

tional base pair on the DNA oligomer caused the RD complex to “disappear,” presumably because the repressor could slide back and forth along the extended DNA and thus prevent the determination of a defined static (on the NMR time scale) RD complex structure.

The *lac* repressor and its complexes with DNA have long served as a central paradigm in the quest for an overarching molecular basis for protein-DNA recognition and for the mechanisms of transcription regulation. The study by Kalodimos *et al.* (2) provides a thoroughly satisfying structural conclusion to this saga.

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OCEAN SCIENCE

The Fate of Industrial Carbon Dioxide

Taro Takahashi

The atmospheric CO₂ concentration has increased from about 280 parts per million (ppm) in 1800—the beginning of the industrial age—to 380 ppm today (1). During this time, the observed annual rate of increase has been about 50% of that expected from the estimated industrial CO₂ emission rate into the atmosphere. This means that an amount of CO₂ equivalent to about one-half of the industrial CO₂ emitted each year has been missing, and thus Earth’s atmosphere is receiving only one-half the full impact of the anthropogenic CO₂ emissions. What process has been taking up the “missing carbon”? An answer to this question is fundamental not only for our understanding of the natural carbon cycle, but also for formulating a sound global CO₂ emission strategy. As reported on page 367 of this issue, Sabine *et al.* (2) used an extensive data set obtained for CO₂ concentration and other chemical properties during recent global oceanographic programs, together with a computational method developed by Gruber *et al.* (3), and provided a solid estimate for the total amount of CO₂ taken up by the global oceans from 1800 to 1994. Their results

show that the oceans store a major proportion of the anthropogenic CO₂ and provide a better understanding of the carbon cycle. In an accompanying report on page 362, Feely *et al.* (4) show how the acidification of ocean waters that resulted from the dissolution of anthropogenic CO₂ has changed an important carbon pathway in the oceans—the production, dissolution, and accumulation of biogenic CaCO₃.

Ocean waters are stratified according to their density. In subsurface regimes, waters flow from polar regions toward lower latitudes along constant-density horizons, with little mixing between different densities. A parcel of water that is found at depths today was located at some past time near the sea surface, where it acquired CO₂ and oxygen from the overlying atmosphere (see the figure). During its course of subsurface travel, CO₂ was added from the oxidation of biogenic debris and dissolved organic compounds as well as from the dissolution of skeletal CaCO₃ falling through the water column. To compute the amount of CO₂ addition attributable to the atmospheric CO₂ increase, the background and biogenic additions must be subtracted from the measured value. Sabine *et al.* used several assumptions for estimating the biogenic contributions. The P:N:C:O₂ stoichiometry for decomposing organic matter is assumed to be constant. The amount of oxygen used for the oxidation is estimated to be the difference between the observed

concentration and the original oxygen concentration, which in turn is obtained by assuming saturation with the atmosphere at the temperature of water. The amount of CaCO₃ dissolution is estimated from the difference between the observed alkalinity value and the original at-surface (or preformed) value that is estimated as a function of salinity, phosphate, and oxygen concentration (3). The background CO₂ concentration in seawater is estimated assuming that the water contained the preformed alkalinity and was in equilibrium with the preindustrial air for waters at depths below about 2000 m, or with atmospheric CO₂ at the time of the last contact with air for depths above about 2000 m. The age of the water sample is estimated from chlorofluorocarbon or tritium data. The overall uncertainty of the global inventory of anthropogenic CO₂ has been estimated to be about ±20% (3).

In table 1 of the Sabine *et al.* report (2), the 1800–1994 inventory for anthropogenic CO₂ thus estimated for the global ocean and other carbon pools is summarized. Two well-known quantities in the global carbon cycle are the emissions from fossil fuel combustion plus cement production of 244 ± 20 Pg C (petagrams of carbon; 1 Pg = 10¹⁵ g) and the amount of excess carbon in the atmosphere of 165 ± 4 Pg C as of 1994. The 1800–1994 ocean inventory of 118 ± 19 Pg C reported by Sabine *et al.* yields the following important information. First, the land biosphere carbon pool has decreased by 39 ± 28 Pg C (244 – 165 – 118 = –39) since 1800. This means that the ocean is the major repository of anthropogenic CO₂ and stores nearly 48% of hitherto emitted CO₂ into the atmosphere. Second, if the change in carbon emission from land use of 100 to 180 Pg C (5) is accepted, the terrestrial biosphere should have accordingly in-

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creased by 61 to 141 Pg C. This suggests that the land biosphere growth has been nearly balanced by the loss caused by land use changes. The inventory ratio for ocean/land biosphere growth ranges from 0.8 to 1.9. The inventory ratios may be compared with the results of one of the most direct methods for obtaining net CO_2 uptake rates for the oceans and land biosphere: time-series measurements of the atmospheric concentrations of CO_2 and O_2 . These methods yield a range of 1.5 to 3.4 (6, 7) for the ocean/land biosphere annual flux ratios in the 1990s. The differences are attributed to the respective estimates for oxygen flux out of the oceans. Thus, the recent carbon flux estimates are broadly consistent with the post-1800 inventory of carbon in these reservoirs. This paper provides an important constraint for identifying the missing carbon sink.

