

Chemische Methoden

Elemente und Elementgruppen

Alkali- & Erdalkalimetalle

Stark elektropositiv, geringe Ionisierungsenergie,
reaktiv, bilden ionische Verbindungen

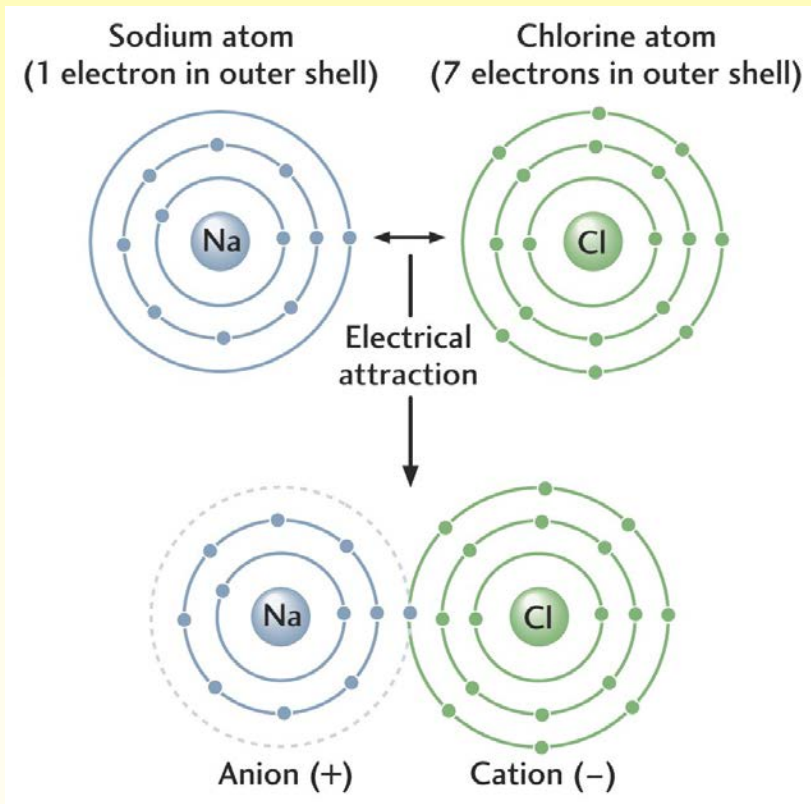
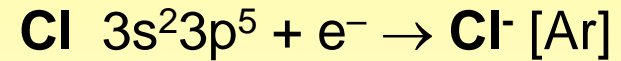
Oxide sind basisch

H																		He
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub							
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Alkali- & Erdalkalimetalle: Ionische Verbindungen

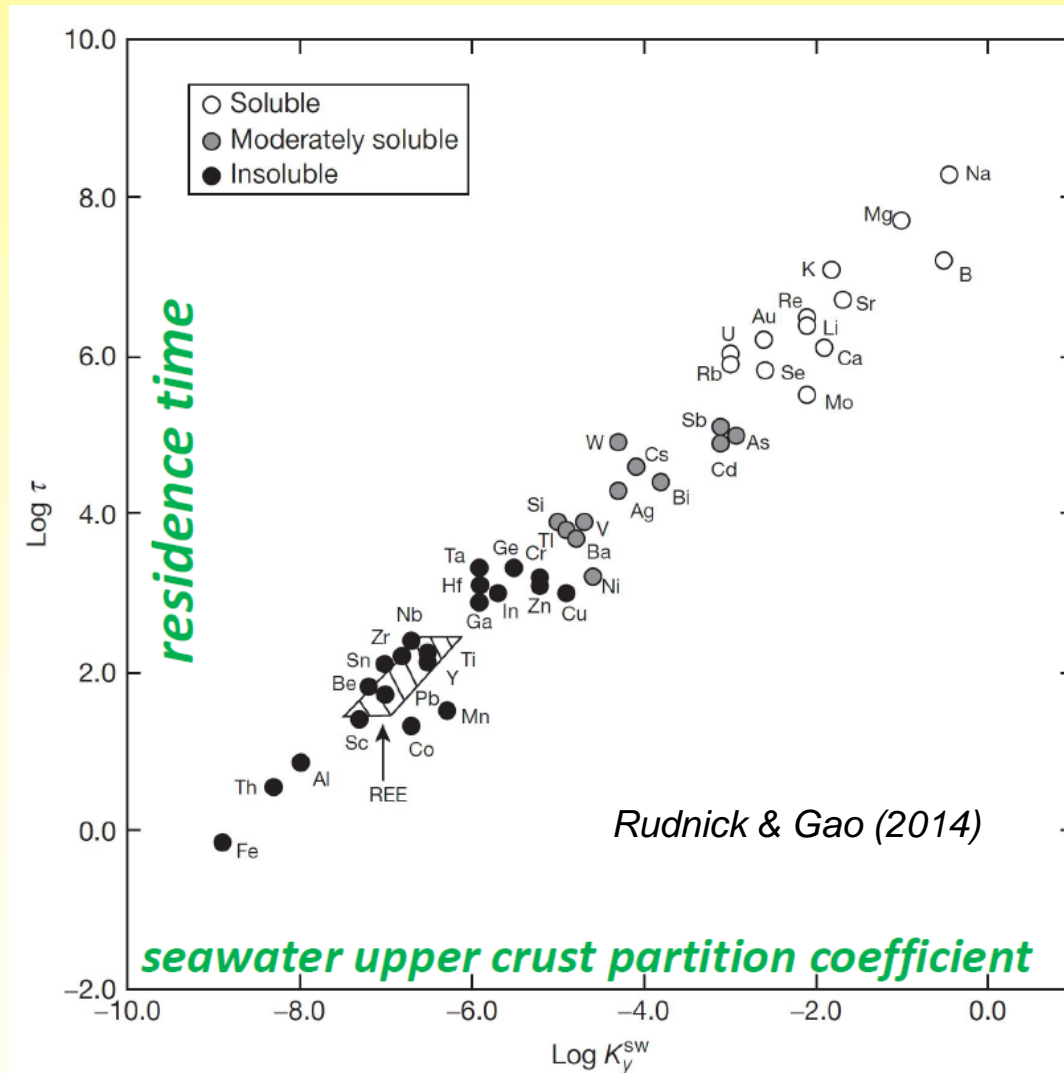
Ionenbindung zwischen Alkalimetallen und Elementen, die rechts im PSE stehen, den Nichtmetallen. Natriumchlorid klassischer Fall der Ionenbindung
Na: e^- Donator (wird zu Kation), Nichtmetall (z.B. Cl) e^- Akzeptor (wird zu Anion)

Die Ionenbindung ist elektrostatischer Natur aber nicht orientiert bzw. nicht gerichtet



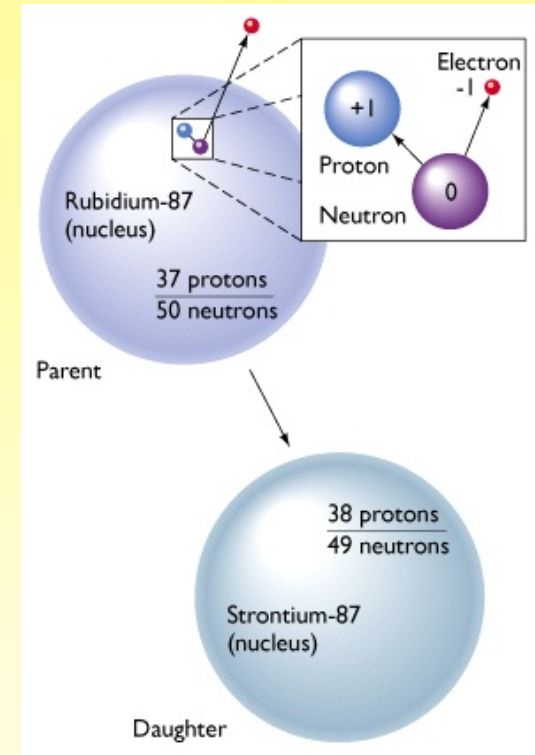
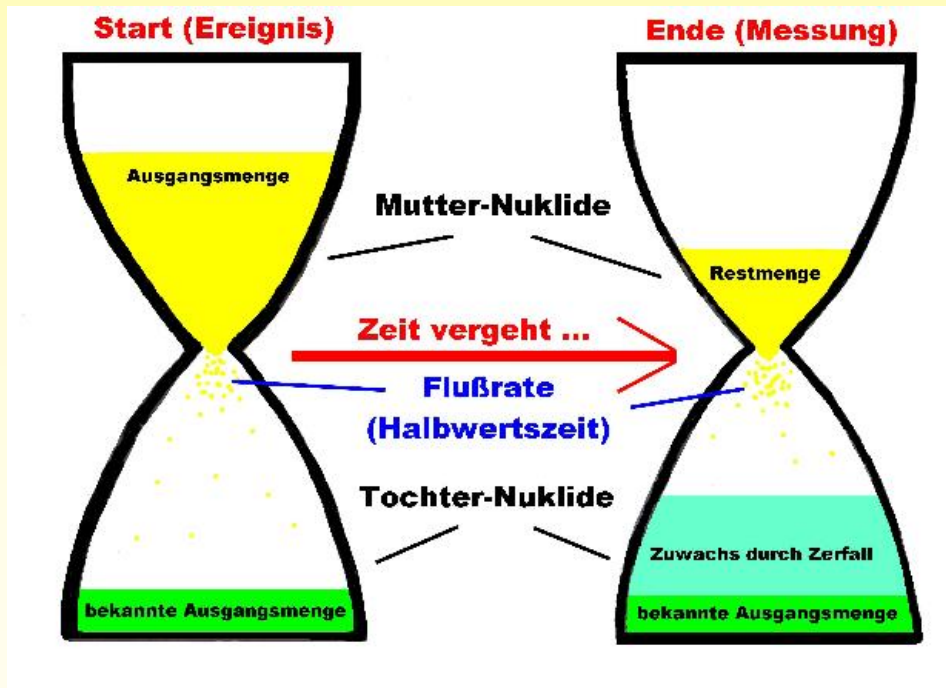
Alkali- & Erdalkalimetalle

Hohe Löslichkeiten im Meerwasser



Radioaktive Alkalimetalle

Von großer Bedeutung sind ^{40}K und ^{87}Rb
Beide Isotope weisen große Halbwertszeiten
auf (1.25 bzw. 48.8 Ga) und sind daher
geeignet Erdalter zu bestimmen \rightarrow
isotopische Altersdatierung, Geochronologie



$$D = N(e^{\lambda t} - 1)$$

$$t = \frac{1}{\lambda} \ln \left(1 + \frac{D}{N} \right)$$

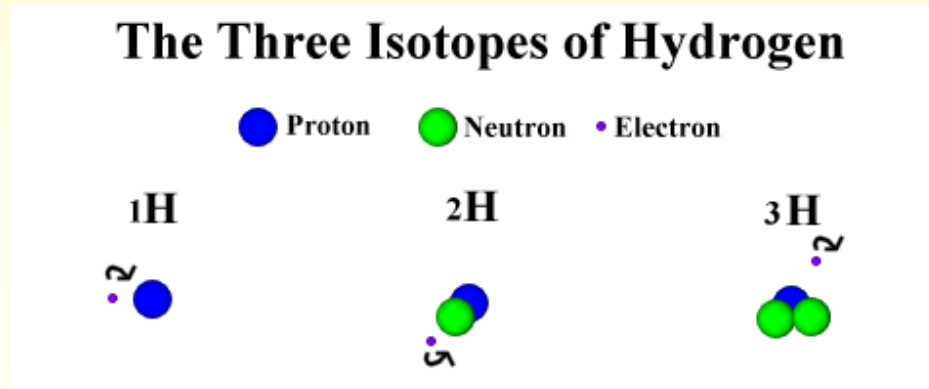
Wasserstoff (H)

H verhält sich **nicht** wie die anderen Alkalimetalle (besitzt z.B. eine viel höhere Ionisierungsenergie und keine Metalleigenschaften)

Geowissenschaftlich wichtig als **OH⁻** (in wasserhaltigen Mineralen wie Glimmern) und als **Wassermolekül (H₂O)**

Elementarer Wasserstoff besteht aus den beiden stabilen Isotopen ¹H (99.984%) und ²H (0.016%) bzw. D (Deuterium).

Ein drittes Isotop, Tritium, ist radioaktiv

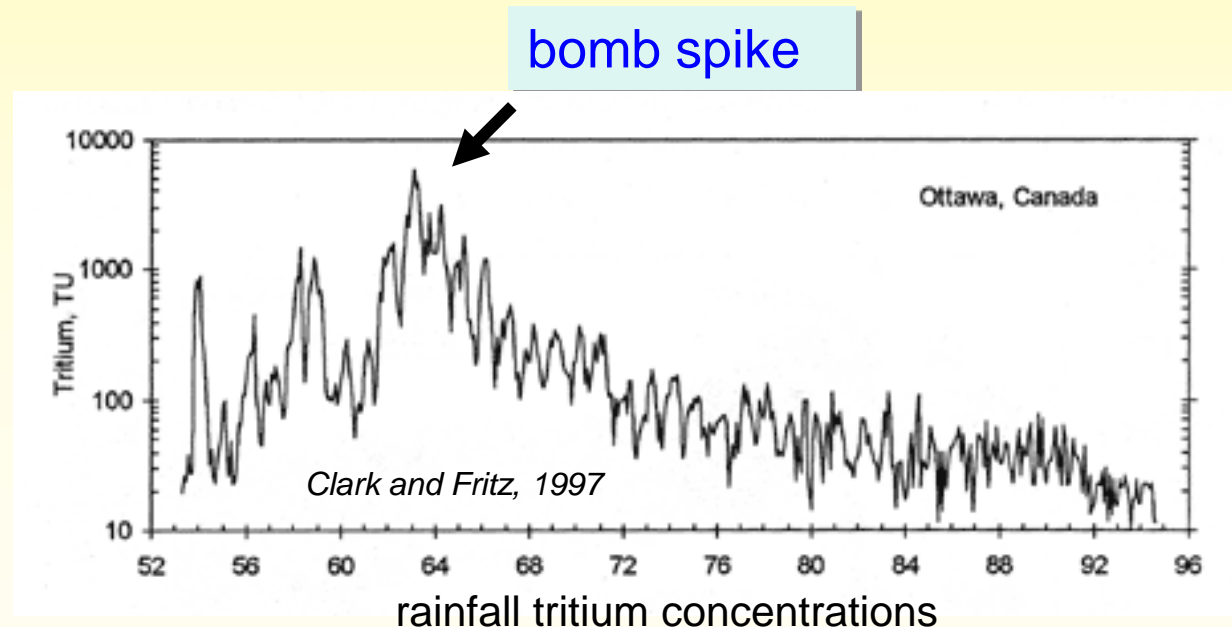


Tritium – ein hydrologischer Tracer

Bomb Tritium

Most of the tritium in the world today was produced by atmospheric testing of nuclear devices that began in 1952 and reached a maximum in 1963/1964.

The bulk of this tritium was released in the northern hemisphere, and entered the oceans.



Tritium dating

- Tritium forms in the atmosphere by the interaction of ^{14}N with cosmic-ray neutrons:



- Tritium rapidly combines with oxygen, forming water (HTO).
Then it mixes with all other water

Reported in units of tritium units (TU):
1 TU = 1 atom of tritium per 10^{18} atoms of hydrogen

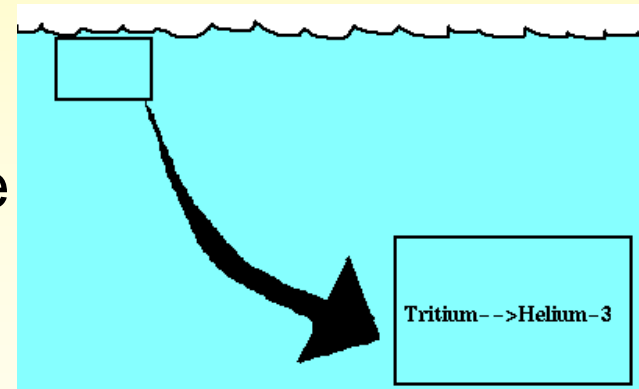
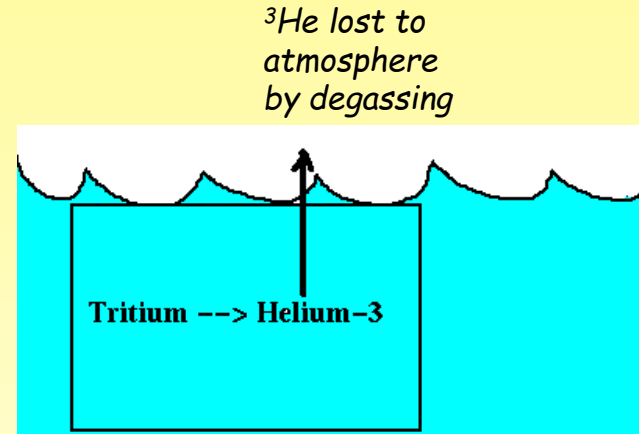
- Tritium decays to Helium-3; $T_{1/2} = 12.3$ years
- Low activity ~ 1 part in 10^{18} (varies by region)
- Used to trace water sources; age of „recent“ materials
- Sources directly fed by rainwater will contain the same tritium levels as rainwater

Tritium /³He age

The tritium/³He age is an **apparent age**

Advantage: It is independent of the initial tritium concentration of the water sample.

Potential problem: tritium/³He age is affected by mixing and dispersion



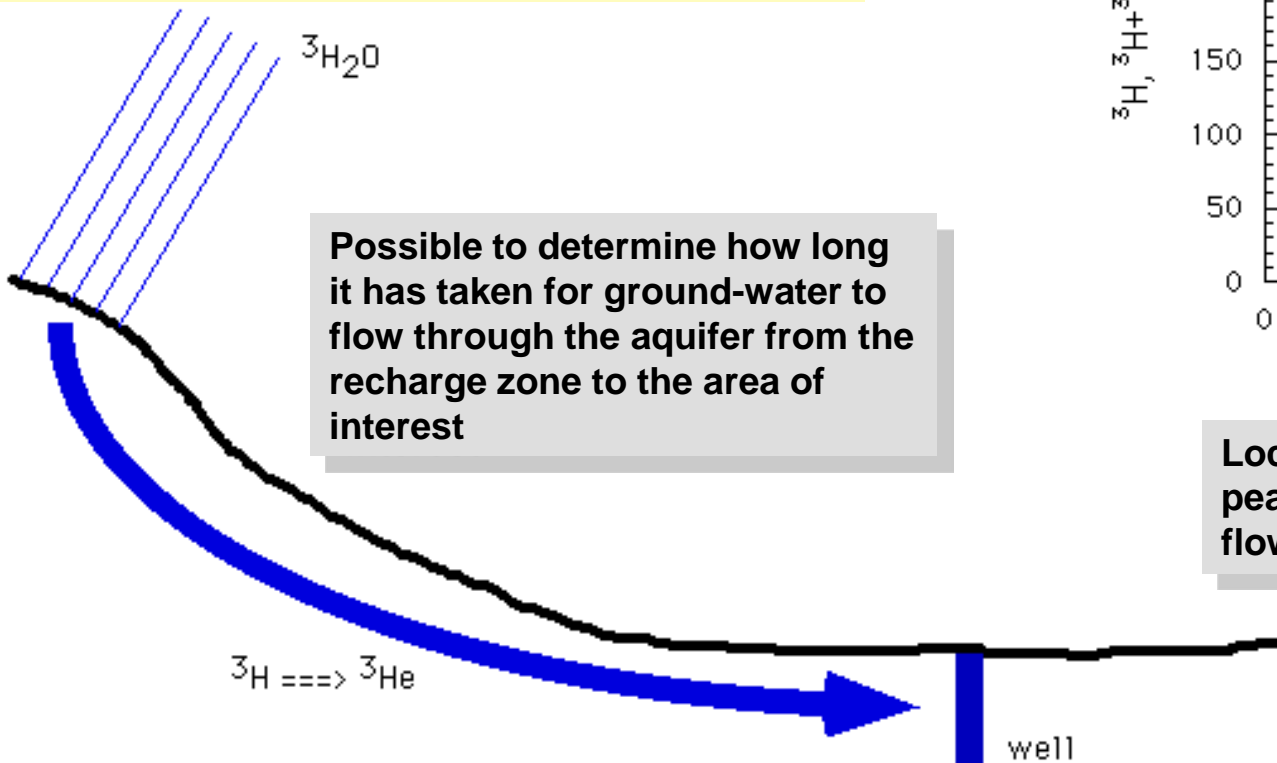
³He accumulates after parcel is removed from surface

Tritium dating

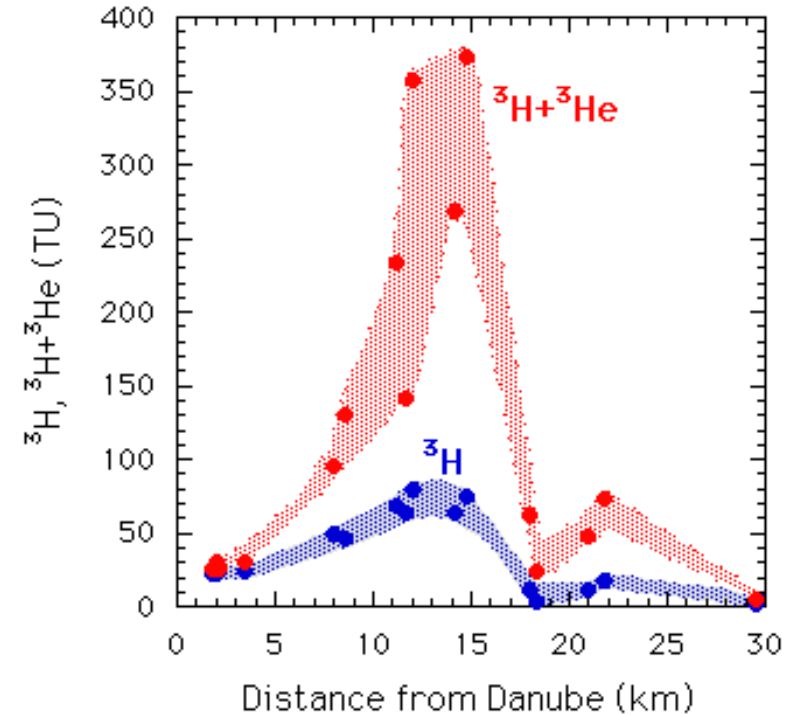
Dating of ground waters

Assumptions:

- (1) tritium of water was in equilibrium with atmospheric levels
- (2) decrease in tritium levels is only due to radioactive decay



Possible to determine how long it has taken for ground-water to flow through the aquifer from the recharge zone to the area of interest



Location of the mid-1960s bomb peak provides information on the flow velocity

$^3\text{H}/^3\text{He}$ age is defined as the time elapsed since the water was isolated from the atmosphere

Erdalkalimetalle, Leichte Elemente

Periodensystem der Elemente

1																	18
1	2											13	14	15	16	17	18
1.01 H Wasserstoff																	4.00 He Helium
6.94 Li Lithium	9.01 Be Beryllium											10.81 B Bor	12.01 C Kohlenstoff	14.01 N Stickstoff	15.999 O Sauerstoff	18.998 F Fluor	20.18 Ne Neon
22.99 Na Natrium	24.31 Mg Magnesium											26.98 Al Aluminium	28.09 Si Silicium	30.97 P Phosphor	32.07 S Schwefel	35.45 Cl Chlor	39.95 Ar Argon
39.10 K Kalium	40.08 Ca Calcium	4.96 Sc Scandium	47.88 Ti Titan	50.94 V Vanadium	52.00 Cr Chrom	54.94 Mn Mangan	55.85 Fe Eisen	58.93 Co Cobalt	58.70 Ni Nickel	63.55 Cu Kupfer	65.38 Zn Zink	69.72 Ga Gallium	72.61 Ge Germanium	74.92 As Arsen	78.96 Se Selen	79.90 Br Brom	83.80 Kr Krypton
85.47 Rb Rubidium	87.52 Sr Strontium	8.91 Y Yttrium	91.22 Zr Zirkonium	92.91 Nb Niobium	95.94 Mo Molybdän	(98) Tc Technetium	101.07 Ru Ruthenium	102.91 Rh Rhodium	106.42 Pd Palladium	107.87 Ag Silber	112.41 Cd Cadmium	114.82 In Indium	118.71 Sn Zinn	121.76 Sb Antimon	127.60 Te Tellur	126.90 I Iod	131.29 Xe Xenon
132.91 Cs Cäsium	137.33 Ba Barium	La-Lu	178.49 Hf Hafnium	180.95 Ta Tantal	183.84 W Wolfram	186.21 Re Rhenium	190.23 Os Osmium	192.22 Ir Iridium	195.08 Pt Platin	196.97 Au Gold	200.59 Hg Quecksilber	204.38 Tl Thallium	207.2 Pb Blei	208.98 Bi Bismut	(209) Po Polonium	(210) At Astat	(222) Rn Radon
(223) Fr Francium	(226) Ra Radium	Ac-Lr	(261) Rf Rutherfordium	(262) Db Dubnium	(263) Sg Seaborgium	(262) Bh Bohrium	(265) Hs Hassium	(266) Mt Meitnerium	(269) Ds Darmstadtium								

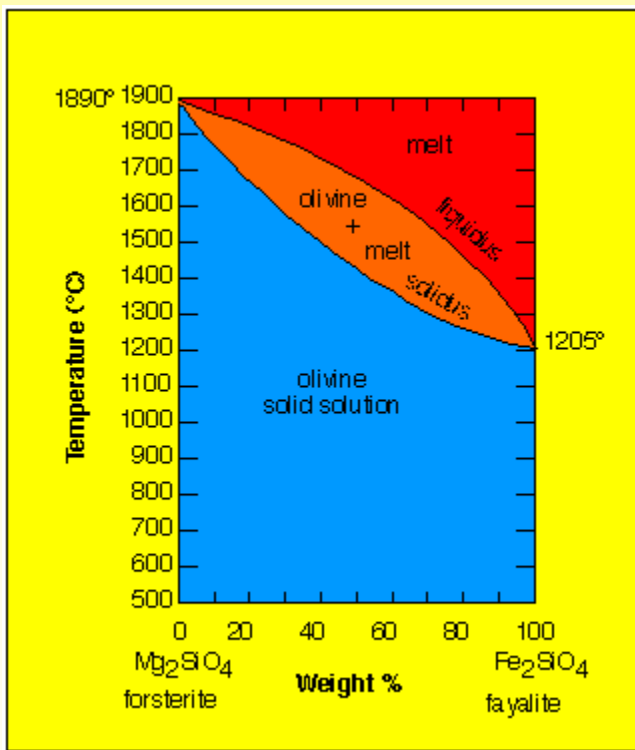
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138.91 La Lanthan	140.12 Ce Cer	144.24 Pr Praseodym	144.24 Nd Neodym	(145) Pm Promethium	150.36 Sm Samarium	151.97 Eu Europium	157.25 Gd Gadolinium	158.93 Tb Terbium	162.50 Dy Dysprosium	164.93 Ho Holmium	167.26 Er Erbium	168.93 Tm Thulium	173.04 Yb Ytterbium	174.97 Lu Lutetium
227.03 Ac Actinium	232.04 Th Thorium	231.04 Pa Protactinium	238.03 U Uran	(237) Np Neptunium	(244) Pu Plutonium	(243) Am Americium	(247) Cm Curium	(247) Bk Berkelium	(251) Cf Californium	(252) Es Einsteinium	(257) Fm Fermium	(258) Md Mendelevium	(259) No Nobelium	(260) Lr Lawrencium

Fe-Mg Austausch

Mg²⁺ hat ähnlichen Ionenradius wie Fe²⁺

Eisen-Magnesium Minerale wie **Olivin** (s. Abbildungen unten) oder **Pyroxen** zeigen vollständige Mischkristallbildung

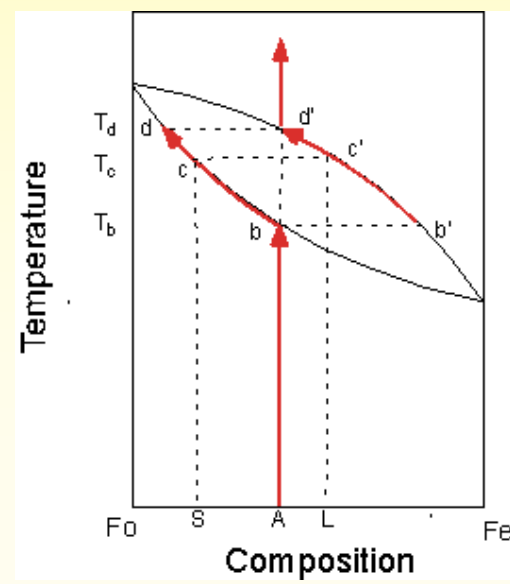


Erdmantel besteht aus Peridotit, der wiederum zu ca. 60% aus Mg-reichen Olivin

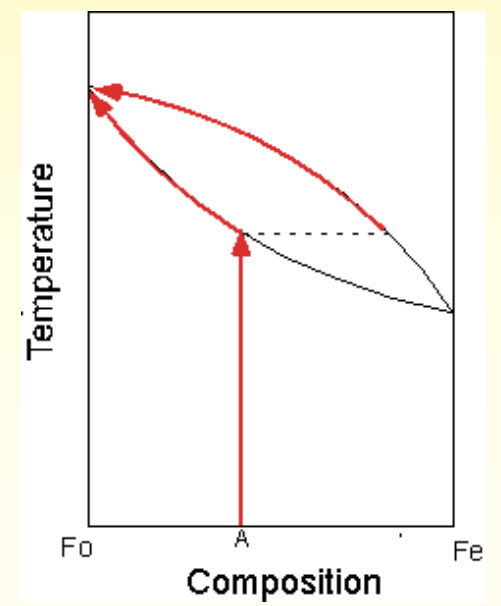
Erdmantelgestein (grün) in Basaltlava



Gleichgewichts-Schmelzbildung



Fraktionierte Aufschmelzung



Fe-Mg Austausch zwischen Mineralen

Partitioning of Fe, Mg with Temperature: The Garnet-Biotite Geothermometer

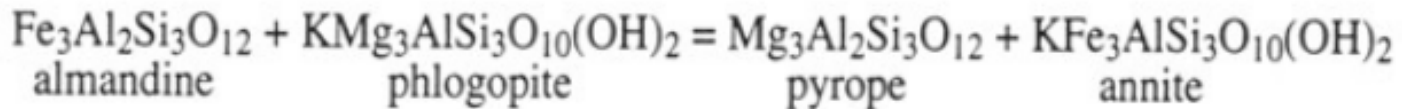
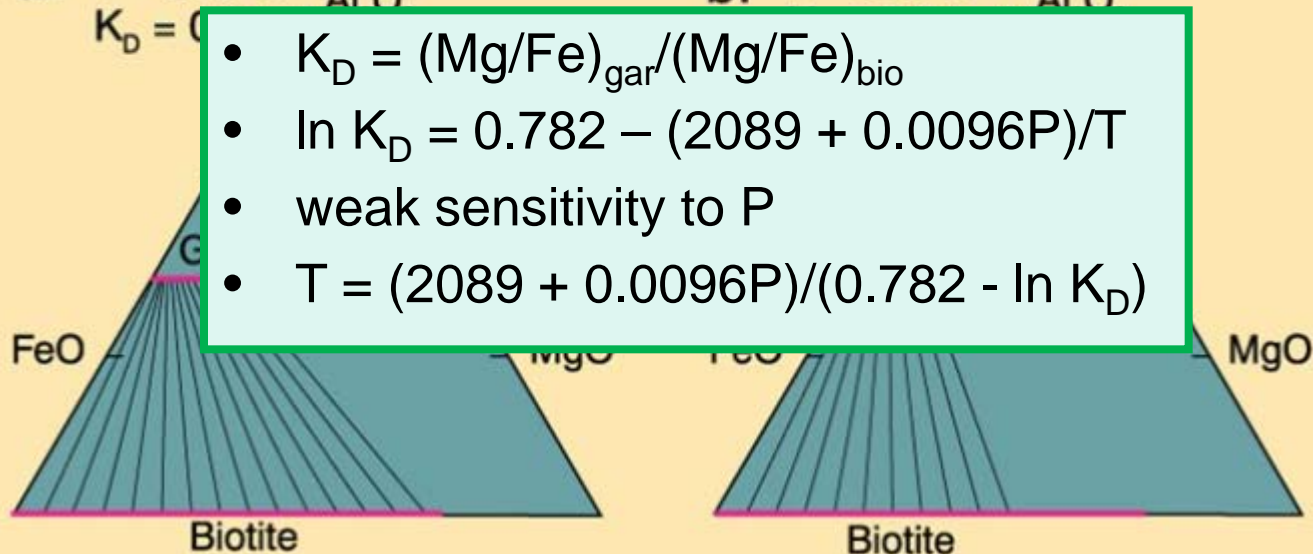
Fe, Mg have similar ionic radii, therefore volume change small

a. $T \gg 500^\circ\text{C}$

$K_D = 0$

b. $T \gg 800^\circ\text{C}$

Al₂O₃



Fe-Mg Zahl

Wichtiger Gesteinsparameter

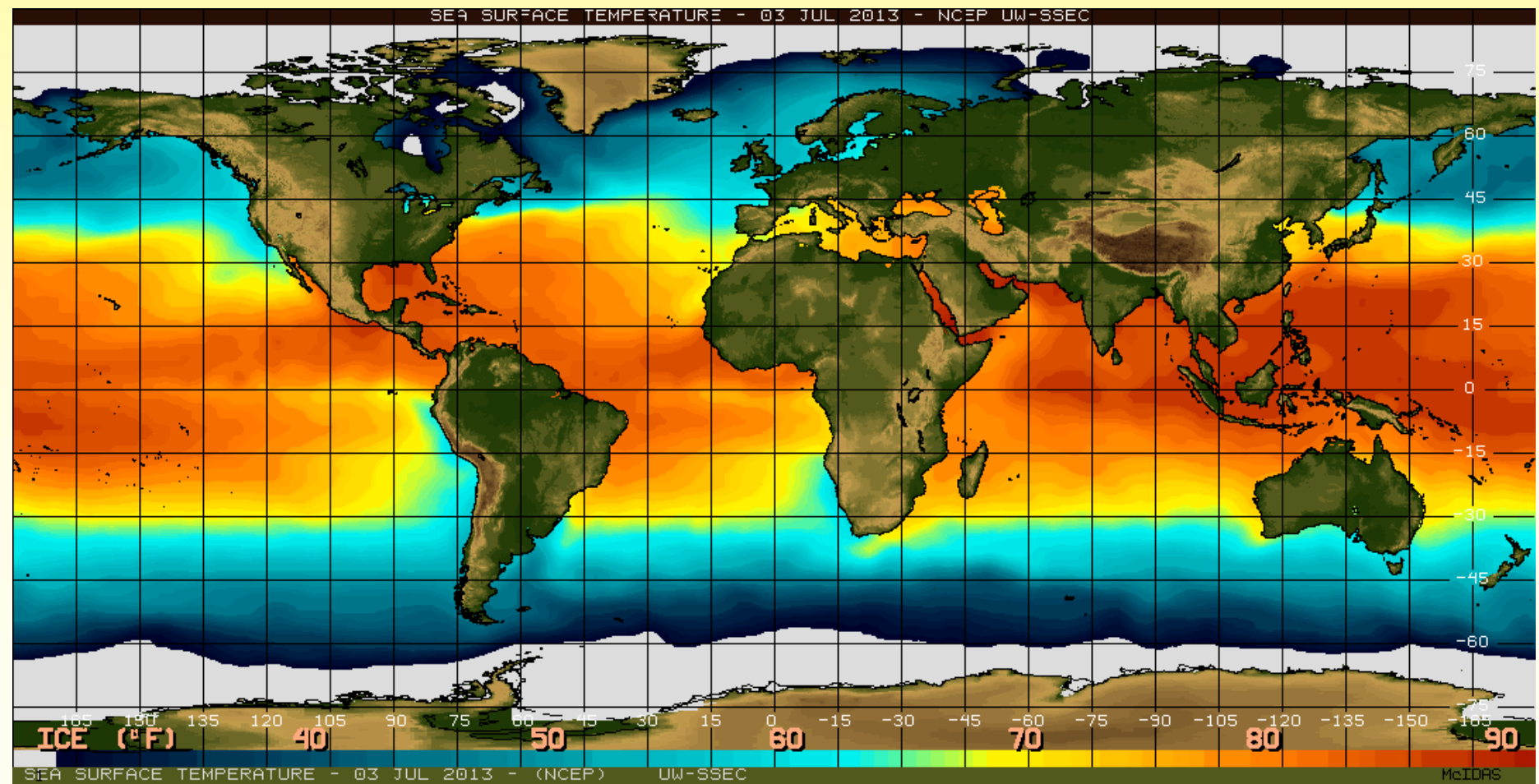
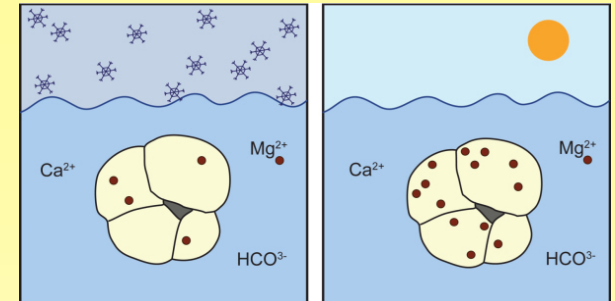
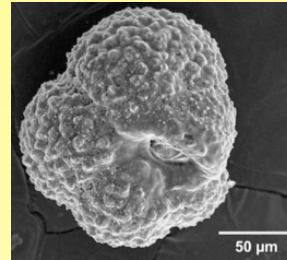
$$Mg' = \frac{\text{mol } Mg^{2+}}{\text{mol } Mg^{2+} + \text{mol } Fe^{2+}}$$

$$Mg' = \frac{\frac{1}{40,32} MgO}{\frac{1}{40,32} MgO + \frac{0,9}{79,8} Fe_2O_3(Total)}$$

