EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
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Geochemistry on the Earth's surface for analytical geochemists

1b.

Mineral stability and structure

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

Topic outline

- Building particles of matter
- Bonds in crystals
  - Ionic
  - Covalent
- Basic minerals on Earth's surface

IONIC MODEL OF CHEMICAL BONDS

Ionic crystals

- We assume that ions are spherically symmetric particles
- The internal structure of ionic crystals is determined by the stacking of spherical particles in three dimensions
- There are three rules leading to maximum stabilization:
  1. The ions must combine in proportions resulting in an electrically neutral crystal.
  2. The closer the distance of adjacent nuclei of oppositely charged ions is to the lowest energy equilibrium distance, the more stable the arrangement (not enough attract when too far and too much of repel when too close).
  3. Each ion should be surrounded by as many oppositely charged ions as possible - *coordination number*.
- Decisive effect of size and charge of building particles – **ionic potential** (ratio of charge to size).

Energy arrangement

$$E_p = -\underbrace{\frac{e^2}{r}}_{\substack{\text{long–range}\\ \text{attraction}}} + \underbrace{\frac{be^2}{r^{12}}}_{\substack{\text{short–range}\\ \text{repulsion}}}$$

e ... difference in charges
r … the distance between the nuclei

Total *potential energy* **E $_p$** arrangement is a sum of

A. Attractive forces between oppositely charged ions (negative terms)
B. Repulsive forces between ions with the same charge (positive terms)

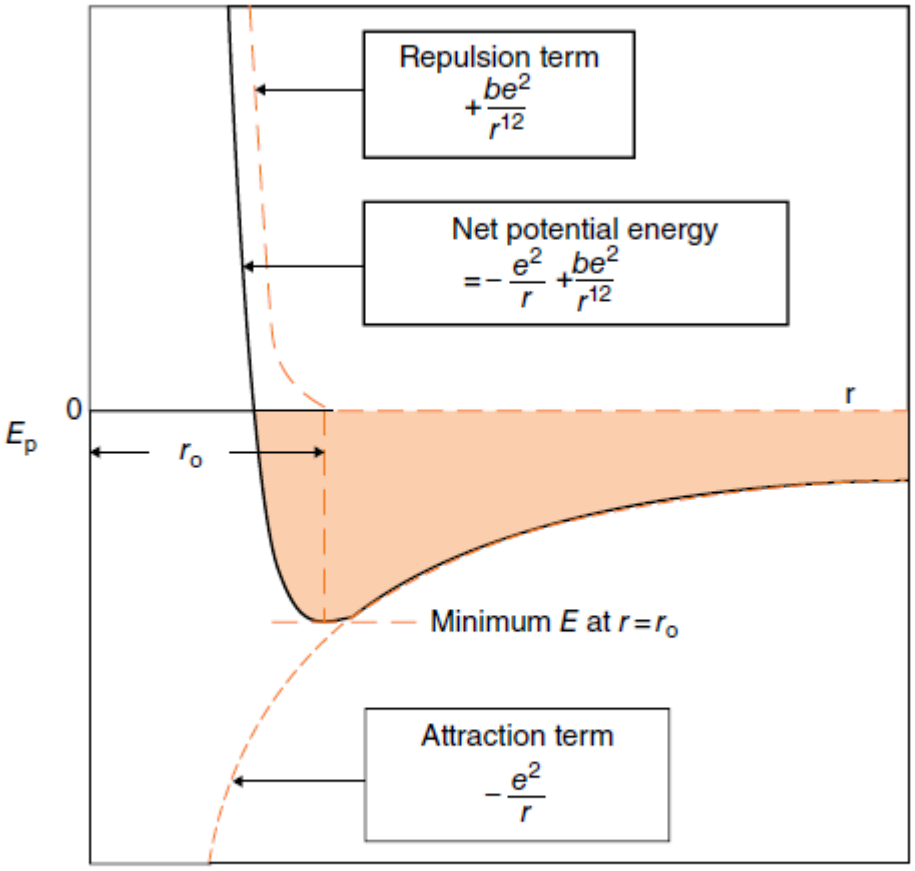
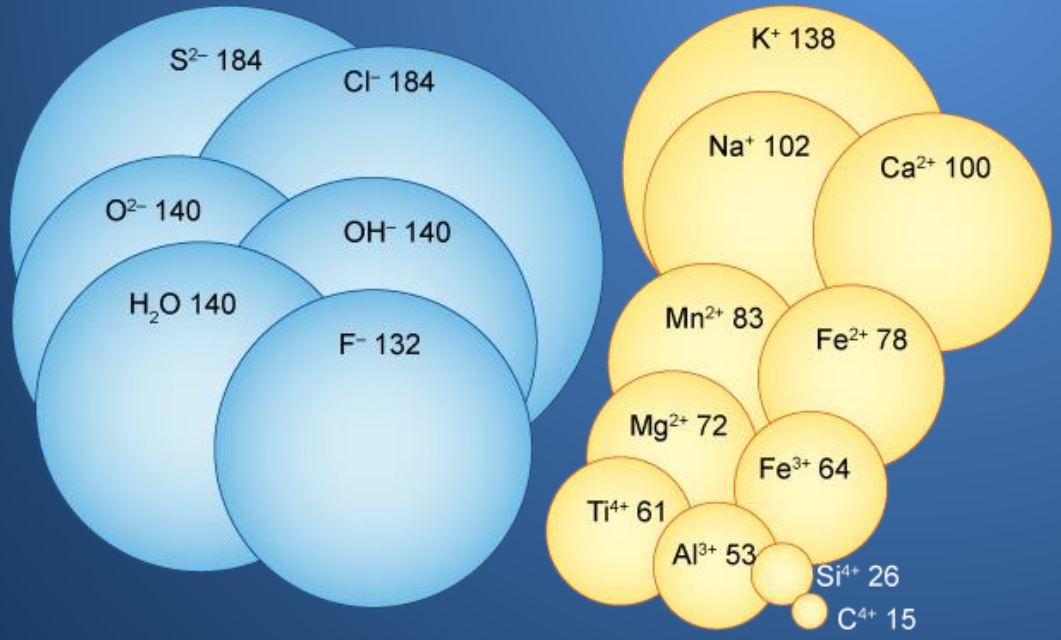


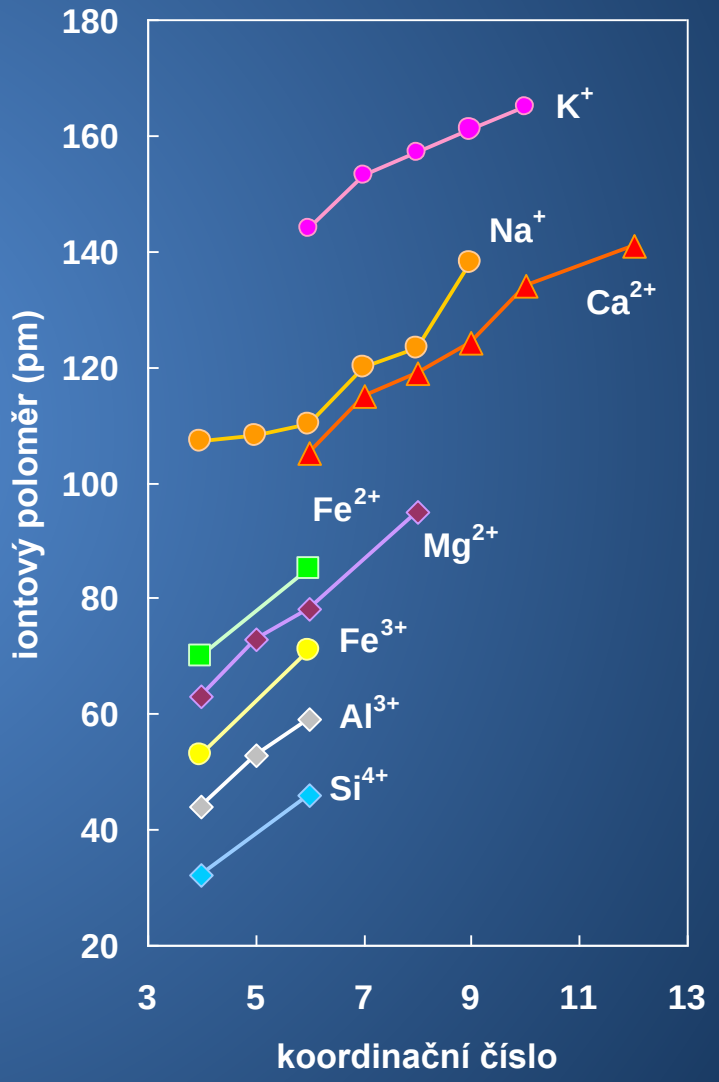
Figure 7.1.1 How the potential energy E_p of two oppositely charged ions varies with internuclear distance r.

Adapted from Gill (2015)

Sizes

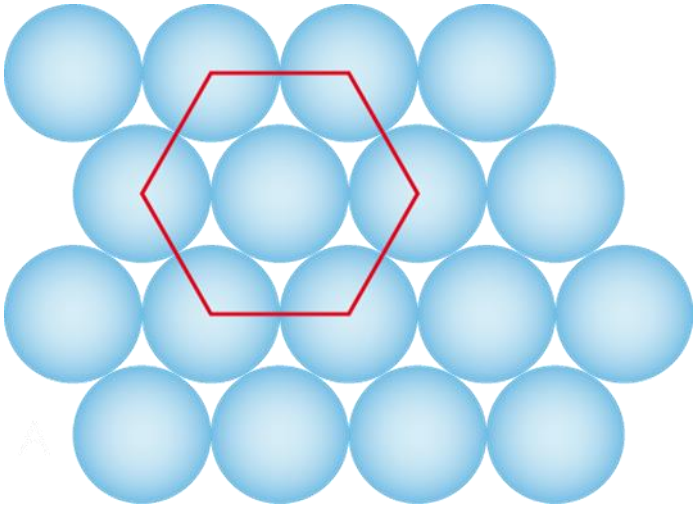
- The higher the positive charge, the smaller the ions
  - significant attraction by the positive charge of the nucleus.
- The higher the negative charge, the larger the ions
  - mutual repulsion of electrons.



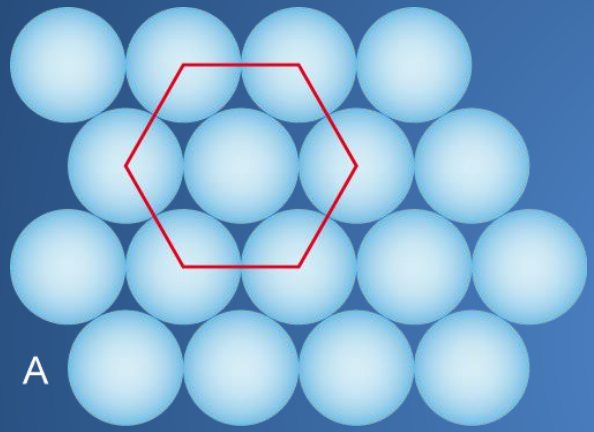


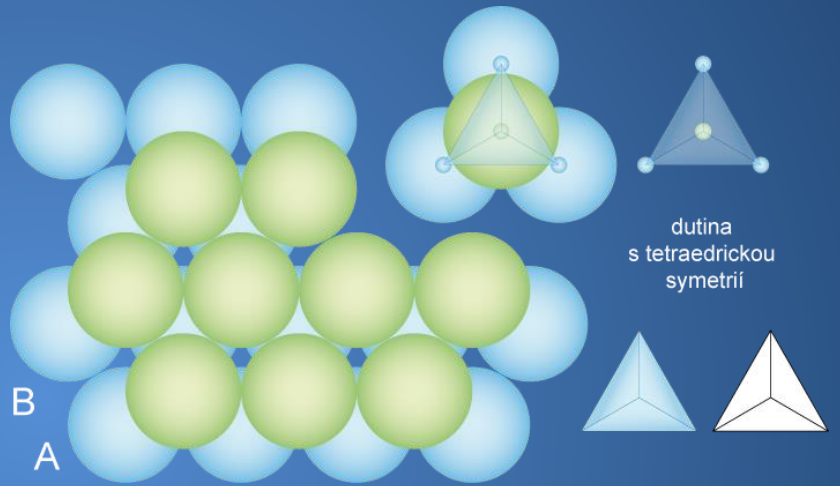
Arrangement

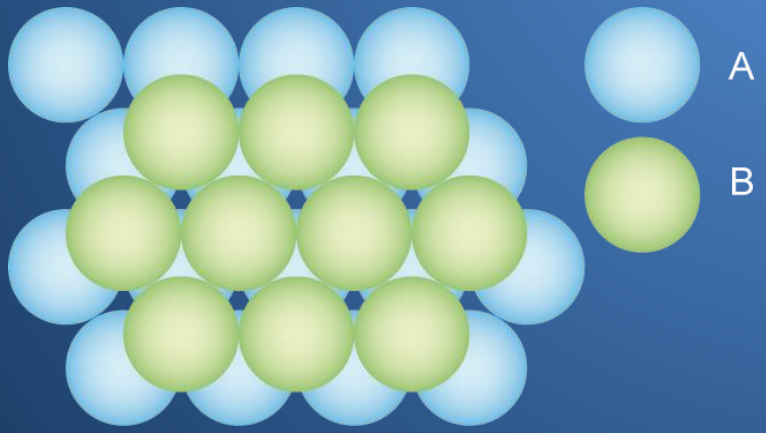
- When stacking spherical particles of the same size, the tightest arrangement is stacks of regular layers.
- Each layer has hexagonal symmetry.
- Another layer is placed on top of it with each particle placed in a dimple between the three particles in the lower layer

