The Impact of Anthropogenic CO\textsubscript{2} on the CaCO\textsubscript{3} System in the Oceans

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Method for Estimating CaCO\textsubscript{3} Dissolution Rates

To estimate in situ CaCO\textsubscript{3} dissolution rates in waters where values of $\Delta$CaCO\textsubscript{3} are positive, we have plotted $\Delta$CaCO\textsubscript{3} against water parcel ages derived from CFC-11 of CFC-12 for the upper ocean, and $^{14}$C for deep waters where CFC-11 or CFC-12 is not detected. The CFC age is calculated by converting the CFC concentrations (in pmol kg$^{-1}$) in the subsurface water to partial pressure ($p$CFC) at the potential temperature and salinity ($S_1$) and then matching $p$CFC of the subsurface water with the $p$CFC of the atmosphere for the appropriate year. In this calculation, the subsurface water parcel is assumed to have been in solubility equilibrium when it was in contact with the overlying atmospheric $p$CFC. Thus, the age of the subsurface water is defined as the time difference between the measurement date and the date when the water parcel was last in contact with the atmosphere. The use of CFC age is limited to upper waters with CFC ages that are less than 35 years because systematic biases in CFC ages due to dilution and nonlinear mixing effects tend to be larger for older waters ($S_2$-$S_4$).

For waters with CFC-based ages greater than 35 years, we used age estimates from natural $\Delta^{14}$C. For waters that contained bomb-generated $^{14}$C, this was subtracted from the total radiocarbon ($\Delta^{14}$C) to derive the natural $\Delta^{14}$C component using the separation method of Rubin and Key ($S_5$) based on the strong correlation between natural $\Delta^{14}$C and potential alkalinity ($P_{TA} = (TA + nitrate) \times 35/S$). We used their $P_{TA} - \Delta^{14}$C
algorithm along with PTA data calculated from the WOCE/JGOFS/OACES dataset to estimate naturally occurring $\Delta^{14}$C. Resulting estimates of natural $\Delta^{14}$C were then used to calculate the age of water parcels. If CaCO$_3$ dissolution occurs in a given water parcel, values of $\Delta$CaCO$_3$ will increase as the water parcel ages. If the effects of mixing between different water masses are taken into account accurately, the slope between values of $\Delta T$ CaCO$_3$ and corresponding ages of water parcels can be used to determine the in situ dissolution rate of CaCO$_3$ particles. An alternative method for estimating the dissolution rate is to divide each value of $\Delta$CaCO$_3$ by its age. However, the rate determined by this method might include a large error if there is systematic age biasing. Therefore, we estimated the in situ CaCO$_3$ dissolution on isopycnal surfaces by determining the slope between values of $\Delta$CaCO$_3$ and ages of water parcels. Systematic age biasing does not significantly affect our slope-based results as long as its magnitude is constant over the period of analysis.

**Biological Impacts of Exposure to Increased CO$_2$ Levels**

Recent field and laboratory studies (Table S1) reveal that the degree of supersaturation has a profound effect on the calcification rates of individual species and communities in both planktonic and benthic habitats. The calcification rate of almost all calcifying organisms investigated to date decreased in response to decreased CaCO$_3$ saturation state, even when the carbonate saturation level was >1. This response holds across multiple taxa—from single-celled protists to reef-building corals—and across all CaCO$_3$ mineral phases.
The effects of chronic exposure to increased CO$_2$ on calcifiers, as well as the long-term implications of reduced calcification rates within individual species and their ecological communities are unknown. Calcification probably serves multiple functions in carbonate producers. Decreased calcification would presumably compromise the fitness of these organisms and could shift the competitive advantage towards noncalcifiers. Carbonate skeletal structures will likely be weaker and more susceptible to erosion (S6) and dissolution. Reduced calcification in planktonic species could have cascading effects through food webs and, coupled with other expected climatic changes in seawater temperature, salinity, and upwelled nutrients, could substantially alter ecosystem structure and interactions.

Pteropod molluscs will be first among the major groups of calcifiers to experience <1 saturation states in parts of their present-day geographical ranges (Fig. S1). If we assume that these animals are restricted to aragonite-saturated waters, then pteropod habitat would become increasingly limited latitudinally and vertically in the water column by shoaling of the aragonite saturation horizon. We predict that the distribution of subarctic Pacific pteropod species will shift southwards toward the equator. The elimination of pteropods from the subarctic Pacific would impact the downward organic carbon flux associated with pteropod fecal pellets (S7) and remove the only source of aragonite production and flux in the region (e.g., S8-S10). Most of the carnivorous zooplankton and fishes that feed on pteropods (S11-S13) would be able to switch to other prey types, which could result in greater predation pressure on juvenile fishes such as salmon (S14). Gymnosomes, the shell-less planktonic molluscs that are believed to prey exclusively on pteropods (S15), would likely shift their geographic distribution in concert
with their pteropod prey (S16). Undersaturated waters are currently impinging upon the
depth ranges of pteropods in several other regions such as the Antarctic Polar Front and
Ross Sea, where pteropods account for more than half of the carbonate flux (S17) and
contribute substantially to the export of organic carbon (S18,S19); and upwelling areas
associated with the Benguela Current, western Arabian Sea, and Peru Current, where
pteropod abundances can be high (e.g., S20-S24). Over the next several centuries, the
progressive shoaling of the aragonite saturation horizon and the decreasing calcite
saturation state of the euphotic zone in these regions will impact trophic dynamics and
other ecosystem processes, including the cycling of CaCO$_3$ and organic matter.
Some benthic ecosystems such as coral reefs have evolved to take advantage of the
accumulated calcium carbonate production of the community, which enables the
community to keep up with sea level rise and to create the structural complexity required
to support high biodiversity. Although no studies have directly measured the effect of
decreased calcification on coral reef systems, decreased carbonate production and
increased dissolution are likely to decrease the overall ability of coral reefs to accumulate
or maintain reef structures (S25).

