Structural Chemistry of Silicates

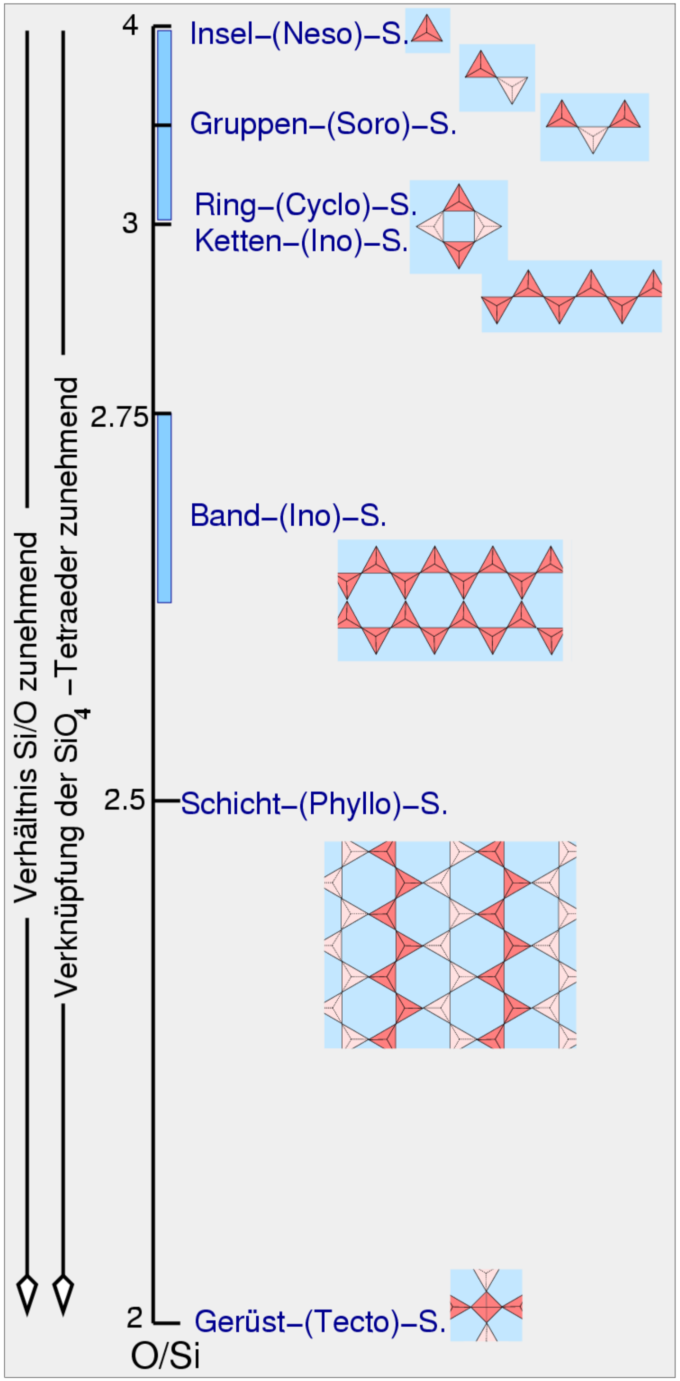
Thomas Lunkenbein

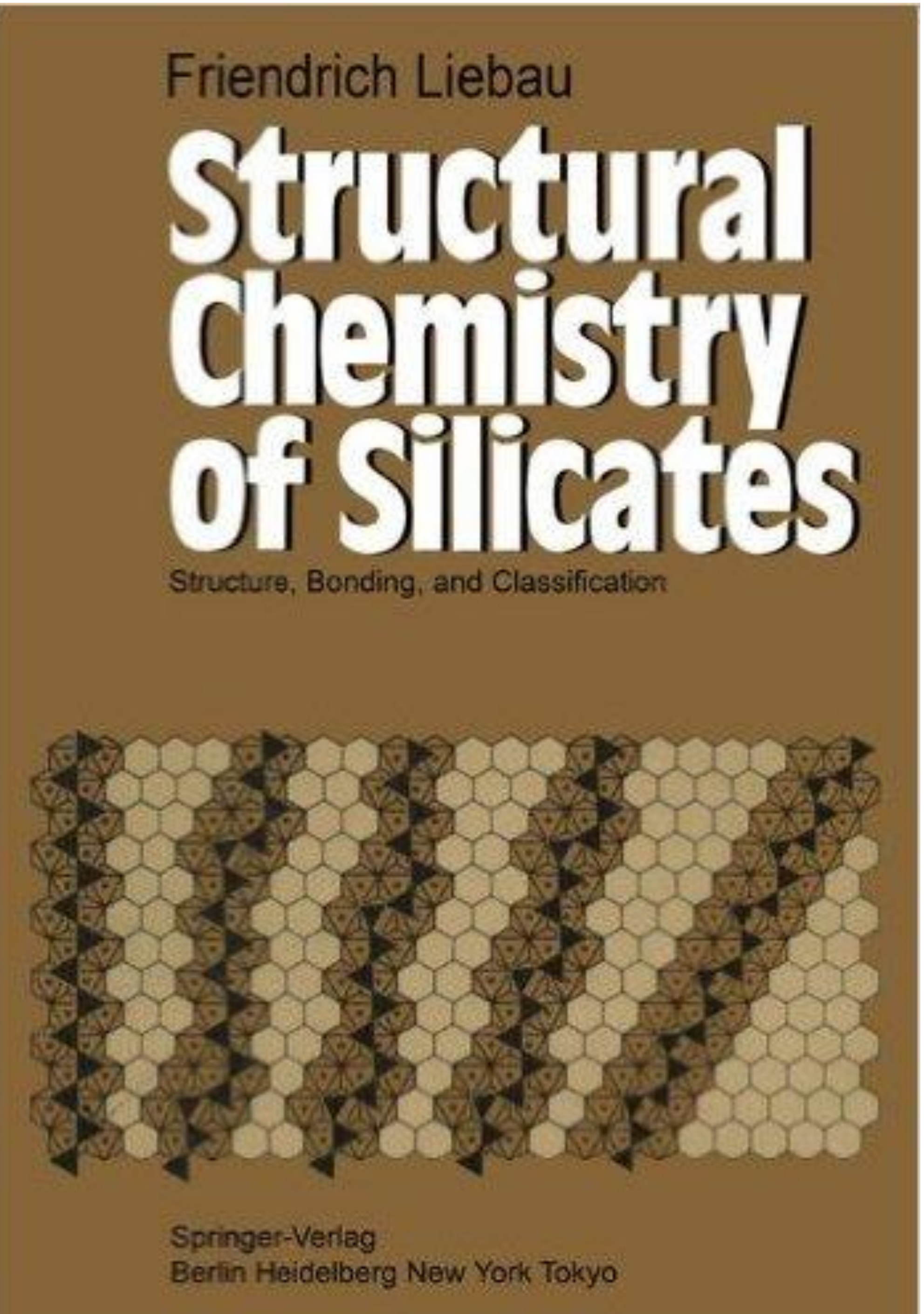
27.01.2017

Silicate Chemistry

- How are silicate structures connected and constructed?
- What is the influence of the Si/O-ratio on the silicate structure
- How do kind, number and size of counterions influence the structure

Short outline





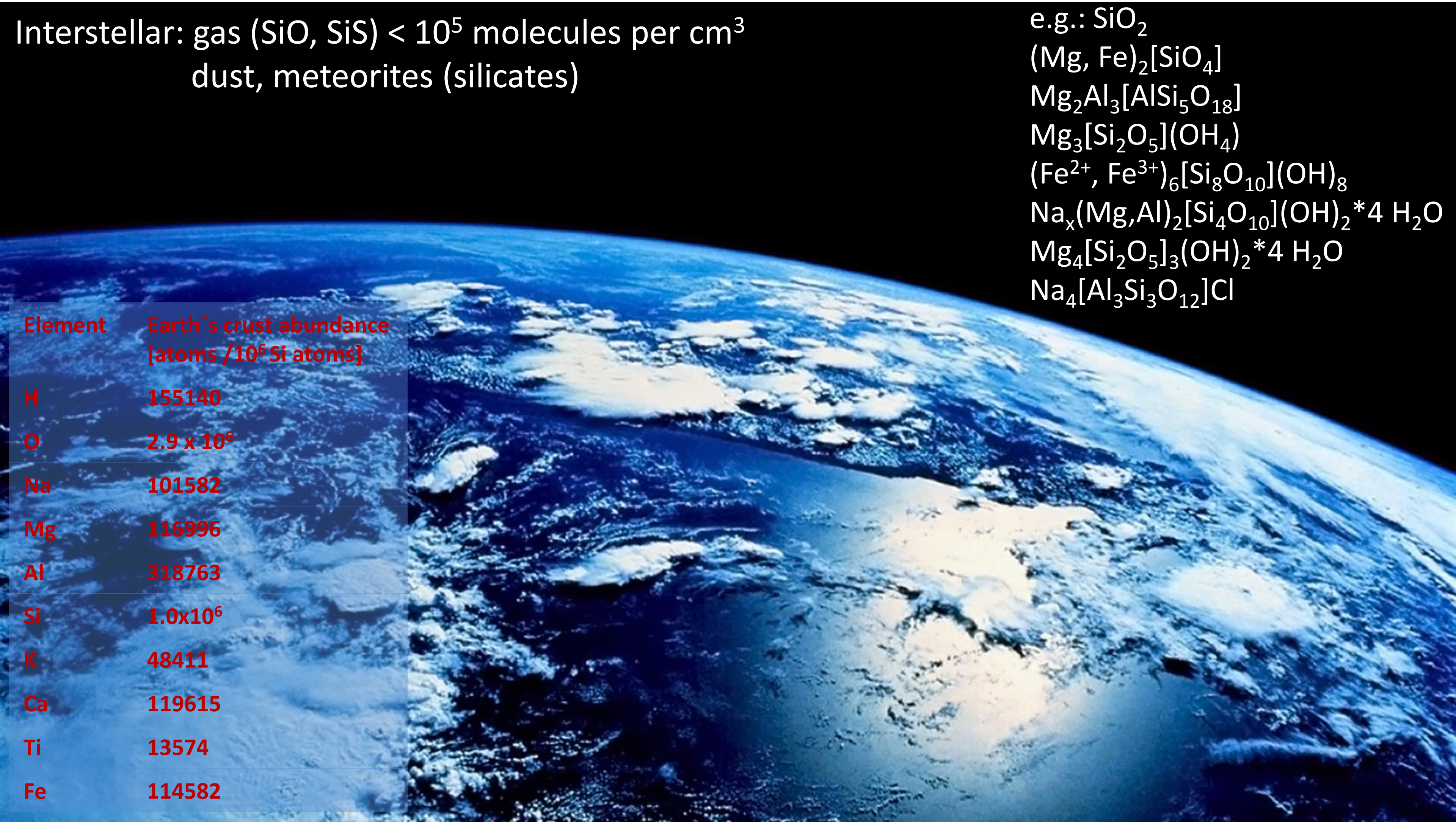
What are silicates?
What is the chemistry behind those compounds?

