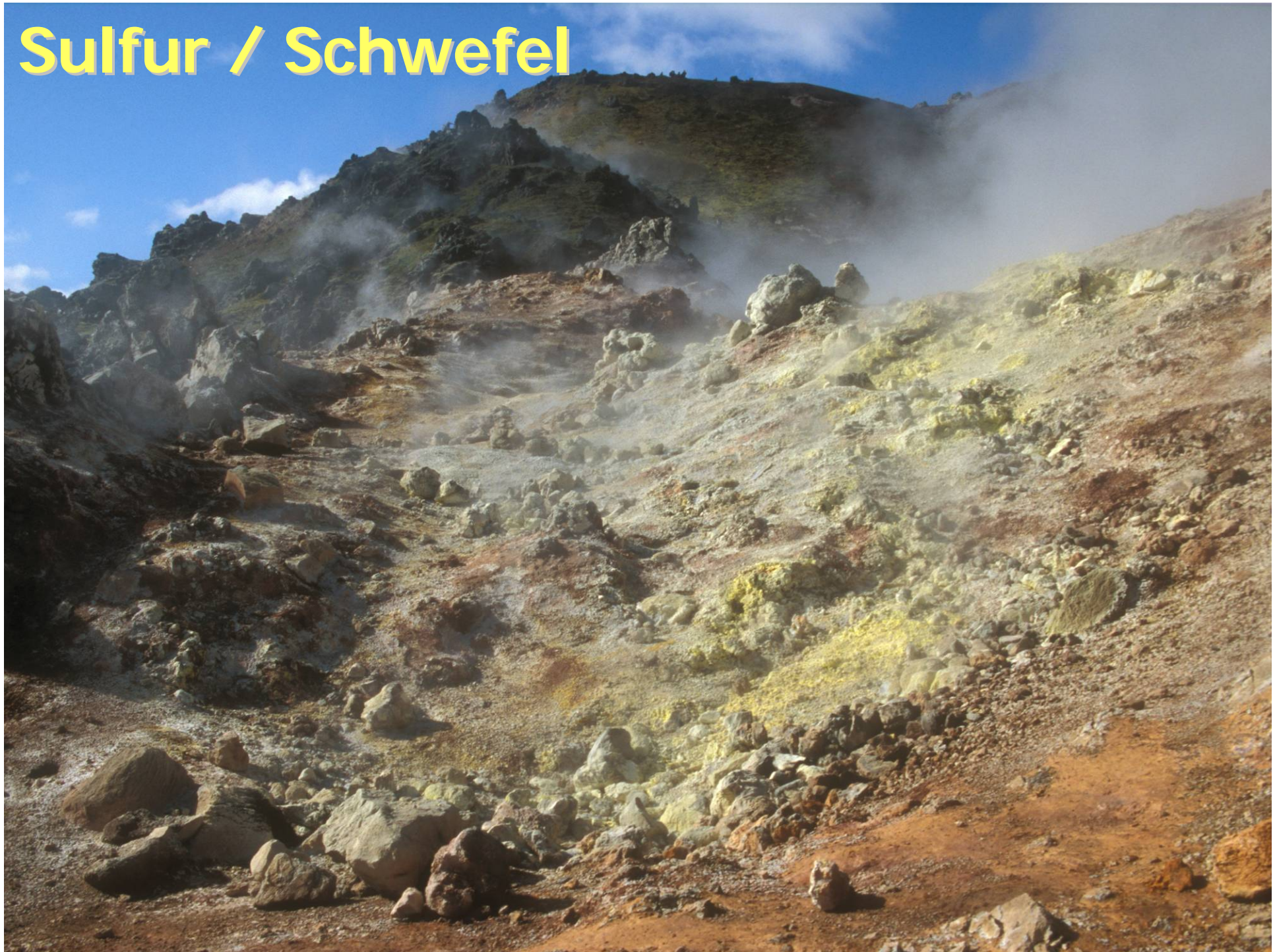


# Fragen

- Wo befindet sich weltweit der meiste "aktive" Stickstoff?
  - Welche typischen C/N-Verhältnisse haben
    - Holz
    - Blätter
    - Bakterien
    - Pilze
    - Organische Substanz im Mineralboden
- In welchen chemischen Formen liegt Stickstoff im Boden vor?
- Worin unterscheiden sich C- und N-Umsätze im Boden?
- Wie beeinflussen N-Umsätze im Boden den pH-Wert?

# Sulfur / Schwefel

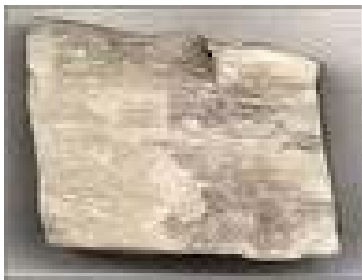


# Sulfur / Schwefel

- Essential nutrient for plants, animals and humans
- Sources for plants: Atmosphere ( $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$ ) and minerals
- Exists in various oxidation levels depending on the soil redox status  
+6 in  $\text{SO}_4^{2-}$  ... 0  $\text{S}^0$  ... -2 in  $\text{S}^{2-}$

## Sulfates $\text{SO}_4^{2-}$

- in aerobic sediments,
- easily dissolved,
- highly mobile



Gips ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

## Sulfur



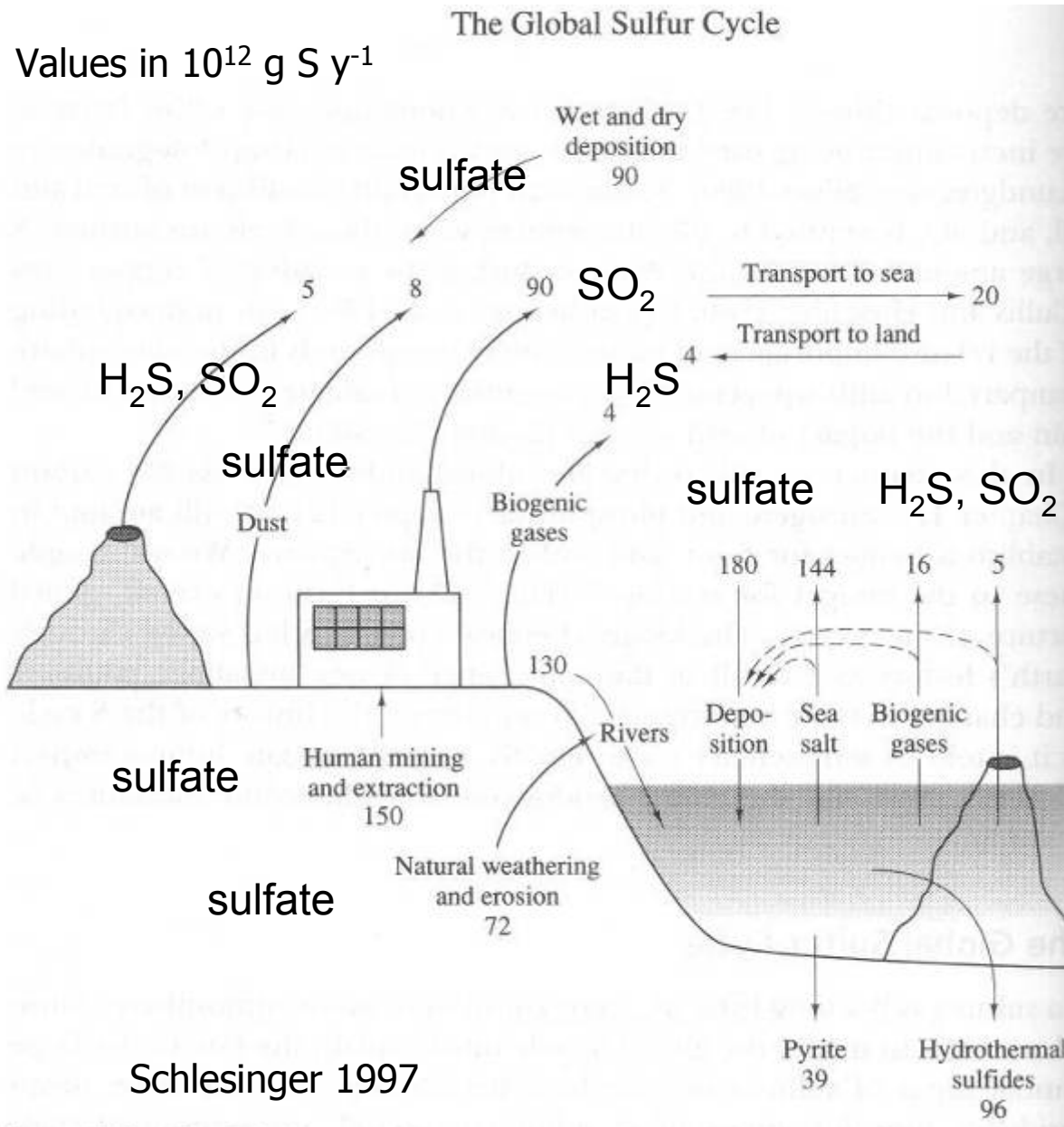
## Sulfides $\text{S}^{2-}$

- anaerobic sediments
- easily oxidized:  
soil acidification!



Pyrit ( $\text{FeS}_2$ )

# Global sulfur cycle



## Global S pools

	$10^{18}$ gS
Atmosphere	0,0000028
Seawater	1280
Sedimentary rocks	
Evaporites	2470
Shales	4970
Land plants	0,0085
Soil organic matter	0,0155

# Sulfur / Schwefel in soils

- Typical binding forms of S in soils:  
organic layer and A horizon: 60...98 % organic S  
Subsoil: mineral S dominates  
In acid soils (< pH 4)  $\text{SO}_4\text{-S}$  it can be adsorbed or precipitated
- $\text{SO}_4\text{-S}$  solubility depends on ion concentrations in soil solution and  
formation of salts: Al-  $\text{SO}_4$  a lot less soluble than Ca- $\text{SO}_4$

# Sulfur / Schwefel in soils

- Organic S
  - Sulfate ester: C-O-S
  - Salze der Sulfaminsäure: -R-NH-SO<sub>3</sub><sup>-</sup>
  - S-containing amino acids:
    - Cystein      R-CH<sub>2</sub>-SH
    - Cystin      R-CH<sub>2</sub>-S-S-CH<sub>2</sub>-R
    - Methionin    R-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>3</sub>

Up to 30% of organic S in soils

# Sulfur / Schwefel in plants

- Uptake mainly as  $\text{SO}_4^{2-}$  via roots, and  $\text{SO}_2$  adsorption by leaves

- Oxidized

$\text{SO}_4^{2-}$ : sulfolipids in membranes

- Reduced

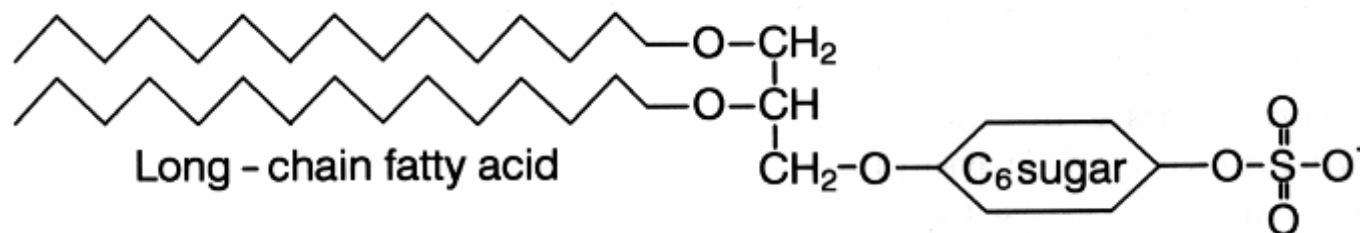
-SH: ~ amino acids (cystein, cystin, methionin)

~ co-enzymes (active parts bound to enzyme proteine structures)

