Introduction to early Earth Geoscience

What do we know?
What do we not know?
How do we know?

Bettina Scheu, Earth & Environmental Sciences LMU

How did the Early Earth look alike?

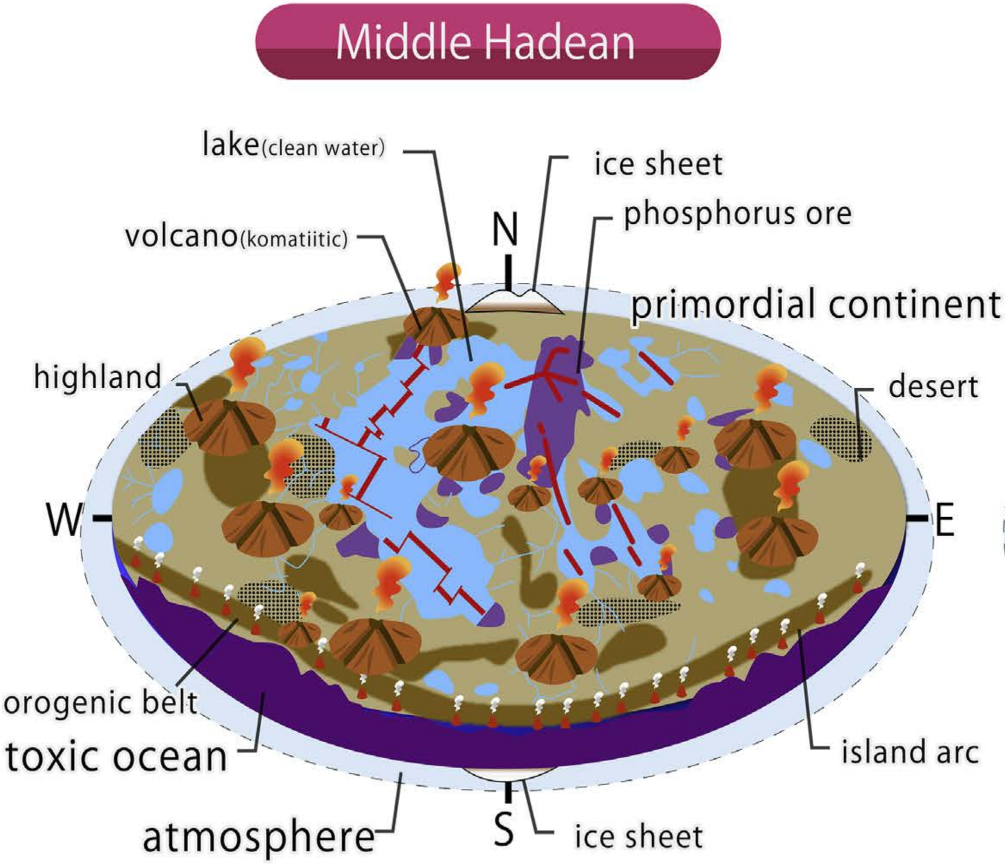
How did the Early Earth look alike?

Hot (hell like planet) <-> cold (icy world) ?
Only a water world? Ocean chemistry?
Which atmosphere?
.....

Source: invited Talk by Prof Martin van Kranendonk (University of New south Wales), Brixen February 2020

Diversified earth vs. monotonous earth

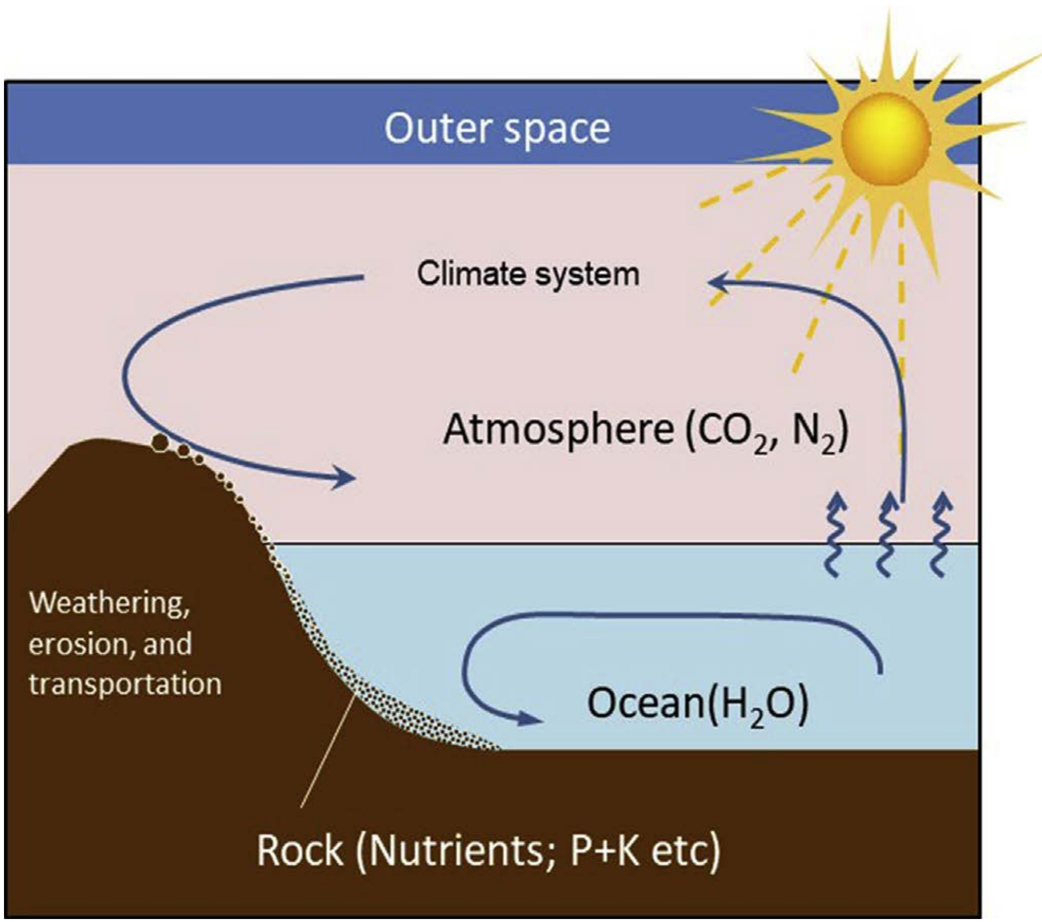
Hadean Earth is thought to be a highly diversified environment (left).
If an ocean covers whole Earth (right), it would be monotonous, with no diversified surface environment and hence, no possibility for the emergence of life.



Source: Maruyama et al. (2019)

Habitable Trinity model

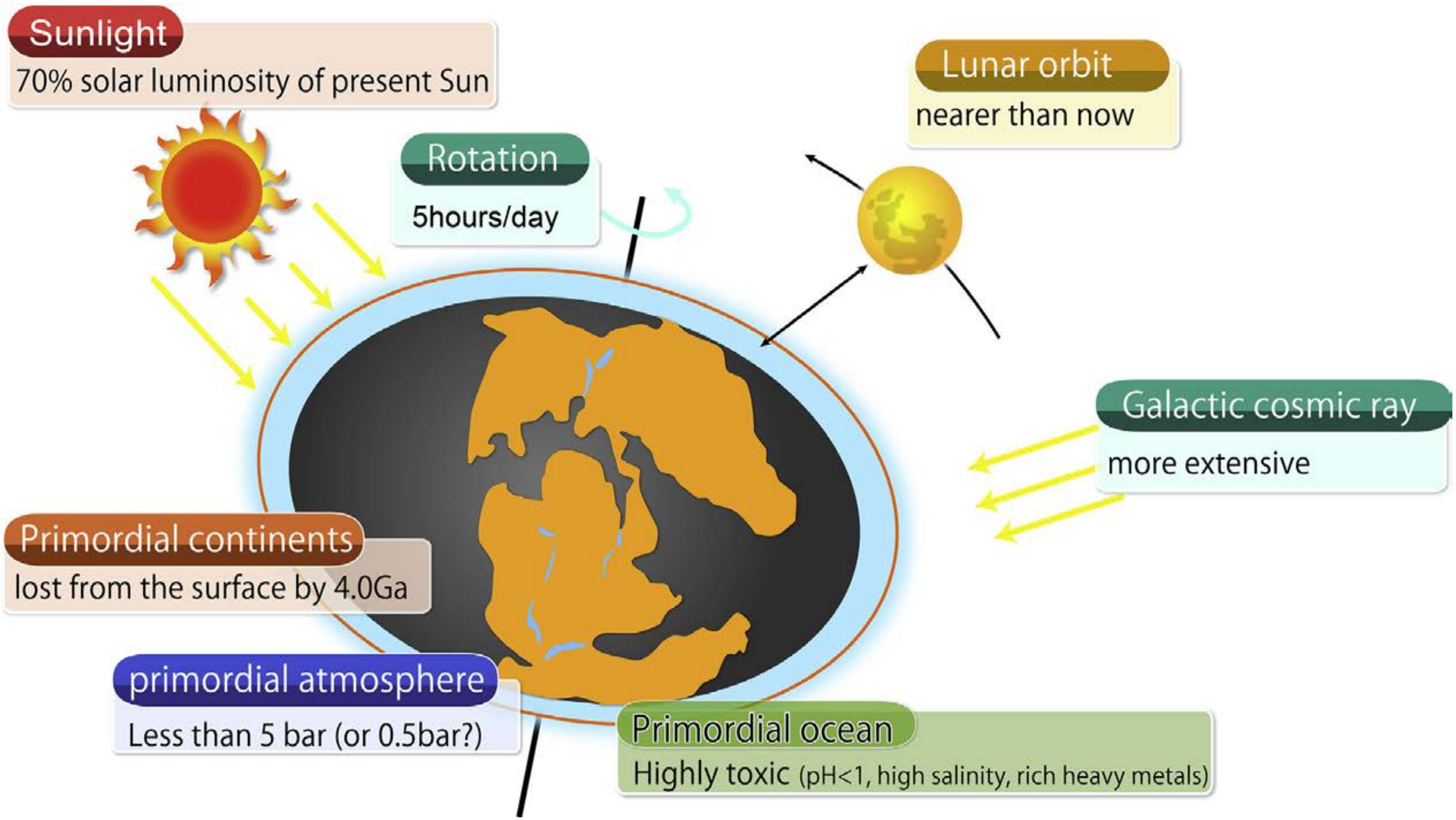
To evolve into a habitable planet, co-existence of atmosphere, ocean, and landmass with a driving force (Sun) is one of the most critical condition. It is obvious that life cannot live with water only. The supply of nutrients derived from landmass is critical for the emergence of life



Source: Maruyama et al. (2019)

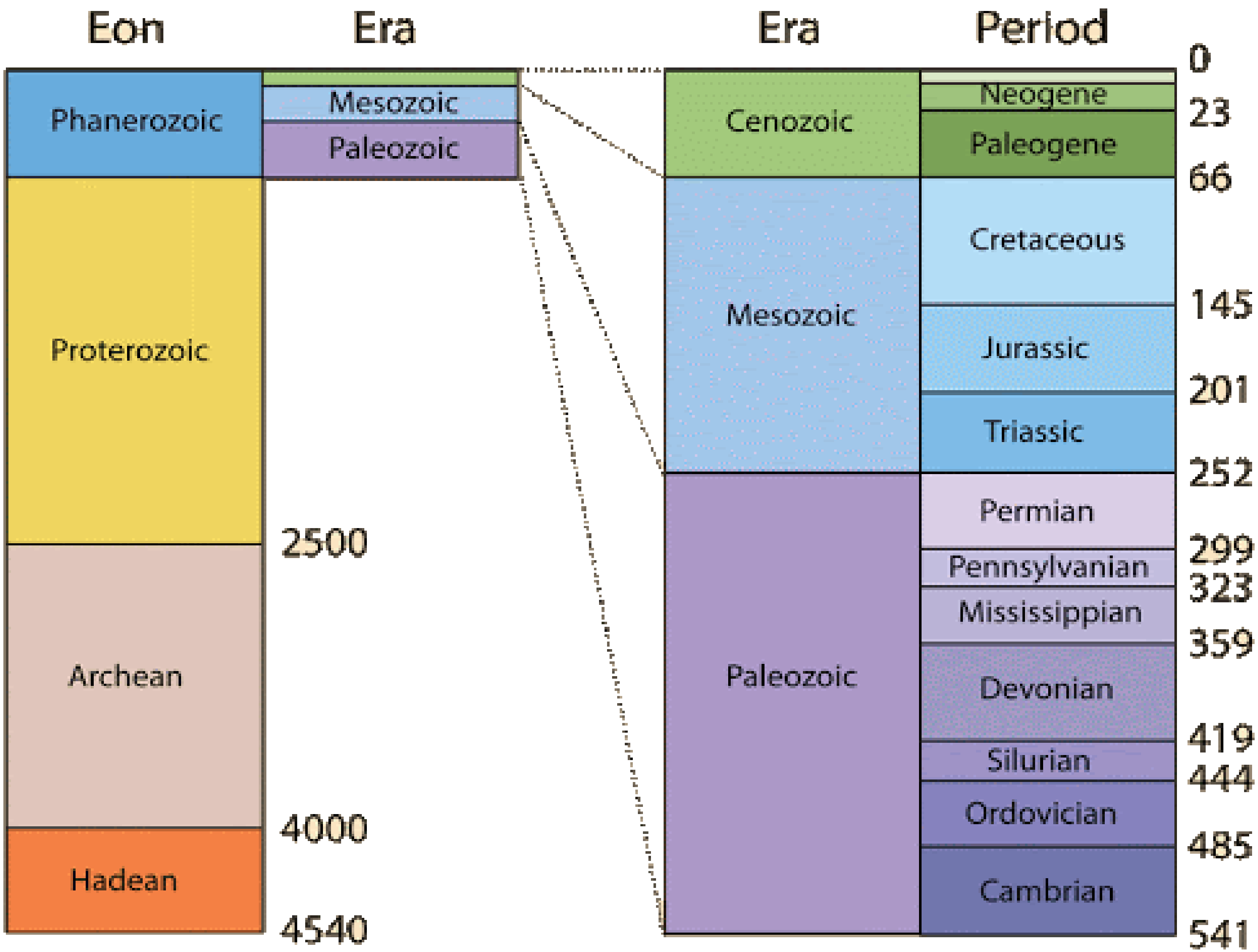
Likely Hadean surface environments of the Earth

Hadean surface environment experienced various types of cyclic phenomena, associated with a closer Moon, faster self-rotation of the Earth, and the faint young Sun



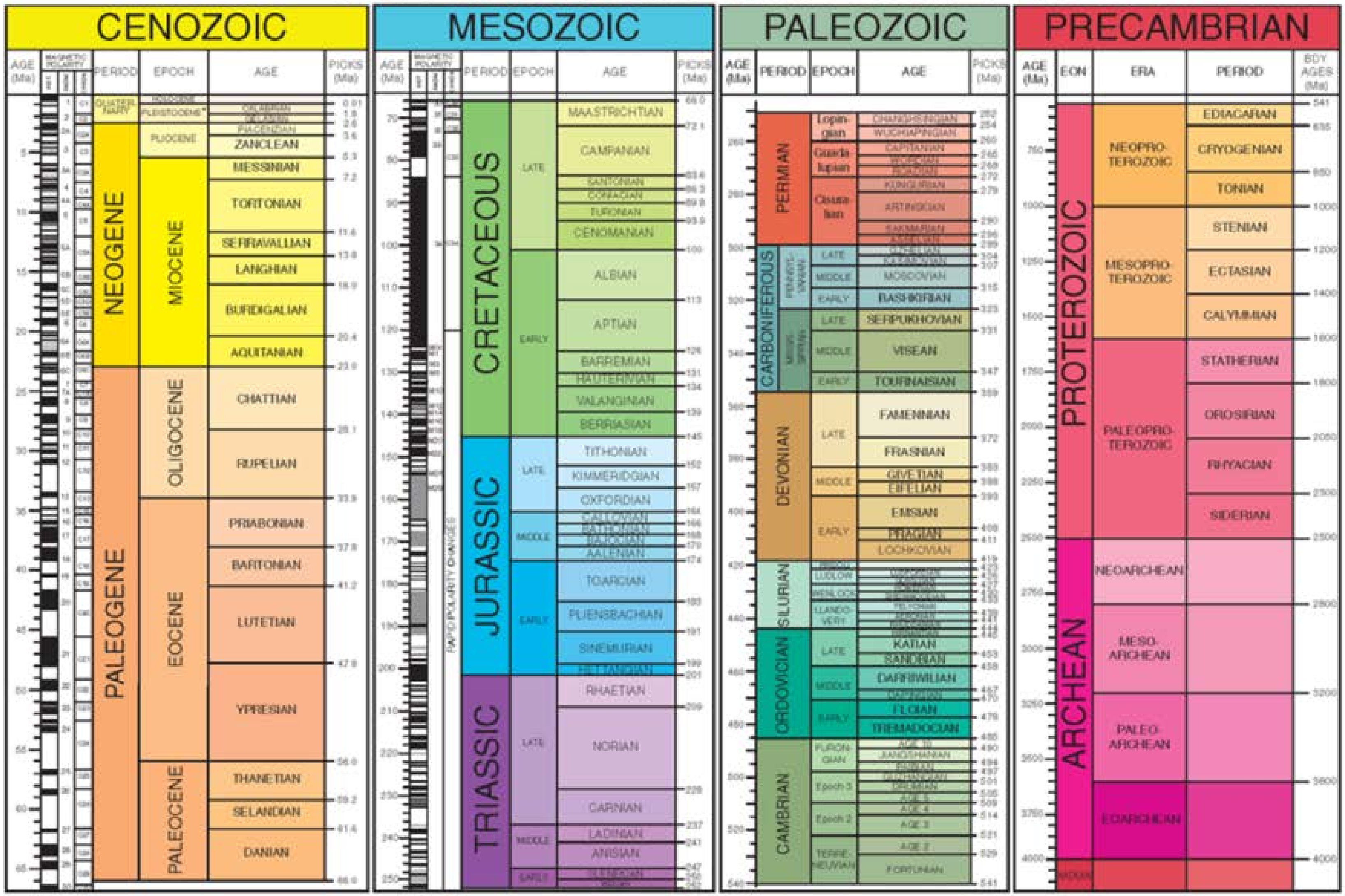
Source: Maruyama et al. (2019)

Geologic time



Geologic time and the geologic column

GSA GEOLOGIC TIME SCALE v. 4.0



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*The Pleistocene is divided into four ages, but only two are shown here. What is shown as Calabrian is actually three ages—Calabrian from 1.8 to 0.78 Ma, Middle from 0.78 to 0.13 Ma, and Late from 0.13 to 0.01 Ma.

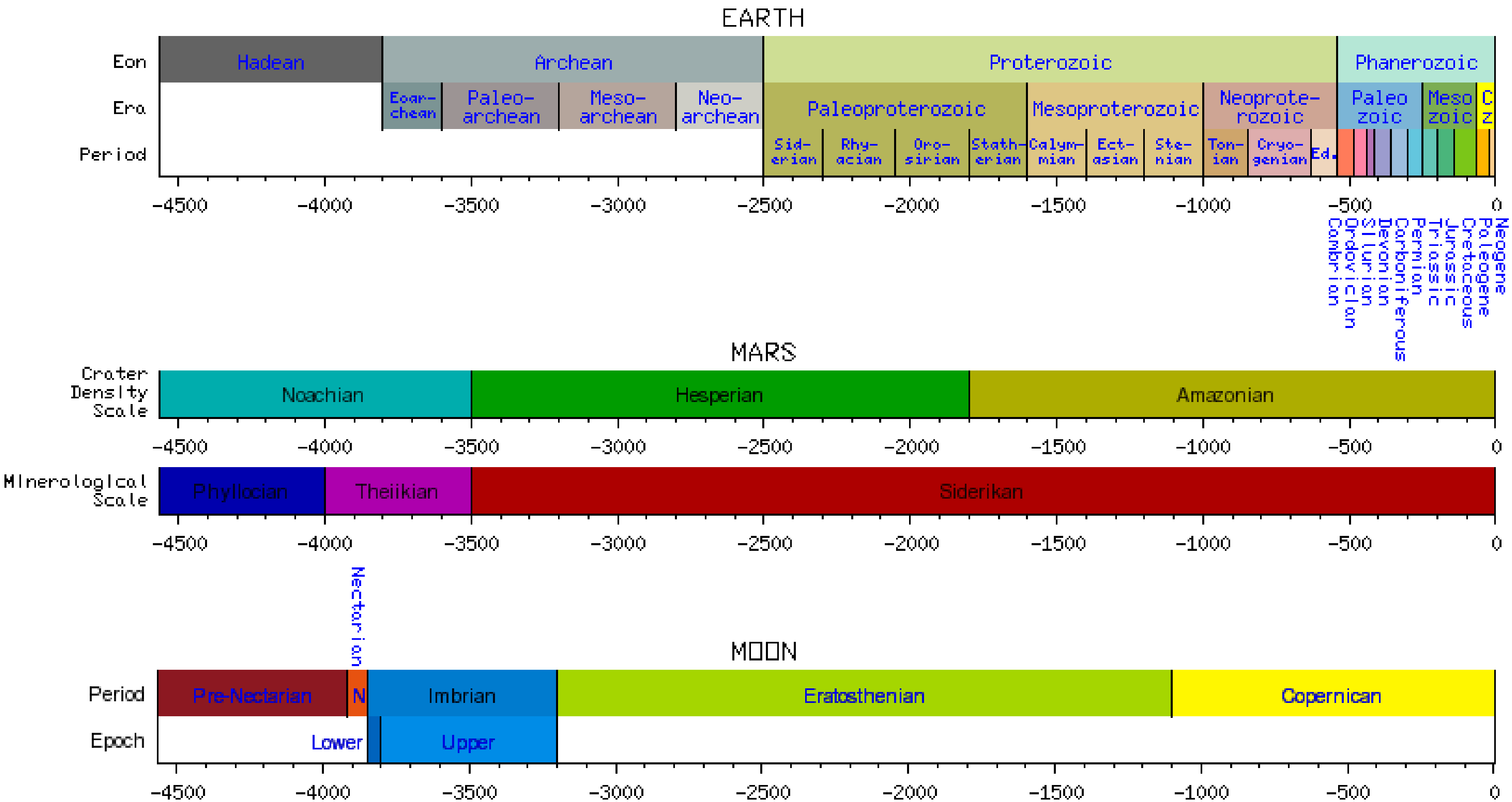
Walker, J.D., Geissman, J.W., Bowring, S.A., and Babcock, L.E., compilers, 2012, Geologic Time Scale v. 4.0: Geological Society of America, doi: 10.1130/2012.CTS004R3C.

The Cenozoic, Mesozoic, and Paleozoic are the Eras of the Phanerozoic Eon. Names of units and age boundaries follow the Gradstein et al. (2012) and Cohen et al. (2012) compilations. Age estimates and picks of boundaries are rounded to the nearest whole number (1 Ma) for the pre-Cenomanian, and rounded to one decimal place (100 ka) for the Cenomanian to Pleistocene interval. The numbered epochs and ages of the Cambrian are provisional.

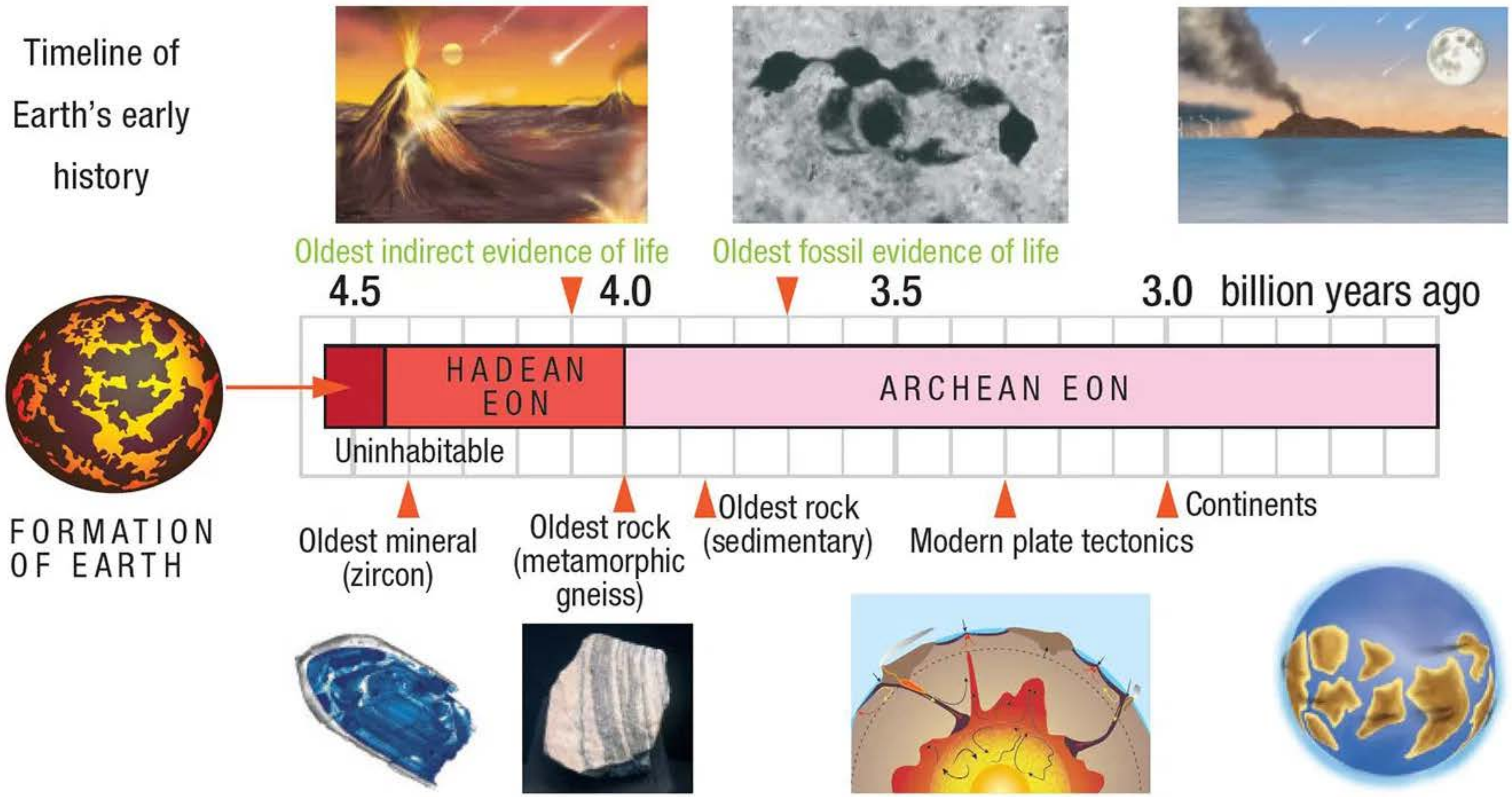
REFERENCES CITED: Cohen, K.M., Finney, S., and Gibbard, P.L., 2012, International Chronostratigraphic Chart: International Commission on Stratigraphy, www.stratigraphy.org (last accessed May 2012). (Chart reproduced for the 34th International Geological Congress, Brisbane, Australia, 5–10 August 2012.)

