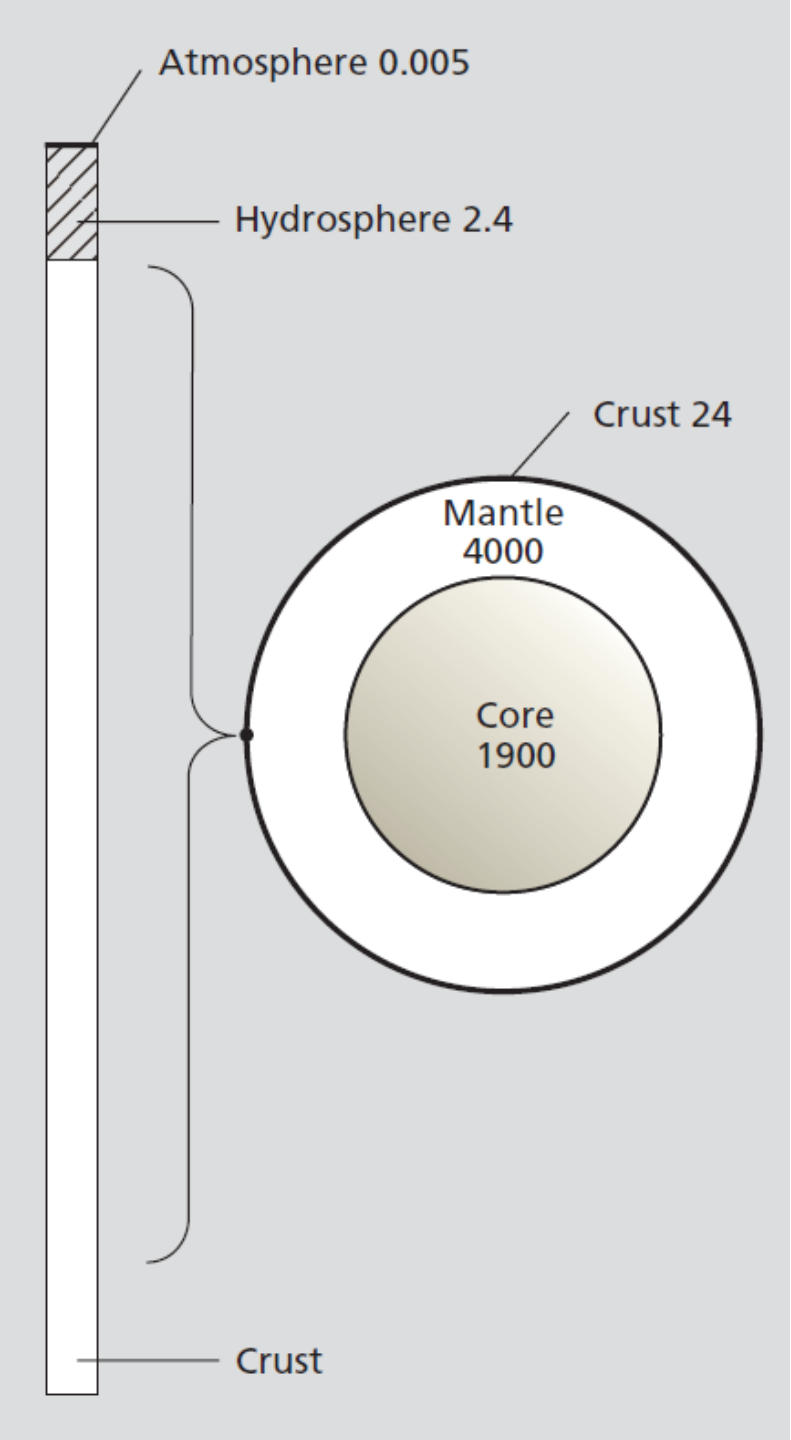
Systembezogene Themen

1. Atmosphäre
2. Kontinentale Kruste
3. Böden und Verwitterungsprozesse
4. Binnengewässer
5. Ozeane (Marine Geochemie)

Die Atmosphere

Relative Größen der wichtigsten Reservoire der Erde

Einheiten: 10^{24}g



Vertikale Unterteilung der Atmosphäre

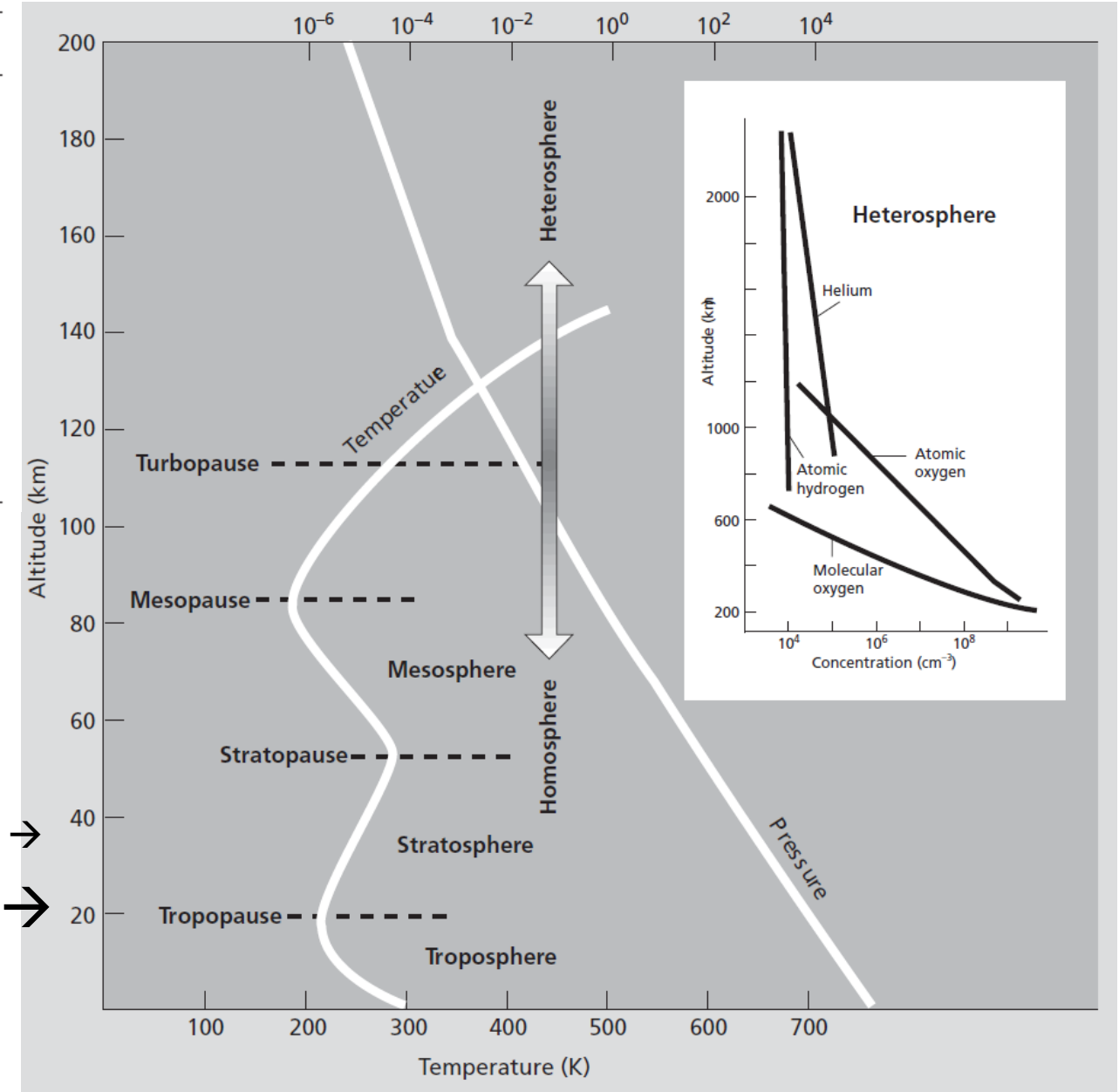
Gas	Concentration
Nitrogen	78.084%
Oxygen	20.946%
Argon	0.934%
Water	0.5–4%
Carbon dioxide	360 ppm
Neon	18.18 ppm
Helium	5.24 ppm
Methane	1.7 ppm
Krypton	1.14 ppm
Hydrogen	0.5 ppm
Xenon	0.087 ppm

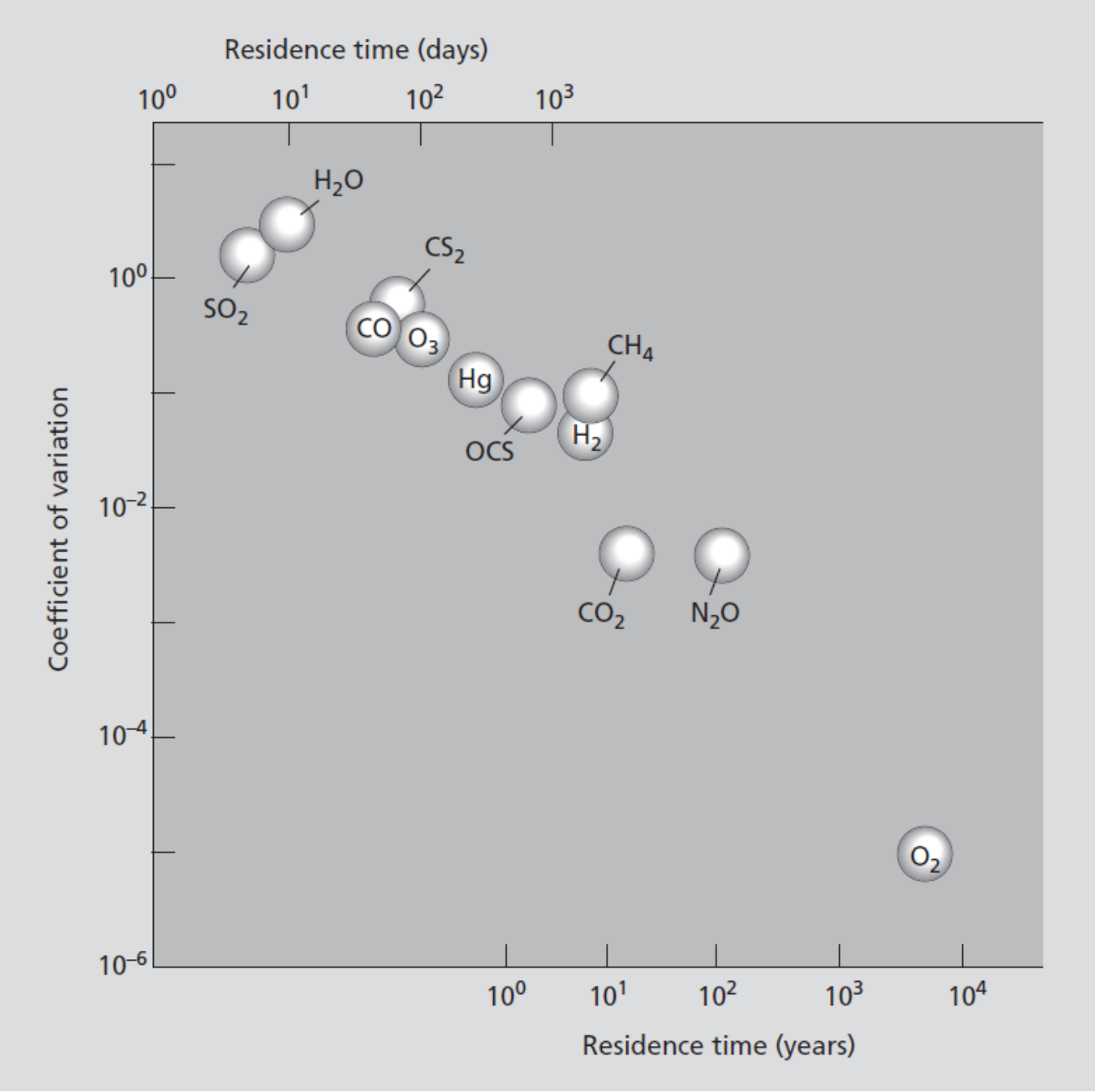
Barometrische Höhenformel:

$$p(H) = p_0 \exp\left(\frac{-H}{7990\,\mathrm{m}}\right)$$

Red Blue Stratos →

Ozonschicht →




Residence time (days)
10^0
10^1
10^2
10^3
H_2O
CS_2
SO_2
CO
O_3
CH_4
Hg
OCS
H_2
CO_2
N_2O
O_2
Coefficient of variation
10^0
10^{-2}
10^{-4}
10^{-6}
10^0
10^1
10^2
10^3
10^4
Residence time (years)

Atmosphären heute

Die Atmosphären der Planeten heute:

	Venus	Erde	Mars
Luftdruck Oberfläche [bar]	100	1	0.06
Oberflächentemperatur [°C]	480	15	-60
Kohlendioxid	**93-98 %**	0.03 %	**95.3 %**
Stickstoff	2-5 %	**78.1 %**	2.7 %
Sauerstoff	~30 ppm	**20.9 %**	0.13 %
Kohlenmonoxid	~20 ppm	0.05-0.2 ppm	0.07 %
Wasserdampf	0.1 %	1.00 %	0.03 %
Argon	~60 ppm	0.93 %	1.60 %

Uratmosphäre

Wasserstoff (H_2)
Helium (He)
wenig Methan (CH_4), Ammoniak (NH_3) und Edelgase

Atmosphäre vor 4 Ga

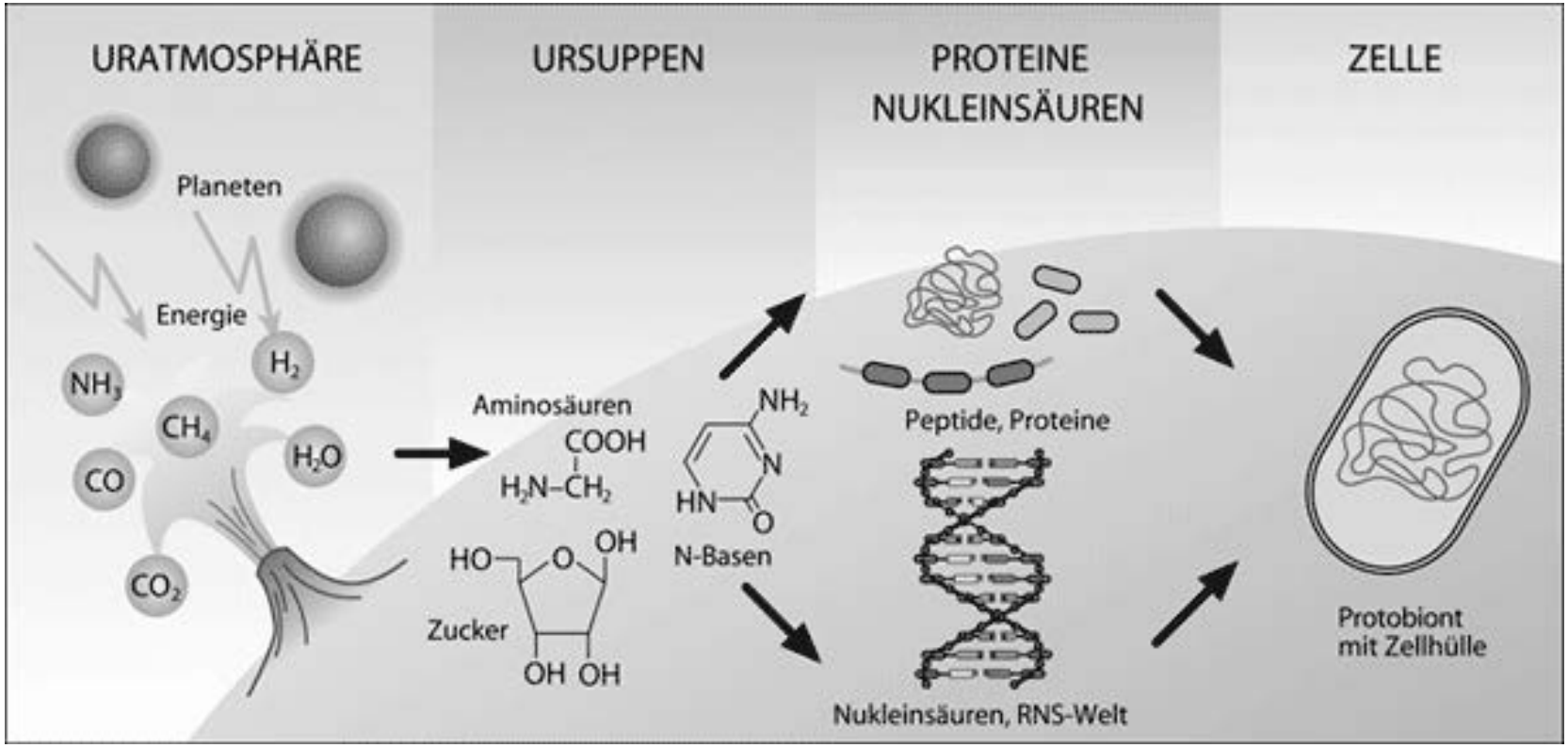
Wasserdampf (H_2O) 80%
Kohlenstoffdioxid (CO_2) 10 %
Schwefelwasserstoff (H_2S) 5-7%
Stickstoff (N_2)
Wasserstoff (H_2),
Kohlenmonoxid (CO), Helium, Methan, Ammoniak

Entstehung des Lebens

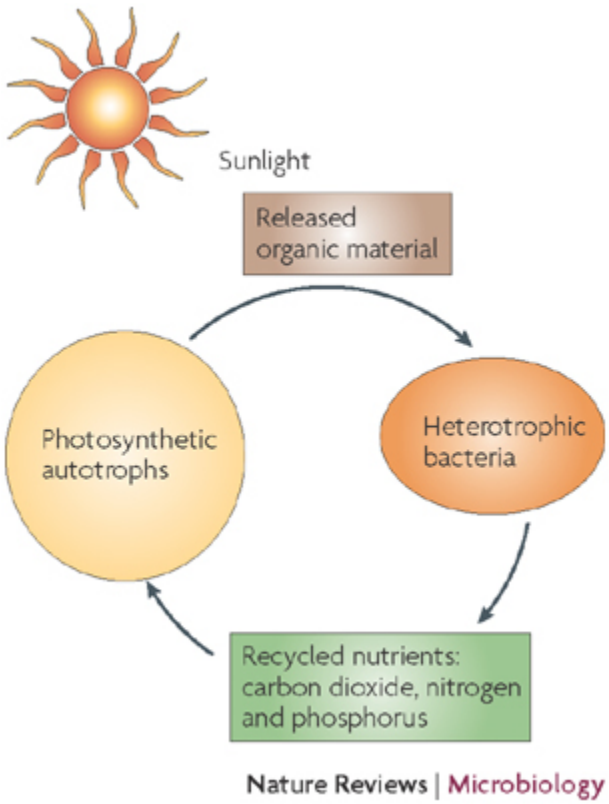
Geochemie – Biochemie

“lebend”: ein sich (auf einer Mineraloberfläche) vervielfältigendes Reaktionssystem

“Zutaten”: NH_3, CH_4, KCN, CO, Fe^{2+}, Ni^{2+}



Entstehung des Lebens



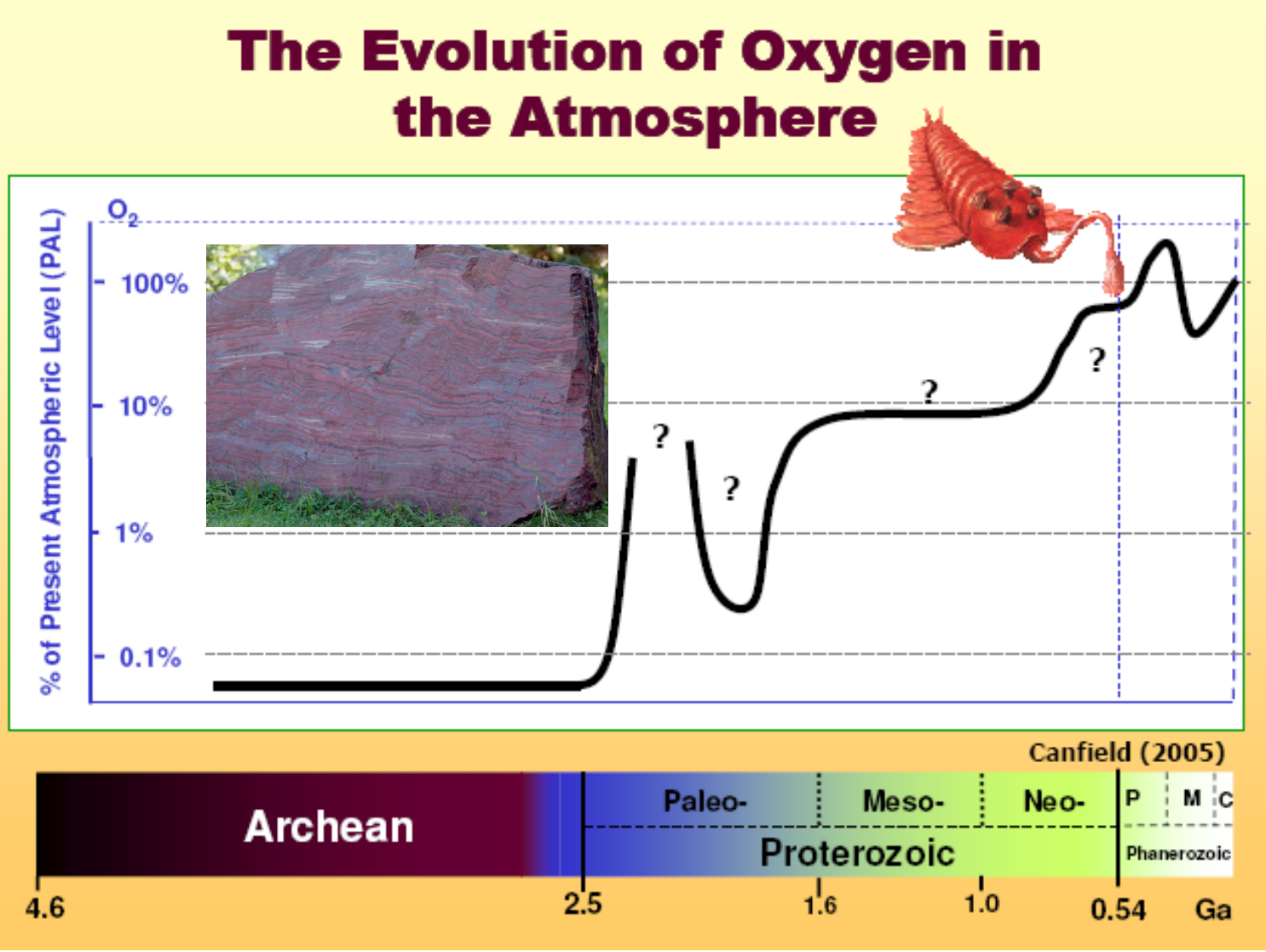
Does the Earth act like a single living entity (Gaya theory, James Lovelock) or as a randomly driven geochemical system?

Autotrophe (selbsternährend) Reaktionen

$$6H_2S + 6CO_2 \longrightarrow 6S + C_6H_{12}O_6 + 6H_2O$$

$$6H_2O + 6CO_2 \longrightarrow C_6H_{12}O_6 + 6O_2$$

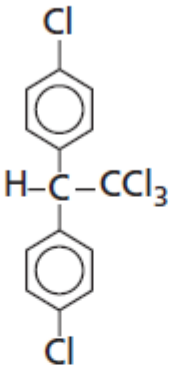
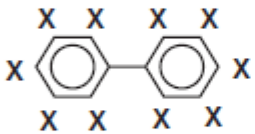
Freier Sauerstoff in der Atmosphäre



Eintrag und Veränderung durch anthropogene Aktivitäten

1. Eintrag neuer „Umweltchemikalien“
2. Veränderung natürlicher Kreisläufe

Antropogene Schadstoffe in der Atmosphäre

Name	Formula	Use	Environmental impact
DDT (2,2-bis (*p*-chlorophenyl)-1,1,1-trichloroethane		Pesticide	Unselective poison, concentrates up food chain
PCBs (polychlorinated biphenyls)	 (x are possible chlorine positions)	Dielectric in transformers; hydraulic fluids and many other uses	Resistant to breakdown carcinogens
TBT (tributyl tin)	$(CH_3(CH_2)_3)_3Sn$	Antifouling agent in marine paints	Affects sexual reproduction of shellfish
CFCs (chlorofluorocarbons)	e.g. F-11, CCl_3F	Aerosol propellant, foam blower	Destruction of stratospheric ozone

System Atmosphäre

Austausch durch:

1. geochemische
2. biologische
3. anthropogene

Prozesse

Table 3.2 Sources for particulate material in the atmosphere. From Brimblecombe (1986).

Source	Global flux (Tg yr^{-1})
Forest fires	35
Dust	750
Sea salt	1500
Volcanic dust	50
Meteoritic dust	1

$$H_2SO_{4(\text{in aerosol})} + NaCl_{(\text{in aerosol})} \rightarrow HCl_{(g)} + NaHSO_{4(\text{in aerosol})}$$

Biologen gebildete Spurengase

Biogene Stickstoffquellen:

Ammoniak und CO_2:

$$NH_2CONH_{2(aq)} + H_2O_{(l)} \rightarrow 2NH_{3(g)} + CO_{2(g)}$$

Lachgasfreisetzung durch mikrobielle Aktivität in Böden:

$$2NH_{3(g)} + 2O_{2(g)} \rightarrow N_2O_{(g)} + 3H_2O_{(g)}$$

Organosulfide:

Dimetylsulfid, Quelle: marines Phytoplankton:

$$(CH_3)_2S^+CH_2CH_2COO^+_{(aq)} \rightarrow (CH_3)_2S_{(g)} + CH_2CHCOOH_{(aq)}$$

Carbonylsulfid:

$$CS_{2(g)} + H_2O_{(g)} \rightarrow OCS_{(g)} + H_2S_{(g)}$$

Spurengase in der Atmosphäre

Table 3.3 Naturally occurring trace gases of the atmosphere. From Brimblecombe (1986).

	Residence time	Concentration (ppb)
Carbon dioxide	4 years	360 000
Carbon monoxide	0.1 year	100
Methane	3.6 years	1600
Formic acid	10 days	1
Nitrous oxide	20–30 years	300
Nitric oxide	4 days	0.1
Nitrogen dioxide	4 days	0.3
Ammonia	2 days	1
Sulphur dioxide	3–7 days	0.01–0.1
Hydrogen sulphide	1 day	0.05
Carbon disulphide	40 days	0.02
Carbonyl sulphide	1 year	0.5
Dimethyl sulphide	1 day	0.001
Methyl chloride	30 days	0.7
Methyl iodide	5 days	0.002
Hydrogen chloride	4 days	0.001

Reaktivität von Spurensubstanzen

Das Hydroxyl-Radikal (OH-Radikal) spielt eine wichtige Rolle für den Abbau von Treibhausgasen wie Methan, von Ozon und Luftverunreinigungen

→ *chemisches Waschmittel* der Atmosphäre

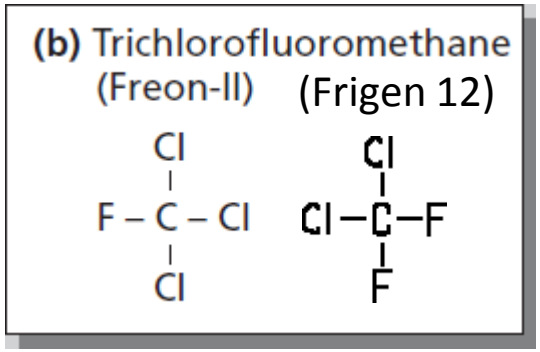
$$O_{3(g)} + h\nu \rightarrow O_{2(g)} + O_{(g)}$$

$$O_{(g)} + H_2O_{(g)} \rightarrow 2OH_{(g)}$$

Reaktivität von Spurensubstanzen

Ozon – nützlich und gefährlich

Flourchlorkohlenwasserstoffe (FCKW)



reagieren nicht mit OH. Reagieren mit Ozon-Molekül in der Stratosphäre:

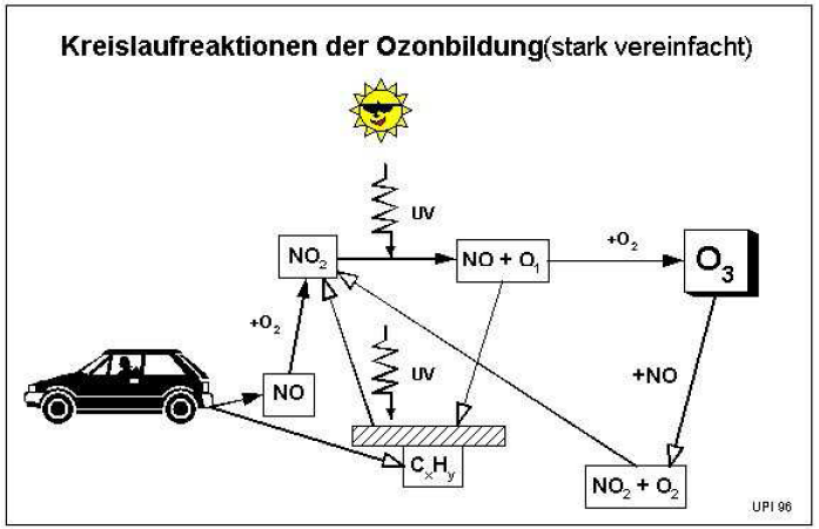
$Cl + O_3 \rightarrow ClO + O_2$

Chloroxid zerfällt wieder in ein Chlor-Atom und Sauerstoff und kann erneut ein Ozon-Molekül angreifen. Auf diese Weise kann ein einziges Chlor-Atom bis zu 100 000 Ozon-Moleküle zerstören!

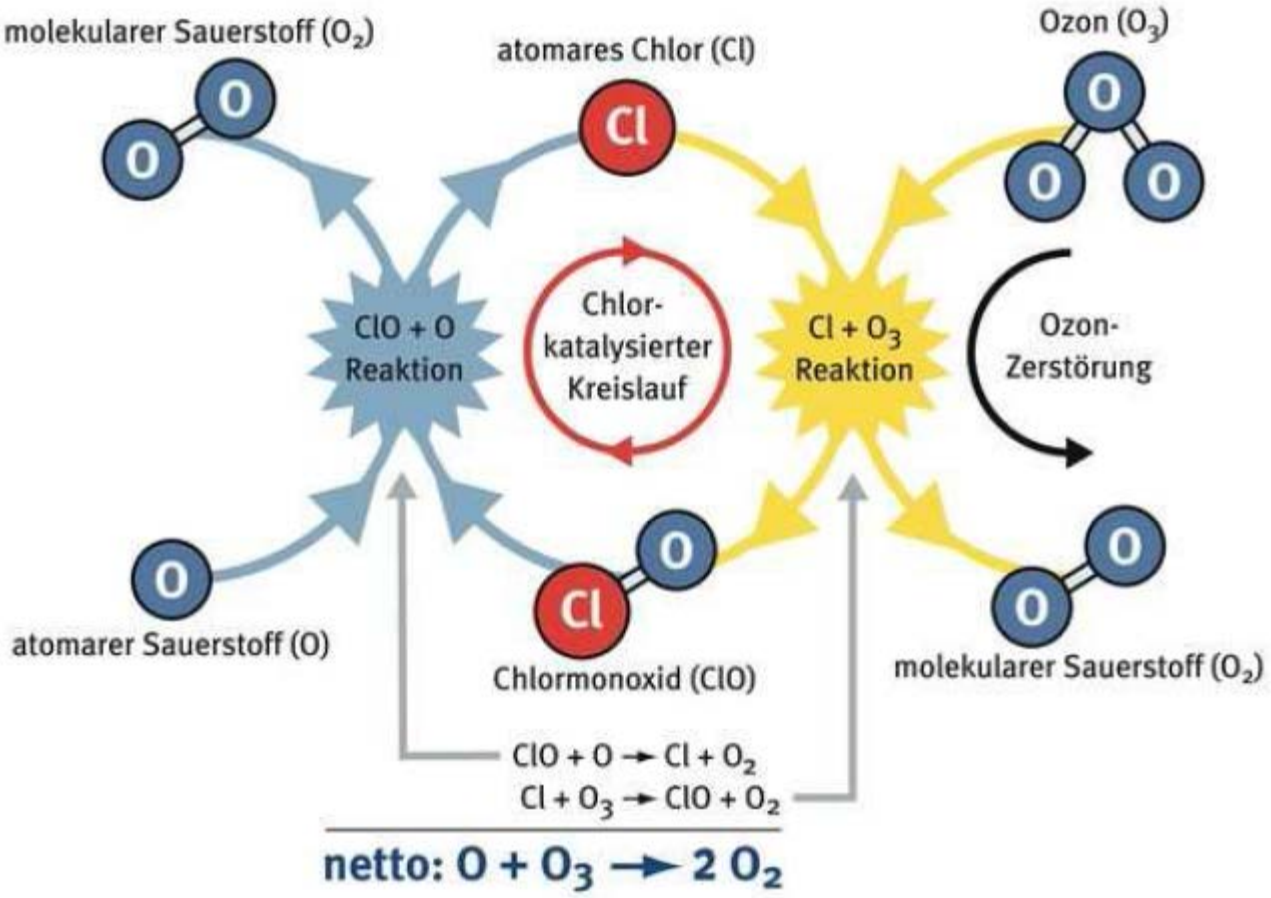
Ozonbildung in Bodennähe durch Reaktionen von Stickstoffoxiden (NO, NO_2) aus Abgasen unter dem Einfluß von UV-Licht:

$NO_2 \rightarrow NO + O$

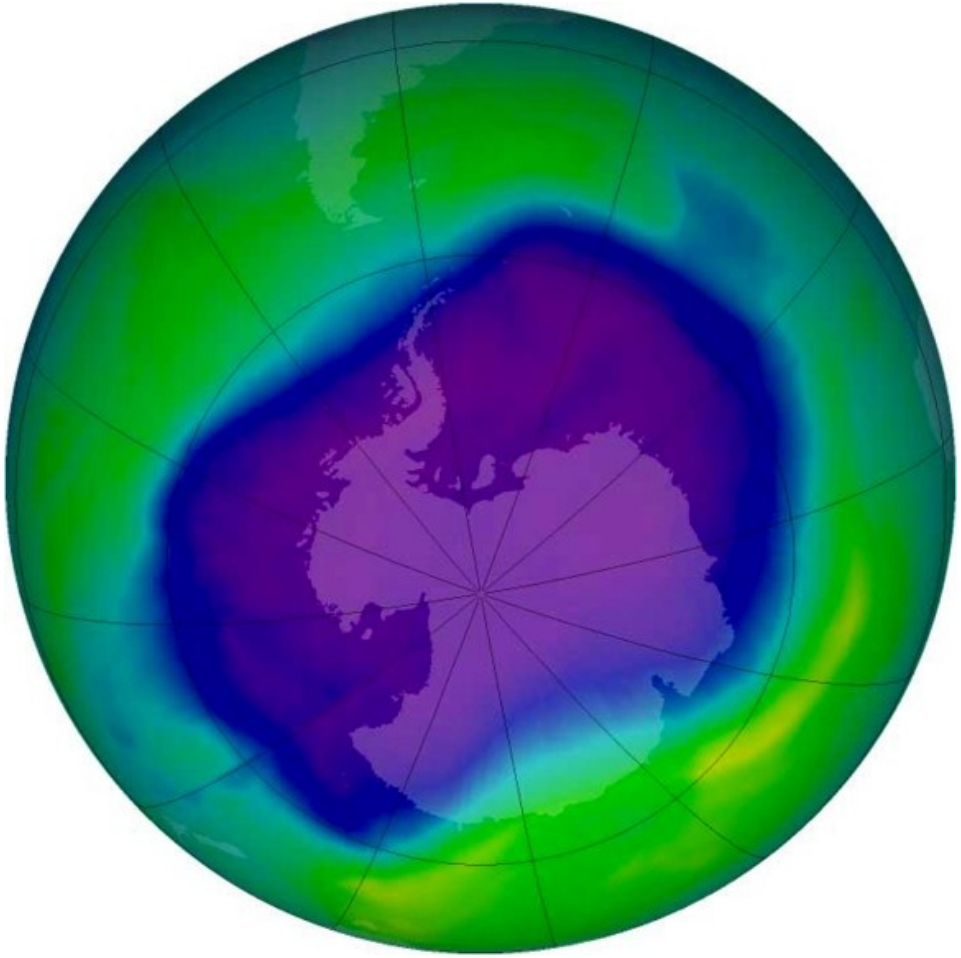
$O + O_2 \rightarrow O_3$



Chemischer Ozonabbau



Chemischer Ozonabbau



Ozonloch über der Antarktis im September 2006

Table 3.3 Naturally occurring trace gases of the atmosphere. From Brimblecombe (1986).

