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# Geochemical Consequences of Increased Atmospheric Carbon Dioxide on Coral Reefs


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**A coral reef represents the net accumulation of calcium carbonate ($CaCO_3$) produced by corals and other calcifying organisms. If calcification declines, then reef-building capacity also declines. Coral reef calcification depends on the saturation state of the carbonate mineral aragonite of surface waters. By the middle of the next century, an increased concentration of carbon dioxide will decrease the aragonite saturation state in the tropics by 30 percent and biogenic aragonite precipitation by 14 to 30 percent. Coral reefs are particularly threatened, because reef-building organisms secrete metastable forms of $CaCO_3$, but the biogeochemical consequences on other calcifying marine ecosystems may be equally severe.**


Atmospheric $CO_2$ is expected to reach double preindustrial levels by the year 2065 (*1*). $CO_2$ research in the marine environment has focused on the ocean's role in sequestering atmospheric $CO_2$ (*2, 3*), but the potential effects of the resulting ocean chemistry changes on marine biota are poorly known.

Dissolved inorganic carbon occurs in three basic forms: $CO_2$* ($CO_{2(aq)} + H_2CO_3$), $HCO_3^-$, and $CO_3^{2-}$. Under normal seawater conditions (pH 8.0 to 8.2), $[HCO_3^-]$ is roughly 6 to 10 times $[CO_3^{2-}]$. When $CO_2$ dissolves in seawater, less than 1% remains as $CO_2$*; most dissociates into $HCO_3^-$ and $CO_3^{2-}$, and the acid formed by dissolution of $CO_2$ in seawater lowers the pH so that some $CO_3^{2-}$ combines with $H^+$ to form $HCO_3^-$. Thus, addition of fossil fuel $CO_2$ decreases $[CO_3^{2-}]$.

The seawater-mediated interaction of $CO_2$ and calcium carbonate ($CO_2 + H_2O + CaCO_3 \leftrightarrow 2HCO_3^- + Ca^{2+}$) illustrates how addition of $CO_2$ enhances $CaCO_3$ dissolution and removal of $CO_2$ enhances its precipitation. Calcium carbonate saturation state ($\Omega$) is

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K'_{sp}}$$

where $K'_{sp}$ is the stoichiometric solubility product for a particular mineral phase of $CaCO_3$ [calcite (calc), aragonite (arag), or high-magnesian calcite (hmc)]. $\Omega$ is largely determined by $[CO_3^{2-}]$ because $[Ca^{2+}]$ is near conservative in seawater. Tropical surface waters are supersaturated ($\Omega > 1.0$) with respect to all mineral phases, but the degree of saturation varies: $\Omega$-calc is 5 to 6, $\Omega$-arag is 3 to 4, and $\Omega$-hmc is 2 to 3. Under the worst case global change scenarios of the Intergovermental Panel on Climate Change (IPCC), the surface ocean will remain almost entirely supersaturated with respect to $CaCO_3$, but the decreased saturation state could result in reduced calcification rates, a shift toward calcite secretors, or a competitive advantage for noncalcifying reef organisms (*4*).

Shifts in carbonate mineralogy over geologic time appear to coincide with inferred atmospheric $CO_2$ concentrations (*5*), and the latitudinal trends of Phanerozoic carbonate accretion rates correlate well with saturation state (*6*). Current reef distribution also correlates with saturation state (*7*), and large-scale biogeochemical studies have found a positive relationship between saturation state and calcification (*8*). Fragile coral skeletons have been reported from high-latitude, low $\Omega$-arag reefs and coral communities (*9*), and reefs in well-mixed, highly supersaturated waters such as the Red Sea tend to have abundant internal carbonate cements (*10*), whereas those in low saturation waters such as the eastern Pacific have none (*11*). Modern aragonitic ooids and "whitings" also form only where $\Omega$-arag is high (for example, Bahama Banks, Persian Gulf).

Experimental studies of calcification versus saturation state in marine organisms or communities are rare. In a recent review (*12*), six such studies on corals and marine algae (the major reef-building taxa) were identified, and, despite methodological differences, all showed a significant positive correlation between saturation state and calcification. Recent experiments in the Biosphere 2 coral reef mesocosm show a strong dependence of community calcification on saturation state (*13*).

