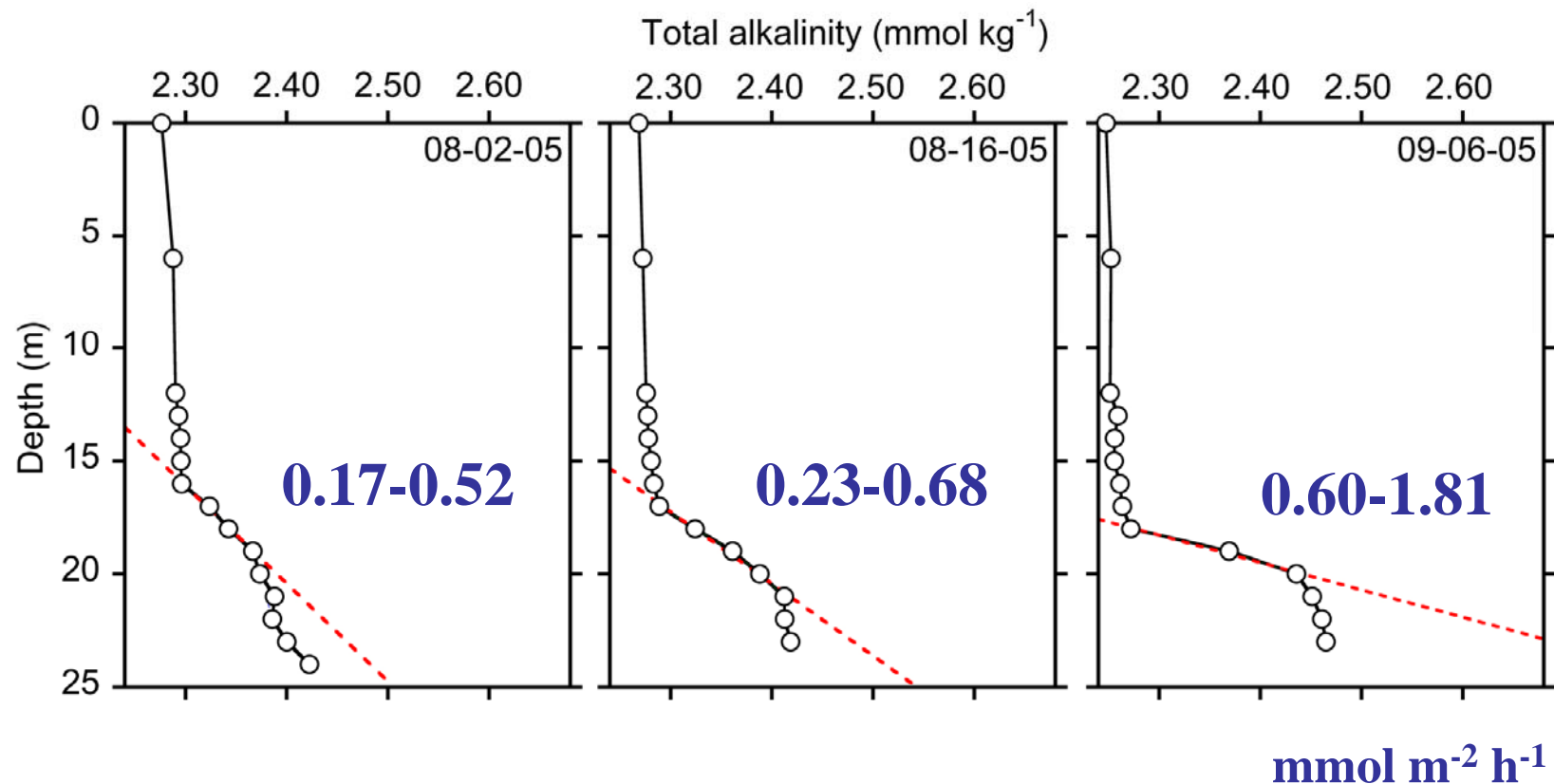
*What is the rate of dissolution of carbonate minerals in Devil's Hole?*

Changes in excess alkalinity;  $R_{\text{Diss}} = \frac{\Delta \text{TA}^* + \bar{F}_{\text{TA}}}{2}$



