Seawater Carbonate System

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Carbon dioxide is present in the atmosphere:

Eq C-1:

$$P_{CO_2} \sim 10^{-3.5}\,\text{atm} \sim 350\,\text{ppmv}$$

The volume mixing ratio ppmv is the ratio of the number of moles of a substance to the number of moles of dry air contained in the volume V occupied by the mixture.

ppmv = n_v / n_a x 10^6 (parts per million)

n_a = p_a V / RT

Carbon dioxide is soluble in water:

Eq C-2:

$$CO_2(g) \Leftrightarrow CO_2(aq)$$
$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3{}^0 \text{ (carbonic acid)}$$

Because water is present in excess, we generally do not distinguish between these two forms, and define:

Eq C-3:

$$CO_2(aq) + H_2CO_3{}^0 \equiv H_2CO_3{}^*$$

At equilibrium:

Eq C-4:

$$\left[H_2CO_3{}^*\right] = K_H P_{CO_2} \sim 10^{-1.5} 10^{-3.5} \sim 10^{-5}$$

Carbonic acid is a weak diprotic acid:

Eq C-5:

$$H_2CO_3{}^* \Leftrightarrow H^+ + HCO_3{}^-$$

Eq C-6:

$$K_1 = \frac{\left[H^+\right]\left[HCO_3{}^-\right]}{\left[H_2CO_3{}^*\right]} \approx 10^{-6} = f(T, P, S)$$

Eq C-7:

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{-2}$$

Eq C-8:

$$K_2 = \frac{[H^+][CO_3^{-2}]}{[HCO_3^-]} \approx 10^{-9} = f(T, P, S)$$

The equilibrium constants are defined for seawater medium and are functions of temperature, pressure and salinity. For completeness, water also acts as an acid:

Eq C-9:

$$H_2O \Leftrightarrow H^+ + OH^-$$

Eq C-10:

$$K_w \approx 10^{-13.7} = [H^+][OH^-]$$

We have 3 equations with 5 unknowns, therefore to solve the system of equations we need to specify two more conditions.

One is mass conservation in carbon, DIC = C_T:

Eq C-11:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$$

The other is a parameter called alkalinity, Alk:

Eq C-12:

$$Alk = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+] + (\text{smaller terms})$$

C_T and Alk are measurable quantities. If they are known then the system is completely defined.

These two parameters vary systematically in the ocean:

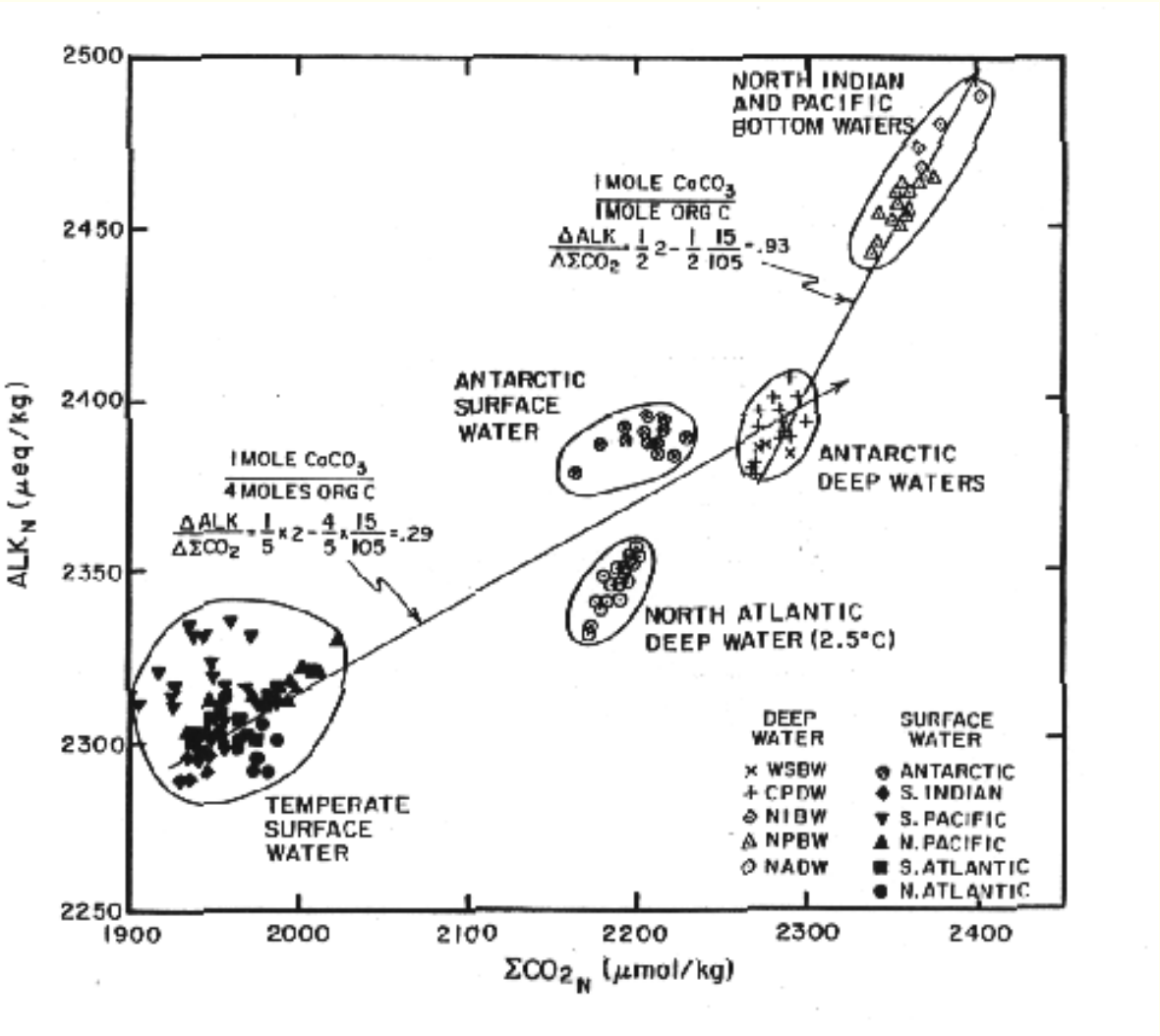

Figure C-1, from [(20)]

Our particular interest here is in the interaction of seawater with solid $CaCO_3$ (s). There are two crystalline forms of calcium carbonate, calcite and aragonite. Calcite is the more stable and more common of the two. Thermodynamically:

Eq C-18:

$$CaCO_3(s) \Leftrightarrow Ca^{+2} + CO_3^{-2}$$

Eq C-19:

$$K_s = \left[Ca^{+2}\right]\left[CO_3^{-2}\right] = f(T,P,S)$$

To establish where calcium carbonate is stable, we need to compare this value of the carbonate ion concentration at thermodynamic equilibrium (which will be a function of temperature, pressure and salinity) with the distribution of carbonate ion in the ocean.
