Seawater Chemistry Change in a Greenhouse Earth and Why Some Scientists Worry About It

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History of Calcification v. CO_2 Issue

1966
Broecker &
Taka
Bahar

1973
Zimen & Altenhein
(Z. Naturforsch.)
&
pre
un
su
Y2

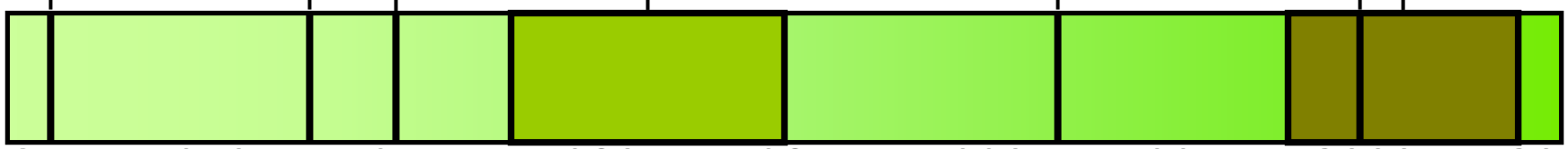
1975
Skirrow & Whitfield
(L&O)
& **Whitfield** *(Nature)*
Recalculate
& predict no
undersatura
10x increase

1979-1985
Several studies illustrate calcification rate dependent on *degree* of saturation state.

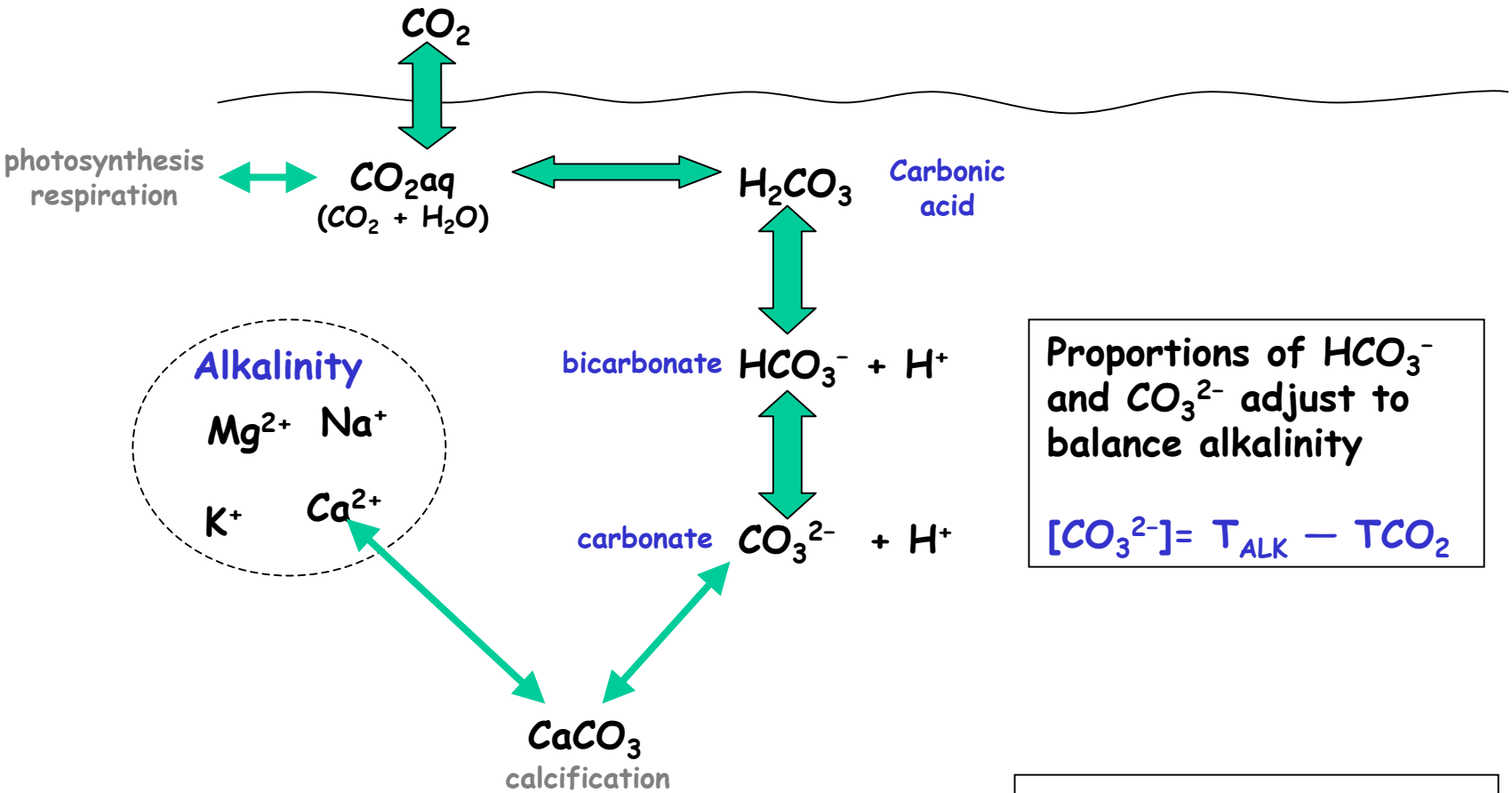
1992
Smith & Buddemeier
(Ann. Rev. Ec
Point out pos
of increased
reef calcificat

1998-present
Numerous lab & mesocosm studies show 10-50% decrease in
coral/alga
calcificatio
2x pCO_2

