Carbon Dioxide, Carbonic Acid, and Carbonate Equilibria

IPOL 8512

Raindrop Equilibria

$$2H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(l)$$

$$CO_2(g) \rightleftharpoons CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$\upharpoonleft\downharpoonright H_2O(l)$$

$$HCO_3^-(aq) + H_3O^+(l)$$

$$\upharpoonleft\downharpoonright H_2O(l)$$

$$CO_3^{2-}(aq) + H_3O^+(l)$$

Raindrop Equilibria

- Water molecules dissociate.

  $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

  or $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

- When CO_2 and H_2O are in contact, some of the CO_2 dissolves and forms H_2CO_3

  $CO_2(g) \rightleftharpoons CO_2(aq)$

  $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

- H_2CO_3 is a weak acid, so it to forms H_3O^+ and HCO_3^-.

  $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$

  or $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

- HCO_3^- in turn ionizes into H_3O^+ and CO_3^{2-}

  $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

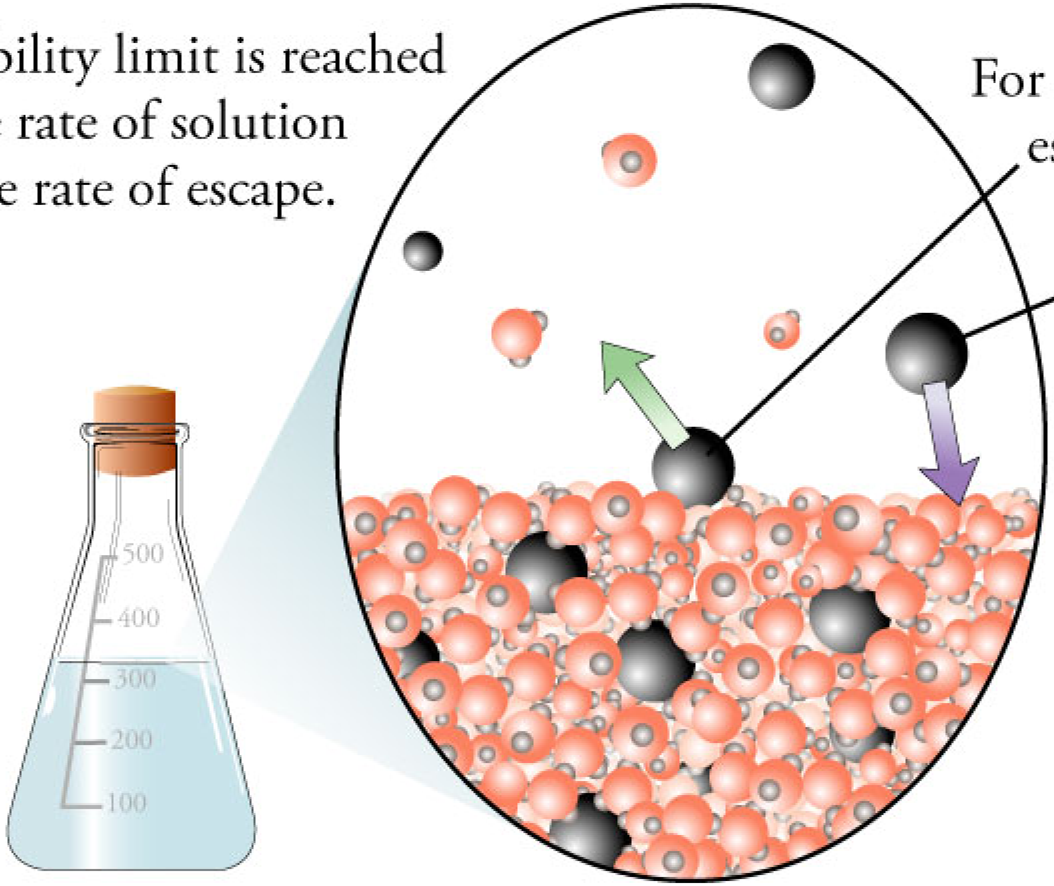
  or $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

Carbonate Equilibria

- If other sources of these species are present in the solution - for example, dissolved $CaCO_3$ from limestone or sea shells - then these must also be taken into account in finding the concentrations.

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

Dynamic Equilibrium for Gas Dissolved in Liquid



The solubility limit is reached when the rate of solution equals the rate of escape.

For every gas particle that escapes from the liquid, another gas particle collides with the surface and goes into solution.

Gas Solubility

Add a gas above a liquid in a closed container

↓

Initially, the rate of solution is greater than the rate of escape → Net shift of particles into solution

↓

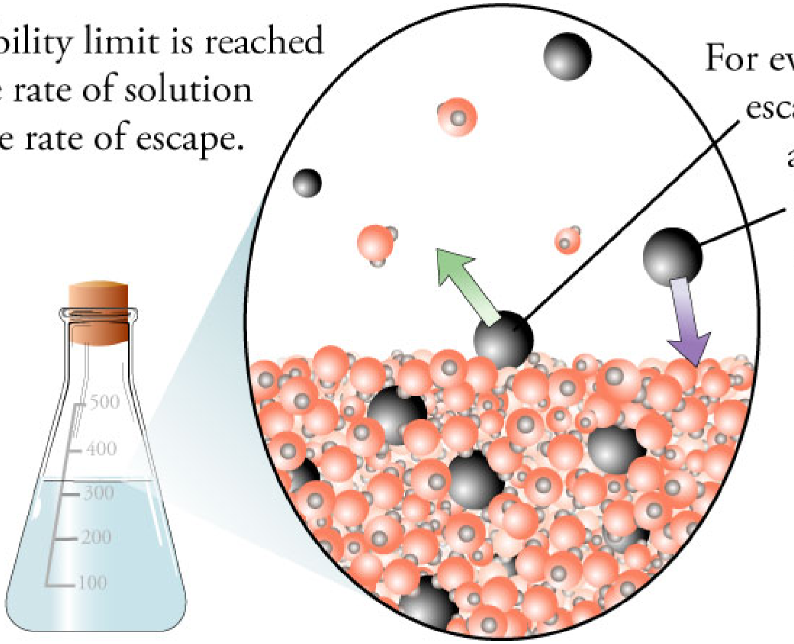
Increased rate of escape… ← Increased concentration of dissolved gas

↓

…Until the rate of escape equals rate of solution → Constant changes between dissolved and undissolved gas, but no net change in amount of either

↙

Dynamic equilibrium (solubility limit)



The solubility limit is reached when the rate of solution equals the rate of escape.

