Altering Seawater Chemistry to Mitigate CO_2 and Ocean Acidification

Greg H. Rau

Institute of Marine Sciences, University of California, Santa Cruz, and
Carbon Management Program, Lawrence Livermore National Laboratory

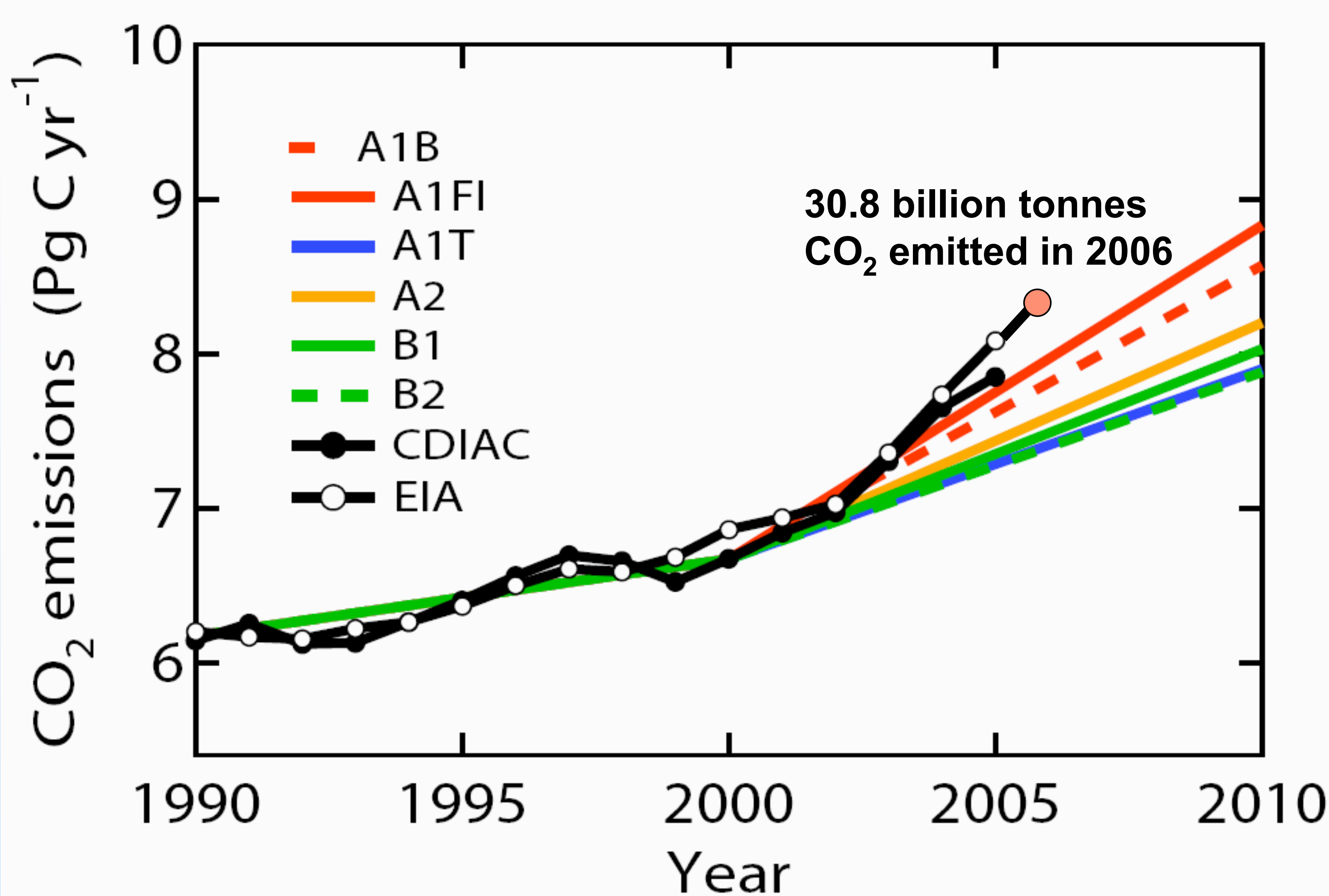
rau4@llnl.gov

Thanks to:
Ken Caldeira
Bob Thronson
Julio Friedmann
CEC's EISG Program

Summary:

- Direct mitigation of fossil energy CO_2 (e.g. sequestration) is essential for stabilizing atmospheric CO_2.
- In addition to climate effects, anthropogenic CO_2 impacts ocean chemistry.
- Ocean-based CO_2 mitigation must be considered:
  - Land-based efforts may prove inadequate.
  - The ocean has a large CO_2 capture/storage potential.
  - Various potentially safe, marine-based options have been proposed and need to be evaluated.
- The preceding realities and possibilities need to be incorporated into CO_2 mitigation policy, decision-making, and R&D funding.

Efforts to reverse CO_2 emissions have thus far failed:
Emissions for 2000-2007 well above worst case scenarios



Renewable energy is losing ground to fossil energy:

Units: GW

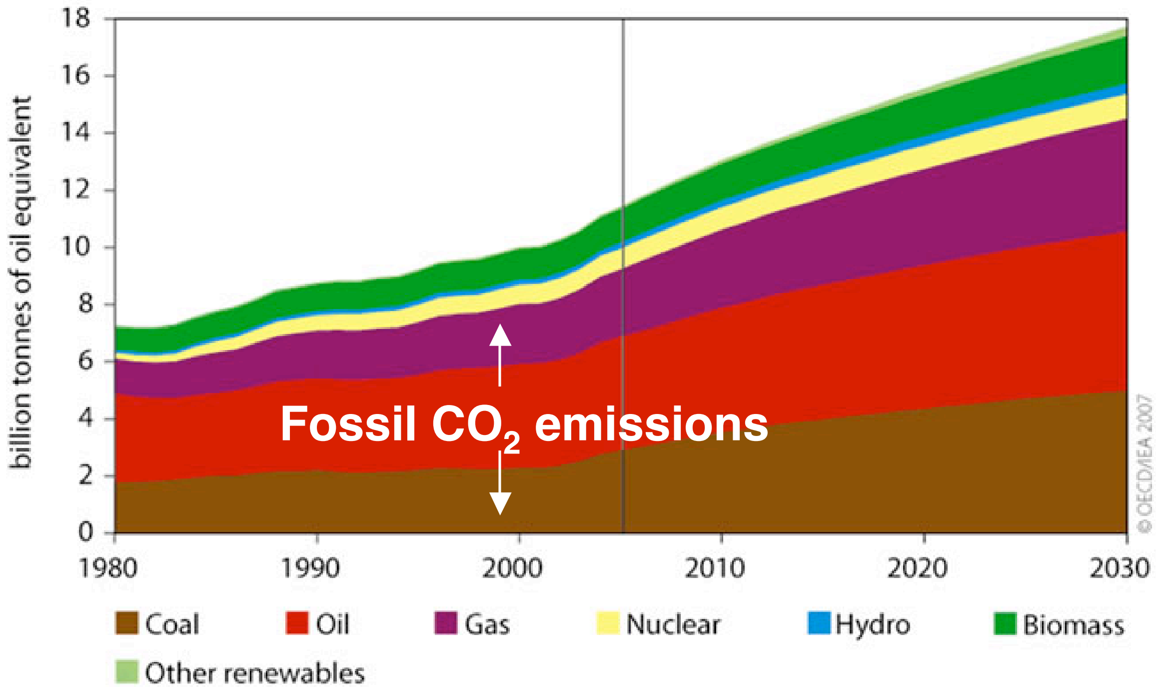
Energy Source:	***World 2001***	***World 2006***	***% Change***
Fossil	**10883**	**12724**	**16.9**
Non-Fossil	**1628**	**1849**	**13.6**