2000
Lough & Barnes
(JEMBE)
No decrease in *Porites* calc'n between 1880-1929 & 1930-1979



Carbonate Chemistry

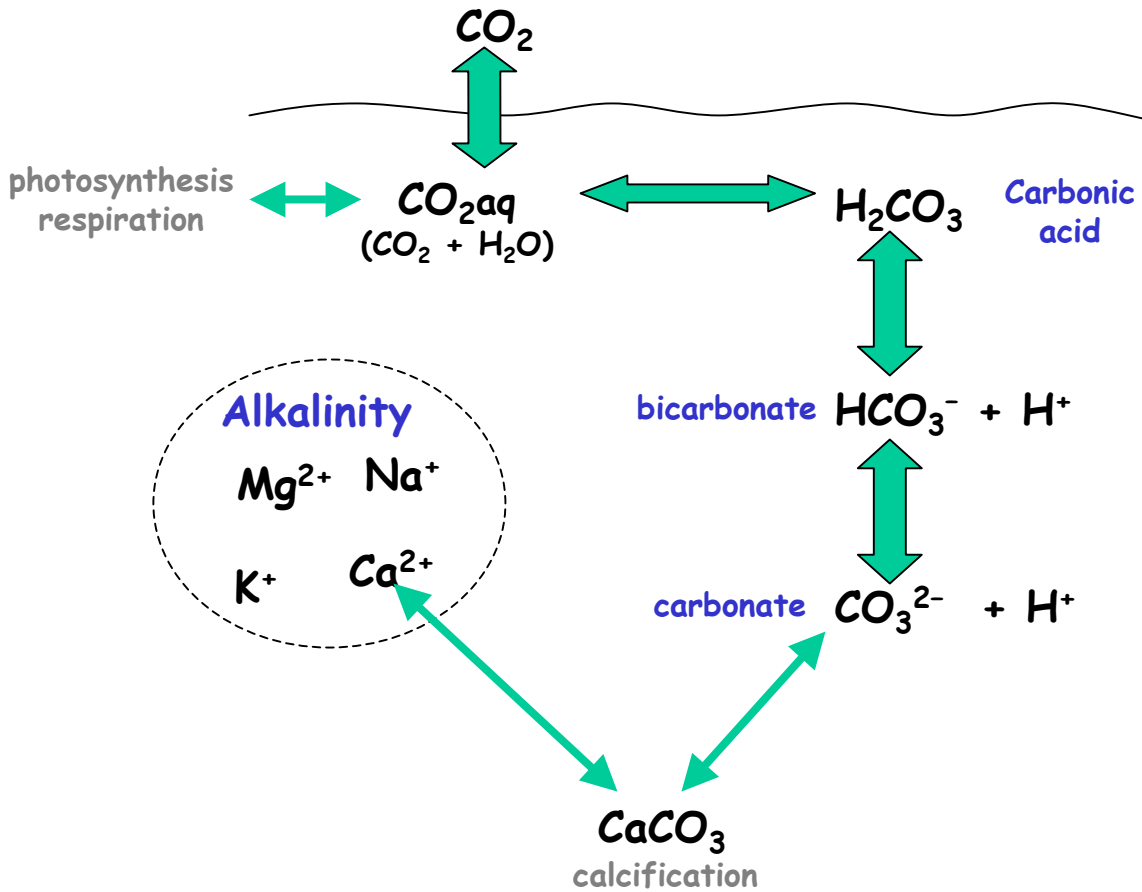


Proportions of HCO_3^- and CO_3^{2-} adjust to balance alkalinity

$[CO_3^{2-}] = T_{ALK} - TCO_2$

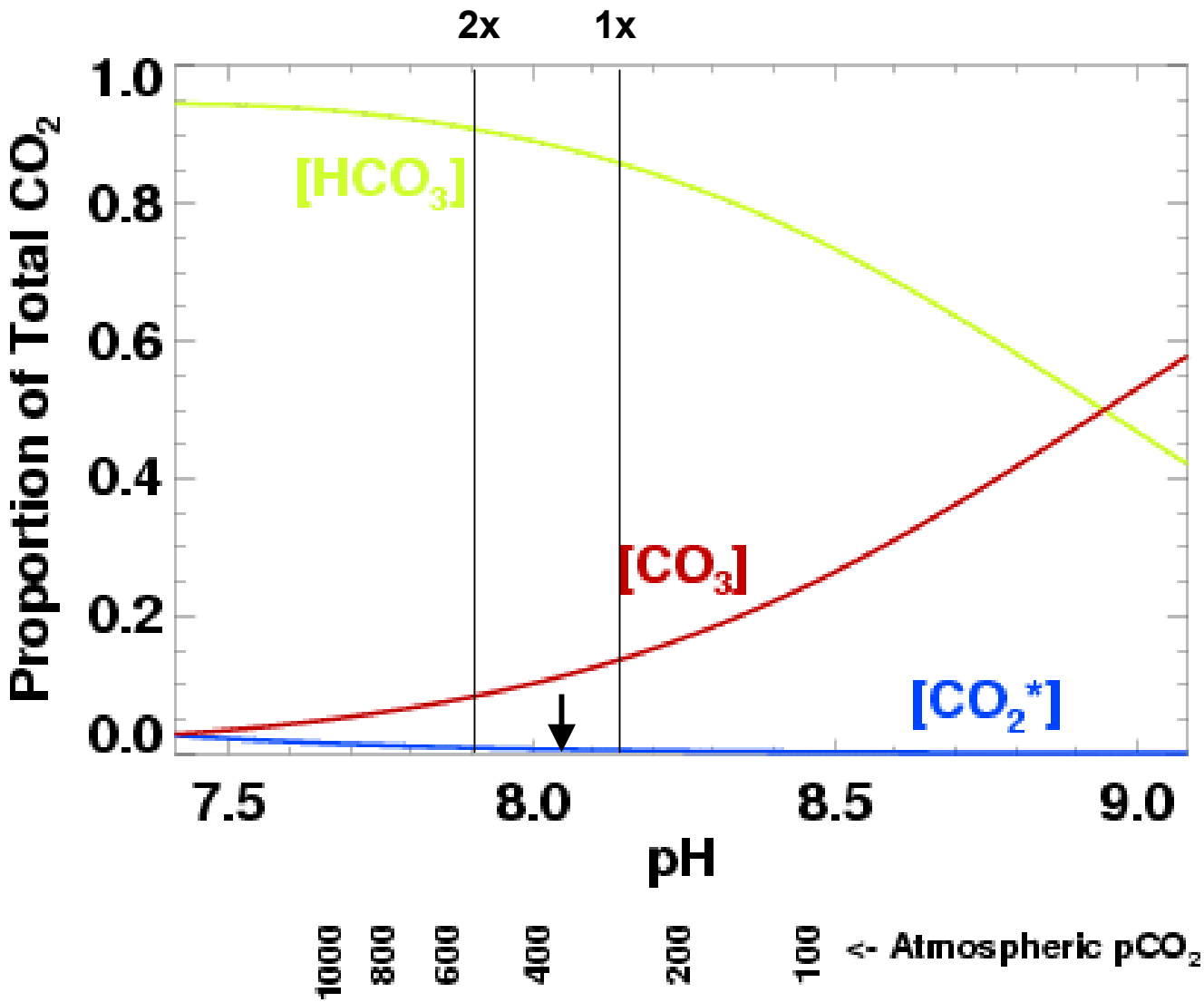
$\Omega = [Ca^{2+}][CO_3^{2-}]/Ksp$

Carbonate Chemistry

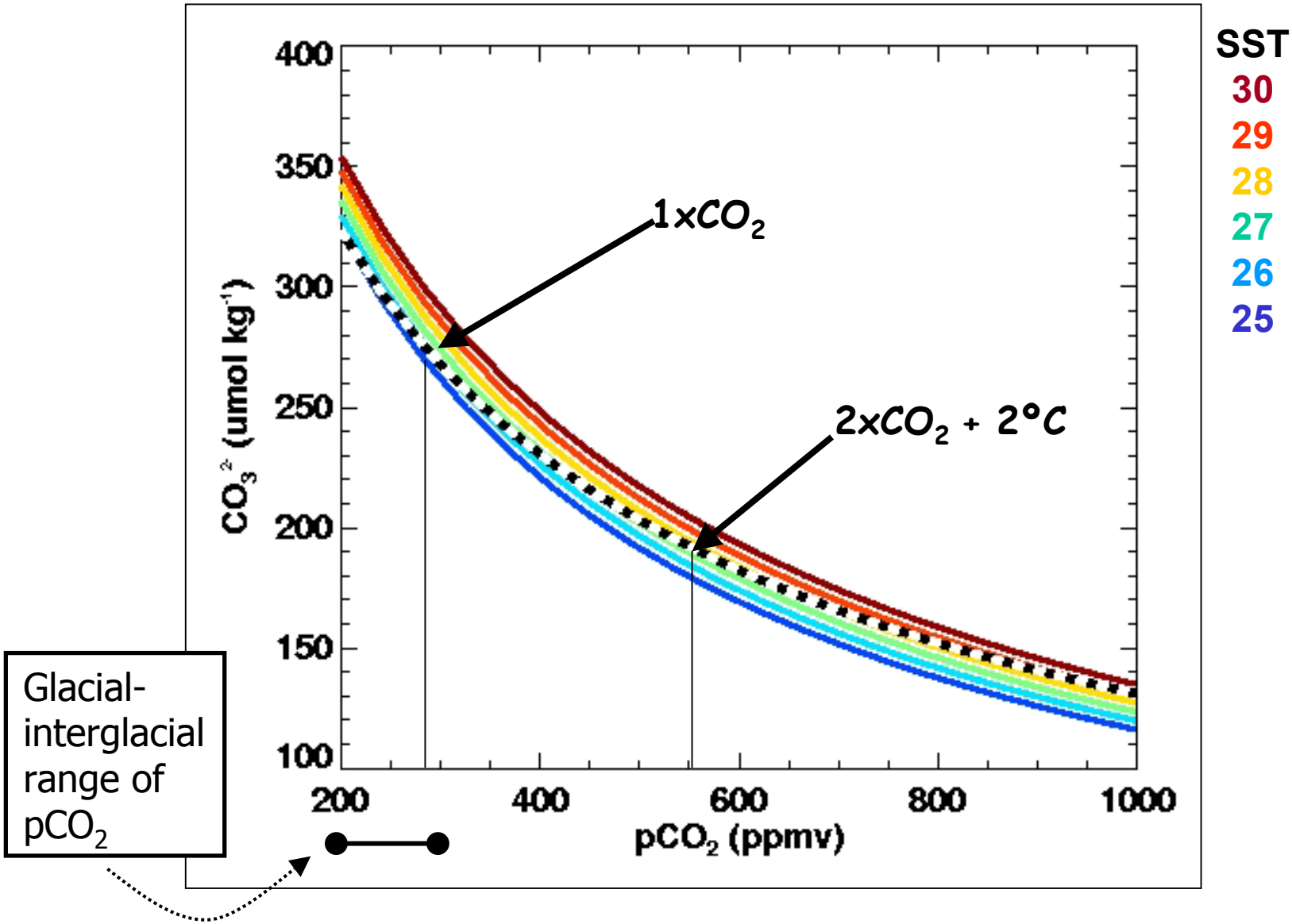


	1xCO_2	2xCO_2
CO_2	280	560
CO_2aq (CO_2 + H_2O)	8	16
HCO_3^- + H^+	1635	1867
CO_3^{2-} + H^+	272	177
TCO_2	1915	2061
T_{alk}	2300	2300
pH	8.17	7.93
Ω-arag	4.3	2.8

