# Mitigating the Atmospheric CO<sub>2</sub> Increase and Ocean Acidification by Adding Limestone Powder to Upwelling Regions

#### Presentation to

Ocean Carbon and Biogeochemistry
Scoping Workshop on Ocean Acidification Research,
Scripps Institution of Oceanography, La Jolla California, 9-11 October 2007

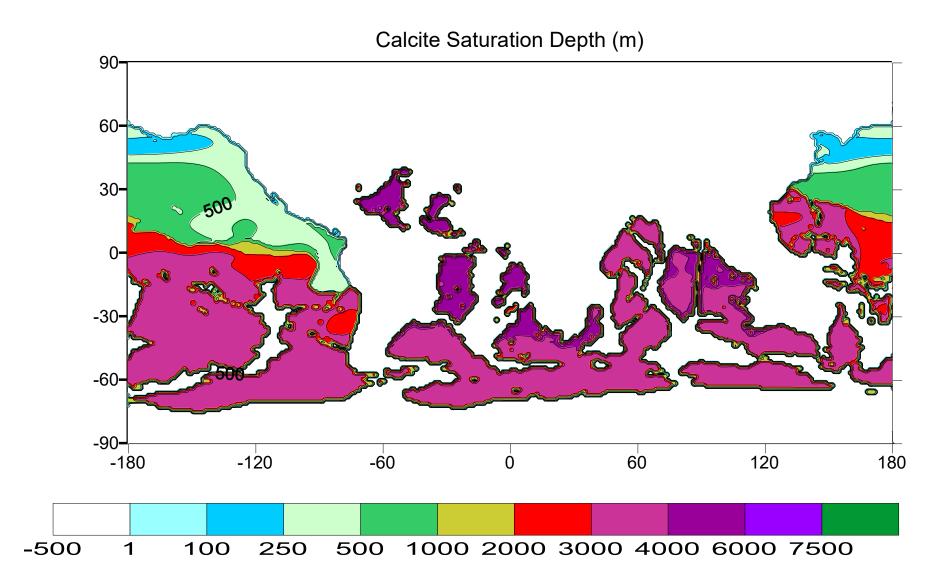
By

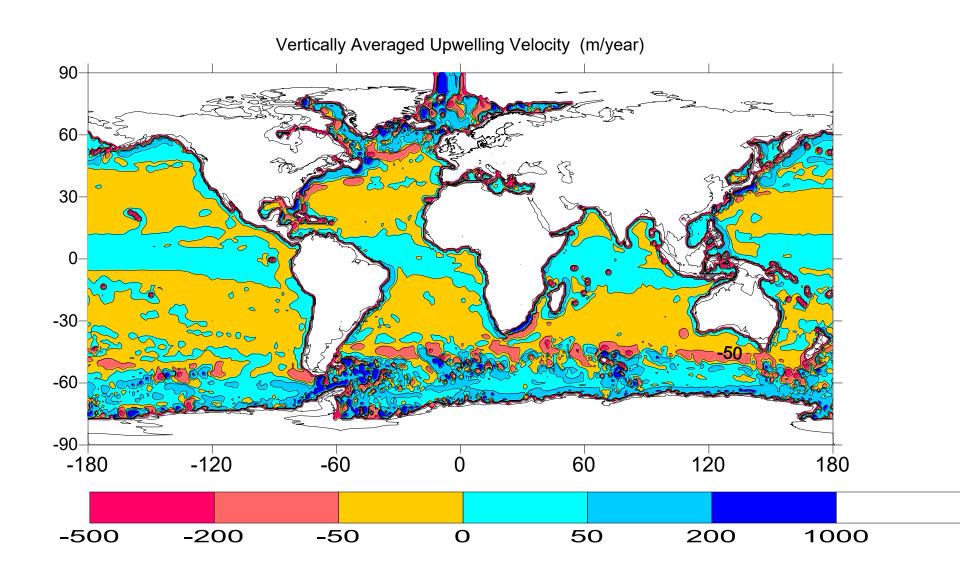
L.D Danny Harvey
Department of Geography
University of Toronto