Gradstein, F.M, Ogg, J.G., Schmitz, M.D., et al., 2012, The Geologic Time Scale 2012: Boston, USA, Elsevier, DOI: 10.1016/B978-0-444-59425-9.00004-4.

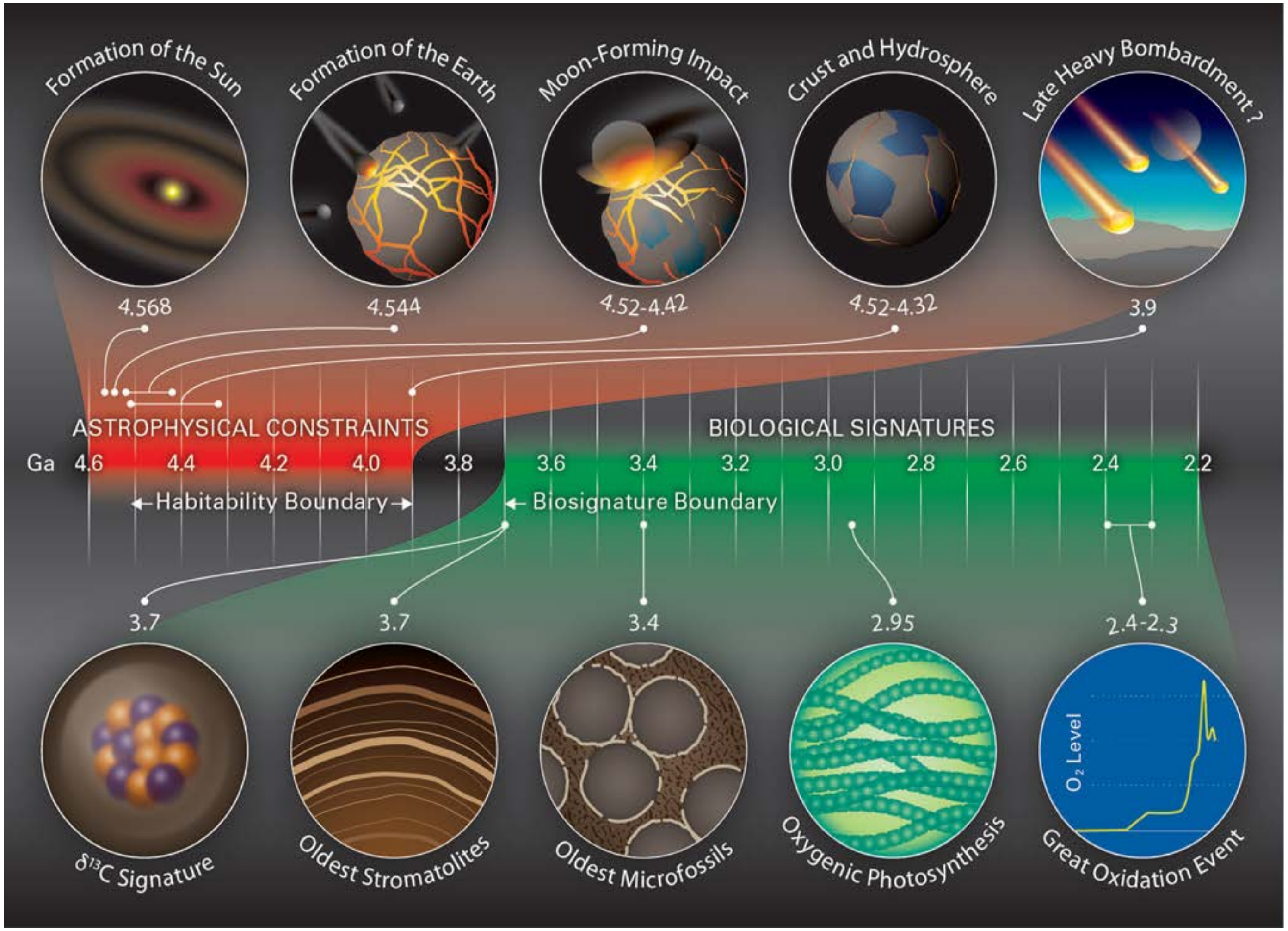
Geologic time – Earth – Mars - Moon



Geologic time – Earth Evolution



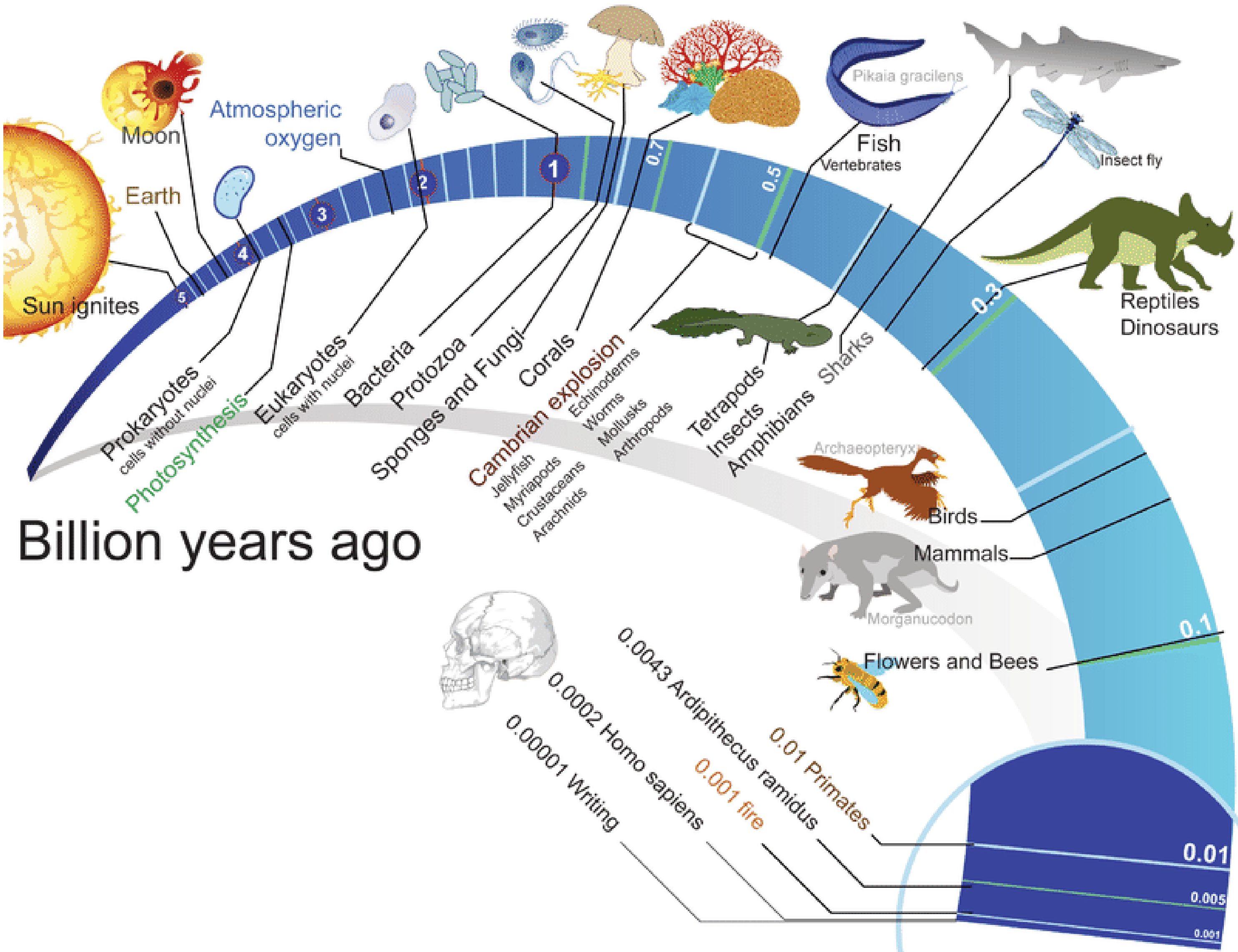
Timeline - Habitability Boundary



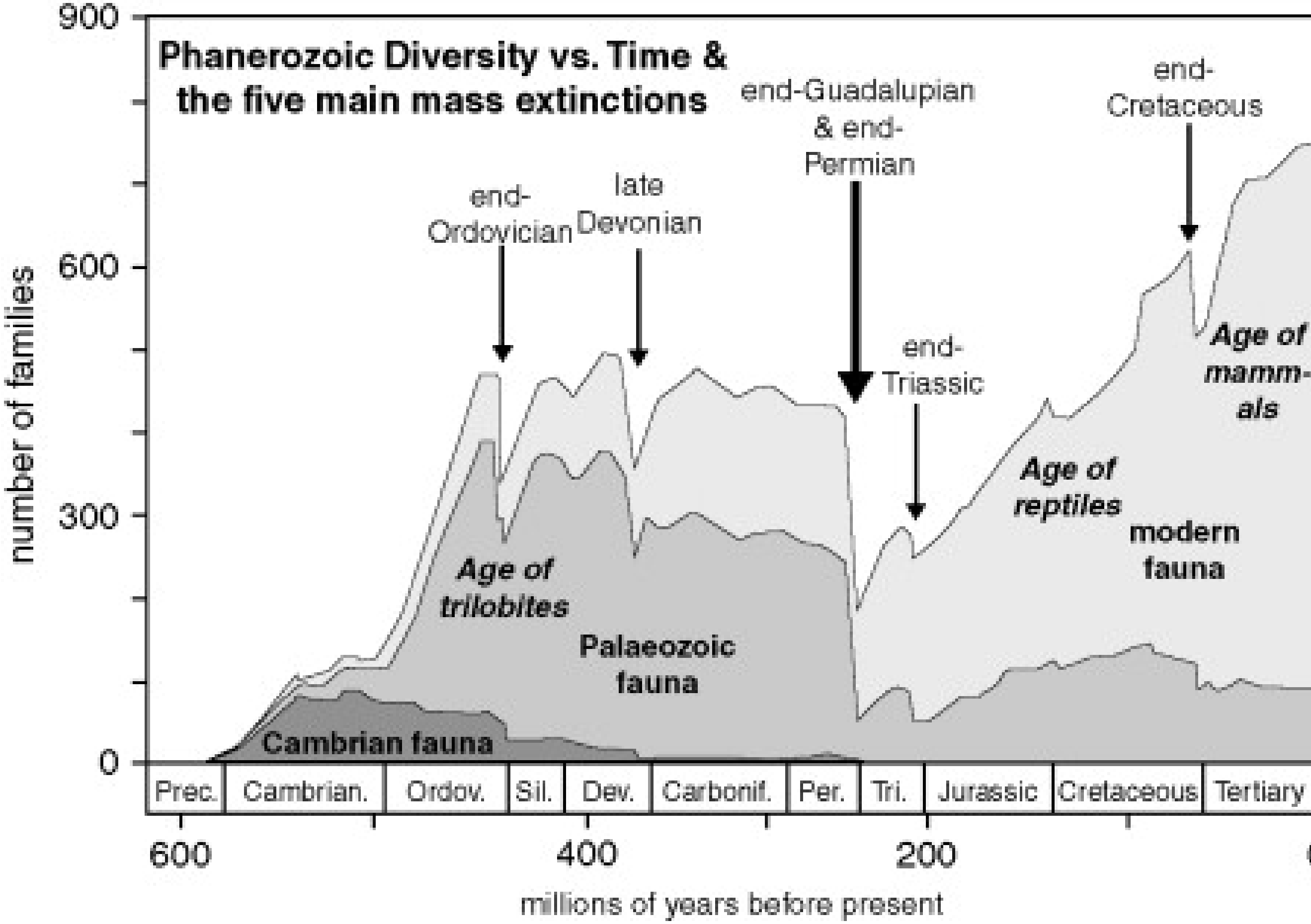
Pearce et al. (2018) Astrobiology

Astrophysical constraints on the time of the habitability boundary and the bio-signature boundary. Uncertainties about whether there was a LHB mean that the position of the habitability boundary is still poorly constrained, whereas the evidence for the bio-signature boundary is beginning to converge..

Evolution of Life – Mass Extinctions



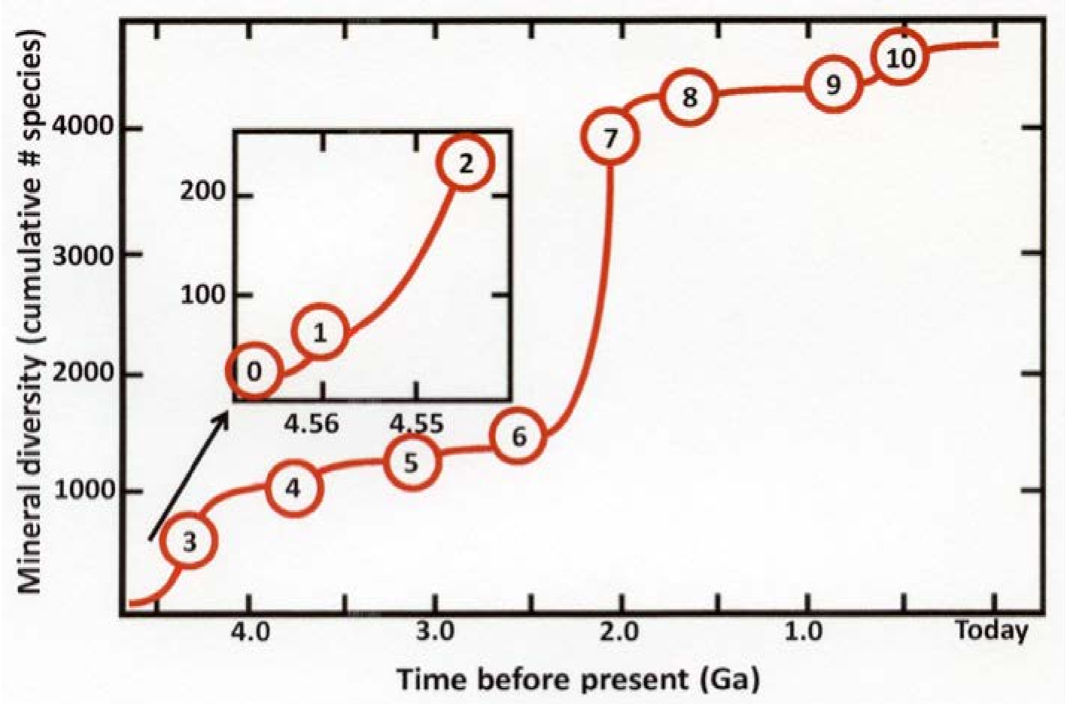
Evolution of Life – Mass Extinctions



From Metcalf & Isozaki (2009), courtesy of Ian Metcalf.

440mya:	End-Ordovician extinction devastates marine invertebrates
360mya:	End-Devonian extinction devastates reef-building organisms
250mya:	End-Permian extinction devastates trilobites, pelycsaurs, placoderms
200mya:	End-Triassic extinction devastates conodonts and large amphibians
65mya:	End-Cretaceous extinction devastates non-avian dinosaurs, pterosaurs, ammonites & many plants

Minerals – Evolution of Diversity



Stage	Age (Ga)	~Cumulative no. species
1. Primary chondrite minerals	>4.56 Ga	60
2. Achondrite and planetesimal alteration	>4.56 to 4.55 Ga	250
3. Igneous rock evolution	4.55 to 4.0 Ga	350 to 500*
4. Granite and pegmatite formation	4.0 to 3.5 Ga	1000
5. Plate tectonics	>>3.0 Ga	1500
6. Anoxic biological world	3.9 to 2.5 Ga	1500
7. Great Oxidation Event	2.5 to 1.9 Ga	>4000
8. Intermediate ocean	1.9 to 1.0 Ga	>4000
9. Snowball Earth events	1.0 to 0.542 Ga	>4000
10. Phanerozoic era of biomineralization	0.542 Ga to present	4300+

Note: Note that the timings of some of these stages overlap, and several stages continue to the present (after Hazen et al. 2008).

* Depending on the volatile content of the planet or moon.

Source: Hazen at al. (2008)

3 Eras & 10 stages of the evolution of minerals on earth

Era/Stage	Age (Ga)	Cumulative no. of species
Prenebular "Ur-Minerals"	>4.6	12
Era of Planetary Accretion (>4.55 Ga)		
1. Primary chondrite minerals	>4.56 Ga	60
2. Achondrite and planetesimal alteration	>4.56 to 4.55 Ga	250
Era of Crust and Mantle Reworking (4.55 to 2.5 Ga)		
3. Igneous rock evolution	4.55 to 4.0 Ga	350 to 500*
4. Granite and pegmatite formation	4.0 to 3.5 Ga	1000
5. Plate tectonics	>3.0 Ga	1500
Era of Biologically Mediated Mineralogy (>2.5 Ga to Present)		
6. Anoxic biological world	3.9 to 2.5 Ga	1500
7. Great Oxidation Event	2.5 to 1.9 Ga	>4000
8. Intermediate ocean	1.9 to 1.0 Ga	>4000
9. Snowball Earth events	1.0 to 0.542 Ga	>4000
10. Phanerozoic era of biomineralization	0.542 Ga to present	4400+

* Depending on the volatile content of the planet or moon

Source: Hazen at al. (2008)

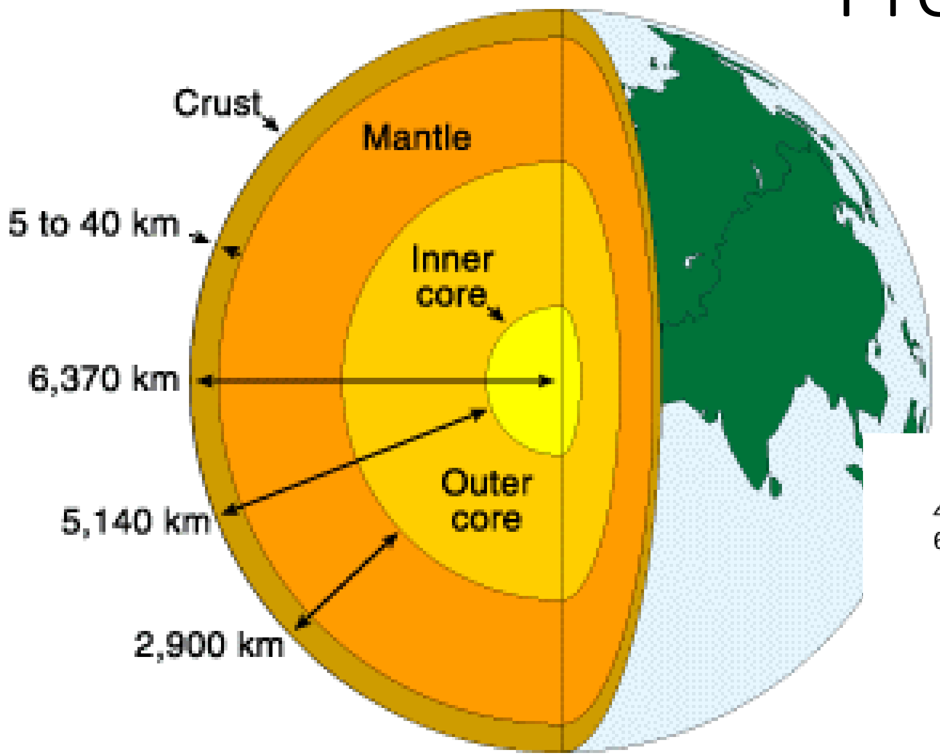
Mineral Assemblage of Present-day Earth

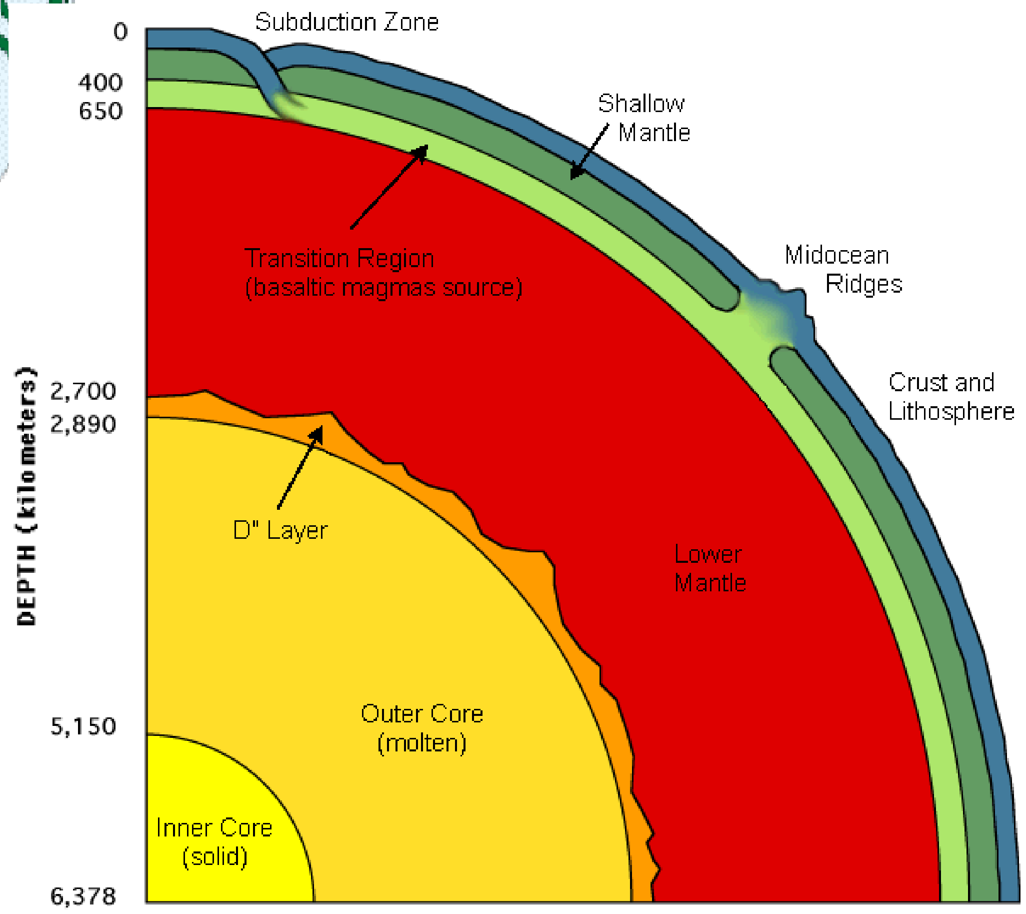
Tabelle 1.5. Häufigkeit wichtiger Minerale und Mineralgruppen in der Erdkruste (in Masse-%)

Feldspäte	58.0 %	Silikate 91.5 %
Pyroxene	16.5 %	
Amphibole		
Olivin		
Quarz	12.5 %	
Glimmer (3.5 %) und silikatische Tonminerale	4.5 %	
Eisenoxide	3.5 %	
Calcit	1.5 %	
alle anderen Minerale	3.5 %	
Summe	100 %	

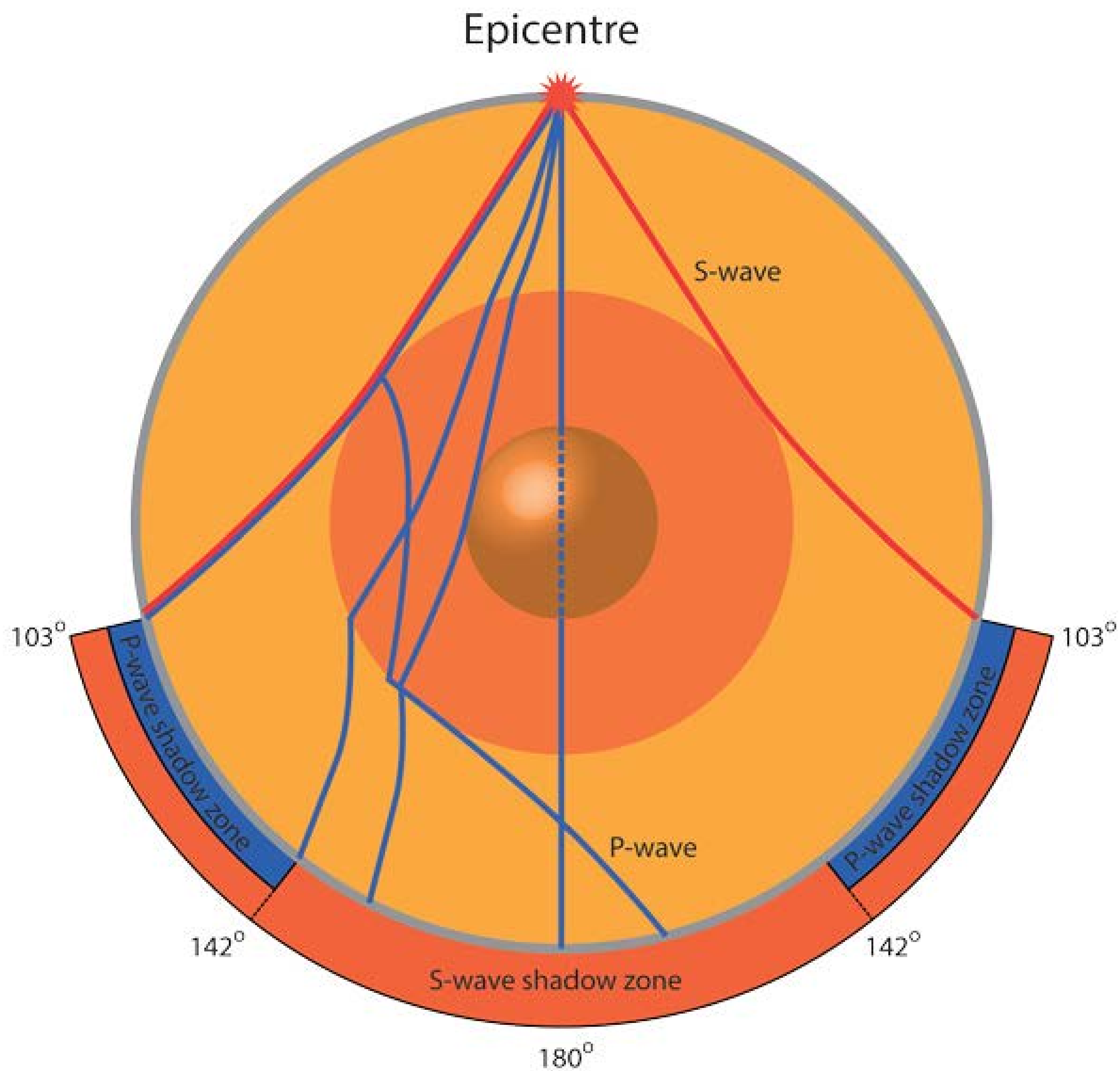
(nach Rösler, 1991, S. 182)

Present-day Earth Interior





Present-day Earth Interior – How do we know?



before we go on with Early Earth...

.... we need to catch up on some basic geoscience knowledge (mainly in the field of geology, petrology, mineralogy, geochemistry, physics and chemistry of melts, volcanology, ...)

join me on a tour de Geo!