For every gas particle that escapes from the liquid, another gas particle collides with the surface and goes into solution.

Partial Pressure and Gas Solubility

Increased partial pressure of a gas over a liquid in a system initially at dynamic equilibrium (Rate of solution = Rate of escape)

↓

Increased rate of collision between gas particles and liquid → Increased rate of solution

↓

Net movement of gas particles into solution ← Rate of solution greater than rate of escape

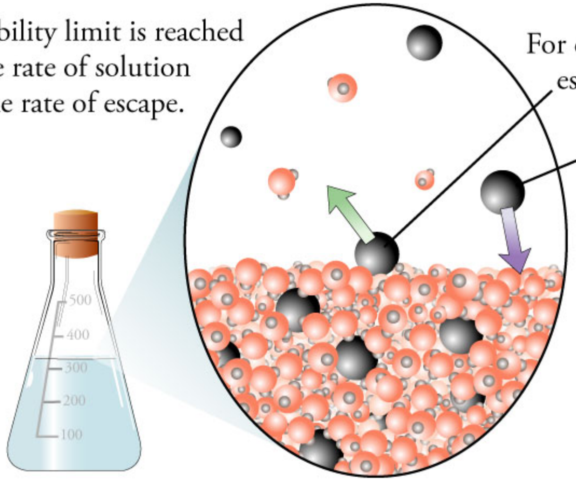
↓

Increased concentration of solute in solution → Increased rate of escape until it equals the higher rate of solution

↙

Greater solubility

The solubility limit is reached when the rate of solution equals the rate of escape.



For every gas particle that escapes from the liquid, another gas particle collides with the surface and goes into solution.

Henry's Law

- **Henry's law** states that *at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.*
- Henry's law can be put into mathematical terms (at constant temperature) as

  $$c = p\,k_H$$

  c is the concentration of the solute in mol/L

  p is the partial pressure of the solute in the gas above the solution

  k_H is Henry's constant, which is different for each gas/solvent combination.
- For carbon dioxide and water, k_H is 0.03400 mol/L·atm
- As of June, 2012, the CO_2 concentration in the atmosphere was 395 ppm. We can use this and Henry's Law to calculate the concentration of CO_2 in water.

CO_2 Concentration in Water

$$\frac{P_{CO_2}}{P_{atm}} = \frac{n_{CO_2}}{n_{atm}} = \frac{395\text{ mol}}{10^6\text{ mol}} = 3.95 \times 10^{-4}$$

$$P_{CO_2} = 3.95 \times 10^{-4} P_{atm} = 3.95 \times 10^{-4}(1\text{ atm}) = 3.95 \times 10^{-4}\text{ atm}$$

$$c = p\,k_H = 3.95 \times 10^{-4}\text{ atm}\,(0.03400\text{ mol/L}\cdot\text{atm})$$

$$= 1.34 \times 10^{-5}\text{ mol/L}$$

CO_2 Solution

- When carbon dioxide dissolves in water, it exists in a chemical equilibrium with carbonic acid:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

- The hydration equilibrium constant, K_h, at 25 °C is

$$[H_2CO_3]/[CO_2] = 1.70 \times 10^{-3}$$

- This shows that the majority of the carbon dioxide is not converted into carbonic acid. Most of it remains as CO_2 molecules.
- H_2CO_3* can be used to represent the CO_2 and the H_2CO_3 together.

$$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+ \quad K_{a1}(\text{app}) = 4.6 \times 10^{-7} \text{ at } 25\ °\text{C}$$

$$K_{a1(\text{app})} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 4.6 \times 10^{-7}$$

H_2CO_3 Equilibrium

- Because H_2CO_3 is a diprotic acid, there is a second ionization that forms carbonate ion CO_3^{2-}:

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

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

at 25 °C

Summary of Equations

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

$$P_{CO_2} = \frac{n_{CO_2}}{n_{atm}} P_{atm}$$

$$[CO_2] = P_{CO_2}\,(0.03400\ \text{mol/L}\cdot\text{atm}) = [H_2CO_3^*]$$

$$K_{a1(app)} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 4.6 \times 10^{-7}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

pH Natural Water

$[H^+][OH^-] = 1.0 \times 10^{-14}$ $\qquad [OH^-] = \dfrac{1.0 \times 10^{-14}}{[H^+]}$

$[CO_2] = P_{CO_2}(0.03400 \text{ mol/L·atm}) = 1.34 \times 10^{-5} \text{ mol/L} = [H_2CO_3^*]$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = \frac{[H^+][HCO_3^-]}{1.34 \times 10^{-5}} = 4.6 \times 10^{-7} \qquad [HCO_3^-] = \frac{4.6 \times 10^{-7}(1.34 \times 10^{-5})}{[H^+]} = \frac{6.2 \times 10^{-12}}{[H^+]}$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