We used two methods to predict changes in surface saturation state. The first assumed constant alkalinity through the middle of the next century and that ocean surface response to increased $P_{CO_2}$atm is strictly thermodynamic ($P_{CO_2}$surf is near equilibrium with $P_{CO_2}$atm) (*14*). This is valid in the tropics except for upwelling regions (*3*). The second method employed the HAMOCC (Hamburg Ocean Carbon Cycle) global model (*15*), which simulates response of the entire carbon system to increased $P_{CO_2}$atm and can thus be used to project further into the future. In this model biogeochemical tracers are advected with a frozen present-day climatological flow field, neglecting the possibility of future changes in ocean circulation (*16*).

Both methods indicate a significant drop in $\Omega$-arag as $P_{CO_2}$atm increases (Fig. 1, A and B). The HAMOCC model $\Omega$-arag values are consistently lower than the thermodynamic calculations because of slightly different global change scenarios and differences between modeled and measured alkalinity. Otherwise the two methods produce similar trends (Fig. 1C). Average $\Omega$-arag in the tropics 100 years ago


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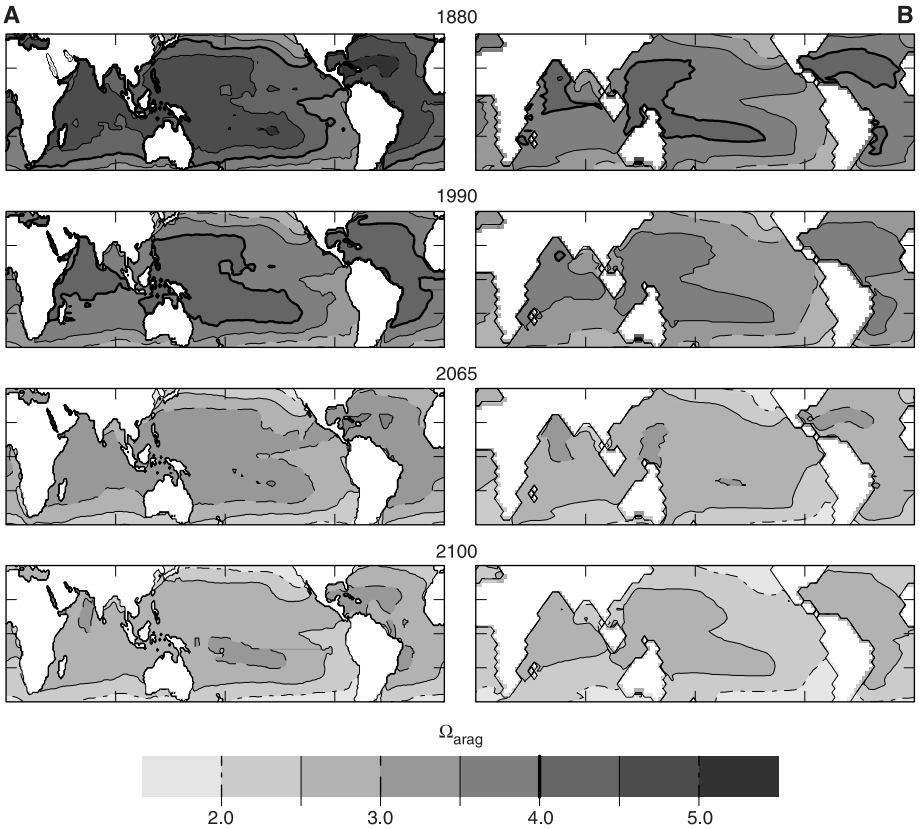
was 4.6 ± 0.2 (1 SD) and is currently 4.0 ± 0.2. It is projected to drop to 3.1 ± 0.2 by the year 2065 and to 2.8 ± 0.2 by 2100 (Fig. 1C). High-saturation areas will experience the greatest decrease in saturation state (for example, Ω-arag in the Red Sea will decrease from 6.0 to 4.0 by 2100). Based on the thermodynamic calculation and the period of modern coral reef growth (since 8000 to 10,000 years ago in many cases), coral reef development is associated with an Ω-arag value of at least 4.0.

Projected changes in Ω-arag were used to predict how reef calcification might change over the next century. Changes in calcification rate ($\Delta G$) were calculated by using the average calcification response of tropical species (*12, 13*) to aragonite saturation state and the thermodynamic calculations of Ω-arag. $\Delta G$ is expressed as percent of average "preindustrial" (1880) calcification rate (Fig. 2). These calculations indicate that aragonite and high-magnesian calcite precipitation in the tropics has already decreased an average of 6% to 11% and will be another 8% to 17% lower under doubled $CO_2$ conditions. Total preindustrial to 2100 calcification decrease could be as high as 17% to 35%.

