Aqueous Carbon Chemistry

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1 Carbon system: 8 variables and 10 equations

Ocean is a great pot of soup. Carbon system inside is therefore complex because it is coupled with multiple reactions. Although we cannot isolate the carbon part with other reactions, the mostly consided reactions are still the processes where ${H_2CO_3}^*$ (i.e., $CO_{2(aq)} + H_2CO_3$) dissociate (电离) into bicarbonate and carbonate.

$$CO_2(g) + H_2O \xrightleftharpoons{K_0} {H_2CO_3}^* \xrightleftharpoons{K_1} H^+ + {HCO_3}^- \xrightleftharpoons{K_2} 2\,H^+ + {CO_3}^{2-} \tag{1}$$

Consequently we have three equilibrium relationships between different carbon species:

$$K_0 = \frac{{H_2CO_3}^*}{pCO_2} \tag{2}$$

$$K_1 = \frac{H^+ \cdot {HCO_3}^-}{{H_2CO_3}^*} \tag{3}$$

$$K_2 = \frac{H^+ \cdot {CO_3}^{2-}}{{HCO_3}^-} \tag{4}$$

Now we get 3 equations and 5 unkown variables ($pCO_2, {H_2CO_3}^*, {HCO_3}^-, {CO_3}^{2-}, H^+$). Although we often measure pH and pCO_2, they are not conservative to temperature, pressure and salinity, and thus cause some unncessary complication. However, oceanographiers mostly use [DIC] and [ALK] of which the former consider the carbon system and the latter consider the charge balance.

Alkalinity: The ability of an object to absorb protons, and an indicator of the charge balance.
Acidity: The ability of an object to donate protons.
pH: the concetration of protons (H+).

$$\mathrm{DIC} = \mathrm{H_2CO_3}^* + \mathrm{HCO_3}^- + \mathrm{CO_3}^{2-} \tag{5}$$

$$\mathrm{ALK} = \mathrm{HCO_3}^- + 2\mathrm{CO_3}^{2-} + \mathrm{OH}^- - \mathrm{H}^+ + \mathrm{B(OH)_4}^- + \text{minor bases} \tag{6}$$

Note each mole of $\mathrm{CO_3}^{2-}$ can deprotonate 2 mole H^+, which is why calcification remove ALK and DIC at 2:1 ratio.

Alternatively, total alkalinity also can be viewed as the excess of bases over acids, i.e., the charge balance of all strong acids and bases unaffected by titration (滴定).

$$\mathrm{ALK} = \mathrm{Na}^+ + \mathrm{K}^+ + 2\,\mathrm{Mg}^+ + 2\,\mathrm{Ca}^{2+} + \text{minor cations} \tag{7}$$

$$-\mathrm{Cl}^- - 2\,\mathrm{SO_4}^{2-} - \mathrm{Br}^- - \mathrm{NO_3}^- - \text{minor anions} \tag{8}$$

Now we introduce [OH-] and $[\mathrm{B(OH)_4}^-]$, therefore, more equations needed!

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] \tag{9}$$

$$K_B = \frac{[\mathrm{H}^+][\mathrm{B(OH)_4}^-]}{[\mathrm{H_3BO_3}]} \tag{10}$$

Finally because boron is conservative and only changed with net exchange of water by evaporation and precipitation, it can be assumed to be proportional to salinity.

$$[\mathrm{B(OH)_4}^-] + [\mathrm{H_3BO_3}] = c * S \tag{11}$$

In conclusion, we have 10 unknown variables and 8 equations now. To solve this simultaneous equation, we just need to measure two variables and then infer all the other ions. But the analytical solution cannot be get because the existence of high-order polynomial equation.

1.1 Quick estimation

According to (4) we can estimate the general

$$\mathrm{HCO_3}^- \approx 2\,\mathrm{DIC} - \mathrm{ALK} \tag{12}$$

$$\mathrm{CO_3}^{2-} \approx \mathrm{ALK} - \mathrm{DIC} \tag{13}$$

$$\mathrm{H}^+ = \frac{\mathrm{HCO_3}^- \cdot K_2}{\mathrm{CO_3}^{2-}} \propto \frac{\mathrm{HCO_3}^-}{\mathrm{CO_3}^{2-}} \approx \frac{2DIC - ALK}{ALK - DIC} \tag{14}$$

$$p\mathrm{CO_2} = \frac{\mathrm{H_2CO_3}^*}{K_0} = \frac{\mathrm{H}^+\ \cdot \mathrm{HCO_3}^-}{K_0 K_1} \propto \mathrm{H}^+\ \cdot \mathrm{HCO_3}^- \tag{15}$$

$$p\mathrm{CO_2} = \frac{[DIC]}{K_0} \frac{1}{1 + \frac{K_1}{H+} + \frac{K_1 \cdot K_2}{H+ \cdot H+}} \tag{16}$$

2 Soft-tissue pump

When organisms extract DIC from surface water, pCO2 is influenced by (1) DIC and (2) pH. Although DIC removal is very intuitive, but pH reduction is more determinant. Also in organic carbon pump, [ALK] is not greatly changed. Therefore, HCO3 decreases, CO3 rises, H+ declines, pCO2 declines.