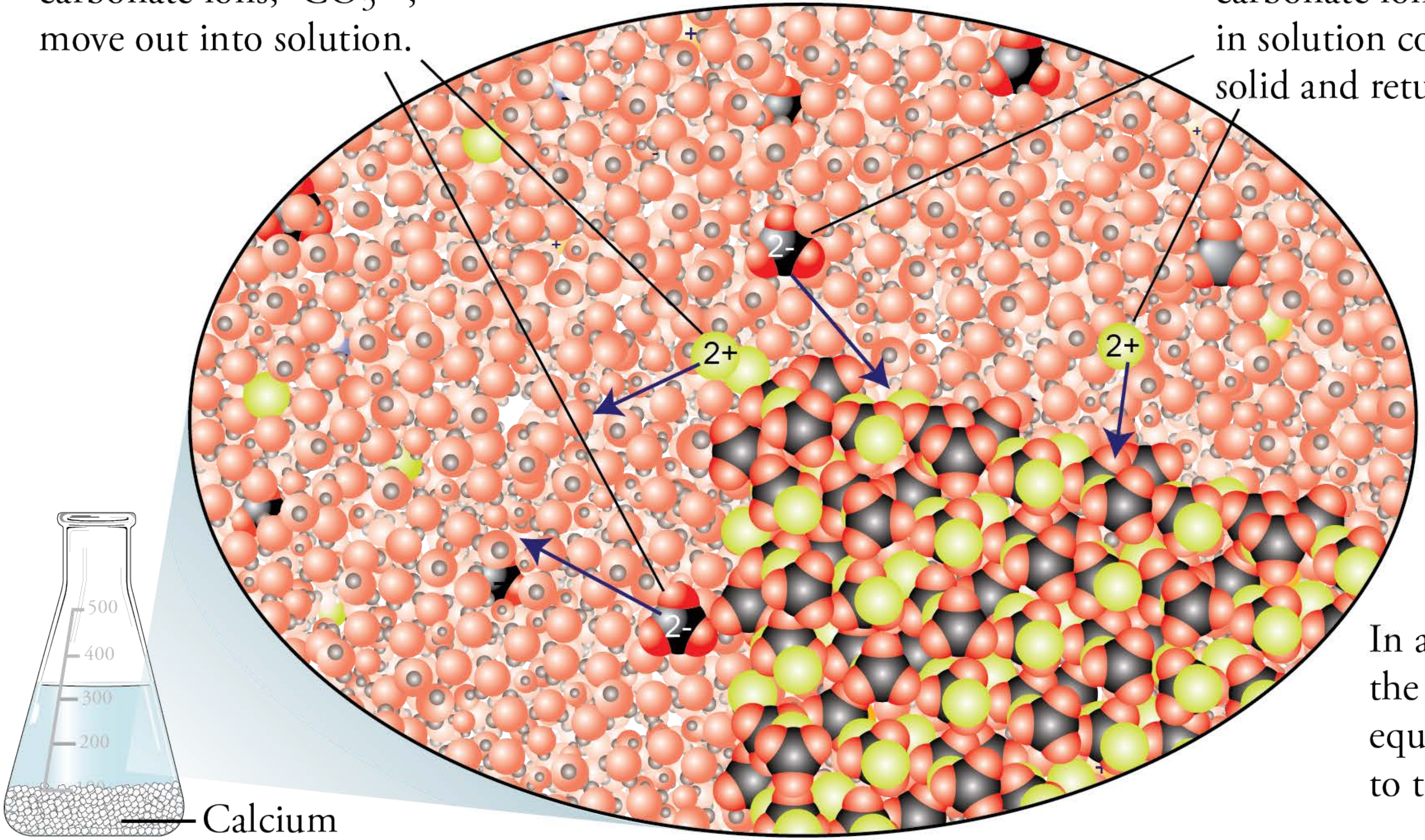
$$[CO_3^{2-}] = \frac{4.69 \times 10^{-11}[HCO_3^-]}{[H^+]} = \frac{4.69 \times 10^{-11}(6.2 \times 10^{-12})}{[H^+] \qquad [H^+]} = \frac{2.9 \times 10^{-22}}{[H^+]^2}$$

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{[H^+]} + \frac{6.2 \times 10^{-12}}{[H^+]} + 2 \times \frac{2.9 \times 10^{-22}}{[H^+]^2} \approx \frac{6.2 \times 10^{-12}}{[H^+]} = [H^+]$$

$[H^+]^2 = 6.2 \times 10^{-12}$ $\qquad [H^+] = 2.5 \times 10^{-6}$ $\qquad$ pH = -log(2.5×10^{-6}) = **5.60**

Saturated Calcium Carbonate Solution



Calcium ions, Ca^{2+}, and carbonate ions, CO_3^{2-}, move out into solution.

Calcium ions, Ca^{2+}, and carbonate ions, CO_3^{2-}, in solution collide with the solid and return to the solid form.

In a saturated solution, the rate of solution equals the rate of return to the solid.

Calcium carbonate solid

Dissolution of solids

- In a saturated solution of calcium carbonate, the rate of solution and the rate of precipitation are equal, so the system is at equilibrium. The equilibrium constant for this process is called the solubility product, K_{sp}.