~ in proteins for forming spatial structure

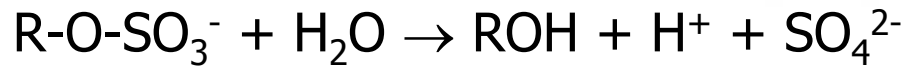
~ various redox and metal binding functions

Example for sulfolipids, S is an important component of all biomembranes

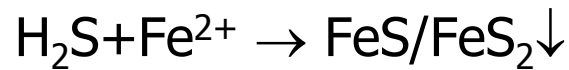


# Microbial S transformations

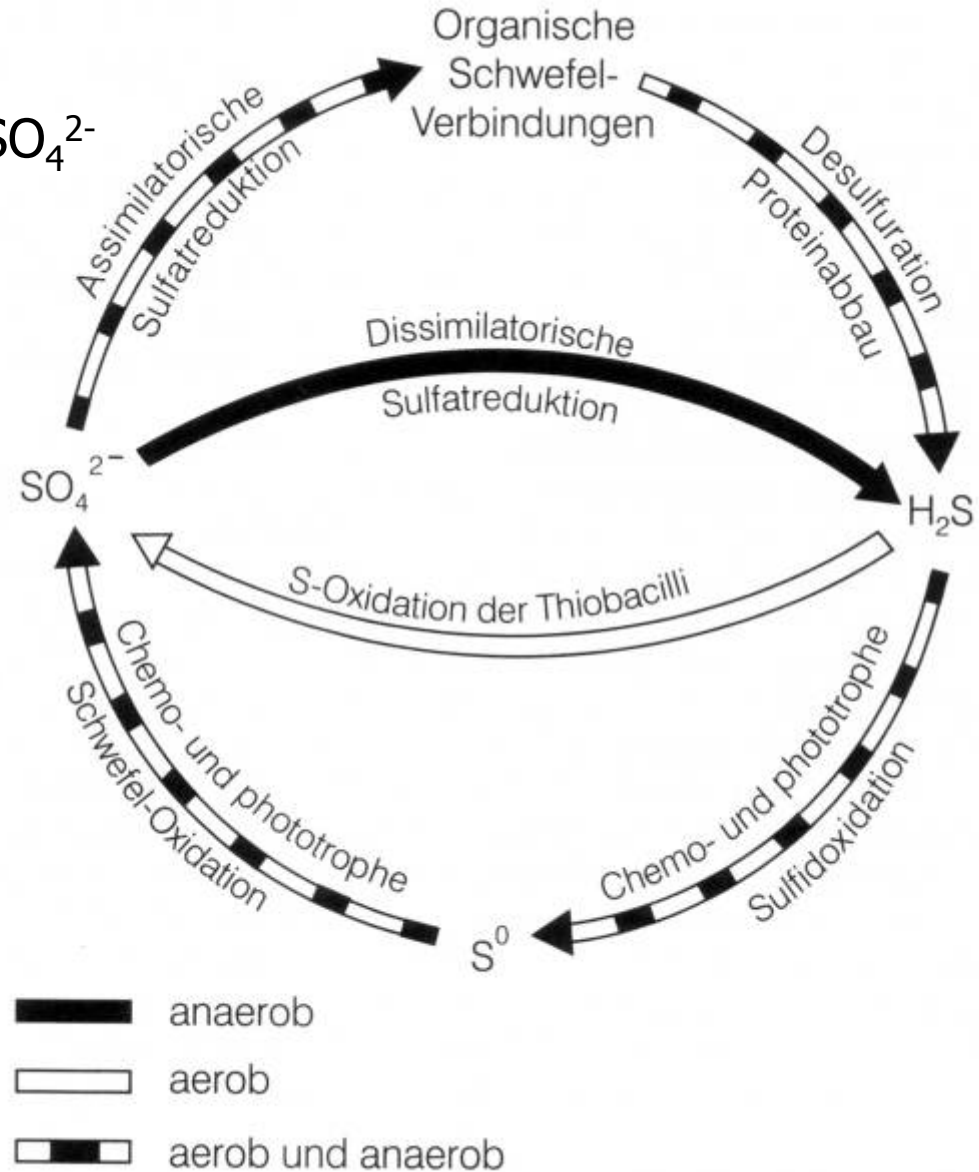
Sulfatase:



Reisböden:



dunkler Horizont,  
Wurzelschäden



Fritsche 1998



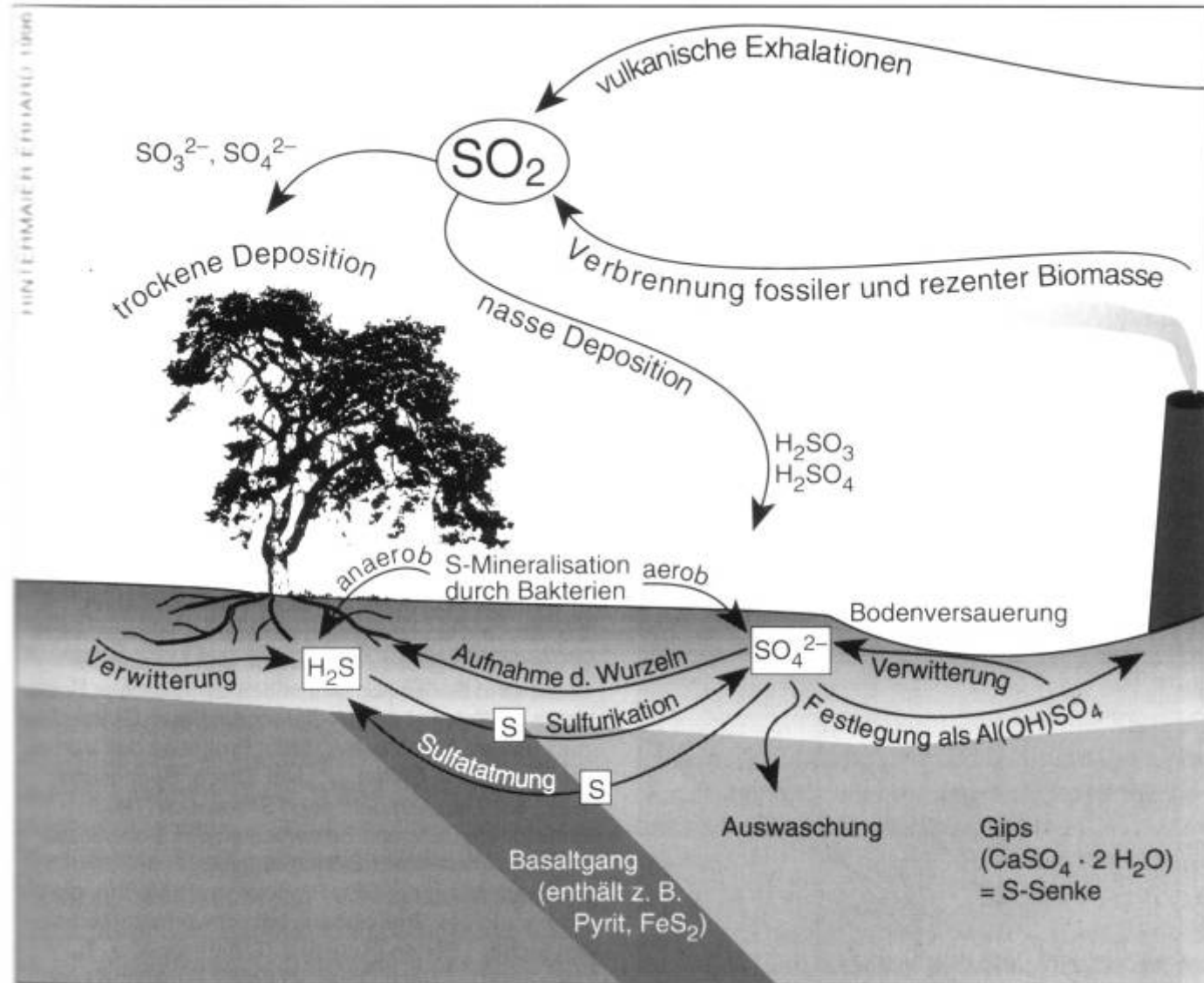
# Microbial S<sup>2-</sup> oxidation

- **Chemolithotrophe Bakterien:** aerob  
→ obtain energy by the oxidation of reduced S (e.g. Thiobacillus)  
some are able to fix CO<sub>2</sub> → autotroph  
 $S^{2-} \rightarrow S \rightarrow SO_4^{2-}$   
sulfidische Eisenerze → H<sub>2</sub>SO<sub>4</sub> → Versauerung der Bergwerksabwässer
- **Phototrophe Schwefelpurpurbakterien** oder grüne S-Bakterien  
oxidieren H<sub>2</sub>S zu S und SO<sub>4</sub><sup>2-</sup> mit Hilfe von Lichtenergie in Seen, anaerob  
 $6CO_2 + 12 H_2S \rightarrow C_6H_{12}O_6 + 12 S + 6 H_2O$  (anoxygene Photosynthese)
- **Heterotrophe Bakterien und Pilze**  
Arthrobacter, Bacillus, etc, also some fungi  
important for S oxidation in aerob soils, but they get their energy from organic substances

# Frage

- Wie gelangt Schwefel in Ökosysteme?
- Was sind die wichtigsten Oxidationsstufen des Schwefels und in welchen Verbindungen tritt er dann auf ?
- Unter welchen Umständen und wozu werden S-Verbindungen von Mikroorganismen oxidiert oder reduziert?

# Sulfur cycle



Schwefelkreislauf. Einfaches Modell des terrestrischen Schwefelkreislaufs mit besonderer Berücksichtigung der Pedosphäre.

# Sulfur / Schwefel in the atmosphere

- Sources of S compounds in the atmosphere
  1. Industry



# Sulfur / Schwefel in the atmosphere

- Sources of S compounds in the atmosphere  
2. Volcanic activity,



Pinatubo 1991:  
 $\sim 10 * 10^{12}$ g S as  $\text{SO}_2$   
in the stratosphere

annual average:  
 $10^{12}$  g S,  
70% passive leaks

# Sulfur / Schwefel in the atmosphere

- Sources of S compounds in the atmosphere

## 3. Biogenic emissions

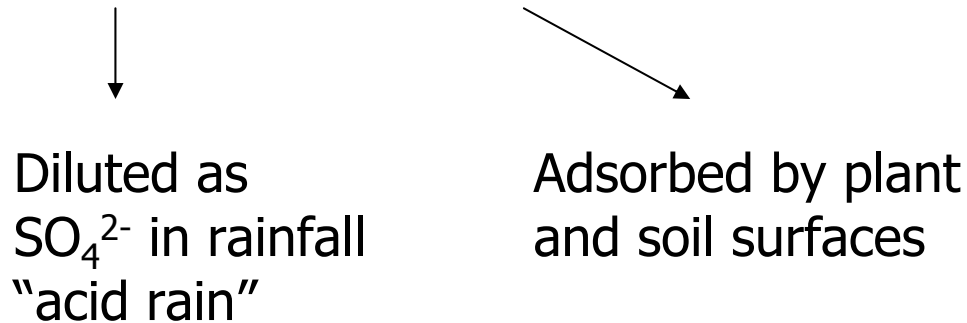


## 4. Fire



# Role of atmospheric S

## 1. Wet and dry deposition



- ↓
- Forest soils:
- increased leaching of nutrients
  - soil acidification
  - < pH 4,5 release of toxic Al ions

- Soils under cultivation:
- liming of soils (Kalkung)
  - Sulfate acts as fertilizer

Total deposition:

up to 150 kg S ha<sup>-1</sup> y<sup>-1</sup>

today: < 30 kg S ha<sup>-1</sup> y<sup>-1</sup>

New Zealand: 1 kg S ha<sup>-1</sup> y<sup>-1</sup>

→ risk of S deficiency

# Role of atmospheric S

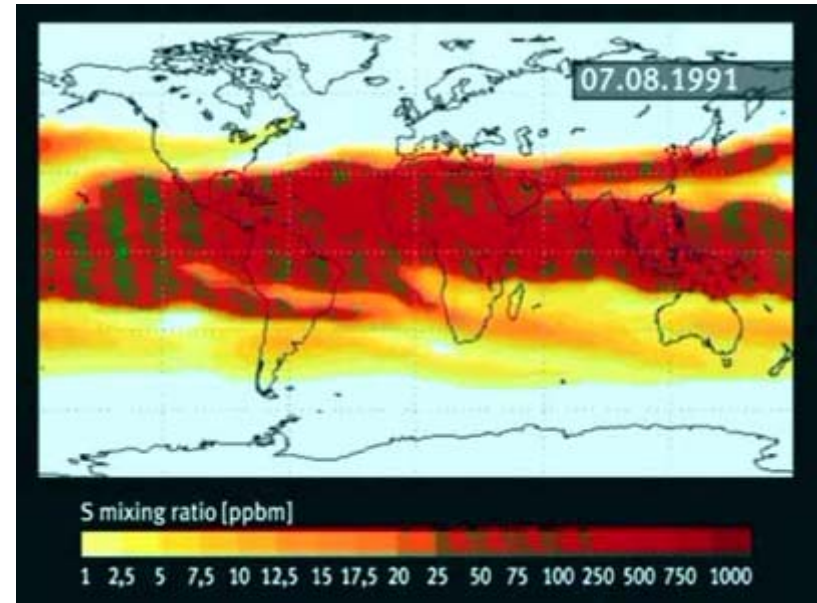
2. Formation of  $\text{H}_2\text{SO}_4$  aerosols (SAT)



Enhance planetary albedo



Reduction of global warming?