Oxid Gew. %	Trachyt	Phonolith	Granit	Granodiorit	Andesit	Diorit	Basalt	Basanit	N-MORB	Inselbogentholeiit	Boninit	Nephelinit	Harzburgit	MORB-Pyrolith	Lherzolith	Dunit
SiO ₂	62,31	57,43	71,84	66,91	58,7	58,34	49,97	45,16	50,35	49,00	53,00	41,81	43,73	44,74	44,16	41,03
Fe ₂ O ₃	3,04	2,85	1,22	1,40	3,31	2,54	3,85	4,02				5,64	6,0			
FeO	2,33	2,07	1,65	2,76	4,09	4,99	7,24	7,65	11,30	9,79	7,54	6,35	7,09	7,55	8,14	6,26
MgO	0,94	1,09	0,72	1,76	3,37	3,77	6,84	8,71	8,65	11,62	13,08	6,58	36,34	39,57	41,05	51,88
Mg#	0,28	0,33	0,36	0,48	0,50	0,52	0,58	0,62	0,63	0,72	0,79	0,82	0,86	0,92	0,92	0,95

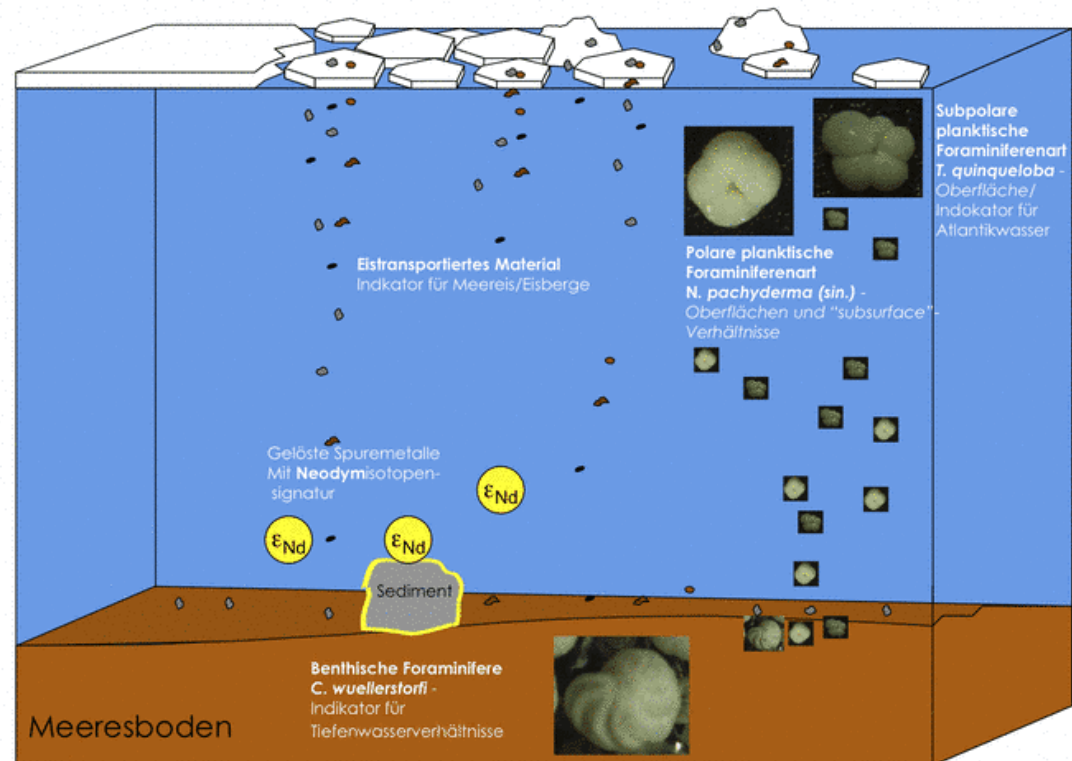
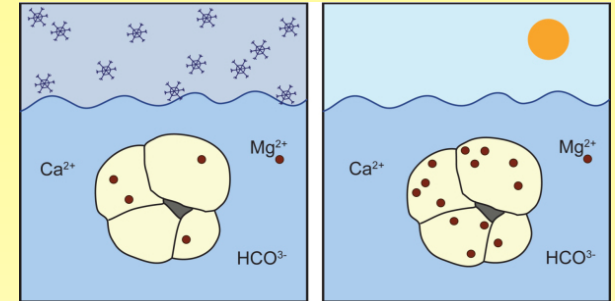
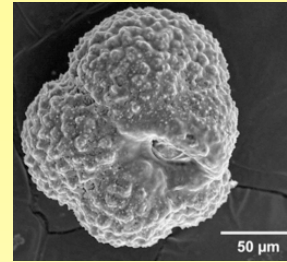
Mg/Ca-Verhältnisse als Temperaturproxies

- Einbau von Mg in Calcit (CaCO_3) → Diadochie
- **Mg/Ca** Verhältnis in Foraminiferen ist temperaturabhängig



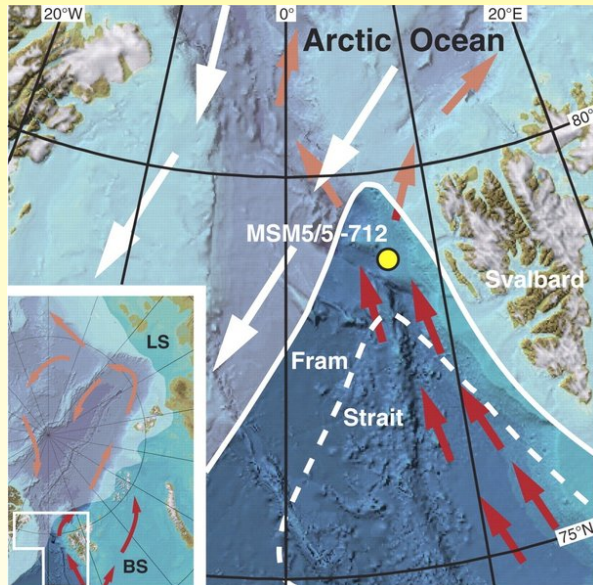
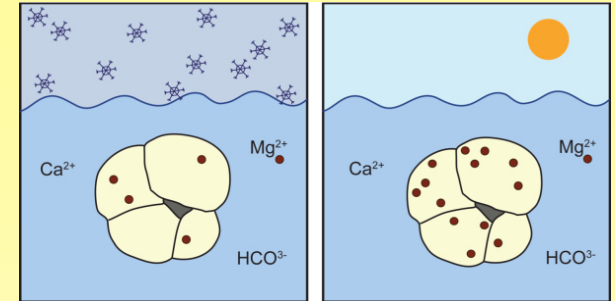
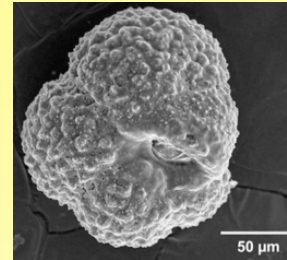
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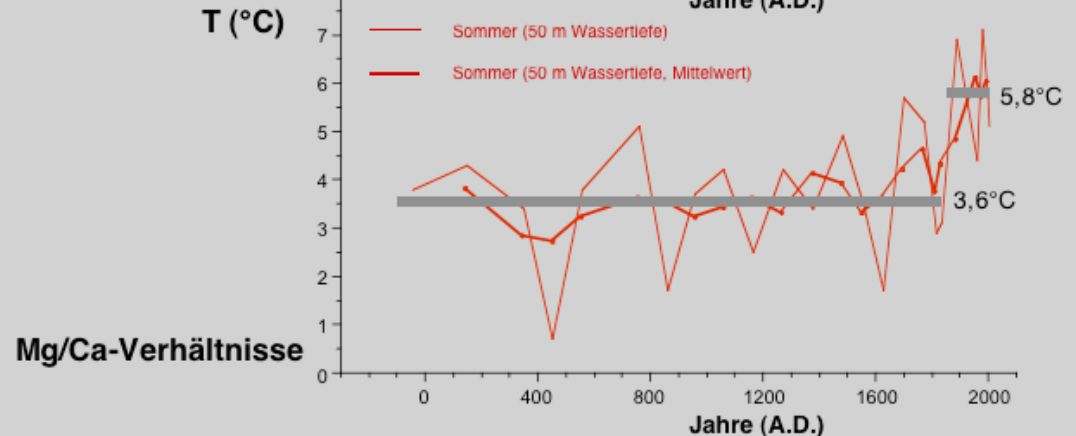
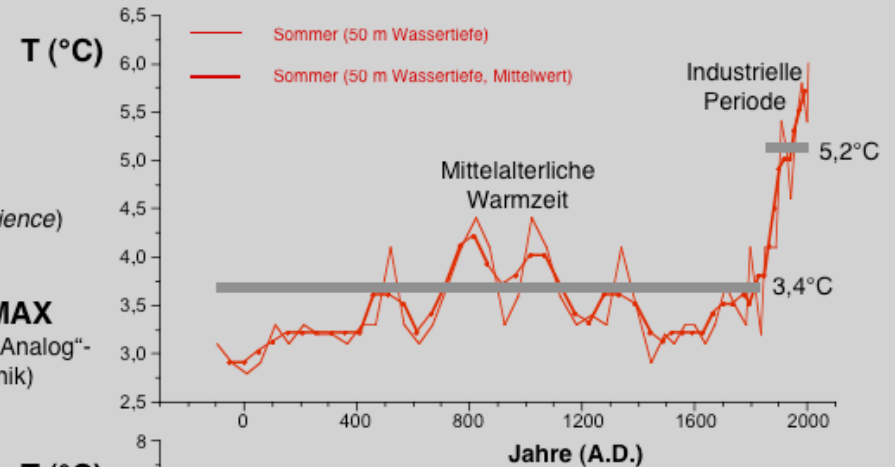
In der östlichen Framstraße dringt relativ warmes Nordatlantikwasser in den Arktischen Ozean ein (rote Pfeile)

Spielhagen et al. (2011) Science, 331, 450-453

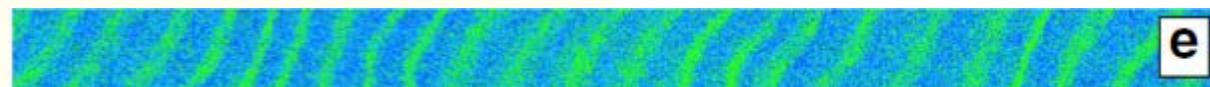
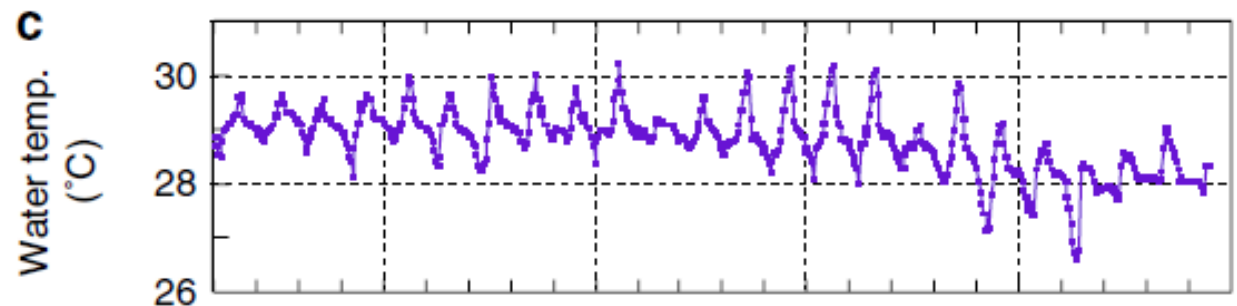
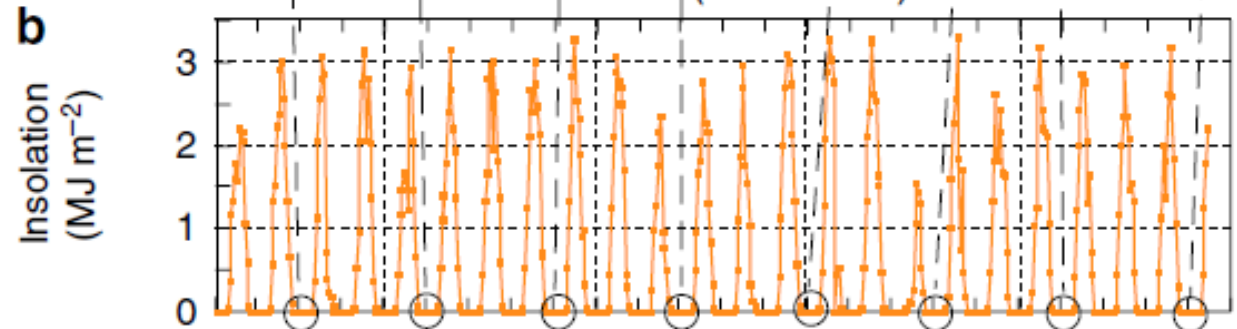
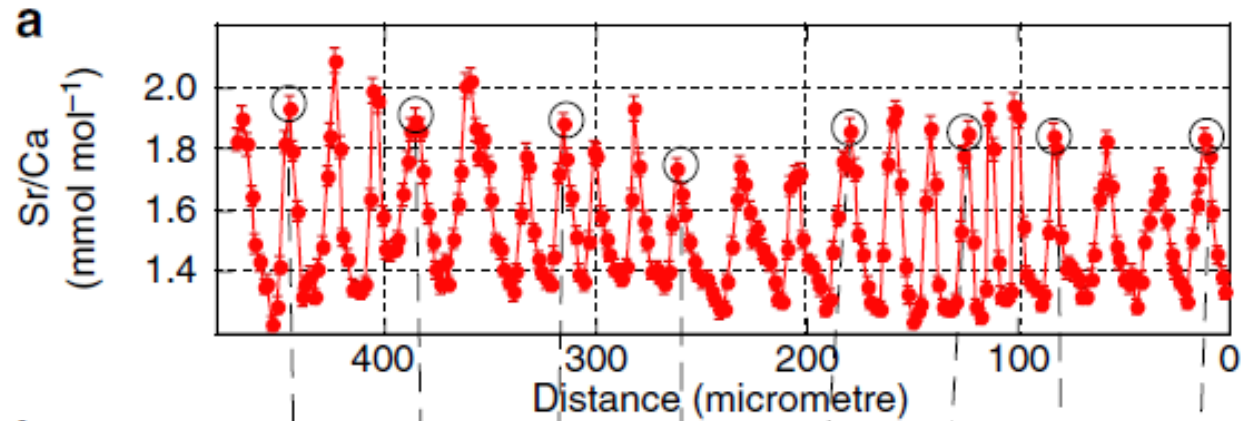
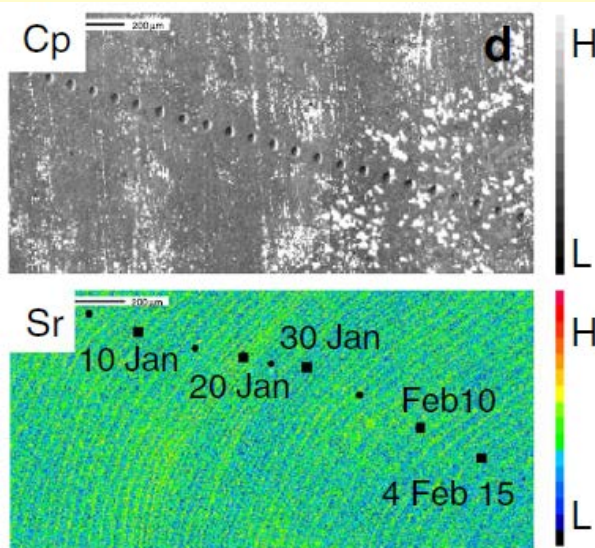
Atlantikwasser-Temperatur-Rekonstruktion

Spielhagen et al. (2011, *Science*)

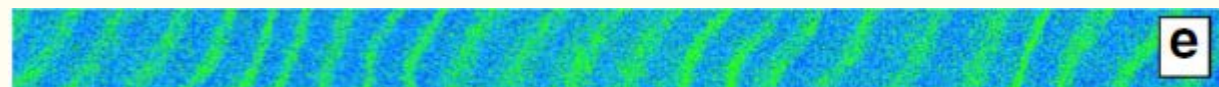
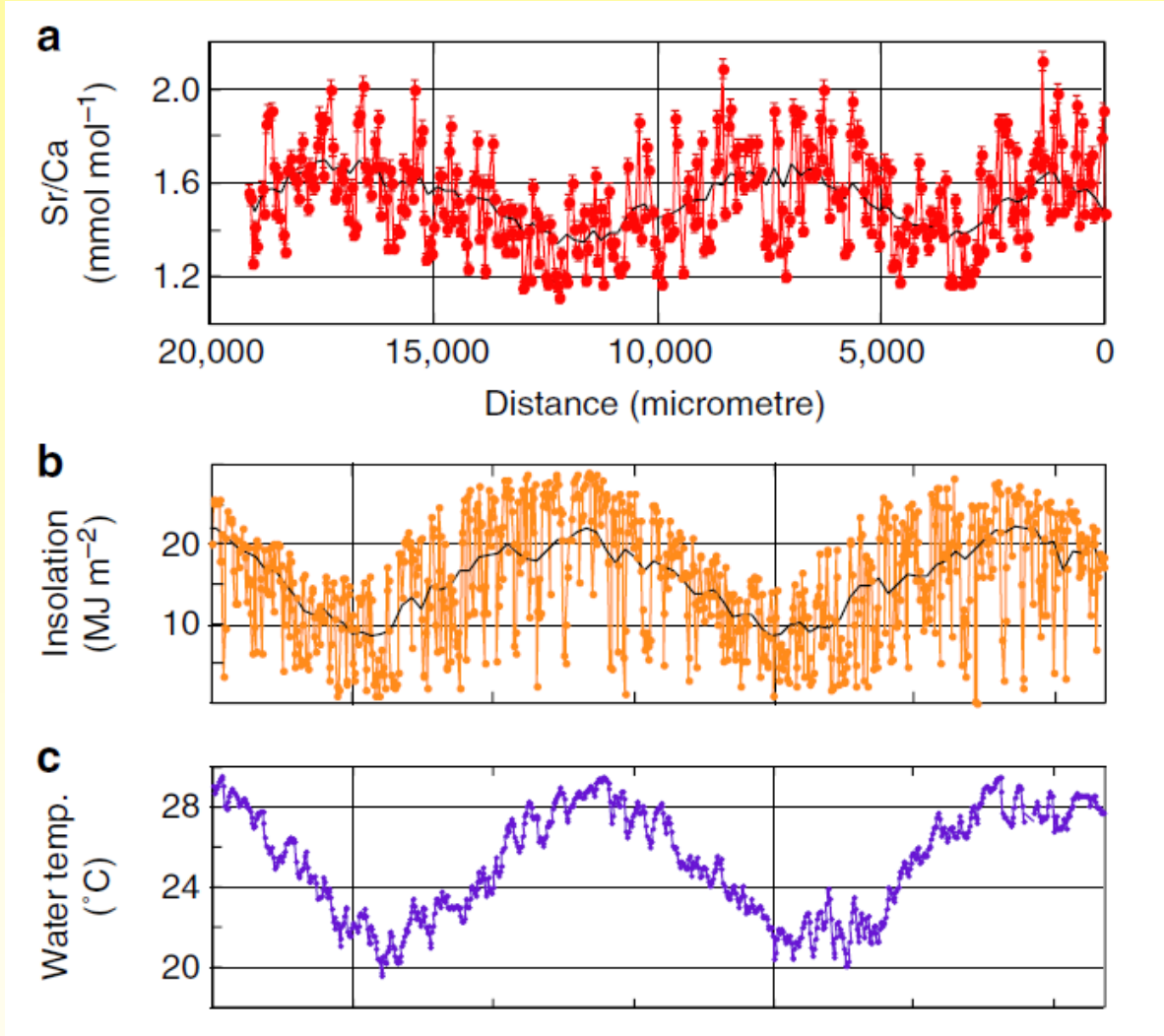
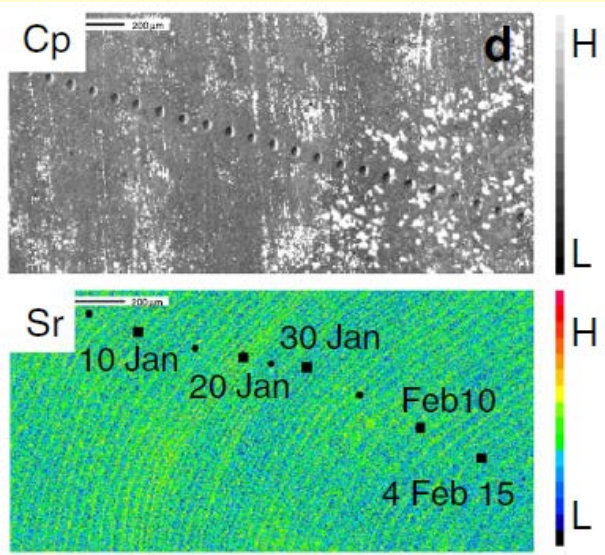
SIMMAX
 („Modern Analog“-Technik)



Sr/Ca-Verhältnisse in Muschelschalen als proxie für Hell-Dunkel Zyklus?



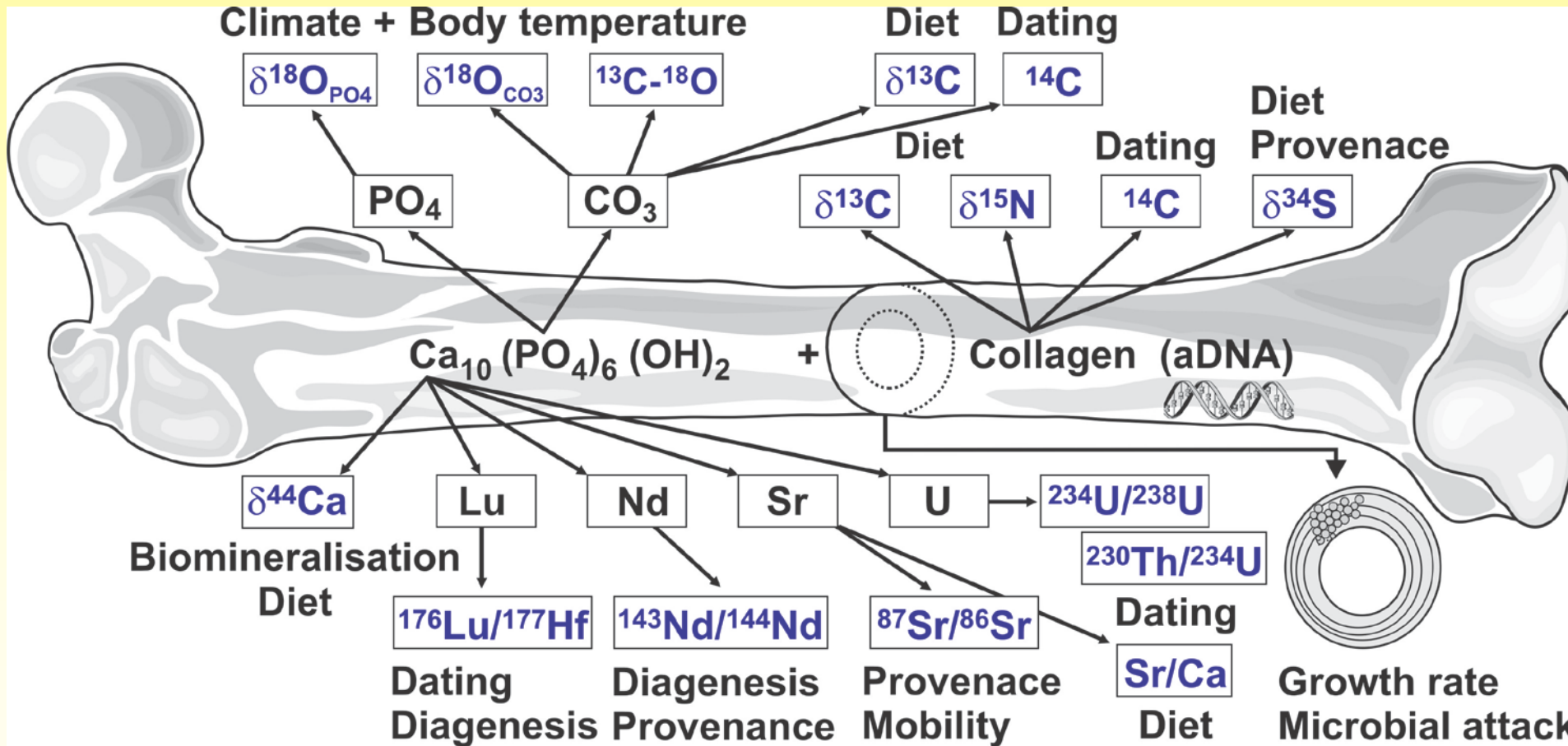
Sr/Ca-Verhältnisse in Muschelschalen als proxie für Hell-Dunkel Zyklus?



“Knochenarbeit”

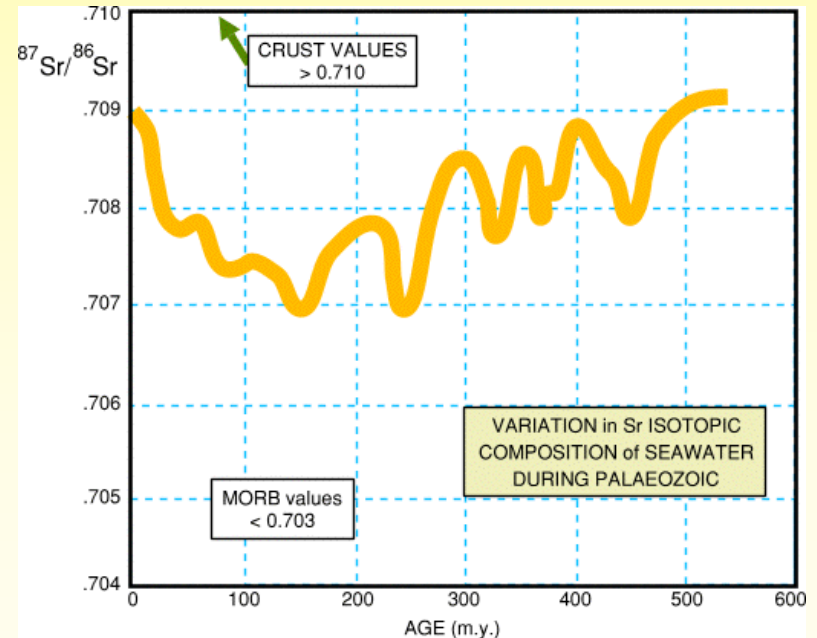
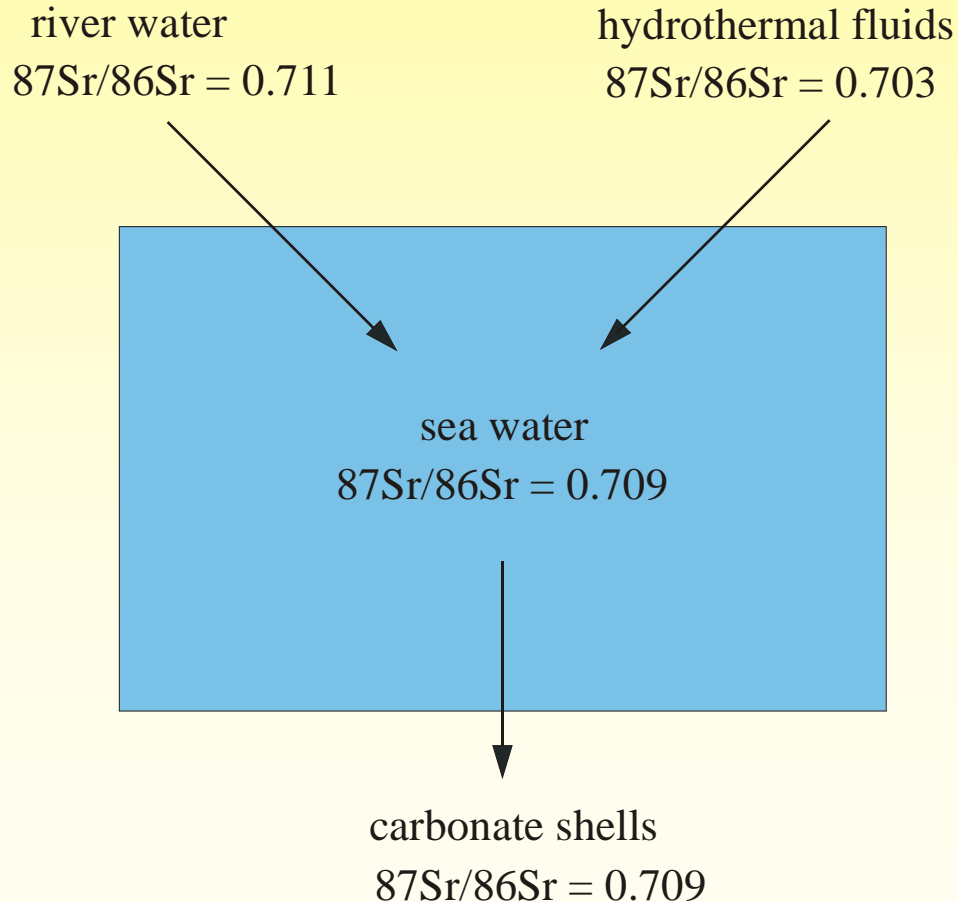
Die Physiologie fossiler Vertebraten

↓ ‚clumped isotopes‘ ↓

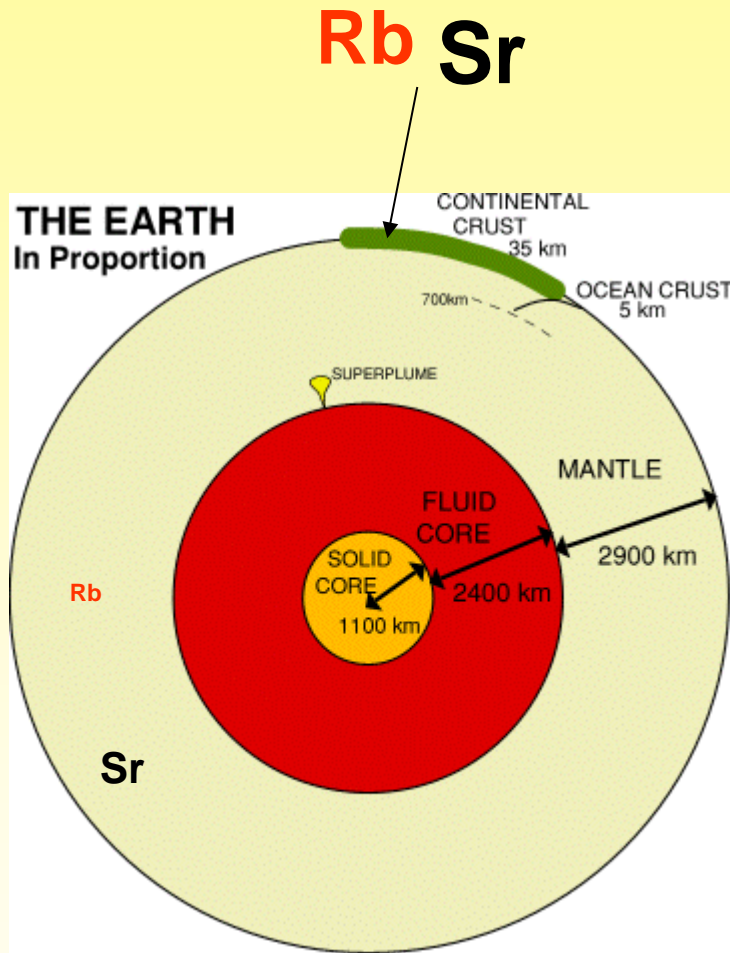


Sr im Meerwasser

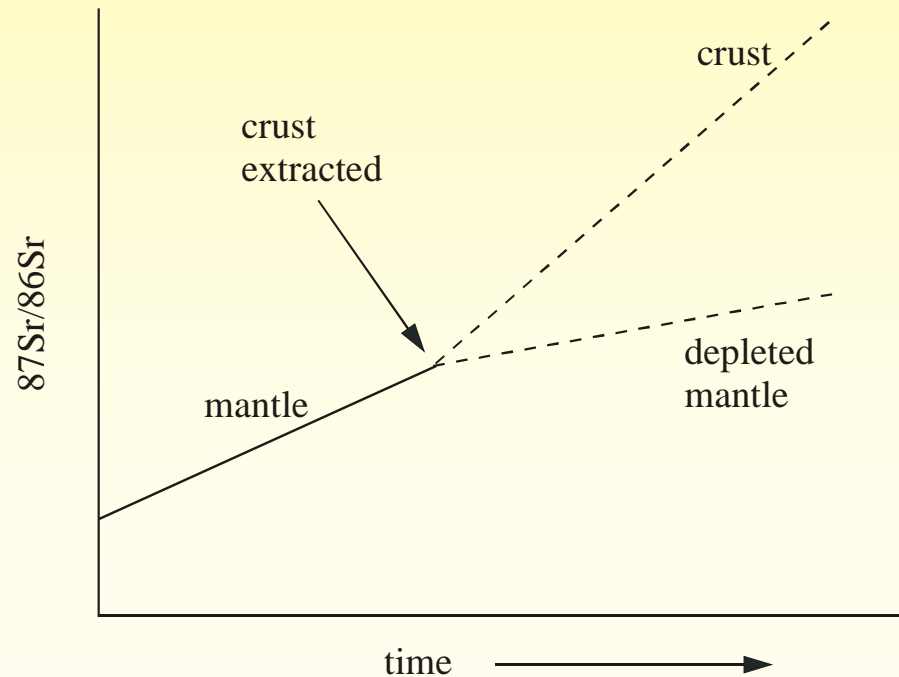
Sr isotope composition of the oceans is determined by the relative contributions of Sr from river waters and hydrothermal sources



Sr-Isotopenentwicklung



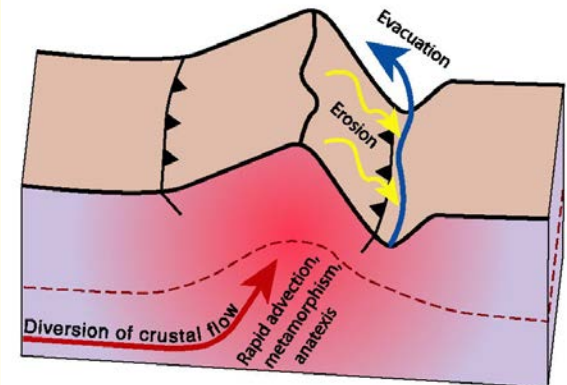
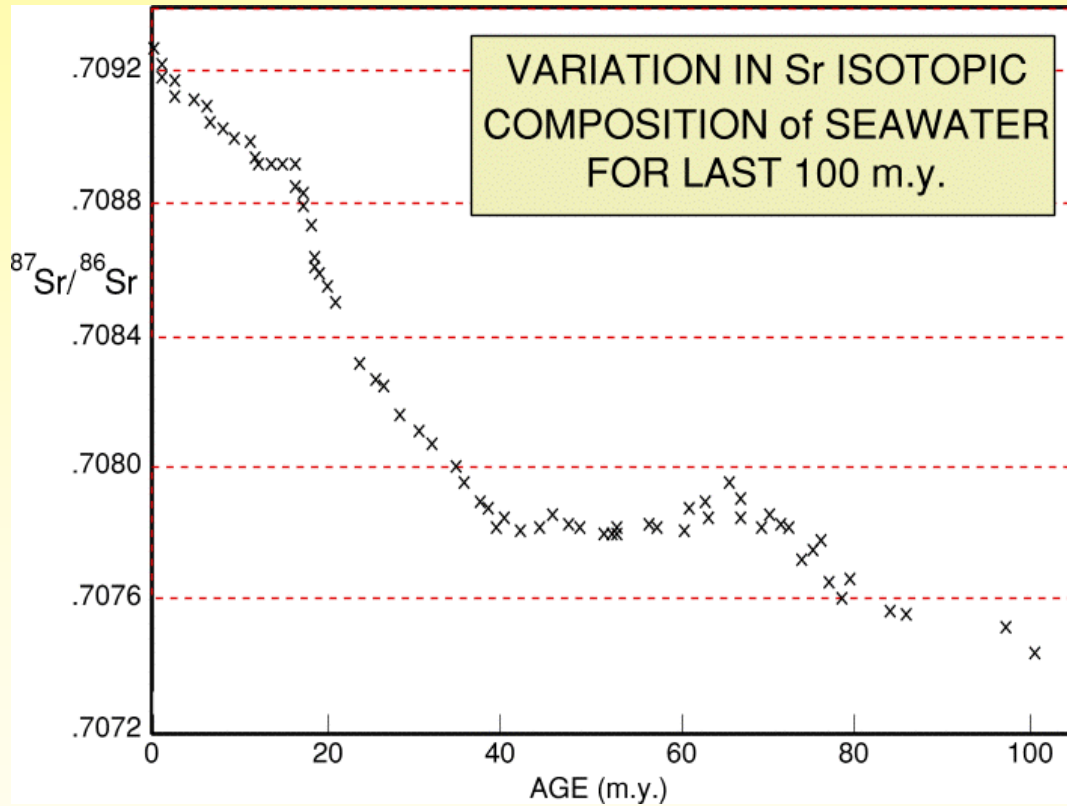
$^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the crust is higher than that of the mantle due to the preferential partitioning of Rb into the crust relative to Sr.