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

  $K_{sp} = [Ca^{+2}][CO_3^{-2}] = 4.47 \times 10^{-9}$ mole^2/liter^2 in fresh H_2O

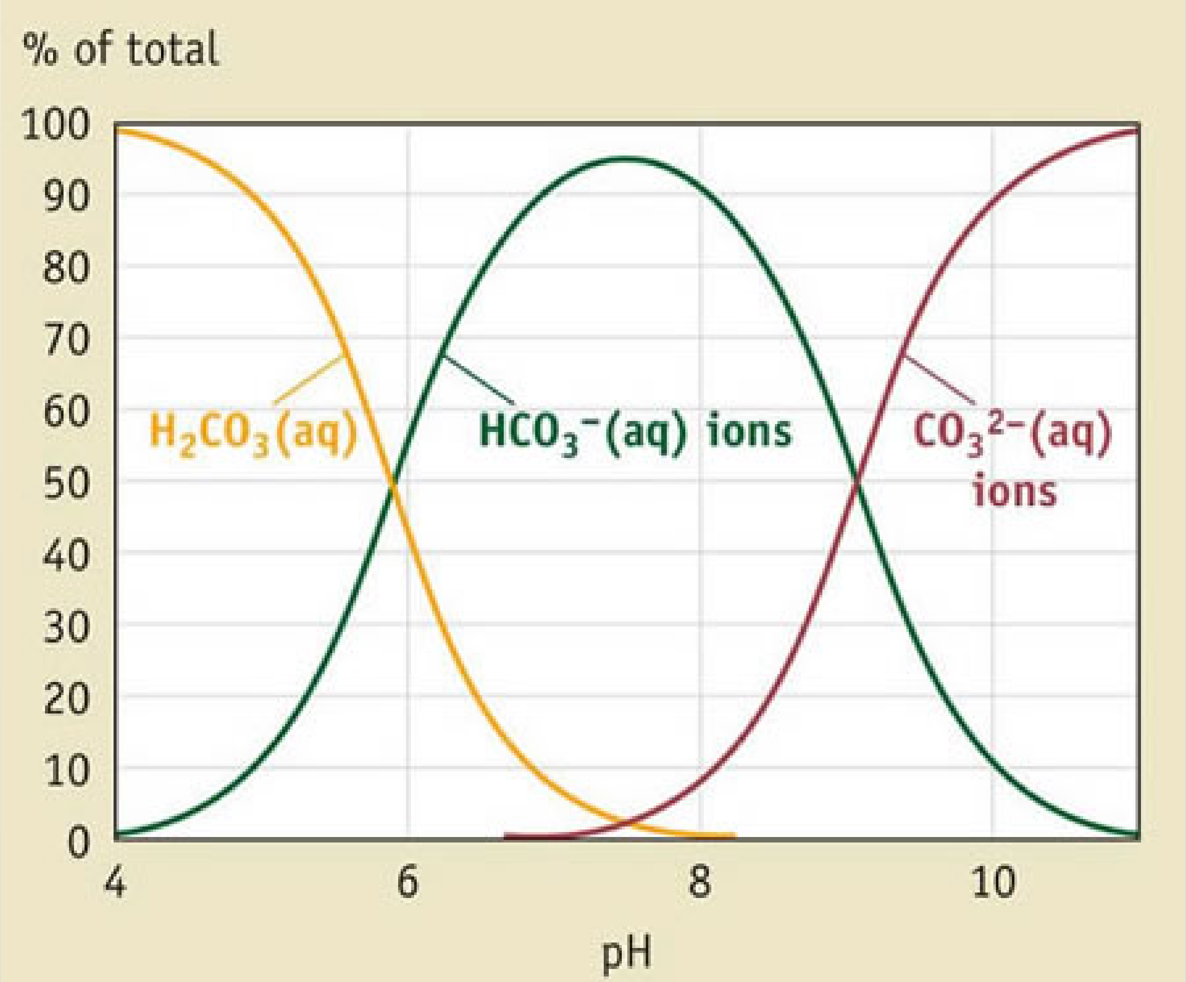
- If you have water in contact with the atmosphere and fully saturated with calcium carbonate, you have 5 unknowns in the charge balance equation and 5 equations to determine them.

  $[H^+] + 2[Ca^{+2}] = [OH^-] + [HCO_3^-] + 2[CO_3^{-2}]$

- If you solve this system, you find pH = 8.1, which is very close to the pH of seawater, which is not surprising since the ocean is saturated with dissolved seashells.

Carbonate Equilibria and pH

The following graph shows the variation in [H_2CO_3], [HCO_3^-], and [CO_3^{2-}] with changes in pH.



Carbonate Buffering

- Weathering reactions with carbonate minerals (calcite, dolomite, various limestones, etc.):

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

$$CaSiCO_3 + 2CO_2 + H_2O \rightleftharpoons Ca^{2+} + SiO_2 + 2HCO_3^-$$

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

- When acid is added to water, equilibria shift and bicarbonate neutralizes some of the acid:

$$HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2$$

- If soils and sediments are rich in carbonates, weathering will supply additional HCO_3^-

Alkalinity

- Alkalinity is a measure of the “buffering” or “acid-neutralizing capacity” (ANC) of a solution:

$$\mathrm{ANC} = [\mathrm{HCO_3^{-}}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^{-}}] - [\mathrm{H^{+}}]$$

- Water saturated with $CaCO_3$:

$$\mathrm{ANC} = 970 \times 10^{-6}\ \mathrm{Eq/L} = 970\ \mu\mathrm{eq/L}$$

  - For bases, an equivalent (Eq) is the amount of a substance which will react with one mole of hydronium ions (H_3O^+).
  - 1 mol CO_3^{2-} = 2 Eq CO_3^{2-}
- ANC depends on watershed soil characteristics.

Buffer Solutions

- A **buffer** is an aqueous solution a weak acid (H_2CO_3) and its conjugate base (HCO_3^-) or a weak base (CO_3^{2-}) and its conjugate acid (HCO_3^-).
  - Conjugate base = acid less one H^+
  - Conjugate base = base plus one H^+

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$[H^+] = K_{a1}\frac{[H_2CO_3]}{[HCO_3^-]}$$

$$[H^+] = K_a\frac{[\text{weak acid}]}{[\text{conjugate base}]}$$

- As long as there are significant concentrations of the weak acid (H_2CO_3) and the conjugate base (HCO_3^-), changing one or the other does not change the ratio of acid to base much so the $[H^+]$ and pH stay relatively constant.