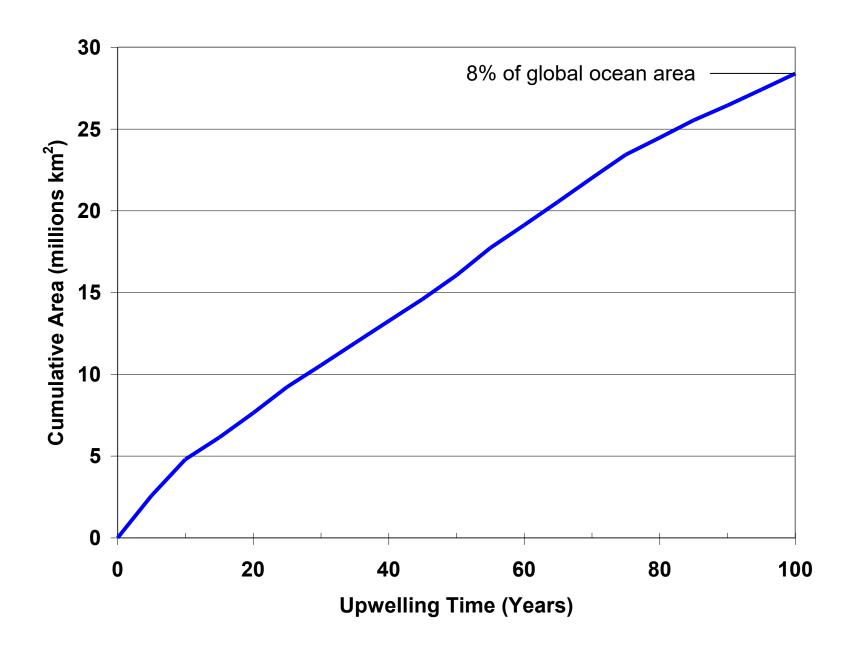
#### Basic Idea:

- Add finely ground (40-um radius) limestone powder to regions of the ocean where the boundary between saturated (upper) and unsaturated (lower) water wrt calcite is relatively shallow (250-500 m depth) and the upwelling velocity relatively large (50-100 m/year)
- The limestone powder will dissolve within the first few hundred meters of the saturation boundary, restoring CO<sub>3</sub><sup>2-</sup>, increasing the pH, and reducing pCO<sub>2</sub>
- When this water upwells to the surface, additional CO<sub>2</sub> will be absorbed from the atmosphere, pushing pH back down, thereby offsetting some of the beneficial increase in pH

In the analysis to follow, I use the 7-component carbonate chemistry algorithm of Peng et al. (1987), and use global datasets on a 1° x 1° latitude-longitude grid and at 33 depths for total dissolved inorganic carbon (TDIC), total alkalinity (TALK), dissolved phosphate, temperature, salinity, and upwelling velocity







### The analysis to follow consists of 3 phases

- Simulation of the dissolution of falling CaCO<sub>3</sub> particles in a single column, calculation of the impact on mixed layer pCO<sub>2</sub> when the carbonate-enriched water upwells to the surface, and calculation of the amount of atmospheric CO<sub>2</sub> that would need to be absorbed in order to restore the original mixed layer pCO<sub>2</sub>
- Analysis of the effect of feedback between atmospheric and mixed layer pCO<sub>2</sub>
- Simulations with a global-scale coupled climate-carbon cycle model

## Simulations with 5 Representative Columns

The reaction when CaCO<sub>3</sub> dissolves is

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \tag{1}$$

This induces the following reactions:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \tag{2}$$

$$H_2CO_3(aq) \to H^+ + HCO_3^- \tag{3}$$

$$CO_2 + H_2O \to H_2CO_3(aq) \tag{4}$$

If reactions 2-4 are fully carried out, the net result is

$$CaCO3 + CO2 + H2O \rightarrow Ca2+ + 2HCO3-$$
 (5)

That is: **one mole** of CO<sub>2</sub> absorbed for every mole of CaCO<sub>3</sub> dissolved, and **no net effect on acidity.** 

In reality, less than one mole of CO<sub>2</sub> is absorbed from the atmosphere for every mole of dissolved CaCO<sub>3</sub> entering the mixed layer, and there is a net reduction in acidity.