Continental crust: 32-78 ppm Rb, 260-333 ppm Sr
Depleted mantle: 0.6 ppm Rb, 19.9 ppm Sr

Sr im Meerwasser

Increase in the global ocean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio since India-Asia collision



Lithium, Beryllium, Bor

leicht und selten

Schrägbeziehung im PSE

zwischen

Li – Mg

Be – Al

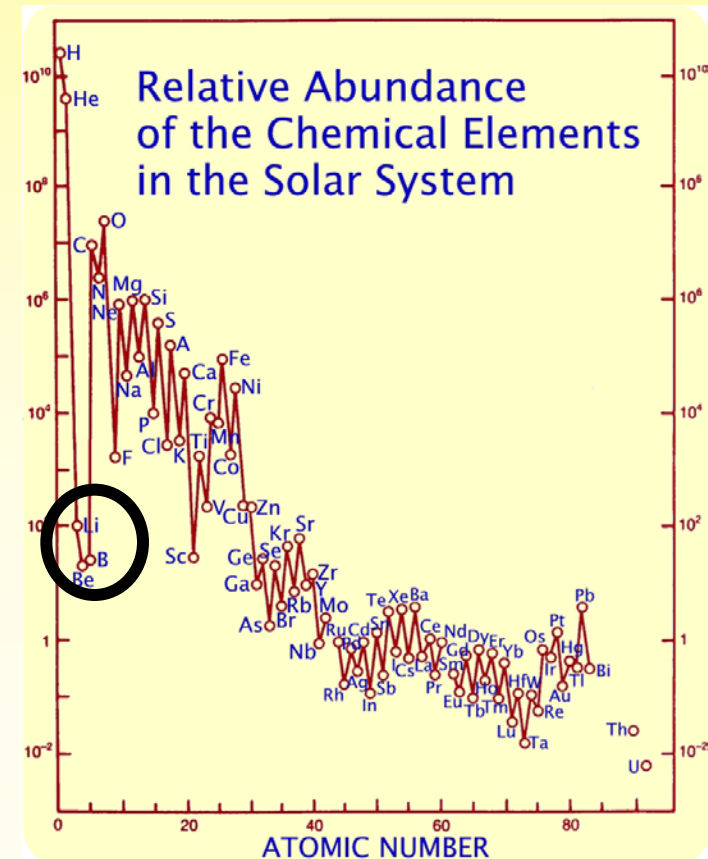
B – Si

ist auf vergleichbare Atomradien
und ähnliche Ladungsdichten,
also ähnliches Ionenpotential
zurückzuführen

Wir erinnern uns:

Li, Be und B sind ungewöhnlich
selten auf der Erde und im
Sonnensystem

Symbol			
Ionenpotential			
Li 1.2	Be 5.7	B 15.0	
Na 0.8	Mg 2.5	Al 4.9	Si 11.8
K 0.6	Ca 1.7	Ga 4.3	Ge 8.3



Lithium, Beryllium und Bor

inkompatibel, mobil und lithophil

werden über Schmelzen und Fluide transportiert

Meerwasser: Quelle und Reservoir für Li, B und Be

Kontinentale Kruste: Li in Glimmer, Bor in Turmalin und Be in ?

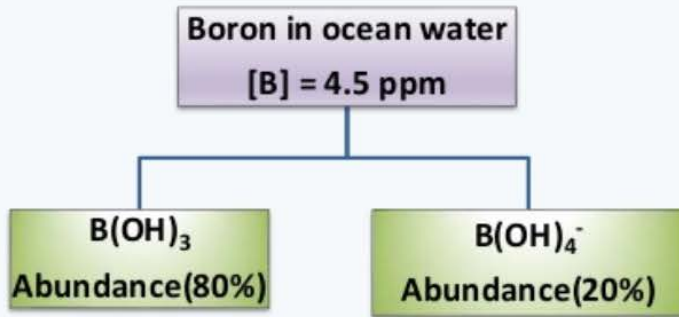
Tracer zur Erforschung geodynamischer Prozesse, lang- und kurzzyklische Stoffkreisläufe (z.B. in Subduktionszonen), Paläoproxy

Isotopenfraktionierung ($^6\text{Li}/^7\text{Li}$, $^{10}\text{B}/^{11}\text{B}$)

Be besitzt ein wichtiges cosmogenes Isotop (^{10}Be)

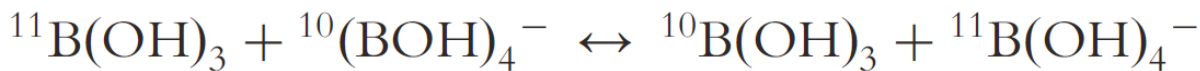


Bor Isotope als Paläo-pH Proxie

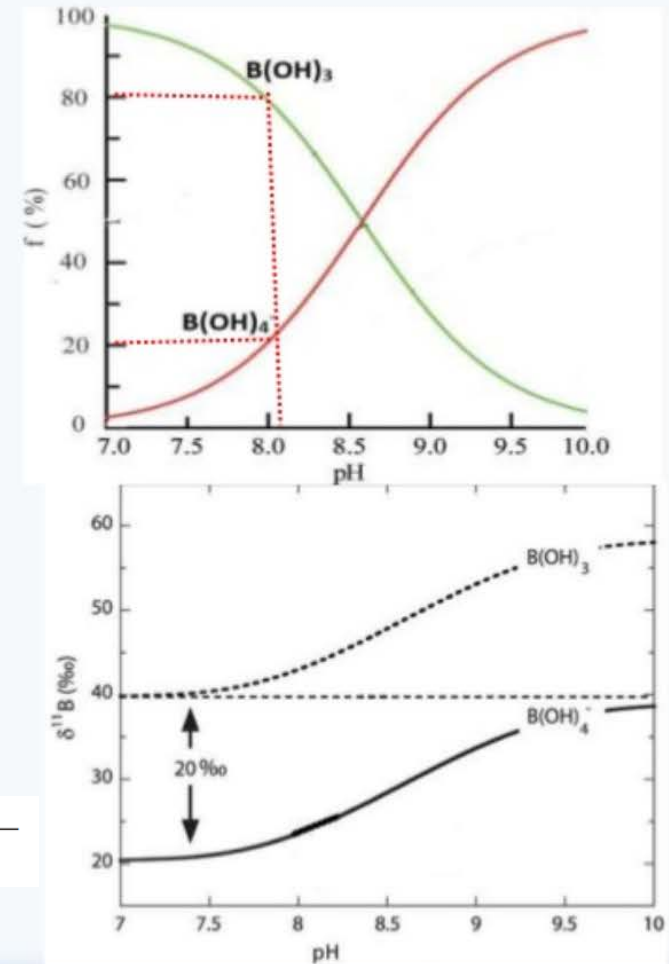


$$K_B = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]}$$

$$\log \left(\frac{[\text{B(OH)}_4^-]}{[\text{B(OH)}_3]} \right) = \text{pH} - \text{p}K_B$$

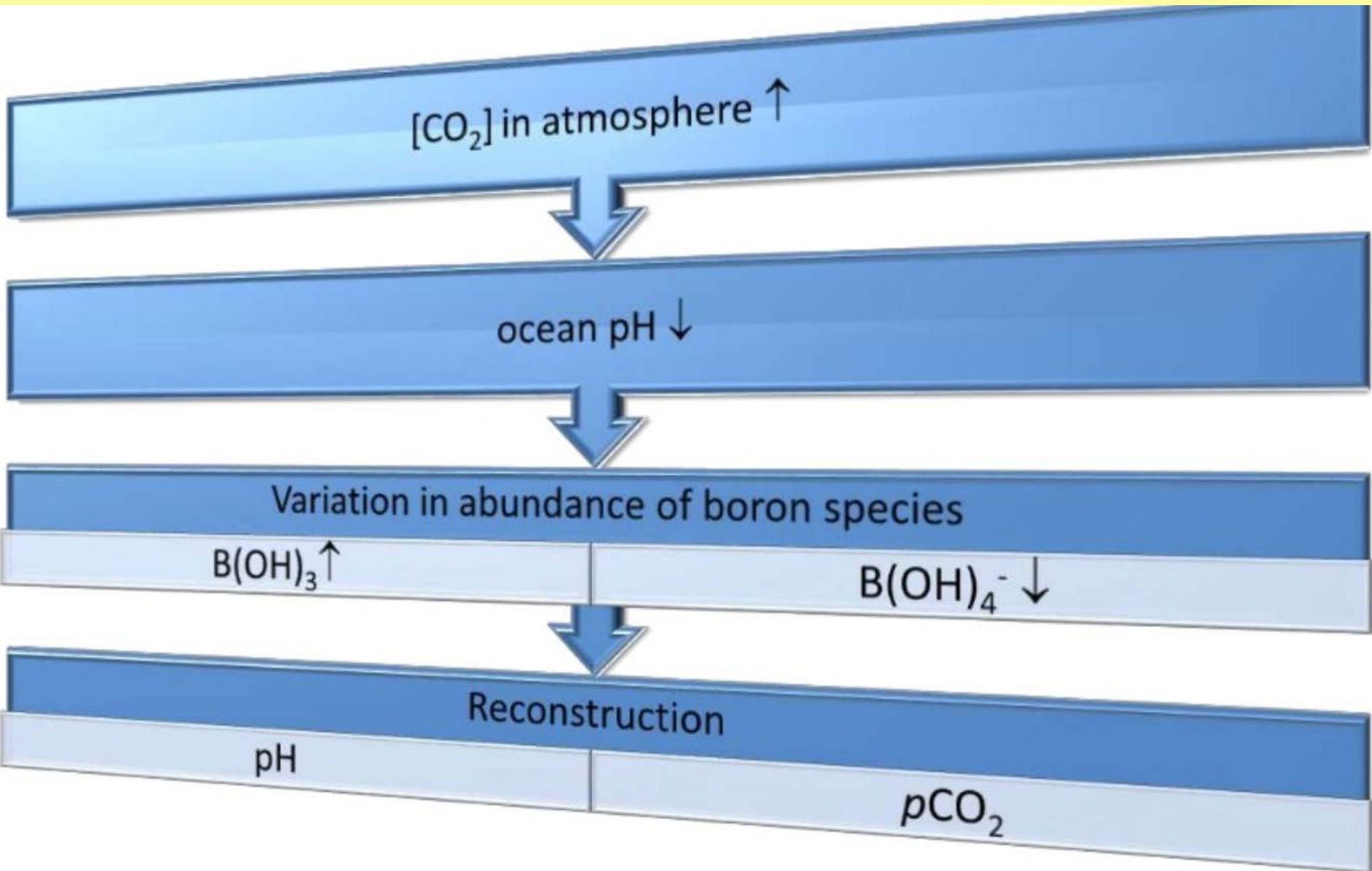


K = Gleichgewichtskonstante < 1, d.h. trigonale Spezies ist isotopisch schwerer im Vergleich zur tetraedrisch koordinierten Spezies;

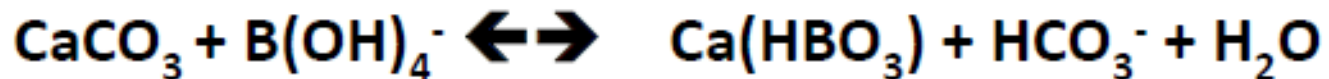
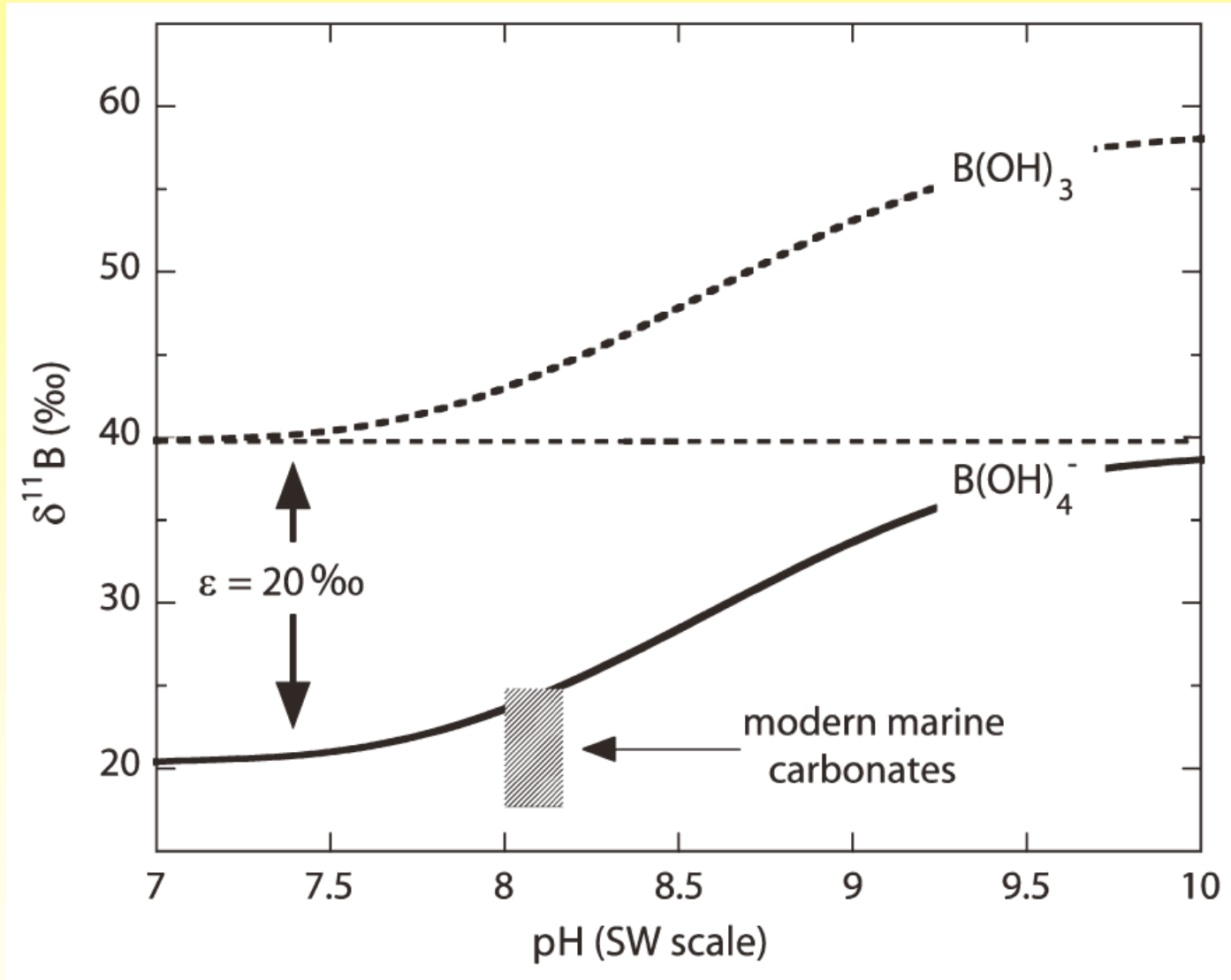


Hemming & Hanson 1992, *Geochimica et Cosmochimica Acta*

Bor Isotope als Paläo-pH proxy

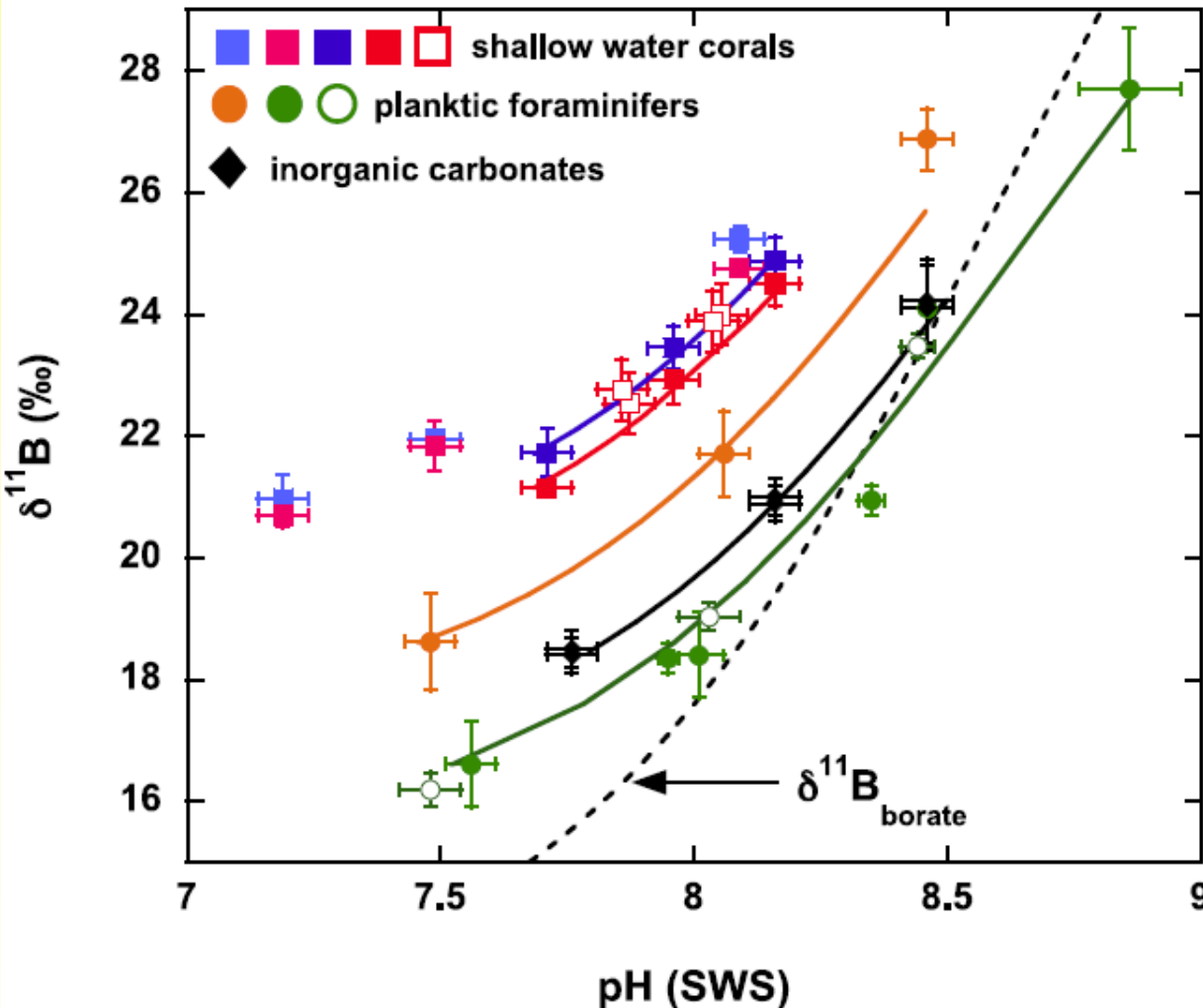


Bor Isotope als Paläo-pH Proxie



Bor Isotope als Paläo-pH proxy

Laboratory calibrations of marine carbonates



MC-ICP-MS

S. pistillata (Krief et al. 2010)

Porites sp. (Krief et al. 2010)

O. universa (Hönisch & Rae, unpubl.)

N-TIMS

P. cylindrica (Hönisch et al. 2004)

Acropora sp. (Reynaud et al., 2004)

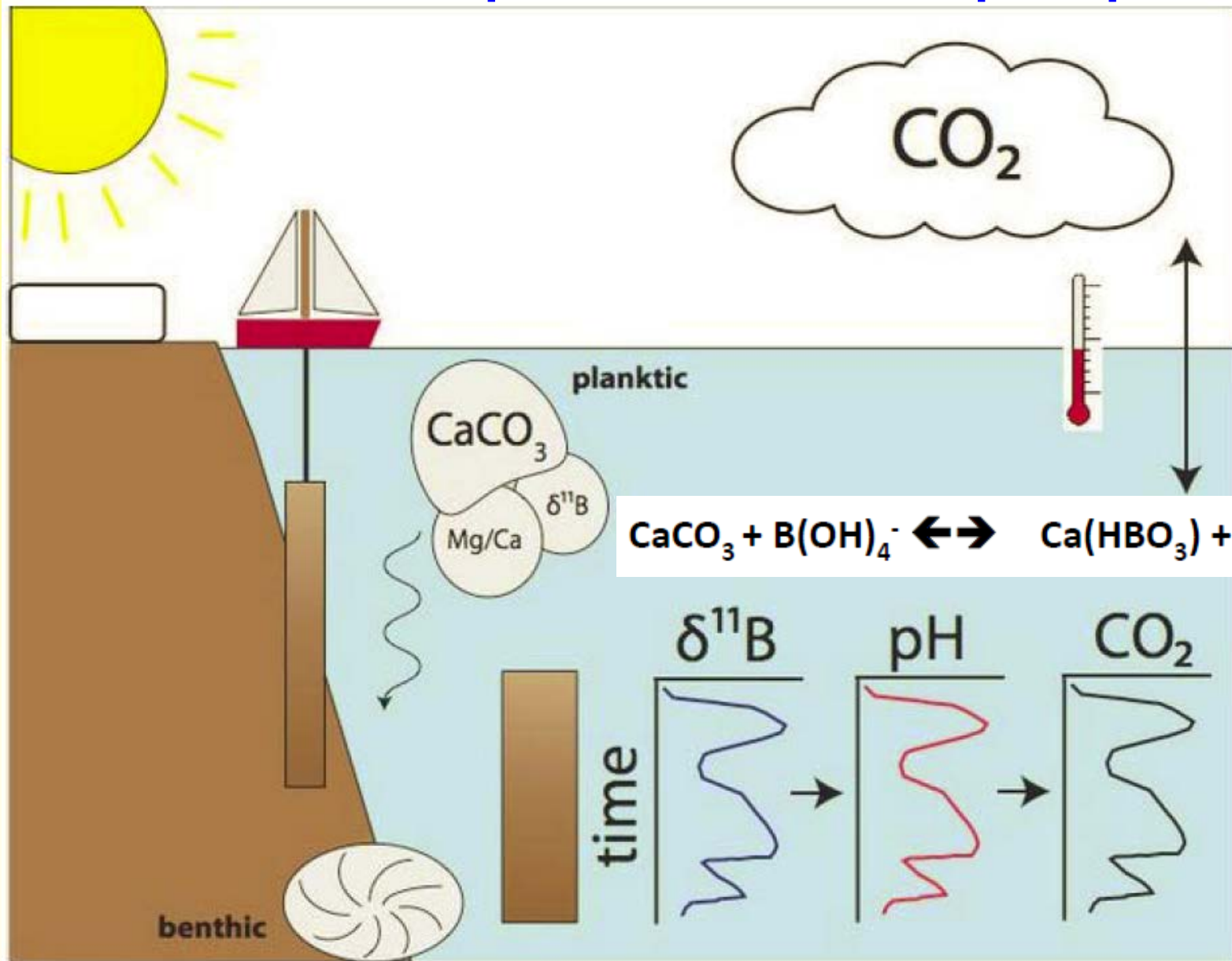
A. nobilis (Hönisch et al. 2004)

G. sacculifer (Sanyal et al. 2001)

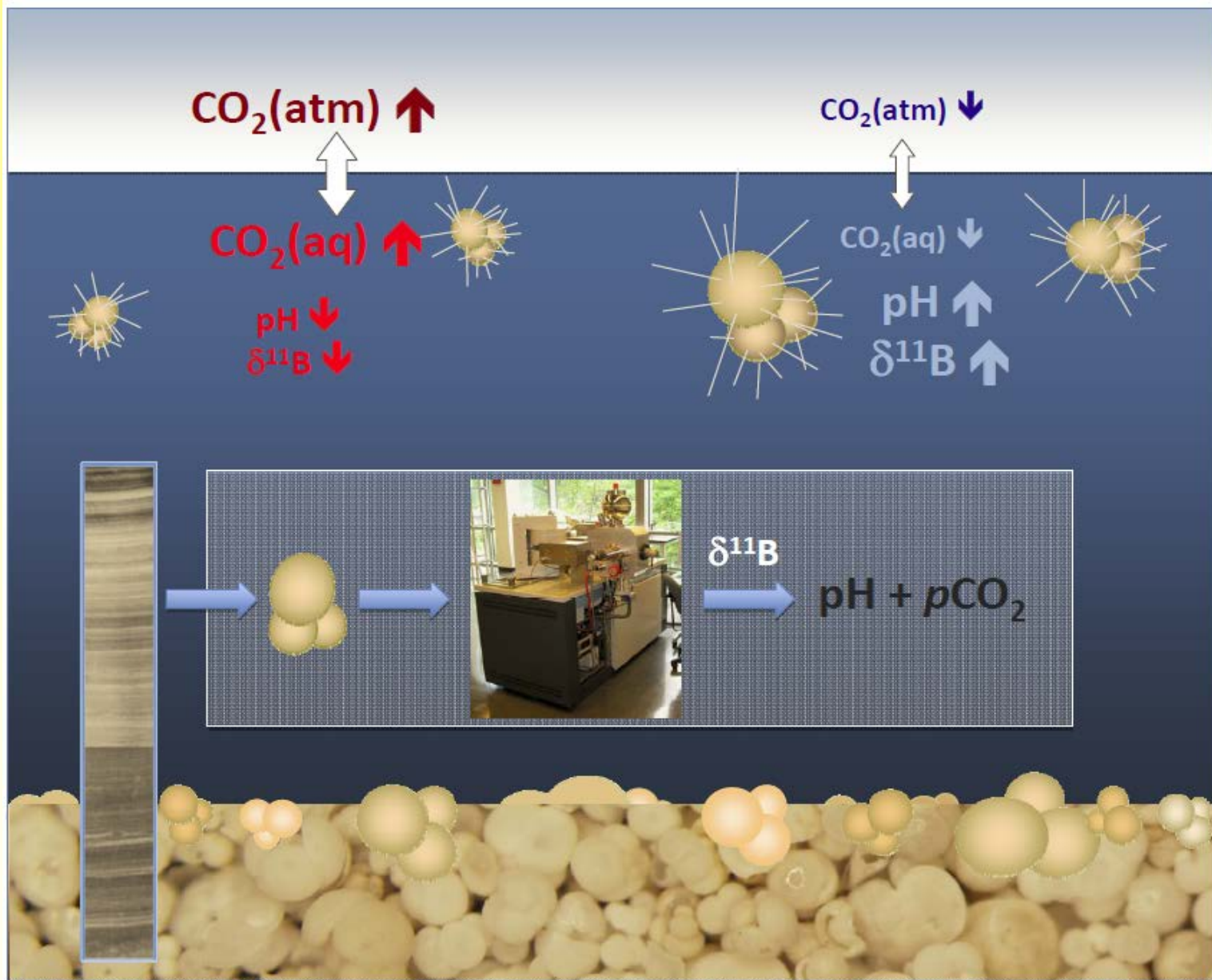
inorganic calcite (Sanyal et al. 2000)

O. universa (Sanyal et al. 1996)

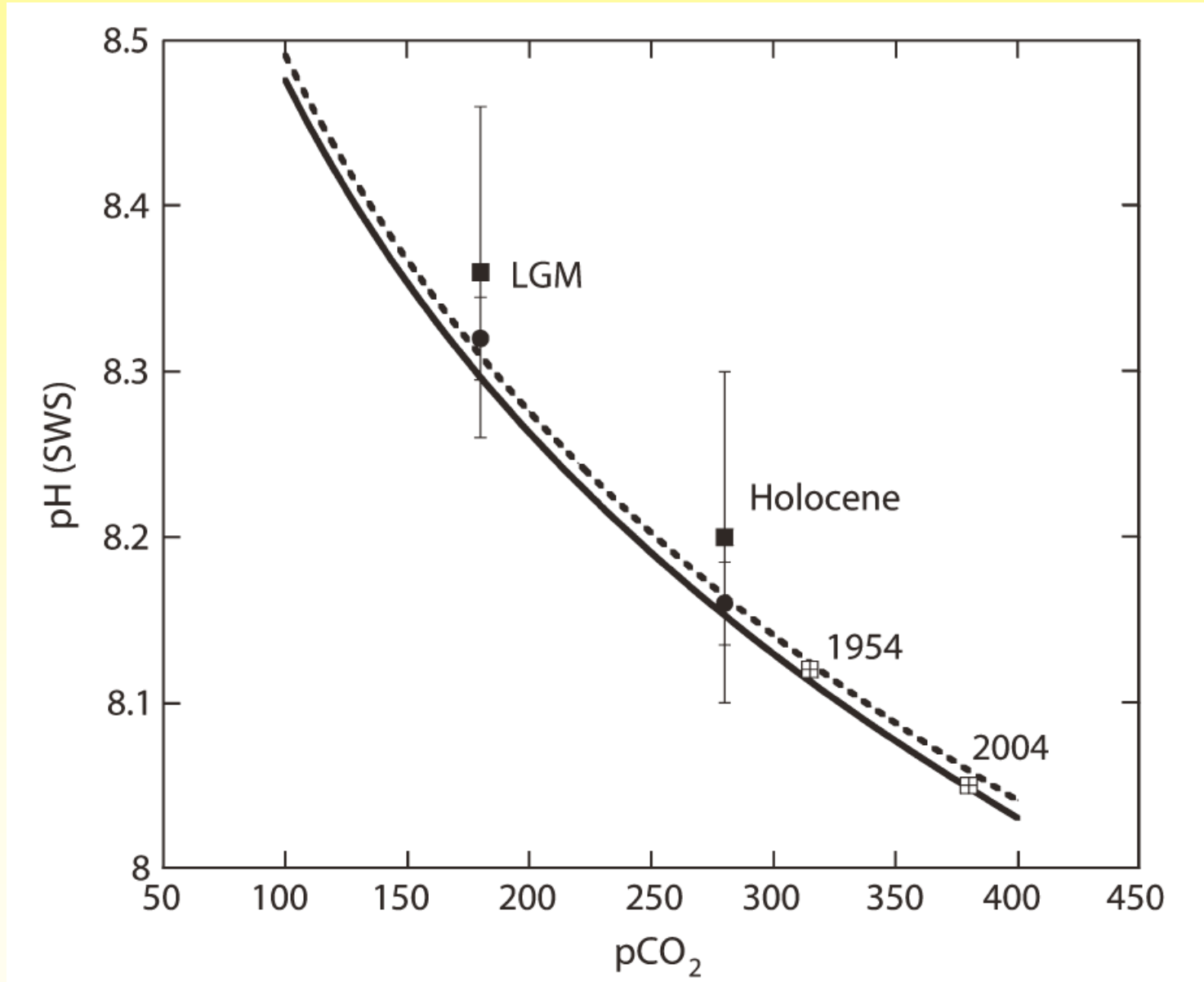
Bor Isotope als Paläo-pH proxy



Bor Isotope als Paläo-pH proxy



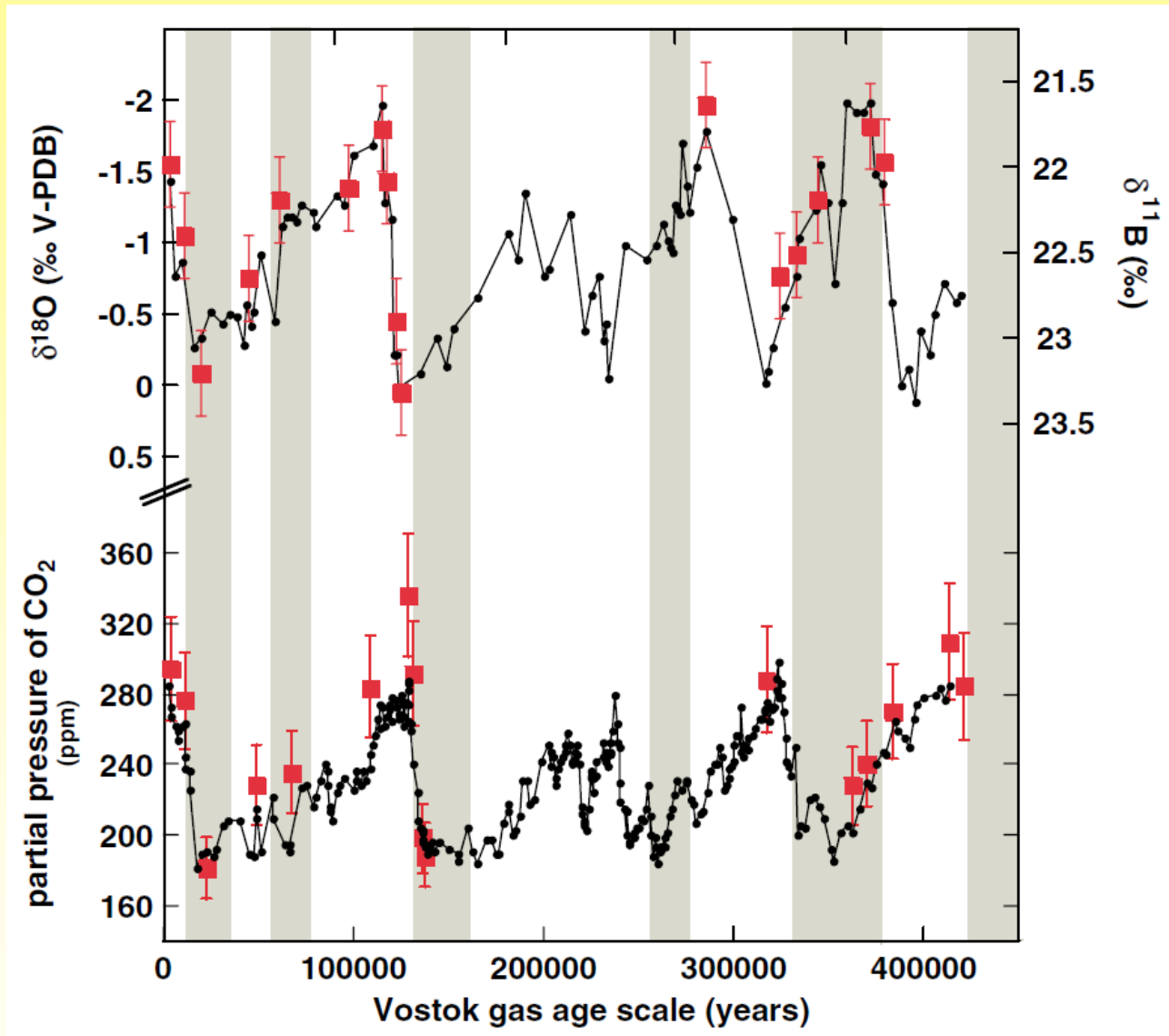
Bor Isotope als Paläo-pH proxy



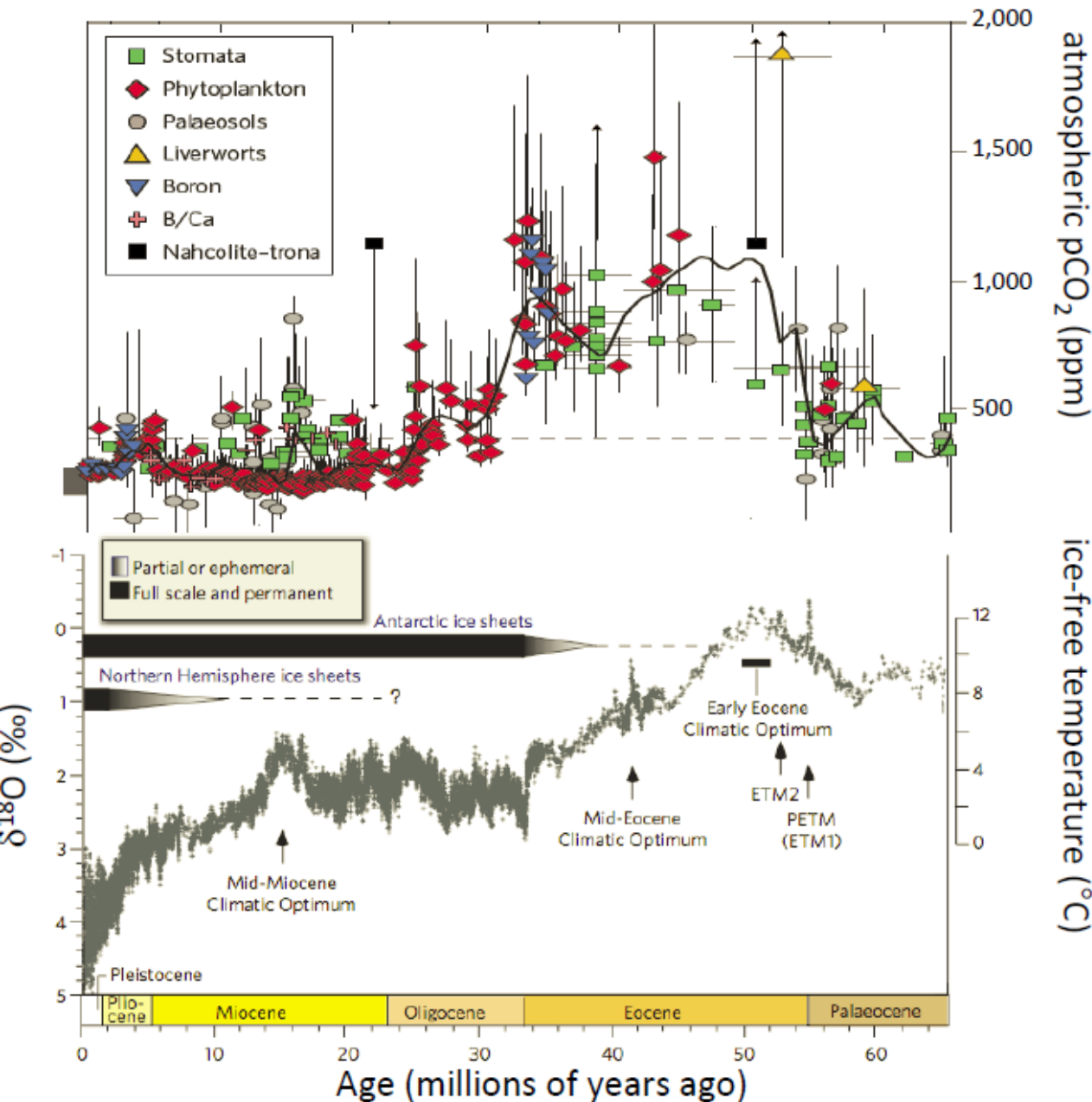
Source: Hemming & Hönisch (2007)

Bor Isotope als Paläo-pH proxy

Data from ODP site 668B, eastern equatorial Atlantic (sediment core) with atmospheric pCO₂ variations (Vostok ice core)



Bor Isotope als Paläo-pH proxy

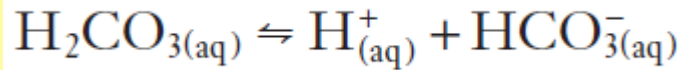


Beerling & Royer,
Nature Geoscience, 2011

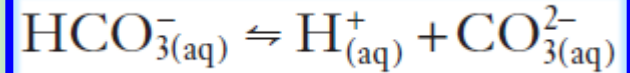
Streuung der Mess-
werte durch ^{11}B
Sekularvariation im
Meerwasser?