Change in albedo due to aerosols is not yet well quantified  
→ uncertainty in climate models

One year after Pinatubo eruption: average cooling of 0.5 °C

**But:** Ozone destruction, acid rain... unknown risks



# Sulfur / Schwefel in the atmosphere

- SO<sub>2</sub> emissions in Germany (Reduction following „Abgasentschwefelung“)

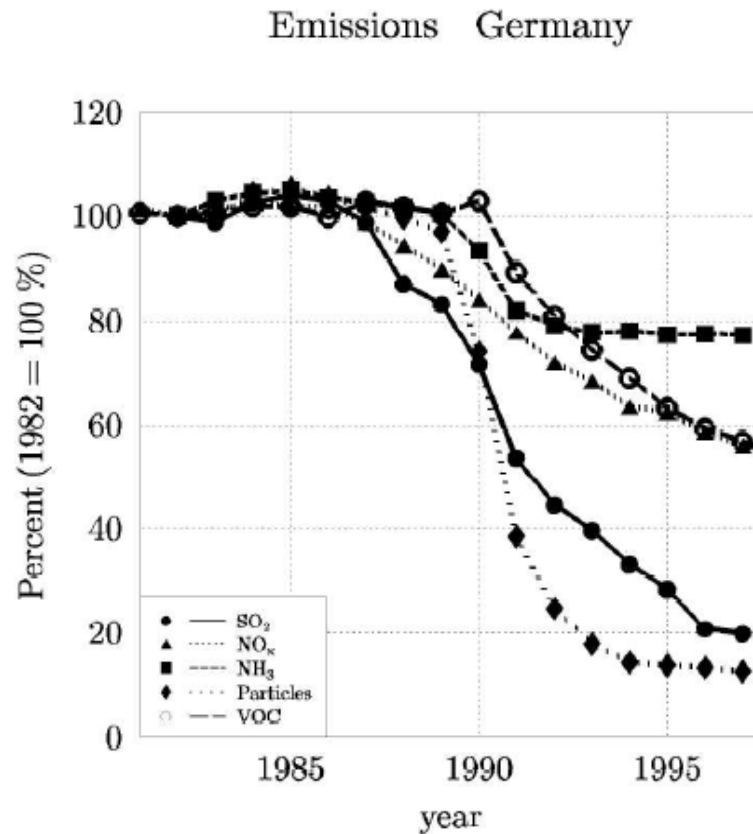
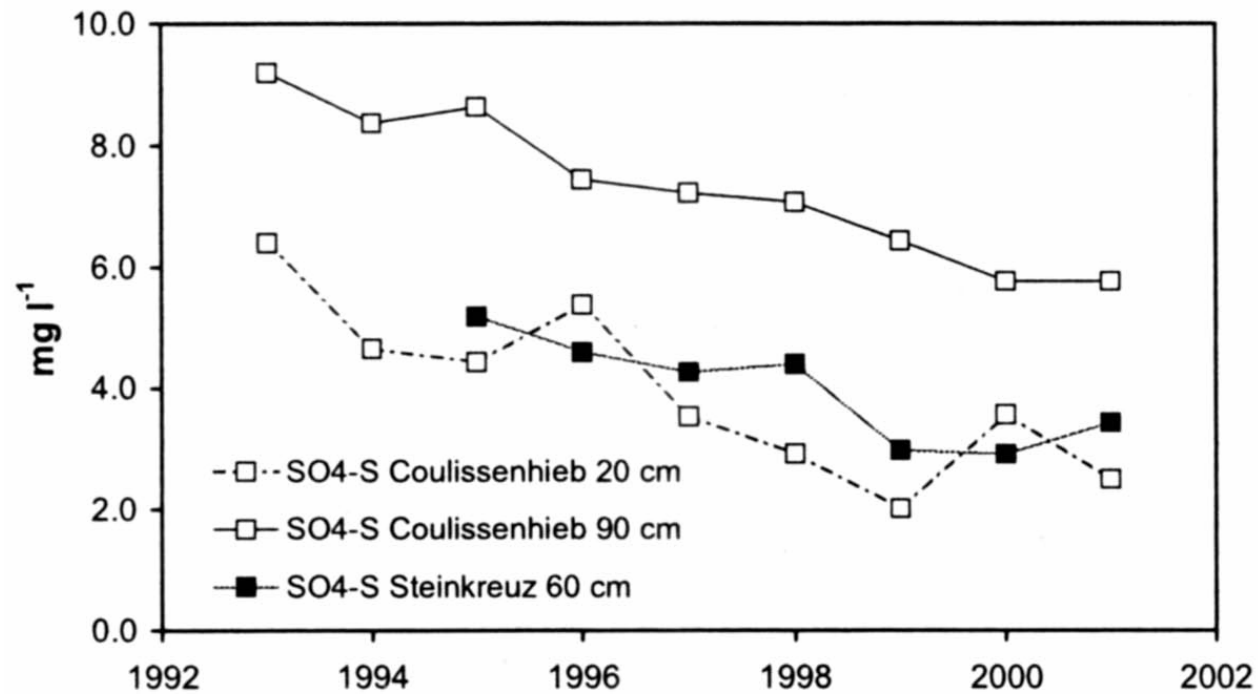


Fig. 1. Emissions in Germany relative to the values of the year 1982.

# Sulfur / Schwefel in the atmosphere

- $\text{SO}_4^{2-}$  concentration in the soil solution of german forest sites



Matzner 2004

# Sulfur deficiency

- S deficiency hampers the synthesis of proteins and chlorophyll
- Symptoms:
  - similar to N deficiency, reduced growth and harvest
  - rape gets white flowers



- In some regions  $\text{SO}_4$  fertilization is required due to reduced S deposition

# Frage

- Wie hat sich der Schwefeleintrag in Ökosysteme in den letzten 20 Jahren entwickelt?
- S Deposition ist jetzt in D so niedrig, dass S wieder gedüngt werden muß.
- S „kühlt“ als Aerosol.
- Also: wieder mehr S-Emissionen?