Modern Origins of Geology & Geochemistry

- James Hutton (1726-1797), is known as the "Father of Geology"
- Alfred Wegener 1915 Theory of continental drift
  -> plate tectonics
- Physical Chemistry and Geology were effectively combined by establishment in 1907 of the Geophysical Laboratory of the Carnegie Institute of Washington.
  → N.L. Bowen, a MIT-trained scientist, published "The Evolution of the Igneous Rocks" (1928)
- V.M. Goldschmidt (1888-1947) is known as the father of Modern Geochemistry. His collected efforts are summarized in the book "Geochemistry", Clarendon Press, Oxford, 1954.

Definitions

- **Crystals** = Solid phase with periodic and strictly regular arrangement of atoms and molecules. The strictly ordered structure is called crystal lattice.
- **Minerals** = Natural, homogeneous solids, usually in crystallized form (some also crypto-crystalline or amorphous).
- **Rocks** = Any natural material consisting essentially of mineral components. This also includes natural glasses.
  there are solid rocks and unconsolidated rocks.

- **Natural Glass** = Inorganic solid without crystalline order formed by geological processes (= amorphous state).

Minerale - Einteilung

Kristallchemische Gliederung

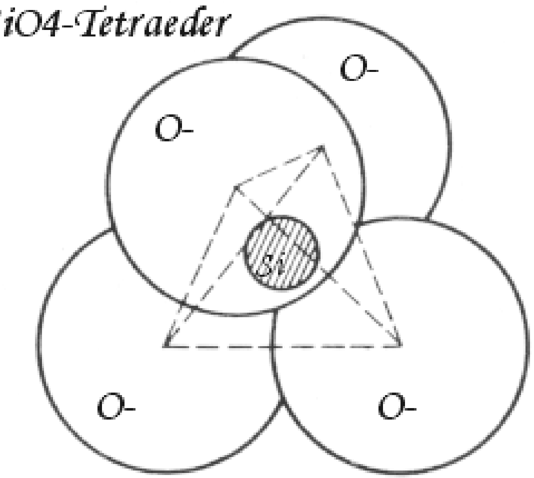
→ 9 Klassen

→ Beruht auf der dominierenden Stellung der Anionen

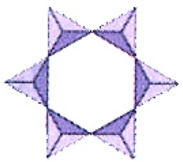
1. **Elemente**
2. **Sulfide**
3. **Halogenide**
4. **Oxide**, Hydroxide
5. Nitrate, **Karbonate,** Borate
6. **Sulfate**, Chromate, Molybdate, Wolframate
7. **Phosphate**, Arsenate, Vanadate
8. **Silikate**
9. Organische Minerale

Silikatstrukturen

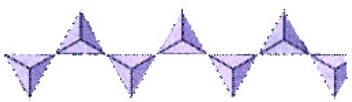
Tetraeder-Polymerisation



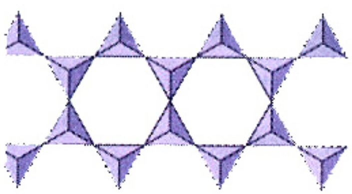
- Inselsilikate z.B. Olivin
- Gruppensilikate z.B. Epidot
  (ohne Grafik)



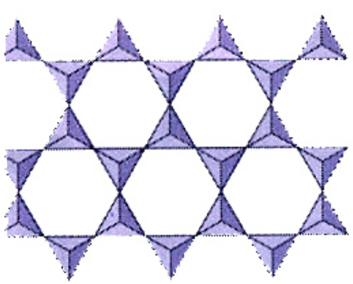
- Ringsilikate z.B. Beryll



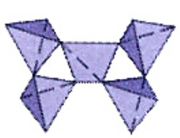
- Kettensilikate z.B. Pyroxene (Augit)



- Bandsilikate z.B. Amphibole (Hornblende)



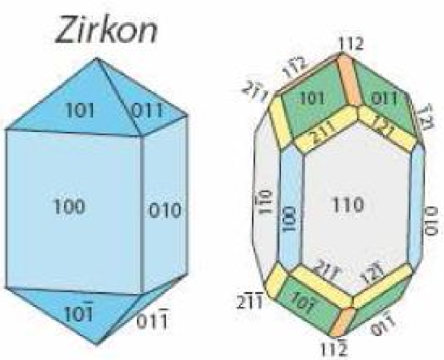
- Schichtsilikate z.B. Glimmer, Tonminerale



- Gerüstsilikate z.B. Feldspäte, Quarz*

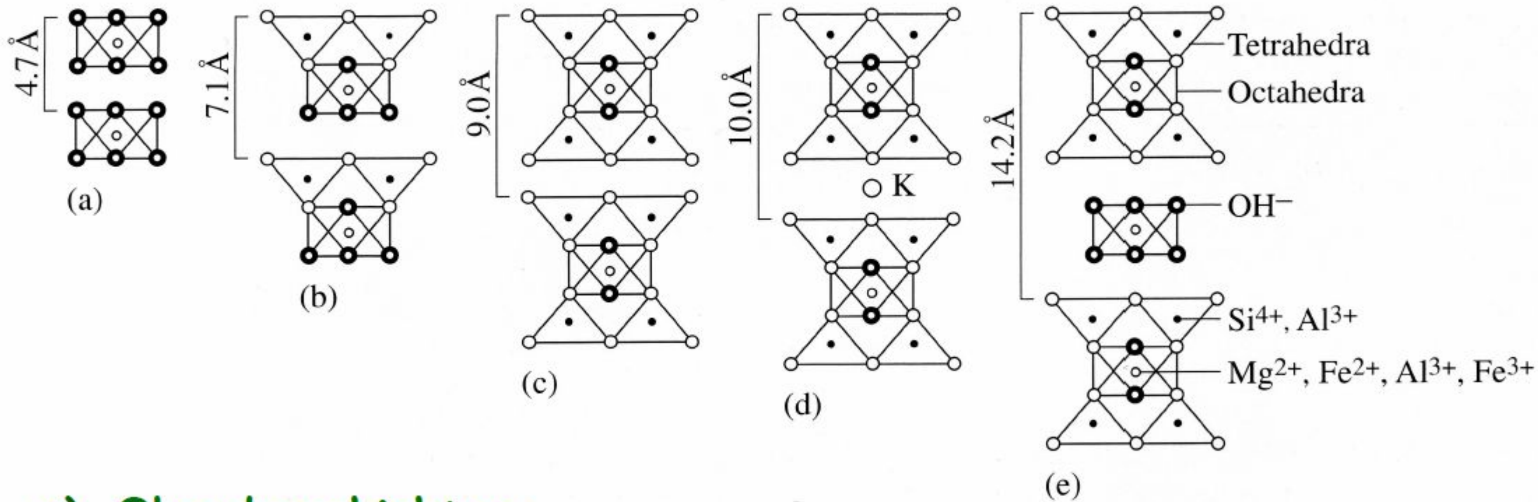
Inselsilikate: Zirkon

Zirkon	$ZrSiO_4$
Kristallsystem:	tetragonal (Klasse 4/mmm)
Ausbildung:	Kristalle von prismatischem bis pyramidalem Habitus
Bruch:	eine unvollkommene Spaltbarkeit
Härte:	$7^1/_2$
Kristalle:	gut ausgebildete Kristallflächen selten; fast immer eingewachsen; sekundär in abgerollten Körnern
Glanz:	nichtmetallischer hoher Glanz
Farbe:	grau, braun, braunrot, seltener gelb, grün oder farblos
Vorkommen:	magmatisch und metamorph; sekundär in Sedimenten (wichti-



Schichtsilikate (sheet silica)

Einteilung: Oktaeder-/Tetraederschichten



a) **Okaederschichten**:
Brucitschicht $Mg(OH)_2$ bzw. Gibbsitschicht $Al(OH)_3$

b) **Zweischichtsilikat**, z.B. Serpentin $Mg_3[Si_2O_5(OH)_4]$

c) **Dreischichtsilikat**, z.B. Talk $Mg_3[Si_4O_{10}(OH)_2]$

d) **Glimmer** (große Kationen zwischen den Schichten)

e) **Chlorit** (Vierschichtsilikat aus Talk-ähnlicher Schicht (TOT) und Brucit-ähnlicher Zwischenschicht)

Schichtsilikate

Systematik der Schichtsilikate

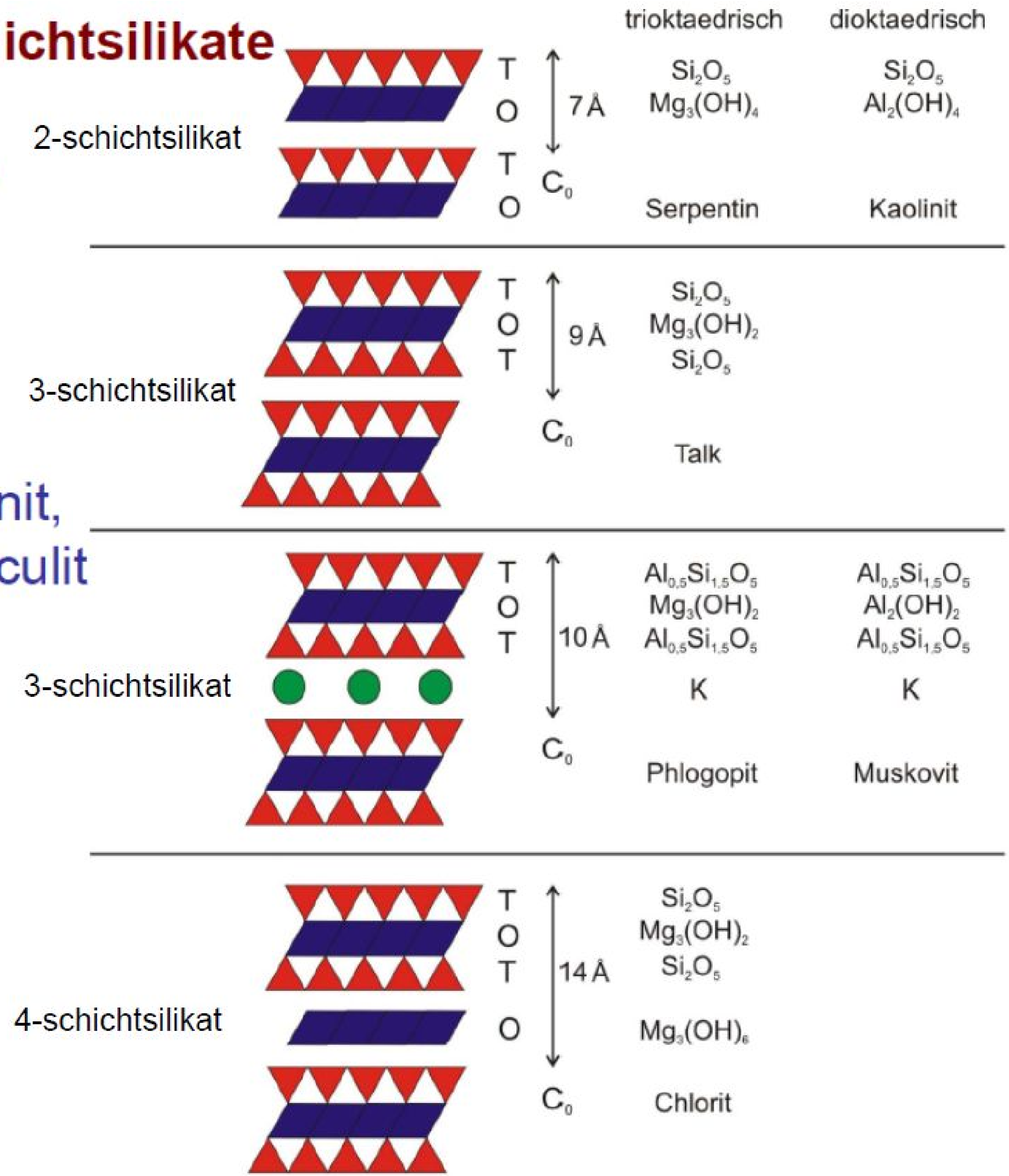
Serpentin, **Kaolin**

Talk

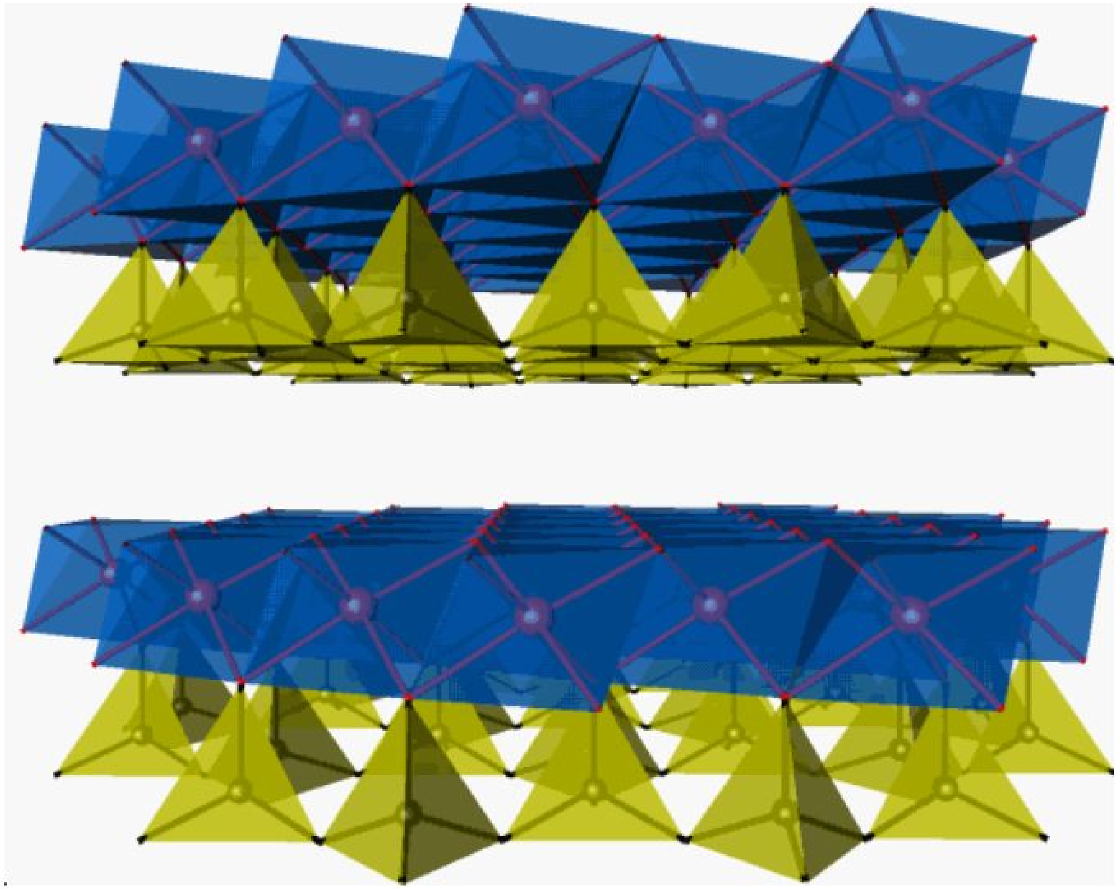
„Tonminerale“
z.B. Montmorillonit,
Nontronit, Vermiculit

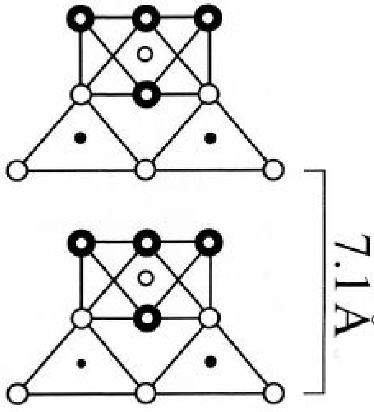
Biotit, **Muskovit**

Chlorit



Serpentin $Mg_3[Si_2O_5(OH)_4]$





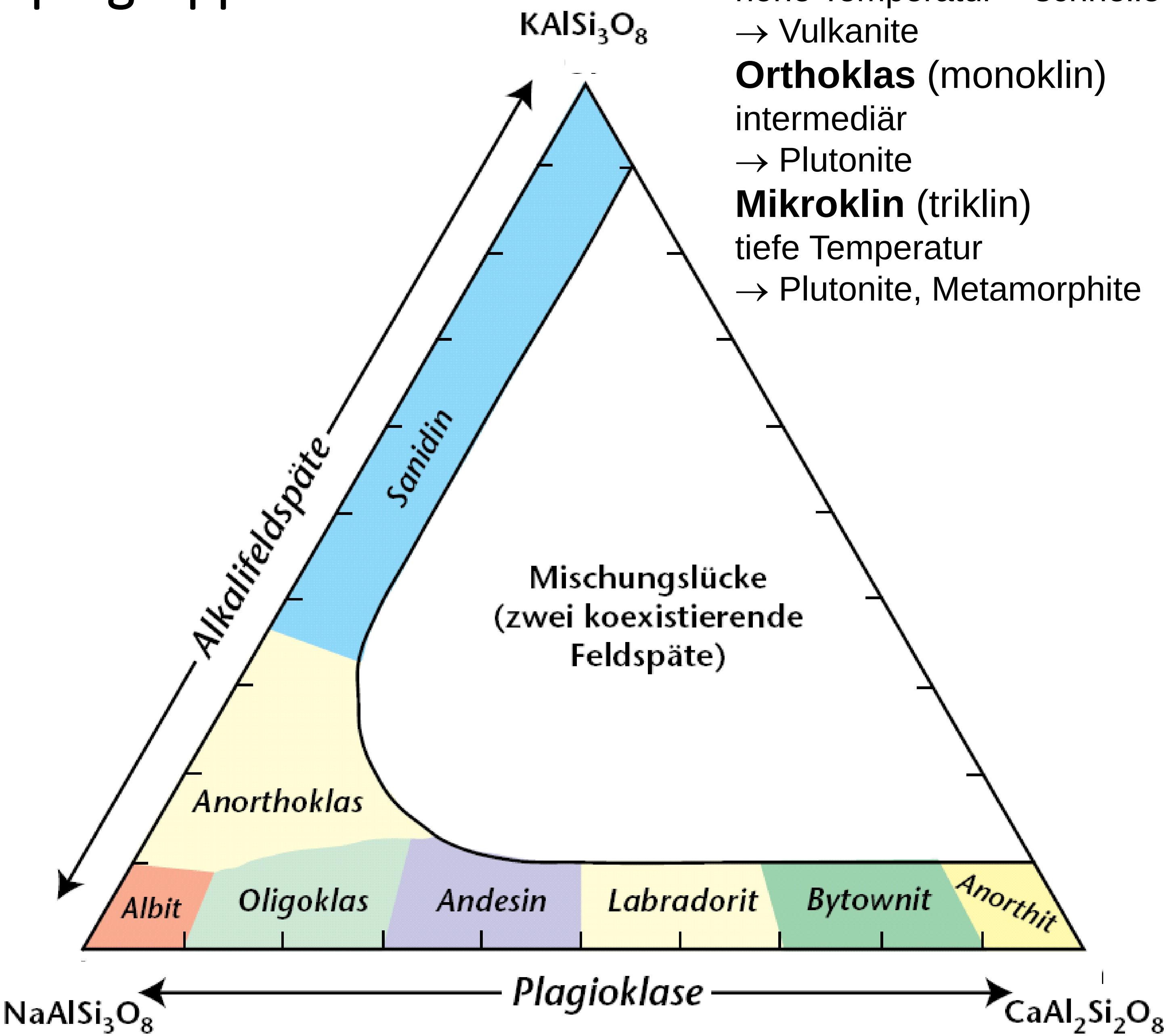
2-Schicht-Silikat

Feldspatgruppe

Sanidin (monoklin)
hohe Temperatur + schnelle Abkühlung
→ Vulkanite

Orthoklas (monoklin)
intermediär
→ Plutonite

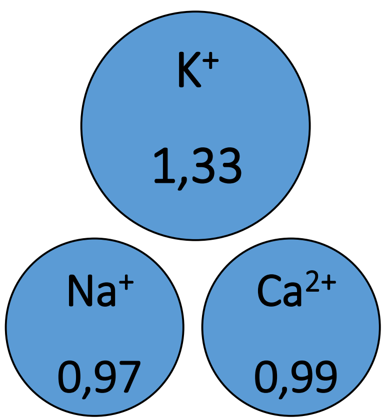
Mikroklin (triklin)
tiefe Temperatur
→ Plutonite, Metamorphite

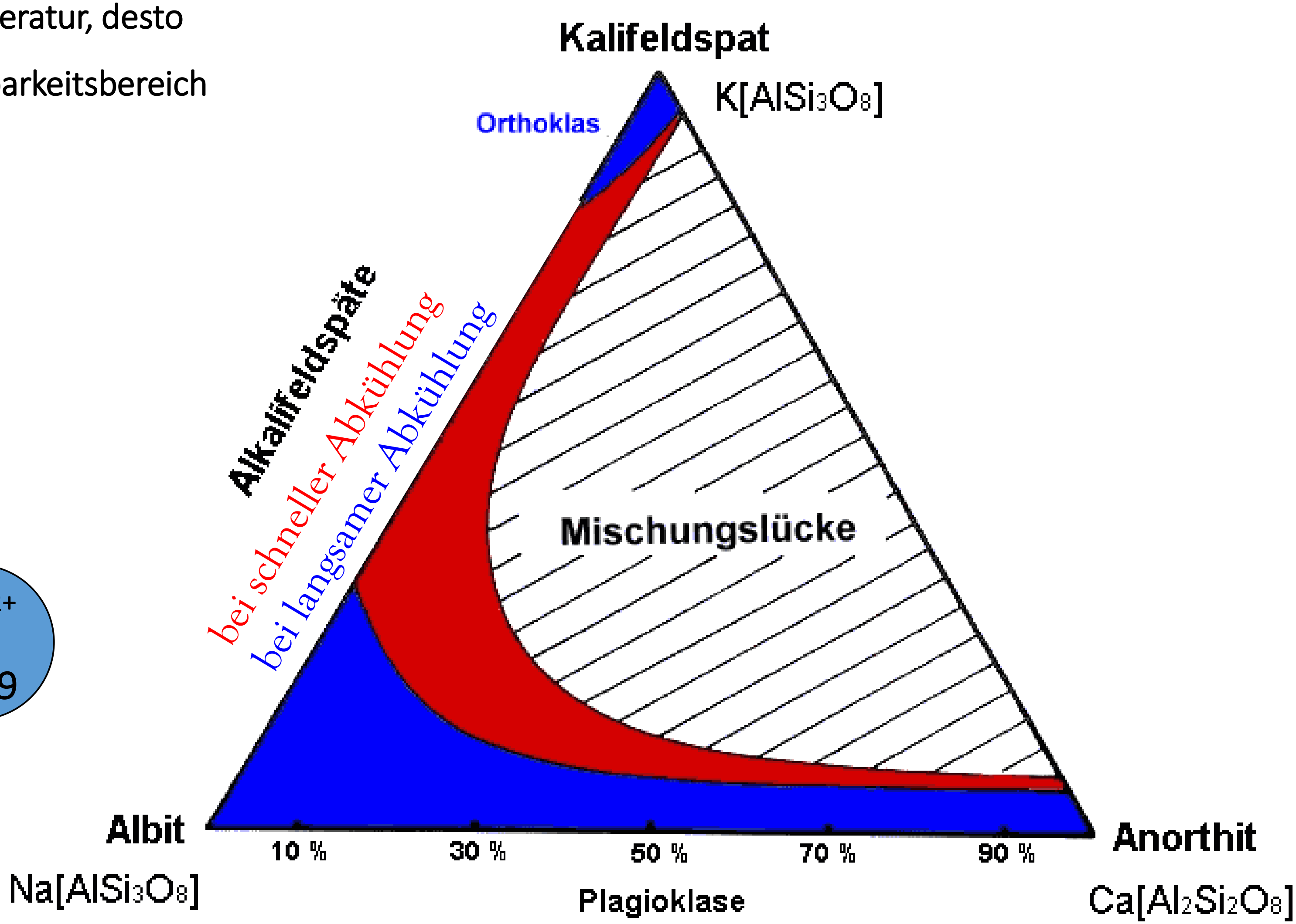


Einfluss der Temperatur auf die Mischbarkeit von Feldspäten

Je höher die Temperatur, desto größer der Mischbarkeitsbereich

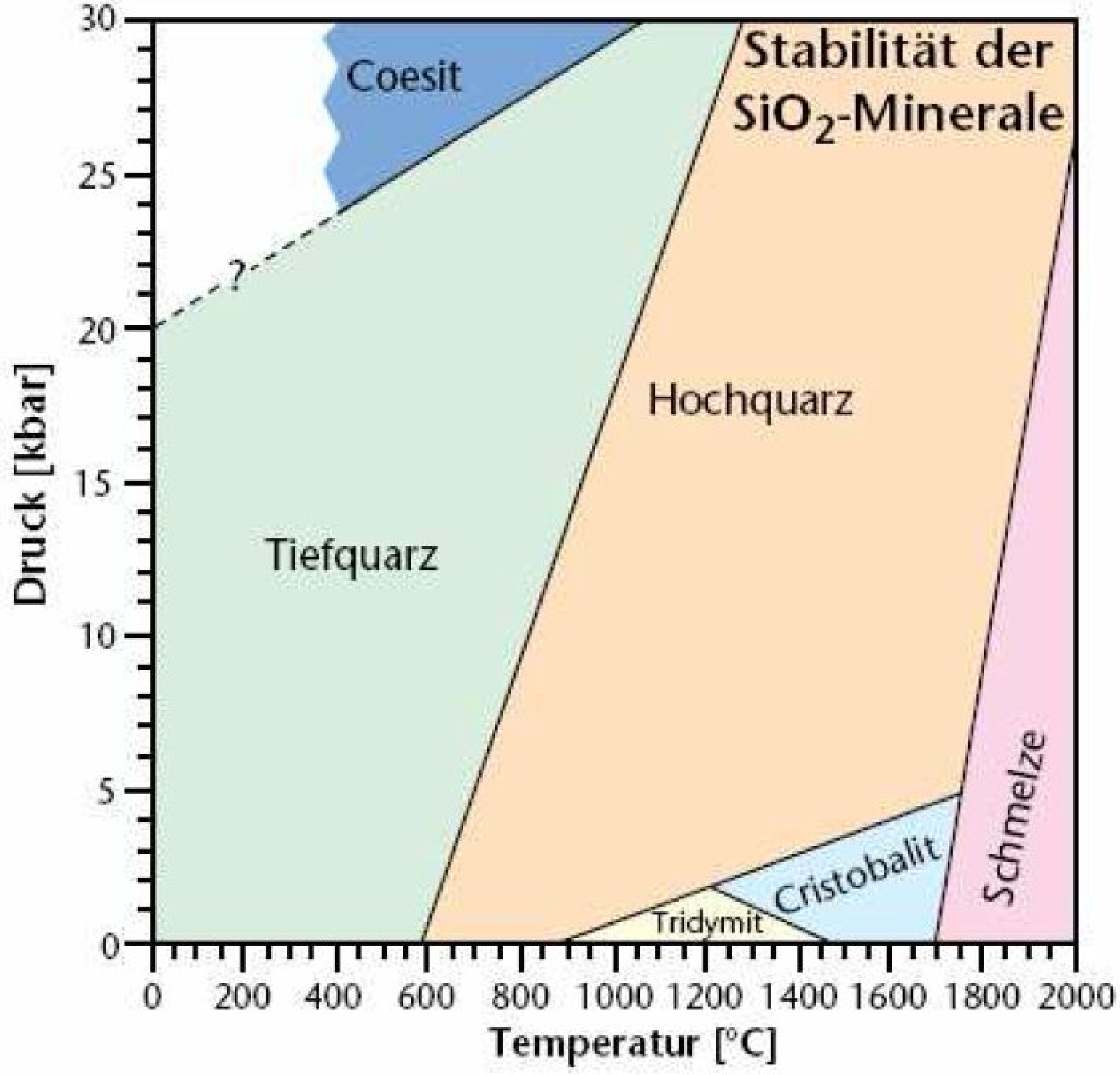
Ionenradien [Å]





Die Prozentangaben in der Plagioklasreihe beziehen sich auf den Anorthitgehalt.