Another important pathway of carbon in the oceans is the growth and settling of biogenic CaCO_3 , which is produced in surface waters by plankton as well as corals. During their posthumous descent through water columns, the shells dissolve in seawater because of the greater pressures in deep waters and the increasing acidity resulting from respired CO_2 . Feely *et al.* (4) estimated that 45 to 65% of skeletal CaCO_3 produced in surface waters was dissolved in ocean waters and recycled. They also showed that the invasion of industrial CO_2 has caused the zone of CaCO_3 undersaturation in subsurface waters to expand by 50 to

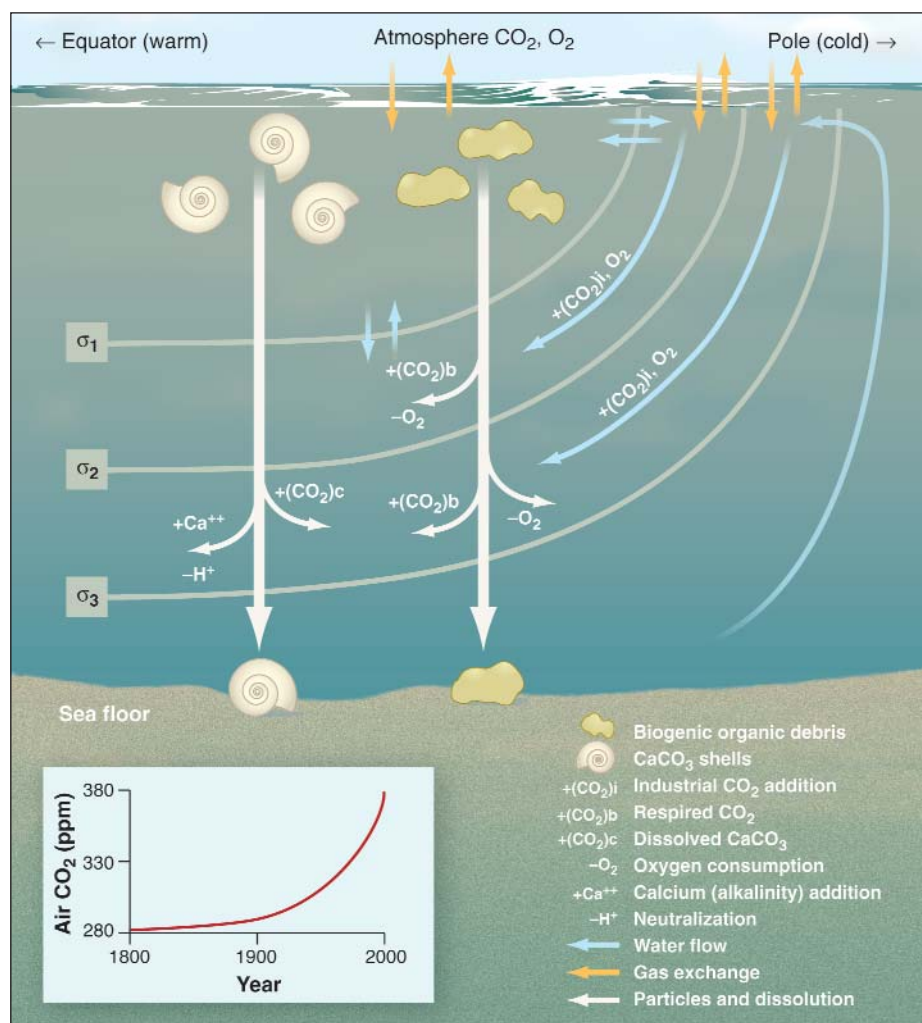
200 m in depth, and suggested that the dissolution rate would increase in the future.

The effects of increasing CO_2 on oceanic CaCO_3 are multifaceted. First, the precipitation of CaCO_3 causes seawater to become more acidic and increase its partial pressure of CO_2 ($p\text{CO}_2$), because this is the reverse of the dissolution of limestone (CaCO_3) used for the neutralization of acid. Although the ocean surface waters are supersaturated with respect to CaCO_3 minerals, the growth rates of organisms are reduced with the decreasing degree of supersaturation by CO_2 -induced acidification (8, 9). Hence, a reduction of CaCO_3 production in the oceans would slow down the rate of increase in surface water $p\text{CO}_2$. Had the present oceanic production of skeletal CaCO_3 (0.8 to 1.4 Pg carbon from CaCO_3 per year) been totally shut down, the surface ocean $p\text{CO}_2$ would be reduced by 10 to 20 μatm , and hence the oceanic CO_2 uptake from the atmosphere would more than double the present flux of about 2 Pg C per year. Second, CaCO_3 shells that are settling through water columns are being dissolved over a wider range of water depths, thus partially neutralizing the industrial CO_2 . When these subsurface waters return to the surface and interact with the atmosphere, they would take up more CO_2 . These processes would provide a negative climate feedback mechanism that counteracts the increasing atmospheric CO_2 . However, Feely *et al.* caution that ecological responses for a reduced production of CaCO_3 -secreting organisms as well as acidification of the oceans are unknown.

Further improvements in the accuracy of the global carbon pool inventory could help to constrain the future course of atmospheric CO_2 level. Characterization of climate feedback processes and assessment of impacts of the CO_2 -induced acidification of seawater on the complex marine ecosystems are important tasks for the future.

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Pathways for carbon dioxide in the oceans. At the sea surface, ocean waters have absorbed carbon dioxide from the air, which has exhibited an increasing concentration of CO_2 from 280 ppm in 1800 to 380 ppm in 2004 (shown schematically in the inset graph). The arrows in the diagram indicate directions of ocean water flow (blue) and of sinking biogenic organic debris and CaCO_3 shells (white) as well as gas exchange with the atmosphere (orange). The seawater density (without the pressure effect) is indicated by $\sigma_1 < \sigma_2 < \sigma_3$ to show stratification according to density. The amount of CO_2 added to subsurface waters by the oxidation of falling organic debris and the dissolution of CaCO_3 shells is estimated from the oxygen and alkalinity data, respectively, and subtracted from the measured concentration to remove the natural biological additions. The dissolution of CaCO_3 partially neutralizes the carbonic acid added to waters by respired CO_2 and industrial emissions.