# **Impacts of Ocean Acidification on the calcium carbonate cycle**

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## Motivation



In seawater: Changes in  $[Ca^{2+}]$  are small  $\rightarrow$  changes in W largely controlled by changes of  $[CO_3^{2-}]$ 

▷ [CO<sub>2</sub>] ↑ → [CO<sub>3</sub><sup>2-</sup>] ↓ → CaCO<sub>3</sub> dissolution ↑
 ▷ [CO<sub>2</sub>] ↓ → [CO<sub>3</sub><sup>2-</sup>] ↑ → CaCO<sub>3</sub> precipitation ↑

# Modeling Flux and Dissolution of CaCO<sub>3</sub>

$$\frac{\mathrm{d}F}{\mathrm{d}z} = P - \frac{1}{l}F$$
Fin
$$F^{\mathrm{in}} = F(\Delta z) = F^{\mathrm{in}}e^{-\Delta z/l} + lP\left(1 - e^{-\Delta z/l}\right)$$
Prod - Loss
$$\Delta z \qquad \mathrm{cm} \qquad \mathrm{cell \ thickness}$$

$$F^{\mathrm{in}} \qquad \mathrm{nmol \ cm^{-2} \ s^{-1}} \qquad \mathrm{particle \ flux \ at \ top \ of \ cell}$$

$$F_{\mathrm{out}} \qquad F(z) \qquad \mathrm{nmol \ cm^{-2} \ s^{-1}} \qquad \mathrm{particle \ flux \ at \ bottom \ of \ cell}$$

$$P \qquad \mathrm{nmol \ cm^{-3} \ s^{-1}} \qquad \mathrm{production \ of \ particulate \ matter}$$

$$R \qquad \mathrm{nmol \ cm^{-3} \ s^{-1}} \qquad \mathrm{production \ of \ particulate \ matter}$$

$$R \qquad \mathrm{nmol \ cm^{-3} \ s^{-1}} \qquad \mathrm{remineralization \ length \ scale}$$

## CaCO<sub>3</sub> and POC fluxes in previous studies

|                                     | Berelson et<br>al, 2007 | Feely et al,<br>2004 | Honjo et al,<br>2008 | Gangsto et<br>al, 2008 | Dunne et<br>al, 2012 | Dunne et<br>al., 2007 |
|-------------------------------------|-------------------------|----------------------|----------------------|------------------------|----------------------|-----------------------|
| annual caco3_prod<br>(PgCaCO3/yr)   | 0.5-1.6                 | 0.8-1.4              |                      | 0.57                   |                      |                       |
| total remin<br>(PgCaCO3/yr)         |                         |                      |                      | 0.38                   |                      |                       |
| remin (0-2000m)<br>(PgCaCO3/yr)     |                         |                      |                      | 0.18                   |                      |                       |
| total burial<br>(PgCaCO3/yr)        |                         | 0.1-0.14             |                      |                        |                      |                       |
| caco3_flux out 100m<br>(PgCaCO3/yr) |                         |                      |                      | 0.41                   | 0.371                | 0.52                  |
| caco3_flux, 2000m<br>(PgCaCO3/yr)   | 0.6                     | 0.4                  | 0.41                 | 0.39                   |                      | 0.29                  |
| annual caco3_prod<br>(PgCaCO3/yr)   | 0.4-1.8                 |                      | 5.73                 |                        |                      | 9.6                   |

- Lack of observational data;
- Large uncertainties remain.

## **Vertical Profiles**





Blue: control case; Red: with  $\Omega$  feedback

CaCO3 dissolution rate increases when undersaturated

# Sediment burial of CaCO3



Standard CESM: all CaCO<sub>3</sub> gets buried in sediments shallower than 3300 m and dissolves in deeper sediments

Modification:  $CaCO_3$  dissolves if undersaturated.  $CaCO_3$  gets buried in sediments shallower than saturation depth.

