Vulnerabilities of the calcium-carbonate cycle: positive and negative feedbacks

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UNESCO, Paris, France
Current level of understanding, projected into the future:

- Predictive models differ significantly in future predictions.
- Cannot improve predictions without better understanding of the controlling processes.
- This is no longer just an academic issue.
- Disagreements in predictions impact baseline targets for emissions reduction.
- Sequestration cost targets are $10-35/t of C.
- Differences between models imply differences in ecosystem services of trillions of dollars.
- = big incentive for research.

- A. Gnanadesikan, GFDL
The Global Carbon Budget [Pg C]. Positive values represent atmospheric increase (or ocean/land sources), negative numbers represent atmospheric decrease (sinks).

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Atmospheric increase</td>
<td>116 ± 4</td>
<td>65 ± 1</td>
</tr>
<tr>
<td>Emissions (f. fuel, cement)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ocean Inventory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net terrestrial</td>
<td>+50 ± 28</td>
<td>-15 ± 9</td>
</tr>
<tr>
<td>Land-use change</td>
<td>+82 to +162</td>
<td>+24 ± 12</td>
</tr>
<tr>
<td>*Resid. terrestrial sink</td>
<td>-32 to -112</td>
<td>-39 ± 18</td>
</tr>
</tbody>
</table>

First 180 years the ocean absorbed 57% of FF emissions
Last 20 years the ocean absorbed 31% of FF emissions
Relative to total emissions the ocean absorbed 44% and 36%
There are a number of feedbacks in the global carbon cycle and between the carbon and climate systems that we must understand if we are ever to predict the future role of the ocean as a sink for $CO_2$

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<td>Increased greenhouse forcing</td>
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2005 Headlines on CO2 & Coral Reefs

Ocean acidification represents “potentially a gigantic problem for the world.” -Dr. Carol Turley, Plymouth Marine Laboratory, Feb. 7, 2005.

“Scientists warn growing acidity of oceans will kill reefs” Paul Brown, environment correspondent, The Guardian

“As an ecosystem our grandchildren will not see coral reefs any more” - Professor Jonathan Erez, Hebrew University of Jerusalem - BBC News, Feb. 13, 2005

“If CO2 levels continue to rise, the oceans could be more acidic in 2100 than they have been for 400 million years.” Ulf Riebesell - BBC News, Feb. 07, 2005.


“The world scientific community is only just waking up to this.” Cape Argus, Feb. 5, 2005
\[ \text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3 \]
\[ \text{Ca}^{2+} + 2\text{HCO}_3^- = \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]
\( \text{CO}_2 \) is an acid gas...as we add \( \text{CO}_2 \) to the surface waters we are reducing the buffering capacity of the ocean and its ability to continue to take up \( \text{CO}_2 \) from the atmosphere

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Under IPCC “Business as Usual” the pH of surface seawater drops by 0.4 pH units by 2100. \(\text{CO}_3^{2-}\) in surface water drops by 48% from pre-industrial values.

Modified from Feely et al., (2001)

Average Surface Water DIC Increase in 2000 ~ 1.2 \(\mu\text{mol kg}^{-1}\text{yr}^{-1}\)
Global Distribution of Surface Revelle Factor

R. Revelle, H. E. Suess, Tellus 9, 18 (1957)

\[
\text{Revelle Factor} = \frac{\Delta fCO_2}{\Delta TCO_2} \cdot \frac{fCO_2}{TCO_2}
\]
Modern Revelle Factors have already increased by 1 since preindustrial
**Carbon Cycle Change** | **Climate Feedback** | **direction**
--- | --- | ---
$CO_3^{2-}$ decrease | Less efficient uptake | positive
**Calcification decrease** | lower natural $CO_2$ production | negative
$CaCO_3$ dissolution-sed. | higher $CO_3^{2-}$ increasing uptake | negative
$CaCO_3$ dissolution-water | higher $CO_3^{2-}$/lower org. transport | Neg./pos.
Increasing SST | Convert ocean $HCO_3^-$ to $CO_2$ | positive
Increased stratification | Reduced mixing and transport | positive
Increased stratification | Lower productivity and uptake | positive
Increased dust input | Increased productivity-N fixers | negative
Ecosystem structure | Lower or higher productivity | Pos./neg.
$CH_4$ hydrate release | Increased greenhouse forcing | Positive

$CaCO_3$ prod. currently releases $\sim$1 PgC yr$^{-1}$ to the atmosphere, as $CO_3^{2-}$ concentrations drop calcification is expected to decrease.
Warm water corals have primarily formed in aragonite saturation levels > 4, can survive at levels > 3.5, and generally stop growing < 3
### Effects of doubled $\text{CO}_2$ on coral calcification

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

* dominated by coralline algae
There appears to be a linear decrease in the calcification rate of coral reef systems with decreasing carbonate ion concentrations.

