Review Articles

The Ocean as Part of the Global Carbon Cycle

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Abstract

The ocean plays a central role in the global carbon cycle being by far the largest active reservoir. Atmospheric CO_2 level depends on the CO_2 concentration in the ocean surface layer, which is relatively low compared to mean oceanic values due to biological and physical carbon pumps. Although the ocean may take up much of the carbon released by the increased burning of fossil fuels, this capacity is limited because of the chemical buffering and a mismatch in time scales (oceanic mixing is much slower than anthropogenic perturbations).

1 Introduction

The burning of fossil fuels (oil, coal, gas) results in an input of carbon dioxide to the atmosphere of 5.4 GtC[1] per year [19] (mean over period 1980 – 89). In addition, approximately 1.9 GtC are supplied by tropical deforestation [11]. The atmospheric CO_2 concentration has increased from 280 ppmv[2] during pre-industrial times to a current value of 355 ppmv. The concentration raises further at a rate of about 1.7 ppmv or 3.4 GtC per year. Concentrations as high as present-day values have not occured in the past millions of years [5].

Following water vapor carbon dioxide is the most important greenhouse gas. From Antarctic [2, 12, 20] and Greenland ice cores we now know that atmospheric temperature and CO_2 concentrations are strongly correlated: during the last glacial period the CO_2 concentration was as low as 200 ppmv. In the near future climatic changes are expected due to anthropogenic perturbations of the chemical composition of the atmosphere. One of the major conclusion of the 1992 report of the Intergovernmental Panel on Climatic Change (IPCC) is that "the evidence from the modelling studies, from observations and the sensitivity of global mean surface temperature to doubling CO_2 is unlikely to lie outside the range 1.5 to 4.5 °C" [11, p.5].

I will discuss only the present-day carbon cycle which encompasses the atmosphere, biosphere and the ocean. In contrast the 'geochemical' carbon cycle describes the transfer of carbon between rocks and the ocean-atmosphere system on a multimillion-year time scale, including processes such as weathering and plate tectonics (see the papers of BERNER (1990, 1993) and references therein). The distribution of carbon in the ocean can be explained only if physical and chemical, as well as biological processes are taken into ac-

count. The biological and physical carbon pumps will be discussed in some detail. Finally the response of the ocean to anthropogenic perturbations is addressed. The quantitative aspects of the carbonate system may be found in an appendix.

2 The Global Carbon Cycle

Before focusing on the ocean the main components of the global carbon cycle should be considered. **Fig. 1** shows the various carbon reservoirs and the fluxes between them. Currently the atmosphere contains 750 GtC in the form of carbon dioxide. Similar amounts are stored in land biota (550 GtC) as well as in organic soils (1,500 GtC). The ocean is by far the largest active reservoir, containing 50 times more carbon (40,000 GtC) than the atmosphere[3].

There is a vigorous exchange between the various reservoirs: Plants take up CO_2 from the atmosphere and photosynthetically fix carbon in the form of organic compounds (the land biota take up 100 GtC per year). Approximately half of this returns to the atmosphere through respiration. The other half goes into the organic soils, which slowly decay releasing 50 GtC per year to the atmosphere. The yearly exchange among these reservoirs amounts to 5 – 10 % of their contents.

The ocean is subdivided in a well mixed upper layer, which is permanently in contact with the atmosphere, and into the middle and abyssal ocean, whose water masses are replenished by surface waters on time scales of hundreds to thousand years. From the contents of the reservoirs and the fluxes one can calculate time scales (τ = content / flux) which may be interpreted as mean residence times of carbon atoms between exchange with other reservoirs. Most of these time constants are of the order of a few years ($\rightarrow$ *Fig. 1*)

$$\tau\text{atmosphere} = \frac{750 \text{ GtC}}{(100 + 92) \text{ GtC/yr}} \approx 4 \text{ yr}$$

$$\tau\text{surface ocean} = \frac{1020 \text{ GtC}}{(100 + 92) \text{ GtC/yr}} \approx 5 \text{ yr}$$

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[1] GtC = gigatons carbon = billion tons of carbon = 10^9 tons of carbon

[2] ppmv = parts per million per volume; 1 ppmv CO_2 in the atmosphere corresponds approximately to 2 GtC (exact values: 1 ppmv = 2.12 GtC)

[3] these numbers (except for the atmosphere) should be taken with larger error margins (see, for example, LONGHURST (1991))

