EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Geochemistry on the Earth's surface for analytical geochemists

3a.
Carbonate system in the environment
&
Geochemistry of karst processes

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

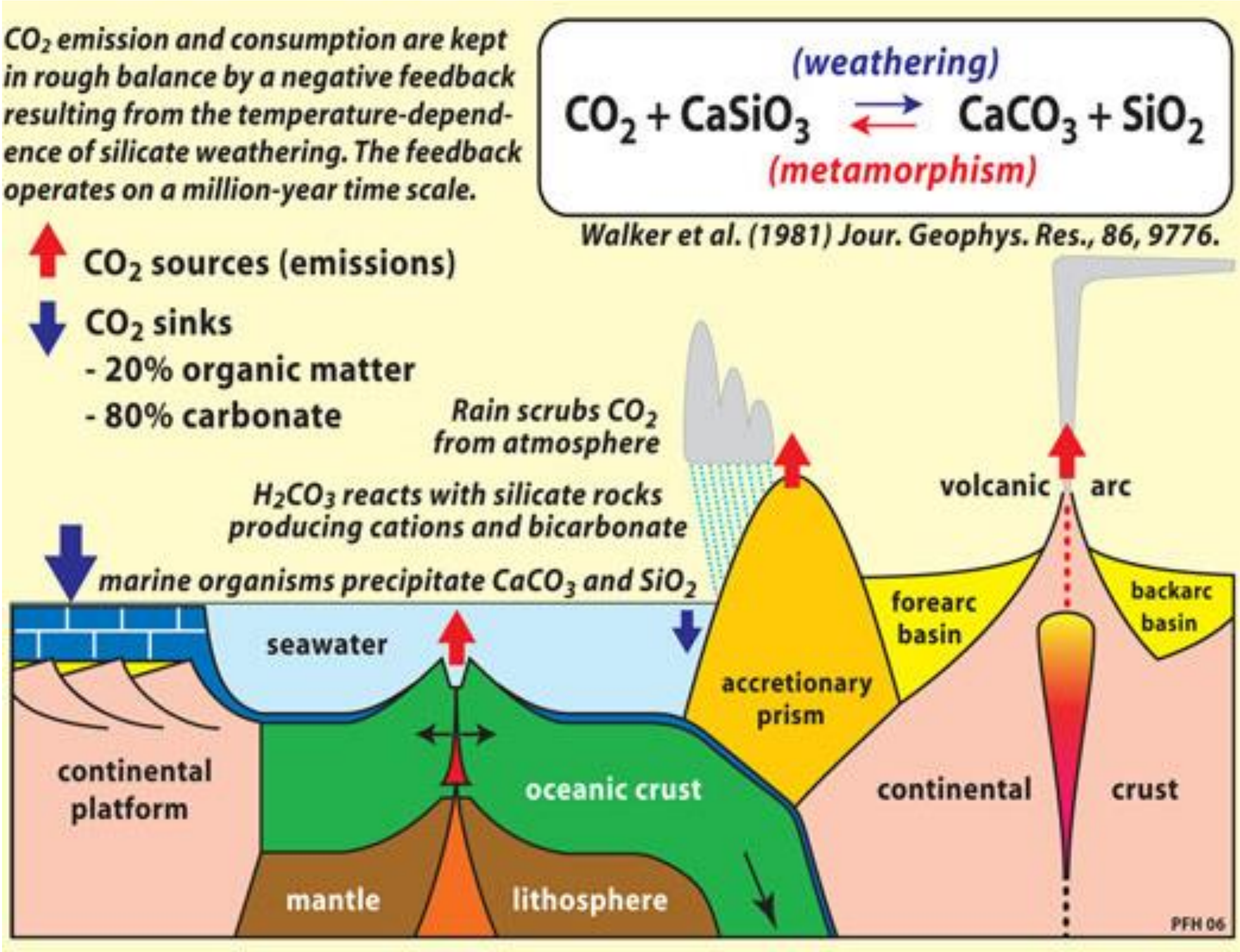
Outline topic

- Importance
- Carbonate system
- Alkalinity and acidity
- Geochemistry of karst processes
  - Equilibrium water-air-mineral
  - Karst formations

Carbonate system

Carbonate system

- Based on CO_2 and derived compounds
- Essential role in weathering
- Greenhouse gas – impact on the climate
- Organic matter – biosphere
- Biogeochemistry



CO_2 emission and consumption are kept in rough balance by a negative feedback resulting from the temperature-dependence of silicate weathering. The feedback operates on a million-year time scale.

$$CO_2 + CaSiO_3 \underset{\text{(metamorphism)}}{\overset{\text{(weathering)}}{\rightleftarrows}} CaCO_3 + SiO_2$$

Walker et al. (1981) Jour. Geophys. Res., 86, 9776.

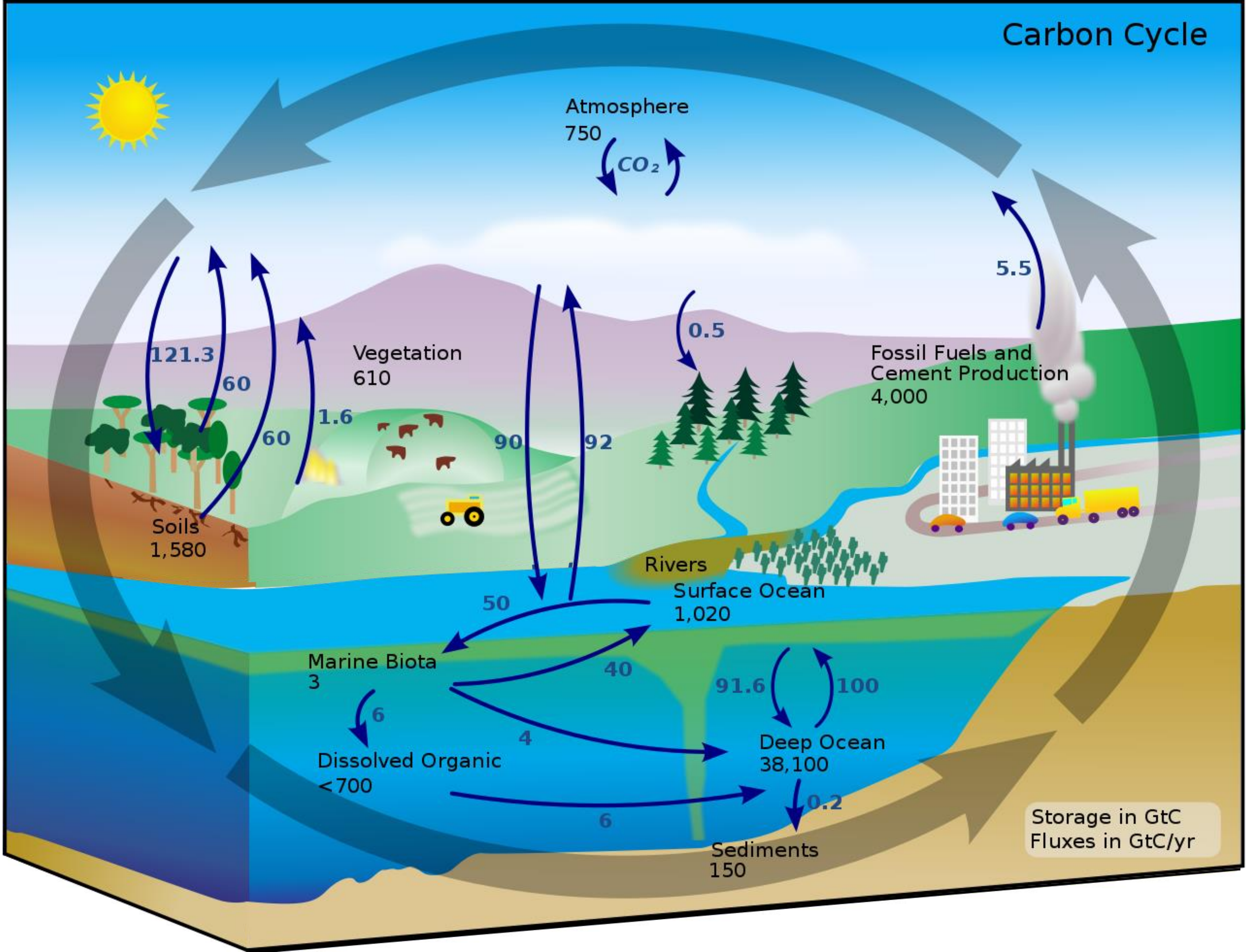
- 🡅 CO_2 sources (emissions)
- 🡇 CO_2 sinks
  - 20% organic matter
  - 80% carbonate

Rain scrubs CO_2 from atmosphere

H_2CO_3 reacts with silicate rocks producing cations and bicarbonate

marine organisms precipitate $CaCO_3$ and SiO_2

Snowball Earth.org


Carbon Cycle
Atmosphere
750
CO_2
121.3
60
60
1.6
Vegetation
610
90
92
0.5
5.5
Fossil Fuels and
Cement Production
4,000
Soils
1,580
Rivers
Surface Ocean
1,020
50
40
Marine Biota
3
6
4
91.6
100
Deep Ocean
38,100
Dissolved Organic
<700
6
0.2
Sediments
150
Storage in GtC
Fluxes in GtC/yr