Since anthropogenic CO$_2$ has already lowered the carbonate ion concentration by ~15%, these systems are already being affected by anthropogenic CO$_2$.

After Turley et al., 2005
There appears to be a linear decrease in the calcification rate of coral reef systems with decreasing carbonate ion concentrations.

At carbonate ion concentrations of ~100-120 µmol/kg this reef system switches from net growth to net dissolution.

After Turley et al., 2005
# Major planktonic calcifiers

<table>
<thead>
<tr>
<th>group</th>
<th>mineral form</th>
<th>generation time</th>
<th># of extant species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coccolithophores</td>
<td>autotroph</td>
<td>calcite</td>
<td>~250</td>
</tr>
<tr>
<td>Foraminifera</td>
<td>heterotroph</td>
<td>calcite</td>
<td>~4000</td>
</tr>
<tr>
<td>(many with autotrophic symbionts)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pteropods</td>
<td>heterotroph</td>
<td>aragonite</td>
<td>~30</td>
</tr>
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Response to elevated $CO_2$ (decreased pH, $\Omega$ or $[CO_3^{2-}]$)

**Today’s world**  
pCO$_2$: 280-380 ppmV

- Gephyrocapsa oceanica
- Emiliana huxleyi
- Calcidiscus leptoporus

**High-CO$_2$ world**  
pCO$_2$: 580-720 ppmV

Riebesell et al. (2000), Nature; Langer et al. subm.
$\text{CO}_2$ out-gassing as a consequence of $\text{CaCO}_3$ production

Changes in calcification out-gassing in the future result in an uncertainty of at least 1 Pg C yr$^{-1}$

Figure 4. Potential $\text{CO}_2$ release in Gt C yr$^{-1}$ from 1850 to 2150 when annual $\text{CaCO}_3$ production remains constant at 1 Gt C yr$^{-1}$ (scenario 1, solid line), PIC/POC ratio decreases as in $E. \text{huxleyi}$ at a 16/8 L/D cycle (scenario 5, dashed line), or at a 24/0 L/D cycle (scenario 6, dashed line), and PIC/POC ratio decreases as in $G. \text{oceanica}$ (scenario 7, dashed-dotted line).

Zondervan et al. (2001)
40% reduction in CaCO₃ export corresponds to 10 ppm reduction in atmospheric CO₂

(assuming CaCO₃ export = 1Pg C yr⁻¹)
In addition to reduced $\text{CaCO}_3$ production, exported $\text{CaCO}_3$ particles are dissolving at shallower depths

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The available sediment trap and water chemistry data indicate that as much as 60% of CaCO₃ production dissolves in shallow waters.

Table 1. Sediment trap particulate CaCO₃ dissolution fluxes in the Pacific Ocean. The difference between the mean carbonate flux in the upper trap and the lower trap defines the dissolution flux. In all but one of the deepwater cases, the CaCO₃ flux collected in the midwater trap is higher than the carbonate flux collected in the deepwater trap. The dissolution rates are derived from the differences in CaCO₃ sediment trap fluxes between the upper and lower sediment traps divided by the depth range between the traps.

<table>
<thead>
<tr>
<th>Location</th>
<th>Trap depth range (m)</th>
<th>Dissolution rate (μmol kg⁻¹ year⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shallow sediment traps</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Northwestern Pacific</td>
<td>100–1000</td>
<td>0.12</td>
</tr>
<tr>
<td>Equatorial Pacific</td>
<td>105–320</td>
<td>0.67</td>
</tr>
<tr>
<td>Northwestern Pacific</td>
<td>500–1000</td>
<td>0.02</td>
</tr>
<tr>
<td>Northeastern Pacific</td>
<td>200–1000</td>
<td>0.10</td>
</tr>
<tr>
<td><strong>Deep sediment traps</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Northwestern Pacific</td>
<td>2000–4000</td>
<td>0.003–0.006</td>
</tr>
<tr>
<td>Equatorial Pacific</td>
<td>2300–3600</td>
<td>0.005–0.014</td>
</tr>
<tr>
<td>2°59.8′N 135°10.0′E</td>
<td>1592–3902</td>
<td>0.012</td>
</tr>
<tr>
<td>4°7.5′N 136°16.6′E</td>
<td>1769–4574</td>
<td>0.013</td>
</tr>
<tr>
<td>0°0.2′N 175°09.7′E</td>
<td>1357–4363</td>
<td>0.005</td>
</tr>
<tr>
<td>0°01′N 175°02′E</td>
<td>2200–4300</td>
<td>—</td>
</tr>
<tr>
<td>13°00′N 175°01′E</td>
<td>1500–5100</td>
<td>0.006</td>
</tr>
<tr>
<td>00°04′N 139°45′W</td>
<td>2284–3618</td>
<td>0.005–0.014</td>
</tr>
<tr>
<td>11°58′S 135°02′W</td>
<td>1292–3594</td>
<td>0.003</td>
</tr>
<tr>
<td>50°0′N 145°0′W</td>
<td>1000–3800</td>
<td>0.024</td>
</tr>
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![Graph](image)
Feely et al. (2004) Anthropogenic CO2 is already shoaling aragonite (and calcite) saturation horizons in all of the major ocean basins!

