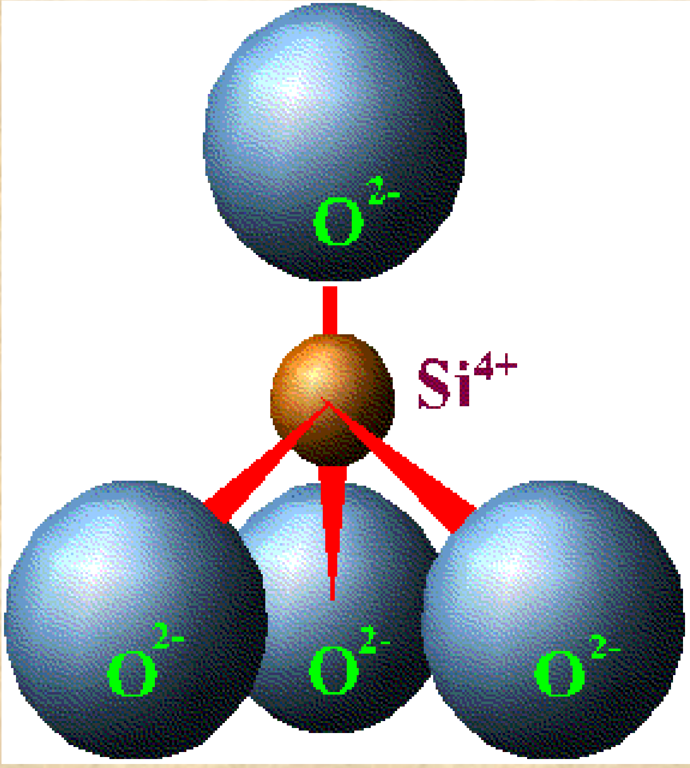
4. Mineralogical background II: Silicates (among others Nesosilicates, Cyclosilicates, Inosilicates)

The manuscript is under construction. Please suggestions an kilian@uni-trier.de

Thank you,

Rolf Kilian

SiO_4-Tetrahedron: basic module silicates



Silicium has here the coordination number four, and it is surrounded by four oxygen-ligand ➔ Tetrahedron

Charges and proportions are illustrated.

Classification of silicates

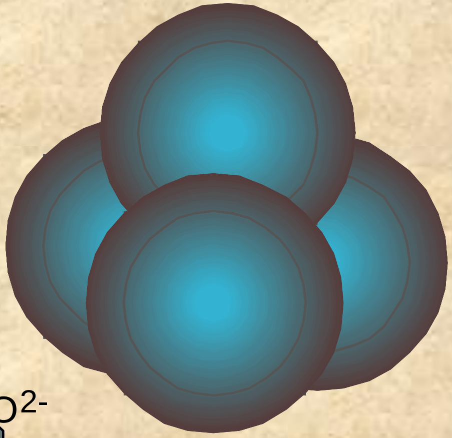
In the silicates are SiO_4-Tetrahedrons not linked or are linked unidimensional, two-dimensional and three dimensional on common oxygen atoms:

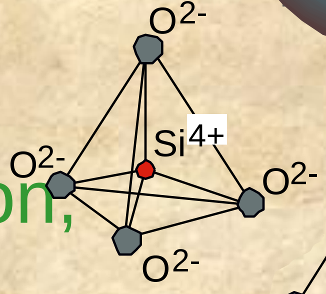
- Nesosilicate (isolated SiO_4-Tetrahedron)
- Sorosilicate (two cross-linked Tetrahedron)
- Cyclosilicate (ring-shaped crosslinking)
- Inosilicate (unidimensional crosslinking)
- Phyllosilicate (two-dimensional crosslinking)
- Tectosilicate (three-dimensional crosslinking)

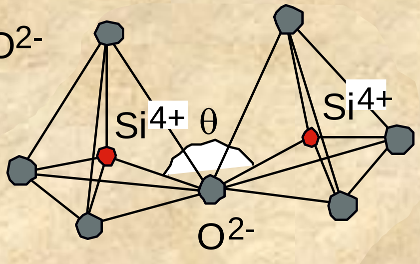
Nesosilicates (Nesosilicate, Orthosilicate)

- isolated $[SiO_4]^{4}$-Tetrahedron
- Si : O -ratio = 1 : 4
- Connection through intermediate cations

Basic module
SiO_4-Tetrahedron







For example: olivine, garnet, zircon, andalusite, disthene, sillimanite, staurolithe, topaz, titanite


disthene
Mineralienkabinett (c) MZ 2000 http://www.min.uni-bremen.de


Ideomorphic garnet
Mineralienkabinett (c) MZ 2000 http://www.min.uni-bremen.de


staurolithe-
cruciform twin
Mineralienkabinett (c) MZ 2000 http://www.min.uni-bremen.de


titanite (sphene)
Mineralienkabinett (c) MZ 2000 http://www.min.uni-bremen.de

Olivine

Mantelperidotit, vorwiegend aus Olivin

- $(Mg,Fe^{2+})_2[SiO_4]$
- orthorhombic

- Series of mixed crystals between forsterite ($Mg_2[SiO_4]$) and fayalite ($Fe_2[SiO_4]$)

Olivine

- Hardness 6 $^{1}/_{2}$ – 7
- Density 3,2 g/cm^3 (forsterite); 4,3 g/cm^3 (fayalite) subject to Fe content
- Poor cleavage (shelly breakage)

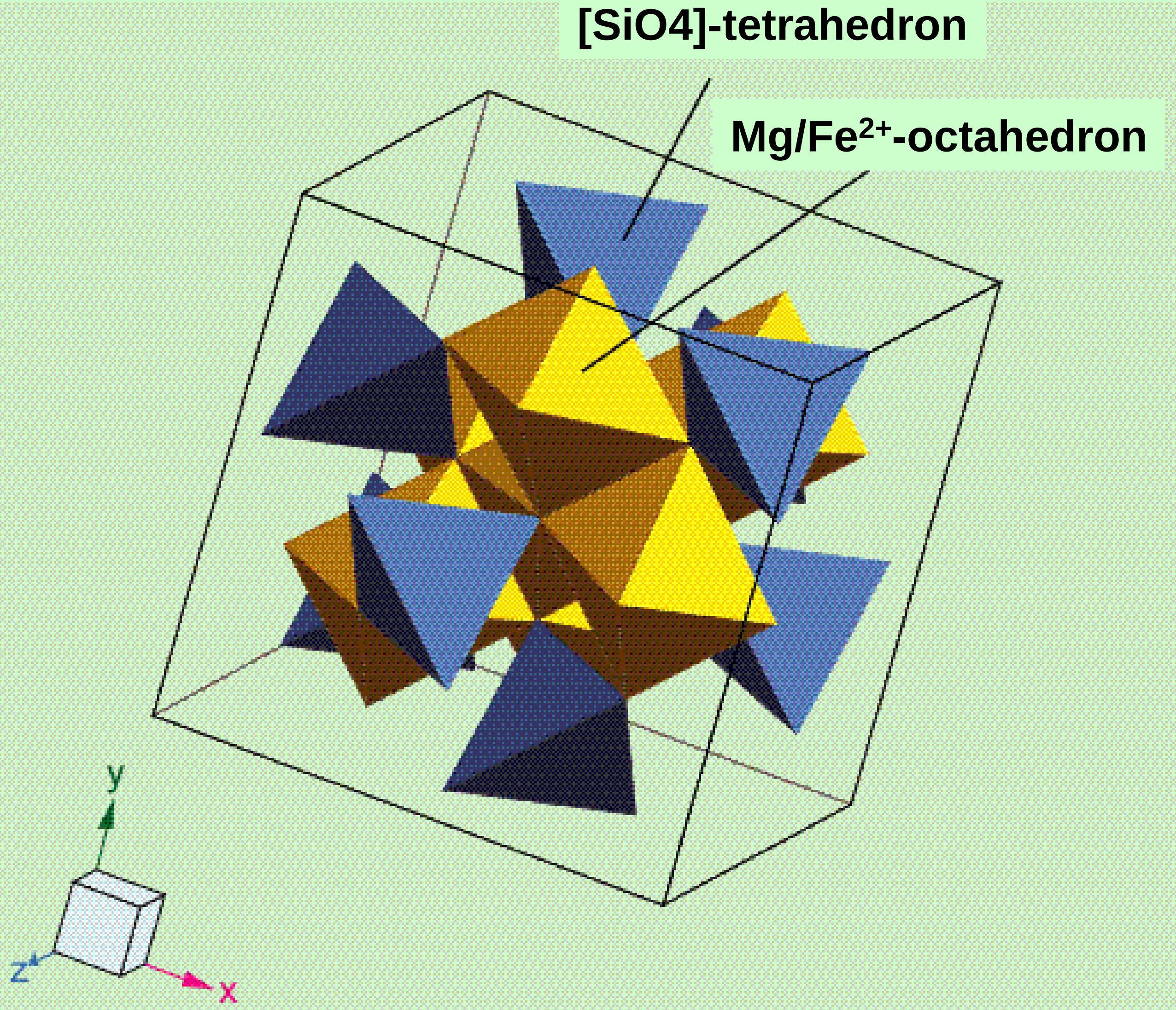
Olivine occurs in

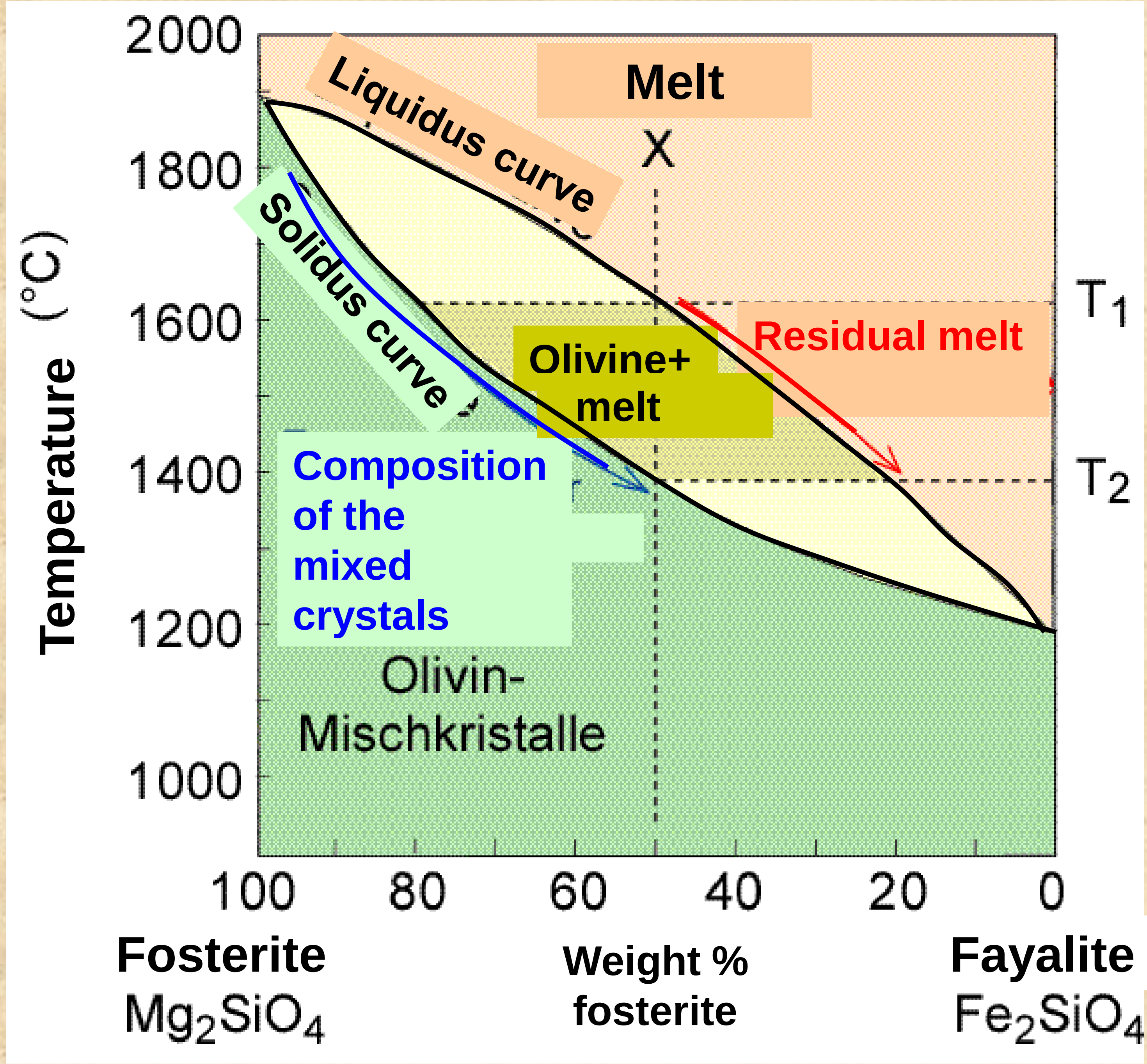
- In mantle peridotites: prevalent in the upper mantle crustal rocks
- mafic cumulates
- Marbles
- magmatic rocks, but only in SiO_2-poor, especially in basanitic und basaltic fusion