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Carbon monoxide	0.1 year	100
Methane	3.6 years	1600
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Nitrous oxide	20–30 years	300
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Nitrogen dioxide	4 days	0.3
Ammonia	2 days	1
Sulphur dioxide	3–7 days	0.01–0.1
Hydrogen sulphide	1 day	0.05
Carbon disulphide	40 days	0.02
Carbonyl sulphide	1 year	0.5
Dimethyl sulphide	1 day	0.001
Methyl chloride	30 days	0.7
Methyl iodide	5 days	0.002
Hydrogen chloride	4 days	0.001

CH_3Cl

Beispiel Freon 11:

$$CFCl_{3(g)} + h\nu \rightarrow CFCl_{2(g)} + Cl_{(g)}$$

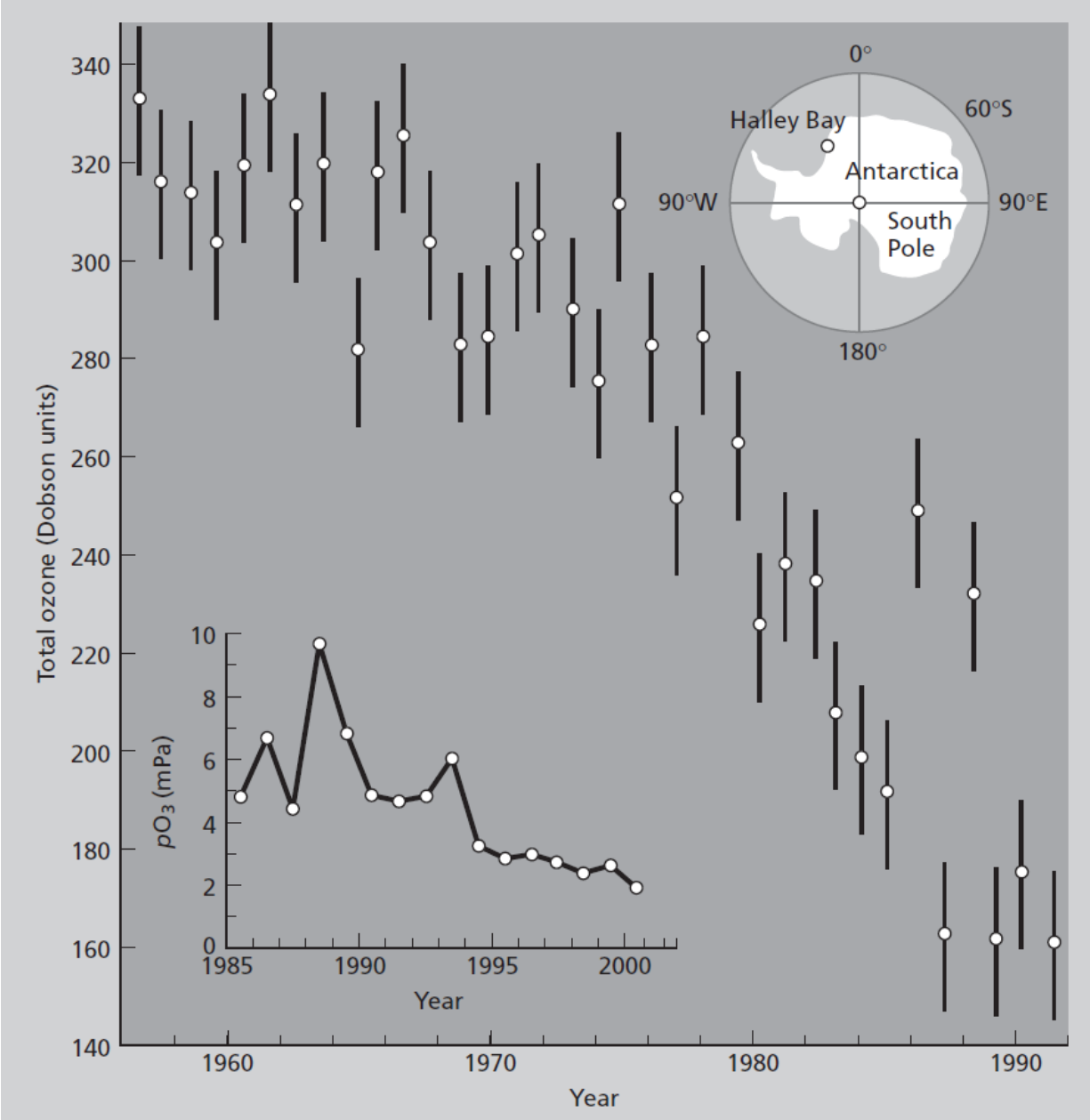
$$CF_2Cl_{2(g)} + h\nu \rightarrow CF_2Cl_{(g)} + Cl_{(g)}$$

Bildung freier Cl-Atome:

$$O_{3(g)} + Cl_{(g)} \rightarrow O_{2(g)} + ClO_{(g)}$$

$$ClO_{(g)} + O_{(g)} \rightarrow O_{2(g)} + Cl_{(g)}$$

Das Ozonloch über der Antarktis



Abschied vom Ozonloch

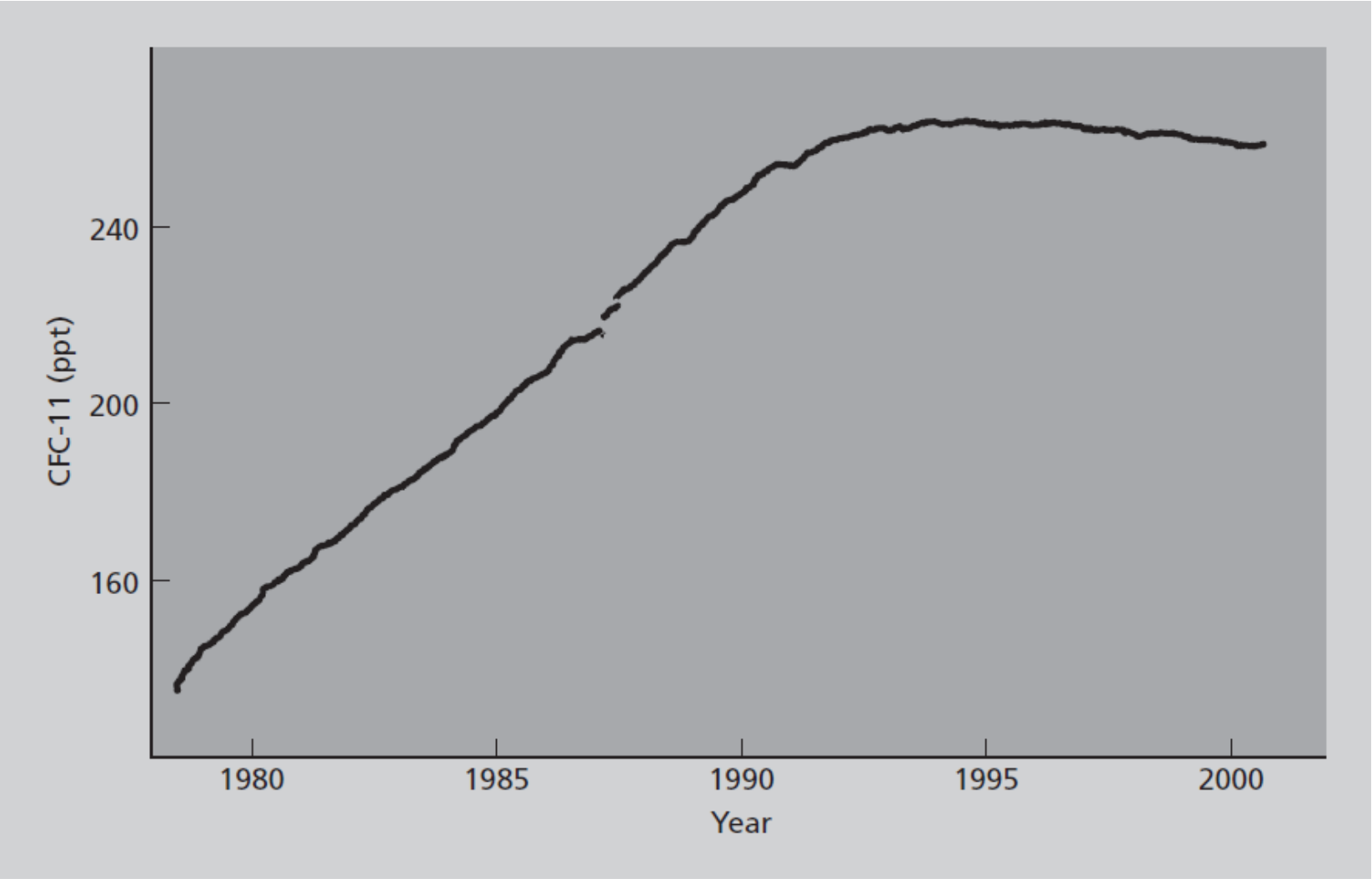
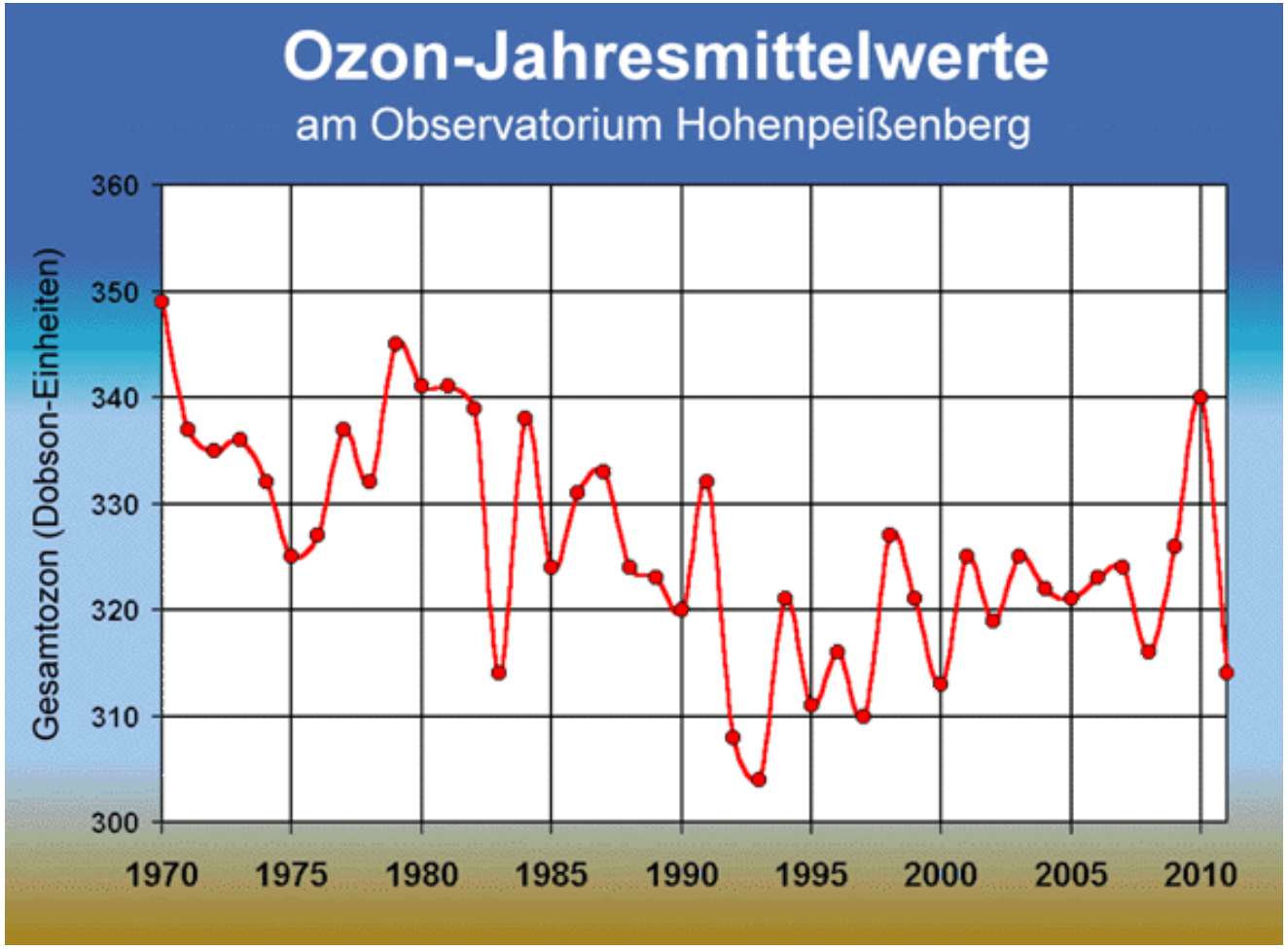


Fig. 3.7 Concentrations of CFC-11 measured at ground level, Cape Grim, Tasmania. Note that concentrations of CFC-11 have been falling in the 1990s following the rapid increase during the 1980s. Copyright CSIRO Australia, May 2002.



Der Knick im Jahre 1991 durch Ausbruch des Vulkans Pinatubo (Philippinen). Abnahme im Jahre 1982 durch Ausbruch des Vulkans El Chichón (Mexiko).

London smog (sm[oke and f]og)

Jack the Ripper in the London Fog

London smog (sm[oke and f]og)

$$\text{‘4CH’} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(g)}$$

fuel + oxygen → carbon dioxide + water

$$\text{‘4CH’} + 3O_{2(g)} \rightarrow 4CO_{(s)} + 2H_2O_{(g)}$$

coal + oxygen → carbon monoxide + water

Fuel	S (% by weight)
Coal	7.0–0.2
Fuel oils	4.0–0.5
Coke	2.5–1.5
Diesel fuel	0.9–0.3
Petrol	0.1
Kerosene	0.1
Wood	Very small
Natural gas	Very small

London smog (sm[oke and f]og)

$$4FeS_{2(s)} + 11O_{2(g)} \rightarrow 8SO_{2(g)} + 2Fe_2O_{3(s)}$$

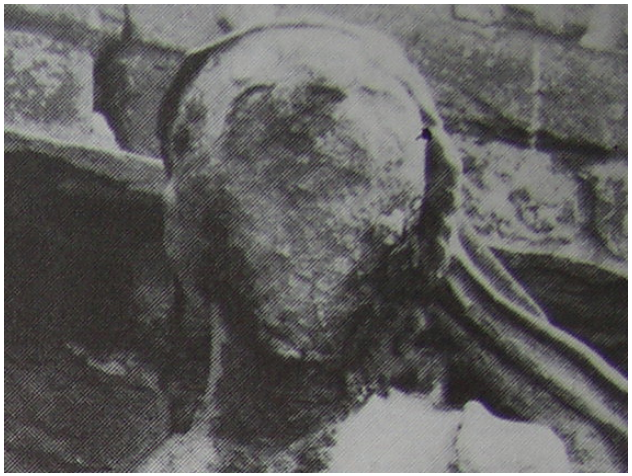
$$SO_{2(g)} + H_2O_{(l)} \leftrightharpoons H^+_{(aq)} + HSO^-_{3(aq)}$$

$$2HSO^-_{3(aq)} + O_{2(aq)} \rightarrow 2H^+_{(aq)} + 2SO^{2-}_{4(aq)}$$

Auswirkungen der Luftverschmutzung

Portalfigur (Schloß Herten)

1908



1969

$$H_2SO_{4(aq)} + CaCO_{3(s)} + H_2O_{(l)} \rightarrow CO_{2(g)} + CaSO_{4(s)} \cdot 2H_2O_{(l)}$$

Anwesenheit von Stickoxiden kann H_2SO_4-Bildung beschleunigen:

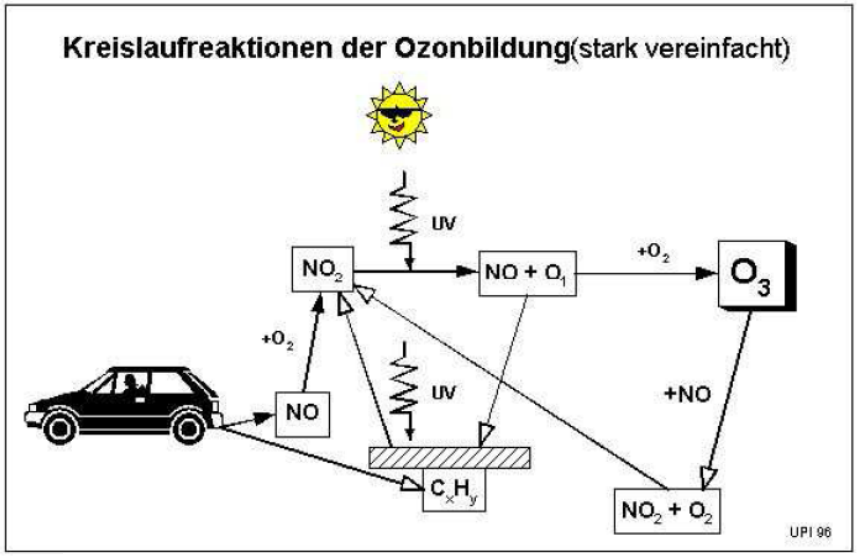
$$SO_{2(g)} + NO_{2(g)} + H_2O_{(l)} \rightarrow NO_{(g)} + H_2SO_{4(aq)}$$

Los Angeles smog – secondary pollution

$$O_{(g)} + N_{2(g)} \rightarrow NO_{(g)} + N_{(g)}$$

$$N_{(g)} + O_{2(g)} \rightarrow NO_{(g)} + O_{(g)}$$

an der Luft wird NO zu braunem NO_2 oxidiert



NO_2 dissoziiert bei Bestahlung mit Sonnenlicht:

$$NO_{2(g)} + hv \rightarrow O_{(g)} + NO_{(g)}$$

Ozonbildung:

$$O_{(g)} + O_{2(g)} \rightarrow O_{3(g)}$$

Ozon - sekundärer Schadstoff

$$CH_{4(g)} + 2O_{2(g)} + 2NO_{(g)} \xrightarrow{hv} H_2O_{(g)} + HCHO_{(g)} + 2NO_{2(g)}$$

Table 3.5 Comparison of Los Angeles and London smog. From Raiswell *et al.* (1980).

Characteristic	Los Angeles	London
Air temperature	24 to 32°C	–1 to 4°C
Relative humidity	<70%	85% (+ fog)
Type of temperature inversion	Subsidence, at 1000 m	Radiation (near ground) at a few hundred metres
Wind speed	$<3\,m\,s^{-1}$	Calm
Visibility	<0.8–1.6 km	<30 m
Months of most frequent occurrence	Aug. to Sept.	Dec. to Jan.
Major fuels	Petroleum	Coal and petroleum products
Principal constituents	O_3, NO, NO_2, CO, organic matter	Particulate matter, CO, S compounds
Type of chemical reaction	Oxidative	Reductive
Time of maximum occurrence	Midday	Early morning
Principal health effects	Temporary eye irritation (PAN)	Bronchial irritation, coughing (SO_2/smoke)
Materials damaged	Rubber cracked (O_3)	Iron, concrete

Wichtigste Bestandteile des photochemischen Smogs

Ozon (O_3)

Peroxidradikale (R-CH2O2)

Peroxyacetylnitrat (PAN) $C_2H_3NO_5$

Air Pollution in Beijing

In winter when coaled fired heating is used and there is no wind or rain to remove the pollution, the levels of pollution measured by the US embassy (the most reliable source) is off the charts and at least 30 to 45 times the recommended safety levels.

Verteilung der Edelgase in der Atmosphäre

Tabelle 5.3. Berechnung des Ar/He-Verhältnisses auf Grund des radioaktiven Zerfalls der primordialen Nuclide ^{40}K, ^{232}Th, ^{235}U und ^{238}U

M	H	$t_{1/2}$	Zerfallsart	D
^{238}U	99,28%	$4{,}49 \cdot 10^9$a	8α	$^{206}Pb + 8\,He$
^{235}U	0,715%	$7{,}13 \cdot 10^8$a	7α	$^{207}Pb + 7\,He$
^{232}Th	100%	$1{,}39 \cdot 10^{10}$a	6α	$^{206}Pb + 6\,He$
^{40}K	0,011%	$1{,}26 \cdot 10^9$a	β-Zerfall K-Eingang	89% ^{40}Ca 11% ^{40}Ar

$$He_h = \sum_i n(\alpha,i)\,\Delta M_i = \sum_i n(\alpha,i)\,M_{h,i}\left(\exp\left\{\frac{\ln 2}{t_{1/2,i}}\theta\right\} - 1\right)$$

He_h = jetzige Anzahl der He-Atome
$M_{h,i}$ = jetzige Anzahl der Mutteratome der Sorte i
$n(\alpha,i)$ = Multiplikator, der aus der Zerfallsart folgt
θ = Erdalter ($= 4{,}5 \cdot 10^9$a)
H_i = Isotopenhäufigkeit von i

Nuklid	Elementkonzentration in der Lithosphäre	Edelgas-Produktion in $4{,}5 \cdot 10^9$a mol g^{-1}-Gestein
^{238}U	2,5 ppm	$8{,}3 \cdot 10^{-8}$
^{235}U		$4{,}1 \cdot 10^{-8}$
^{232}Th	13 ppm	$8{,}4 \cdot 10^{-8}$
		$He_h = 20{,}8 \cdot 10^{-8}$
^{40}K	2,5%	$Ar_h = 3{,}3 \cdot 10^{-7}$
daraus folgt:		$(Ar/He)_{rad} \simeq 1{,}6$

$(Ar/He)_{Atmosphäre}$ = 1790

Bildung von Stromatolithen (seit ~3 Ga)

Zunahme von O_2 und Abnahme von CO_2 in der Atmosphäre

$$6\ CO_2 + 6\ H_2O + \text{Lichtenergie} \rightarrow C_6H_{12}O_6 + 6\ O_2$$

Aufg.: CO_2 Emission durch Autos

Der durchschnittliche Benzinverbrauch eines Autos sei 5L pro 100km.

A) Wieviel g CO_2 emittiert dieses Auto pro Kilometer?

Mol-Masse Benzin C_7H_{16} = (7 x 12 g/mol + 16 x 1 g/mol) = 100 g/mol

1 kg Benzin enthält: - 10 mol C_7H_{16} Moleküle
- 70 mol Kohlenstoff C

Daraus folgt:

Das Verbrennen von 1 kg Benzin (ungefähr 1 Liter) setzt 70 mol CO_2 frei!

Auf 100 km setzt unser Auto ***350 mol CO_2***...

Mol-Masse CO_2 = (1 x 12 g/mol + 2 x 16 g/mol) = 44 g/mol

...oder 15400 g CO_2 frei!

Pro gefahrenem Kilometer emittiert unser Auto 154 Gramm CO_2 in die Atmosphäre!

Aufg.: CO_2 Emission durch Autos

B) Wieviel g $CaSiO_3$ muss verwittert werden, damit dieses CO_2 (154 g) der Atmosphäre wieder entzogen wird?

entzogen

$$CaSiO_3 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2 + H_2O$$

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

freigesetzt

Pro 1 mol verwittertes $CaSiO_3$ wird der Atmosphäre 1 mol CO_2 entzogen.

Unser Auto emittiert 350 mol CO_2 pro 100 km oder ***3.5 mol CO_2 pro km***. Also müssen ***3.5 mol $CaSiO_3$ verwittert*** werden um der Atmosphäre diese emittierte Menge CO_2 wieder zu entziehen.

Mol-Masse $CaSiO_3$ = 116 g/mol (1 x 40 g/mol + 1 x 28 g/mol + 3 x 16 g/mol)

Pro gefahrenem Kilometer müssen 3.5 mol x 116 g/mol = <u>406 Gramm $CaSiO_3$</u> verwittert werden um das emittierte CO_2 zu kompensieren.

Es gilt zu beachten, dass bei dieser Rechnung das ***durch Photosynthese verbrauchte CO_2*** vollständig vernachlässigt wird.

Kontinentale Kruste

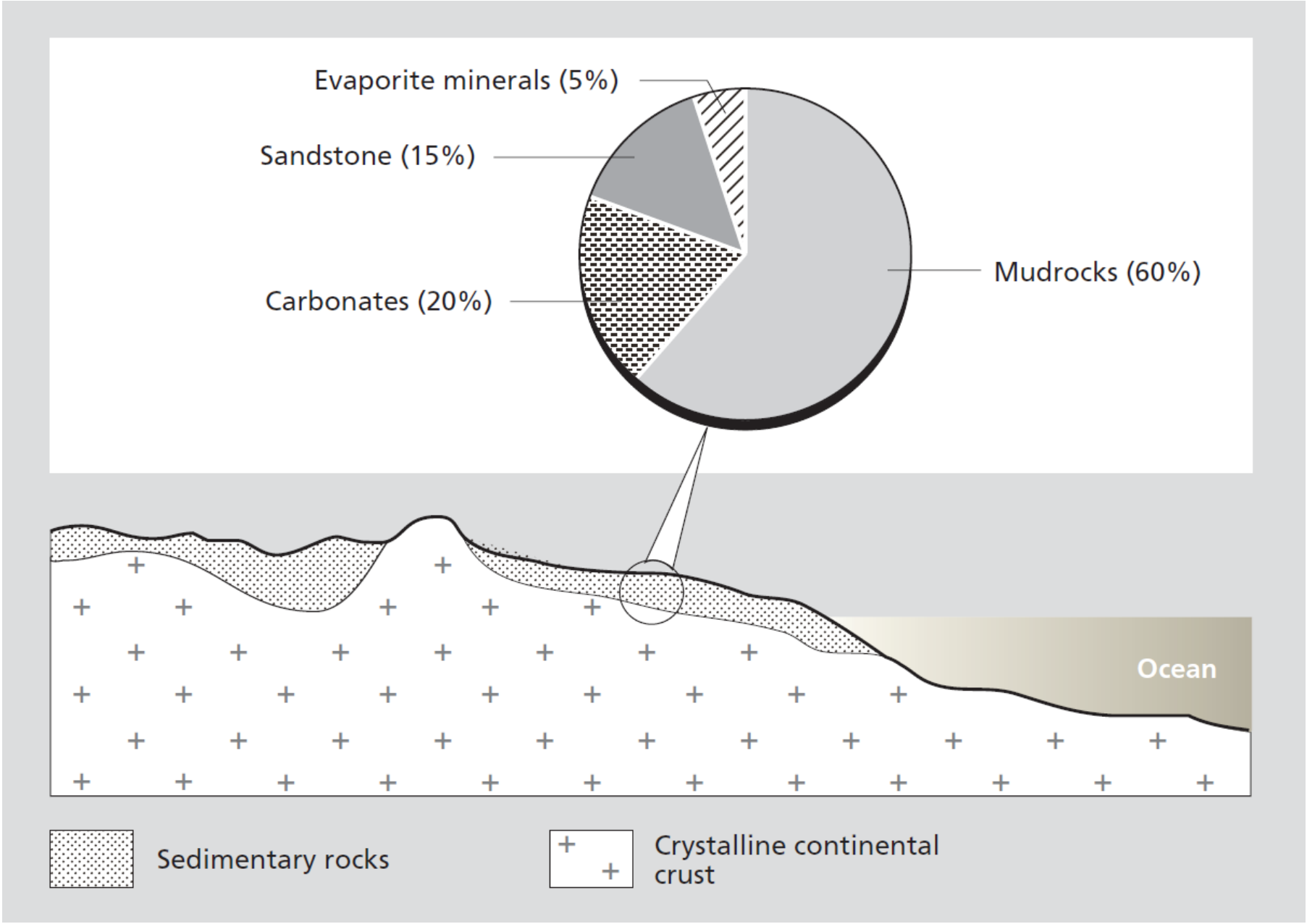

Evaporite minerals (5%)
Sandstone (15%)
Carbonates (20%)
Mudrocks (60%)
Ocean
Sedimentary rocks
Crystalline continental crust

Table 4.1 Average chemical composition of upper continental crust, sedimentary mudrock and suspended load of rivers. Data from Wedepohl (1995) and Taylor and McLennan (1985).

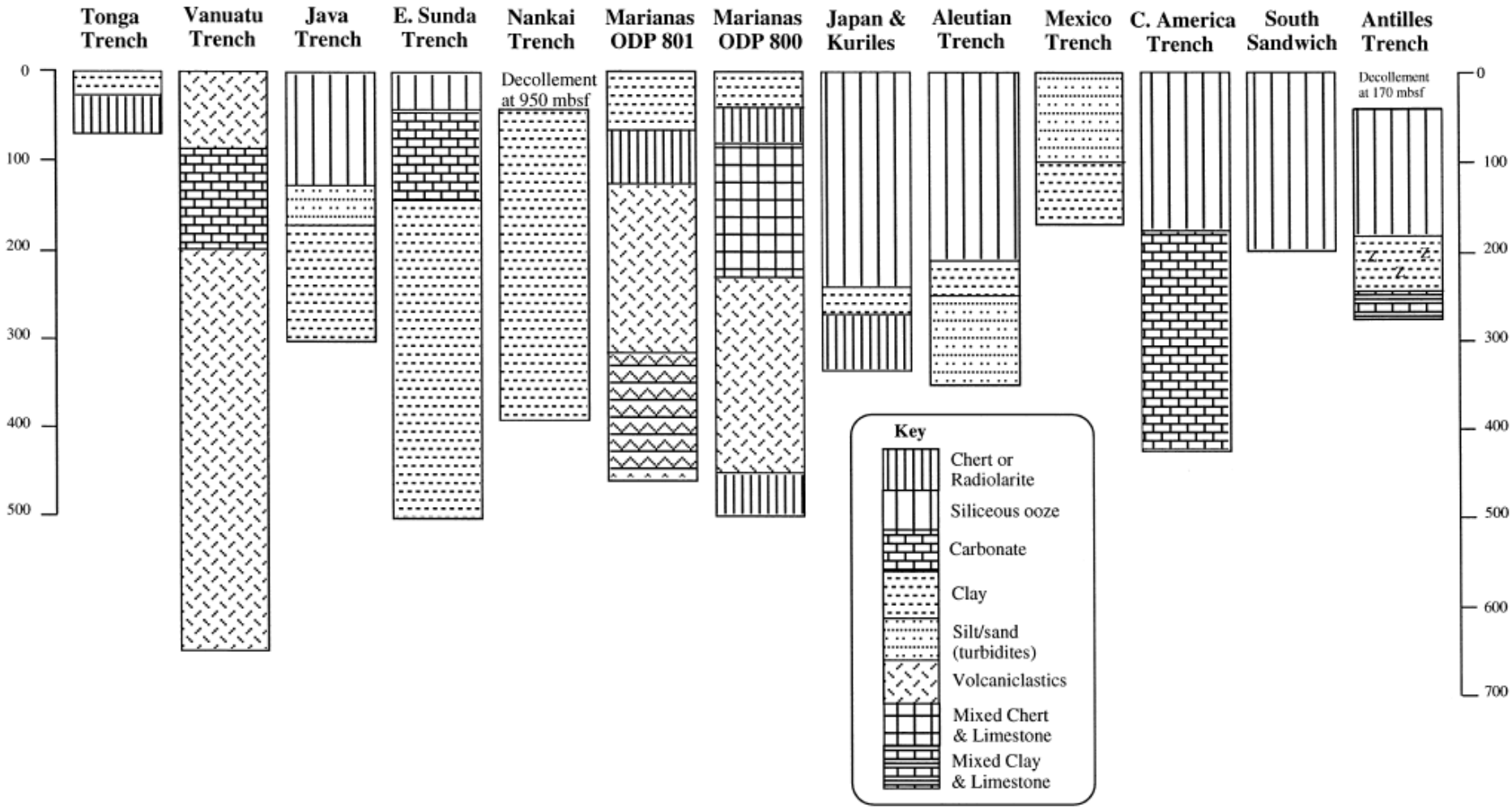
	Average upper continental crust (wt%)*	Average sedimentary mudrock† (Tonstein) (wt%)	Average suspended load (rivers)‡ (wt%)
SiO_2	65.0	62.8	61.0
TiO_2	0.6	1.0	1.1
Al_2O_3	14.7	18.9	21.7
FeO	4.9	6.5	7.6
MgO	2.4	2.2	2.1
CaO	4.1	1.3	2.3
Na_2O	3.5	1.2	0.9
K_2O	3.1	3.7	2.7
Σ	98.3	99.9	99.4

*A silicate analysis is usually given in units of weight% of an oxide (grams of oxide per 100 g of sample). As most rocks consist mainly of oxygen-bearing minerals, this convention removes the need to report oxygen separately. The valency of each element governs the amount of oxygen combined with it. A good analysis should sum (Σ) to 100 wt%.

†This analysis represents terrigenous mudrock (i.e. does not include carbonate and evaporite components), a reasonable representation of material weathered from the upper continental crust.

‡Average of Amazon, Congo, Ganges, Garronne and Mekong data.

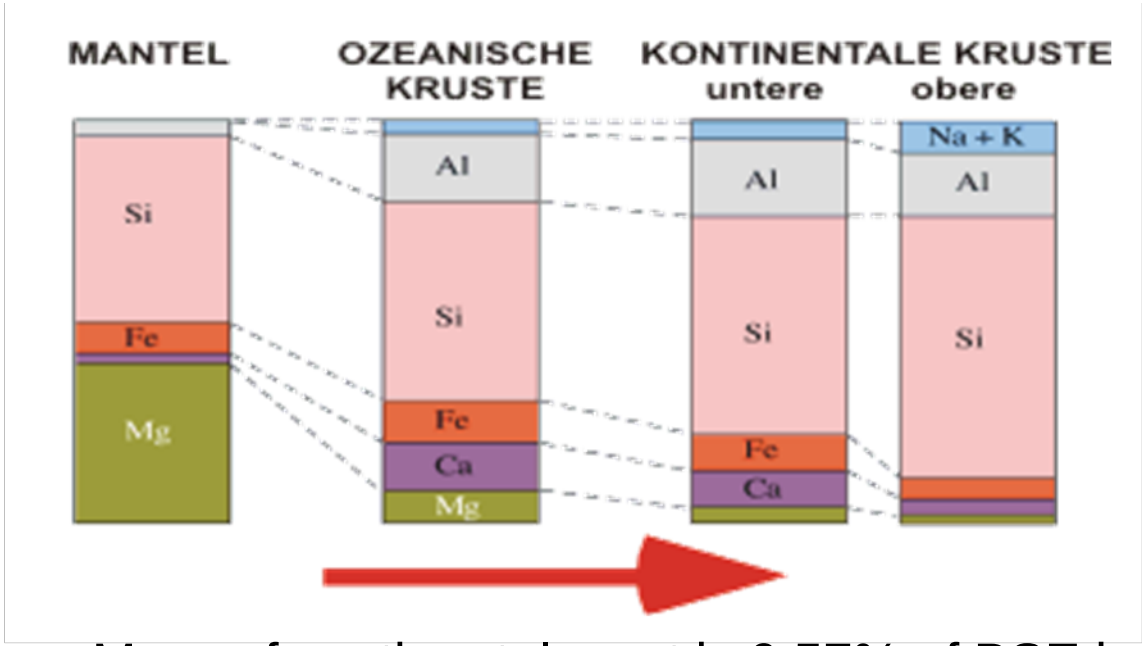
Global sediment subduction (GLOSS)



GLOSS dominated by terrigenous material: 76 wt% terrigenous, 7 wt% calcium carbonate, 10 wt% opal, 7 wt% mineral-bound H_2O^+, and therefore similar to upper continental crust

Plank & Langmuir: Chem Geol 1998

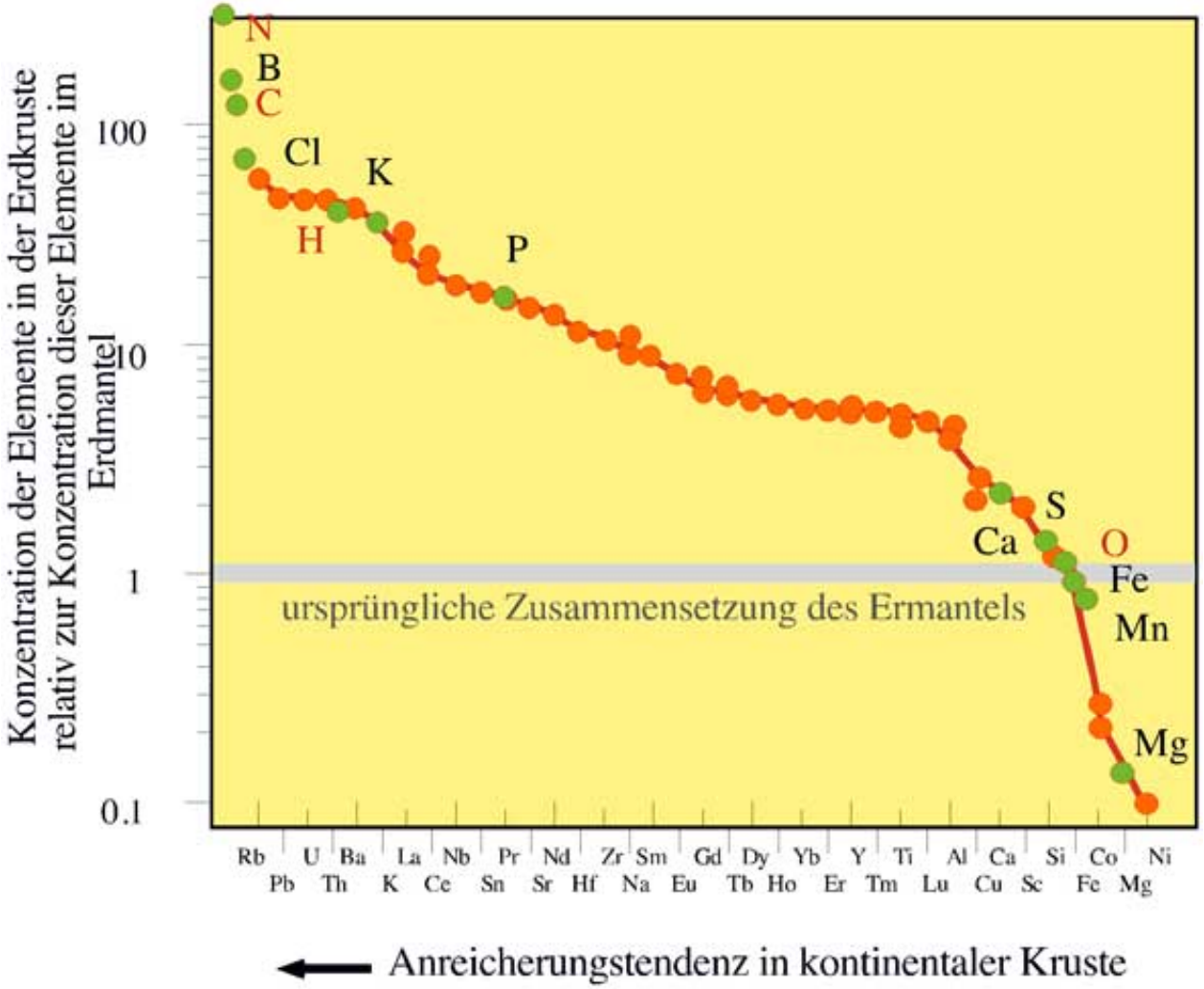
Geochemie der Kruste



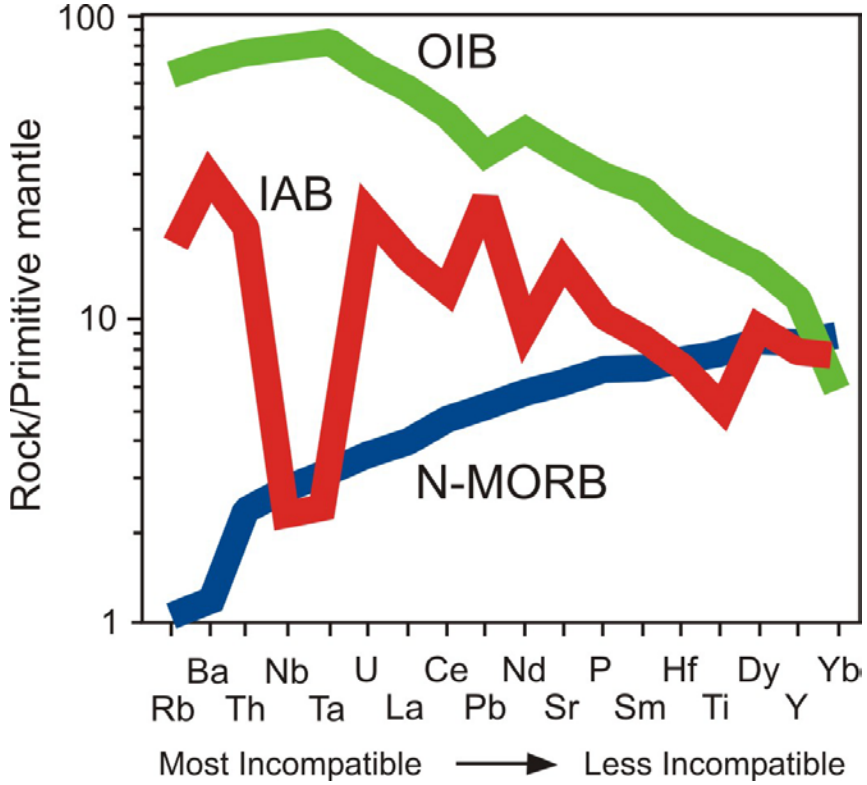
Mass of continental crust is 0.57% of BSE but it contains 35% of ist potassium!

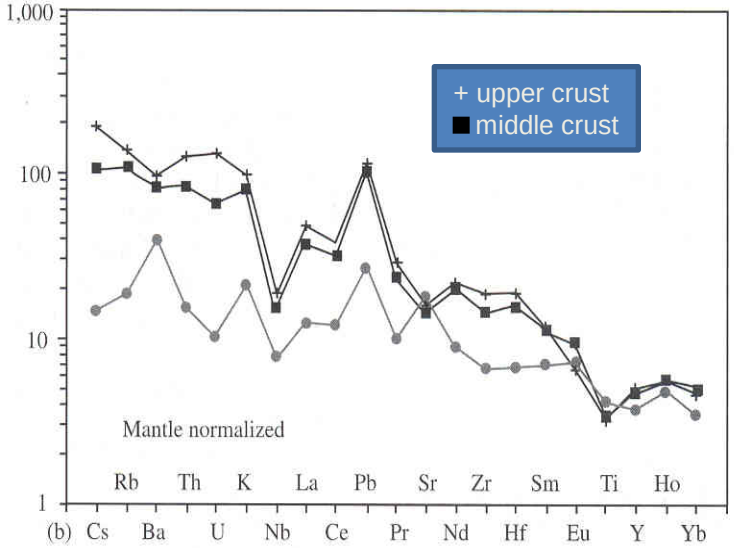
Mass of continental crust is 0.57% of BSE but it contains 35% of ist potassium!