Proportion of Carbonate Species

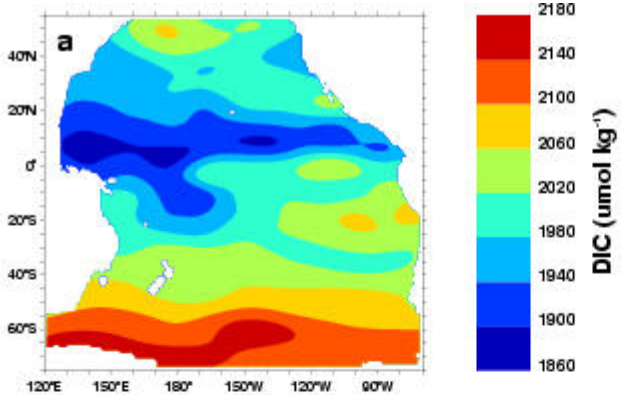


Effect of Temperature on $[CO_3^{2-}]$



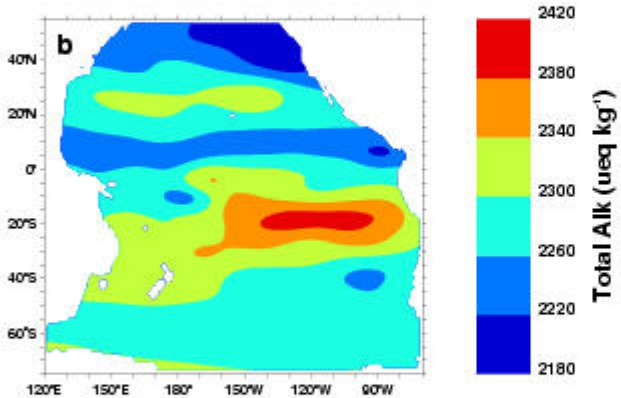
Approximating $[CO_3^{2-}]$ in the Pacific Ocean

Total CO_2

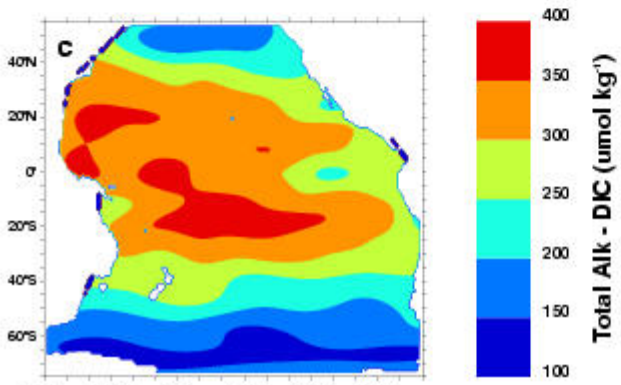


Data from synthesis of CO_2 survey data: WOCE, JGOFS & OACES (Lamb et al. 2001)