3   The Carbon Distribution in the Ocean
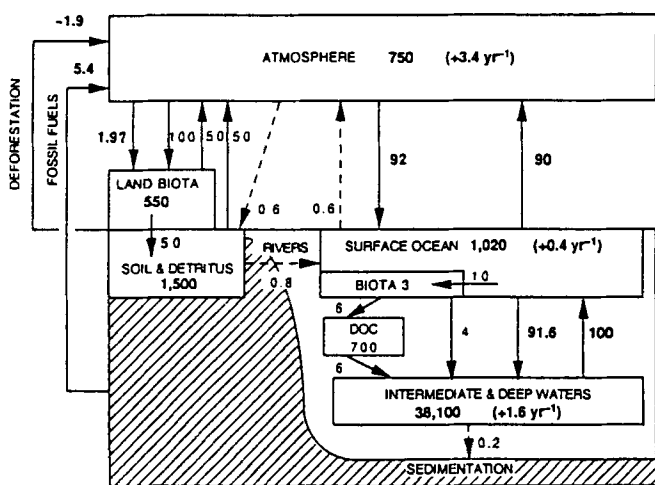
CARBON CYCLE 1980-89

Fig. 1: The global carbon-cycle: estimates of the major reservoirs (in GtC = 10^9 t carbon) and fluxes (in GtC/a = 10^9 t carbon per year) for the period 1980 – 89 (from SIEGENTHALER and SAR-MIENTO 1993)

and even soils and detritus have an appreciable fast component

$$\tau_{soil} = \frac{1500\ GtC}{50\ GtC/yr} = 30\ yr$$

We now know from analysis of air bubbles trapped in Antarctic ice shields that the CO_2 concentration in the atmosphere has been nearly constant with a mean value of 280 ppmv and fluctuations of only $\pm$ 10 ppmv during the time period (at least) starting at 900 AD until 1800. This time period is very long compared to the exchange time scales. Therefore one should expect to find some efficient (negative) feedback mechanisms which keep the components in balance.

At first sight the flux due to the burning of fossil fuels appears small compared to the fluxes among the reservoirs. However there is a fundamental difference: this carbon is added to the system and perturbes a well established steady state. Fortunately not all of the added carbon dioxide remains in the atmosphere: an increase of 1.7 ppmv/yr or 3.4 GtC/yr implies that more than half of it is transfered to other reservoirs like, for example, the ocean.

Table 1: Anthropogenic carbon fluxes in GtC/yr: mean values for 1980 – 89 [38, p. 13]. For 1988 MARLAND and BODEN (1993) gave a value of 5.9 for burning of fossil fuels

Emissions from fossil fuels into the atmosphere	5.4 $\pm$ 0.5
Emissions from deforestation and land use	1.6 $\pm$ 1.0
Accumulation in the atmosphere	3.4 $\pm$ 0.2
Uptake by the ocean	2.0 $\pm$ 0.8
Net imbalance ('missing sink')	1.6 $\pm$ 1.4

The carbon content of the atmosphere and its change from year to year could be estimated from measurements at one remote station, for example, Mauna Loa (Hawaii). This is possible because of the fast mixing of the atmosphere with time scales for interhemispheric exchange of less than a year. Of course there are seasonal fluctuations with amplitudes of up to 10 ppmv especially in the northern hemisphere due to the breathing of the extratropical land vegetation and also an interhemispheric gradient of a few ppmv [13] due to the fact that by far most of the fossil fuels are burned in the northern hemisphere (50 % in the USA, USSR and China [19]). In the ocean, the situation is much more complicated. Here carbon exists in various forms. Dissolved organic carbon (DOC) is a name for a complex cocktail of compounds whose composition is still largely unknown [3]. Even the estimates of the carbon content of the DOC pool have been revised by a few hundred GtC in the last few years [32, 33].

In contrast to the other main gases of the atmosphere (nitrogen, oxygen) CO_2 is not simply 'dissolved' in the ocean: it really undergoes chemical reactions and forms bicarbonate HCO_3^- and carbonate CO_3^{2-}. Together these three forms (bicarbonate, carbonate and the gas in solution CO_2 (aq)) are called dissolved inorganic carbon (DIC) or total CO_2 (TCO2). The relative amounts of the three forms depend on pH and, to a much lesser extend, on temperature and salinity. A more quantitative discussion of the carbonate system is given in the appendix. Here I will mention only two aspects.

1. When considering the gas content of atmosphere and ocean together, more than 95 % of oxygen or nitrogen resides in the atmosphere and only a minor fraction is dissolved in the ocean whereas the reverse situation applies to CO_2.

2. The carbonate system in the ocean is a strong buffer: when the concentration of one of the three forms is decreased by some process (uptake of CO_2 by algae, for example), part of the deficit is replenished by conversion of the other components. This effect may be quantified by the buffer or Revelle[4] factor which is defined as the relative change in CO_2 (aq) compared to the relative change in DIC (compare the appendix).

The distributions of both the three different inorganic carbon forms as well as their sum are strongly heterogeneous. Vertical DIC profiles ($\rightarrow$ *Fig. 2*) show a minimum at the surface, a maximum at intermediate depths of 1000 to 2000 m, and a weak decline towards the bottom. This is due to the long mixing time scales combined with other physical, chemical and biological processes (see chapters on biological and physical pumps).