Zachos et al., Nature, 2008

Übung – Alkalinität und pH



$$K_1 = \frac{a\text{H}^+ \cdot a\text{HCO}_3^-}{a\text{H}_2\text{CO}_3} = 10^{-6.4}$$



$$K_2 = \frac{a\text{H}^+ \cdot a\text{CO}_3^{2-}}{a\text{HCO}_3^-} = 10^{-10.3}$$

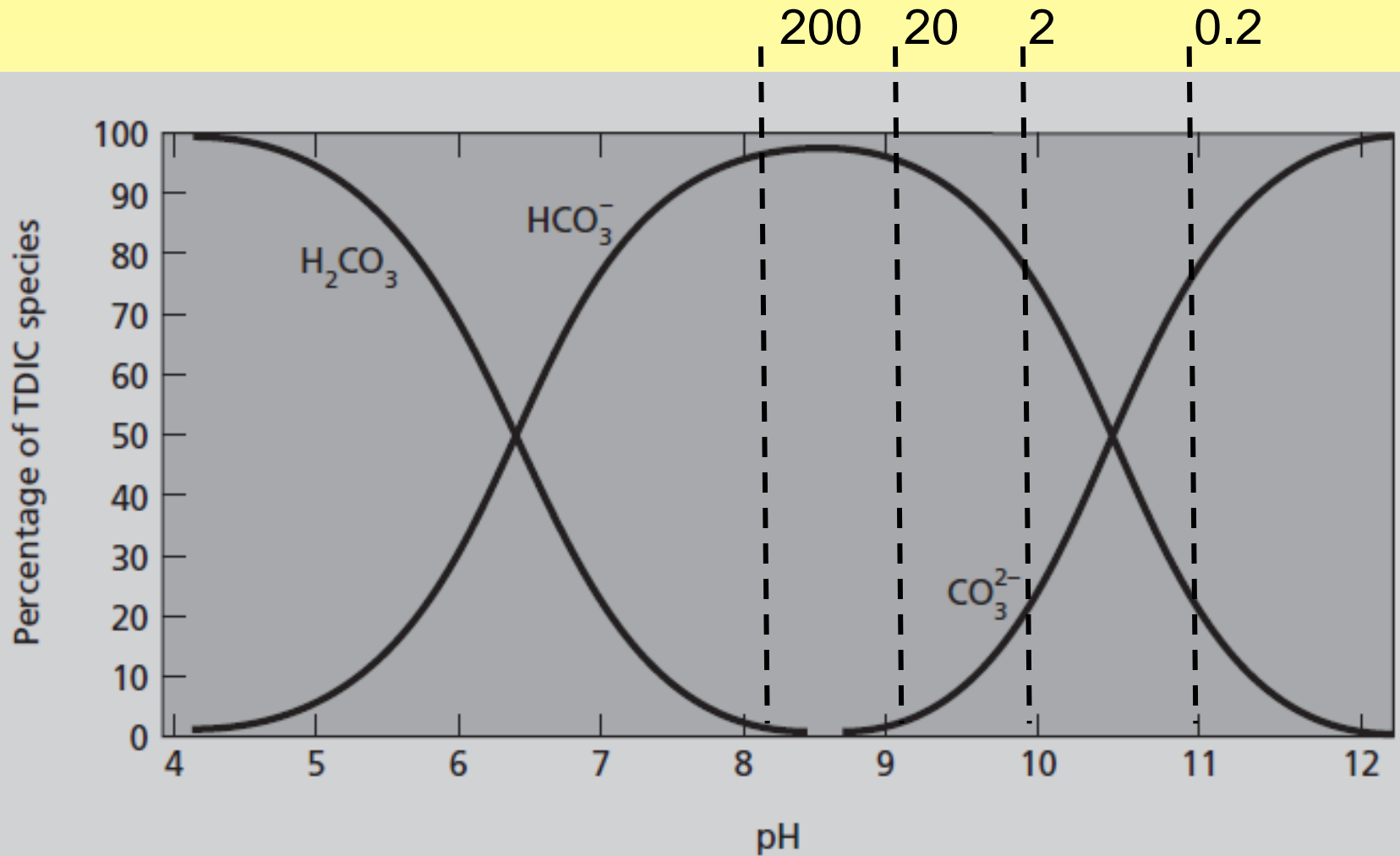
Berechnen sie das Verhältnis Hydrogenkarbonationen (HCO_3^-) zu Karbonationen (CO_3^{2-}) für Gewässer mit pH-Werten von 8, 9, 10 & 11 und zeichnen sie ein Diagramm mit den prozentualen Anteilen der beiden Ionenarten für die verschiedenen pH-Werte

$$\text{pH} = -\log_{10} a\text{H}^+$$

für pH 8 ($\text{pH} = -\log_{10} a\text{H}^+$) gilt:

$$a\text{HCO}_3^- = \frac{10^{-8} \cdot a\text{CO}_3^{2-}}{10^{-10.3}} = \frac{1 \times 10^{-8} \cdot a\text{CO}_3^{2-}}{5 \times 10^{-11}} = 200 a\text{CO}_3^{2-}$$

Alkalinität



Li-, Be- und B-Kreislauf

Li-, Be-, B- Stoffkreislauf:

Meerwasser →
ozeanische Kruste →
Subduktionszone →
Fluide →
Mantelkeil →
Schmelze →
Vulkanischer Bogen →
Verwitterung, Erosion →
Meerwasser
(hier schließt sich der
Kreislauf)

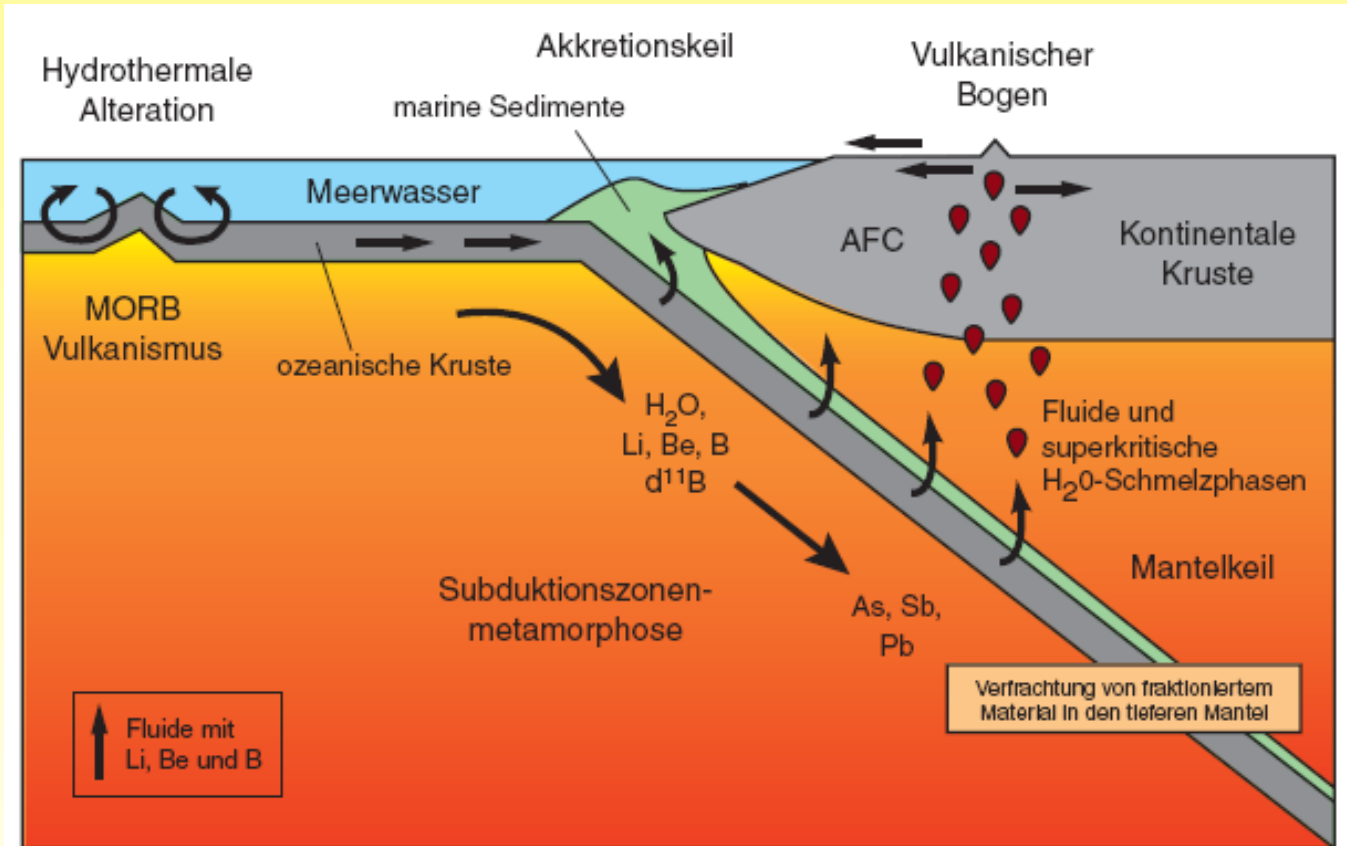


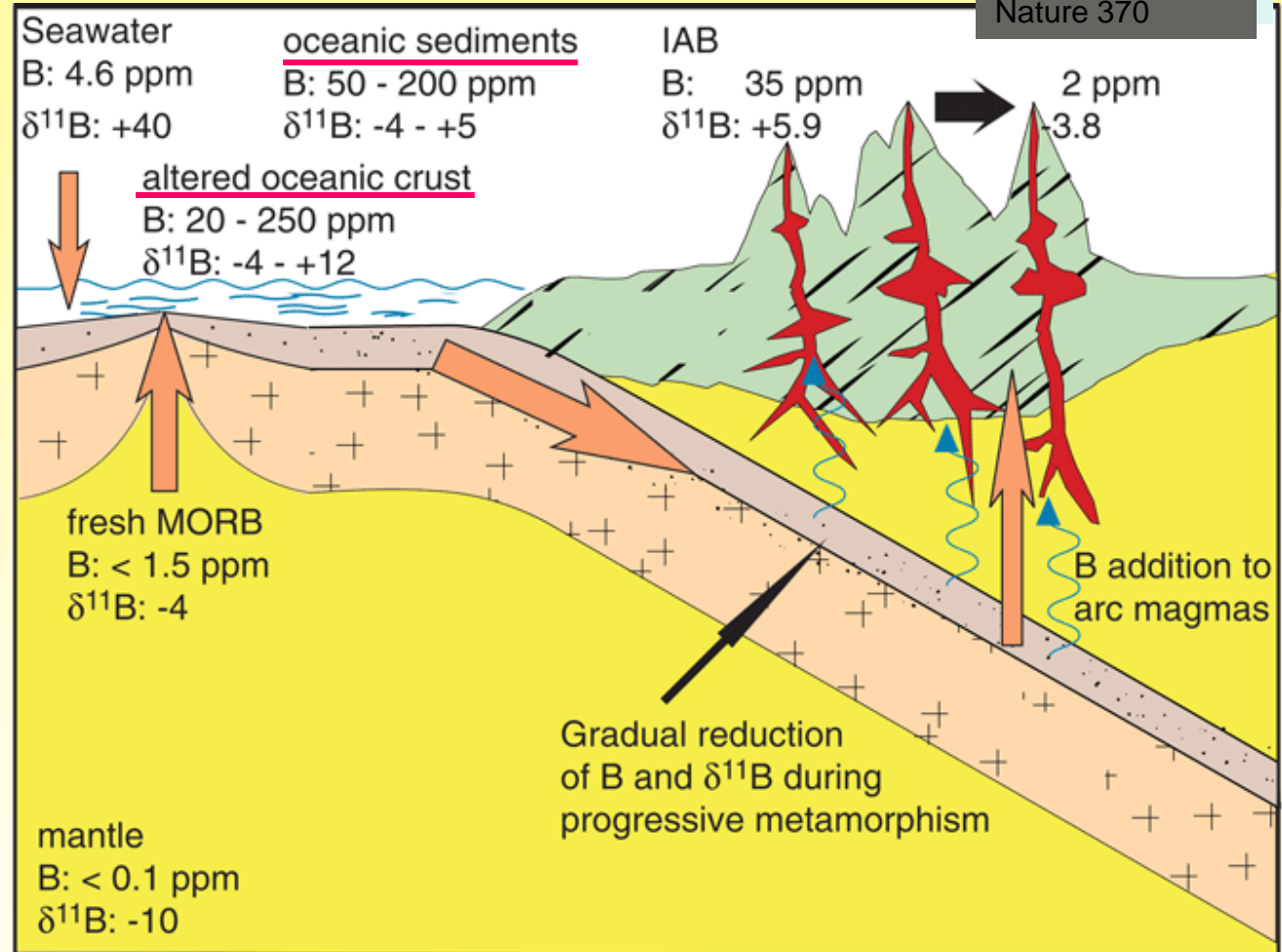
Abb. 1-1 Stoffkreislauf leichter Elemente (Li, Be, B) an Subduktionszonen (nach Bebout 1996)

Li-, Be-, B-Trägerphasen in Subduktionszonen: Tonminerale, Lawsonit, Omphazit, Phengit, Amphibol, Chlorit, Chloritoid, Paragonit, Epidot, Serpentin, d.h. viele OH-haltige Minerale

Bor-Konzentrations- und Isotopenvariationen

$$\delta^{11}\text{B} = \left\{ \left[\frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{standard}}} \right] - 1 \right\} \times 1000$$

e.g. Izu arc:
Ishikawa &
Nakamura (1993)
Nature 370



Quelle: GFZ

Meerwasser wichtige
Quelle für Bor

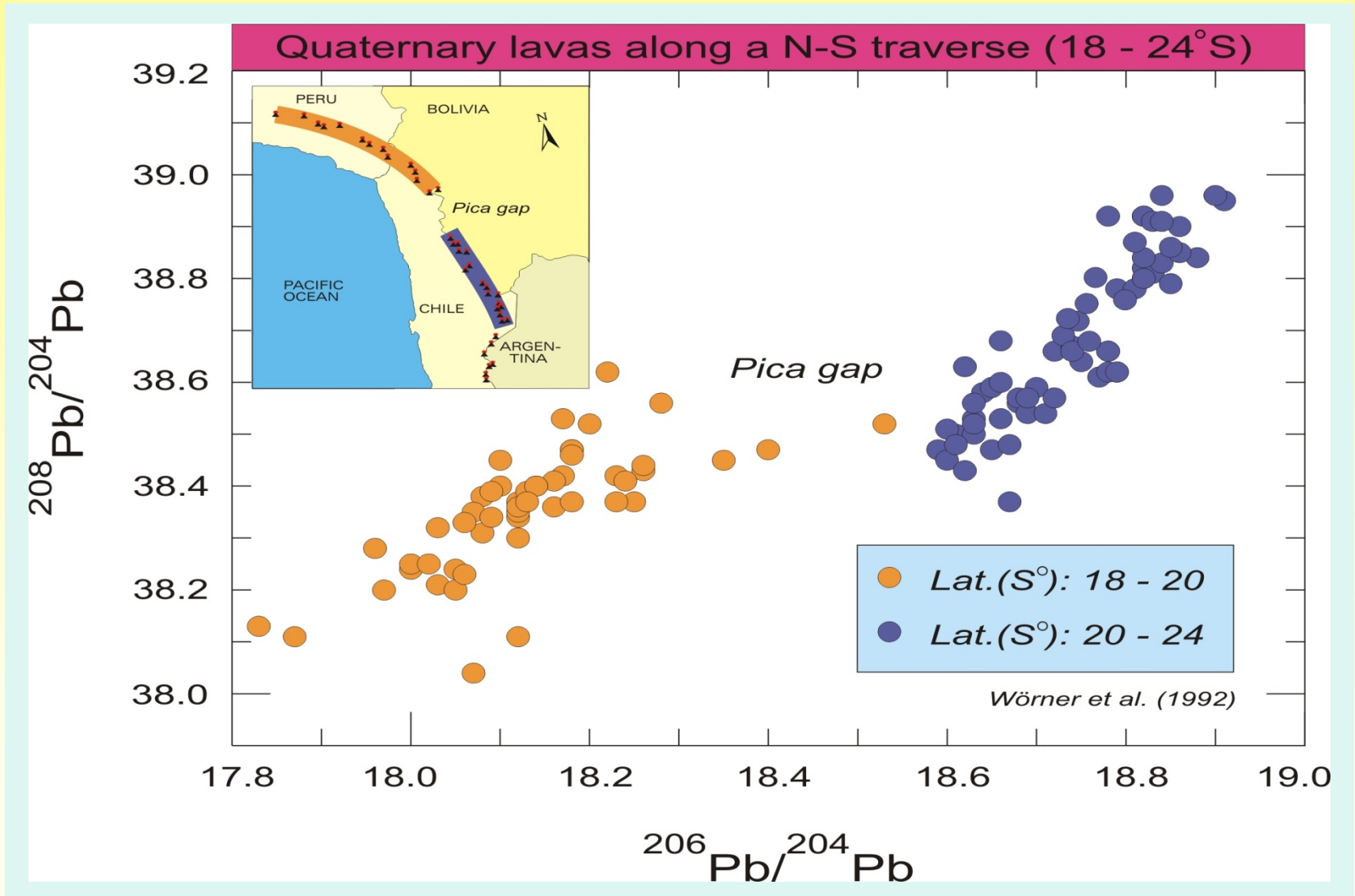
Alterierte ozeanische
Lithosphäre mit hoher
Bor-Konzentration

In Subduktionszone
entwässern Bor-haltige
Fluide \rightarrow temperatur-
abhängige) B-Isotopen-
fraktionierung

Frontale Arc-Magmatite
mit hohen Bor-Gehalten

in wässrigen Fluiden ($T > 50^\circ\text{C}$) ist Bor trigonal koordiniert – angereichert an ^{11}B

Bleisotope – andere Methode andere Aussagen

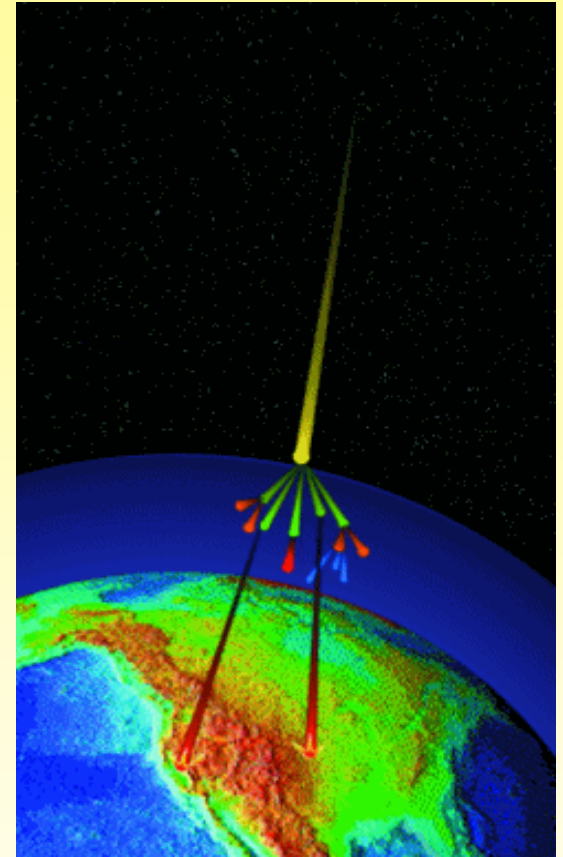


Cosmogene Nuklide

Discovery of cosmic-rays



Victor Hess
discovered the
„cosmic rays“ in
his balloon
voyages of
1911-1912
(received Nobel
Prize in physics
in 1936)

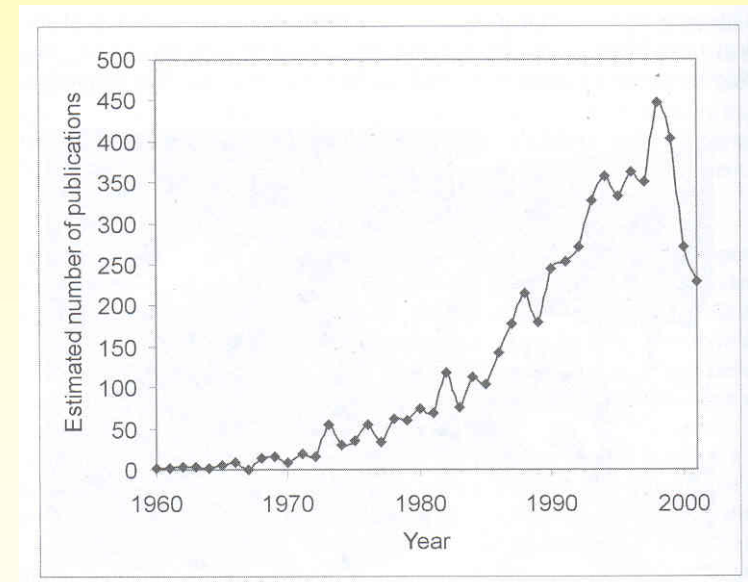


Libby introduced **radiocarbon dating** (^{14}C) in 1947 (Nobel Prize in 1960)

Discovery of ^{10}Be , ^7Be (1956-1957) Arnold (Chicago) Peters, Lal (Bombay)

Terrestrial cosmogenic isotopes

The “centre of mass” of many geoscience departments has shifted from solid Earth subfields towards surface processes (Bruce Watson, Elements 2009)

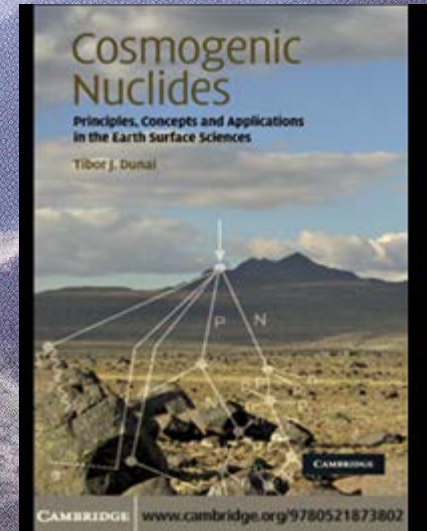
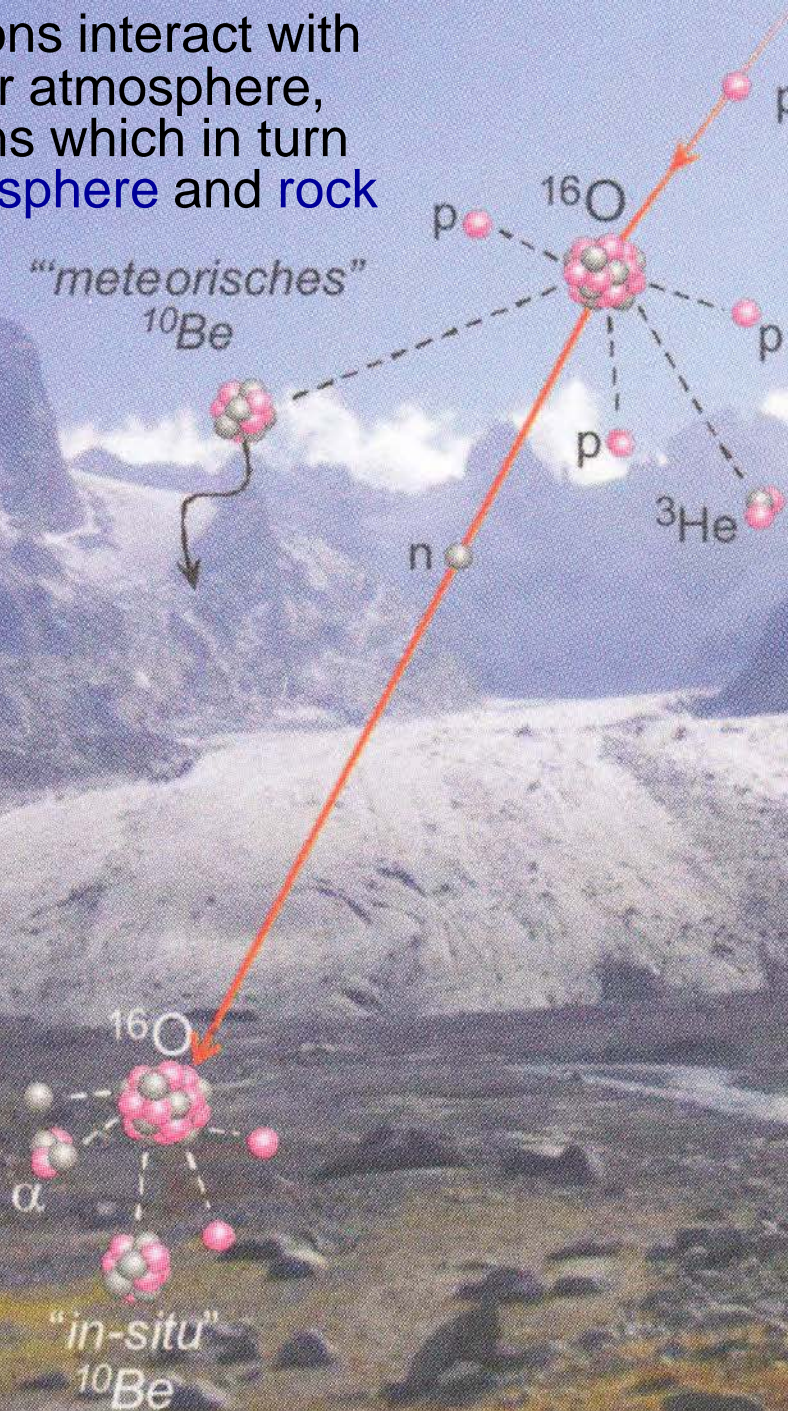


Cockburn & Summerfield 2004

Davis et al. 2003: papers containing “U-Pb” and “zircon” as key words

Cosmic rays protons interact with nuclei in the upper atmosphere, producing neutrons which in turn interact with atmosphere and rock surface

GMIT 33, 2008



Cosmic-rays

Galactic cosmic rays derive their energy from supernova explosions

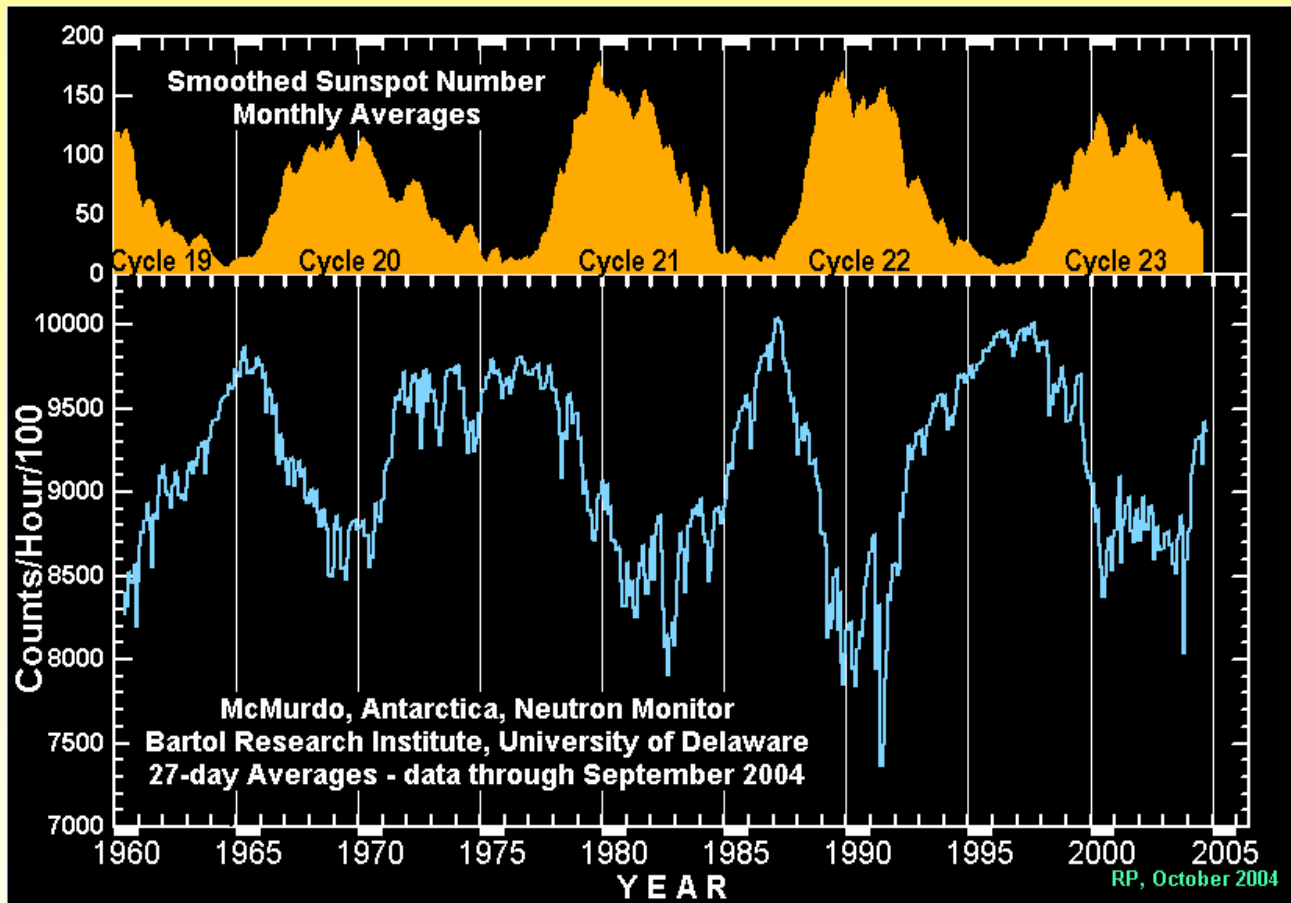
*Crab nebula
(Krebsnebel)*

Galactic cosmic rays: originate in sources outside the solar system, throughout our Milky Way galaxy.