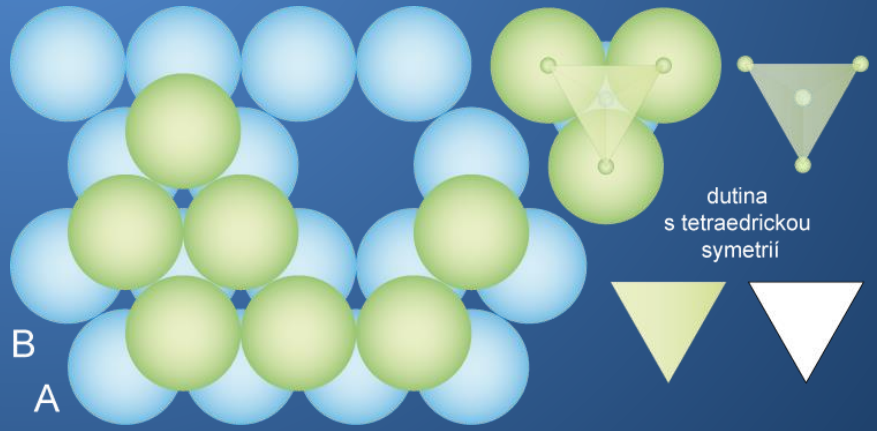


Layout – 2 layers









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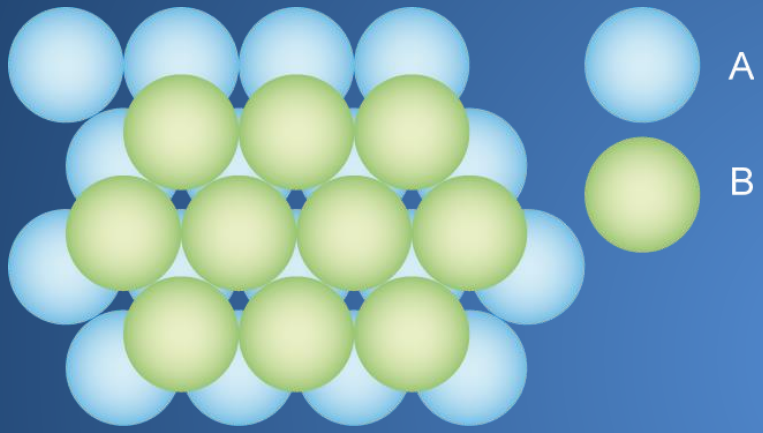
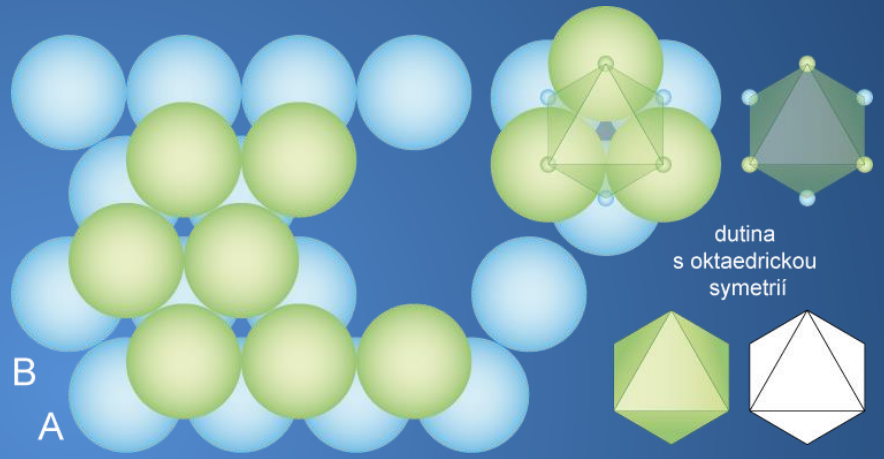
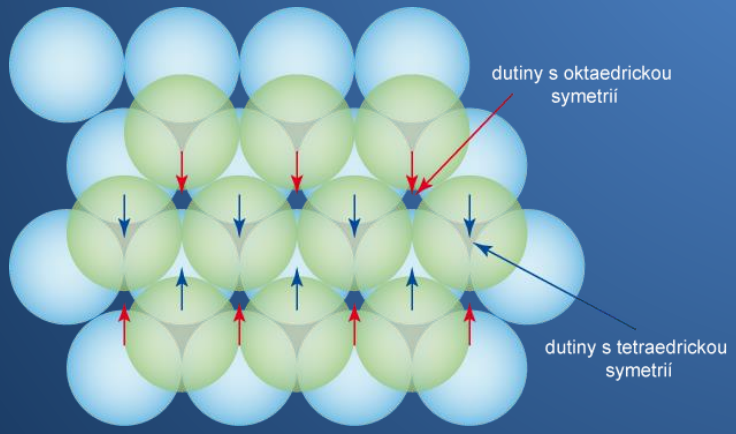
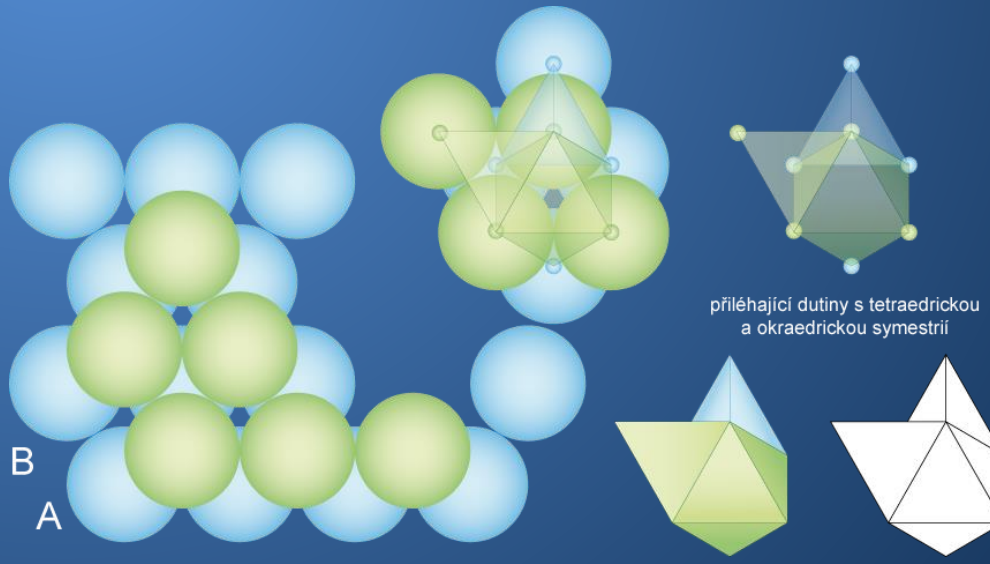
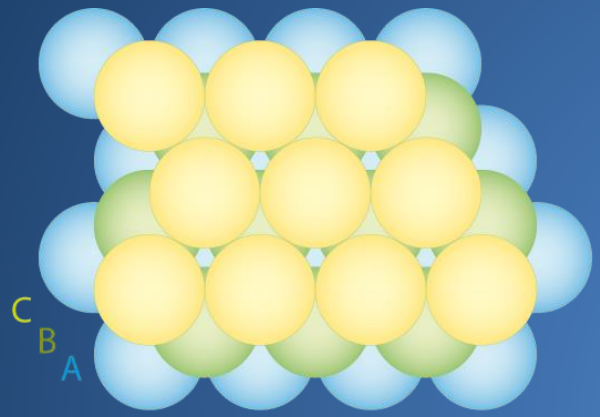


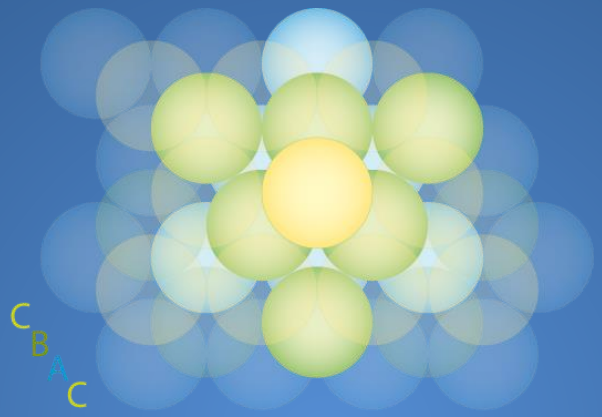


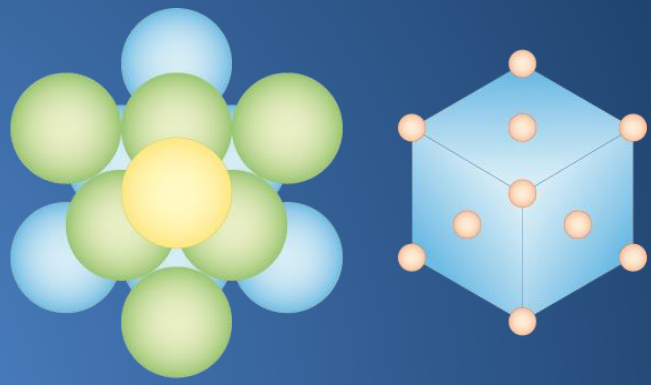




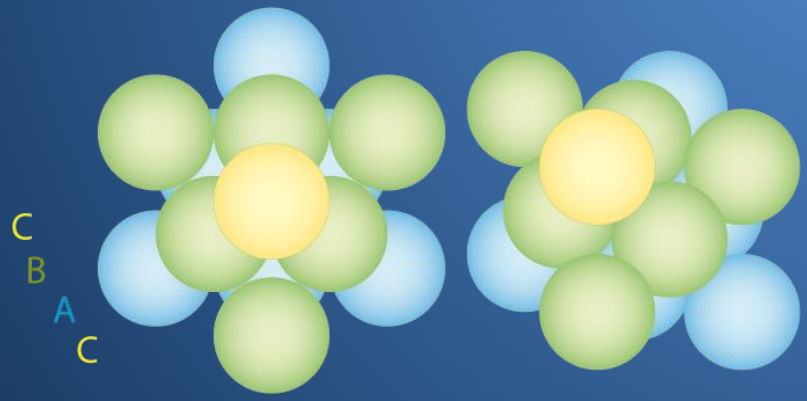
Layout – 3 layers

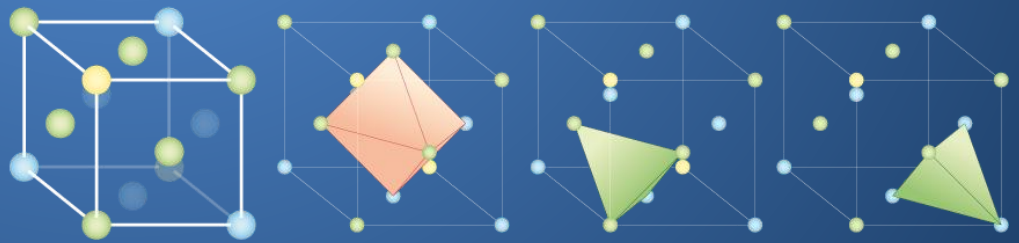






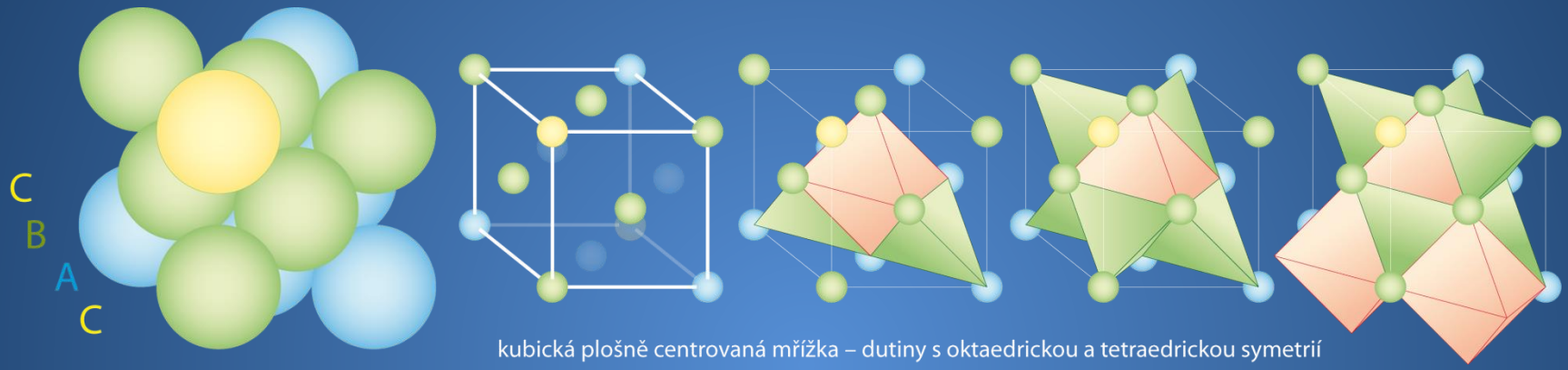
kubická plošně centrovaná mřížka





kubická plošně centrovaná mřížka – dutiny s oktaedrickou a tetraedrickou symetrií

Layout – 3 layers



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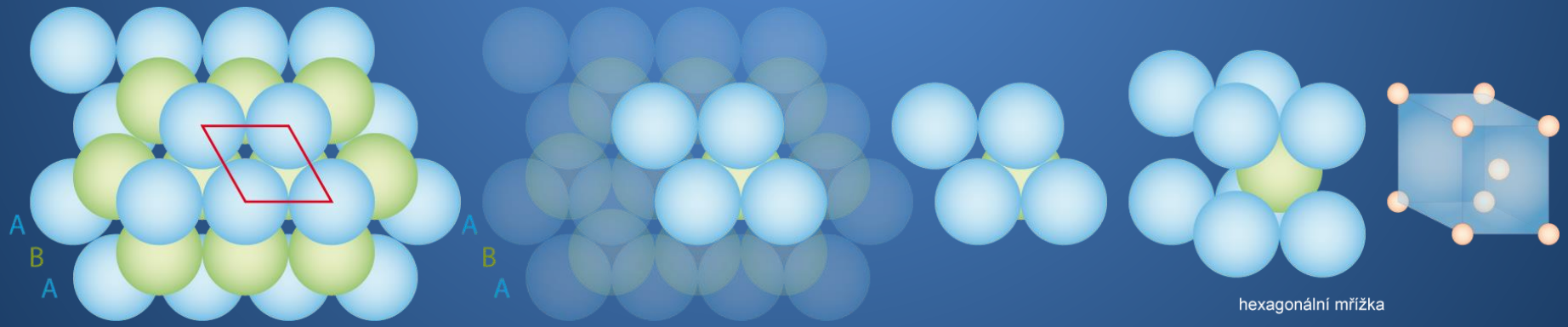
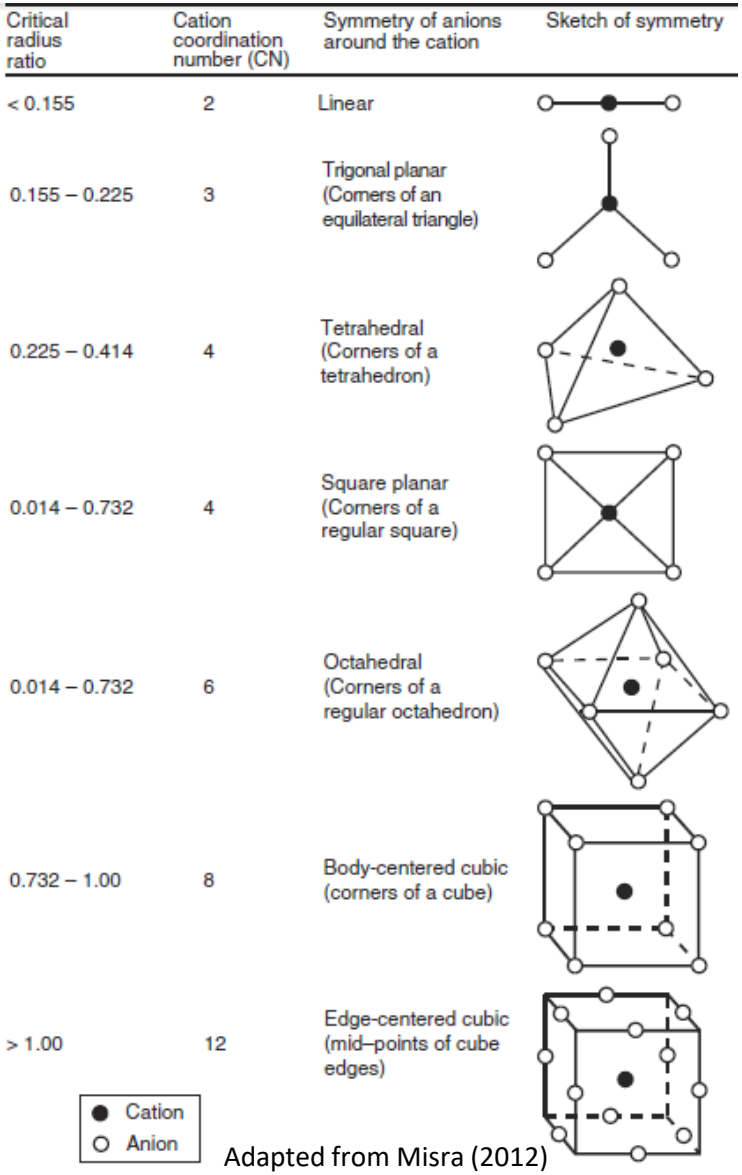


hexagonální mřížka

Arrangement

ratio r_{cat}/r_{O2}	Coord. Nr.	coord. polyhedron
1	12	centers of the edges of the cube
0.73 – 1	8	hexahedron
0.41–0.73	6	octahedron
0.22 - 0.41	4	tetrahedron
0.15 – 0.22	3	middle of triangle

- Both types of positions are significantly larger than the spaces between particles in a monolayer.
- In most crystals, there are cations in these positions.
- C^{4+} always occupies spaces between three oxygens (carbonates).
- Si^{4+} occupies positions in tetrahedral cavities (may also be substituted by Al^{3+} – aluminosilicates, exceptionally Ti^{4+} – pyroxenes, amphiboles).
- Other ions (Fe^{3+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Ca^{2+}, Na^{+}) occupy octahedral positions in the tightest arrangement of oxygens, while well substituting in the structures (they occupy the same structural positions): Fe^{3+}–Mg^{2+}–Fe^{2+}–Mn^{2+}, Ca^{2+}–Na^{+}.
- K^{+} occupies oxygen positions, as well as OH^{-} groups.



