
CARBON DIOXIDE, DISSOLVED (OCEAN)

The ocean contains about sixty times more carbon in the form of dissolved inorganic carbon than in the pre-anthropogenic atmosphere (~600 Pg C). On time scales $<10^5$ yrs, the ocean is the largest inorganic carbon reservoir (~38,000 Pg C) in exchange with atmospheric carbon dioxide (CO_2) and as a result, the ocean exerts a dominant control on atmospheric CO_2 levels. The average concentration of inorganic carbon in the ocean is $\sim 2.3 \text{ mmol kg}^{-1}$ and its residence time is $\sim 200 \text{ ka}$.

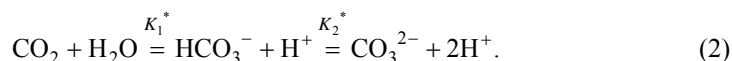
Dissolved carbon dioxide in the ocean occurs mainly in three inorganic forms: free aqueous carbon dioxide ($\text{CO}_2(\text{aq})$), bicarbonate (HCO_3^-), and carbonate ion (CO_3^{2-}). A minor form is true carbonic acid (H_2CO_3) whose concentration is less than 0.3% of $[\text{CO}_2(\text{aq})]$. The sum of $[\text{CO}_2(\text{aq})]$ and $[\text{H}_2\text{CO}_3]$ is denoted as $[\text{CO}_2]$. The majority of dissolved inorganic carbon in the modern ocean is in the form of HCO_3^- (>85%), as described below.

Carbonate chemistry

In thermodynamic equilibrium, gaseous carbon dioxide ($\text{CO}_2(\text{g})$), and $[\text{CO}_2]$ are related by Henry's law:

$$\text{CO}_2(\text{g}) \stackrel{K_0}{=} [\text{CO}_2] \quad (1)$$

where K_0 is the temperature and salinity dependent solubility coefficient of CO_2 in seawater (Weiss, 1974). The concentration of dissolved CO_2 and the fugacity of gaseous CO_2 , $f\text{CO}_2$, then obey the equation $[\text{CO}_2] = K_0 \times f\text{CO}_2$, where the fugacity is virtually equal to the partial pressure, $p\text{CO}_2$ (within $\sim 1\%$). The dissolved carbonate species react with water, hydrogen and hydroxyl ions and are related by the equilibria:



The pK^* 's ($= -\log(K^*)$) of the stoichiometric dissociation constants of carbonic acid in seawater are $pK_1^* = 5.94$ and $pK_2^* = 9.13$ at temperature $T=15^\circ\text{C}$, salinity $S=35$, and surface pressure $P = 1 \text{ atm}$ (Prieto and Millero, 2001). At typical surface seawater pH of 8.2, the speciation between $[\text{CO}_2]$, $[\text{HCO}_3^-]$, and $[\text{CO}_3^{2-}]$ is 0.5%, 89%, and 10.5%, respectively, showing that most of the dissolved CO_2 is in the form of HCO_3^- and not in the form of CO_2 (Figure 1). The sum of the dissolved carbonate species is denoted as total dissolved inorganic carbon (ΣCO_2):

$$\Sigma\text{CO}_2 = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] . \quad (3)$$

This quantity is also represented as DIC, TIC, TCO₂, and C_T. Another essential parameter to describe the carbonate system is the total alkalinity (TA), a measure of the charge balance in seawater:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] \\ + \text{minor compounds} . \quad (4)$$

ΣCO_2 and TA are conservative quantities, i.e. their concentrations measured in gravimetric units (mol kg⁻¹) are unaffected by changes in pressure or temperature, for instance, and they obey the linear mixing law. Therefore they are the preferred tracer variables in numerical models of the ocean's carbon cycle. Of all the carbon species and carbonate system parameters described above, only $p\text{CO}_2$, $p\text{H}$, ΣCO_2 , and TA can be determined analytically. However, if any two parameters and total dissolved boron are known, all parameters ($p\text{CO}_2$, $[\text{CO}_2]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, $p\text{H}$, ΣCO_2 , and TA) can be calculated for a given T , S , and P (cf. Zeebe and Wolf-Gladrow, 2001).