Solar energetic particles: nuclei and electrons accelerated in association with energetic events on the Sun

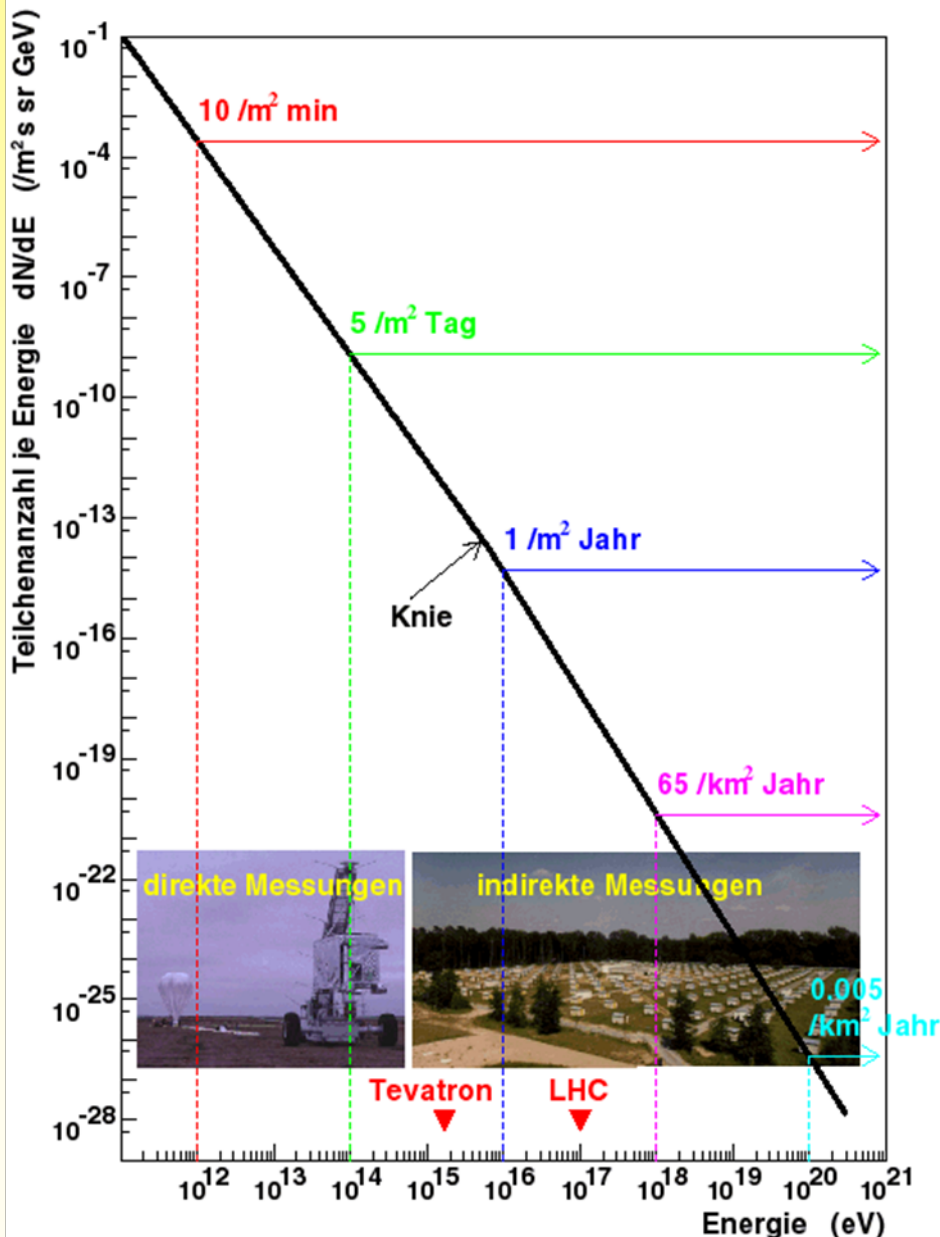


Variation of production rate



When the sun is active, we get fewer cosmic rays here

Energy of cosmic-rays



Components of galactic cosmic-rays

87-89% protons
 10-12% α -particles
 1-2% electrons
 1% heavier elements

Secondary cosmic-rays

Pions \rightarrow muons, neutrinos, γ -rays
 electrons
 positrons

Particle colliders

Tevatron, Fermilab, Chicago, USA
 LHC, CERN, Geneva, Switzerland

Cosmogenic isotopes

Major *in-situ* produced cosmogenic nuclides in terrestrial materials

Isotope	Production rate (atoms / g / year)	Half-life (years)	Target elements in terrestrial rocks
^3He	75 – 100 (olivine)	stable	O, Si, Al, Mg
^{10}Be	5 – 7 (quartz)	1.5×10^6	O, Si, Al, C
^{14}C	18 – 20	5730	C, O
^{21}Ne	18 – 21 (quartz)	stable	Mg, Na, Si, Al
^{26}Al	30 – 36 (quartz)	0.71×10^6	Si, Al
^{36}Cl	8 – 10 (basalt)	0.30×10^6	Cl, K, Ca
^{53}Mn	?	3.7×10^6	Fe

Cerling & Craig (1994) Annu. Rev. Earth Planet. Sci. 22

Major target minerals:

^3He : olivine, pyroxene hornblende

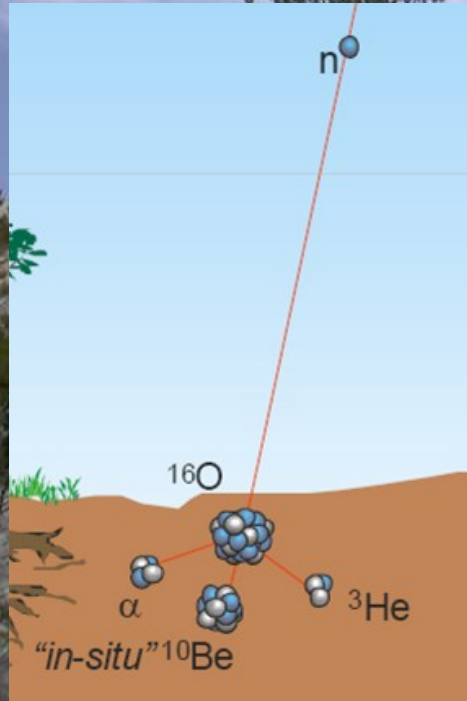
^{10}Be , ^{14}C , ^{21}Ne , ^{26}Al : quartz

^{36}Cl : calcite, K-feldspar

Cosmogenic isotopes are produced in near surface rocks by collisions of high energy neutrons and muons with specific target elements in rocks and minerals. All production rates scaled to sea-level high latitude (>60°)

Production of cosmogenic isotopes

Cosmic radiation



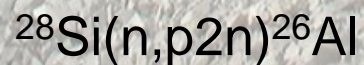
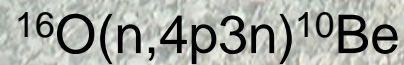
^{21}Ne

^3He

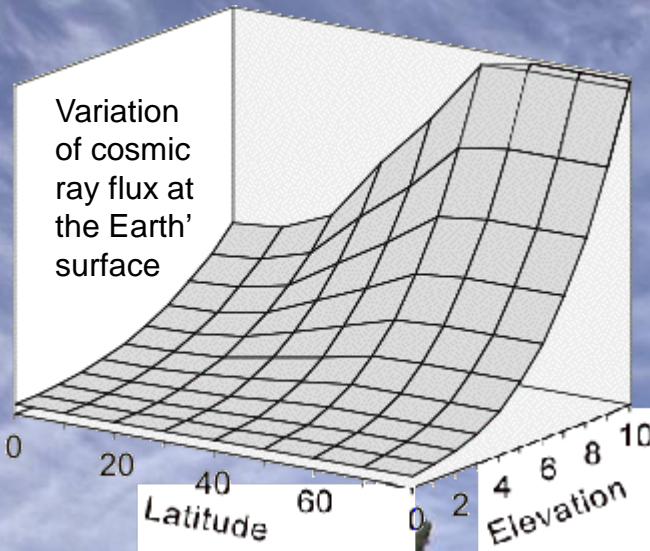
^{26}Al

^{10}Be

Spallation reactions:



Variation of production rate



The **rate of production** of cosmogenic isotopes depends on the concentrations of the target elements (O, K, Ca, Mg), elevation, surface orientation, and geomagnetic latitude

Comparison with redness of a person's skin (suntan)

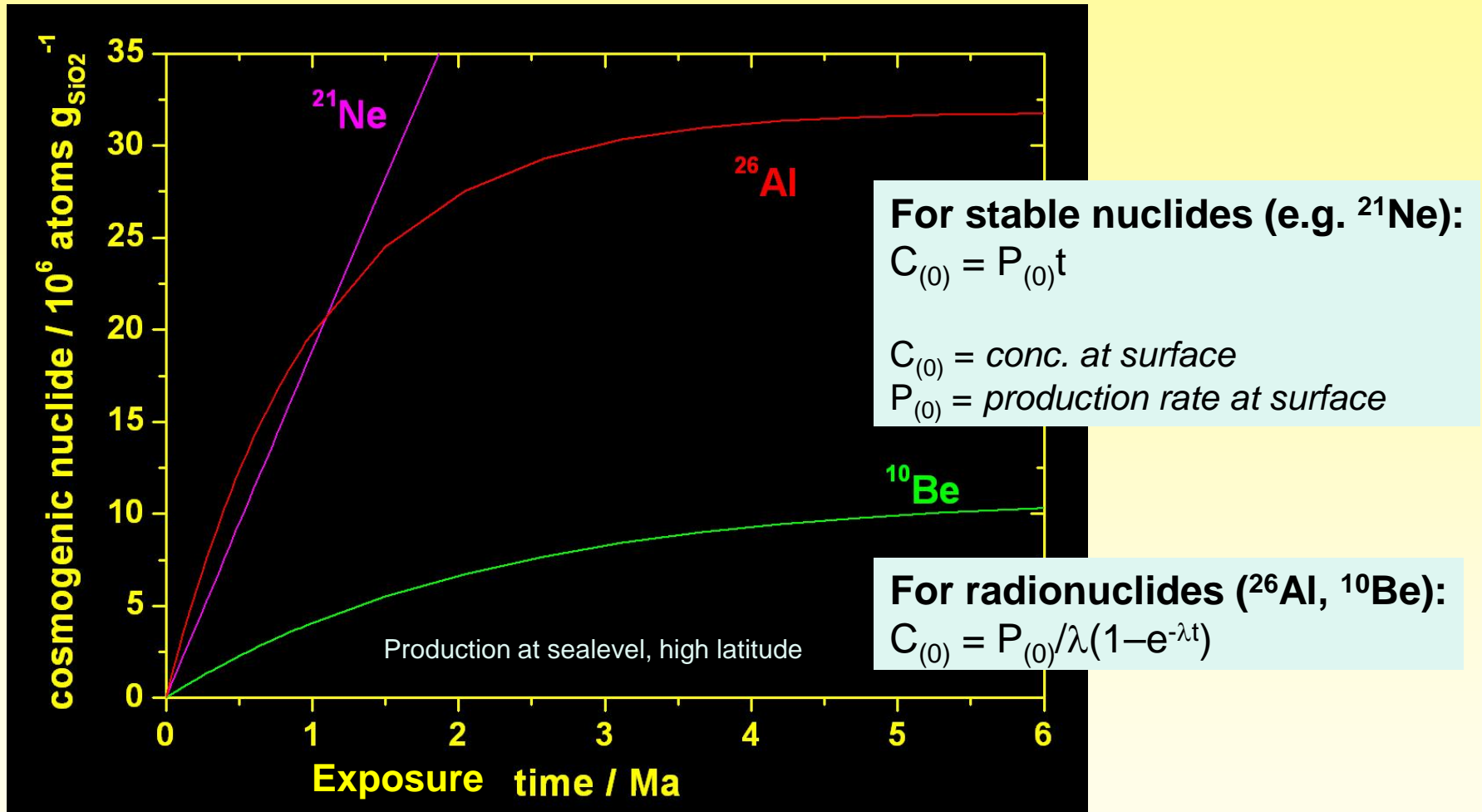
Gosse and Phillips (2001)

Suntan – wears away
Cosmogenic nuclide – decays

Suntan lotion shields skin from radiation
Atmosphere and snow shields a landform from radiation

Not everybody tans to the same degree of redness
Nuclide production varies in different minerals

Production rates



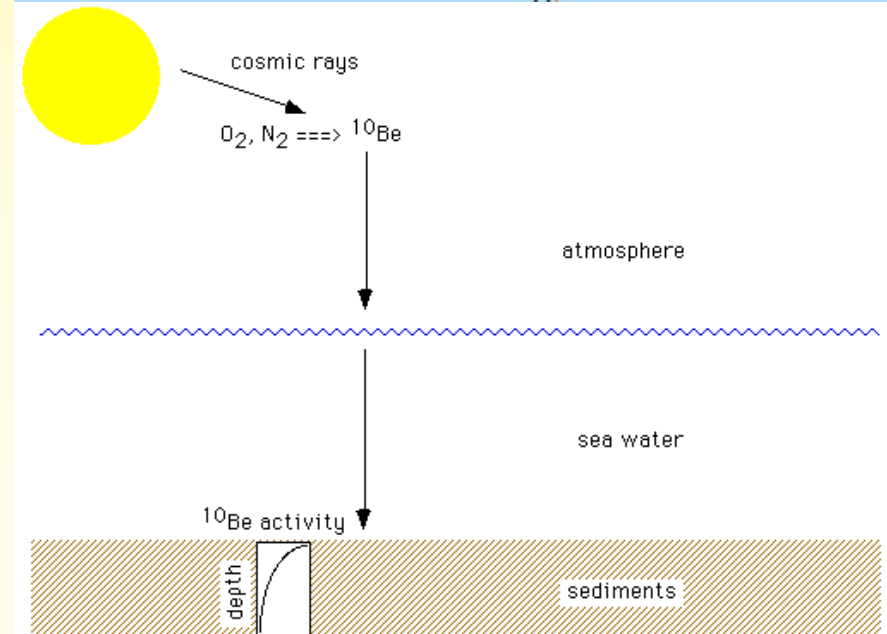
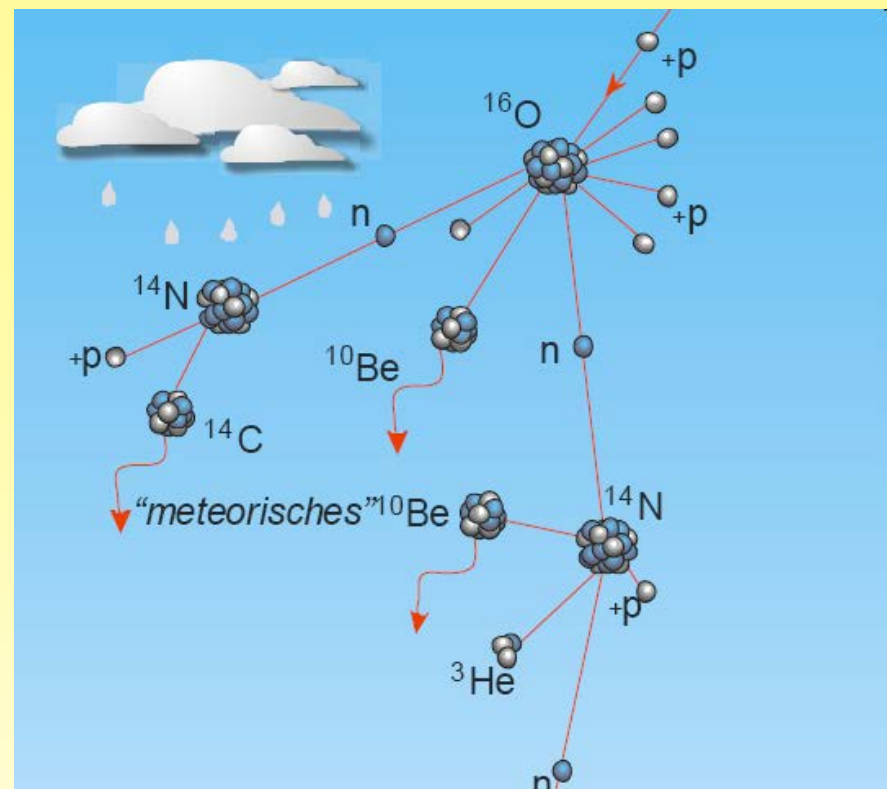
build-up of cosmogenic nuclides in case of **no erosion**

^{10}Be

^{10}Be is produced by reactions of cosmic ray protons with N_2 and O_2 in the upper atmosphere

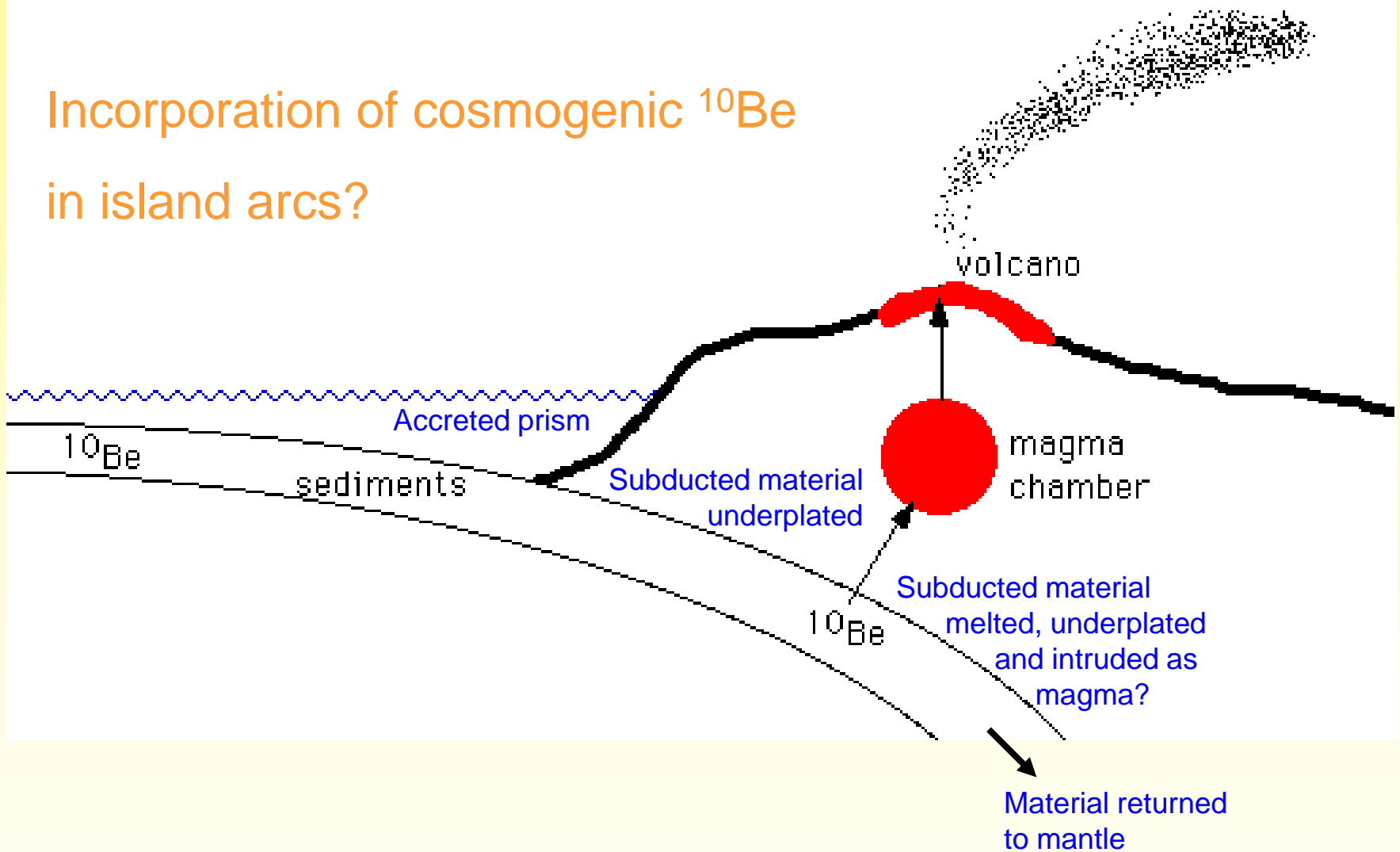
Be is a particle reactive element \rightarrow becomes concentrated in clay-rich oceanic sediments

^{10}Be then undergoes decay to ^{10}B with a half-life of about 1.5 Ma (long enough to be subducted, but quickly lost to mantle systems)



^{10}Be

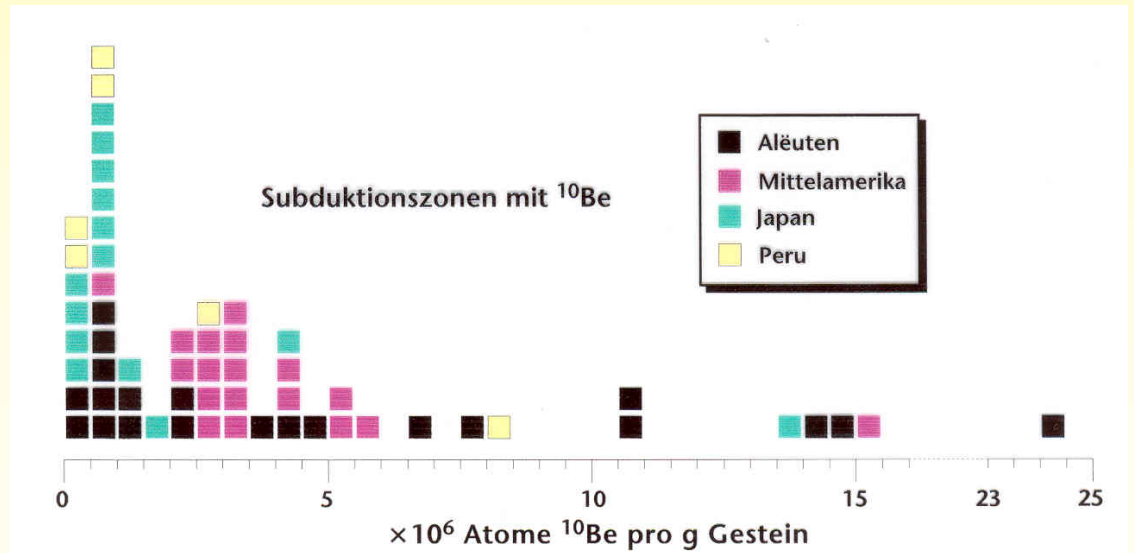
Incorporation of cosmogenic ^{10}Be in island arcs?



^{10}Be in arc lavas



Smoking gun evidence for sediment subduction



Measurement



Accelerator mass spectrometer

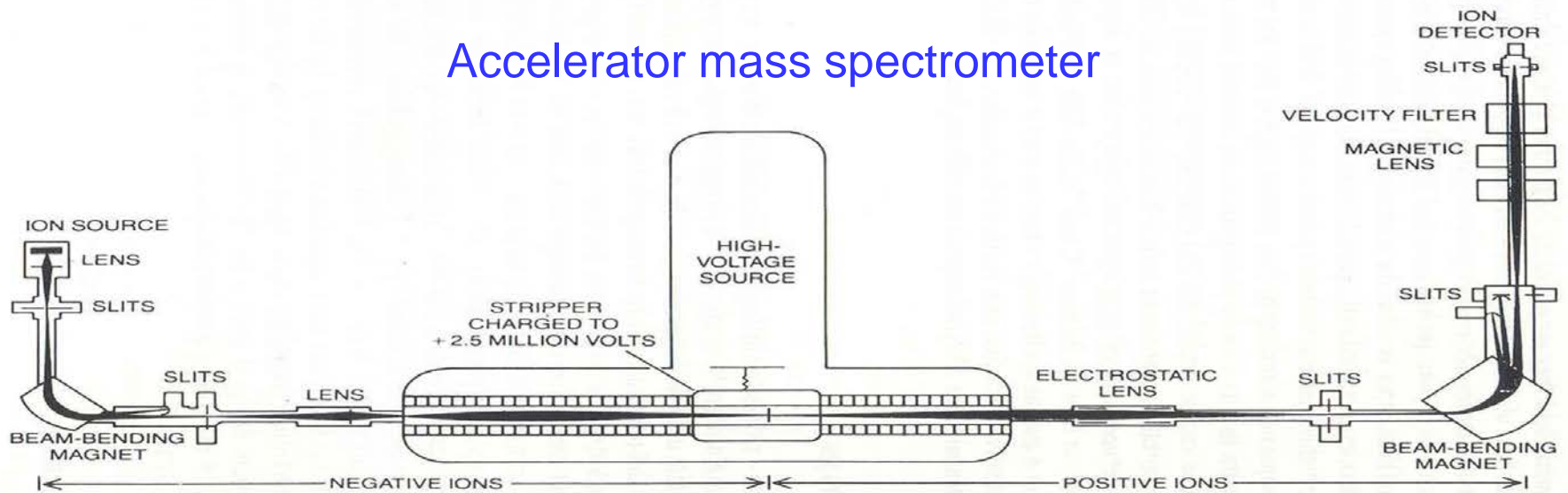
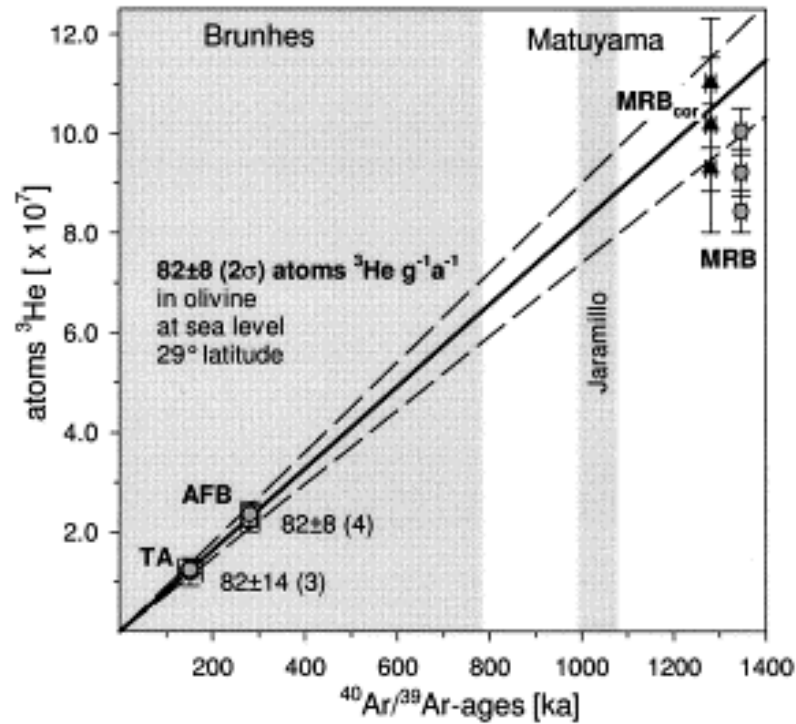


Fig. 37. Principal components of an accelerator mass spectrometer. (After Hedges and Gowlett 1986)

AMS has a factor of a million lower detection limit for ^{14}C , ^{36}Cl , ^{10}Be , ^{26}Al compared to counting methods

How to determine production rates of TCN?



Production rate of ^3He in olivine derived from 3 lava flows dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique at 152, 281 and 1350 ka (from Dunai & Wijbrans 2000).

Production rates

Nucleonic production profile with depth

$P(d)$:

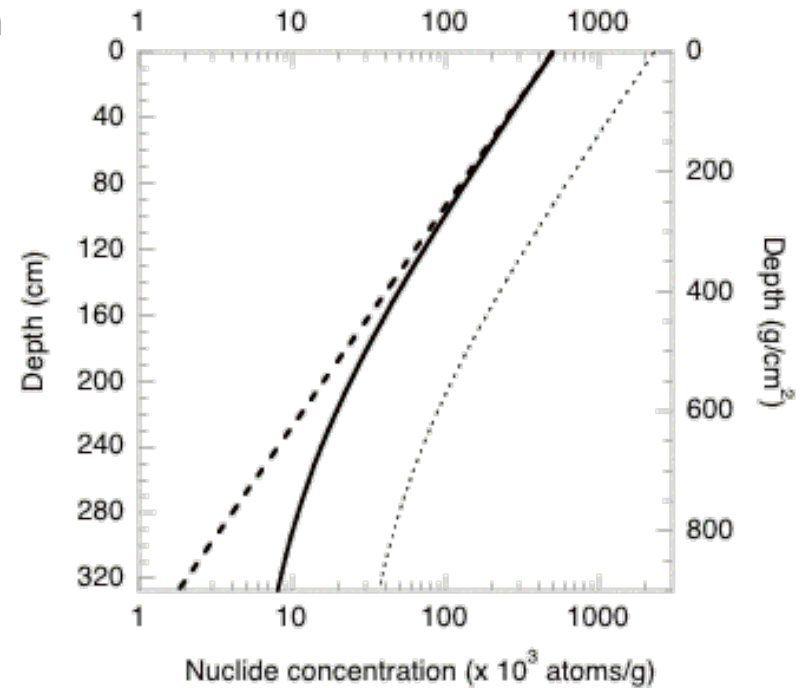
$$P(d) = P_{(0)} e^{-d/L}$$

$P_{(0)}$ = production rate at surface

d = depth

L = absorption length scale

$L = 160/\rho$ cm (ρ = overburden pressure)



^{10}Be concentration vs. depth after 100 ka exposure calculated for nucleon production (dashed line) and for combined nucleon and muon production (solid curve) with a surface production rate of $5.1 \text{ atoms g}^{-1} \text{ a}^{-1}$, a rock density of 2.75 g cm^{-3} and **no erosion**.

Production rates

Nucleonic production profile with depth

P(d):

$$P(d) = P_{(0)} e^{-d/L}$$

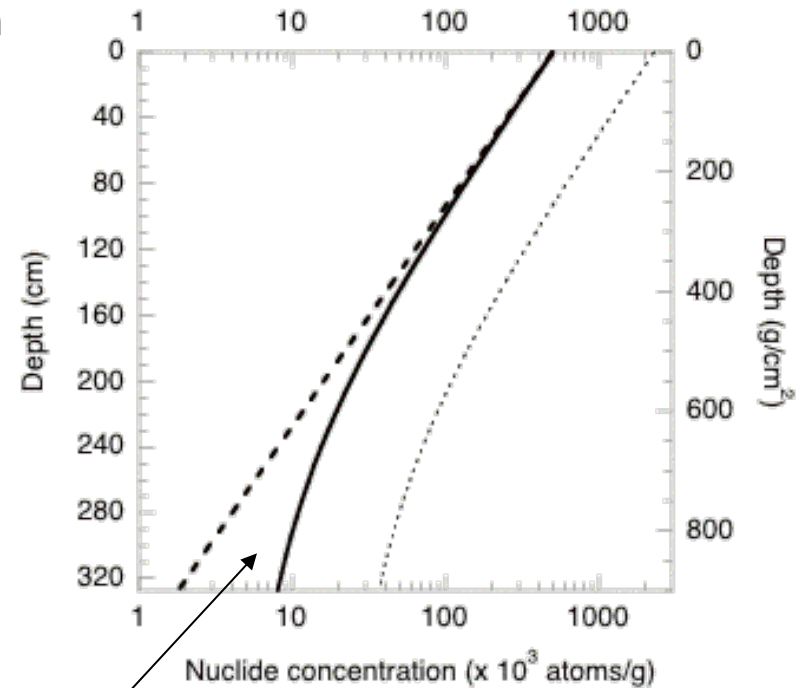
$P_{(0)}$ = production rate at surface

d = depth

L = absorption length scale

$L = 160/\rho$ cm (ρ = density of overburden)

In situ cosmogenic isotopes are produced near the surface of the earth because the cosmic flux is attenuated by rock at depths that exceed 2-3 m.



For nucleon and muon production (solid curve in fig.):

$$P(d) = P_{(0)} e^{-d/L_0} + P_{(1)} e^{-d/L_1} + P_{(2)} e^{-d/L_2} + P_{(3)} e^{-d/L_3}$$

Production rates

Production profile with depth $P(d)$:

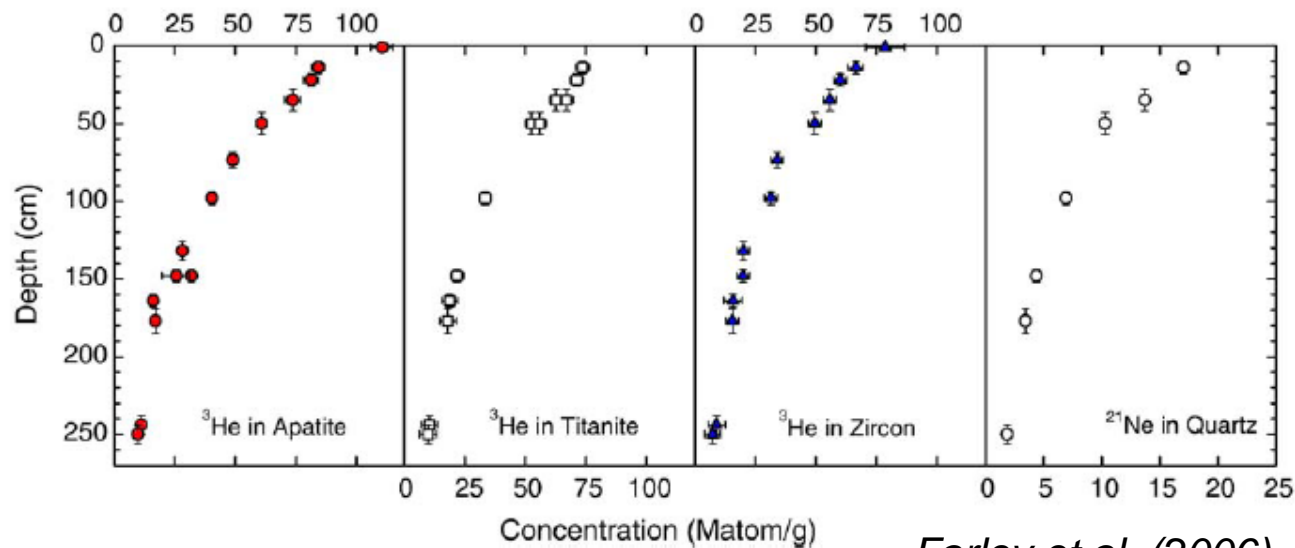
$$P(d) = P_{(0)} e^{-d/L}$$

$P_{(0)}$ = production rate at surface

d = depth

L = absorption length scale

$$P(d) = P_{(0)} e^{-d/L_0} + P_{(1)} e^{-d/L_1} + P_{(2)} e^{-d/L_2} + P_{(3)} e^{-d/L_3}$$



Farley et al. (2006)

Übung 1: Produktionsratenberechnung

^{23}Na wird bei einer konstanten Neutronenflußdichte von $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ in radioaktives ^{24}Na umgewandelt

Der Wirkungsquerschnitt beim Einfang thermischer Neutronen (*Neutroneneinfangsquerschnitt*) für diese Reaktion beträgt $0.53 \times 10^{-24} \text{ cm}^2$ pro Atom

Wieviel ^{24}Na Atome werden pro g Natrium und pro Sekunde produziert?

Übung 1: Produktionsratenberechnung

^{23}Na wird bei einer konstanten Neutronenflußdichte von 10^{12} $\text{cm}^{-2} \text{ s}^{-1}$ in radioaktives ^{24}Na umgewandelt: $^{23}\text{Na}(n,\gamma)^{24}\text{Na}$

Der Wirkungsquerschnitts für den Einfang thermischer Neutronen (*Neutroneneinfangsquerschnitt*) für diese Reaktion beträgt 0.53×10^{-24} cm^2 pro Atom

Wieviel ^{24}Na Atome werden pro g Natrium und pro Sekunde produziert?

Pro Sekunde werden $0.53 \times 10^{-24} \times 10^{12} = \mathbf{0.53 \times 10^{-12}}$

^{24}Na Atome produziert

Übung 1

In einer Sekunde werden $0.53 \times 10^{-24} \times 10^{12} = \mathbf{0.53 \times 10^{-12}}$

^{23}Na Atome produziert

1 Mol Na enthält 6.023×10^{23} Atome (Avogadro-Zahl)

Na hat das Atomgewicht 23 \rightarrow Gewicht von 6.023×10^{23} Atomen entspricht also 23 g

$\rightarrow 0.53 \times 10^{-12} \times 6.023 \times 10^{23} / 23 = \mathbf{1.387 \times 10^{10}}$ Atome ^{24}Na werden pro Sekunde pro g Natrium produziert

Übung 2: Berechnung der Probenmenge für Expositionsaltersbestimmung

^{10}Be Produktionsrate in Quarz: 5 Atome pro Jahr

Geschätztes Alter der Oberfläche 6000 Jahre

^{10}Be Konzentration in Quarz?

Für AMS Messung:

Gewünschtes $^{10}\text{Be}/^9\text{Be}$ -Verhältnis: 5×10^{-14}

gewünschte Menge an (reinem) BeO : 0.5 mg

Vieviel g Quarz wird für die Messung gebraucht?

Assuming no erosion....