Carbonates

- CO_2(g) dissolves into water proportionally to the partial pressure in the air (P_{CO2})

$$\mathrm{CO_2}(g) \leftrightarrow \mathrm{CO_2}(aq)$$

- CO_2reacts with water to form acid

$$\mathrm{CO_2}(aq) + \mathrm{H_2O}(l) = \mathrm{H_2CO_3}(aq)$$

- CO_2(aq) is about 600x more abundant, yet for simplicity we express all CO_2 as H_2CO_3*

$$\mathrm{H_2CO_3^*}\ (aq) = \mathrm{CO_2}(aq) + \mathrm{H_2CO_3}(aq)$$

Carbonic acid

- We can simplify the dissolution to:

$$\mathrm{CO_2}(g) + \mathrm{H_2O}(l) = \mathrm{H_2CO_3^*}(aq)$$

- With the equilibrium constant

$$\mathrm{K}_{CO_2} = \frac{a_{H2CO3(aq)}}{P_{CO2}}$$

- Each P_{CO2} thus corresponds to a specific a_{H2CO3*}
- CO_2 content in water is often expressed as P_{CO2} even if the gas phase isn‘t present

Dissociation

- Carbonic acid dissociates to the 1st degree:

$$\mathrm{H_2CO_3^* = HCO_3^- + H^+}$$

$$\mathrm{K_1} = \frac{a_{\mathrm{HCO_3^-}}\ a_{\mathrm{H^+}}}{a_{\mathrm{H_2CO_3^*}}} = 10^{-6.35}$$

- And to the 2nd degree:

$$\mathrm{HCO_3^- = CO_3^{2-} + H^+}$$

$$\mathrm{K_2} = \frac{a_{\mathrm{CO_3^{2-}}}\ a_{\mathrm{H^+}}}{a_{\mathrm{HCO_3^-}}} = 10^{-10.33}$$

Speciation

- $a_{\mathrm{H2CO3*}}/a_{\mathrm{HCO3-}}$ and $a_{\mathrm{HCO3-}}/a_{\mathrm{CO32-}}$ are pH dependent and can be simplified to:

$$\frac{a_{\mathrm{H_2CO_3^*}}}{a_{\mathrm{HCO_3^-}}} = \frac{a_{\mathrm{H}^+}}{\mathrm{K_1}} = 10^{+6,35}\ a_{\mathrm{H}^+} \text{at 25 °C}$$

- H_2CO_3* and HCO_3^- are in equilibrium at pH = 6.35 (neglecting CO_3^{2-})

Speciation

- Analogously for $a_{\text{HCO3−}}/a_{\text{CO32−}}$

$$\frac{a_{\mathrm{HCO_3^-}}}{a_{\mathrm{CO_3^{2-}}}} = \frac{a_{\mathrm{H}^+}}{\mathrm{K_2}} = 10^{+10{,}33}\ a_{\mathrm{H}^+} \text{at 25 °C}$$

- CO_3^{2-} and HCO_3^- are in equilibrium at pH = 10.33 (neglecting H_2CO_3*)

Carbonate speciation

- In natural waters dominates HCO_3^-

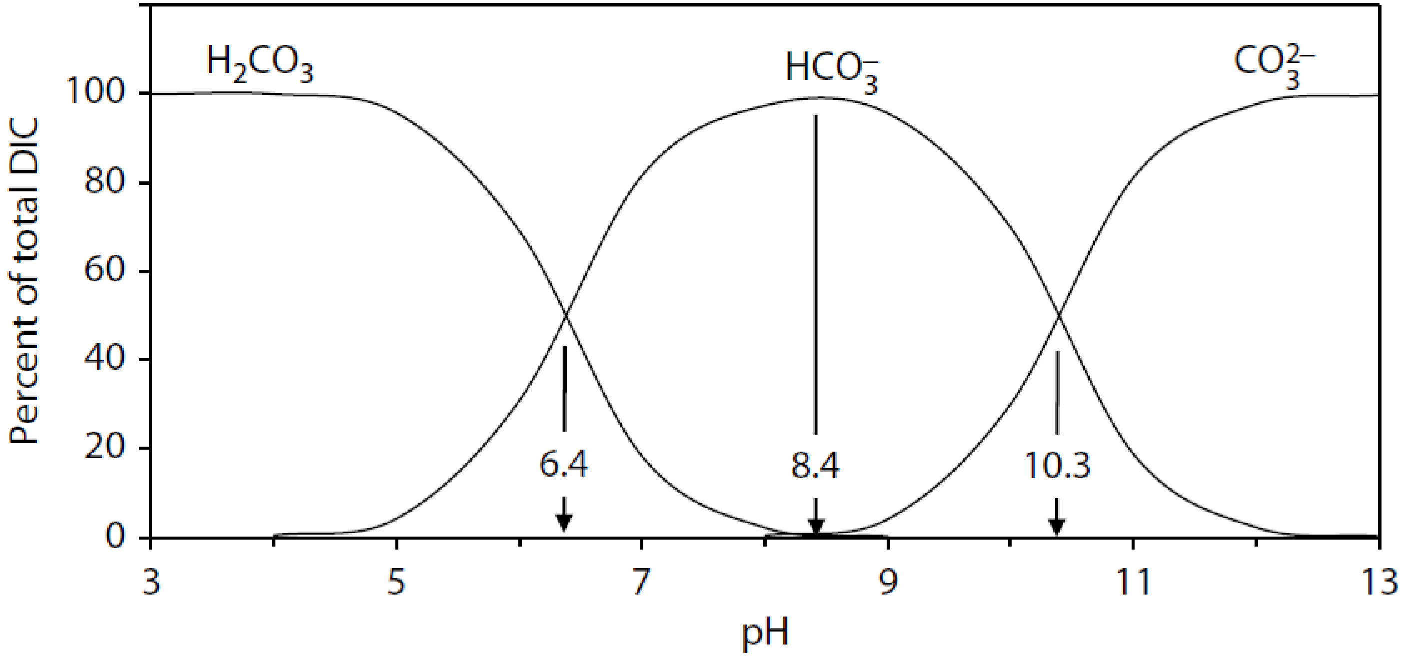


FIGURE 3.15 Relative distribution of dissolved inorganic carbon species in pure water as a function of pH, at 25°C.

Adapted from Clark (2015)

Example 1

- What will be the pH of water in equilibrium with atmospheric CO_2 at 25 °C, assuming ideal behavior and no other dissolved substances?
- The partial pressure of CO_2 is 4×10^{-4}
- $K_{CO2} = 10^{-1,47}$
- $K_1 = 10^{-6,35}$
- Based on the charge balance

$$[H^+] = [OH^-] + [HC03^-]\, {}^{+}2[CO_3{}^{2-}]$$

Calcium carbonates

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

- The solubility product is

$\mathrm{K}_c = a_{\mathrm{Ca^{2+}}}\, a_{\mathrm{CO_3^{2-}}} = 10^{-8{,}48}$ **calcite** (25 °C)

$\mathrm{K}_a = a_{\mathrm{Ca^{2+}}}\, a_{\mathrm{CO_3^{2-}}} = 10^{-8{,}34}$ **aragonite** (25°C)

- We can solve the systems by adding the appropriate equations to the carbonate system
  - K_{CO2}, K_1, K_2, K_W, K_c, PEN and one other condition
    - Fixed P_{CO2} for an open system or sum of carbonates for a closed system

Example 2

- What will be the pH of water in equilibrium with atmospheric CO_2 and calcite at 25 °C, assuming ideal behavior and no other solutes?
  - 6 unknowns (P_{CO2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ and $[H^+]$)
  - 6 equations (P_{CO2}, K_{CO2}, K_1, K_2, K_C and charge balance)

$$P_{CO2} = 10^{-3.4}$$

Charge balance: $[H^+]+2[Ca2^+]=[HCO_3^-]+2[CO_3^{2-}]+[OH^-]$

- At neutral pH simplified to

$$2[Ca2^+] = [HCO3^-]$$

- By substituting the equations, we express $[H^+]$

Example 2

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$$P_{CO2} = 10^{-3.4}$$

Charge balance: $[H^+]+2[Ca2^+]=[HCO_3^-]+2[CO_3^{2-}]+[OH^-]$

- At neutral pH simplified to

$$2[Ca2^+] =[HCO3^-]$$

- By substituting the equations, we express $[H^+]$
- $[H^+] = 10^{-8.2}$ pH = 8.2

Weathering of carbonates

GEOCHEMISTRY OF KARST PROCESSES

The importance of karst

- Landscape system
- Cultural-economic
  - Tourism, aesthetic significance
  - Source of raw materials (limestone, iron ore, wood)
  - Agriculture
  - Groundwater collectors
- A source of information about the environment in the geological past

Source: http://www.slovenia-explorer.com/wp-content/uploads/6-Predjama-castle_Predjama-castle_Postojna-cave9.jpg

Predjama Castle (SLO)