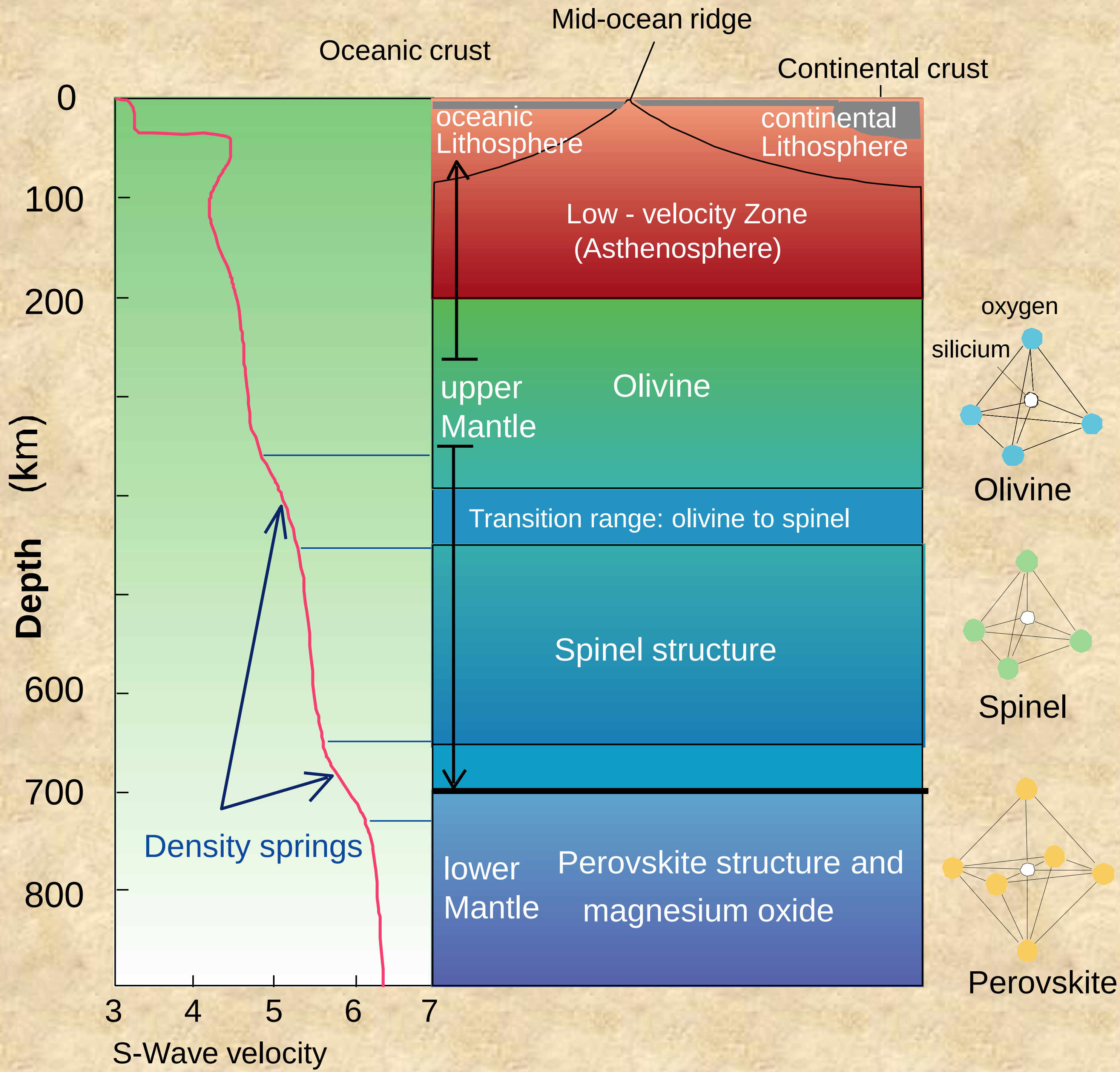
Serpentinization

- Olivine can be to changed in magnetite and serpentine.
- $3\ Fe_2SiO_4 + O_2 \rightarrow 2\ Fe_3O_4 + 3\ SiO_2$
- $3\ Mg_2SiO_4 + SiO_2 + 2H_2O \rightarrow 2\ Mg_3Si_2O_5(OH)_4$

Polyhedron model of the crystal structure of olivine
The isolated $[SiO_4]$-tetrahedrons are linked by the corners with the Mg oder Fe^{2+} octahedrons (yellow)




Melt
Liquidus curve
Solidus curve
X
T1
T2
Residual melt
Olivine+ melt
Composition of the mixed crystals
Olivin-Mischkristalle
Temperature (°C)
2000
1800
1600
1400
1200
1000
100
80
60
40
20
0
Fosterite
Mg2SiO4
Weight % fosterite
Fayalite
Fe2SiO4



Mid-ocean ridge
Oceanic crust
Continental crust
0
100
200
600
700
800
Depth (km)
3
4
5
6
7
S-Wave velocity
oceanic Lithosphere
continental Lithosphere
Low - velocity Zone
(Asthenosphere)
upper Mantle
Olivine
Transition range: olivine to spinel
Spinel structure
lower Mantle
Perovskite structure and magnesium oxide
Density springs
oxygen
silicium
Olivine
Spinel
Perovskite

Garnet

- The group of the garnet forms a complete mixed crystal series with the generic formula

$$A_2{+}3B_3{+}2[SiO_4]_3$$

with A^{2+} = Ca, Mg, Fe^{2+}, Mn, Na

B^{3+} = Al, Fe^{3+}, Cr^{3+} , Ti^{4+} u.a.

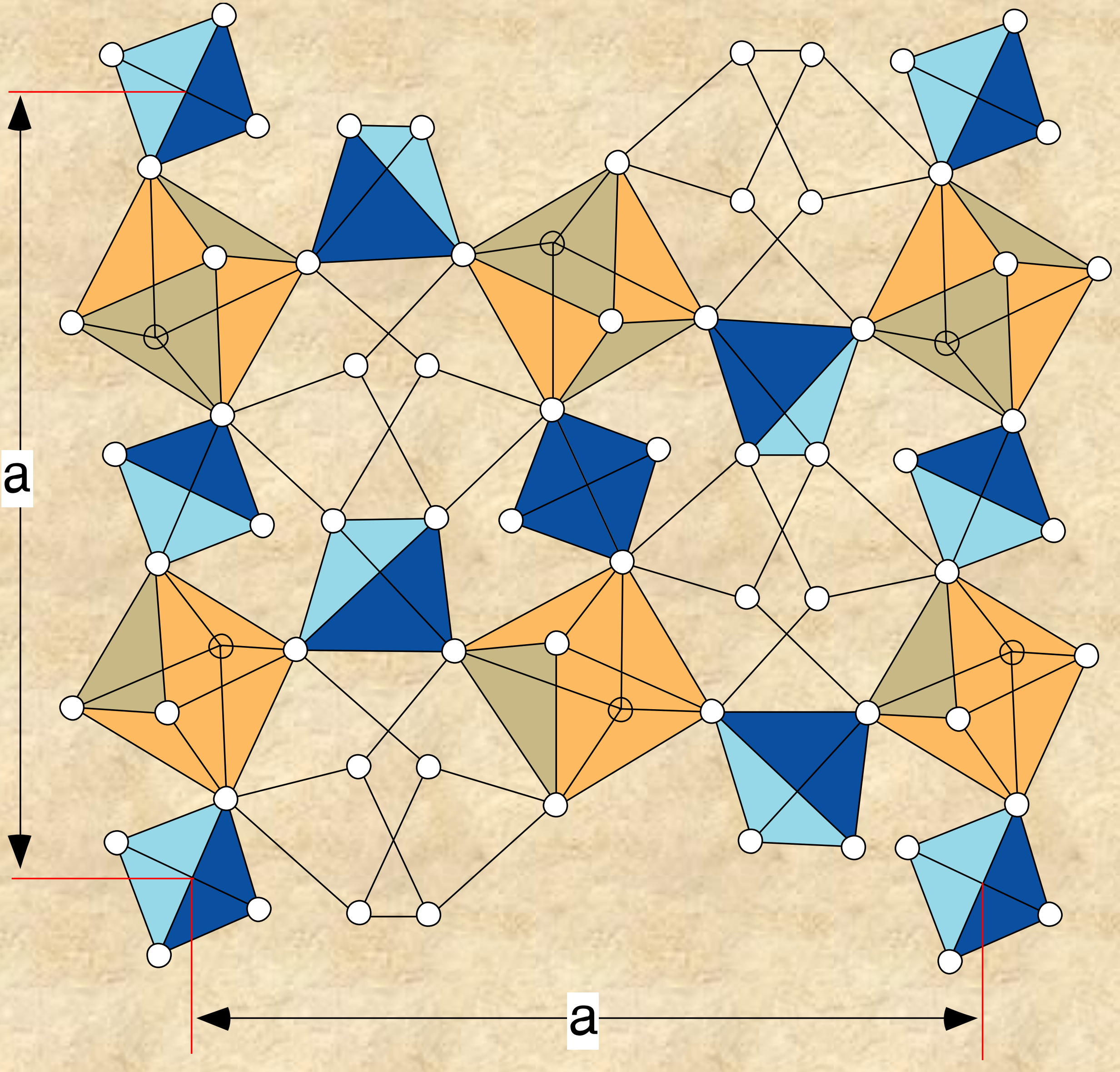
- $Mg_3Al_2[SiO_4]_3$ **Pyrope** **(in mantle peridotites)**
- $Fe_3Al_2[SiO_4]_3$ **Almandine** **(in mica schist)**
- $Mn_3Al_2[SiO_4]_3$ **Spessartine**
- $Ca_3Al_2[SiO_4]_3$ **Grossularite** **(in marble)**
- $Ca_3Fe_2[SiO_4]_3$ **Andradite**
- $Ca_3Cr_2[SiO_4]_3$ **Uvarovite**

Garnet

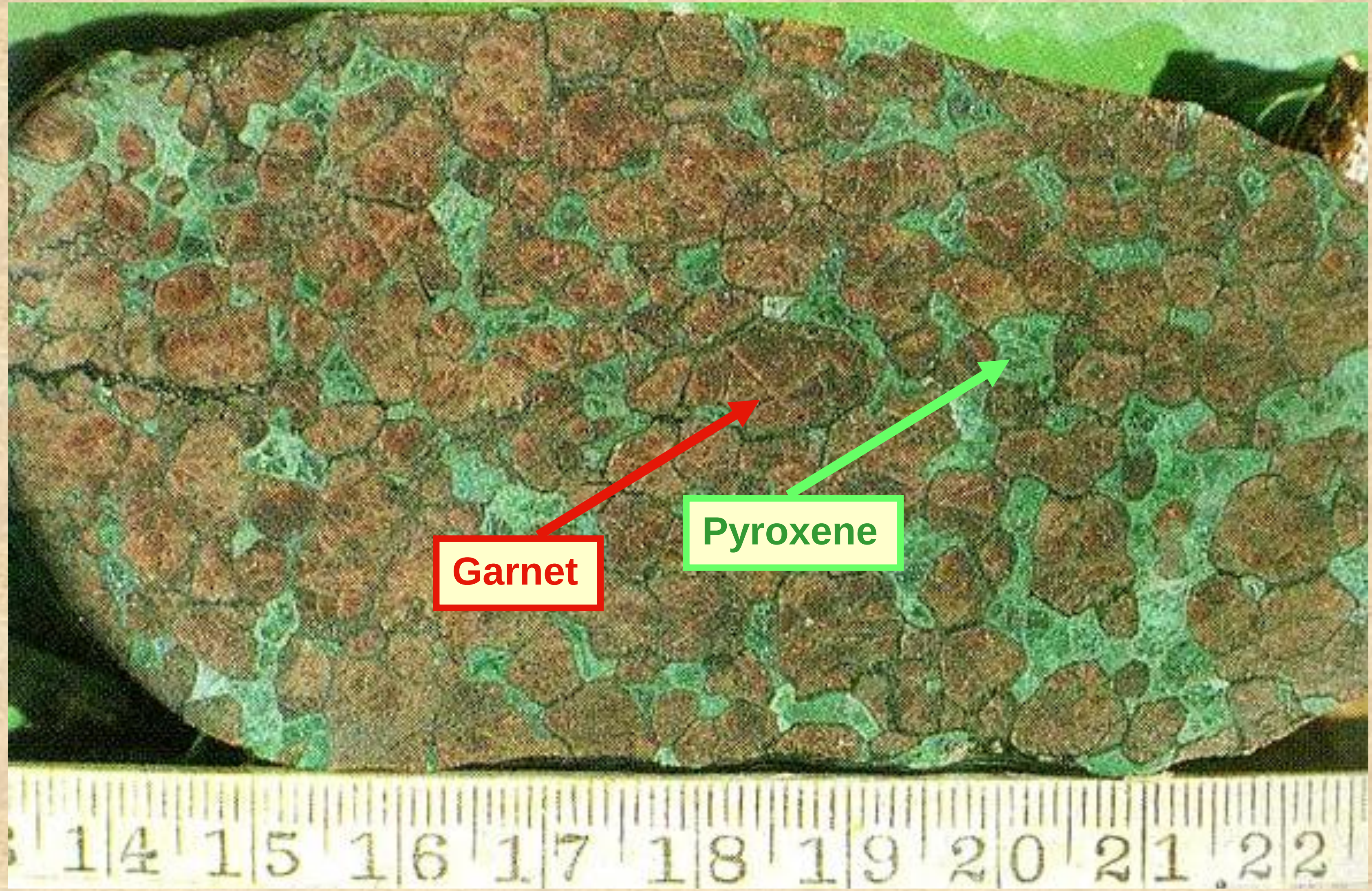
- crystallize cubic
- hardness 7
- density 3,3 - 4,4 g/cm^3

Allmandin-Granat, (Fe-Al-Silicat), Stapfenalpe/Zillertal/Ö, Foto: T. Seilnacht

- Formed mainly metamorphic; for example in schist, gneisses, amphibolites, eclogites, granulites, peridotites
- To form necessary different high pressures
- In pelitic system: already in the upper to middle cruste
- in mica schist often as idioblast

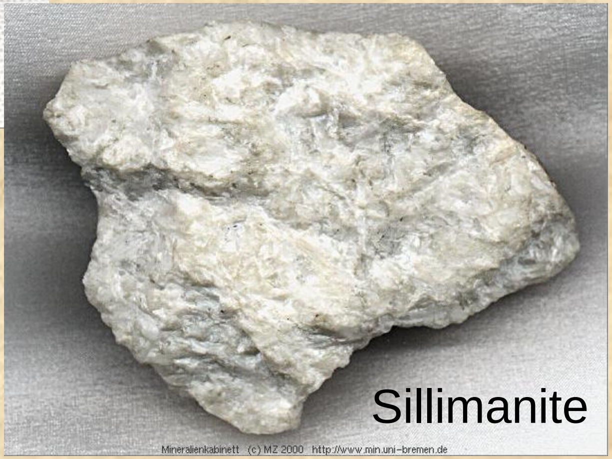


Garnet structure characterized by insular SiO_4^{4-}- oder AlO_4^{4-}-tetrahedrons (blue) as well as octahedric coordinated cations.



Eclogite xenolith from the Roberst Victor Mine, South Africa.