Total Alkalinity

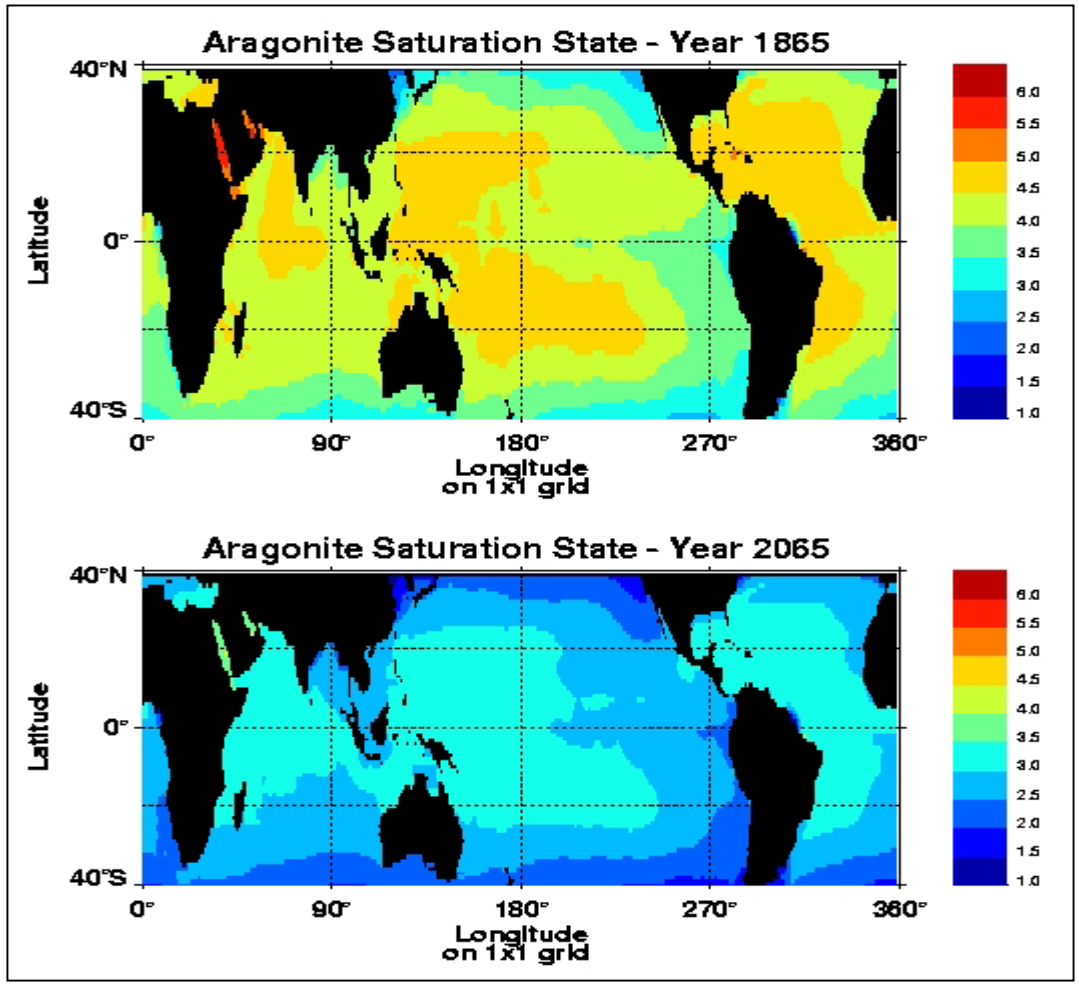


$\sim CO_3^{2-}$



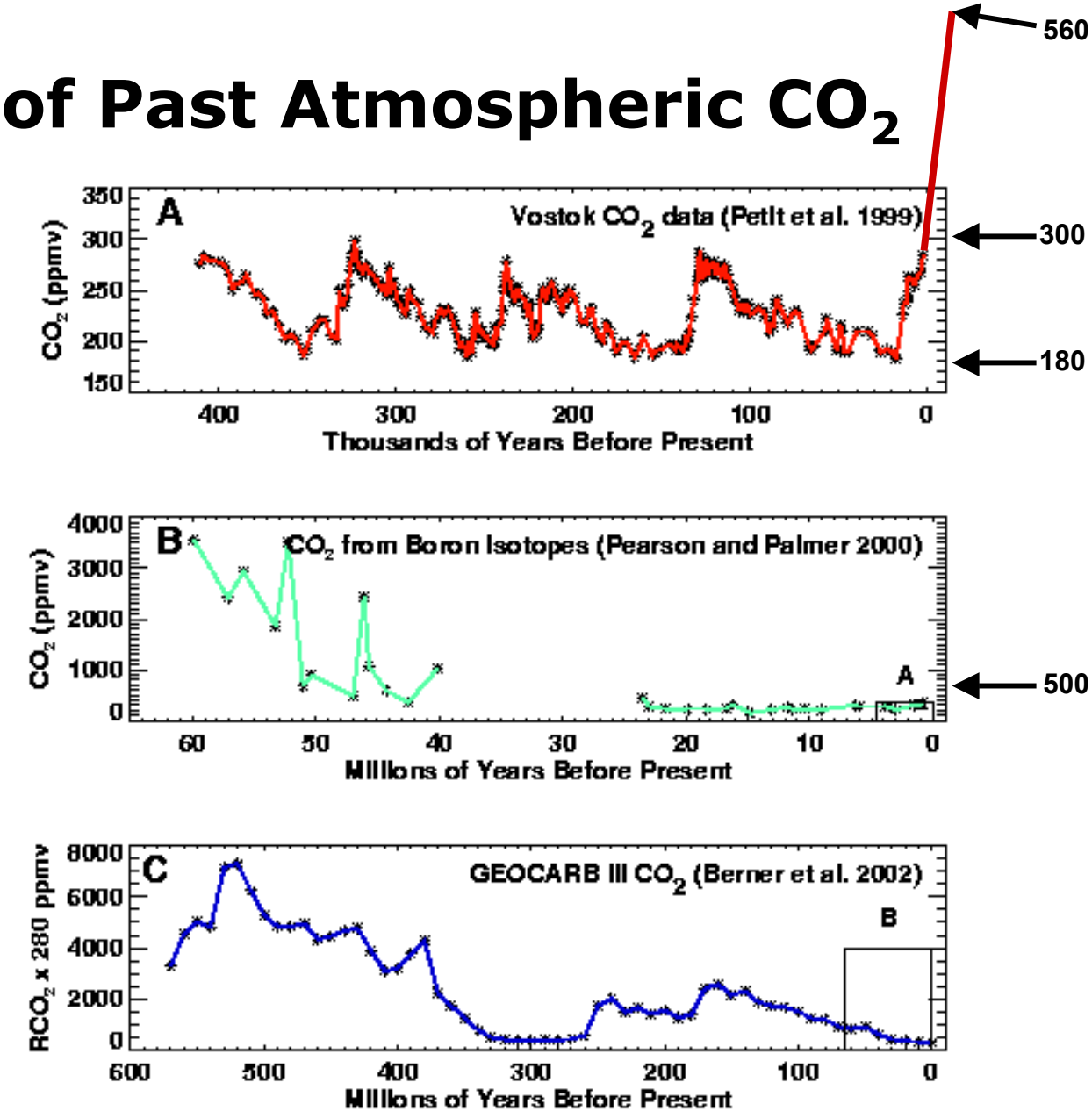
$[CO_3^{2-}] = T_{ALK} - TCO_2$

Changes in Aragonite Saturation State 1865 - 2065

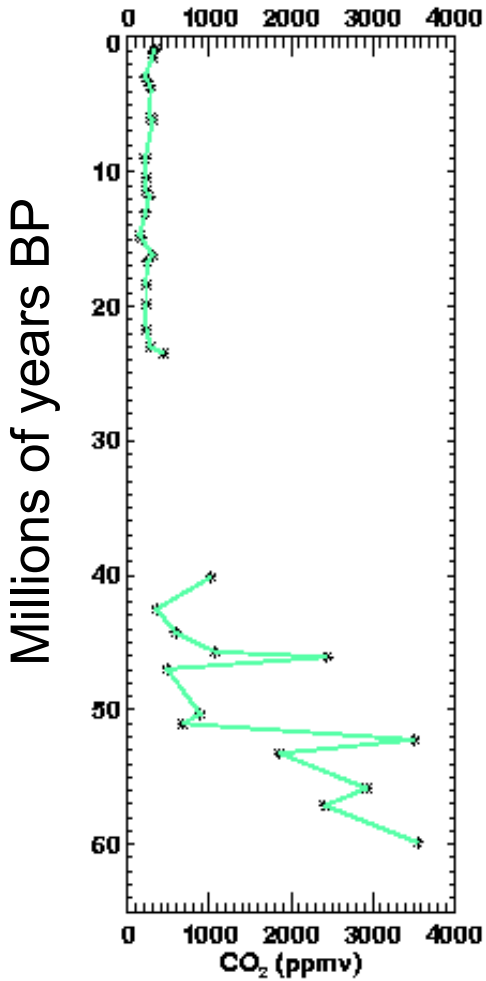


Records of Past Atmospheric CO_2

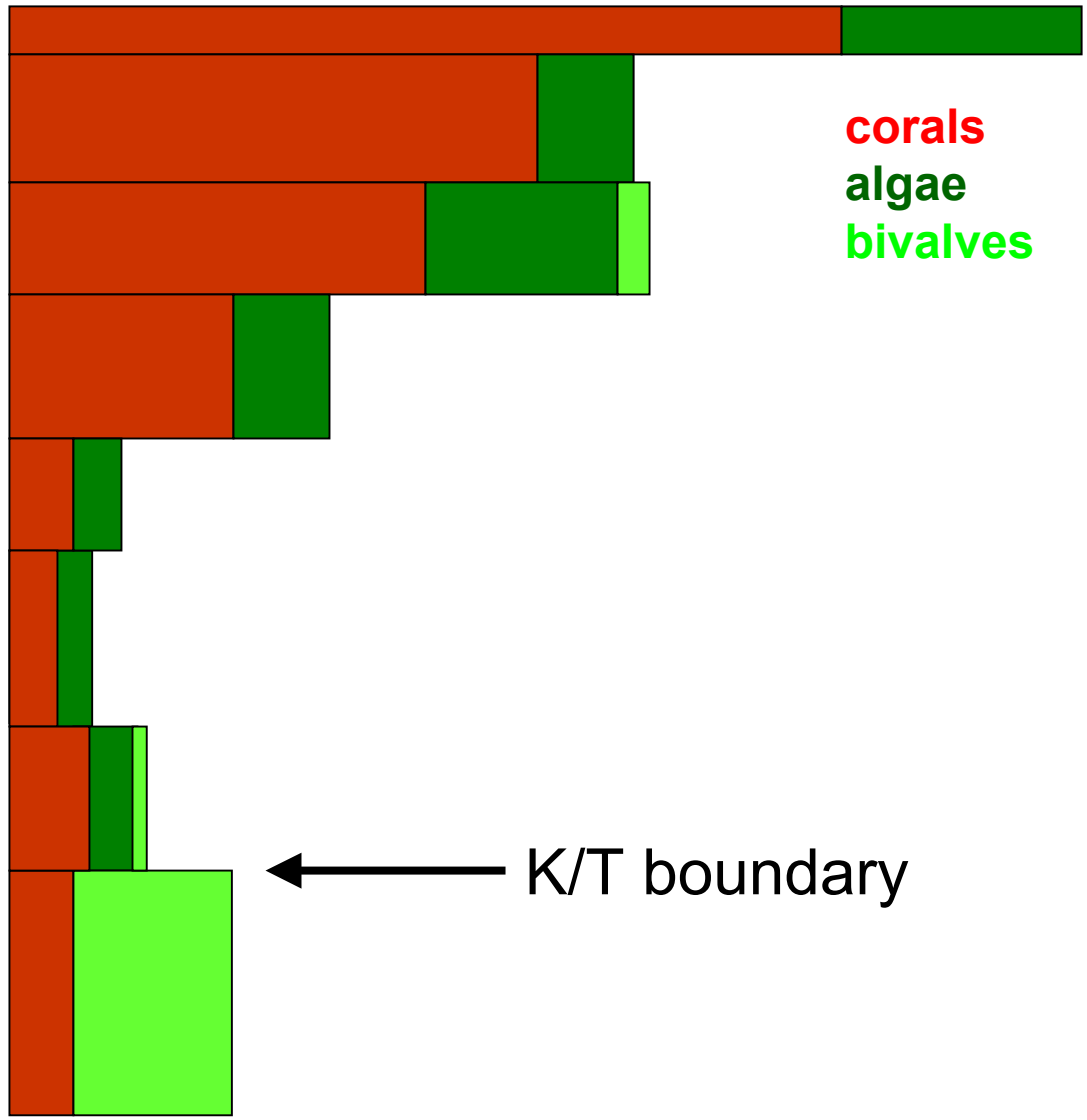
Latest lines of evidence suggest that CO_2 levels have been below 500 ppmv since the Miocene (~24 my ago)