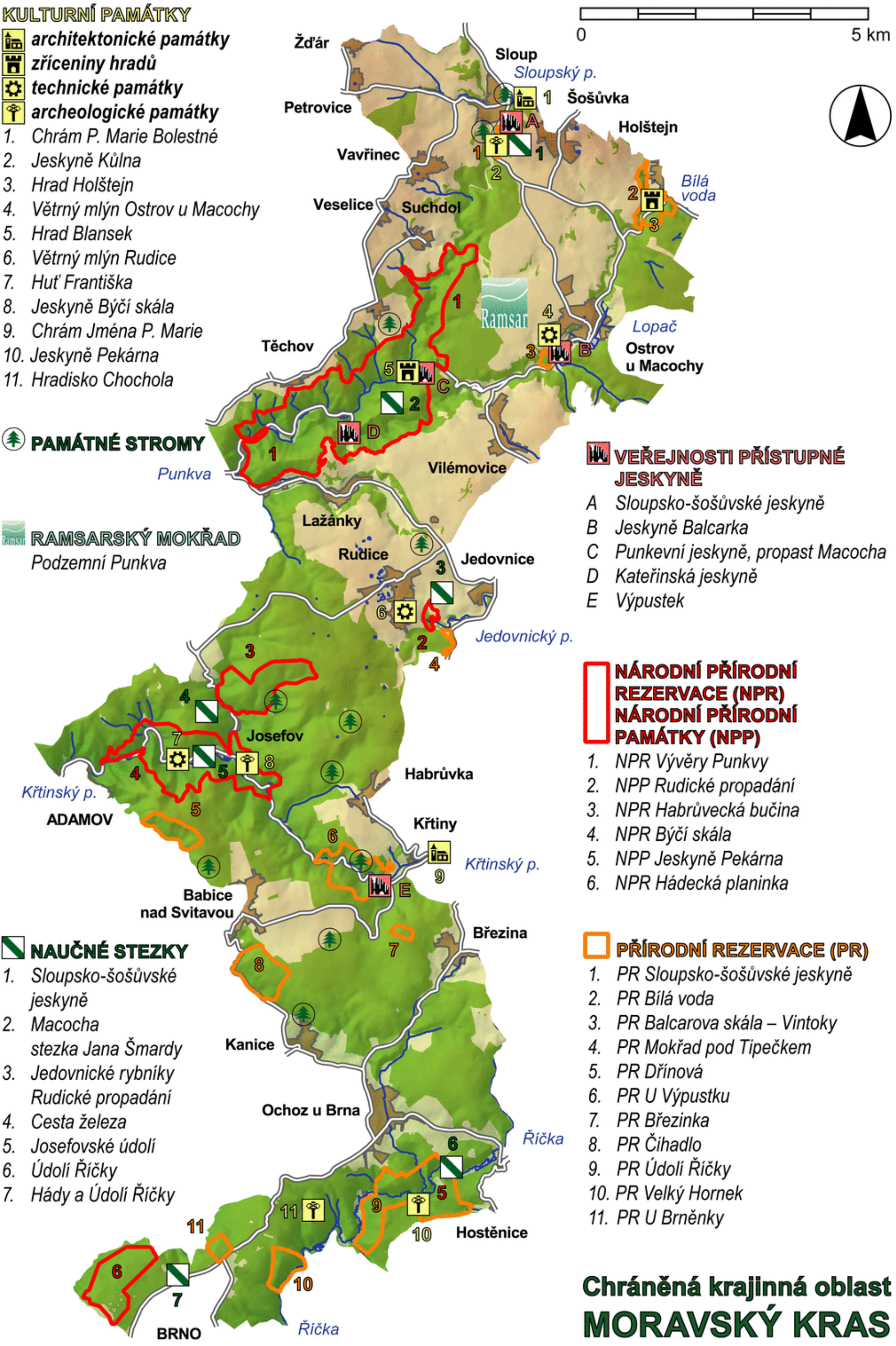
Karst

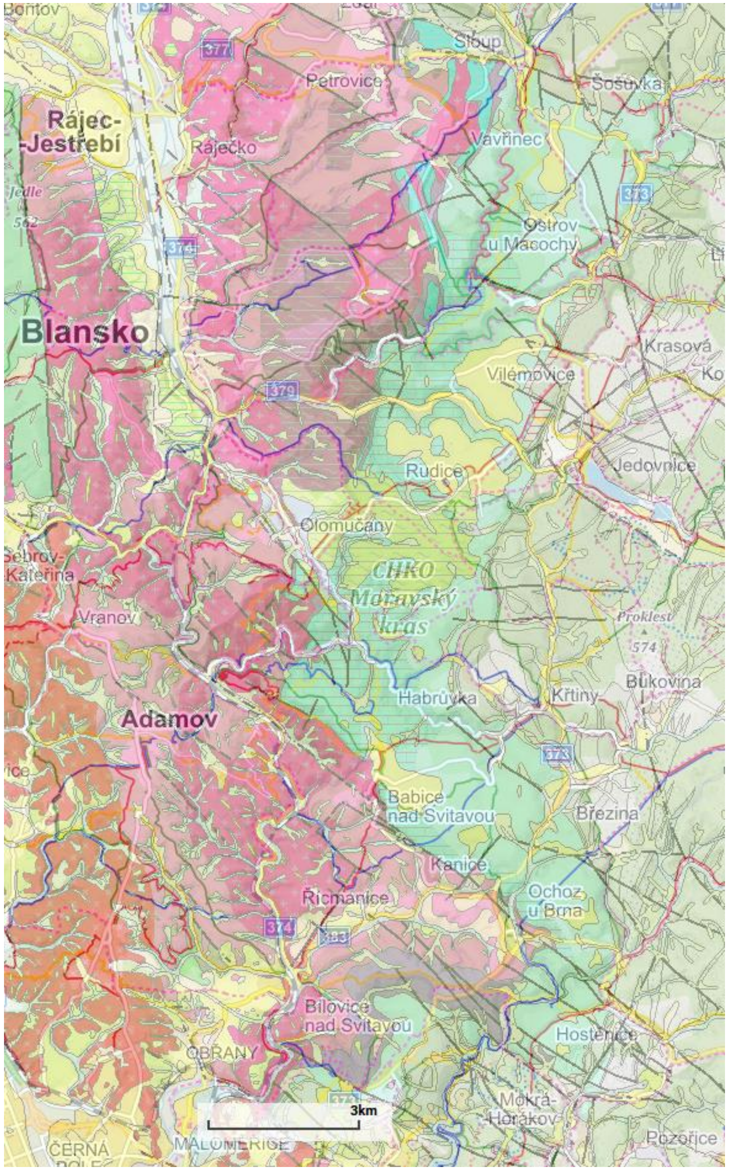
- Geological formation
- A landscape formed by the dissolution of the bedrock
    - Mostly carbonate rock, but evaporites as-well
- Key role of CO_2

Source: http://wordsmith.org/words/images/karst_large.

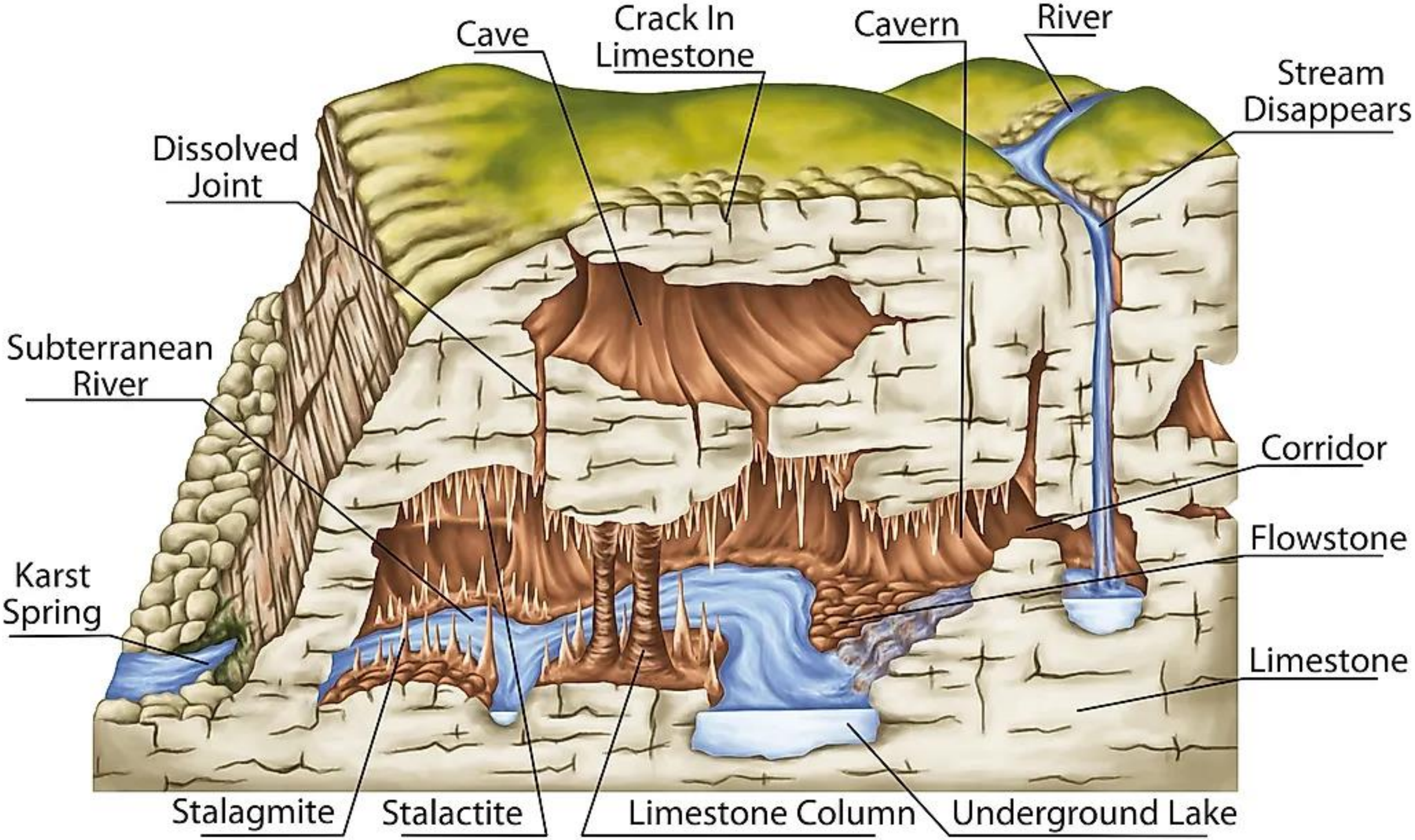
Karst (SLO)