# Phosphorus / Phosphor

# Phosphorus / Phosphor



Apatit  
 $\text{Ca}_5(\text{PO}_4)_3\text{OH}$



Apatit – Mine Rußland



Apatit



Variszit  
 $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$

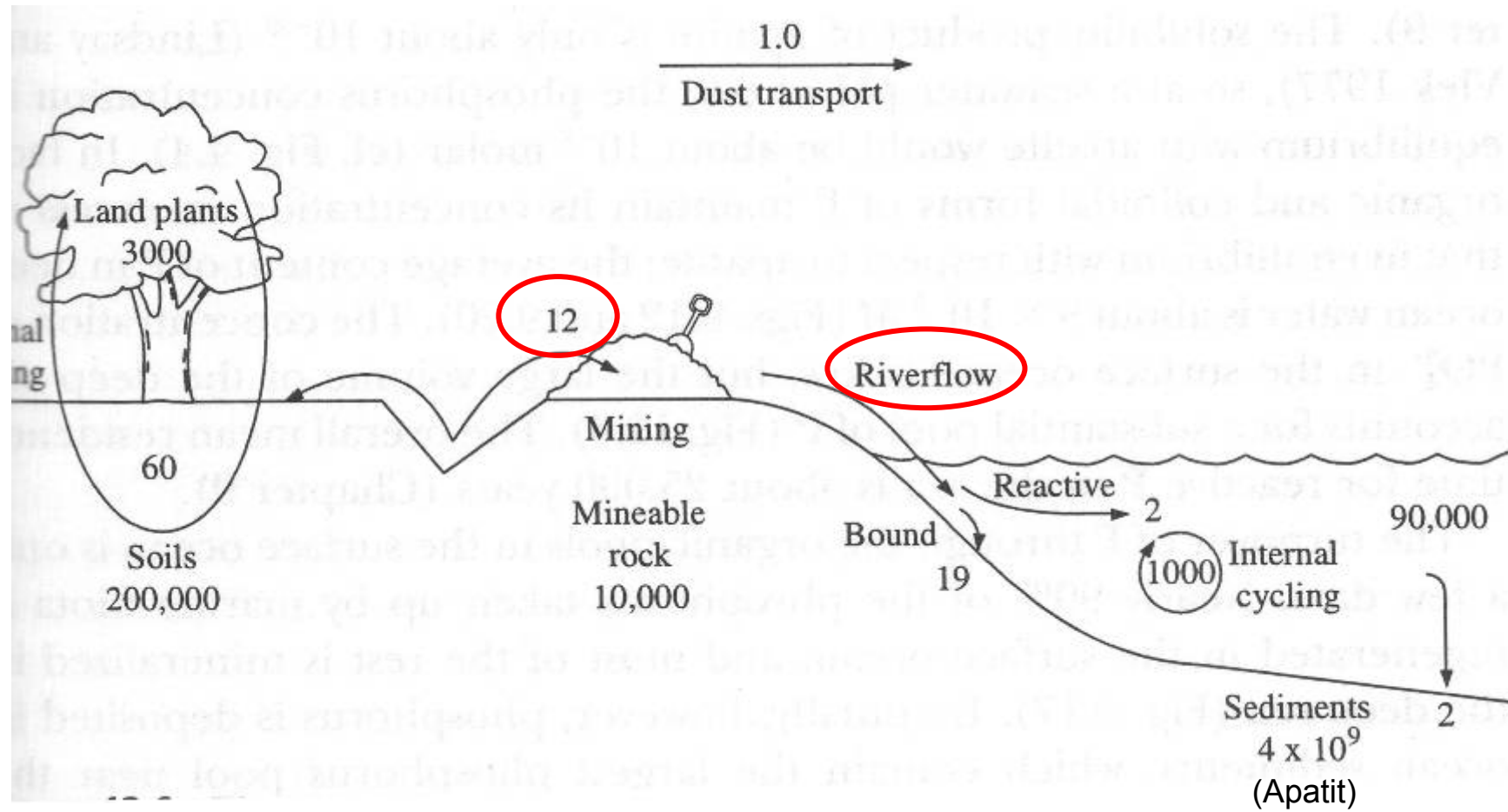


Strengit  
 $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$

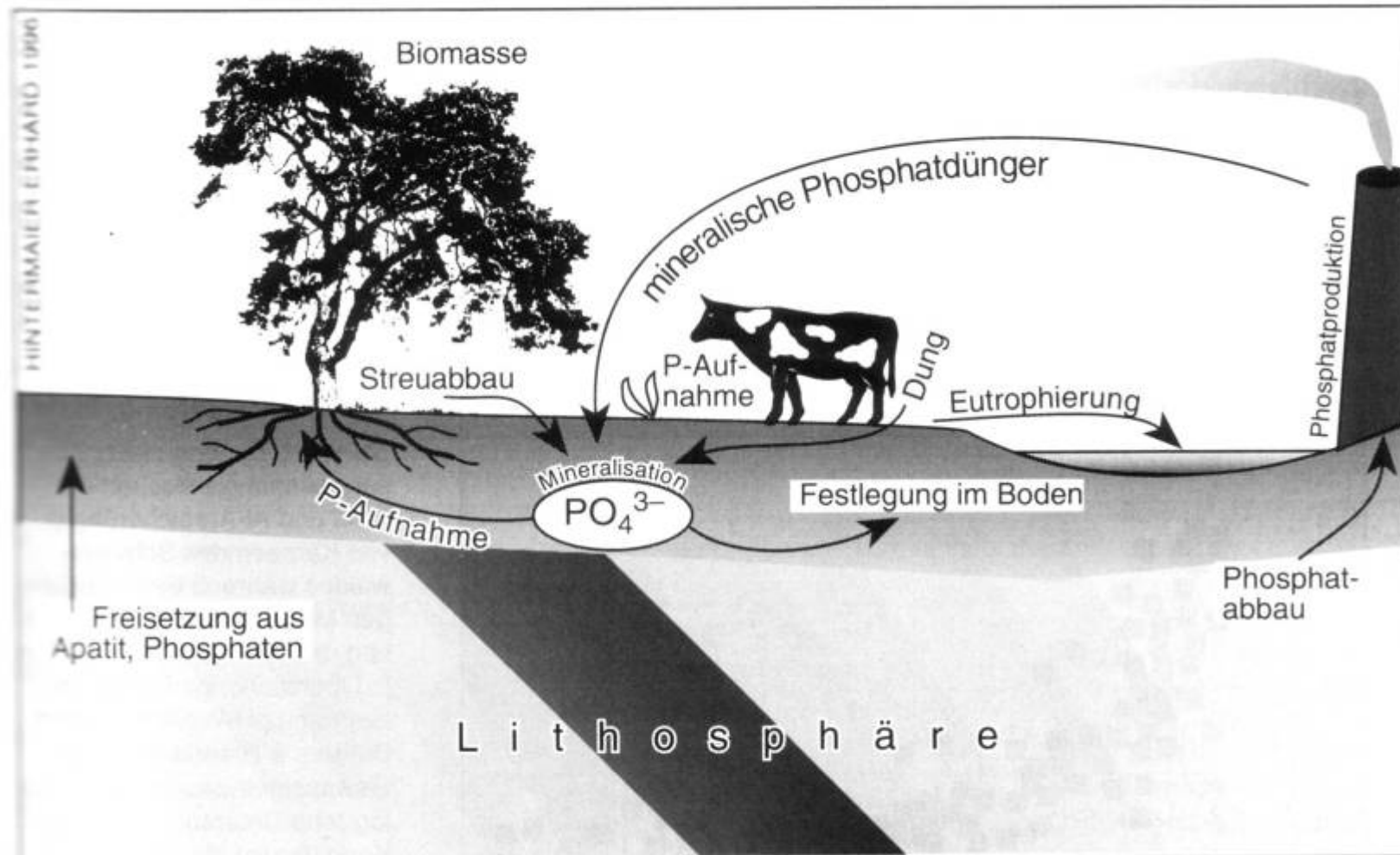


Vivianit  
 $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ <sup>22</sup>

# Global phosphorus cycle



# Ecosystem P cycle



Phosphorkreislauf. Einfaches Modell des terrestrischen P-Kreislaufs mit bes. Berücksichtigung der Pedosphäre.



# Role of P in plants

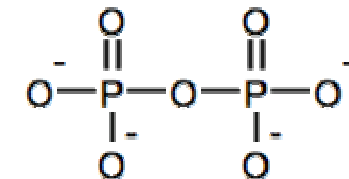
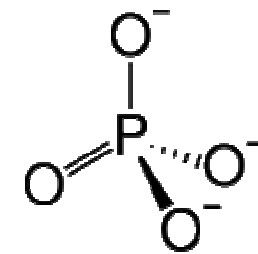
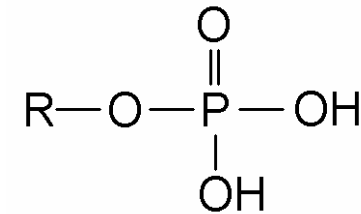
## Central element of energy metabolism in all organisms

### Metabolic functions

- Important as energy store and transporter:  
e.g. ATP (Phosphatester mit Adenosin)
- Activation of substrates in the nutrient cycle

### Structural functions:

- P is important for the formation of DNA, RNA
- Phospholipids in biomembranes



# Phosphorus forms in the soils

- Nur Orthophosphat  $\text{PO}_4^{3-}$
- Oft an elektrophile Kationen gebunden:  
 $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  (Apatit:  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ )

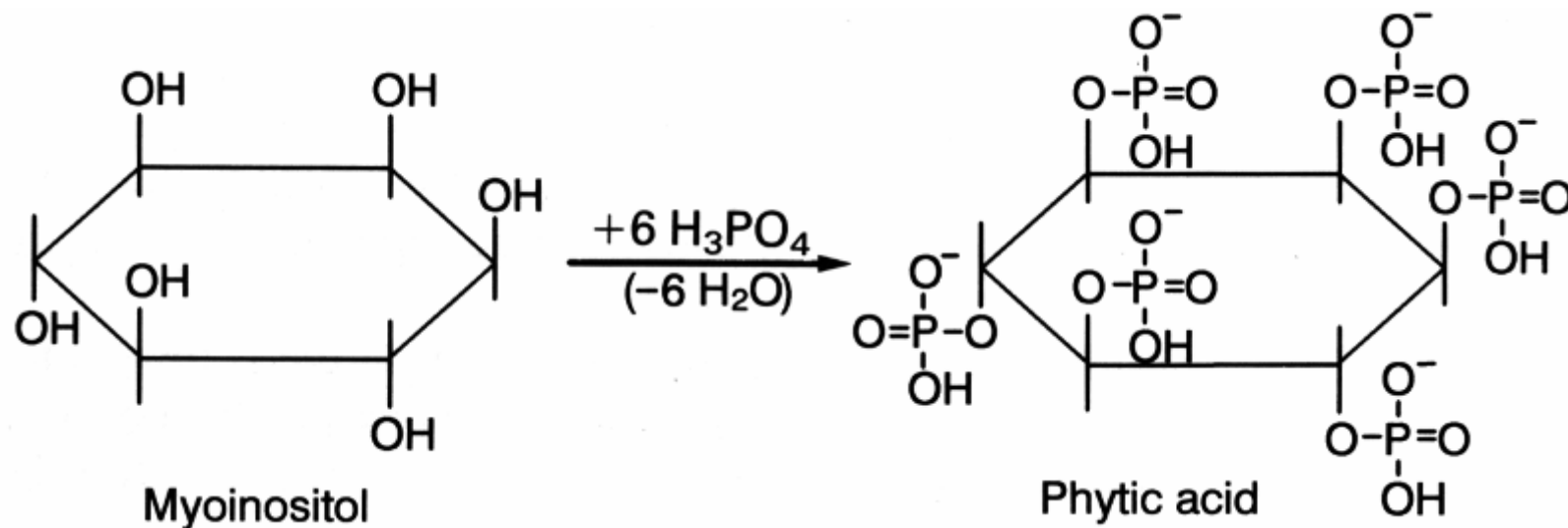
Allgemein: 99,9% fixiert / gebunden

Bindungsformen im Boden:

- Lithogen in Mineralen (Apatit)
- Anorganische Phosphate (Orthophosphat  $\text{PO}_4^{3-}$ )  
anorganisch gefällt ( $\text{FePO}_4$ ,  $\text{AlPO}_4$ ) – verschiedene Salze, z.T. sehr schwer löslich
- Adsorbierte Phosphate (austauschbar oder spezifisch)
- Organische Phosphate (25-65% des P in A-Horizonten)

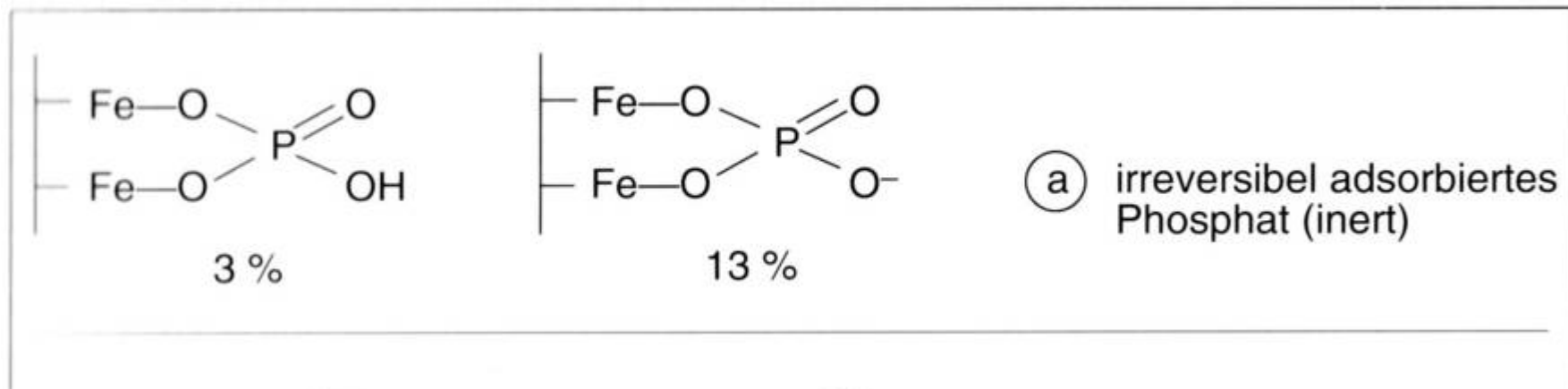
# Phosphate types in the soil

- P in organic forms
  - about 50% as Phytin (Inositphosphat)
  - Phospholipids <1-2%
  - Nuclein acids 5-10%