Aluminum silicates

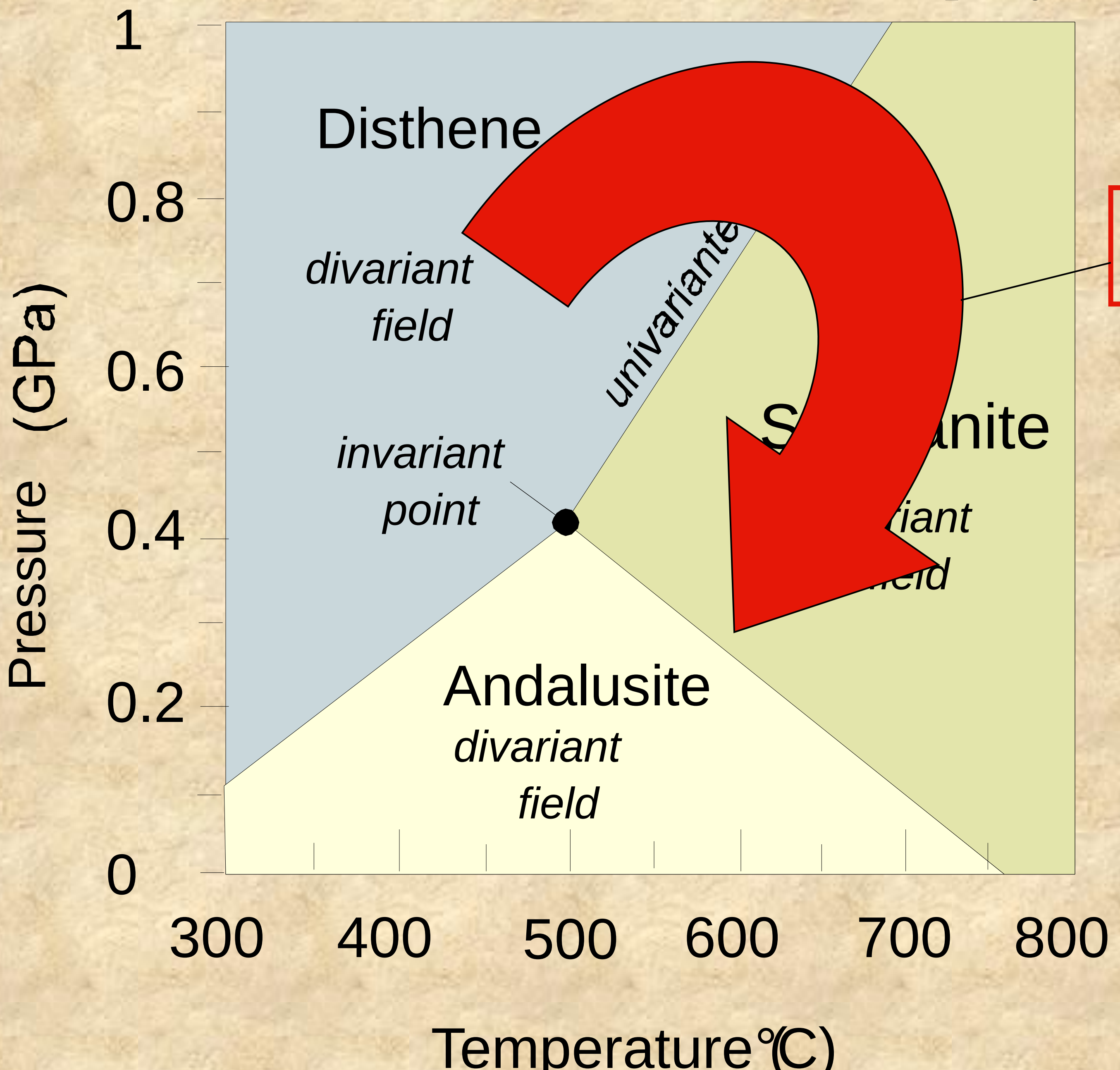


- Al_2SiO_5 with the three modifications:

  andalusite, disthene, sillimanite

- Differences in cristallographic, physical properties and formation conditions.
- predominant metamorphic in pelitic (clayey) systems

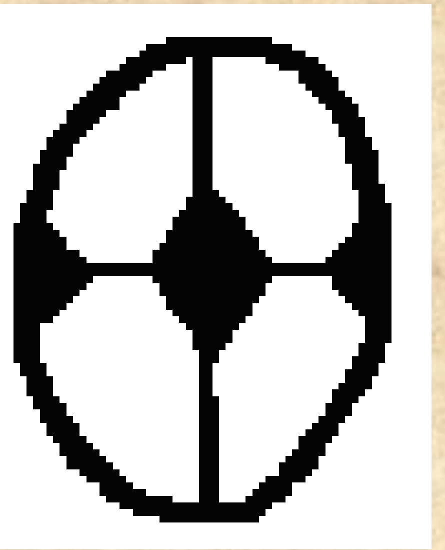
Experimentally determined phase diagram of the **Al_2SiO_5-Polymorphous**



PT-path a sinking and ehxumation

Andalusite

- Al_2SiO_5 or $Al^{[6]}Al^{[5]}[O/SiO_4]$
- hardness $7^1/_2$
- predominant metamorphic in pelitic (clayey) systems

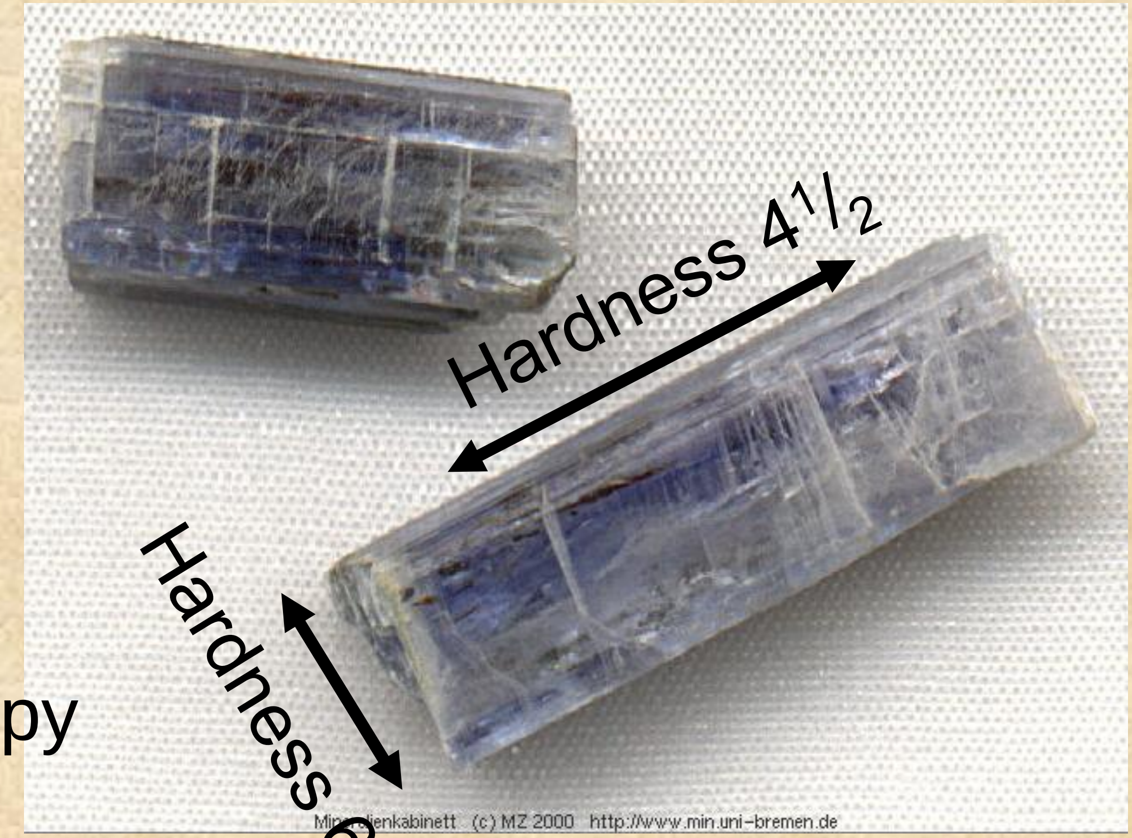


Andalusite-Chiastolite
from Lancaster Massachusetts

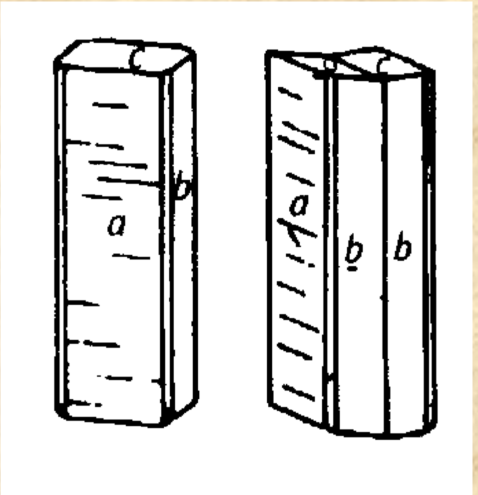
often thick-columnar crystals with rectangular section
sometimes with dark cross through embedded inclusions
(often graphite → variety chiastolite)

Disthene

- Al_2SiO_5 or $Al^{[6]}Al^{[6]}[O/SiO_4]$
- triclinic
- pronounced hardness anisotropy



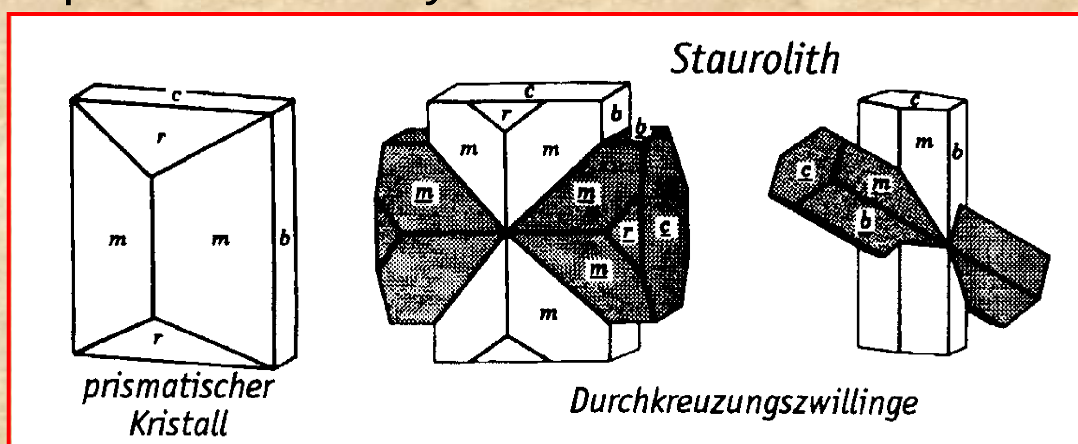
Disthene from the Ural



Acicular sillimatite crystals from Williamstown, Australia

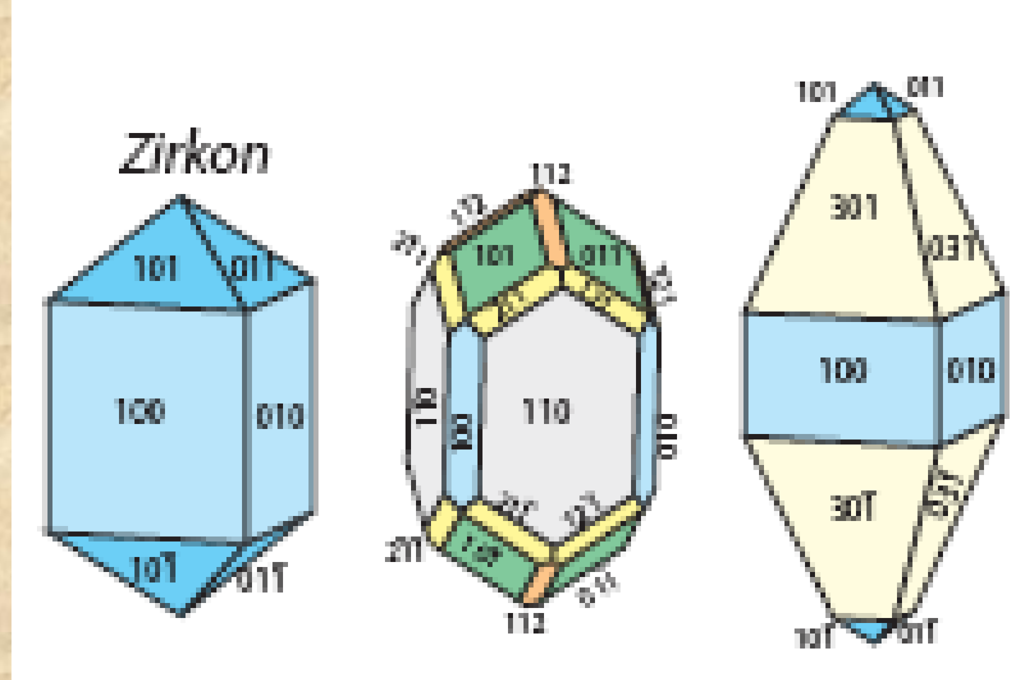
Staurolite

- hardness 7
- density 3.8 g/cm^3
- monocline, pseudorhombic
- $(Fe^{2+},Mg,Zn)_2(Al,Fe^{3+},Ti)_9O_6[(Si,Al)O_4]_4(O,OH)_2$
- predominant formed metamorphic in Al-rich systems
- Cruciform twin are frequent ➔



Zircon

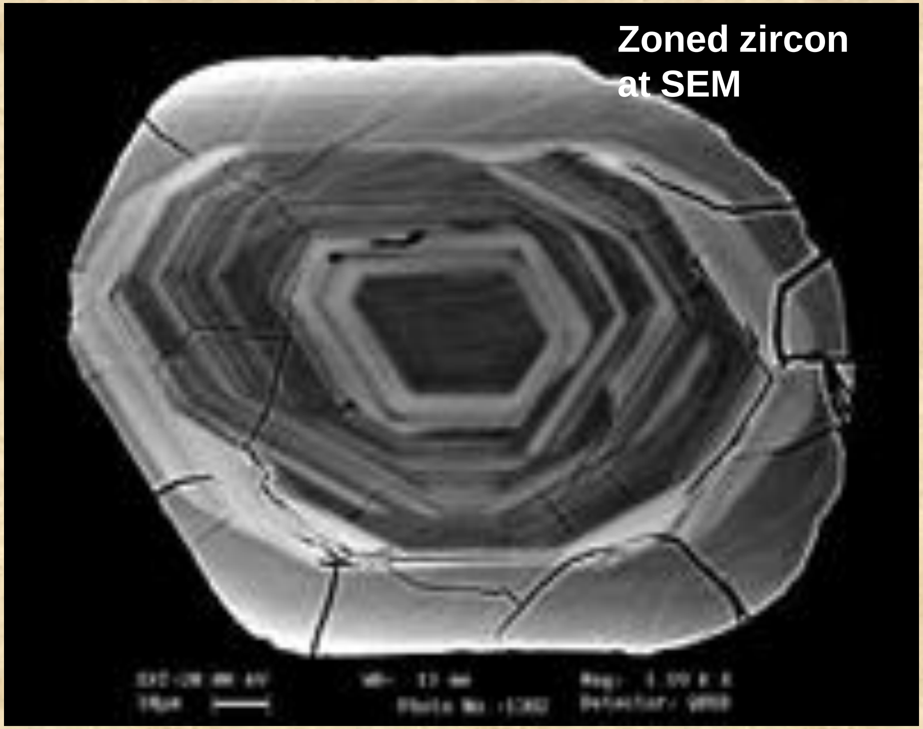
- $Zr[SiO_4]$



- **ca. 32.8 Gew.% SiO_2**
- **67 wt.% ZrO_2**
- **a high percentage of Hf ($HfO_2 \geq 1$ wt.%)**
- **many zircons contain U and Th and can therefore be used as chronometer ($^{235}U \rightarrow {}^{207}Pb$; $^{238}U \rightarrow {}^{206}Pb$; $^{232}Th \rightarrow {}^{208}Pb$).**
- **especially heavy rare earth (SEE^{3+}) can be incorporated at the place of Zr^{4+}.**

