

01

**Geochemical mechanisms of
carbonate equilibria in the
system**

CO_2 - H_2O - CaCO_3

Contents:

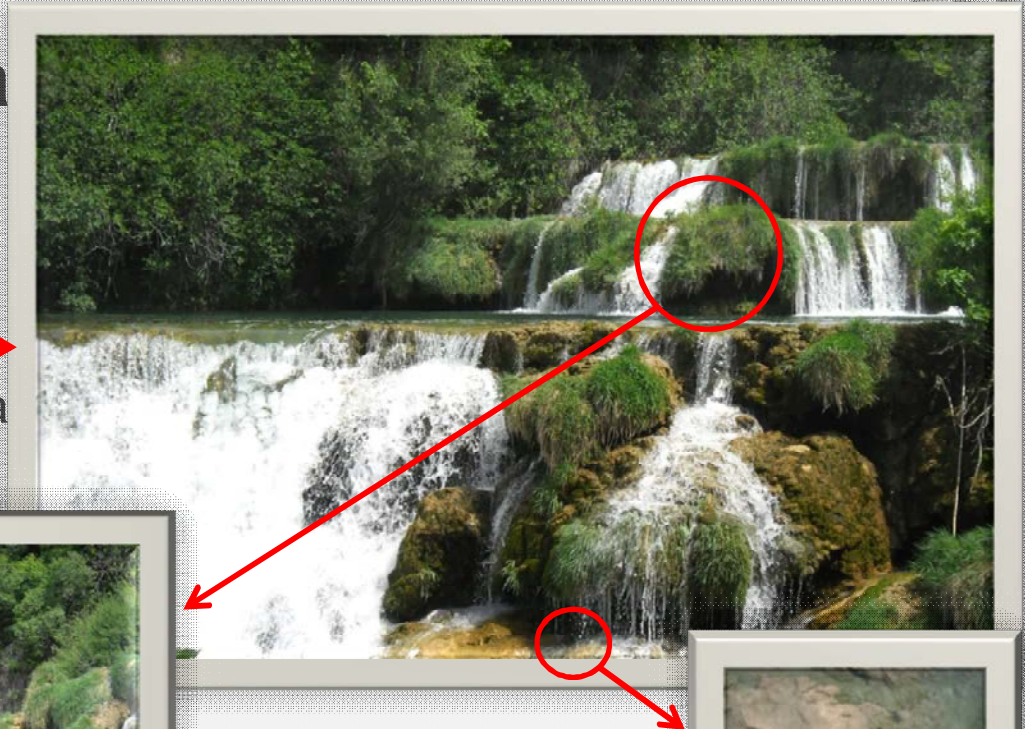
02

- Basic geological facts
- Basic chemical terms
- Simple system (CO_2 - H_2O)
- Resources of CO_2 dissolved in soil
- Dissolution of CaCO_3
- Precipitation of CaCO_3
- Physicochemical precipitation of limestone
- Biochemical precipitation of limestone

Basic geological facts

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carbonate sediments:



Basic chemical terms

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Chemical equilibrium (Le Chatelier):

