Amphiboles

Amphibology (from the Greek *amphibolia*) is an ambiguous grammatical structure in a sentence

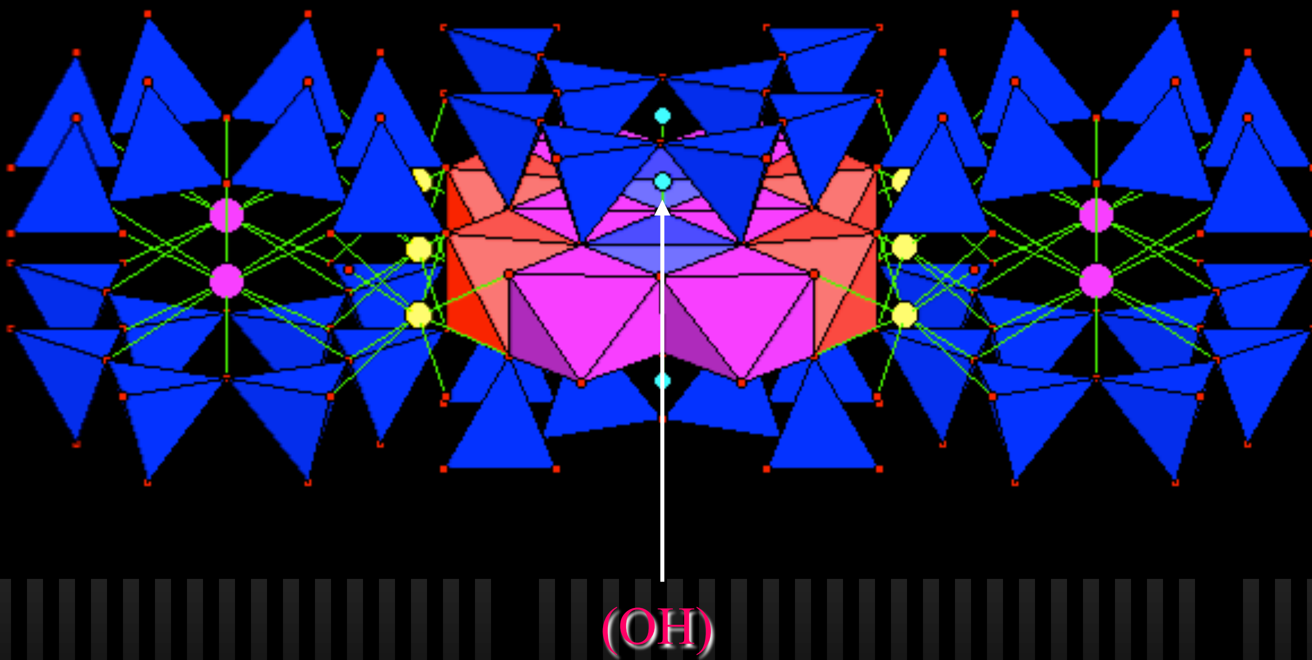
Some examples:

I once shot an elephant in my pajamas

Why are amphiboles so ambiguous?

Inosilicates: double chains- **amphiboles**
Perspective view of crystal structure

Hornblende: □(Ca, Na)$_{2\text{-}3}$ (Mg, Fe, Al)$_5$ [(Si,Al)$_8$O$_{22}$] (OH)$_2$



M1-M3 are small sites

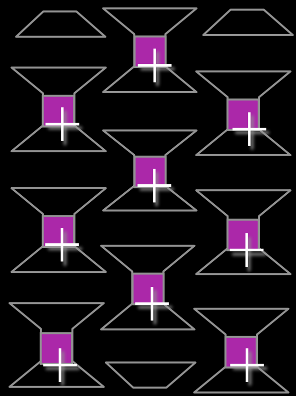
M4 is larger (Ca)

A-site is really big

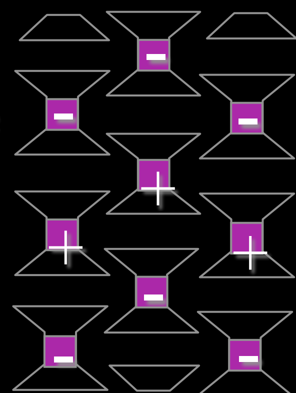
Variety of sites → great chemical range

dark blue = Si, Al purple = M1 pink = M2
light blue = M3 (all Mg, Fe) yellow ball = M4 (Ca) purple ball = A (Na)
little turquoise ball = H