# Phosphate types in the soil

- P adsorbed to Al/Fe oxides / hydroxides, clay minerals



# Phosphorus contents in soils

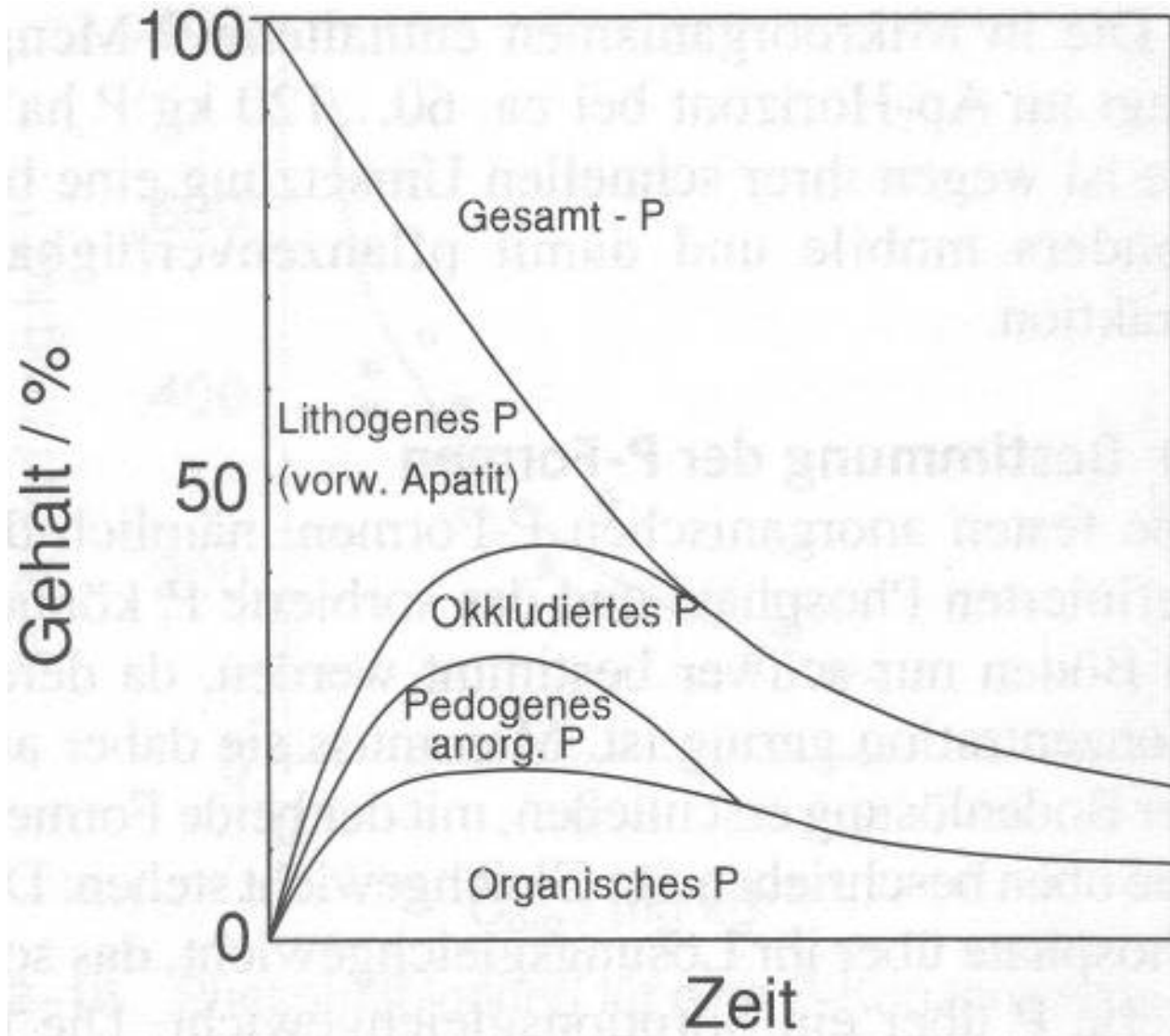
Sandy soils, Vertisols (smectite), highly weathered soils  
(Ultisols, Oxisols):  
P-poor:  $< 100 \text{ mg P kg}^{-1}$  soil

Loamy moderately weathered soils in temperate regions:  
P-rich:  $200\text{-}800 \text{ mg P kg}^{-1}$  soil

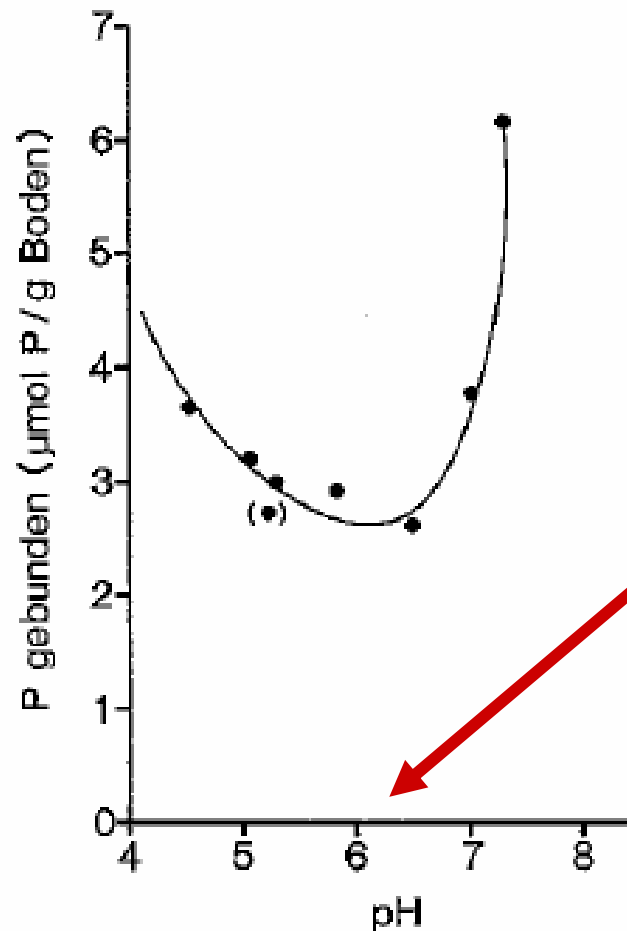
Soils lose geogenic P during weathering.

P contents of A horizons typically  $0.02\text{-}0.08\%$  P

# Changes of P forms with soil genesis



# pH dependant Phosphate availability

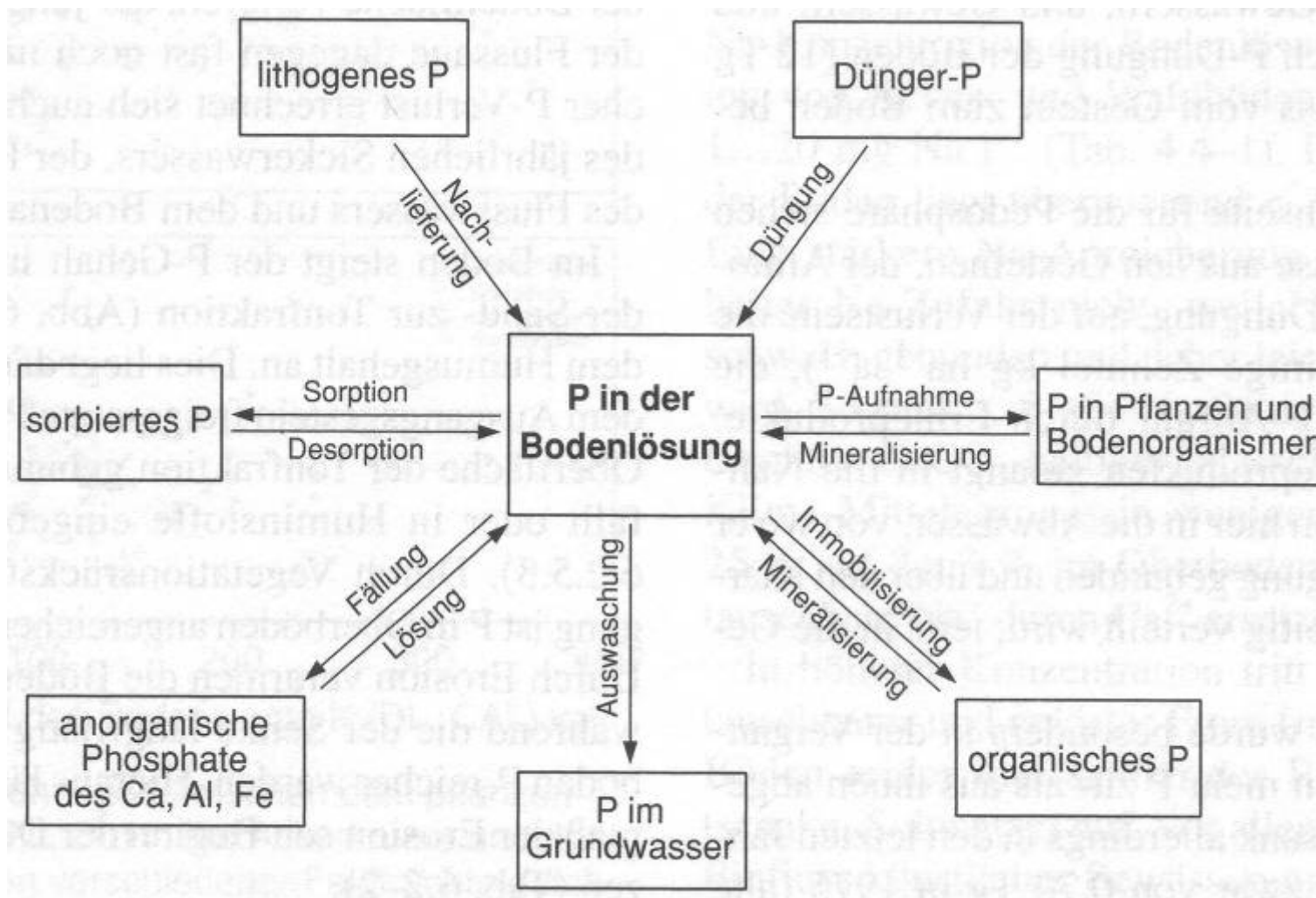


Optimal pH for  
P availability: pH 6-6.5

higher pH  $\rightarrow$  precipitation as Ca-phosphate  
lower pH  $\rightarrow$  more sorption to Fe oxides  
(more positive charge),  
precipitation as  
Al / Fe-phosphate

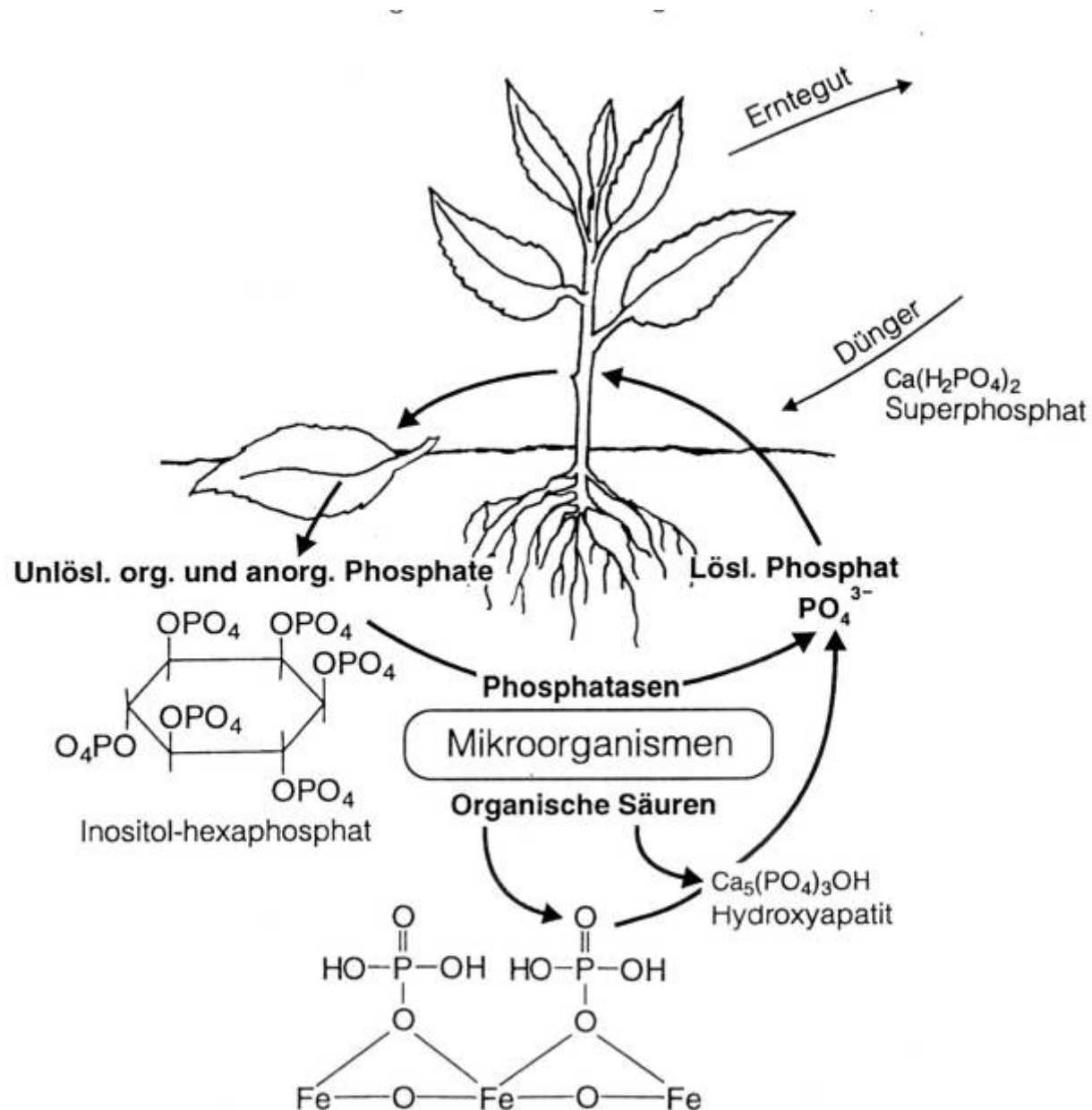
Abb. 60 Phosphatadsorption eines Lößbodens, dessen pH (5,2) durch Zugabe von HCl oder  $\text{Ca}(\text{OH})_2$  erniedrigt bzw. erhöht wurde [Konz. der P-Gleichgewichtslösung 0,2 mmol/l; (●) = ursprünglicher Boden] (Schwertmann, U. & H. Amann, unveröff.)