Buffering

The dissolved carbonate species in seawater provide an efficient chemical buffer for various processes that change the properties of seawater. For instance, the addition of a strong acid such as hydrochloric acid (naturally added to the ocean by volcanism), is strongly buffered by the seawater carbonate system. In distilled water, the addition of HCl leads to an increase of $[\text{H}^+]$ and $[\text{Cl}^-]$ in solution in a ratio 1:1. This is not the case in seawater. For example, the addition of 1 $\mu\text{mol kg}^{-1}$ HCl to distilled water at $p\text{H}$ 7 reduces the $p\text{H}$ to very close to 6. The same addition to seawater at $p\text{H}$ 7 and $\Sigma\text{CO}_2 = 2000 \mu\text{mol kg}^{-1}$ at $T=15^\circ\text{C}$ and $S=35$ only reduces the $p\text{H}$ to 6.997. The seawater $p\text{H}$ buffer is mainly a result of the capacity of CO_3^{2-} and HCO_3^- ions to accept protons.

One specific buffer factor, the so-called Revelle factor, is important in the context of the oceanic uptake of anthropogenic CO_2 . The Revelle factor, R , is given by the ratio of the relative change of atmospheric $p\text{CO}_2$ (in equilibrium with dissolved CO_2) to the relative change of ΣCO_2 in seawater:

$$R = (d[p\text{CO}_2] / [p\text{CO}_2])_a / (d\Sigma\text{CO}_2 / \Sigma\text{CO}_2)_{sw} \quad (5)$$

and varies roughly between 8 and 15, depending on temperature and $p\text{CO}_2$. As a consequence, the current increase of ΣCO_2 in surface seawater occurs not in a 1:1

ratio to the increase of atmospheric CO₂ (the latter being mainly caused by fossil fuel burning). Rather, a doubling of *p*CO₂ will only lead to an increase of ΣCO₂ of the order of 10%.

ΣCO₂ and TA of a water parcel

Important processes that can change the carbonate chemistry of a water parcel in the ocean can be described by considering changes in ΣCO₂ and TA (Figure 2). Invasion of CO₂ from (or release to) the atmosphere increases (or decreases) ΣCO₂, respectively, while TA stays constant. This leads to a rise and drop of [CO₂], respectively, with opposite change in *p*H (since CO₂ is a weak acid). Respiration and photosynthesis lead to the same trends, except that TA changes slightly due to nutrient release and uptake. CaCO₃ precipitation decreases ΣCO₂ and TA in a ratio 1:2, and, counterintuitively, increases [CO₂] although inorganic carbon has been reduced. For a qualitative understanding, consider the chemical reaction



which indicates that during CaCO₃ precipitation CO₂ is liberated. Quantitatively, however, the conclusion that [CO₂] in solution is increasing by one mole per mole CaCO₃ precipitated is incorrect because of buffering. The correct analysis takes into account the decrease of ΣCO₂ and TA in a ratio 1:2 and the buffer capacity of seawater. That is, the medium gets more acidic because the decrease in alkalinity outweighs that of total carbon and hence [CO₂] increases. For instance, at surface water conditions (ΣCO₂ = 2000 μmol kg⁻¹, *p*H = 8.2, T = 15°C, S = 35), [CO₂] increases by only ~0.03 μmol per μmol CaCO₃ precipitated.

Measurements and data

As stated above, the following parameters of the carbonate system can be determined experimentally: *p*CO₂, *p*H, ΣCO₂, and TA. The *p*CO₂ of a seawater sample refers to the *p*CO₂ of a gas phase in equilibrium with that seawater sample. It is usually measured by equilibrating a small volume of gas with a large volume of seawater at given temperature. Then the mixing ratio of CO₂(g) in the gas phase is determined either using a gas chromatograph or an infrared analyzer. Finally, the *p*CO₂ is calculated from the mixing ratio. *p*H is routinely measured using a glass / reference electrode cell or spectrophotometrically using an indicator dye. ΣCO₂ is usually measured by an extraction / coulometric method or a closed cell titration. A potentiometric titration is used to determine TA. For summary, see DOE (1994) and Grasshoff et al. (1999).