Moravian karst





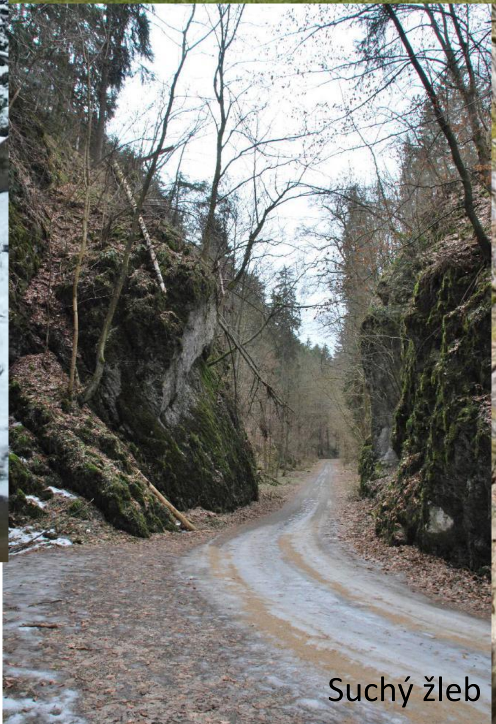
Karst phenomena



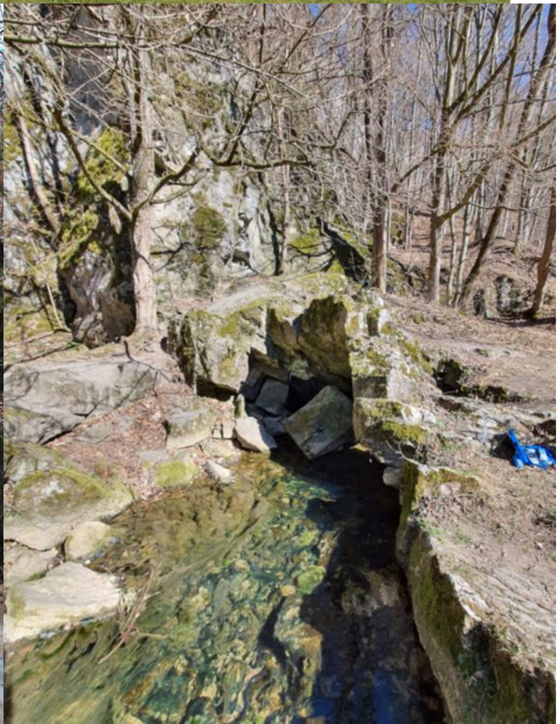
Surface landforms

Sinkhole

Rudické propadání



Suchý žleb



Vývěr Jedovnického potoka

Surface landforms

Autor: User:Serinde – Vlastné dielo, CC BY 2.5, https://commons.wikimedia.org/w/index.php?curid=170897

Underground phenomena

Kateřinská jeskyně

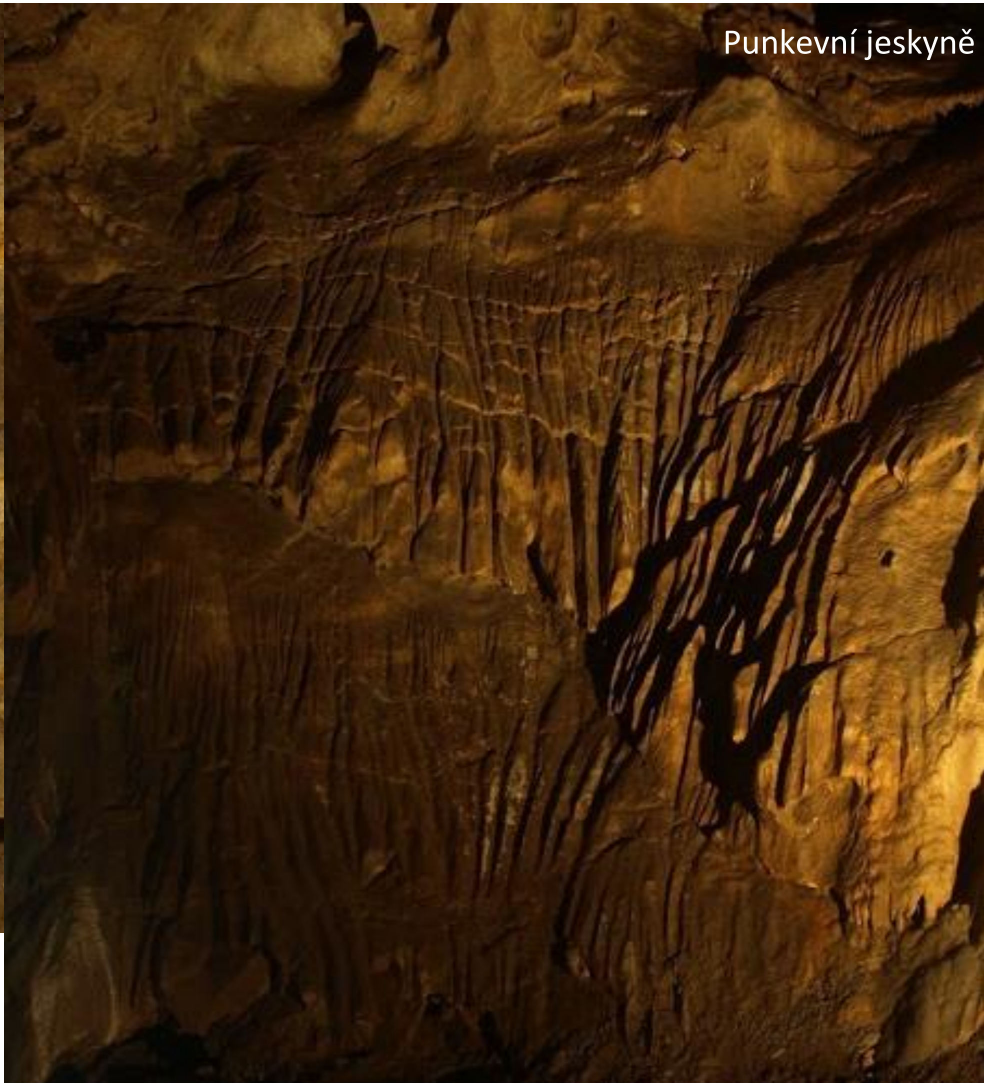
Caves

Punkevní jeskyně

Jeskyně Jáchymka

Corrosion

Císařská jeskyně



Punkevní jeskyně

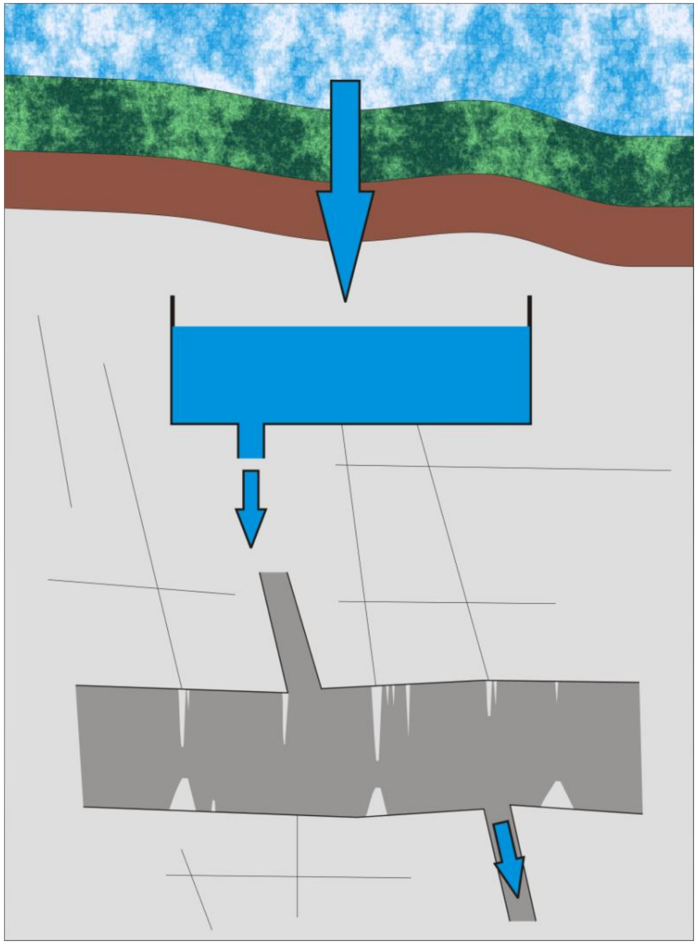
Cave sediments

- Cave deposits:
  - allochthonous (sand, clay)
  - autochthonous (cave sinters – **speleothems**)