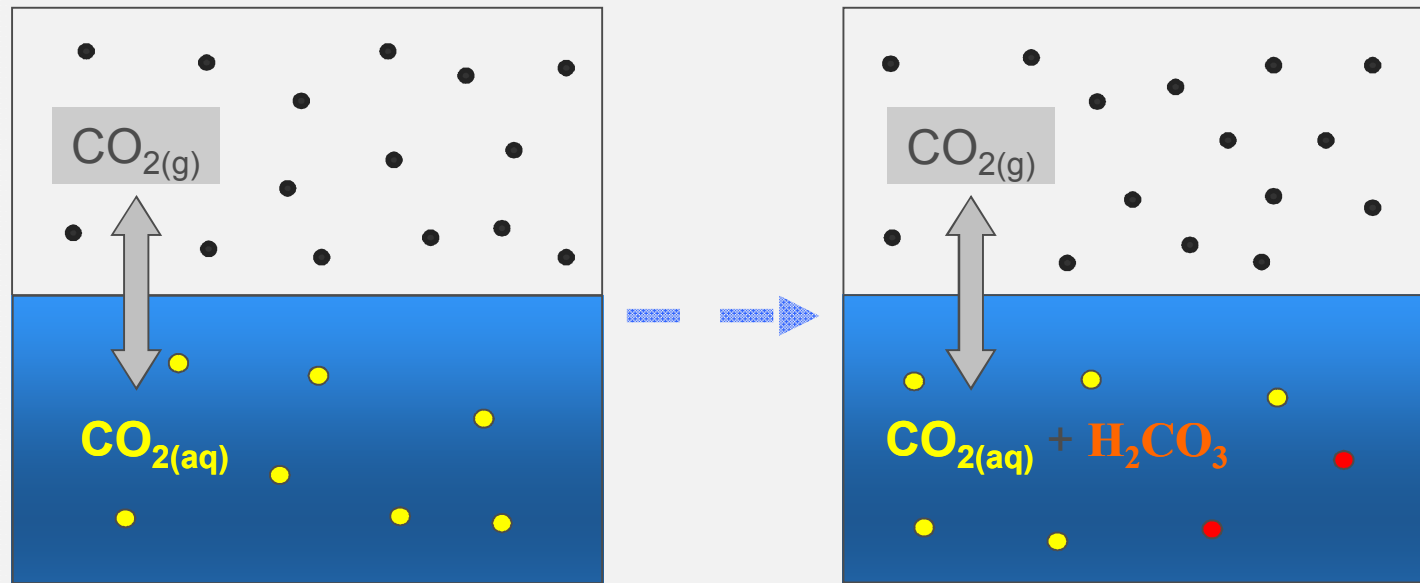


Instead of $K = \frac{[C][D]}{[A][B]}$ we use $K = \frac{a_C a_D}{a_A a_B}$

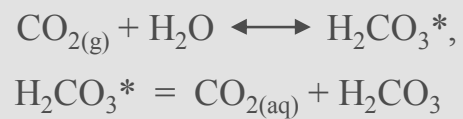
***a** - activity (=effective 'availability' of component)

Simple system (CO₂ - H₂O)

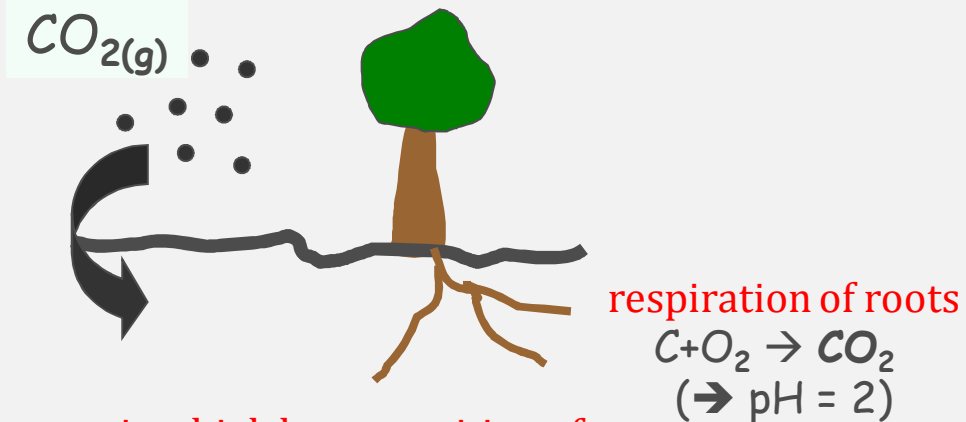
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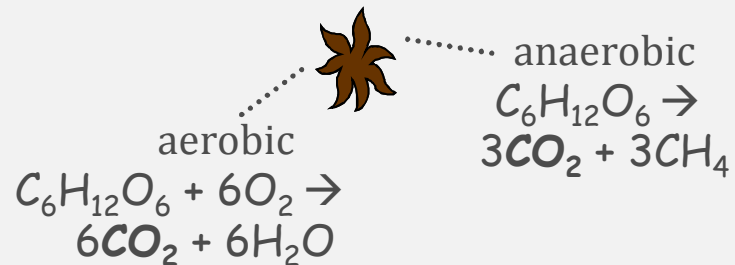
Total reaction:



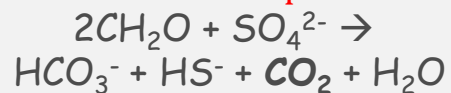
$$K_{\text{CO}_2} = \frac{a_{\text{H}_2\text{CO}_3^*}}{P_{\text{CO}_2}} = 10^{-1.5}$$

Resources of CO₂ dissolved in soil

microbial decomposition of
the non-living organic substances



reduction of sulphates



Results of these processes:

$$P_{\text{CO}_2(\text{tlo})} = 10 - 100 \times P_{\text{CO}_2(\text{g})}$$

The positive factors :

SUMMER

-highest biological activity

WINTER

-low temperatures

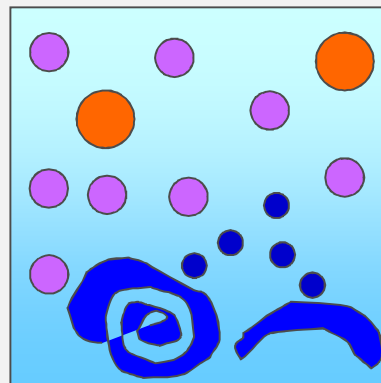
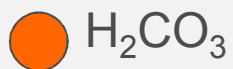
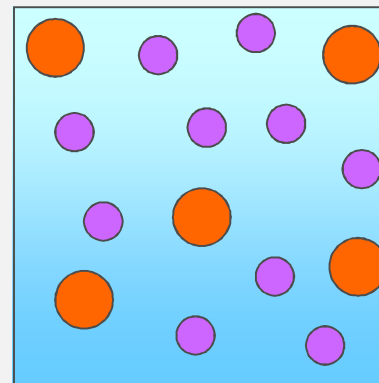
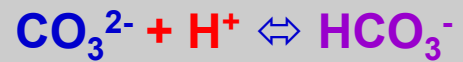
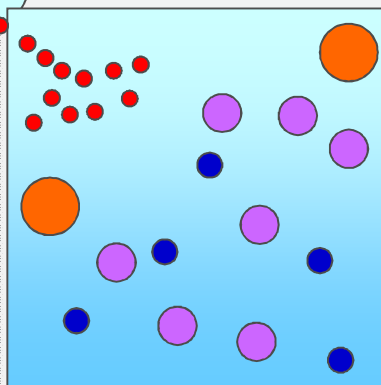
(acceleration of the dissolution of gas)