...the exposure age can be determined using the following equation:

$$T = \frac{\ln(1 - C\lambda/P)}{-\lambda}$$

T = the length of irradiation (i.e., exposure age),

C = number of cosmogenically produced atoms

P = cosmogenic isotope production rate

λ = decay constant

Production rates, considering erosion

$$C = P_{\Lambda}/D$$

C = concentration of cosmogenic nuclide

P = production rate

Λ = penetration length scale

D = denudation rate

$$N_{(0)} = [P_{(0)}/(\lambda + \rho\varepsilon/L_0)]$$

$N_{(0)}$ = concentration at surface

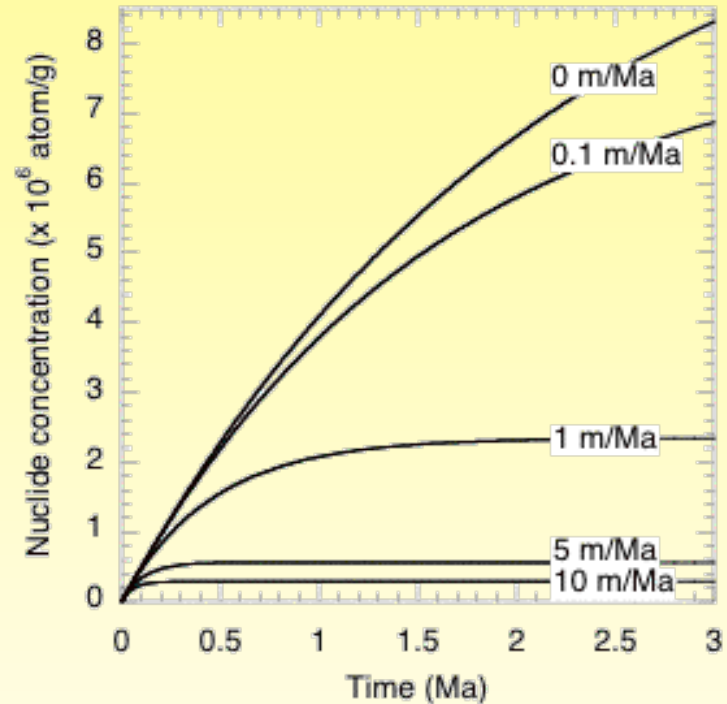
$P_{(0)}$ = production rate at surface

λ = decay constant

ε = (constant) erosion rate

ρ = density

L_0 = attenuation length



Surface concentration of in-situ cosmogenic stable isotope (¹⁰Be) for steady-state erosion rates ranging from 0 to 10 m/Ma.

Exposure age dating and erosion

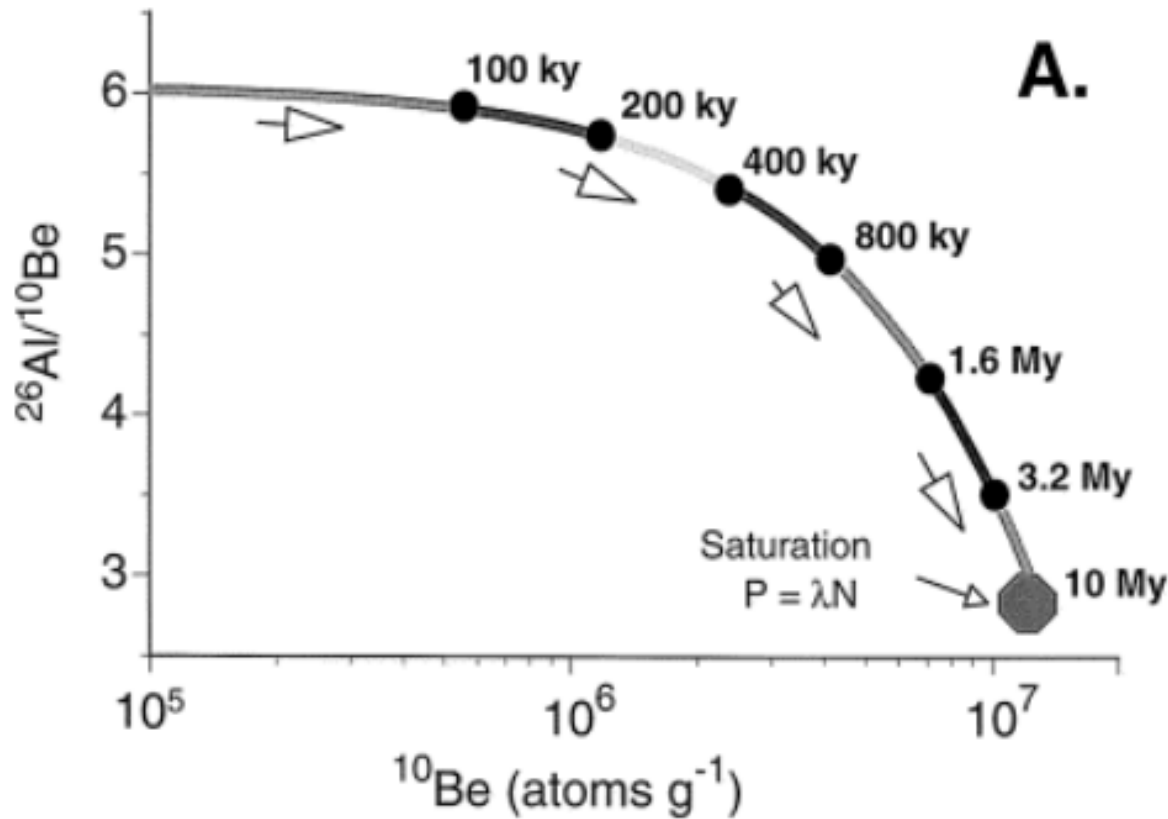
Assumptions:

- No *inheritance* of nuclide concentrations
- Steady state erosion or no erosion
- Simple exposure history (e.g. no shielding)
- Production rate can be constrained

Questions:

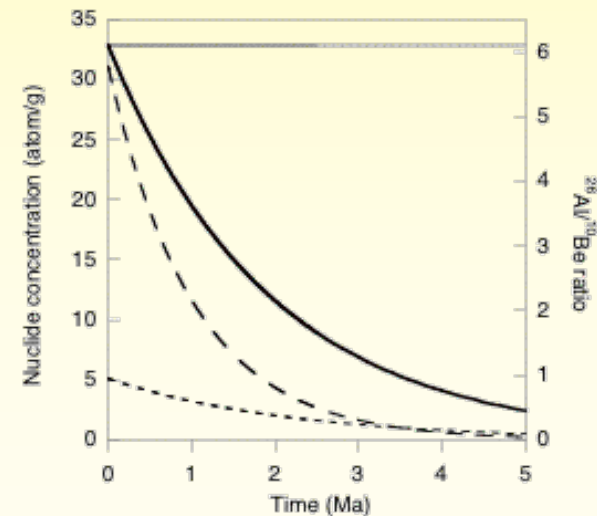
- Exposure age of a surface
- Exposure age of terraces (bedrock and deposits)
- Erosion rate of exposed bedrock
- Soil production rates

Banana plot 1/2

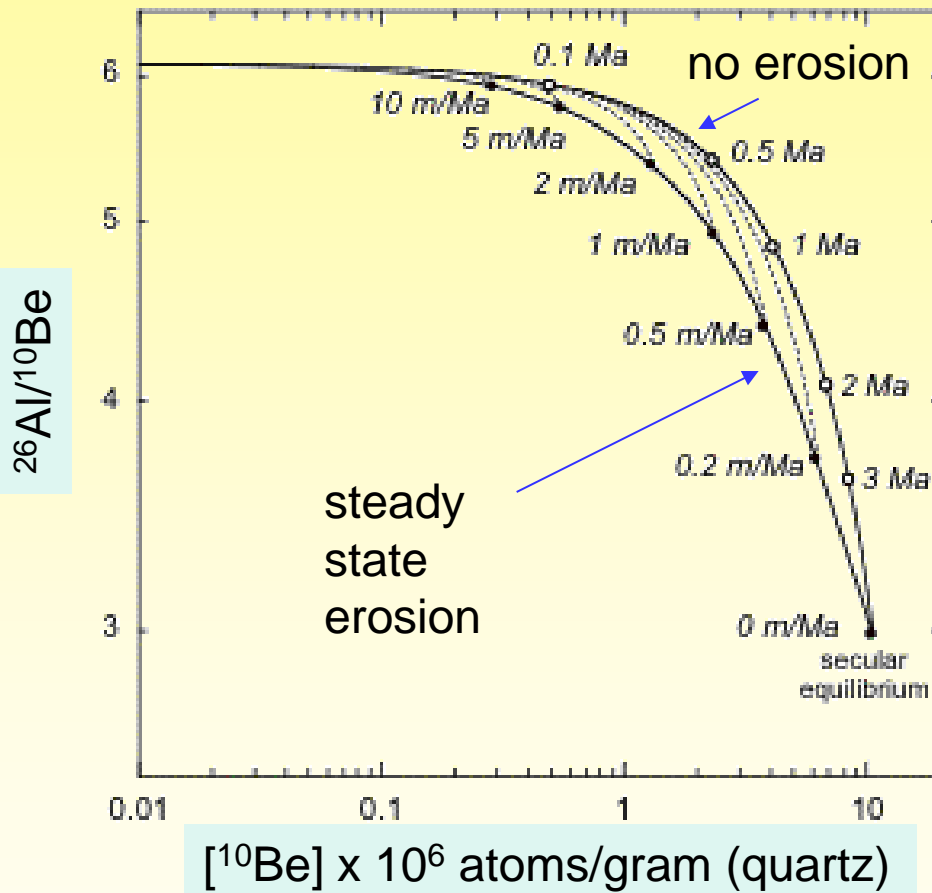


^{26}Al is produced six times faster than ^{10}Be , but ^{26}Al decays more quickly (half-life = 0.71 Ma) than ^{10}Be (half-life = 1.5 Ma)

The line is the isotopic trajectory of non-eroding sample exposed continuously at the surface. Numbers to right of curve are exposure ages. Trajectory ends at saturation where in situ production is equal to decay. In reality, saturation is rarely reached as nuclides are lost by surface erosion.



Banana plot 2/2



Continuously exposed samples fall on the curve connecting the open circles labelled with exposure time (same as in last figure)

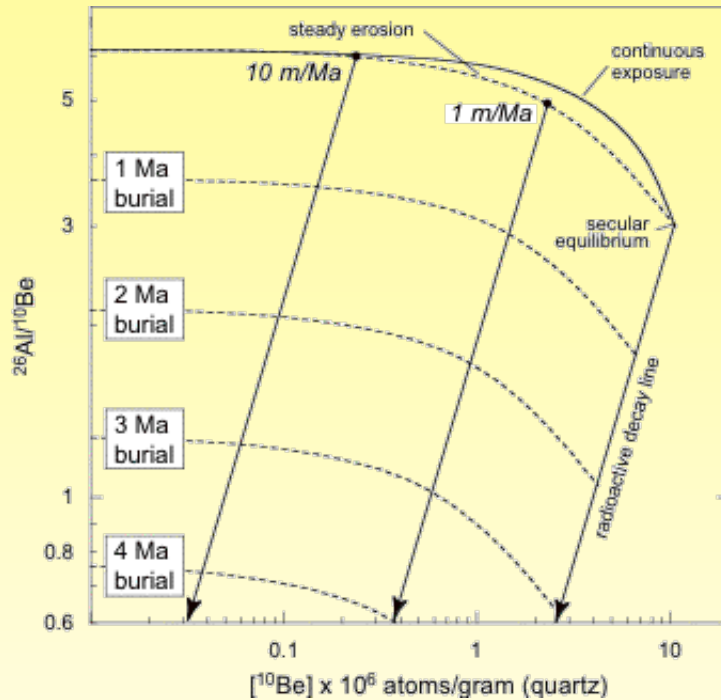
Steadily eroding samples lie on the lower curve connecting the labelled steady-state erosion end points (solid dots).

Dashed curves show the trajectory of samples within the ^{10}Be concentration vs. $^{26}\text{Al}/^{10}\text{Be}$ space for the given steady-state erosion rates.

Samples that have been shielded will plot below the "banana-window" i.e., below the line of steady-state erosion

Burial dating

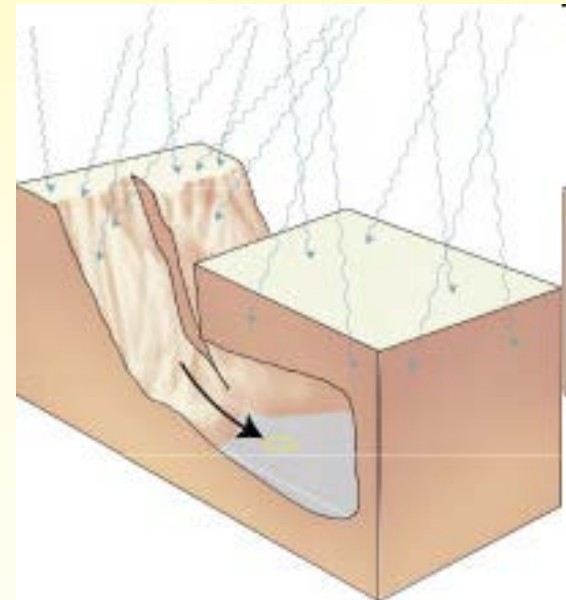
Burial dating plot



A mineral with no burial history should plot between the steady erosion and continuous exposure curves (i.e., in the “banana-window”)

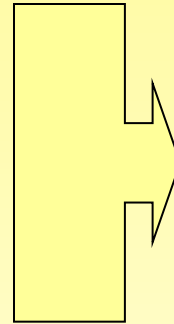
For completely buried and shielded minerals, the $^{26}\text{Al}/^{10}\text{Be}$ decreases along a line parallel to the solid "radioactive decay line".

Measured $^{26}\text{Al}/^{10}\text{Be}$ ratio in a sample determines the burial time, and can also be used to calculate the pre-burial erosion rate.



Applications

1. Dating Quaternary basalt volcanism
2. Timing of landslides
3. Tectonic displacement
4. Glaciers and ice-sheets
5. Meteorite impacts
6. Sedimentation rates
7. Ground water dating
8. (Sea water dating)
9. Age of landscapes
10. Erosion rates



Exposure age
dating

1. Dating Quaternary volcanism

Radiocarbon dating (if charcoal in between)
or: cosmogenic ^3He

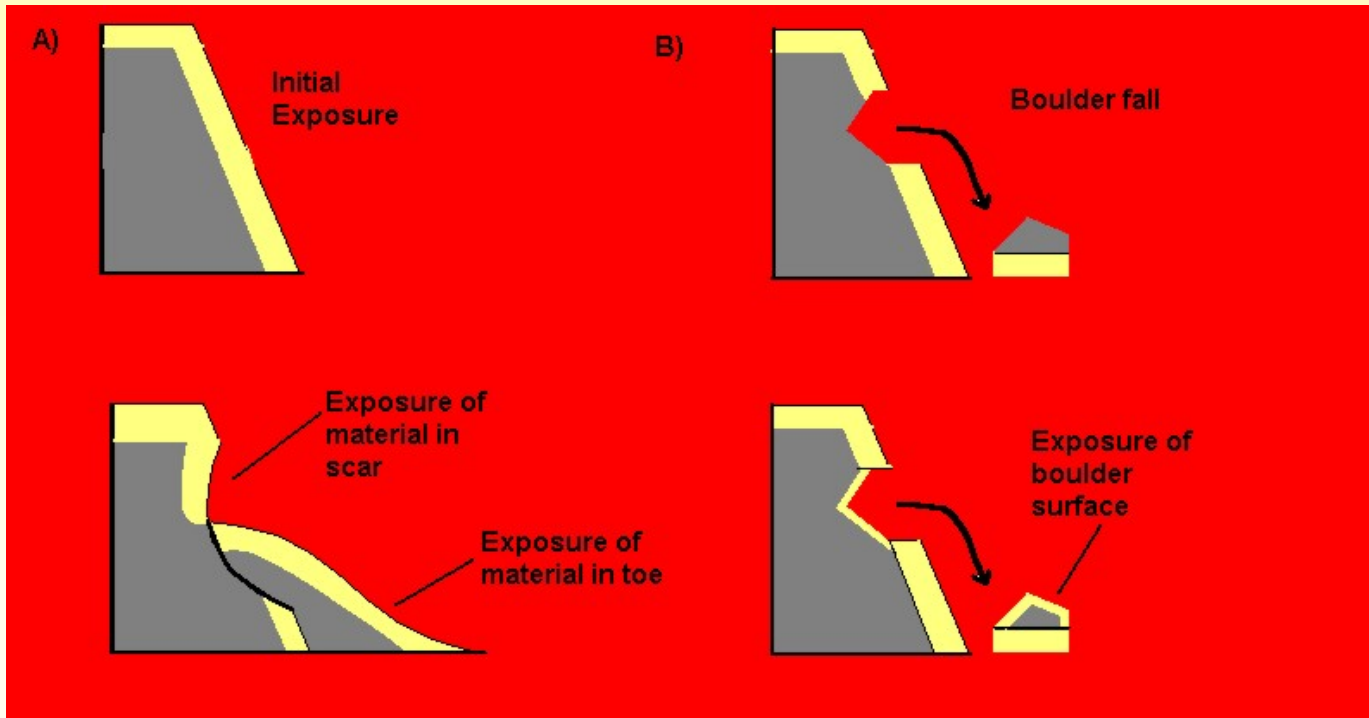


Lascar, N-Chile

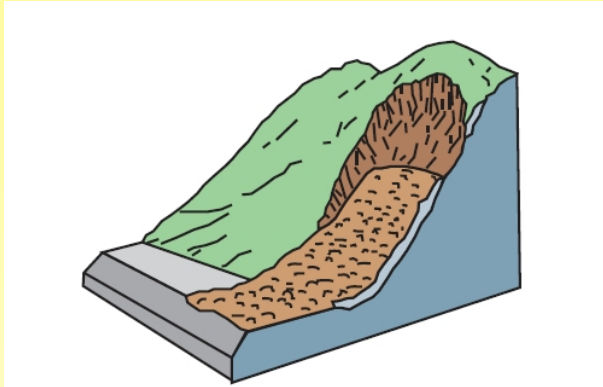
2. Timing of landslides

A: After landslide, cosmic rays build up in the rocks exposed in the landslide scar and on the surface of the deposit

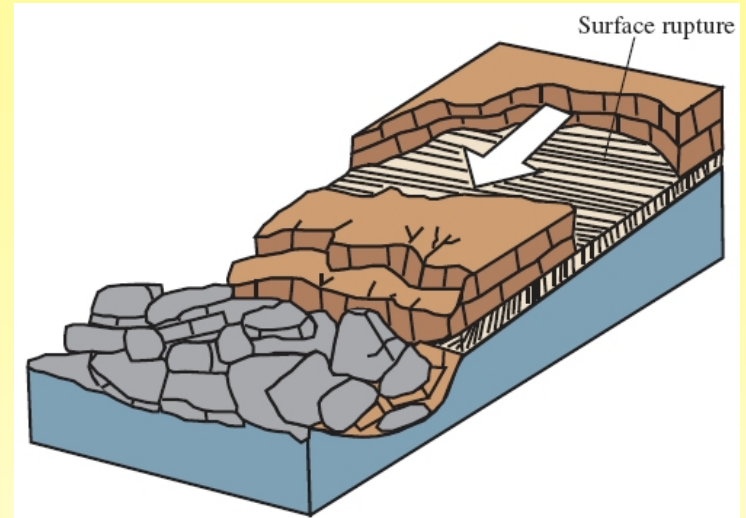
B: after boulder fall, cosmogenic isotopes build up on the upper surface of the boulder and in the scar left behind



2. Timing of landslides



La Conchita landslide (1995) California



Panoche Hills, California

2. Timing of landslides



3. Tectonic displacement

dating of ancient earthquakes

Movement along fault planes usually occurs during earthquakes.

Exposure ages increase from bottom to top, and can cluster into discrete groups or steps representing the episodic nature of faulting events.

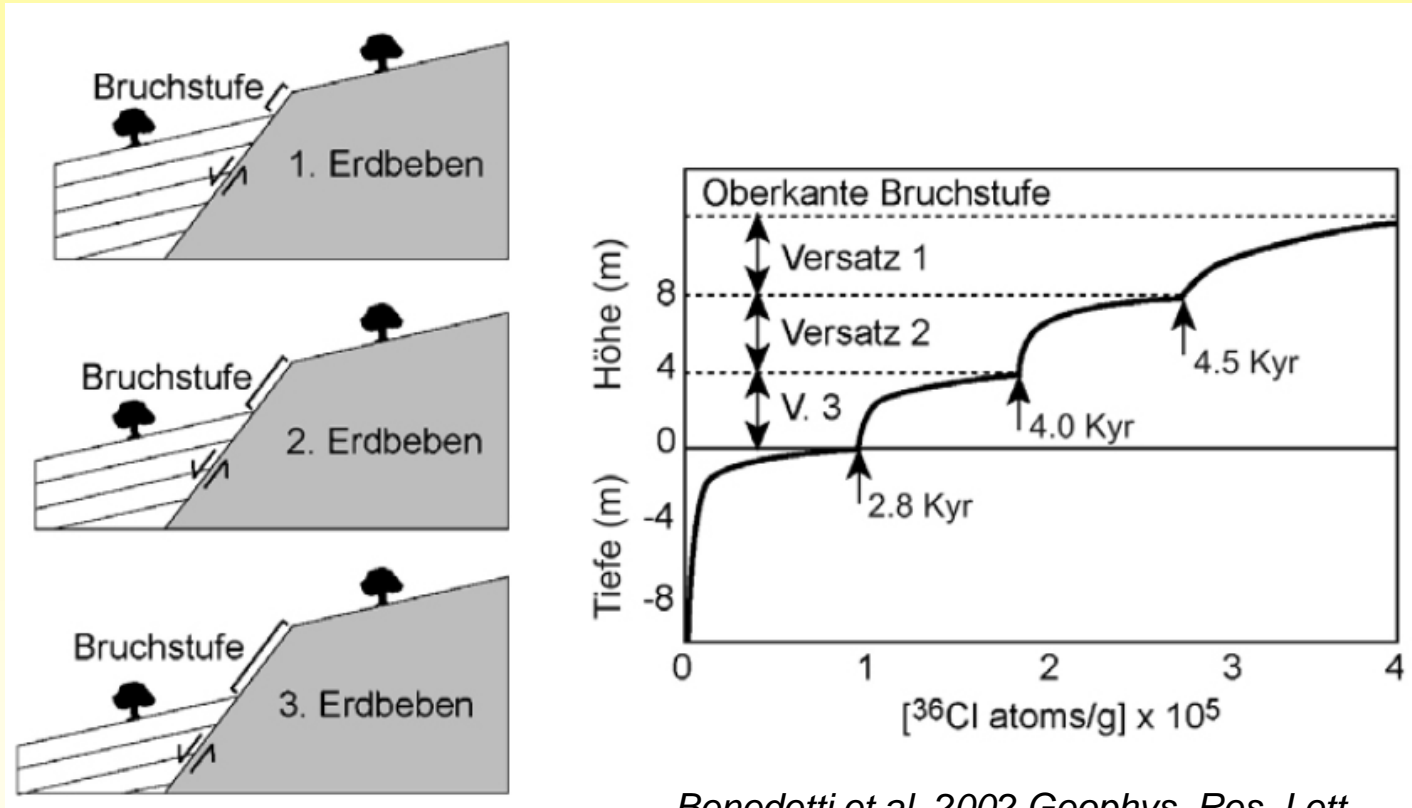
The number and magnitude and recurrence interval of the faulting events which produced the scarp can be determined.



(Zreda & Noller 1998, Science 282)

3. Tectonic displacement

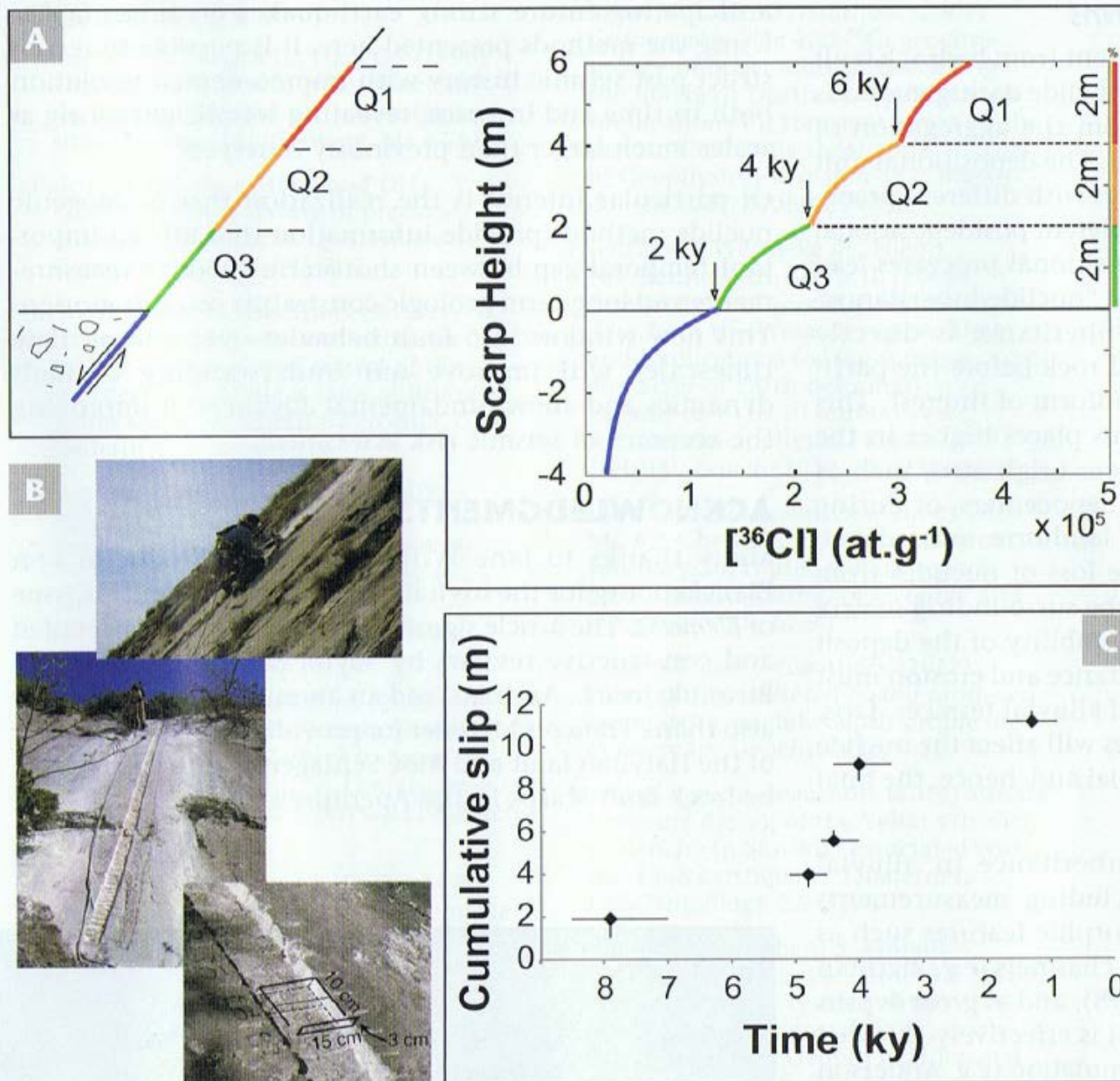
Sparta fault, Greece



Benedetti et al. 2002 Geophys. Res. Lett.

3. Tectonic displacement

Magnola fault, Apennines



Schlagenhauf et al.
(2011), EPSL 307

4. Glaciers and ice sheets



Courtsey H. Hann

4. Glaciers and ice sheets

Pasterzengunge, Großglockner (3798 m)



1900



2000

Assuming that boulders have been exposed continuously since the retreat of the ice, the glacial retreats can be dated

4. Glaciers and ice sheets

Morteratsch



1867

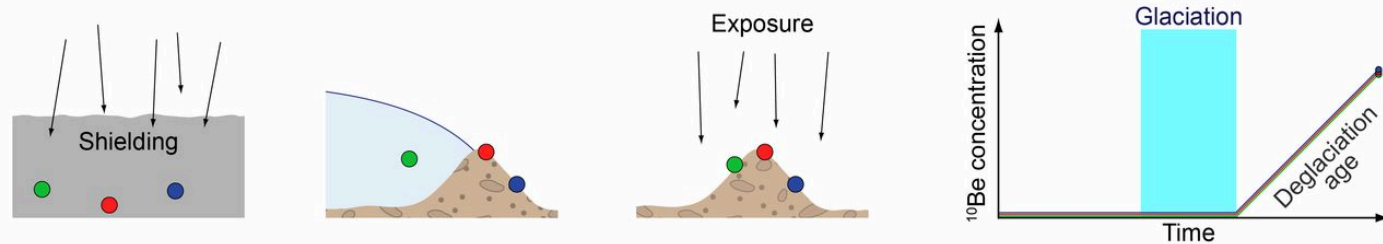


2007

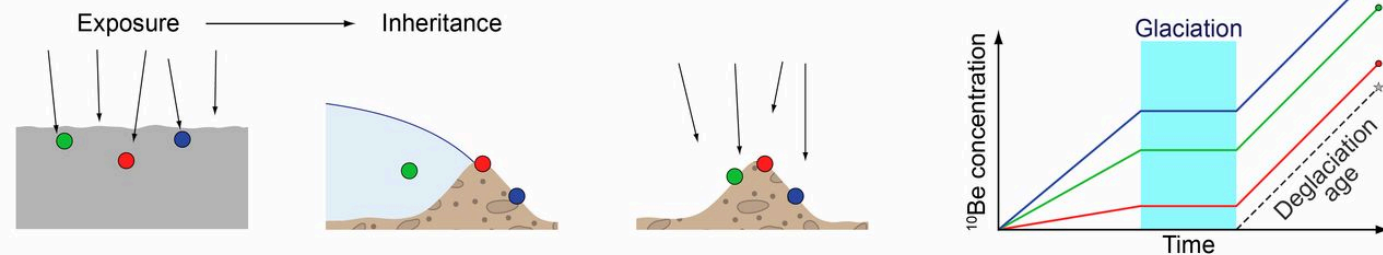
4. Glaciers and ice sheets



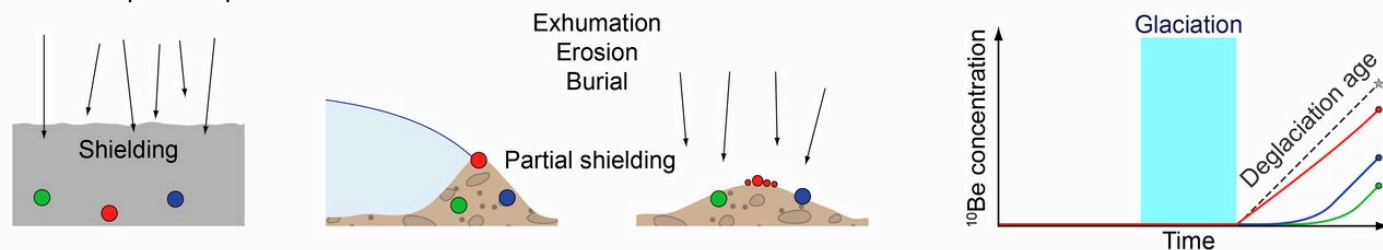
a Ideal case



b Prior exposure

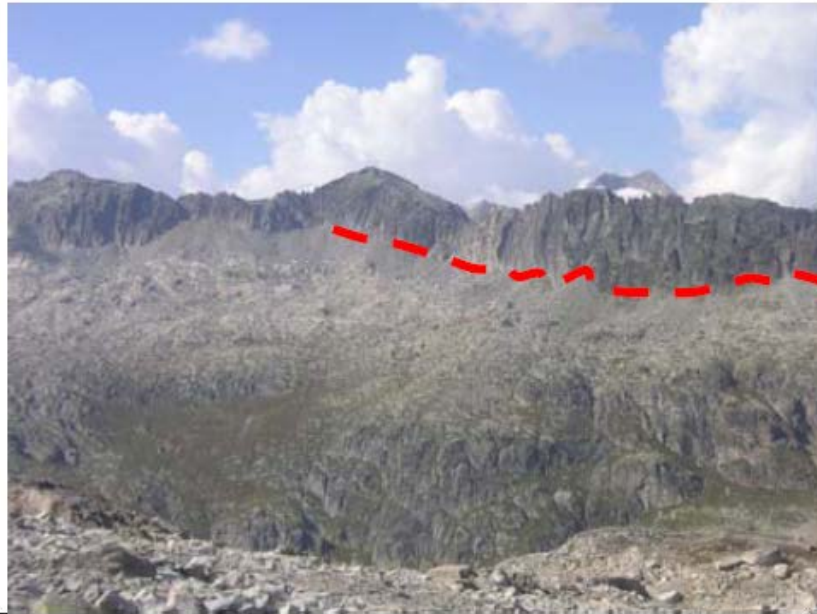


c Incomplete exposure



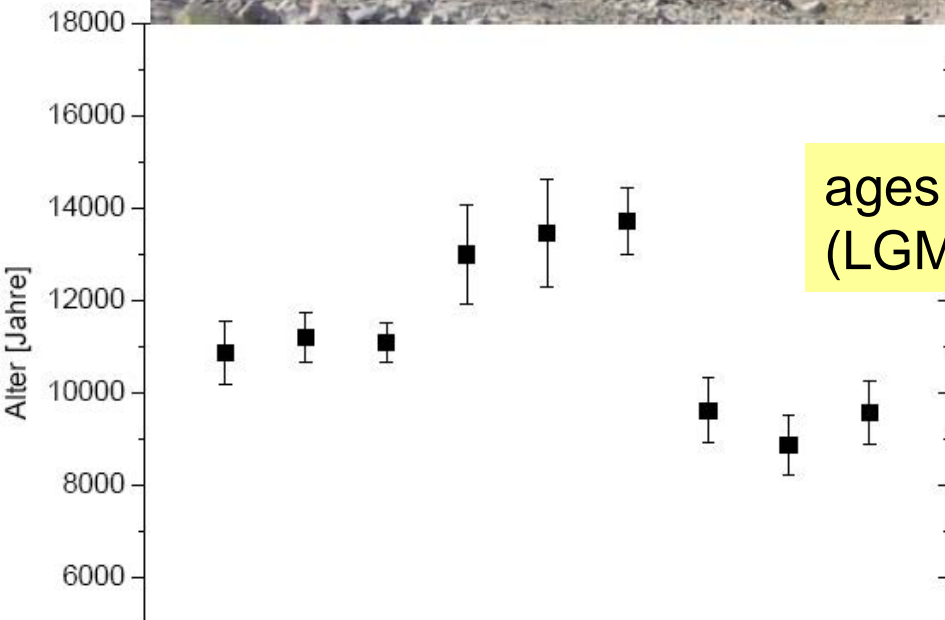
Ivy-Ochs & Briner:
Elements (2014)

4. Glaciers and ice sheets



Grimselpass, Schweiz

← former active ice surface



ages correspond to the last glacial maximum (LGM) → Younger Dryas

5. Meteorite impacts

Dating a hole in the ground



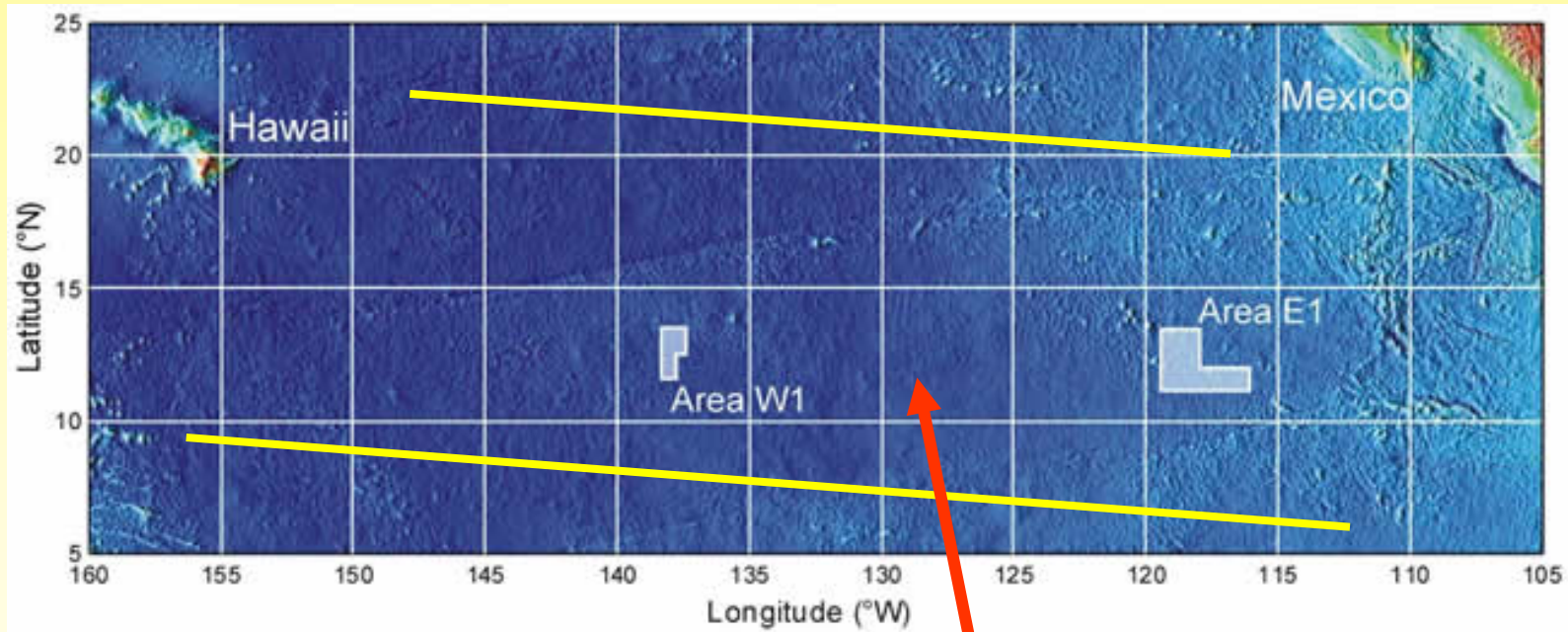
The Barringer Meteorite Crater of the Arizona desert.