Coral/algal reef development over time

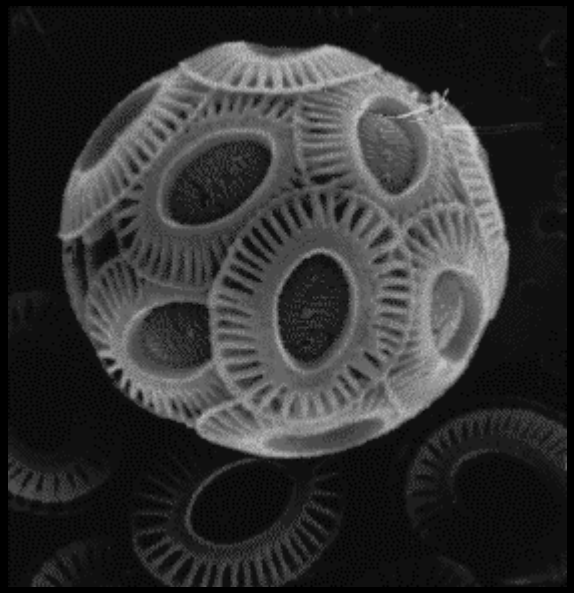


Pearson & Palmer 2000



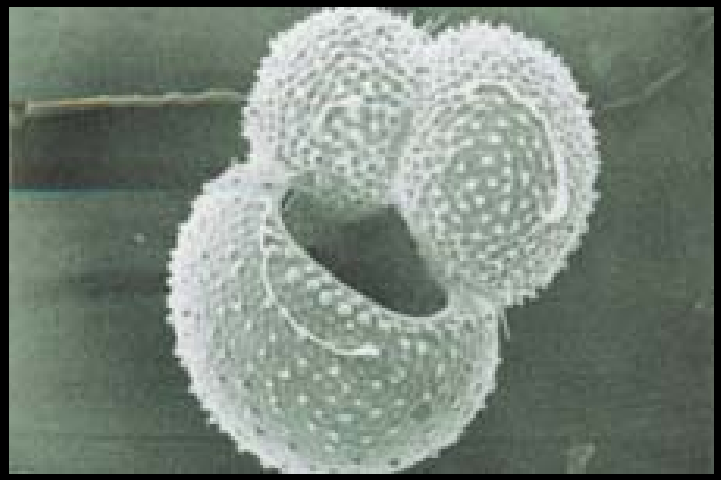
Kiessling et al. 1999

Coccolithophores
calcite



T. Tyrrel

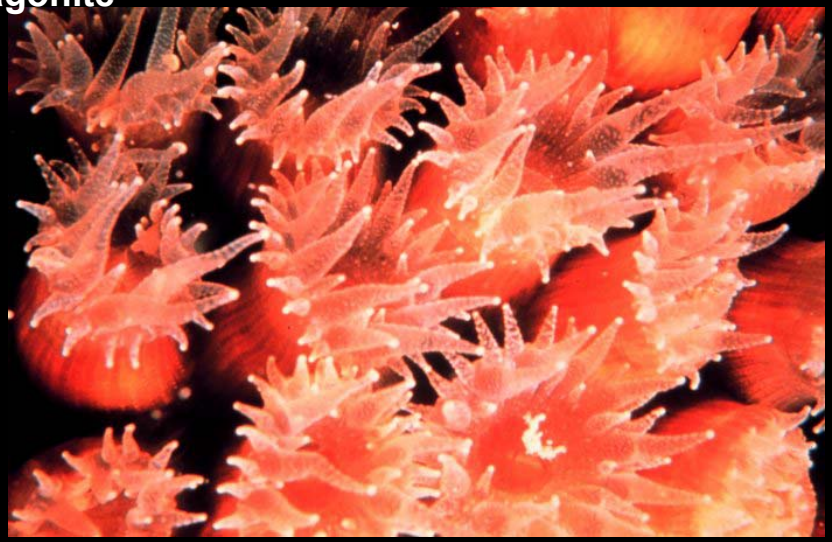
Forams
calcite



Calcareous algae
High-Mg calcite

Nancy Sefton

Corals
aragonite



NOAA

Effects of doubled CO_2 on calcification

Organism/ System	Manipulation
Corallina	1
Porolithon	2
Amphiroa	3
Turbinaria	2
Stylophora	2
Goniastrea	2
Acropora	2
Porites	2
	1
Acropora	2
Porites	2
Porites/ Montipora	2
Montipora	3
Gr. Bahama Banks*	4
B2 mesocosm*	1,3,4
Monaco mesocosm	1

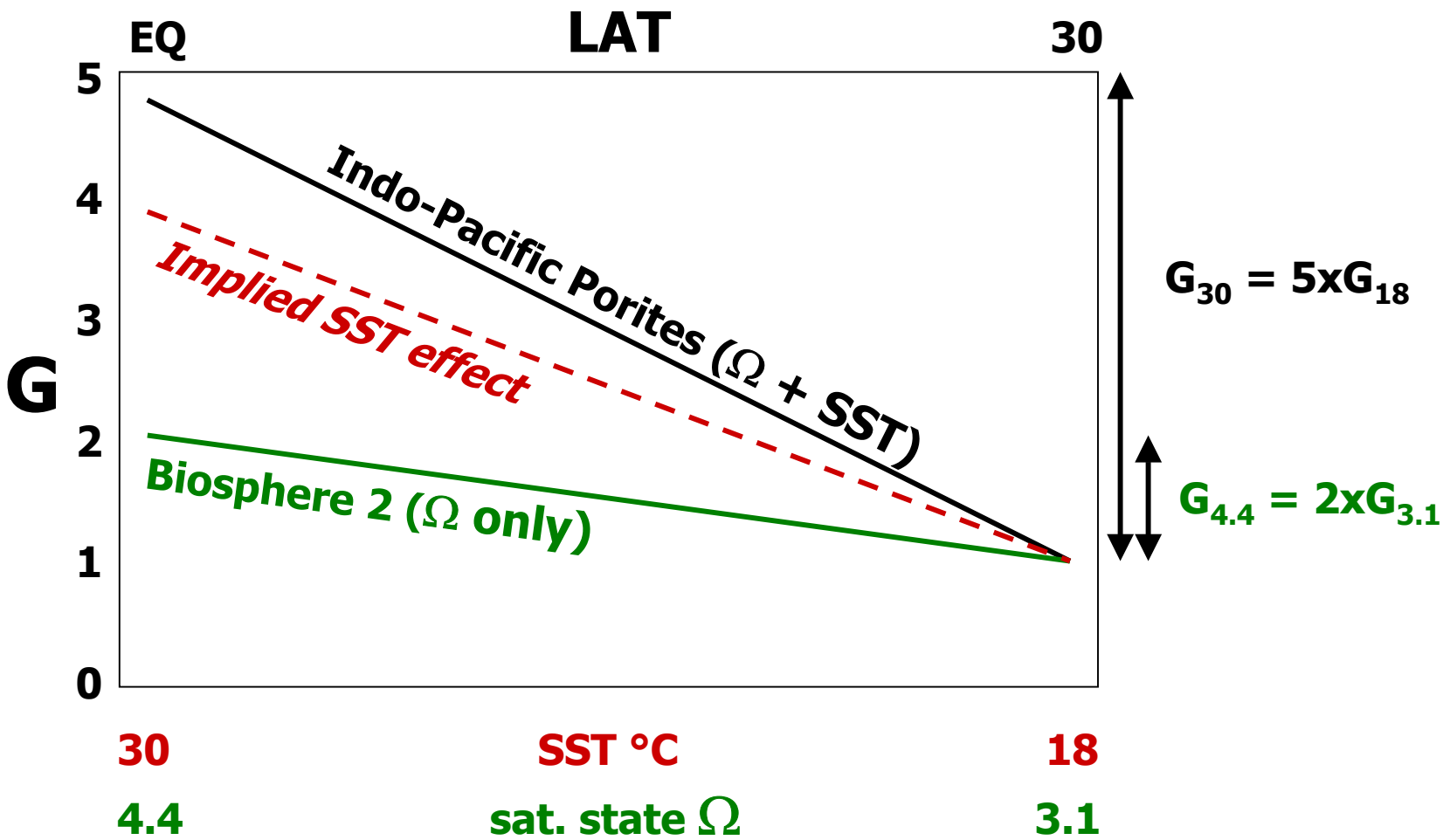
I.	Constant TA	Adjust TCO_2 with CO_2 gas
2.	Constant TCO_2	Adjust TA with acid / base
3.	Constant pH	Adjust TA and TCO_2
4.	Natural	Let organism or community change chemistry