Zircon occurrence

- in intermediated to acid magmatites
- in all clastic sediments
- in heavy metal placers
- as detritic zircon-grains, which remain by metamor-phose and partial dissolution and further form grow seaming at old grains ➔



Zircon crystals from Frederiksvärn, Norway

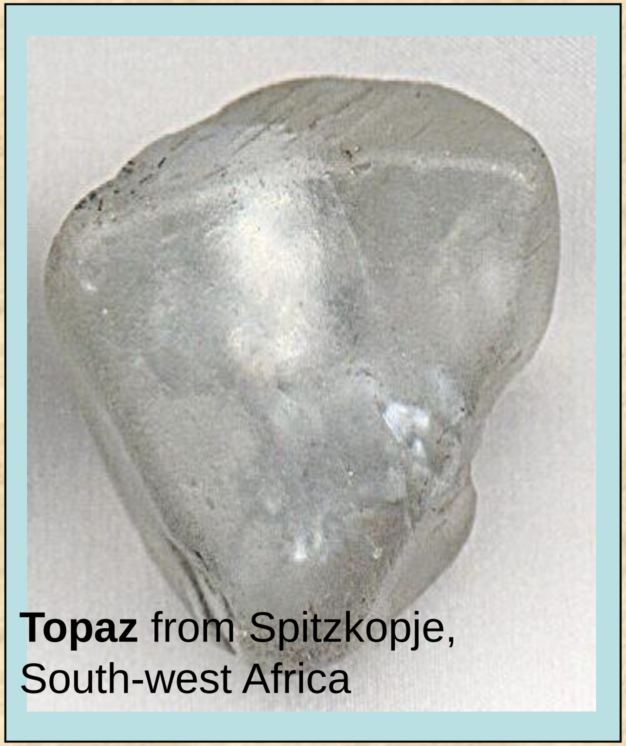
The economic significance:

Raw material for the extraction of Zr and Hf; gemstone industry.

Titanite

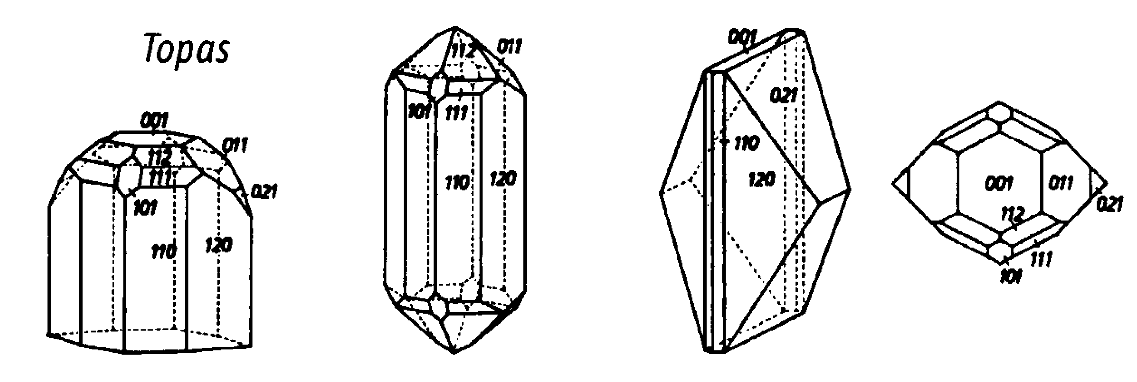
- CaTi [SiO_4] (O,OH,F)
- hardness 5
- yellow, brown, red brown greenish
- in differentiated alkaline-rich Ca-rich magmatites
- in metamorphites: green schist, amphibolites, gneisses, eclogites

Topaz



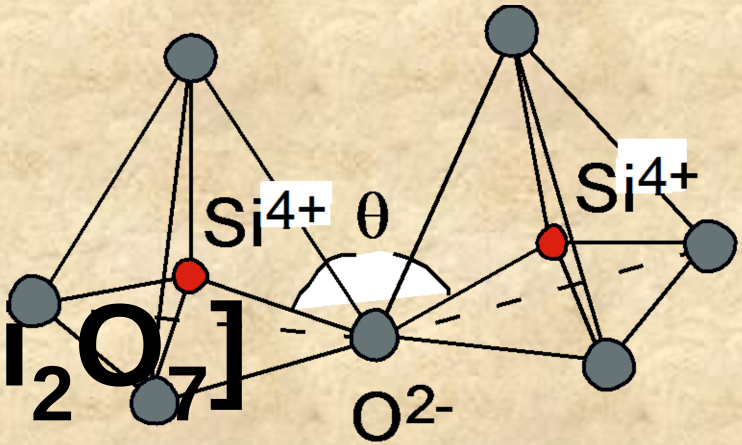
Topaz from Spitzkopje, South-west Africa

- $Al_2[SiO_4](F,OH)_2$
- hardness 8
- Gemstone varieties
- in pegmatites or as secondary form in Al-rich acid granites



Sorosilicates

$[Si_2O_7]$

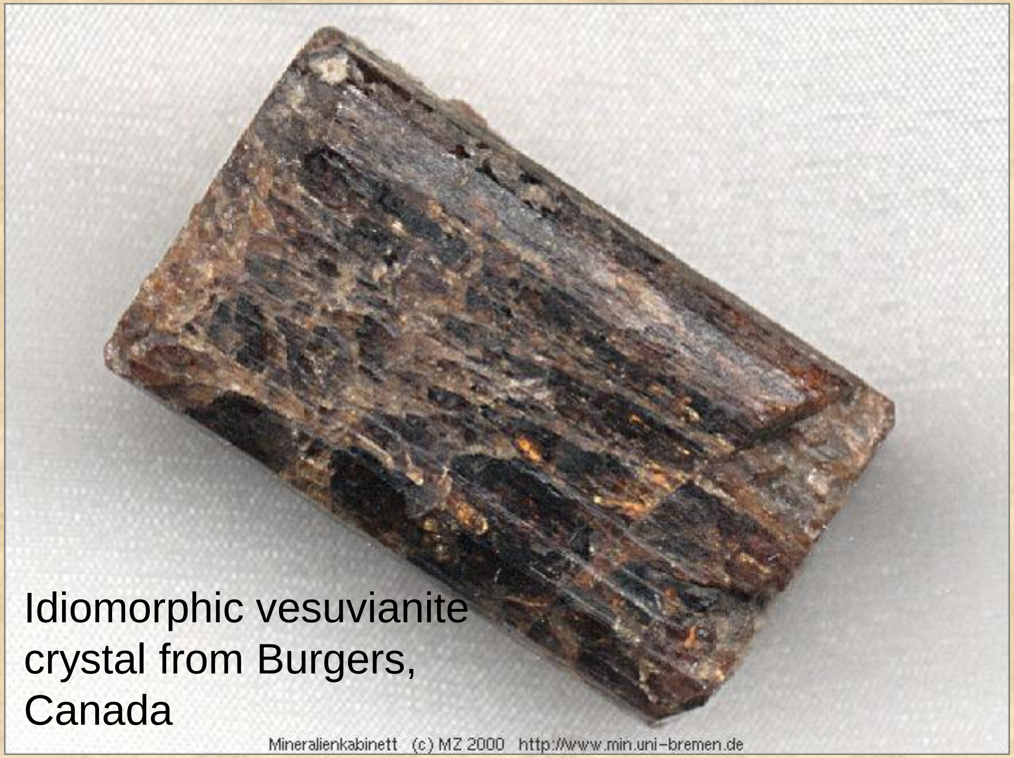


To form by low metamorphic conditions: **epidote group, vesuvianite, pumpellyite, lawsonite**

In well silica-poor high temperature metamorphic and magmatic systems

➔ **melilite group**

Vesuvianite
tetragonal



Idiomorphic vesuvianite crystal from Burgers, Canada

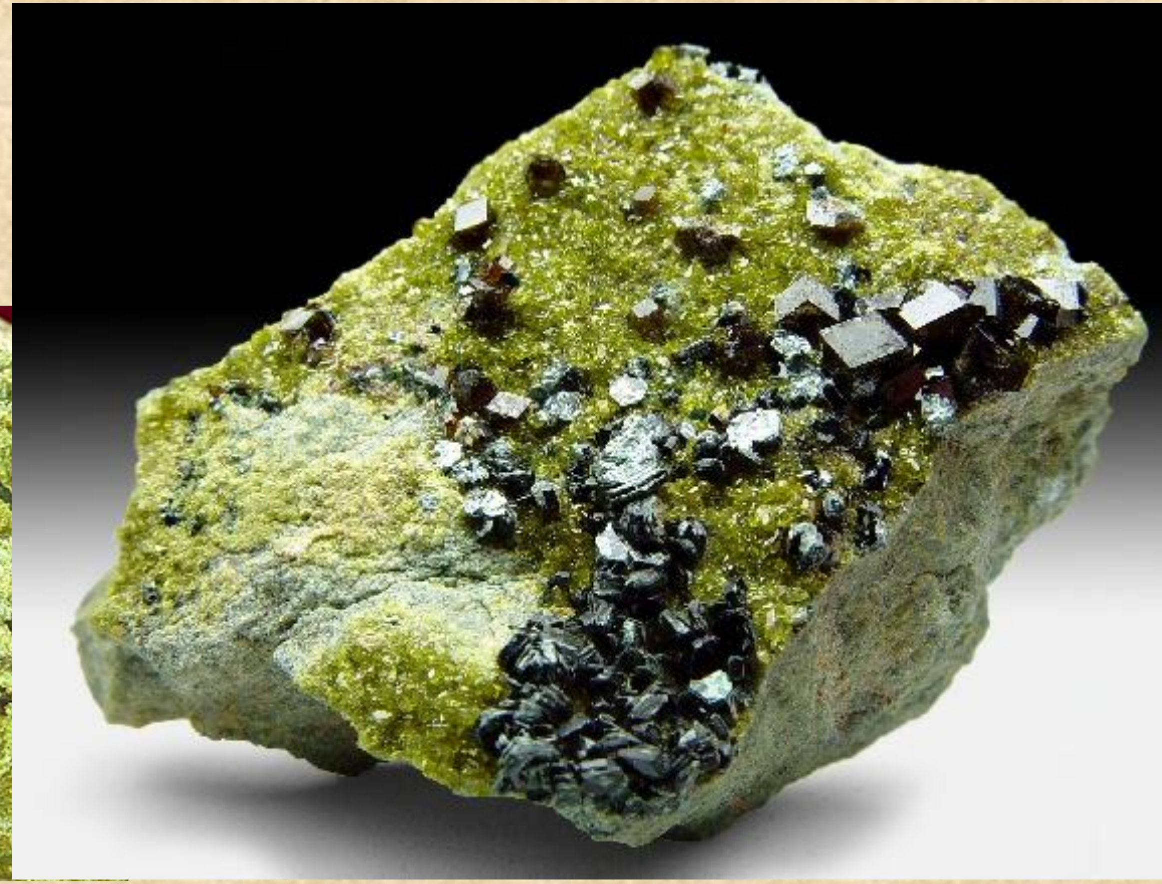
$Ca_{19}(Al,Fe^{3+},Ti)_{10}(Mg,Fe^{2+},Mn)_3[Si_2O_7]_4[SiO_4]_{10}(O,OH,F)_{10}$

Hardness 6-7 with many colors depending on chemism

<u>Occurrence:</u> as concretions in sediments of the Eifel maars

By high temperatures in SiO_2 and calc-rich material components

Epidote / Zoisite



www.mineralium.com

- $Ca_2(Al,Fe^{3+})Al_2[O/OH/SiO_4/Si_2O_7]$
- Yellow-green to dark green, pistachio green ("Pistazite")
- metamorphic, mainly occurring in green schist, often in diaclases

Lawsonite orthorhombic

- **$CaAl_2[Si_2O_7](OH)_2 \cdot H_2O$**

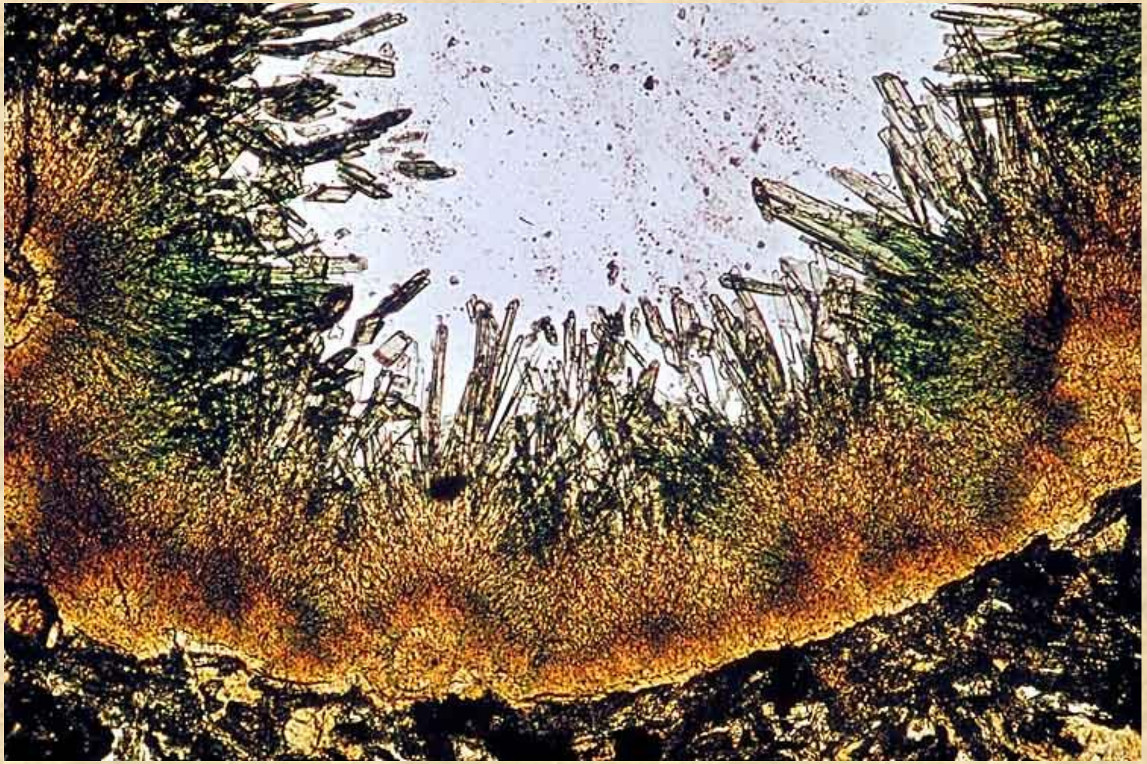
- can be formed in the subducted oceanic crust and by low geothermic gradient and is stable up to very high pressure (10 GPa = 300 km depth).