Stabilitätsfelder der SiO_2 - Modifikationen

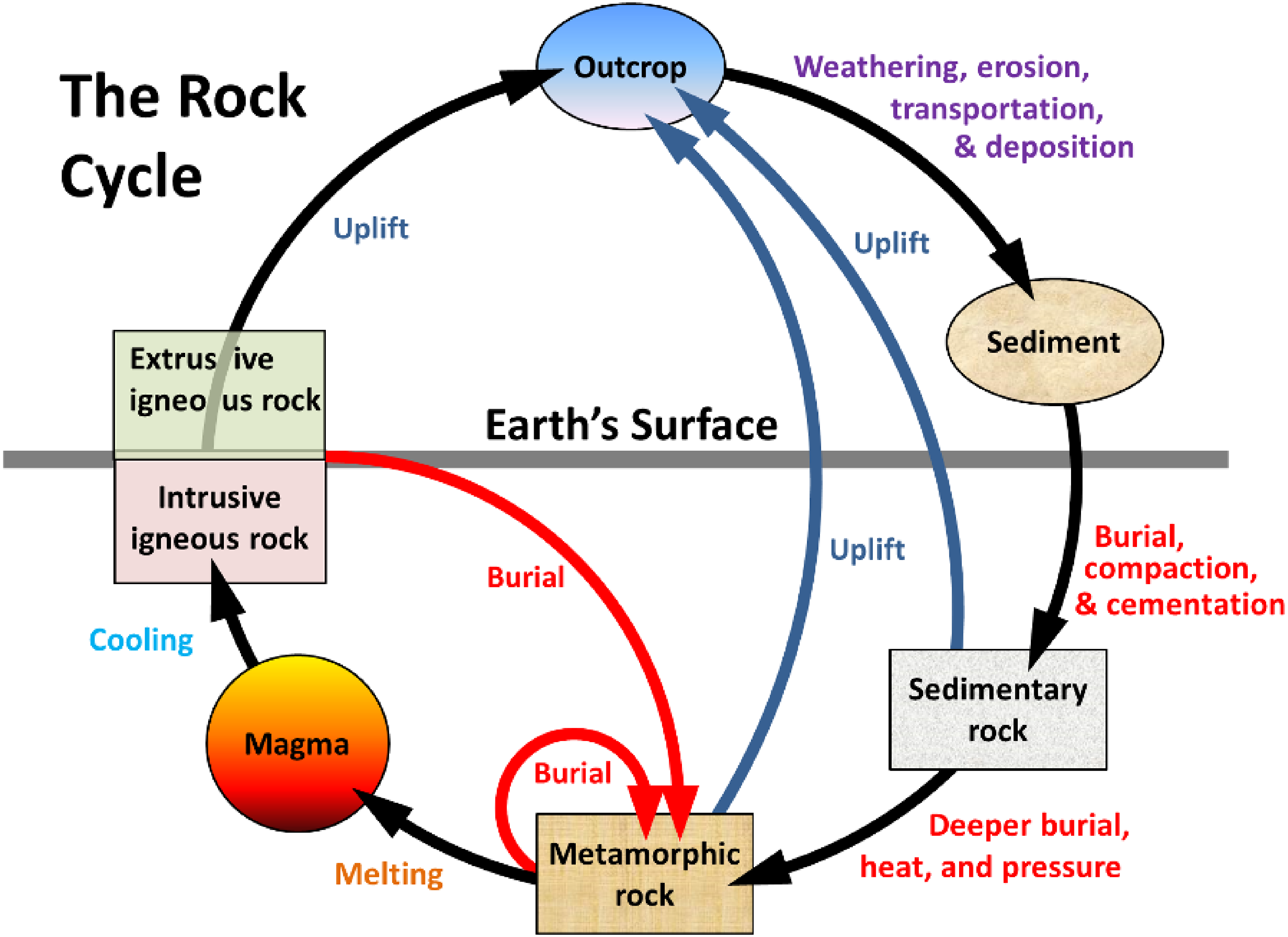


Gesteine - Rocks

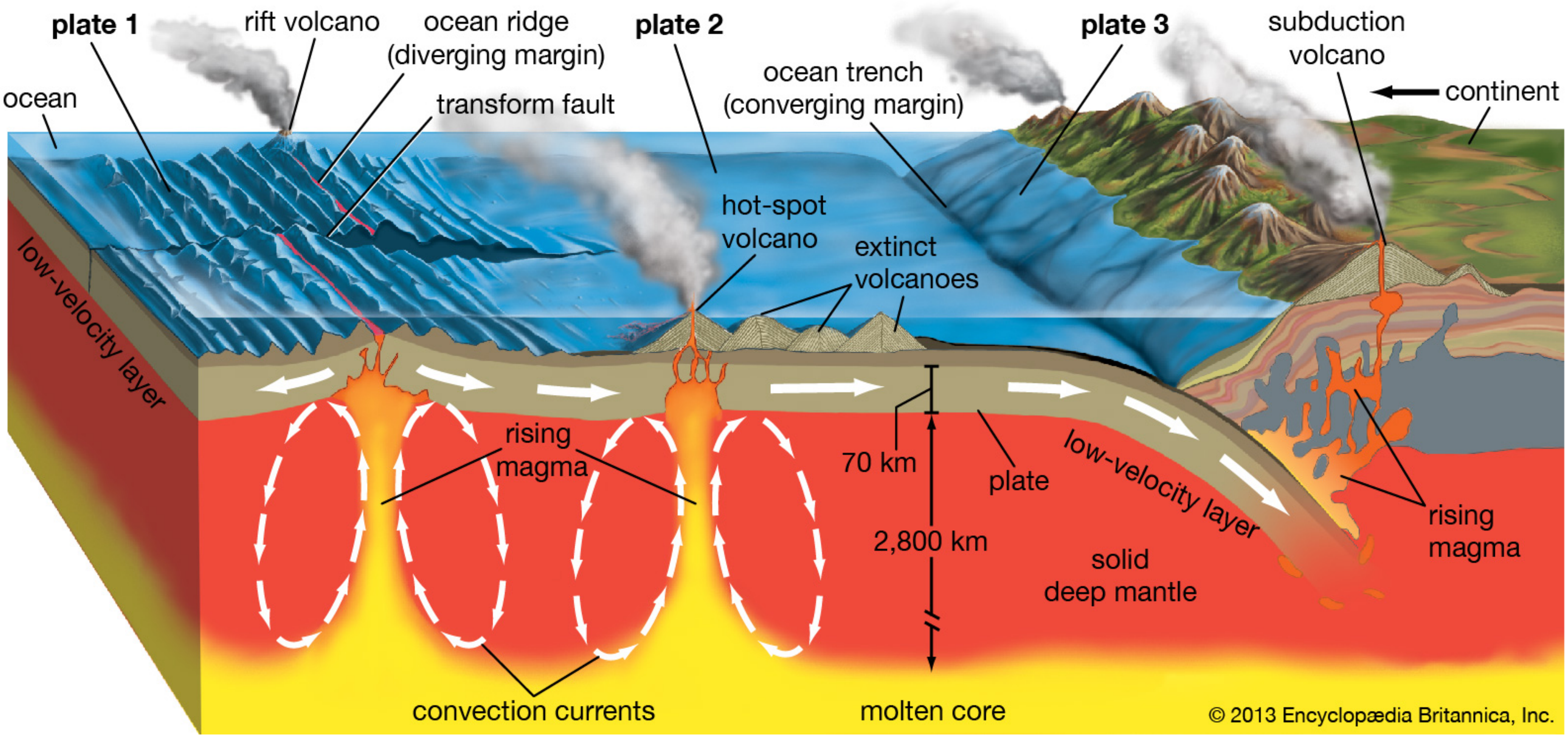
- 3 major types:

1) igneous rocks
2) sedimentary
3) metamorphic rocks

→ Geological rock cycle


The Rock Cycle
Outcrop
Weathering, erosion, transportation, & deposition
Uplift
Sediment
Uplift
Extrusive igneous rock
Earth's Surface
Intrusive igneous rock
Burial
Uplift
Burial, compaction, & cementation
Cooling
Sedimentary rock
Magma
Burial
Metamorphic rock
Deeper burial, heat, and pressure
Melting

Volcanoes and tectonics



The lithosphere slides over the asthenosphere which is weakened due to it being near its solidus. The asthenosphere, though solid, flows by convection

Plate tectonics and magma composition

1. Divergent margins: Decompression melting
-> low volatile abundance, low SiO_2 (~50%), low viscosity basaltic magmas (e.g. Krafla, Iceland)

2. Convergent margins: Addition of volatiles
Melting of the mantle wedge below the continental crust, magmas commonly differentiate during their rise through the thicker and chemically distinct continental crust. High volatile abundance, intermediate SiO_2 (60-70%), high viscosity andesites and dacites (e.g. Montserrat, West Indies)

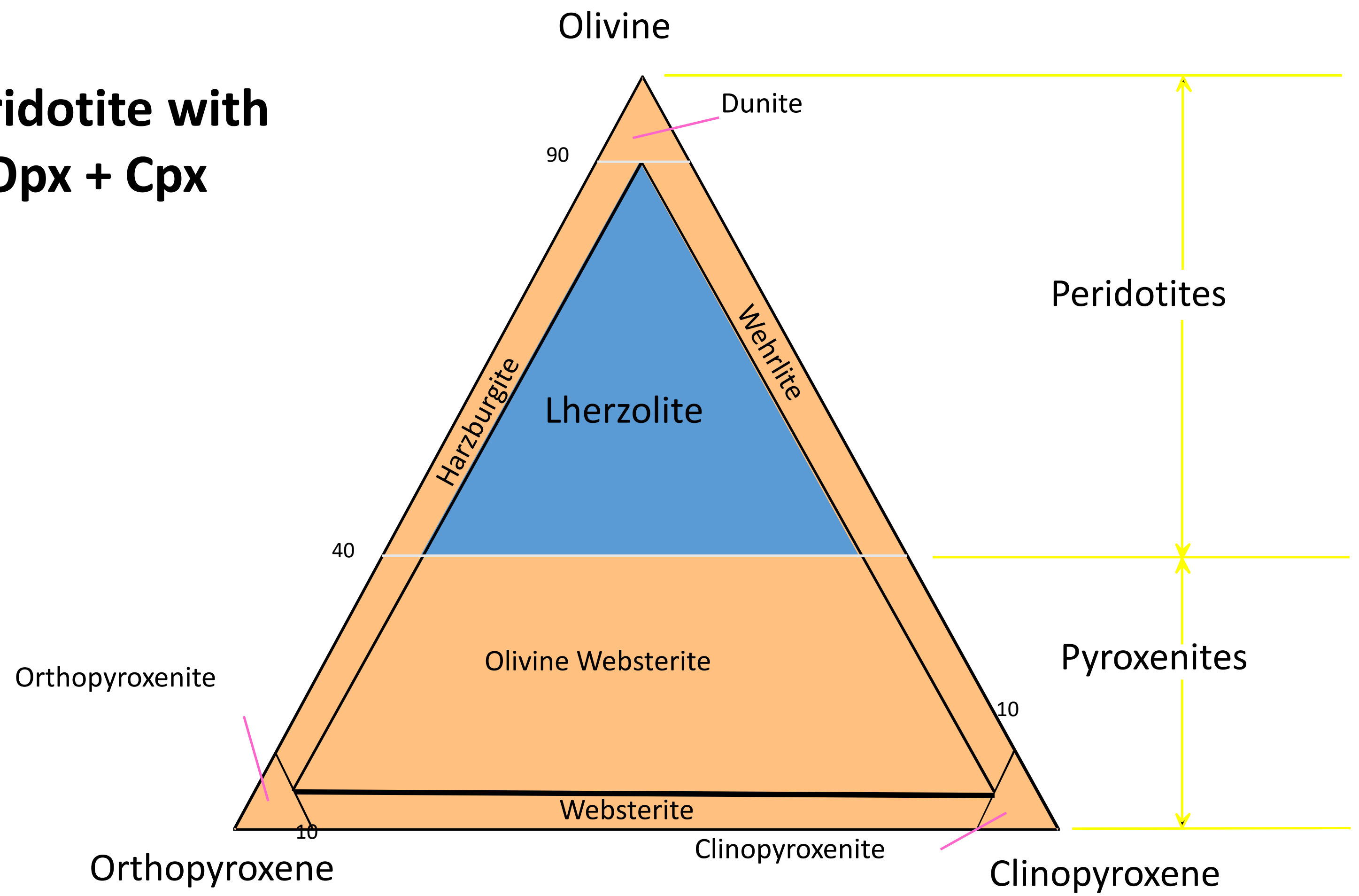
3. Intraplate \`Hot-spot\` settings: Temperature increase

A. Oceanic: Mantle plumes melt thin oceanic crust producing low viscosity basaltic magmas (e.g. Kilauea, Hawaii)

B. Continental: Mantle plumes melt thicker, silicic continental crust producing highly silicic (>70% SiO_2) rhyolites (e.g. Yellowstone, USA)

The Earth's mantle is a lherzolite

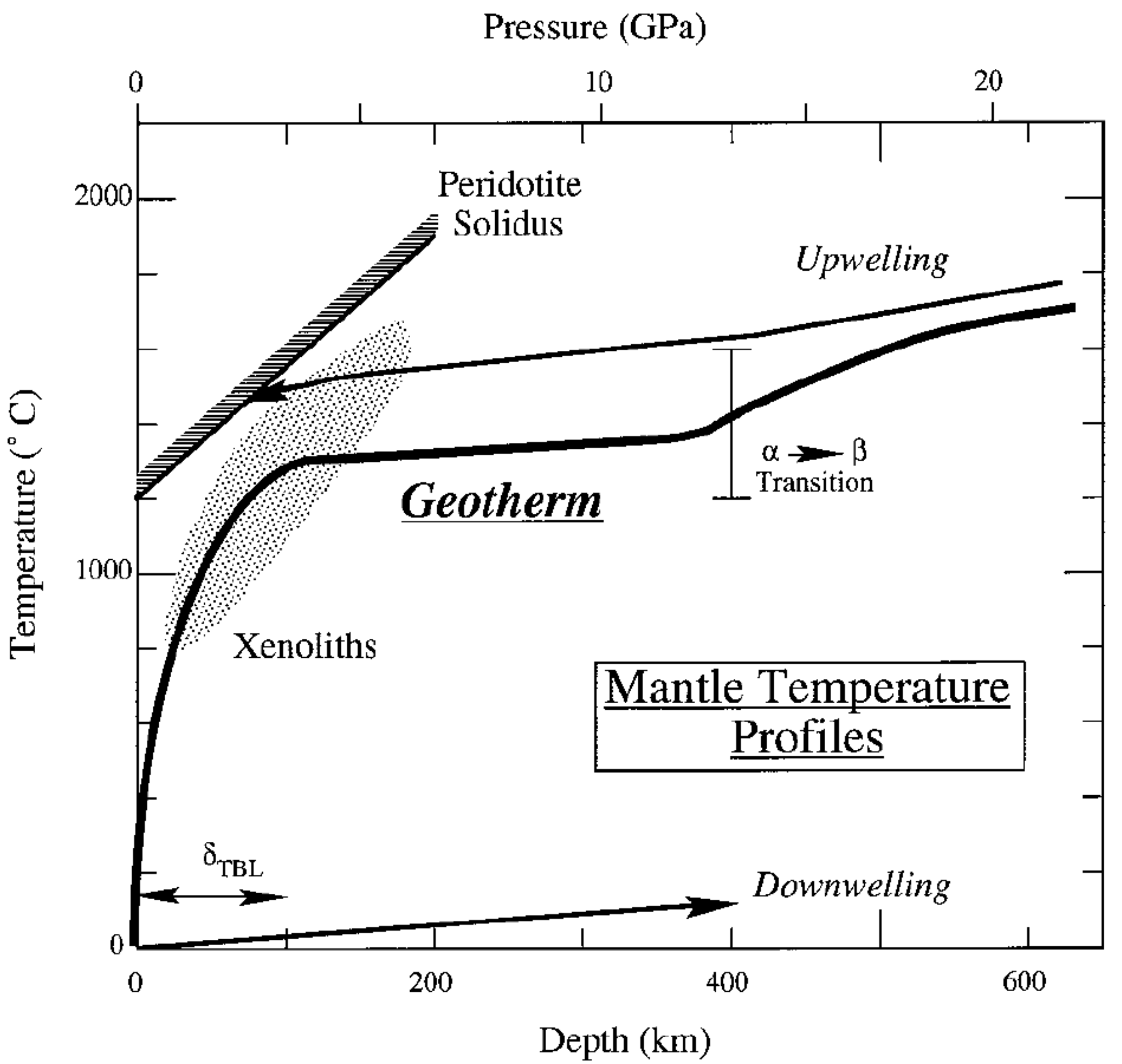
A type of peridotite with Olivine > Opx + Cpx



Conductivity

The lithosphere cools conductively

The asthenosphere is very near to the solidus



Melting by temperature increase

Impact melting

- meteorite

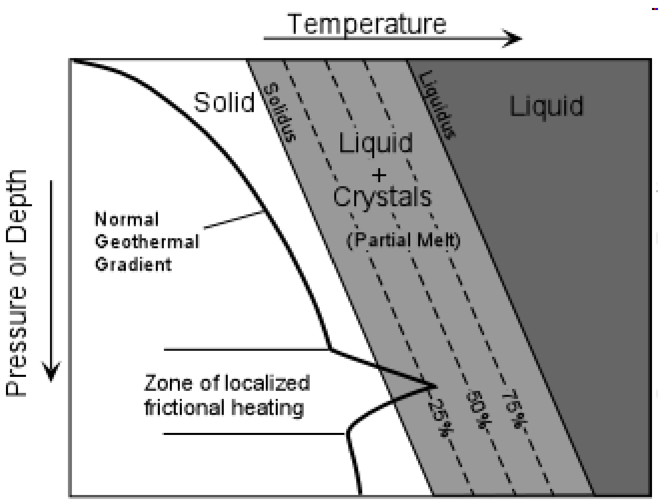
Radioactive heat generation

- planetary formation

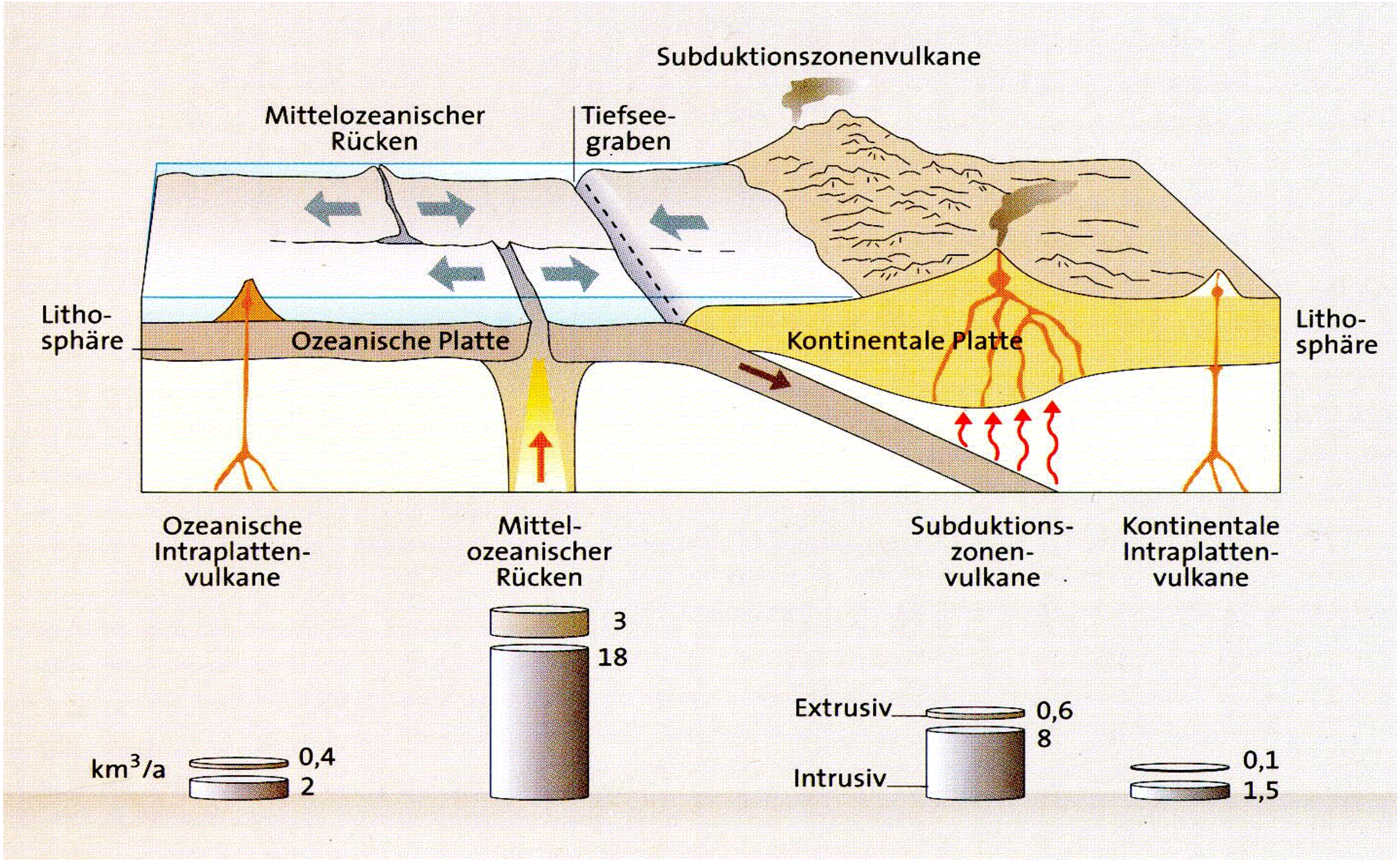
Conduction

- dyke/sill intrusion
- migmatism
- partial melting

Frictional heating and viscous dissipation

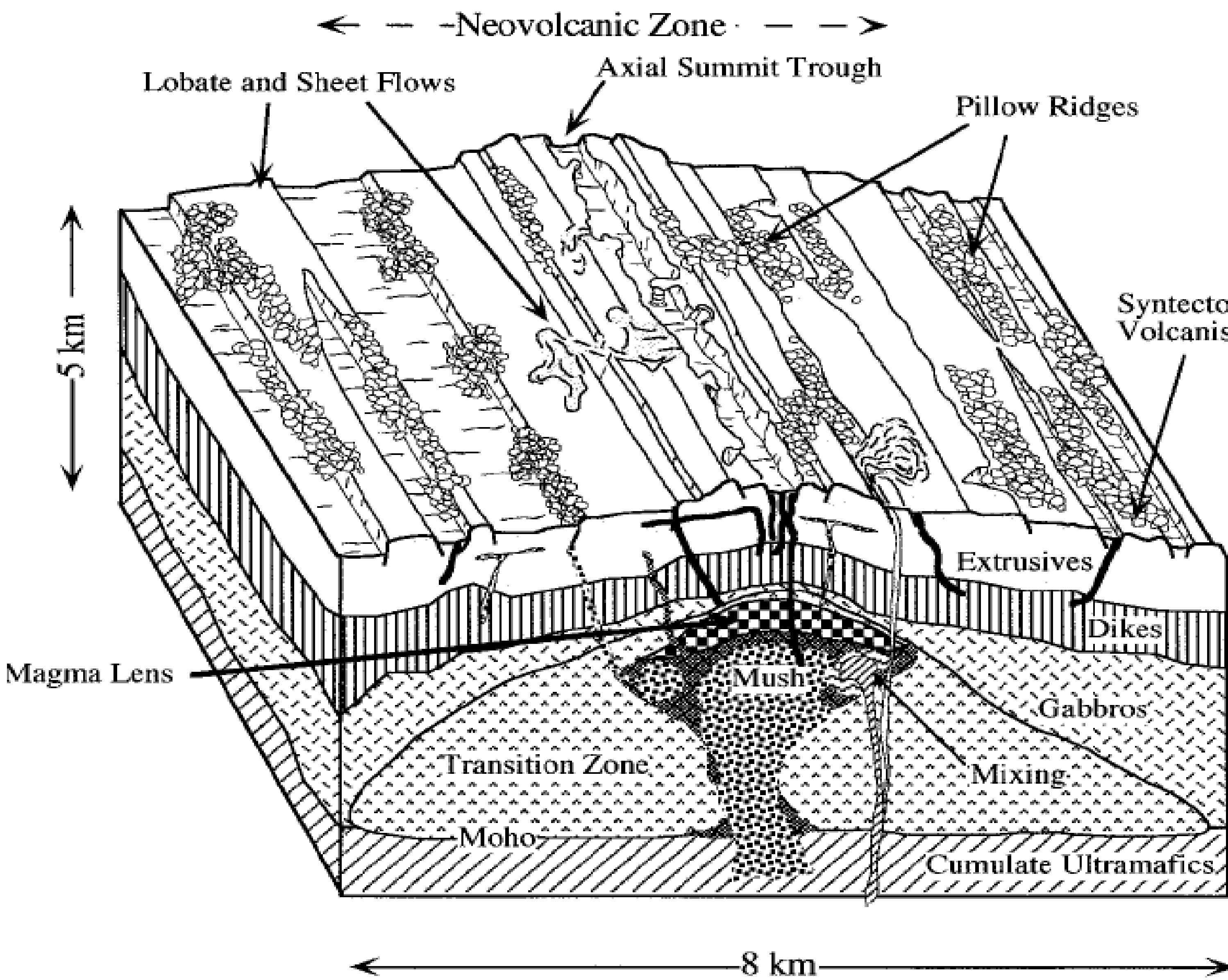


Melting by decompression



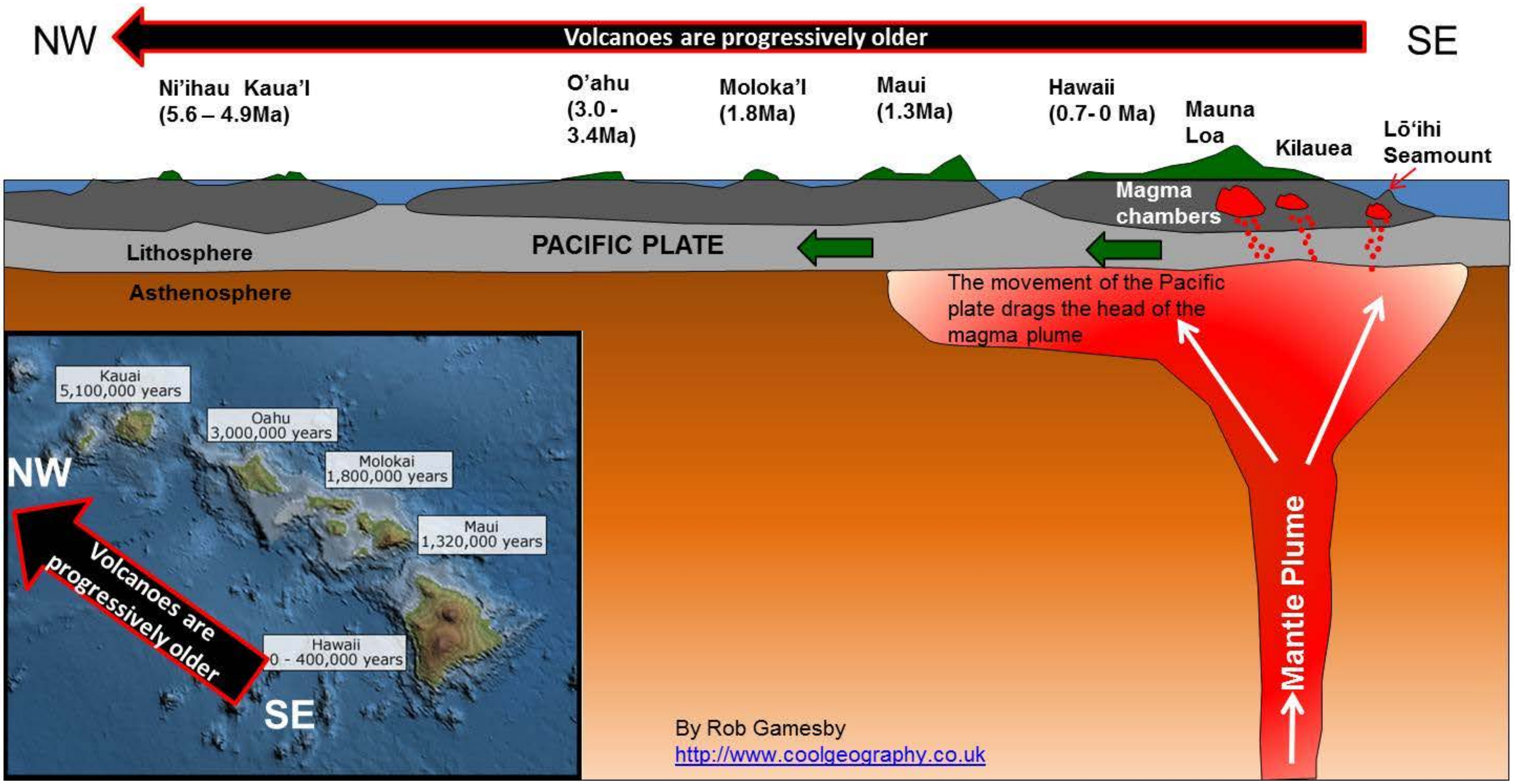
Melting by decompression prevails at Mid Ocean Ridges