Today and in the near future we cannot hope to get enough measurements to estimate the content and yearly changes of the DIC with an accuracy in the GtC range (John WOODS proposed to rerun a program like the World Ocean Circulation Experiment (WOCE) every year with automatic measur-

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[4] after Roger REVELLE (1909 – 1991)

ing devices which might improve the situation). A much better strategy would be to determine the flux through the surface and the influx by rivers. But even that seems to be a very difficult task because of the small scales in space and time of variations of CO_2 concentrations [29].

Recently Ralph KEELING developed a new interferometric technique for measuring the concentration of oxygen in the atmosphere with an extremely high precision [14]. These measurements potentially allow to infer the integrated uptake of CO_2 by the ocean [15].

3 shows a section in the equatorial Pacific. Near the surface one observes potential pCO_2 values similar or a little bit higher than atmospheric partial pressures of carbon dioxide. But in the upper 1000 m there is an extremely strong gradient (compare with the much weaker gradient of DIC in *Fig. 2)* which leads to values of up to 2000 ppmv $pCO_2^{potential}$ at a depth of only 400 m.

This CO_2-enriched water contains a lot of nitrate and phosphate which serve as nutrients for the phytoplankton in the euphotic zone, when upwelling occurs.
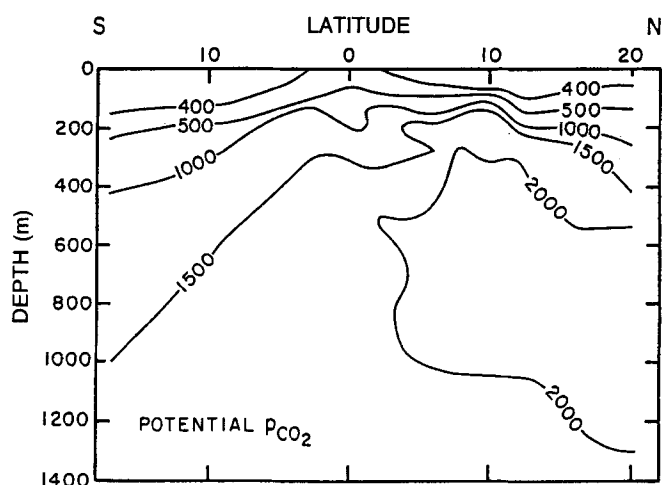

Fig. 2: Depth distribution of DIC-concentration in the North and South Atlantic (NA, SA), North and South Pacific (NP, SP), North and South Indian Oceans (NI, SI) and in the Antarctic Ocean (AA). (From TAKAHASHI 1989)

Fig. 3: Potential CO_2 pressure in the equatorial pacific. Potential CO_2 pressure is the CO_2 pressure a sample would achieve if it were isochemically depressurized (to 1 atm at the ocean surface) and warmed (to 25 °C at the equator). (From BROECKER and PENG 1982)

4   Does Marine Biology Play an Important Role in the Carbon Cycle?

At first sight one could get the impression that the effect of marine biota in the global carbon cycle is negligible because of its standing stock of only about 3 GtC. In addition we know from general ocean circulation models (OCGMs) [17, 25] that the ocean takes up 2 GtC/yr CO_2 simply by dissolution due to higher atmospheric concentrations. Sometimes this has been interpreted as an indication that marine biology is not important at all in regulating the atmospheric carbon dioxide concentration.

4.1   The Strangelove Ocean

The contrary is true as outlined by BROECKER and PENG in 'Tracer in the Sea' (1982). They developed the 'Strangelove ocean' scenario (named after the movie "Dr. Strangelove, or, How I Learned to Stop Worrying and Love the Bomb" (1964) by Stanley KUBRICK): what happens when the marine biology is abruptly turned off either by radioactive pollution due to KUBRICK's doomsday machine or, more pleasantly, only in a thought experiment? The atmospheric concentration of CO_2 would increase by a factor of about three (!!!) on a time scale of a few decades. This can be illustrated by the distribution of potential pCO_2, i.e. the partial CO_2 pressure a water sample would achieve if it were isochemically depressurized (to surface pressure of 1 atm) and warmed to surface temperature (25 °C at the equatorial Pacific). Fig.

4.2   The Biological Carbon Pump

Starting point and bottle neck of the food web is the phytoplankton which takes up CO_2 and photosynthetically fixes it in the form of organic compounds. Part of the fixed carbon sinks in form of algal-aggregates ("marine snow", see *Fig. 4)* or, at higher trophic levels, as fecal pellets of zooplankton and is partly remineralized on its way down [22]. Only a small portion is buried in the sediments. This transport of carbon from the surface (DIC minimum) to depths (regions with higher DIC concentrations) has been named 'biological carbon pump' by VOLK and HOFFERT (1985) (transport against a carbon concentration gradient). The details of the biological carbon pump are not yet well understood [4]. From sediment trap studies it is known that the vertical particle flux shows strong variations during the year. This is correlated with biological processes in the euphotic zone, namely algal blooms [1, 10].