[Fossil sources **increased** as % of total: 87.0 -> 87.3%]

Source: BP Statistical Review of World Energy 2007

Forecast: Continued increases in CO_2 emissions

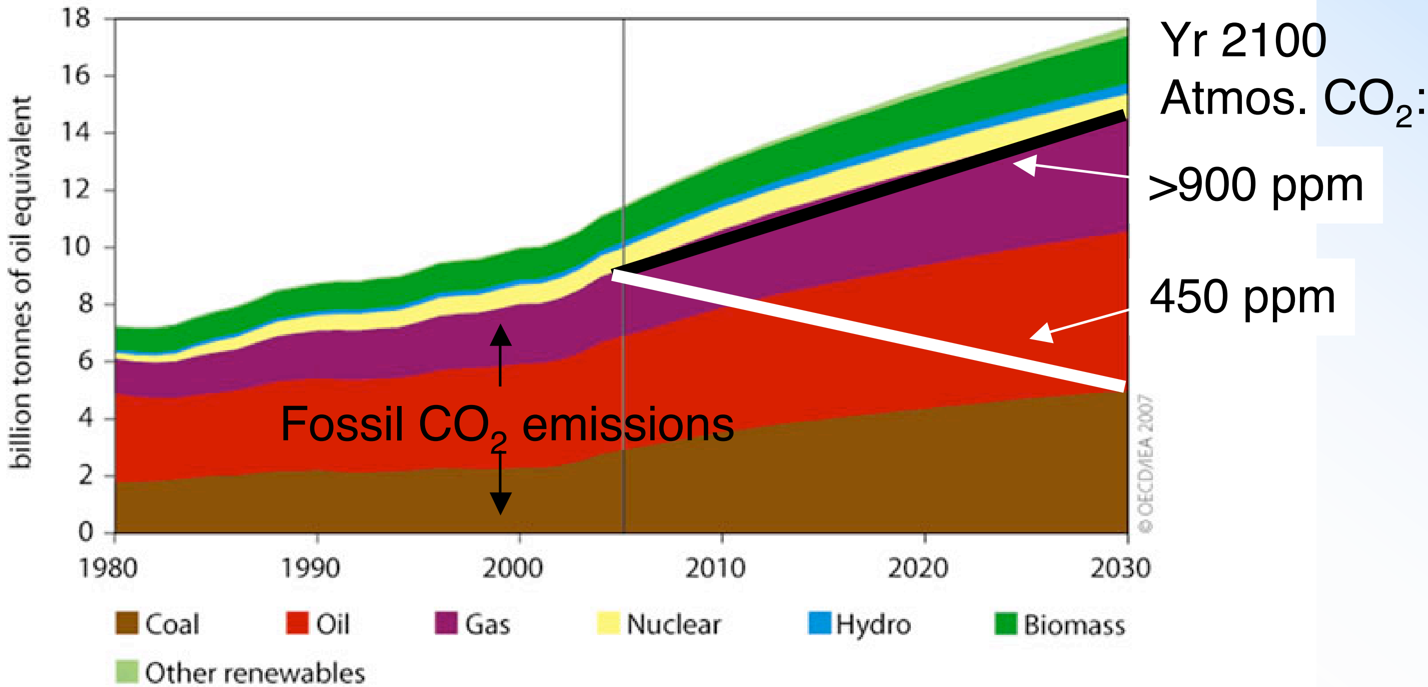
International Energy Agency projected energy use and sources to 2030 -



http://www.iea.org/textbase/country/graphs/weo_2007/Fig01-01.jpg

Forecast: Continued increase in atmospheric CO_2

Increasing fossil energy use without mitigation guarantees increasing atmospheric CO_2



http://www.iea.org/textbase/country/graphs/weo_2007/Fig01-01.jpg

Conclusion:

- Despite significant gains in low/no-carbon energy generation, these have been and will likely continue to be woefully inadequate for mitigating CO_2 emissions from energy production.

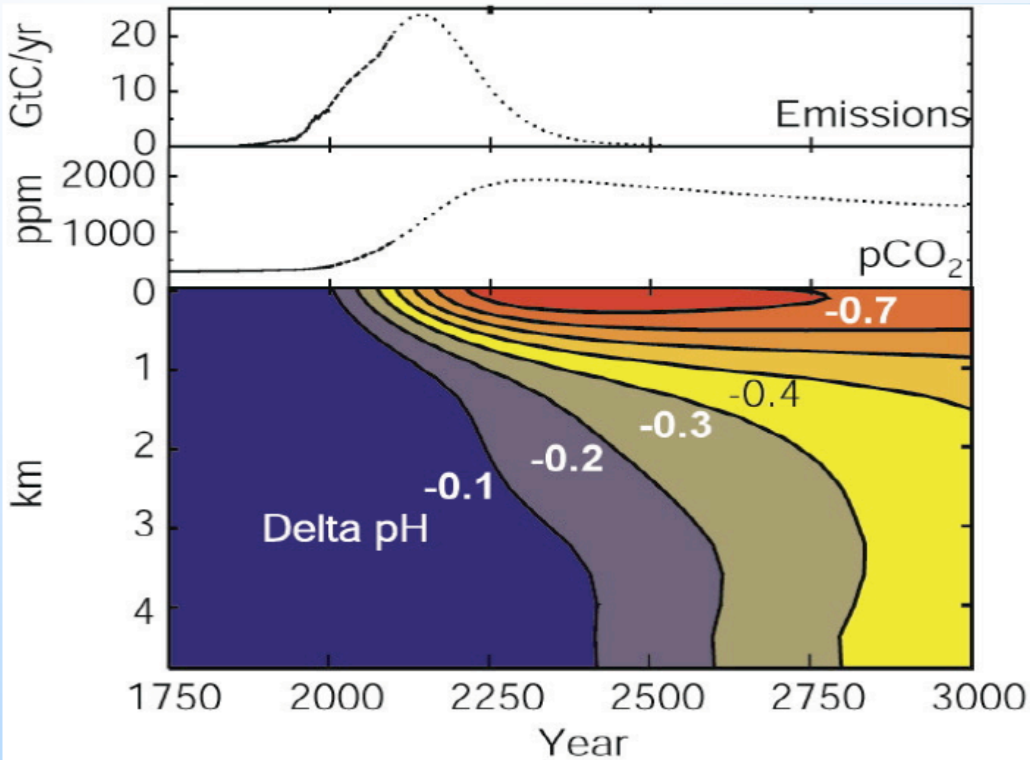
- Therefore, direct or indirect CO_2 mitigation of fossil energy is urgently needed for atmospheric CO_2 stabilization.

- Mitigation strategies must be applicable to developing countries, the primary source of future CO_2 emissions.