Adapted from Misra (2012)

Ionic substitution

1. Ions of one element can normally replace ions of another element if they differ in size by less than approx. 15%.
2. If the charge of the ions differs by 1, they can normally be substituted if the electroneutrality of the crystal is preserved. Substitution occurs to a much smaller extent when the charge difference is larger.
3. If two different ions can occupy a position, the ion with the higher ionic potential forms a stronger bond with the surrounding ions.
4. Mutual substitution of similar ions can be limited by different electronegativity and the formation of bonds of different ionic nature.

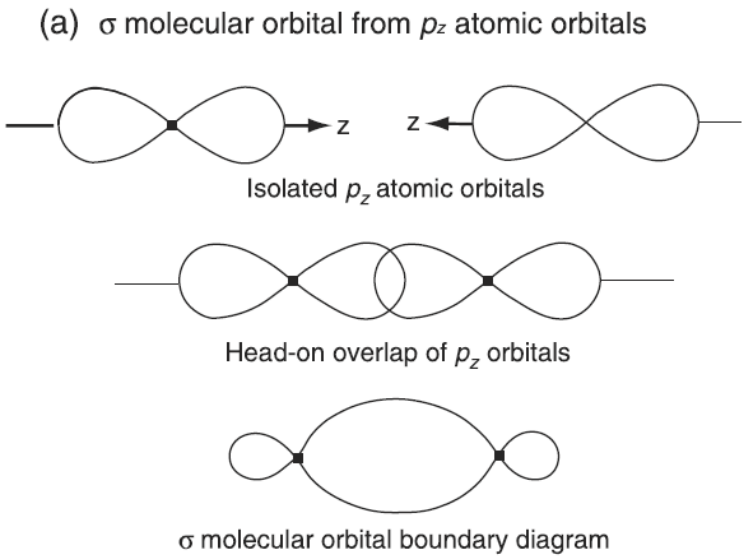
COVALENT BONDS

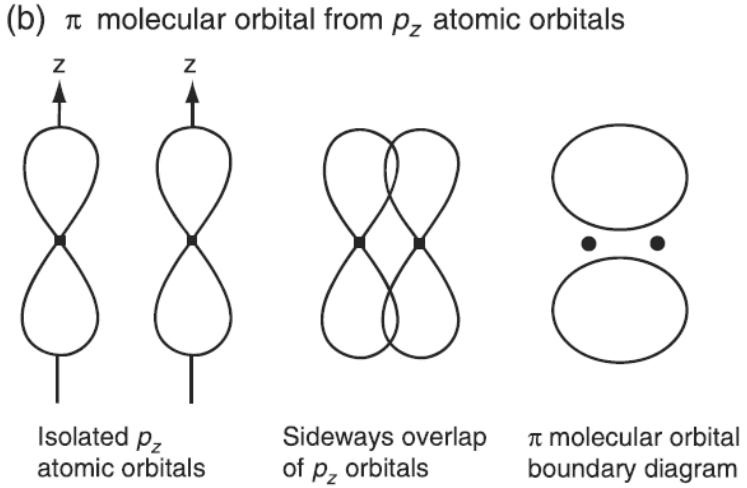
Covalent bond

- Sharing unpaired electrons between neighboring atoms.
- If the orbitals overlap, a molecular orbital is formed.
  - Shared orbitals have a lower total energy than each one separately
- Bonds stronger, directional
- Small stable molecules (O_2, H_2O, CH_4 …)

σ and π

- Orbital σ is symmetric according to the line connecting the nuclei of the bonded atoms.
  - High density of electrons between nuclei
  - Simple bonding
- The orbital axes are parallel and lie above and below the junction of the nuclei (nodal plane)
  - Electrons above the nodal plane
  - Double bond





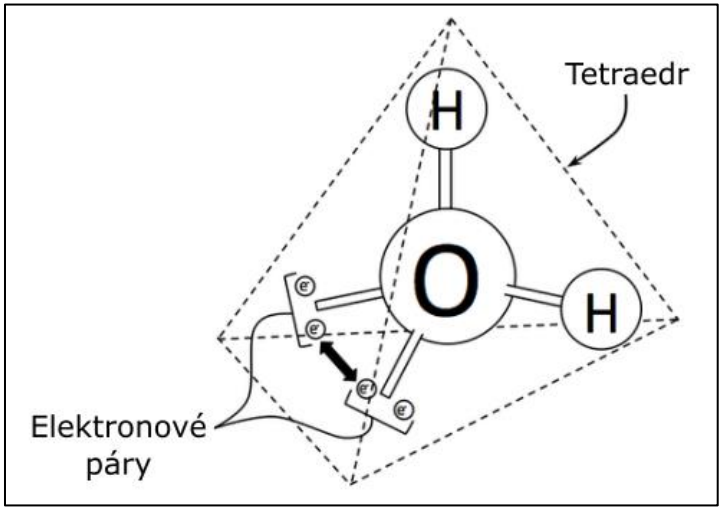
Adapted from Misra (2012)

Coordination bond

- Link between donor and acceptor:
  - The donor has an electron pair.
  - The acceptor has an empty orbital.
- Overlapping creates complex compounds.
- A central atom (often a transition metal - acceptor) and several ligands (donors) around it.
- Complexes are important for the mobility of metals in the environment.

Covalent crystals

- Structure determined by the shape of bonds (hybridization of orbitals).
- In a diamond, each carbon is bonded to 4 others in a grid of tetrahedra.
  - Strong bonds, strong materials



The irregular shape of the water molecule

The free electron pairs in the water molecule cause a deformation of the shape – the molecule is not a linear HOH, the electron pairs and hydrogens try to fit into the vertices of the tetrahedron. The result is a partially deformed (all angles are not equal) tetrahedron.

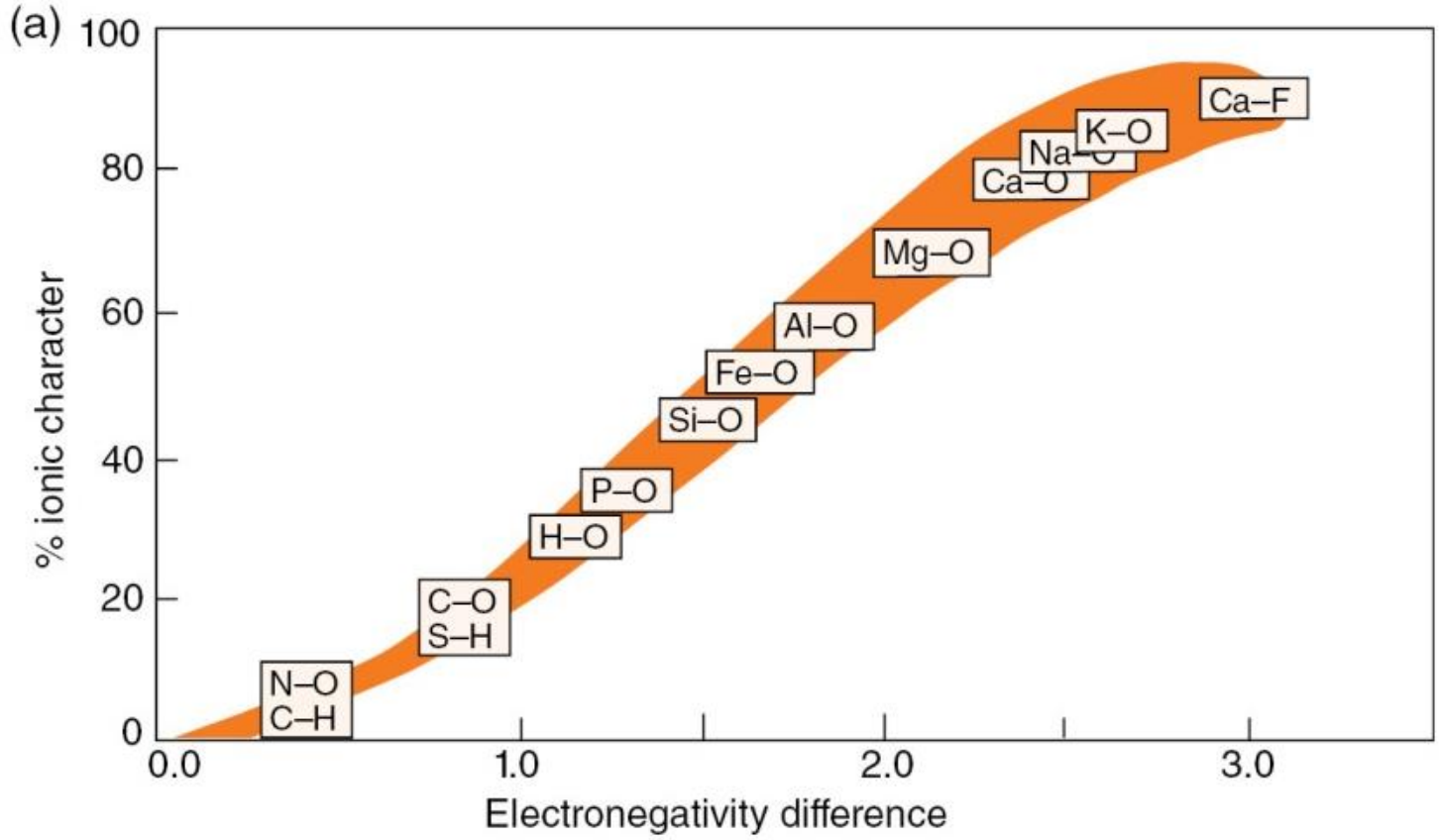
BONDS IN MINERALS

Non-ideal bonds

- Most compounds fall between the extremes of ionic and covalent bonding.
- Real ties differ from ideal models.
- In every **ionic bond** , the occurrence of an electron is deflected due to the electrostatic force.
  - The smaller the cation, the closer it is to the anion and the greater the effect (Si^{4+} vs K^{+}).
  - The effect of the size of the charge of the cation.
- The difference in electronegativity causes one atom to attract more of the bonding electrons of a **covalent bond .**
  - Polarization of the bond causes it to show a certain degree of "ionicity".

The nature of the bonds

- The nature of the bonds is continuous, and ionic and covalent bonds represent the extremes.



Correlation between the ionic character of the bond and the electronegativity difference of the atoms according to Pauling. Geologically significant bonds are marked. Adapted from Gill (2015)

Oxygen compounds

- Carbonates, phosphates, nitrates...
- Ionic bond between anion and cation (e.g. Ca^{2+} and CO_3^{2-}).
- Covalent bonds in the anion (in carbonates between carbon and oxygens).

A very large group that deserves its own chapter

SILICATE CRYSTALS

Silicate bonds

- The Si-O bond has an ionic character of approx. 50% and thus exhibits approximately equally ionic and covalent character.
- In the real structure of silicates, the Si cation accounts for roughly half the charge (Si^{2+}).
- The covalent nature of the bond allows the structural strength of the silicate chains and structures.
  - Silicon determines the construction of silicate structures.
- Other bonds in silicate minerals are of a more ionic nature (Al-O, Mg-O, Na-O, Ca-O, K-O) – their structure is well described by the ion model.
  - Ions limit the mutual arrangement of Si-O structures in the mineral.
- Due to its size, aluminum can enter both octahedral and tetrahedral positions.

Polymerization

- SiO_4 tetrahedra share oxygens with each other.
- A polymer structure with chains is formed.
- -Si-O-Si-O-Si-O-
- While no oxygen is shared by silicon in olivine, all oxygens are shared in quartz.
- Great structural diversity of silicate minerals.

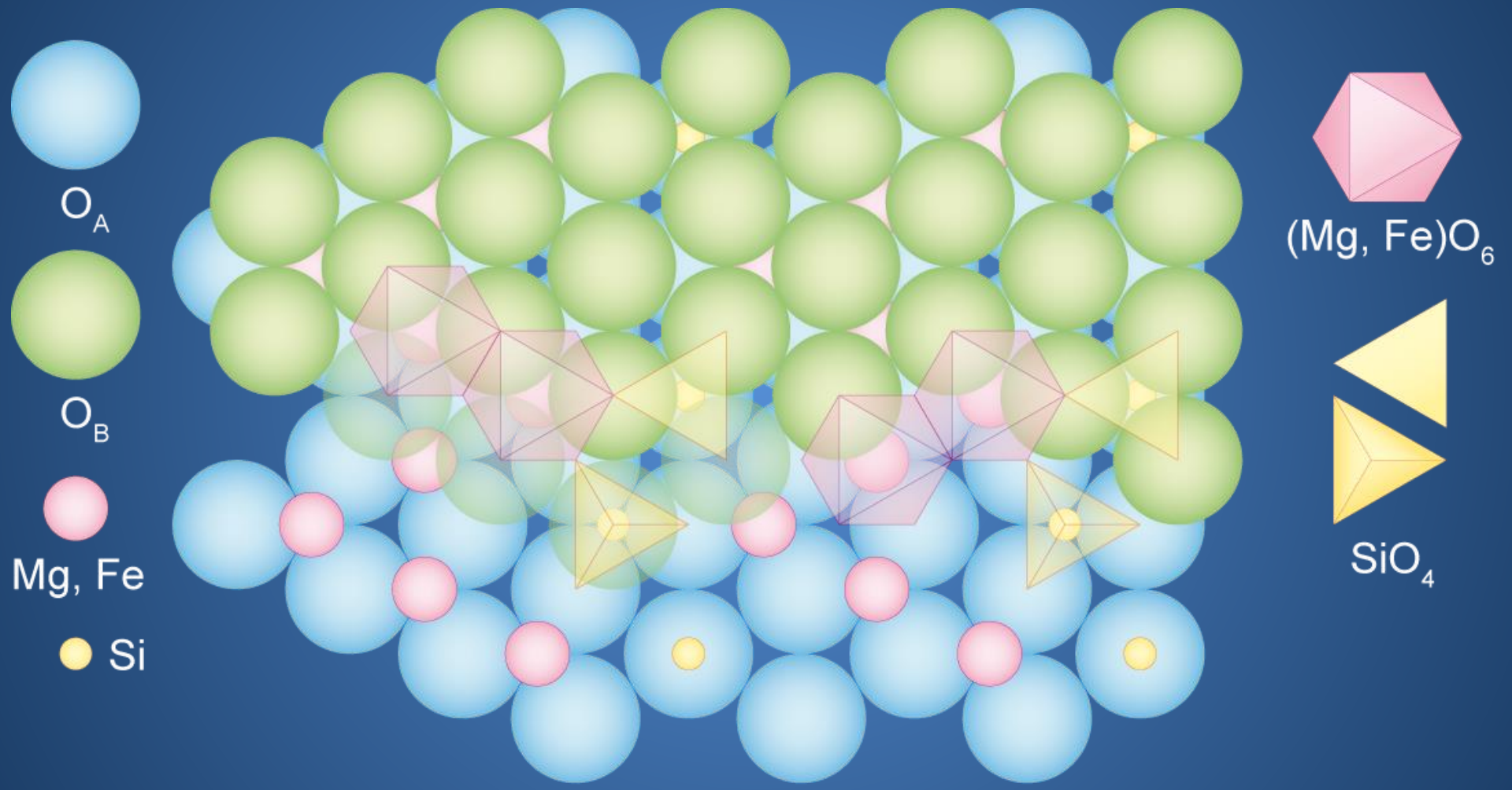
Arrangement

group	general formula	valence O	Si bonds	Cation bonds	ratio	mineral	formula
	SiO_2	4	4	0	4:0	silica	SiO_2
tecto-	$M^{I}Si_3AlO_8$	16	12	4	3:1	albite	$NaSi_3AlO_8$
phylo-	$M_3Si_4O_{10}(OH)_2$	22	16	6	2.7:1.3	talc	$Mg_3Si_4O_{10}(OH)_2$
ino-	$M_2Si_2O_6$	12	8	4	2:1	diopside	$CaMgSi_2O_6$
neso-	M_2SiO_4	8	4	4	1:1	olivine	$(Fe, Mg)_2SiO_4$