- The mineral can incorporate up to 10 wt. % water in crystal lattice and can resist the pressures according about 200 km depth ➔ **Water transport in the Earth's mantle!**

Pumpellyite

- **$W_2XY_2[Si_2(O,OH)_7][SiO_4](OH,O)_3$**
  often:
  $(Ca,Na,K)_2(Al,Fe^{3+},Fe^{2+},Mg)Al_2[Si_2(O,OH)_7][SiO_4](OH,O)_3$

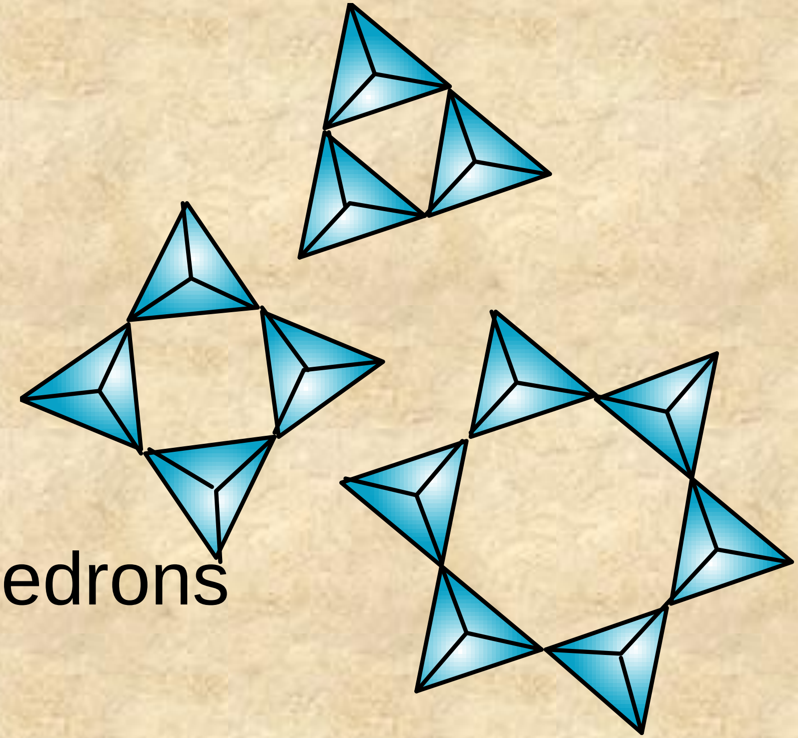
- Example for a chemical very variable crystal lattice



Reaction rim between diabase and quartz grain together with plagioclase, smectite and Fe-Hydroxide

Foto: Dr. Alfred Schuster

Cyclosilicates



- annular linked $[SiO_4]^{4-}$-tetrahedrons
- Si : O -ratio = 1 : 3
    - $[Si_4O_{12}]^{8-}$- and $[Si_6O_{18}]^{12-}$ -rings
- Common characteristics are a very high hardness (7-8) and diverse cations, especially placed in the ring structures. This results in very different colors and gemstone varieties.
- For example beryl, tourmaline, cordierite

Cyclosilicates

cordierite, rounded

beryl

Beryl

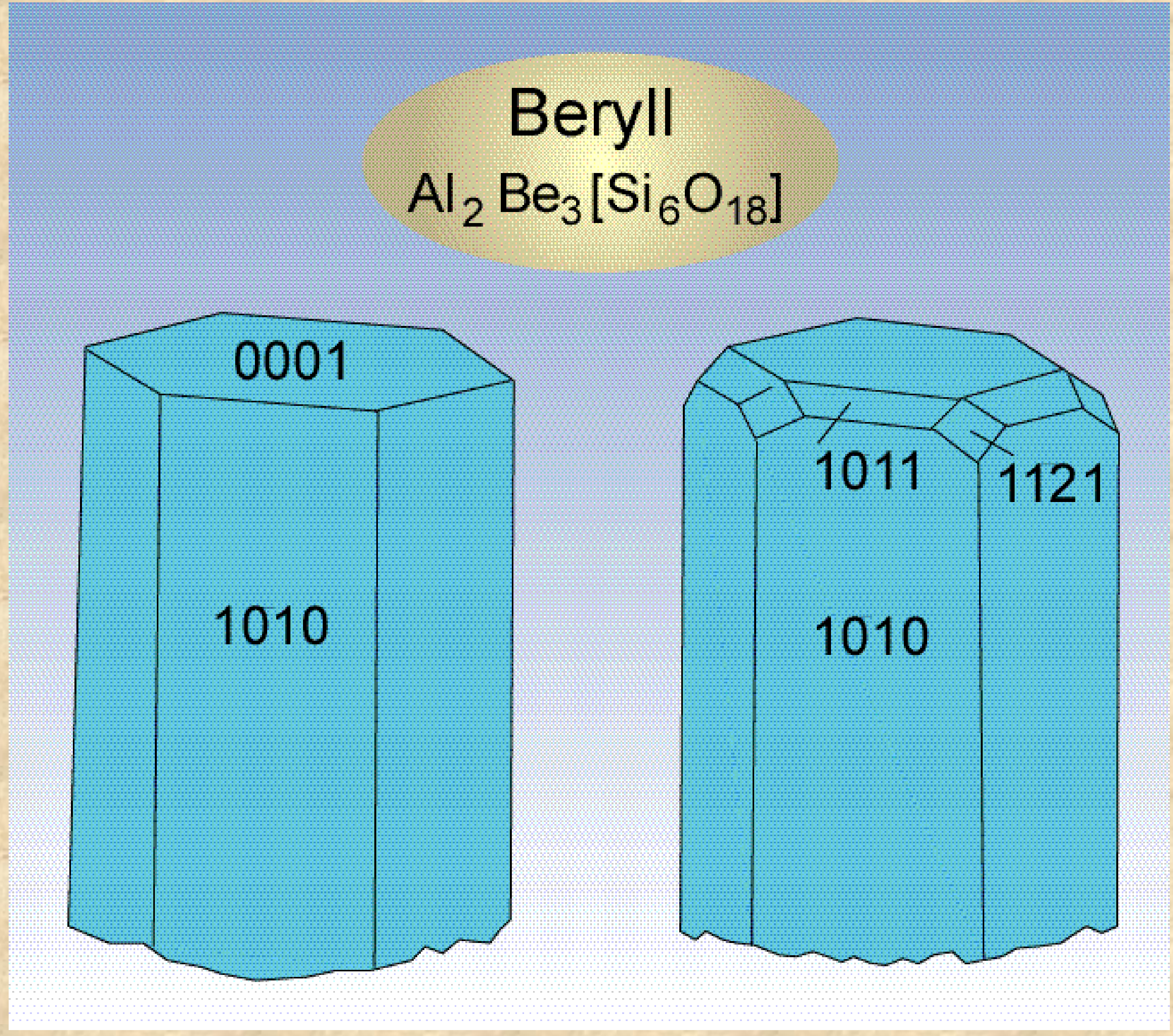

Aquamarin (Be-Al-Silicat), Pakistan, Foto und Copyright: T. Seilnacht

- $Be_3Al_2[Si_6O_{18}]$
- hexagonal
- Gemstone varieties:

  green (= emerald)

  blue (= aquamarine)

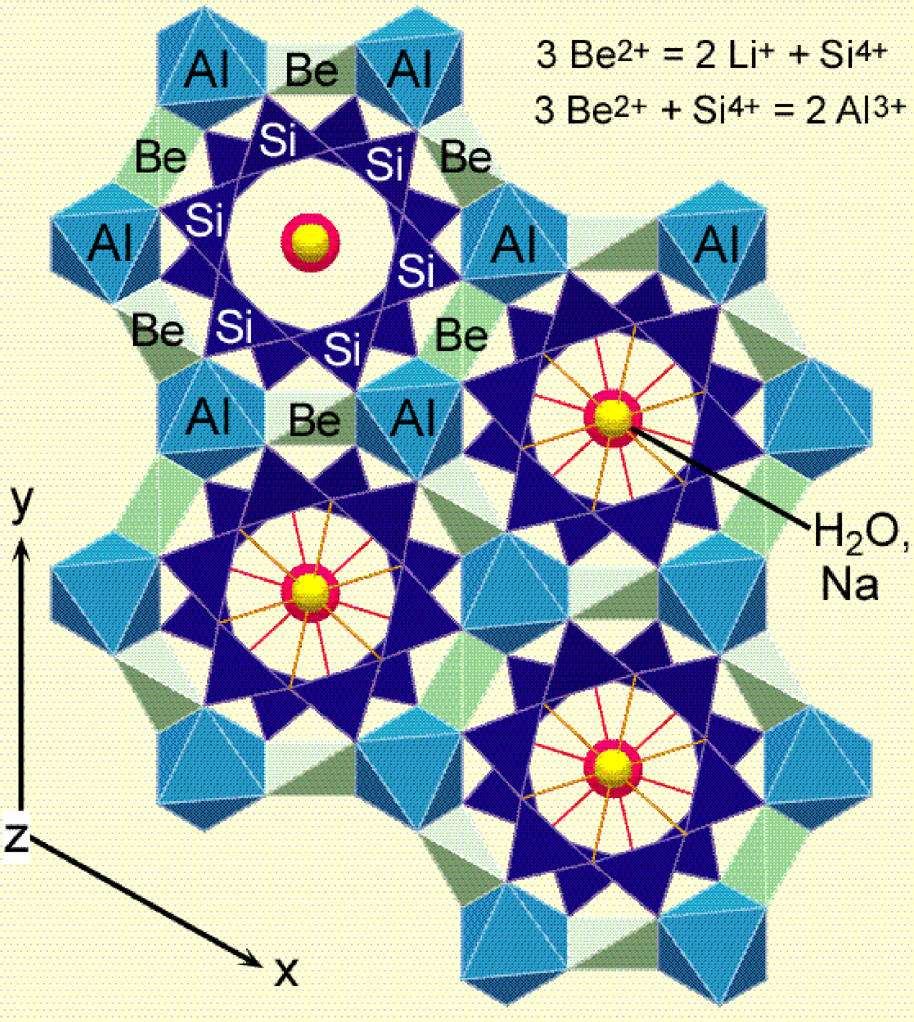
- green, blue, yellow, reddish; transparent to opaque
- Hardness $7^1/_2$ - 8
- Occurrence in pegmatites