Why mitigate CO_2: It's not just about climate change - CO_2 emissions impact ocean chemistry

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow 2\,H^+ + CO_3^{2-}$$

(% of initial CO_2) : (+ 9 %) (+151 %) (– 60%)



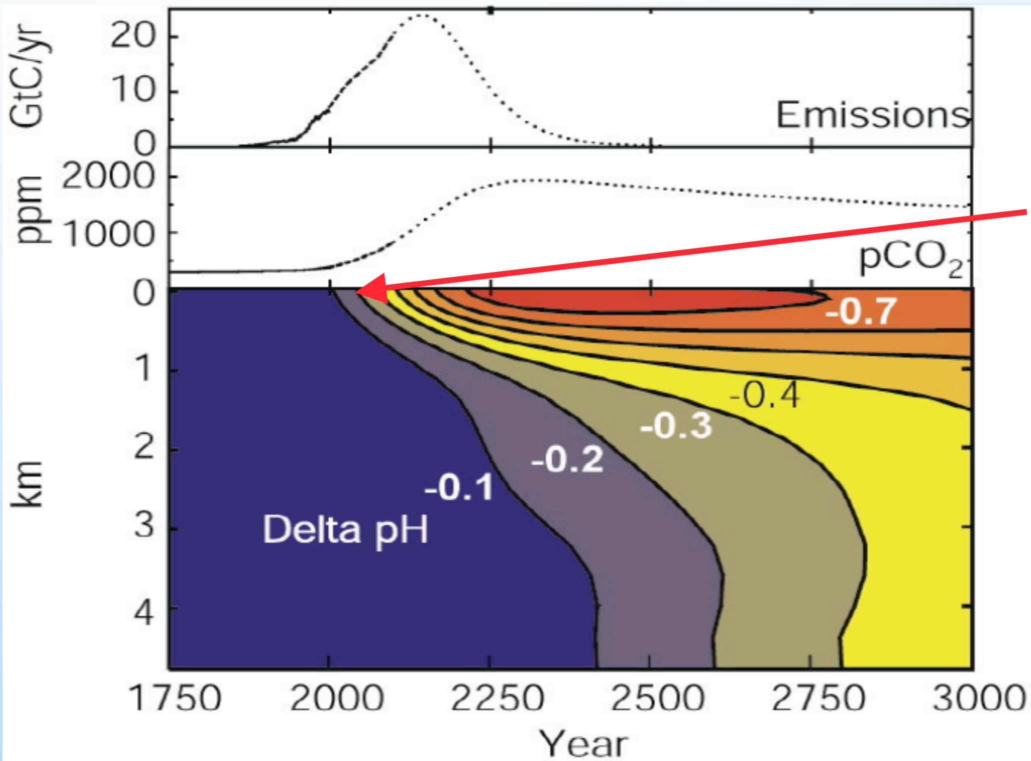
(Caldeira and Wickett, 2003, *Nature* 425:365)

Therefore unlike climate effects, ocean acidification is guaranteed under BAU emissions scenarios

Why mitigate CO_2: It's not just about climate change - CO_2 emissions impact ocean chemistry

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow 2\,H^+ + CO_3^{2-}$$

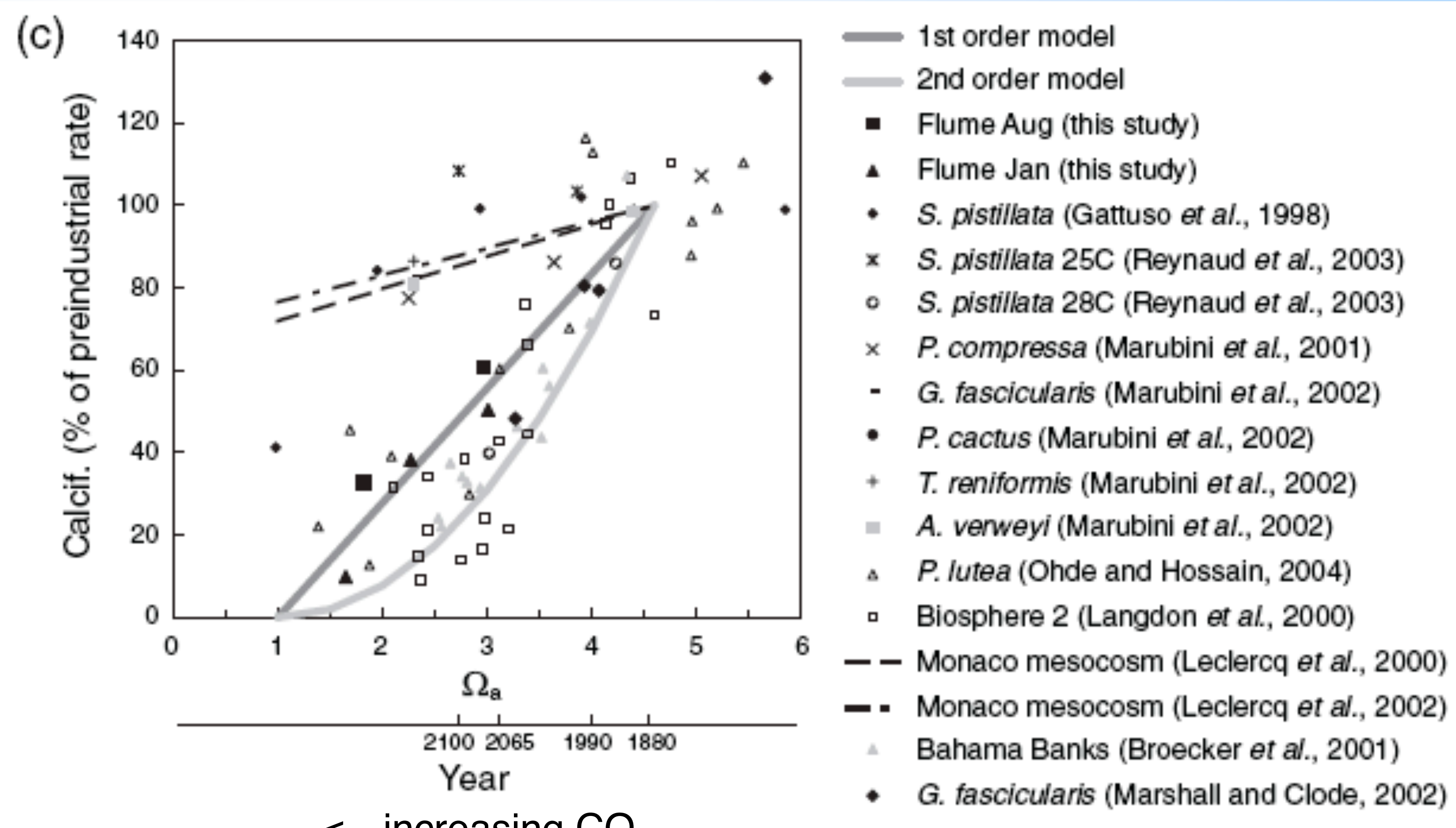
(% of initial CO_2) : (+ 9 %) (+151 %) (– 60%)



(Caldeira and Wickett, 2003, *Nature* 425:365)

CO_2 emissions will alter ocean pH (0.2 units) to the point where it will violate U.S. Environmental Protection Agency Quality Criteria [1976] by mid-century if emissions are not dramatically curtailed. (e.g., see Zeebe et al., Science, 321:51-2)

CO_2 affects many calcifying species

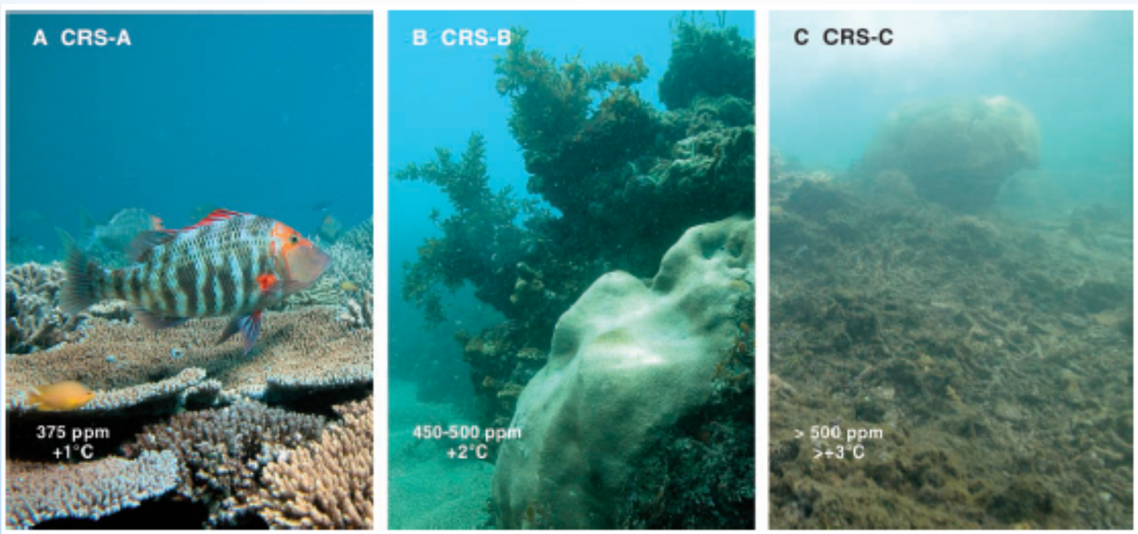


<---increasing CO_2

Klepas et al. 2006. NOAA/NSF/NOAA report . http://www.ucar.edu/communications/Final_acidification.pdf

The consequences of increasing ocean acidity

- Significant impacts observed on calcifying organisms such as corals and shellfish
- Significant potential for impacts on marine ecosystems and biogeochemistry that are essential to a habitable planet, i.e. food and O_2 production, carbon and nitrogen cycling, etc.