Nesosilicates

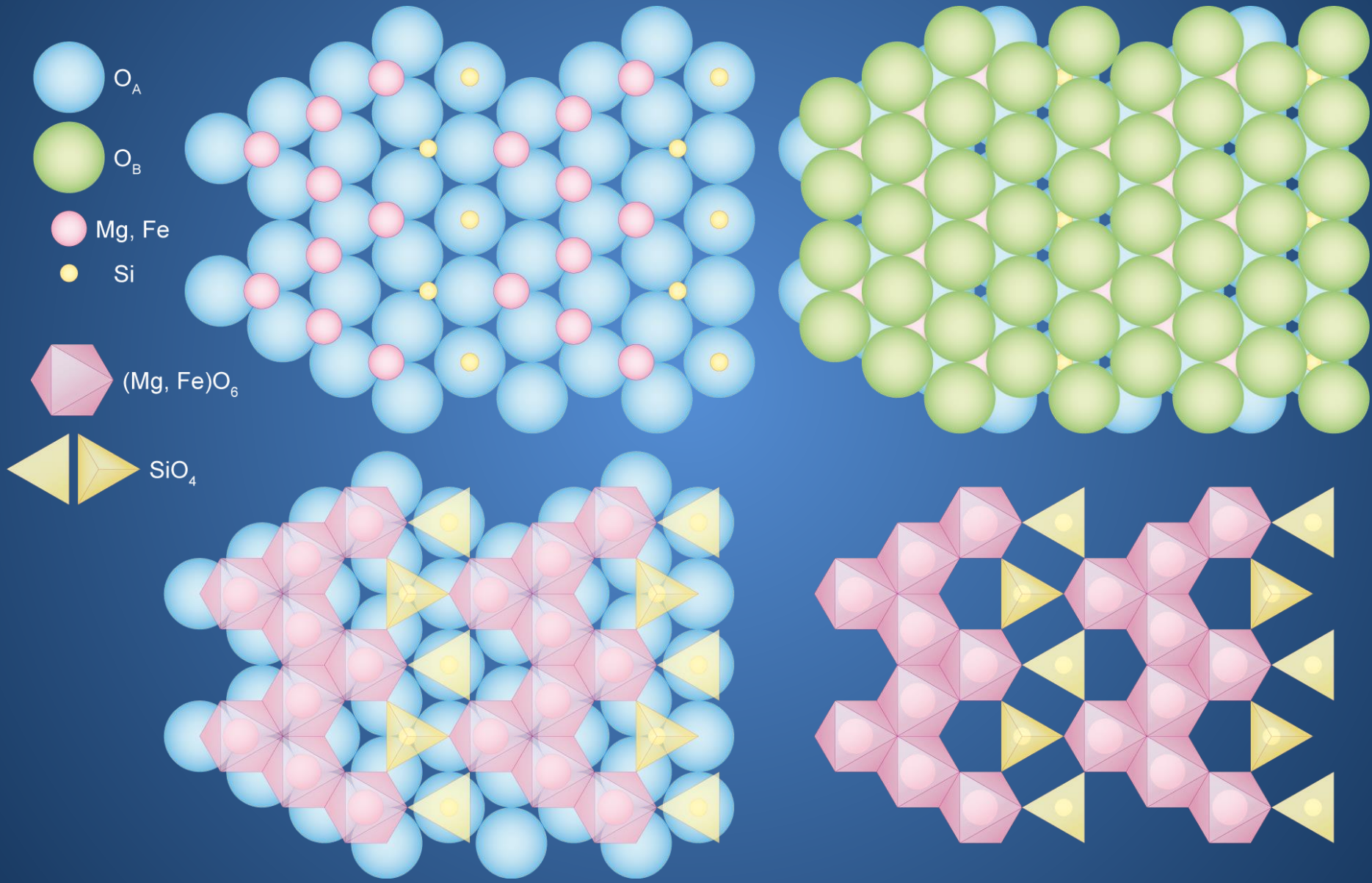
- SiO_4 tetrahedra have only half of the oxygen bonds covered:
- One Si^{4+} to four O^{2-} => SiO_4^{4-}
- If a free electropositive ion (typically Mg^{2+}) is abundantly present in the melt, it will bind the SiO_4^{4-} tetrahedra
- A typical olivine structure (especially forsterite Mg_2SiO_4) is formed, which does not contain any direct bonds between adjacent tetrahedra.
  - The cohesion of the crystal is determined by the ionic bond between Mg^{2+} and SiO_4^{4-}
- Other examples are garnets (e.g. $Ca_3Al_2Si_3O_{12}$), zircon ($ZrSiO_4$) or topaz ($AlSiO_4F_2$).
- Typically high temperature crystallization from magma.

Olivine – $(Mg, Fe)_2SiO_4$



Mezi vrstvou A a B jsou střídavě obsazovány oktaedrické (Mg-Fe) a tetraedrické dutiny (Si).

Olivine – $(Mg, Fe)_2SiO_4$



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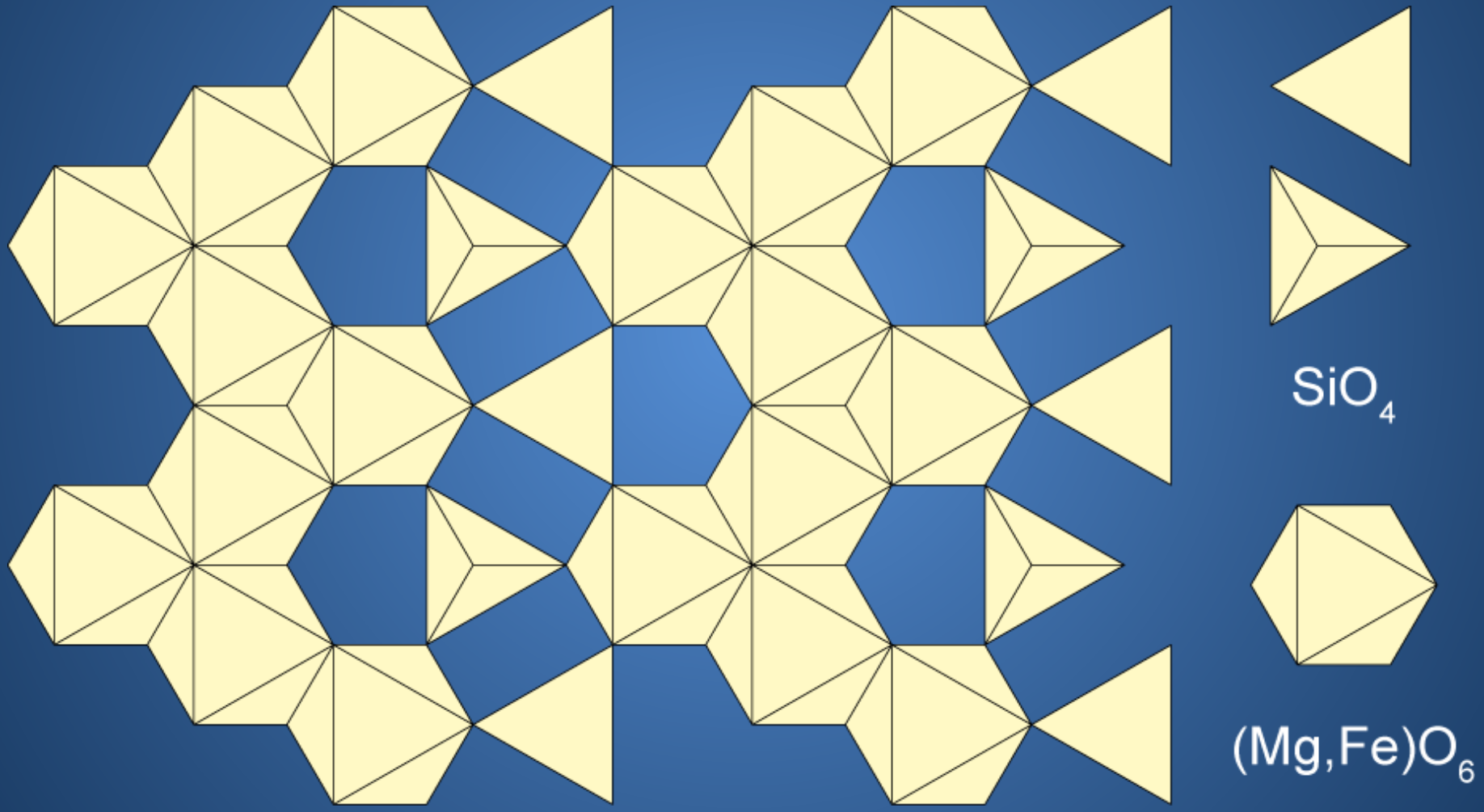
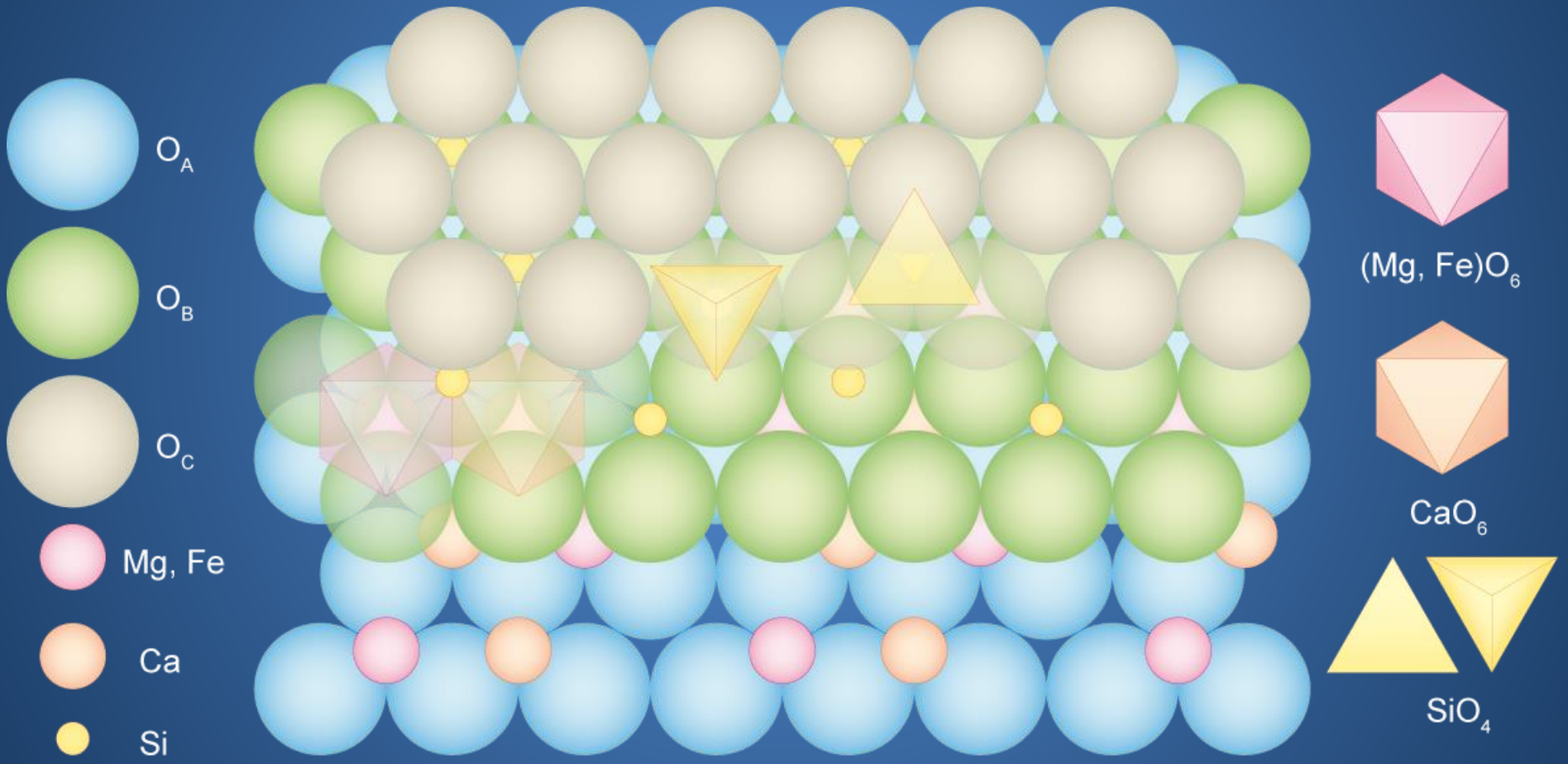


Inosilicates

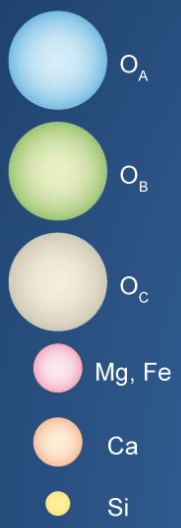
- **Pyroxenes**
  - Each Si shares two oxygens with neighboring tetrahedra.
  - Structurally, we can write it as $(SiO_3)_n$, where n is the number of tetrahedra in the chain.
  - The negative charge is mostly balanced by divalent cations, sometimes also by pairs (Na^+ and Al^{3+} or Fe^{3+}).
  - Common rock-forming minerals (diopside, augite, enstatite ...).

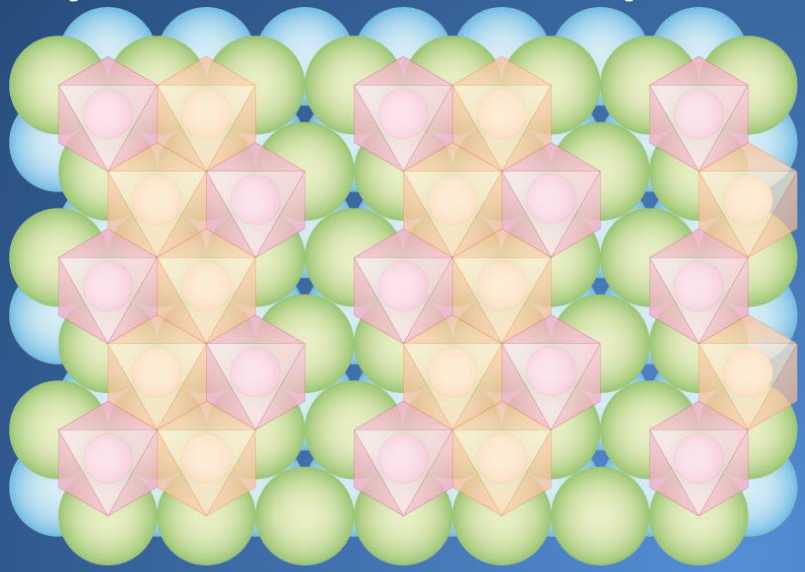
Pyroxenes – diopside $Ca(Mg, Fe)Si_2O_6$

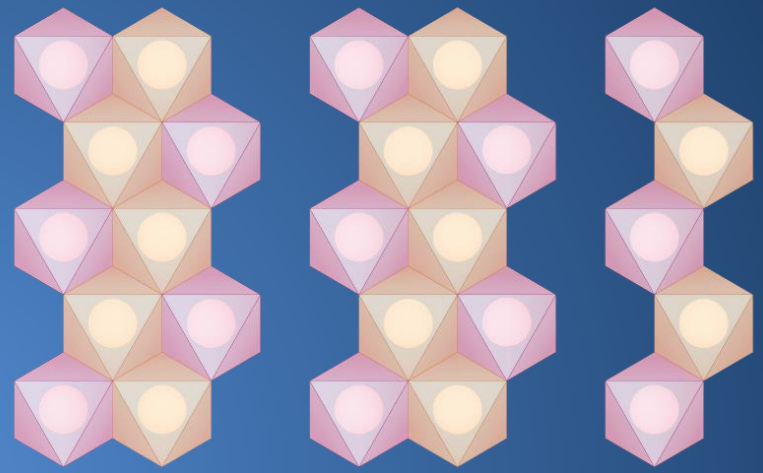


Mezi vrstvou A a B jsou obsazovány jen oktaedrické dutiny (Ca, Mg-Fe), mezi vrstvou B a C pouze tetraedrické dutiny (Si).