Holstein Cave

By chris 論. Ampliated by Nachosan - Own work, CC BY 3.0, https://commons.wikimedia.org/w/index.php?curid=8300377

Water in karst



An ideal path of water through karst

- Infiltration
- Flow through soil
- Water retention in epikarst
- Flow along fissures
- Discharge into the cave
- Drainage into phreatic zone

Karst processes

- Soil CO_2 dissolution

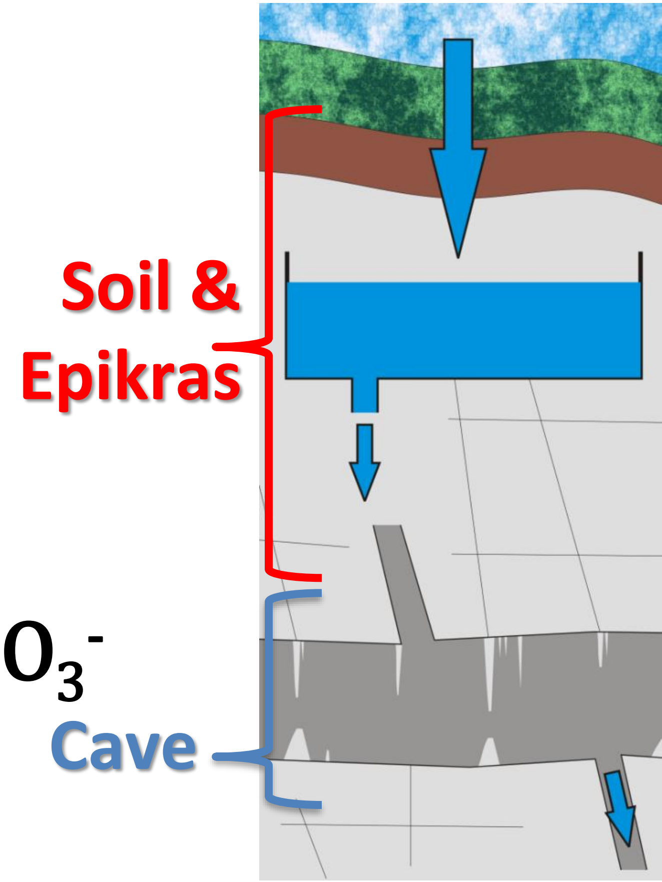
$$H_2O+CO_2 \rightleftarrows H_2CO_3^*$$

- CO_2 degassing

- Carbonate rock dissolution

$$CaCO_3+H_2CO_3 \rightleftarrows Ca^{2+}+2HCO_3^-$$

- Calcite precipitation



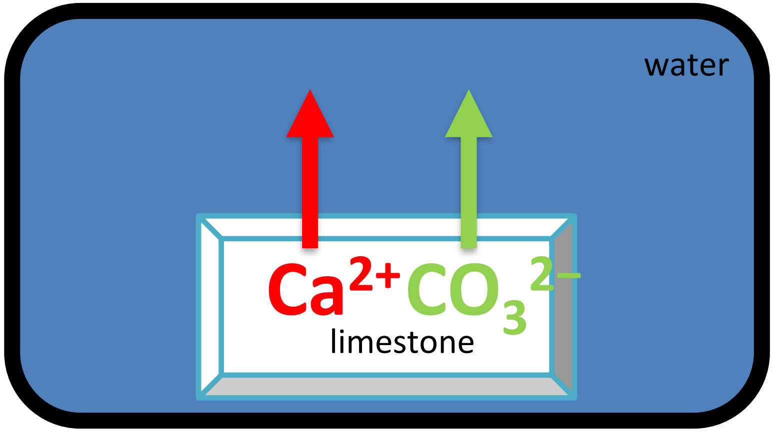
Open/closed system

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

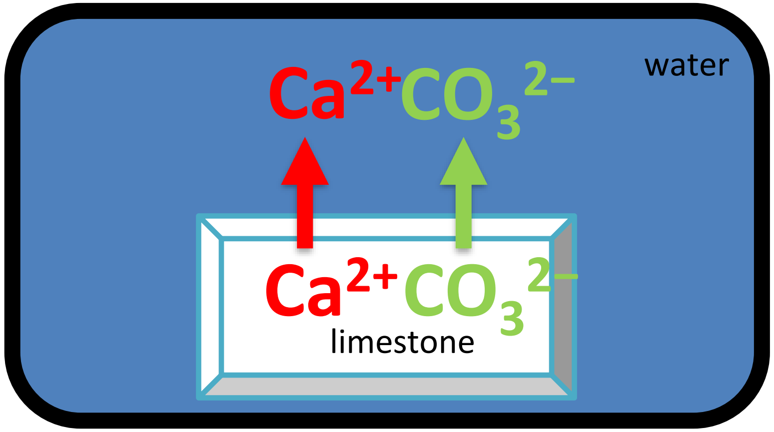
- **Open system**: P_{CO2} of the water remains constant, CO_2 from air replaces CO_2 consumed by dissolution
- **Closed system**: The ammount of calcite solution can dissolve is limited by the CO_2 initially present in the water

Dissolution

Closed system



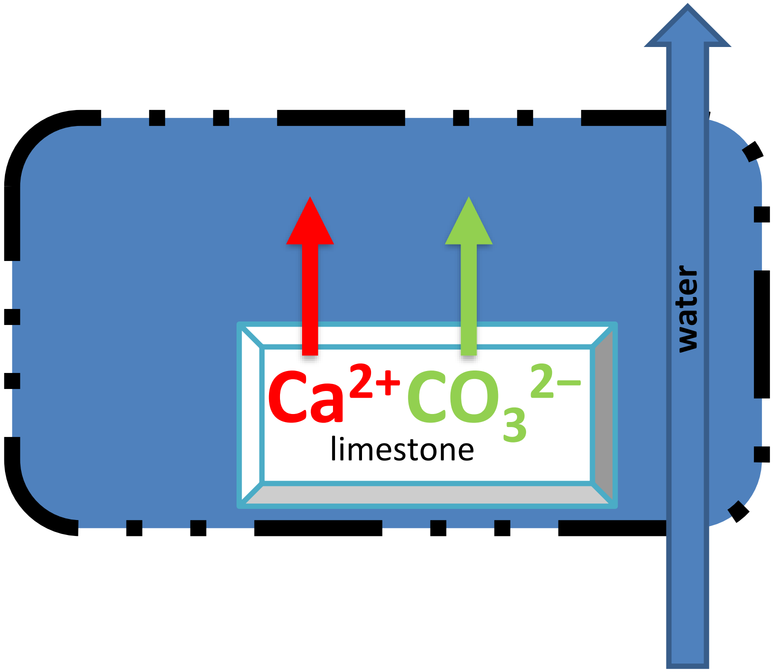
Equlibrium



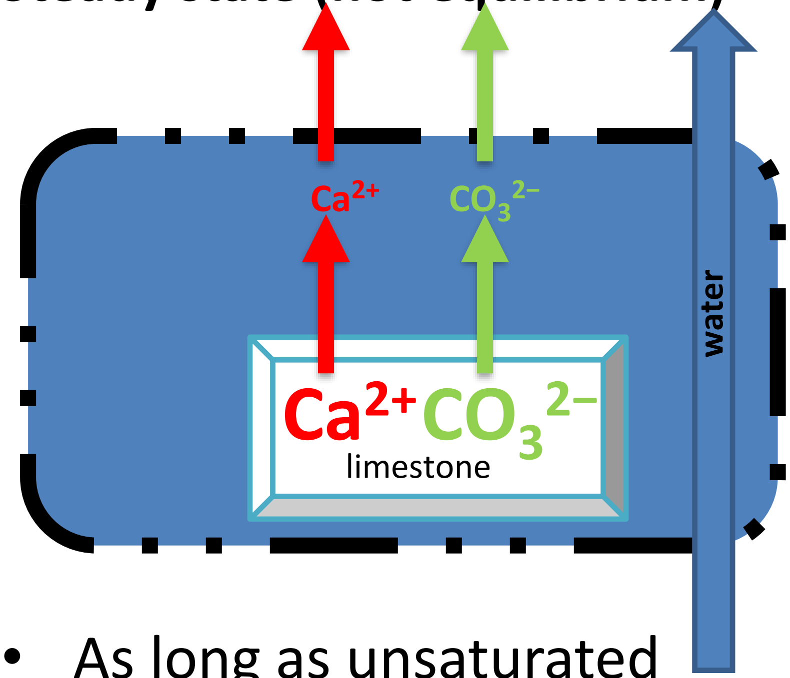
- Only a small amount of limestone dissolves.

Dissolution

Open system



Steady state (not equilibrium)



- As long as unsaturated water flows, it can dissolve limestone.