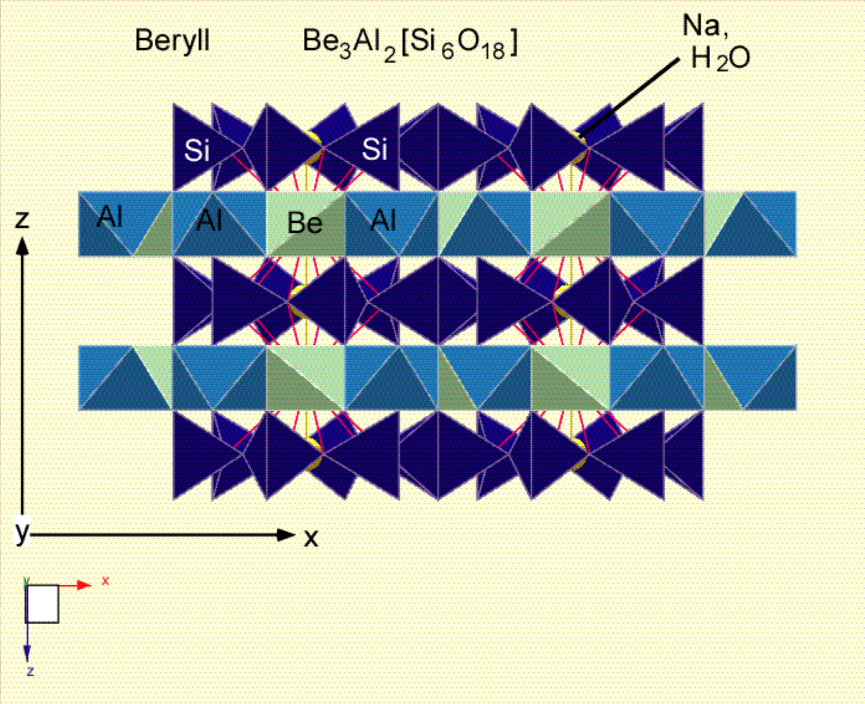


hexagonal, columnar crystals

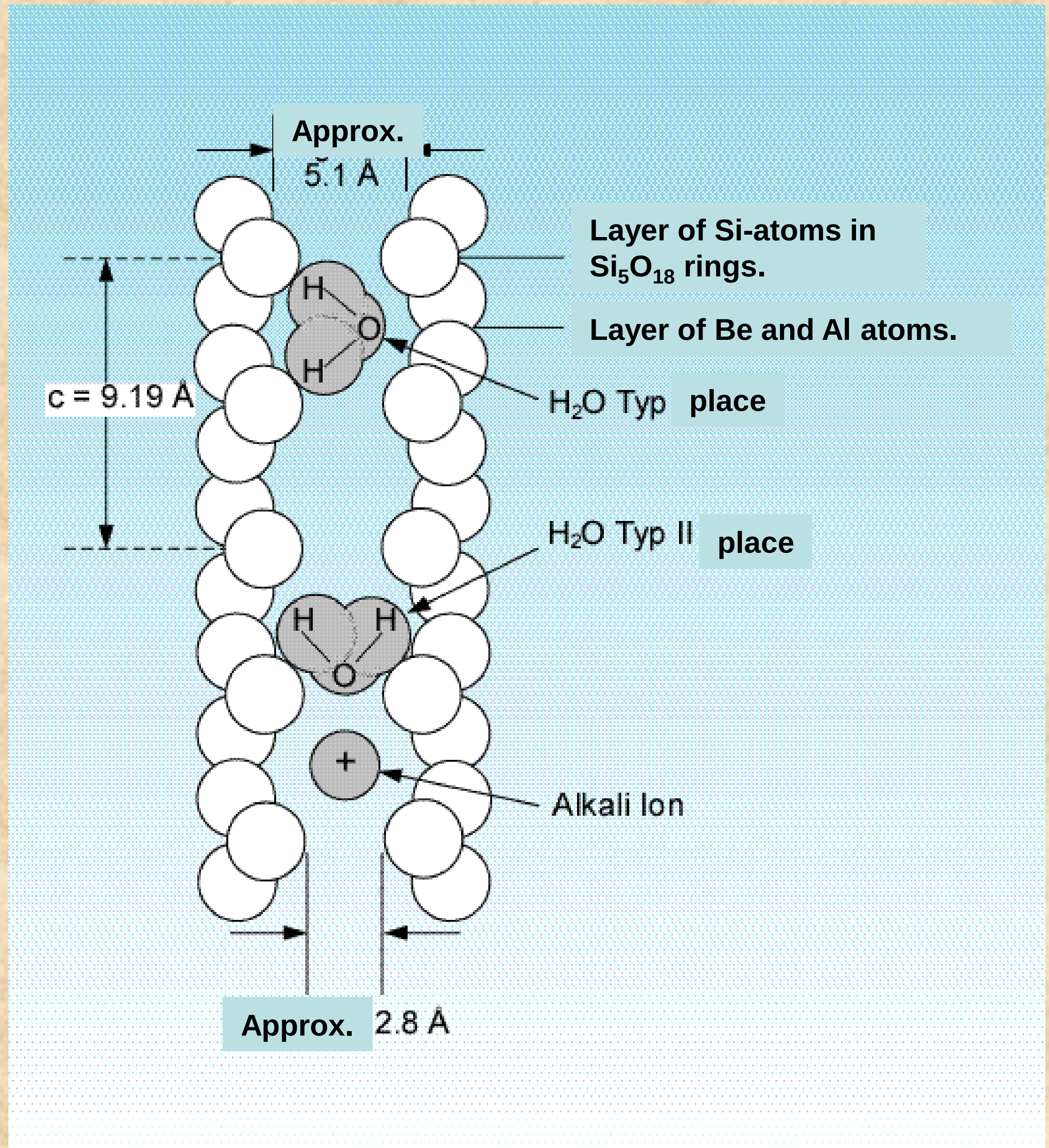
Beryl $Be_3Al_2[Si_6O_{18}]$

Projection at (0001)

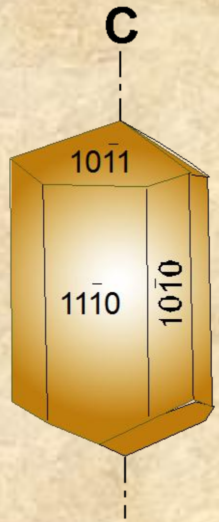




Beryl- channels



Turmalin



- Härte $7^1/_2$
- Dichte 2.9 bis 3.2 g/cm^3
- triklin
- oft chemisch zonariert
- unterschiedliche Kationen beteiligt
- $(Na,K,Ca)(Mg,Fe,Mn,Li,Al)_3(Al,Mg,Fe^{3+})_6$

$[Si_6O_{18}](BO_3)_3(O,OH)_3(OH,F)$

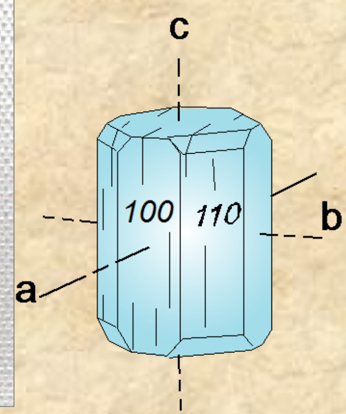
Turmalin, Stak Nala/Pakistan, Foto und Copyright: T. Seilnacht

Cordierit

$(Mg,Fe^{2+})_2[Al_4Si_5O_{18}]$

„Luchssaphir“ bzw
„Wassersaphir“ aus Ceylon

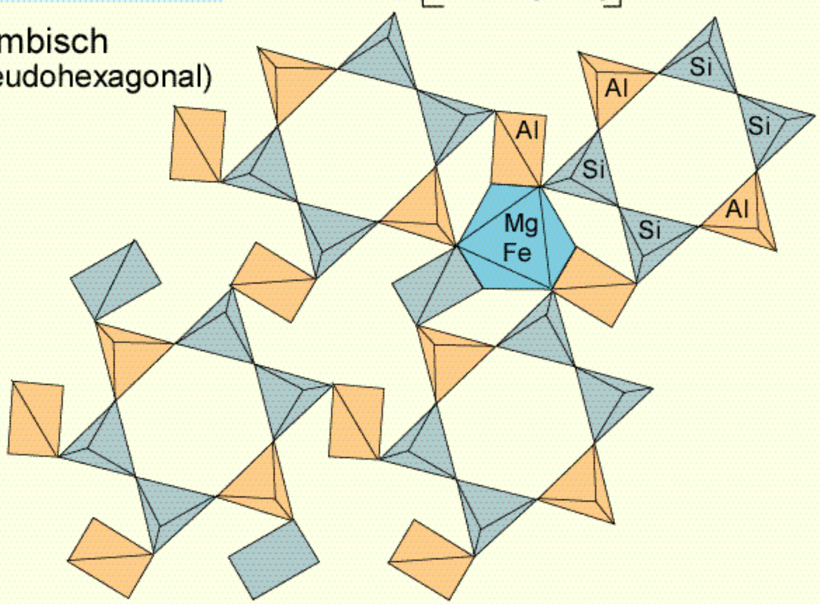
- Entsteht bei hohen Temperaturen (T ≥ 520 °C) in Al-reichen Metamorphiten und Magmatiten



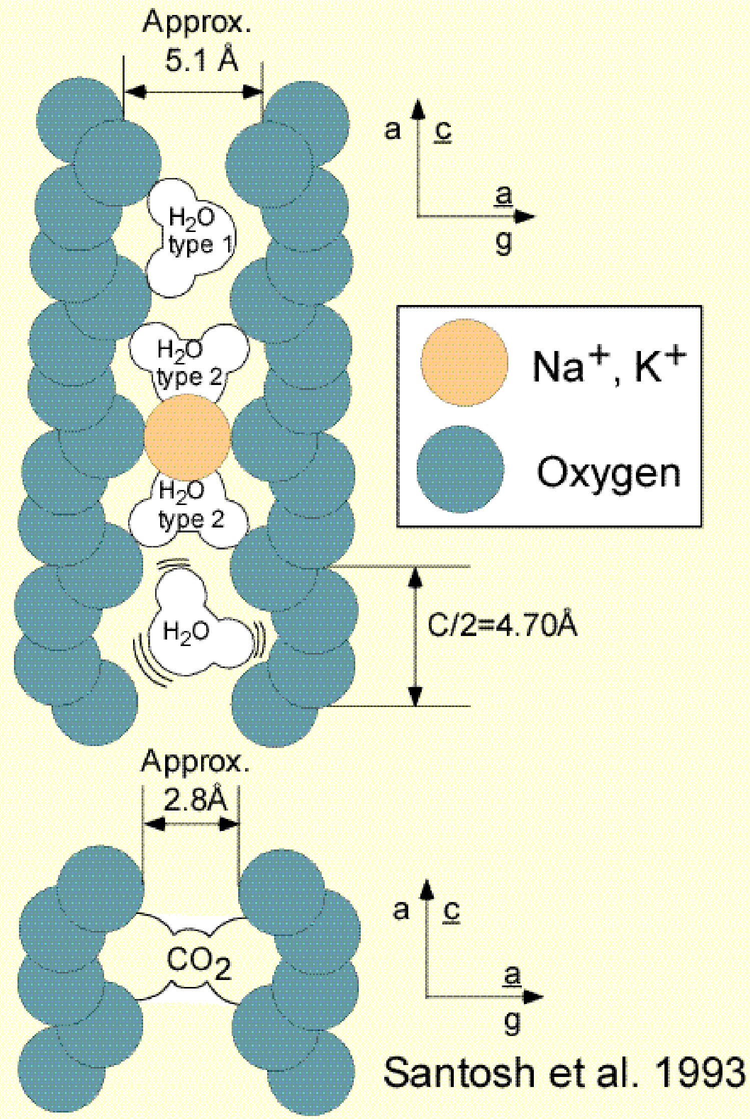
„Luchssaphir“ bzw
„Wassersaphir“ aus Ceylon

CORDIERIT $(Mg, Fe)_2 [Al_4Si_5O_{18}] \times nH_2O$

rhombisch
(pseudohexagonal)



Cordierit



Santosh et al. 1993

Kettensilikate (Inosilikate)

- zu Ketten verknüpfte $[SiO_4]^4$-Tetraeder auf
- 2 Sauerstoffatome eines Tetraeders gehören gleichzeitig zwei Tetraedern an
- Si : O -Verhältnis = 1 : 3
- negativ geladene Ketten werden durch Kationen zusammengehalten.

Beispiele: Pyroxene, Wollastonit.

- Pyroxene:

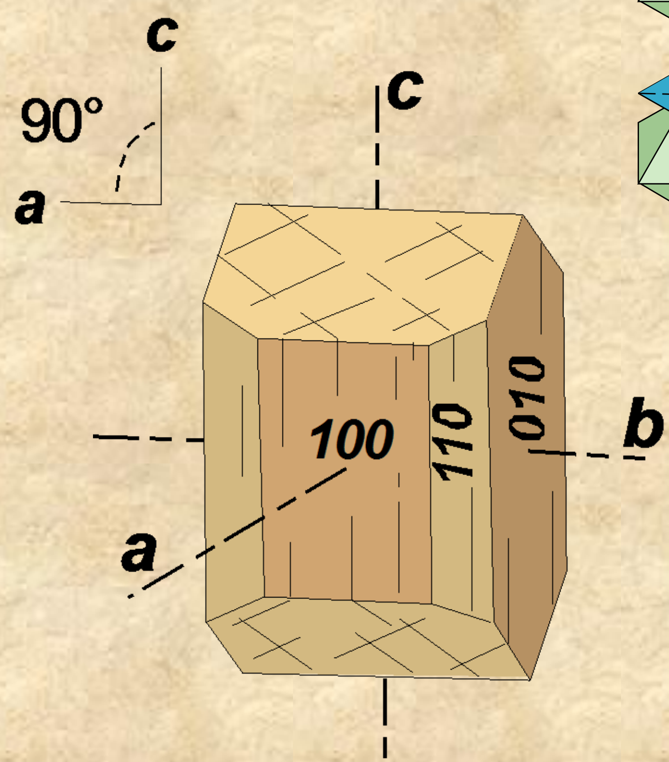
Allgemeine Formel: $A_2B_2[(Si,Al)_2O_6]$