O. Hoegh-Guldberg, et al., *Science*, December 2007

Action items needed on ocean acidity

- Determine full scope of biogeochemical and habitability impacts from ocean acidification.
- Incorporate these impacts into the cost/benefit equations for CO_2 mitigation.
- Incorporate preceding into policy and action plans at state (e.g., ARB, CEC), national (e.g. Congress, DOE, EPA), and international (e.g. UN, World Bank, G-8) levels.

The ocean as part of the CO_2 solution

Rationale:

- Largest potential for CO_2 absorption and storage on earth:
  - 7 GT CO_2/yr absorbed by the ocean
  - 1/3-1/2 of all anthropogenic CO_2 emissions have thus far been absorbed by the ocean
- Land-based CO_2 mitigation efforts alone may prove ineffective in reversing CO_2 emissions
- Various methods of ocean CO_2 mitigation exist or have been proposed, for example ----->

Ocean CO_2 Sequestration Options

- Physical: Deep ocean CO_2 injection (Marchetti, ‘77)
  issues - Cost of CO_2 capture and transport; Bio effects
- Biological: Ocean fertilization (Martin, ‘90)
  issues - Bio and eco effects; Mitigation effectiveness?
- Chemical:
  - Alkalinity addition (Kheshgi ‘95; House et al. ‘07; Harvey ‘08)
  - Enhanced limestone weathering (Rau et al. ‘99-’07)
- Other? E.g., crop waste stored in marine anoxic zones (Metzger and Benford, 2001)

Nature's own CO_2 capture and storage

Atmospheric CO_2

Photosynthesis

$nCO_2 + nH_2O$ + photons

---> $(CH_2O)n + nO_2$

Weathering Reactions

e.g.:

$CO_2 + Ca/MgOSiO_2$ --->

$Ca/MgCO_3 + SiO_2$

$CO_2 + H_2O + CaCO_3$ --->

$Ca^{2+} + 2HCO_3^-$

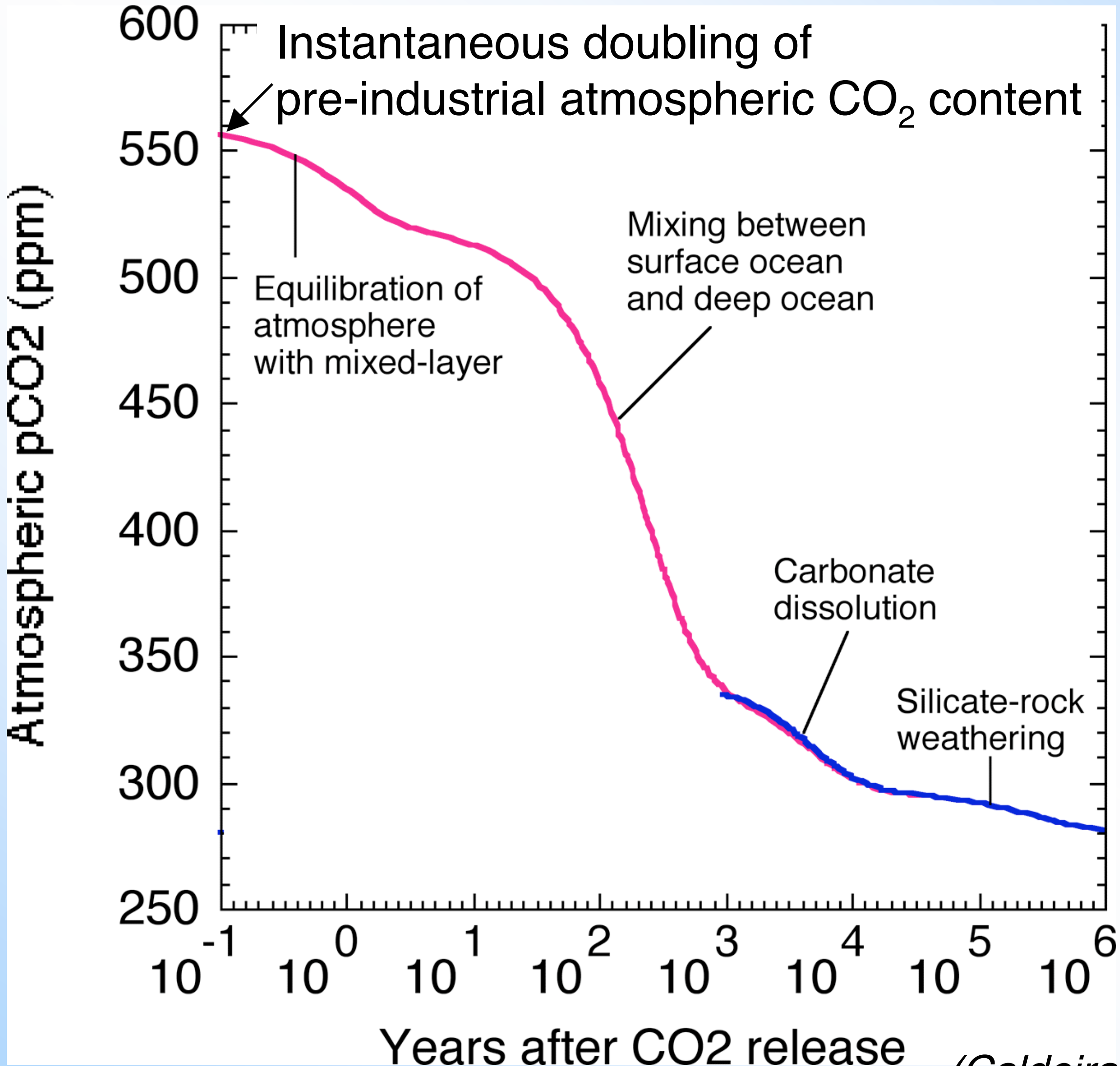
Ocean uptake

$CO_2 + 2H_2O + CO_3^{2-}$

---> $2H^+ + 2HCO_3^-$

Nature will sequester all anthropogenic CO_2

but over tens of thousands of years and with significant climate and environmental impacts



(Caldeira and Rau, 2000)

Why not speed up carbonate weathering?