Elementverteilung zwischen Kruste & Mantel



Elementanomalien der Kruste





Merkmale kontinentaler Kruste

Continental crust growths magmatically,

constitutes only 0.6% of the silicate Earth,

has an average andesitic composition,

is highly differentiated and buoyant

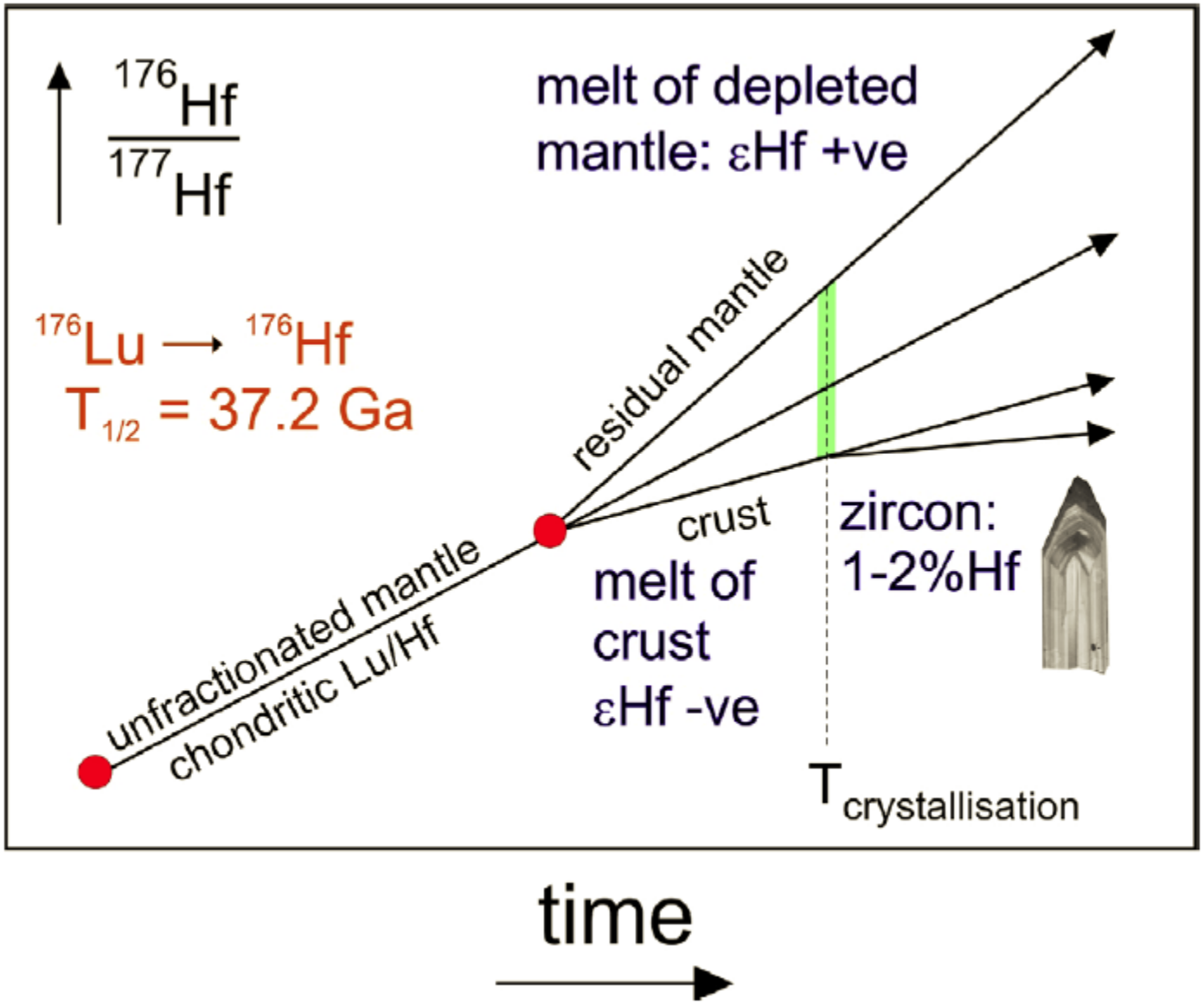
Enriched in incompatible components compared to primeval chondritic composition, i.e.:
→ Important reservoir for many scarce elements (ore deposits)

Other features: negative anomalies for Nb and Ta and high Pb contents, low Nb/U…

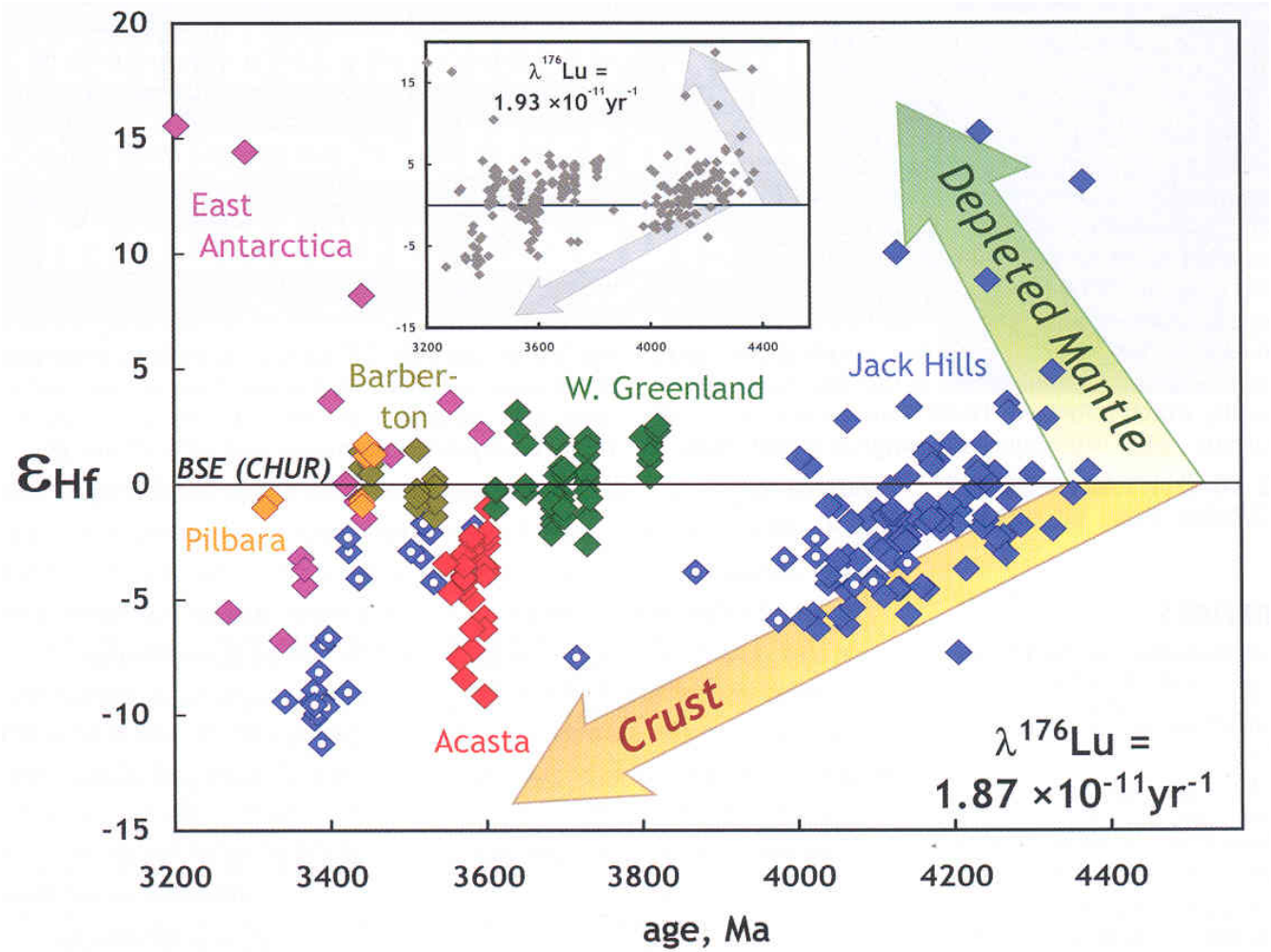
Old average age: ~2 Ga
→ Archean magmatism contributed greatly to the formation of the continental crust

Earth has considerably cooled since its formation
→ rates and processes of magma generation (plume-related versus arc-related) and crust formation have changed

Hf-Isotopie


$^{176}Hf / ^{177}Hf$
melt of depleted mantle: εHf +ve
$^{176}Lu \rightarrow ^{176}Hf$
$T_{1/2}$ = 37.2 Ga
residual mantle
crust
zircon: 1-2%Hf
melt of crust εHf -ve
unfractionated mantle
chondritic Lu/Hf
$T_{crystallisation}$
time

Mantel-Kruste Differentiation der Erde – Hf Zirkon



$$\varepsilon_{Hf} = \left[\frac{\left({}^{176}Hf / {}^{177}Hf \right)_{Probe}}{\left({}^{176}Hf / {}^{177}Hf \right)_{Chondrite}} - 1 \right] \times 10^4$$

Scherer, Whitehouse, Münker: Elements 3, 2007

Krustenwachstum

The most dramatic shift in the generation of continental crust began ~2.7 by ago.
This crust formation period was followed by additions of continental crust at:

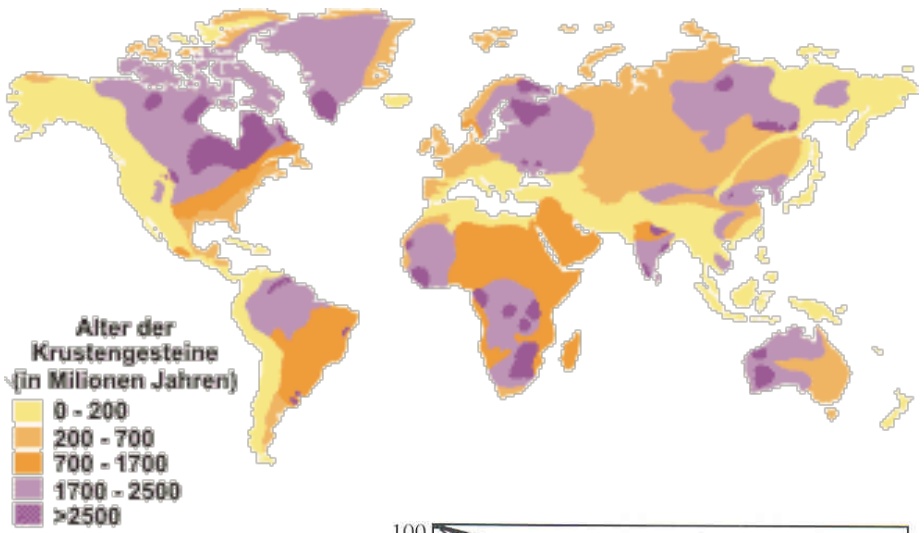
~1.9 by
~1.2 by
0.5 – 0.3 by

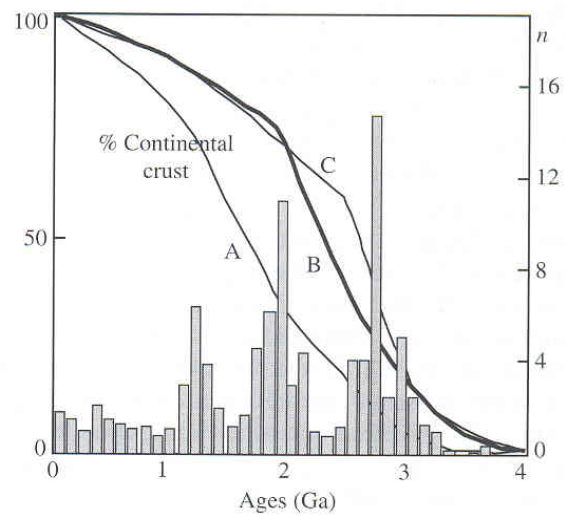
Large crustal volumes formed during short time periods

Global episodicity explained by:

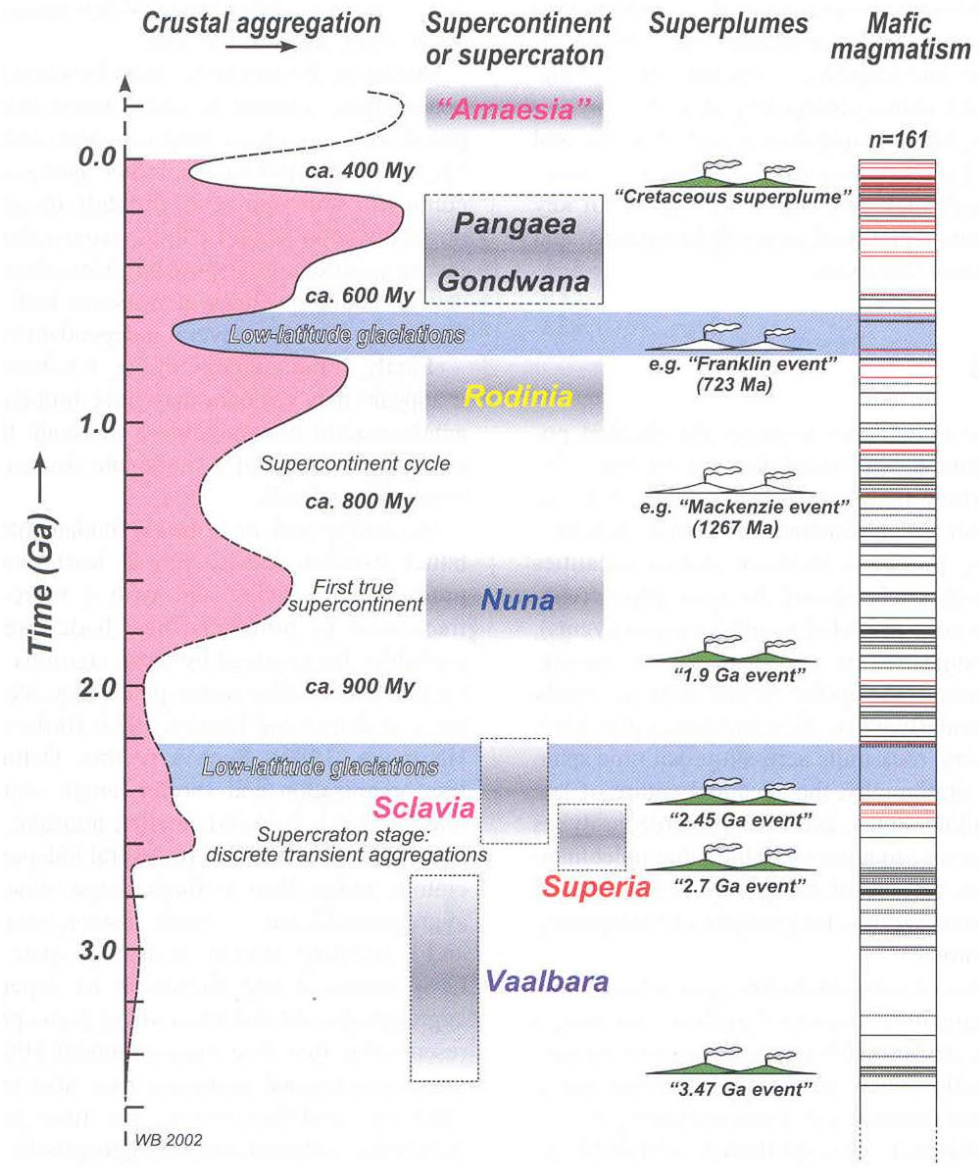
1. Supercontinent cycle hypothesis

a) Break apart of supercontinent
b) Higher subduction rates
c) Formation of new continental crust





Superkontinente der Erdgeschichte



Bleeker: Lithos 71, 2003

Die 3 Schritte bis zur modernen Kruste

Basaltic crust generated by partial melting of mantle peridotite
1st. crust formation step – separation of basaltic rocks from the mantle

This crust was locally hydrated and transferred (in greater depth) into amphibolite/eclogite

Melting of basaltic crust during (1) subduction and/or (2) magmatic underplating (high heat flow) → generation of tonalites, trondhjemites and (differentiated) granodiorites
2nd. crust formation step – stratification into more evolved upper crust and mafic residual lower crust

Melting of TTG‘s and of sedimentary rocks → granite production and enrichment of SiO_2, Na_2O und K_2O
3rd. crust formation step – evolved modern continental crust

Die heutige Kruste

Modern Earth's crust has a bulk andesitic composition: ~61% SiO_2
Mg number (Mg#, molar Mg/(Mg + Fe)) is ~ 55

modern crust is stratified
But bulk crust is more differentiated than any magma in equilibrium with the upper mantle

<u>Crustal growth by:</u>

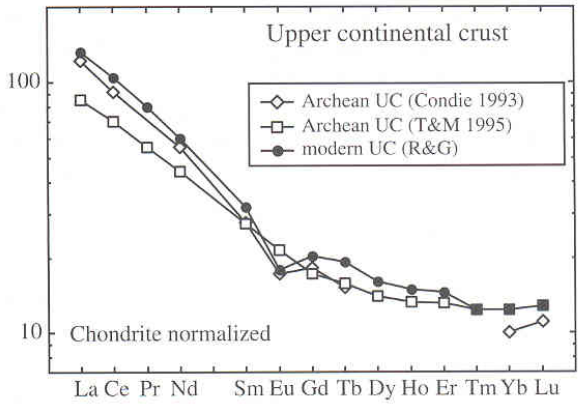
-- tectonic accretion of island arcs or oceanic plateaus i.e.,
addition of basalt. The basalts are ultimately reprocessed into felsic continental crust by intracrustal differentiation (fractional crystallization, remelting, weathering and erosion, etc.)

→ crust formation takes place in several stages

Oberkruste

-- enriched in light REE
-- Eu-anomaly
-- flat heavy REE

This is different from TTG‘s but similar to most post-Archean granitic rocks → fundamental role of such granites in shaping the compositional structure of the crust



Treatise on Geochemistry, Vol 3: The Crust

Eu (like Sr) accommodated in plagioclase, and thus is sensitive to intracrustal differentiation processes

Can granitic plutons represent new crust? – yes, by

-- fractional crystallization of basaltic liquid
-- mixing between crustal and mantle-derived magmas
-- partial melting of young, mantle-derived mafic protoliths in the crust

Die Pedosphäre

Verwitterung – physikal., chem., biol.

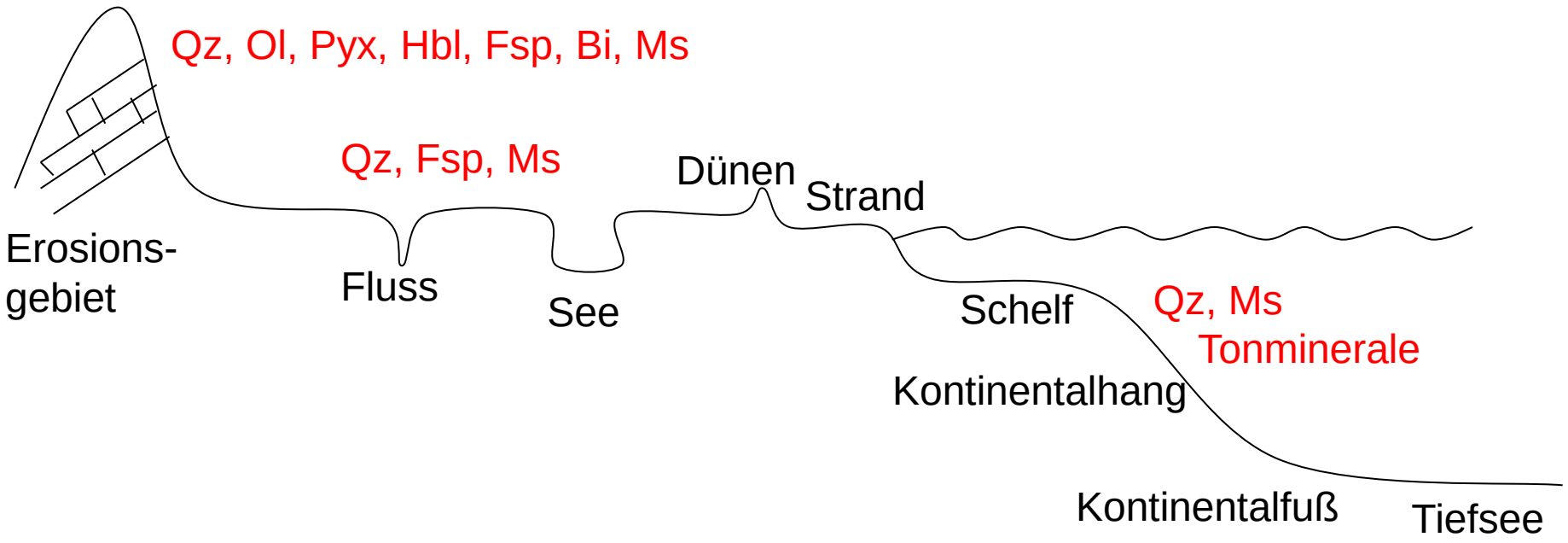
Wenig weit transportiert
(proximal)

Weiter Transport
(distal)

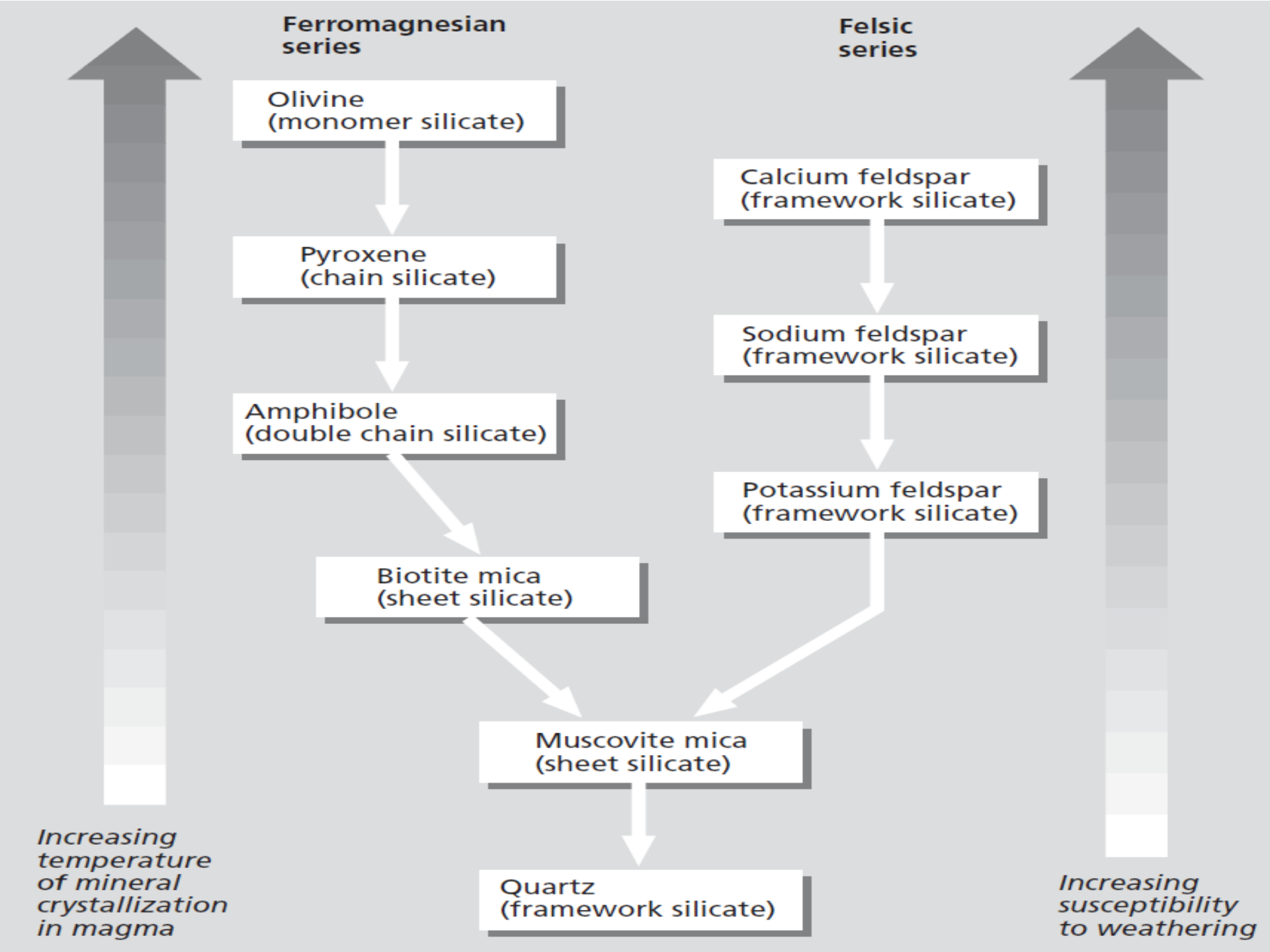
Glimmer
Feldspäte
Quarz

Feldspäte
(+/- Tonminerale)
Quarz

Quarz



Orthoklas → Kaolinit (Verwitterungsneubildung)


Ferromagnesian series
Felsic series
Olivine (monomer silicate)
Pyroxene (chain silicate)
Amphibole (double chain silicate)
Biotite mica (sheet silicate)
Calcium feldspar (framework silicate)
Sodium feldspar (framework silicate)
Potassium feldspar (framework silicate)
Muscovite mica (sheet silicate)
Quartz (framework silicate)
Increasing temperature of mineral crystallization in magma
Increasing susceptibility to weathering

Chem. Verwitterung: Lösungsverwitterung

Die Lösungsverwitterung bewirkt die Lösung (Korrosion) von Gesteinen, die relativ leichtlösliche Alkali- und Erdalkalisalze wie z.B. Chloride, Nitrate, Sulfate und/oder Karbonate enthalten

$$NaCl_{(s)} \overset{H_2O}{\rightleftharpoons} Na^+_{(aq)} + Cl^-_{(aq)}$$

Die Vorstufe der Lösungsverwitterung ist die **Hydratation**; die randlichen Ionen des Kristallgitters werden in Kontakt mit Wasser hydratisiert

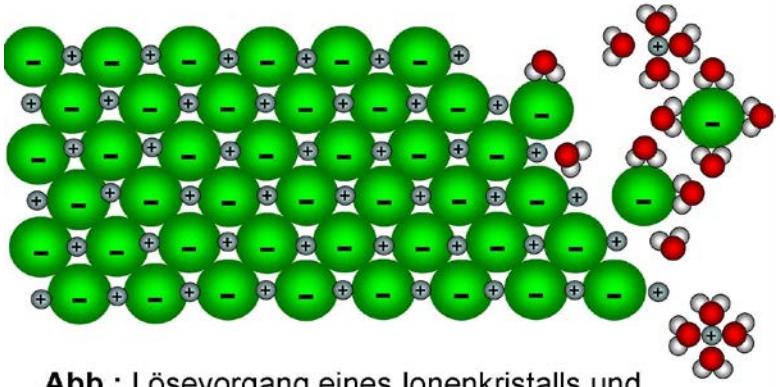


Abb.: Lösevorgang eines Ionenkristalls und Hydratation der Ionen

Chem. Verwitterung: Karbonatverwitterung

Die **Karbonatverwitterung** ist ein besonderer Fall der Lösungsverwitterung

Zur Lösung der Karbonate muß **kohlensäurehaltiges Wasser** vorhanden sein

$$CaCO_3 + H_2O + CO_2\ (H_2CO_3 \text{ oder } H^+ + HCO_3^-) \rightarrow Ca^{2+} + 2HCO_3^-$$

CO_2 entsteht im Boden durch Organismen. Im Boden ist die CO_2-Konzentration wegen der Atmung (Dissimilation) der Bodenorganismen wesentlich höher als in der Atmosphäre.

Die **Kohlensäure** wird durch die Atmung der Pflanzenwurzeln und Bodenorganismen ständig neu gebildet (daher auch Kohlensäureverwitterung oder saure Hydrolyse).

Zerfall organischer Substanz

$$CH_2O_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} + H_2O_{(l)}$$

$$CO_{2(g)} + H_2O_{(l)} \leftrightharpoons H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} \leftrightharpoons H^+{}_{(aq)} + HCO^-_{3(aq)}$$

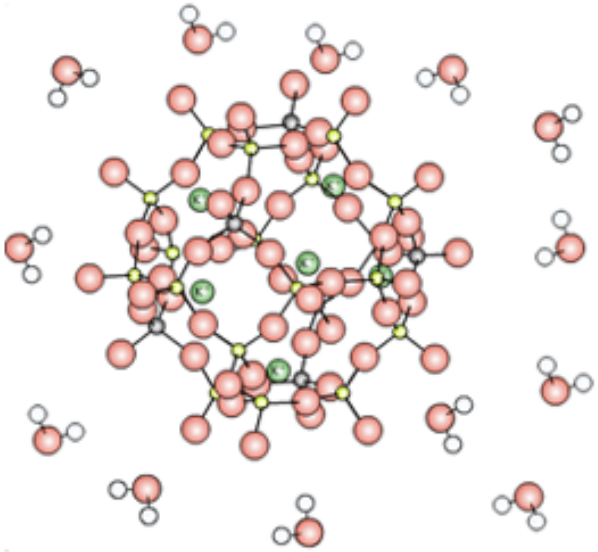
CO_2 Partialdruck im Bodengas kann den in der Atmosphäre um 2 Größenordungen übersteigen → Porenlösungen saurer als Oberflächenwässer → Kaolinitminerale

Chem. Verwitterung: Hydrolyse

- **Hydrolyse** bezieht sich auf Reaktionen bei denen eine (oder beide) der O-H Bindungen des Wassers bricht.
- Die Hydrolyse gehört zu den wichtigsten Reaktion der chemischen Verwitterung. Triebkraft dieser Verwitterungsart ist die Reaktion eines Minerals mit den Wassermolekülen bzw. H^+-Ionen der Lösung, die sich an die Grenzflächenionen von Kristallen anlagern und Kationen (z.B. K) aus dem Kristallgitter ersetzen:

$$KAlSi_3O_8 + H^+ + 9/2H_2O \rightarrow 1/2Al_2Si_3O_5(OH)_4 + K^+ + 2H_4SiO_4$$

Kaolinit



Orthoklas, umgeben von Wassermolekülen

Wichtiger Schritt bei der Hydrolyse ist die Dissoziation von Wasser zu H^+ und OH^-.

Der Betrag der Hydrolyse nimmt mit sinkendem pH und steigenter Temperatur zu, was zu einem vermehrten Abbau des Kalifeldspats führt.

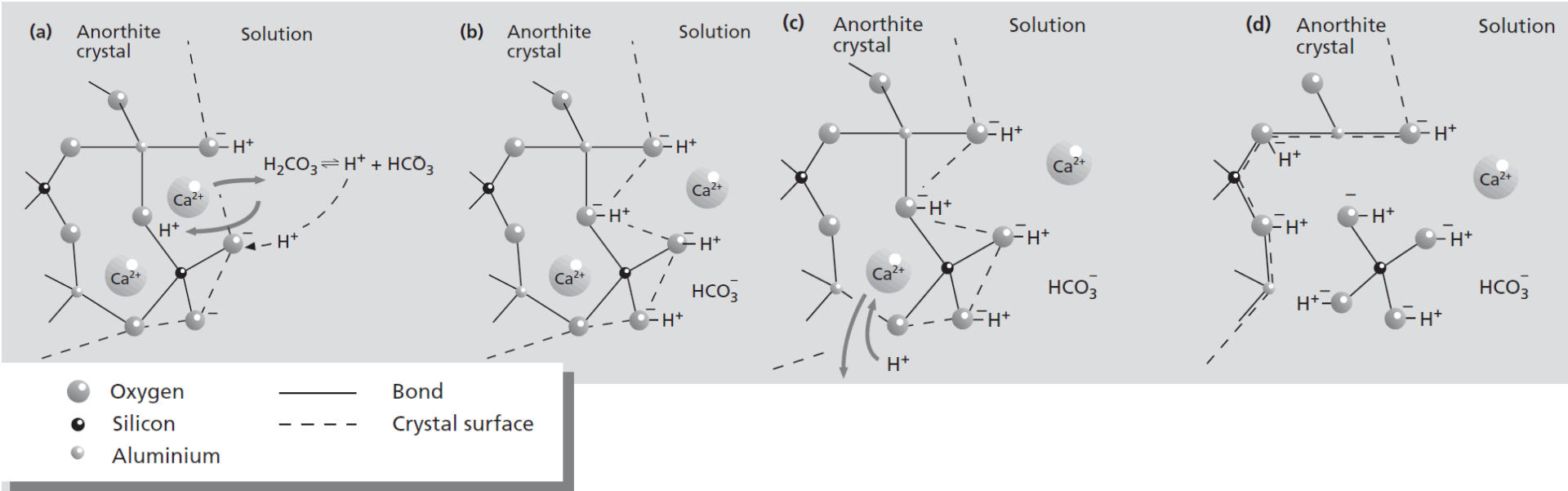
Chem. Verwitterung: Saure Hydrolyse

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

CO_2 entsteht im Boden durch Organismen

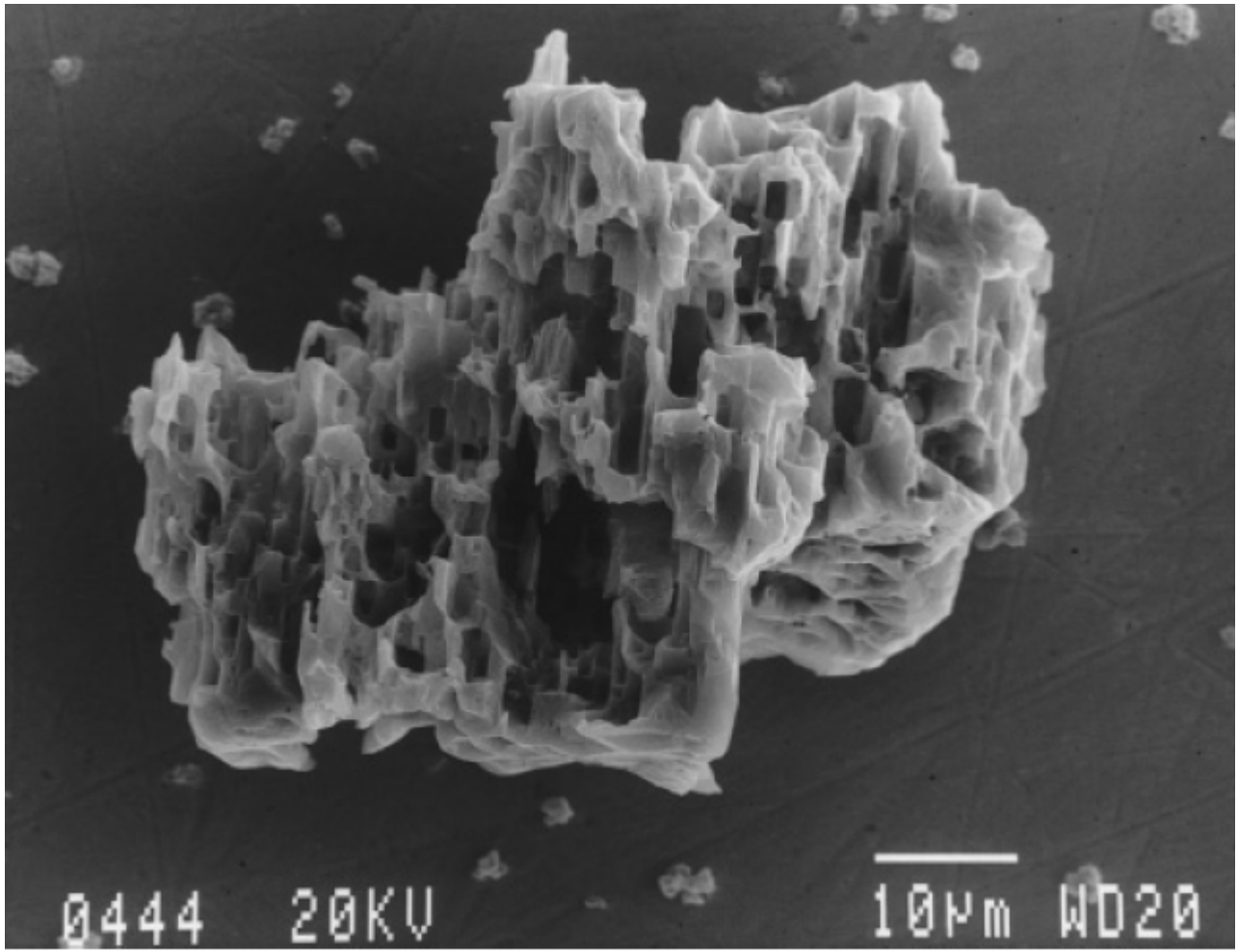
$$Mg_2SiO_{4(s)} + 4H_2CO_{3(aq)} \rightarrow 2Mg^{2+}_{(aq)} + 4HCO^-_{3(aq)} + H_4SiO_{4(aq)}$$

$$CaAl_2Si_2O_{8(s)} + 2H_2CO_{3(aq)} + H_2O_{(l)} \rightarrow$$
$$Ca^{2+}_{(aq)} + 2HCO_{3(aq)} + Al_2Si_2O_5(OH)_{4(s)}$$



Chem. Verwitterung: Saure Hydrolyse, Albit

$$2NaAlSi_3O_{8(s)} + 9H_2O_{(l)} + 2H_2CO_{3(aq)} \rightarrow$$
$$Al_2Si_2O_5(OH)_{4(s)} + 2Na^+_{(aq)} + 2HCO^-_{3(aq)} + 4H_4SiO_{4(aq)}$$



Verwitterung und Klima

Mineralneubildungen:

Feucht-gemäßigte Klimazone:
siallitisch
Illit, Vermiculit, Montmorillonit, Kaolinit, Halloysit

Feucht-tropische Klimazone:
allitisch
Gibbsit, Böhmit, Diaspor, Kaolinit, Goethit, Hämatit

Chem. Verwitterung: Oxidationsverwitterung

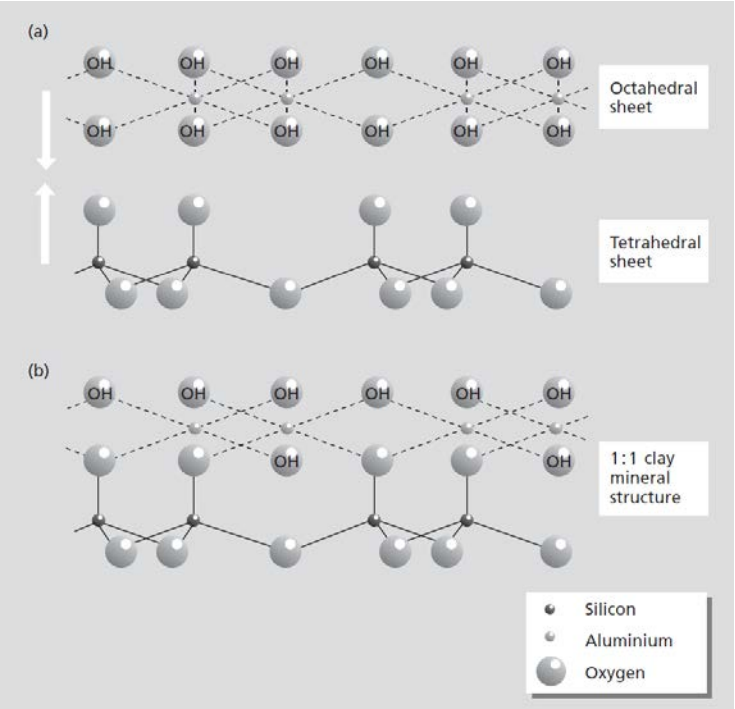
$$2FeS_{2(s)} + 7\tfrac{1}{2}O_{2(g)} + 7H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + 4H_2SO_{4(aq)}$$

$$Fe_2SiO_{4(s)} + \tfrac{1}{2}O_{2(g)} + 5H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + H_4SiO_{4(aq)}$$

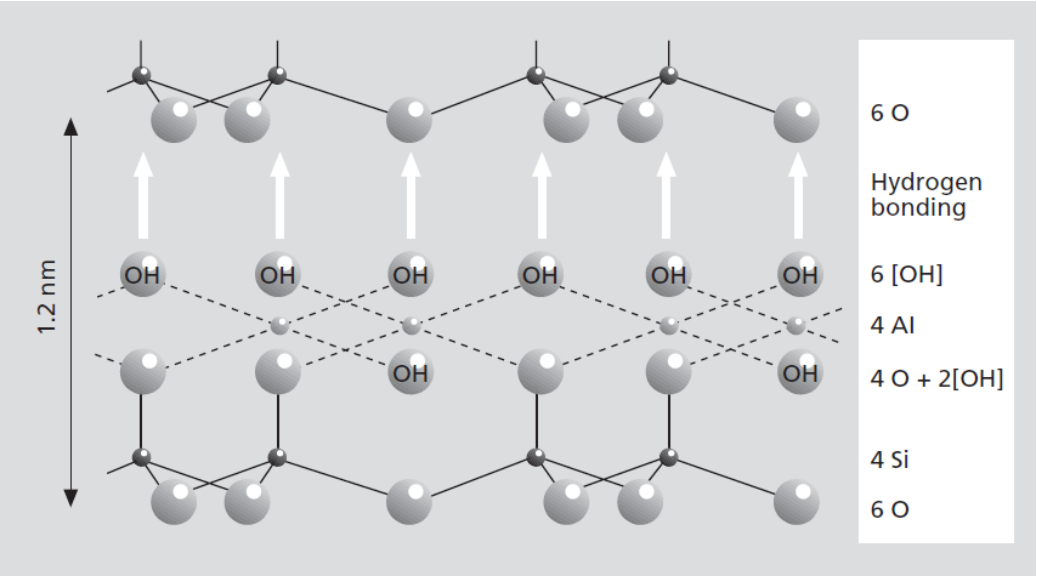
(fayalite)
(Fe(II)) (Fe(III))

Table 4.5 Simplified classification of clay minerals. After Martin *et al.* (1991) with kind permission from the Clay Minerals Society.