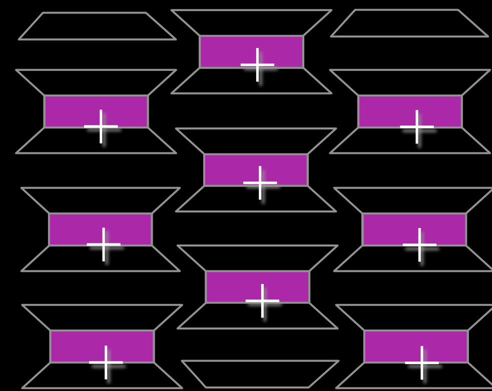
Inosilicates



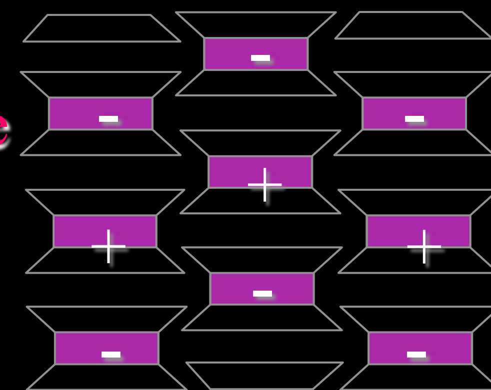
Clinopyroxene



Orthopyroxene



Clinoamphibole

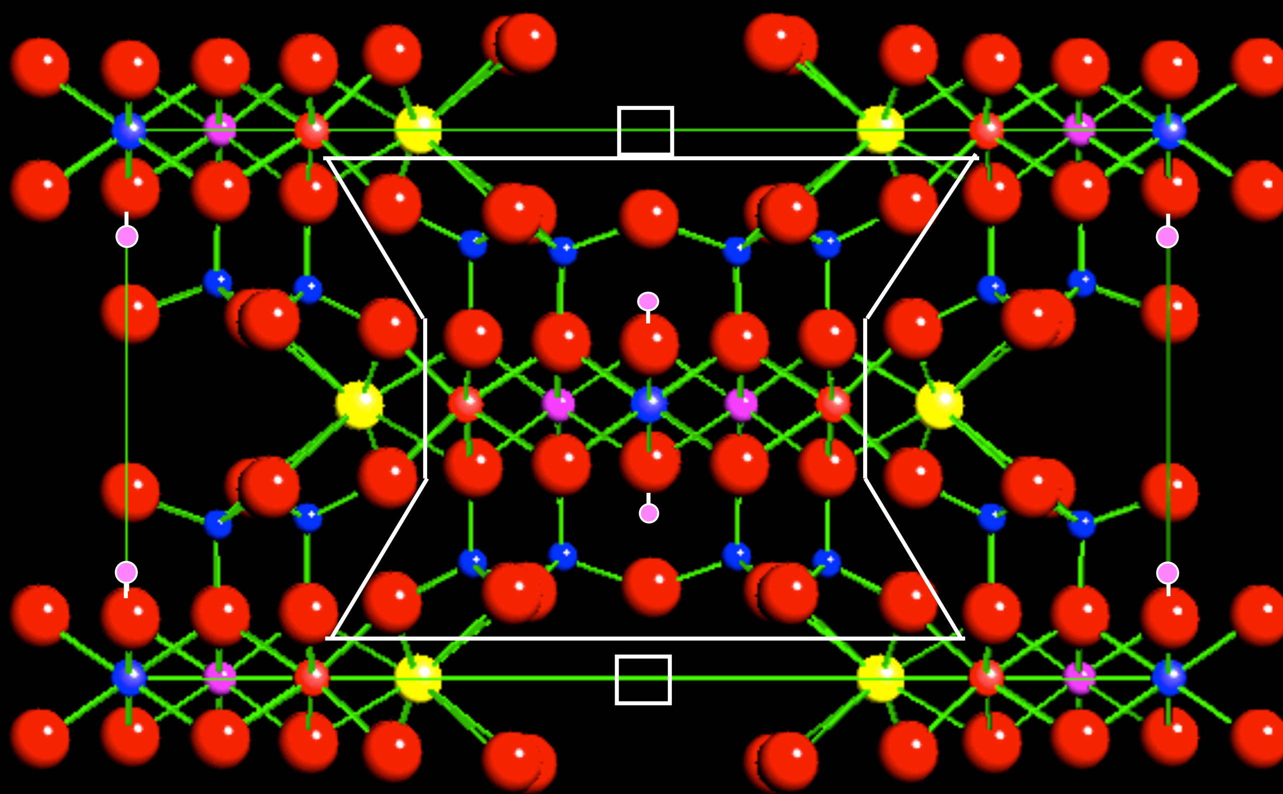


Orthoamphibole

Pyroxenes and amphiboles are very similar:

- Both have chains of SiO_4 tetrahedra
- The chains are connected into stylized I-beams by M octahedra
- High-Ca monoclinic forms have all the T-O-T offsets in the same direction
- Low-Ca orthorhombic forms have alternating (+) and (-) offsets

Main difference between PX and Amph

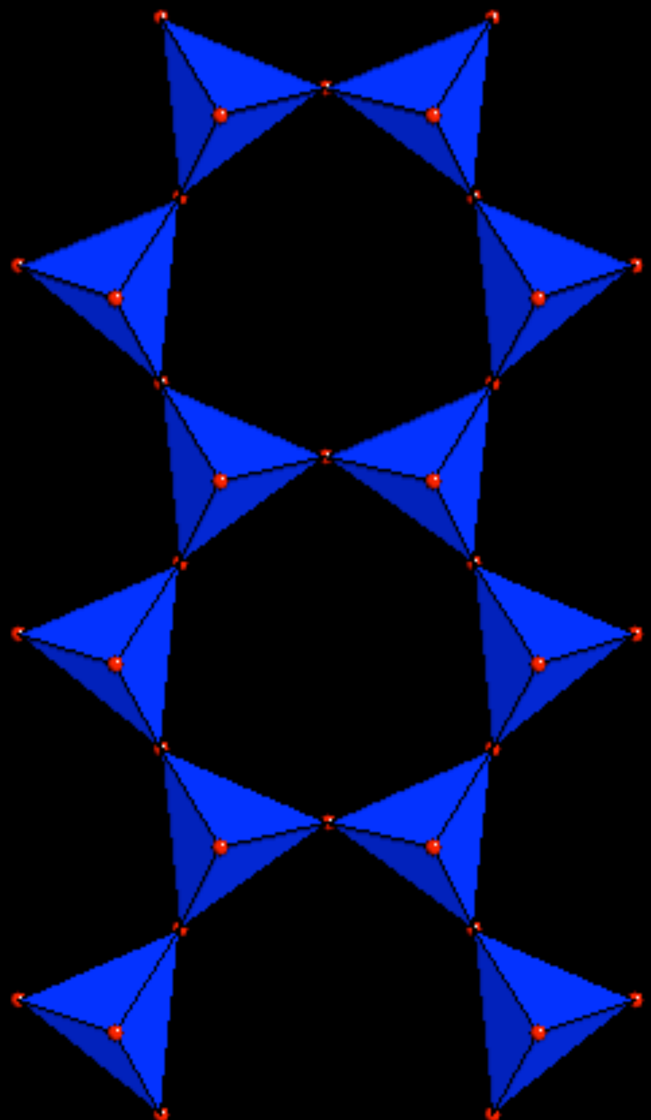


Double chains leads to a big hole and more M sites
More varied, and larger cations can fit
OH site