Vertical DIC profiles are mainly a result of the biological pump: the DIC concentrations show a minimum in the euphotic zone where carbon is fixed and a maximum in deeper levels where most of the remineralization takes place. Superimposed on this simple model, a general increase in DIC at depth is observed from the North Atlantic to the South Atlantic through the Antarctic Ocean towards the Pacific as the water circulation follows the oceanic 'conveyer belt' (see below).
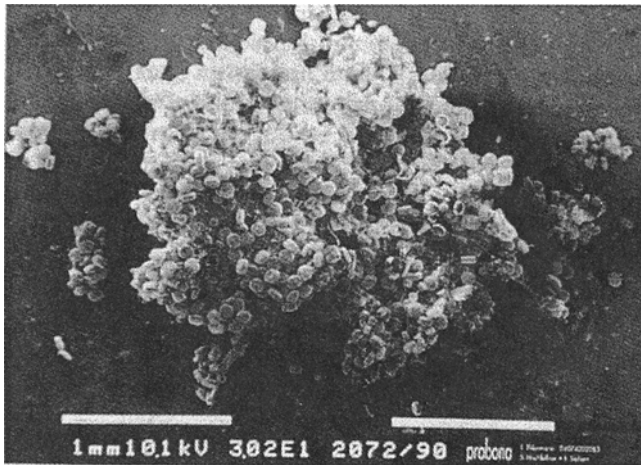
Fig. 4: An aggregate of diatoms *(Thalassiosira eccentrica)* (the scanning electron microscope photography was kindly provided by Ulf RIEBESELL)

The importance of the biological carbon pump is very well demonstrated by two runs of an ocean carbon cycle model with and without biota: the model without biota shows a vertical gradient much too weak (→ *Fig. 5 a*) compared to the GEOSECS measurements of DIC (→ *Fig. 5 c*) The concentrations fit much better (→ *Fig. 5 b*) when the effects of biota are taken into account.
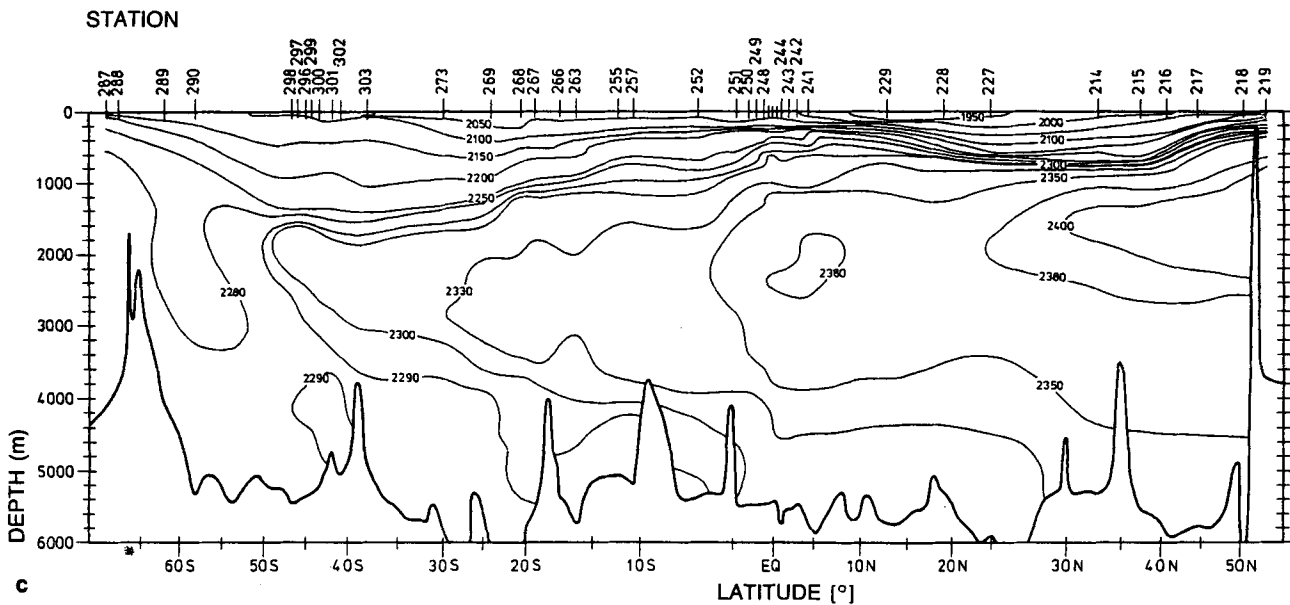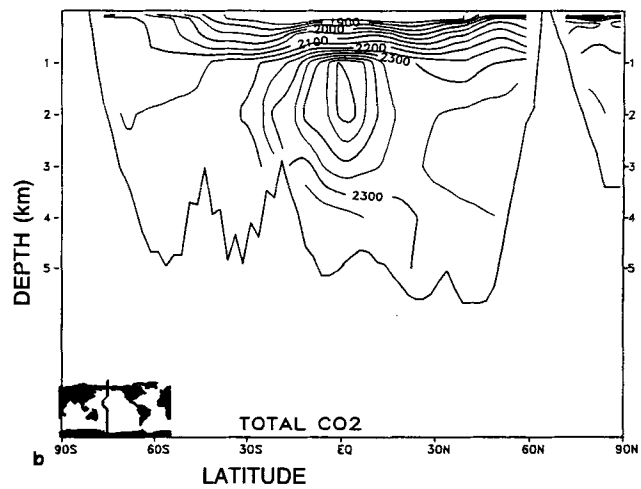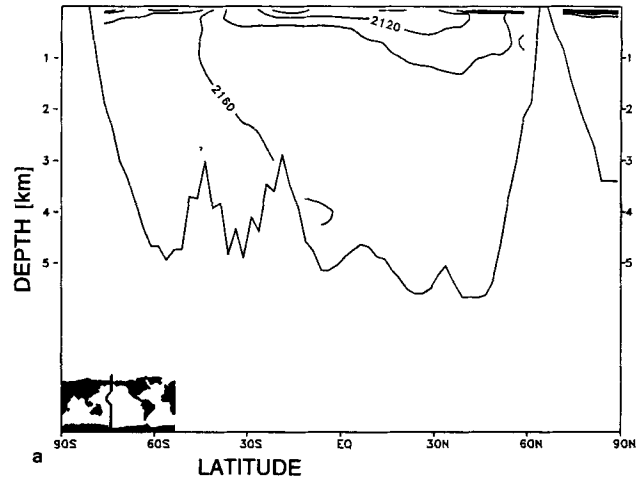