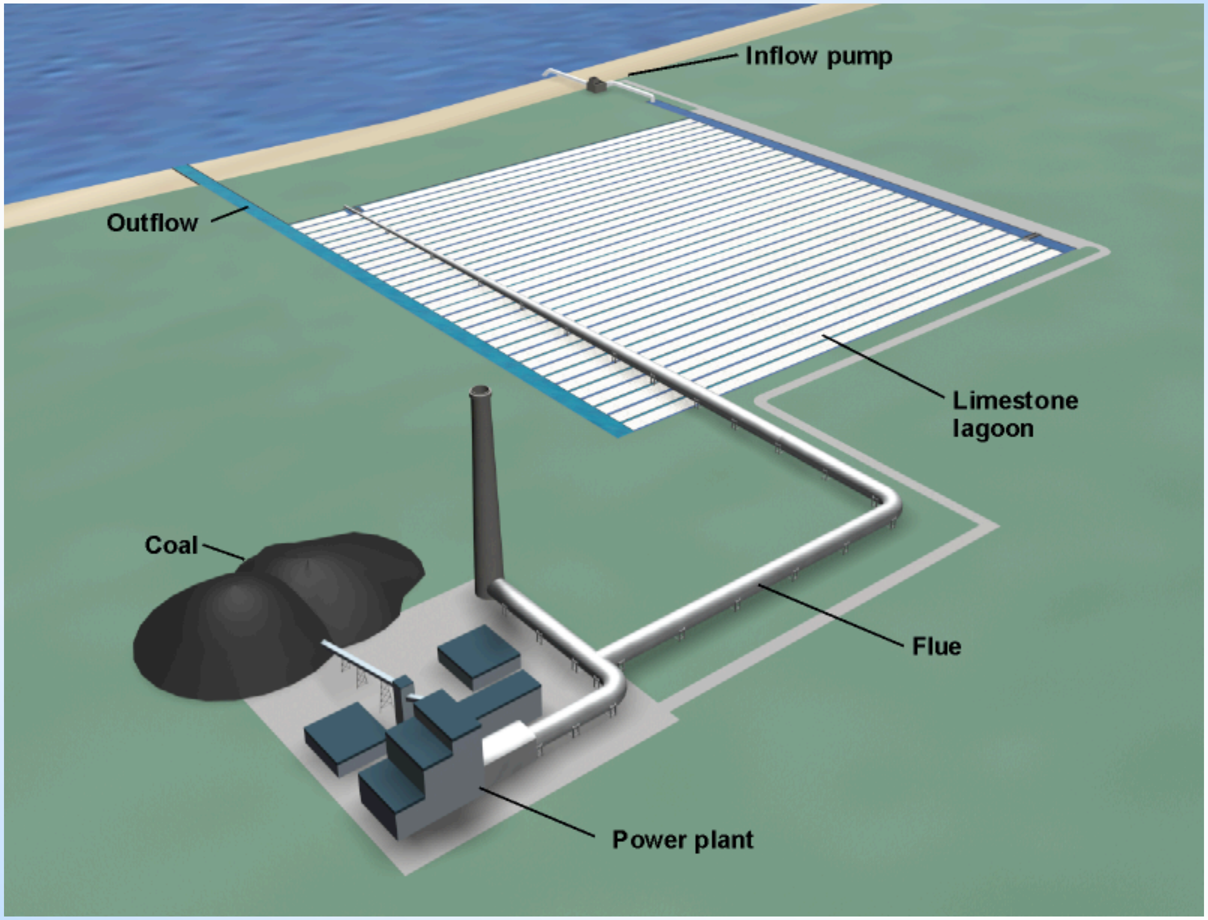
Where cost effective to do so, place limestone and water in direct contact with CO_2-rich waste gas:

$$CO_2 + H_2O + CaCO_3 \dashrightarrow Ca^{2+} + 2HCO_3^-$$

Advantages:

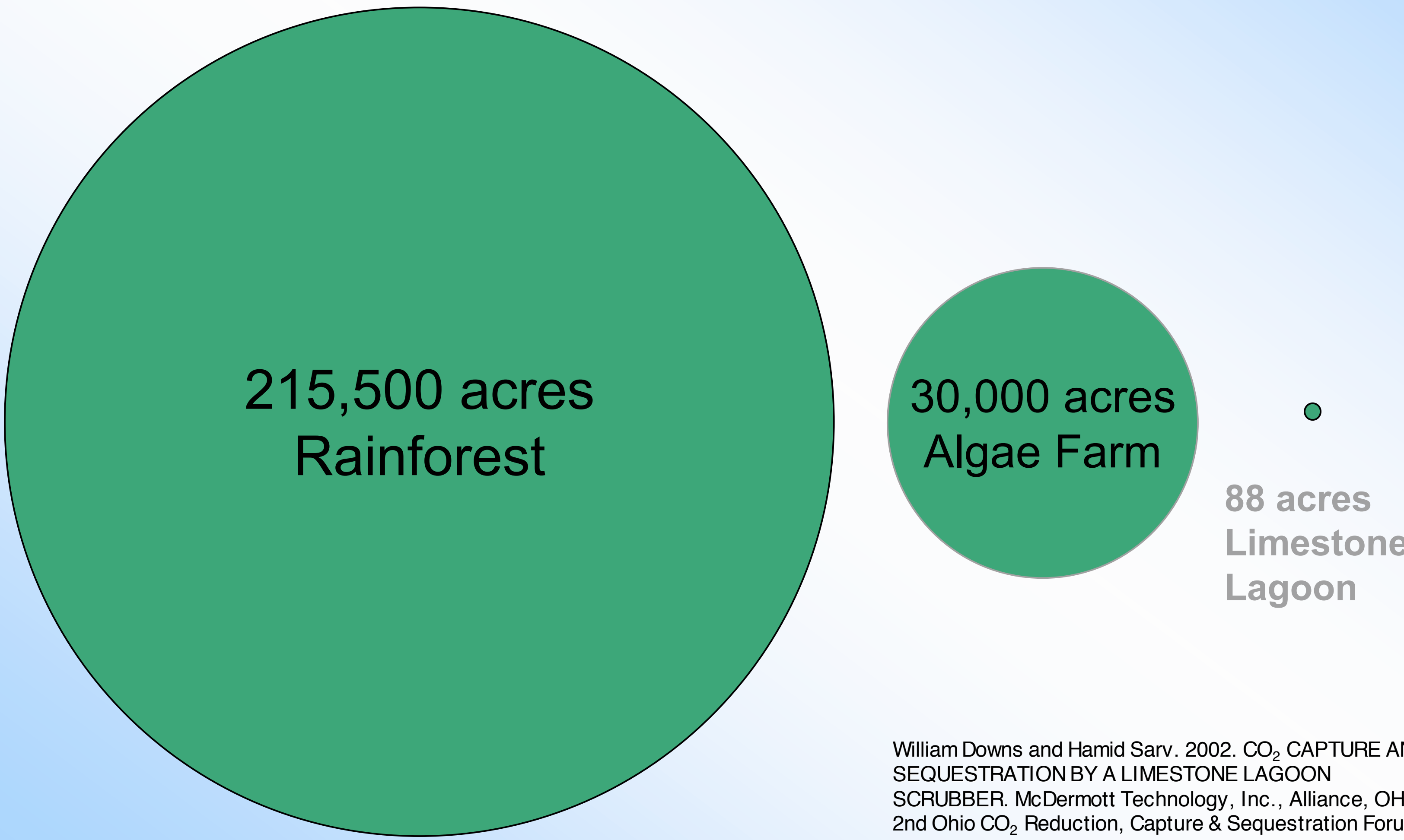
- Low-tech and retrofitable to existing power plants, including those in developing countries
- Already widely used for SO_2 mitigation
- Can have low parasitic energy loss
- Can be low cost
- Safe, benign end product; Counters effects of ocean acidity

McDermott's limestone CO_2 scrubber concept



William Downs and Hamid Sarv. 2002. CO_2 CAPTURE AND SEQUESTRATION BY A LIMESTONE LAGOON SCRUBBER. McDermott Technology, Inc., Alliance, OH. 2nd Ohio CO_2 Reduction, Capture & Sequestration Forum, Ohio University, April 26 2002