DIC ↓ HCO_3^- ↓ H^+ ↓ pCO_2 ↓	CO_3^{2-} ↑ pH ↑	电离平衡向右移动 整体可电离的碳酸和碳酸氢根减少了

3 Carbonate pump

Calcification remove ALK:DIC in 2:1. When Alk is extracted from surface, it make HCO3- rises, CO32- declines and H+ rises, (reaction from right to left). Therefore, pCO2 increases because of (1) higher HCO3- and (2) H+.

DIC ↓ HCO_3^- ↑ H^+ ↑ pCO_2 ↑	2 ALK ↓ CO_3^{2-} ↓ pH ↓	电离平衡向左移动

Remineralisation of biogenic material at depth, after it was exported from the surface, releases DIC and ALK, thereby causing chemical changes in deep water in the reverse direction as their removal causes in surface waters.

3.1 CaCO3 saturation state

Theoretically, $CaCO_3$ is precipitated when $\Omega > 1$ and dissolves when $\Omega < 1$.

Saturation: The extent of solubility (relative)
Solubility: The ability of a substance, the solute, to form a solution with another substance, the solvent (absolute).

The concetration of $Ca_2{}^+$ is almost uniform in the ocean, the expression of Ω then is mostly determined by carbonate ion. And because biological pump removes DIC, the surface water is mostly $CaCO_3$ supersaturated. In the modern Ocean, almost all CaCO3 precipitation is mediated or controlled by organisms growing in highly supersaturated waters near the surface.

$$\Omega = \frac{[Ca_2{}^+][CO_3{}^{2-}]}{CO_{3\,sat}^{2-}} \approx \frac{CO_3{}^{2-}}{[CO_3{}^{2-}]_{sat}} \approx \frac{ALK - DIC}{CO_3{}^{2-}(sat)} \tag{17}$$

However, for three reasons, most of the CaCO3 rain from the surface dissolves rather than being buried in deep-sea sediments. (1) $CO_3{}^{2-}$(sat) increase with water depth (and therefore pressure); (2) because of biological pump, the CO_{32}^{-} is much lower in the ocean interior than at the surface; (3) the respiration of organic matter in seafloor sediments reduces the CO_3^{2-} in the sediment pore water so as to allow for sedimentary CO_3^{2-} dissolution even if the overlying bottom water is supersaturate.

4 Soft-tissue vs. Carbonate pump

Carbonate pump only partially cancels the CO2 drawdown effect of soft-tissue pump. And they are decoupled in (1) different magnitude, not all organic matter that sinks is associated with calcium carbonate; (2) different fate: soft-tissue and carbonate material that sink into the ocean interior would face different pathways.

The nutrient in the interior ocean can be divided into two parts: (1) remineralised (or regenerated) i.e., from organic matter respiration; (2) preformed nutrients emplaced by ocean circulation. Therefore, the **regenerated nutrients distribution can be used to infer the strength of organic pump**. Current studies suggest that every 0.1 μM increased regenerated P leads to 13-20 ppm CO_2 drawdown.

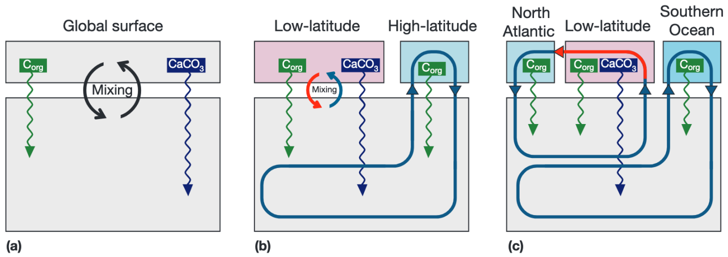
The inorganic pump, certainly cannot be used to estimate this because there is no such globally valid relationship between the export rates of C_org and $CaCO_3$. But the estimation of carbonate pump effect is that every 10 μM alkalinity increase causes 5 ppm CO_2 increase.

The reconstruction of biological pump must consider the effect of ocean circulation which is against the pumps. Generally, greater export of organic matter and/or a greater residence time of remineralised products in the interior result in a transform from preformed P to regenerated P, and cause a atmospheric CO2 drawdown. Likewise, an increased CaCO3 rain act to increase the concentration of sequestered alkalinity which caused atmospheric CO2 to rise.

Is the age of deep ocean always correlated with carbon storage of biological pump? No. For example, increasing surface/deep communication in the low latitude where all the surface nutrients are consumed, inceased upward transport of deeply sequestered CO2 will counter the effects of organic carbon export and does not influence the strength of soft-tissue pump. In contrast, if in a region of incomplete surface nutrient consumption, higher surface/deep communication will mainly improve upwelling than the downward export. i.e., increased ocean ventilation weaken the soft-tissue pump. 这段话说的是, soft-tissue pump 受到生物群落（以及相应的生物量转换率）调控比较大。

For the carbonate pump, it is less corrlated with nutrient supply (because calcifers are less). So the changes of ventilation rate will translate more directly to the changes of carbonate pump. A increased surface/deep communication will likely yield a decrease regenerated alkalinity (i.e., weaker carbonate pump). Therefore it is relatively safe to say younger deep ocean has a weaker carbonate pump.

5 Conceptual views of ocean



Phase 1: two box (surface and deep ocean)

Phase 2: deep ocean + low latitude (strongly stratified) and high latitude (higher ventilation and nutrients)

Phase 3: deep ocean + low lat + North Atlantic (nutrient poor) + Southern Ocean (rich nutrient)