Layer type	Group	Common minerals	Octahedral character	Interlayer material
1 : 1	Serpentine–kaolin	Kaolinite	Dioctahedral	None
2 : 1	Smectite	Montmorillonite	Dioctahedral	Hydrated exchangeable cations
	True (flexible) mica	Biotite	Trioctahedral	Non-hydrated monovalent cations
		Muscovite, illite	Dioctahedral	
	Chlorite	Chamosite	Trioctahedral	Hydroxide sheet



Kaolinitstruktur



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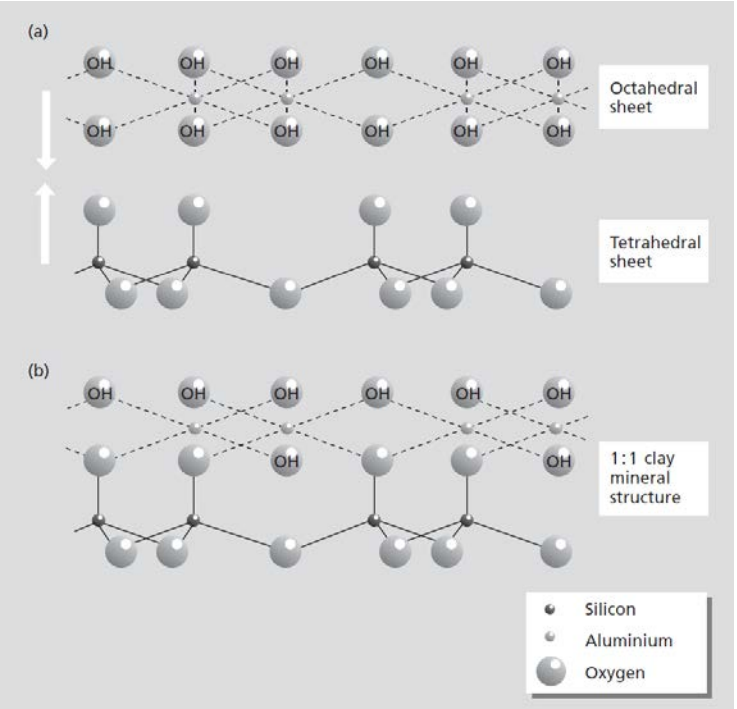
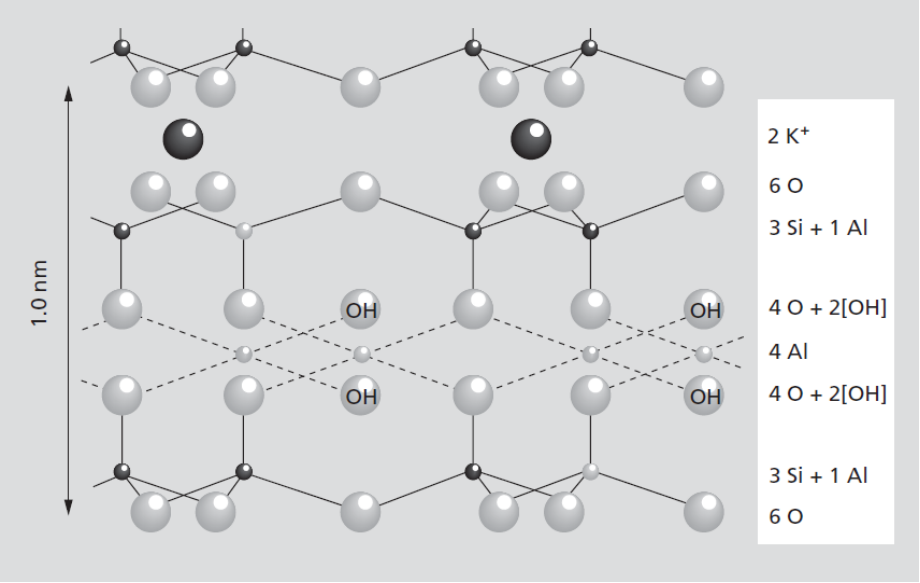


Muskovitstruktur



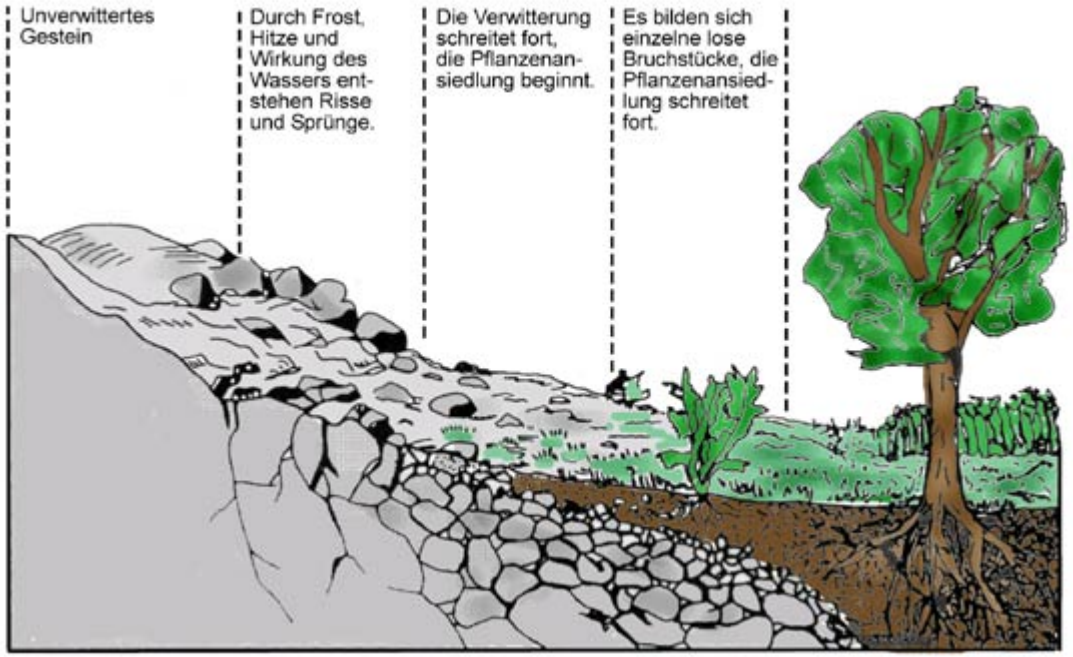
Bodenbildung

$S = f(G, E, B)\ dt$

Faktoren:
G = Geologie
E = Umwelt
B = Biologie

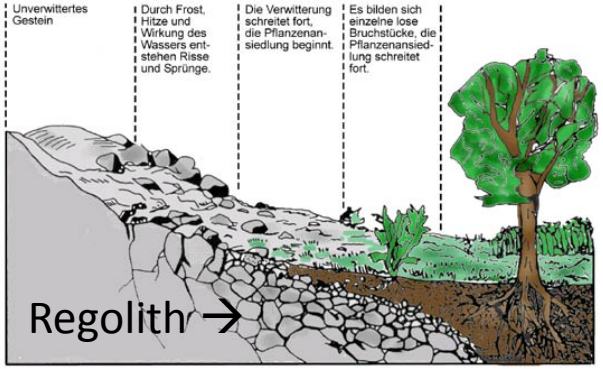
$S = f(a, k, r, v, o)\ dt$

Schlüsselfaktoren:
a = Ausgangsgestein
k = Klima
r = Relief
v = Vegetation
o = Organismen



Vegetation – organische Bodensubstanz

Böden enthalten etwa 5 % organisches Material,
SOM = soil organic matter (partikulär bzw. adsorptiv)
DOM = dissolved organic matter (gelöst)
Humus (Zellulose, Lignin) = Makromoleküle aus C, H, O, P, N und S



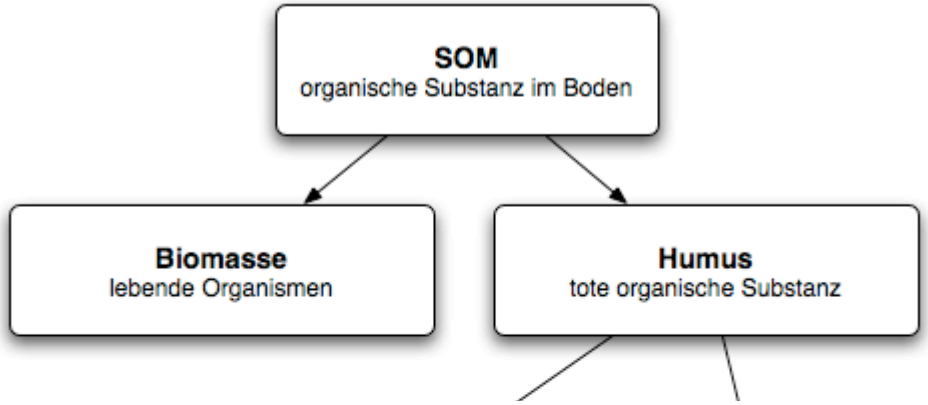
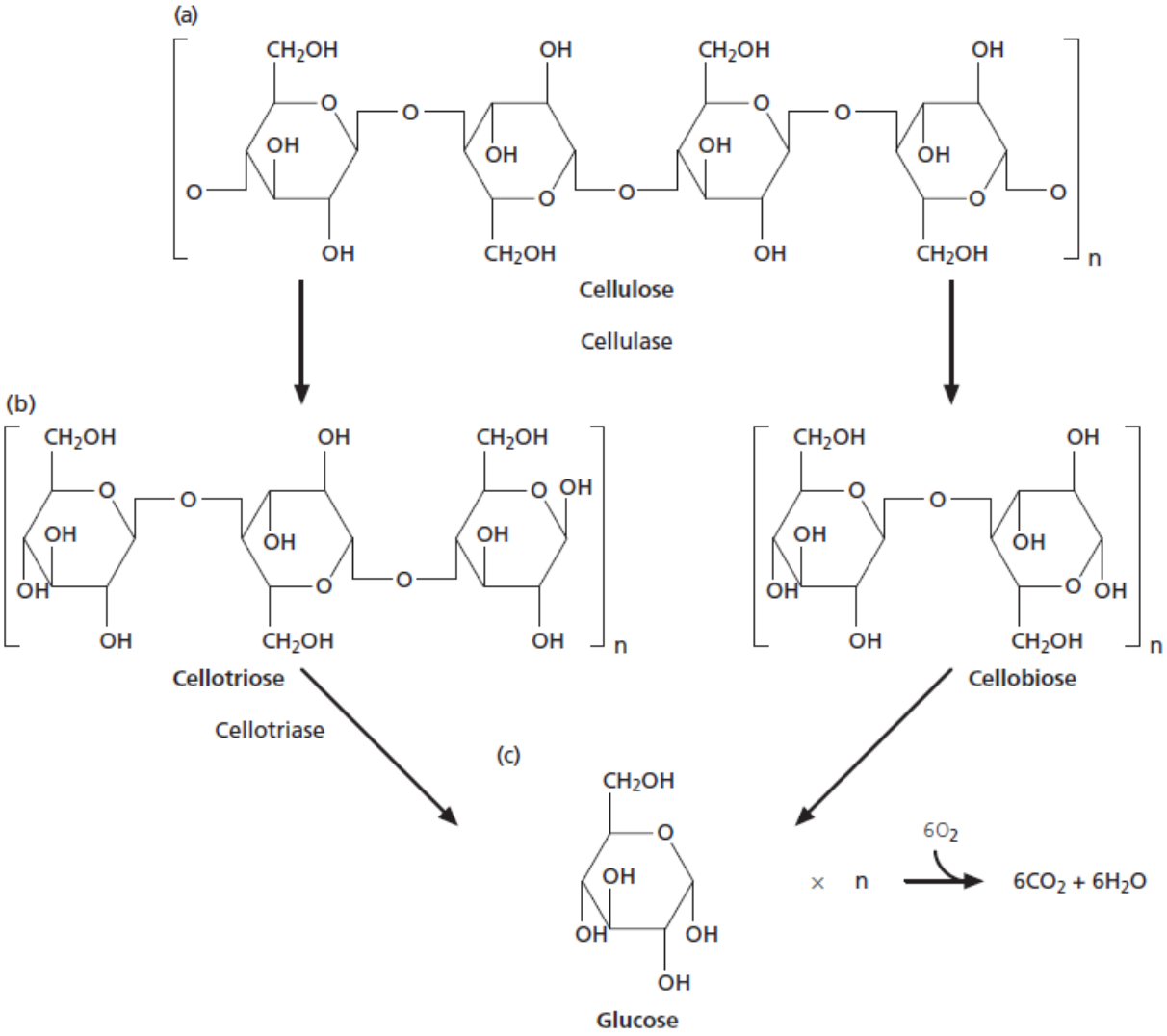


Table 4.6 Relative proportions of biopolymers in plant-derived soil organic matter.

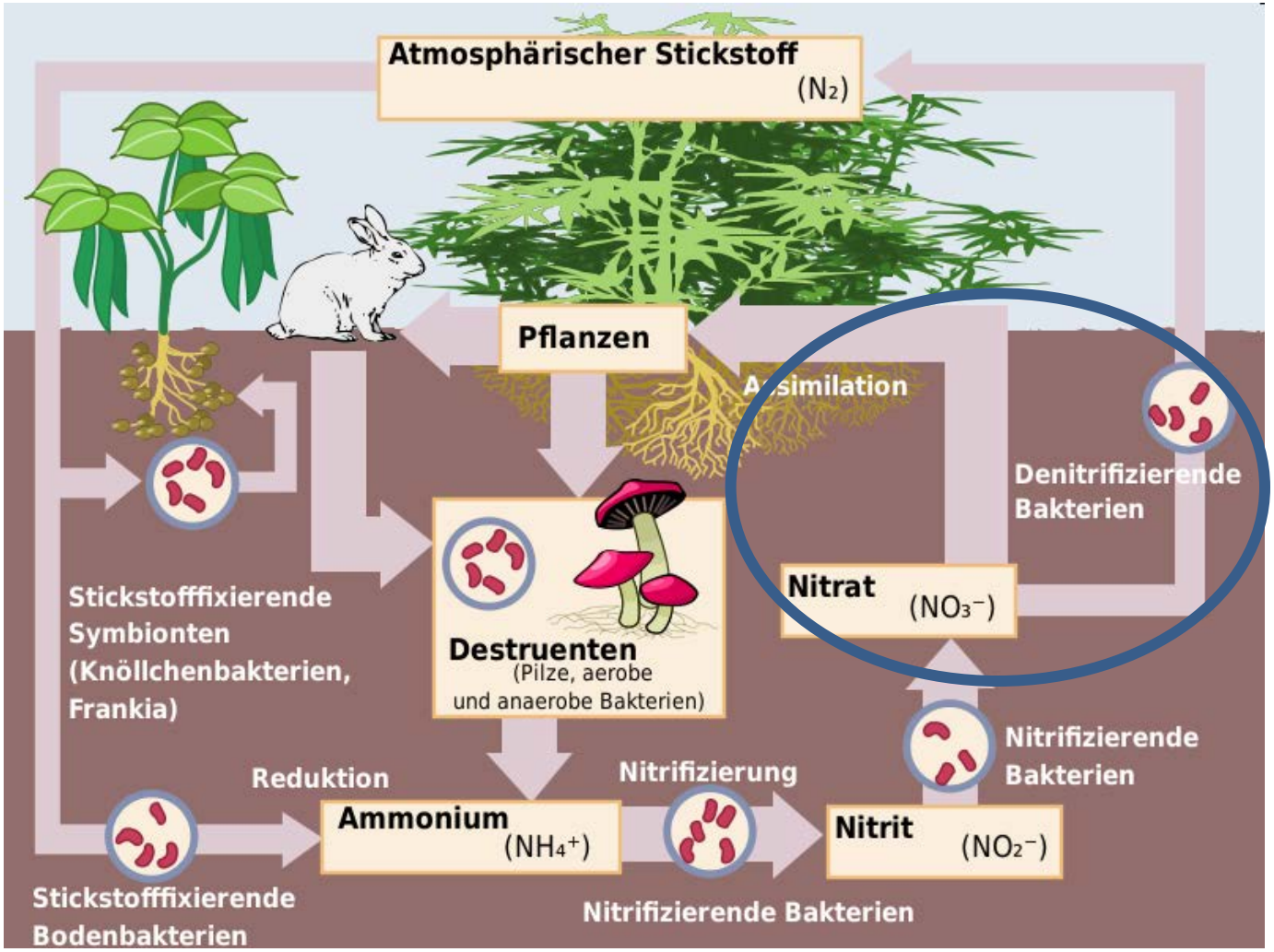
Plant residues	Percentage in soils
Cellulose	50
Hemicelluloses	20
Lignin	15
Protein	5
Carbohydrates and amino acids	5
Pectin	1
Waxes and pigments	1

Aerober Abbau von Zellulose im Boden



Abbau organischer Substanz im Boden

Pilze
Bakterien
Actinomyzeten



(1) $NH_4^+ + 1.5\ O_2 \longrightarrow NO_2^- + H_2O + 2H^+$ (2) $NO_2^- + 0.5\ O_2 \longrightarrow NO_3^-$

(3) $5CH_2O + 4NO_3^- \longrightarrow 2N_2 + 4HCO^{3-} + CO_2 + 3H_2O$

Table 4.7 Order of bacterial reactions during microbial respiration of organic matter based on energy yield. Modified from Berner (1980), reprinted by permission of Princeton University Press.

Bacterial reaction	ΔG° (kJ mol^{-1} of CH_2O)
Aerobic respiration: important in all oxygenated Earth surface environments	
$CH_2O + O_2 \rightarrow CO_2 + H_2O$	–475
Denitrification: most important in terrestrial and marine environments impacted by anthropogenic inputs from fertilizers	
$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	–448
Manganese reduction: minor reaction important in some marine sediments	
$CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3$	–349
Iron reduction: can be significant in some soils and marine sediments with high iron contents from contamination or weathering flux (e.g. Amazon Delta)	
$CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$	–114
Sulphate reduction: major process in anaerobic marine sediments, especially on continental shelves	
$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	–77
Methanogenesis: important process in freshwater wetlands, waterlogged soils and in deeply buried low-sulphate marine sediments	
$2CH_2O \rightarrow CH_4 + CO_2$	–58

Note: Free energy value for organic matter (CH_2O) is that of sucrose.

Reisfelder: Schornsteine für Methan

Für etwa 10 bis 25 Prozent der weltweiten Methan-Emissionen sind Mikroorganismen in den Böden gefluteter Reisfelder verantwortlich. Kohlenstoff für das Methan stammt hauptsächlich aus Wurzeln und Pflanzenresten.

In überschwemmten Reisfeldern tummeln sich Bakterien im Schlamm.

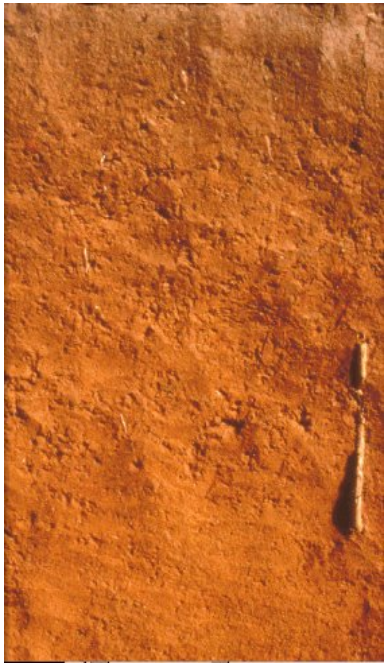
Je länger die Felder überflutet sind, desto geringer sind die Konzentrationen von Sauerstoff und desto mehr Methan wird produziert.

Vertisols swelling clay soil. Through shrinking and swelling deep cracking; soil material consistently mixes itself

Table 4.8 Mobility of different chemical species in relation to rock weathering. Modified from Polynov (1937).

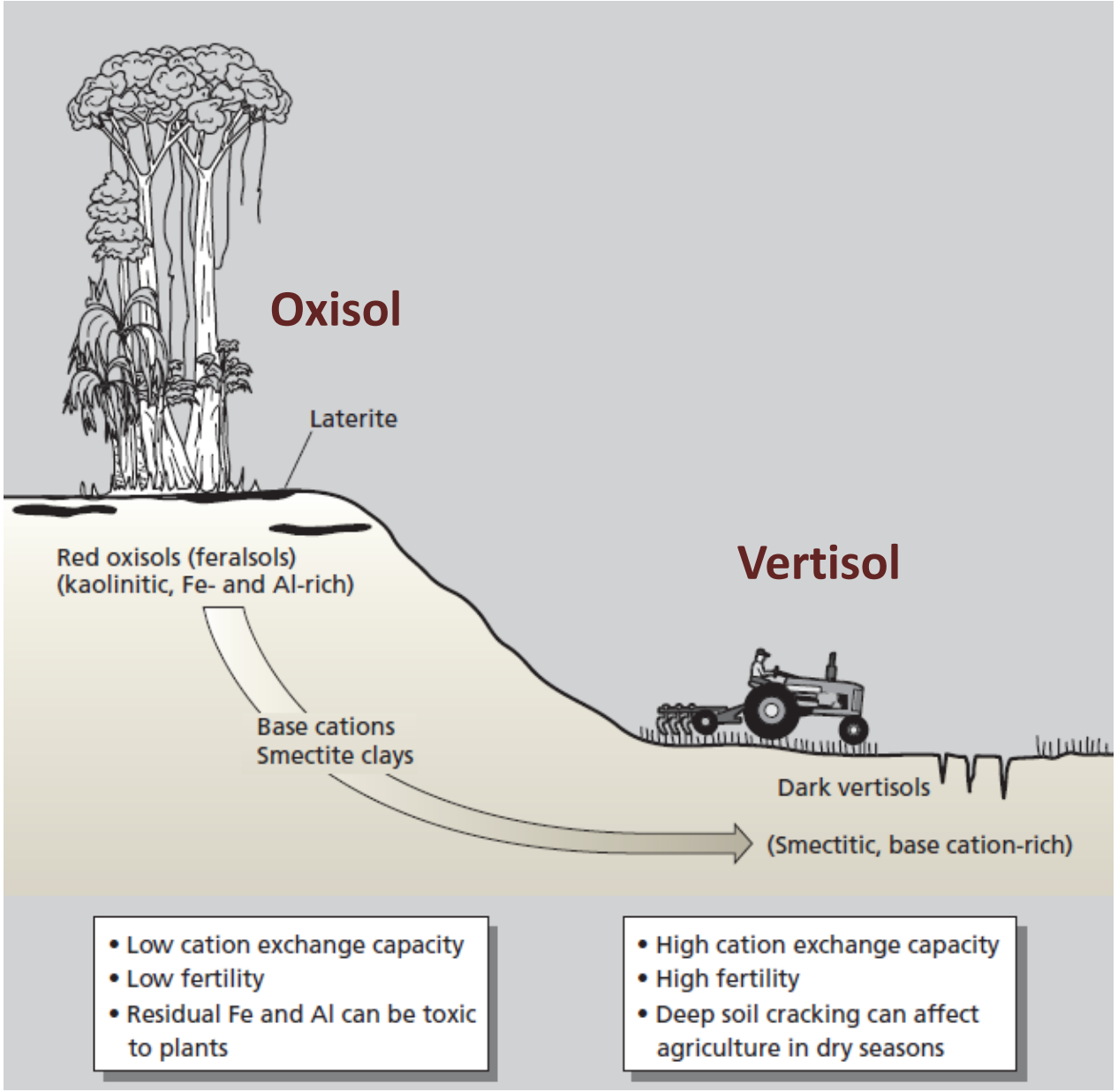
	Species	Mobility*	Comments†
Group I	Cl^-	100	Soluble anions easily leached by water
	SO_4^{2-}	57	
Group II	Ca^{2+}	3.00	Relatively soluble cations, easily leached by water
	Na^+	2.40	
	Mg^{2+}	1.30	
	K^+	1.25	
Group III	SiO_2	0.20	Relatively insoluble element, typically present as quartz grains
Group IV	Fe_2O_3	0.04	Highly insoluble elements present as Fe and Al oxides
	Al_2O_3	0.02	

*Most mobile = 100.



Oxisols (ferralsols and laterite soils) occur in tropical rain forest, 15-25 degrees north and south of the equator

Bodenwelten: Tropische Böden



Chemical Index of Alteration: CIA

$$CIA = Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O) \times 100$$

Table 4.9 Chemical index of alteration (CIA) values for various crustal materials. Data from Nesbitt and Young (1982), Maynard *et al.* (1991) and Taylor and McLennan (1985).

Material	CIA
Clay minerals	
Kaolinite	100
Chlorite	100
Illite	75–85
Smectite	75–85
Other silicate minerals	
Plagioclase feldspar	50
Potassium feldspar	50
Muscovite mica	75
Sediments	
River Garonne (southern France) suspended load	75*
Barents Sea (silt)	65*
Mississippi delta average sediment	64*
Amazon delta muds	70–75
Amazon weathered residual soil clay	85–100
Rocks	
Average continental crust (granodiorite)	50
Average shales	70–75
Basalt	30–40
Granite	45–50

Value calculated using total CaO rather than CaO (see text).

CIA values among the rivers from different continents

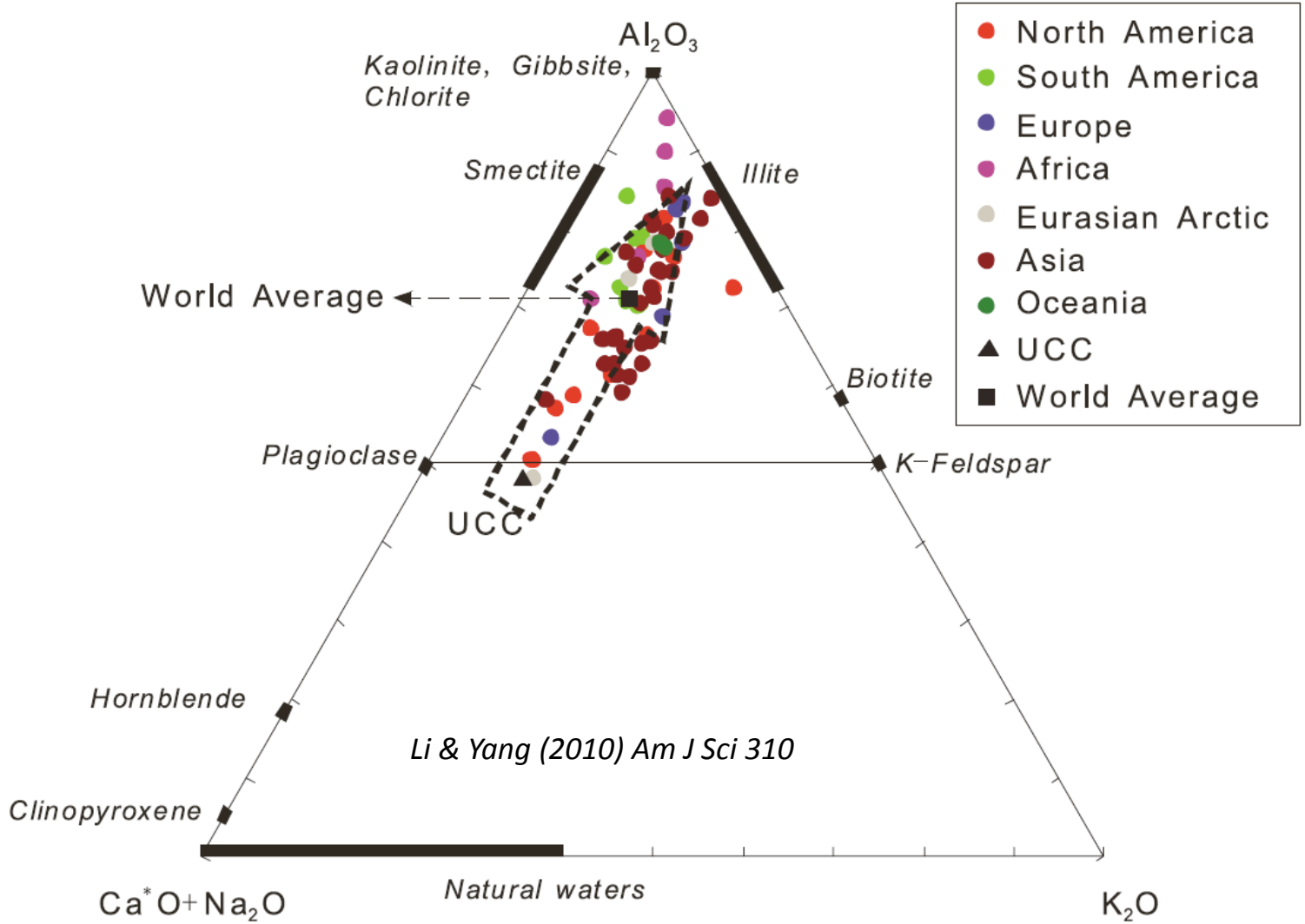
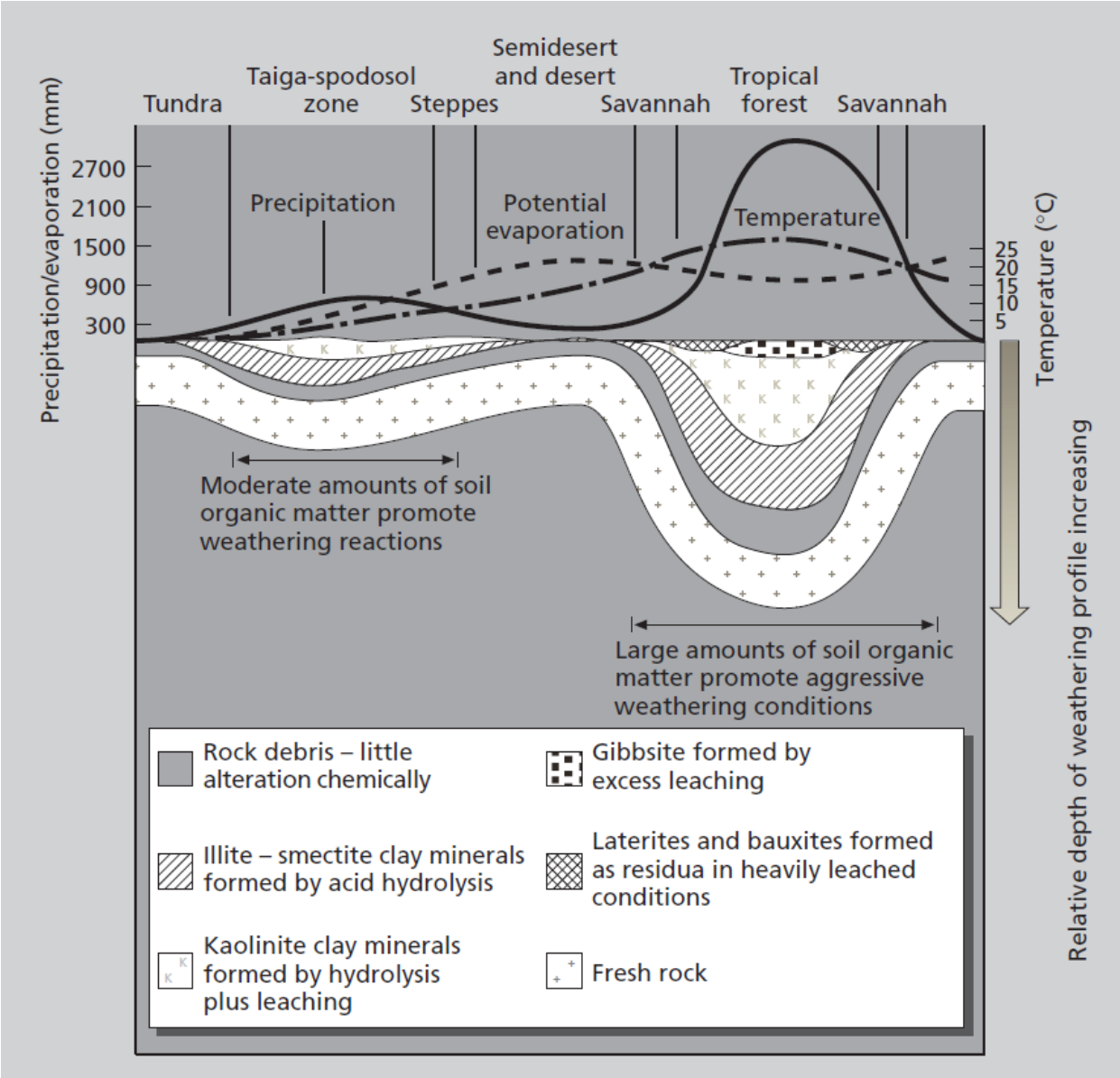
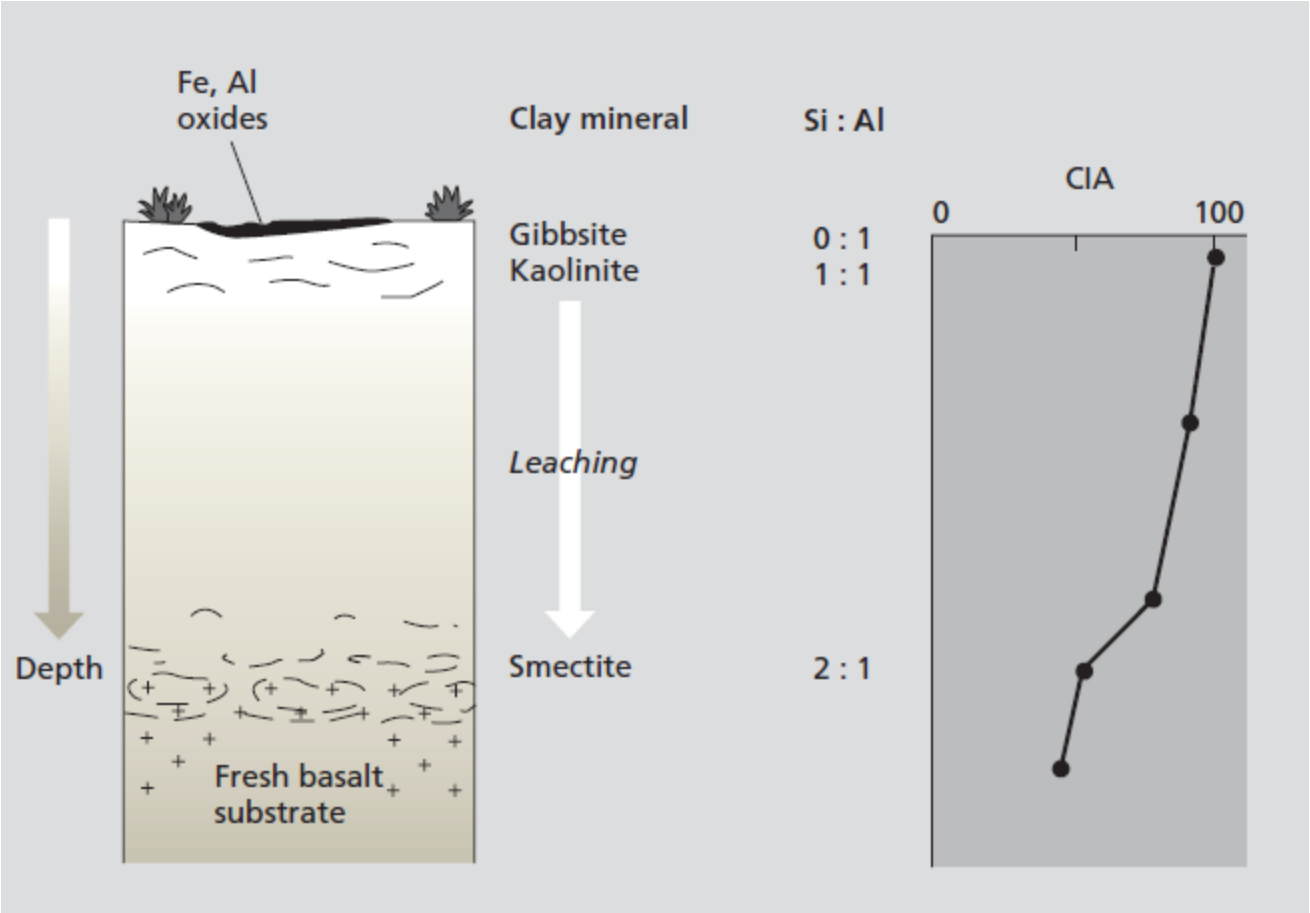


Fig. 3. The A-CN-K diagram of global rivers. Note that most of the investigated rivers show the similar weathering trend in parallel with the A-CN line.

Zusammenhang zwischen Klima, Verwitterung und Tonmineralneubildungen



Basaltverwitterung

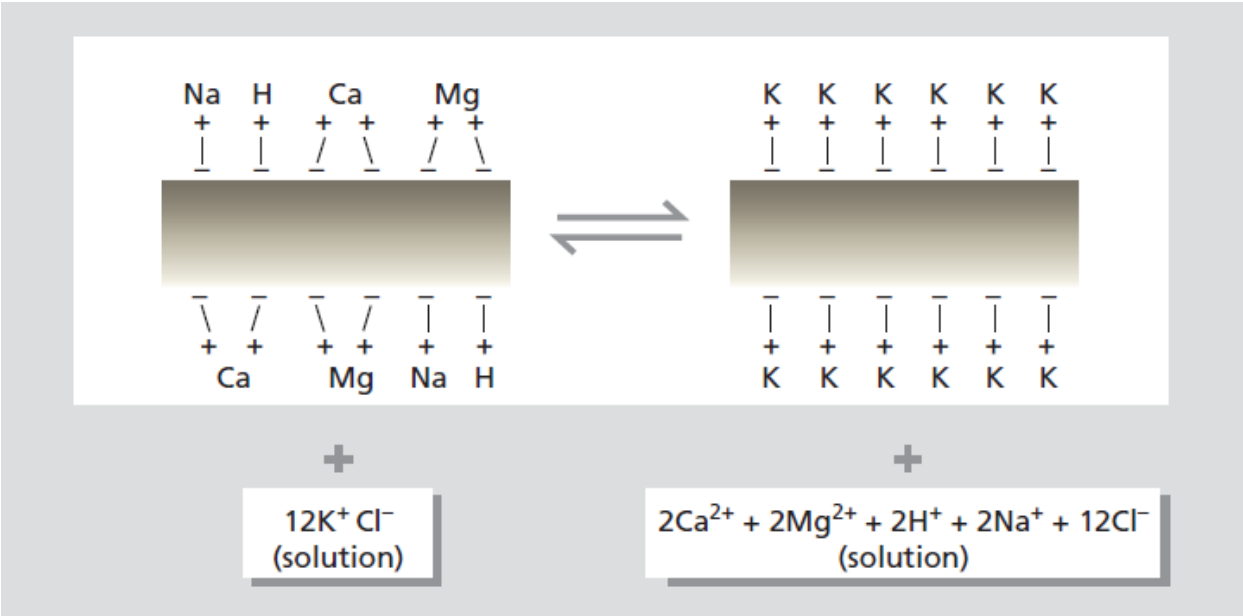


Bodenkolloide & Ionenaustauschkapazität

Bodenpartikel der mineralischen und organischen Bodensubstanz sind an ihren Oberflächen elektrisch geladen.

Tonminerale und Huminstoffe sind wesentliche Ladungsträger und Ionenaustauscher.

Negative Ladungen überwiegen.

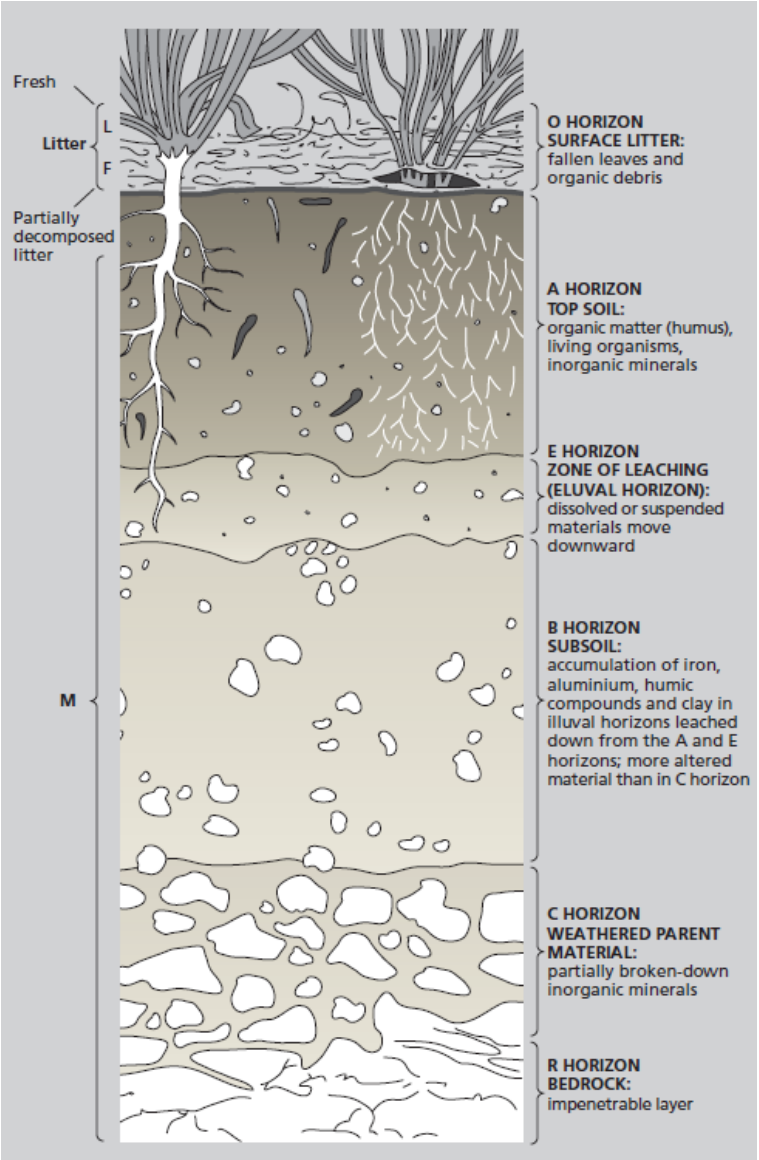


Non-clay materials	CEC
Quartz, feldspars	1–2
Hydrous oxides of Al and Fe	4
Organic matter	150–500

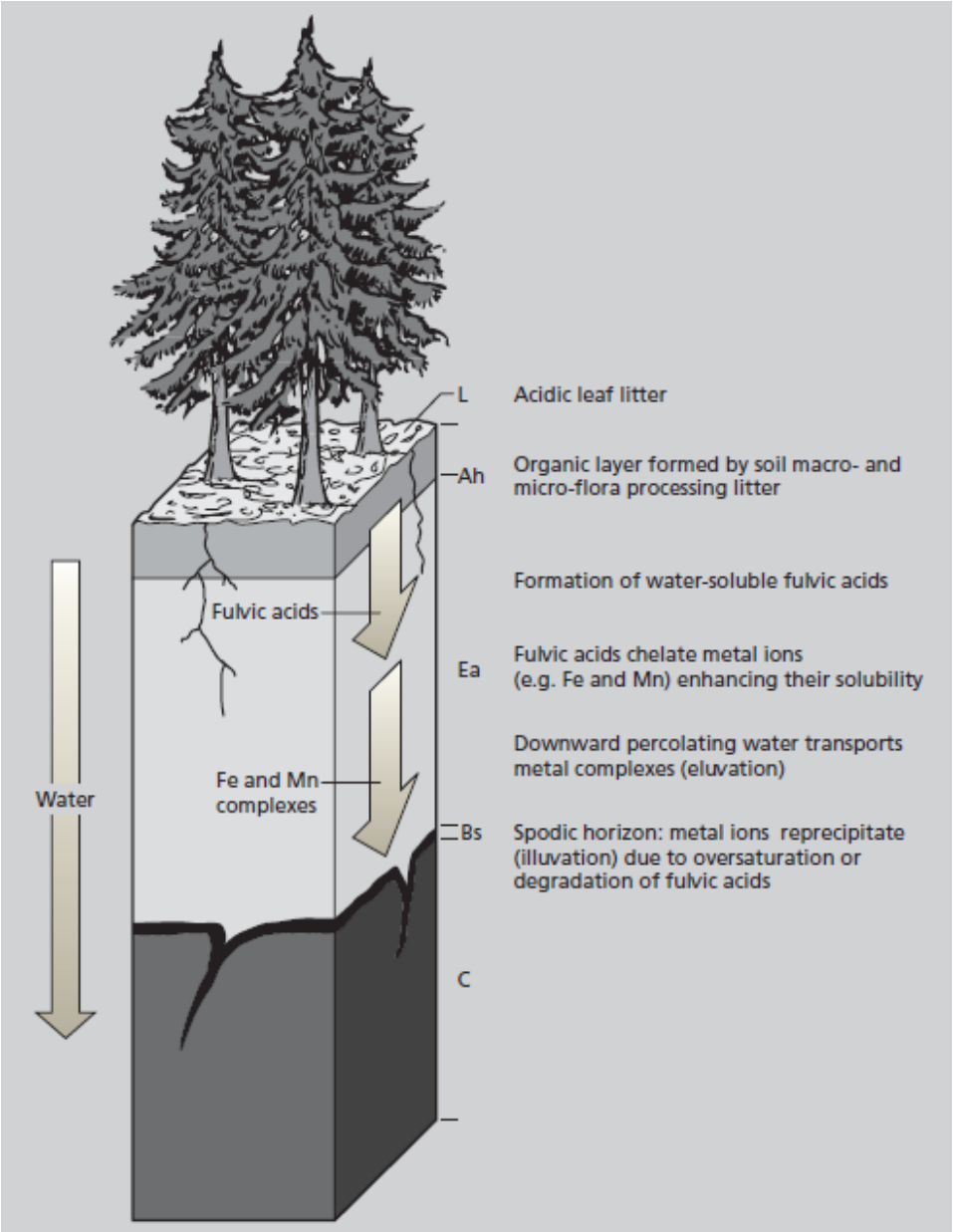
CEC = cation exchance capacity (microäquivalente pro g)

Clay minerals	CEC	Cation exchange site
Kaolinite	3–15	Edge effects
Illite	10–40	Mainly edge effects, plus some interlayer
Chlorite	10–10	
Smectite	80–150	Mainly interlayer plus some edge effects

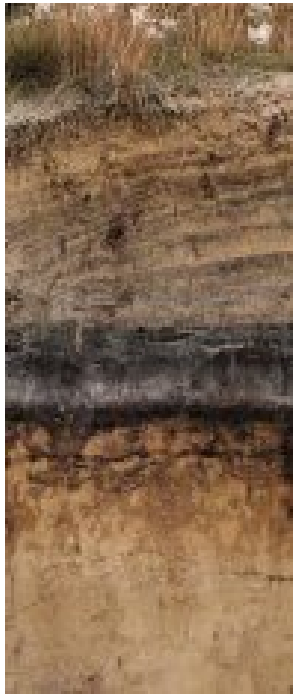
Bodenhorizonte



Podzolböden



entstehen auf sauren Ausgangs-gesteinen wie Buntsandstein, Granit oder Flugsanden (Heide-böden).