Required land for fixation of CO_2 from a 500 MW coal-fired plant



William Downs and Hamid Sarv. 2002. CO_2 CAPTURE AND SEQUESTRATION BY A LIMESTONE LAGOON SCRUBBER. McDermott Technology, Inc., Alliance, OH. 2nd Ohio CO_2 Reduction, Capture & Sequestration Forum, Ohio University, April 26 2002

McDermott's comparison of CO_2 control methods

Power System	CO_2 Removal			
	Method	% Efficiency Loss	% Removal	$/ton Avoided
Conventional PC w/o FGD	None	Base	0	--
Conventional PC w/ FGD	None	1.4	0	--
Conventional PC w/ FGD	Amine scrubbing	40	90	73
O_2 fired PC w/ recycled flue gas	Condensing CO_2-rich exhaust	34	90	60
Conventional PC with limestone lagoon	Wet scrubbing with limestone	2	90	21

William Downs and Hamid Sarv. 2002. CO_2 CAPTURE AND SEQUESTRATION BY A LIMESTONE LAGOON SCRUBBER. McDermott Technology, Inc., Alliance, OH. 2nd Ohio CO_2 Reduction, Capture & Sequestration Forum, Ohio University, April 26 2002

Optimum AWL economics

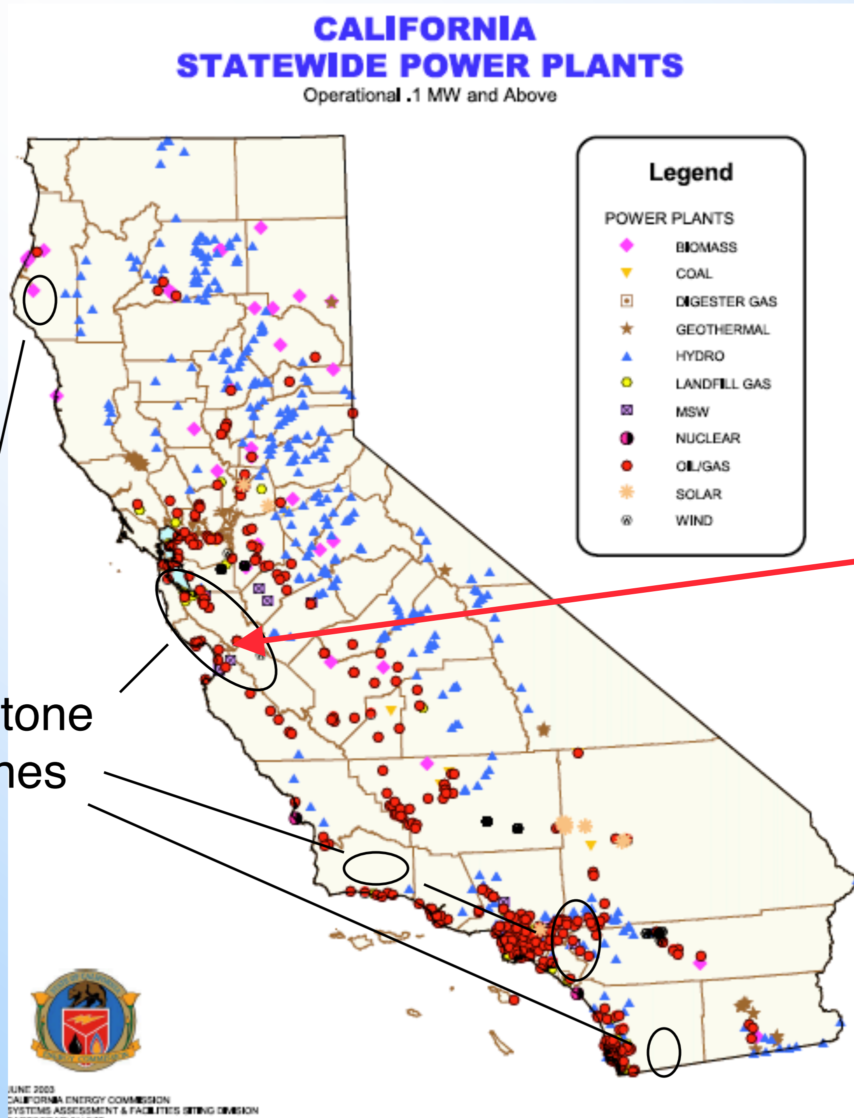
Estimated cost per tonne CO_2 sequestered, assuming coastal location:

- Limestone -
  - 2.3 tonnes @ $4/tonne = ~~$ 9.20~~ *use free, nearby*
  - crushing from 10 cm to 1cm = ~~$ 1.45~~ *waste limestone*
  - transport 100 km by rail = ~~$ 8.00~~
  - Water -
  - 10^4 m^3, pumped 2 vertical meters = ~~$ 7.57~~ *use cooling water*
- Capital and maintenance = $ 2.50