A great volume of data on the carbonate chemistry of the oceans has been obtained over the last few decades through programs such as GEOSECS (Geochemical Ocean Sections Study), TTO (Transient Tracers in the Oceans), and

WOCE (World Ocean Circulation Experiment). Much of these data are available through CDIAC (Carbon Dioxide Information Analysis Center) at <http://cdiac.ornl.gov>.

Distribution of ΣCO_2 and TA

The vertical distribution of ΣCO_2 in the ocean is a result of the so-called biological and physical carbon pumps. Uptake of carbon into organic matter and production of CaCO_3 in the surface ocean, the transport to deeper layers, and the remineralization at depth (biological pump) reduces ΣCO_2 in surface waters while ΣCO_2 in deep water increases (Figure 3a). The increased solubility of CO_2 in high-latitudes at low temperatures where the ocean's deep water forms and descends to the abyss leads to the same vertical trend in ΣCO_2 (physical pump). Vertical profiles of TA in the ocean (Figure 3b) are mostly governed by production and dissolution of CaCO_3 . Generally, uptake of Ca^{2+} and CO_3^{2-} in the surface and release in the deep ocean reduces and increases TA, respectively. This is similar to the cycling of organic carbon and ΣCO_2 but the maximum in TA occurs at greater depth because CaCO_3 is mainly redissolved in deep water. The vertical distribution of ΣCO_2 and TA constitutes one major control on atmospheric CO_2 concentrations. For example, without the biological pump, the pre-anthropogenic atmospheric CO_2 concentration would have been >500 ppmv (parts per million by volume) rather than 280 ppmv (Maier-Reimer et al., 1996).

The horizontal distribution of CO_2 and ΣCO_2 in the surface ocean is mainly governed by the temperature-dependent solubility of CO_2 on interannual timescales. Warm low-latitude surface water generally holds less CO_2 ($\sim 10 \mu\text{mol kg}^{-1}$) and ΣCO_2 ($\sim 2000 \mu\text{mol kg}^{-1}$) than cold high-latitude surface water ($\text{CO}_2 \sim 15 \mu\text{mol kg}^{-1}$ and $\Sigma\text{CO}_2 \sim 2100 \mu\text{mol kg}^{-1}$), because of the enhanced solubility at low temperature. Locally, and on seasonal time scales, however, significant deviations from these general patterns may occur due to changes in salinity and processes such as biological activity, upwelling, temperature variations, river runoff, and other processes which affect ΣCO_2 and TA.

Deep ocean circulation whose mass transport is predominantly from the North Atlantic through the Southern Ocean into the Indian and Pacific Ocean, produces horizontal deep-water gradients in ΣCO_2 and TA. While the details of deep ocean circulation are much more complex in general, the 'youngest' water which was most recently in contact with the atmosphere resides in the Atlantic, whereas the 'oldest' water resides in the Pacific. As a corollary, the water in the deep North Pacific has collected the most respired CO_2 on its way and thus has the highest ΣCO_2 (Figure 3a).

Inventories of ΣCO_2 and TA over time

Under most natural conditions, the global inventories of ΣCO_2 and TA constitute one major control on atmospheric CO_2 concentrations. Understanding changes of these inventories over time is therefore crucial to understanding climate. Thus, the characterization of the dominant carbon and alkalinity fluxes on different time scales is of fundamental importance. [Note that due to our limited knowledge on this subject, the following analysis is to be considered a simplification (Sundquist, 1986)].