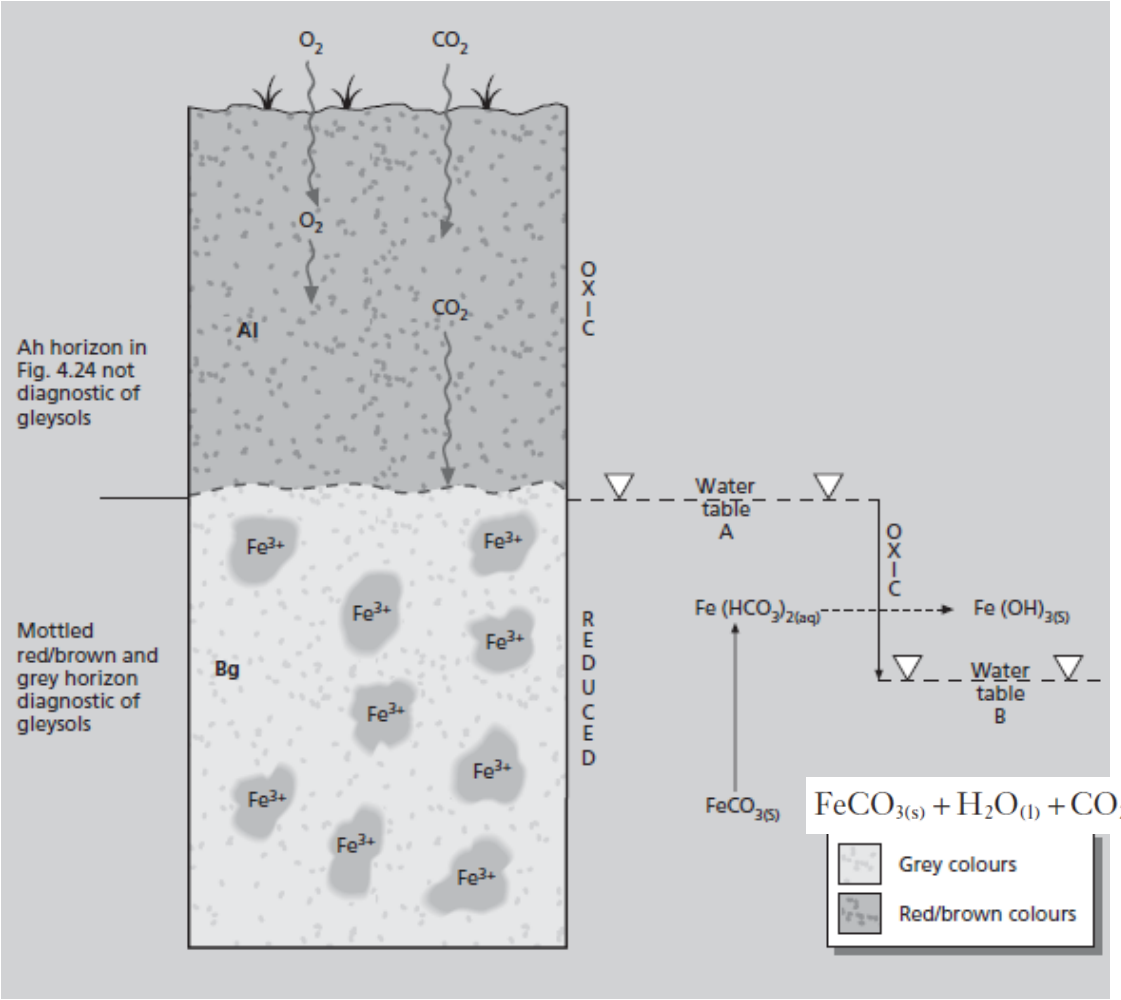
ausgebleichter, aschgrauer Horizont, (Nährstoffe ausge-waschen)

Ortstein (schwarz)

Anreicherungshorizont (ockerbraun)

Grundwasserböden (Gley)

Grundwasserböden sind in der Tiefe ständig mit Wasser gesättigt. Grundwasser führt gelöste Stoffe (Fe) heran und reichert diese in den oberen Bodenhorizonten an

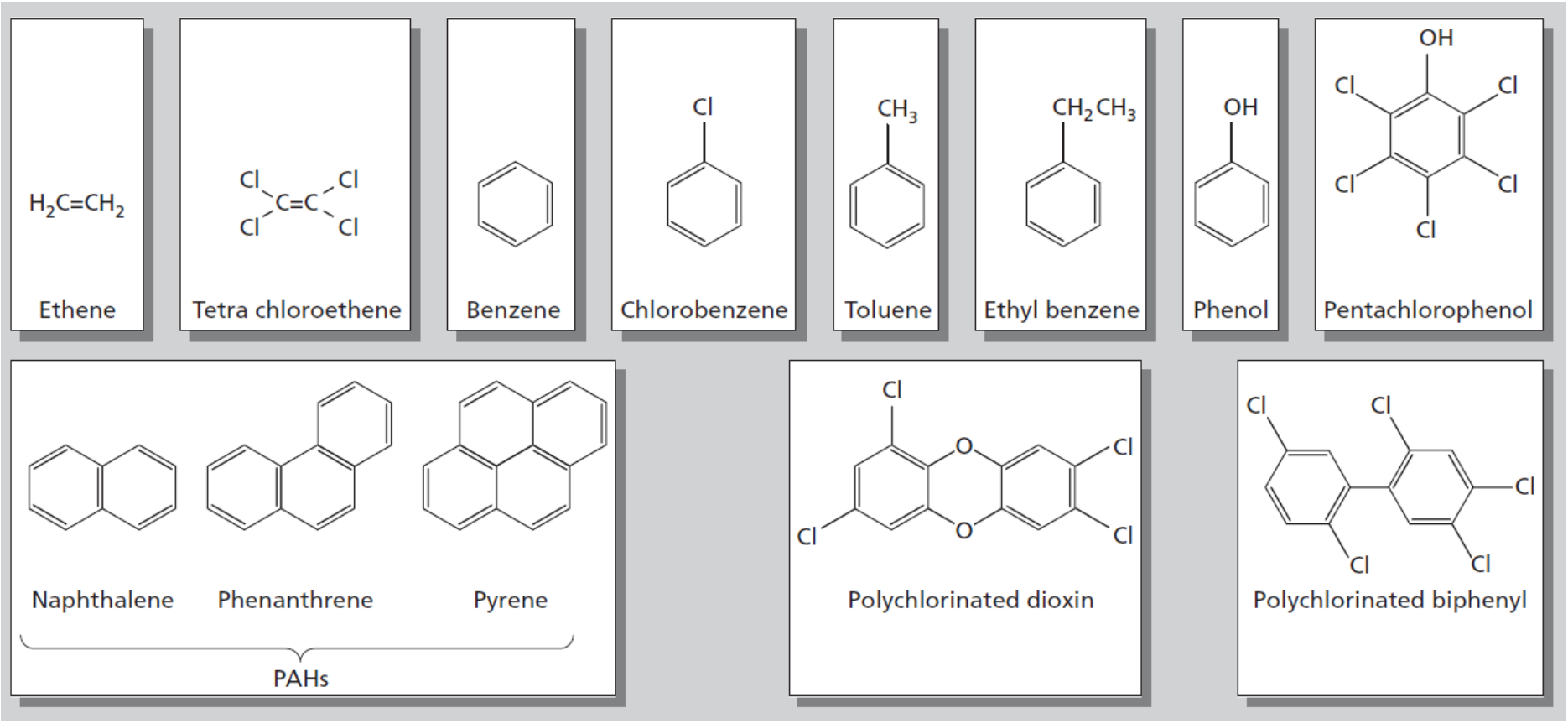


Es entstehen rostfleckige, Oxidations-Horizonte (Go)

Im Unterboden Sauerstoffmangel → Reduktion des Eisens charakteristische, bläulich-graue "Reduktionsfarben" (Gr)

Schadstoffe in Böden

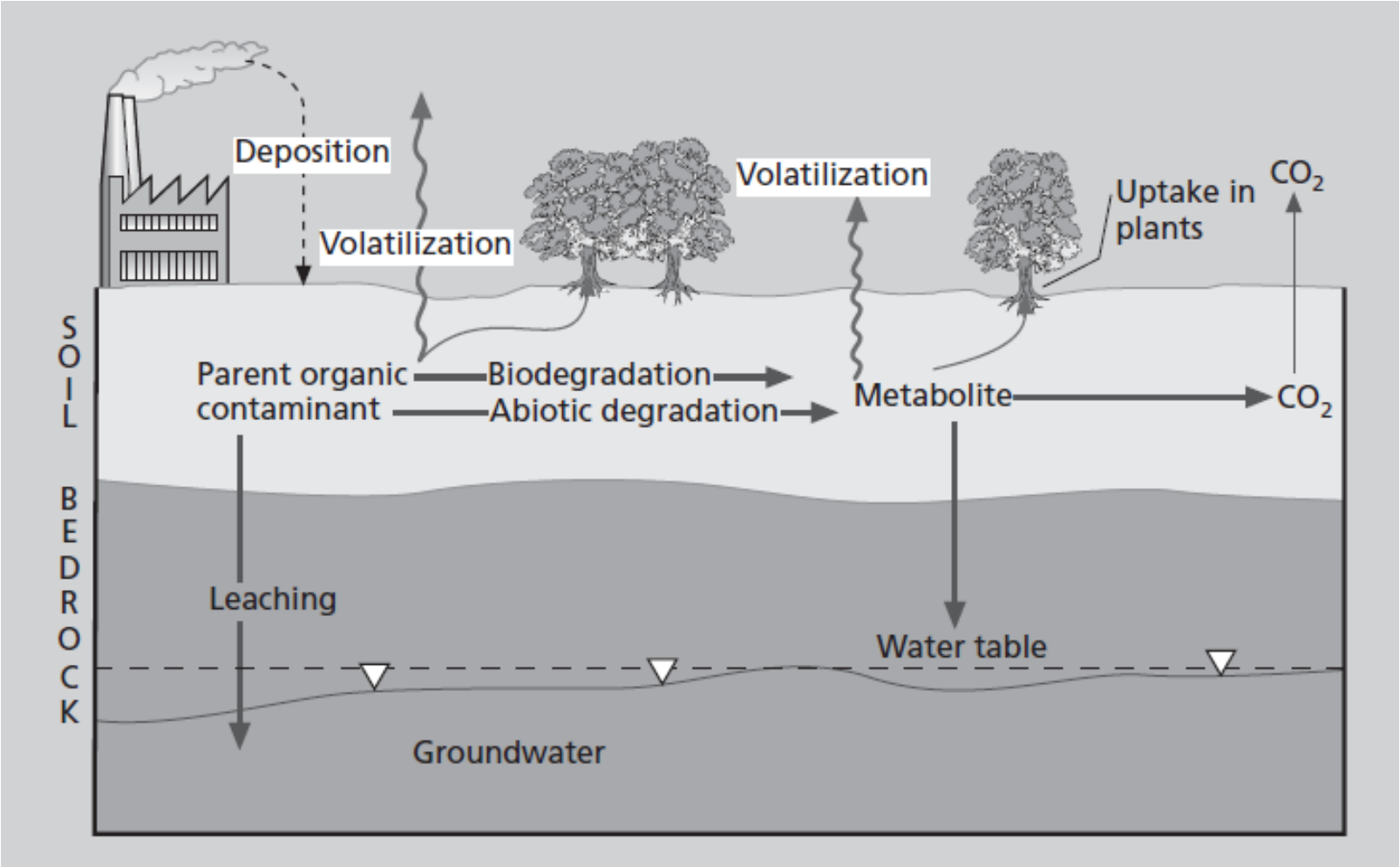
Beispiele für Schadstoffe in Böden



PAHs = polyzyklische aromatische Kohlenwasserstoffe


Cl
O
Cl
Cl
O
Cl

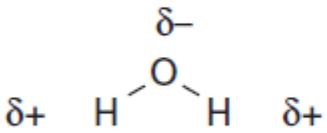
Schadstoffe in Böden



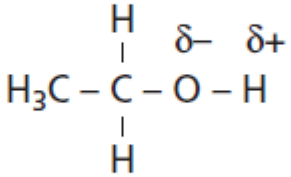
Dampfdruck → Volatilität
Löslichkeit → Polarität
Hydrophobe Eigenschaften

<u>Schadstoff-Abbau</u>
Biogen: Biodegradation
Abiogen: Hydrolyse, Reduktion, Oxidation, Photooxidation

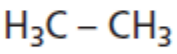
Volatilität, Polarität, Löslichkeit, Hydrophobizität



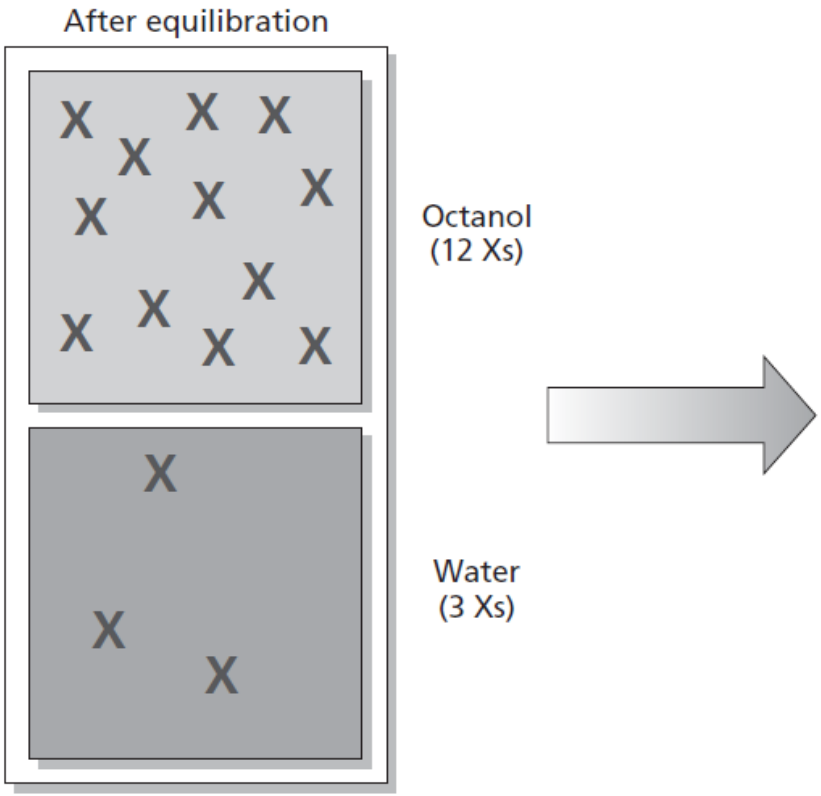
Water



Ethanol



Ethane

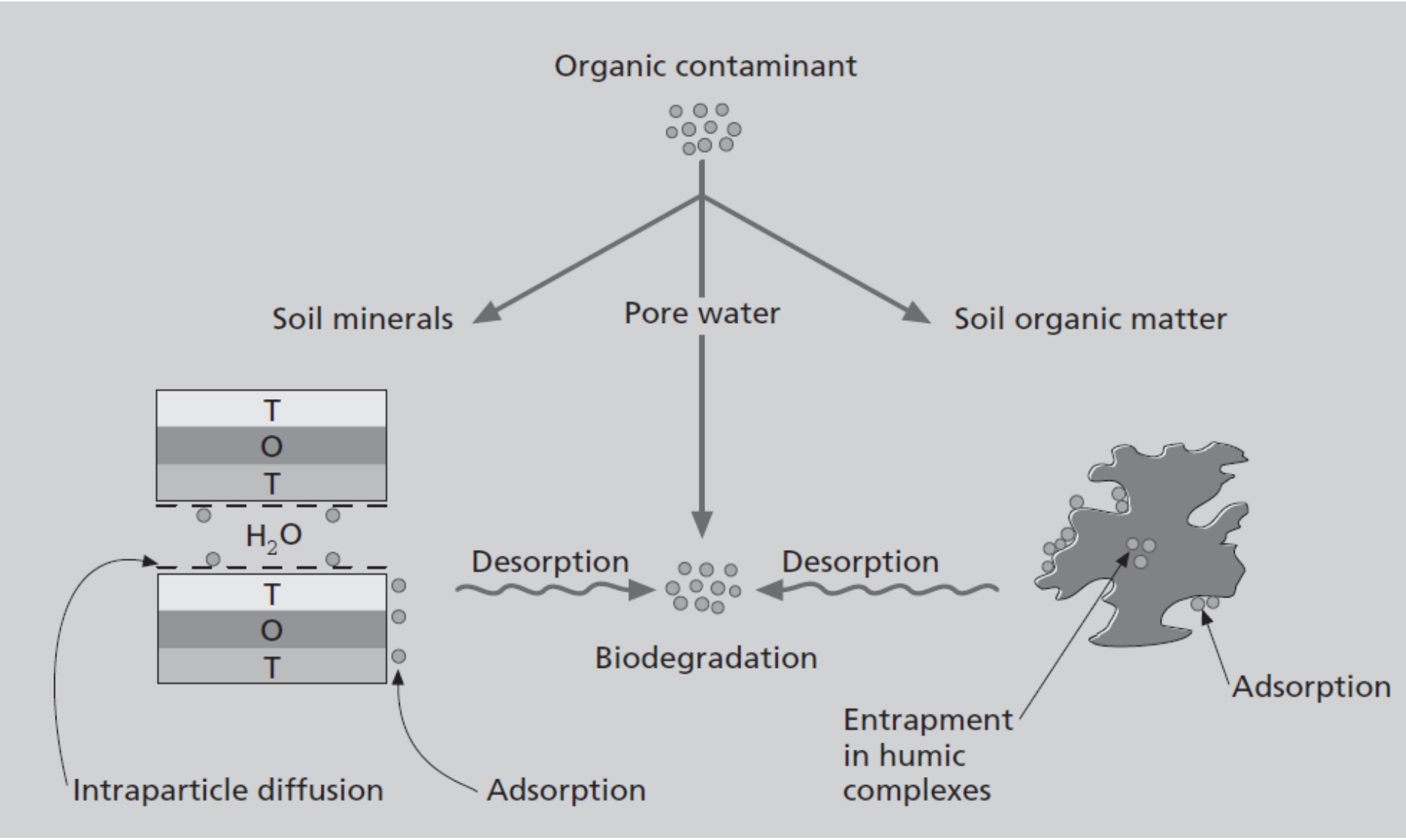


$$K_{OW} = \frac{[\text{octanol}]}{[\text{water}]} = \frac{[12]}{[3]} = 4$$

$$\log K_{OW} = \log 4 = 0.60$$

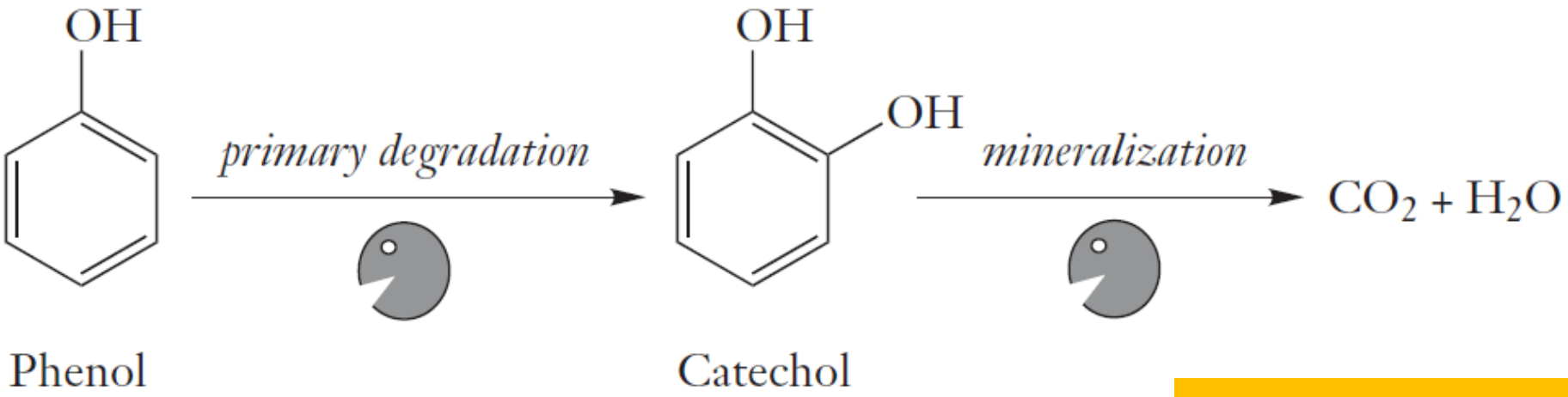
X = Compound of interest

Abbau & Fixierung



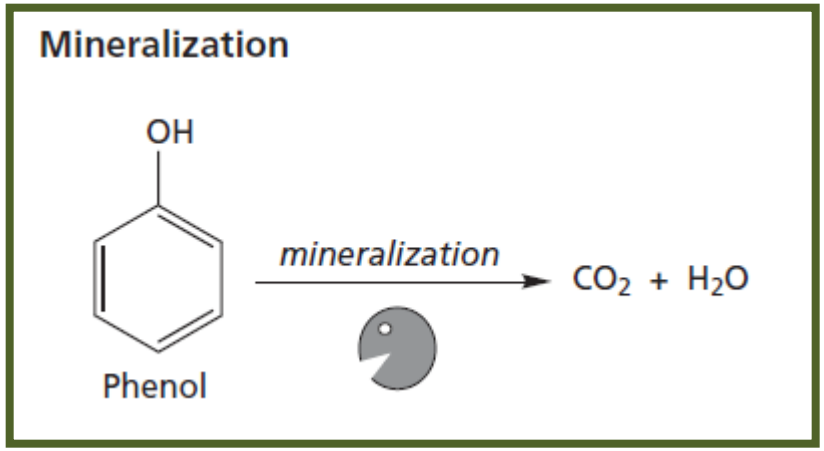
Biologische Verfügbarkeit und “ageing”

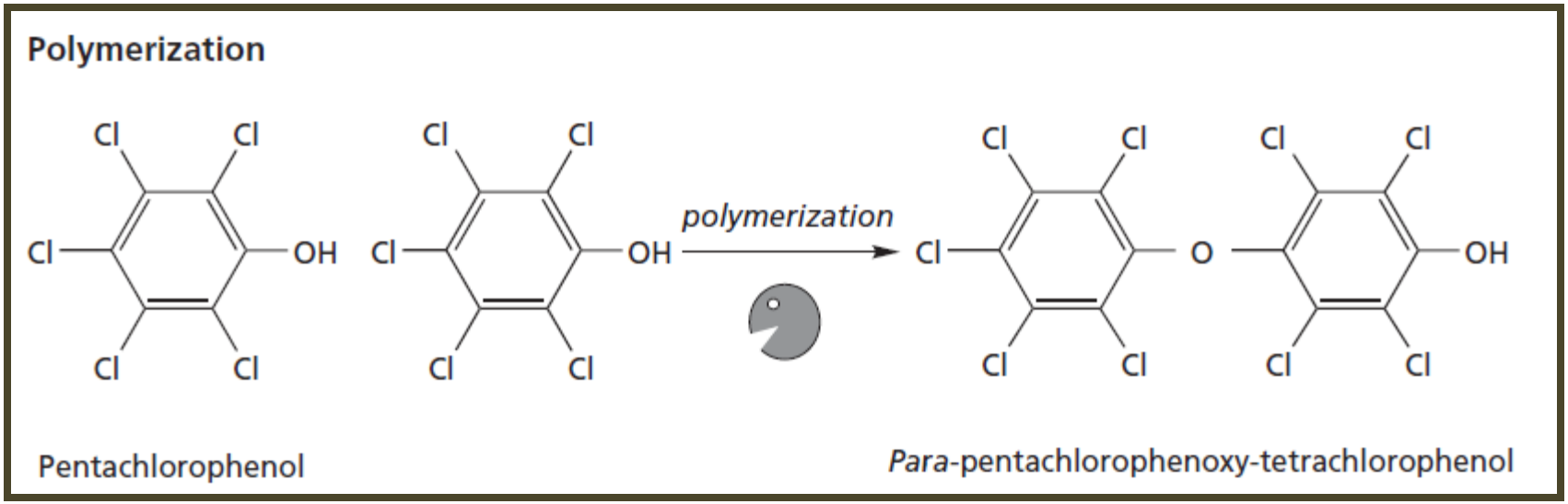
Biodegradation



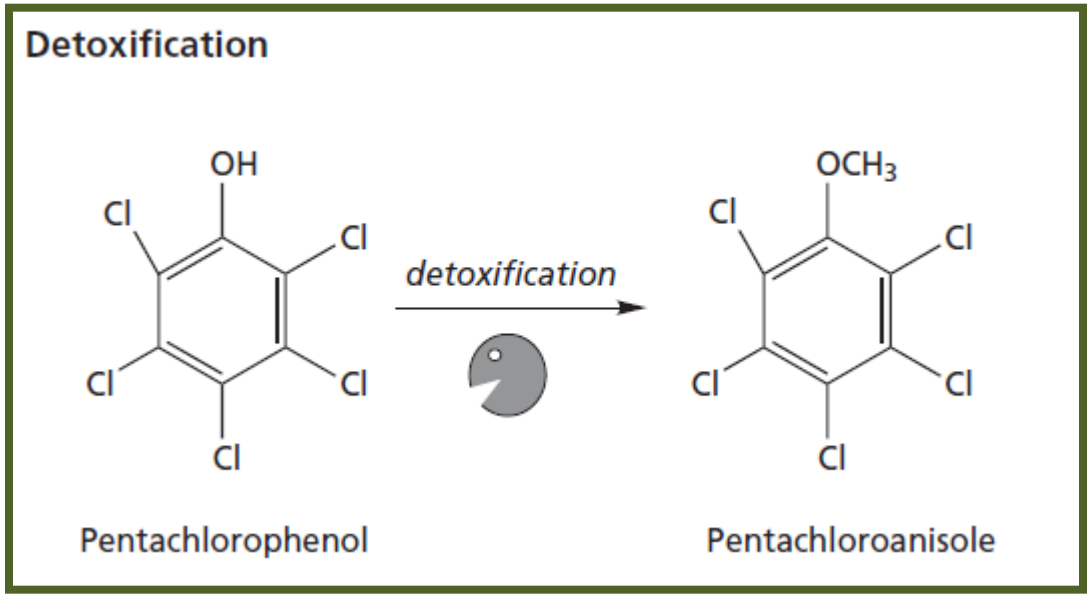
Aerob: $CO_2 + H_2O$
Anaerob: Etanol + CO_2

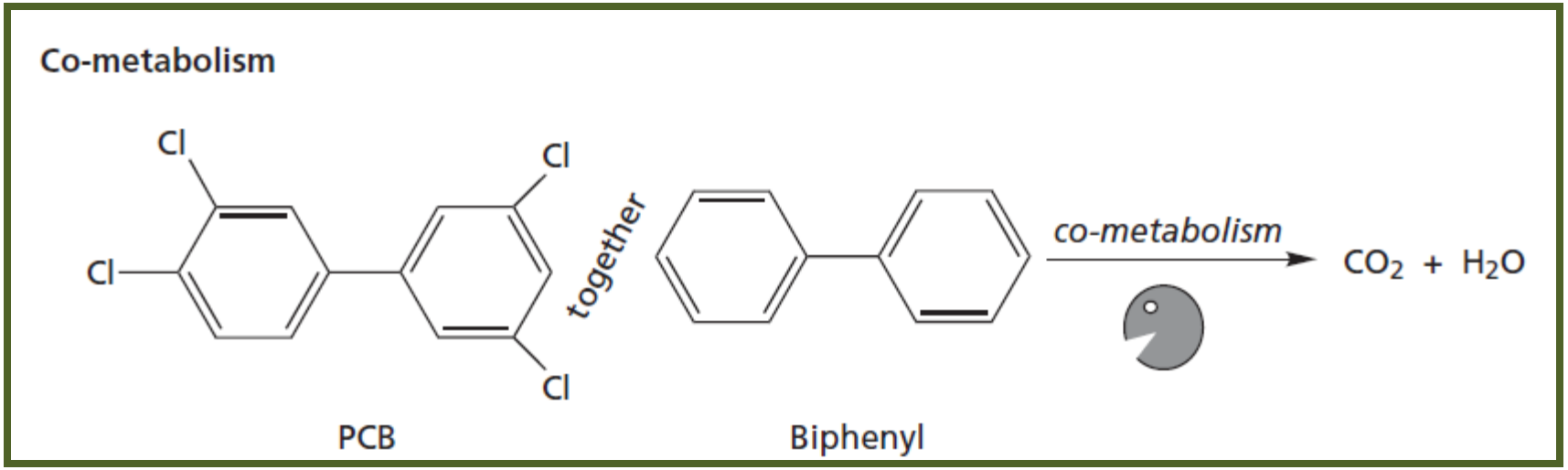
Biodegradative Prozesse



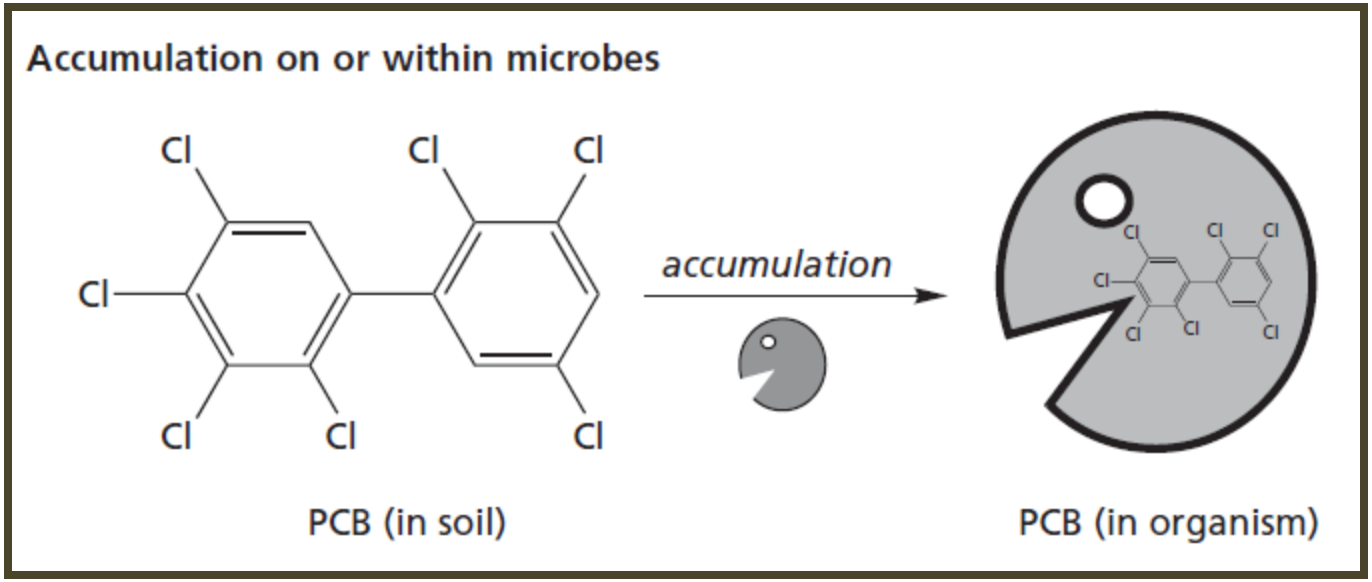


Biodegradative Prozesse





Biodegradative Prozesse



Remediation/

Sanierung

Bodensanierung

Thermische Vor-Ort-Sanierung

Bodensanierung mit Mikroorganismen

Bioremediation

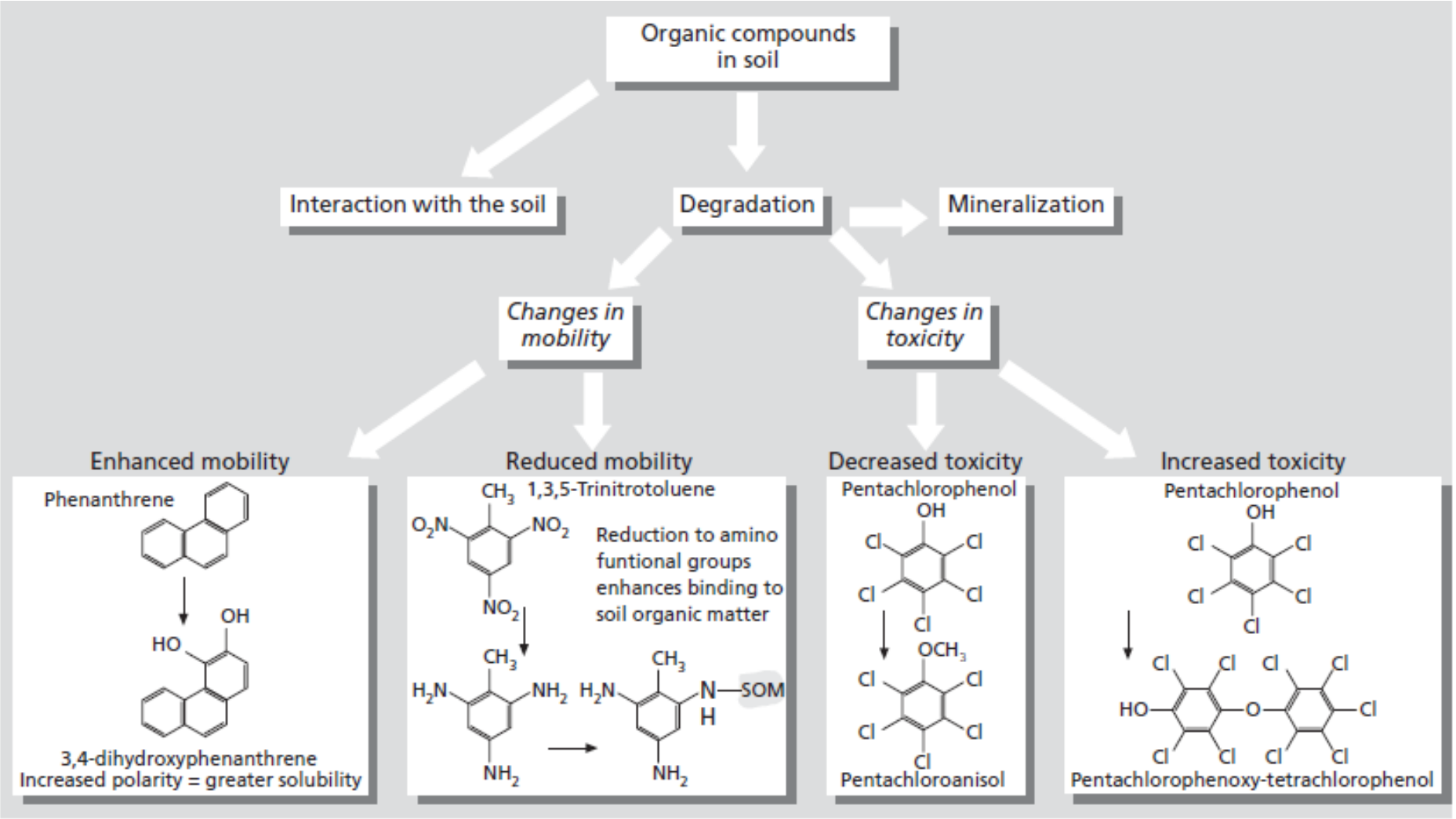
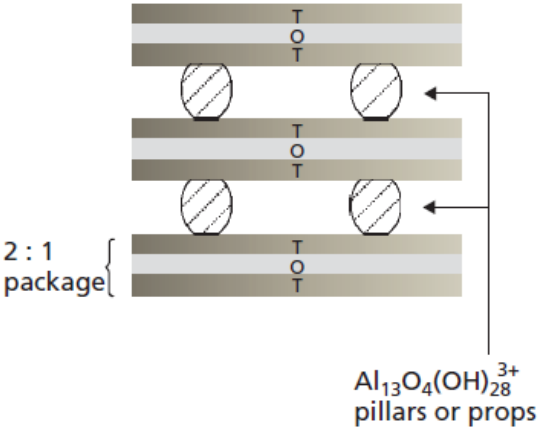
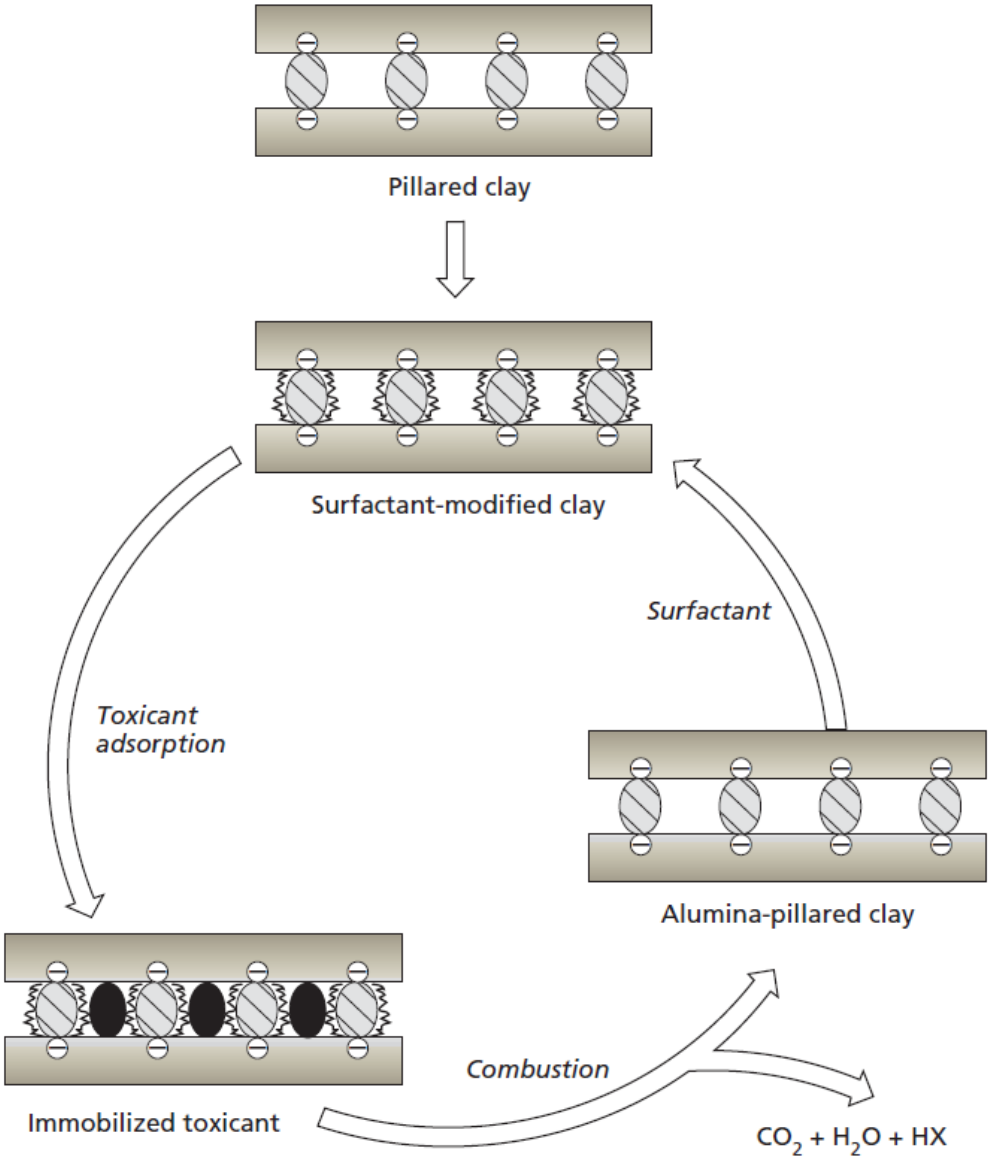


Fig. 4.30 Changes in toxicity and mobility of organic contaminants caused by biodegradation and biotransformation. SOM, soil organic matter.

Tonmineral Doping





<u>Surfactant</u>
Benetzungsmittel (Tensid),
z.B.: $CH_3(CH_2)_{16} – COO^-Na^+$

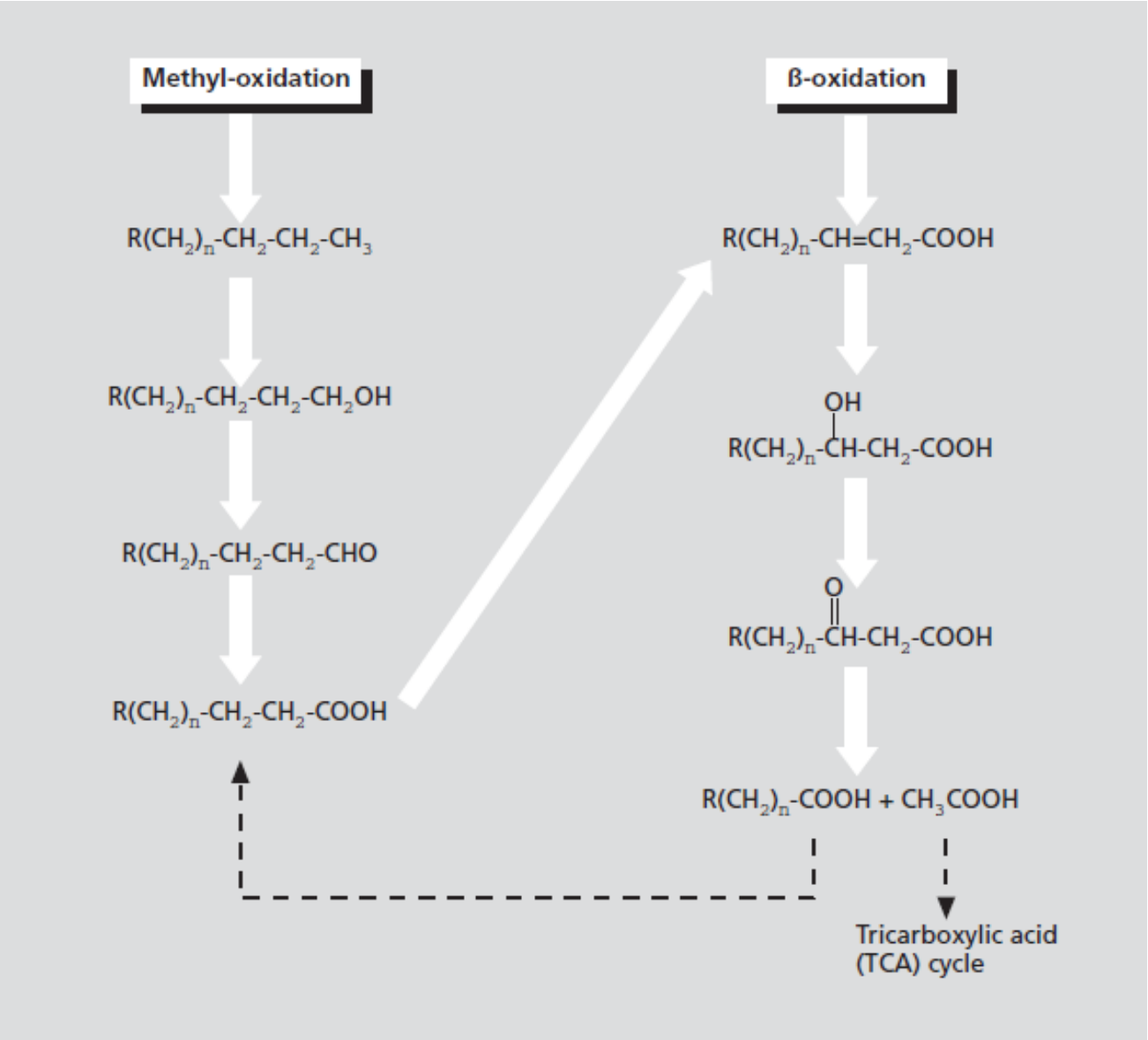
Sanierung: in-situ vs. ex-situ

Table 4.11 Consideration of typical factors relating to *in situ* or *ex situ* treatment of contaminated land.