Si coordinated by oxygen

Neutral: silica (SiO_2)	anionic: silicate	Cationic: (e.g. SiP_2O_7)

Follow the same structural chemical rules
→ Term „silicates“

Occurence of Silicon



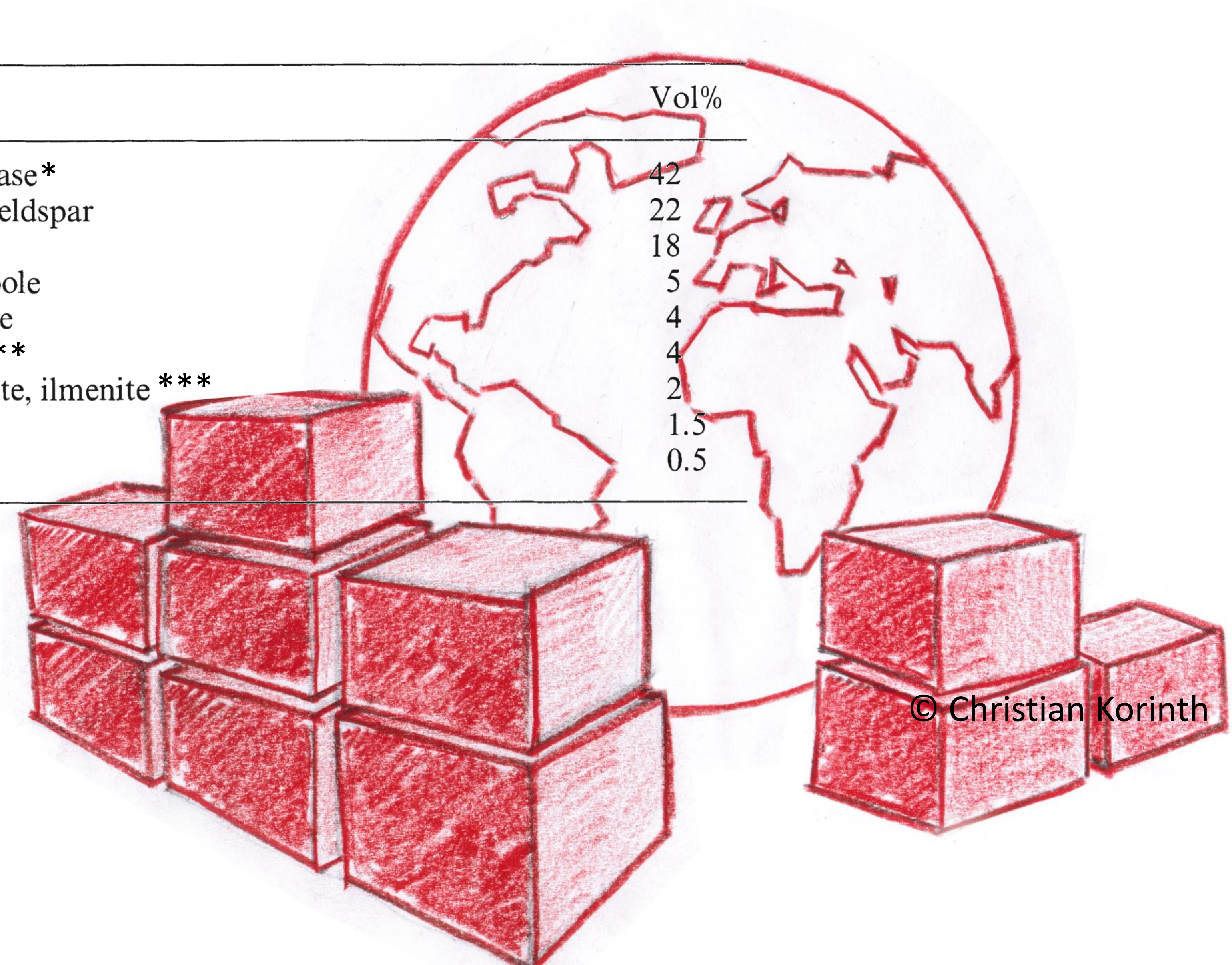
Interstellar: gas (SiO, SiS) < 10^5 molecules per cm^3
dust, meteorites (silicates)

e.g.: SiO_2
$(Mg, Fe)_2[SiO_4]$
$Mg_2Al_3[AlSi_5O_{18}]$
$Mg_3[Si_2O_5](OH_4)$
$(Fe^{2+}, Fe^{3+})_6[Si_8O_{10}](OH)_8$
$Na_x(Mg,Al)_2[Si_4O_{10}](OH)_2*4\ H_2O$
$Mg_4[Si_2O_5]_3(OH)_2*4\ H_2O$
$Na_4[Al_3Si_3O_{12}]Cl$

Element	Earth´s crust abundance [atoms /10^6 Si atoms]
H	155140
O	2.9×10^6
Na	101582
Mg	116996
Al	318763
Si	1.0×10^6
K	48411
Ca	119615
Ti	13574
Fe	114582

Occurence of Minerals

Mineral	Vol%
Plagioclase*	42
Potash feldspar	22
Quartz	18
Amphibole	5
Pyroxene	4
Biotite **	4
Magnetite, ilmenite ***	2
Olivine	1.5
Apatite	0.5



© Christian Korinth

*** $FeTiO_3$

** mica

*Albite/Anorthite solid solution

Properties of Silicates

Mechanical properties (strength, cleavage (layers), soft fibres (asbestos)

Chemical reactivity (swelling, host-guest chemsitry

Optical properties (colors, ultramarine, luminescence)

Magnetism (Granate (ferrimagnetic coupling): YIG)

Electric and dielectric properties

Properties are produced, influenced or modified by the counter-ion

Application of Silicates

Fillers (gas permeability)
Catalysts (Zeolithes)
Ceramics (ceran®, slightly negative coefficient of expansion)
Additive for detergent
Provide raw materials ($Al_2Be_3[Si_6O_{18}]$, Berryl or $Sc_2[Si_2O_7]$, Thortveitite)

Diversity of Silicates

- Larger number of different silicate phases
  → large variability of properties
- 2nd largest number of compunds with other elements
- Is the structural versatility of carbon and silicon a result of the same factors?

→ No!

Table 1.4 Mean bond energies in kJ/mol of several bonds of carbon and silicon (Cottrell 1958)

Bond	C	Si
X–X	346	222
X–O	358	452
X–H	413	318

Same probability

skeleton -C-C-C-C-C- -Si-O-Si-O-Si-

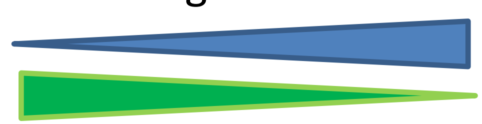
smaller number of compounds

Phosphates,
Sulfates
Chlorates?

Weaker
Metal oxygen
bond

Na-Mg-Al-Si-P-S-Cl

Tendency to link $[AO_n]$ polyhedra
+
Number of compounds

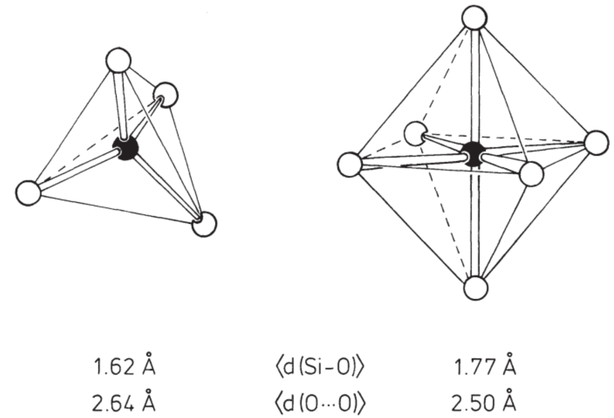


Cationic repulsion in $[AO_n]$ polyhedra

Chemical Bonds in Silicates

Coordination Numbers of Silicon

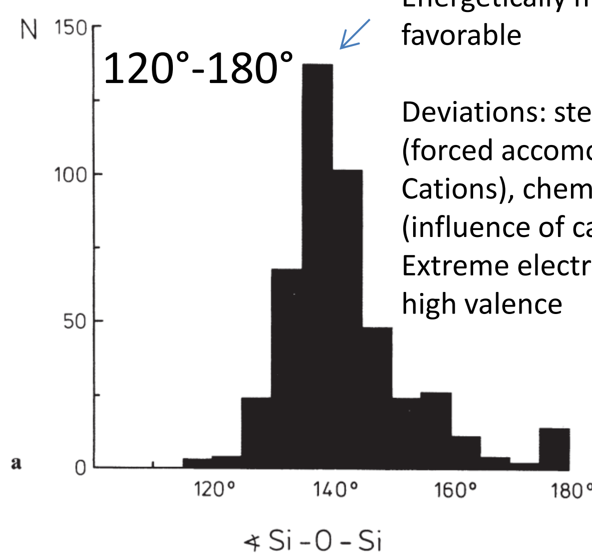
Fig. 3.1. $[SiO_4]$ tetrahedra and $[SiO_6]$ octahedra and their average dimensions



with metal ions

with non-metal ions
High pressure phases
(pressure-distance-paradox)

Si-O-Si Angles (oxygen atoms bridging two Si tetrahedra)



silicate

Energetically most favorable

Deviations: steric effects (forced accomodation of Cations), chemical effects (influence of cation size, Extreme electronegativity, high valence

The Nature of Bonds in Silicates

Si-O bond is partly ionic and partly covalent

15% ionic character according to Pauling $(1-e^{1/4(\chi_A-\chi_B)})$

Si-O bond length

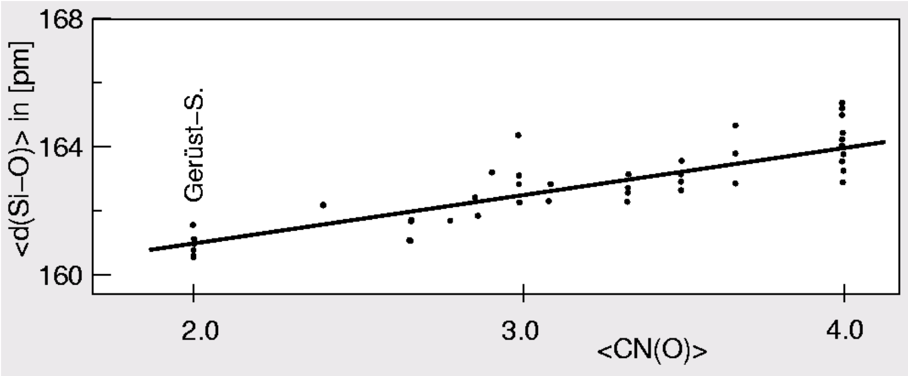
Ionic bond: 176 pm

Covalent bond: 183 pm

Actual bond length: 162 pm (double bond character?)

Partial π- π-bonding between Op and Sip-orbitals

Oxygen coordination number dependency

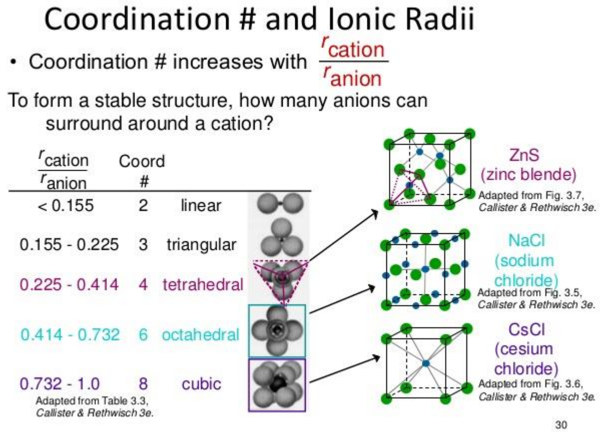


Terminal Si-O bonds are shorter than bridging Si-O-Si bonds

Structural concepts (Pauling rules)

1. *Ratio of ionic radii:*

   Each cation is surrounded by a coordination polyeder. The distance between cation and anion is determined by the sum of the ion radi,
   the coordination number by the ratio of the radii.



2. *Electrostatic sum of valences:*

   The valence of an anion in a stable ionic structure aims to compensate the strength of the electrostatic bonds (S) of the surrounding cations and vice versa.

   e.g. Perowskit $CaTiO_3$

   Ca: Z= +2; CN=12 d.h. Z/CN=1/6
   Ti: Z= +4; CN=6 d.h. Z/CN= 2/3
   *O: coordinated by 2 Ti + 4 Ca cations S(electrostatic bond strength)= 4*1/6+2*2/3=2*

3. *Pauling´s rule: if more cations are presents, the cations with higher charge have the maximum distance from each other. The cation coordination polyeder share the least possible polyeder elements (corner, edge, face)*

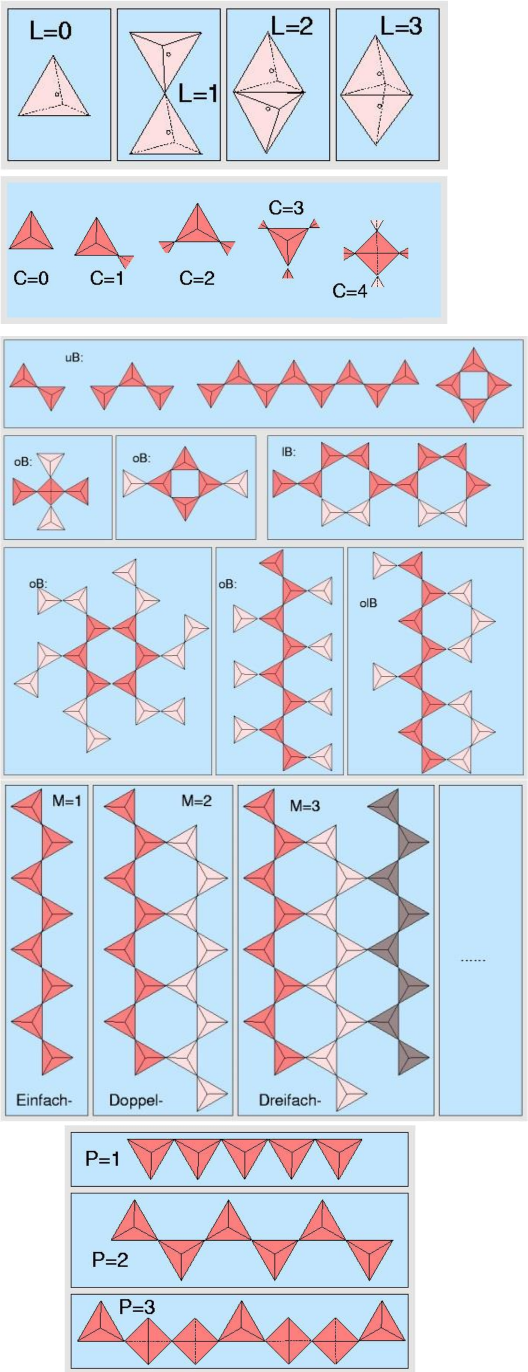
   → *Löwenstein-Rule: two aluminium atoms can not be inserted in neighboring tetrahedra (ordering)*

   → *e.g. Silicates do not share faces and edges of adjacent tetrahedra (either isolated or shared corners)*

4. *Rule of economy*

   The least possible number of coordination polyhedra are realized

Crystal Chemical Classification of Silicate Anions



1. CN = Coordination Number mostly CN=4 !

2. L = Linkedness: Number of oxygen atoms shared between two [SiOn] polyhedra (isolated, corner-, edge-, face-shared polyhedra

- **L=0** isolated
- **L=1** corner-shared

3. C = Connectedness (s): Number of other linked [SiO_n] polyhedra (Symbol: Q^s)

- **C=0** Q^0: isolated polyhedron (singular)
- **C=1** Q^1 (primary): one polyedron is connected to another polyyedron (e.g. disilicates).
- **C=2** Q^2 (secundary): one polyedron is connected to two polyedra (e.g. silicates with chain- or ring strucure).
- **C=3** Q^3 (tertiary) (e.g. in layered silicates).
- **C=4** Q^4 (quaternary): (e.g. L=1 and CN=4 → SiO_2 polymorph)s.