MOR



Neovolcanic Zone
Lobate and Sheet Flows
Axial Summit Trough
Pillow Ridges
Syntectonic Volcanism
5 km
Extrusives
Dikes
Magma Lens
Mush
Gabbros
Transition Zone
Mixing
Moho
Cumulate Ultramafics
8 km

Melting at hotspots



Melting occurs as P-T profile across the plume intersects the solidus (*c.f.*, as for the convecting mantle)

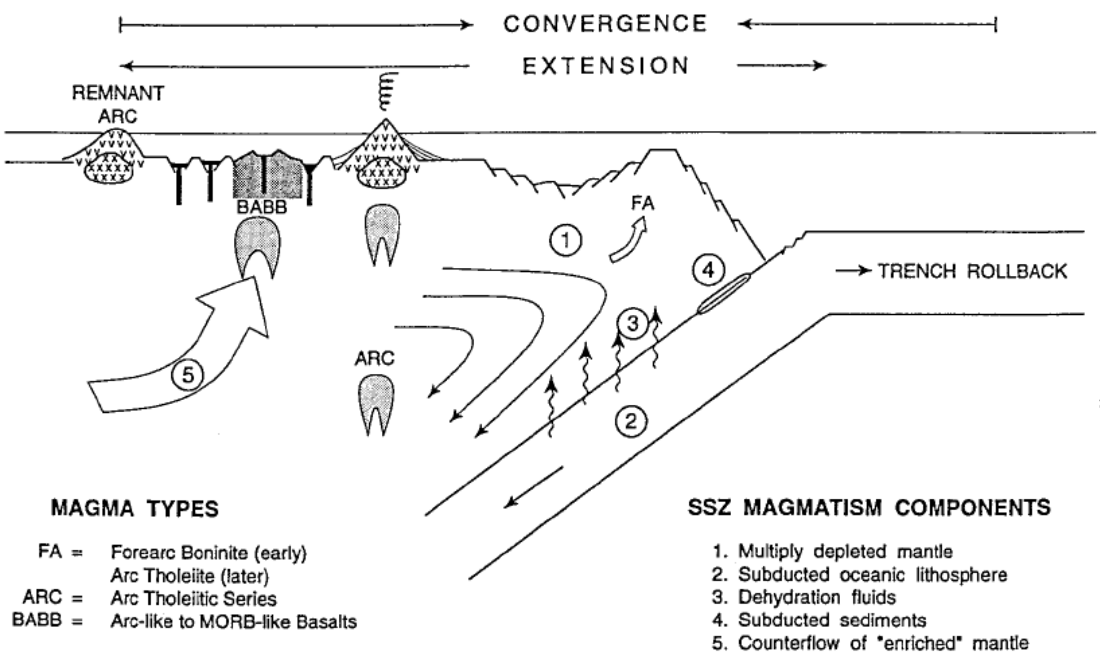
Intraplate magmatism

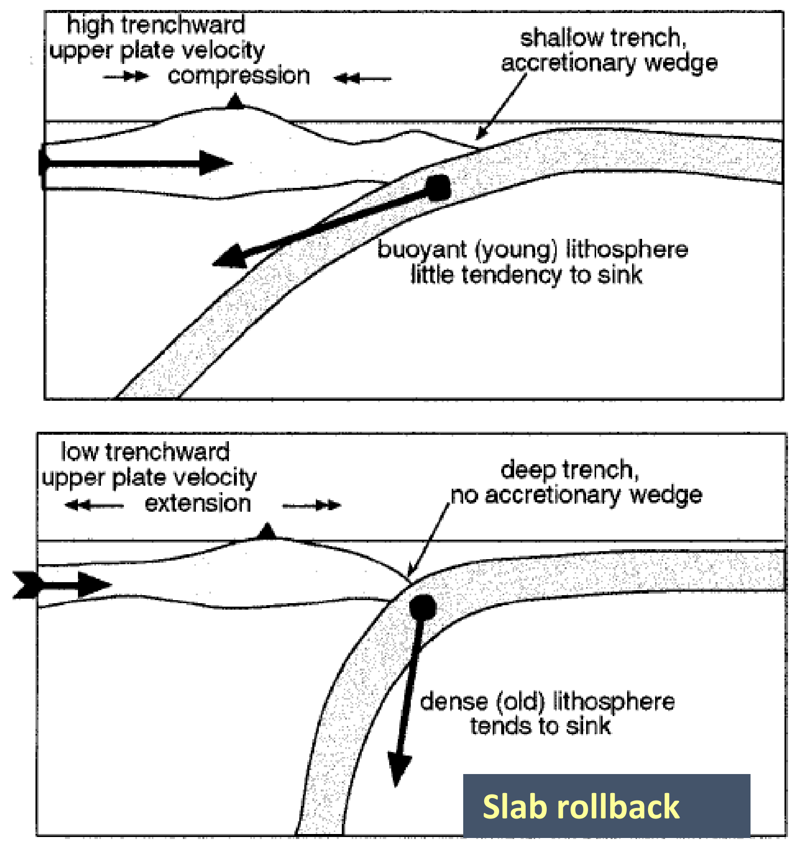
Plumes or Hotspots correlate with Geoid highs (*i.e.*, rise in the gravitational potential surface)

They may originate from the D” layer at the CMB or U/LMB

Hotspots are ‘hotter’ than the surrounding mantle: the generation of melt is accordingly high

Melting by chemical changes

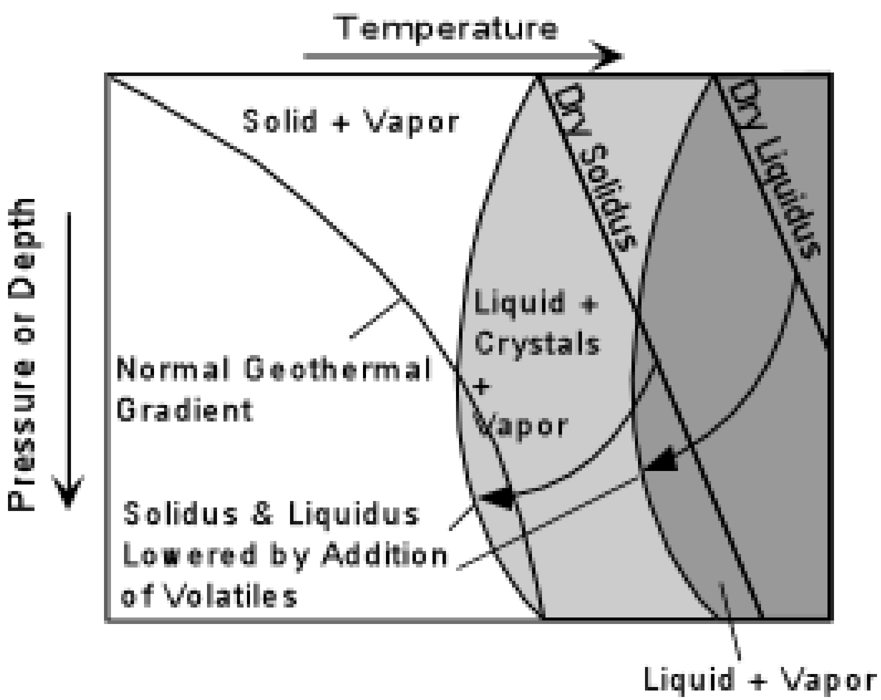


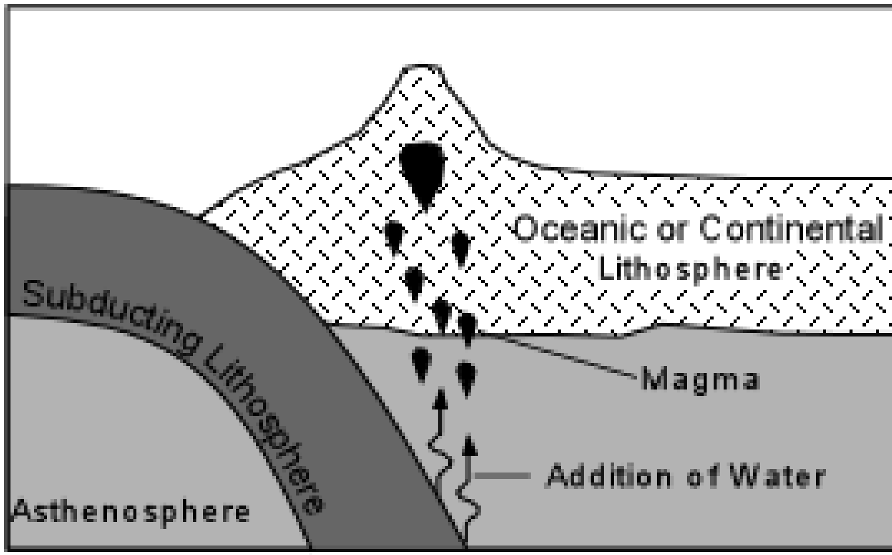


- Volcanic arcs parallel the trench
- Segmentation of the arc due to structure in the upper plate:
  - –Ridge (NVZ)
  - –Windows (CVZ)
  - –Flat subduction (SVZ) – may produce adakite
  - –Lateral motion (W Aleutian)

Melting by chemical changes

Water in the melt <u>decreases the viscosity</u> and may favor diapirism.

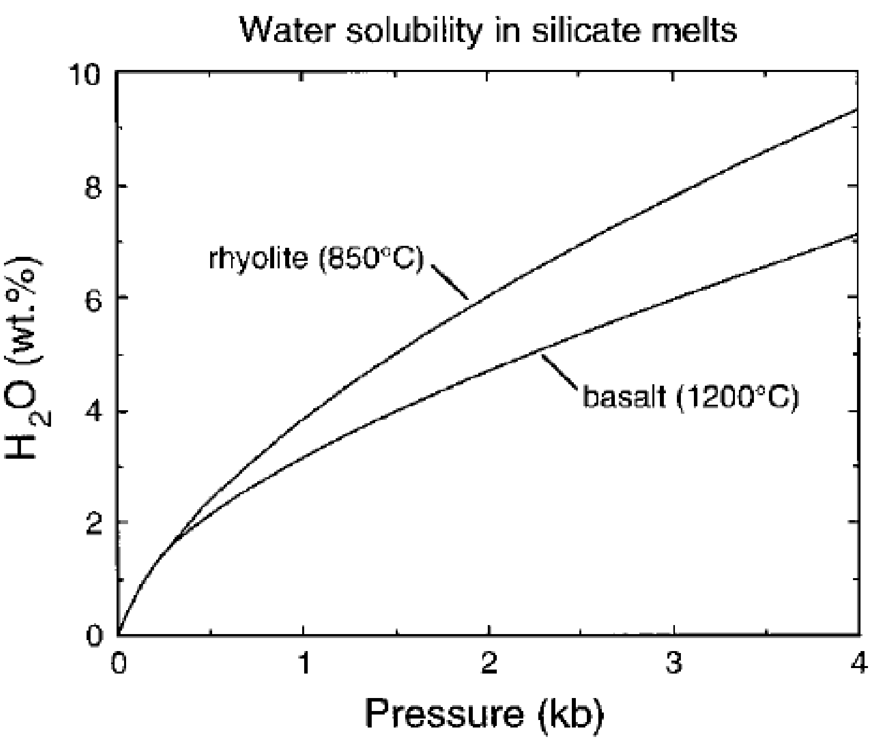


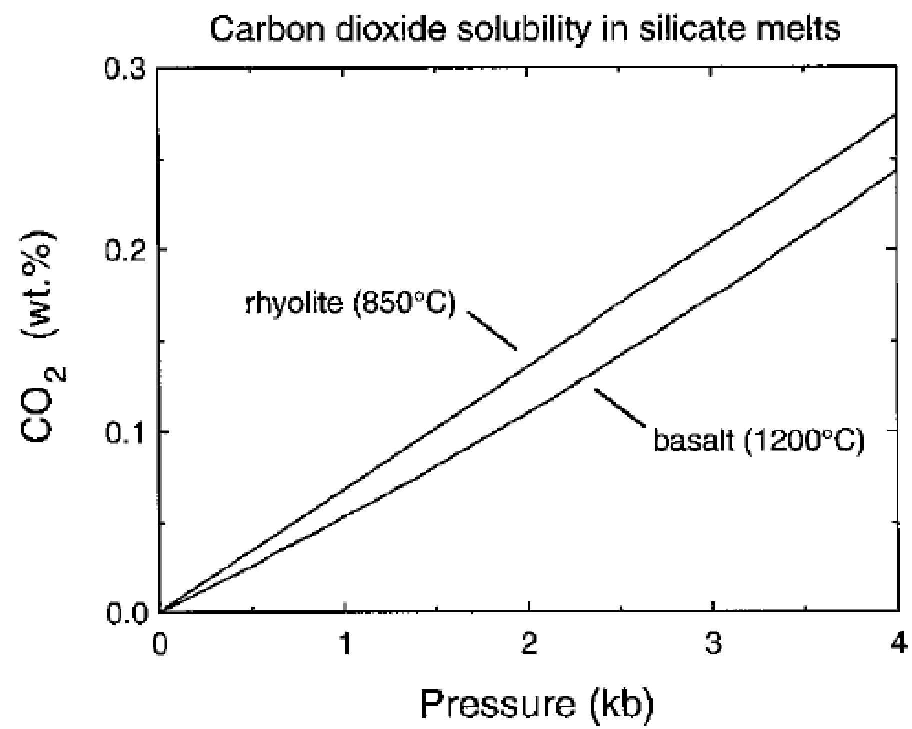


Solubility of Volatiles in Magmas

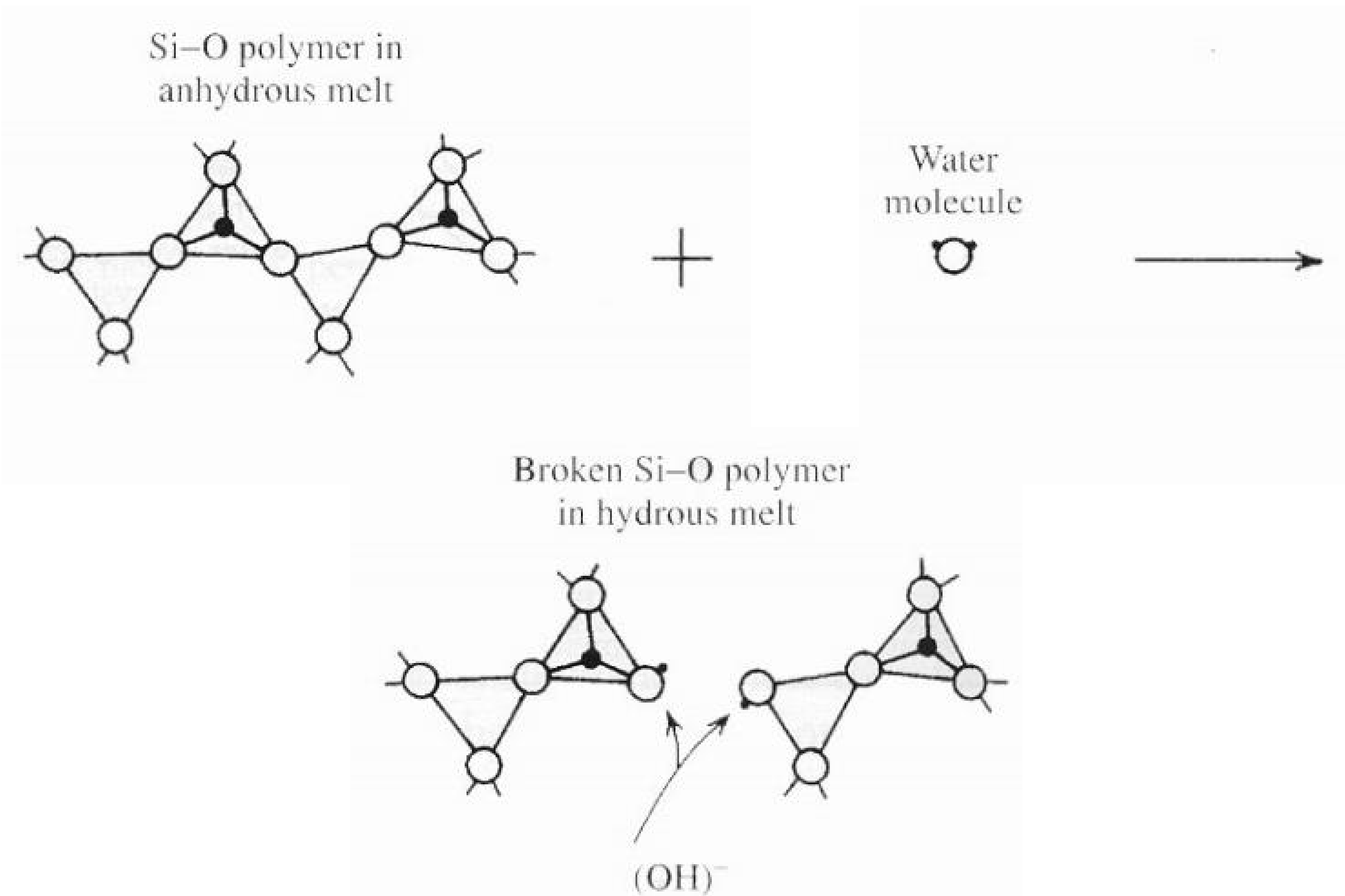
Solubility: max. amount of volatiles that can dissolve under given P, T, X

→ H_2O is 50-100 x more soluble than CO_2 !!



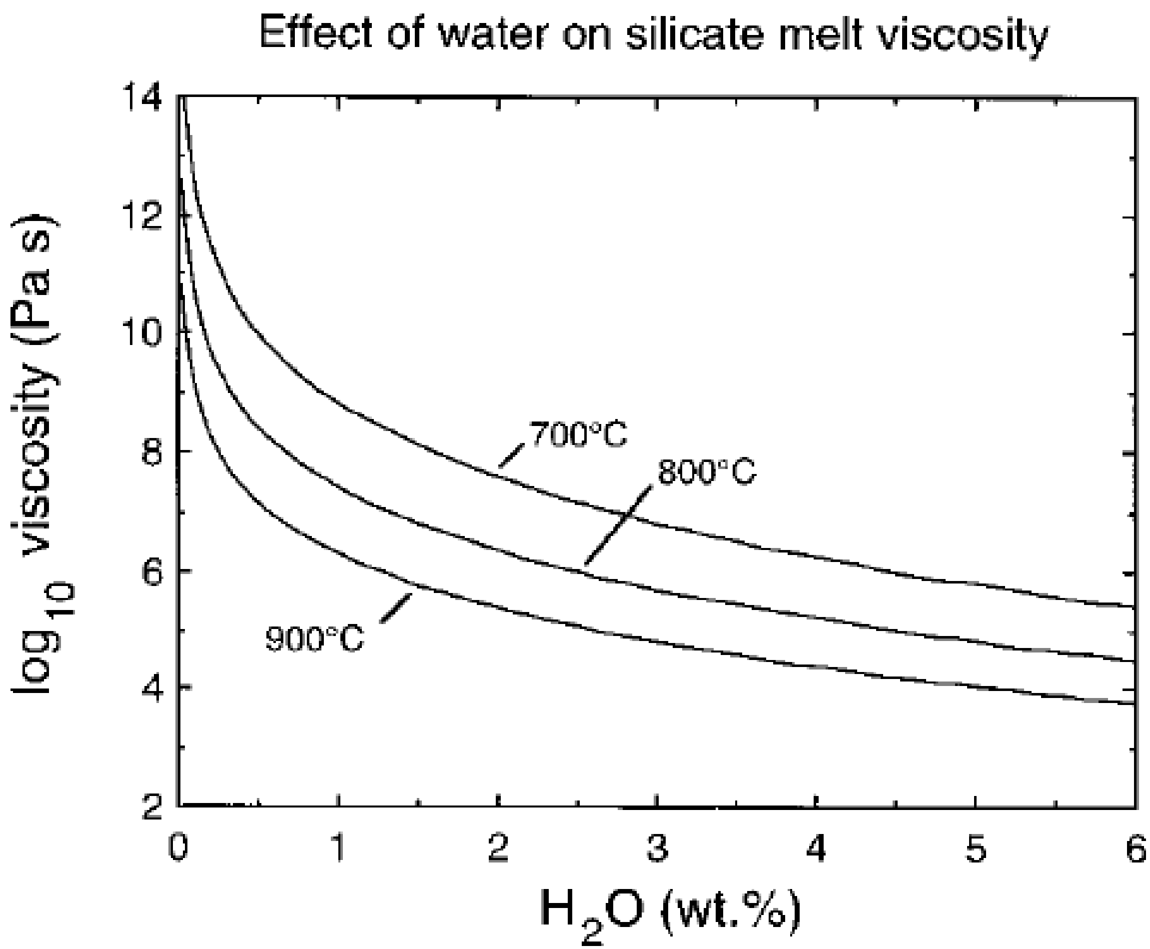


Effect of Water:
Depolymerization of Silicate Melts



Viscosity: effects of water

- As magma ascents, it looses water (to bubbles) and becomes more viscous
- Decrease the activation energy and the Si-O bonds



Why study volatile species?

→ **Play a fundamental role in forcing magma to ascend, and erupt**

For example:
typical percentage by mass might be 0.1%

↕

equivalent to 90% bubbles in magma!

↓

Volume increase !!