In situ	*Ex situ*
For	*Against*
Less expensive	More expensive
Creates less dust	Creates dust during excavation
Causes less release of contaminants	May disperse contaminants
Treats larger volumes of soil	Limited in scale—batches treated individually
Against	*For*
Slower	Faster
Difficult to manage	Easier to manage—ensure results
Not suited to high clay soils or compacted sites	Suited to a variety of sites including high clay and compacted sites

Bioremediation - marine Ölteppiche

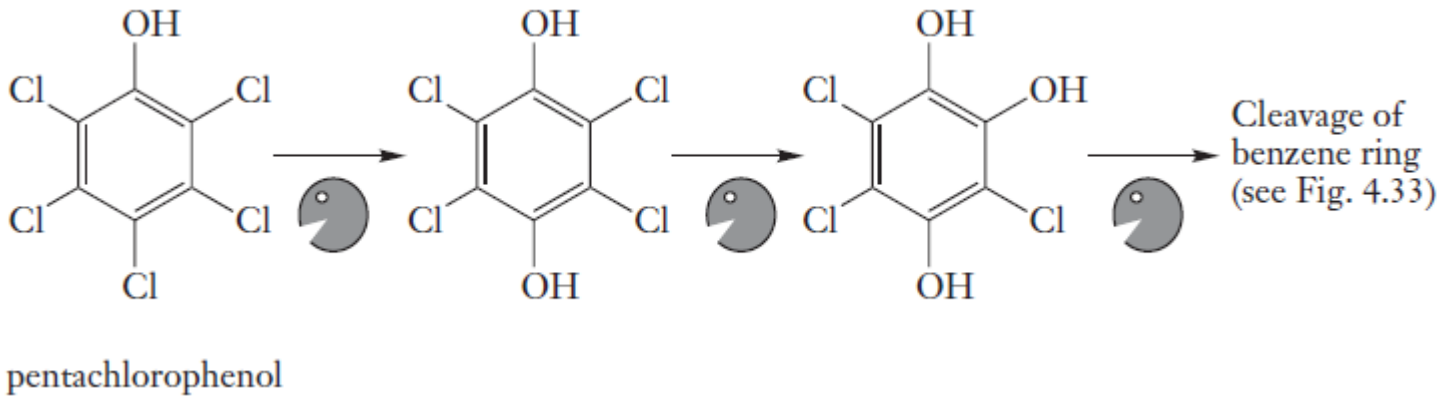
Beispiel: Exxon Valdez 1989



Sägewerke Finnland

Ex-situ compost bioremediation

Chlorphenole



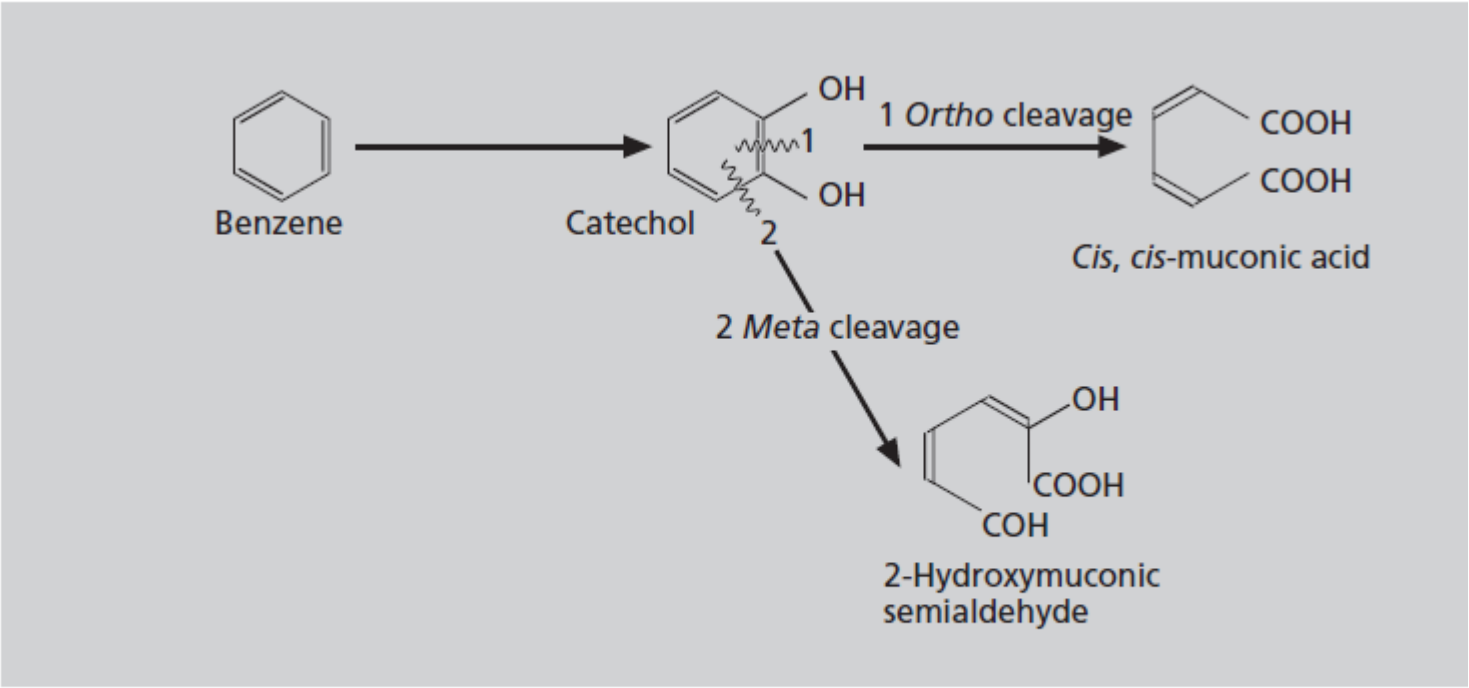


Fig. 4.33 Aerobic biodegradation pathways for benzene.

Kreosot-Kontaminationen

Burlington Northern
United States Environmental Protection Agency (EPA) Superfund site

Kreosot eingesetzt als Holzschutzmittel für Eisenbahnschwellen und Telefonmasten.

Enthält zahlreiche toxische Verbindungen u.a. polyzyklische aromatische Kohlenwasserstoffe.

Kreosotentfernung im Bioreaktor

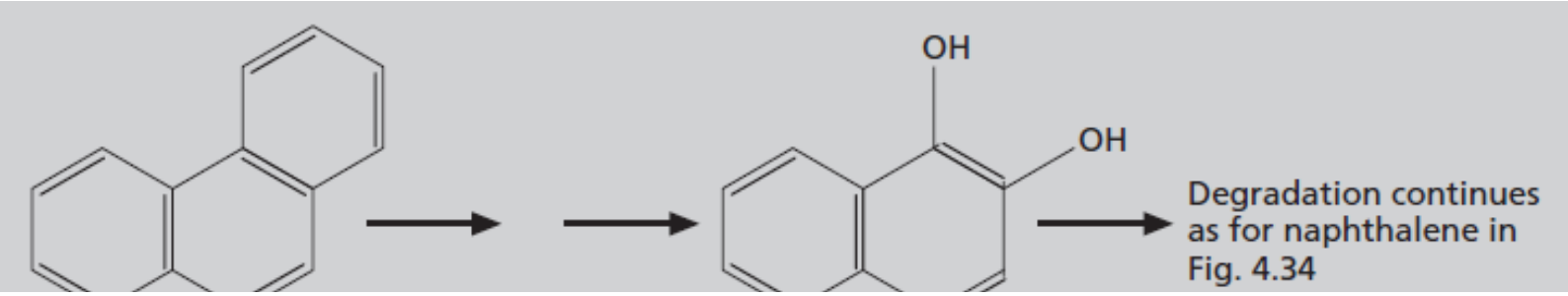
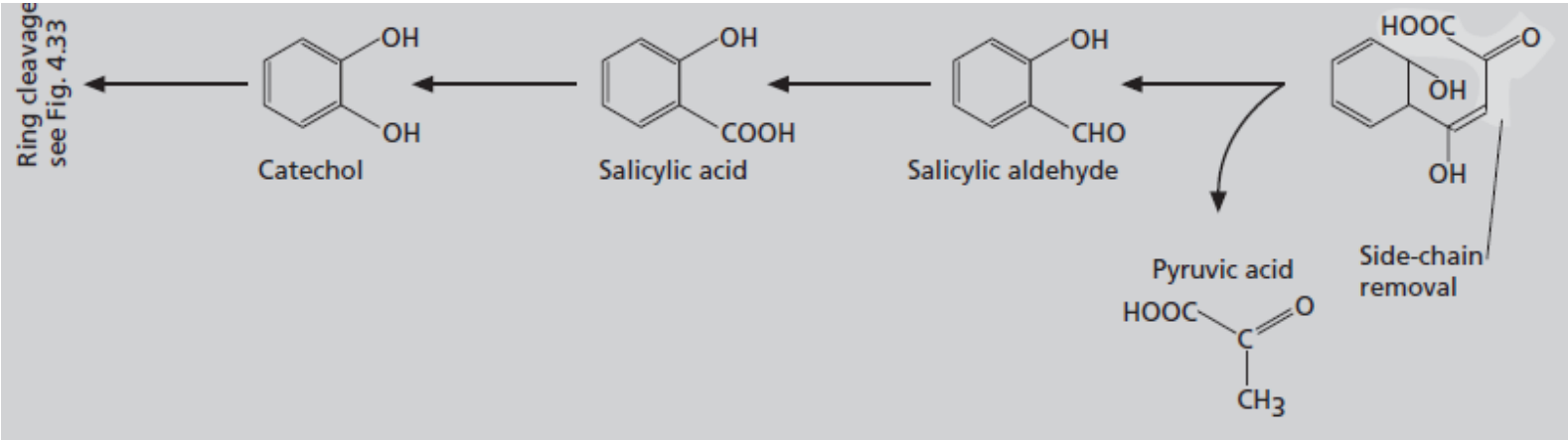


Table 4.12 Bioreactor remediation of creosote (PAH) contaminated soil, adapted from US Environmental Protection Agency technology demonstration sheet EPA/540/S5-91/009.

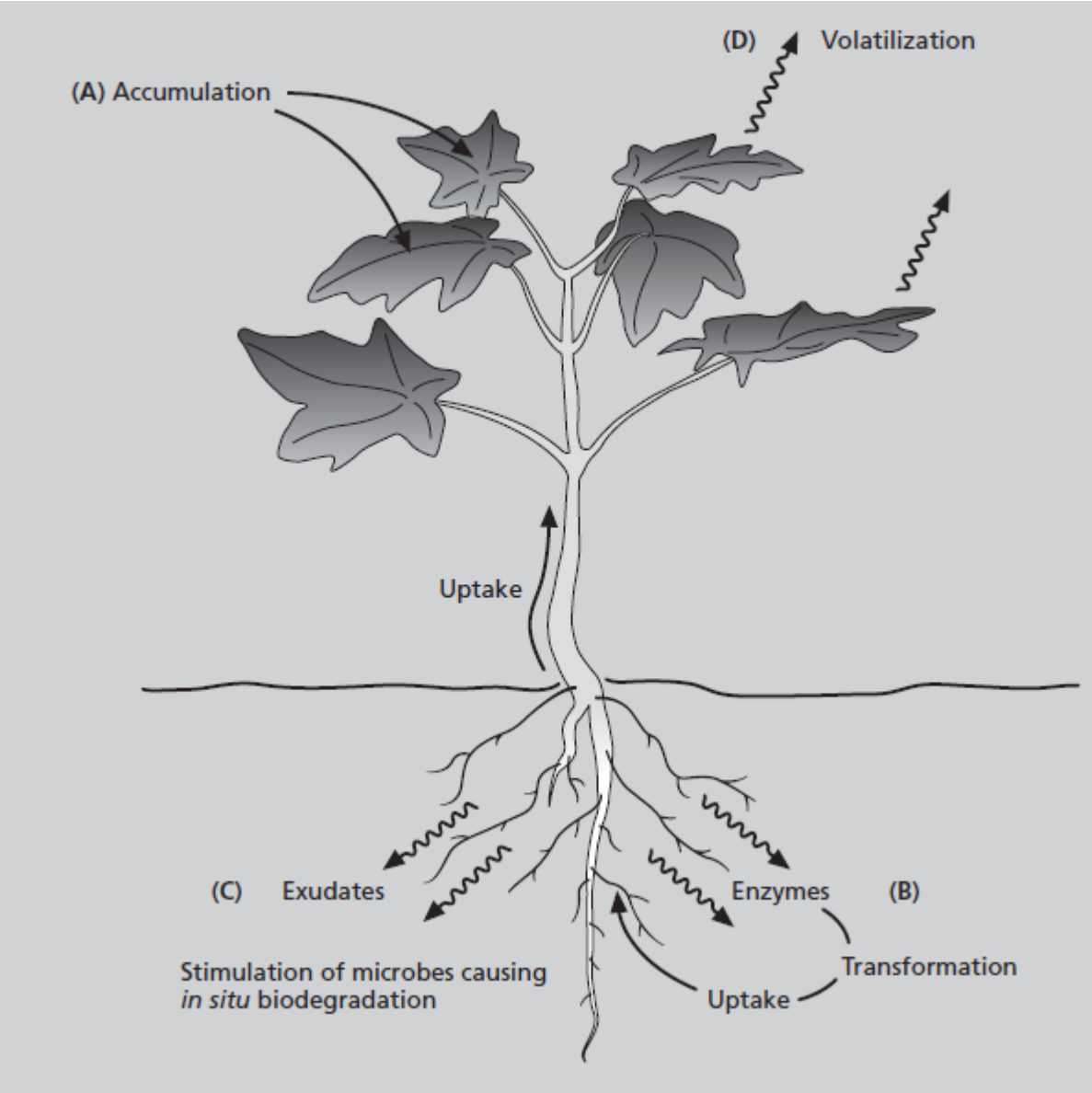
	Initial PAH concentration (mg kg^{-1})	Residual PAH concentration after 12 weeks' treatment (mg kg^{-1})	PAH reduction (%)
Two- and three-ring PAHs	1500	30	98
Four- through six-ring PAHs	960	280	70
Total PAHs*	2460	310	87

* Sixteen PAHs listed as priority pollutants by the US EPA (see Fig. 4.32).



Phytoremediation

Metall- und Schadstoffakkumulation durch Pflanzen

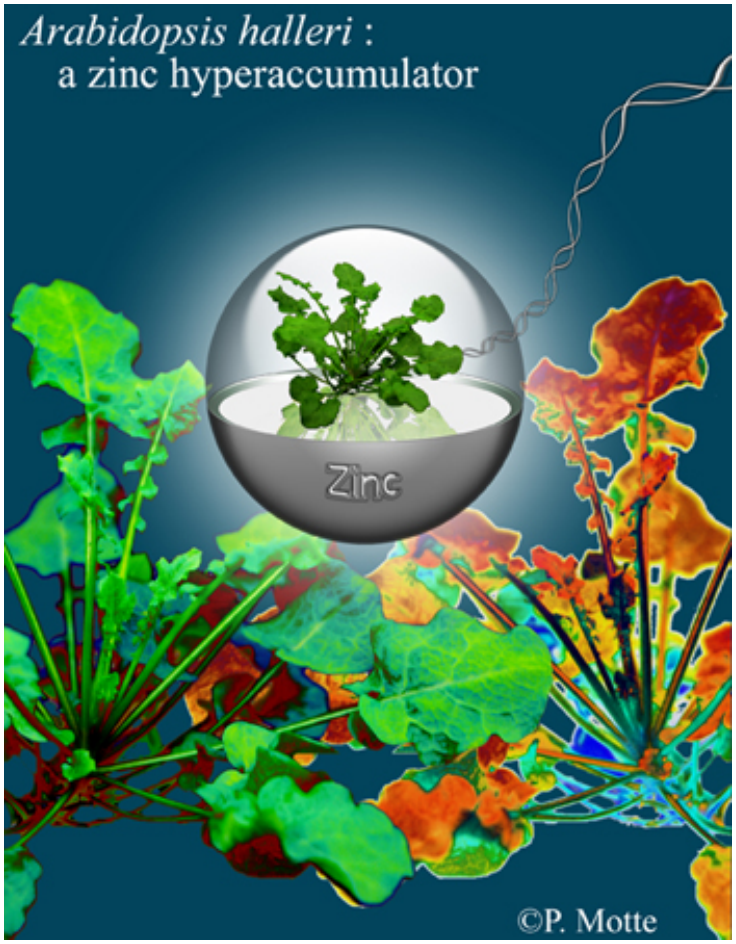


Phytoremediation durch Hyperakkumulation

Metallhunger von Pflanzen

Einige Pflanzenarten zeigen die Fähigkeit zur Hyperakkumulation von Schwermetallen → einsetzbar zur Sanierung von schwermetall-belasteten Böden und Gewässern

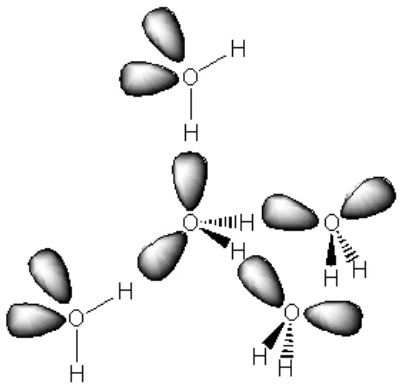
Arabidopsis halleri ist ein Hyperakkumulierer, der auf vielen metallbelasteten Standorten in Mitteleuropa wächst (z.B. im Harz), die aufgrund geologischer oder anthropogener Einflüsse metallreich sind.



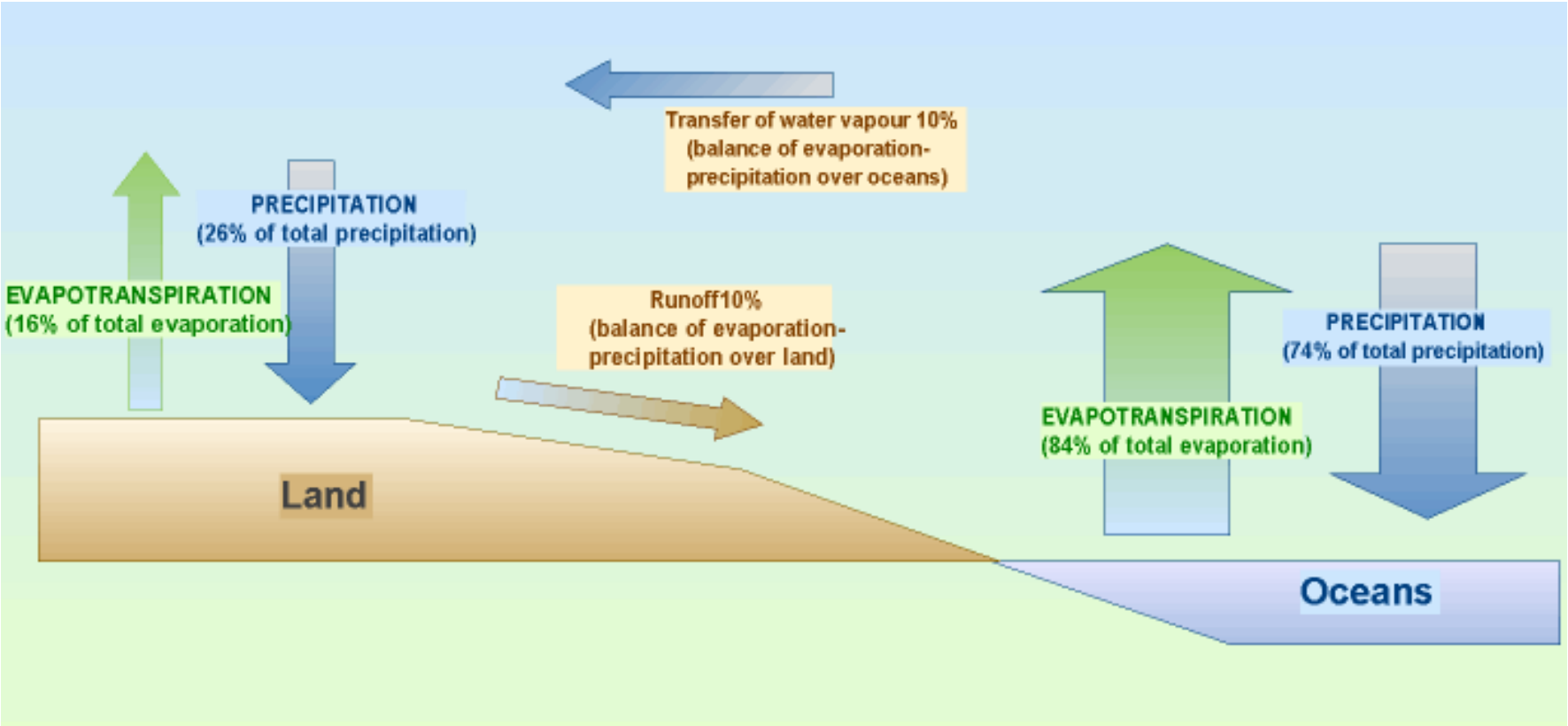
Hydrosphäre

Wasser

- Wasser bedeckt 71% der Erde
- 97% davon in den Ozeanen
- Wassermolekül – polar
  Wasserstoffbrückenbindung
- Hohe Löslichkeit (Ausnahme: Öl!)
- Hohe Wärmekapazität
- Hohe Verdunstungswärme
- Transportmedium
- Salinität (variiert um 35g Salz pro kg Meerwasser)



World Water Balance



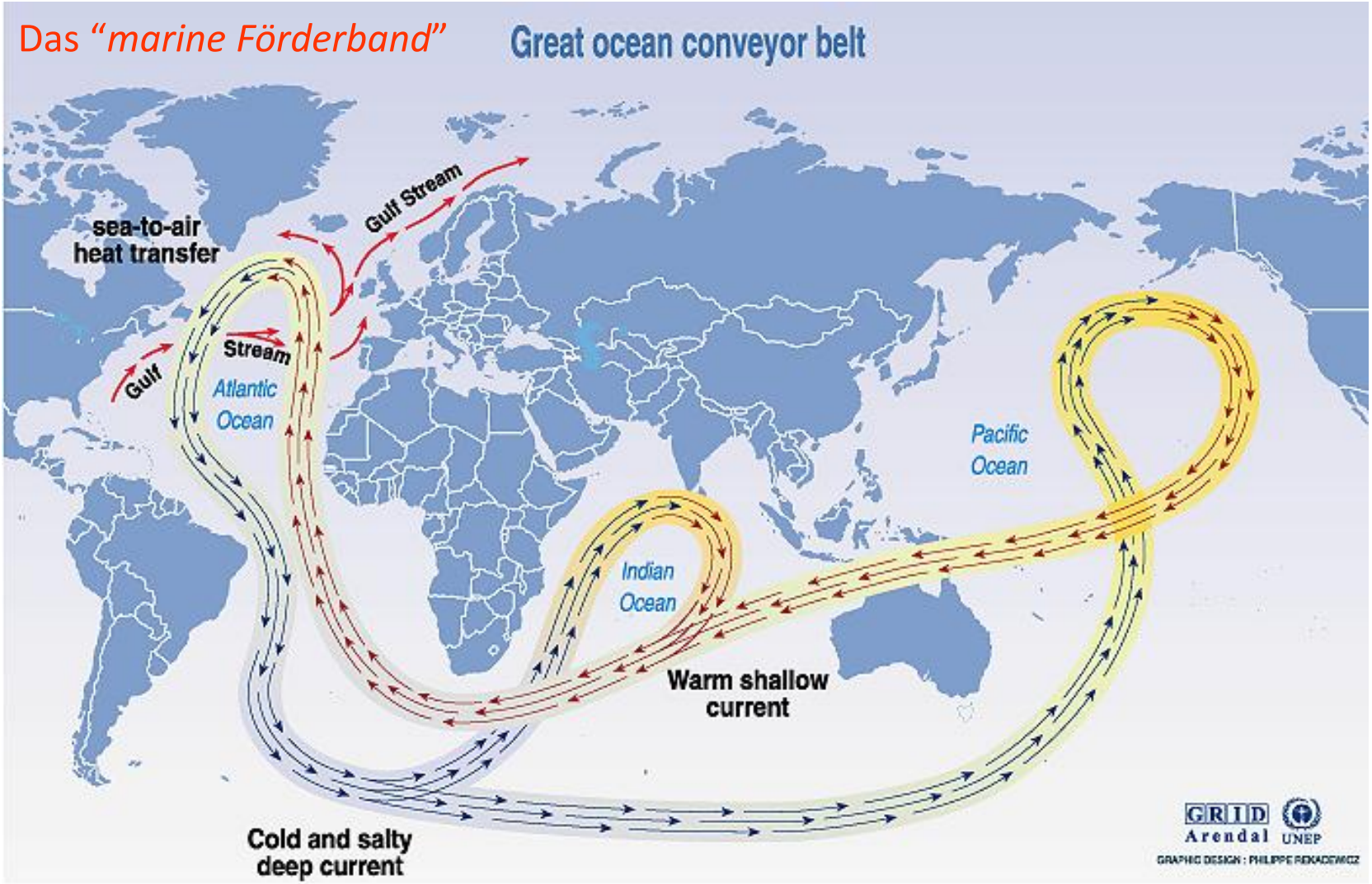
Waugh 1990

Hydrosphäre

- Oceans are the main reservoir of water on the Earth ~97% by volume.
- Much higher contents of dissolved solids than most other natural waters (35 g / kg water)
- Compared to other natural waters, seawater is remarkably homogeneous in composition

Total dissolved solids (g/kg)	
Rain	0.005
River	0.1
Ocean	35

Thermohaline Zirkulation



Source: Broecker, 1991, in Climate change 1995, Impacts, adaptations and mitigation of climate change: scientific-technical analyses, contribution of working group 2 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.

Das "conveyor-belt"-Modell von Gordon (1986) und Broeker (1987)

Hydrosphäre

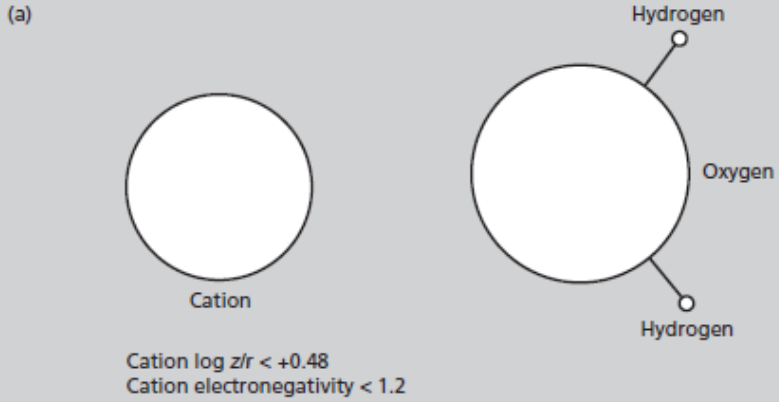
- **Georg Forchhammer (1794-1865)**
  Danish Mineralogist

"*The quantity of different elements in seawater is **not** proportional to the quantity of elements which river water pours into the sea…*"

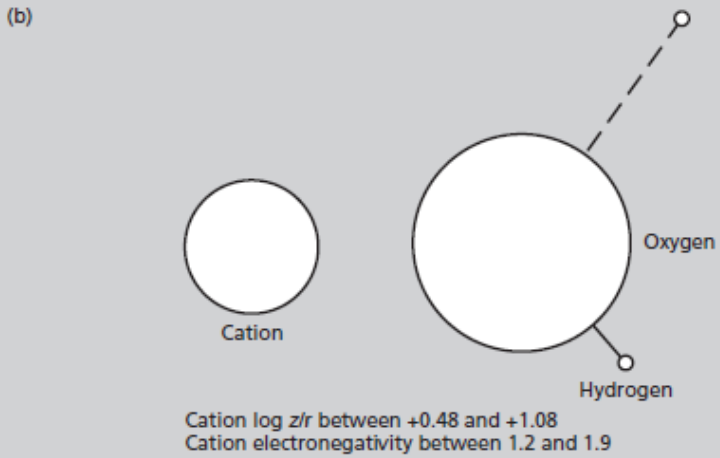
Binnengewässer (Süßwasser)

Table 5.1 Comparison of the major cation composition of average upper continental crust (from Wedepohl 1995) and average riverwater (from Berner & Berner 1987); except aluminium and iron from Broecker and Peng (1982).

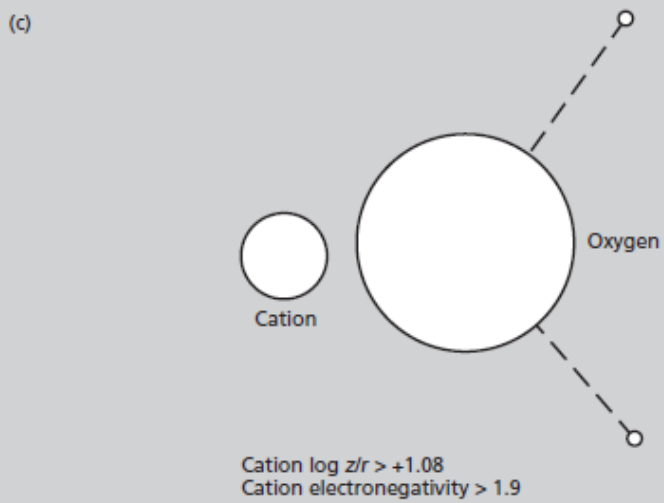
	Upper continental crust ($mg\,kg^{-1}$)	Riverwater ($mg\,kg^{-1}$)
Al	77.4	0.05
Fe	30.9	0.04
Ca	29.4	13.4
Na	25.7	5.2
K	28.6	1.3
Mg	13.5	3.4



Ca^{2+}, Na^{+}, K^{+} and Mg^{2+}



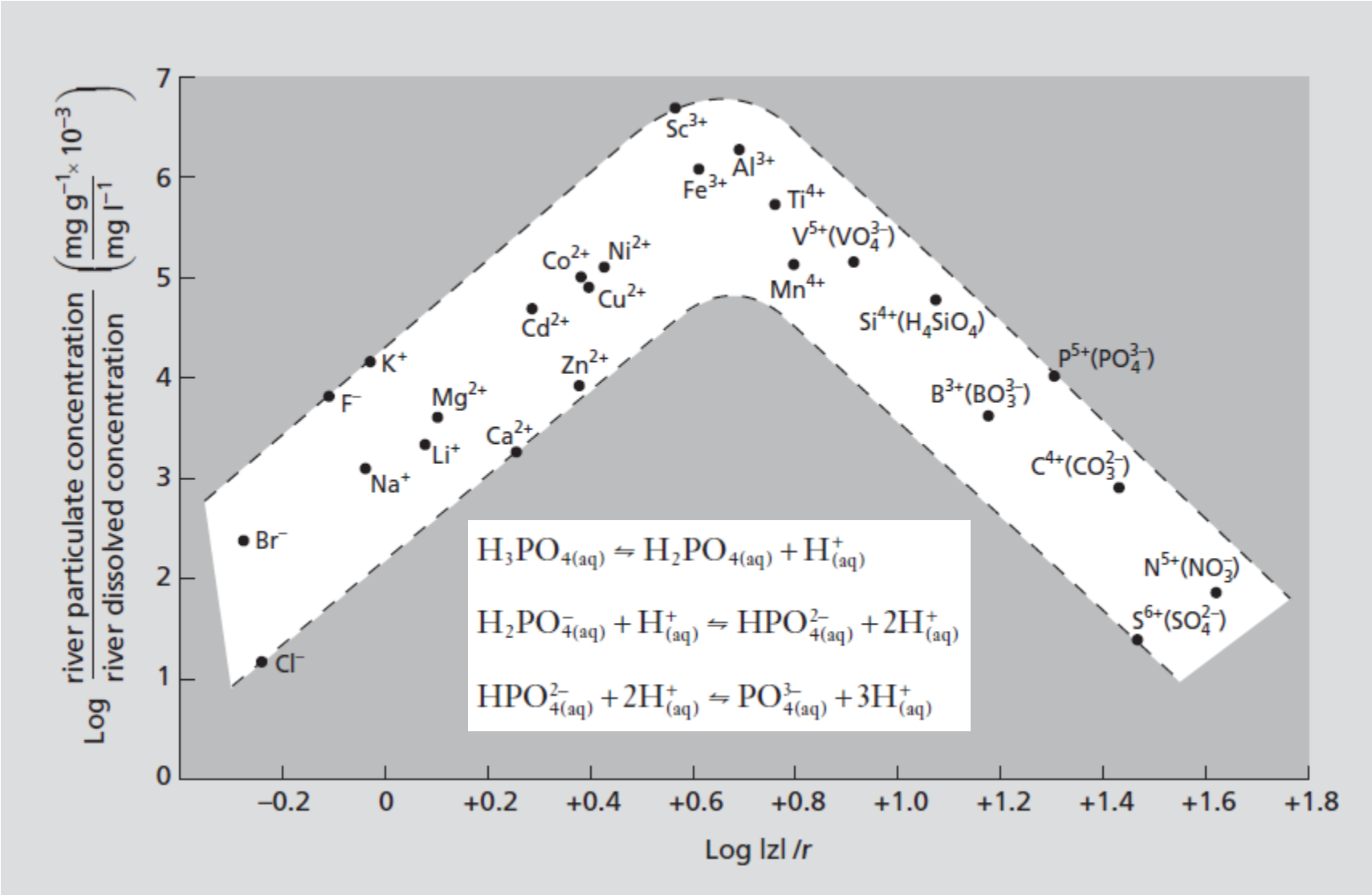
$$Fe^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow FeOH_{3(s)} + 3H^{+}_{(aq)}$$



$$S(VI)_{(s)} + 4H_2O_{(l)} \rightarrow SO^{2-}_{4(aq)} + 2H^{+}_{(aq)}$$

Oxyanion

Elementchemie Süßwasser



Beispiel Phosphor

P: 0.1 Gew.% in Erdkruste; wichtiger Nährstoff

Phosphatminerale: Apatit: $Ca_5(PO4)_3(F,Cl,OH)$

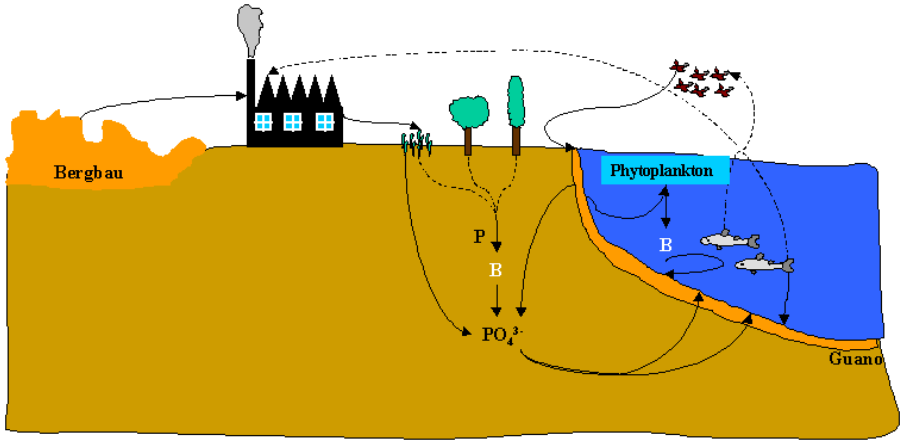
im Wasser oder in Bodenlösung: Phosphat-Anionen

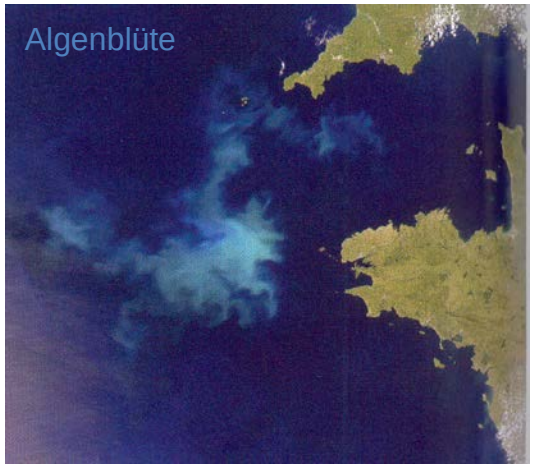
schwach basische Wässer **Hydrogenphosphat**-Anion (HPO_4^{2-})

schwach saure Wässer **Dihydrogenphosphat**-Anion ($H_2PO_4^-$)

Dünngungsmittel (Überdüngung → Eutrophierung)

entgegenwirken durch chemische P-Fällung, z.B.: $Fe^{3+} + PO_4^{3-} \rightarrow FePO_4$





Grundwasserchemie

Table 5.3 Chemical analyses of US groundwater from various rock types (mmol l^{-1}). Adapted from Todd (1980). This material is used by permission of John Wiley & Sons, Inc.

	Granite South Carolina	Metamorphic schist Georgia	Limestone Texas
Ca^{2+}	0.3	0.7	1.8
Mg^{2+}	0.2	0.2	0.4
Na^{+}	0.4	0.7	1.0
K^{+}	0.1	0.2	0.2
Cl^{-}	0.1	0.1	0.7
SO_4^{2-}	0.1	0.1	0.2
HCO_3^{-}	1.2	2.3	4.5
Al	0.004	0	—
Fe	0.003	0.002	0.001
SiO_2	0.6	0.35	0.18
$Na^{+}/(Ca^{2+} + Na^{+})$	0.57	0.50	0.36

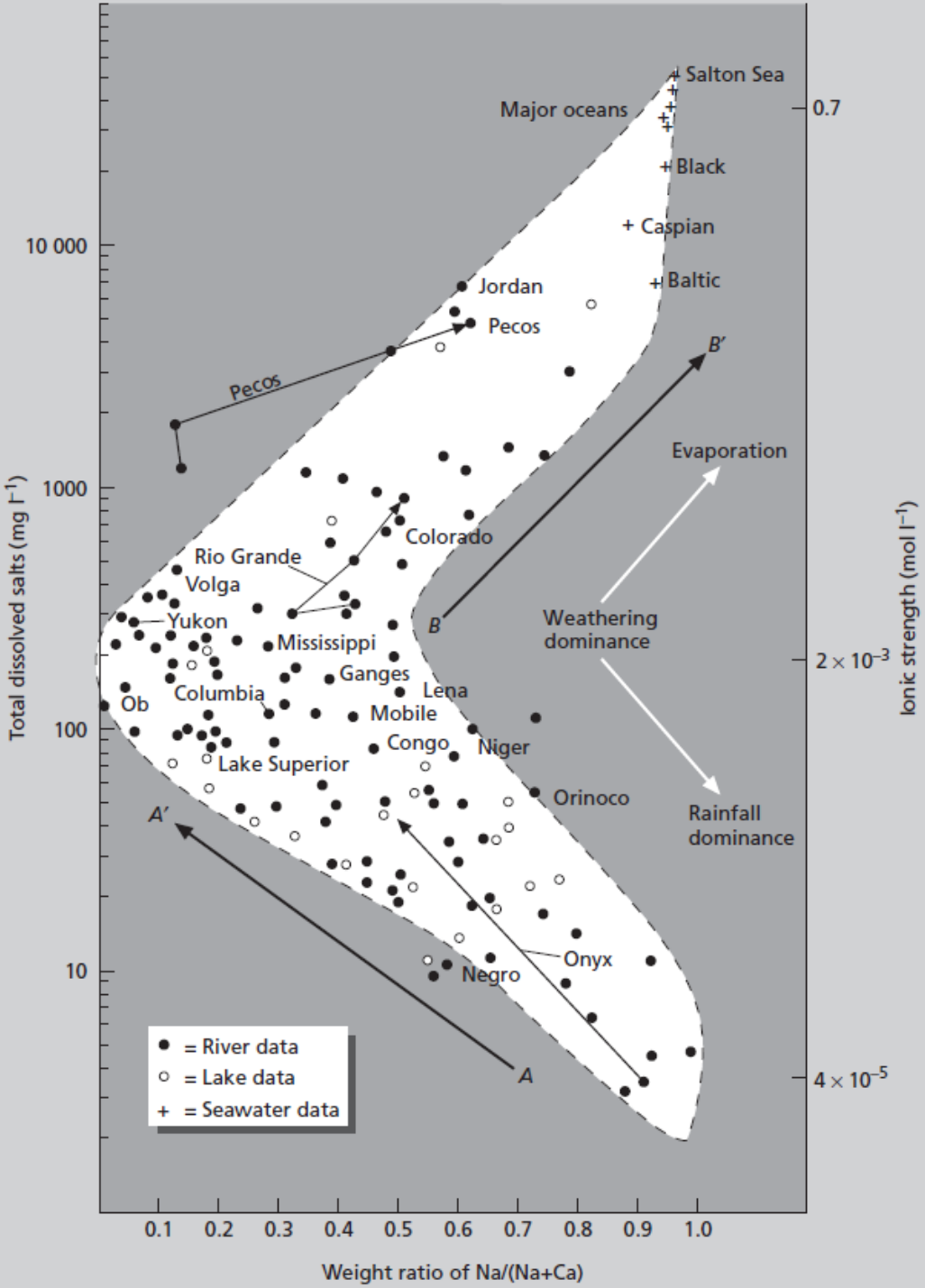
Wasserchemie und Verwitterungsregime

Table 5.2 Dissolved major ion composition (mmol l^{-1}) of some major rivers. Data from Meybeck (1979); except Rio Grande from Livingston (1963).