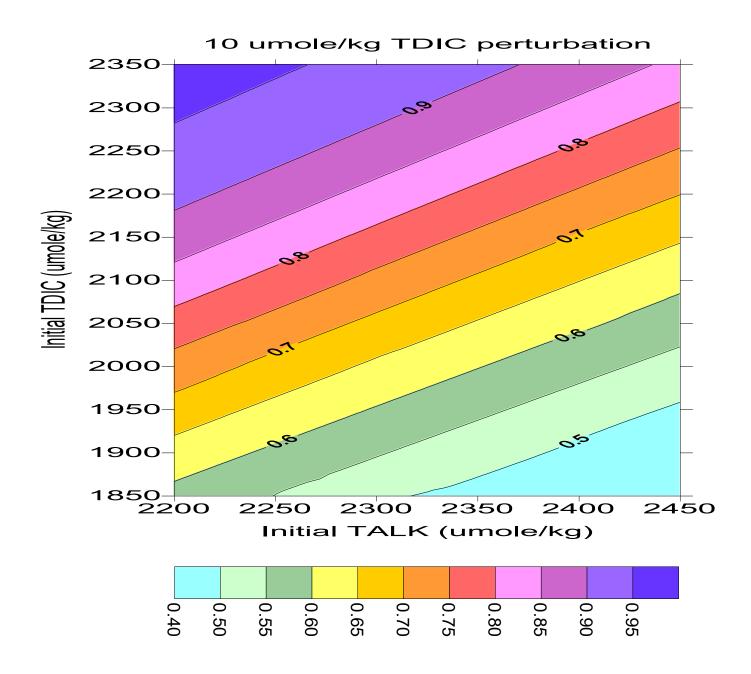
#### Why?

Because only as much CO<sub>2</sub> will enter the mixed layer from the atmosphere as is required to restore the initial pCO<sub>2</sub> difference between the mixed layer and atmosphere. For fixed atmospheric pCO<sub>2</sub>, the following applies after adjustment of mixed layer pCO<sub>2</sub> to the dissolution of CaCO<sub>3</sub>:

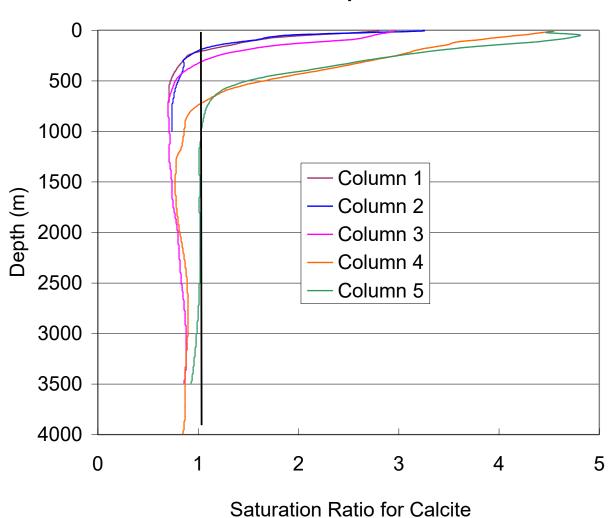
$$\Delta TDIC_a \frac{\partial pCO_2}{\partial TDIC} + \Delta TDIC_p \frac{dpCO_2}{dTDIC} = 0$$

Thus, the molar ratio  $M_R$  is given by

$$M_{R} = \frac{\Delta TDIC_{a}}{\Delta TDIC_{p}} = -\frac{dpCO_{2} / dTDIC}{\partial pCO_{2} / \partial TDIC}$$



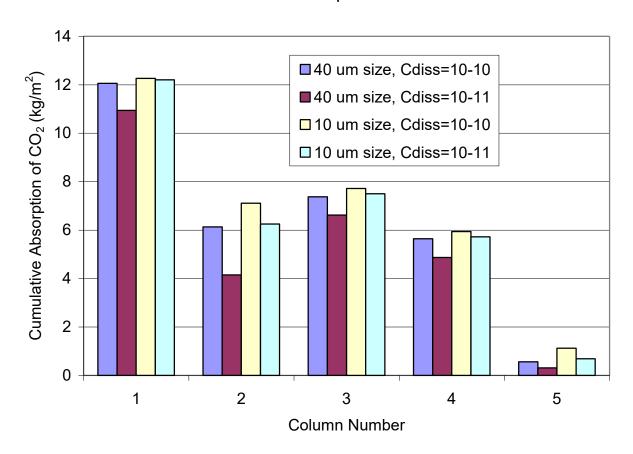
#### **Initial Profiles for 5 Representative Columns**