-snow

(prevention of the CO₂ outgassing)

Dissolution of CaCO_3

07

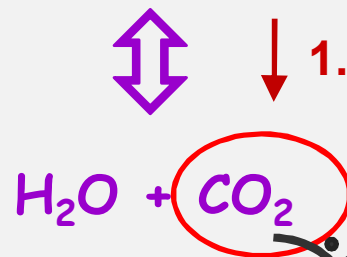
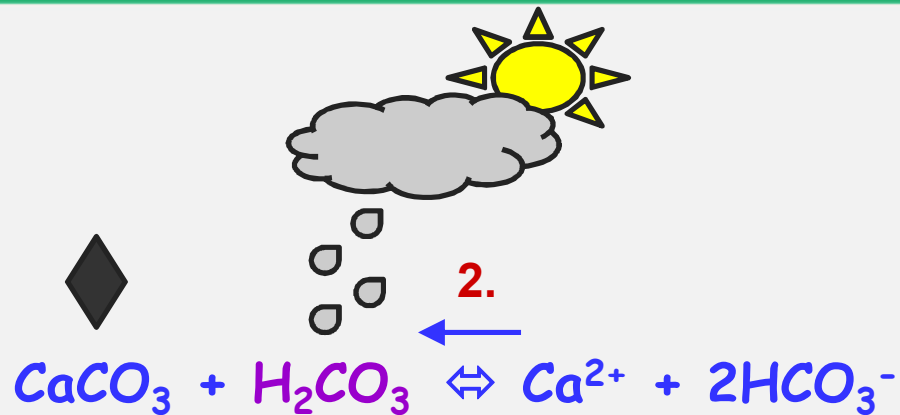


Total reaction:

Equilibrium shift:
-dissociation of the weak acid
-dissolution of the ionic compound of relatively low solubility

Precipitation of CaCO_3

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CO₂ outgassing:

1. equilibrium shift 'down'
(to compensate for CO₂)
2. equilibrium shift to the 'left'
(to compensate for H₂CO₃)

$$a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} > K_{SP} (= 10^{-8.3})$$

Precipitation of CaCO_3

Physicochemical precipitation of limestone

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CO₂ outgassing and its transfer over the water /bubble surface:

- by temperature increase

(reduction of the dissolution of gas)

- by water turbulence

(numerous water droplets increase the contact with the atmosphere)

waterfalls: Krka (tufa)

waves: shallow sea (oid)

- By water springing into the environment with lower P_{CO₂}

caves: stalagmites and stalactites

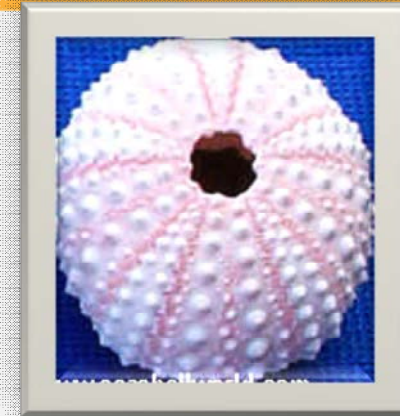
hot springs : travertine



Biochemical precipitation of limestone

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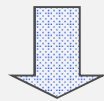
- Mediation of the organic matrix (skeletons of organisms)



- Biologically induced mineralization



photosynthetic
absorption of CO₂



increase in microenvironment pH



Encrustation of mosses and algae



- pH of most natural waters is controlled by chemical reactions in the system $\text{CO}_2\text{-H}_2\text{O-CaCO}_3$



- Limestone/carbonate aquifers of high capacity
 - Carbonate minerals: accessory or as a cement in sandy aquifers
-
- dissolved CO_2 = main agent of weathering of limestones/carbonate sediments
 - equilibrium shifts of dissolved carbon species
→ dissolution / precipitation of limestone
 - carbonate species adjust mutual ratios according to $K_{\text{SP}}(\text{CaCO}_3)$ and $K_{1,2}(\text{H}_2\text{CO}_3)$

References:

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- BROWNLOW, ARTHUR H. (1979): Geochemistry. Prentice Hall, p. 498, New Jersey.
- KRAUSKOPF, K.B., BIRD, K. (1995): Introduction to Geochemistry. McGraw-Hill International.



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