Simplistic Calculation to Illustrate Buffering

- pH pristine natural water is about 5.6.
- Calculate the pH of a solution where enough strong acid is added to water to yield a 0.1 M H^+ solution.

  $pH = -\log(10^{-1}) = 1$

- Calculate the pH of a solution of 1 M H_2CO_3 and 1 M HCO_3^-.

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

$$[H^+] = 4.5 \times 10^{-7} \frac{[H_2CO_3]}{[HCO_3^-]} = 4.5 \times 10^{-7} \frac{1\ M\ H_2CO_3}{1\ M\ HCO_3^-}$$

$$[H^+] = -\log 4.5 \times 10^{-7} = \mathbf{6.35}$$

Simplistic Calculation to Illustrate Buffering

- Calculate the pH of a solution of 1 M H_2CO_3 and 1 M HCO_3^- when enough strong acid is added to the solution to make the solution 0.1 M strong acid.

$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$

$[HCO_3^-] = 1\text{ M} – 0.1\text{ M} = 0.9\text{ M } HCO_3^-$

$[H_2CO_3] = 1\text{ M} + 0.1\text{ M} = 1.1\text{ M } H_2CO_3$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

$$[H^+] = 4.5 \times 10^{-7} \frac{[H_2CO_3]}{[HCO_3^-]} = 4.5 \times 10^{-7} \frac{1.1\text{ M } H_2CO_3}{0.9\text{ M } HCO_3^-}$$

$$[H^+] = -\log 5.5 \times 10^{-7} = \mathbf{6.26}$$

Buffer Solution – Base and Conjugate Acid

- A lake might contain a buffer solution of the base carbonate from the solution of calcium carbonate in limestone and hydrogen carbonate in runoff from weathering of the limestone.

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

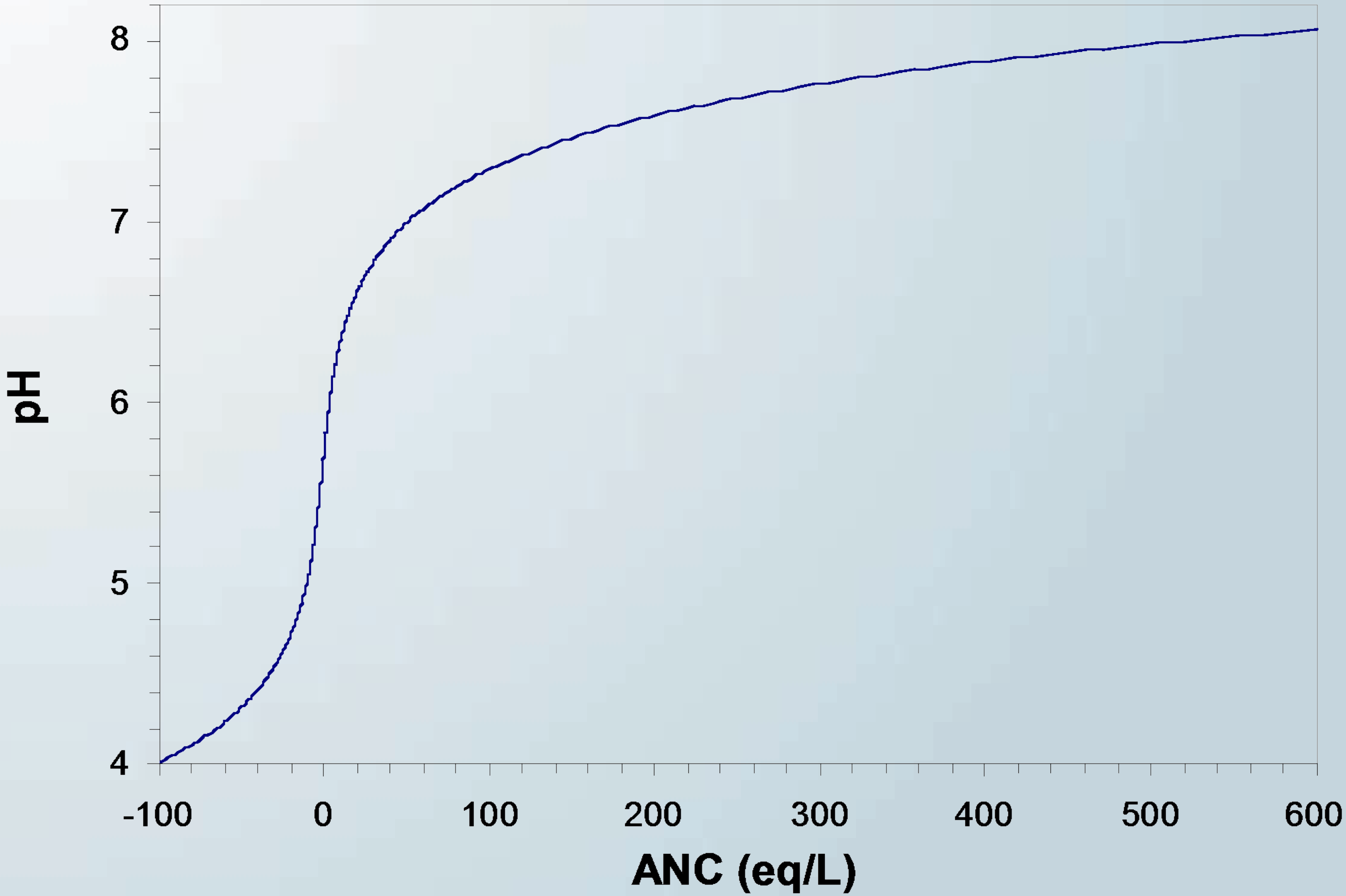
  $$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^{-}$$

- Many life forms thrive only in a relatively small pH range so buffer solutions are important for maintaining a near constant pH.