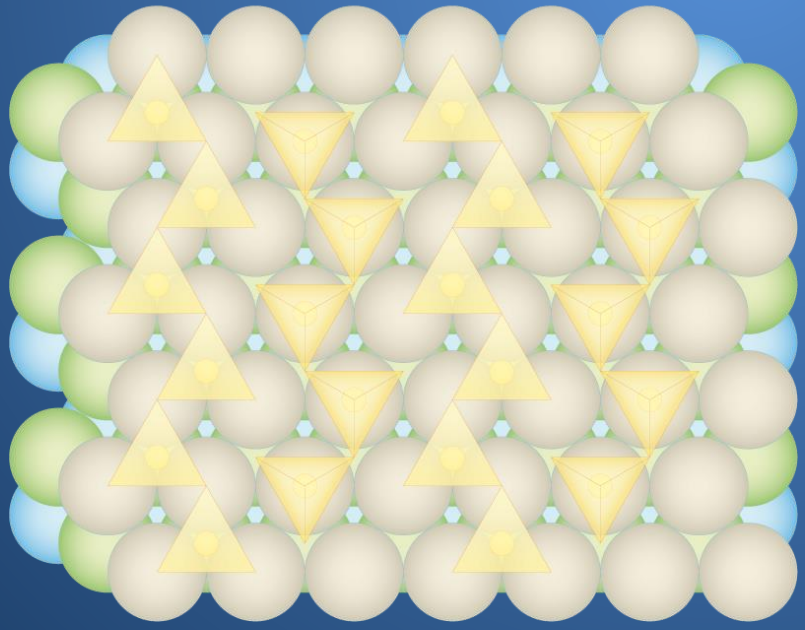
Pyroxenes – diopside $Ca(Mg, Fe)Si_2O_6$

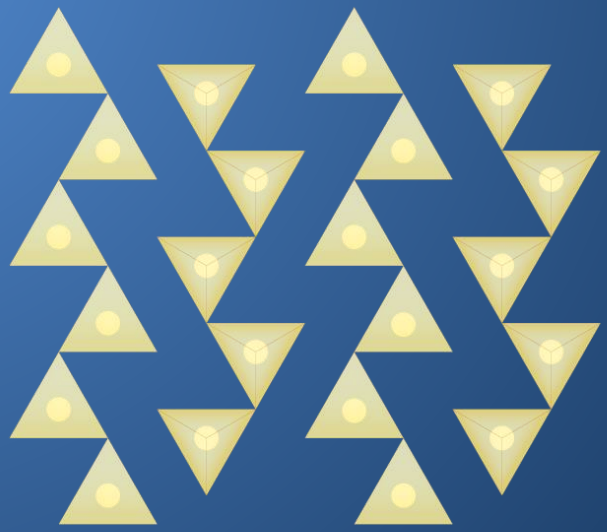






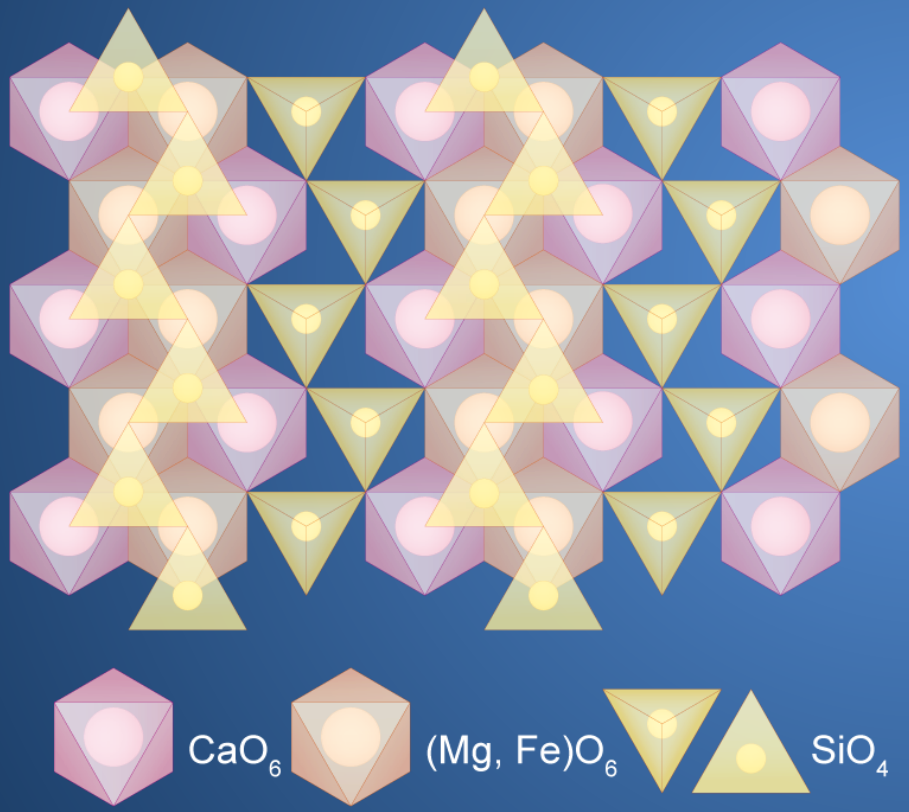
Mezi vrstvou A a B jsou obsazovány jen oktaedrické dutiny (Ca, Mg-Fe).

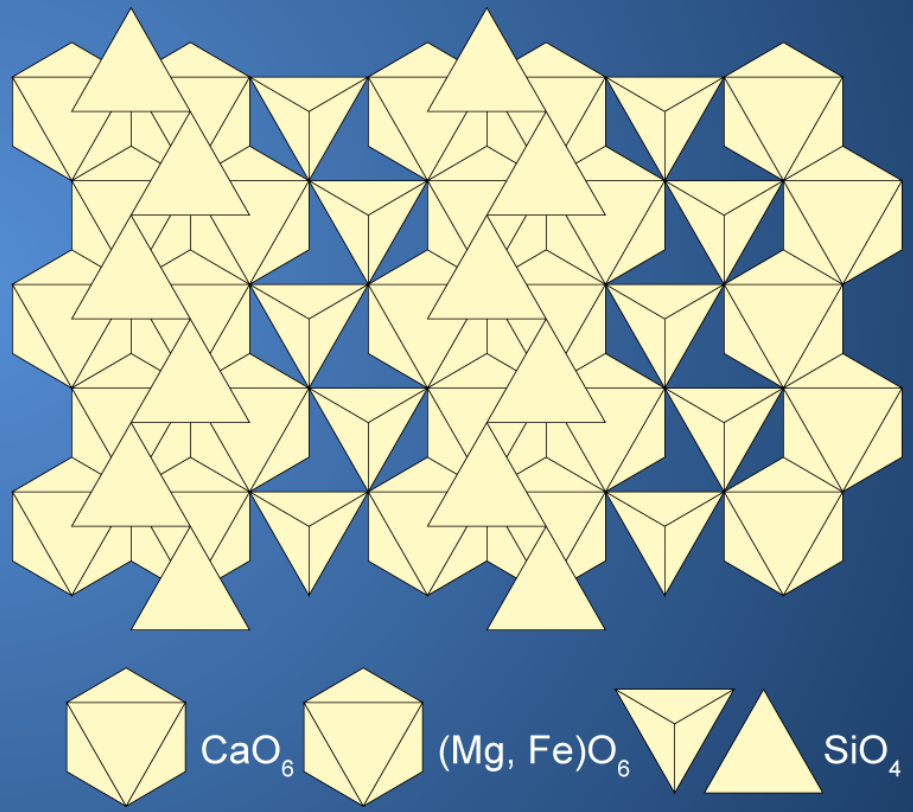




Mezi vrstvou B a C jsou obsazovány pouze tetraedrické dutiny (Si).

Pyroxenes – diopside $Ca(Mg, Fe)Si_2O_6$

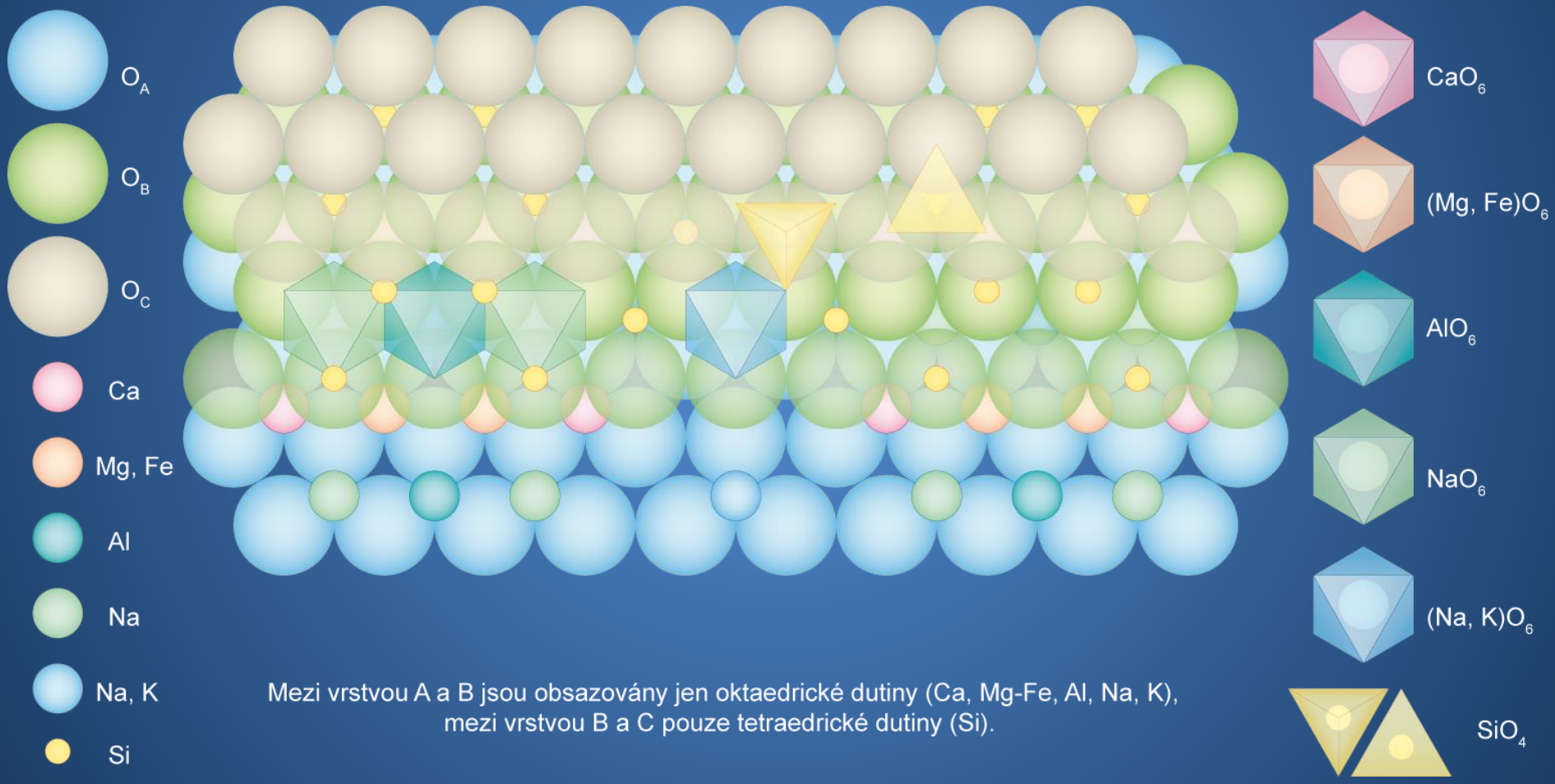




Inosilicates

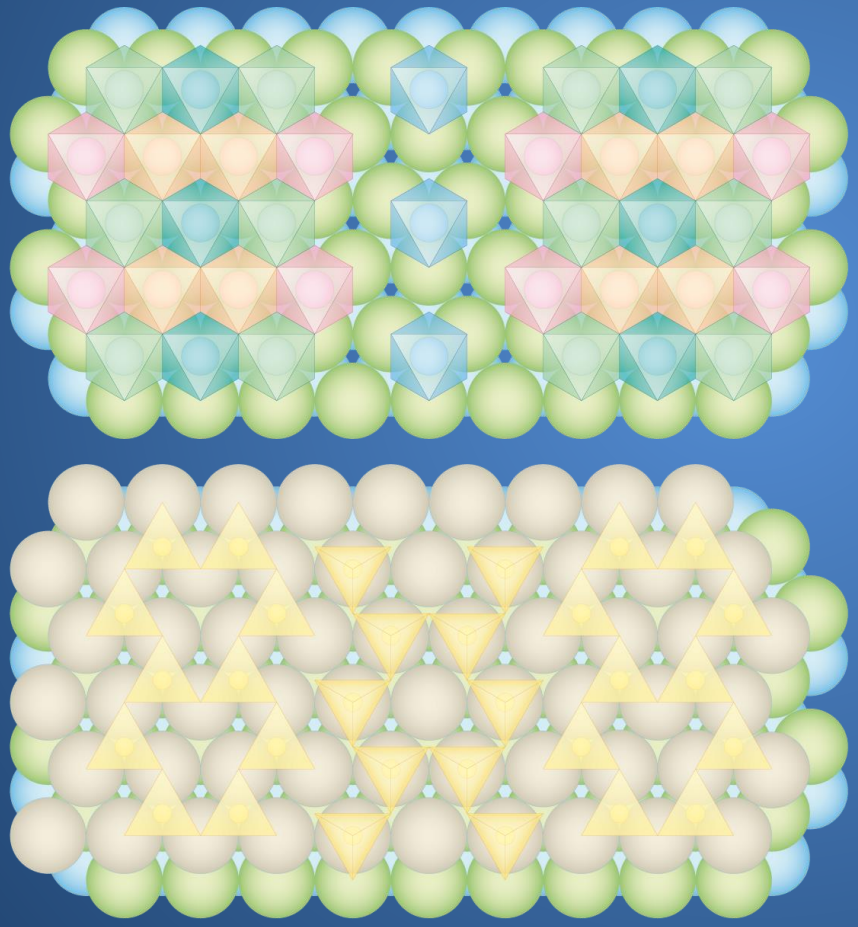
- **Amphibole**
  - Half of the tetrahedra share two oxygens, the other half share three oxygens.
  - Two connected pyroxene chains, between which larger cavities are formed, into which large anions (OH^- or F^-) can enter.
    - Thanks to them, lower stability at high temperatures.
    - Very complex stoichiometry.
  - Structurally, we can write it as $(Si_4O_{11})_n$.
  - Tremolite, hornblende...

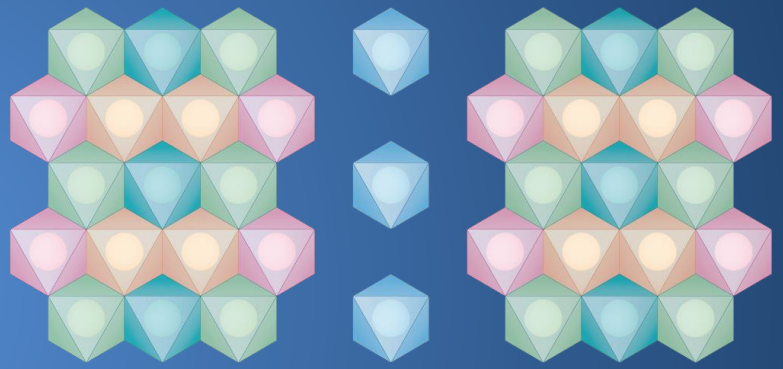
Amphibole – $NaCa_2(Mg, Fe, Al)_5(OH)_2(Si, Al)_8O_{22}$



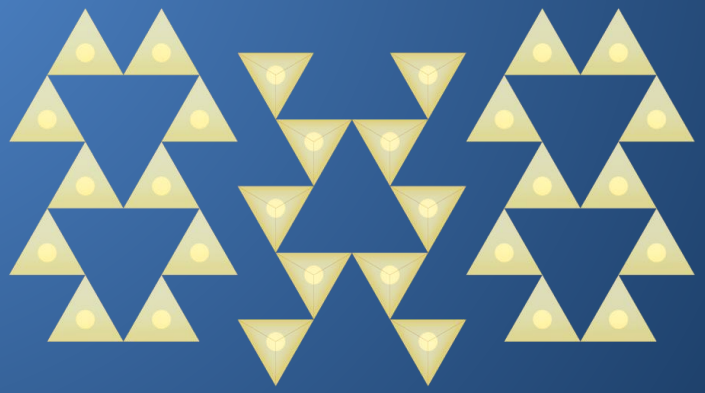
Mezi vrstvou A a B jsou obsazovány jen oktaedrické dutiny (Ca, Mg-Fe, Al, Na, K), mezi vrstvou B a C pouze tetraedrické dutiny (Si).