Effects of doubled CO_2 on calcification

Organism/ System	Manipulation	% Change in Calc'n	Reference
Corallina	1	-44	Gao 1993
Porolithon	2	-25	Agegian 1985
Amphiroa	3	-36	Borowitzka 1981
Turbinaria	2	-15	
Stylophora	2	-15	
Goniastrea	2	-16	Marubini et al. 2003
Acropora	2	-18	
Porites	2	-18	
	1	-19	Marubini et al. 2001
Acropora	2	-37	Schneider & Erez 2000
Porites	2	-27	Marubini & Atkinson 1999
Porites/ Montipora	2	-51	Langdon & Atkinson (in prep)
Montipora	3	-22	Langdon (in press)
Gr. Bahama Banks*	4	-82	Broecker & Takahashi 1964
			Broecker et al. 2001
B2 mesocosm*	1,3,4	-54	Langdon et al. 2000
Monaco mesocosm	1	-21	Leclercq et al. 2000

* dominated by coralline algae

Porites Calcification
Ω versus SST

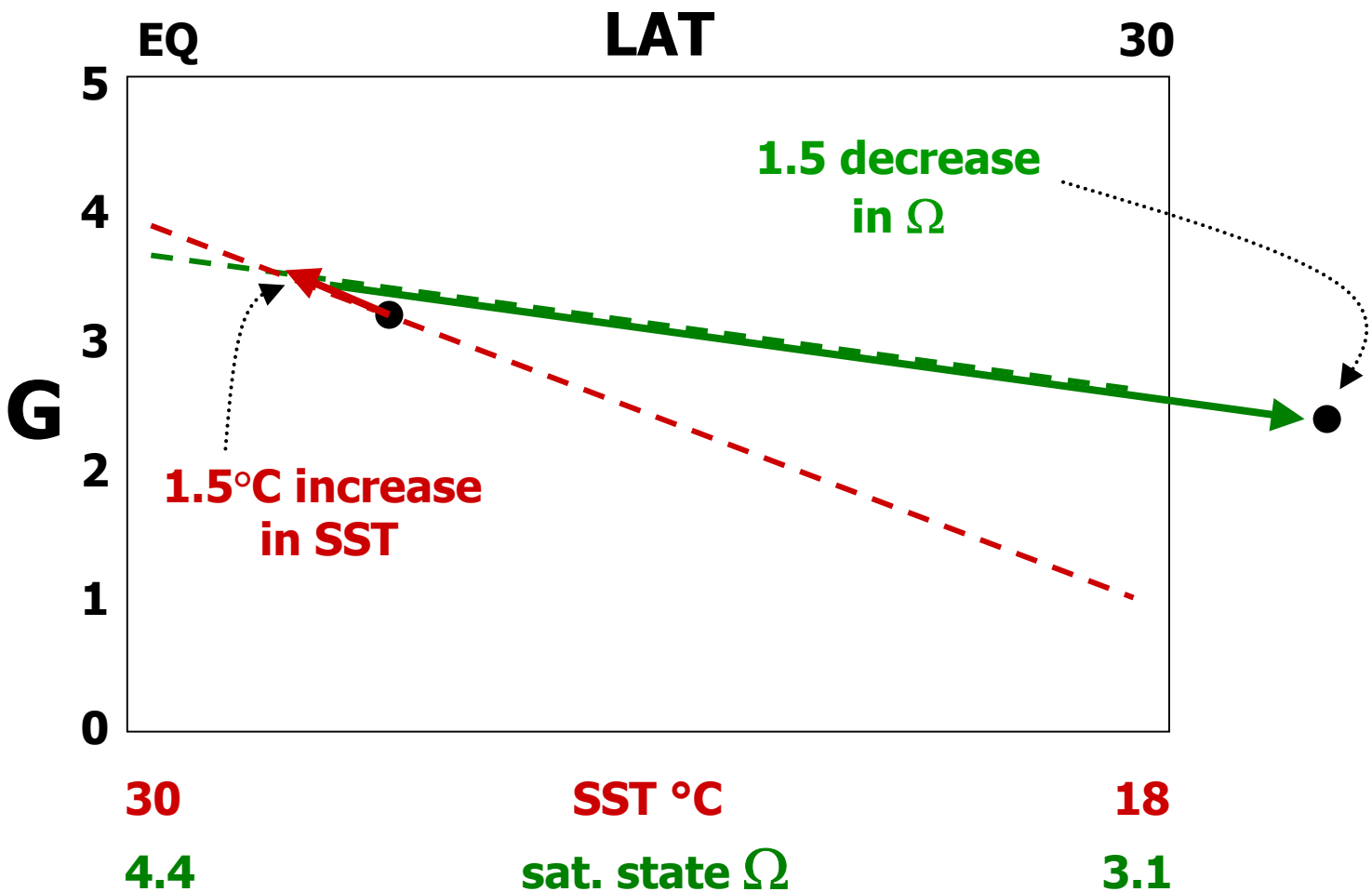


Porites Calcification

Ω versus SST

when pCO_2 ↑ 560 μatm

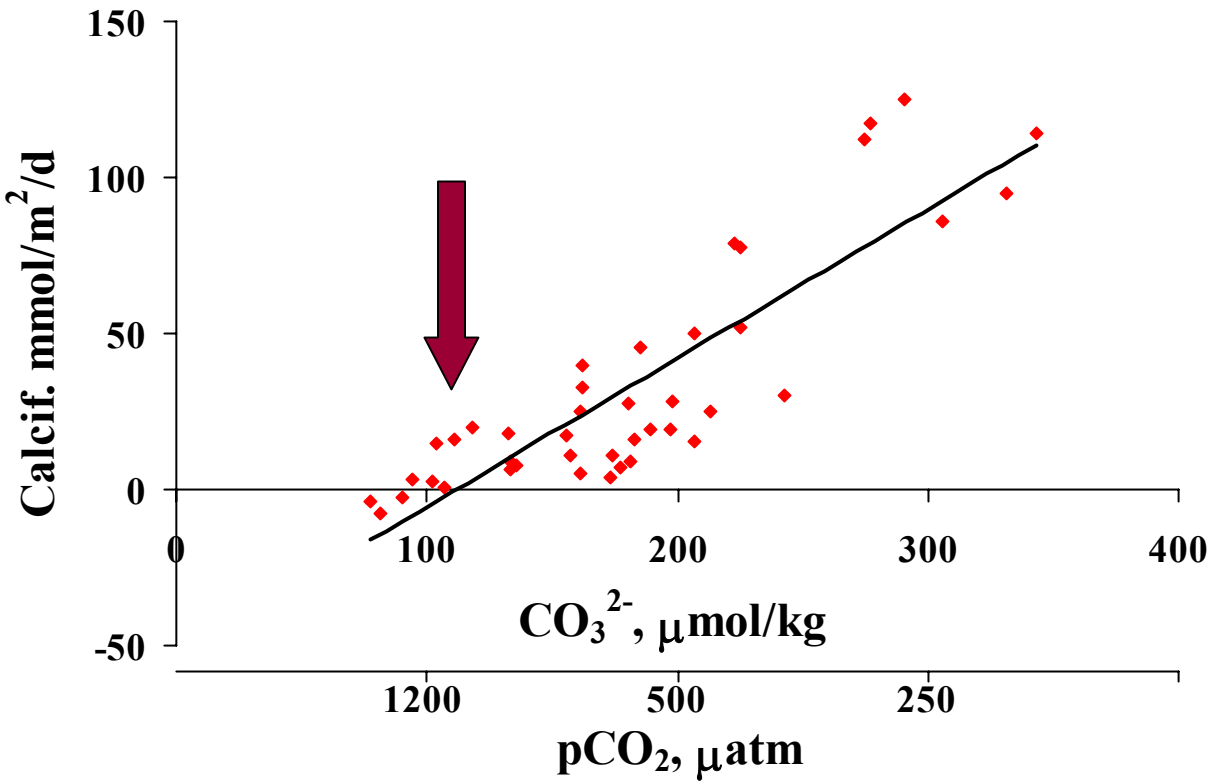
SST ↑ 1.5°C
Ω ↓ 1.5



What is role of $CaCO_3$ dissolution in buffering the system?