# Factors determining P in the soil solution





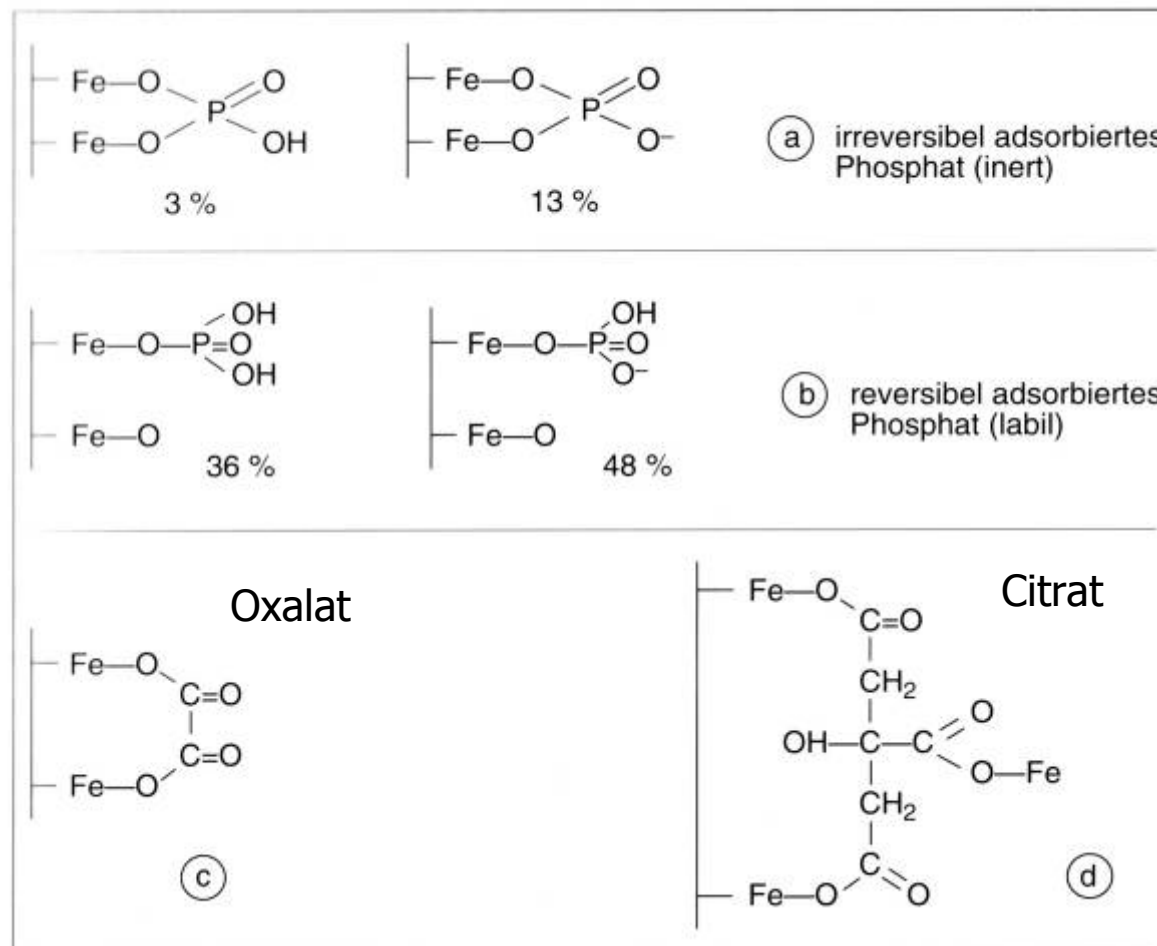
# Phosphate mobilization by microbes



# Phosphate mobilization by microbes and plants

Exudation of organic acids and other complex forming agents:

- sorbed P is replaced
- binding sites for sorption of new P are reduced



Examples:

- Gluconsäure
- Citronensäure
- α-Ketoglutar Säure
- Oxalsäure

# Phosphor deficiency

## Symptoms:

- reduced growth and root formation
- violet leaf chlorosis



schwacher P-Mangel



starker P-Mangel



# Questions

In welchen Formen kommt Phosphor im Boden vor?

Warum ist wenig P in der Bodenlösung?

Warum können Pflanzen nur zwischen 10 und 30% des Dünger-Phosphats direkt nutzen?

Wie können Pflanzen fixierten Phosphor mobilisieren?

Welche Rolle spielt P für die Pflanze?

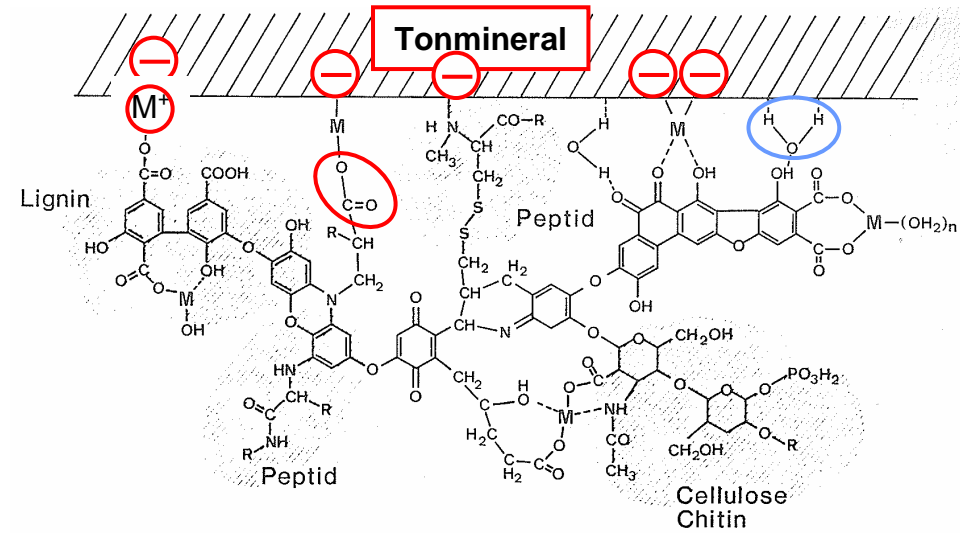
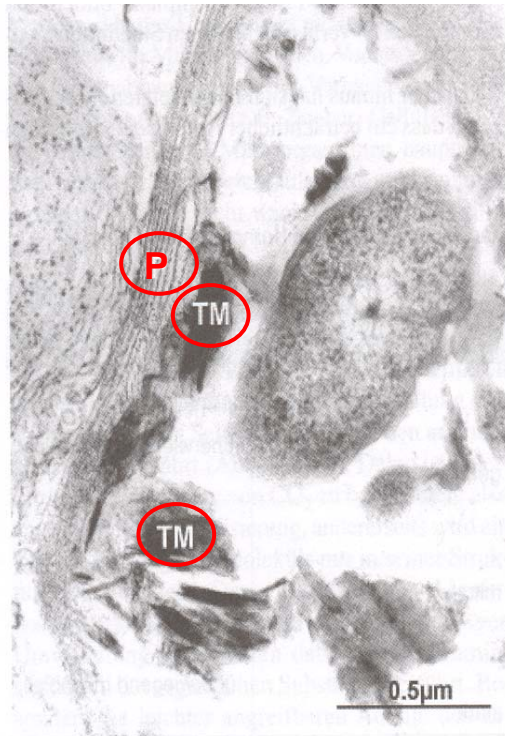
# Tonminerale

## Kationenaustausch

### Makronährelemente: K, Ca, Mg



# Tonminerale

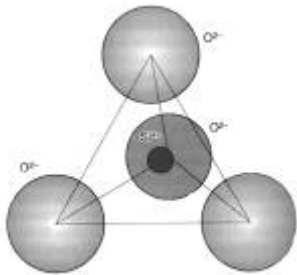


P: Polysaccharidfragment  
TM: Tonmineral

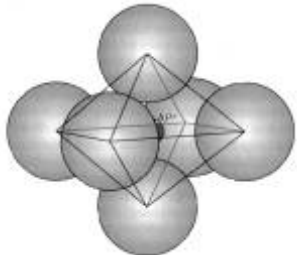
# Clay minerals / Tonminerale: wichtigste Bodenminerale

- Basic units of clay minerals

$\text{SiO}_4$  Tetraeder



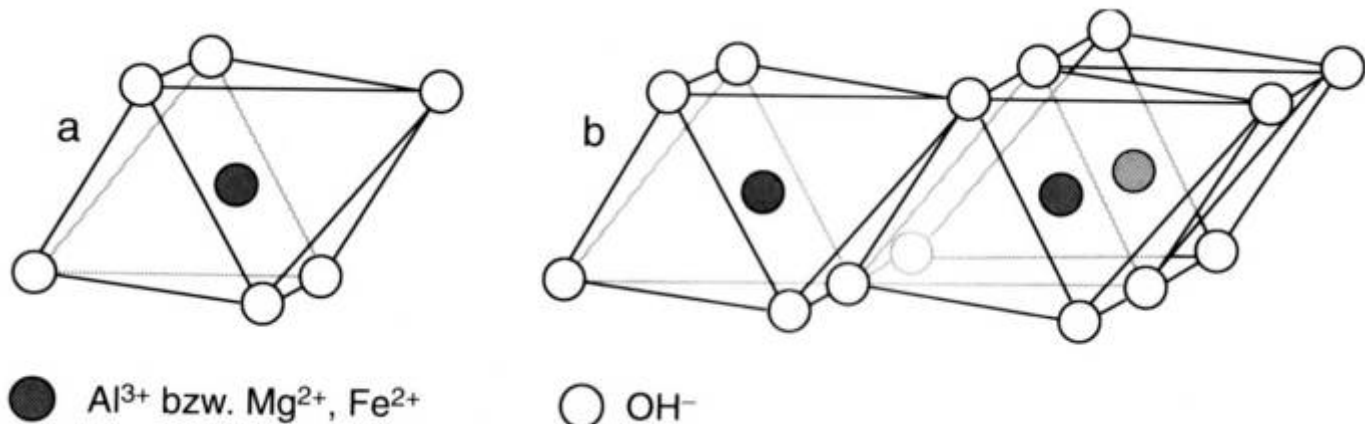
$\text{Al}(\text{OH})_6$  Octaeder



- Isomorpher Ersatz

Austausch von  $\text{Si}^{4+}$  durch  $\text{Al}^{3+}$  in Tetraedern oder von  $\text{Al}^{3+}$  durch  $\text{Mg}^{2+}$  oder  $\text{Fe}^{2+}$  in Oktaedern