Millennial ($<10^3$ yr) time scale

On time scales shorter than $\sim 10^3$ yrs, the natural reservoirs that exchange carbon with the ocean are the atmosphere (pre-anthropogenic inventory ~ 600 Pg C), the biosphere (~ 550 Pg C), and soils ($\sim 1,500$ Pg C) and thus the oceanic inventory of ΣCO_2 ($\sim 38,000$ Pg C) can be considered essentially constant. Exceptions to this are potential rapid carbon inputs from otherwise long-term storage reservoirs. Examples are the current combustion of fossil fuel carbon by humans (which will eventually be mostly absorbed by the ocean), and catastrophic events such as possible impact events over carbonate platforms, or abrupt methane releases from gas hydrates (as postulated for the Late Paleocene Thermal Maximum).

10^3 – 10^5 yr time scale

On time scales of 10^3 – 10^5 yrs, fluxes between reactive carbonate sediments ($\sim 5,000$ Pg C) and the ocean's inventories of ΣCO_2 and TA have to be considered as well. Oceanic inventories may vary, for instance, during glacial cycles (see so-called calcite compensation below). The magnitude of these changes is, however, limited and so are associated changes in atmospheric CO_2 .

Tectonic ($>10^5$ yr) time scale

A large amount of carbon is locked up in the Earth's crust as carbonate carbon ($\sim 70 \times 10^6$ Pg C) and as elemental carbon in shales and coals ($\sim 20 \times 10^6$ Pg C). On time scales $>10^5$ yrs, this reservoir is active and imbalances in the fluxes to and from this pool can lead to drastic changes in ΣCO_2 and TA and atmospheric CO_2 . The balance between CO_2 consumption by subduction of marine sediments, weathering, subsequent carbonate burial and volcanic degassing of CO_2 are the dominant processes controlling carbon fluxes on this time scale (Berner et al., 1983). This so-called rock cycle is driven by tectonic processes which lead to changes in seafloor spreading rates and continental uplift.

$[\text{CO}_3^{2-}]$ and CaCO_3 saturation

The accumulation and dissolution of reactive CaCO_3 sediments in the deep sea provide a powerful feedback to regulating the carbonate ion content ($[\text{CO}_3^{2-}]$) and thus the concentration of dissolved CO_2 in the ocean. The inventory of carbonate ion

in the ocean cannot be viewed independently of carbonate sediments because of the control of CO_3^{2-} on the solubility of CaCO_3 . In today's ocean there is a close correspondence between $[\text{CO}_3^{2-}]$ of deep water and the observed distribution of CaCO_3 in deep sea sediments. Depending on the geographic location, there is a certain depth above which the ocean floor is mainly covered with calcite while below it is largely calcite-free. The depth at which the sediments are virtually free of calcium carbonate is called the calcium carbonate compensation depth (CCD). The transition from calcite-rich to calcite-depleted sediments is not abrupt but gradual and the depth of rapid increase in the rate of dissolution as observed in sediments is called the calcite lysocline. Aragonite is more soluble than calcite and the aragonite lysocline occurs at shallower depth than the calcite lysocline. In the Pacific, the aragonite lysocline can be as shallow as 500 m and ~ 3 km in the Atlantic. The calcite lysocline lies at ~ 3 –4 km in the Pacific and between 4 and 5 km in the Atlantic.

The reason for the disappearance of CaCO_3 at depth is the increase of solubility with pressure and thus with depth. The CaCO_3 saturation state of seawater is expressed by Ω :

$$\Omega = \frac{[\text{Ca}^{2+}]_{\text{sw}} \times [\text{CO}_3^{2-}]_{\text{sw}}}{K_{\text{sp}}^*} \quad (7)$$

where $[\text{Ca}^{2+}]_{\text{sw}}$ and $[\text{CO}_3^{2-}]_{\text{sw}}$ are the concentrations of Ca^{2+} and CO_3^{2-} in seawater and K_{sp}^* is the solubility product of calcite or aragonite at the in situ conditions of temperature, salinity and pressure. Values of $\Omega > 1$ signifies supersaturation, $\Omega < 1$ signifies undersaturation. Because K_{sp}^* increases with pressure (the temperature effect is small) there is a transition of the saturation state from $\Omega > 1$ (calcite-rich) to $\Omega < 1$ (calcite-depleted) sediments at depth.