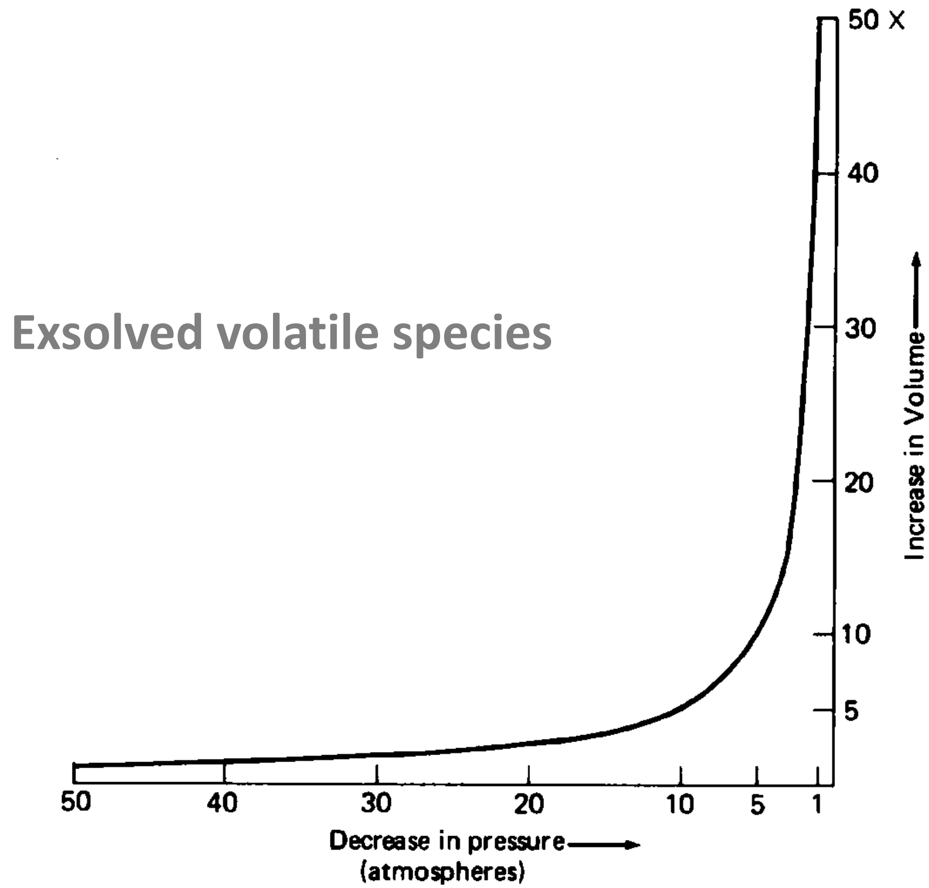
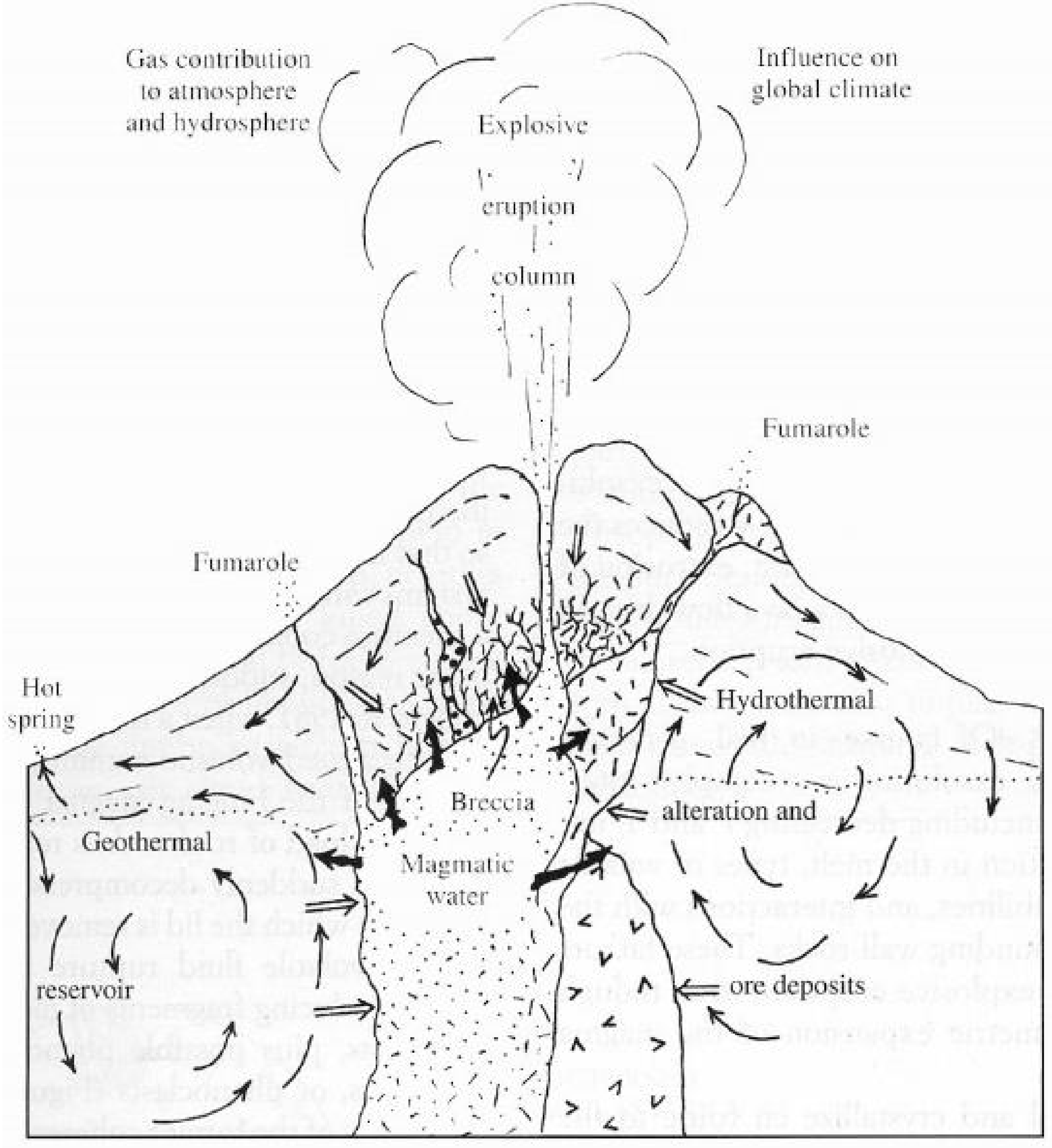
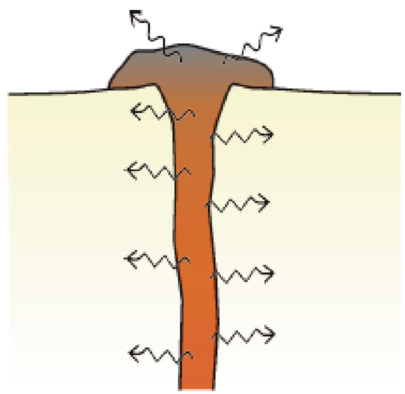


Figure 3.4. Graph showing the approximate volume of volcanic gases at a constant high temperature and varying pressure. For each 10 meters of depth below sea level, or about 4 meters of depth below ground level, pressure increases by 1 atmosphere. For example, volcanic gas bubbles in magma at a depth of 36 meters below ground surface (10 atmospheres) would expand approximately 10 times in volume as they approach the surface (1 atmosphere).

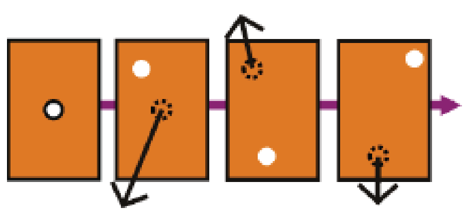
Volatiles, hydrothermal systems and volcanic eruptions



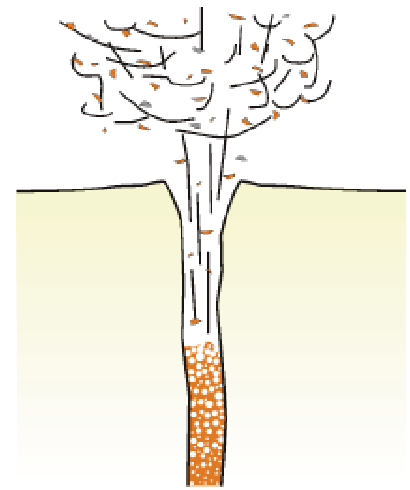
Volatiles influence eruptive style



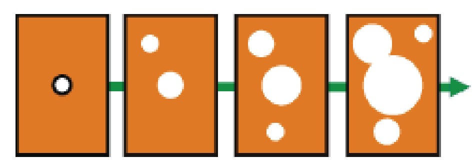
Open-system degassing



- gas is removed from the system as it is exsolved from the melt



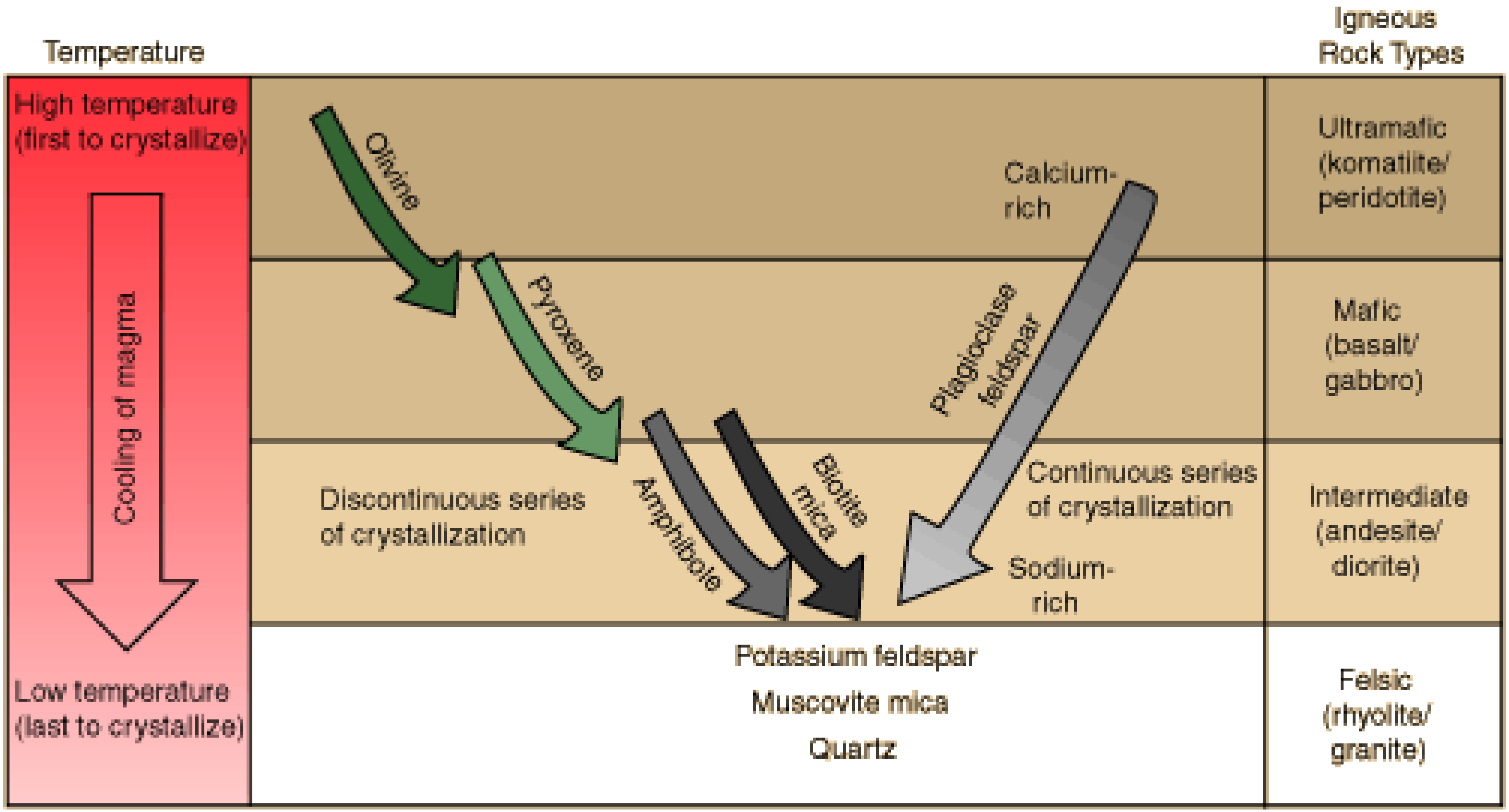
Closed-system volatile exsolution



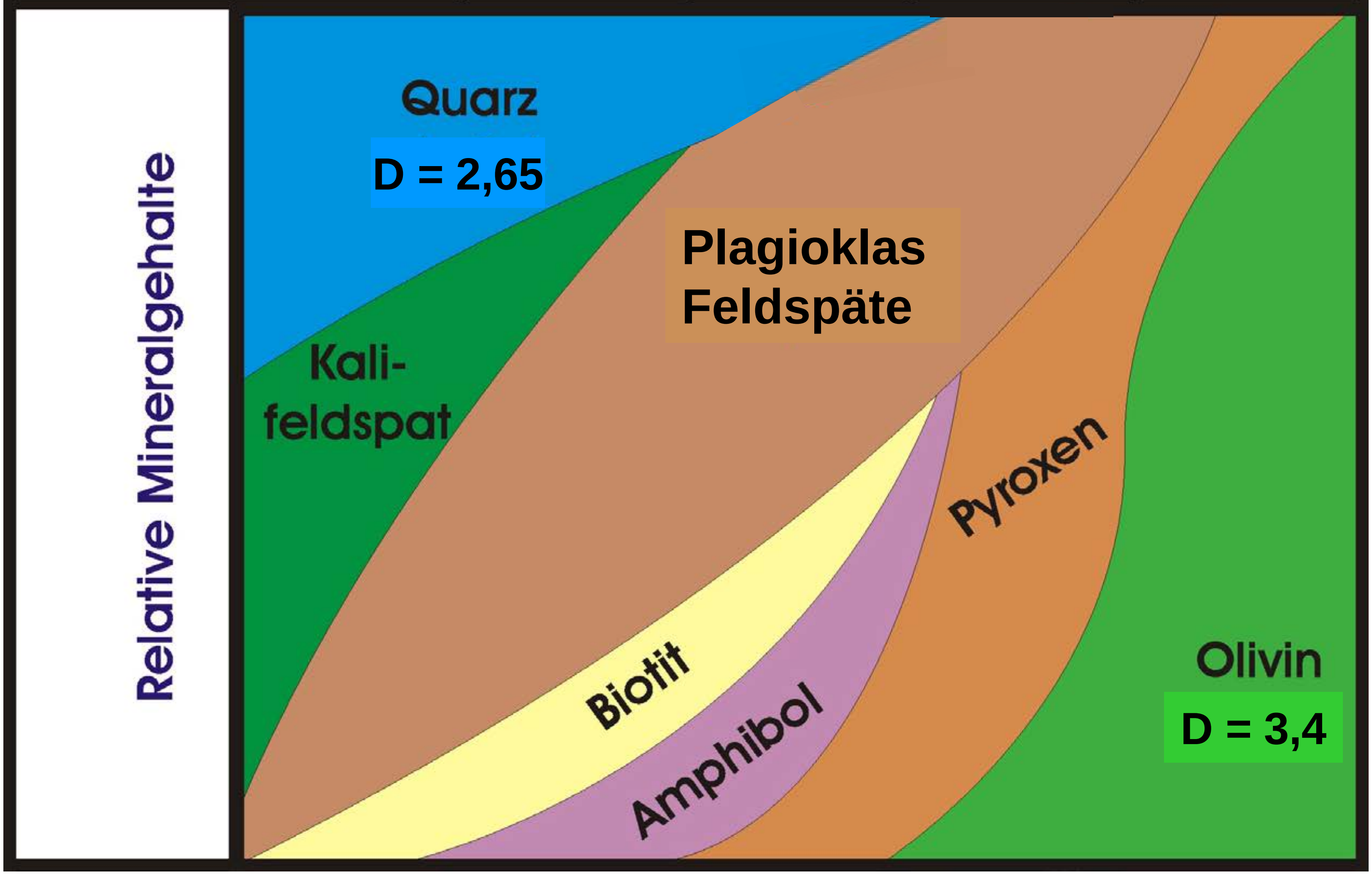
- exsolved gas remains in contact with the melt

From melts to igneous rocks

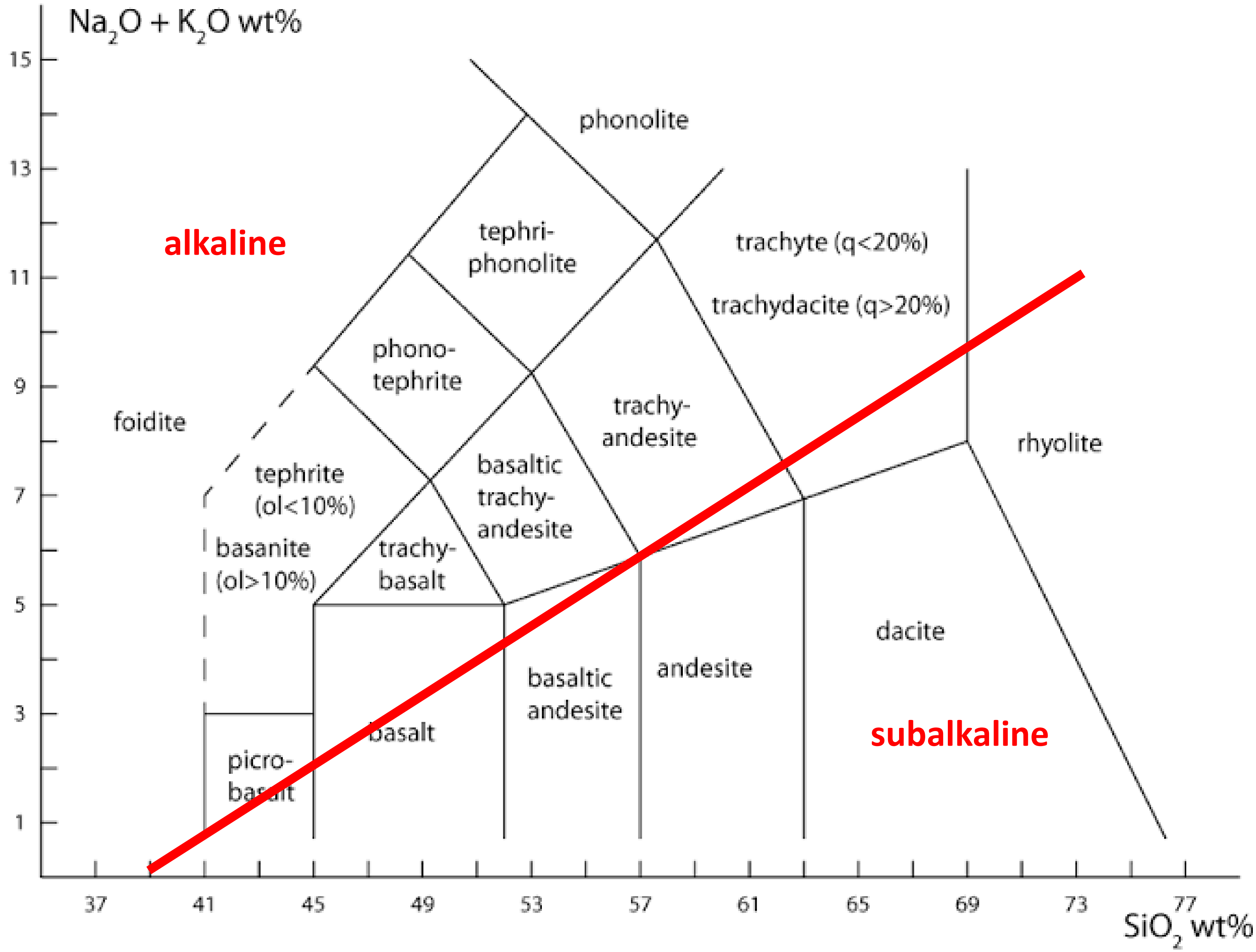
Bowen's Reaction Series for fractional crystallization



Intrusiv	Granit	Grano-diorit	Diorit	Gabbro	Peridotit
Extrusiv	Rhyolith	Dacit	Andesit	Basalt	-



Chemical classification of igneous rocks (TAS-Diagram)



Metamorphose

Isochemische Umwandlung des Mineralbestandes von Gesteinen durch Druck- und Temperaturänderungen unter Beibehaltung des festen Zustands (Lösungs-Fällungs-Reaktion) und Wachstum neuer, P- und T-angepasster Minerale.

Temperaturbereich > 220 ± 20 °C bis 640 °C (beginnende Anatexis)

Metamorphite = Gesteine der Metamorphose

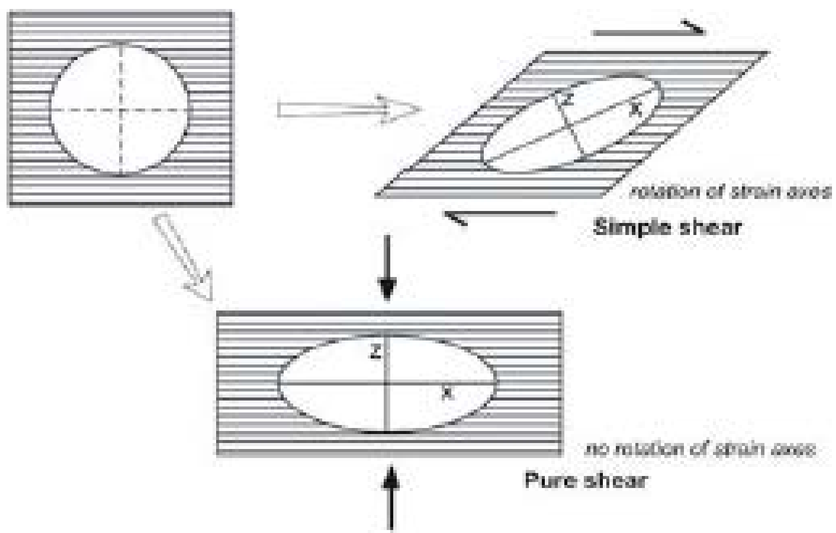
Faktoren der Prägung metamorpher Gesteine:

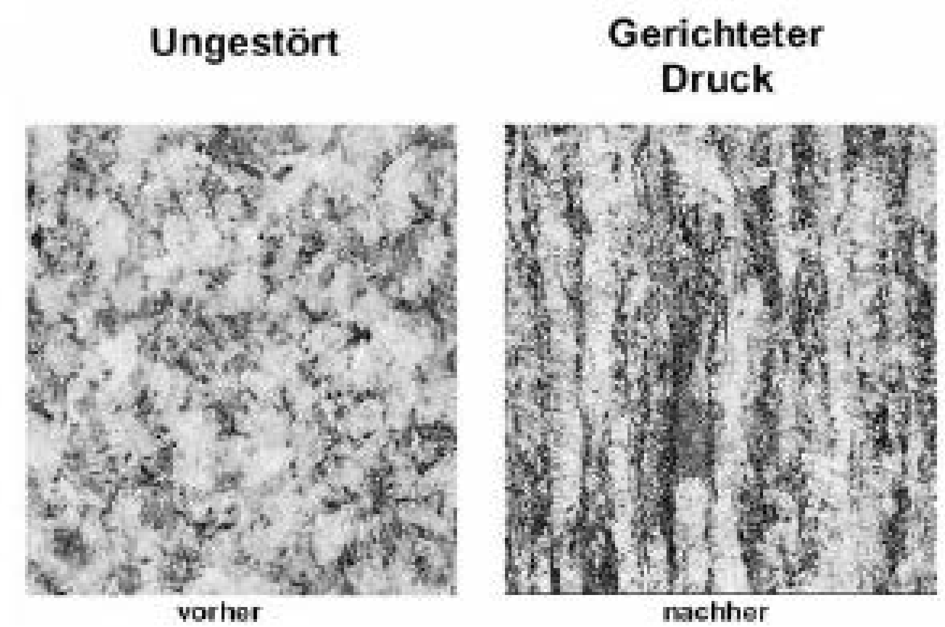
- Druck (P) und Temperatur (T)
- Zeit (t)
- Zusammensetzung der fluiden Phase
- Deformation

Wie entsteht Schieferung/Foliation in Metamorphiten?

Schieferung = Ausbildung von Trennflächen im Gestein

<u>Ursache:</u> Wachstum von blättrigen und stängeligen Mineralen in Richtung des minimalen Stresses





Mineral changes during metamorphic processes

Kornvergröberung durch Korngrenzwanderung:

- Kalk → Marmor
- Sandstein → Quarzit

Texturänderung:

- Glimmerschiefer

Umkristallisation durch Deformation:

- Granit → Gneis

Isochemische Strukturänderung (Phasenumwandlung):

- Calcit → Aragonit

Mineralreaktionen:

- Muskovit + Biotit + Quarz →
  Fe-Granat + Kalifeldspat + Fluid

Metamorphose-Typen

Regionalmetamorphose (Mitteldruckmetamorphose):

gleicher Anstieg von Druck und Temperatur (Normaltyp)

Druckbetonte Metamorphose (Hochdruckmetamorphose):

Niedrige Temperaturen und hoher Druck

Temperaturbetonte Metamorphose (Kontaktmetamorphose):

Gesteinsumwandlung im heißen Kontaktbereich zu Magmatiten

Metasomatose (Sonderfall):

Veränderung des Chemismus des Metamorphits durch bedeutende Stoffzufuhr bzw. Stoffabfuhr.

z.B. im hydrothermalen Kreislauf an mittelozeanischen Rücken (Ozeanboden-Metamorphose).