4. B = Branchedness (br):

- *uB = unbranched, simple chains or rings*
- *br = branched,*

  to be distinguished:
  oB = open branched
  lB = loop-branched
  olB = mixed
  hB = Hybrid-type

5. D = Dimensionality of silicate anions: (extension to infinity in 1,2 or 3 dimensions)

- *D=0* isolated anions

  t: terminated polyeder
  r: ring

- *D=1* chains
- *D=2* layers
- *D=3* frameworks

6. M = Multiplicity

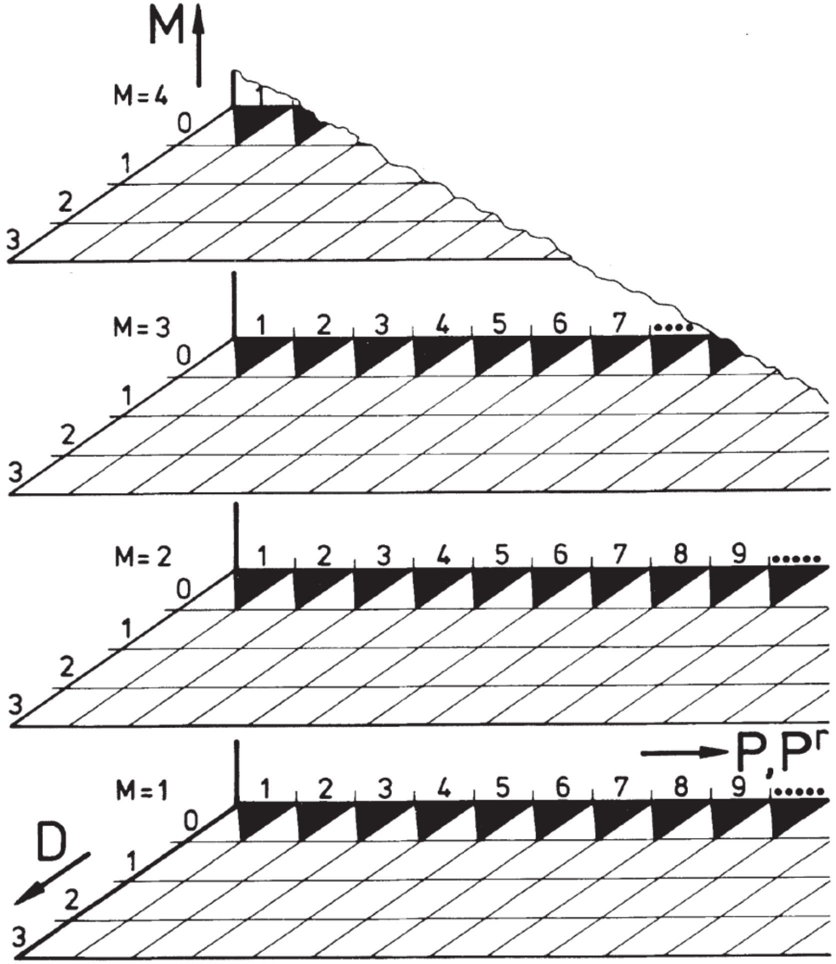
Connecting limited number M of [SiOn] polyedra, chains, rings, layers that lead to the formation of multiple anions of the same dimensionality (e.g. double chain, triple chain).

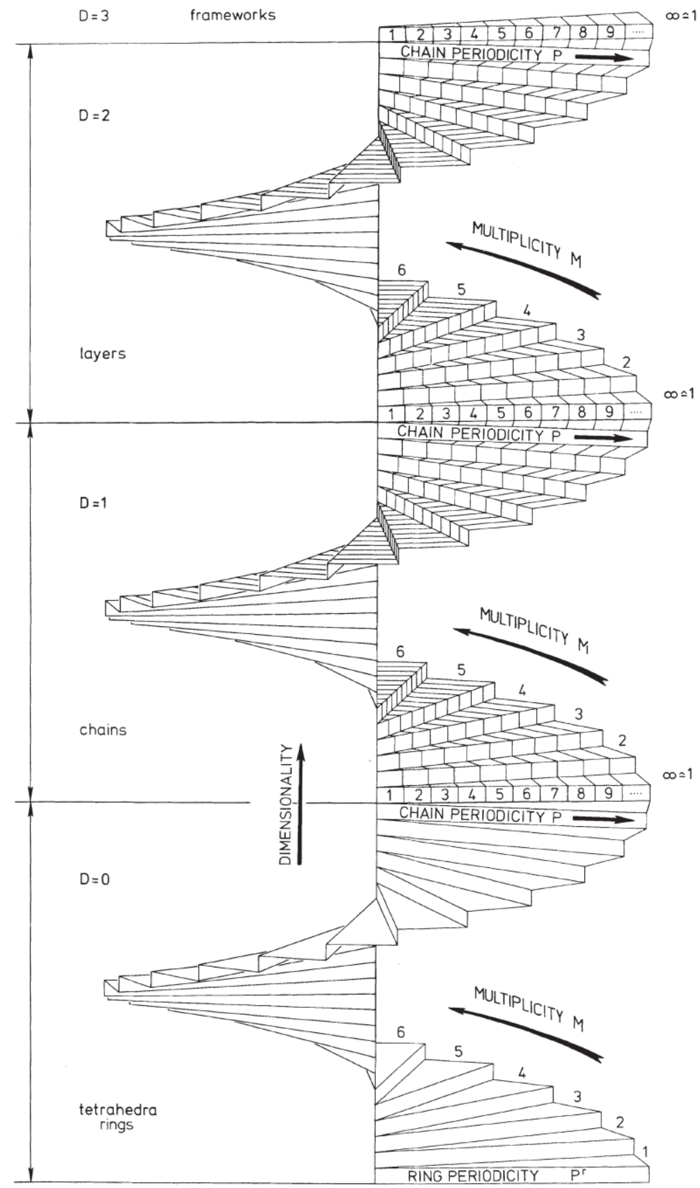
7. P = Periodicity Number of tetrahedra, rings or layers after which the structural motif repeats Einer- (P=1), Zweier- (P=2), Dreier- (P=3), etc.

Crystal Chemical Classification of Silicate Anions

3D representation of the subdivision of silicate anions

Cell → familiy of silicates





Crystal chemical systematic of silicates

Parameter squence

Class	CN	4
Subclass	L	L=0 (isolated) or L=1 (corner shared)
Branches	B	ub, ob, lb, hb
order	M	Repetitive unit
group	D	dimensionality
supgroup	r or t	Ring or terminated
family	P	periodicity

Nomenclature
Nomenclature –Chemical-

$\chi_{M1} < \chi_{Si}\ (1.74) < \chi_{M2}$

SiO_2 is acidic + anionic
Vast majority of
Compounds

Salts of silicic acid

Si in octahedral
coordination
$ZnSiO_3 (\chi_{Zn}=1.66)$

SiO_2 is basic + cationic
$Si[P_2O_7]$ $(\chi_P=2.06)$

Silicon salts of the
Corresponding acid

$(\chi_P=2.06)$

Multiplicity / Dimensionality	1	2	3	4	. . .
0 Oligo- silicates	Mono- silicates	Disilicates	Trisilicates	Tetra- silicates	. . .
0 Cyclo- silicates	Monocyclo- silicates	Dicyclo- silicates	Tricyclo- silicates	Tetracyclo- silicates	. . .
1 Poly- silicates	Monopoly- silicates	Dipoly- silicates	Tripoly- silicates	Tetrapoly- silicates	. . .
2 Phyllo- silicates	Monophyllo- silicates	Diphyllo- silicates	Triphyllo- silicates	Tetraphyllo- silicates	. . .
3 Tecto- silicates	Tecto- silicates				

Nomenclature –Mineralogist-

by morphology, color (olivine = olive green), changes due to heating or chemical composition (Sodalite: sodium-rich silicate), place (Vesuviante) or person (Gmelinite)of discovery:

actinolite→ aktis (gr. Ray) and lithos (gr. Stone) often found as prismatic crystals in radiating groups (German: Strahlstein).
chrysotile → fibrous crystals with silky, yellow-brownish luster (chrysos, gr. gold)

Intuitive group names

Multiplicity / Dimensionality	1 (island)		2	3	4	. . .
0	Nesosubsilicates	Nesosilicates	Sorosilicates (group)			
0	Cyclosilicates (ring)					
1	Inosilicates (fiber)					
2	Phyllosilicates (layer)					
3	Tectosilicates (framework)					

Structural Formulae

Complex anions are written in „[]“
Coordnation numbers are in „[]“

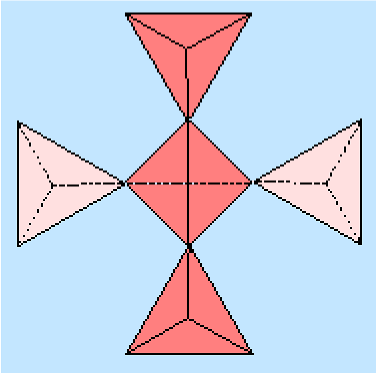
$K_2Si^{[6]}[Si_3{}^{[4]}O_9]$: ¼ of Si six fold coordination
¾ of Si tetrahedral coordination
(cyclic anion)

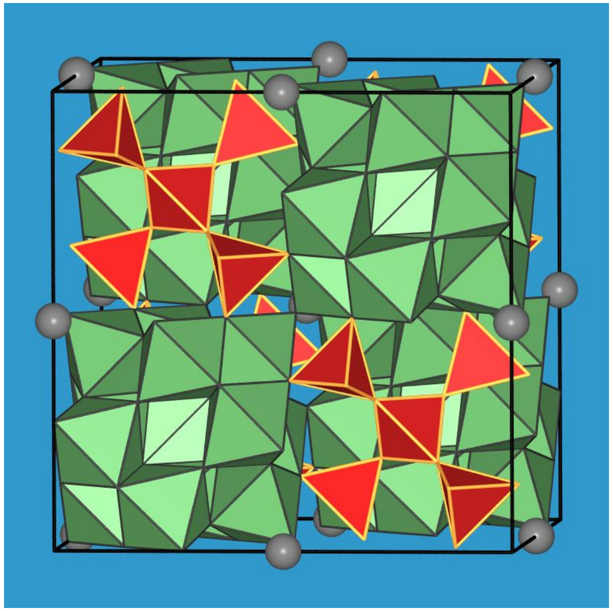
Suffixes may occur (lT), (mT), (hT), (lP), (mP), (hP)

Degree of condensation is written in „{}“ : $M_r\{B, M^D{}_\infty\}[Si_xO_y]$

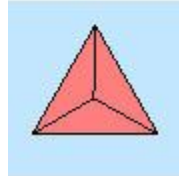
e.g. Zunyite:

$Al^{[6]}{}_{12}Al^{[4]}\{oB, 3t\}[Si_5O_{16}](OH,F)_{18}O_4Cl$

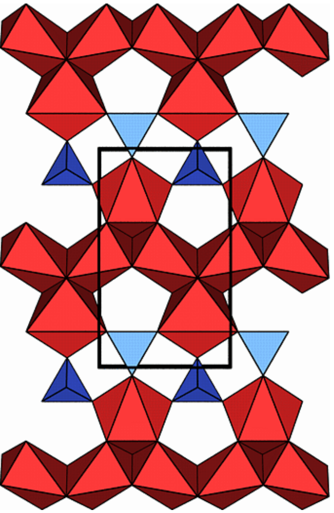




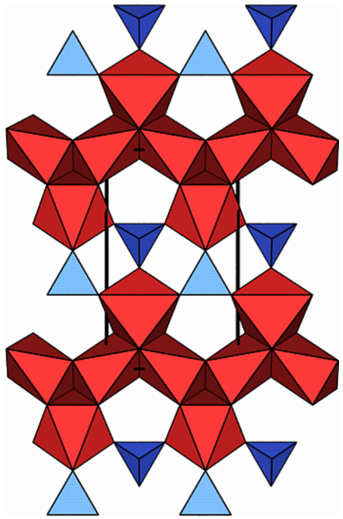
5.1 ortho (Neso)-Silicate:



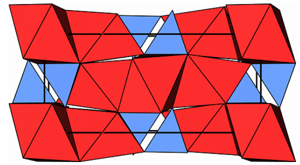
isolated $[SiO_4]^{4-}$–Tetrahedra



A



B



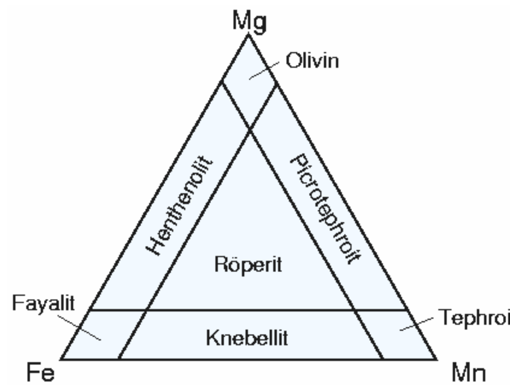
Olivine $Mg_2[SiO_4]$:

hcp of oxygen anions (ABAB stacking)

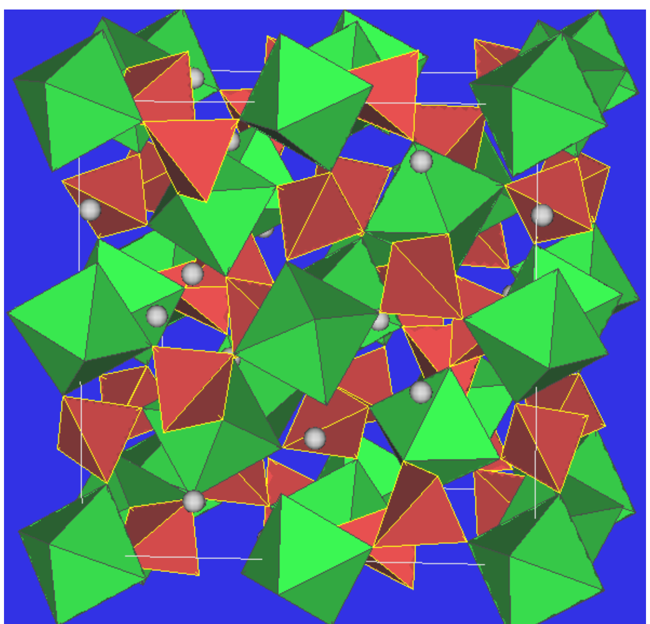
Si in $^1/_8$ tetrahedra

Mg in $^1/_2$ Octahedra

$\Rightarrow$ No common faces in the crystal structure



solid soultions



Granate: $A_3^{2+}B_2^{3+}[SiO_4]_3$

A = Ca, Mg, Fe, Mn: distorted cubic (CN=8)

B = Al, Fe, Cr: octahedra (CN=6)

Corner shared octahedra and tetrahedra

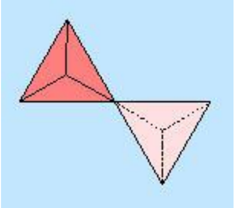
Yttrium-Iron-Granate (YIG; $Y_3^{III}Fe_2\ [Fe^{III}O_4]_3$) ferrimagnetic coupling of tetraedron- and octaedron position

Frequency multiplyer in microwave applications

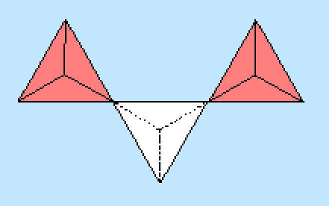
Yttrium-Aluminium-Granate (YAG; $Y_3^{III}Al_2[AlO_4]_3$) Laser material for weld or medical applications.

+ Ln (e.g.Nd) on Y-positions → IR long-wave Nd-YAG laser

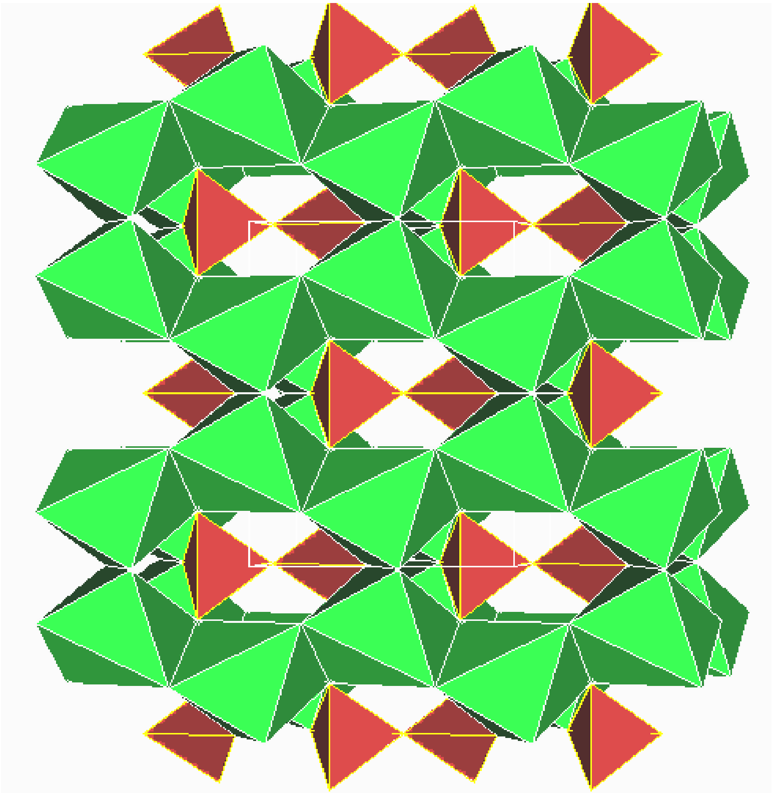
5.2 Group(Soro)-Silicate:

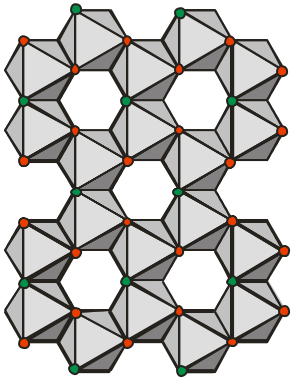


$[Si_2O_7]^{6-}$



$[Si_3O_{10}]^{8-}$





BiI_3 (hcp)
gibbsitisch ($Al(OH)_3$)

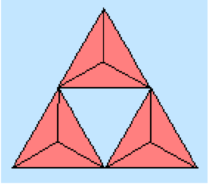
Thortveitite $Sc_2[Si_2O_7] \equiv (ScO_3)_2Si_2O$

$\Rightarrow$ BiI_3–analogue edge-shared octahedra layers connected by isolated disilicats–anions

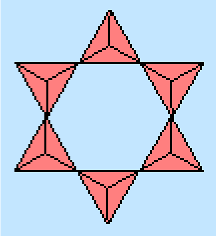
Natural: Sc substituted by Ln

$\Rightarrow$ Important material for rare-earth materials

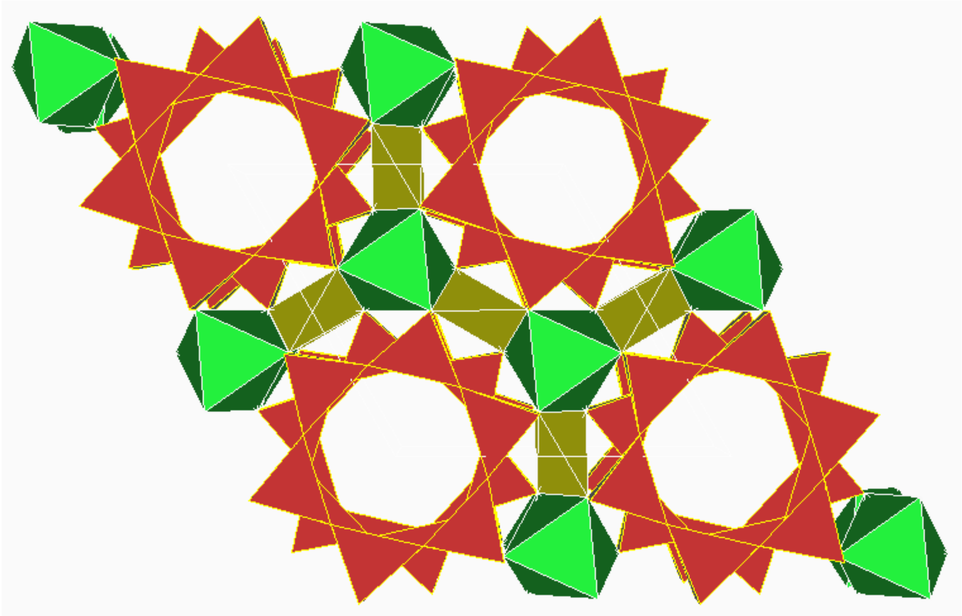
5.4 Ring(Cyclo)-Silicate:



$[SiO_3]_3^{6-}$



$[SiO_3]_6^{12-}$



Beryll $Al_2Be_3[Si_6O_{18}]$

Most important mineral for Be

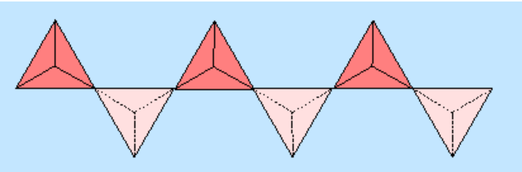
Gem-stone varieties:

•Emerald: strong green partial substitution of Al by Cr

•Aquamarin: pale blau (mixed valent Fe^{2+}/Fe^{3+})

5.5 Fibrous(Ino)-Silicate:

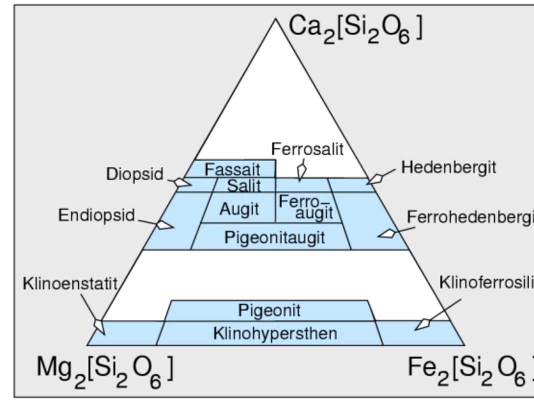
5.5.1 Chain-Silicate:

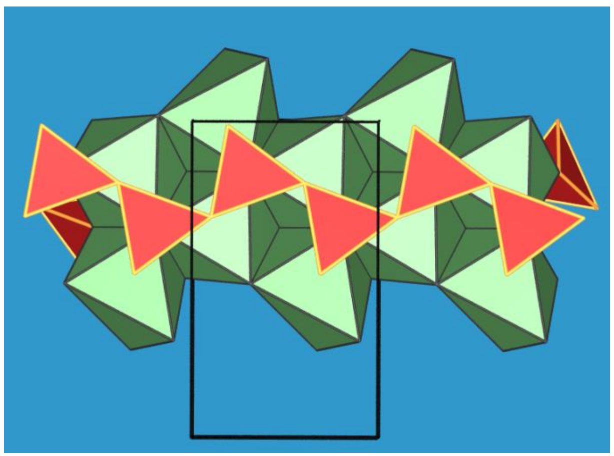


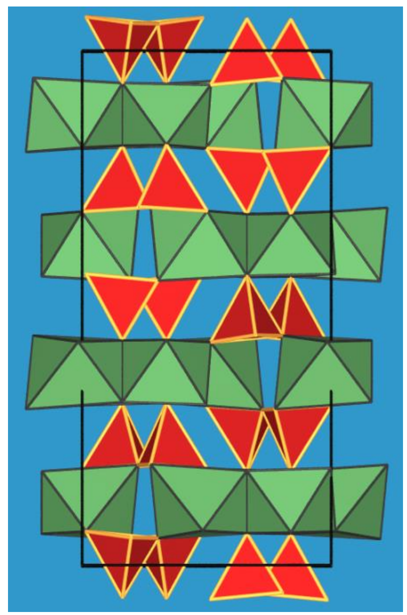
$$^{1}_{\infty}[SiO_2O_{2/2}]^{2-} \Rightarrow {}^{1}_{\infty}[SiO_3]^{2-}$$