- The amount of dissolved calcite depends critically on the availability of the gas phase with CO_2 at dissolution

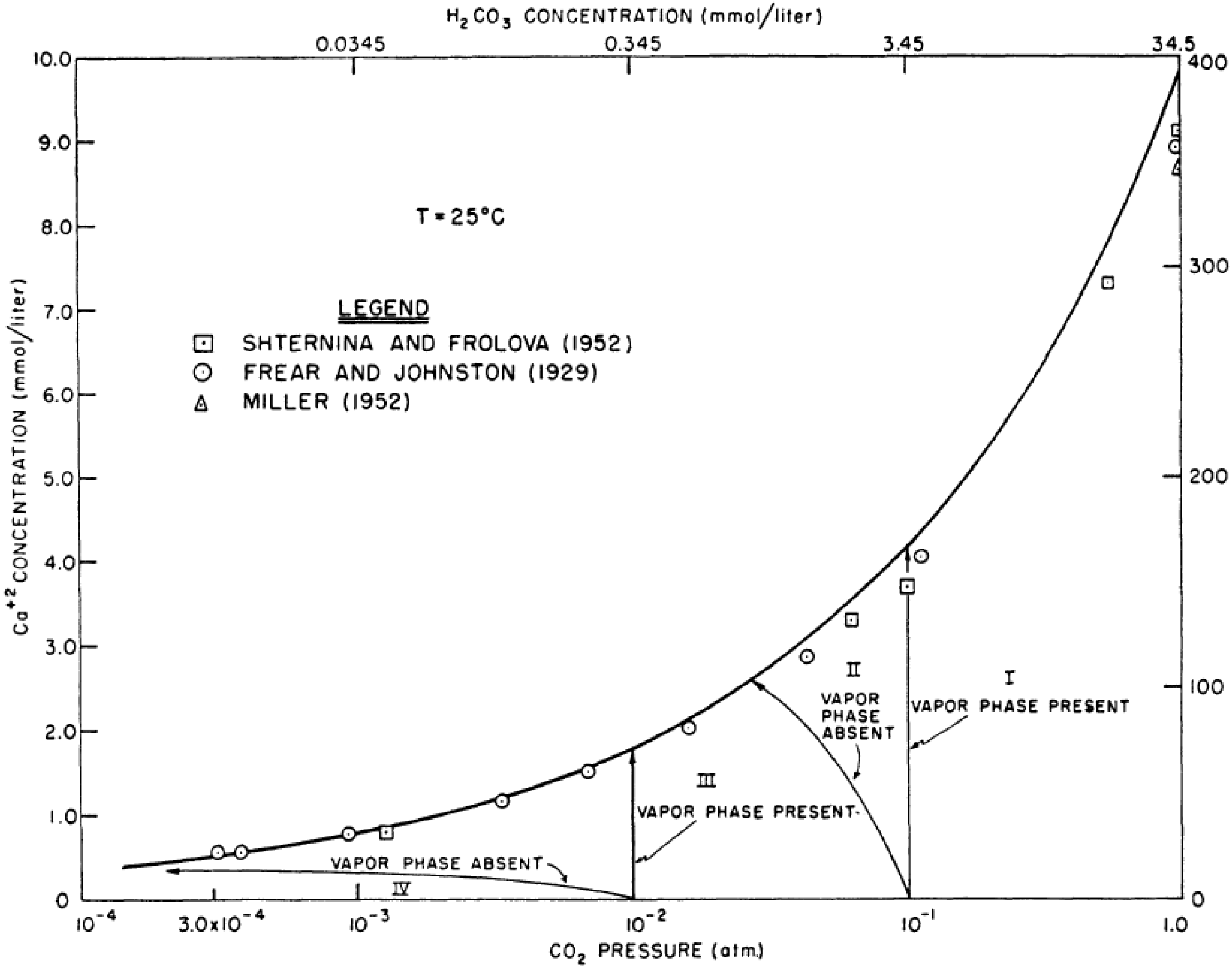


FIG. 2.—Changes in composition of carbonated water during equilibration with calcite at 25° C. in the presence and in the absence of a vapor phase. Curves I and II describe the behavior of a solution which was originally in equilibrium with a vapor phase with a CO_2 pressure of 0.10 atm., curves III and IV describe the behavior of a solution that was originally in equilibrium with a vapor phase with a CO_2 pressure of 0.01 atm.

Holland et al. (1964)

Example 3

- Pure water in equilibrium with $P_{CO2} = 10^{-2}$
  a) How much calcite will be dissolved in a closed system?

6 unknowns (P_{CO2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ a $[H^+]$)

6 equations (K_{CO2}, K_1, K_2, K_C, Ch. Bal. a ΣCO_2)

$\Sigma CO_2 = \Sigma CO_2^o + \Sigma CO_{2\ diss}$

$\Sigma CO_2 = [H_2CO_3^*]^o + [Ca^{2+}]$

We assume negligible $[CO_3^{2-}]$ in ΣCO_2 and get

$[H_2CO_3^*]^o = [HCO_3^-] + [H_2CO_3^*] - [Ca^{2+}]$

Example 3

- Pure water in equilibrium with $P_{CO2} = 10^{-2}$
  a) How much calcite will appear in a closed system?

  6 unknowns (P_{CO2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ and $[H^+]$)

  6 equations (K_{CO2}, K_1, K_2, K_C, PEN and ΣCO_2)

  $\Sigma CO_2 = \Sigma CO_2{}^o + \Sigma CO_{2\,diss}$

  $\Sigma CO_2 = [H_2CO_3^*]^o + [Ca^{2+}]$

  We assume negligible $[CO_3^{2-}]$ in ΣCO_2 and obtain

  $[H_2CO_3^*]^o = [HCO_3^-] + [H_2CO_3^*] - [Ca^{2+}]$

  Substituting the remaining equation gives

  $$[Ca^{2+}] = 3.34 \times 10^{-4}\ \text{mol/l}$$

  Approximately 33.4 mg of calcite is dissolved per liter of water

Example 3

- Pure water in equilibrium with $P_{CO2} = 10^{-2}$
  b) How much do you appear in the open system?
  - A system we have already dealt with

    6 neznámých (P_{CO2}, $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[Ca^{2+}]$ a $[H^+]$)

    6 rovnic (P_{CO2}, K_{CO2}, K_1, K_2, K_C and Ch. Bal.)

$$P_{CO2} = 10^{-2}$$

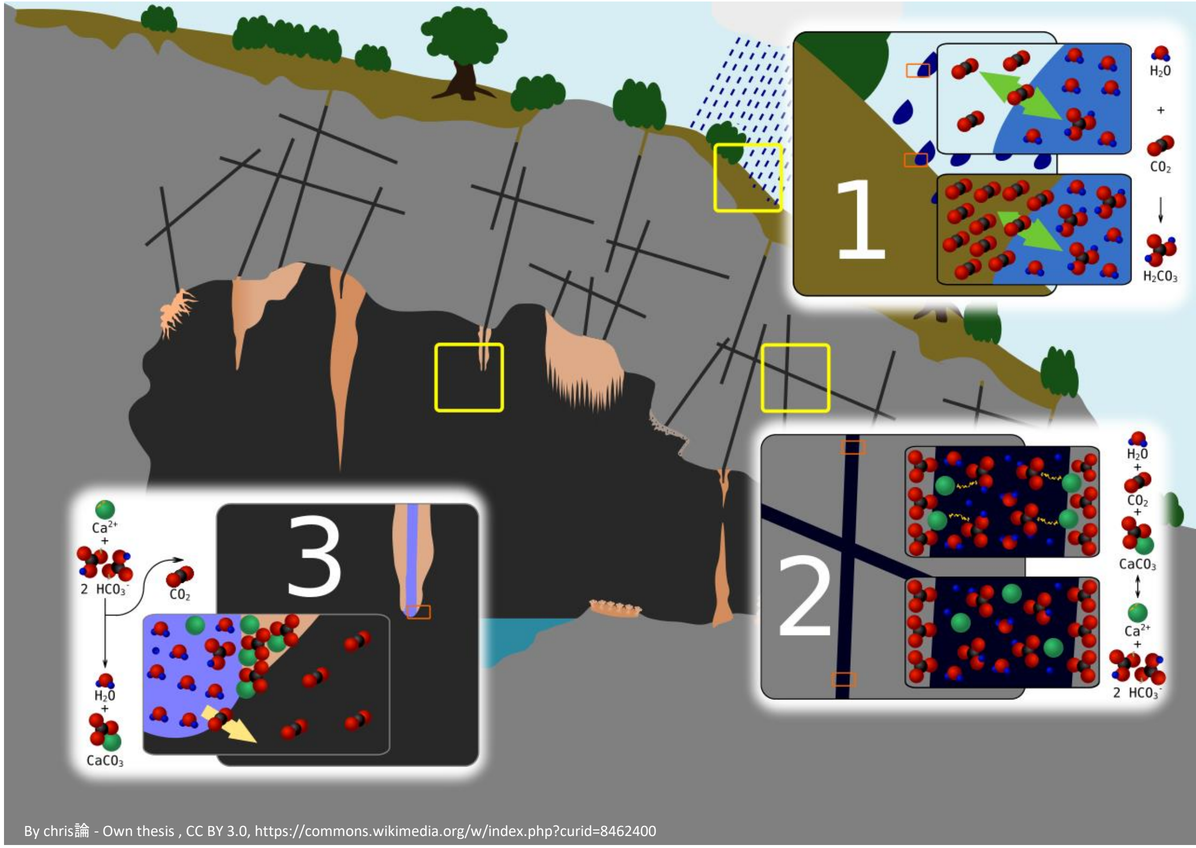
We express $[Ca^{2+}]$ from the equations and substitute the parameters