49.2 ± 1.7 ka, based on ^{10}Be and ^{26}Al exposure age of samples from the crater walls and ejecta blocks at the crater rim (*Nishiizumi et al. 1991*).

49 ± 0.7 ka, based on ^{36}Cl exposure age of for dolomite ejecta on the crater rim (*Phillips et al. 1991*).



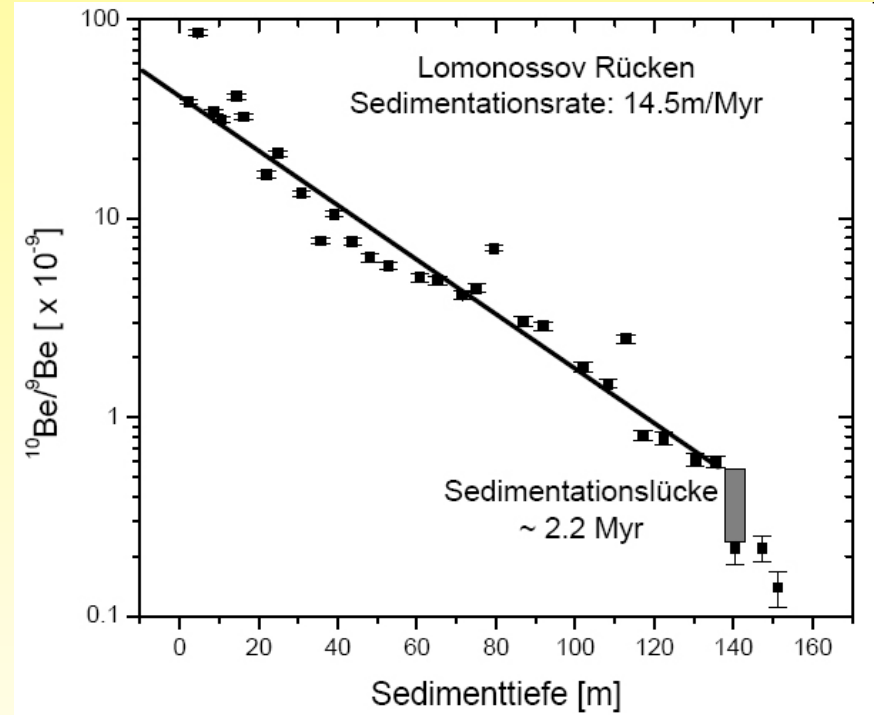
6. Sedimentation and growth rates



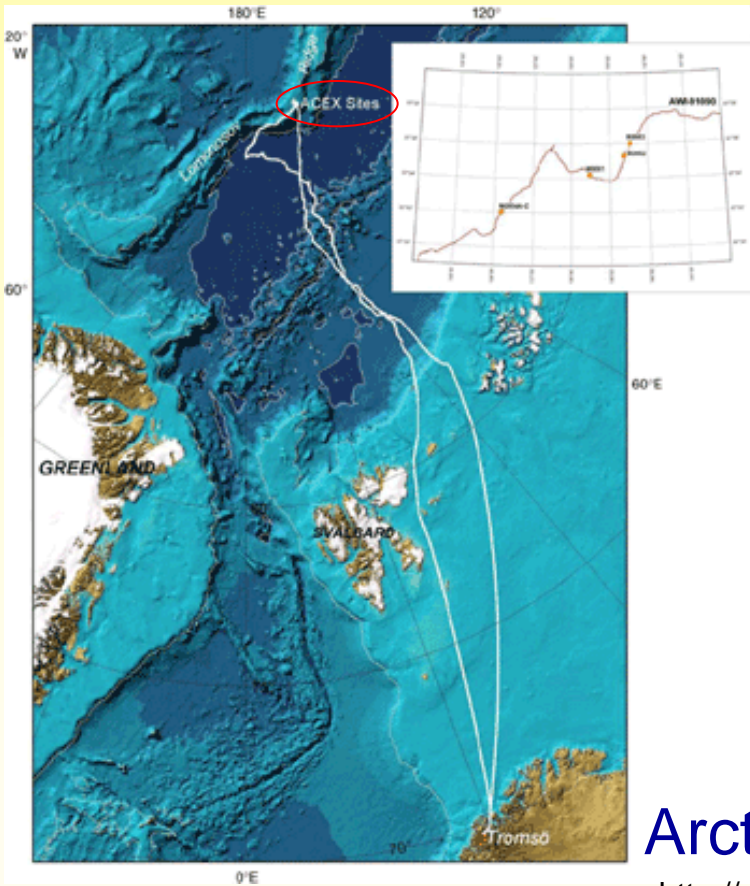
Manganese nodules

6. Sedimentation rates

The down-core decrease of $^{10}\text{Be}/^9\text{Be}$ yields an average sedimentation rate of 14.5 ± 1 m/Ma and a gap in sedimentation between 9.4 and 11.6 Ma



Frank et al. 2008



Arctic Coring Expedition 2004

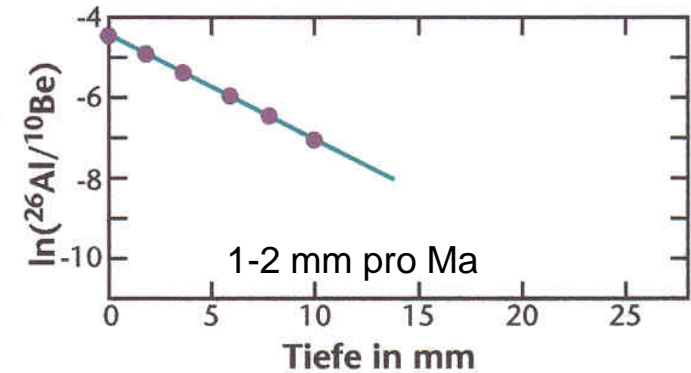
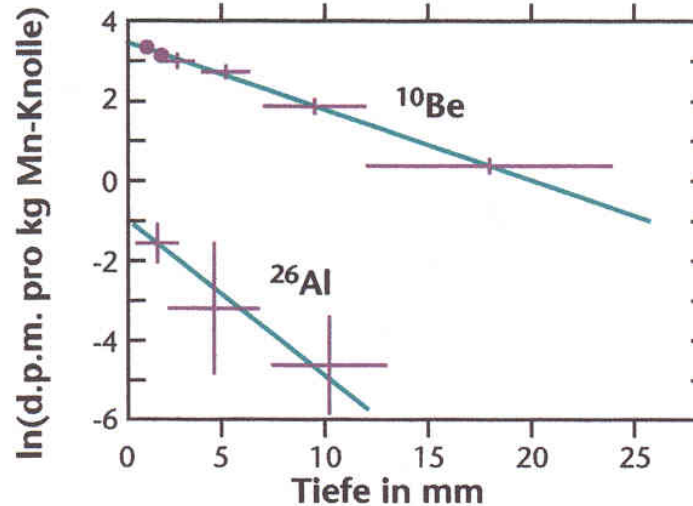
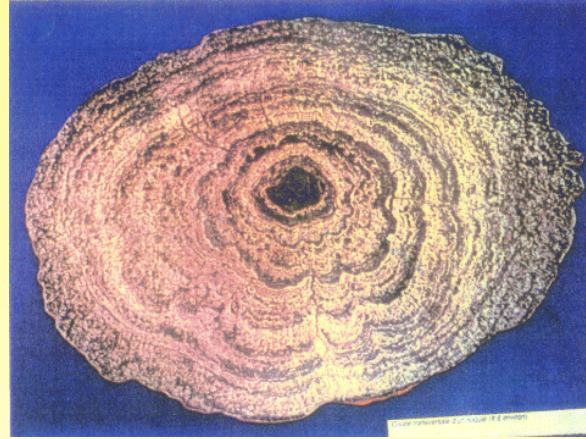
<http://www.eso.ecord.org/expeditions/302/302.htm>

6. Growth rates

Manganese nodules

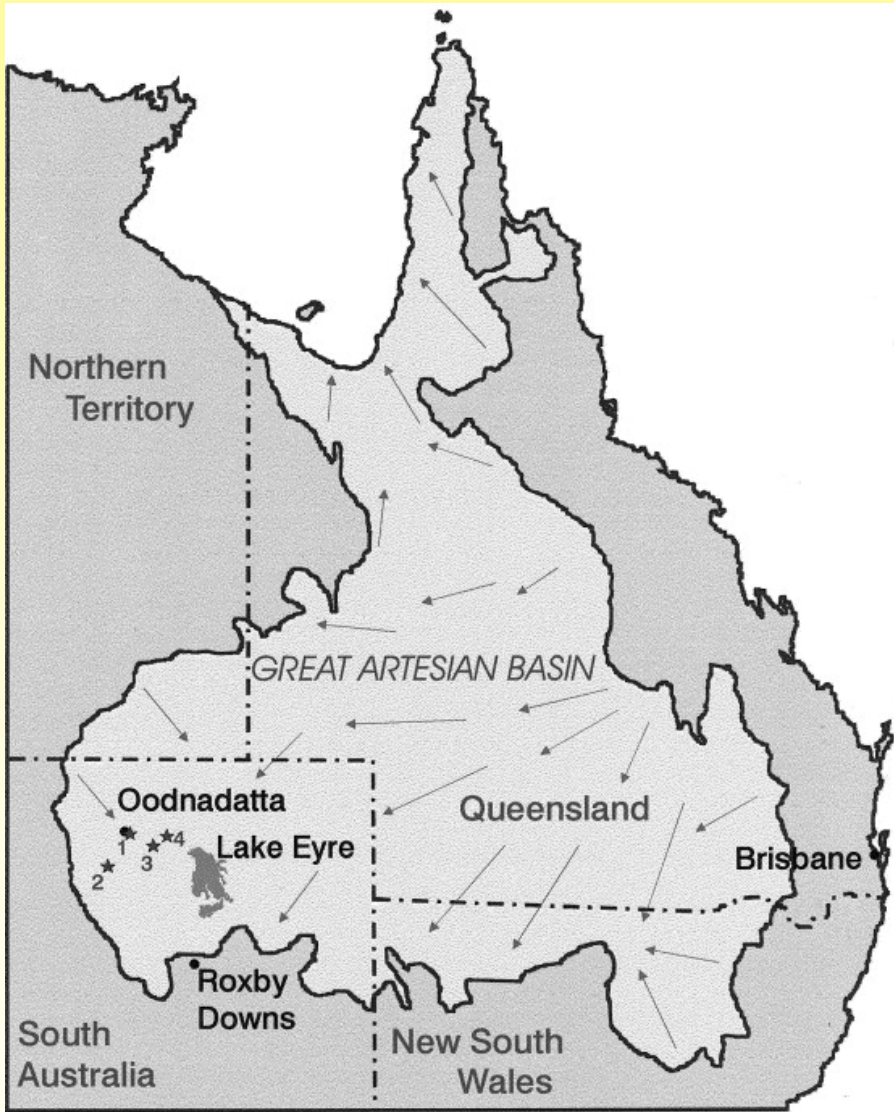
Manganese nodules are dark, potato-shaped little balls where metals and other minerals have accumulated around a core.

They contain a relatively high percentage of metals, i.e. **Nickel, Copper, Cobalt, Manganese** and **Iron** and are mostly found in water depths of 4000-6000 metres a few thousand km from the closest continent shores.



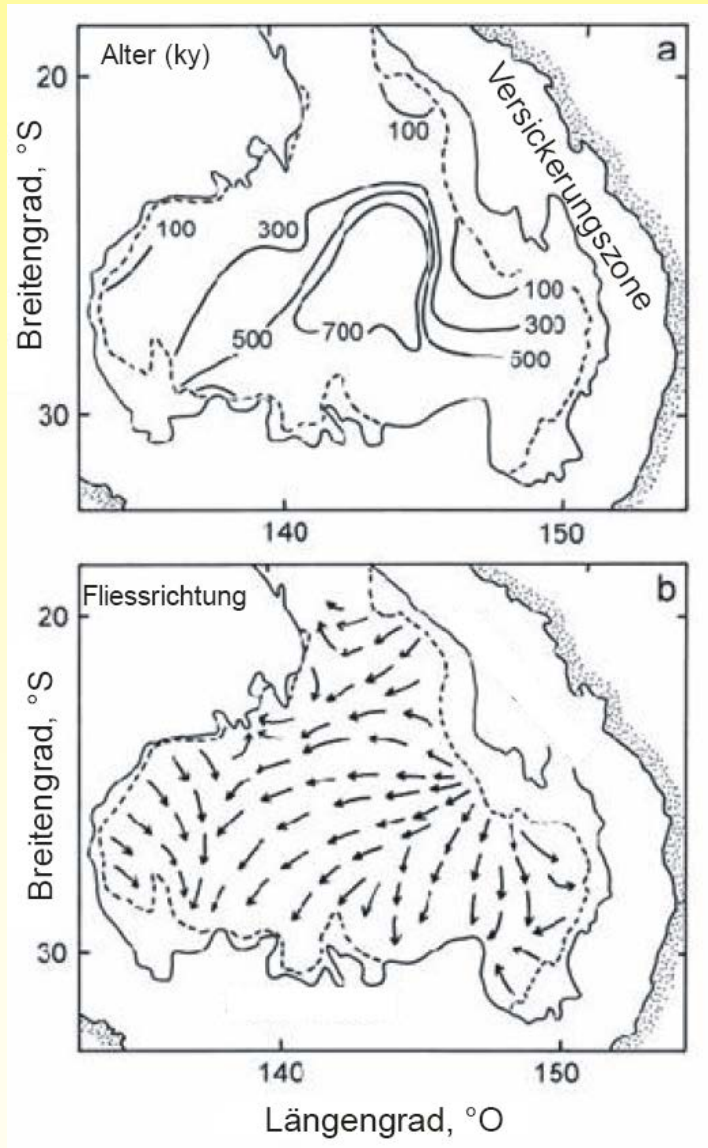
7. Ground water dating – ^{36}Cl

Great Artesian Basin (Eastern Australia)



7. Ground water dating – ^{36}Cl

Great Artesian Basin (Eastern Australia)

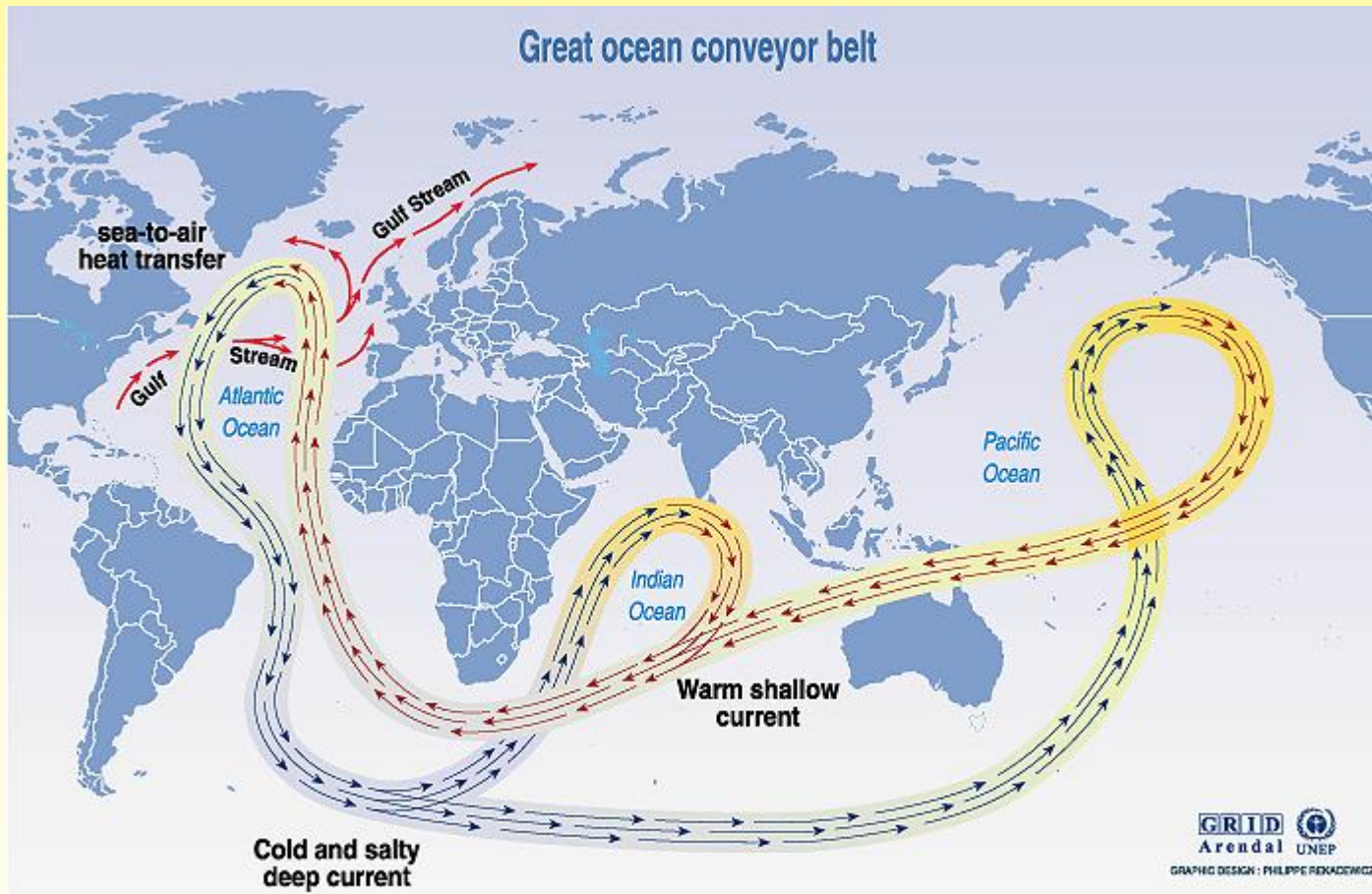


a) ^{36}Cl ground water dating (ages in 10^3 years)

b) reconstructed ground water flow directions

8. Sea water dating – ^{14}C

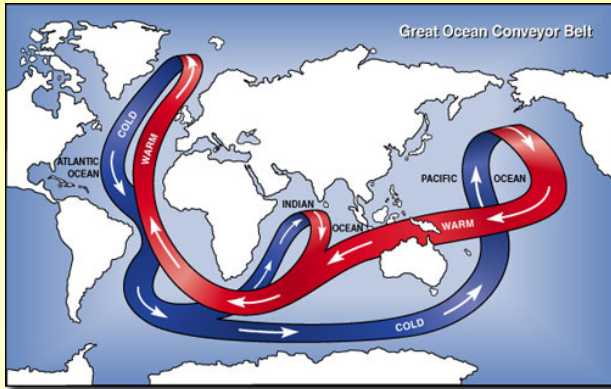
Great Ocean Conveyor



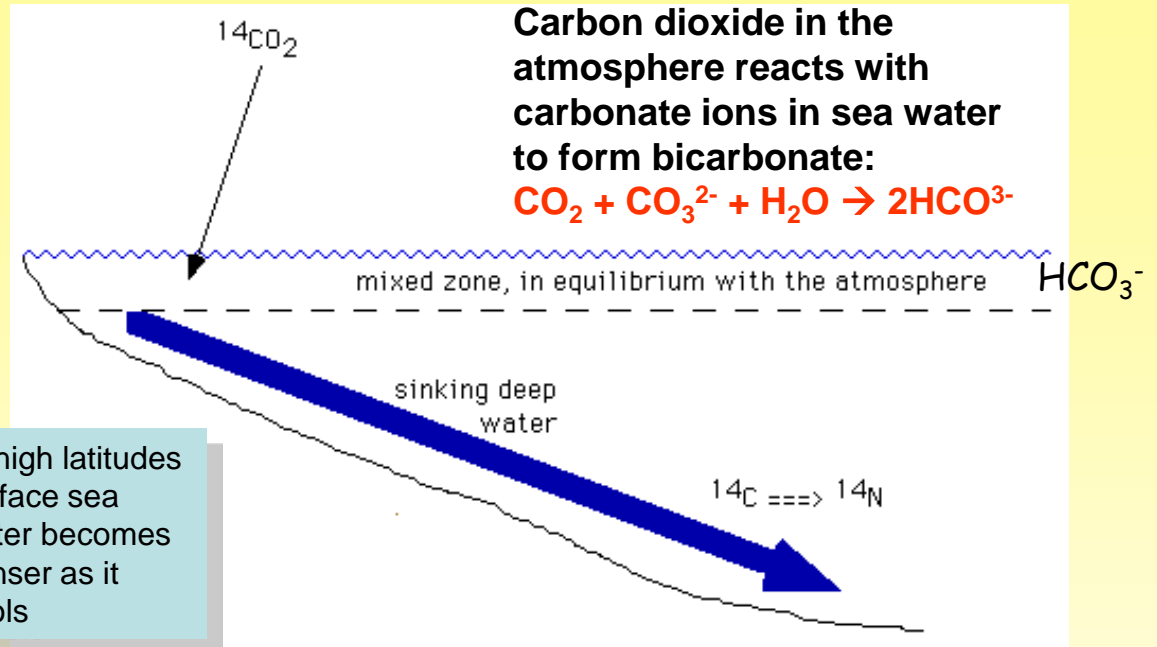
Source: Broecker, 1991, in *Climate change 1995, impacts, adaptations and mitigation of climate change: scientific-technical analyses, contribution of working group 2 to the second assessment report of the intergovernmental panel on climate change*, UNEP and WMO, Cambridge press university, 1996.

8. Sea water dating – ^{14}C

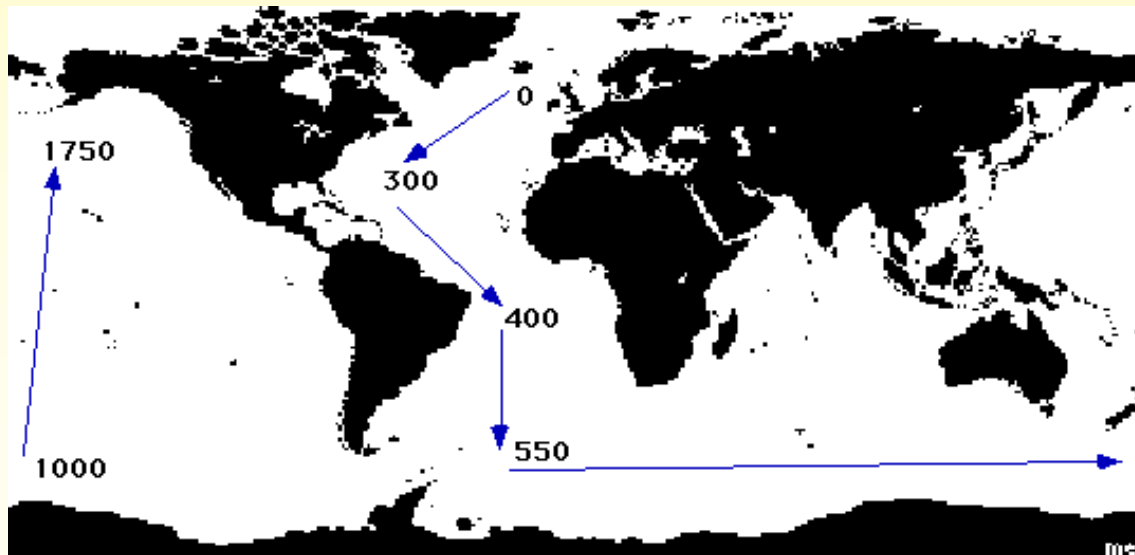
Great Ocean Conveyor



At high latitudes surface sea water becomes denser as it cools



The major source of this bottom water is in the North Atlantic

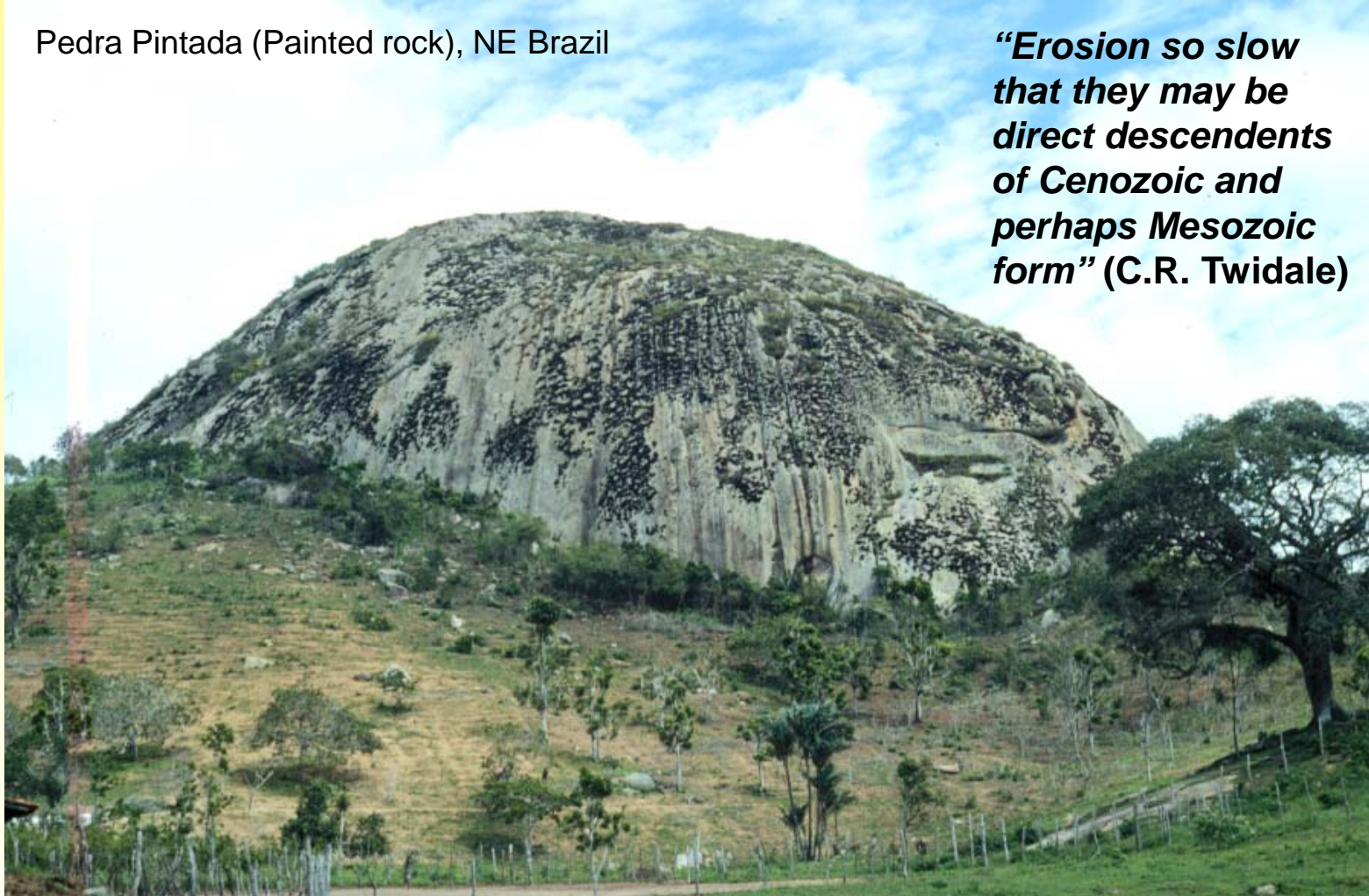


9. Age of landscapes

Tropical inselbergs

Pedra Pintada (Painted rock), NE Brazil

“Erosion so slow that they may be direct descendents of Cenozoic and perhaps Mesozoic form” (C.R. Twidale)



9. Age of landscapes

Arid environments

Inselbergs in the central Namib desert:
mean denudation rate of the order of 5 m/m.y.
(Cockburn et al., 1999)



Atacama desert, Chile:
~2 m/m.y. to <0.2 m/m.y.
(Caffee, 2005)



9. Age of landscapes

Martian surface: 78 ± 30 Ma (*Farley et al. 2013 Science 24*)



10. Erosion rates

How many years must a mountain exist
Before it is washed to the Sea?

The answer, my friend, is blowing in the wind...

Bob Dylan's song cited in:

Cerling and Craig (1994): *Annu. Rev. Earth Planet. Sci* 22: 273-317

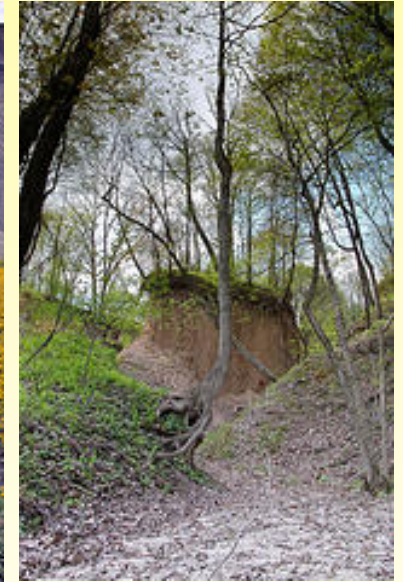
...for geomorphologists the answer is provided
by cosmogenic isotopes...

10. Erosion rates

What processes regulate **chemical weathering** and **physical erosion**?

What are the driving forces for landscape denudation?

Climate?
Precipitation?
Tectonics?
or combination?



Does erosion drive weathering or does weathering drive erosion?

10. Catchment wide denudation rates

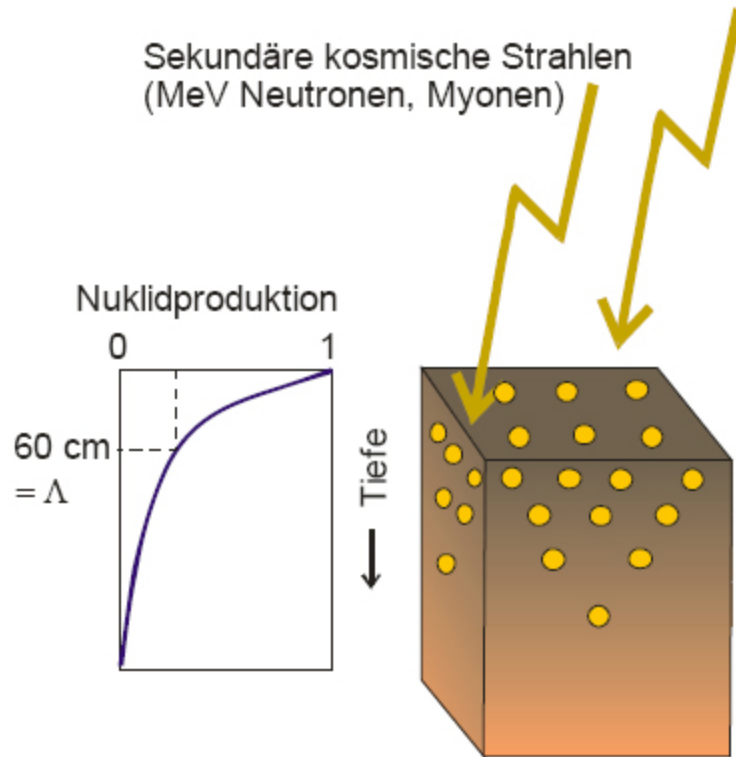


10. Catchment wide denudation rates



10. Catchment wide erosion rates

Erosionsraten aus *in situ*-produzierten kosmogenen Nukliden



$$C = \left(\frac{P_0}{\varepsilon/\Lambda + \lambda} \right)$$

ε : Erosionsrate

C : Nuklidkonzentration

P_0 : Nuklid Produktionsrate
an der Gesteinsoberfläche

Λ : Mittlere Abschirmtiefe

λ : Zerfallskonstante

10. Catchment wide erosion rates

derived from river loads:

derived from alluvial sediments:

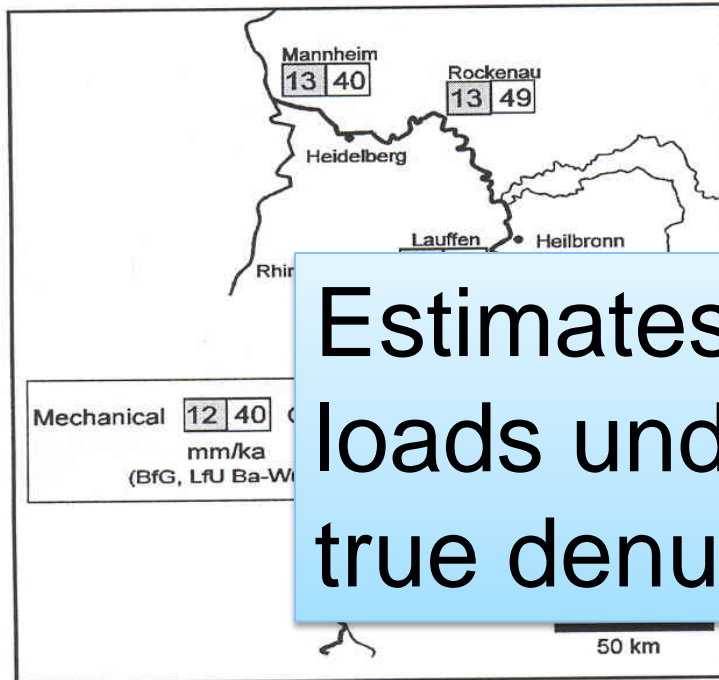


Fig. 1: Neckar denudation rates from river load data

von Blanckenburg et al.