$\{uB,1^1{}_{\infty}\}[SiO_2O_{2/2}]^{2-}$

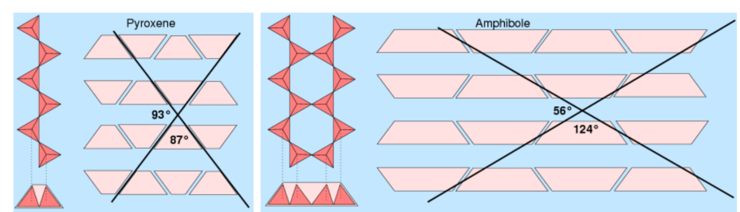
Zweier single chains:
Identity after two tetraeda (approx. 520 pm)
Very common for natural silicates







Cleavage properites



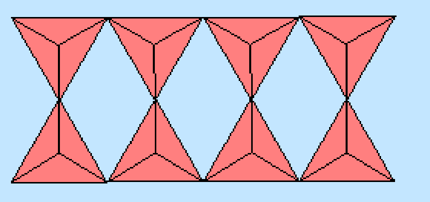
Pyroxene: $AB[Si_2O_6]$

A = Ca, Na etc.
B = Mg, Fe, Al etc.
A=B=Ca ≡ Pyroxen
crystallographic: Ortho-Pyroxene (orthorhombisch) z.B. Enstatit (A=B=Mg)
Klino-Pyroxene (monoklin) z.B. Diopsid (Ca/Mg)

5.5 Fibrous(Ino)-Silicate:

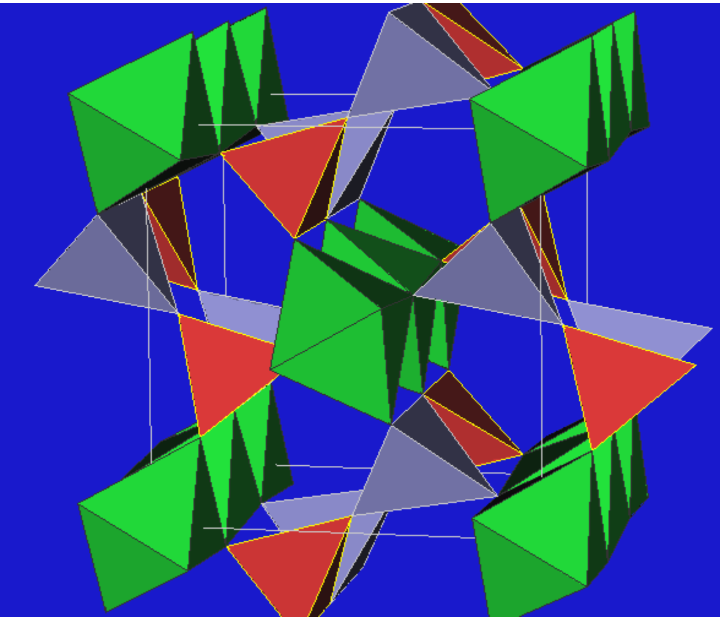
5.5.2 Band-Silicate:

Einer double chains



$$ {}^{1}_{\infty}[Si_2O_2O_1O_{4/2}]^{2-} $$

$$ \Rightarrow {}^{1}_{\infty}[Si_2O_5]^{2-} $$

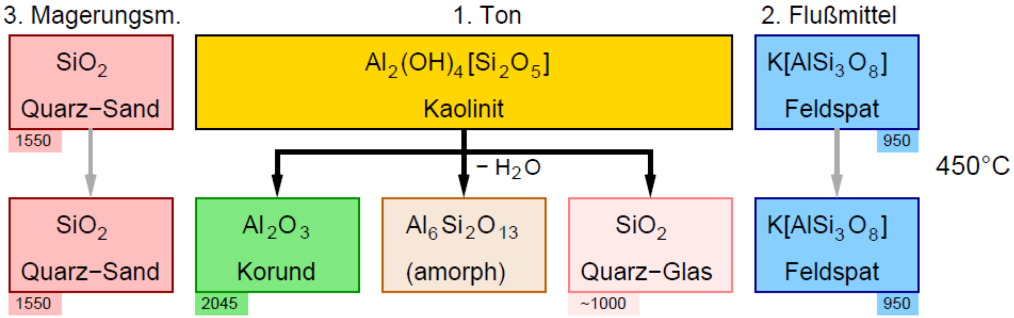


Sillimanite: $Al^{[6]}[(AlSi)^{[4]}O_5]$

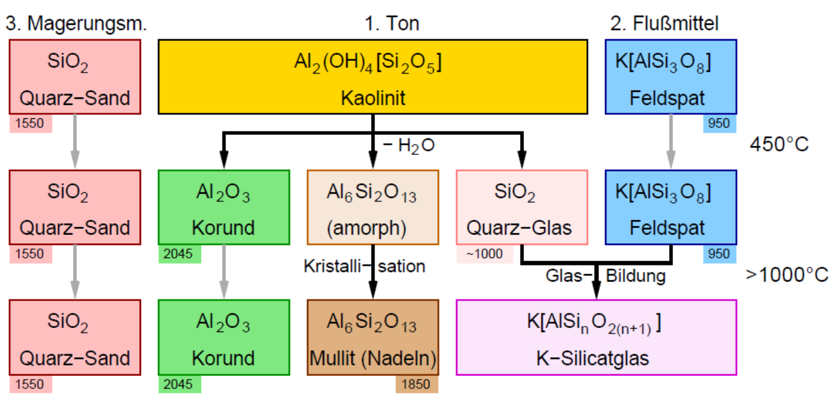
Mullite: $Al_2^{[6]}[(Al_{2+2x}Si_{2-2x})O_{10-x}]$

⇒Porzellan $\text{mit } x = 0.25 : 3Al_2O_3 \bullet 2SiO_2$

bis ca. 450°C

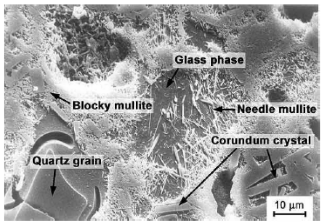


- ca. 20% Volumenverlust (Schrumpfung)
- $Al_2(OH)_4[Si_2O_5] \xrightarrow[-H_2O]{450^\circ C} \underbrace{Al_2O_3}_{\text{Korund,kris.}} + \underbrace{3Al_2O_3 \cdot 2SiO_2}_{\text{Mullit,amorph}} + \underbrace{SiO_2}_{\text{Glas,amorph}}$
- Mullit ($Al_6Si_2O_{13} = 3\ Al_2O_3 + 2\ SiO_2$) als amorphe Phase



ab ca. 1000°C

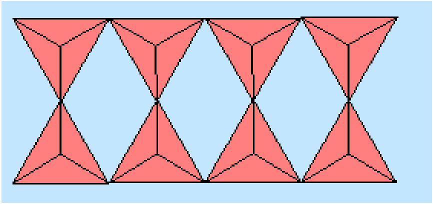
- Feldspatverflüssigung: Feldspat (Flußmittel) löst alle amorphen Anteile (SiO_2-Glas + 'Mullit')
- Mullit kristallisiert Nadel-förmig (verfilzte Nadeln)
- K-Alumiosilicat-Gläser 'verkitten' die Kristallite



5.5 Fibrous(Ino)-Silicate:

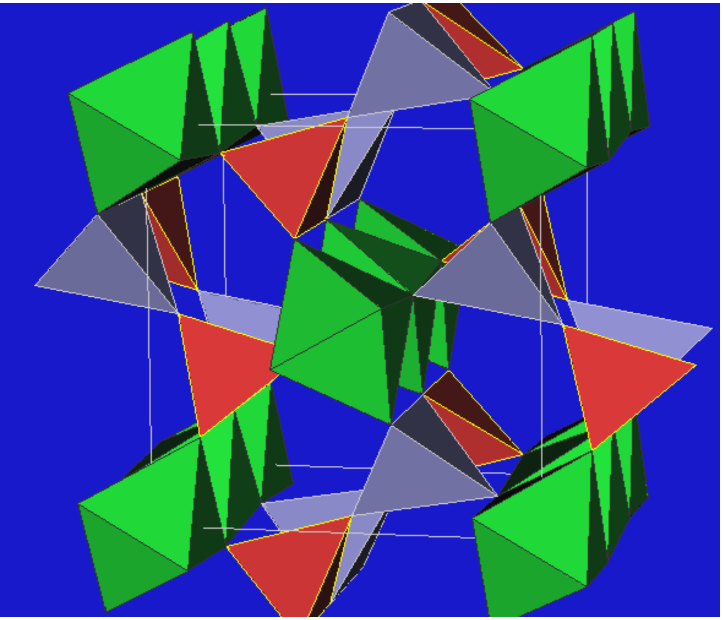
5.5.2 Band-Silicate:

Einer double chains



$$ {}^{1}_{\infty}[Si_2O_2O_1O_{4/2}]^{2-} $$

$$ \Rightarrow {}^{1}_{\infty}[Si_2O_5]^{2-} $$



Rare case for silicates, but technological importance

Sillimanit: $Al^{[6]}[(AlSi)^{[4]}O_5]$

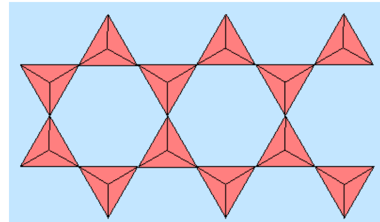
Mullit: $Al_2^{[6]}[(Al_{2+2x}Si_{2-2x})O_{10-x}]$

⇒Porzellan $\text{mit } x = 0.25 : 3Al_2O_3 \bullet 2SiO_2$

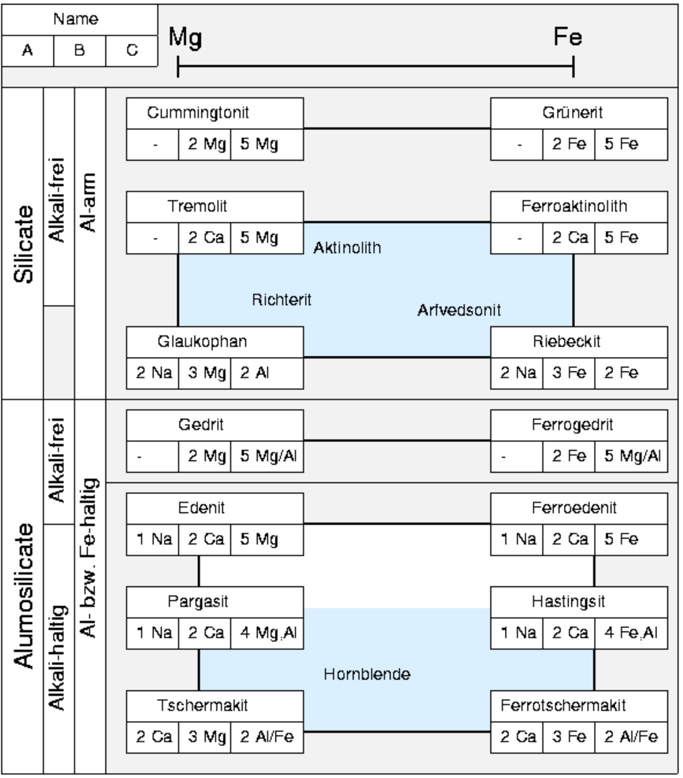
5.5 Fibrous(Ino)-Silicate:

5.5.2 Band-Silicate:

Zweier double chains

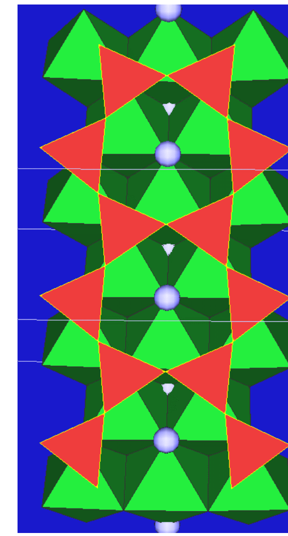


$$^{1}_{\infty}[SiO_1O_{3/2}SiO_2O_{2/2}]^{3-} \xrightarrow{\times 2} {}^{1}_{\infty}[Si_4O_{11}]^{6-}$$