**Table 3.** Steady state impact on mixed layer properties of applying 200 gm/m<sup>2</sup>/yr of CaCO<sub>3</sub> (assumed to be calcite) at 40  $\mu$ m radius with  $C_{dis} = 10^{-10}$  m/s/ $\mu$ mole/kg.

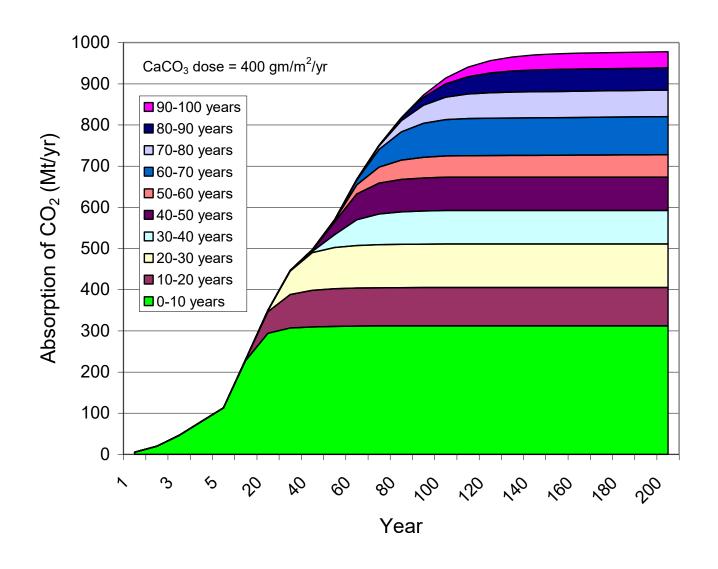
	Changes prior to absorption					
	of atmospheric CO <sub>2</sub>		Equilibrium	Moles CO <sub>2</sub>	Fraction of	Mass of CO <sub>2</sub>
	(changes in TALK are		adjustment	absorbed	added CaCO <sub>3</sub>	absorbed over
Column	twice those of TDIC)		of TDIC	over moles	in the mixed	mass of CaCO <sub>3</sub>
	TDIC	$pCO_2$	(µmole/kg)	CaCO <sub>3</sub> added	layer (F)	added (R)
	(µmole/kg)	(µatm)				
1	39.8	-40.5	28.9	0.727	0.943	0.302
2	37.6	-27.5	26.2	0.696	0.501	0.153
3	44.4	-48.7	31.7	0.714	0.587	0.184
4	33.4	-26.7	20.5	0.613	0.522	0.141
5	8.5	-10.3	5.2	0.615	0.052	0.014
	Changes in pH			Changes in Supersaturation		
	Initial	Adjustment	Final	Initial	Adjustment	Final
1	0.073	-0.059	0.014	55%	-36%	19%
2	0.063	-0.050	0.013	63%	-34%	20%
3	0.078	-0.063	0.015	62%	-41%	22%
4	0.044	-0.033	0.011	51%	-28%	23%
5	0.012	-0.009	0.003	13%	-7%	6%