→ permanente negative Ladung



# Clay minerals / Tonminerale

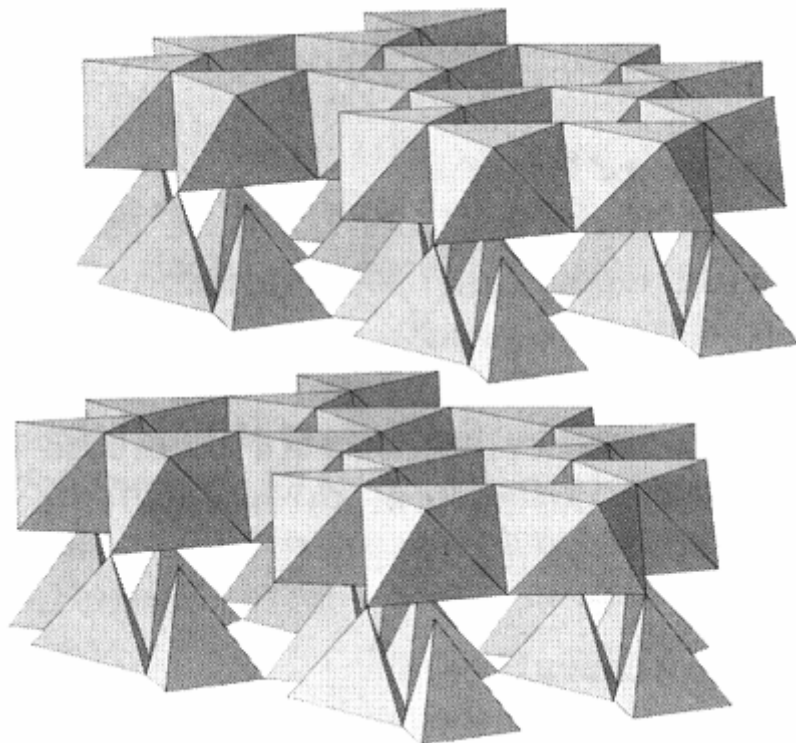
- Zweischichttonminerale

(1:1): z.B. Kaolinit

Schichtpakete aus

1 Schicht  $\text{AlO}_4(\text{OH})_2$  Oktaeder +

1 Schicht  $\text{SiO}_4$ -Tetraeder



- Dreischichttonminerale (2:1):

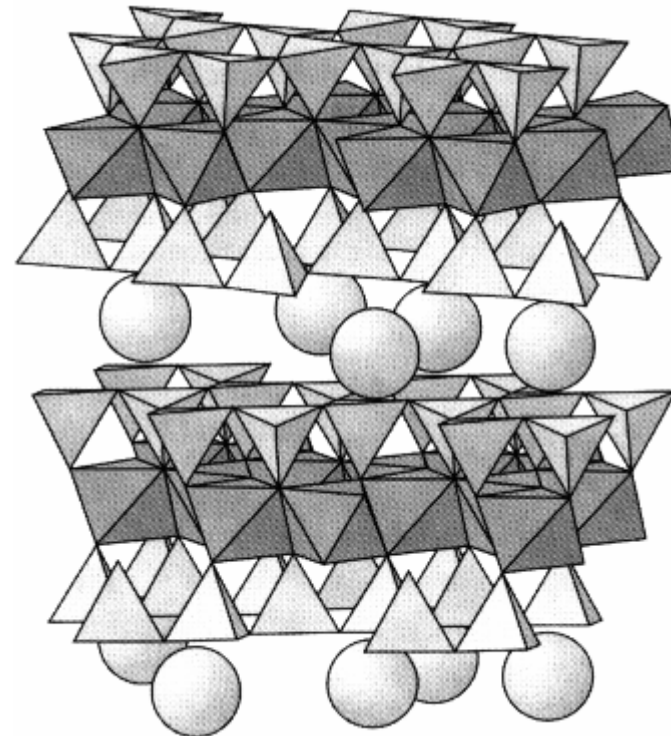
Vermikulit, Smektit, Chlorit

Schichtpakete aus

2 Schichten  $\text{SiO}_4$ -Tetraeder +

1 Schicht  $\text{AlO}_4(\text{OH})_2$  Oktaeder

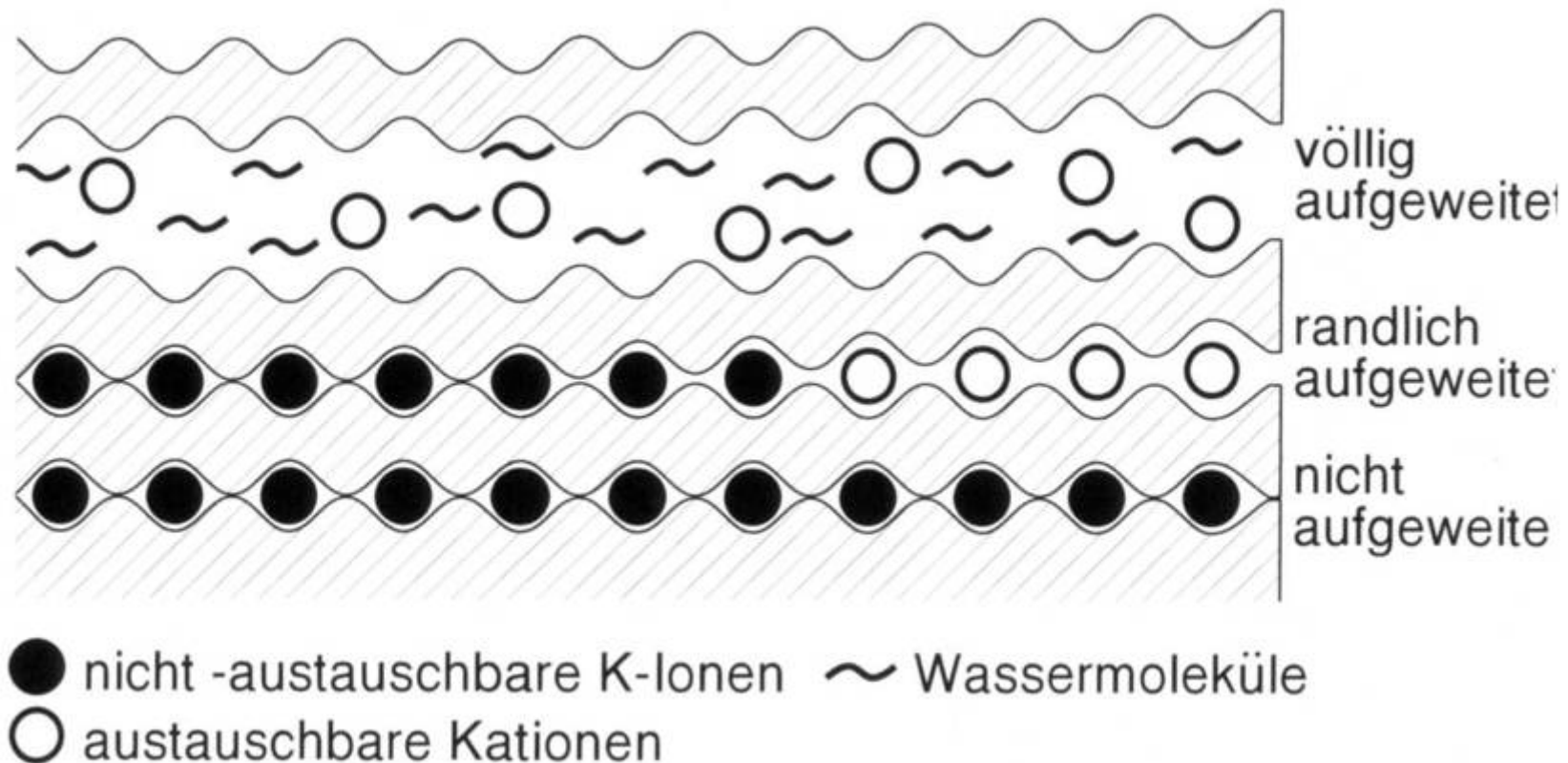
dazwischen





# Clay mineral weathering

- Example of an Illite with increasing space between layers caused by weathering



# Interlayer space of different clay minerals

Schichtladung sinkt, Aufweitbarkeit steigt,  
mehr innere Oberflächen für KAK



## Kaolinite (1:1)

0,72 nm, no cations between layers

CEC 3...15  $\text{cmol}_c \text{ kg}^{-1}$

## Illite (2:1)

1.0 nm fixed for  $\text{K}^+$

CEC 20...50  $\text{cmol}_c \text{ kg}^{-1}$

## Vermiculite (2:1)

1.0 nm for  $\text{K}^+$

1.4 nm for  $\text{Mg}^{2+}$

CEC 150...200  $\text{cmol}_c \text{ kg}^{-1}$

## Smectite (2:1)

1.4 nm for  $\text{Mg}^{2+}$

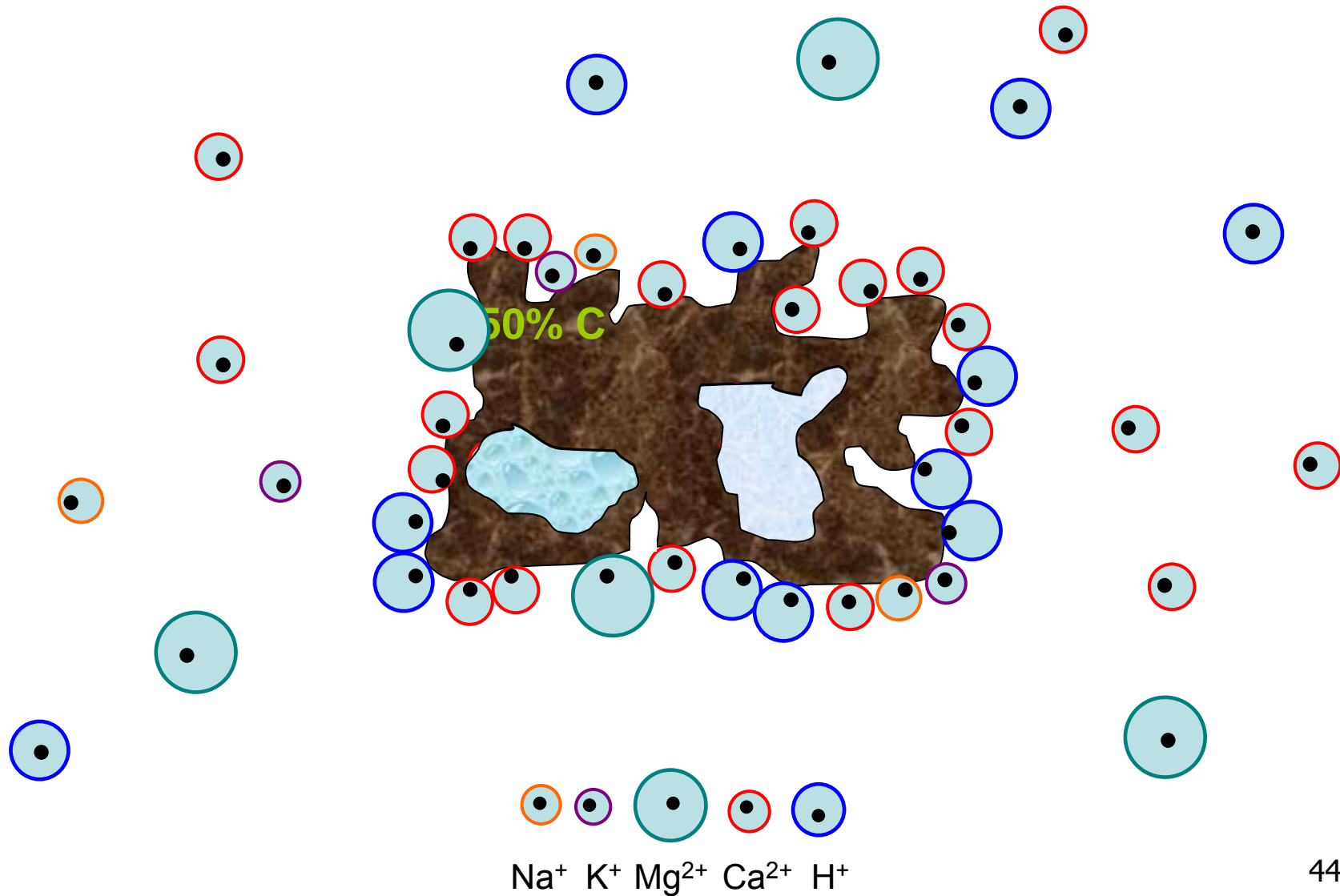
1.8 nm for  $\text{Mg}^{2+}$  + Glycerin