$A_{0\text{-}3}B_{2\text{-}0}C_{4\text{-}5}[Si_8O_{22}](OH/F)_2$:

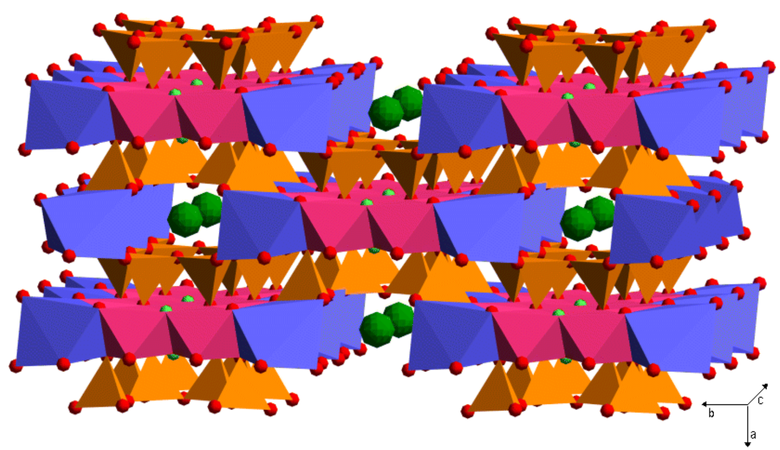
- A: Ca oder Na
- B: Ca, Mg, Fe^{2+}
- C: Mg, Al, $Fe^{3+/2+}$
- Si ist oft partiell durch Al ersetzt

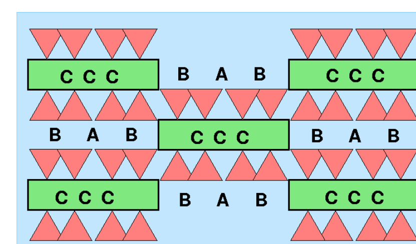


Beispiele: Tremolite: $Ca_2Mg_5[Si_8O_{22}](OH)_2$
Fluororichterite: $Na_2Ca(Mg,Fe)_5[Si_8O_{22}(F)_2]$
Grunerite: $Fe^{2+}_2\ Fe^{2+}_5\ [Si_8O_{22}(OH)_2]$

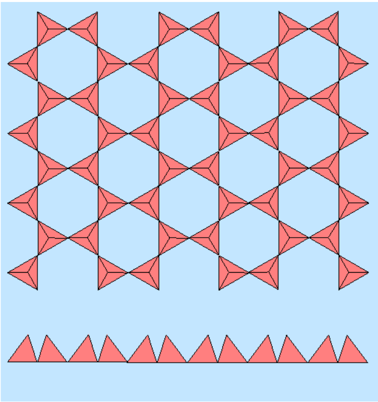
fibrous amphiboles = asbestos of amphibole

Nomenclature: difficult



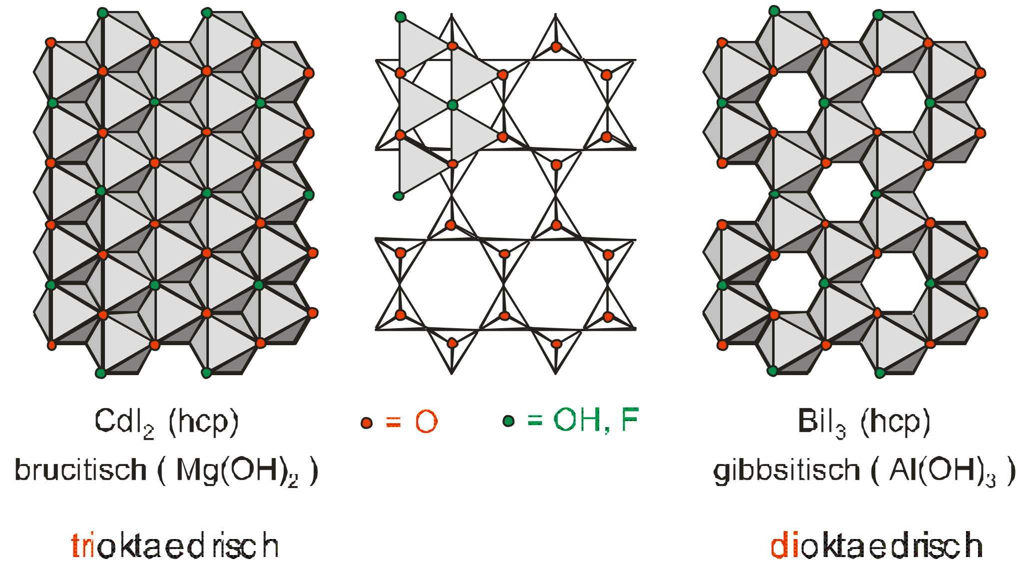


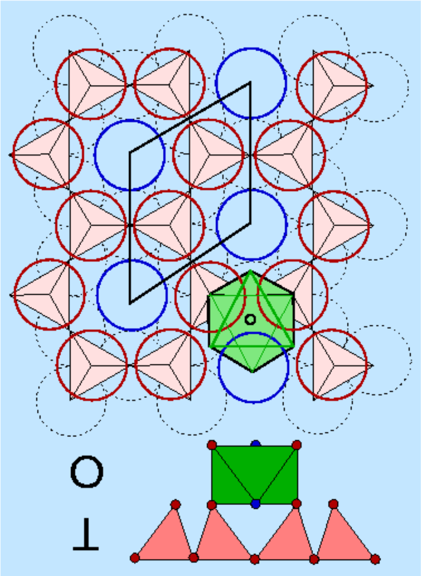
5.6 Layer(Phyllo)-Silicate:



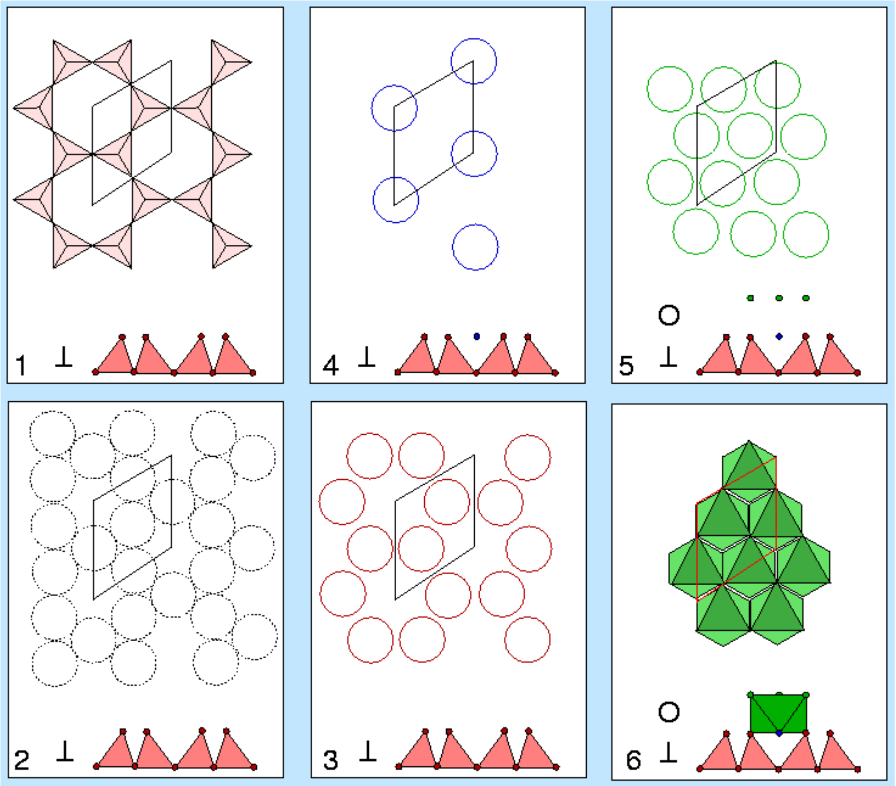
$$^2_\infty[SiO_1O_{3/2}]^{1-}$$

$$\xrightarrow{\times 2} {}^2_\infty[Si_2O_5]^{2-}$$

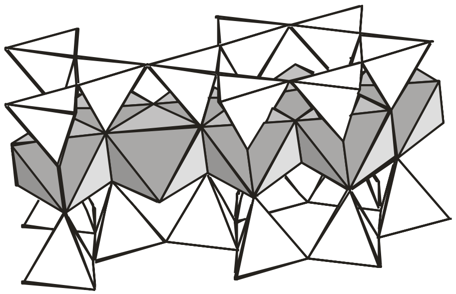




Green B-layer



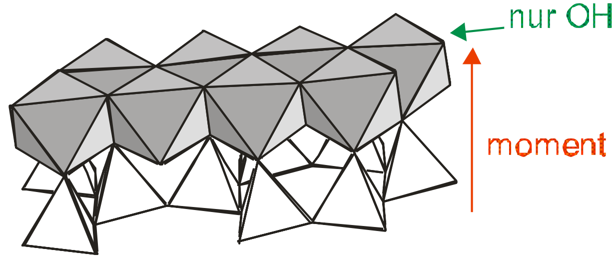
Dreischichttonminerale



Pyrophyllit: Al_2 _ $Si_4O_{10}(OH)_2$

Talk: $Mg_3 Si_4O_{10}(OH)_2$

Zweischichttonminerale



Kaolinit: Al_2 _ $Si_2O_5(OH)_4$

Chrysotil: $Mg_3 Si_2O_5(OH)_4$

Serpentine

Interlayer charges:

0 → talk, pyrophyllite
>0 → mica-like layered silicates
Montmorillonitic type (Al→ Mg)
Beidellitic type (Al→Si); charge
Balance → cations (hydrated)
$(Al_{2-y}Mg_y)[Si_{4-x}Al_xO_{20}(OH)_2]^{(x+y)-}$

Hardness increases and cleavage decreases with interlayer charge

Silicates with x+y between 0.2 – 1.2 are
Swellable by cations
<0.2: too less cations are available for swelling
>1.2: layer charge is too high for swelling

x+y	Family 2:1	
0-0.25	Hectorite TO	
0.25-0.55	Smectite: (frequent 0.33)	Montmorillonite (DO, $T=Si_4$)
		Beidellite DO
0.55-0.70	Vermiculite (TO, also DO; häufig: 0.66)	
0.70-1.20	Mica (Muskovite DO, Biotite TO)	
	x+y=0.70-0.90	Illite (DO)
	x+y=0.90-1.2	Serizite
2	Calcium mica	Margarite (DO) $CaAl_2[Al_2Si_2]$
		Xanthophyllite $CaMg_3[Al_2Si_2]$

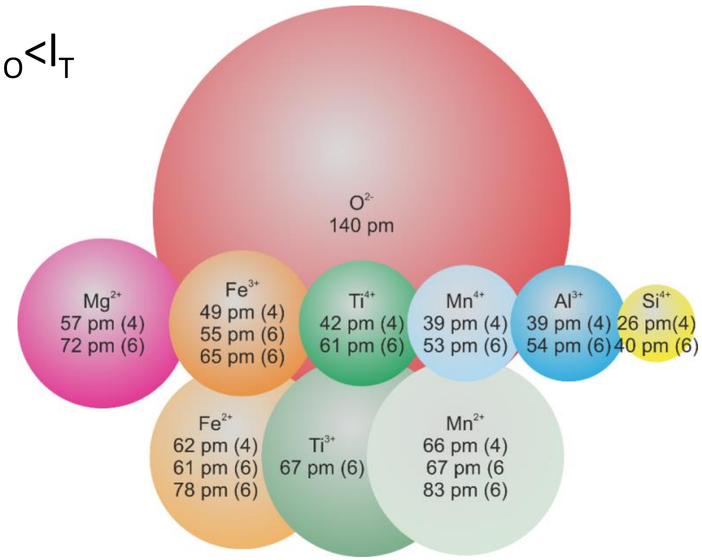
double layer clays:

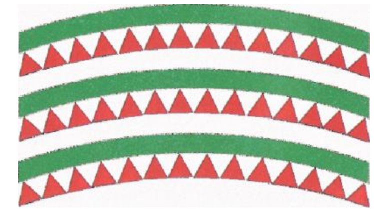
Crystotilasbest (Weißasbest)

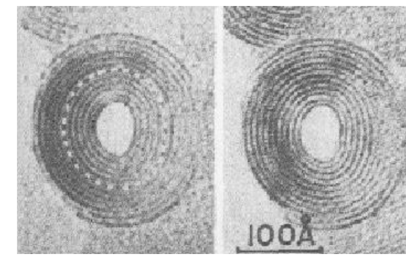
Mismatch error between TL and OL → strain in the double layer