$$[Ca^{2+}] = 1{,}39 \times 10^{-3}\ \mathrm{mol/L}$$

Approximately 139 mg of calcite dissolves per liter of water

Schematics of karst dissolution

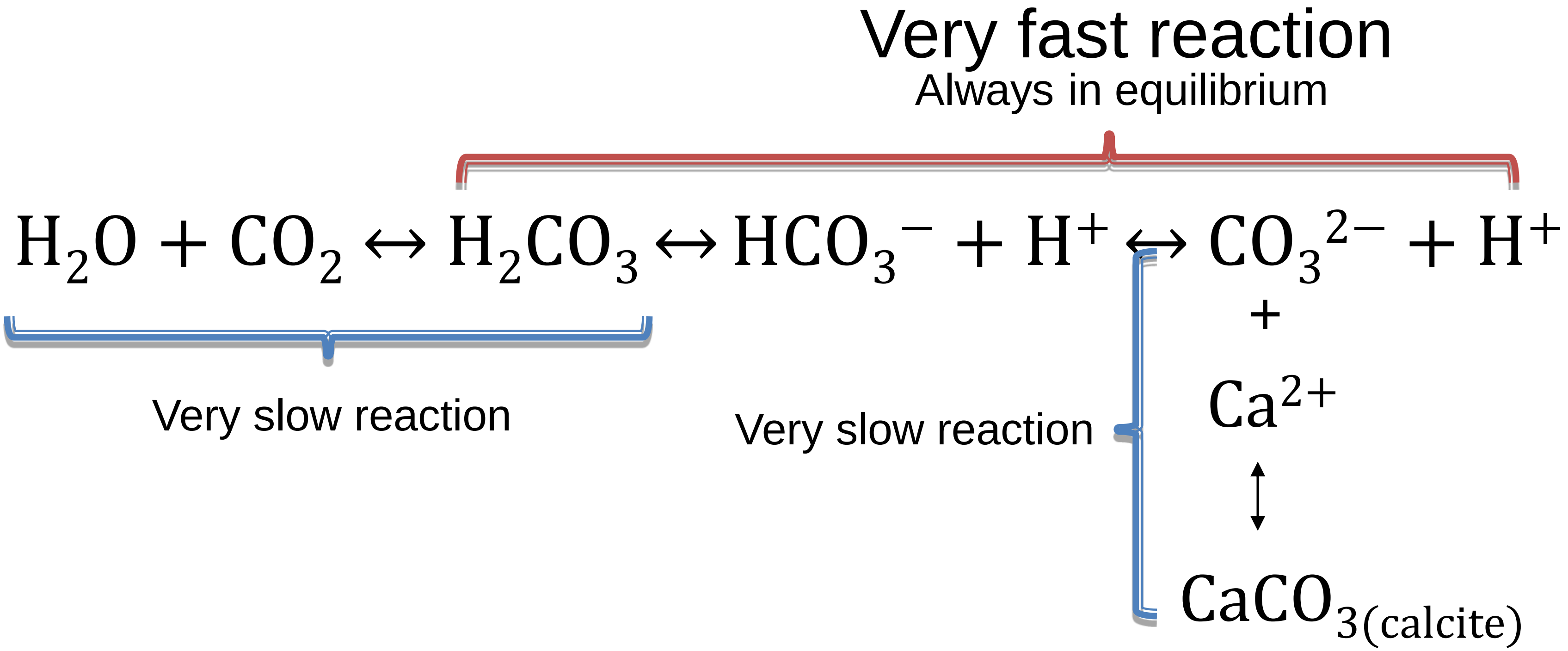
- Precipitation
- Infiltration
- Percolation
- Dissolving CO_2 from the soil
- Dissolving limestone
- (Cave)
  - Degassing and speleothem growth
- Discharge



By chris論 - Own thesis , CC BY 3.0, https://commons.wikimedia.org/w/index.php?curid=8462400

Karst processes

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



Very fast reaction

Always in equilibrium

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + H^+$$

Very slow reaction

Very slow reaction

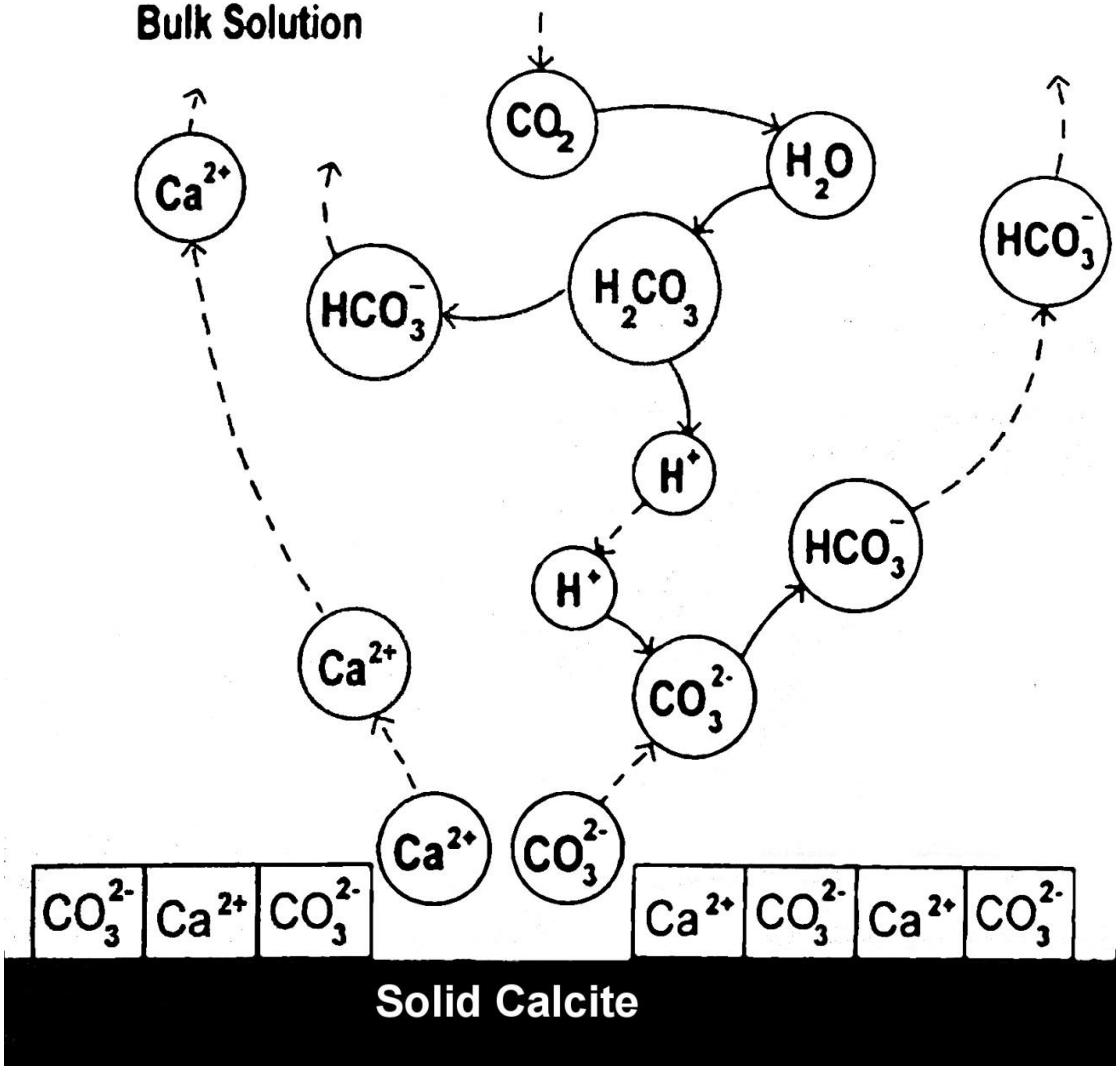
$$+$$

$$Ca^{2+}$$

$$\updownarrow$$

$$CaCO_{3(calcite)}$$

Diagram of calcite dissolution



Dreybrodt & Eisenlohr (2000)

Surface concentration

- $F_S = \alpha_S f(c_{eq} - c_s)$ … flux released from surface
  - α_S … constant

- $F_D = \alpha_D (c_s - c_B)$ … diffusional flux
  - α_D … combined diffusion coef. and thickness of concentration boundary

$$F_S = F_D$$

Steady state

Calcite surface processes

1. $CaCO_3 + H^+ \xrightarrow{k_1} Ca^{2+} + HCO_3^-$
2. $CaCO_3 + H_2CO_3^* \xrightarrow{k_2} Ca^{2+} + 2HCO_3^-$
3. $CaCO_3 + H_2O \xrightarrow{k_3} Ca^{2+} + CO_3^{2-} + H^+ \rightarrow Ca^{2+} + HCO_3^- + OH^-$
4. $Ca^{2+} + HCO_3^- \xrightarrow{k_4} CaCO_3 + H^+$

PWP Equation (Plummer et al. 1978)