Fig. 5: DIC along a section in the Pacific: results of an ocean carbon general circulation model a) without biota and b) with biota; c) GEOSECS measurements. (From MAIER-REIMER and HASSELMANN 1987)

4.3   The CaCO₃-Pump

The effects of chalk formation are counterintuitive. The statement "removal of carbon in the form of $CaCO_3$ leads to a decrease of CO_2" is wrong, and is the source of much confusion.

Carbon is fixed in the form of calcite or aragonite by calcifying organisms like, for example, coccolithophorids or foraminifera. Carbon is removed from the surface layer when this chalk ($CaCO_3$) sinks down towards the bottom of the oceans. But that does not imply a decrease in the CO_2 concentrations. On the contrary, CO_2 goes up! This is easy to grasp with the chemical reaction equation for chalk formation

$$Ca^{2+} + 2\ HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$
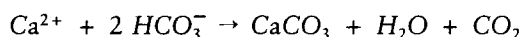
or in words: one calcium ion reacts with two bicarbonate ions and forms chalk, water and carbon dioxide. So for every $CaCO_3$ formed one CO_2 is released. Fortunately also in this case the buffering effect of the carbonate system applies: one may calculate a Revelle factor for this case and will find that most of the newly formed CO_2 is converted to bicarbonate and only 10 % remains as CO_2 (compare *Fig. 8*). Of course biogenic calcification is not possible without formation of soft tissue. The change of CO_2 in the euphotic zone depends on the amount of carbon removed and on the ratio of carbon in chalk (skeletons, tests) and in organic compounds (soft tissue) known as the 'rain ratio'. The buffer factor as a function of the rain ratio is shown in **Fig. 8**. Note that important bloom forming algae are noncalcifying. Diatoms, for example, build their frustules out of silicate. They lower the mean oceanic rain rate.

5   The Physical Pump

In winter Greenland Sea surface water cools down and salt is released when sea-ice forms (only a small part of the dissolved salt remains in the sea-ice). The water becomes dense, breaks through the underlying water masses and forms deep water. Because of the higher solubility of gases at lower temperature these dense waters contain large amounts of CO_2. The water formed by deep convection in the Greenland Sea flows southward, crosses the equator and finds its way through the South Atlantic to the Indian and Pacific Ocean, where upwelling to the surface occurs mainly in equatorial regions. This flow system is closed by currents near the surface (→ *Fig. 6*). This oceanic "conveyer belt" (BROECKER) needs approximately 1000 years for a full cycle. The upwelling water in the equatorial regions of the Pacific releases large amounts of carbon dioxide when it reaches the surface and is heated up. Because the cycling period of the conveyer belt is long compared to the rapid increase of the atmospheric CO_2 level there can be currently no steady state: the newly formed deep water contains more CO_2 than the deep water formed in past times. The amount of DIC along the conveyer belt increases further in load by the biological pump (→ *Fig. 2*).
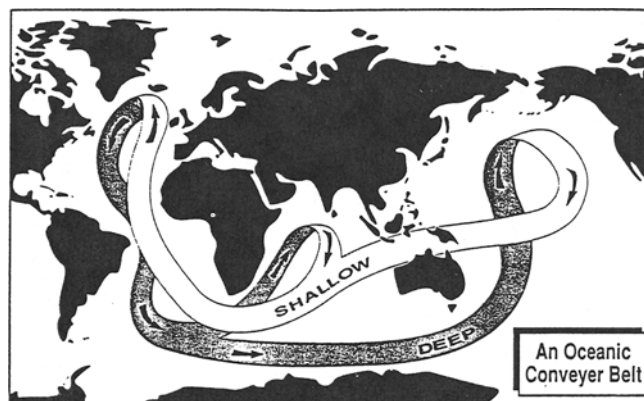