~~$ 29/tonne CO_2~~

TOTAL: **<$3/tonne CO_2**

Limestone availability vs. CA coastal power plant locations

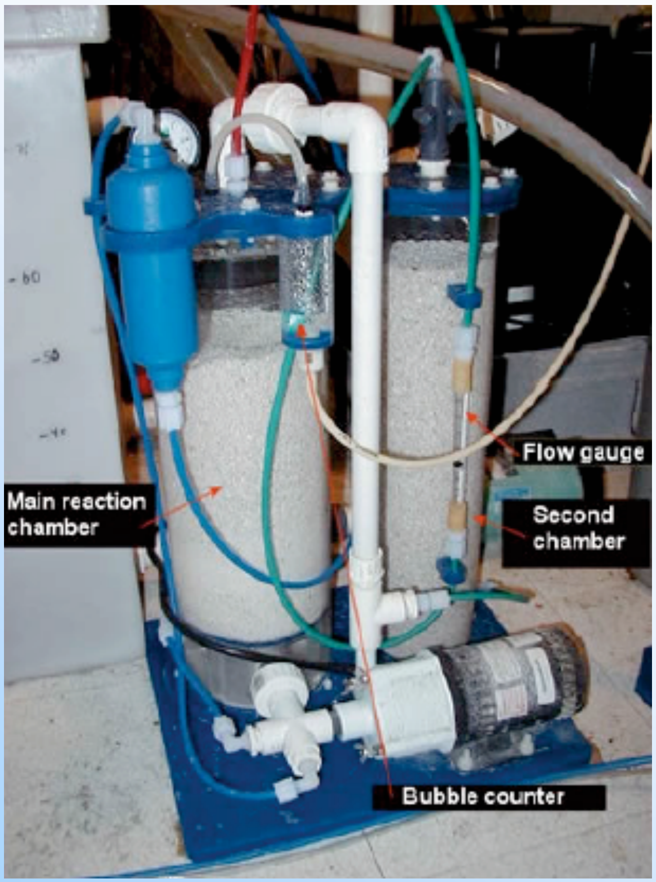


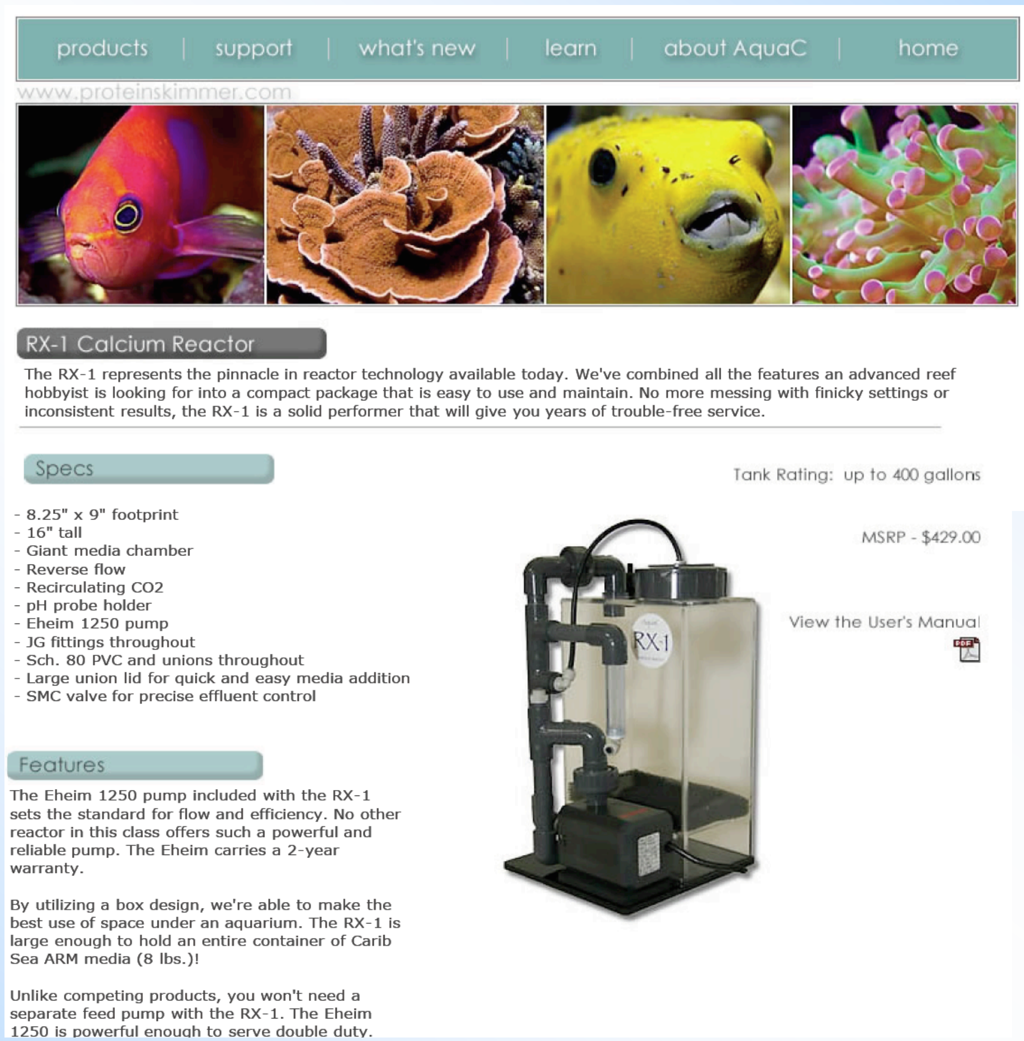
Major Limestone Deposits/Mines

E.g., Moss Landing 2.5 GW power plant complex - largest single CO_2 emitted in state?

Safety of AWL effluent?

In-home tank CO_2 + carbonate reactors routinely used to add alkalinity to saltwater aquariums!





products | support | what's new | learn | about AquaC | home

www.proteinskimmer.com

RX-1 Calcium Reactor

The RX-1 represents the pinnacle in reactor technology available today. We've combined all the features an advanced reef hobbyist is looking for into a compact package that is easy to use and maintain. No more messing with finicky settings or inconsistent results, the RX-1 is a solid performer that will give you years of trouble-free service.

Specs

Tank Rating: up to 400 gallons

- 8.25" x 9" footprint
- 16" tall
- Giant media chamber
- Reverse flow
- Recirculating CO2
- pH probe holder
- Eheim 1250 pump
- JG fittings throughout
- Sch. 80 PVC and unions throughout
- Large union lid for quick and easy media addition
- SMC valve for precise effluent control

MSRP - $429.00

View the User's Manual

Features

The Eheim 1250 pump included with the RX-1 sets the standard for flow and efficiency. No other reactor in this class offers such a powerful and reliable pump. The Eheim carries a 2-year warranty.

By utilizing a box design, we're able to make the best use of space under an aquarium. The RX-1 is large enough to hold an entire container of Carib Sea ARM media (8 lbs.)!

Unlike competing products, you won't need a separate feed pump with the RX-1. The Eheim 1250 is powerful enough to serve double duty.

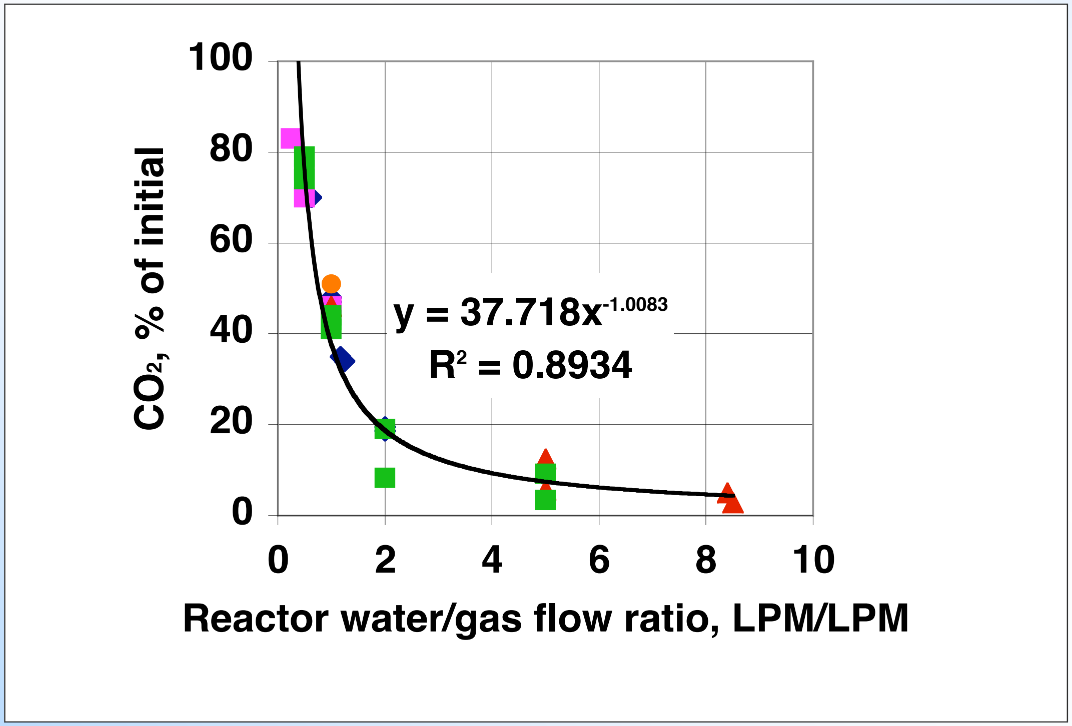
Current EISG/CEC funded project

Bench-scale evaluation of AWL concept at UCSC's Long Marine Laboratory →

- Adaptation of commercial seawater calcium/alkalinity generator to test effectiveness and safety of wet carbonate scrubbing of a 10% CO_2 stream:

Project results thus far

- >95% removal CO_2 stream depending on water/gas flow ratio:



Implications for Moss Landing Power plant:

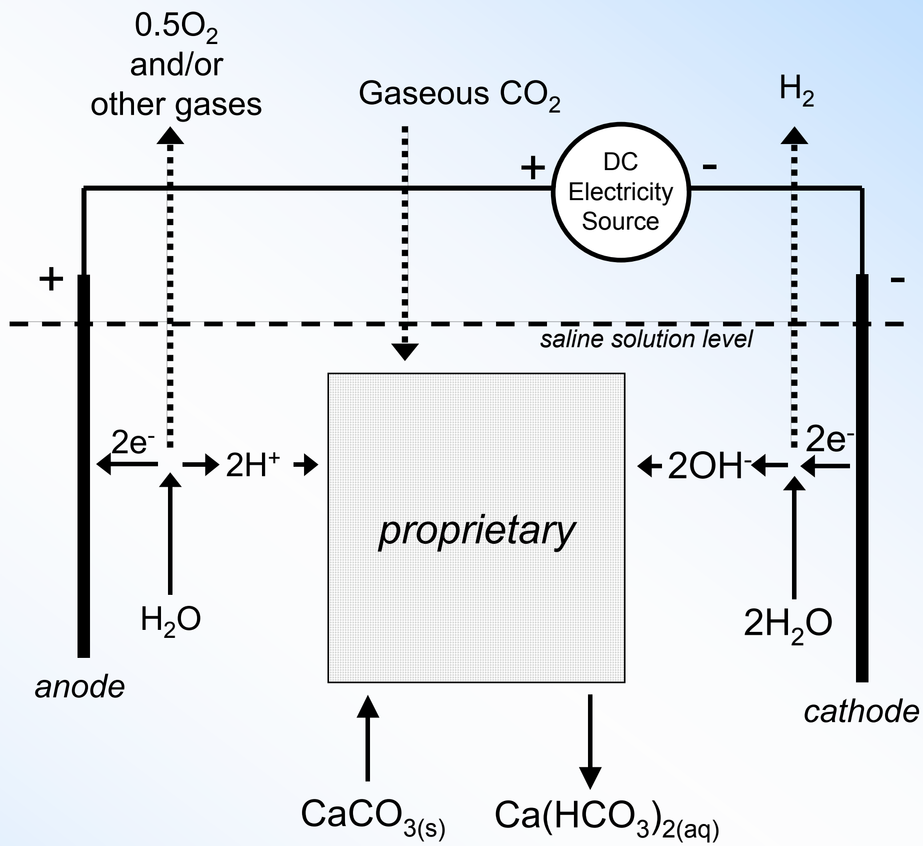
Optimized, full-scale reactor using once-through cooling seawater ($4x10^6$ tonnes seawater/day) might allow 25% CO_2 emissions reduction at <$15/tonne CO_2.

- Planned downstream bio testing of effluent water on selected marine invertebrates (with Prof. D. Potts, UCSC)

Air CO_2 capture with “Juiced” AWL (JAWL)

Add renewable DC electricity to AWL chemistry to allow:

- Production of air CO_2 absorbing solutions while generating “super green” hydrogen
  - 22 tonnes CO_2 absorbed per tonne H_2 produced
  - thus, novel production of <u>carbon-negative hydrogen</u>
- Addition of alkalinity to seawater neutralizes or offsets ocean acidity



JAWL Requirements, Yields, Costs

(tonnes/tonne CO_2 consumed)

Atmos. (1) CO_2

Reactants:

(2.3) $CaCO_3$-->

(0.64) Seawater-->

DC Electricity:

2300 kWh_e-->

Seawater Electrolysis cell

Products:

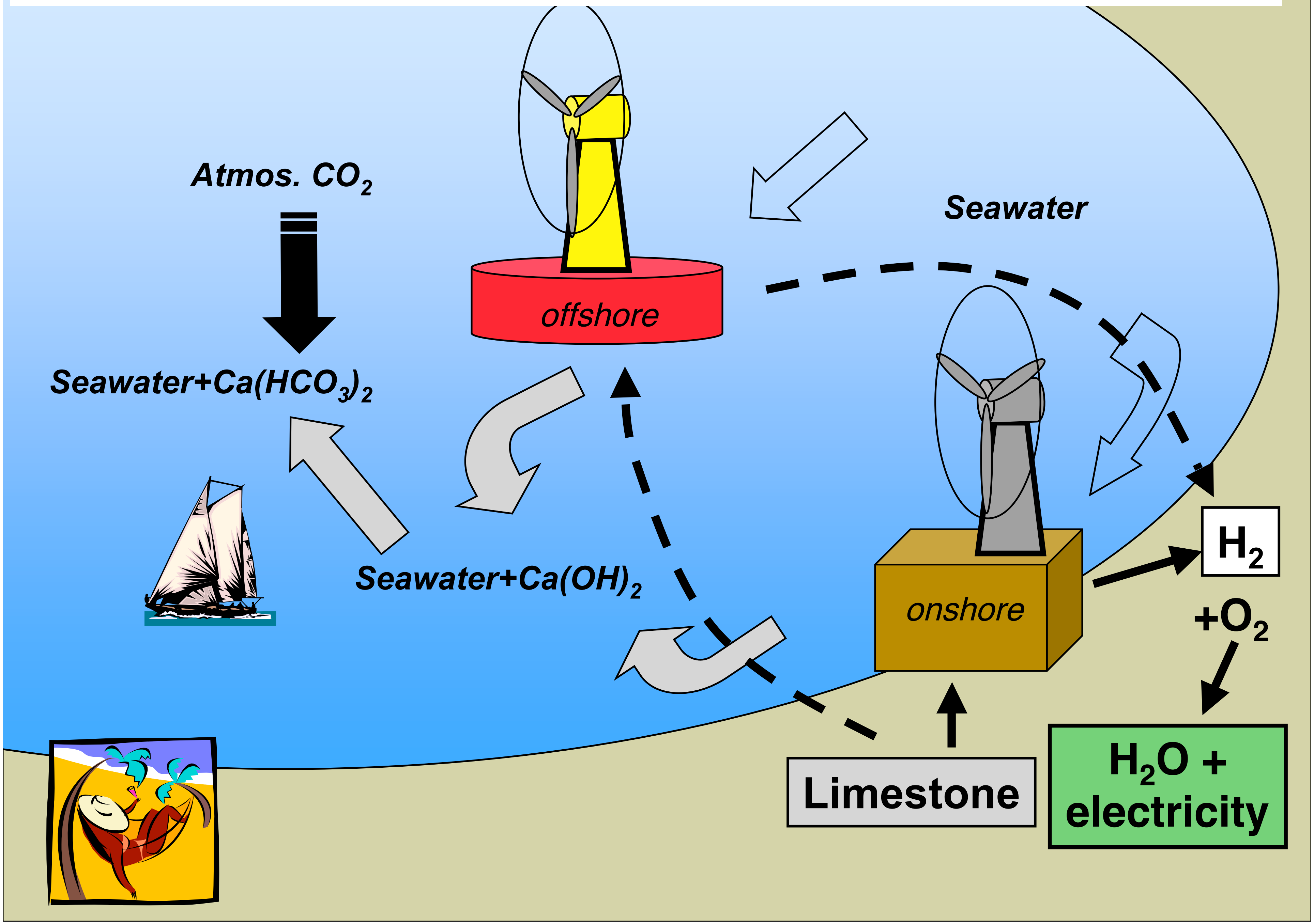
--> (1.7) $Ca(OH)_2$ --> (2.7) $Ca(HCO_3)_2$

--> (0.045) H_2 = 1/0.045 = 22 t CO_2/t H_2

--> (0.18) O_2/Cl_2

Estimated net cost = $187 (cost) - $87 (product value) = $100/tonne CO_2 mitigated

For Example: Ocean-based, carbon-negative wind hydrogen



Summary:

- Direct mitigation of fossil energy CO_2 (e.g. sequestration) is essential for stabilizing atmospheric CO_2.
- In addition to climate effects, anthropogenic CO_2 impacts ocean chemistry.
- Ocean-based CO_2 mitigation must be considered:
  - Land-based efforts may prove inadequate.
  - The ocean has a large CO_2 capture/storage potential.
  - Various potentially safe, marine-based options have been proposed and need to be evaluated.
- The preceding realities and possibilities need to be incorporated into CO_2 mitigation policy, decision-making, and R&D funding.