#### Cumulative Absorption after 200 Years

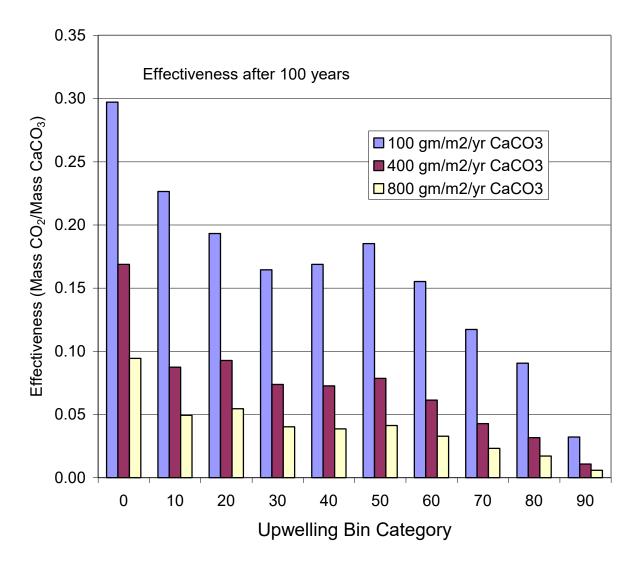


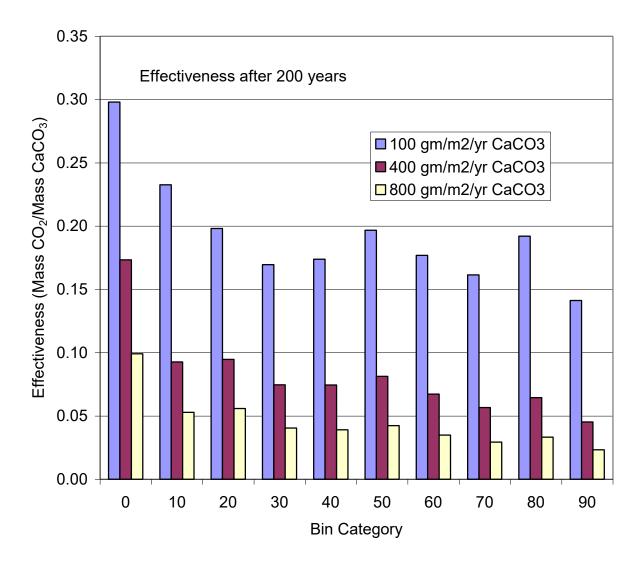
# Simulations with all 3713 1° x 1° columns having an upwelling time of 100 years of less

## Rate of absorption of CO<sub>2</sub> for one uniform rate of application of limestone powder, showing contributions from groups of columns with different upwelling times



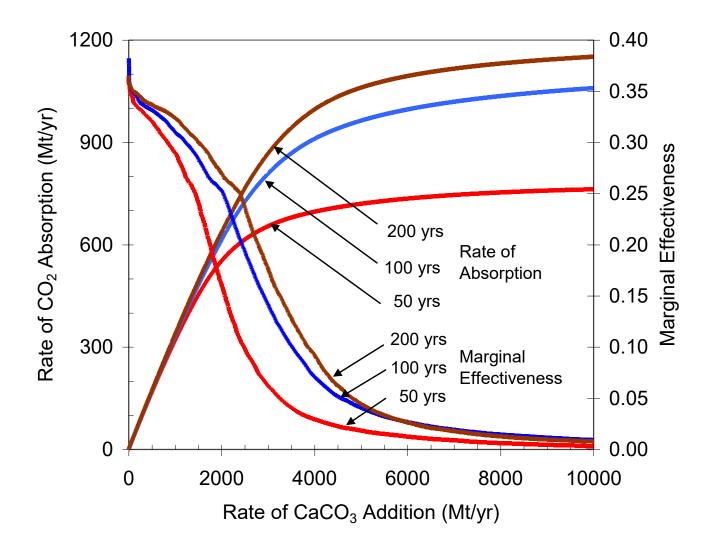
The effectiveness of adding limestone powder in terms of absorbing atmospheric CO<sub>2</sub> decreases with increasing rate of application, varies between columns in different upwelling bins, and varies over time



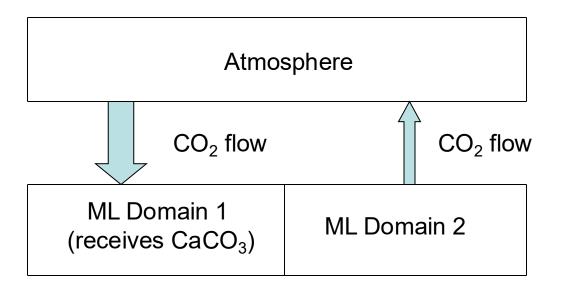


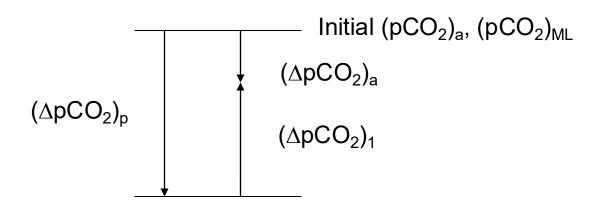
## Optimization Strategy:

- Compute the marginal effectiveness of adding limestone powder in each of 3713 columns for successively greater rates of limestone addition
- Sort all of the column/limestone-increment combinations in order of decreasing effectiveness
- Prepare a plot of rate of absorption of CO<sub>2</sub> vs total rate of addition of limestone, as the rate of addition of limestone is increased according to the order established in step (2).



## Global-scale Interactions





#### **Balance Equations:**

Domain 1 pCO<sub>2</sub>

$$\Delta(pCO_2)_1 - (\Delta pCO_2)_a + (\Delta pCO_2)_p = 0$$

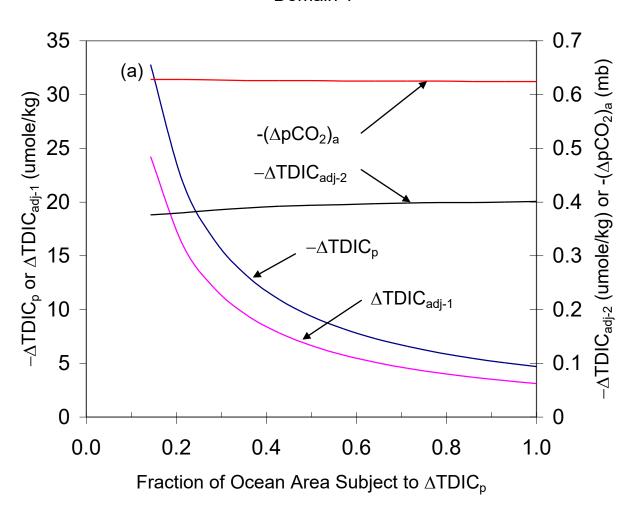
#### Domain 2 pCO<sub>2</sub>

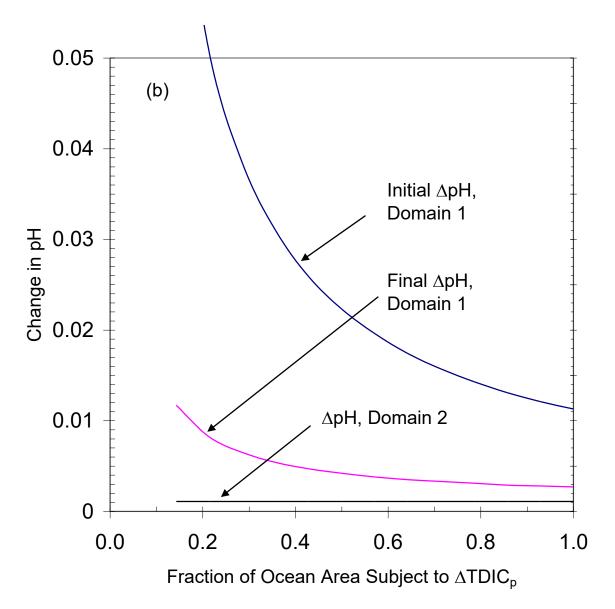
$$\Delta(pCO_2)_2 - (\Delta pCO_2)_a = 0$$