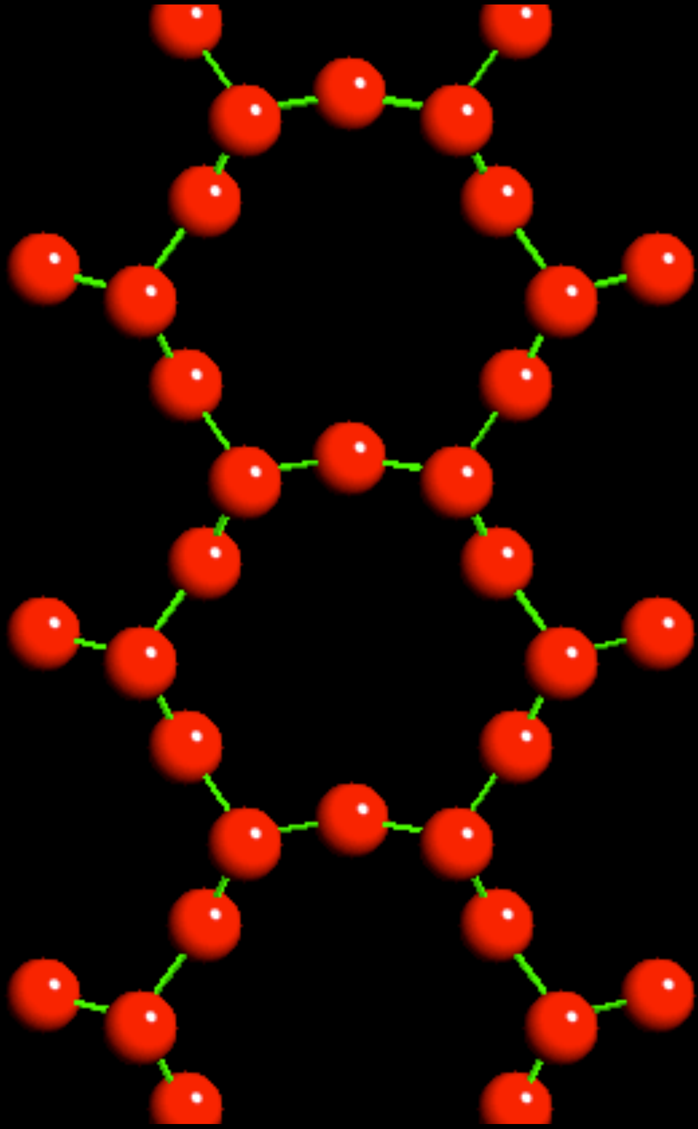
Inosilicates: Double chain structures: **Amphiboles**

Compositional unit: $(Si_4O_{11})^{6-}$ or $(Si_8O_{22})^{12-}$

Polyhedral model



"Ball and stick" model



Amphibole Compositions

General formula:

$W_{0-1} X_2 Y_5 [Z_8O_{22}] (OH, F, Cl)_2$

W = **Na** K (this site is vacant in many amphiboles, called the 'A' site)
X = **Ca** **Na** Mg Fe^{2+} Mn (called the M4 site)
Y = **Mg** **Fe^{2+}** Mn **Al** Fe^{3+} Ti (called the M1, M2 and M3 sites)
Z = **Si** **Al** (the T site)