### Simulation results

|                                     | Berelson<br>et al, 2007 | Feely et<br>al, 2004 | Honjo et<br>al, 2008 | Gangsto<br>et al,<br>2008 | Dunne<br>et al,<br>2012 | Dunne et<br>al. <i>,</i> 2007 | control | OA-run |
|-------------------------------------|-------------------------|----------------------|----------------------|---------------------------|-------------------------|-------------------------------|---------|--------|
| annual caco3_prod<br>(PgCaCO3/yr)   | 0.5-1.6                 | 0.8-1.4              |                      | 0.57                      |                         |                               | 1.29    | 0.71   |
| total remin<br>(PgCaCO3/yr)         |                         |                      |                      | 0.38                      |                         |                               | 1.133   | 0.55   |
| remin (0-2000m)<br>(PgCaCO3/yr)     |                         |                      |                      | 0.18                      |                         |                               | 0.84    | 0.22   |
| total burial<br>(PgCaCO3/yr)        |                         | 0.1-0.14             |                      |                           |                         |                               | 0.15    | 0.15   |
| caco3_flux out<br>100m (PgCaCO3/yr) |                         |                      |                      | 0.41                      | 0.371                   | 0.52                          | 0.92    | 0.64   |
| caco3_flux, 2000m<br>(PgCaCO3/yr)   | 0.6                     | 0.4                  | 0.41                 | 0.39                      |                         | 0.29                          | 0.35    | 0.4    |
| 100m (PgC/yr)                       | 0.4-1.8                 |                      | 5.73                 |                           |                         | 9.6                           | 7.29    | 7.27   |

CaCO3 production is reduced to maintain alkalinity balance;

• > ~ 21% of CaCO3 produced is buried, and ~45% dissolved in bottom cells.•





- More CaCO3 fluxes below ~1000m;
- CaCO3 dissolution increases in undersaturated conditions

# Changes in DIC distribution



- DIC concentrations slightly decrease in surface seawater and increase in deeper waters;
- Changes in DIC concentrations and alkalinity are small.

### Saturation Depth



Changes of CaCO3 dissolution profiles lead to changes of  $[CO_3^{2-}]$ . This changes  $\Omega$  and saturation depths.

Calcite Saturation Depth, CTRL (m) Latitude -50 Longitude Calcite Saturation Depth, EXP (m) Latitude -50 Longitude Saturation Depth (EXP-CTRL)(m) Latitude -100 -50 -200 -300 

Longitude

# CaCO<sub>3</sub> Burial

CaCO3 Flux to Sediments, CTRL (gCaCO 3/m2/year)



CaCO3 Flux to Sediments, EXP (gCaCO 3/m2/year)



CaCO3 Flux to Sediments (EXP-CTRL)(gCaCO 3/m2/year)







(Dunne et al., 2012)

CaCO<sub>3</sub> burial flux increases in Atlantic Ocean and decreases in Pacific Ocean, controlled by the saturation state in the bottom cell above sediments.

# CaCO<sub>3</sub> Burial

CaCO3 Flux to Sediments, CTRL (gCaCO  $_{\rm 3}/m^2/year)$ 



a<sup>-1</sup>)

### Saturation Depth

#### Changes of saturation depths due to increasing CO<sub>2</sub>









Increasing  $CO_2$  since 1850 leads to shoaling lysocline in N. Pacific and Southern Ocean



CaCO3 Flux to Sediments, CTRL (gCaCO ,/m<sup>2</sup>/year)



- Since 1850, Changes in Ω and [DIC] mainly happen in upper ocean, where Ω>1
- $\succ$  There is no significant changes in the amount of CaCO<sub>3</sub> burial

## Summary

- With Modifications:
  - Simulation CaCO3 fluxes (2000m and bottom) basically agree with previous studies;
  - Distribution of CaCO3 burial changes: increased burial in Atlantic Ocean
  - Small changes in DIC and alkalinity distributions
- ▶ 1850-2009:
  - ► Increasing  $CO_2$  mainly affected the upper ocean, where  $\Omega > 1$ . There is no significant changes in  $CaCO_3$  dissolution
- > Next Step:
  - Incorporating explicit calcifiers,
  - Incorporating effects of Ω on calcification
  - Studying impacts of ocean acidification on the carbon cycle on longer timescales.

## **Dissolution Length Scale**

### **Dissolution of CaCO<sub>3</sub> in standard CESM/BEC:**

 $DECAY_CaCO3 = exp(-dz(k) / (scalelength*P_CaCO3%diss))$ 

DECAY\_CaCO3 is remineralization length scale of CaCO3; dz is the thickness; P\_CaCO3%diss is dissolution length; scalelength is a parameter varying with depth

### **Dissolution of CaCO<sub>3</sub> in modified CESM/BEC:**

DECAY\_CaCO3 = exp(-dz(k) \* max(c0, 1-OMEGA\_CALC) /
(scalelength\*P\_CaCO3%diss))

#### Pre-industrial part: POC flux