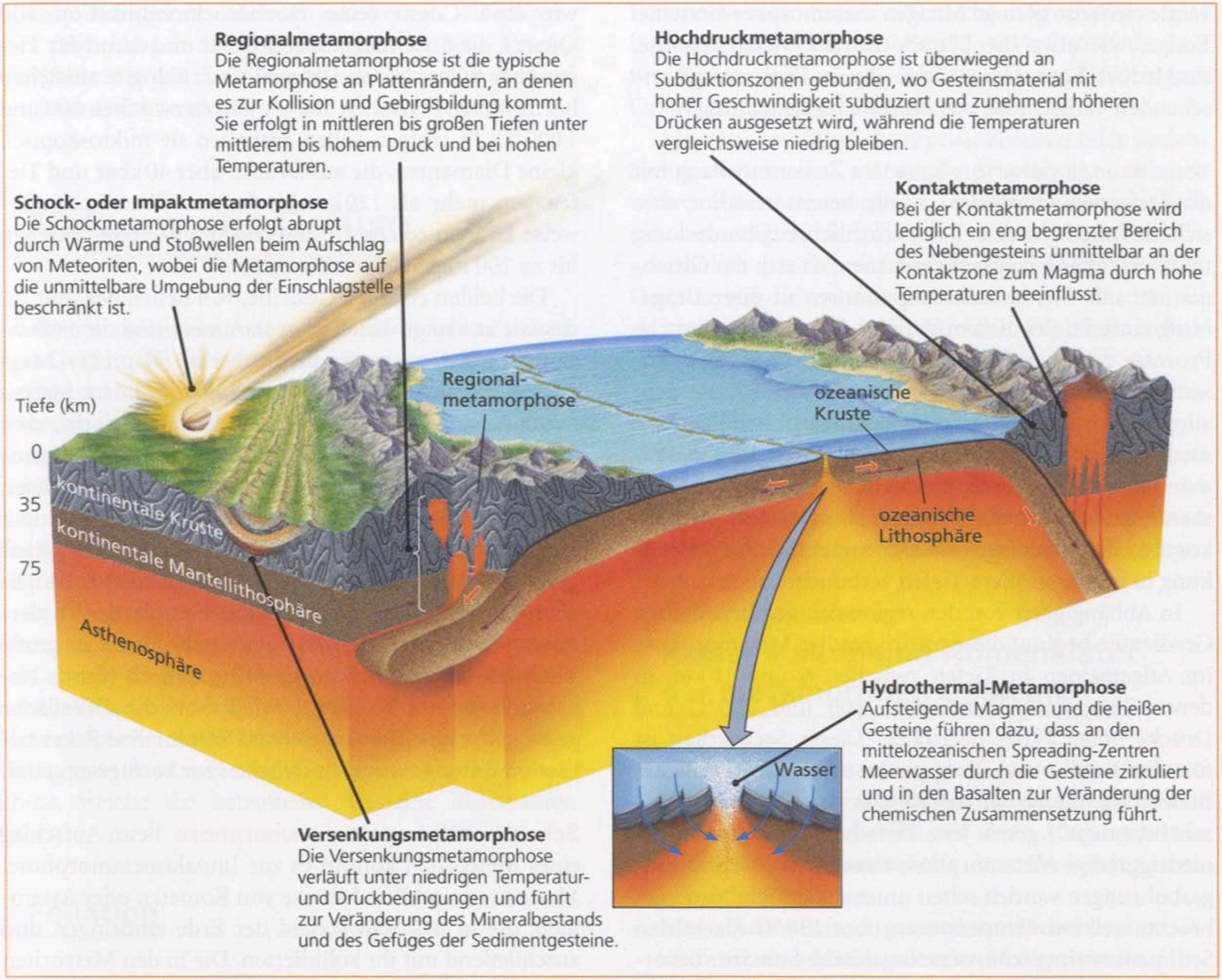
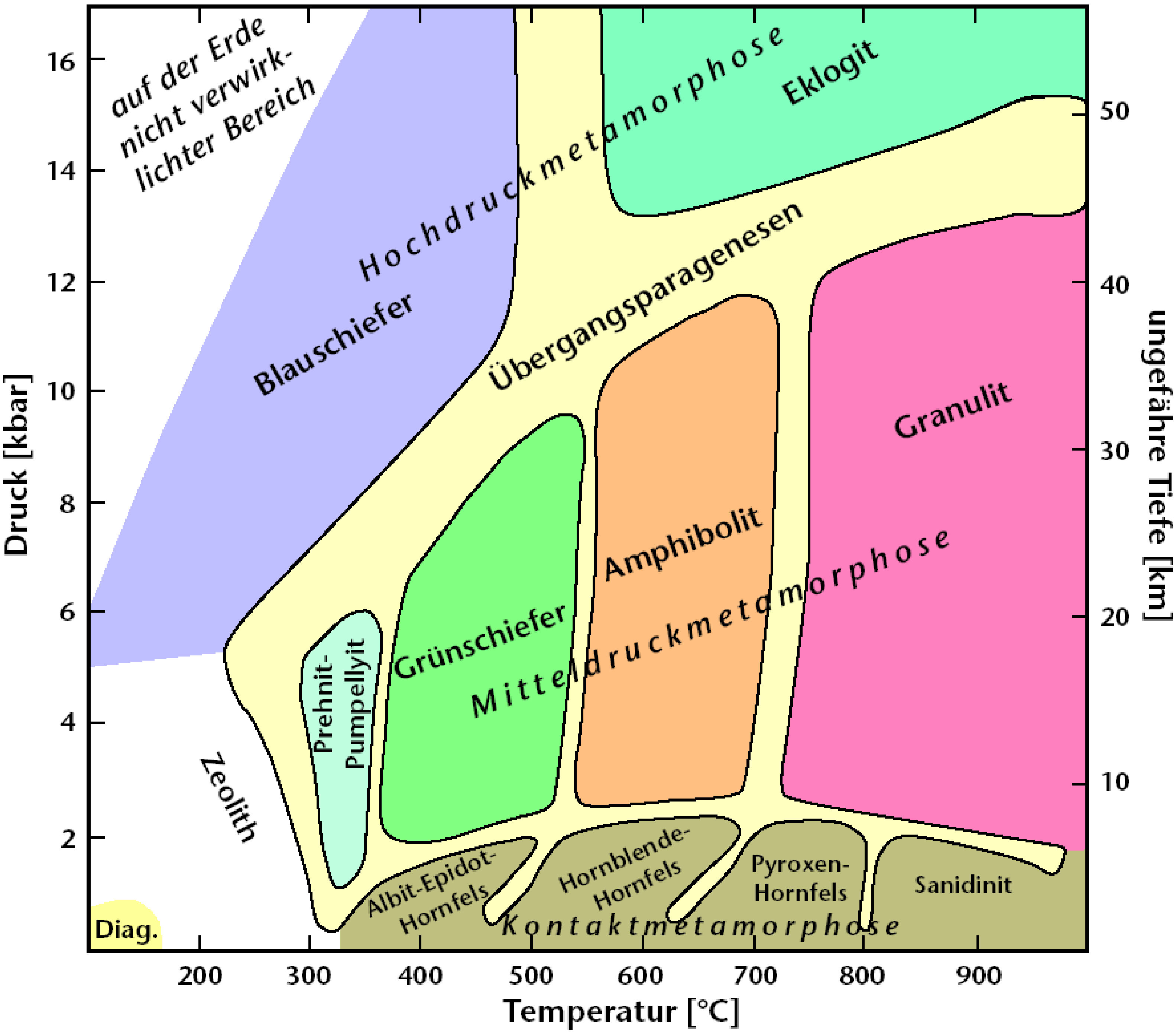


Abb. 6.3 Die Interaktion von Lithosphäre und Asthenosphäre führt zur Bildung metamorpher Gesteine.



auf der Erde nicht verwirklichter Bereich
Blauschiefer
Hochdruckmetamorphose
Eklogit
Übergangsparagenesen
Granulit
Amphibolit
Grünschiefer
Prehnit-Pumpellyit
Mitteldruckmetamorphose
Zeolith
Albit-Epidot-Hornfels
Hornblende-Hornfels
Pyroxen-Hornfels
Sanidinit
Kontaktmetamorphose
Diag.
Druck [kbar]
ungefähre Tiefe [km]
Temperatur [°C]
16
14
12
10
8
6
4
2
50
40
30
20
10
200
300
400
500
600
700
800
900

Major and Trace Elements

No rigorous definition of a trace element, but typically 11 elements are described as major elements because they form more than 99 wt% of most igneous rocks;

- the relative abundance of major elements determines the proportions of rock-forming minerals such as feldspar, quartz, micas, olivine, pyroxenes and amphiboles.
- major elements (ME) in order of increasing atomic number: O, Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe.

→ all other elements typically occur in lower abundance, <0.1 wt.%, and are described as Trace Elements

Major and Trace Elements

- Abundances of trace elements are used to test petrogenetic hypotheses
- No universal definition of TE: Concentration usually less than 100 ppm, often < 10 ppm
- Useful trace elements:

a)First transition series: Sc Ti V Cr Mn Fe Co Ni Cu Zn

Ti and Fe are usually major elements, Cr, Mn, and Ni are minor elements

Progressive filling of 3d orbitals

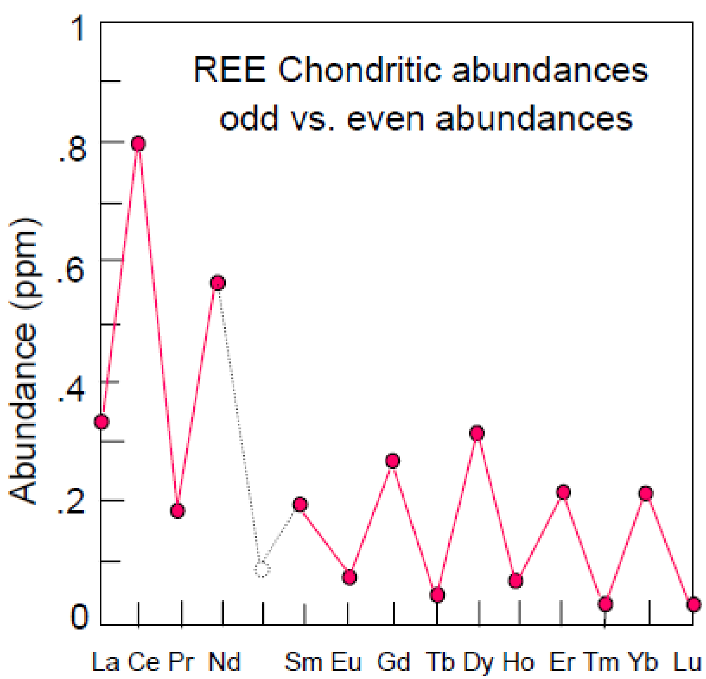
Variable crystal field stabilization

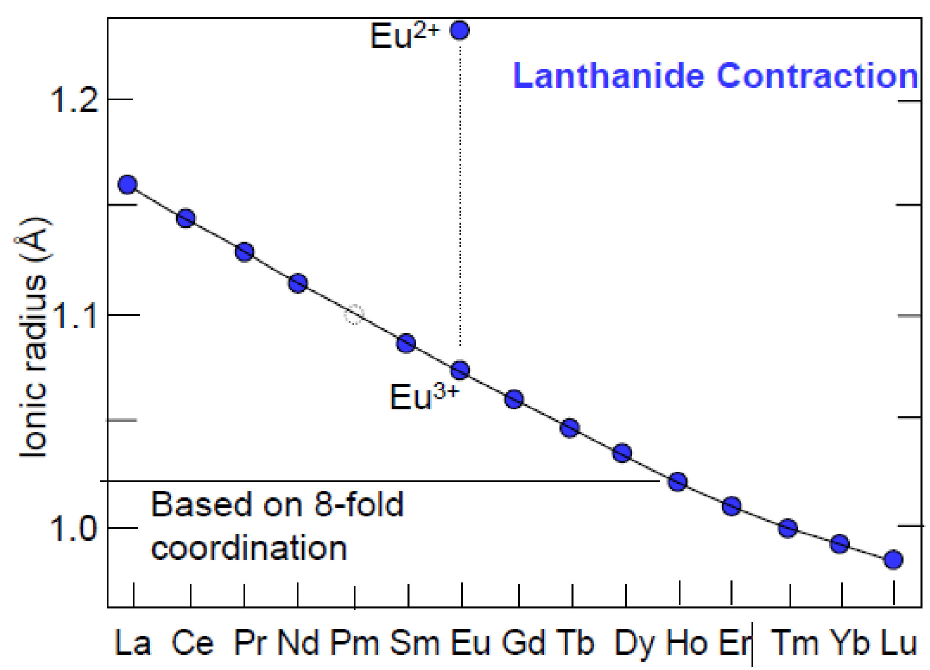
Commonly multivalent (Sc^{3}, $Ti^{4,3}$, $V^{2,3,4,5}$, $Cr^{2,3,6}$, $Mn^{2,3}$, $Fe^{2,3}$, Co^{2}, Ni^{2}

b) Lanthanides (REE): La Ce Pr Nd (Pm) Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Light REE and heavy REE (Y behaves like a HREE)

normalization factors (chondrites)





Major and Trace Elements

(c) Large Ion Lithophile Elements (LILE): may also be partitioned into fluid phase
Alkalis: K Rb Cs (monovalent)
Alkaline earths: Ba Sr (divalent)
Actinides: U, Th, Ra, Pa (multiple valency)

(d) High field strength elements (HFSE): small, highly-charged ions
Zr, Hf (4 valent) Nb, Ta (4 and 5 valent)

(e) Chalcophile elements: Cu, Zn, Pb, Ag, Hg, PGE, (Fe, Co, Ni)

(f) Siderophile elements: Fe, Ni, Co, Ge, P, Ga, Au (PGE)…

- Decoupled from major elements: lack of stoichiometric constraints (not strictly true)
- Goldschmidt's Rules
- Generalities: **Incompatible** elements are elements that tend to be excluded from common minerals (olivines, pyroxenes, garnets, feldspars, oxides…) in equilibrium with a melt, i.e., they have low **D** values.
  - Numerous exceptions, e.g., Sr, Eu in plag, Cr, Sc in pyroxene, Ni in olivine, HREE in garnet..
- Empirical (not thermodynamic) definition of D

$$D_i^{C/L} = \frac{C_i^C}{C_i^L}$$

where $D_i^{C/L}$ *is the weight distribution coefficient,* C_i^C *is concentration (ppm) of trace element i in liquid, and* C_i^L *is concentration (ppm) of trace element i in the liquid*

GOLDSCHMIDT'S RULES

1. The ions of one element can extensively replace those of another in ionic crystals if their radii differ by less than approximately 15%.
2. Ions whose charges differ by one unit substitute readily for one another provided electrical neutrality of the crystal is maintained. If the charges differ by more than one unit, substitution is generally slight.
3. When two different ions can occupy a particular position in a crystal lattice, the ion with the higher ionic potential forms a stronger bond with the anions surrounding the site.

RINGWOOD'S MODIFICATION OF GOLDSCHMIDT'S RULES

4. Substitutions may be limited, even when the size and charge criteria are satisfied, when the competing ions have different electronegativities and form bonds of different ionic character.

→ *proposed 1955 to explain discrepancies from rules above..*

Example: Na^+ and Cu^+ have the same radius and charge, but do not substitute for one another.

Major and Trace Elements

INCOMPATIBLE VS. COMPATIBLE TRACE ELEMENTS

Incompatible elements: Elements that are too large and/or too highly charged to fit easily into common rock-forming minerals that crystallize from melts. These elements become concentrated in melts.

Large-ion lithophile elements (LIL's): Incompatible owing to large size, e.g., Rb^+, Cs^+, Sr^{2+}, Ba^{2+}, (K^+).

High-field strength elements (HFSE's): Incompatible owing to high charge, e.g., Zr^{4+}, Hf^{4+}, Ta^{4+}, Nb^{5+}, Th^{4+}, U^{4+}, Mo^{6+}, W^{6+}, etc.

Compatible elements: Elements that fit easily into rock-forming minerals, and may in fact be preferred, e.g., Cr, V, Ni, Co, Ti, etc.

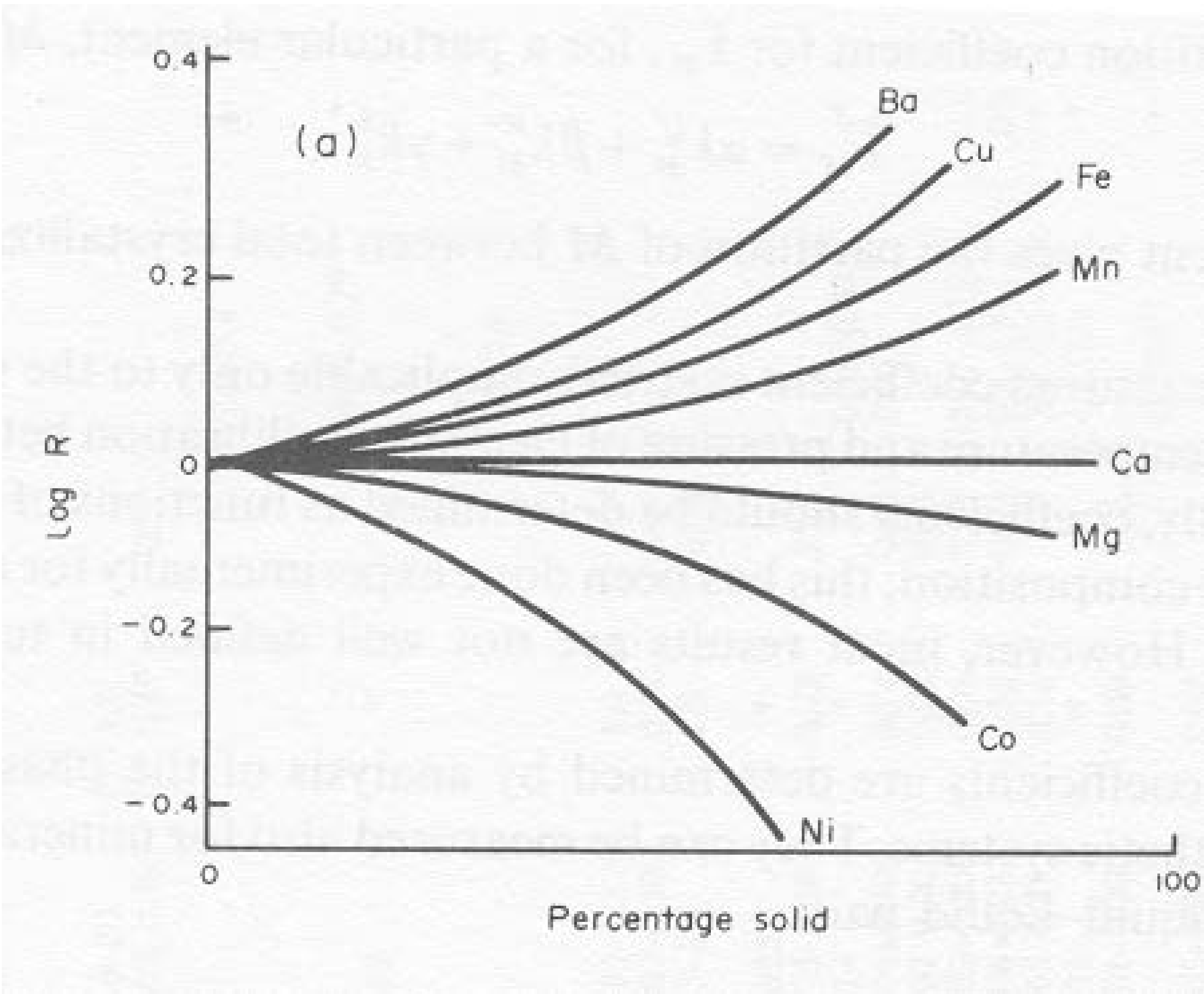
Table 7.1. Goldschmidt's Classification of the Elements

Siderophile	Chalcophile	Lithophile	Atmophile
Fe*, Co*, Ni*	(Cu), Ag	Li, Na, K, Rb, Cs	(H), N, (O)
Ru, Rh, Pd	Zn, Cd, Hg	Be, Mg, Ca, Sr, Ba	He, Ne, Ar, Kr, Xe
Os, Ir, Pt	Ga, In, Tl	B, Al, Sc, Y, REE	
Au, Re†, Mo†	(Ge), (Sn), Pb	Si, Ti, Zr, Hf, Th	
Ge*, Sn*, W‡	(As), (Sb), Bi	P, V, Nb, Ta	
C‡, Cu*, Ga*	S, Se, Te	O, Cr, U	
Ge*, As†, Sb†	(Fe), Mo, (Os)	H, F, Cl, Br, I	
	(Ru), (Rh), (Pd)	(Fe), Mn, (Zn), (Ga)	

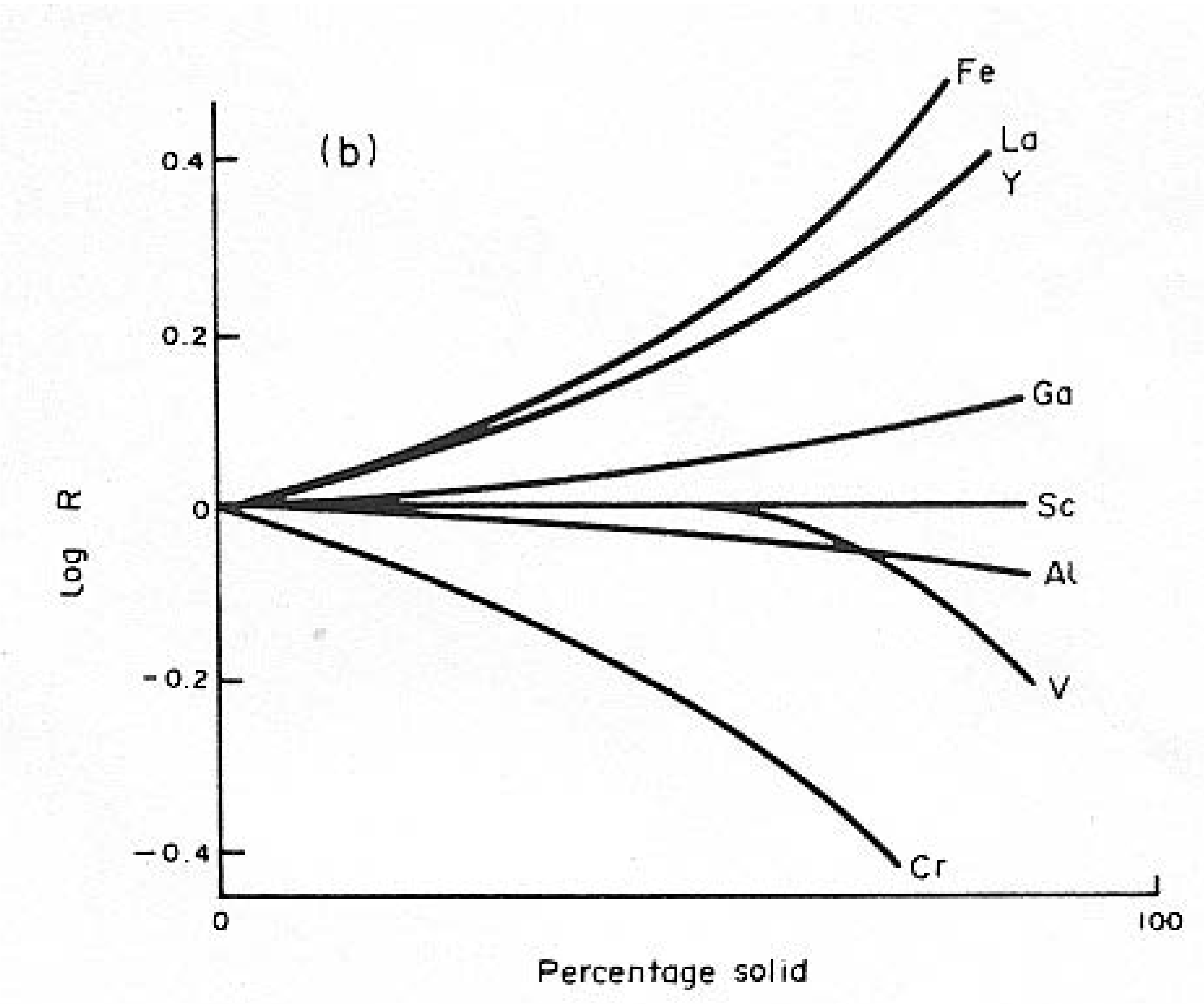
*Chalcophile and lithophile in the earth's crust
†Chalcophile in the earth's crust
‡Lithophile in the earth's crust

- *Atmophile* elements are generally extremely volatile
- *Lithophile* elements are those showing an affinity for silicate phases
- *Siderophile* elements have an affinity for a metallic liquid phase.
- *Chalcophile* elements have an affinity for a sulfide liquid phase.

Changes in element concentration in the magma during crystal fractionation of the Skaergaard intrusion: Divalent cations



Changes in element concentration in the magma during crystal fractionation of the Skaergaard intrusion: Trivalent cations



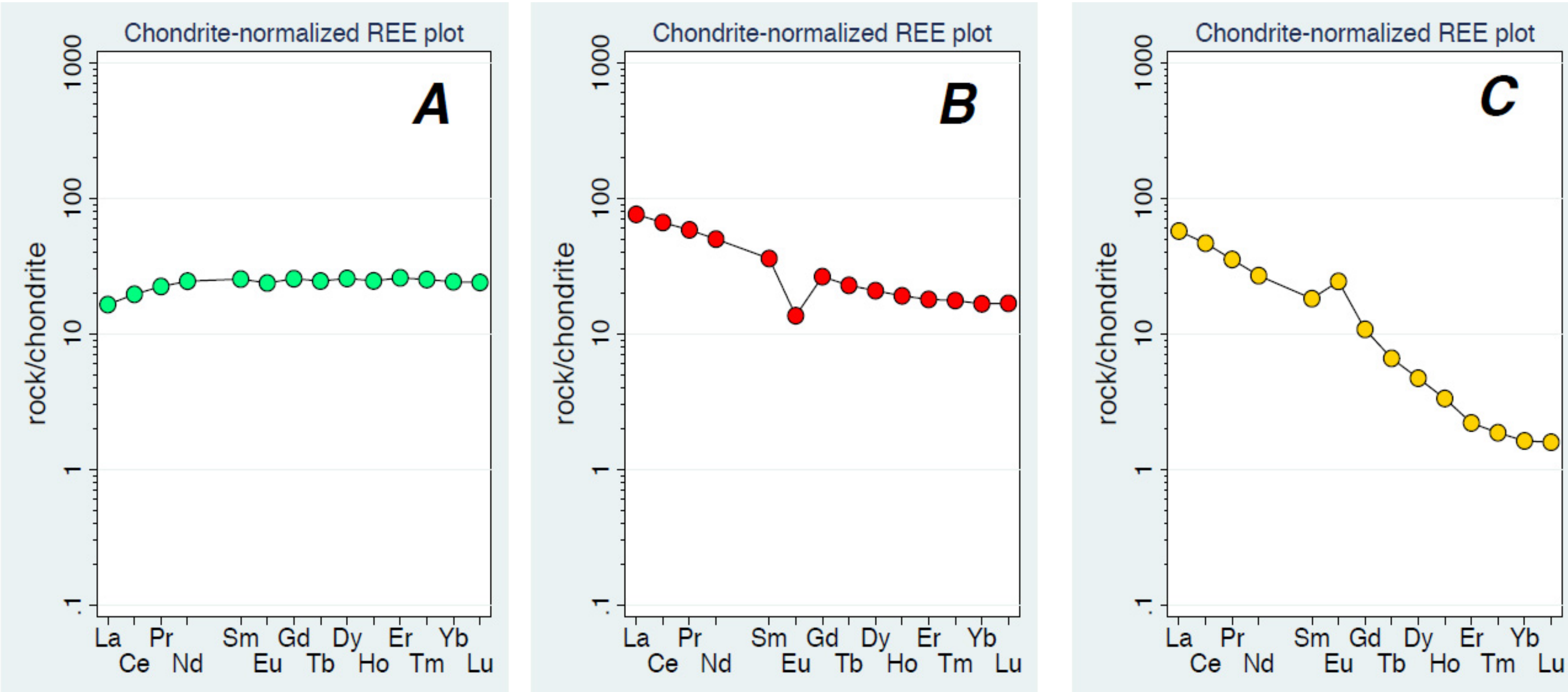
REE abundances in some important geological materials

C1-chondrites and Silicate Earth from McDonough and Sun (1995).
N-MORB from Hoffman (1988). Average Continental Crust from Rudnik and Fountain (1995)

	C1-condrites	Silicate Earth	N-MORB basalts	Continental Crust
La	0.237	0.648	3.895	18
Ce	0.613	1.675	12.001	42
Pr	0.0928	0.254	2.074	5
Nd	0.457	1.25	11.179	20
Sm	0.148	0.406	3.752	3.9
Eu	0.0563	0.154	1.335	1.2
Gd	0.199	0.544	5.077	3.6
Tb	0.0361	0.099	0.885	0.56
Dy	0.246	0.674	6.304	3.5
Ho	0.0546	0.149	1.342	0.76
Er	0.16	0.438	4.143	2.2
Tm	0.0247	0.068	0.621	0.3
Yb	0.161	0.441	3.9	2
Lu	0.0246	0.0675	0.589	0.33

REE are shown normalized to C1 chondritic composition

->chondrite-normalized diagrams: Spider diagrams



A) N-MORB basalt showing a depletion of the LREE with respect the HREE; the depletion increases with decreasing Z.
B) Monazite-bearing peraluminous granite with LREE > HREE and a marked negative Eu anomaly.
C) An Archean trondheimite (plagiogranite) with LREE >> HREE and a marked Eu positive anomaly.