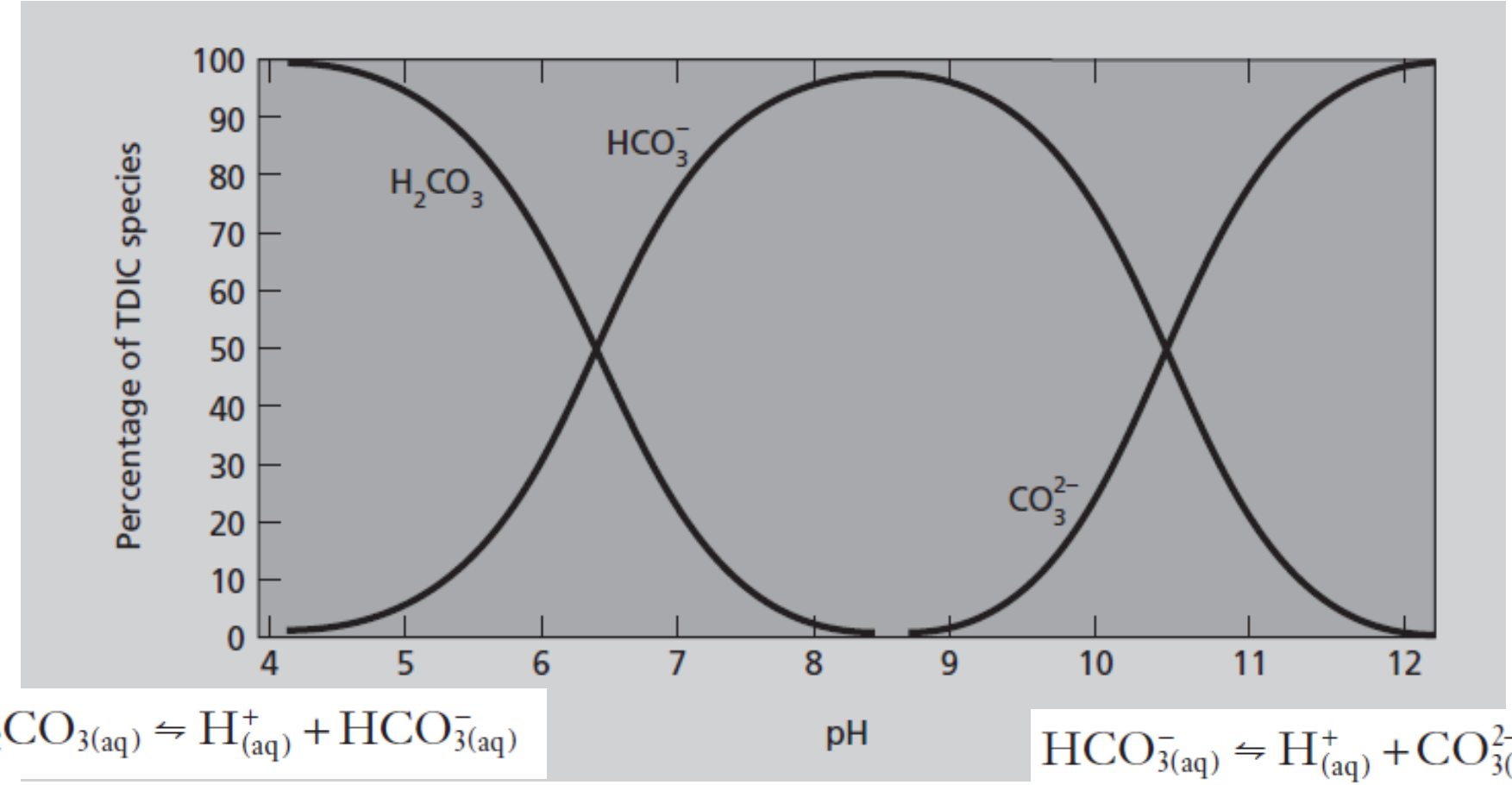
	Mackenzie (1)	Orinoco (2)	Ganges (3)	Rio Grande (4)
Ca^{2+}	0.82	0.08	0.61	2.72
Mg^{2+}	0.43	0.04	0.20	0.99
Na^{+}	0.30	0.06	0.21	5.10
K^{+}	0.02	0.02	0.08	0.17
Cl^{-}	0.25	0.08	0.09	4.82
SO_4^{2-}	0.38	0.03	0.09	2.48
HCO_3^{-}	1.82	0.18	1.72	3.00
SiO_2	0.05	0.19	0.21	0.50

Drainage basin characteristics: (1) northern arctic Canada; (2) tropical northern South America; (3) southern Himalayas; (4) arid southwestern North America.

Lösungsfracht Von Flüssen



Alkalinität



$$H_2CO_{3(aq)} \leftrightharpoons H^+_{(aq)} + HCO^-_{3(aq)}$$

$$HCO^-_{3(aq)} \leftrightharpoons H^+_{(aq)} + CO^{2-}_{3(aq)}$$

$$K_1 = \frac{aH^+ . aHCO_3^-}{aH_2CO_3} = 10^{-6.4}$$

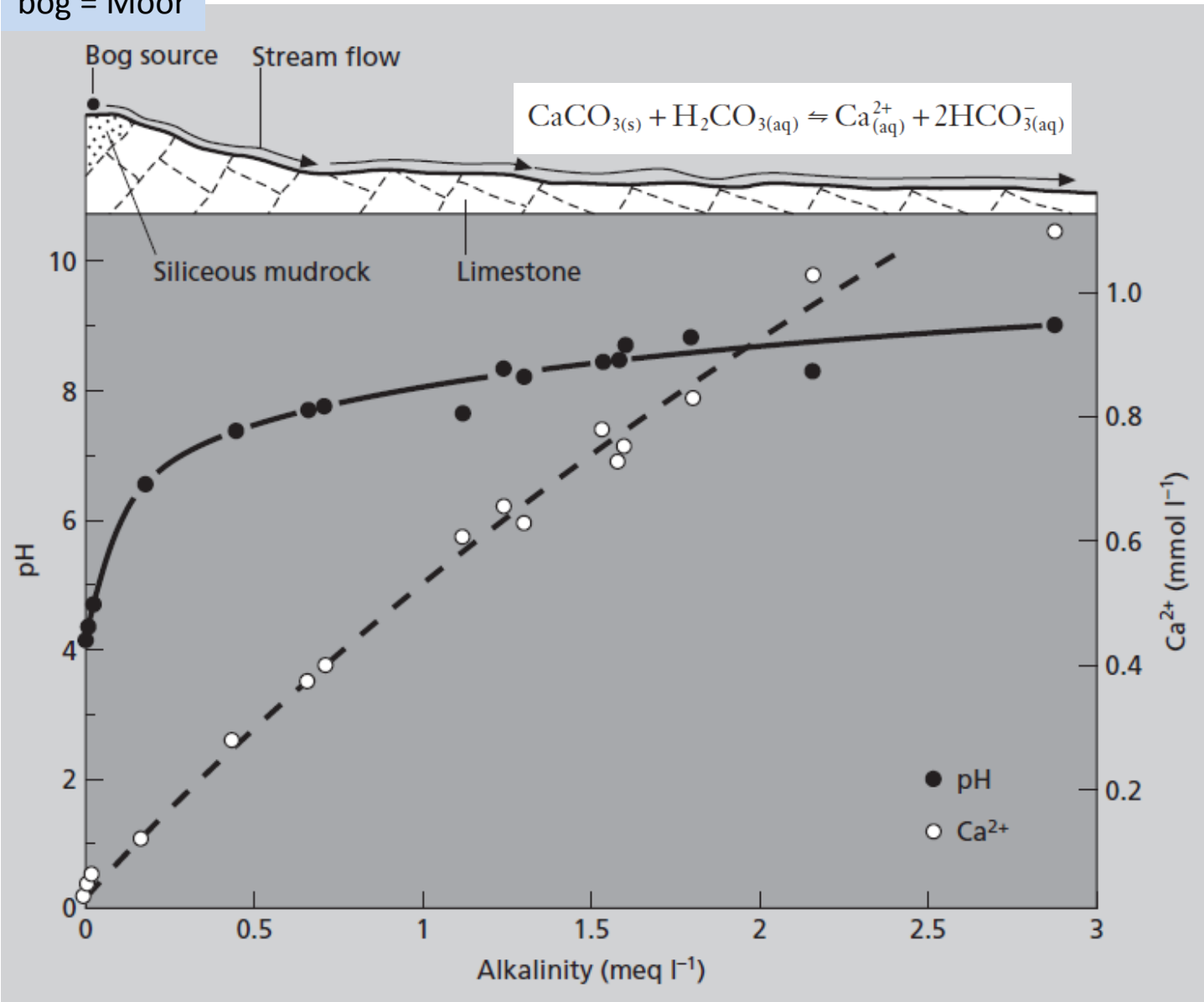
$$K_2 = \frac{aH^+ . aCO_3^{2-}}{aHCO_3^-} = 10^{-10.3}$$

für pH 8 (pH = -log10aH$^+$) gilt:

$$aHCO_3^- = \frac{10^{-8} . aCO_3^{2-}}{10^{-10.3}} = \frac{1 \times 10^{-8} . aCO_3^{2-}}{5 \times 10^{-11}} = 200\, aCO_3^{2-}$$

Alkalinität und pH Puffer

bog = Moor



Aluminiumlöslichkeit und Säuregrad

<u>Al gelöst</u>

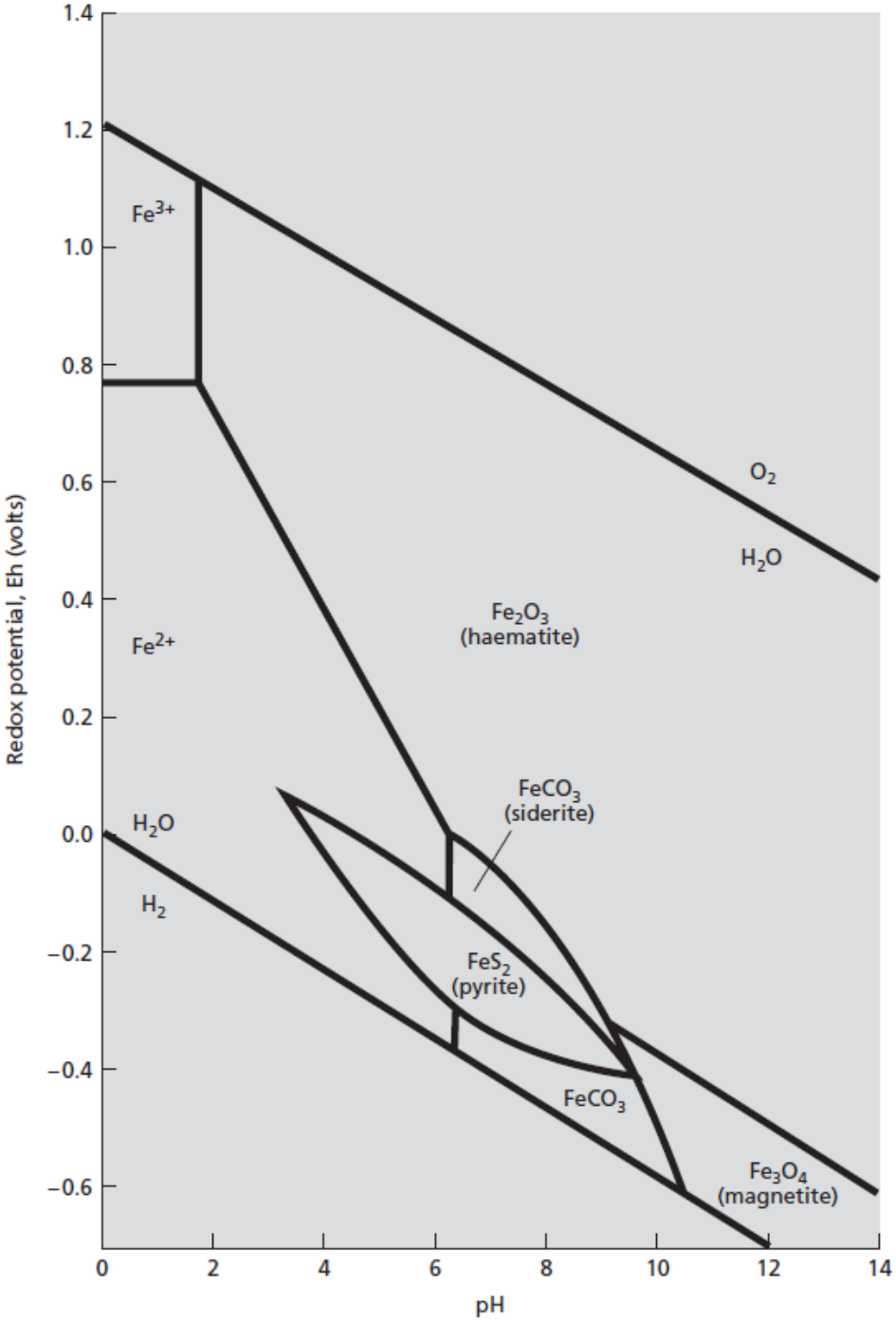
unter sauren Bedingungen als $Al^{3+}(aq)$

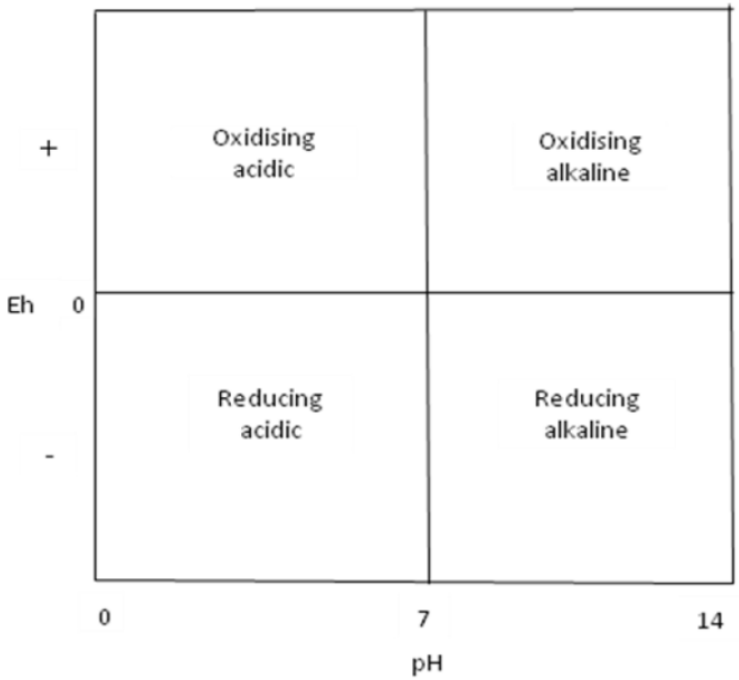
$$Al(OH)_{3(s)} + OH_{(aq)} \leftrightharpoons Al(OH)_4^-$$

unter neutralen oder alkalischen Bedingungen als $Al(OH)_4^-$ (aq)

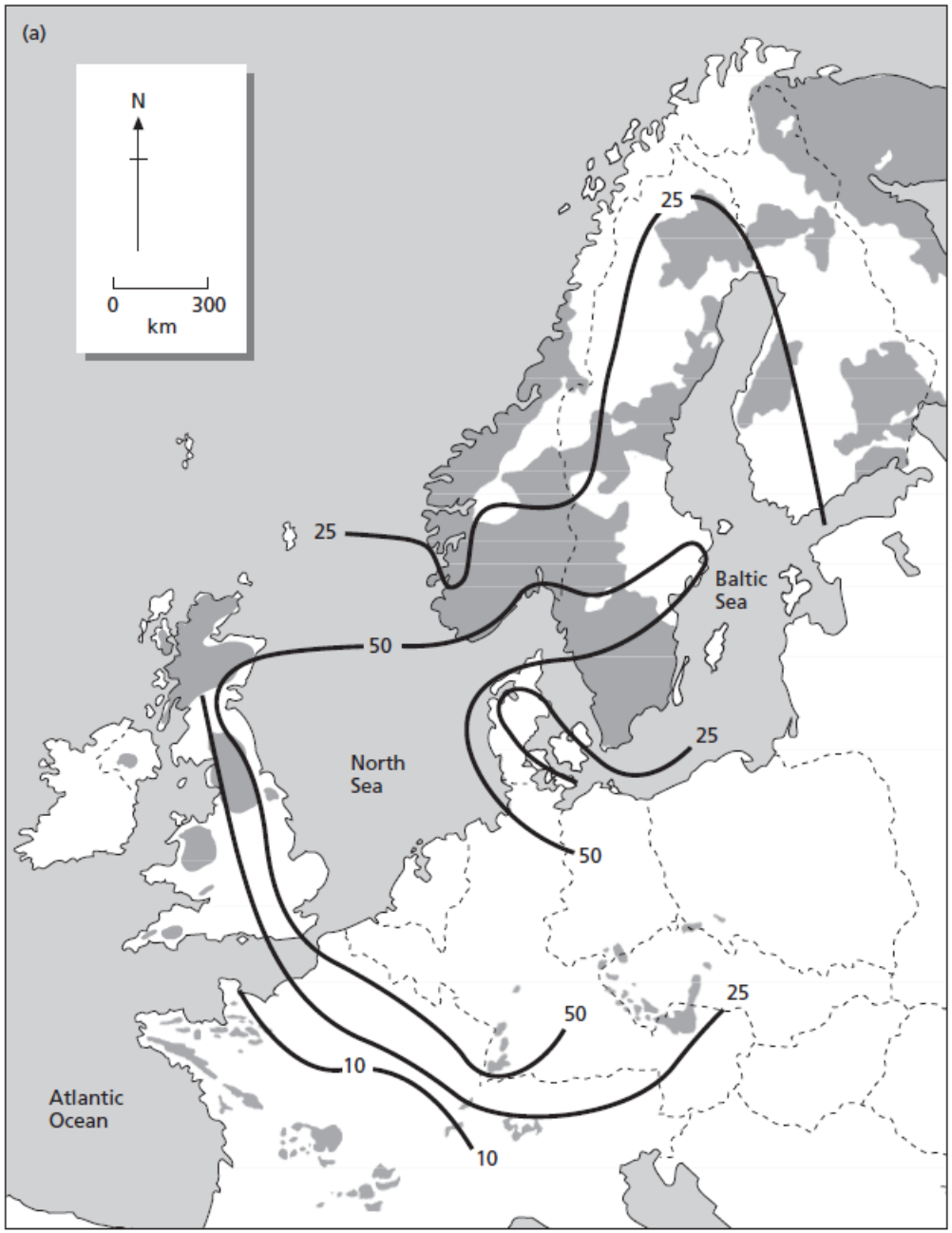
$$Al(OH)_{3(s)} \leftrightharpoons Al^{3+}_{(aq)} + 3OH^-_{(aq)}$$

Eh-pH Diagram





Acid mine drainage / saure Grubenwässer



$$2FeS_{2(s)} + 2H_2O_{(l)} + 7O_{2(g)} \longrightarrow 4H^+_{(aq)} + 4SO^{2-}_{4(aq)} + 2Fe^{2+}_{(aq)}$$

(pyrite oxidation)

Bei pH 3.5 – 4.5 Oxidation von Eisen katalysiert durch Bakterien Metallogenicum, Thiobacillus thiooxidans)

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 10H_2O_{(l)} \longrightarrow 4Fe(OH)_{3(s)} + 8H_{+(aq)}$$

(Fe(II)) (Fe(III))

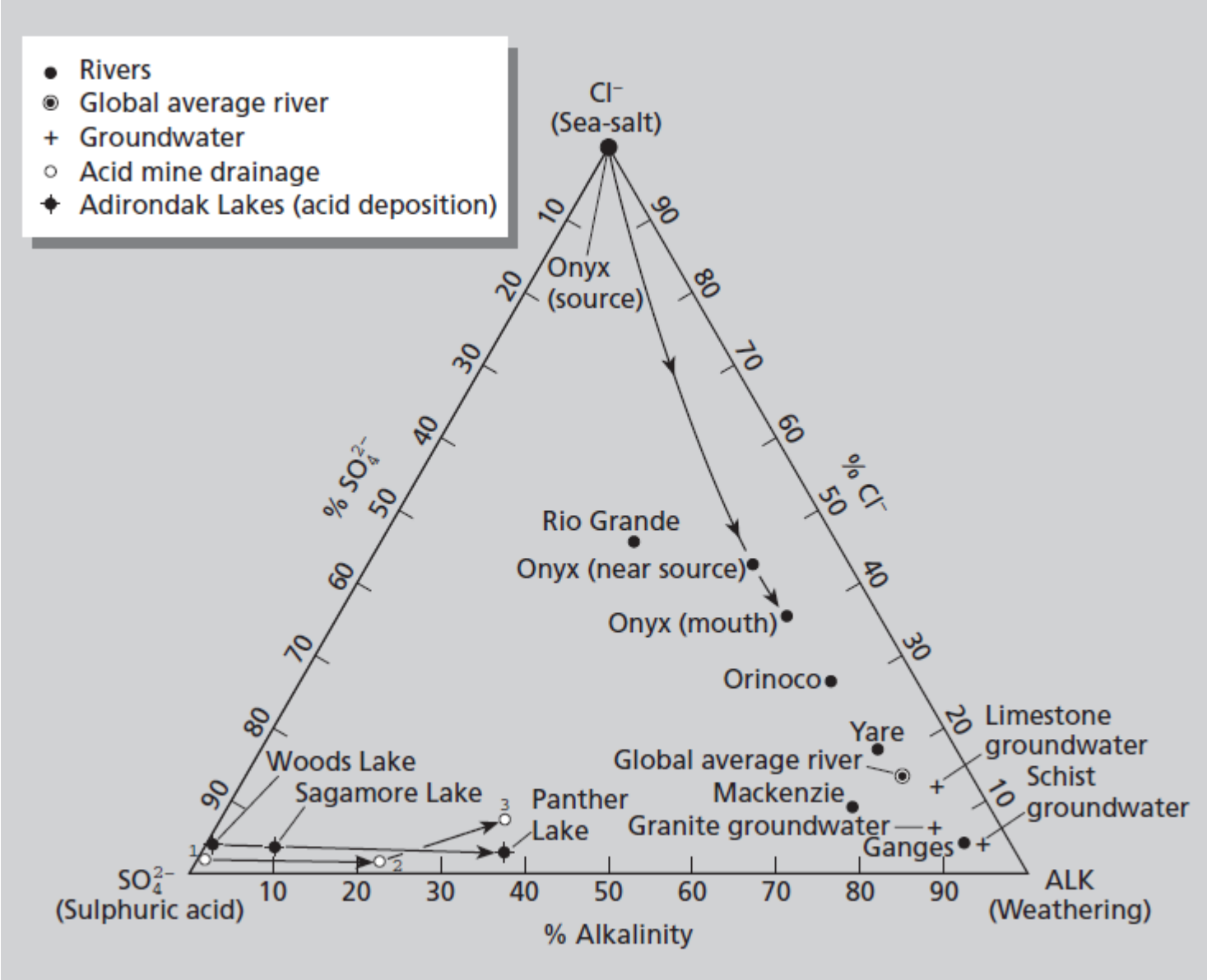
Rio Tinto

Acid mine drainage / saure Grubenwässer

ab pH > 3-4:

$$Fe^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow FeOOH_{(s)} + 3H^{+}_{(aq)}$$

Alkalinität - Cl^- - SO_4^{2-}

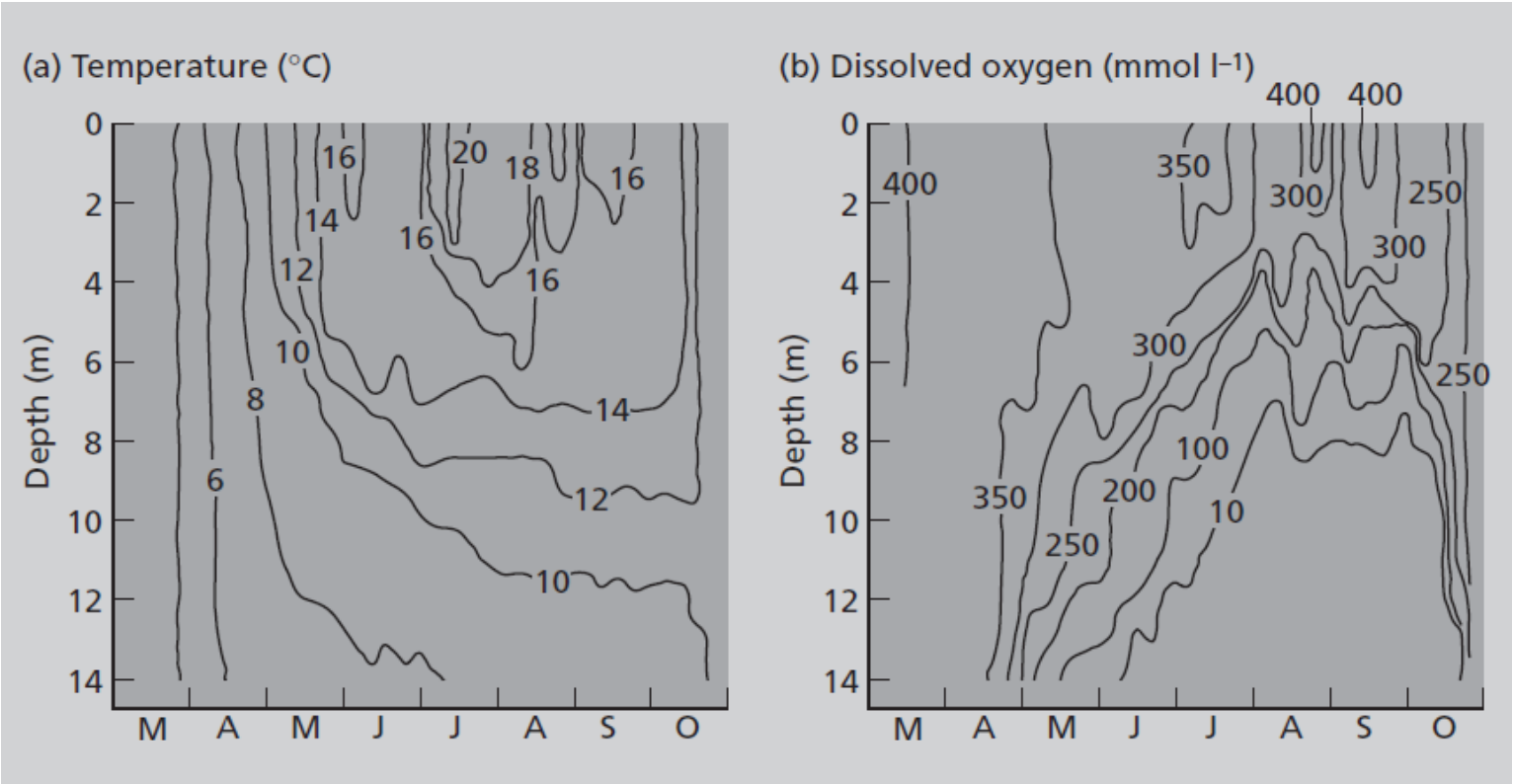


Biologische Prozesse

$$CO_{2(g)} + H_2O_{(l)} \xrightarrow{\text{light}} CH_2O_{(s)} + O_{2(g)}$$

$$CH_2O_{(s)} + O_{2(s)} \rightarrow CO_{2(g)} + H_2O_{(l)} \quad \Delta G^{\circ} = -475\,\text{kJ mol}^{-1}$$

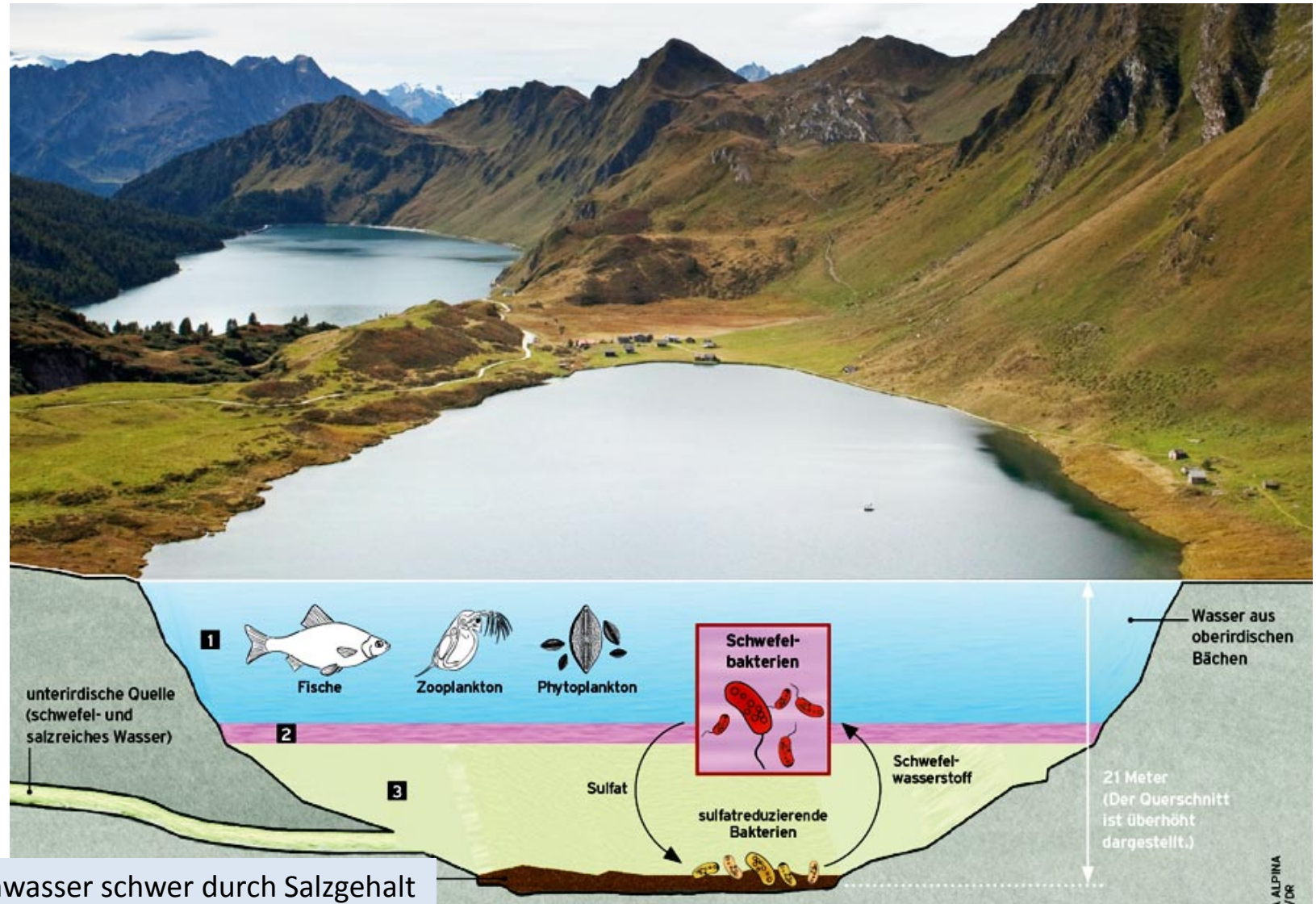
Seewasser: Lake Esthwaite, NW England



Alatsee – meromiktischer See

keine Wasserzirkulation
ab 15 m Tiefe fast sauerstofffrei
Schwefelhaltiges Tiefenwasser
Herkunft des Schwefels?

Lago di Cadagno - geogene Meromixis



Tiefenwasser schwer durch Salzgehalt

Die drei Zonen des Lago di Cadagno

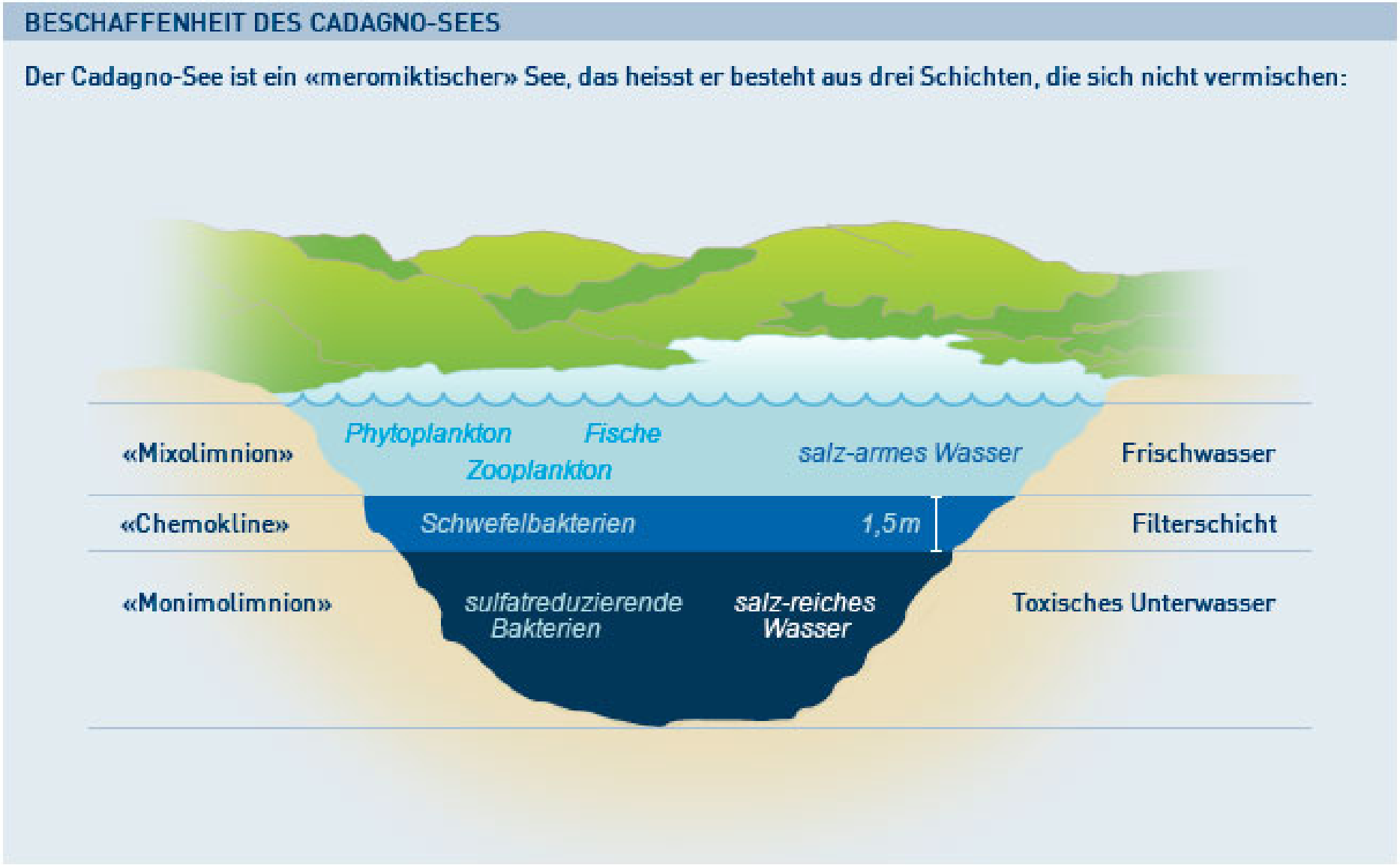
1 Sauerstoffreiches Oberwasser: Diese Zone wird von Bächen gespeist, die über kristallines Gestein fliessen. Das Wasser ist klar, reich an Sauerstoff und bietet zahlreichen Organismen wie Plankton oder Fischen einen Lebensraum.

2 Zwischenschicht mit Schwefelbakterien: Das Wasser dieser eineinhalb Meter tiefen Zone ist stark rosa gefärbt. Die Farbe stammt von Schwefelbakterien, die das toxische Unterwasser filtern und so das Leben in der obersten Zone erst ermöglichen.

3 Toxisches, sauerstofffreies Unterwasser: Hier reichern sich Schwefel und Salze an, die von unterirdischen Quellen in den See gespült werden. Nur einige archaische Bakterien können in dieser Schicht wachsen; sie ernähren sich vom Sulfat.