*What is the rate of dissolution of carbonate minerals in Devil's Hole?*

*Vertical diffusion of alkalinity;*  $R_{\text{Diss}} = \frac{\Delta \text{TA}^* + \bar{F}_{\text{TA}}}{2}$



# *What is the rate of dissolution of carbonate minerals in Devil's Hole?*

$$R_{\text{Diss}} = \frac{\Delta \text{TA}^* + \bar{F}_{\text{TA}}}{2}$$

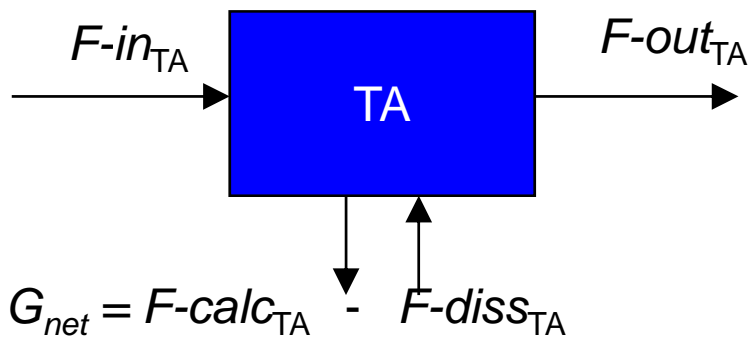
**Table 2.** Calculated excess alkalinity, range of vertical alkalinity diffusion, and rate of dissolution in subthermocline waters of Devil's Hole during August and September 2005

Date	Integration depths	Excess alkalinity (mmol m <sup>-2</sup> )	Δ Excess alkalinity (mmol m <sup>-2</sup> h <sup>-1</sup> )	Vertical alkalinity diffusion (mmol m <sup>-2</sup> h <sup>-1</sup> )		Rate of dissolution (mmol CaCO <sub>3</sub> m <sup>-2</sup> h <sup>-1</sup> )	
				Min	Max	Min	Max
24-aug-2004	13.5-23.5	415	-	0.23	0.70	-	-
16-sep-2004	18.8-23.5	477	0.11	0.31	0.94	0.19	0.47
2-aug-2005	16.0-23.5	499	-	0.17	0.52	-	-
16-aug-2005	16.7-23.7	532	0.10	0.23	0.68	0.15	0.35
6-sep-2005	17.8-23.5	700	0.33	0.60	1.81	0.37	0.79

- *0.15 to 0.79 mmol m<sup>-2</sup> h<sup>-1</sup> - analogue to future CO<sub>2</sub> conditions?*
- *175 to 701 grams CaCO<sub>3</sub> m<sup>-2</sup> yr<sup>-1</sup>*
- *Average coral reef calcification: ~1500 grams m<sup>-2</sup> yr<sup>-1</sup> (Milliman, 1993)*
- *Calcification decrease 42% by 2100 and 90% by 2300*