Fig. 6: The oceanic 'conveyer belt': The deep water formed in the Greenland Sea flows through the Atlantic at shallow depths. A full cycle needs approximately 1000 years. (From STEELE 1989)

6   The Response of the Ocean to Anthropogenic Perturbations

We may now try to answer the following question:

1. How does the ocean respond to an increase of atmospheric CO_2 levels?
2. Is it able to take up large amounts of the added CO_2?

6.1   The Additional Dissolution of CO_2

Air and water get into contact at the surface of the ocean. Under equilibrium conditions the atmospheric partial pressure of CO_2 (pCO_2) and the concentration of the dissolved CO_2 ($[CO_2(aq)]$) are related by the temperature dependent solution constant $K_H\ (T)$

$$[CO_2(aq)] = K_H(T) \cdot pCO_2$$

(known as Henry's law [31]). In case of an increase of the atmospheric CO_2 level the system tries to establish a new equilibrium by dissolving carbon dioxide. The typical time scale of this process is one year [29]. The flux through the interface depends on the concentration differences; it is enhanced by strong winds [37] and hindered by sea-ice. However, the uptake of CO_2 by the ocean is limited by two constraints:

1. Only a small part of the ocean, namely the well mixed upper layer with a thickness of 50 – 500 m, is continuously in contact with the atmosphere. By far the largest part will be ventilated much more slowly by the formation of deep water (mainly in the Greenland and the Weddell Sea) and global ocean circulation (conveyer belt with a time scale of 1000 years). The anthropogenic pertubations of the carbon system are too fast to let the ocean keep pace with it.
2. The second constraint is caused by the buffering of the carbonate system and can be parameterized by the Revelle factor. An additional uptake of carbon dioxide reduces the pH value (the water becomes more acidic) and thereby the partitioning of the three forms $CO_2(aq)$, bicarbonate and carbonate changes (→ *Fig. 7*). A doubling of at-

mospheric CO_2, for example, only leads to an increase of the total dissolved inorganic carbon (DIC) of 5 to 10 % (see the appendix "The carbonate system" for details).
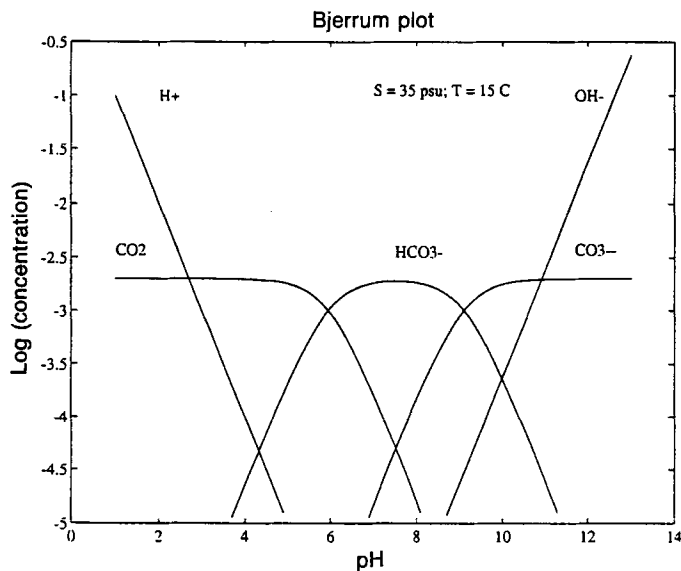

Fig. 7: The ratios of CO_2, bicarbonate, and carbonate as a function of pH value (temperature 10 °C, salinity 35 psu)

Current estimates of net CO_2 uptake rates by the ocean of 1.6 to 2.3 GtC/yr have been calculated with various models (box-diffusion models [26, 27, 28], ocean general circulation model with a perturbation approach [25], or with a carbon model of MAIER-REIMER [29]).

6.2 Changes in the Biological Pump?

From a geochemical point of view, marine biology may be considered as a black (or better: green) box which removes inorganic carbon with the help of nutrients (nitrate, phosphate). The molar ratios of biological relevant elements like C:N:P are constant (Redfield ratios [21], see Fig. 8). During an algal bloom (the most extreme case) the plants can take up not more than 10 % of the DIC; so an increase of CO_2 due to anthropogenic perturbations and thereby a small (1/Revelle factor) increase of DIC should have a negligible effect on the biology. Changes in the biological pump are expected only as a consequence of different ocean circulation patterns due to climatic changes and corresponding variations in the cycling of nutrients.