References and Notes


### Table S1. Measured biogenic calcification responses to increased pCO$_2$.

<table>
<thead>
<tr>
<th>Organism/System</th>
<th>Mineralogy</th>
<th>Approximate % Change in Calcification when pCO$_2$ is</th>
<th>References and notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2X preindustrial</td>
<td>3X preindustrial</td>
</tr>
<tr>
<td>Coccolithophores</td>
<td></td>
<td></td>
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<tr>
<td><em>Emiliania huxleyi</em></td>
<td>Calcite</td>
<td>–25</td>
<td></td>
</tr>
<tr>
<td><em>Emiliania huxleyi</em></td>
<td>Calcite</td>
<td>–9</td>
<td>–18</td>
</tr>
<tr>
<td><em>Gephyrocapsa oceanica</em></td>
<td>Calcite</td>
<td>–29</td>
<td>–66</td>
</tr>
<tr>
<td>Foraminifera</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Oorbicula universa</em></td>
<td>Calcite</td>
<td>–8</td>
<td>–14</td>
</tr>
<tr>
<td><em>Globogeneroides</em></td>
<td>Calcite</td>
<td>–4 to –6</td>
<td>–6 to –8</td>
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<tr>
<td><em>Sacculifer</em></td>
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<tr>
<td>Scleractinian corals</td>
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<tr>
<td><em>Turbinaria reniformis</em></td>
<td>Aragonite</td>
<td>–13</td>
<td></td>
</tr>
<tr>
<td><em>Pavona cactus</em></td>
<td></td>
<td>–18</td>
<td></td>
</tr>
<tr>
<td>Species</td>
<td>Structure</td>
<td>Temperature</td>
<td>Source</td>
</tr>
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<td>-------------------------------</td>
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<td>------------------------------------------------------------------------</td>
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<tr>
<td><em>Galaxea fascicularia</em></td>
<td></td>
<td>–16</td>
<td>pCO$_2$ = 412 ppm and 866 ppm</td>
</tr>
<tr>
<td><em>Acropora verweyi</em></td>
<td></td>
<td>–18</td>
<td></td>
</tr>
<tr>
<td><em>Porites compressa</em></td>
<td>Aragonite</td>
<td>–14 to –20</td>
<td>Marubini <em>et al</em>., 2001 (S33)</td>
</tr>
<tr>
<td><em>Porites porites</em></td>
<td>Aragonite</td>
<td>–16</td>
<td>Marubini and Thake, 1999 (S34)</td>
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<tr>
<td><em>Stylophora pistillata</em></td>
<td>Aragonite</td>
<td>0 to –50</td>
<td>Reynaud <em>et al</em>., 2003 (S35); Corals grown at pCO$_2$ = 460 and 760 ppm; level of response is temperature-dependent</td>
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<tr>
<td><strong>Coralline red algae</strong></td>
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<tr>
<td><em>Porolithon gardineri</em></td>
<td>Magnesian calcite</td>
<td>–25</td>
<td>Agegian, 1985 (S36)</td>
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<td></td>
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<td><strong>Carbonate systems</strong></td>
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</tr>
<tr>
<td>Biosphere 2</td>
<td>Mixed</td>
<td>–40</td>
<td>Langdon <em>et al</em>., 2000 (S37); dominated by coralline algae</td>
</tr>
<tr>
<td>Monaco mesocosm</td>
<td>Mixed</td>
<td>–21</td>
<td>Leclercq <em>et al</em>., 2000 (S38)</td>
</tr>
<tr>
<td>Monaco mesocosm</td>
<td>Mixed</td>
<td>–15</td>
<td>Leclercq <em>et al</em>., 2002 (S39)</td>
</tr>
</tbody>
</table>
Figure Caption

Fig. S1. Shells from live *Clio pyramidata* pteropods collected from the subarctic Pacific (50°N; 145°W). Animals were held in 1-L jars at 9°C for time periods up to 48 hours. All animals were actively swimming when the experiment was terminated. Owing to respiratory CO₂, the ambient seawater in jars became undersaturated with respect to aragonite. (A) Shell of *Clio pyramidata*. Size bar = 1 mm. (B) SEM photograph of shell aperture after 4 hours in undersaturated water. Size bar = 100 um. (C) SEM photograph of shell aperture after 48 hours in undersaturated water. Size bar = 100 um. Note the extensive erosion and pitting of the shell resulting from dissolution.