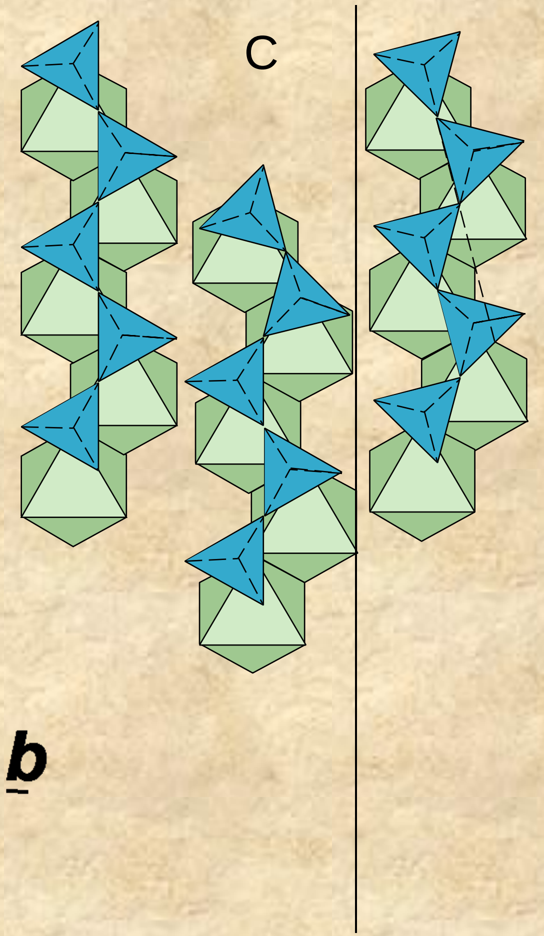
mit A = Na, Ca, Mg, Fe^{2+}, Mn

B = Mg, Fe^{2+}, Mn, Fe^{3+}, Al, Ti, Cr

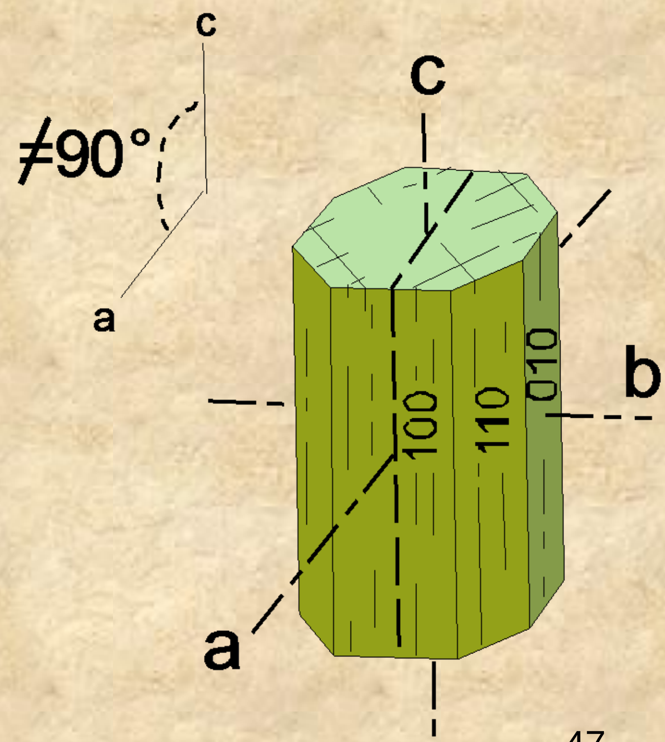
Kristallstruktur von Pyroxenen

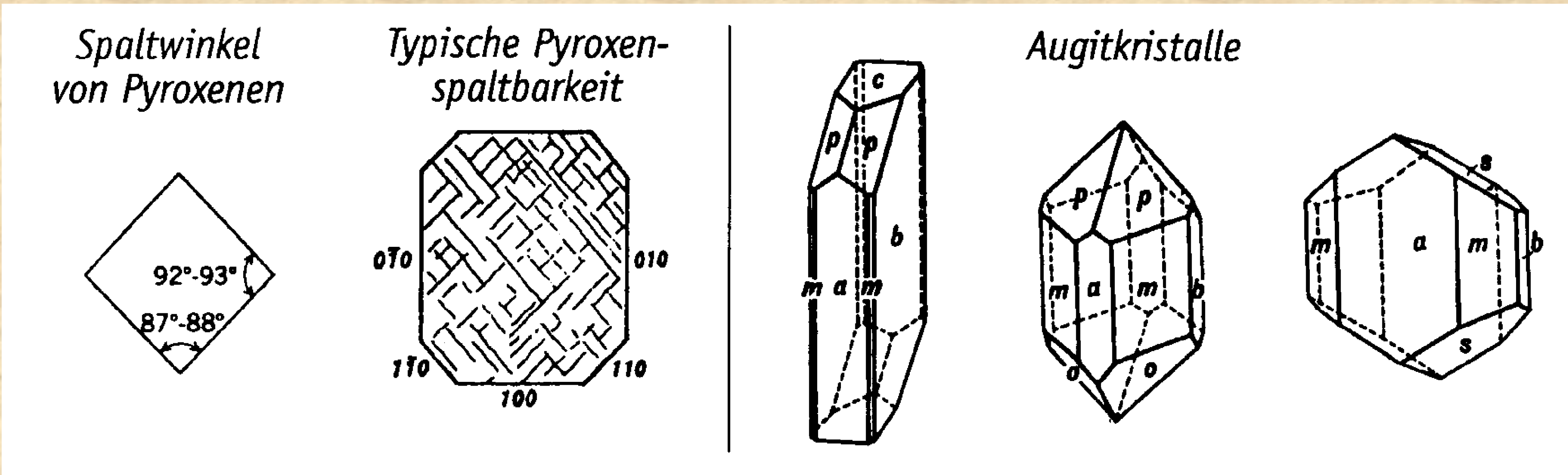
Orthopyroxene
rhombisch



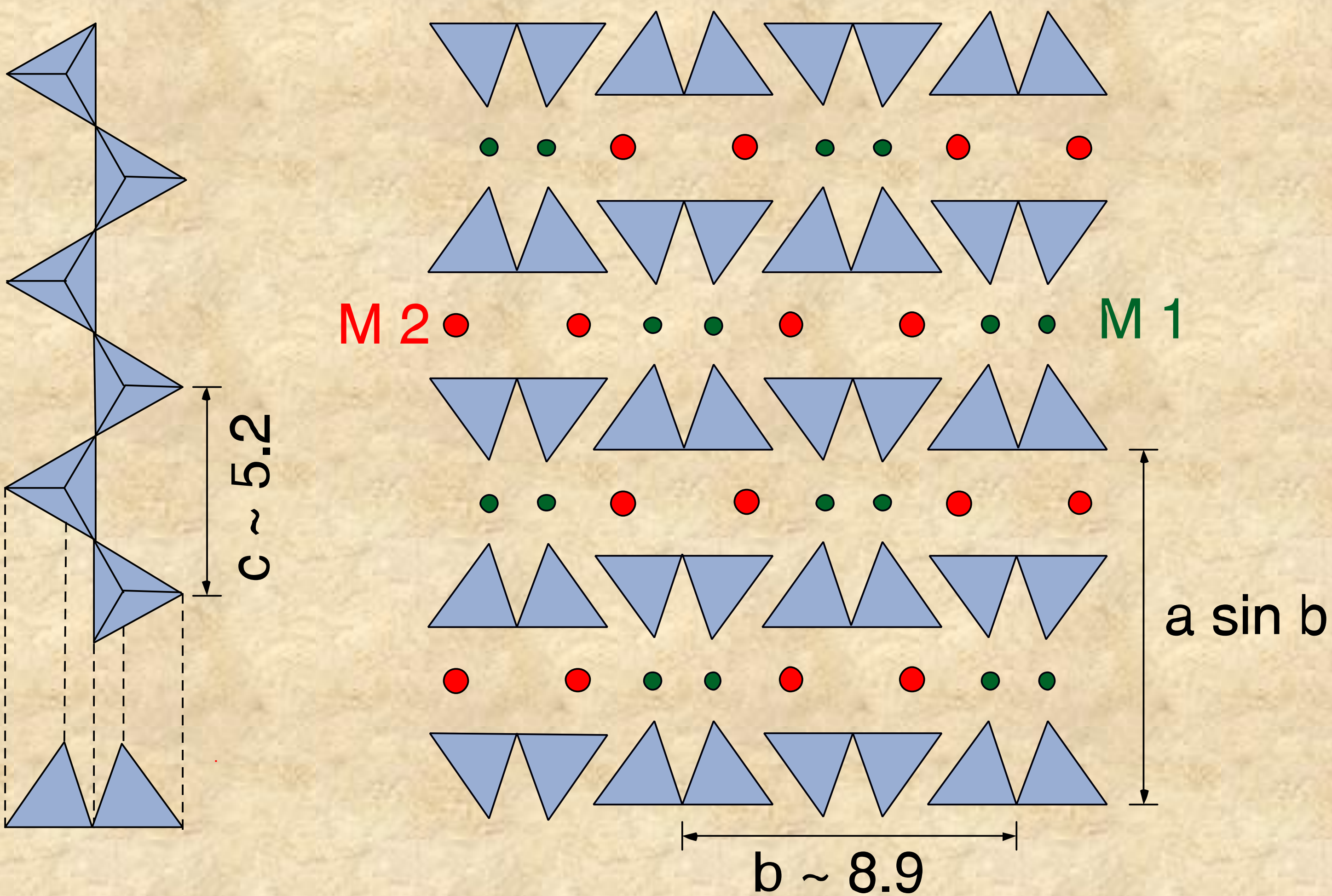


Klinopyroxene
monoklin



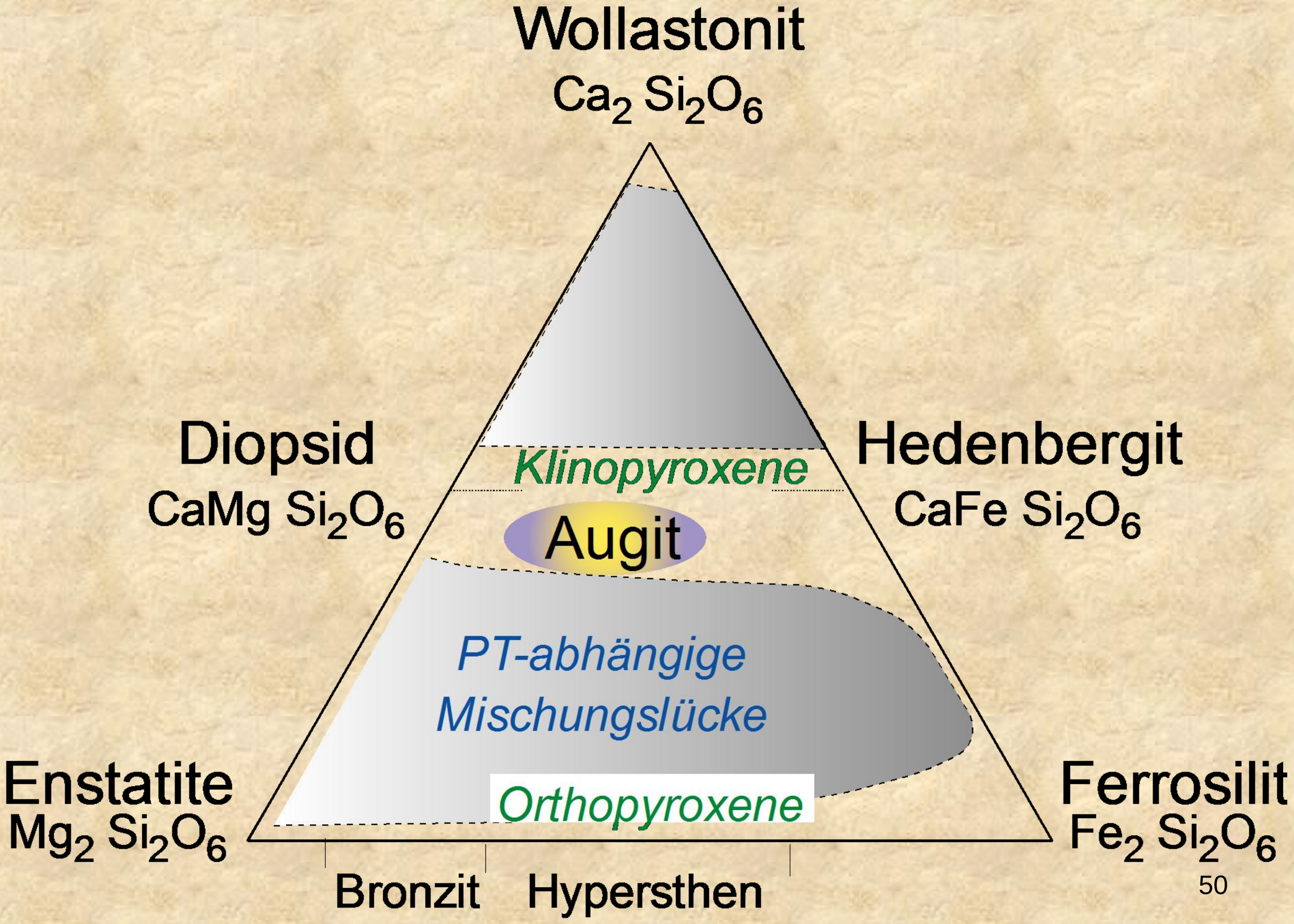

Spaltwinkel von Pyroxenen
92°-93°
87°-88°
Typische Pyroxen-spaltbarkeit
01̄0
010
1̄10
110
100
Augitkristalle
c
p
p
m
a
m
b
p
p
m
a
m
b
o
o
s
m
a
m
b
s

Pyroxenstruktur: [SiO_4]-Verknüpfung zu Ketten



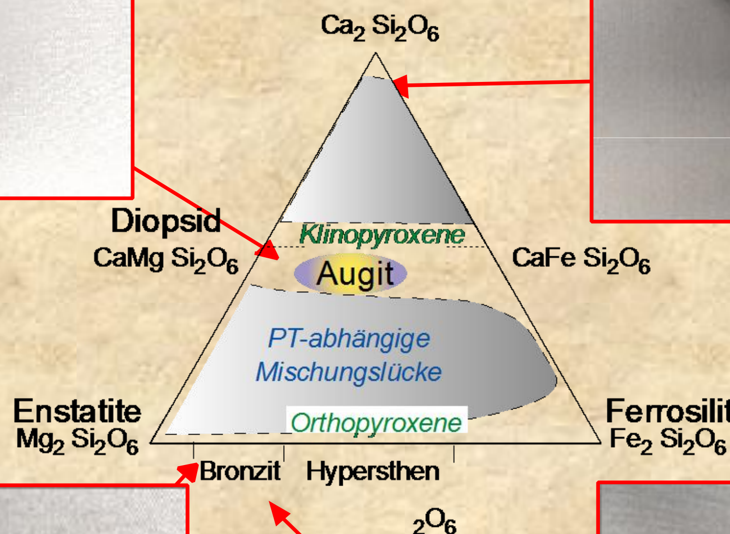
M 1= kleine Kationen (Fe^{2+}, Mg)

M 2= kleine und große Kationen (u.a. Ca)


Wollastonit
$Ca_2 Si_2O_6$
Diopsid
$CaMg Si_2O_6$
Klinopyroxene
Hedenbergit
$CaFe Si_2O_6$
Augit
PT-abhängige
Mischungslücke
Enstatite
$Mg_2 Si_2O_6$
Orthopyroxene
Ferrosilit
$Fe_2 Si_2O_6$
Bronzit
Hypersthen

Idiomorpher Augit

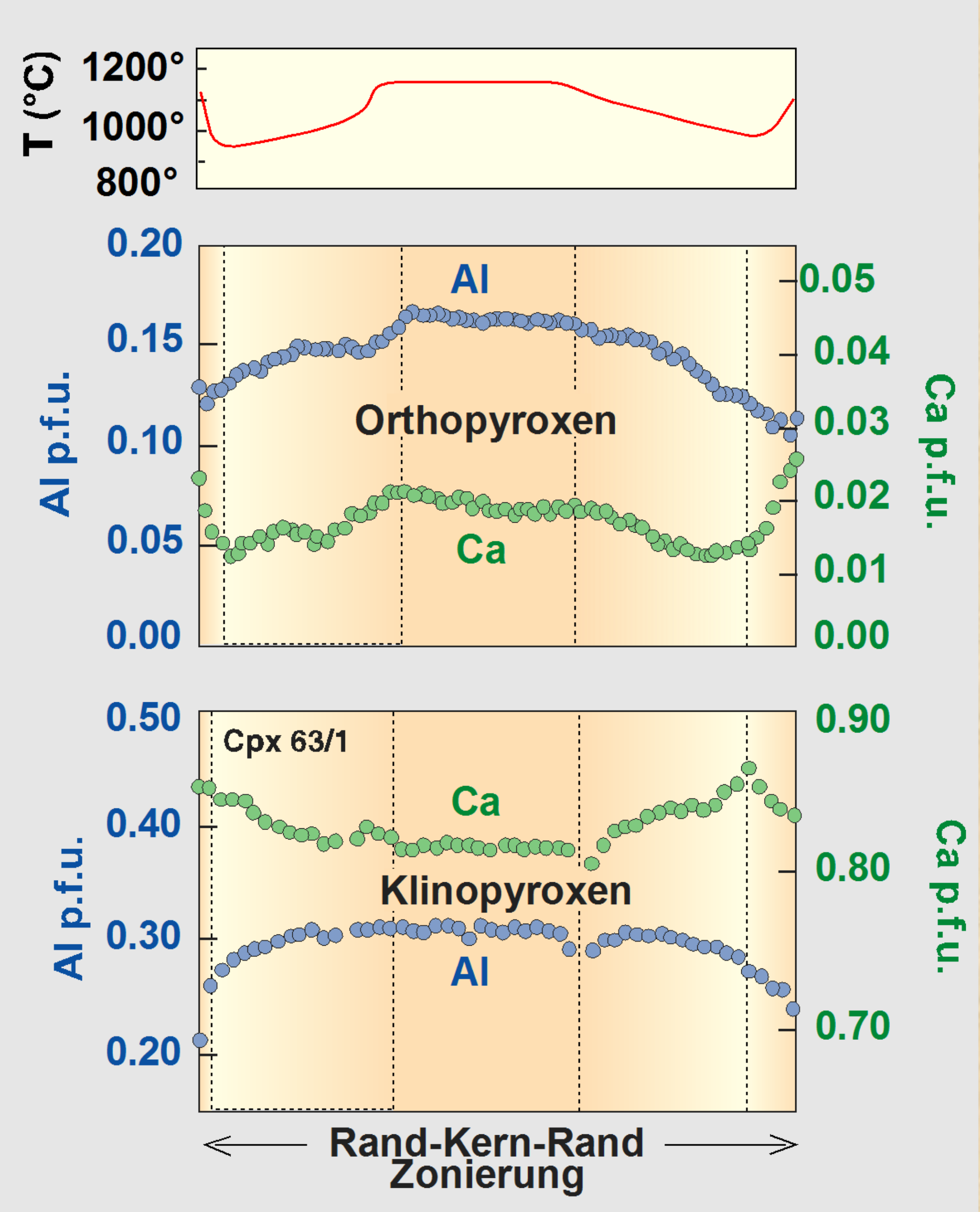
Wollastonit mit Grossular (Schweden)