The variety of sites and cations → a wide chemical range, many end members

Example: □ $Ca_2Mg_5Si_8O_{22}(OH)_2$ Tremolite

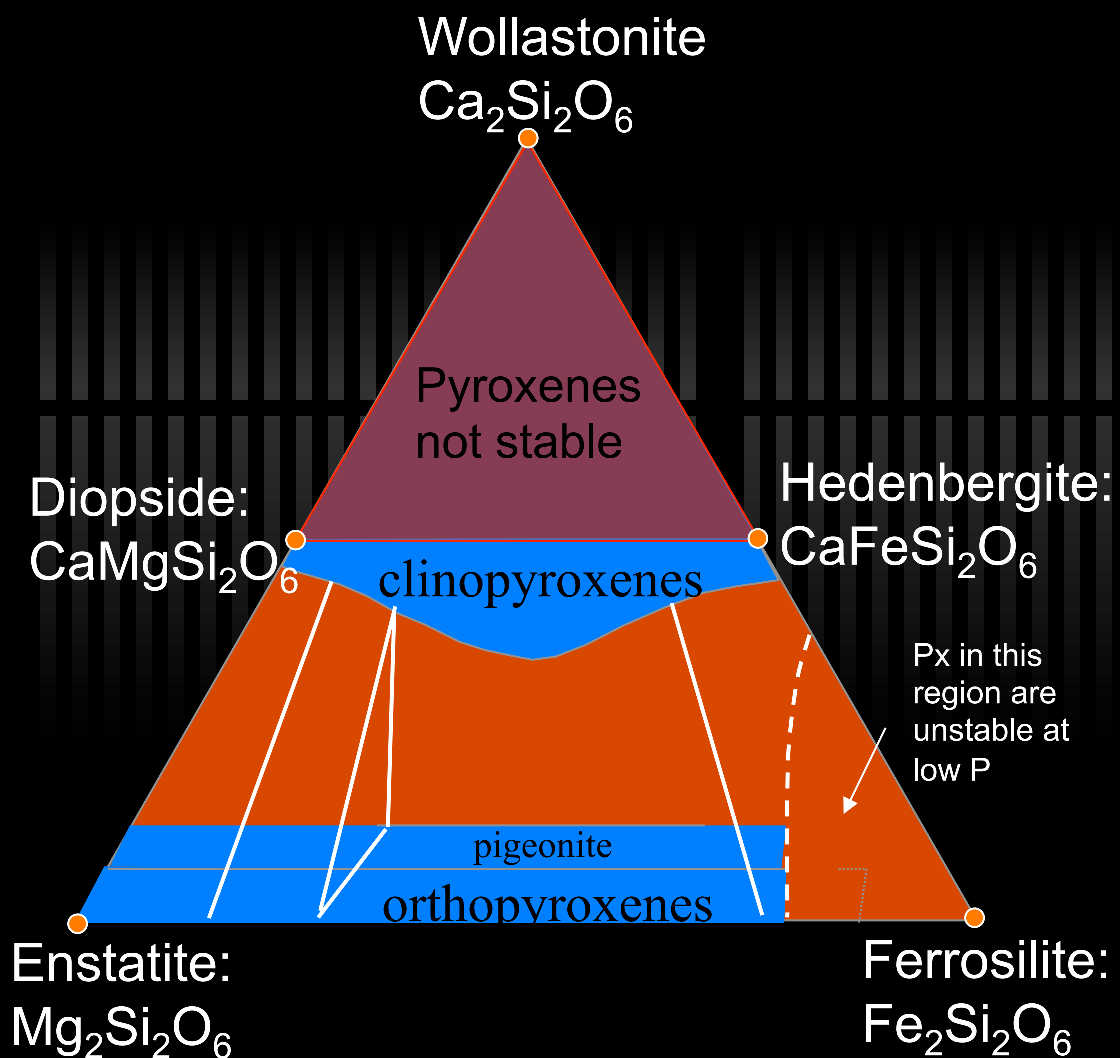
Substitutions:

$Fe^{(M123)} \Leftrightarrow Mg^{(M123)}$
$Na^{(M4)}Al^{(M123)} \Leftrightarrow Ca^{(M4)}Mg^{(M123)}$