Alkalinity

- Surface water with ANC ≈200 μeq/L is normal; healthy lakes have ANC > 100 μeq/L; water with ANC < 50 μeq/L is highly sensitive to acidification.
- Acidified waters have ANC < 0 μeq/L.
- As acidity [H^+] is added to a lake, ANC is consumed. The pH decreases slowly at first, then rapidly as the alkalinity is exhausted.

Titration Curve



Coral Reefs

- Coral reefs - among the most biologically diverse and economically important ecosystems
- Important for
  - fisheries,
  - coastal protection,
  - building materials,
  - new biochemical compounds,
  - tourism

Coral Reefs Under Rapid Climate Change and Ocean Acidification
Ove Hoegh-Guldberg, et al, *Science 14 December 2007: Vol. 318 no. 5857 pp. 1737-1742*

Threat to Coral Reefs

- About 25% (2.2 Pg C year^{-1}) of the CO_2 emitted from all anthropogenic sources enters the ocean.
- CO_2 dissolving in seawater has
  - Decreased pH by about 0.1 pH unit
  - Decreased seawater carbonate concentrations by ~30 mmol/kg seawater, reducing the availability of carbonate to biological systems and reducing the rate of calcification of marine organisms such as reef-building corals

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Threat to Coral Reefs

- Doubling of pre-industrial $[CO_2]_{atm}$ to 560 ppm decreases coral calcification and growth by up to 40% through the inhibition of aragonite formation (the principal crystalline form of calcium carbonate deposited in coral skeletons).
- Carbonate accretion on coral reefs approaches zero or becomes negative when $[CO_2]_{atm}$ approaches 480 ppm and carbonate ion concentrations drop below 200 mmol kg^{-1} in most of the global ocean.

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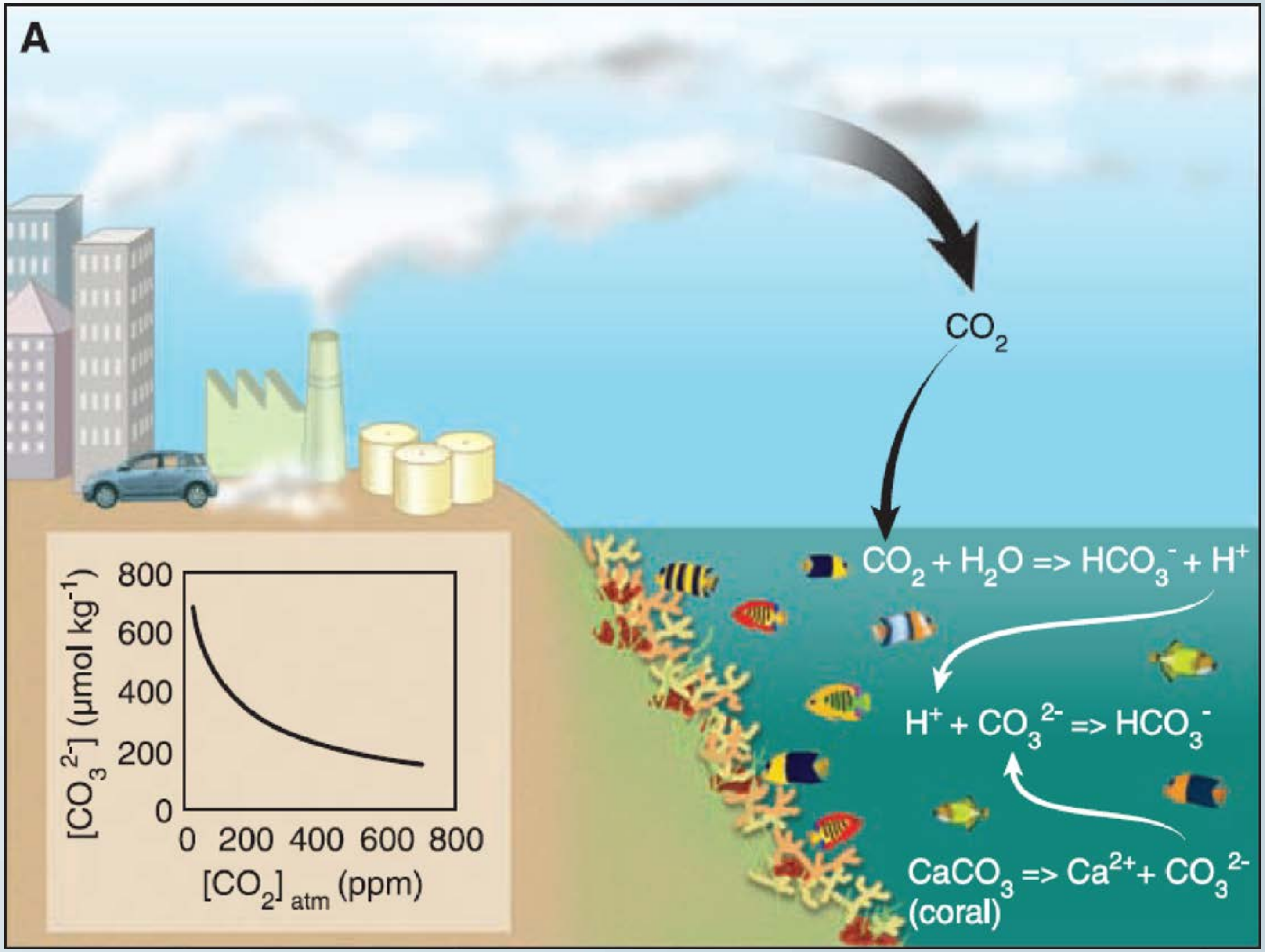