Large cation/Small cations in octahedra layer vs. Tetrahedra layer

$l_O > l_T$ $l_O < l_T$



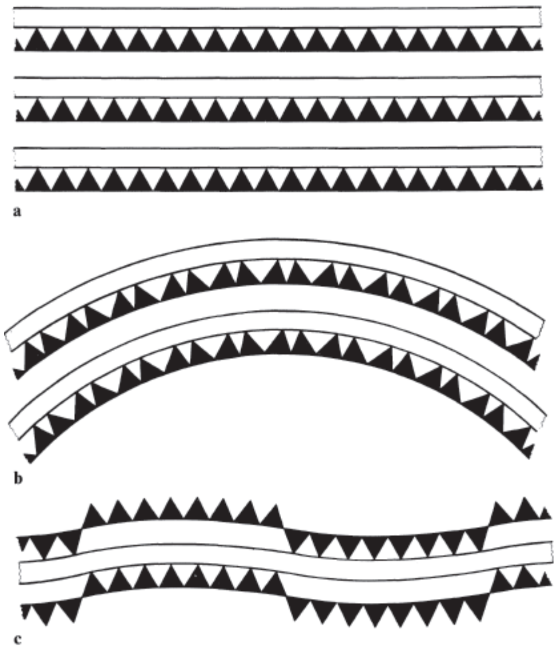




Strain relaxation:

rolling (e.g. Halloysite (Al^{3+} in OL, TL outside), Serpentin (Mg^{2+} in OL, OL outside)
layer distortion: in TL or displacement of the layers
adaption of the OL via combination of cations, i.e. intermixing of large and small cations
corrugation in the TL: reversion of the TL layer → corrugated surfaces

double layer clays:



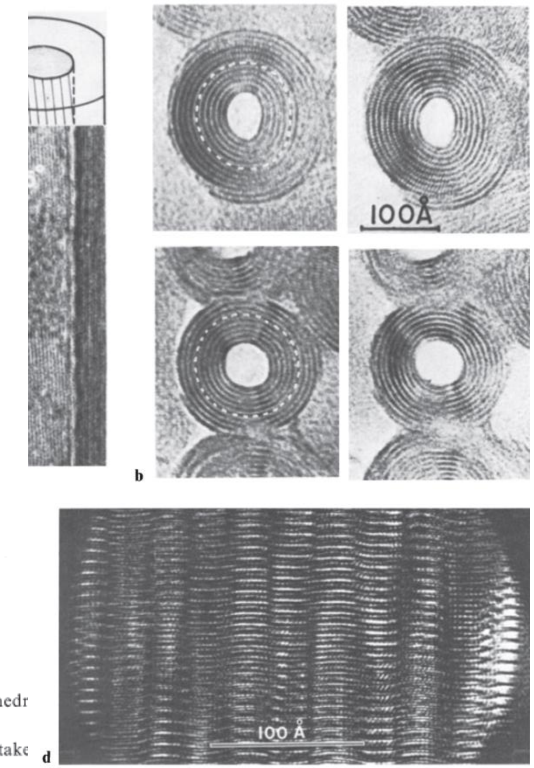


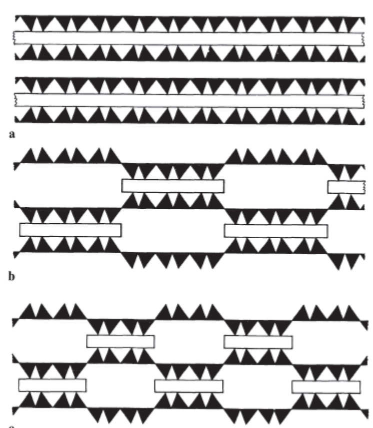
Fig. 10.25 a – c. Reduction of strain between octahedral layers (*white bars*) and tetrahedr (*black triangles*) in hydrous phyllosilicates with kaolinite-like arrangements.

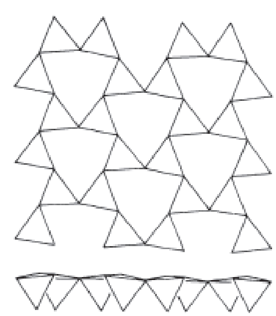
a Kaolinite $Al_2[Si_2O_5](OH)_4$ (Zvyagin 1960); **b** chrysotile $Mg_3[Si_2O_5](OH)_4$ (Whittake **c** antigorite $Mg_{48}[Si_4O_{10}]_{8.5}(OH)_{62}$ (Kunze 1959; Evans et al. 1976)

triple layer clays:

Fig. 10.23 a – c. Reduction of strain between octahedral layers (*white bars*) and tetrahedral layers (*black triangles*) in hydrous magnesium phyllosilicates with mica-like arrangements.

a Talc, $Mg_3[Si_2O_5]_2(OH)_2$ (Perdikatsis and Burzlaff 1981); **b** sepiolite, $Mg_4[Si_2O_5]_3(OH)_2 \cdot 4H_2O$ (Brauner and Preisinger 1956); **c** palygorskite, $Mg_5[Si_2O_5]_4(OH)_2 \cdot 8H_2O$ (Bradley 1940)

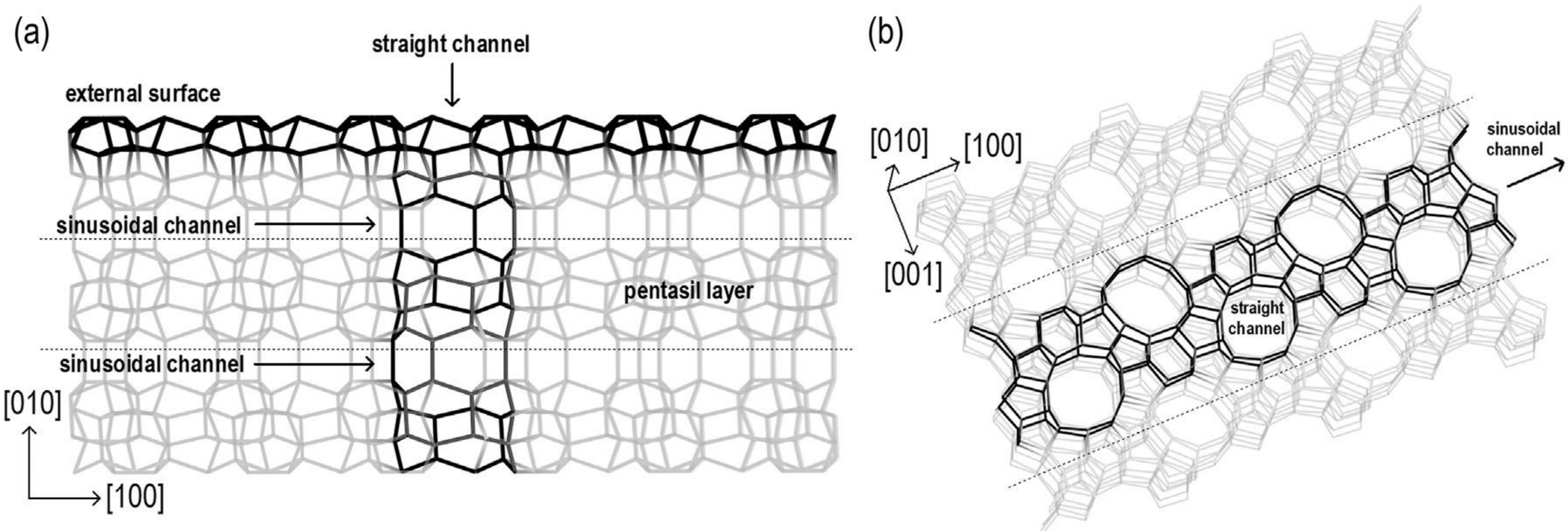




TL corrugation

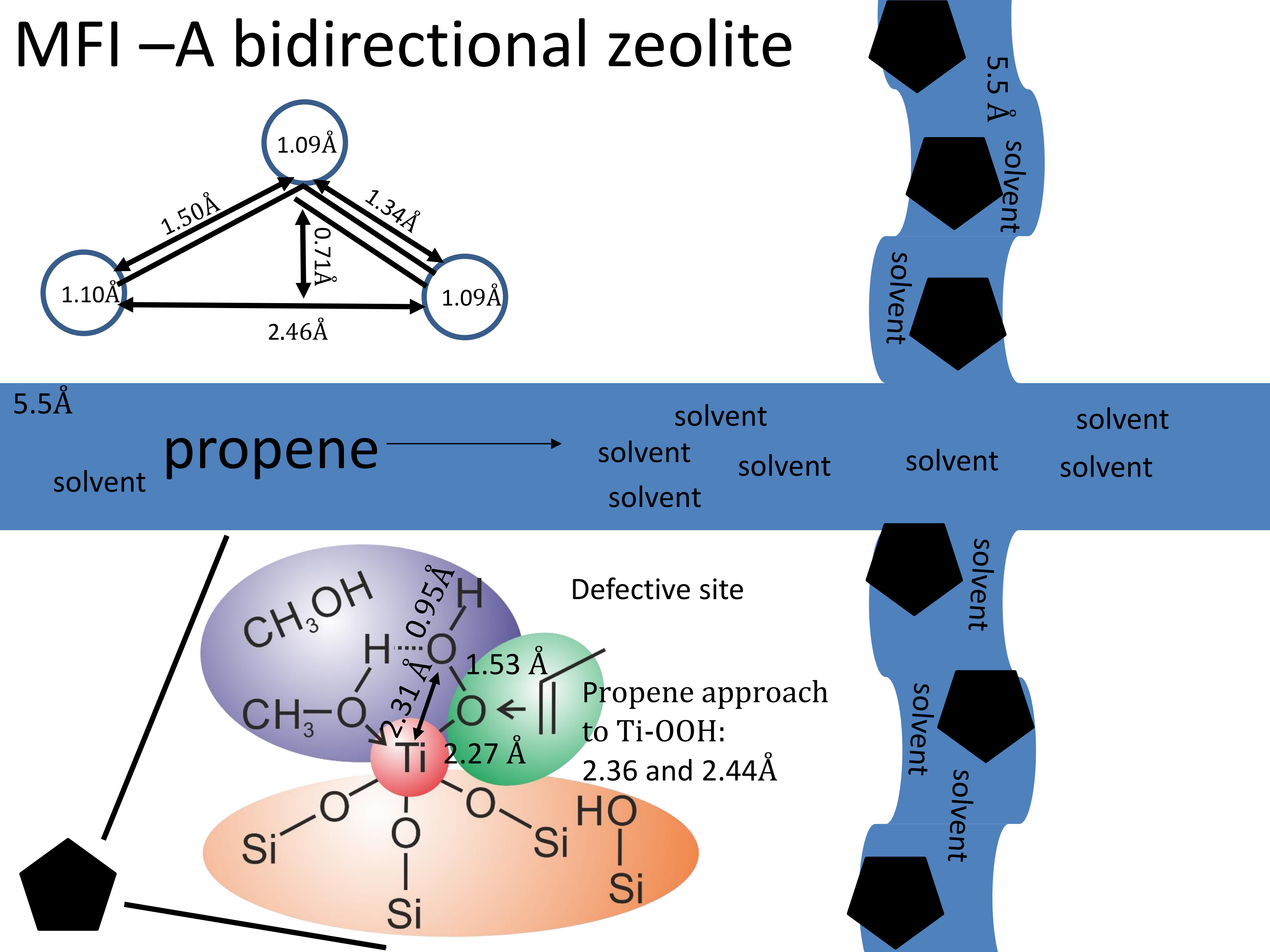
Fig. 10.22. Slight corrugation of the plane of the bridging oxygen atoms in dioctahedral margarite, $CaAl_2[AlSiO_5]_2(OH)_2$ (Takéuchi 1965)

MFI –A bidirectional zeolite



Hernandez-Tamargo, C.E. et al., *Journal of Solid State Chemistry* **2016**, *237*, 192-203

MFI –A bidirectional zeolite



5.7 (Tecto)-Silicate:

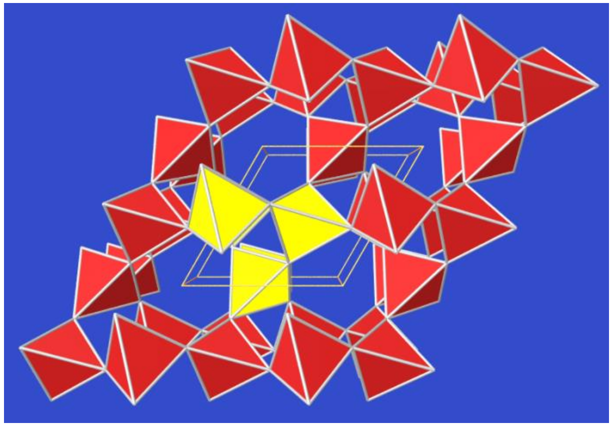
5.7.1 Pyknolite: small voids, small windows