On the other hand one may argue that because of the large effect of the biological pump small variations may cause appreciable consequences. Although the coupling of nutrient chemistry and biology via Redfield ratios is an old concept the details are not well understood (see the paper by SAMBROTTO et al. (1993) and the comment by TOGGWEILER (1993)).

New laboratory studies indicate a direct effect of increased CO_2 concentrations on the growth rates of some bloom forming diatoms [23]. Although this cannot increase the amount of production (which is limited by nitrate or phosphate) it
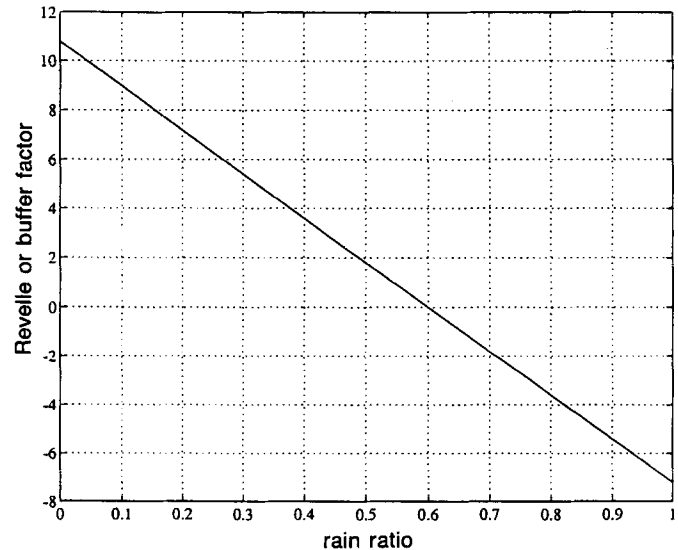

Fig. 8: The Revelle factor as a function of the rain ratio

may lead – in combination with nonlinear processes like decoupling from grazers and physical aggregation of phytoplankton – to increased removal of carbon from the euphotic zone. Maybe marine biology has even more surprises to offer.
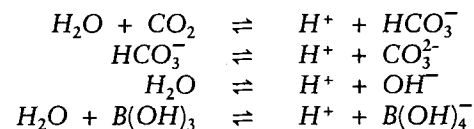
7 Appendix

The Carbonate System (including boron)

Remark: The current chapter follows in many details the appendix of MAIER-REIMER and HASSELMANN (1987) [17].
In the ocean, carbon dioxide exists in three different forms[5]: as free carbon dioxide (CO_2), as bicarbonate[6] (HCO_3^-), and as carbonate (CO_3^{2-}). The sum of the three forms is called dissolved inorganic carbon (DIC):

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]. \qquad (1)$$

In addition to DIC, the carbonate system includes water (H_2O) and its dissoziation products H^+ and OH^-. For quantitative calculations boron compounds ($B(OH)_3$, $B(OH)_4^-$) have to be taken into account. The above mentioned substances are related by the following reactions:

$$
\begin{aligned}
H_2O + CO_2 &\rightleftharpoons H^+ + HCO_3^- \\
HCO_3^- &\rightleftharpoons H^+ + CO_3^{2-} \\
H_2O &\rightleftharpoons H^+ + OH^- \\
H_2O + B(OH)_3 &\rightleftharpoons H^+ + B(OH)_4^-
\end{aligned}
$$

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[5] Refinement: there exists a fourth form namely H_2CO_3; in equilibrium with CO_2 the concentration of H_2CO_3 is much smaller than that of CO_2; the sum of these two electrically neutral forms is sometimes denoted by $H_2CO_3^*$

[6] prefix "bi": the carbonate ion may bind a second single positive ion in addition to H^+

The concentration of water can be considered as constant with negligible error for the calculations, because its concentration is orders of magnitude larger than that of the other components. Under equilibrium conditions the law of mass action reads[7]:

$$[H^+] \, [HCO_3^-] = K_1 \, [CO_2] \qquad (2)$$

$$[H^+] \, [CO_3^{2-}] = K_2 \, [HCO_3^-] \qquad (3)$$

$$[H^+] \, [OH^-] = K_w \qquad (4)$$

$$[H^+] \, [B(OH)_4^-] = K_B \, [B(OH)_3] \qquad (5)$$

The acidity constants K_1, K_2 and K_B depend on temperature, pressure, and salinity. Using eqs. (1) − (4) one can express the concentrations of CO_2, HCO_3^- und CO_3^{2-} as functions of DIC and $h = [H^+]$:

$$[CO_2] = DIC \cdot \alpha_0 = DIC/(1 + \frac{K_1}{h} + \frac{K_1 K_2}{h^2}) \qquad (6)$$

$$[HCO_3^-] = DIC \cdot \alpha_1 = DIC/(1 + \frac{h}{K_1} + \frac{K_2}{h}) \qquad (7)$$

$$[CO_3^{2-}] = DIC \cdot \alpha_2 = DIC/(1 + \frac{h}{K_2} + \frac{h^2}{K_1 K_2}) \qquad (8)$$