#### **Conservation of mass**

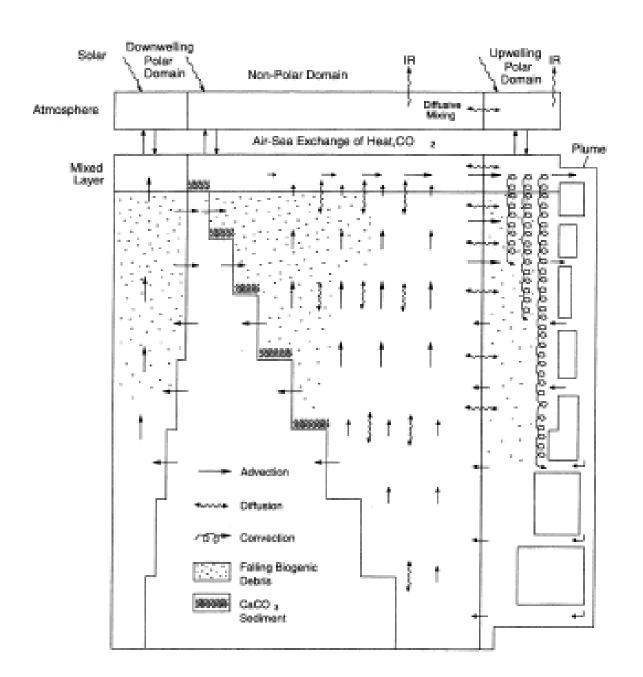
$$\Delta C_1 + \Delta C_2 + \Delta C_a = 0$$

## Impact of Dissolving 2 Gt CaCO<sub>3</sub> into the Mixed Layer of Domain 1



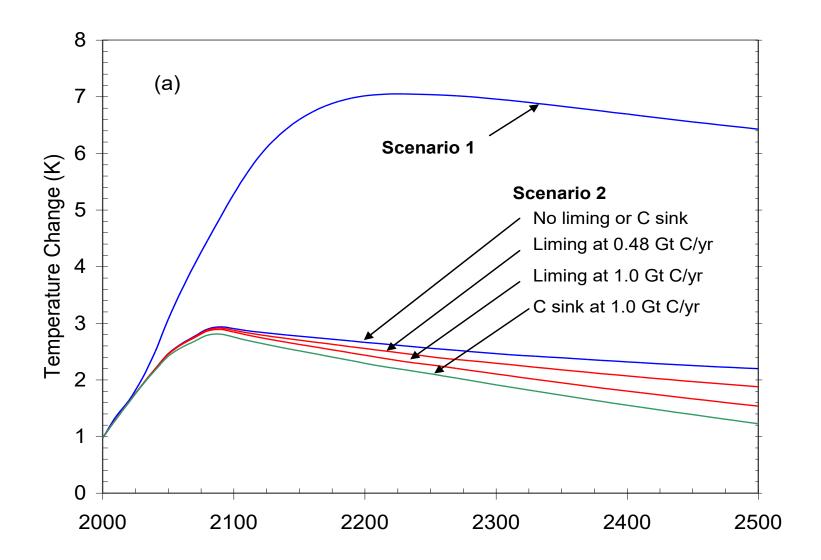


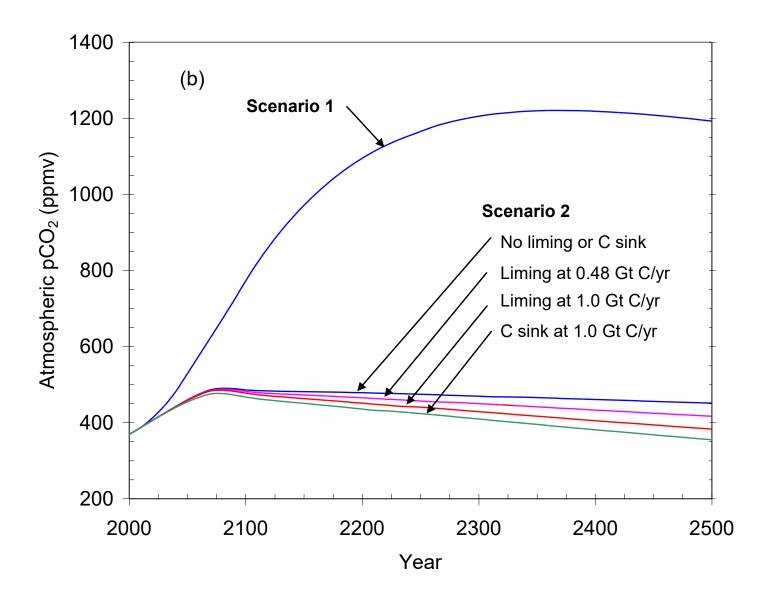
## Simulations with a coupled climatecarbon cycle model