Amphibole – $NaCa_2(Mg, Fe, Al)_5(OH)_2(Si, Al)_8O_{22}$



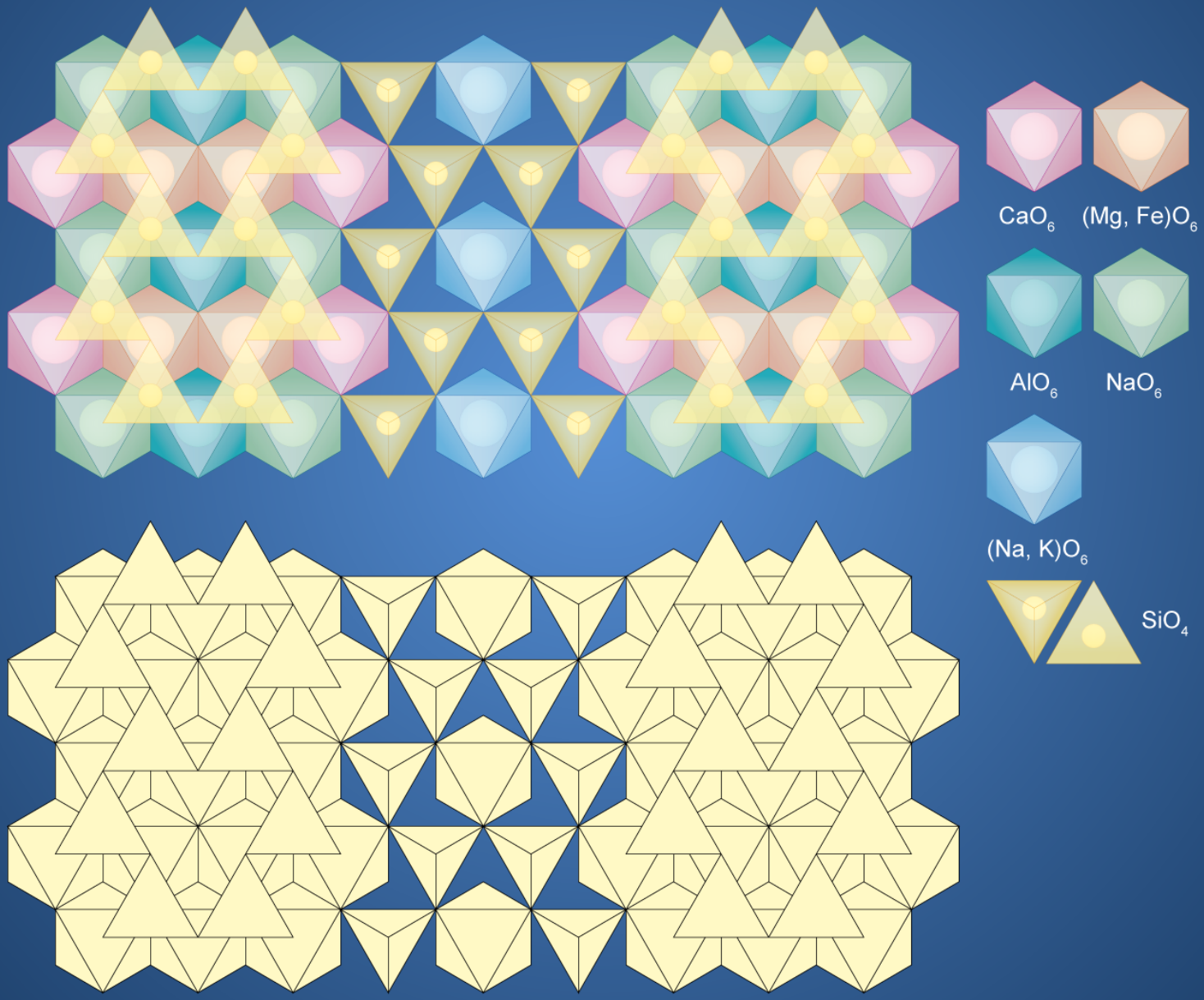


Mezi vrstvou A a B jsou obsazovány jen oktaedrické dutiny (Ca, Mg-Fe, Al, Na, K).



Mezi vrstvou B a C jsou obsazovány pouze tetraedrické dutiny (Si, Al).

Amphibole – $NaCa_2(Mg, Fe, Al)_5(OH)_2(Si, Al)_8O_{22}$



Phyllosilicates

- If all tetrahedra share three oxygens with neighboring tetrahedra, a continuous planar structure is formed.
  - They form sheets, endless planes.
- Anions can again enter the meshes in the network.
- The general formula is Si_4O_{10} or Si_2O_5.
  - Aluminum replaces up to 50% of the tetrahedra, usually less than 25%.
- Different types of phyllosilicates (chlorites, clay minerals) differ in the "filling" between the silicate layers.
- The silicate layers are much more cohesive than the filler – that‘s why they are fissile across the surface (typically micas).

Phyllosilicates

- Significant absorption capacity (especially cations).
- Relatively reactive – they significantly affect the properties of water, soil and sediments.
- 2 main building elements
  - Tetrahedral layers
  - Octahedral layers

2:1 Phyllosilicates

- "Sandwich" tetrahedral lr. – octahedral – tetrahedral.
- Between the cations "sandwiches" – they fit into the hexagonal "mesh" of the tetrahedral layer.
- No interlayer – they are held together by van der Waals forces.

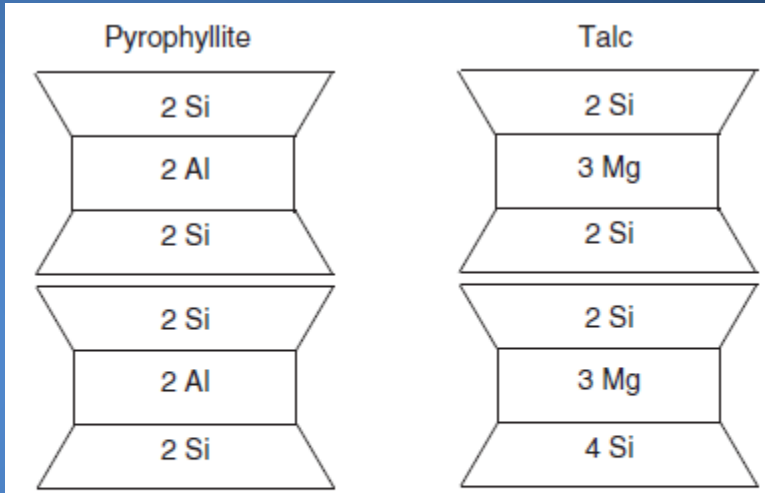
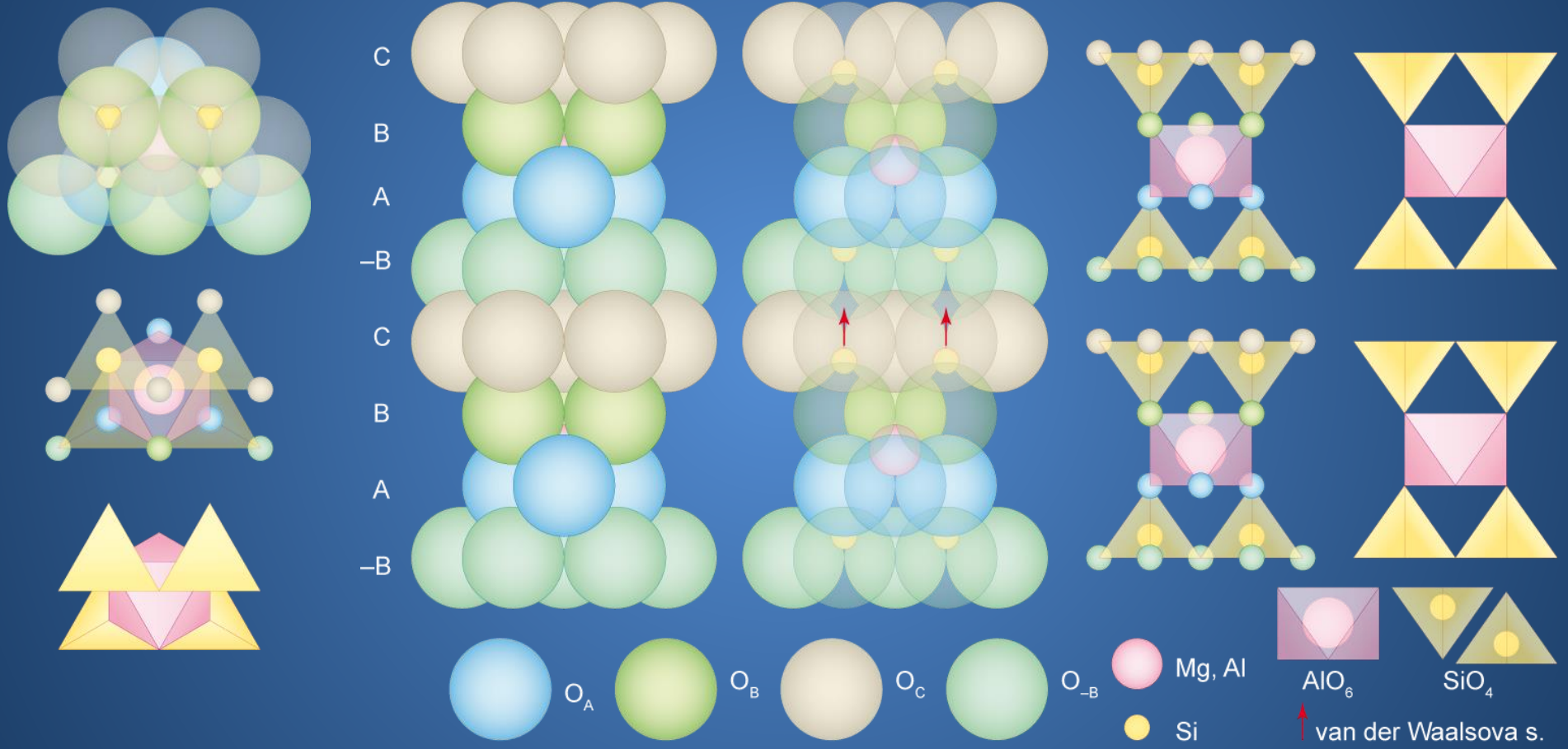


Fig. 2.17 Schematic of pyrophyllite (left) and talc (right). Note (a) substitution of 3 Mg (talc) for 2 Al (pyrophyillite) in octahedral sheet, and (b) absence of interlayer cations in both.

Adapted from Ryan (2014)

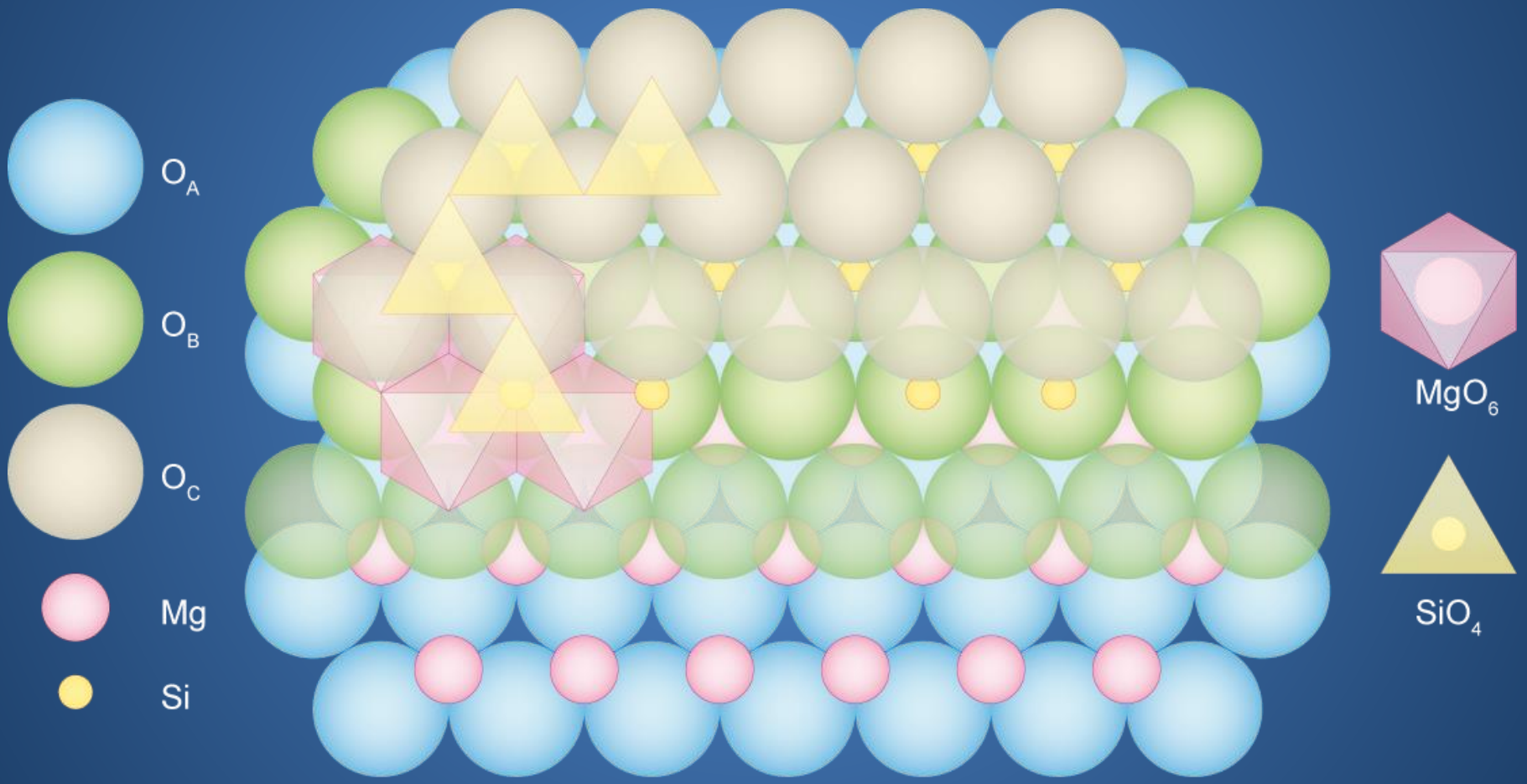
Trioctahedral : 3 Mg^{2+} in the octahedral layer per building unit (talc)
Dioctahedral : 2 Al^{3+} in an octahedral layer per building unit (pyrophyllite)

Phyllosilicates



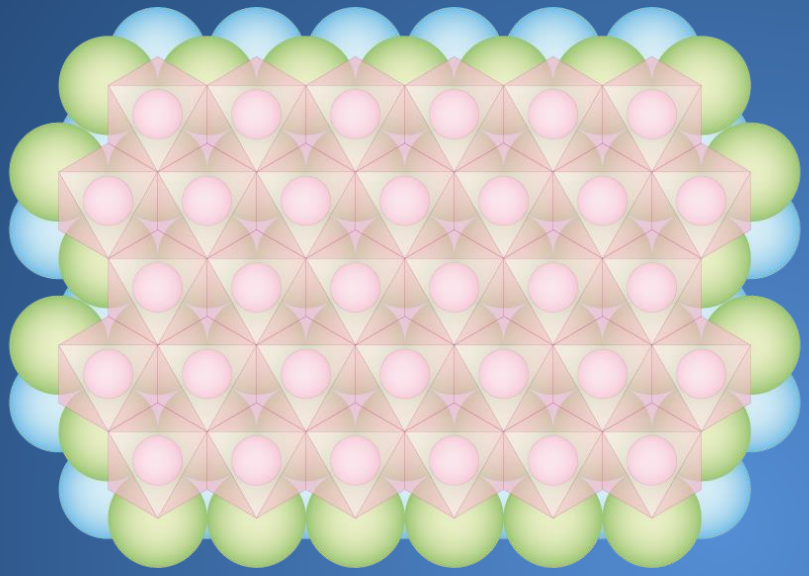
pyrophyllite $Al_2(OH)_2Si_4O_{10}$ (dioctahedral), talc $Mg_3(OH)_2Si_4O_{10}$ (trioctahedral)