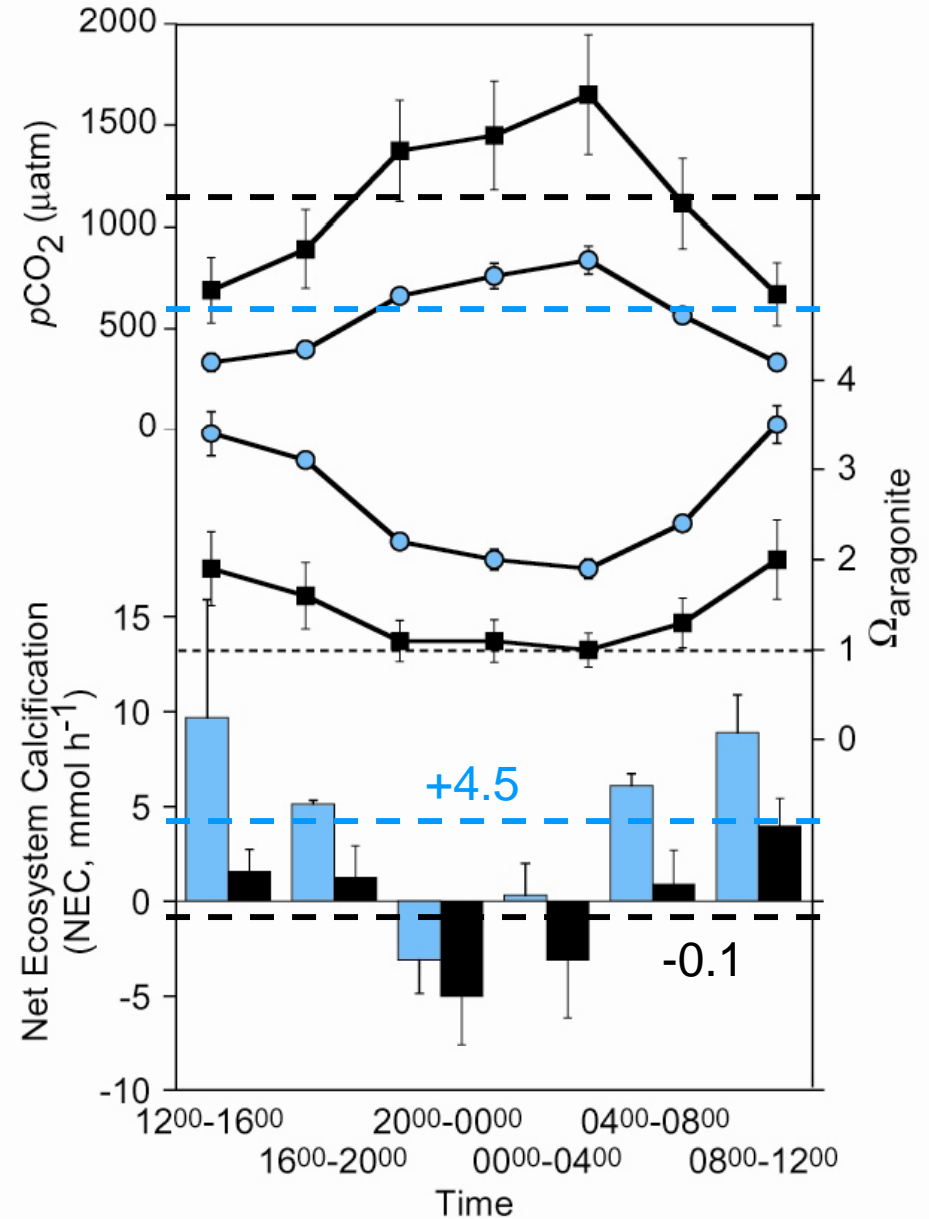
# Mesocosm incubations...

Net Community Calcification,  $G_{net} = \text{calcification} - \text{dissolution}$