In the modern ocean, $[\text{Ca}^{2+}]_{\text{sw}}$ is large (compared to $[\text{CO}_3^{2-}]_{\text{sw}}$) and virtually constant (except for variations in salinity) and thus variations of the saturation state are controlled by variations in $[\text{CO}_3^{2-}]_{\text{sw}}$. The crossover of $[\text{CO}_3^{2-}]_{\text{sw}}$ and the carbonate ion concentration at calcite saturation is called calcite saturation horizon. The feedback that controls the average carbonate ion content of seawater and the distribution of CaCO_3 on multi-millennial time scale via variations of the saturation horizon is called calcite compensation. This in turn exerts a major control on dissolved CO_2 and alkalinity in the ocean.

Calcite compensation

Calcite compensation maintains the balance between CaCO_3 weathering fluxes into the ocean and CaCO_3 burial fluxes in marine sediments on time scales of 10^3 – 10^5 yrs (Broecker and Peng, 1989). In steady state, the riverine flux of Ca^{2+} and CO_3^{2-} ions from weathering must be balanced by burial of CaCO_3 in the sea, otherwise $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ would rise or fall. The feedback that maintains this balance works as

follows. Assume that there is an excess weathering influx of Ca^{2+} and CO_3^{2-} over burial of CaCO_3 . Then, the concentrations of Ca^{2+} and CO_3^{2-} in seawater increase which leads to an increase of the CaCO_3 saturation state. This in turn leads to a deepening of the saturation horizon and to an increased burial of CaCO_3 just until the burial again balances the influx. The new balance is restored at higher $[\text{CO}_3^{2-}]$ than before.

ΣCO_2 and $\delta^{13}\text{C}$

In the ocean, there is an inverse relationship between the vertical distribution of ΣCO_2 and the stable carbon isotope ratio $^{13}\text{C}/^{12}\text{C}$ of ΣCO_2 ($\delta^{13}\text{C}_{\Sigma\text{CO}_2}$). In the surface ocean, phytoplankton takes up inorganic carbon to produce organic carbon via photosynthesis. This process discriminates against the heavy isotope ^{13}C such that the organic carbon is depleted in ^{13}C and, as a result, surface ΣCO_2 becomes enriched in ^{13}C . At depth the process is reversed. The organic carbon settling down to intermediate and deep waters is remineralized and the ‘isotopically light’ carbon is set free, which causes deep ΣCO_2 to become enriched in ^{12}C (i.e. it has relatively less ^{13}C). In today’s ocean the mean difference in $\delta^{13}\text{C}$ of ΣCO_2 between surface and deep is $\Delta\delta^{13}\text{C} \cong 2\%$. In a very simple two-box view of the ocean, one can show that $\Delta\delta^{13}\text{C}$ depends on the strength of the carbon export to deep water (biological pump), the photosynthetic fractionation factor (Δ^{photo}), and mean ΣCO_2 of the ocean (Broecker, 1982):

$$\Delta\delta^{13}\text{C} = \Delta^{\text{photo}} \times \Delta\Sigma\text{CO}_2 / \Sigma\text{CO}_2. \quad (8)$$

where $\Delta\Sigma\text{CO}_2$ is the surface-to-deep difference in ΣCO_2 due to the biological pump. Given information on past $\Delta\delta^{13}\text{C}$ from differences in $\delta^{13}\text{C}$ of planktonic and benthic foraminifera, and assumptions regarding the strength of the biological pump, and Δ^{photo} , estimates of ΣCO_2 of past oceans have been derived (e.g. Shackleton, 1985).

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Bibliography

- Berner, R.A., Lasaga, A.C. and Garrels, R.M. (1983) The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am J. Sci.* **283**, 641-683.
- Broecker, W.S. (1982) Ocean chemistry during glacial times. *Geochim. Cosmochim. Acta*, **46**, 1689-1705.
- Broecker, W.S. and Peng, T.-H. (1987) The role of CaCO_3 compensation in the glacial to interglacial atmospheric CO_2 change. *Global Biogeochem. Cycles*, **1**, 5-29.
- DOE (1994) *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2*, (eds. Dickson, A.G. and Goyet, C.) ORNL/CDIAC-74.
- Grasshoff, K., Kremling, K. and Ehrhardt, M. (eds.) (1999) *Methods of Seawater Analysis*, Wiley-VCH, Weinheim, 600 pp.