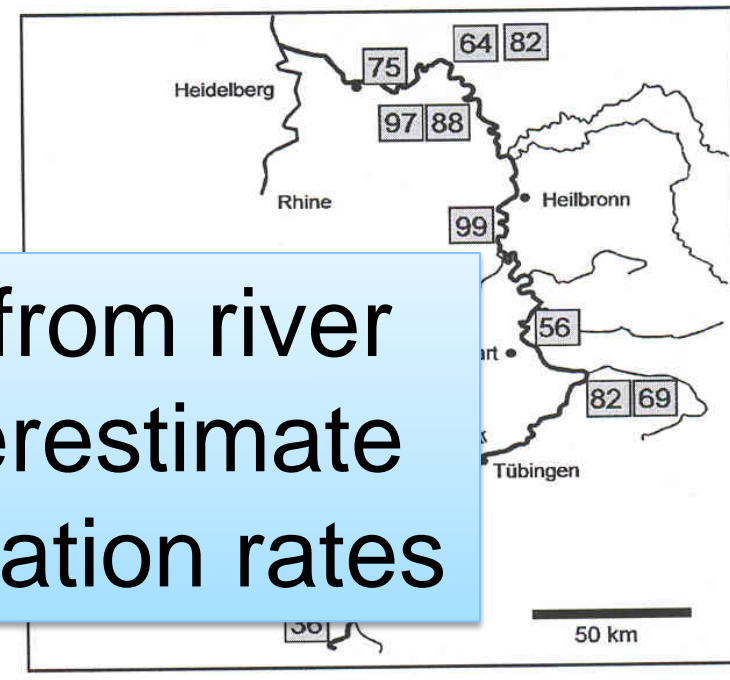
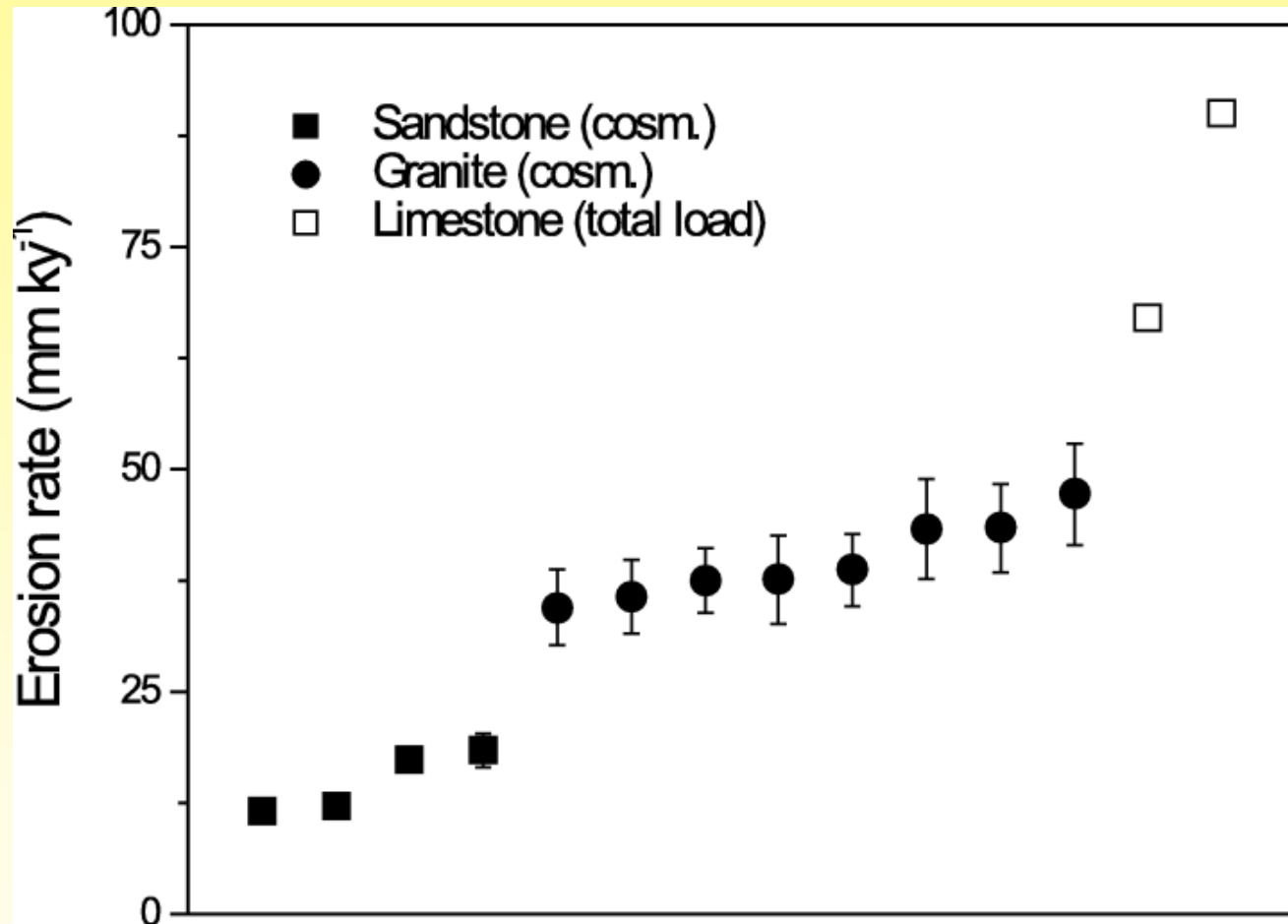


Fig. 2: Neckar total denudation rates from cosmogenic nuclides

Estimates from river loads underestimate true denudation rates

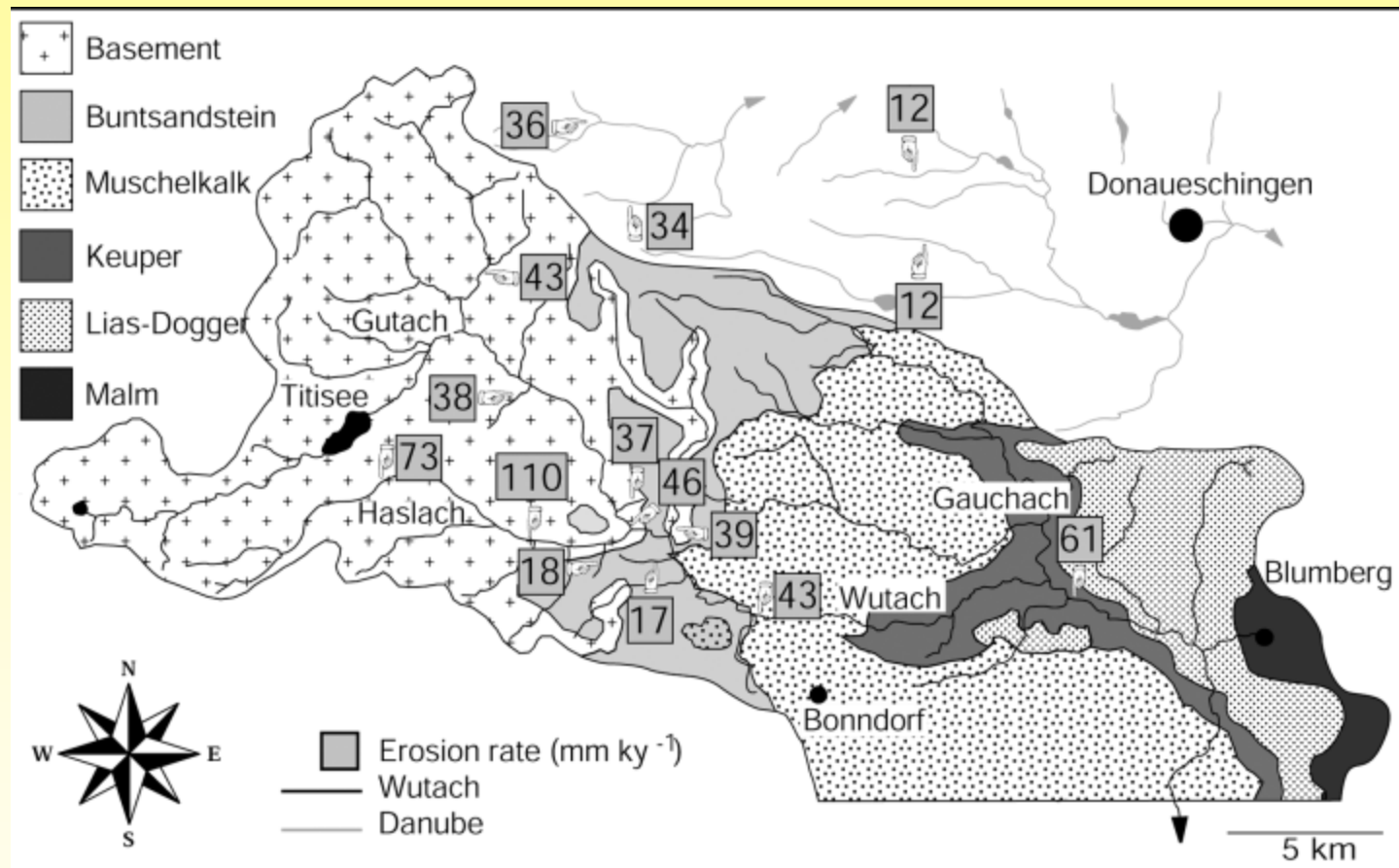
Cosmogenic isotopes measure total denudation rate - chemical part and physical part

10. Catchment wide denudation rates



Lithological dependence of erosion rates as determined from cosmogenic nuclides and river load data (Bauer 1993, Morel et al. 2003)

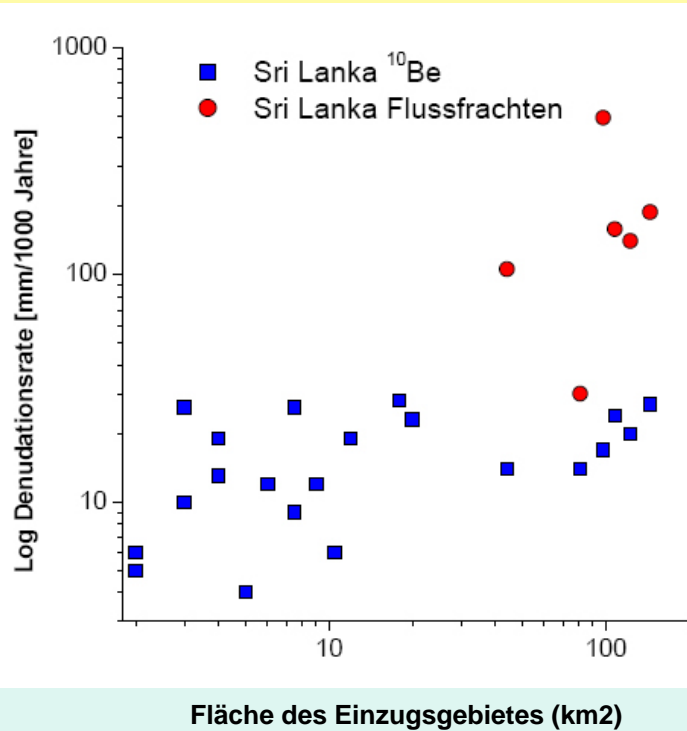
10. Catchment wide denudation rates



Morel et al. 2003 Terra Nova

Geological map of the Wutach basin, with erosion rates from cosmogenic nuclides (mm kyr⁻¹).

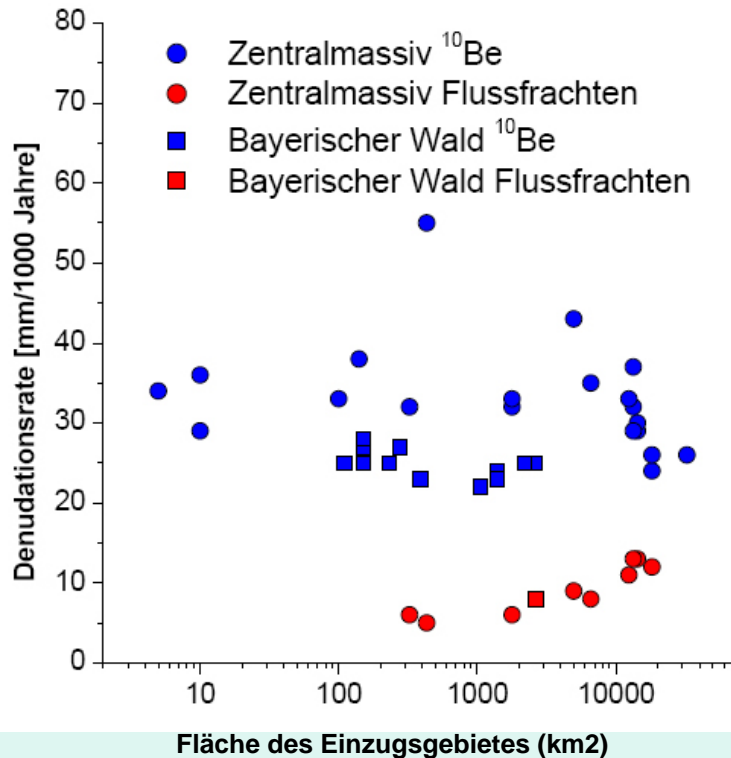
10. Catchment wide erosion rates



Sri Lanka:
antropogenic
increase of soil
erosion

von Blanckenburg 2008 GMT 33

10. Catchment wide erosion rates



von Blanckenburg 2008 GMT 33

European midlands:

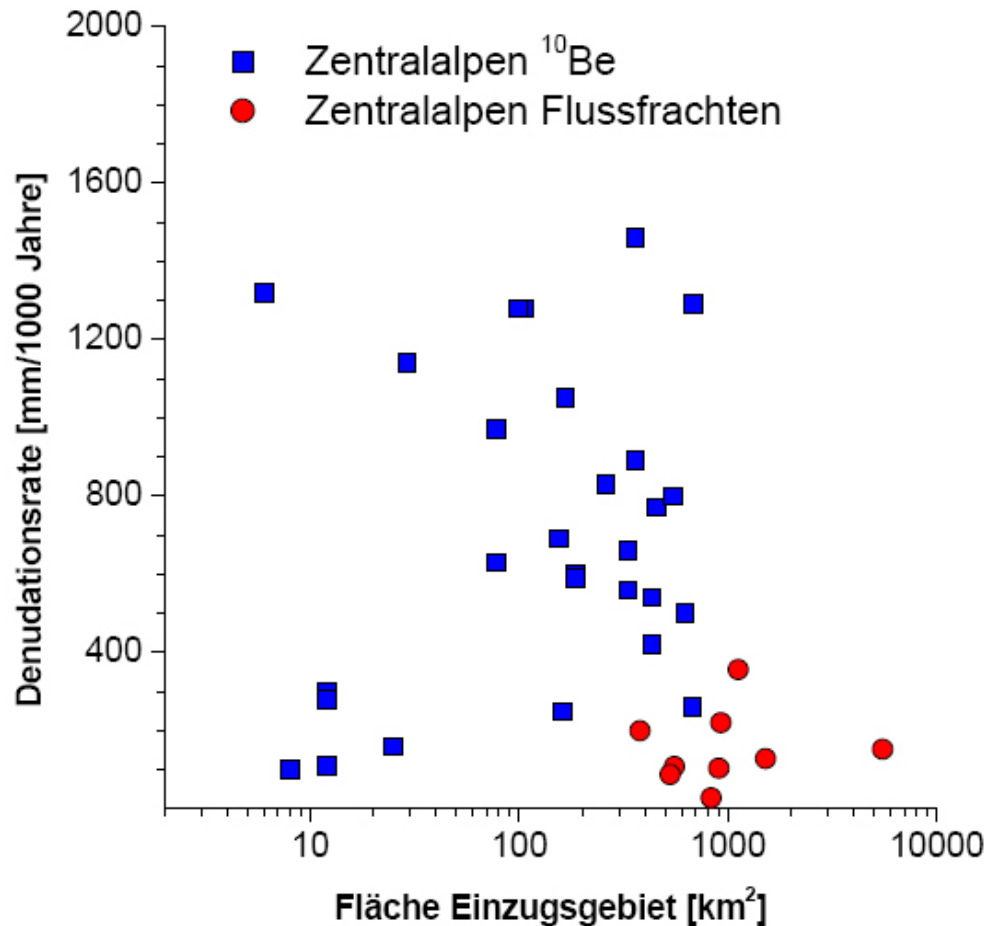
Higher denudation rates
as in Sri Lanka!

Why??????

Quarternary tectonic
activity (uplift and rift
formation) in central
Europe

Sri Lanka: stable shield
area

10. Catchment wide erosion rates



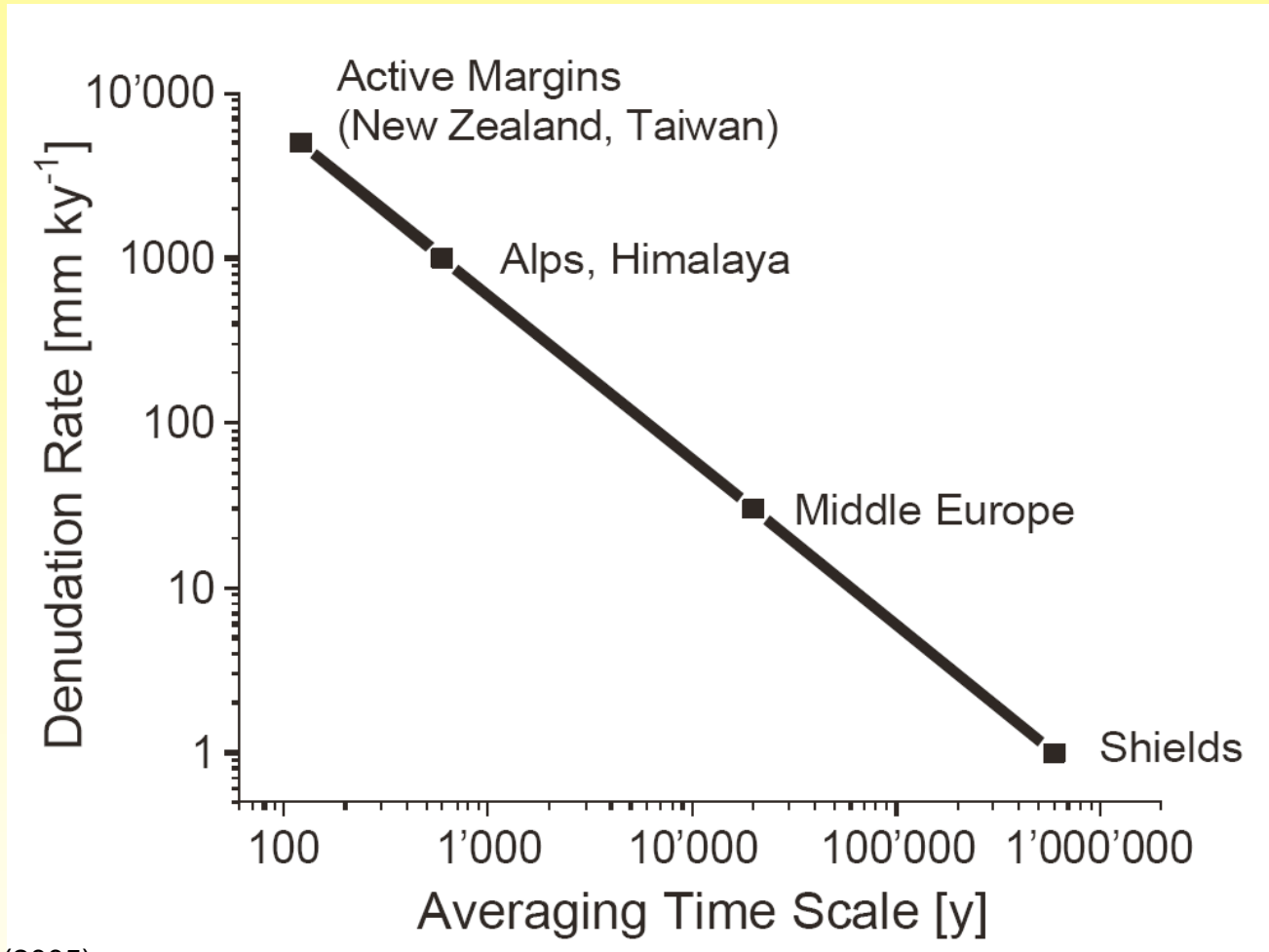
Swiss Alps:

Very high cosmogenic denudation rates

River load underestimates true erosion rates

Reason: isostatic rebound following deglaciation

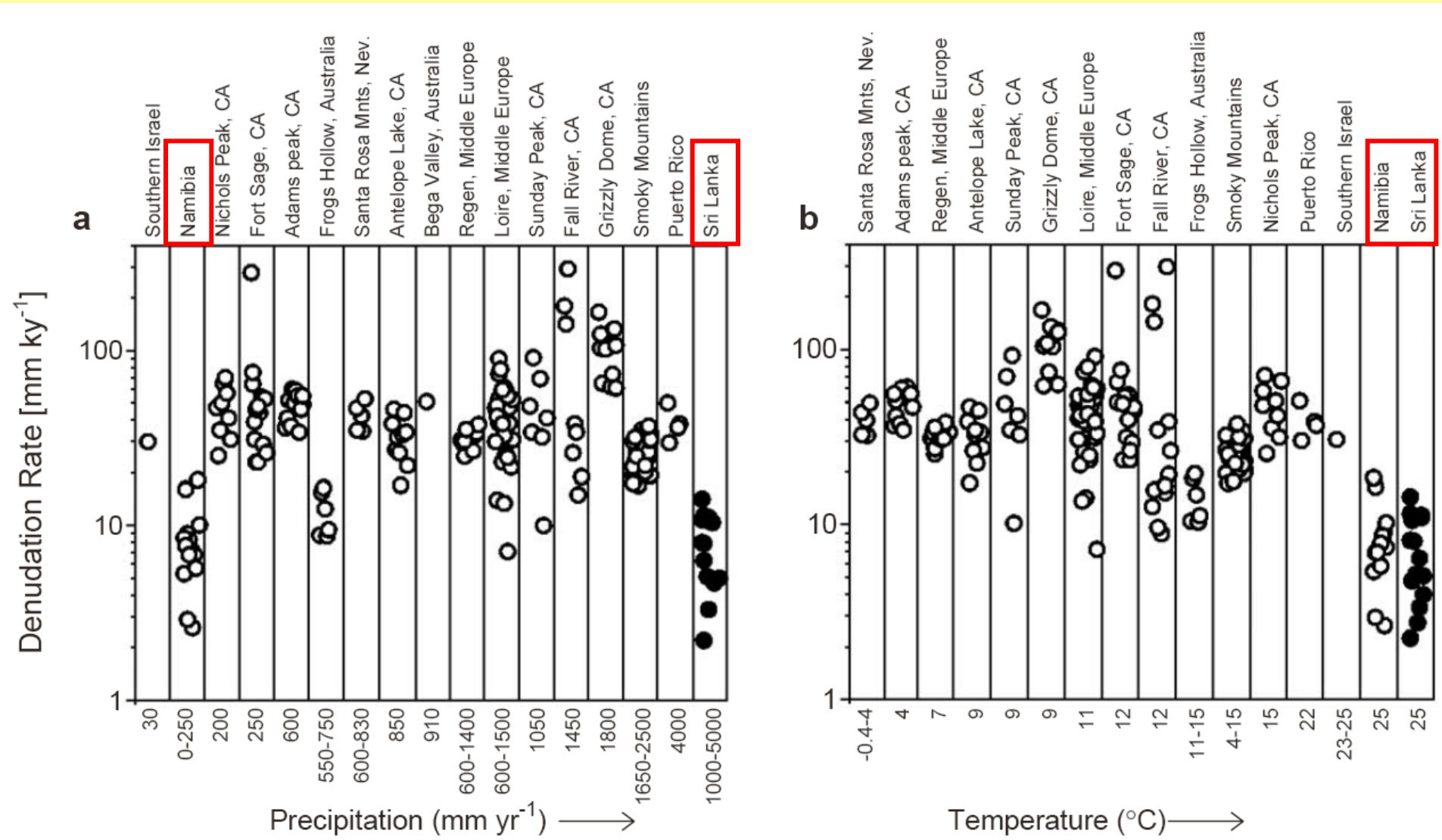
10. Catchment wide erosion rates



von Blanckenburg (2005)

the time it takes to erode the upper 0.6 m of bedrock, or ca. 1.0 m of soil

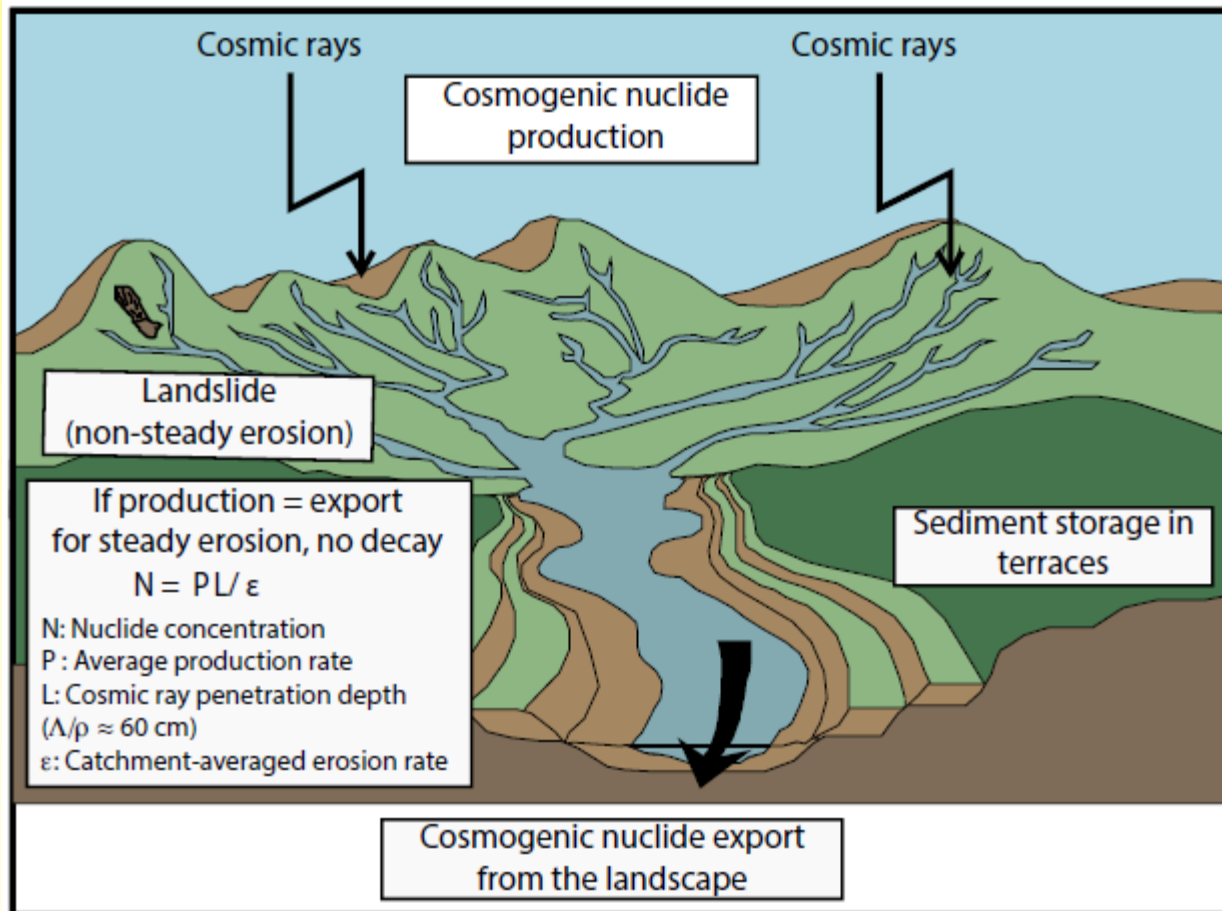
10. Climate, erosion and rock weathering



In order to avoid lithology-dependent effect only granitic catchments are shown

von Blanckenburg 2005

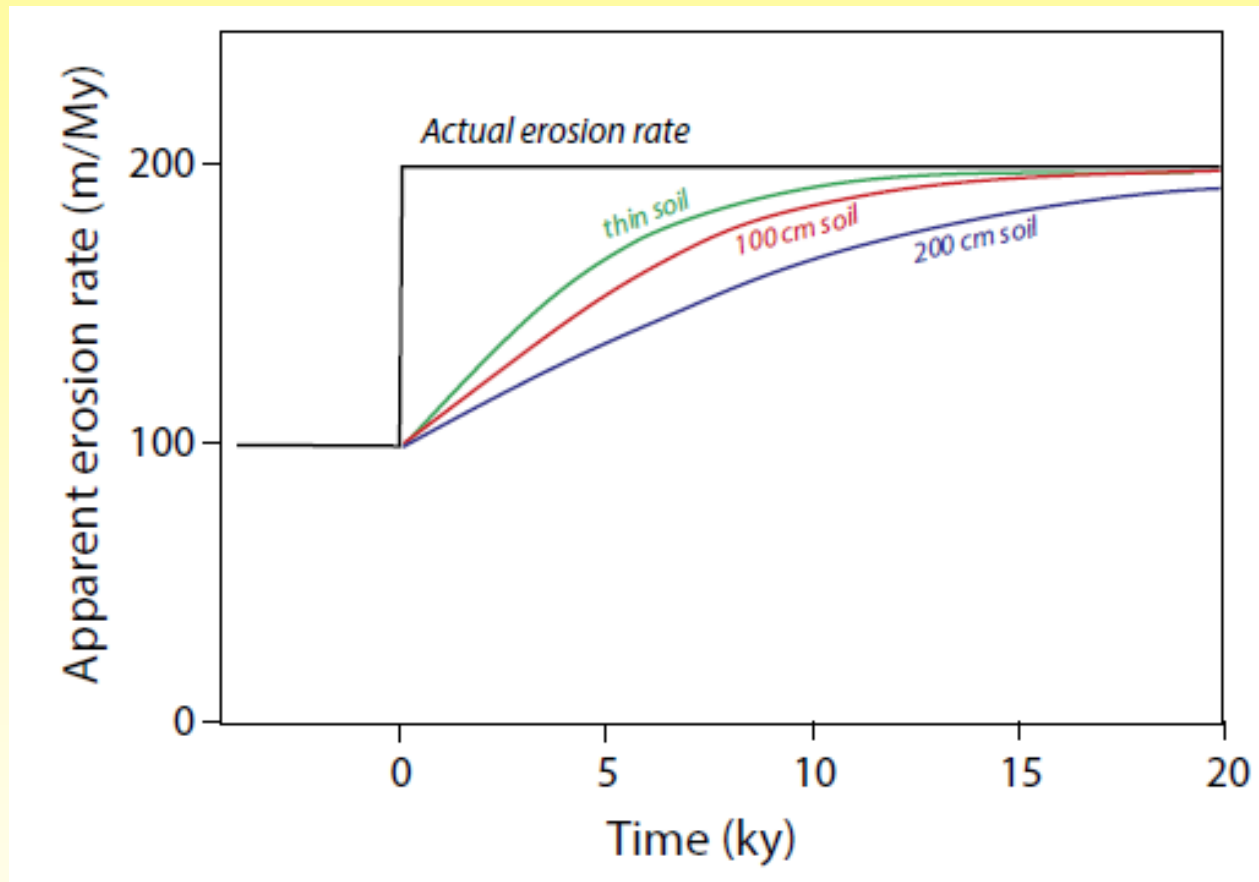
10. Catchment wide erosion rates



Granger & Schaller: Elements (2014)

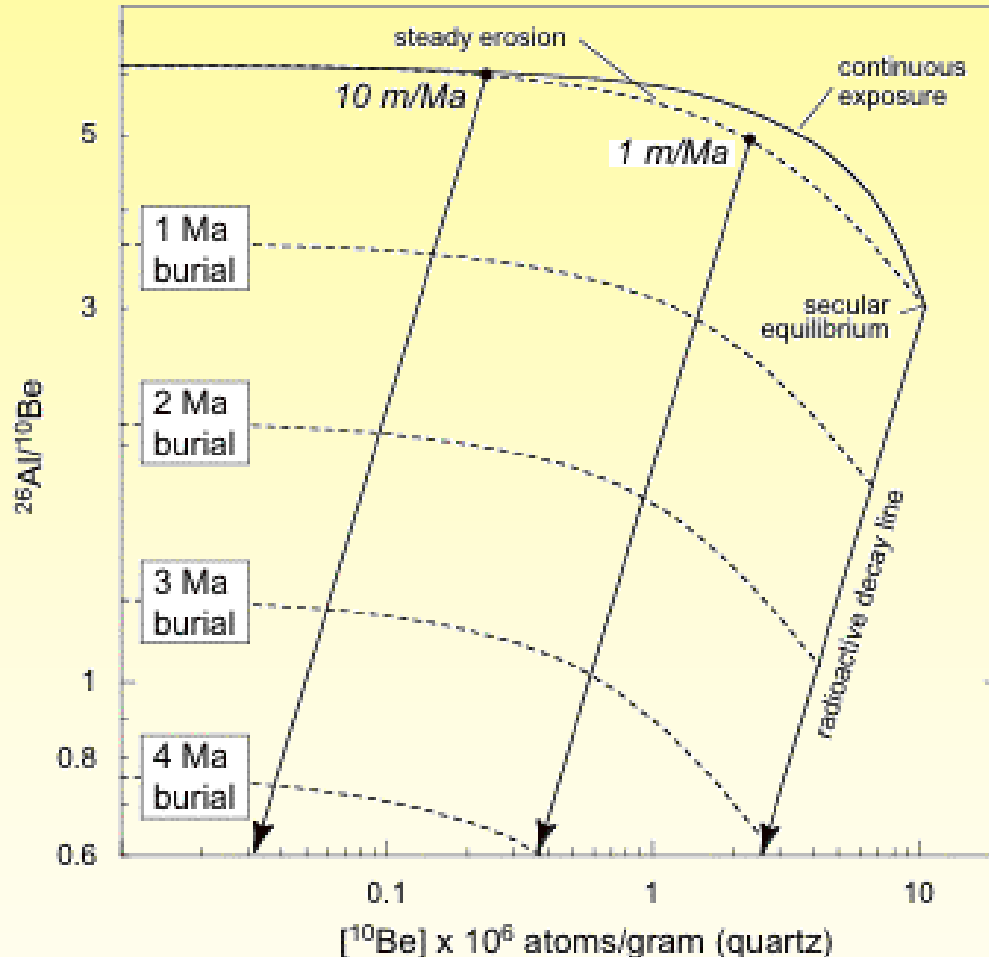
„Nature does the averaging“

10. Catchment wide erosion rates



Granger & Schaller: Elements (2014)

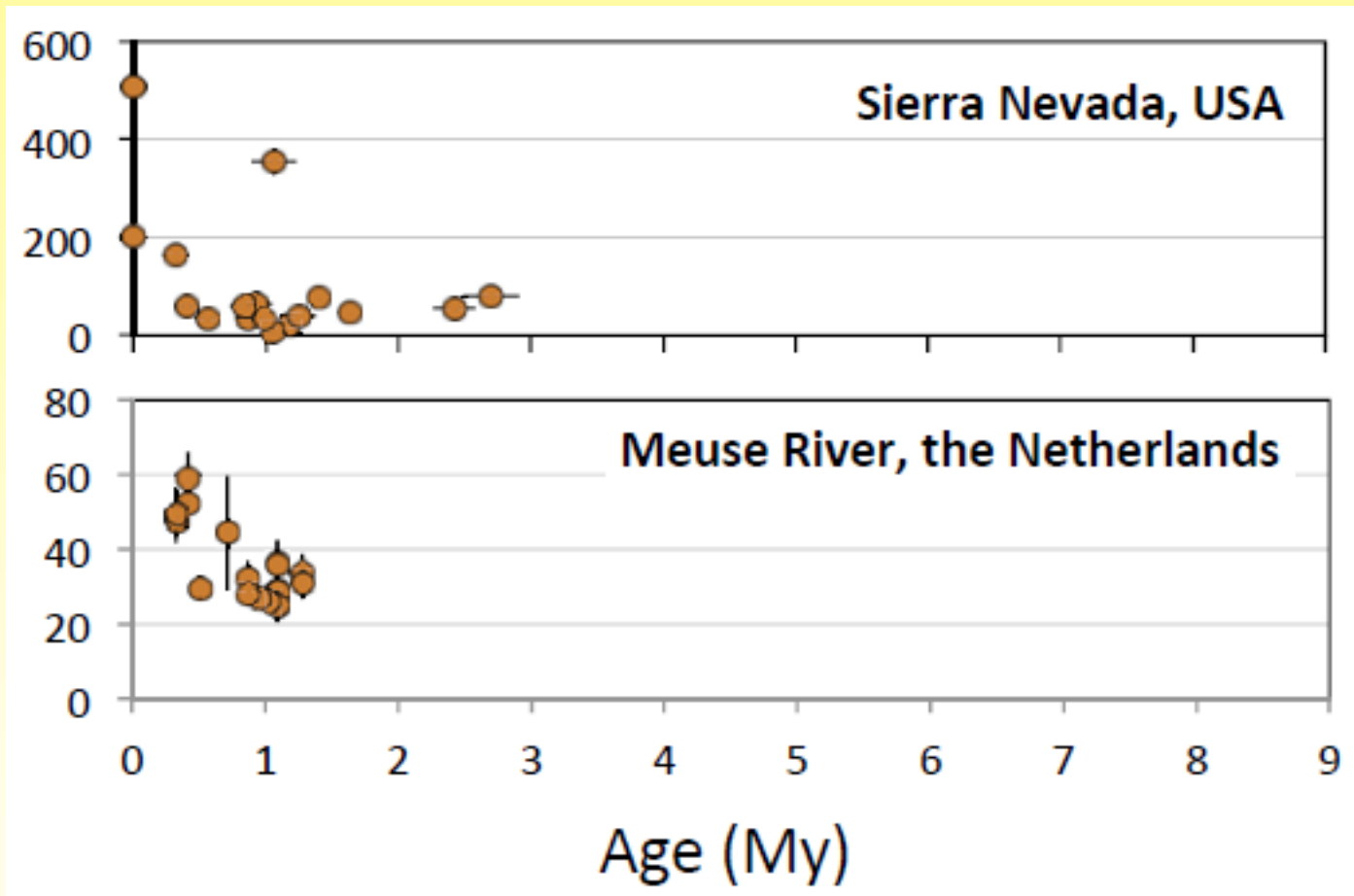
10. Palaeo-erosion rates



For completely buried and shielded minerals, the $^{26}\text{Al}/^{10}\text{Be}$ decreases along a line parallel to the solid "radioactive decay line".

Measured $^{26}\text{Al}/^{10}\text{Be}$ ratio in a sample determines the burial time, and can also be used to calculate the pre-burial (or palaeo) erosion rate.

10. Palaeo-erosion rates



Granger & Schaller: Elements (2014)