The expected primary effects of reduced calcification are weaker skeletons, reduced extension rates, and increased susceptibility to erosion. These primary effects will lead to a host of secondary changes in community structure, reproduction, and overall community function. If saturation state is a limiting variable with importance comparable to temperature (*7*), expansion of tropical sea-surface temperatures into higher latitudes (such as predicted in global warming scenarios) would not imply expanded coral reef development.

Reef building requires that organisms deposit $CaCO_3$ in excess of physical, biological, and chemical erosion. A 10% to 20% decrease in $CaCO_3$ production will pose a significant deficit for many coral reefs. The reefs projected to experience the greatest $\Delta G$ are those currently in high saturation conditions, such as the Red Sea, west central Pacific, and Caribbean. However, reefs with balanced $CaCO_3$ budgets ($CaCO_3$ destruction = production) are likely to be the most affected. These might include high latitude reefs (for example, Bermuda), reefs in upwelling regions (for example, Galápagos), and many reefs experiencing anthropogenic stresses.

Many uncertainties surround the issue of coral reefs and global change. Calcification versus saturation state data are scarce, and the average response presented here is only a first approximation of how coral reefs in general will respond. More studies at the ecosystem level are needed. The shape of the calcification versus saturation curve may be crucial in predicting how reefs will fare over the next 50 to 100 years. The curve used in calculating global calcification is based on a straight-line relationship, but a response curve like that of *Stylophora pistillata* (*17*) indicates that calcification may remain constant over a range of values and then drop precipitously below some threshold value. The response to lowered saturation could be species-specific, so that calcification rates of some species will be affected before those of others—with potentially serious consequences



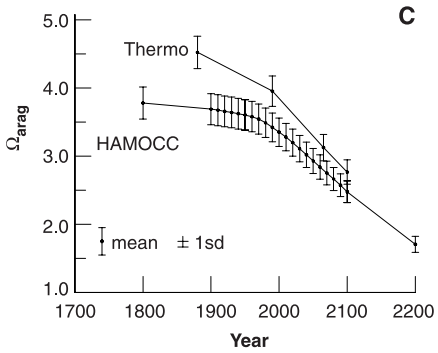




**Fig. 1.** (**A**) Thermodynamic calculations of surface ocean Ω-arag between 1880 and 2100 (*14*). (**B**) HAMOCC model results of surface ocean Ω-arag between 1800 and 2100 (*16*). (**C**) Changes in average tropical Ω-arag between 1800 and 2200 based on thermodynamic calculations and the HAMOCC model.

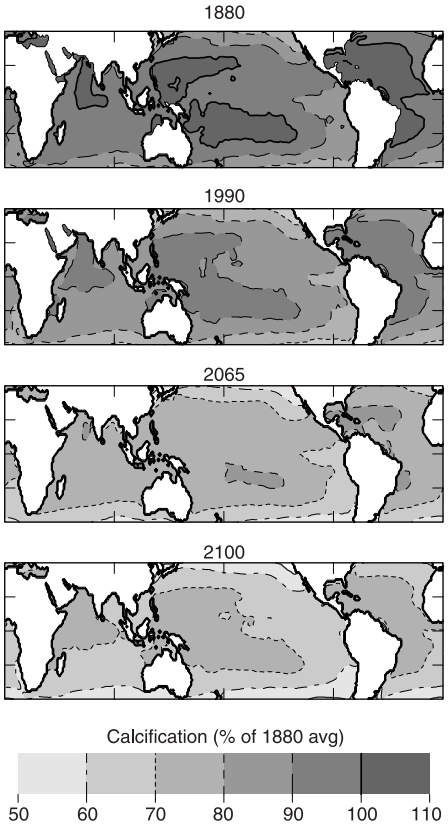



**Fig. 2.** Projected changes in reef calcification rate based on average calcification response of two species of tropical marine algae and one coral (*12*) and a marine mesocosm (*13*).

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at community and ecosystem levels. Calcification versus saturation experiments cited here were conducted over days to weeks. Whether individual reef-building species display an acute versus chronic response to saturation state or whether they can adapt to more gradual changes in carbonate chemistry is unknown. Possible mitigative physiological effects, such as $CO_2$ fertilization of calcareous algae or the symbiotic algae within coral tissues, are addressed elsewhere (*12*). The geological record offers no evidence of either adaptation or mitigative affects; nonetheless, these considerations are important when the effects of global change on photosynthetic and calcifying organisms are being weighed.