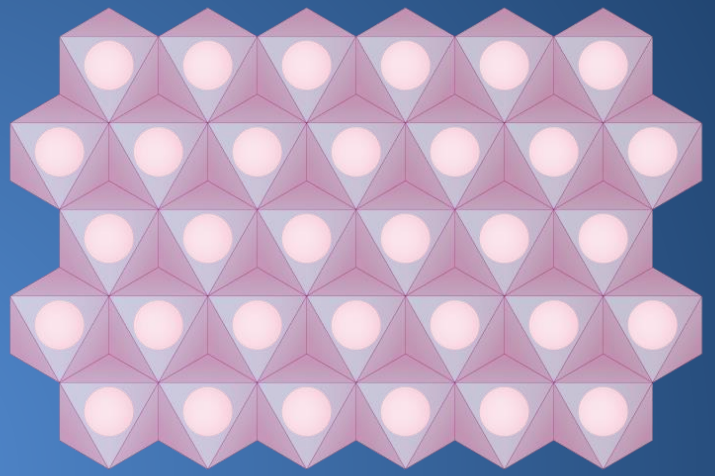
Phyllosilicates – talc $Mg_3(OH)_2Si_4O_{10}$



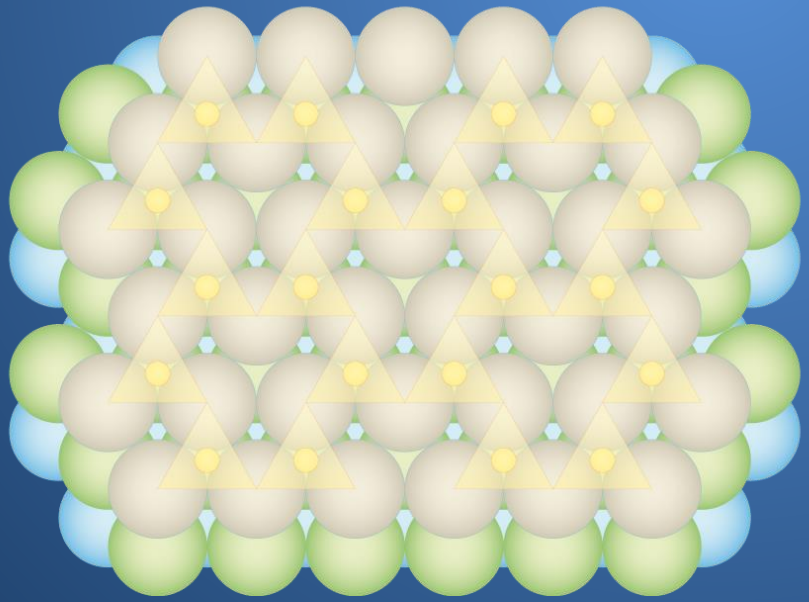
Mezi vrstvou A a B jsou obsazovány jen oktaedrické dutiny (Mg),
mezi vrstvou B a C pouze tetraedrické dutiny (Si).

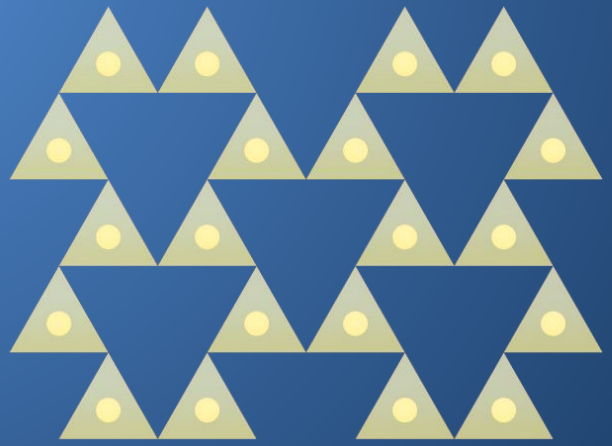
Phyllosilicates – talc $Mg_3(OH)_2Si_4O_{10}$





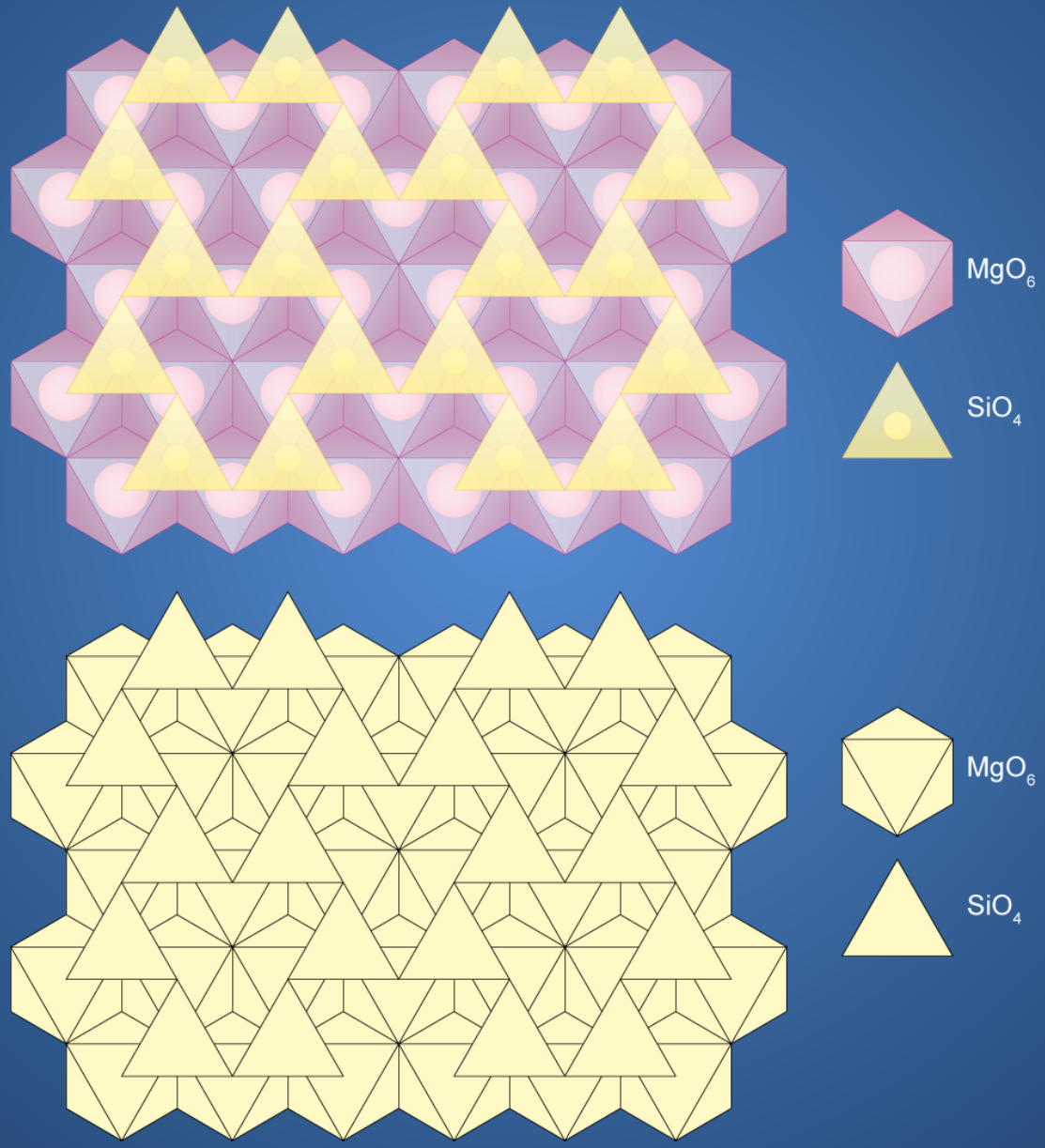
Mezi vrstvou A a B jsou obsazovány všechny oktaedrické dutiny (Mg).



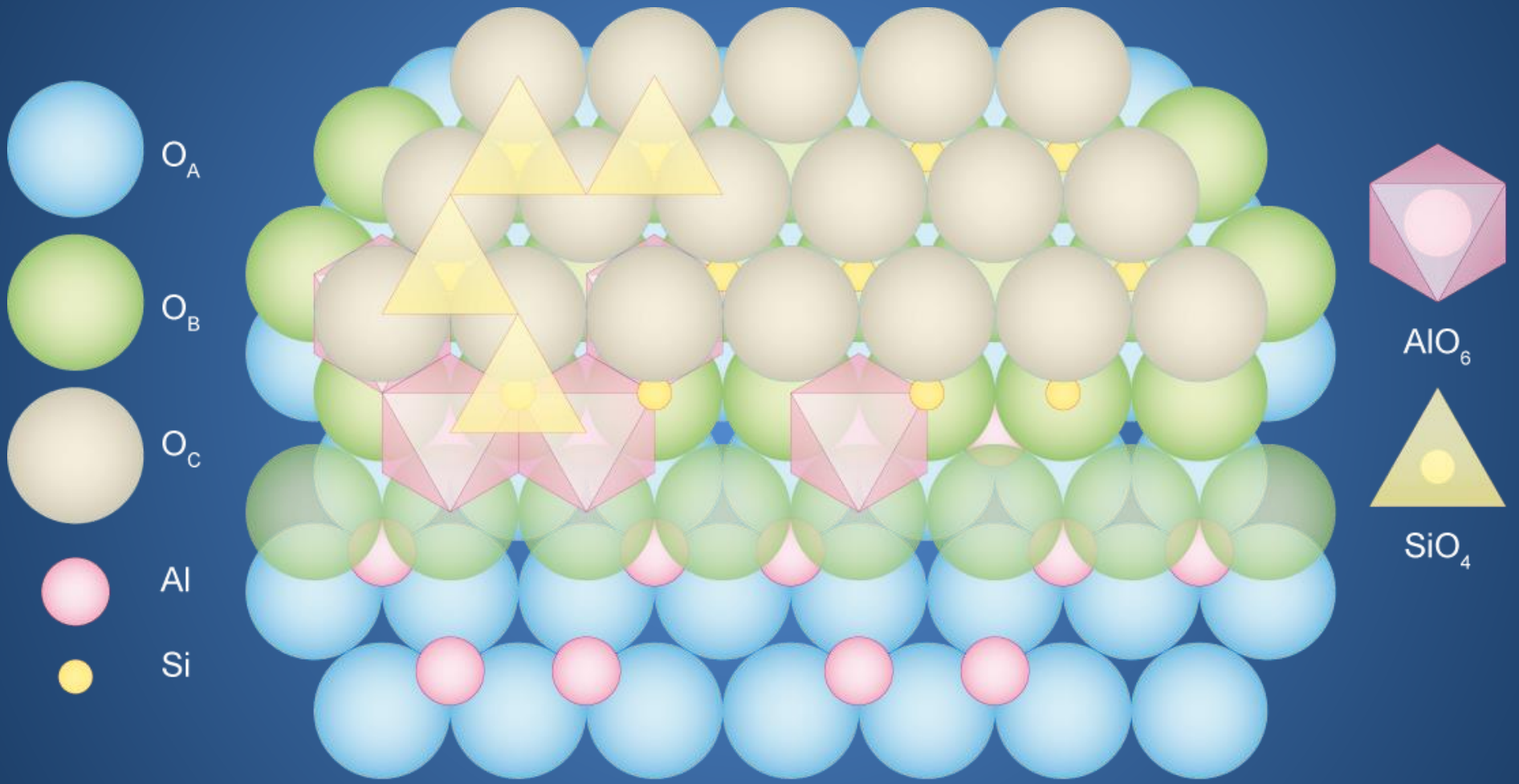


Mezi vrstvou B a C jsou obsazovány pouze tetraedrické dutiny (Si).

Phyllosilicates – talc $Mg_3(OH)_2Si_4O_{10}$

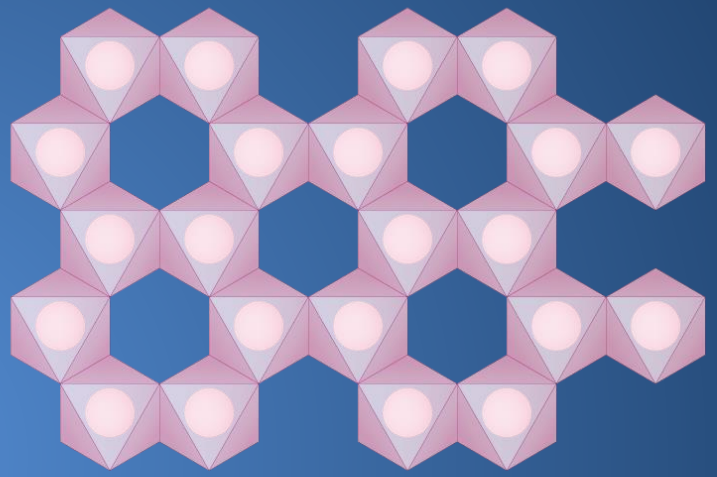


Phyllosilicates – pyrophyllite $Al_2(OH)_2Si_4O_{10}$

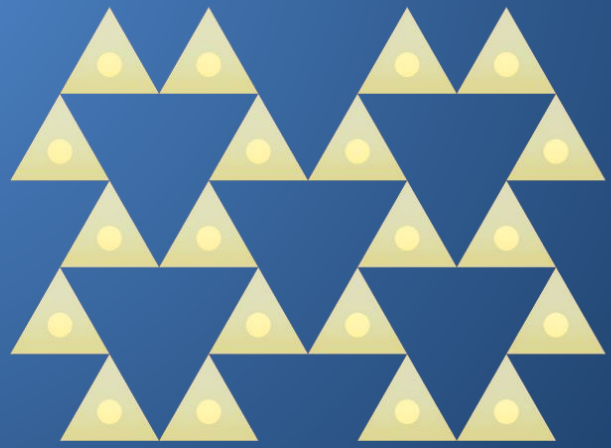


Mezi vrstvou A a B jsou obsazeny 2/3 oktaedrických dutin (Al),
mezi vrstvou B a C jsou obsazovány pouze tetraedrické dutiny (Si).

Phyllosilicates – pyrophyllite $Al_2(OH)_2Si_4O_{10}$

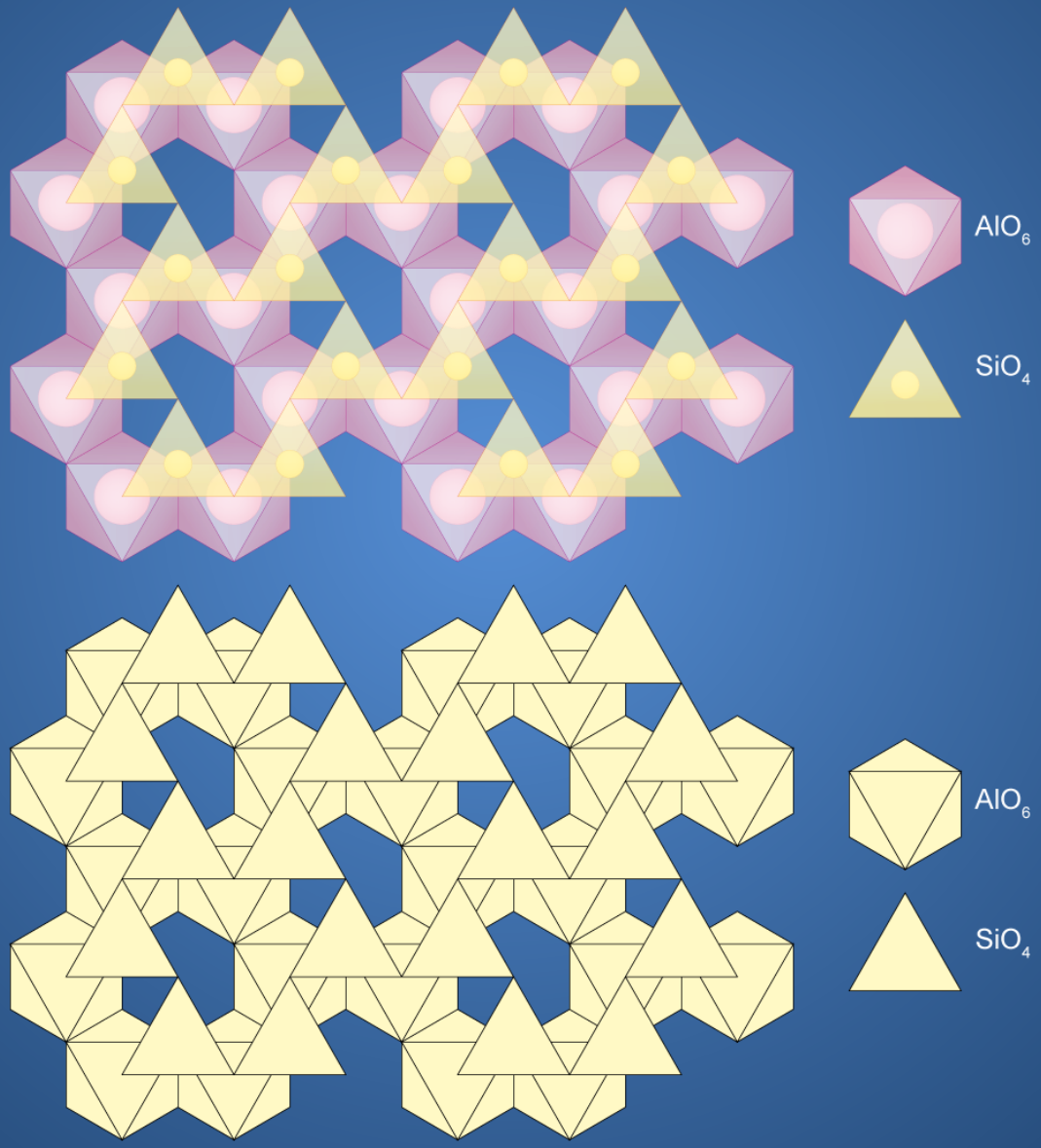


Mezi vrstvou A a B jsou obsazeny 2/3 oktaedrických dutin (Al), jedná se pak o dioktaedrické fylosilikáty.