Enstatit

Bronzit mit Plagioklas

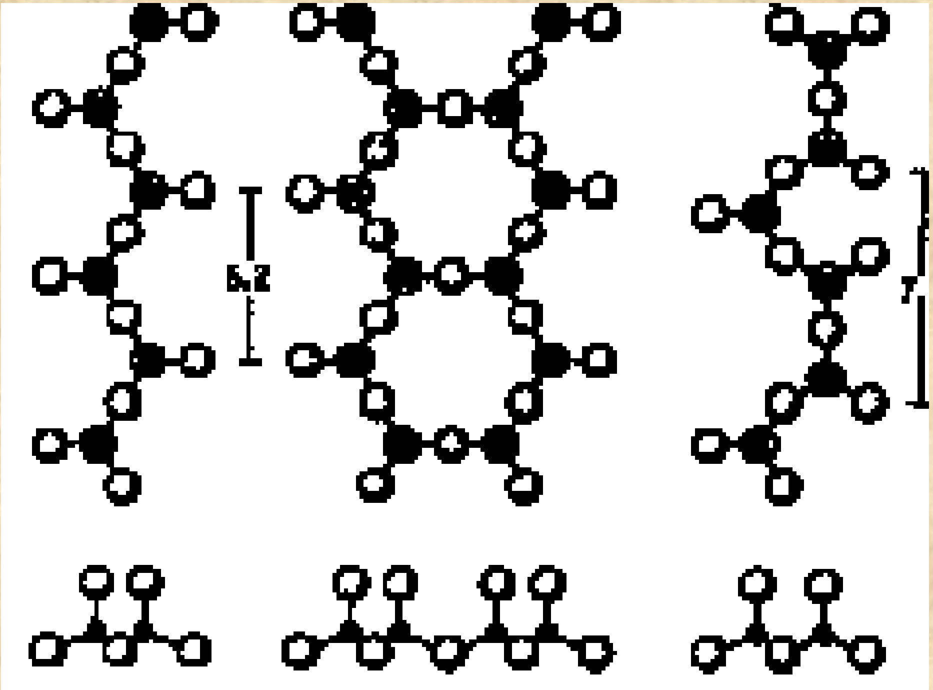
Chemische Zonierungen in Pyroxenen von Mantelxenolithen reflektieren die Abkühlungs- und Aufheizungs-geschichte des Erdmantels



Bändersilikate

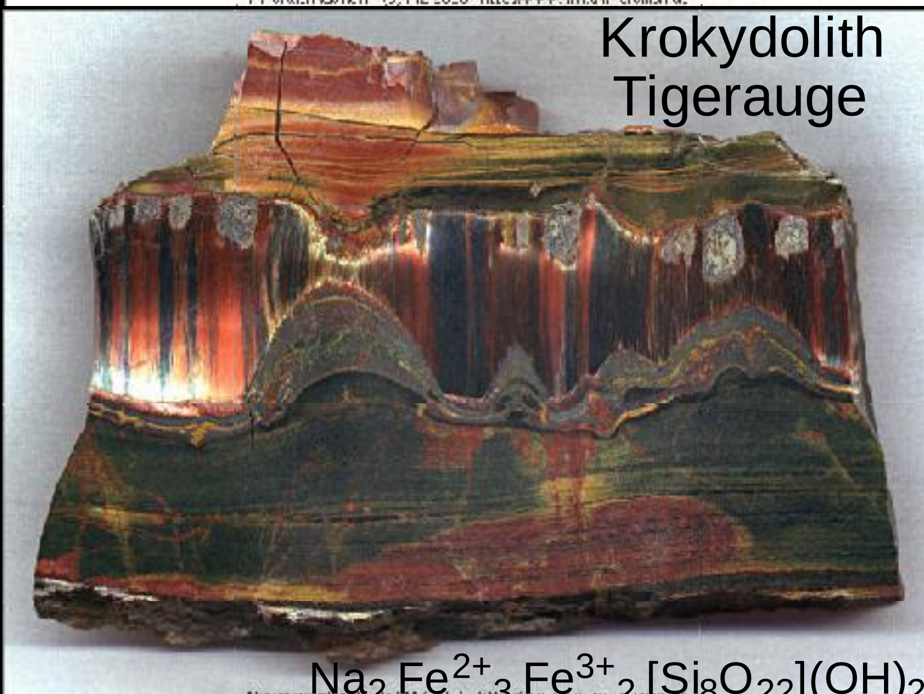
- jeweils zwei Tetraederketten sind zu einem Band oder einer Doppelkette verknüpft
- Si : O -Verhältnis = 1 : 2.75.

- *Beispiele:* Amphibole




$Ca_2(Mg,Fe)_5[Si_8O_{22}](OH)_2$
Aktinolith
Aktinolith
(Tschecheslowakei)


Basaltische
Hornblende
$NaCa_2(Mg,Fe^{2+})_4$ (Ti, Fe^{3+}) $[Al_2Si_6O_{22}](OH)_2$


Krokydolith
Tigerauge
$Na_2Fe^{2+}{}_3Fe^{3+}{}_2[Si_8O_{22}](OH)_2$


Tremolit
$Ca_2(Mg,Fe)_5[Si_8O_{22}](OH)_2$

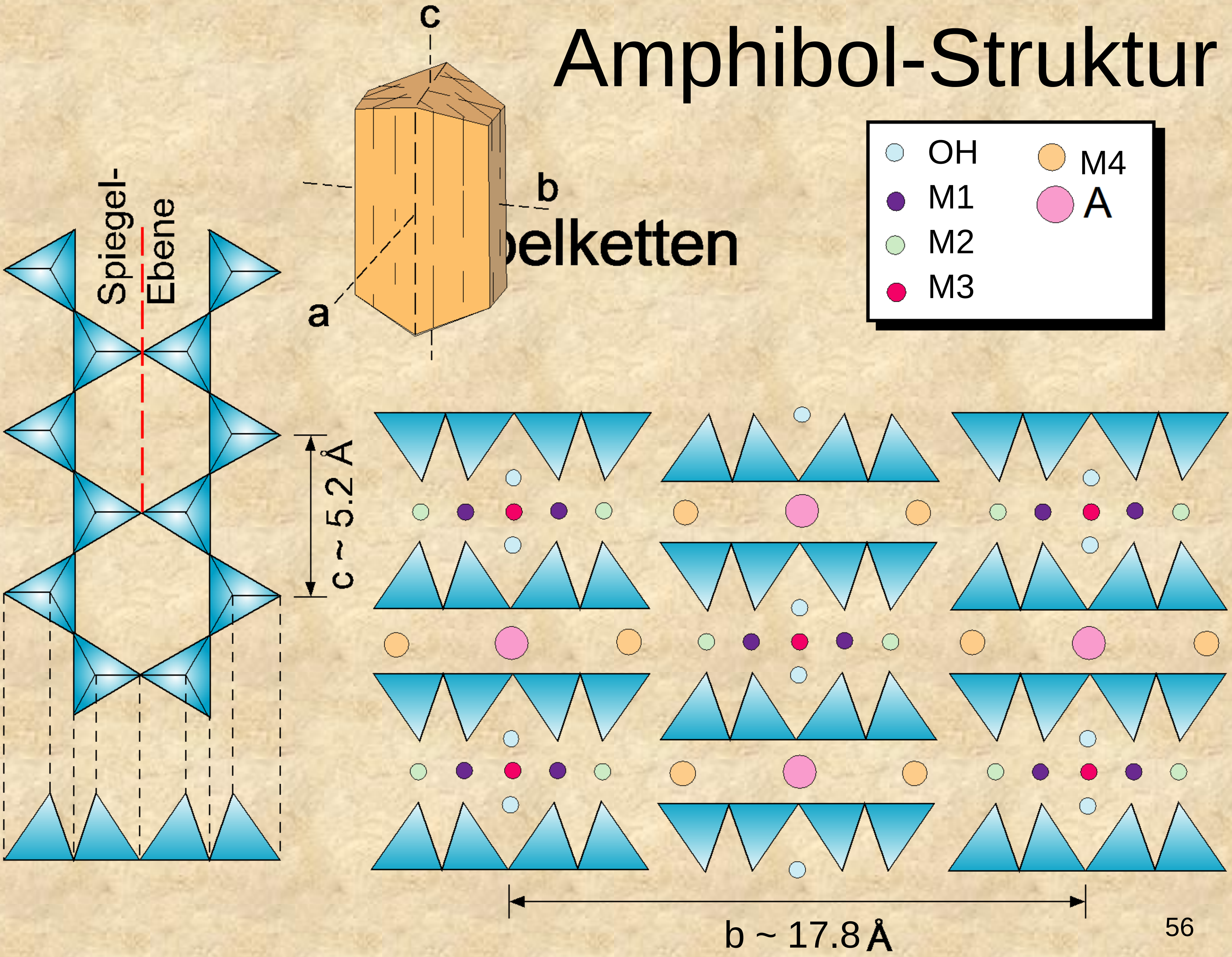
Amphibol-Gruppe

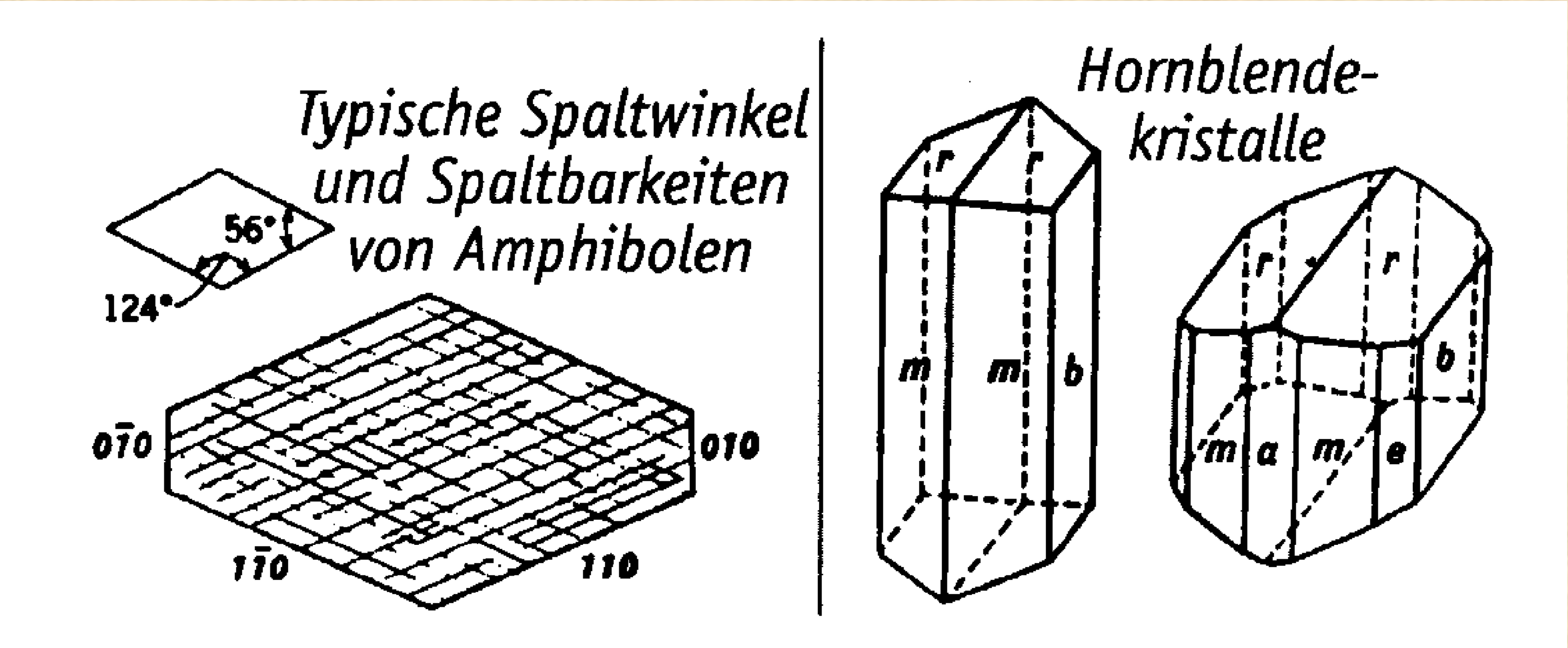
- Allgemeine Formel:

$$A_{0\text{-}1}X_2Y_5[(Si,Al)_8O_{22}(OH,F,Cl)_2]$$

- mit A = K, Na
- X = Na, Ca, Mg, Fe^{2+}, Mn
- Y = Mg,Fe^{2+}, Mn, Fe^{3+}, Al, Ti, Cr

Amphibol-Struktur





- Orthoamphibole = orthorhombisch

  Klinoamphibole = monoklin

- prismatische Kristalle mit meist sechseckigem Querschnitt; oft auch nadelig oder faserig

- 2 gute Spaltbarkeiten im Winkel von ~ 55° bzw. ~ 125°

Amphibole:
Allgemein

- Härte $5^1/_2$
- Dichte 2.9 bis 3.2 g/cm^3
- magmatisch (u.a. Hornblende, Riebeckit)
- metamorph (u.a. Hornblende, Tremolit, Aktinolith, Glaukophan, Riebeckit)

Schichtsilikate (Phyllosilikate)

- zu Schichten vernetzte $[SiO_4]^4$-Tetraeder
- vernetzte Sechserringe
- drei Sauerstoffatome gehören gleichzeitig zwei Tetraedern an
- Si : O -Verhältnis = 1 : 2.5.

- *Beispiele:* Biotit, Muskovit, Chlorit, Serpentin, Talk, Kaolin.

Schichtsilikat-Strukturen

In Schichtsilikaten Wechseln sich Tetraeder- und Oktaeder-Schichten ab.

Rechts:
Tetraeder-Basiseinheit