Sarma et al. (2002)

Figure 2. The change in total alkalinity (μmol/kg) with reference to potential density (σ₀), between GEOSECS and WOCE in the (a) North Pacific [GEOSECS #213, 30.97°N, 168.48°W and WOCE leg P15NA, #50, 31.00°N, 165.00°W (b) North Indian Ocean [GEOSECS #446, 12.6°N, 84.6°E and WOCE leg I09, #241, 13.86°N, 91.5°E]. Horizontal lines show aragonite saturation during GEOSECS (solid line) and WOCE (dashed line). Increase in TA between two horizontal lines represents the influence of dissolution of aragonite skeletal material due to increased anthropogenic carbon inputs during past two decades.

Sarma et al. (2002)

Feely et al. (2004)
By 2100 large changes in saturation state

\[ \Delta [\text{CO}_3^{2-}]_A \text{ in } \mu\text{mol kg}^{-1} \]

- **Surface undersaturation** \(\Delta [\text{CO}_3^{2-}]_A < 0\)
  - Southern Ocean
  - Subarctic Pacific

- **Shoaling of the aragonite saturation horizon** \(\Delta [\text{CO}_3^{2-}]_A = 0\)
  - Southern Ocean (by ~1000 m)
  - North Atlantic (by ~3000 m)

Orr et al., (submitted)
Effect of reduced CaCO$_3$ production and export may be counteracted by decreasing POC export ("ballasting effect")

The long term burial of organic C in the ocean is only $\sim$0.15 PgC yr$^{-1}$, but annual mixed layer export is $\sim$ 7 Pg C yr$^{-1}$
There is ~65 Million Pg C stored as CaCO₃ in ocean sediments

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{HCO}_3^-
\]

Dissolution of these sediments provides a huge potential for CO₂ uptake

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Models predict that on millennial time-scales 65-70% of the emissions would end up in the ocean (no CaCO$_3$ compensation).

Dissolution of CaCO$_3$ sediments increases this number to 80-85%.
The depth of carbonate dissolution affects the timing and magnitude of the atmospheric $CO_2$ signal.

Figure 9.18. Graph illustrating that once $CO_2$ enters the atmosphere because of human activities, the return to original conditions takes a long time, regardless of whether or not CaCO$_3$ minerals are dissolved. (After Bacastrow and Keeling, 1979.)
The majority of CaCO$_3$ sediments are found on shelves and slopes.
Pore water $\text{CaCO}_3$ dissolution flux increases in shallow sediments because of lower saturation states and increased organic matter oxidation.

Organic matter oxidation in sediments increases as ocean temperatures increase.
Big dissolution event at Paleocene-Eocene Thermal Maximum
55Ma sea surface temperatures rose by $\sim 8^\circ$C over a few thousand years

30-40% of deep sea benthic foraminifera went extinct
A commensurate change in $^{13}$C suggests that there was a huge “burp” of methane into the atmosphere.
CONCLUSIONS

1) Many of the ocean carbon cycle and climate feedbacks are tied to the CaCO$_3$ cycle.

2) The CaCO$_3$ cycle is still poorly understood and needs to be studied with a particular emphasis on the magnitudes and timing.

3) We know from thermodynamics that ocean uptake efficiency will decrease, but the real bottle neck is in moving the CO$_2$ into the ocean interior, which is controlled by circulation.

4) There is general consensus that elevated CO$_2$ will reduce calcification and lead to shallower dissolution producing a negative feedback, but the related decrease in organic matter export may counteract some or all of this effect.

5) There is a potentially very large negative feedback associated with dissolving carbonate sediments. This has been thought to be a millennial time scale issue, but there is growing evidence that this dissolution may occur quickly.
Take home message:

We should not limit our vulnerability studies only to positive feedbacks, but we also need to understand potential negative feedbacks.