CEC 70-130  $\text{cmol}_c \text{ kg}^{-1}$

# Role of clay minerals in soils

- Charged due to isomorphous substitution of central ions:  
often negative charge
- Weathering releases ions from inter-layers and later on,  
from all positions
- Sorbents for soil organic matter

# Kationenaustausch



# Cation Exchange Capacity (CEC) Kationenaustauschkapazität

- Definition of Cation Exchange capacity (CEC/KAK):

Sum of cations that can be extracted from a soil using a (neutral) salt solution

Important measure for soil fertility

- exchangeable nutrients are still plant available
- protection against loss of basic nutrients via leaching

Typical exchangeable cations in the soil

$\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{H}^+$ ,  $(\text{NH}_4^+)$ ,  $\text{Fe}^{2+}$ , heavy metal ions

basic cations / basische Kationen (Maß für die Basizität eines Bodens)

→ Anion Exchange Capacity (AEC/AAK):

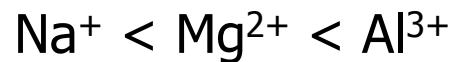
amount of negatively charged ions a soil can reversibly adsorb

In European soils usually less important than CEC

# Cation exchange capacity (CEC)

- Cation exchange: Ions at the adsorber are in equilibrium with the soil solution, but specific binding strength of individual cations:

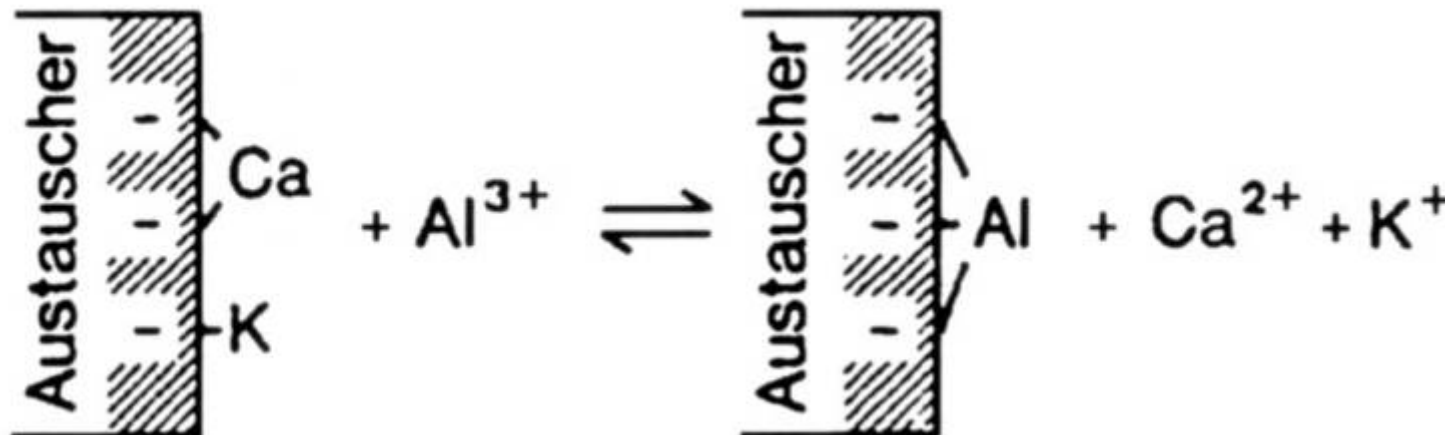
- binding strength increases with increasing charge:



- binding strength increases with decreasing ion size:



For example in a Loess soil:



# Cation exchange capacity (CEC)

Relevant particles for CEC in the soil:

- clay minerals
- organic matter
- Fe and Al oxides

→ the higher the clay and organic matter content,  
the higher is CEC

# Cation Exchange Capacity (CEC)

- permanent negative charge: pH independent  
v.a. durch isomorphen Ersatz in Tonmineralen
- variable negative charge: pH dependent  
in organischer Substanz, Oxiden, und amorphen  
Tonmineralen (Allophan)



# Cation Exchange Capacity (CEC)

## Variable charge

Charge depends on pH: negative charge at high pH due to dissociation of  $H^+$ , neutral to positive charges at low pH values.

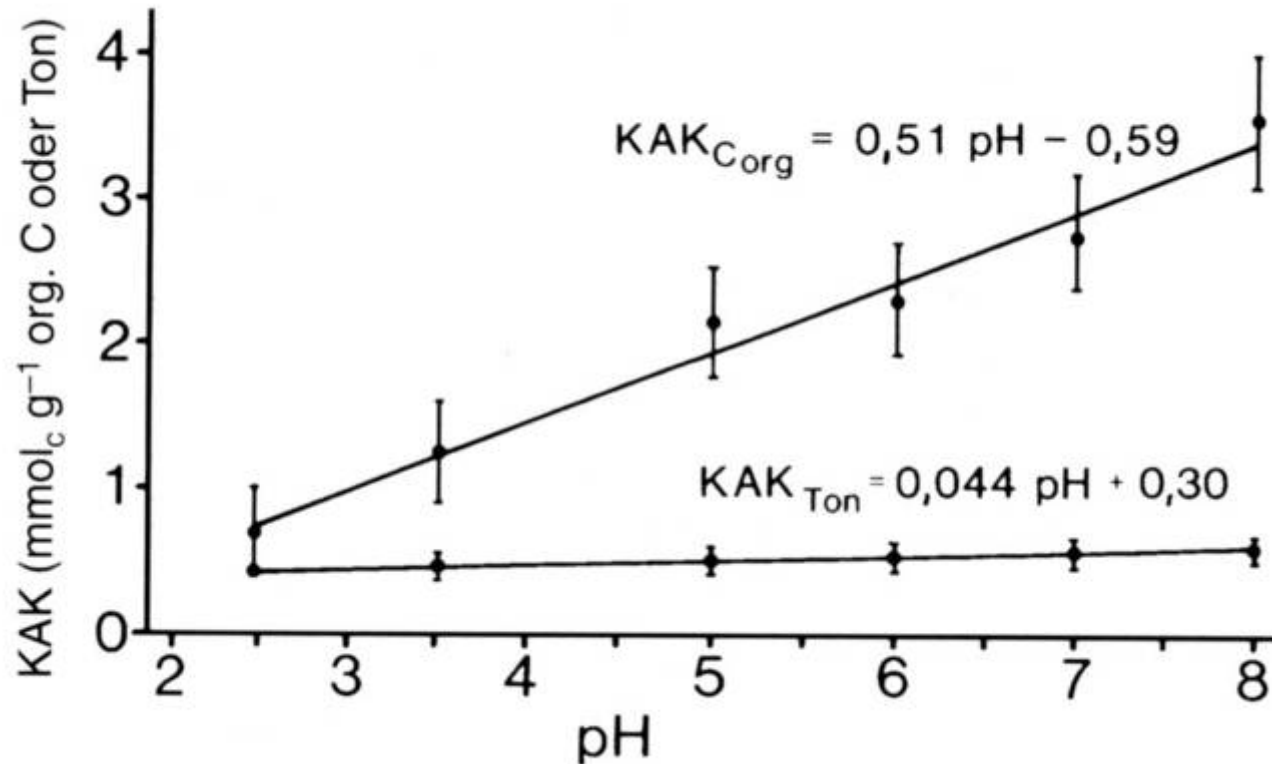
Metal-hydroxides:  $[M-OH]^0 + Ca^{2+} \rightarrow [M-O-Ca^{2+}]^+ + H^+$

Carboxyl-Groups of organic substances:  $[R-COOH]^0 + Ca^{2+} \rightarrow [RCOO^-Ca^{2+}]^+ + H^+$

Examples for substances mit mainly variable charge:

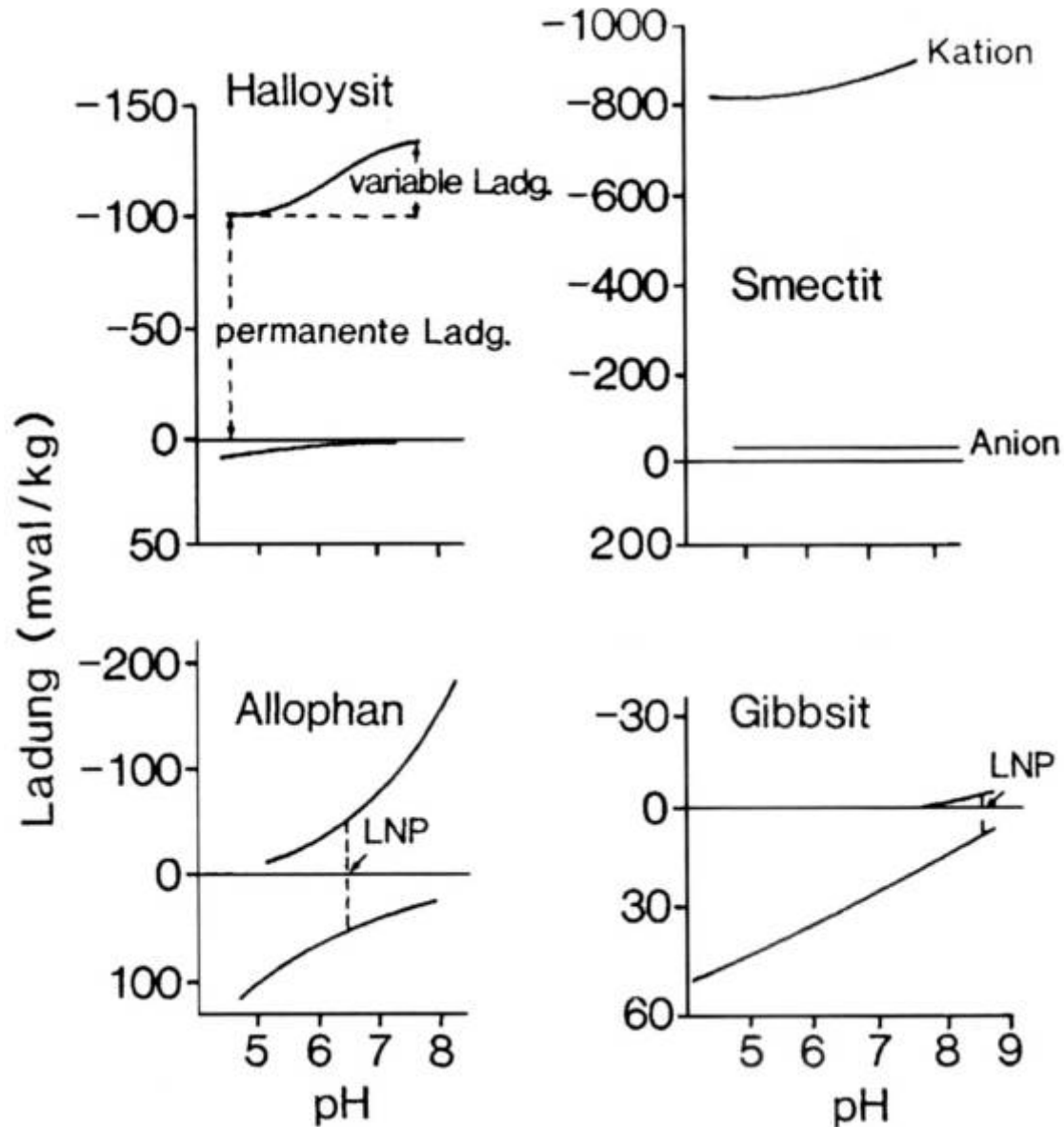
- Allophane / Imogolite: non-crystalline clay minerals
- Fe/Al-Oxides and Hydroxides
- organic matter

# pH dependency of CEC



pH is important for the contribution of organic matter to CEC  
but less for clay

# pH dependency of CEC



# Tonminerale

- Was sind die wichtigsten Eigenschaften von Tonmineralen und Prozesse für
  - Freisetzung von Nährstoffen
  - Speicherung von Nährstoffen
  - Pflanzenverfügbarkeit von Nährstoffen?