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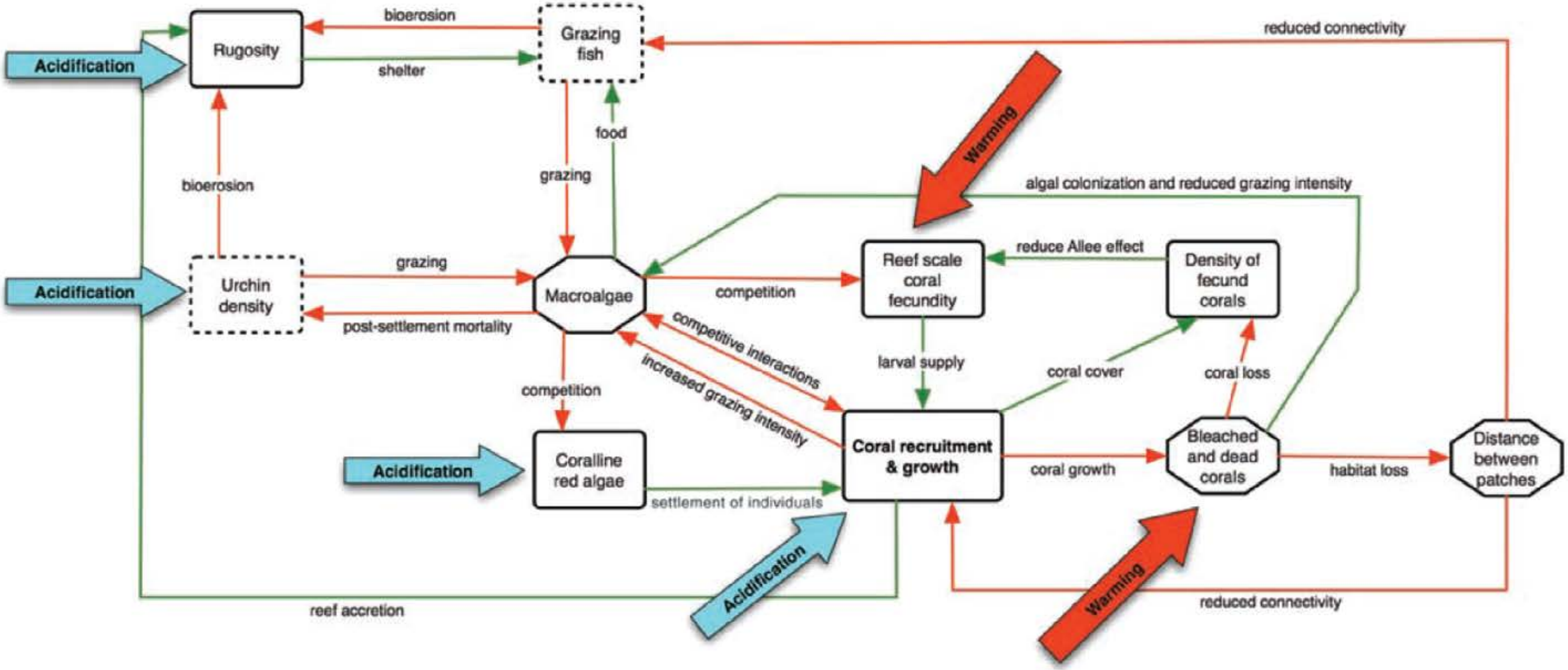

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Threat to Coral Reefs

- Aragonite - the principal crystalline form of calcium carbonate deposited in coral skeletons.
- $\Omega_{\text{aragonite}} = ([\text{Ca}^{2+}]\cdot[\text{CO}_3^{2-}])/K_{\text{sp}}$ aragonite) is used to describe aragonite levels.
- Before the Industrial Revolution (280 ppm), nearly all shallow-water coral reefs had $\Omega_{\text{aragonite}} > 3.25$ (blue regions in the figure), which is the minimum $\Omega_{\text{aragonite}}$ that coral reefs are associated with today; the number of existing coral reefs with this minimum aragonite saturation decreases rapidly as $[\text{CO}_2]_{\text{atm}}$ increases.