- Maier-Reimer, E., Mikolajewicz, U., Winguth, A. (1996) Future ocean uptake of CO₂: Interaction between ocean circulation and biology. *Climate Dynamics*, **12**, 711-721.
- Prieto, F.J.M. and Millero F.J. (2001) The values of pK₁ and pK₂ for the dissociation of carbonic acid in seawater. *Geochim. Cosmochim. Acta*, **66**(14), 2529-2540.
- Shackleton, N.J. (1985) Oceanic carbon isotope constraints on oxygen and carbon dioxide in the Cenozoic atmosphere, in *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*, Geophys. Monogr. Ser., Vol. 32, (eds. Sundquist, E.T. and Broecker W.S.) AGU, Washington DC, pp. 412-417.
- Sundquist, E.T. (1986) Geologic Analogs: Their value and limitations in carbon dioxide research, in *The Changing Carbon cycle: A Global Analysis*, (eds. Trabalka, J.R. and Reichle, D.E.). Springer-Verlag, New York, pp. 371-402.
- Weiss, R.F. (1974), Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Mar. Chem.*, **2**, 203-215.
- Zeebe, R.E. and Wolf-Gladrow D.A. (2001) *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*. Elsevier Oceanography Series. Amsterdam, 346 pp.

Cross-references

Carbon cycle
 Carbon dioxide and methane, Quaternary variations
 Carbon isotopes, stable
 Carbonate compensation depth
 Glacial-interglacial cycles
 Marine carbon geochemistry
 Methane hydrates, carbon cycling, and environmental change
 Paleo-ocean pH
 Quaternary climate transition and cycles
 Thermohaline circulation

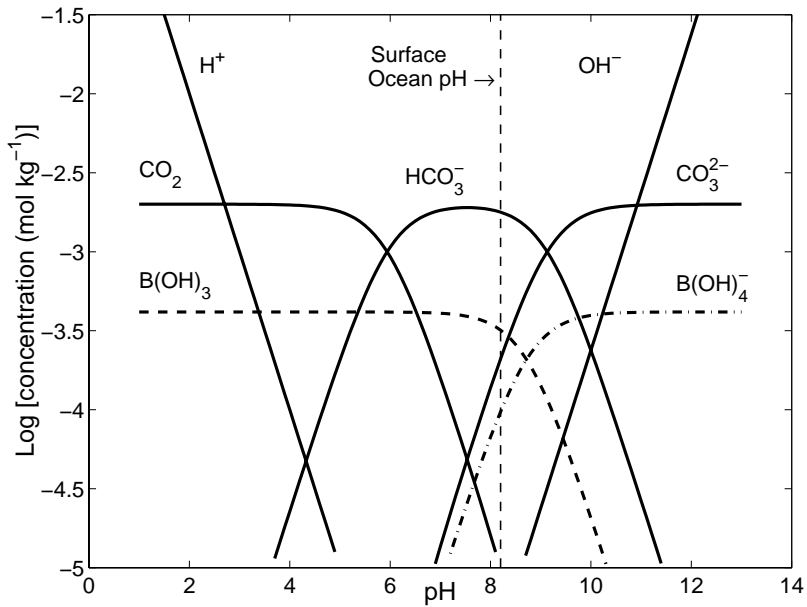


Figure 1 Concentrations of the dissolved forms of the carbonate system in seawater (so-called Bjerrum plot). $\Sigma\text{CO}_2 = 2000 \mu\text{mol kg}^{-1}$, temperature $T=15^\circ\text{C}$, salinity $S=35$, and pressure $P = 1 \text{ atm}$ (after Zeebe and Wolf-Gladrow, 2001).