$Na^{(M4)}\ Si^{(T)} \Leftrightarrow Ca^{(M4)}\ Al^{(T)}$
$Al^{(M123)}\ Al^{(T)} \Leftrightarrow Mg^{(M123)}Si^{(T)}$
$(OH)^- \Leftrightarrow F^- \Leftrightarrow Cl^-$

Pyroxene Composition

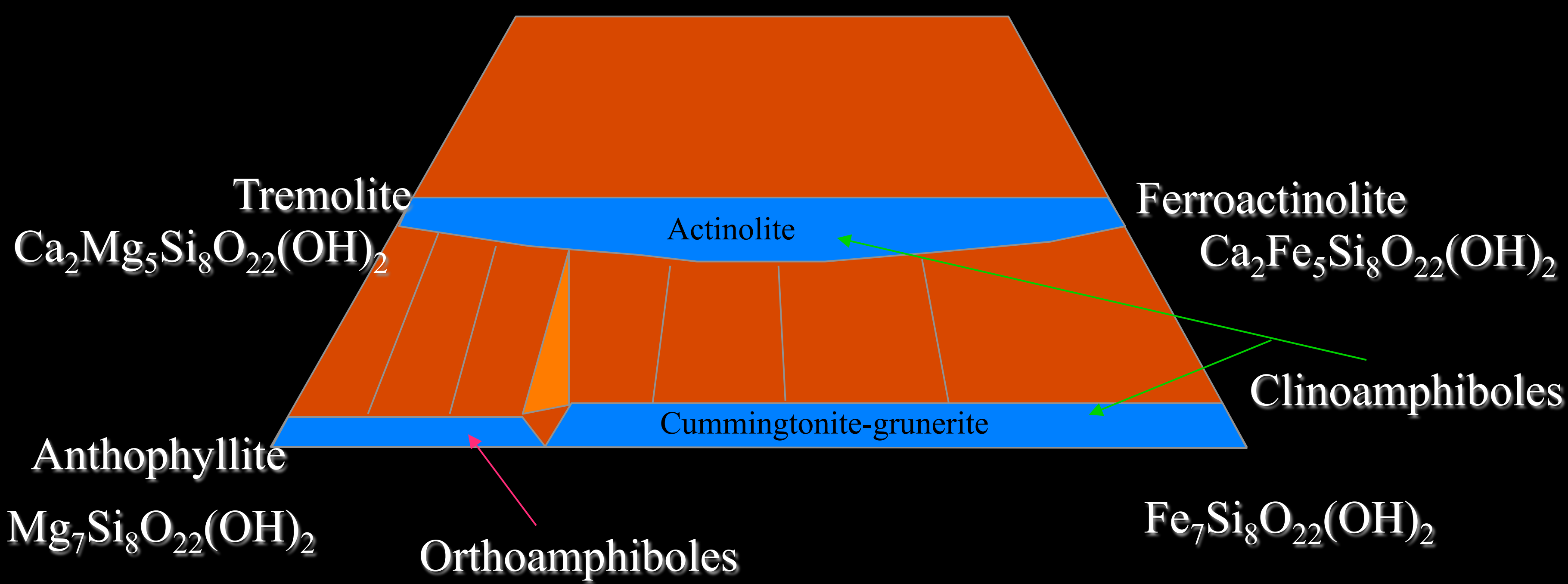
The pyroxene quadrilateral and opx-cpx solvus