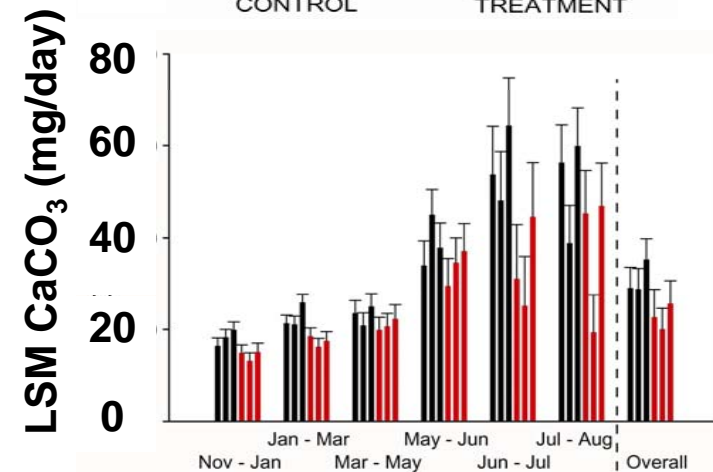
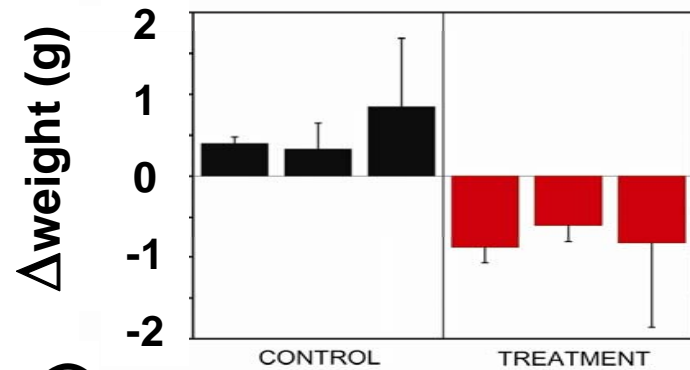
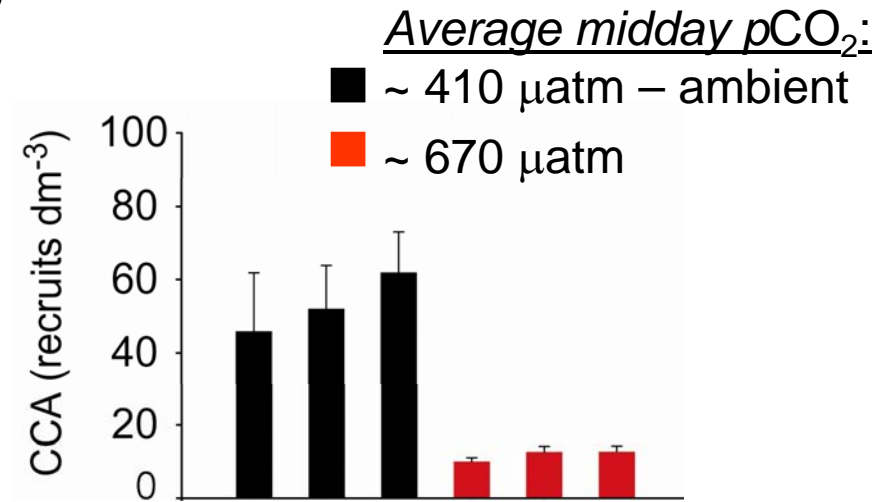
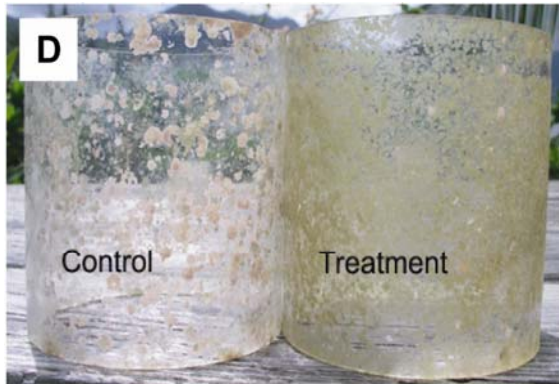


$$dTA/dt = Fin_{TA} - Fout_{TA} - 2 \times G_{net}$$

$$G_{net} = [Fin_{TA} - Fout_{TA} - dTA/dt] / 2$$



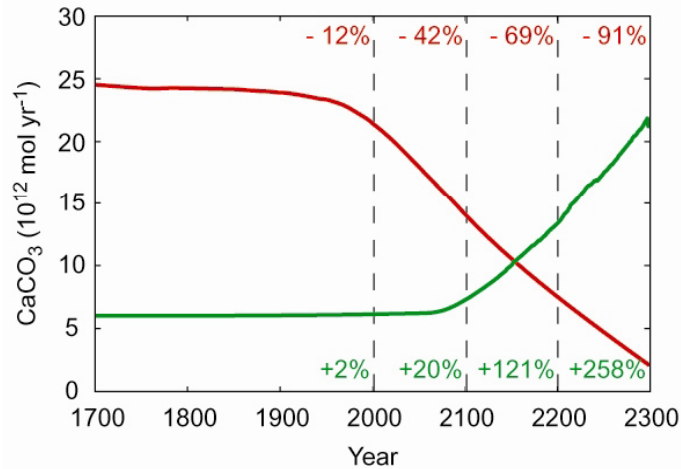
# Long term effects on individual organisms...