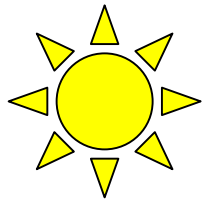
- Dissolution will help maintain system above undersaturation of the most soluble mineral
- Dissolution does not become important until saturation state is already at a level where coral/algal calcification is reduced by 20-50% (Langdon 2003)
- Dissolution will not be effective on reefs which exchange with open ocean water

Dissolution in Biosphere2 mesocosm



C. Langdon, ICRS 2000

‘Aquarium’



Typical aquarium (closed) system

- coral (calcifying surface)
- sediments (mineral composition, grain size)
- water volume, well mixed, open to air-sea gas exchange
- diurnal light cycle

Processes

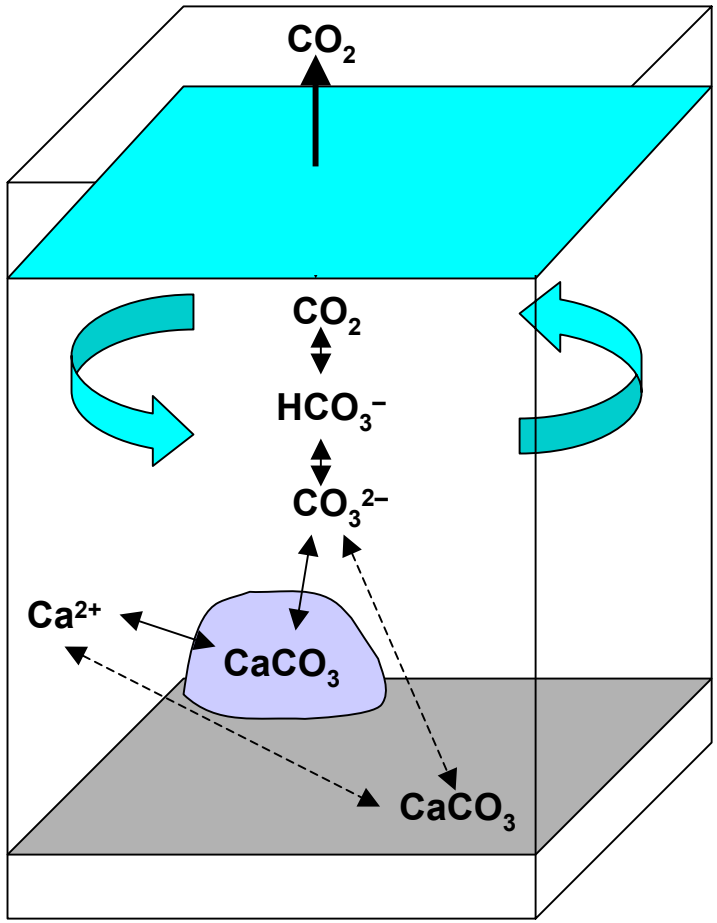
- calcification

  f(I, $CaCO_3$ saturation state)

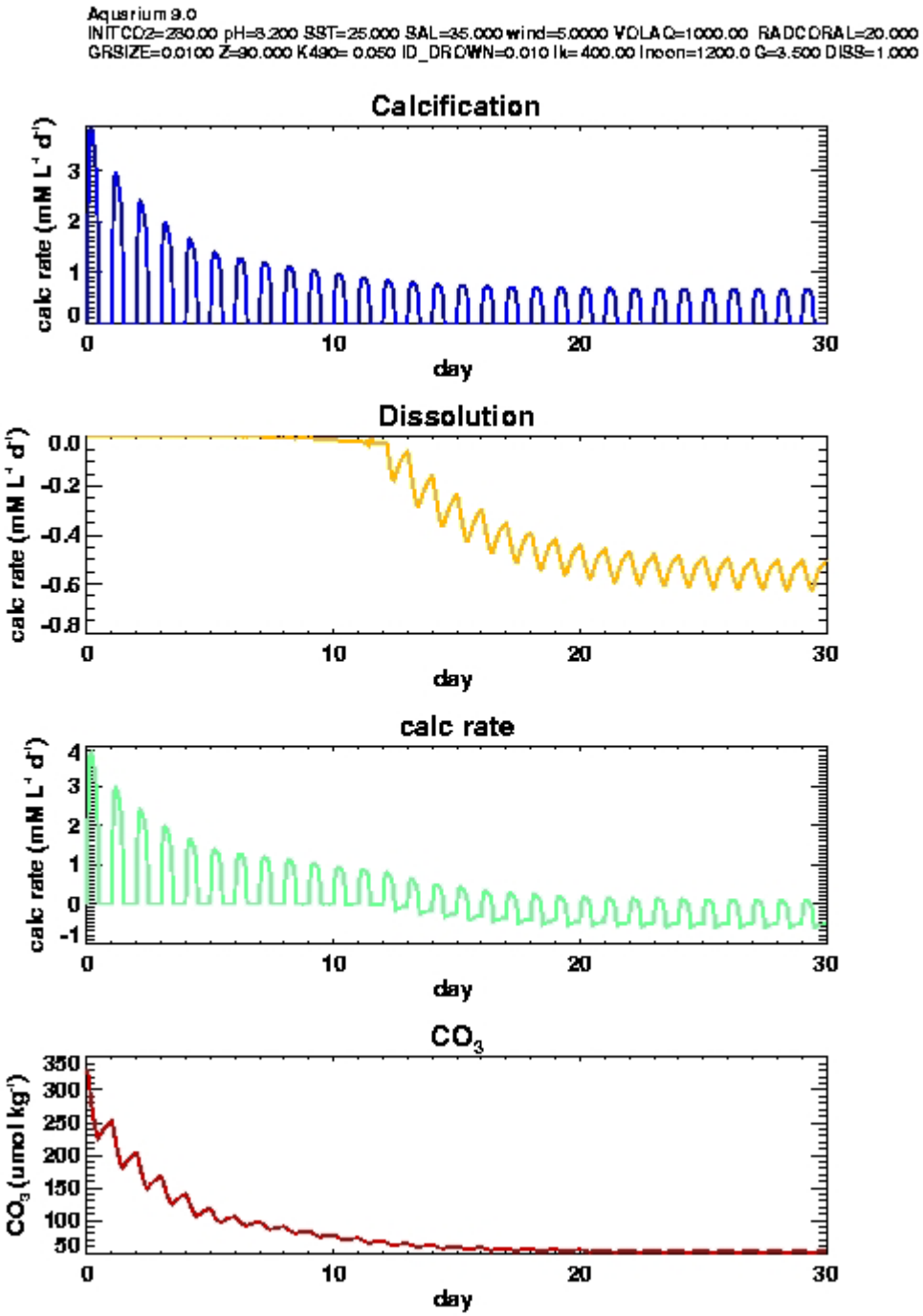
- sediment dissolution

  f($CaCO_3$ saturation state)

- air-sea gas exchange f(T, wind speed, air-sea pCO_2 gradient)
- changes in seawater chemistry are calculated