Mezi vrstvou B a C jsou obsazovány pouze tetraedrické dutiny (Si).

Phyllosilicates – pyrophyllite $Al_2(OH)_2Si_4O_{10}$



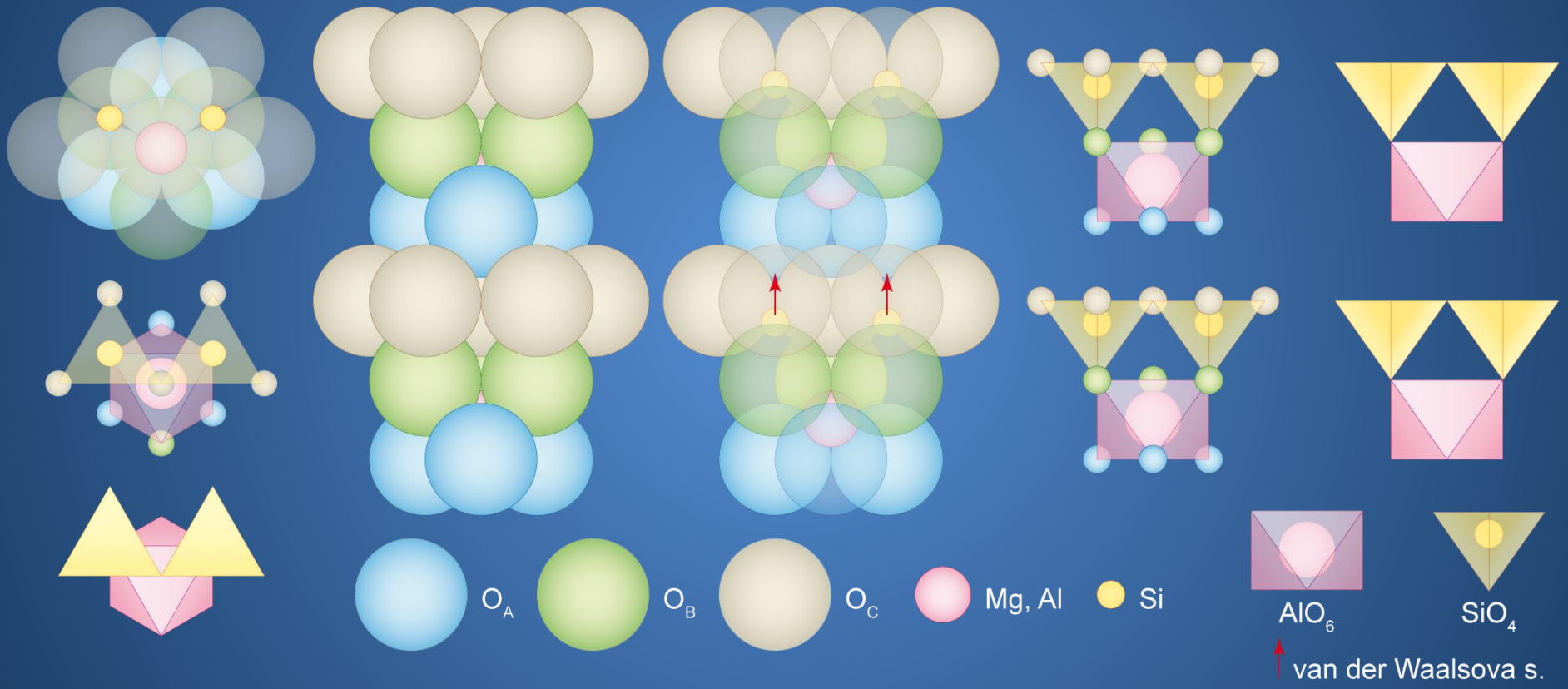
Mica

- Derived from pyrophyllite by replacing one silicon with aluminum
  - One free negative charge in the structure
  - The need for cations in the interlayer – the weakest point of the mineral (that's why they are layered)
  - Typically K^+
  - $Al_2Si_4O_{10}(OH)_2$ -> $KAl_2(Si_3Al)O_{10}(OH)_2$ (muscovite)

1:1 Phyllosilicates

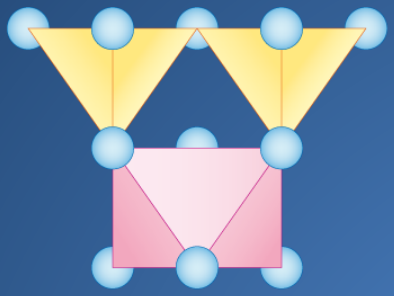
- One octahedral and one tetrahedral sheet is repeated
- **Trioctahedral** – 3 Mg^{2+} in the octahedral layer per structural unit (serpentines)
- **Dioctahedral** – 2 Al^{3+} in an octahedral layer per structural unit (kaolins)

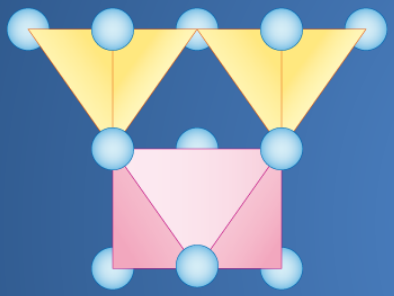
Phyllosilicates



kaolinite $Al_4(OH)_8Si_4O_{10}$ (dioctahedral), serpentine $Mg_6(OH)_8Si_4O_{10}$ (trioctahedral)

Phyllosilicates

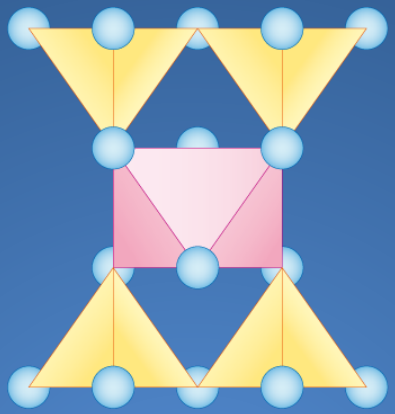


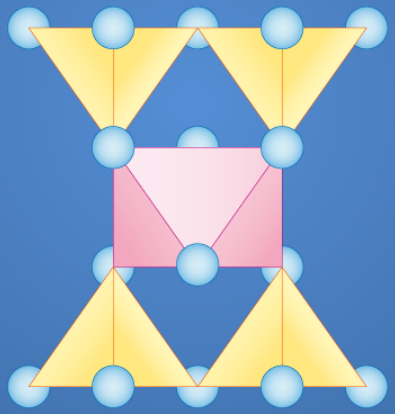


kaolinit $Al_4(OH)_8Si_4O_{10}$ (dioktaedrický)
serpentin $Mg_6(OH)_8Si_4O_{10}$ (trioktaedrický)

T

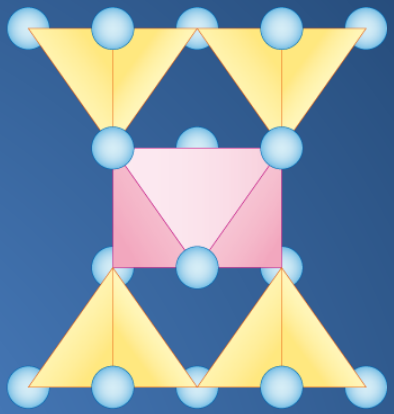
O

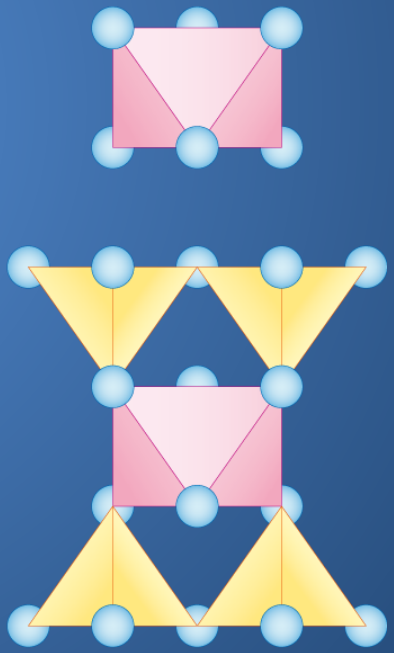




pyrofilit $Al_2(OH)_2Si_4O_{10}$ (dioktaedrický)
mastek $Mg_3(OH)_2Si_4O_{10}$ (trioktaedrický)

muskovit $NaAl_2(OH)_2(Si_3Al)O_{10}$ (dioktaedrický)
flogopit $KMg_3(OH)_2(Si_3Al)O_{10}$ (trioktaedrický)





montmorillonit $(Na, Ca)_x(Al, Mg)_2(OH)_2Si_4O_{10} \times n\,H_2O$ (dioktaedrický)
vermiculit $(Mg, Fe, Al)_3(OH)_2(Si, Al)_4O_{10} \times 4\,H_2O$ (trioktaedrický)

chlorit $(Mg, Fe, Al)_6(OH)_8(Si, Al)_4O_{10}$

T : O = 1 : 1

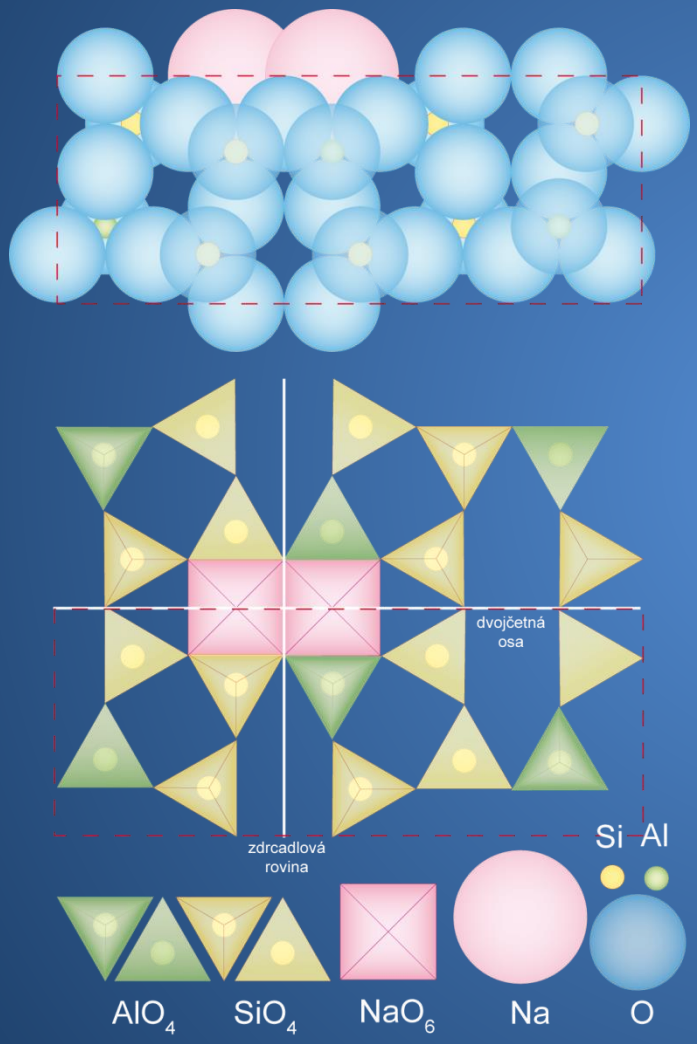
T : O = 2 : 1

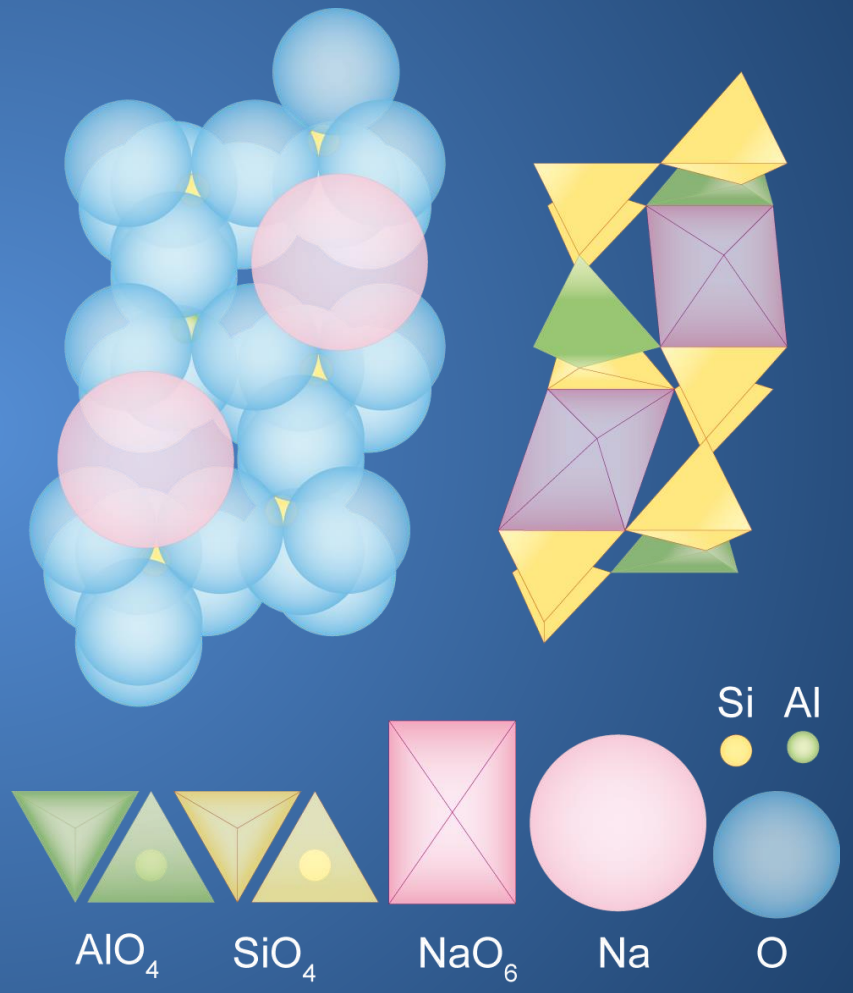
T : O = 2 : 1 : 1

Tectosilicates

- Tetrahedra share all oxygens – each oxygen is shared by two tetrahedra.
- Crystal volume is determined entirely by covalent bonding and not by ion deposition.
  - Poor cleavage.
- The structure contains large spaces and channels through which cations and whole molecules can diffuse.
- The basic structure is SiO_2.
- When silicon is replaced by aluminum (Al^{3+}), relatively large ions (Na^{+}, K^{+}, Ba^{2+}) can enter the structure – feldspars are formed.

Tectosilicates





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Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie

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