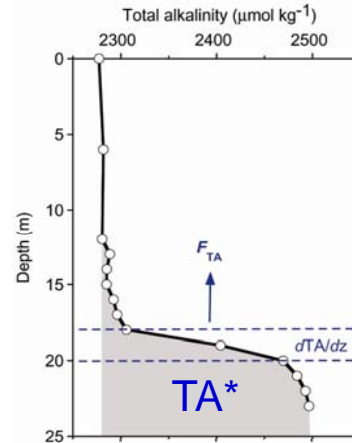
Kuffner et al. 2008; Jokiel et al. 2008

# Summary and conclusions...

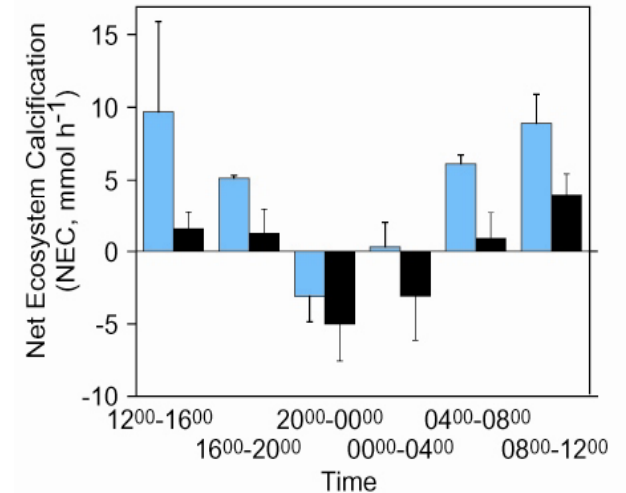
## 1. Numerical model



## 2. Devil's Hole



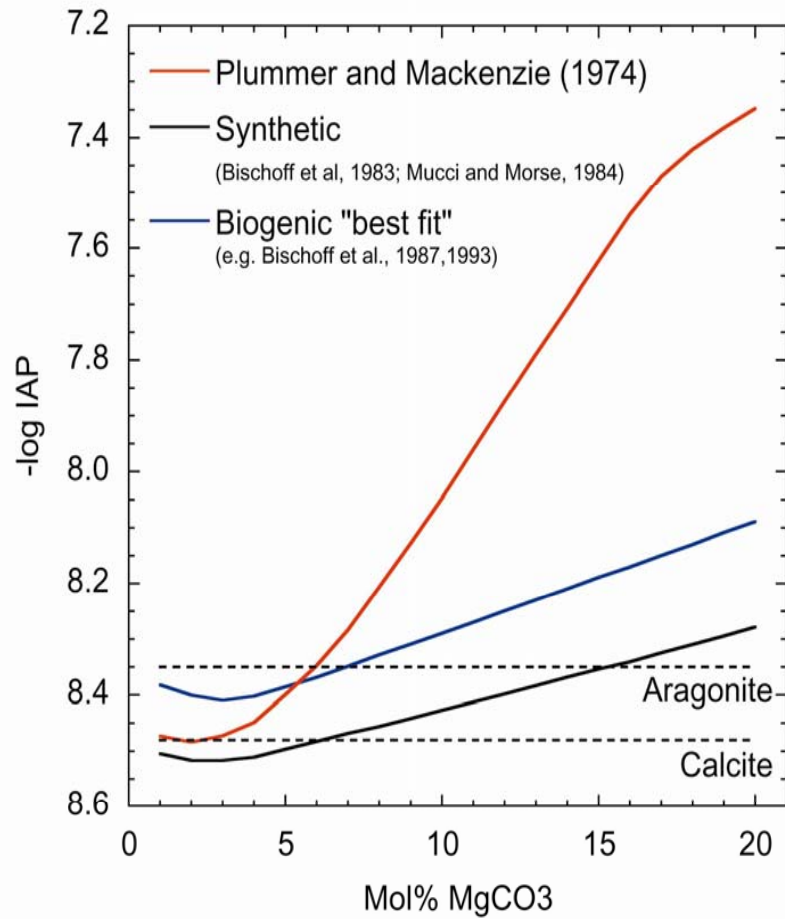
## 3. Mesocosms



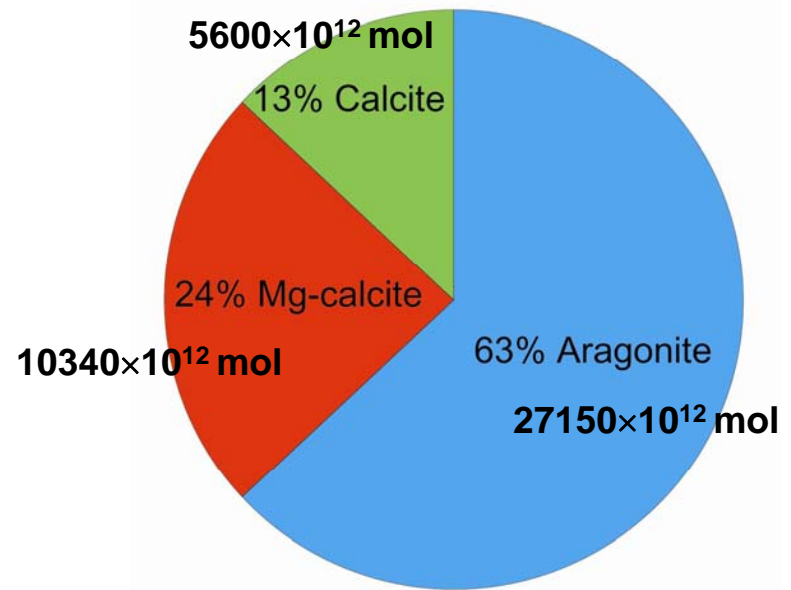
### **As a result of anthropogenic ocean acidification:**