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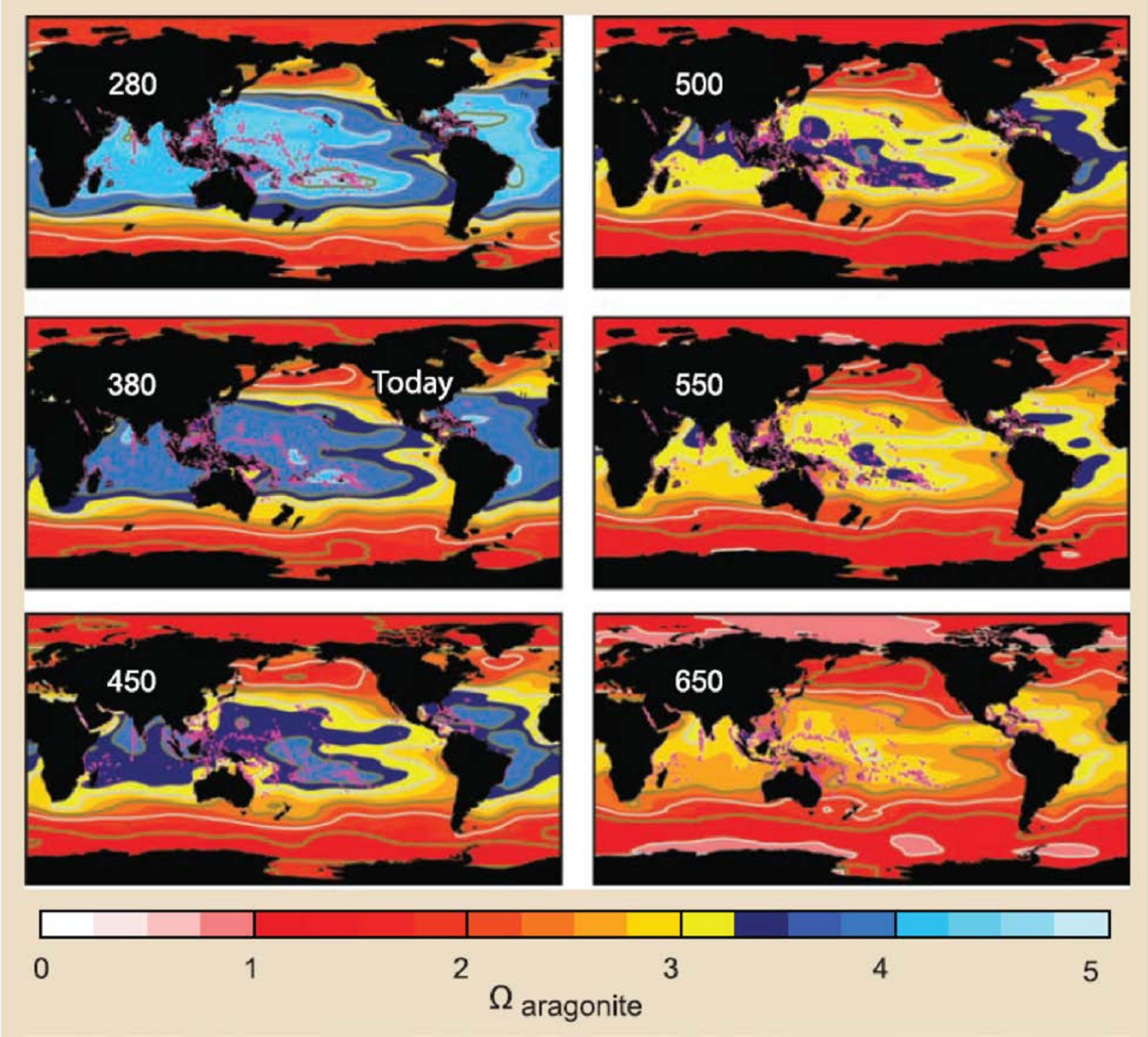
Threat to Coral Reefs



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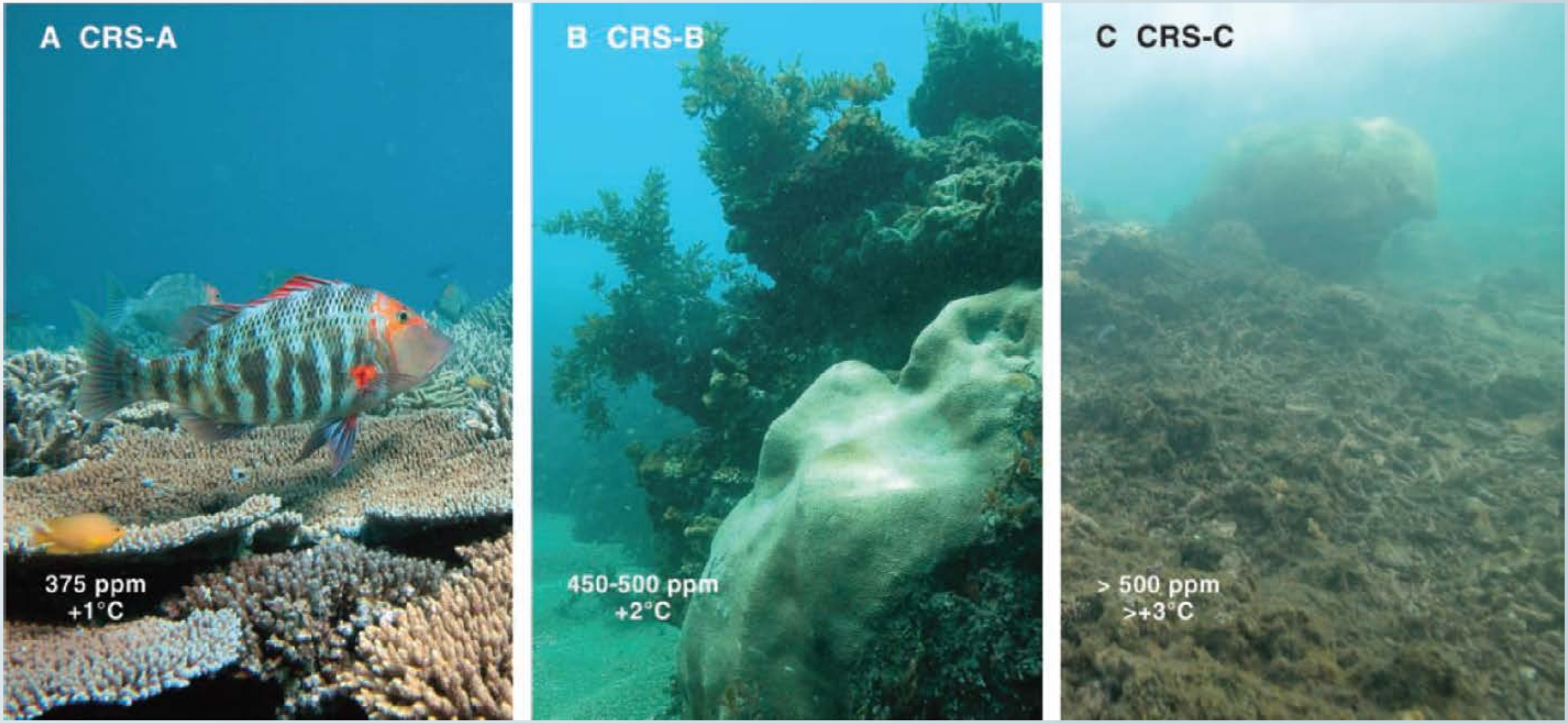

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