The Creation Of Limestone Cave

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Limestone cave

- **Limestone** cave the result of chemical weathering that occur because of the equilibrium reaction between CaCO₃ with CO₂ and H₂O.
- Rain water is acidic.
Limestone

• Main component of limestone is: CaCO$_3$
• CaCO$_3$:
  – Ionic compound that contain anion of a weak acid
  – Slightly soluble in water (Ksp = 3.3x10$^{-9}$)
  – Soluble in acidic solution
2 key facts

1. In natural water, CO$_2$ gas in equilibrium with CO$_2$ (aq)

$$\text{H}_2\text{O}$$

$$\text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq) \quad \ldots \ldots \text{eq. 1}$$

The concentration of CO$_2$ in water is proportional to the partial pressure of CO$_2(g)$ in contact with the water (Henry`s Law)

$$[\text{CO}_2(g)] \approx P\text{CO}_2$$
2 key facts

1. In natural water, CO\textsubscript{2} gas in equilibrium with CO\textsubscript{2} (aq)

   - Because of continual release of CO\textsubscript{2} within the earth (out gassing), \( P_{CO_2} \) in soil trapped is higher than \( P_{CO_2} \) in the atmosphere
2. The present of $\text{H}_3\text{O}^+$ (aq) increases the solubility of ionic compound that contain the anion of a weak acid.

- The reaction of $\text{CO}_2$ and $\text{H}_2\text{O}$ produces $\text{H}_3\text{O}^+$

$$\text{CO}_2(\text{aq}) + 2\text{H}_2\text{O}(\ell) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + 2\text{HCO}_3^-(\text{aq})$$
2. The present of $\text{H}_3\text{O}^+(\text{aq})$ increases the solubility of ionic compound that contain the anion of a weak acid.
   - The present of $\text{CO}_2(\text{aq})$ leads to the formation of $\text{H}_3\text{O}^+$, which increases the solubility of $\text{CaCO}_3$
     
     $$\text{CaCO}_3(\text{s}) + \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) \leftrightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{HCO}_3^-(\text{aq}) \ldots \ldots \text{eq.2}$$
\[ P \text{CO}_2 \text{(sta)} > P \text{CO}_2 \text{ (atm)} \]

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow [\text{CO}_2] \gg \gg \]

Eq. 1 shift to right

Solution more acidic

Eq. 2 shift to right

\[ \text{Ca} \text{(HCO}_3\text{)}_2 \rightarrow \text{CaCO}_3 \text{ dissolved} \rightarrow \text{Ca} \text{(HCO}_3\text{)}_2 \]

Limestone cave formed
Ca(HCO_3)_2 flow

CO_2 come out of solution

eq. 1 shift to left

P CO_2(sta) > P CO_2 (atm)

CO_2 (sta) meet air

CaCO_3 precipitated

stalagtite and stalagmite formed on ceiling and the floor below