- Carbonate mineral dissolution will increase
- Shallow water carbonate environments - state of net dissolution
  - Timing of transition is uncertain, but the trend is robust
  - Negative community calcification – organisms still able to sustain themselves
- Dissolution will not produce sufficient alkalinity to significantly buffer surface ocean from changes in seawater chemistry neither on a global nor a regional scale
  - Rate of CO<sub>2</sub> emissions and oceanic uptake
  - Rate of physical mixing between open ocean and shallow environments

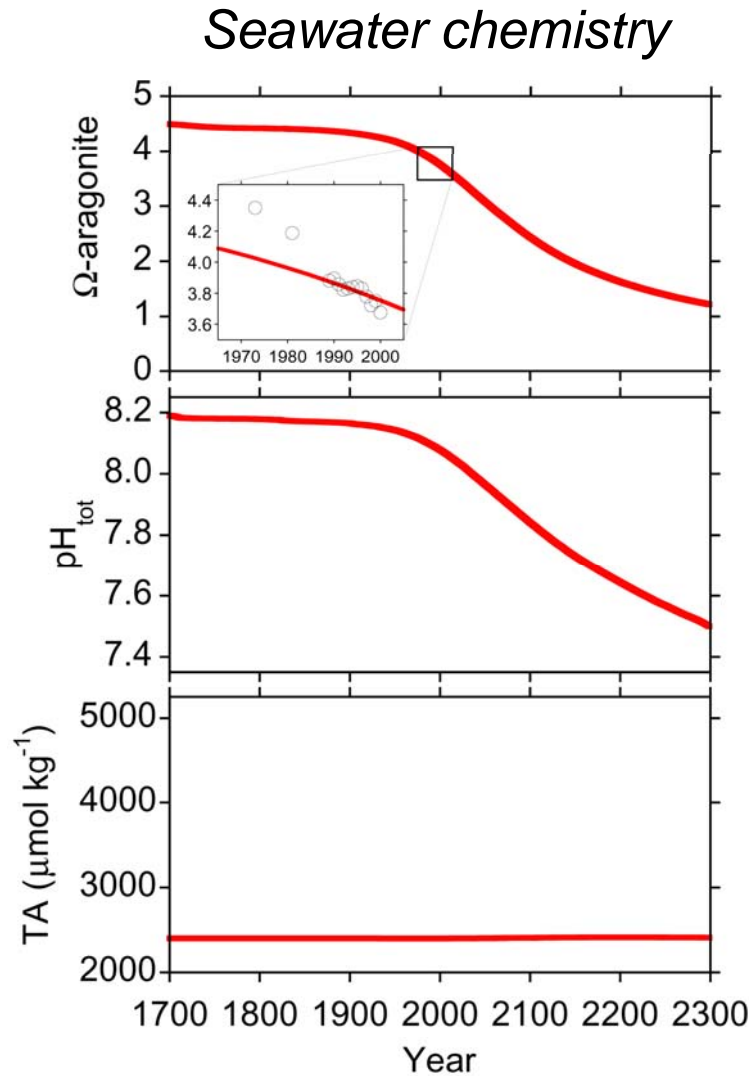
## Mineral solubility



## Shallow water reactive CaCO<sub>3</sub> reservoir



*Will dissolution of Mg-calcite minerals buffer surface ocean pH from changes owing to rising  $p\text{CO}_2$ ?*



*Will dissolution of Mg-calcite minerals buffer surface ocean pH from changes owing to rising pCO<sub>2</sub>?*