QUELLE: CENTRO BIOLOGIA ALPINA
INFOGRAFIK: BEOBACHTER/DR

Lago di Cadagno - geogene Meromixis

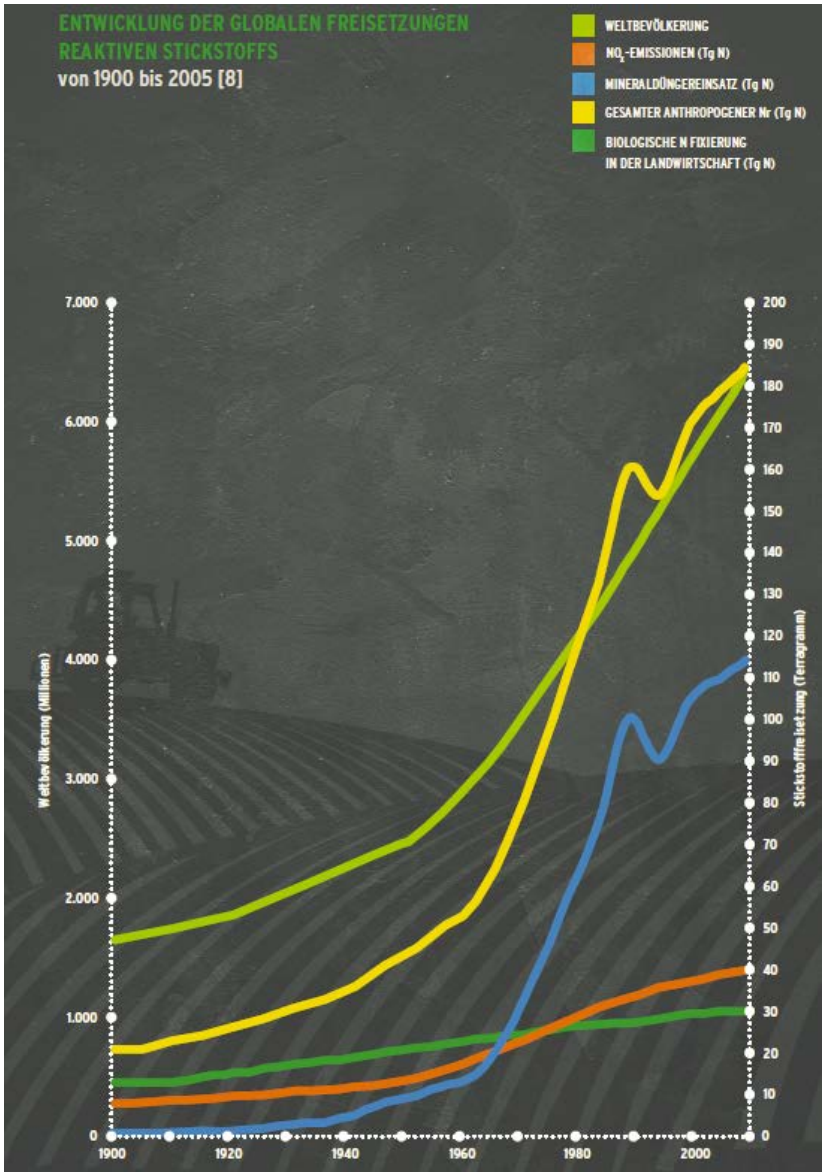


Quelle: Reinhard Bachofen, Helmut Brandl "Val Piora - ein mikrobiologischer Feldführer"

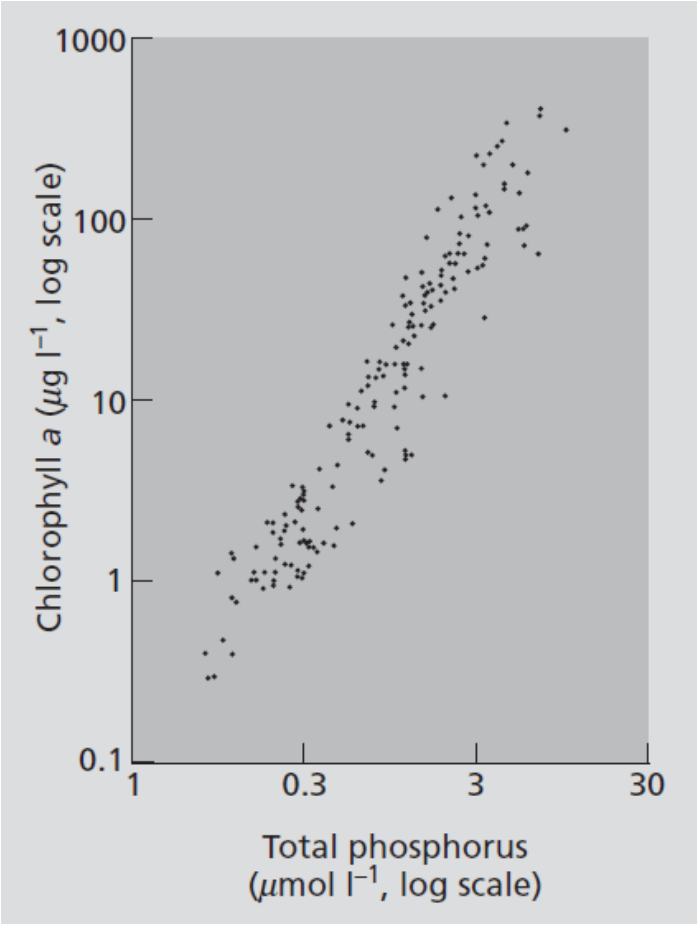
presented by swissinfo

Nährstoffe und Eutropisierung

Mg^{2+} häufig vorhanden; aber: P, N - biokritisch, wachstumslimitierend

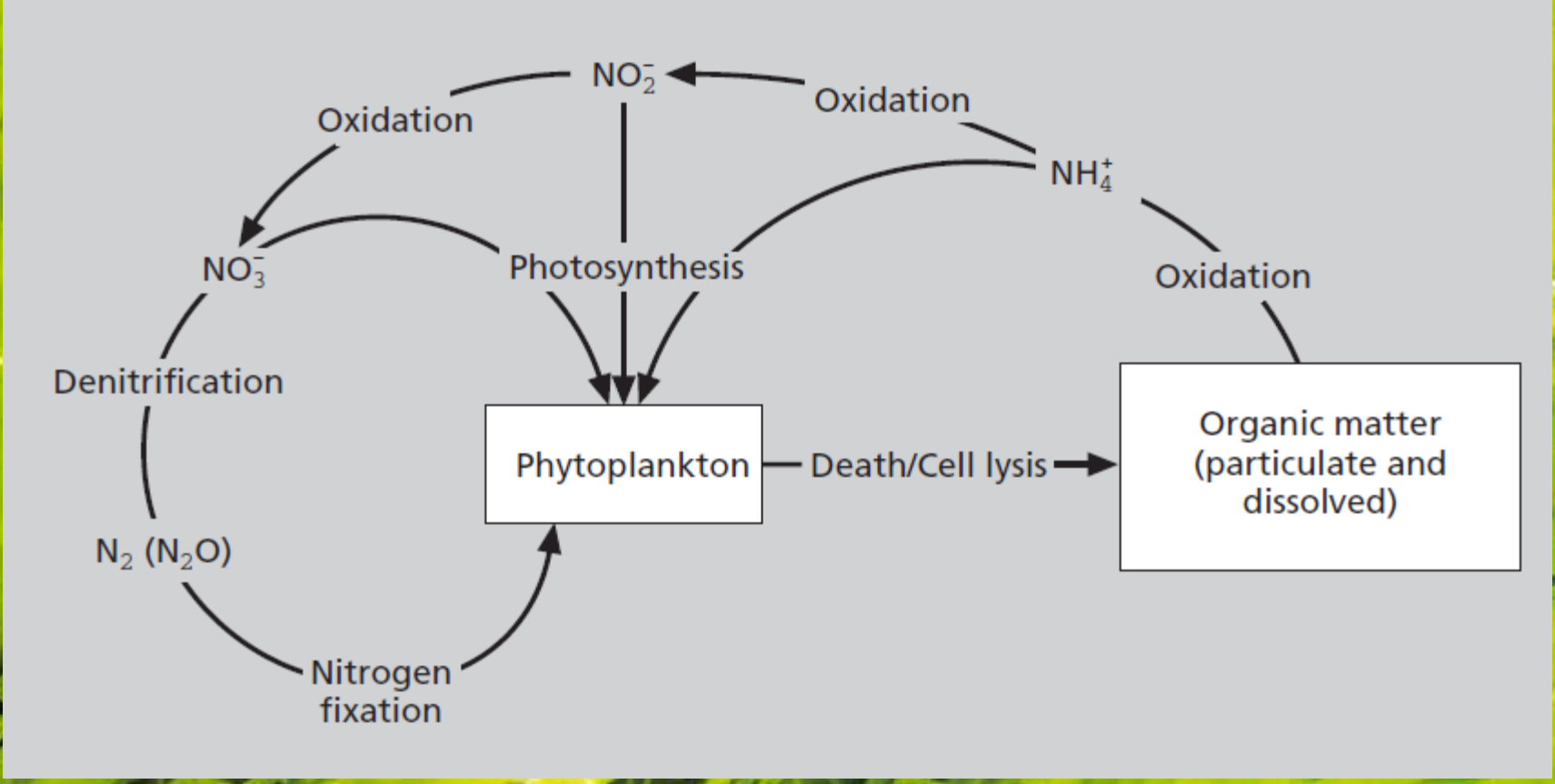


Bioverfügbarkeit
N/P-Verhältnis

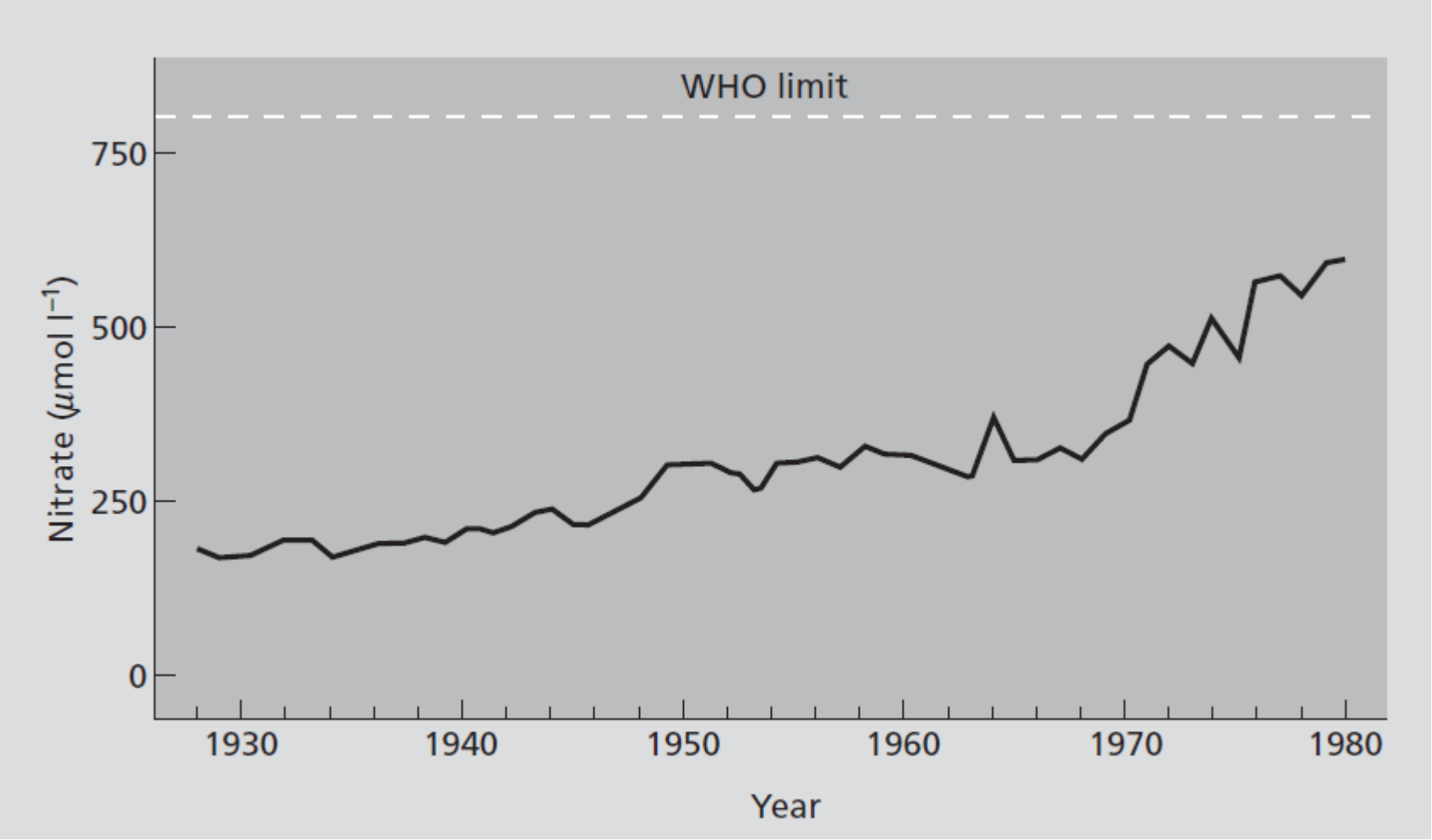


Nährstoffe und Eutropisierung

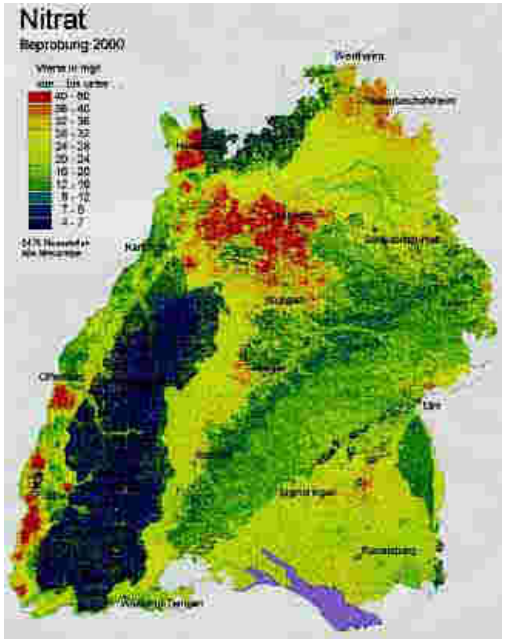
Stickstoffkreislauf im Wasser



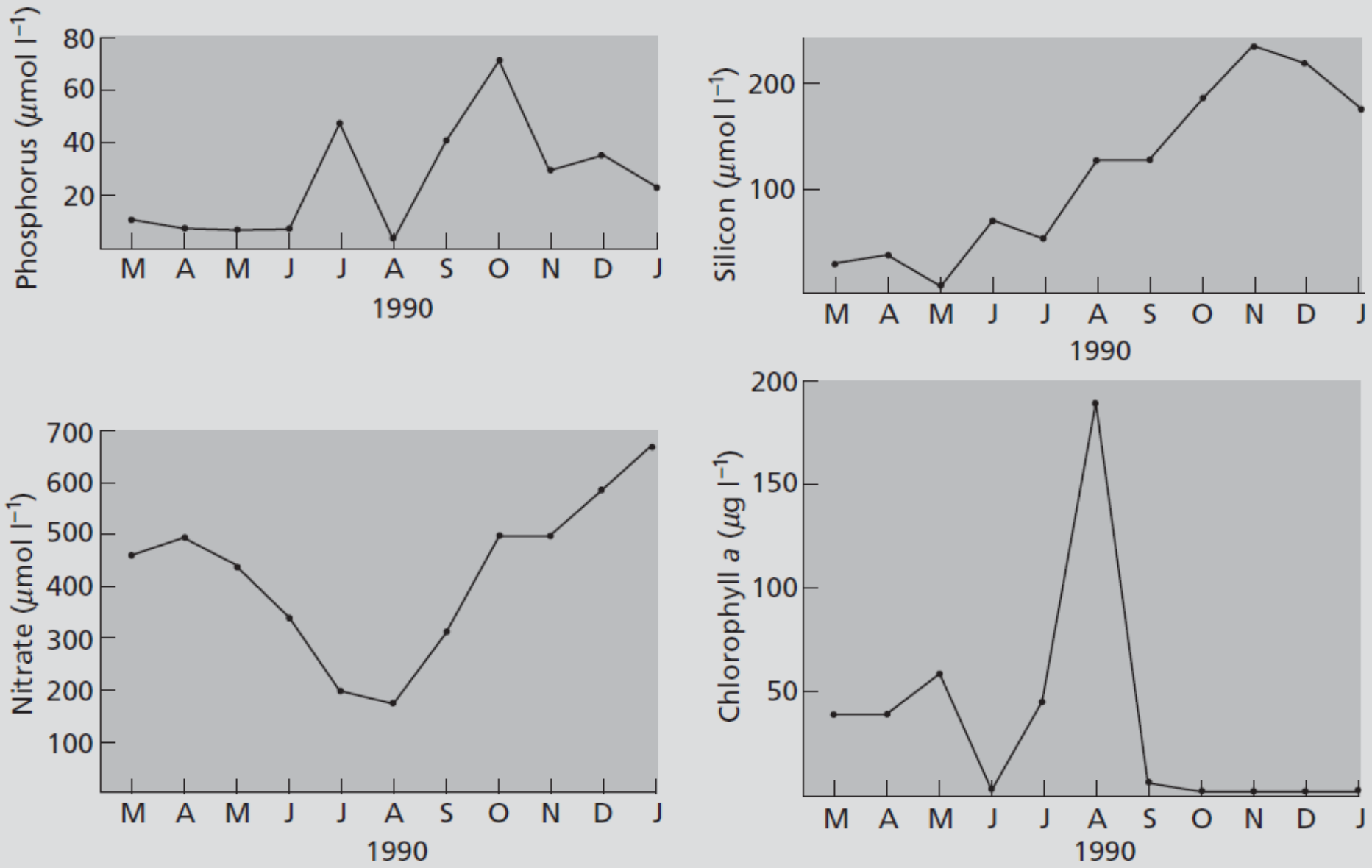
Nitratbelastung in Flüssen



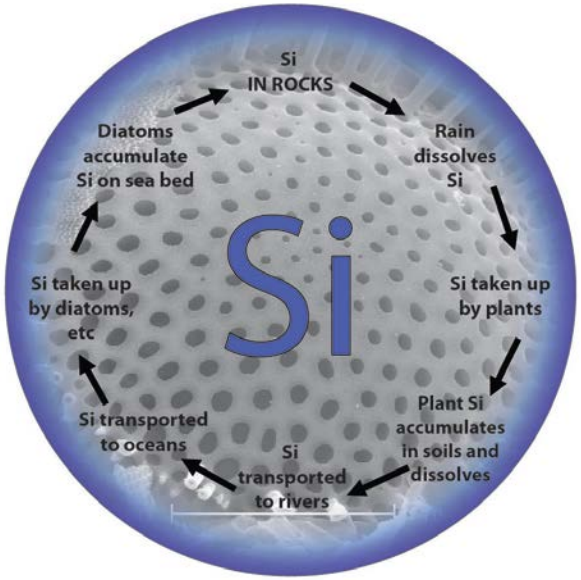
Nitratbelastung

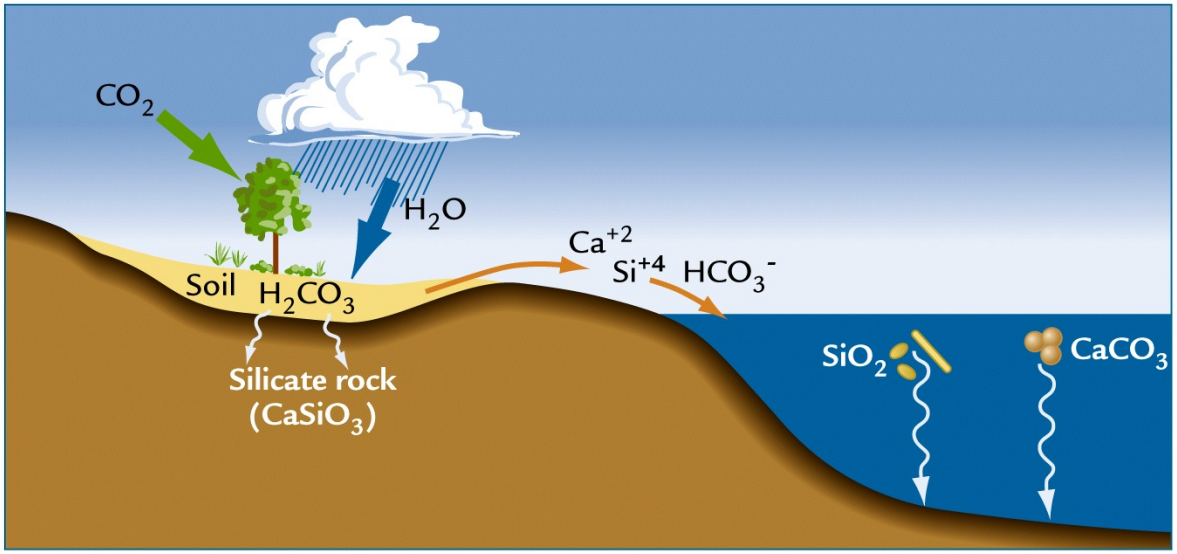


Nitratbelastung in Flüssen



Silizium





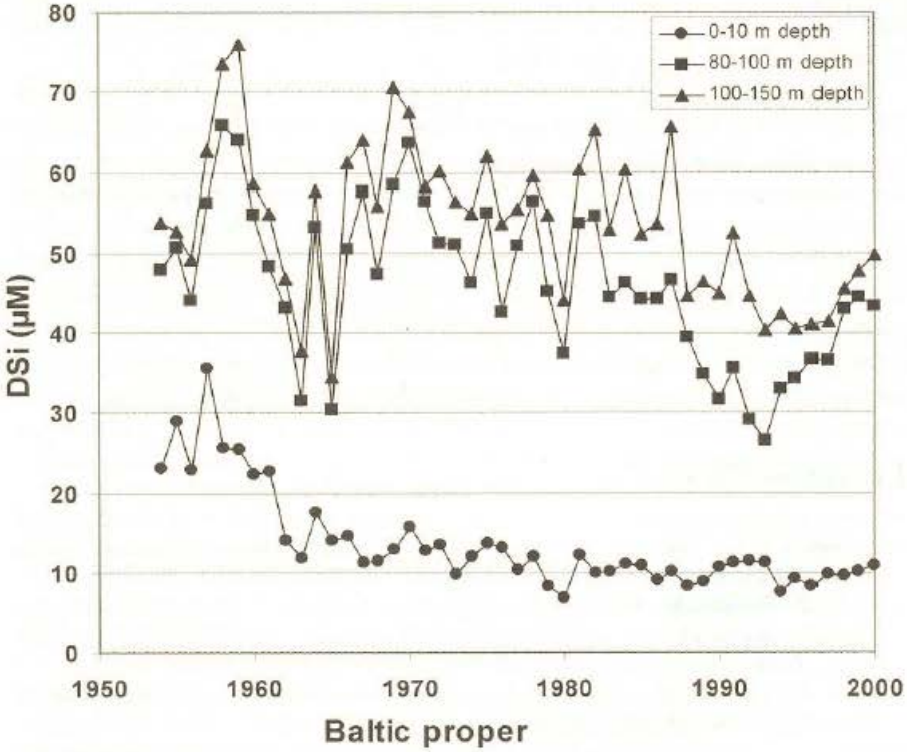
$CaSiO_3$ + H_2CO_3	Ca^{+2} Si^{+4} HCO_3^-	$SiO_2 + CaCO_3$
Silicate bedrock / Carbonic acid in soils	Ions dissolved in river water	Shells of ocean plankton
Weathering on land	Transport in rivers	Deposition in ocean

River damming

Dams:

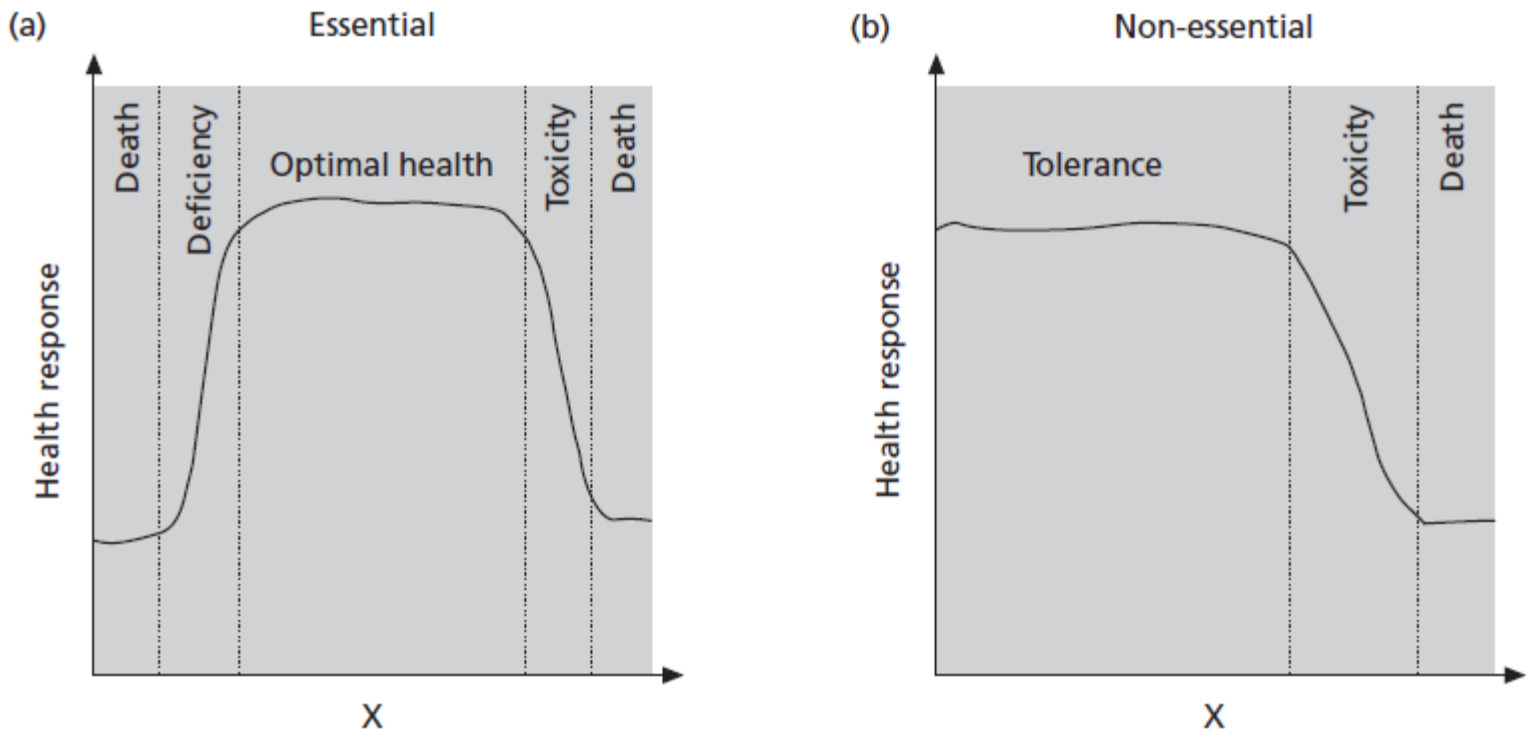
artificial lake effect

Si retention



Humborg et al. (2006)

Schwermetalle



Paracelsus (1493-1541): „Allein die Dosis macht das Gift“

Schwermetalbelastungen

Garimpos, Amazonasgebiet

Einsatz von Quecksilber zur Bindung des Goldes

Amalgamverfahren:

$$Au_{(metal)} + Hg^0 \rightarrow Au\text{-}Hg_{(amalgam)}$$

Schwermetalbelastungen

$$Hg^0 + O_3 \rightarrow HgO + O_2$$

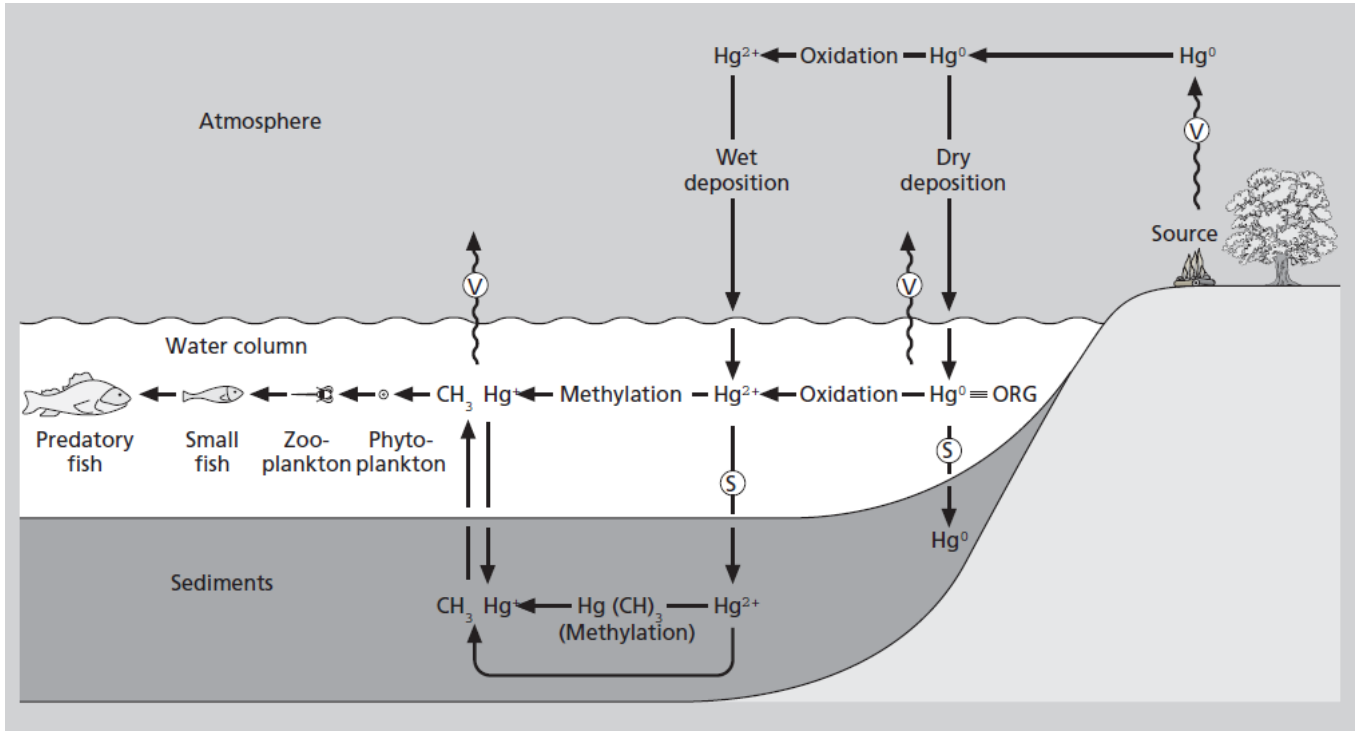
$$2H^+ + HgO \rightarrow Hg^{2+} + H_2O$$

$$Hg^{2+} + 2CH_3^- \longrightarrow Hg(CH_3)_2$$

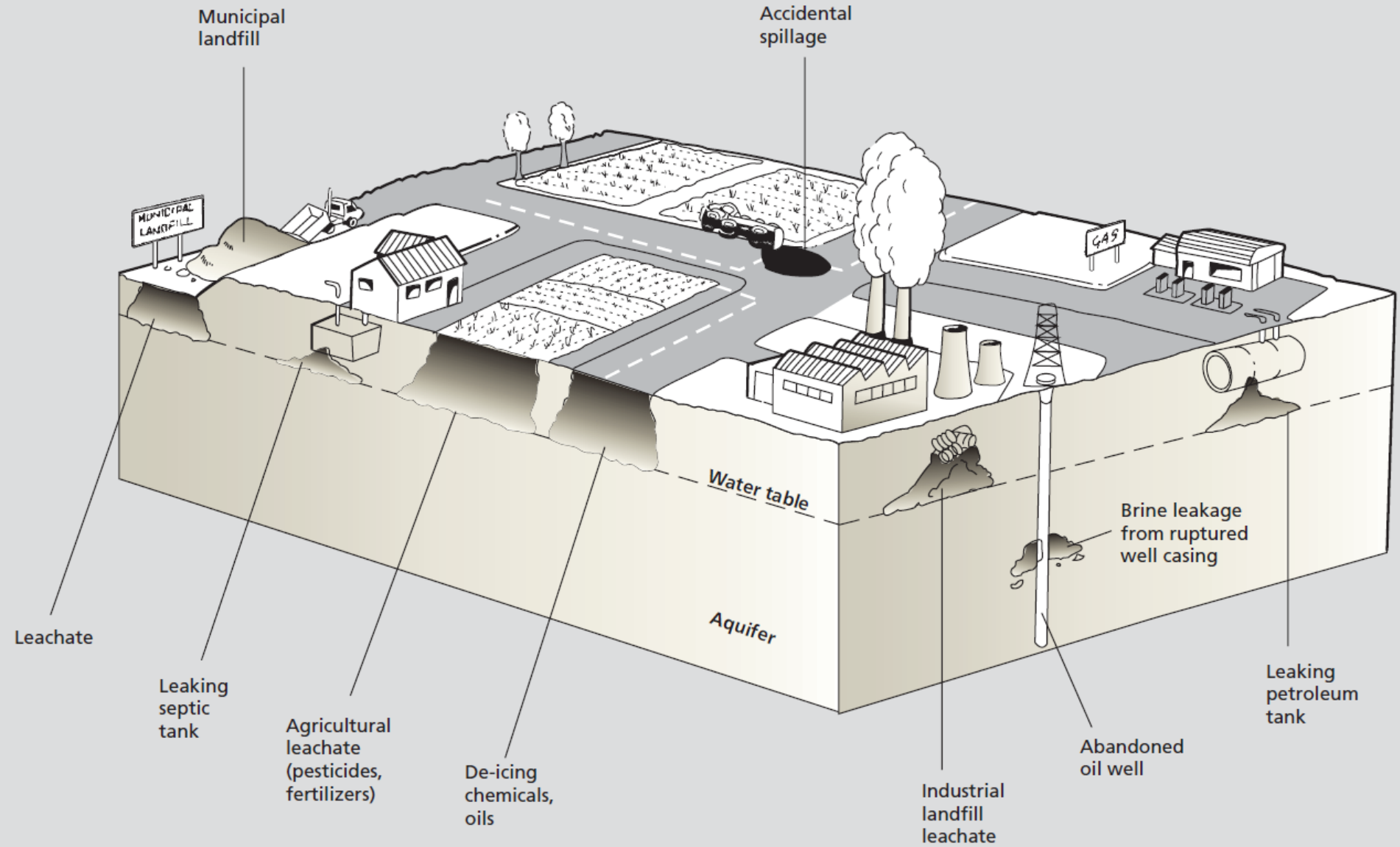
(methylcobalamin)

SRB

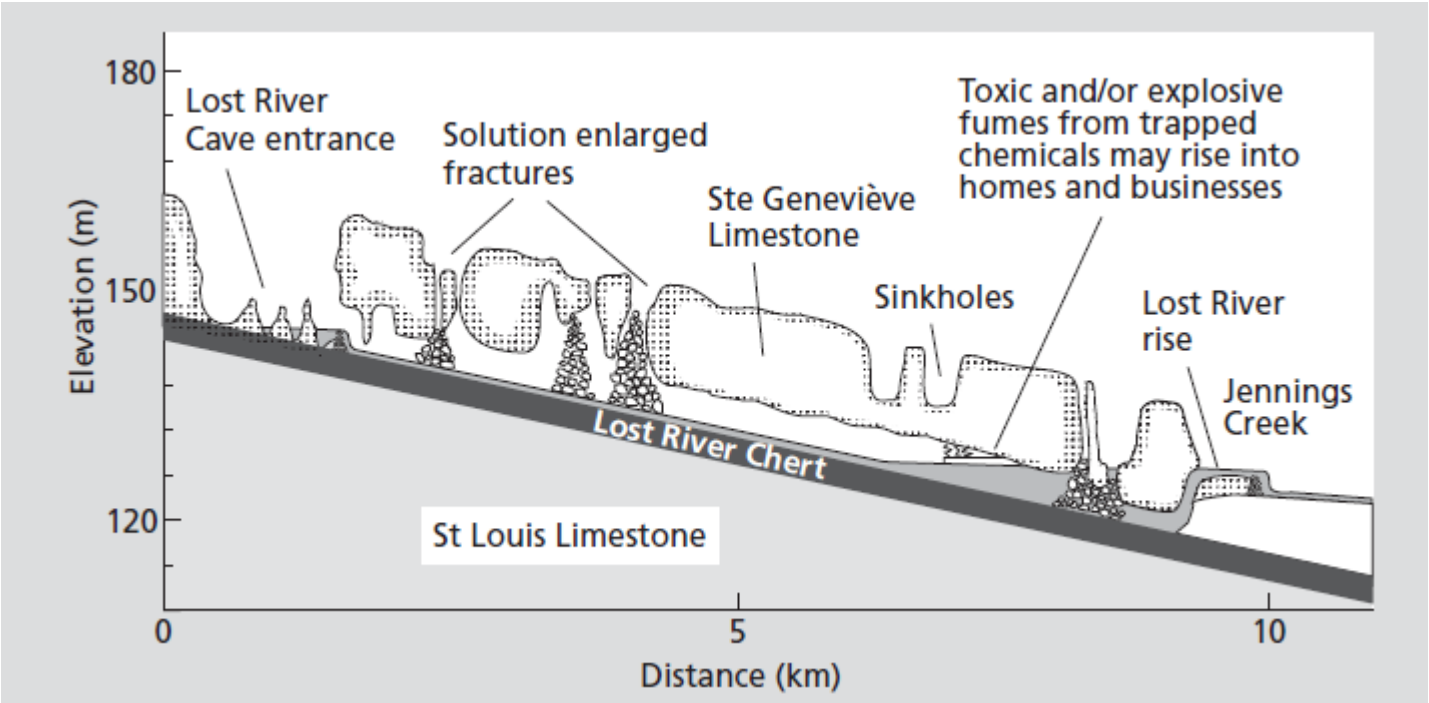
Dimethyl-
quecksilber



Grundwasserkontamination



Grundwasserkontamination

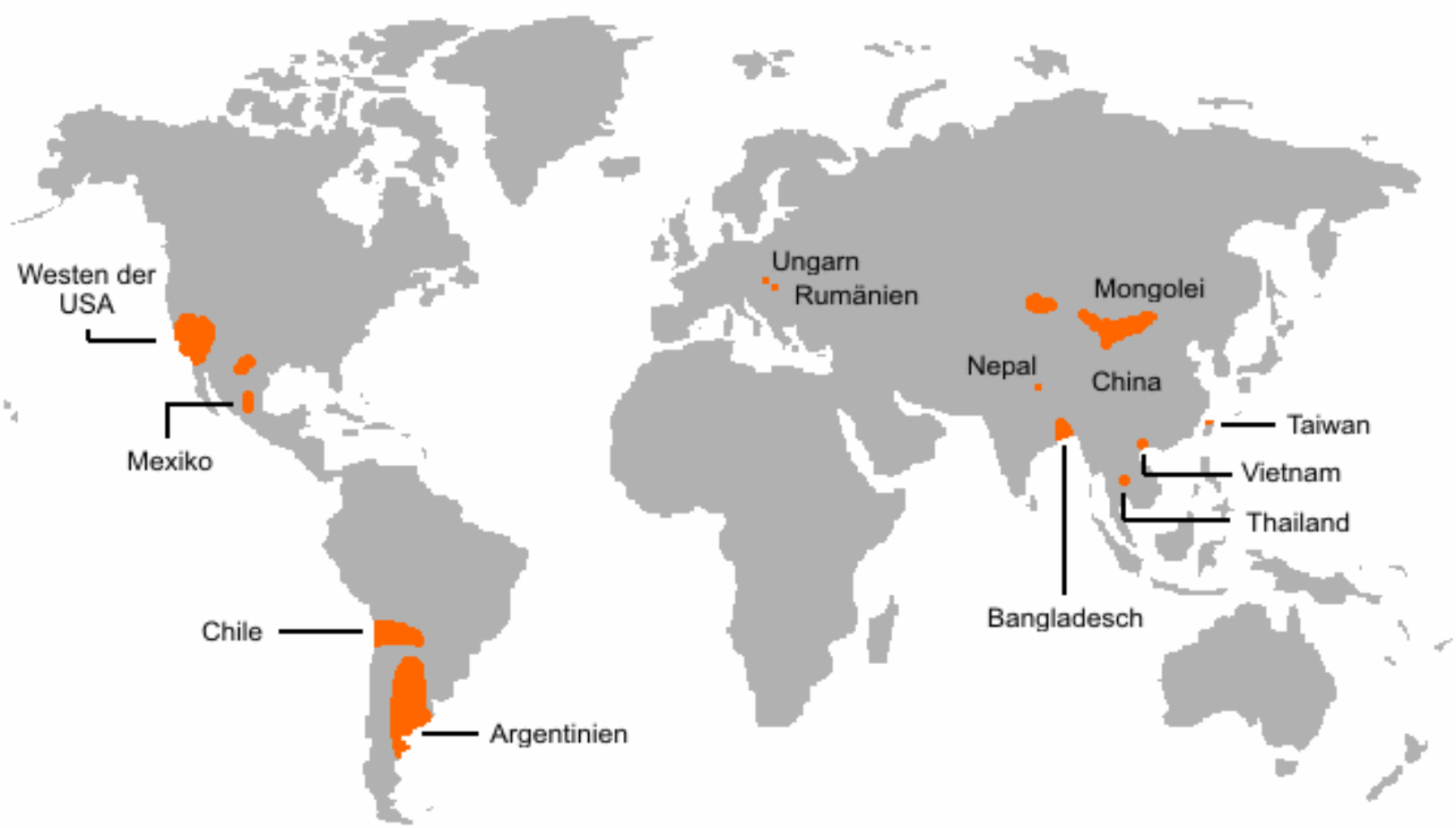


$$C_6H_{6(aq)} + 6NO^-_{3(aq)} + 6H^+_{(aq)} \longrightarrow 6CO_{2(aq)} + 3N_{2(g)} + 6H_2O_{(l)}$$

(benzene)

Dechloromonas aromatica

Arsen im Grundwasser



<u>Beispiel Bangladesh</u>

primäre Arsenquellen: Sedimente, As-führende Kohle, Sulfiderze aus Himalaya

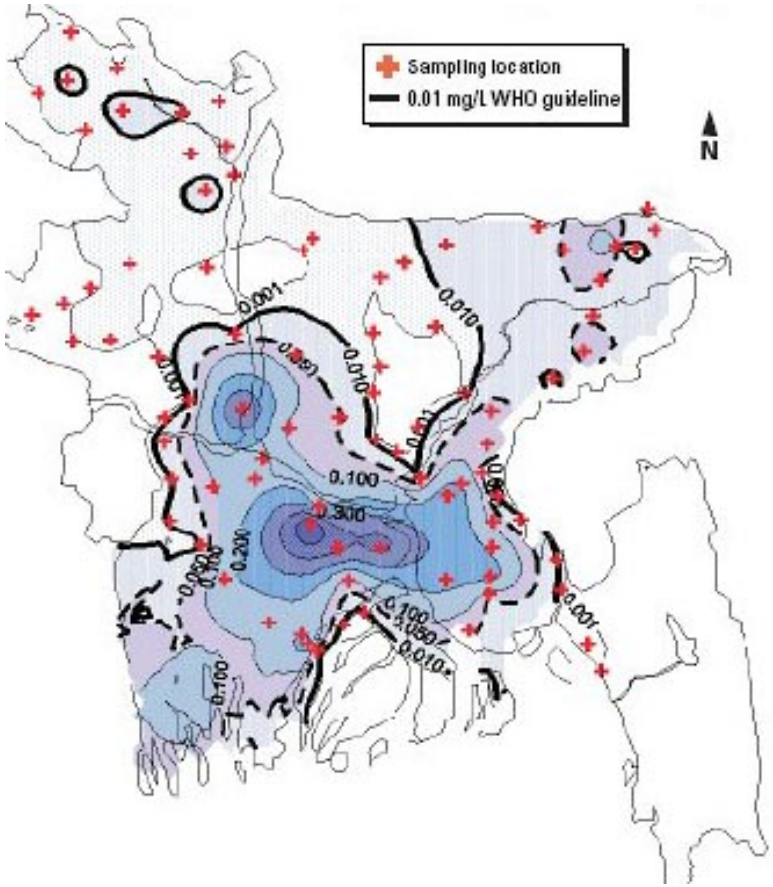
Arsen im Grundwasser

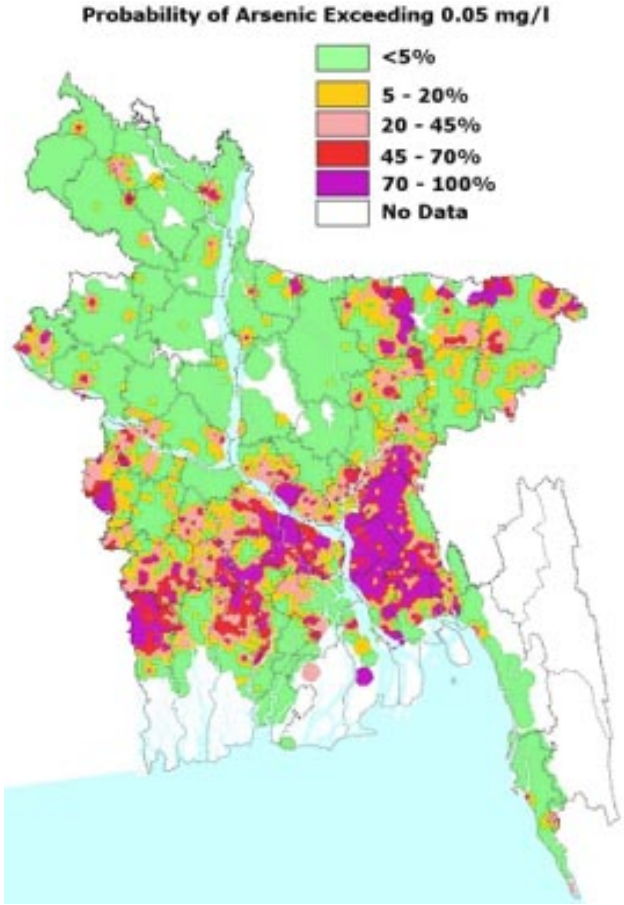
Oberflächenwasser mit Krankheitserregern kontaminiert

Bau von Röhrenbrunnen

Steigende Arsenbelastung

As im Grundwasser, Bangladesh





Röhrenbrunnen in Bangladesh
Ganges, Brahmaputra und Meghna Delta

Freisetzung von As durch:

Änderungen in den Redox-Bedingungen

Übermäßige Grundwassernutzung (Bewässerung), senkt den Grundwasserspiegel ab und gestattet dem Luftsauerstoff, das im Ton befindliche Arsen freizusetzen.

Starkes Redox-Gefälle zwischen belüftetem (Oxidationszone) und wassergesättigtem Sediment führt zur Bildung von Eisen(III)-oxidhydrat, das bis zu 800 ppm Arsenat enthalten kann

mikrobielle Reduktion As-führender Eisenoxide setzt As frei:

$$4FeOOH_{(s)} + CH_2O_{(s)} + 7H_2CO_{3(aq)} \longrightarrow 4Fe^{2+}_{(aq)} + 8HCO^{-}_{3(aq)} + 6H_2O_{(l)}$$

eqn. 5.26