Given the decrease in average tropical Ω-arag from 4.6 to 4.0 over the past century, net calcification has probably already decreased on some reefs. We may be able to detect such changes in coral records through either coral calcification or stable isotope records. For example, $\delta^{13}C$ and $\delta^{18}O$ in several foraminiferans correlate strongly with carbonate saturation state (*18*). Although reduced calcification decreases the ocean-atmospheric $CO_2$ flux, this effect will be small because $CO_2$ evasion from reef calcification is only about 1% that of present-day fossil fuel emissions (*19*).

The possibly dire consequences of reduced reef calcification warrant a much closer look at the biogeochemistry of shallow water carbonate secretors. Better quantification of the calcification-saturation relationship, through laboratory and field studies, and examination of geologic records are needed, as is a mechanistic understanding of calcification physiology in corals and algae (*12*). This analysis has focused on coral reef calcification, but other calcifying marine ecosystems (both neritic and open ocean) may share similar risks.

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14. Atmospheric $PCO_2$ and temperature were adjusted according to projections of IPCC, IS95a (*1*). Surface $PCO_2$ was adjusted by using sea-air $PCO_2$ differences of Takahashi *et al.* (*3*). Total alkalinity (TA) was determined as follows: TA = NTA × (salinity/35), where NTA (normalized total alkalinity) = 2306 μEq $kg^{-1}$ [W. S. Broecker and T. H. Peng, *Global Biogeochem. Cycles* **3**, 215 (1989)]. SST and salinity were from Levitus [S. Levitus, *NOAA Professional Papers*, vol. 13 (Government Printing Office, Washington, DC, 1994)], and $PO_4$ and $SiO_2$ concentrations were from Levitus *et al.* [S. Levitus, M. E. Conkright, J. L. Reid, R. G. Najjar, A. Mantyla, *Prog. Oceanogr.* **31**, 245 (1993)]. $[CO_3^{2-}]$ was calculated by using standard constants for $CO_2$ solubility in water ($K_0$) [R. F. Weiss, *Mar. Chem.* **2**, 203 (1974)] and stoichiometric constants for ionization of carbonic acid in seawater ($K_1$ and $K_2$) [F. J. Millero, *Geochim. Cosmochim. Acta* **59**, 661 (1995)]. Phosphate and silicate were maintained at present-day levels. Ω-arag was calculated by using $K'_{sp}$ adjusted for temperature and salinity [A. Mucci, *Am. J. Sci.* **283**, 780 (1983)]. All calculations were done on a 1° grid.
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20. We thank other members of the workshop Coral Reefs and Global Change: Adaptation, Acclimation, or Extinction (R. Bak, J. Benzie, B. Carlson, T. Done, R. Gates, B. Hatcher, R. Karlson, R. Kinzie III, R. Rowan, J. Pandolfi, A. Pittock, D. Potts, and S. Smith), sponsored by the Society for Integrative and Comparative Biology, Land Ocean Interactions in the Coastal Zone, Scientific Committee on Oceanic Research, and the National Oceanic and Atmospheric Administration.

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# Lateral Variations in Compressional/Shear Velocities at the Base of the Mantle


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**Observations of core-diffracted *P* ($P_{diff}$) and *SH* ($SH_{diff}$) waves recorded by the Missouri-to-Massachusetts (MOMA) seismic array show that the ratio of compressional (*P*) seismic velocities to horizontal shear (*SH*) velocities at the base of the mantle changes abruptly from beneath the mid-Pacific ($V_P/V_S = 1.88$, also the value predicted by reference Earth models) to beneath Alaska ($V_P/V_S = 1.83$). This change signifies a sudden lateral variation in material properties that may have a mineralogical or textural origin. A textural change could be a result of shear stresses induced during the arrival at the core of ancient lithosphere from the northern Pacific paleotrench.**


The core-mantle boundary (CMB) is an important component of the global system of mantle convection (*1*), but direct observations of mantle flow at this depth have been frustratingly difficult to obtain (*2*). The CMB region includes a thick thermal boundary layer (labeled *D″*), large lateral variations at great and small scales (*3, 4*) that likely involve chemical boundary layers, an apparent discontinuous increase in seismic velocity 250 ± 100 km above the core (*5*), an ultralow-velocity zone probably attributable to partial melting (*6*), boundary topography, and seismic anisotropy (*7*). Most studies of the CMB have used observations of

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