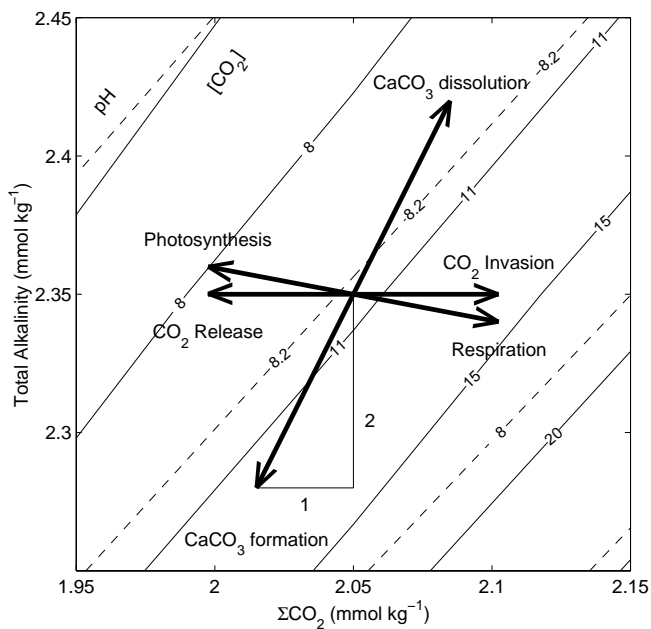


Figure 2 Important processes changing the carbonate chemistry of a water parcel in the ocean (values shown refer to $T=15^{\circ}\text{C}$, $S=35$, and $P=1$ atm). Solid and dashed lines indicate contours of constant dissolved CO_2 and pH , respectively. Many processes are most easily described by considering changes in ΣCO_2 and TA. For example, the invasion of CO_2 increases ΣCO_2 while TA stays constant which leads to an increase of dissolved CO_2 and a decrease of pH (since CO_2 is a weak acid).

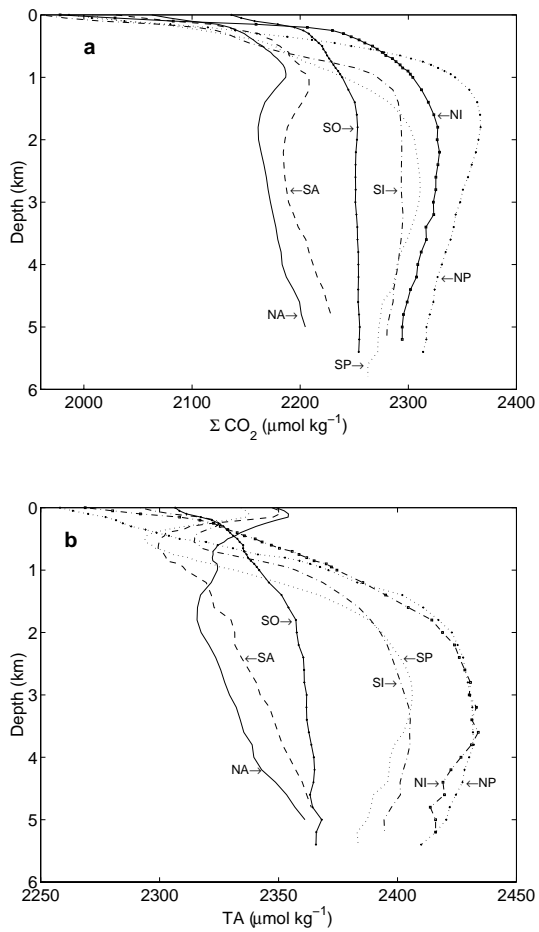


Figure 3 Average vertical distribution of ΣCO_2 (a) and TA (b) in the oceans. NA/SA = North/South Atlantic, SO = Southern Ocean, NI/SI = North/South Indian, NP/SP = North/South Pacific. The data (www.ewoce.org) was compiled using Ocean Data View (Schlitzer, R., www.awi-bremerhaven.de/GEO/ODV).