Isotope Geochemistry

Two principal applications of radiogenic isotope geochemistry:

1) *Geochronology*
uses the constancy of the rate of radioactive decay

→ Dating method

2) T*racer studies*
Uses the differences in the ratio of the radiogenic daughter isotope to other isotopes of an element. (as e.g. in biology)

→Origin of volatiles, minerals & rocks

Isotope Geochemistry

TABLE 4.1: Geologically Useful Long-Lived Radioactive Decay Schemes

Parent	Decay Mode	λ	Half-life	Daughter	Ratio
^{40}K	β^+, e.c, β^-	$5.543 \times 10^{-10} y^{-1}$	1.28×10^{9} yr	^{40}Ar, ^{40}Ca	$^{40}Ar/^{36}Ar$
^{87}Rb	β^-	$1.42 \times 10^{-11} y^{-1}$	4.8×10^{10} yr	^{87}Sr	$^{87}Sr/^{86}Sr$
^{138}La	β^-	$2.67 \times 10^{-12} y^{-1}$	2.59×10^{11} yr	^{138}Ce, ^{138}Ba	$^{138}Ce/^{142}Ce$, $^{138}Ce/^{136}Ce$
^{147}Sm	α	$6.54 \times 10^{-12} y^{-1}$	1.06×10^{11} yr	^{143}Nd	$^{143}Nd/^{144}Nd$
^{176}Lu	β^-	$1.94 \times 10^{-11} y^{-1}$	3.6×10^{10} yr	^{176}Hf	$^{176}Hf/^{177}Hf$
^{187}Re	β^-	$1.64 \times 10^{-11} y^{-1}$	4.23×10^{10} yr	^{187}Os	$^{187}Os/^{188}Os$, ($^{187}Os/^{186}Os$)
^{190}Pt	α	$1.54 \times 10^{-12} y^{-1}$	4.50×10^{11} yr	^{186}Os	$^{186}Os/^{188}Os$
^{232}Th	α	$4.948 \times 10^{-11} y^{-1}$	1.4×10^{10} yr	^{208}Pb, ^{4}He	$^{208}Pb/^{204}Pb$, $^{3}He/^{4}He$
^{235}U	α	$9.849 \times 10^{-10} y^{-1}$	7.07×10^{8} yr	^{207}Pb, ^{4}He	$^{207}Pb/^{204}Pb$, $^{3}He/^{4}He$
^{238}U	α	$1.551 \times 10^{-10} y^{-1}$	4.47×10^{9} yr	^{206}Pb, ^{4}He	$^{206}Pb/^{204}Pb$, $^{3}He/^{4}He$

Note: the branching ratio, i.e. ratios of decays to ^{40}Ar to total decays of ^{40}K is 0.117. ^{147}Sm and ^{190}Pt also produce ^{4}He, but a trivial amount compared to U and Th.

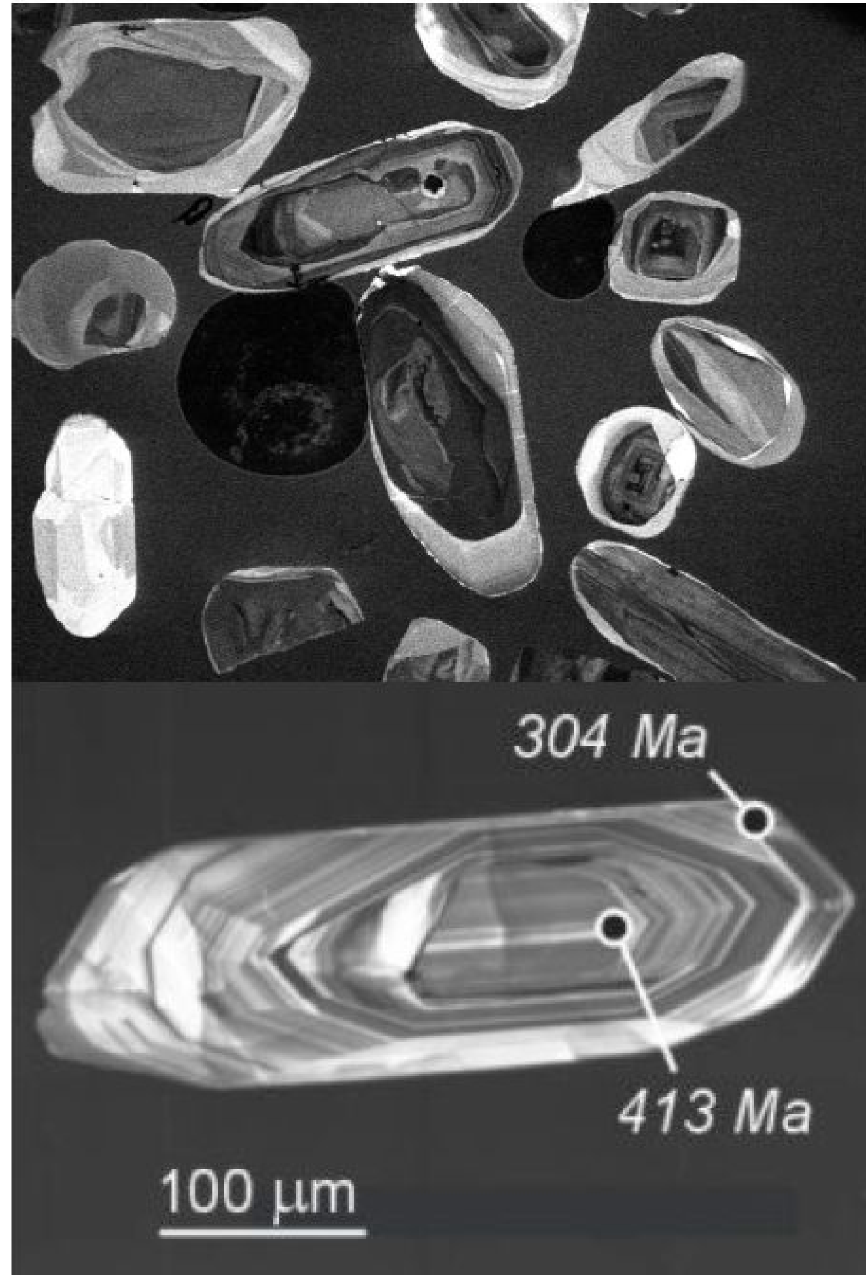
Isotope Geochemistry

Prerequisite:

stable minerals!!

No exchange of parent or daughter elements with surroundings

→ Zircons



Archean-eon craton were found in the area of the Nuvvuagittuq greenstone belt in northern Quebec.

- Different ages determined: ca. 3.7 billion years and ca. 4.3 billion years.
- Dispute so far unsolved…
- Evidence for fossils of microorganisms discovered in these rocks, which would be the oldest trace of life yet discovered on Earth.

Age determination of Nuvvuagittuq Greenstone Belt

- U-Pb dating on zircons → minimum of 3.7 billion years old.

  Done 2007 on zircons found within granitic intrusions that cut portions of the belt, and therefore, are younger than the features it cuts.
  -> This measurement is widely accepted.
  -> It alone does not provide a maximum age.

- Sm-Nd dating and Nd isotope fractionation in 2012→ age of 4.3 billion years

  -> dating of intruding gabbros and measuring neodymium isotope fractionation in less-deformed members of a sub-unit.
  ->The age of 4.3 billion years would make the NGB the oldest known rocks on Earth.

- Detrital zircons from quartz–biotite schists → max age of 3780 Ma.

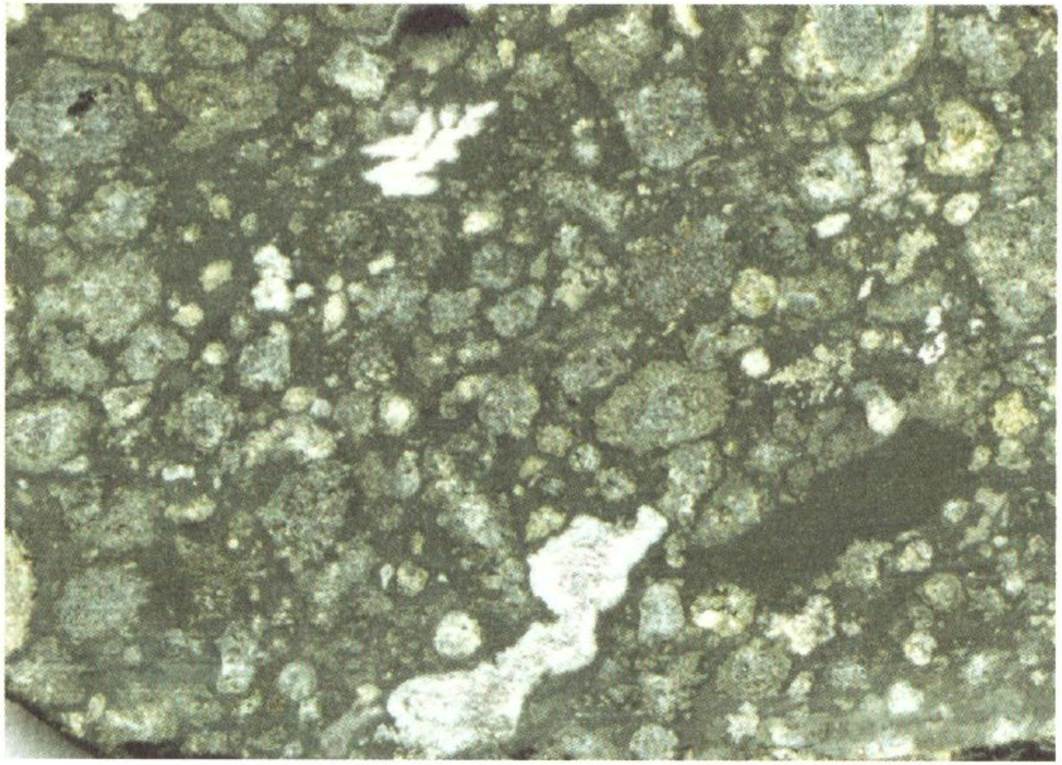
  → This study states that the age of 4.3 billion years reflects isotope ratios inherited from Hadean crust that was melted to form the parent rocks of the NGB.

Chondrites („stone meteorites")

→ provides important clues for understanding the origin and age of the Solar System
→ formed during accretion in the early Solar System to form primitive asteroids
→ Dating using $^{206}Pb/^{204}Pb$ gives an estimated age of 4,566.6 ± 1.0 Ma
→ chondrules, millimetre-sized spherical objects that originated as freely floating, molten or partially molten droplets in space; most chondrules are rich in the silicate minerals olivine and pyroxene. To lesser extend also: Ca minerals and Al, metallic Fe-Ni and sulfides, Phylosilicates, Magnetite, ..

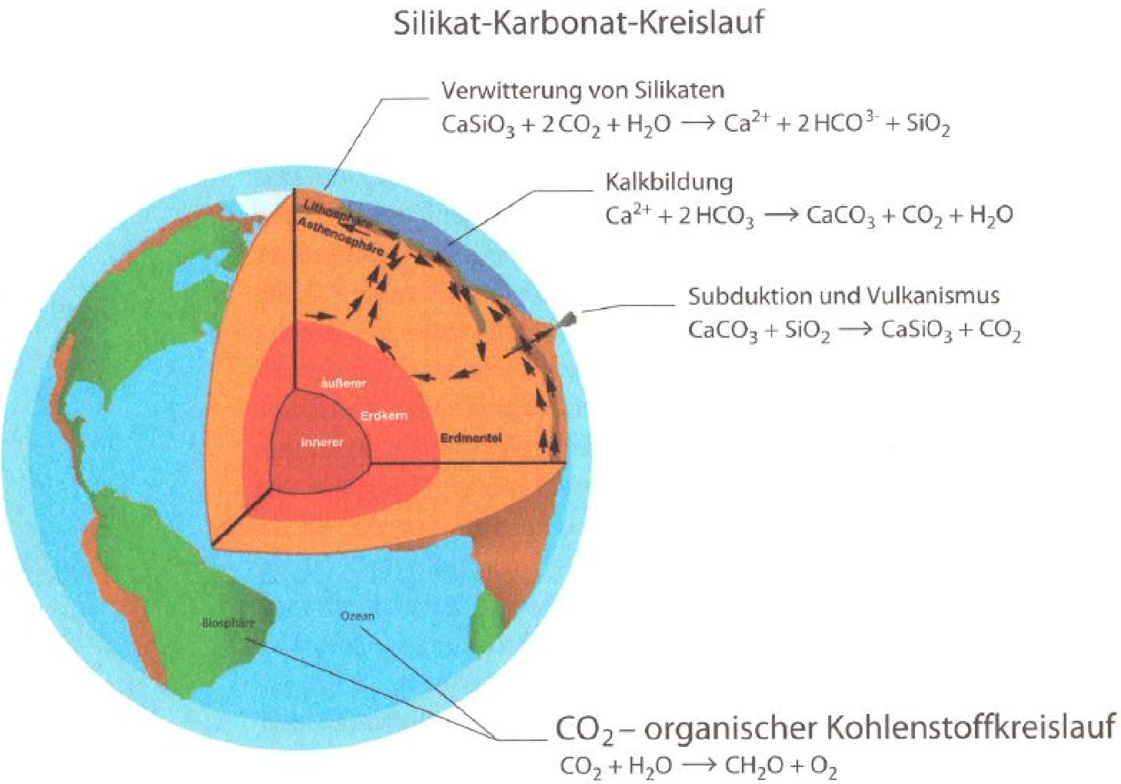
Abb. 2-10

Der kohlige Meteorit Allende (Durchmesser etwa 10 cm) ist aus mm-großen Silikatkügelchen (Chondren) aufgebaut (Basilico Fresco/Wikipedia).



Source: Oschmann, Evolution der Erde (2018)

Prerequisite for silicate-carbonate-cycle: Plate tectonics



Mantel) ausgetauscht. Voraussetzung für den **Silikat-Karbonat-Kreislauf** ist die Plattentektonik. Mit deren Beginn setzte auch der Silikat-Karbonat-Kreislauf ein. Der hohe CO_2-Gehalt der Atmosphäre verursachte einen «sauren Regen» und damit eine hohe Verwitterungsrate an der Erdoberfläche, bei der Kalziumsilikat ($CaSiO_3$) mit CO_2 reagiert. Dabei entstehen Kalzium- (Ca^{2+}) und Hydrogenkarbonationen (HCO_3^-) und Kieselsäure (SiO_2). Ca^{2+} und HCO_3^- werden über die Flüsse in die Ozeane transportiert und reagieren dort zu Kalk ($CaCO_3$), CO_2 und H_2O. Bei der Subduktion reagiert der subduzierte Kalk mit Kieselsäure und bildet wieder Kalziumsilikat und CO_2, das teilweise über den Vulkanismus wieder in die Atmosphäre eingebracht wird. In der Bilanz sind diese Reaktionen ausgeglichen. Allerdings verlaufen die Teilreaktionen in verschiedenen erdgeschichtlichen Abschnitten unterschiedlich schnell ab, was zu starken Schwankungen im CO_2-Gehalt der Atmosphäre führt und damit entweder ein **Treibhaus-** oder ein **Eiszeitklima** fördert. Langfristig ist der Transport in den

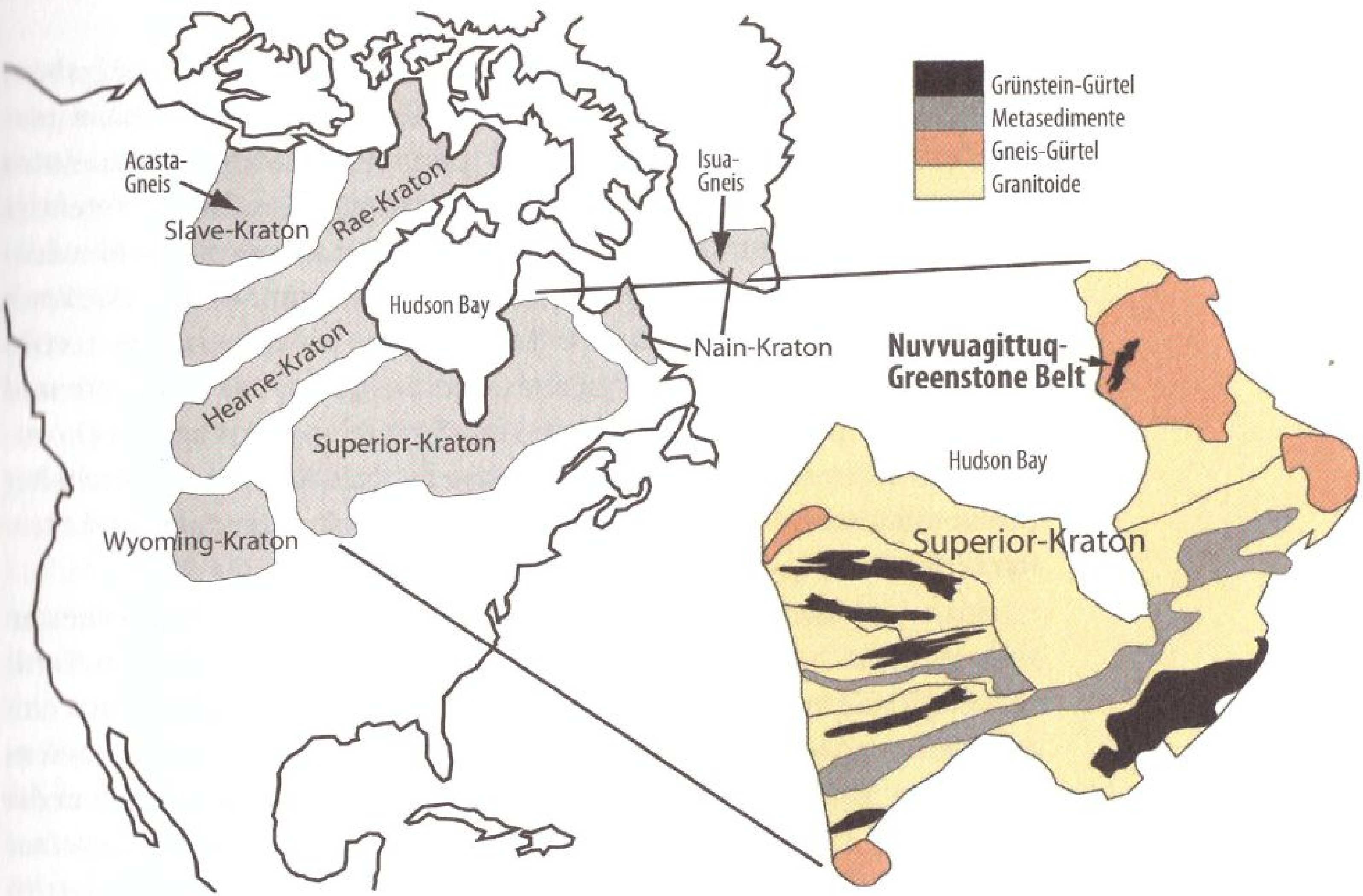
Source: Oschmann, Evolution der Erde (2018)

Abb. 4-3 | Links: Archaische Pillow-Lava aus dem Barberton-Grünsteingürtel von Südafrika. Die Entgasungskanäle belegen eine Entstehung im Flachwasser. Mitte: Kontakt von TTG zu Pillowlaven aus dem Barberton-Grünsteingürtel. Rechts: Sedimentäre Cherts aus dem Barberton-Grünsteingürtel in Südafrika (Photos: Armin Zeh, Frankfurt).

Source: Oschmann, Evolution der Erde (2018)

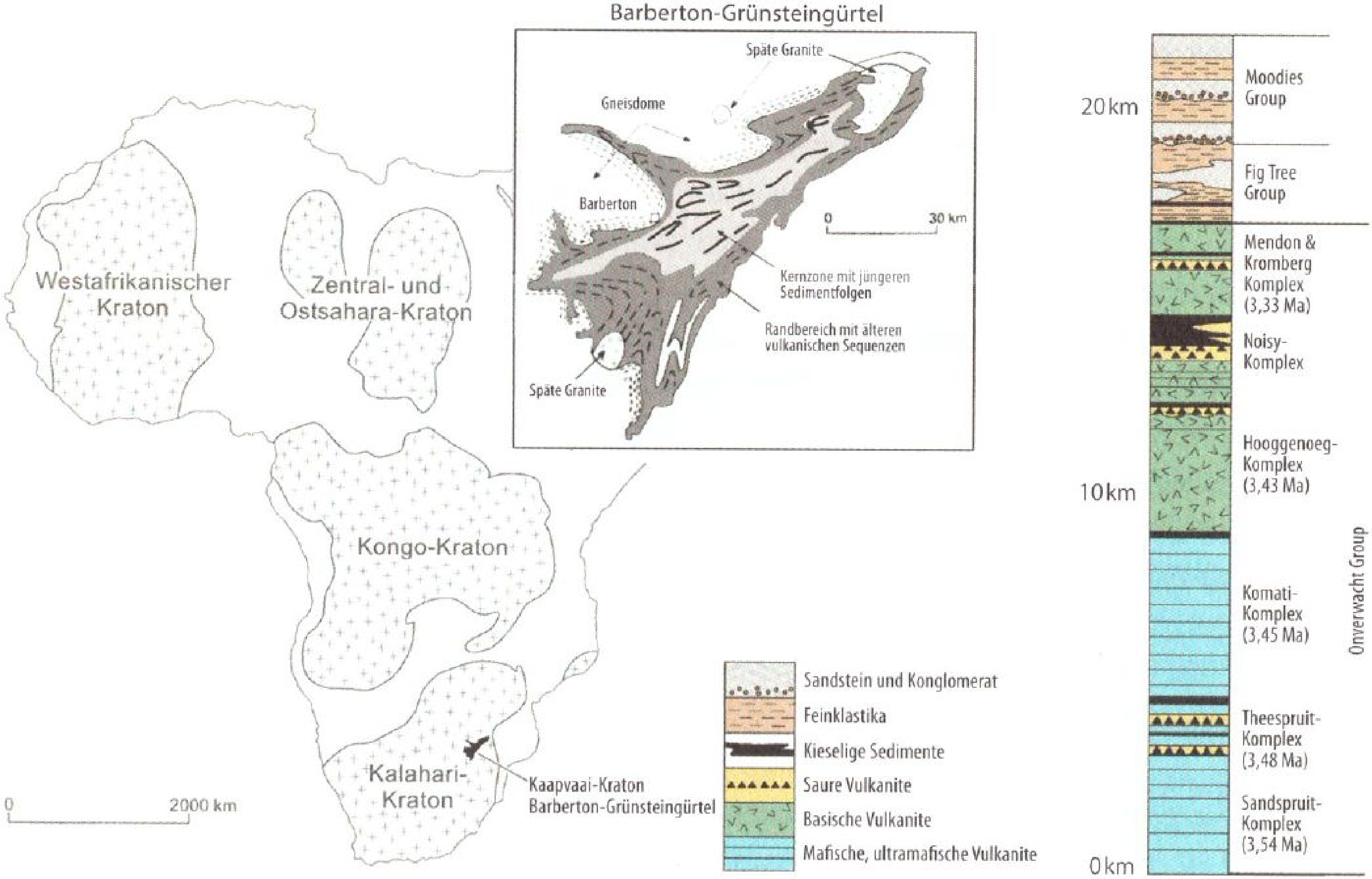
Die ältesten bislang datierten Gesteine stammen alle aus Nordamerika (verändert nach Eisbacher 1996 aus Walter 2014): Der Nuvvuagittuq Greenstone Belt, aus der Superior Provinz (möglicherweise ~ 4.3 Mia. Jahre) und der Acasta-Gneis (~ 4 Mia. Jahre), beide aus Kanada, sowie der Amitsoq-Gneis mit dem Isua-Grünsteingürtel (~ 3.9 Mia. Jahre) aus Südgrönland.

Abb. 4-4



Source: Oschmann, Evolution der Erde (2018)

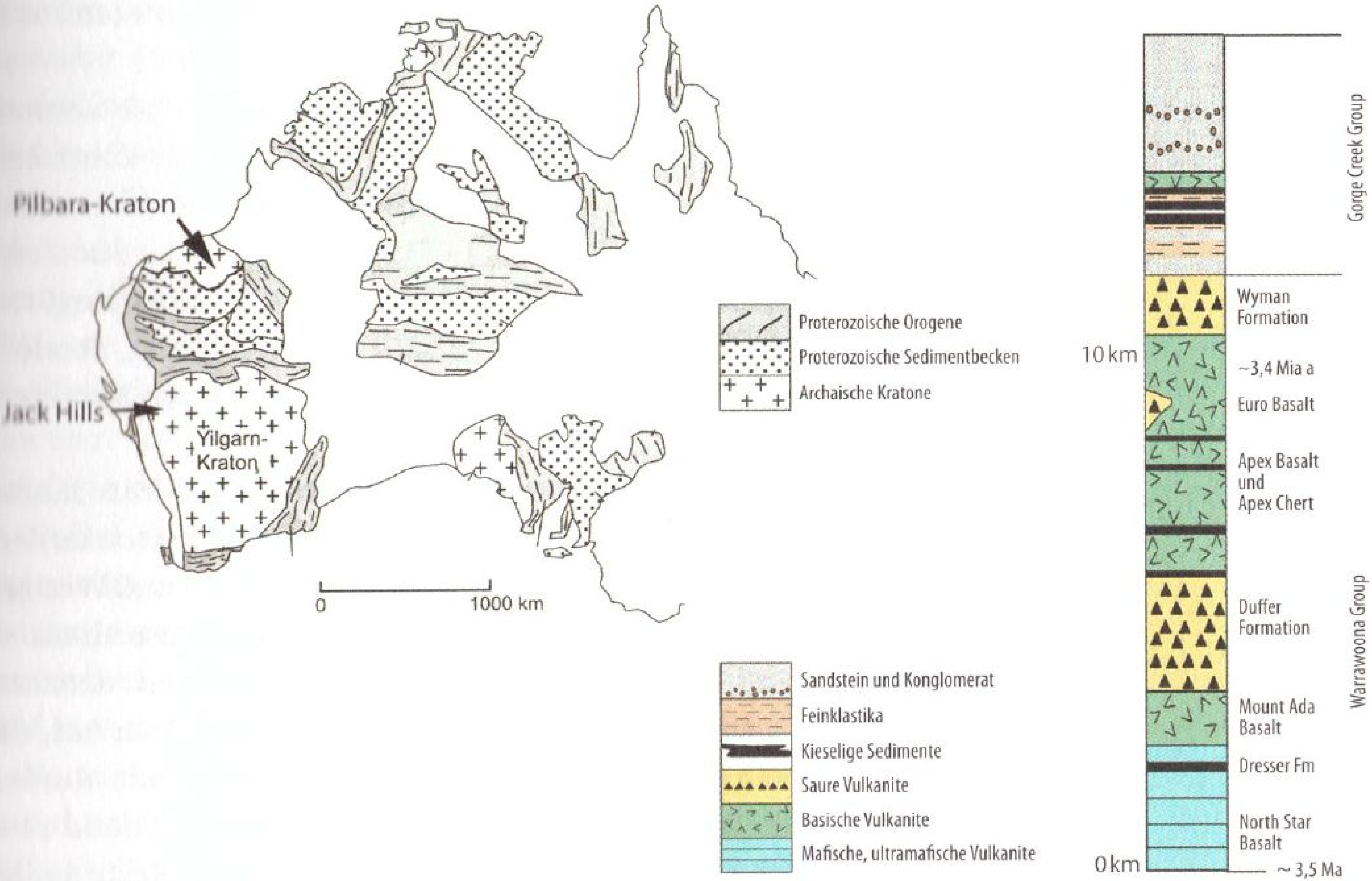
Abb. 4-5 Afrika wird aus mehreren archaischen Kratonen aufgebaut. (modifiziert nach Walter 2014, Stanley 2001 und Furnes et al. 2013).



Source: Oschmann, Evolution der Erde (2018)

Die Kratone in Australien (modifiziert nach Walter 2014 und Stanley 2001).

Abb. 4-6



Source: Oschmann, Evolution der Erde (2018)