At a pH value of 8.2, typical for sea water, one gets ($S = 35$ psu, $T = 15$ °C): $[CO_2] : [HCO_3^-] : [CO_3^{2-}] \approx 0.5\,\% : 88.4\,\% : 11.1\,\%$. The strong dependence of these ratios on the pH values is shown in **Fig. 7**. We already note here that this behavior results in an increase of dissolved CO_2 according to the increase of CO_2 in the atmosphere but only to a relatively small increase in DIC. The description of the carbonate system has to be completed by two additional equations: conservation of alkalinity (ALK)

$$ALK = 2[CO_3^{2-}] + [HCO_3^-] + [B(OH)_4^-] + [OH^-] - [H^+] \qquad (9)$$

and total boron concentration B_T

$$B_T = [B(OH)_4^-] + [B(OH)_3]. \qquad (10)$$

Eliminating all quantities except h and $s = [CO_2]$ the system (1) to (9) can be reduced to two equations:

$$DIC = s(1 + \frac{K_1}{h} + \frac{K_1 K_2}{h^2}) \qquad (11)$$

$$ALK = s(\frac{K_1}{h} + 2\frac{K_1 K_2}{h^2}) + \frac{B_T}{1 + \frac{h}{K_B}} + \frac{K_w}{h} - h \qquad (12)$$

How does DIC change as a consequence of higher atmospheric CO_2 concentrations?
The CO_2 concentration in the surface waters $[CO_2]$ increases by dissolving additional CO_2 from the atmosphere according to Henry's law

$$[CO_2] = K_H(T) \, pCO_2 \qquad (13)$$

where pCO_2 is the partial pressure of atmospheric carbon dioxide and $K_H(T)$ is the temperature dependent solubility. The differentials of DIC and ALK are:

$$dDIC = \frac{\partial DIC}{\partial s} \, ds + \frac{\partial DIC}{\partial h} \, dh \qquad (14)$$

$$dALK = \frac{\partial ALK}{\partial s} \, ds + \frac{\partial ALK}{\partial h} \, dh \qquad (15)$$

The uptake of charge-free CO_2 from the atmosphere does not change the alkalinity ($dALK = 0$) and therefore

$$\frac{dh}{ds} = - \frac{\partial ALK}{\partial s} (\frac{\partial ALK}{\partial h})^{-1}$$

$$= \frac{(\frac{K_1}{h} + 2\frac{K_1 K_2}{h^2})}{1 + \frac{K_w}{h^2} + \frac{B_T}{K_B(1 + h/K_B)^2} + s(\frac{K_1}{h^2} + 4\frac{K_1 K_2}{h^3})} \qquad (16)$$

and

$$\frac{dDIC}{ds} = \left[\frac{\partial DIC}{\partial s} - \frac{\partial DIC}{\partial h} \frac{\partial ALK}{\partial s} (\frac{\partial ALK}{\partial h})^{-1}\right]$$

$$= \frac{4\frac{K_1 K_2}{h^2} + \frac{K_1}{h} + \frac{K_1^2 K_2}{h^3} + \frac{h}{s}(1 + \frac{K_1 K_2}{h^2} + \frac{K_1}{h})(1 + \frac{K_w}{h^2})}{4\frac{K_1 K_2}{h^2} + \frac{K_1}{h} + \frac{h}{s}(1 + \frac{K_w}{h^2} + \frac{B_T}{K_B(1 + h/K_B)^2})} \qquad (17)$$

The right hand side of Eq. (16) is always positive, i.e., with increasing CO_2 concentration the hydrogen ion concentration increases and the pH value decreases. The solution becomes more acidic. As a consequence the concentration ratios among CO_2, bicarbonate, and carbonate change: while the ratios of CO_2 and bicarbonate increase, the ratio of carbonate decreases. The DIC concentration increases with increasing CO_2 concentration (all terms of the right side of Eq. (17) are positive). However, the increment is not proportional to the increment of $[CO_2]$. This fact is due to the change of the pH value. This effect is quantified by the (differential) Revelle or buffer factor RF:

$$RF : = \frac{ds}{s} / \frac{dDIC}{DIC} \qquad (18)$$

The Revelle factor is a measure of the relative change of DIC as a consequence of changing carbon dioxide concentrations. When alkalinity is kept constant (no formation of chalk) the value of RF ranges between 8 and 15, depending on the atmospheric CO_2 concentrations and water temperatures [9]. A doubling of atmospheric CO_2 leads only to a change of DIC by approximately 10 %. When chalk is formed ($\gamma > 0$) the buffer factor may become negative ($\rightarrow$ *Fig. 8*).

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[7] the concentration of water (55.56 mol/l) is hidden in K_1 and K_w

8 Literature

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