‘Aquarium’ results



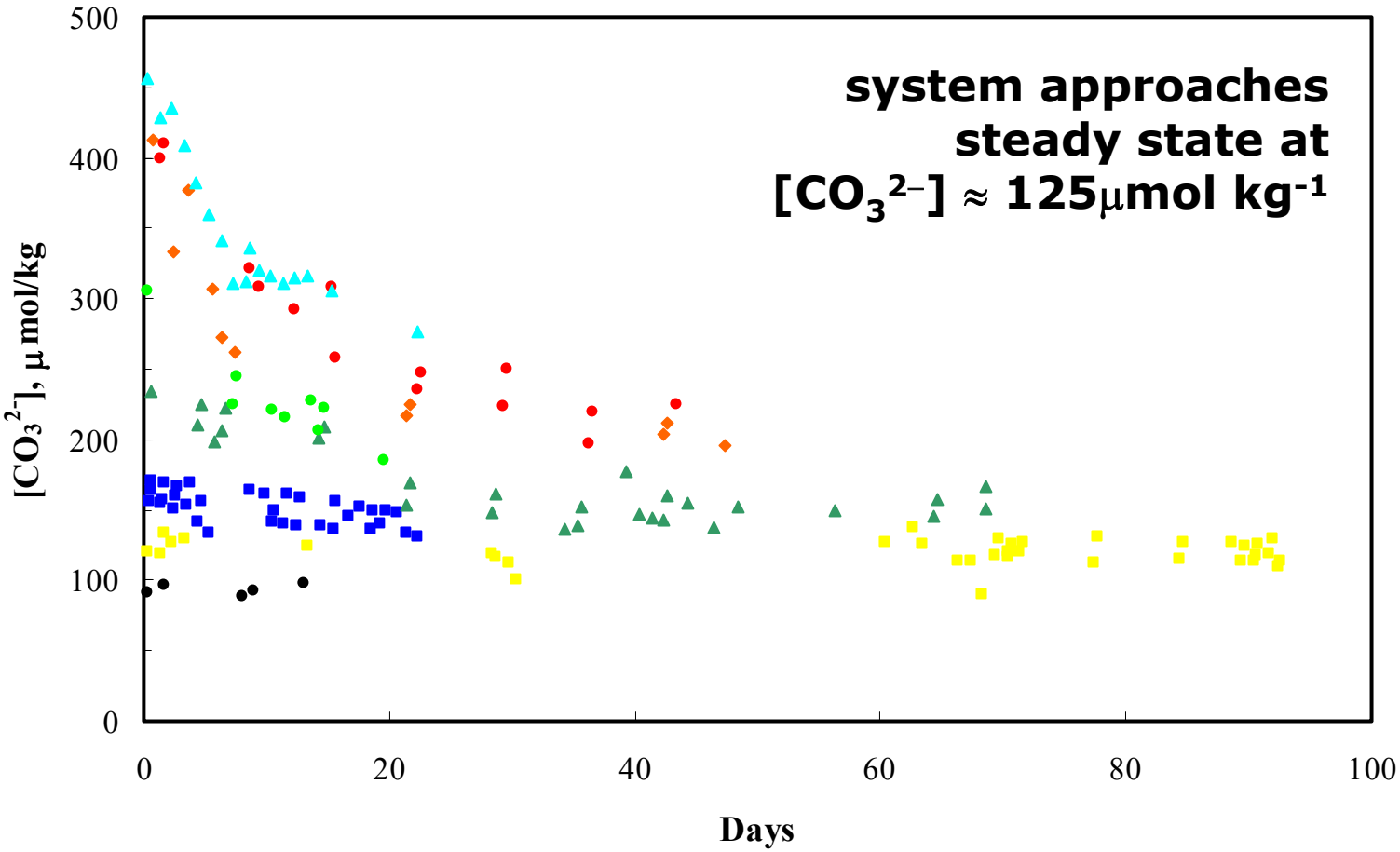
Diurnal cycle of calcification progressively alters seawater chemistry

Dissolution kicks in once saturation state drops below that of high magnesium calcite

Net calcification

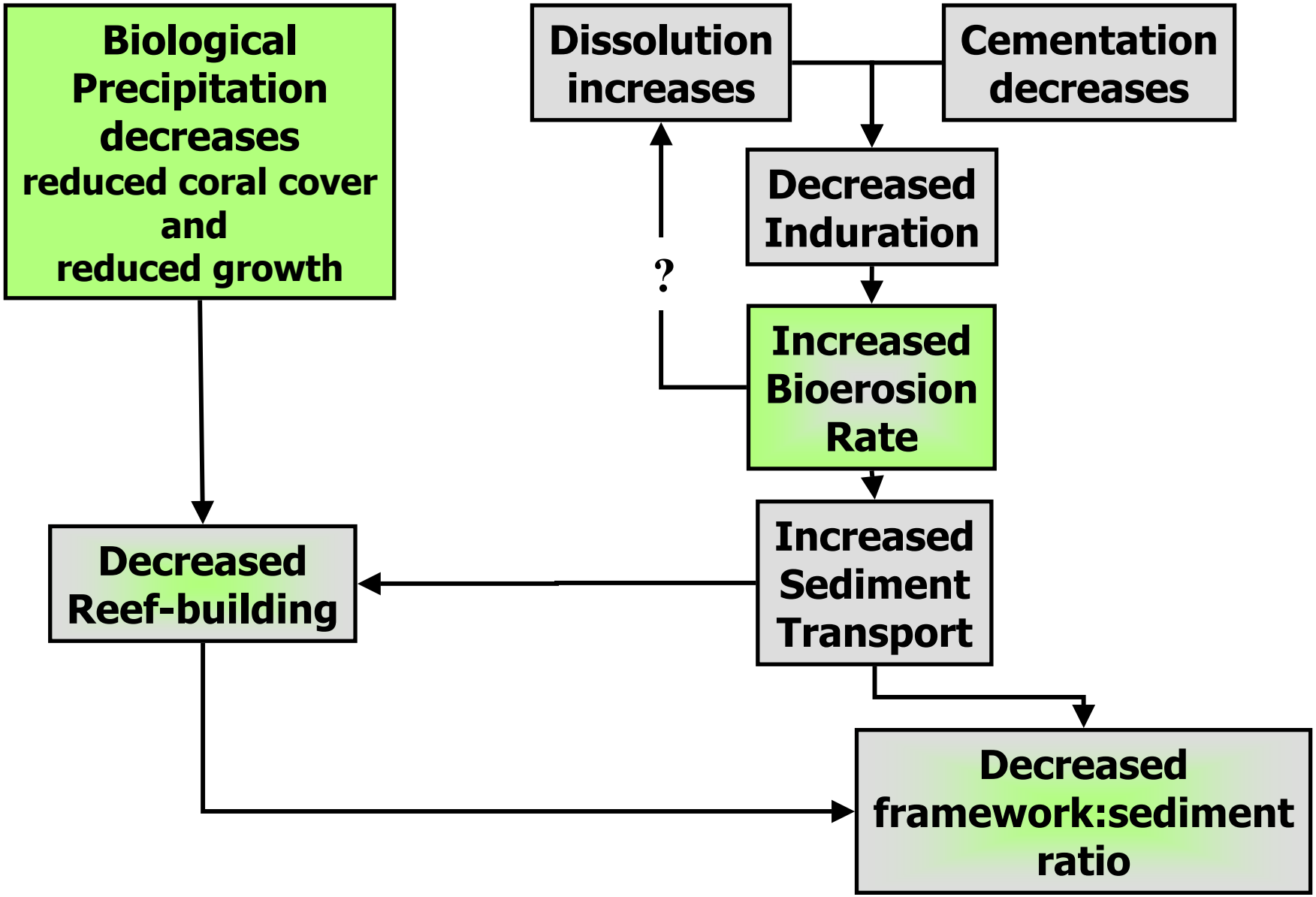
System approaches steady state after about 10-20 days

$[CO_3^{2-}]$ in Biosphere2 Mesocosm



C.Langdon, ICRS 2000

Overall Effects of Increased pCO_2 on Reefs



FINAL COMMENTS

Calcification rates of corals under increased CO_2 respond to multiple variables:

↑ SST ↑ G

↓ Ω ↓ G

Inorganic components of calcification (cementation, dissolution) have no biological component

↓ Ω ↓ cementation

↓ Ω ↑ dissolution

Carbonate budgets on reefs are likely to decrease