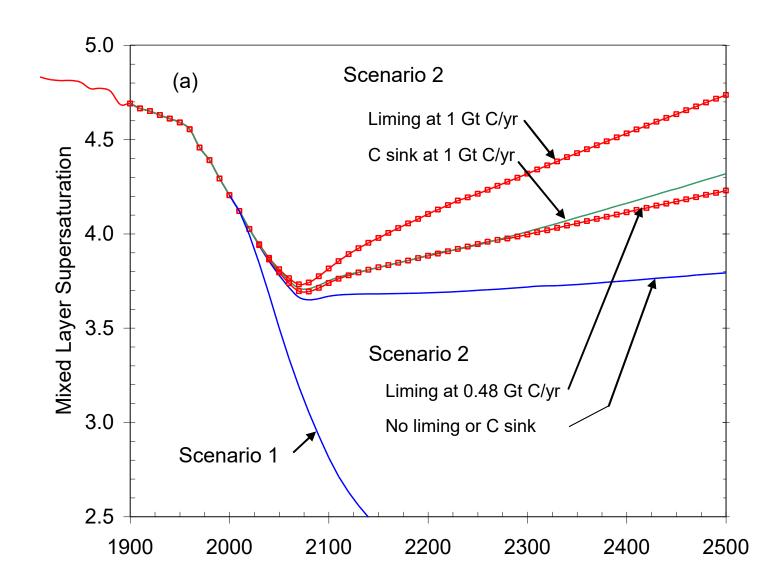


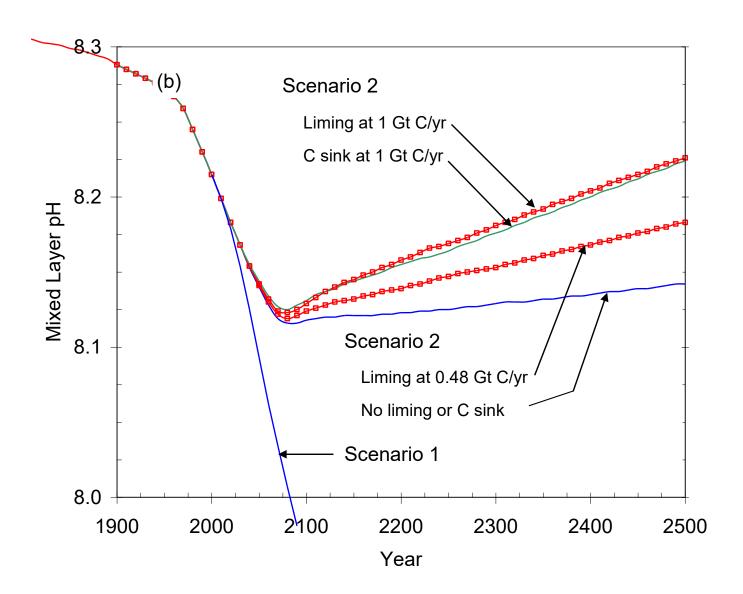
## Scenarios and Assumptions

- Scenario 1: Fossil fuel CO<sub>2</sub> emission peaks at 17.5 Gt C/yr in 2100, then declines by 1%/yr
- Scenario 2: Fossil fuel CO<sub>2</sub> emission peaks at 7.5 Gt C/yr in 2010, drops to zero by 2100, and stringent reductions in emissions of other GHGs or precursors occur
- Climate sensitivity of 3 K









## Conclusions

- Phasing out CO<sub>2</sub> emissions by 2100 has the single largest impact in reducing the ocean acidification that will otherwise occur
- Extraordinary additional measures (adding 4 Gt limestone/yr to the ocean for > 200 years) provides a modest additional benefit
- Compared to sequestering 0.5 Gt C/yr in soils or in geological strata, adding 0.5 Gt C/yr of dissolved CaCO<sub>3</sub> to the mixed layer (by adding 4 Gt/yr of limestone powder) has
- about twice the effect of ML supersaturation,
- about the same effect on ML pH, and
- about ¾ the effect on atm pCO<sub>2</sub> and ΔT