- Dissolution rate at the surface

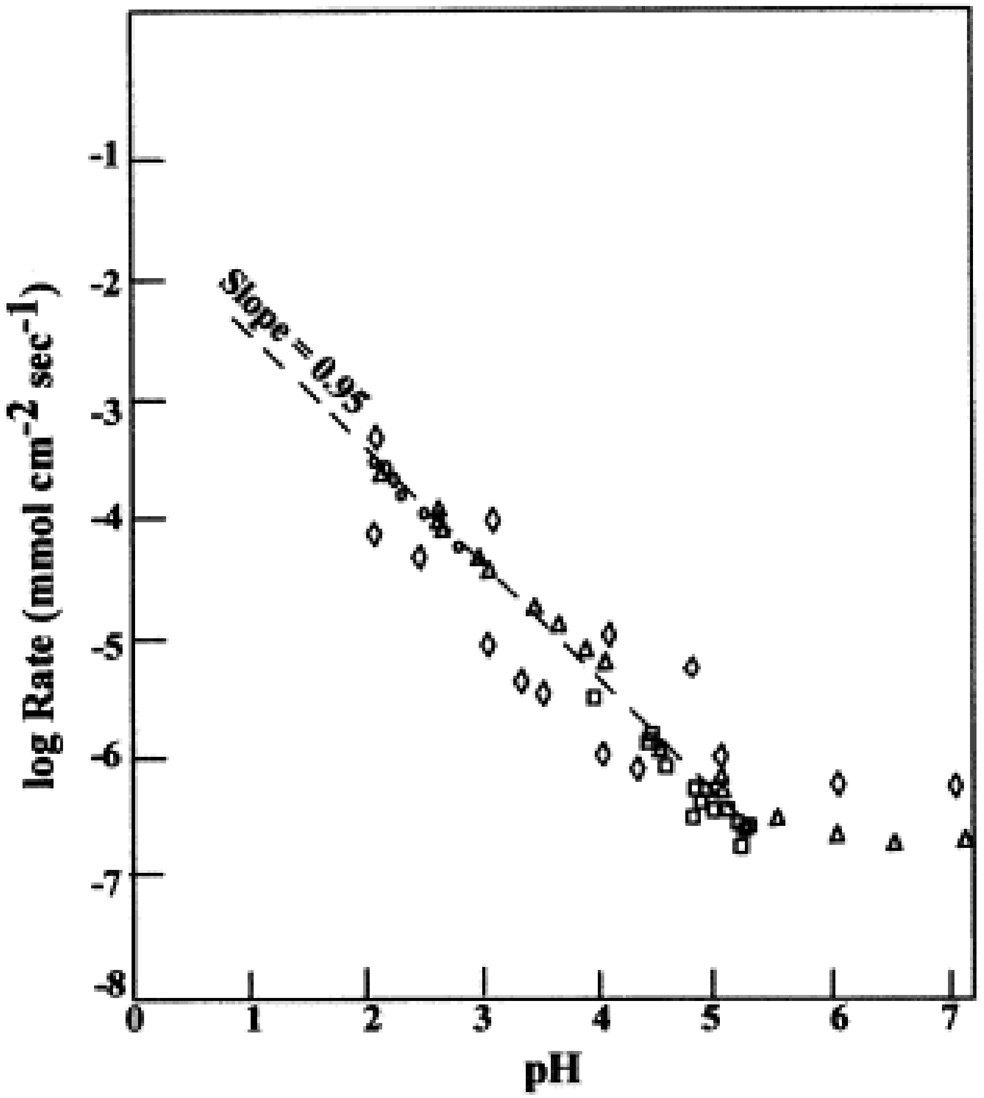
$$F_{PWP} = \boxed{k_1(H^+)_s + k_2\,(H_2CO_3{}^*)_s} + \boxed{k_3 - k_4(Ca^{2+})_s\,(HCO_3{}^-)_s}$$

Reaction-transport control

pH < 5

Surface reaction control

pH > 7



Plummer et. al. 1979

pH dependent

pH independent

Dolomites

$$\mathrm{CaMg(CO_3)_2(s)} = \mathrm{CO_3^{2-}} + \mathrm{Ca^{2+}} + \mathrm{Mg^{2+}}$$

- The solubility product is

$\mathrm{K}_D = a_{\mathrm{Ca^{2+}}} a_{\mathrm{Mg^{2+}}} a_{\mathrm{CO_3^{2-}}} = 10^{-17.2}$ (25 °C)

- The value of $\mathrm{K_D}$ is uncertain and can display very variable values for dolomites of different origins
- Very slow dissolution under standard conditions and almost no growth (highly unsaturated/supersaturated solutions)

Formation of dolomite

- Dolomite is often formed by alteration of calcite

$$\mathrm{CaMg(CO_3)_2 + Ca^{2+} = 2CaCO_3 + Mg^{2+}}$$

$$\mathrm{K}_{CD} = \frac{a_{\mathrm{Mg^{2+}}}}{a_{\mathrm{Ca^{2+}}}}$$

- In solutions where the Mg/Ca ratio is greater than K $_{CD}$, dolomite is more stable than calcite and vice versa
- The process is kinetically very slow
- Calcite changes to dolomite only under large excess of magnesium

Dissolution of dolomite

- Analogous to calcite
- Significantly slower
- Extreme times needed to reach "equilibrium" (thousands of years)
  - Significant uncertainty in equlibrium values
- At low temperatures, based on kinetics and thermodynamics, it should dissolve incongruently

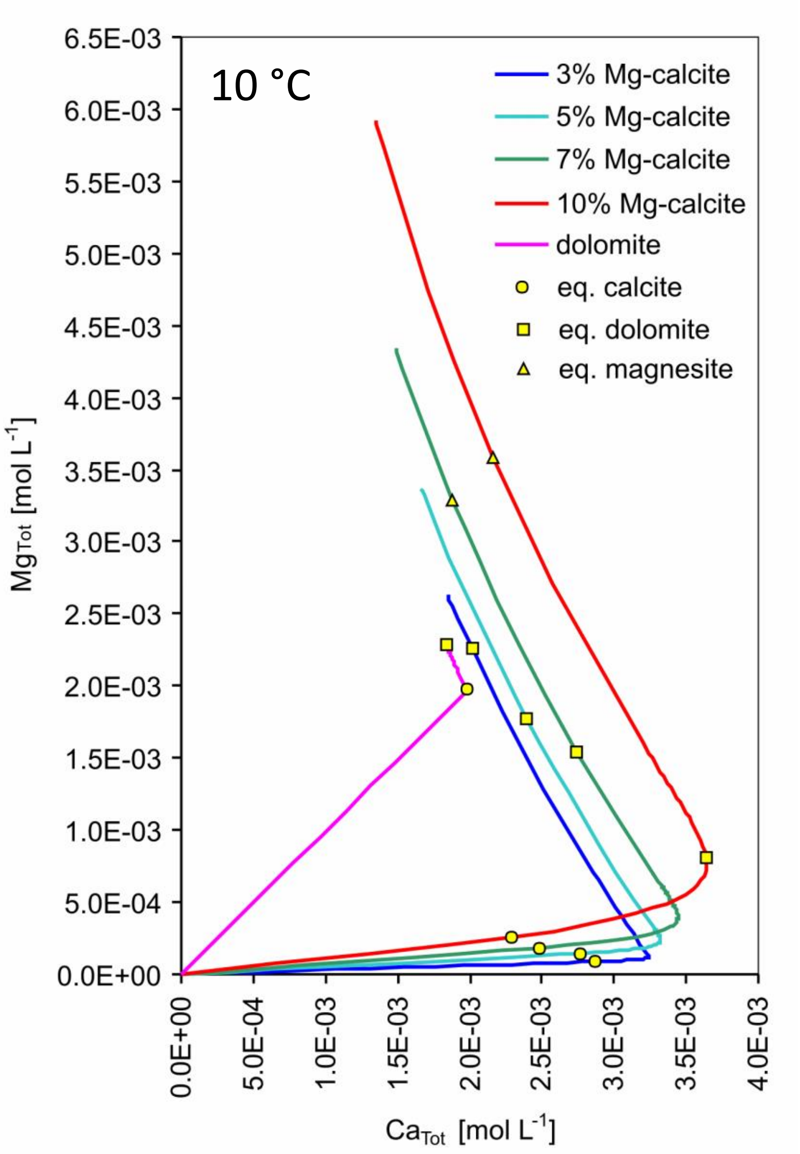
Magnesium calcite

$$\mathrm{Ca}_{(1-x)}\mathrm{Mg}_x\mathrm{CO}_3(\mathrm{s}) = \mathrm{CO}_3^{2-} + (1-x)\mathrm{Ca}^{2+} + x\mathrm{Mg}^{2+}$$

- Low magnesium Mg-calcite (<5%)
- High magnesium Mg-calcite (>10%) – recent deep-sea sediments
- All high-magnesium calcites are unstable (transformation to dolomite and low-magnesium calcite), but under surface conditions this is inhibited by dolomite growth kinetics
- Mg-calcite in seawater more stable than pure calcite

Dissolution of Mg-calcite

- Equilibrium with solution definable as cation exchange or dissolution
  - As a result, both processes must be in balance
- The correctness of the approaches is not clarified, the relationships are very complex
- The determination of K_s complicates the combination of congruent and incongruent dissolution



Pracný et al. 2017

EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie

č. CZ.02.2.69/0.0/0.0/16_018/0002593

Resources

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