5.7.1.1 ‚filled' modifications of SiO_2–polymorphs:

Filled Quartz: **Eukryptite Li [$AlSiO_4$]**

•Weakly negative coefficient of expansion

•Ceran©



Ternate spirals, 3D-networks
Distorted hexagonal cavities

5.7.1.2 Feldspar:

•65 Vol.-% of the earth crust

•Al:Si-ratio > 1:3 ⇒ Al–rich Aluminosilicate

•Often ordered Si/Al-distribution due to the Löwenstein-Rule

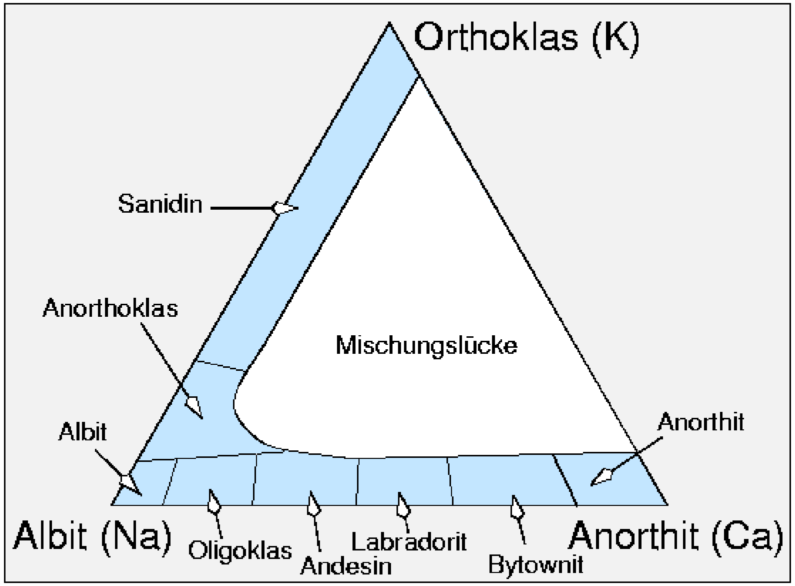
•**Alkaline feldspar**: M[$AlSi_3O_8$] with M=Na, K, Rb, Cs

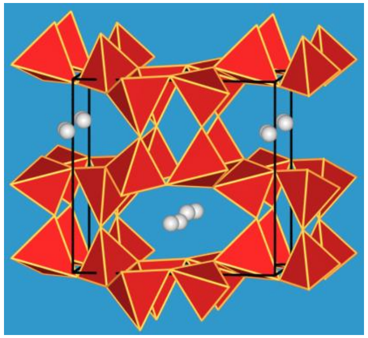
- •Na[$AlSi_3O_8$] (Sodium feldspar, **Albite**)
- •K[$AlSi_3O_8$] (Potassium feldspar, **Orthoklas**)

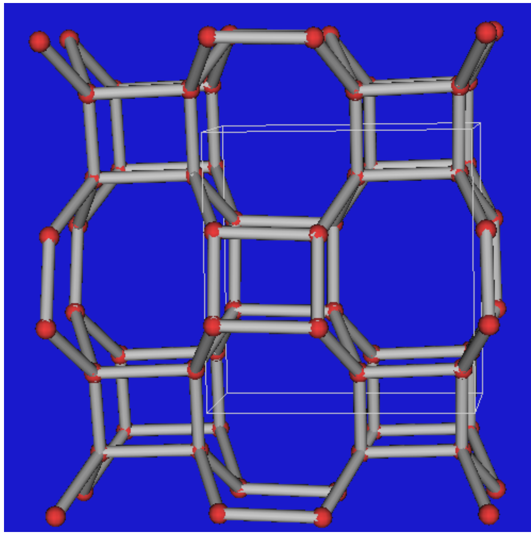
•**Earthalkaline feldspar** M[$Al_2Si_2O_8$] with M=Ca, Sr, Ba

- •Ca[$Al_2Si_2O_8$] (Calciumfeldspar Anorthit)

Solid solution Na[$AlSi_3O_8$] / Ca[$Al_2Si_2O_8$] ⇒ **Plagioklase**







crystall structure:

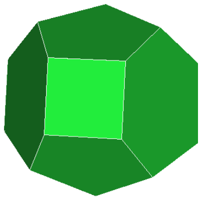
•four-, six-, and eight-membered rings

•or: condensed layer of two adjacent same orientated tetrahedra

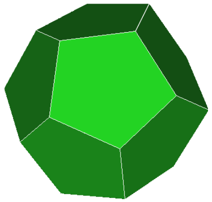
•max. Cation coordination: 9 O^{2-}

5.7.2 Clathrasile: large voids, small windows

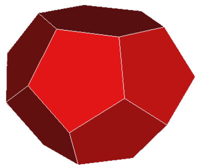
5.7.2.1 neutral framework/neutral guests Gäste:



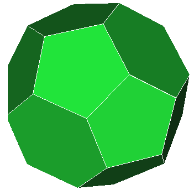
D´
$[4^3 5^6 6^3]$
d = 5.4 Å



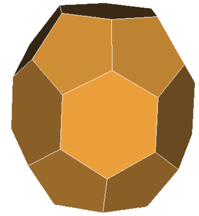
D
$[5^{12}]$
d = 5.2 Å



T
$[5^{12} 6^2]$
d_1 = 5.3 Å
d_2 = 6.4 Å



H
$[5^{12} 6^4]$
d = 6.8 Å

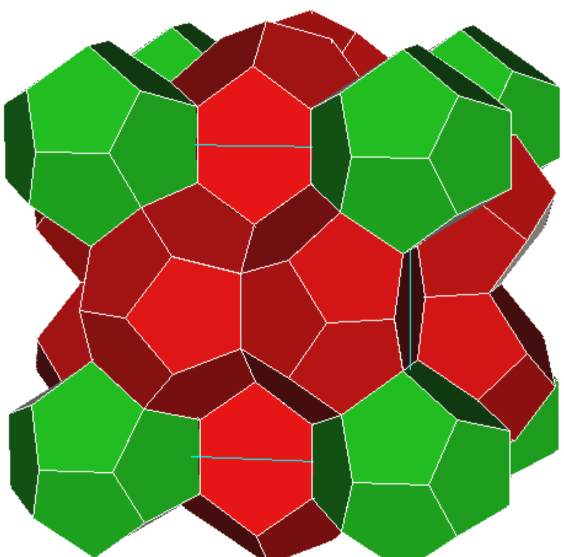


E
$[5^{12} 6^8]$
d_1 = 7.3 Å
d_2 = 9.6 Å

Different structural types are possible using different combinations of the Building blocks:

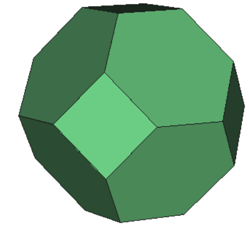
z.B.: **Melanophlogite: Type I (cubic): 2D + 6T ⇒ 8 voids**
black mineral with organics in the cages (natural occurence: Sicily

Zusammensetzung: $(SiO_2)_{46}$ • 8 (N_2, CO_2, CH_4)



Analogy: $SiO_2 \leftrightarrow OH_2$
Economic and ecological importance
Gas hydrates:
Methanhydrate: 46 H_2O •8 CH_4
CO_2–Hydrate: 46 H_2O •8 CO_2

5.7.2.2 anions:

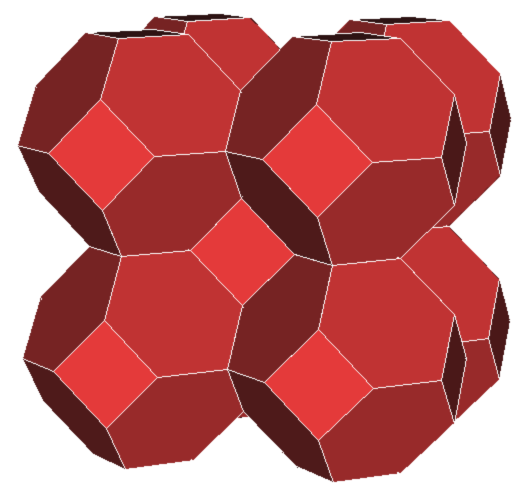


β–cages
$[4^6 6^8]$

colorless: **Sodalith ($Na_4[Al_3Si_3O_{12}]Cl$):**
colored: **Ultramarine**

Anions: Cl^-, SO_4^{2-}, S_2^- (green), S_3^- (blue) in voids

Lapislazuli $Na_4[Al_3Si_3O_{12}]S_x$ (X=2-3)

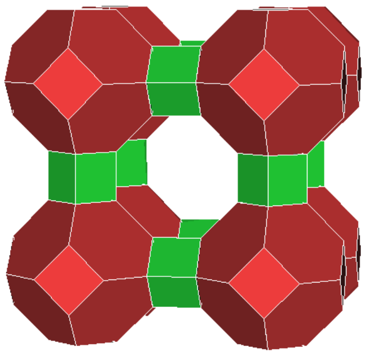


5.7.3 Zeolith: large voids, large windows ⇒ channels

Structure: Combination of a limited of secondary building blocks

General formula:

$\{[M^{n+}]_{x/n} \bullet [mH_2O]\}^{@Hohlraum}\{[AlO_2]_x[SiO_2]_{1-x}\}^{@Gerüst}$

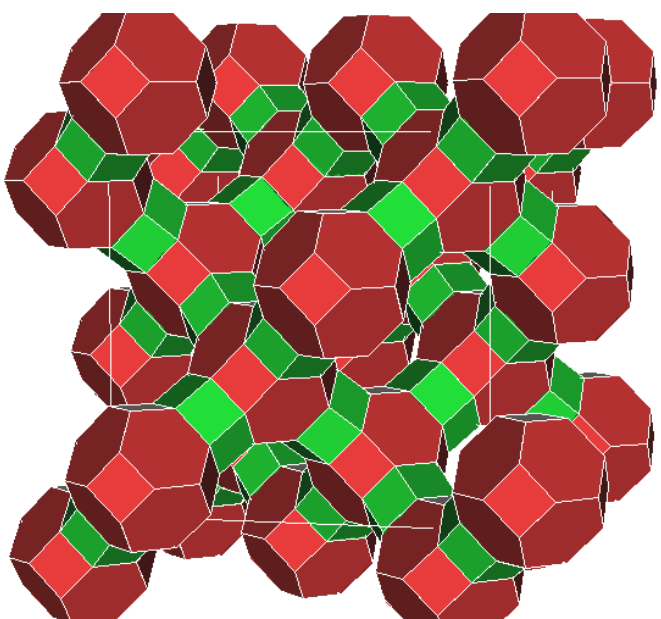


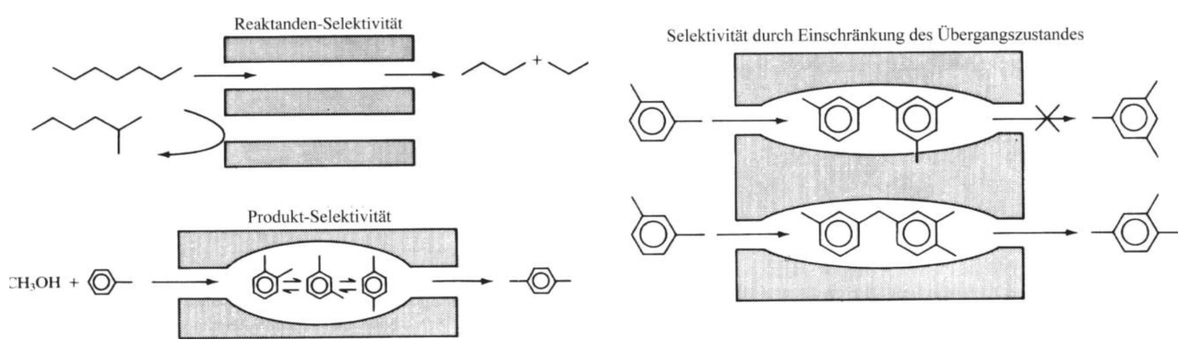
β–cages + cubes: Zeolith (Linde) A

Application:

- Ion exchanger
  - detergent
  - ^{137}Cs-Fixierung mit Clinoptilolith
- water-free Zeoliths are strongly hygroskopic
  - Molsieve
- acidic (Brönsted + Lewis), catalysis (shape-selective)

β–Käfige + hexagonal prism: Faujasite





Tpyical reaktions:

•Cracking •Isomerisation (Xylole, Butene) •Hydrocracking
•alkylation of aromatic compounds •Dehydration