Coexisting opx + cpx in many rocks (pigeonite only in volcanics)

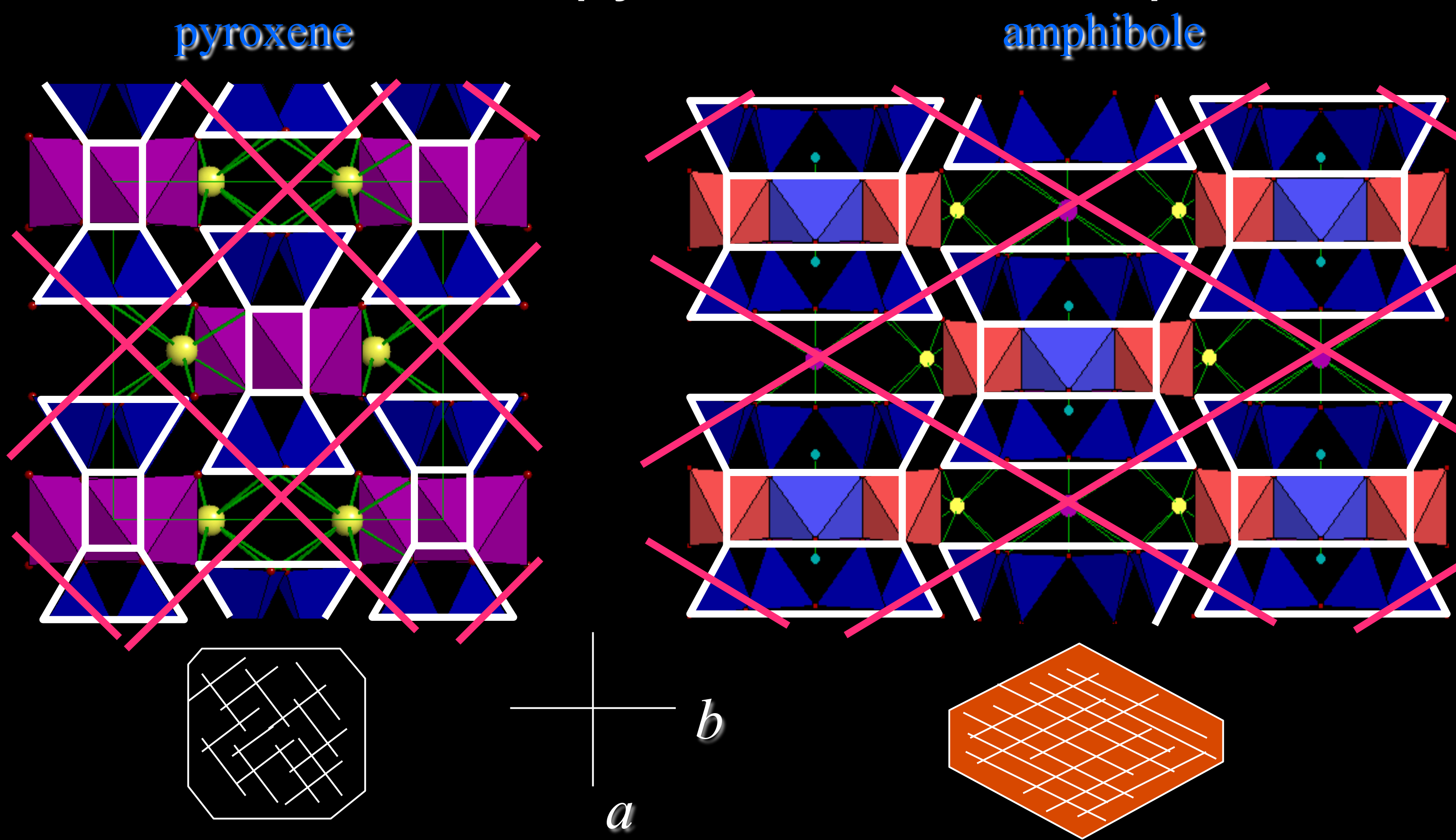


Amphibole Chemistry

Ca-Mg-Fe Amphibole "quadrilateral"



How to differentiate pyroxenes from amphiboles?



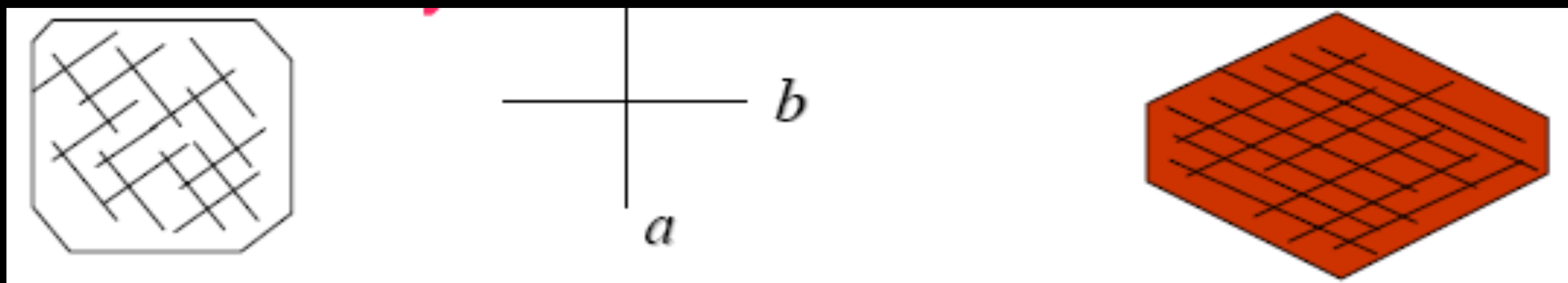
Cleavage angles can be interpreted in terms of weak bonds in M2 sites (around I-beams instead of through them)

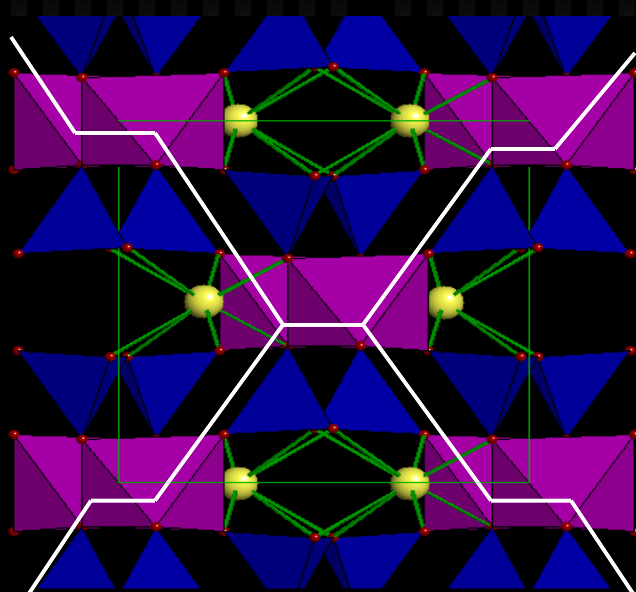
Narrow single-chain I-beams → 90º cleavages in pyroxenes while wider double-chain I-beams → 60-120º cleavages in amphiboles

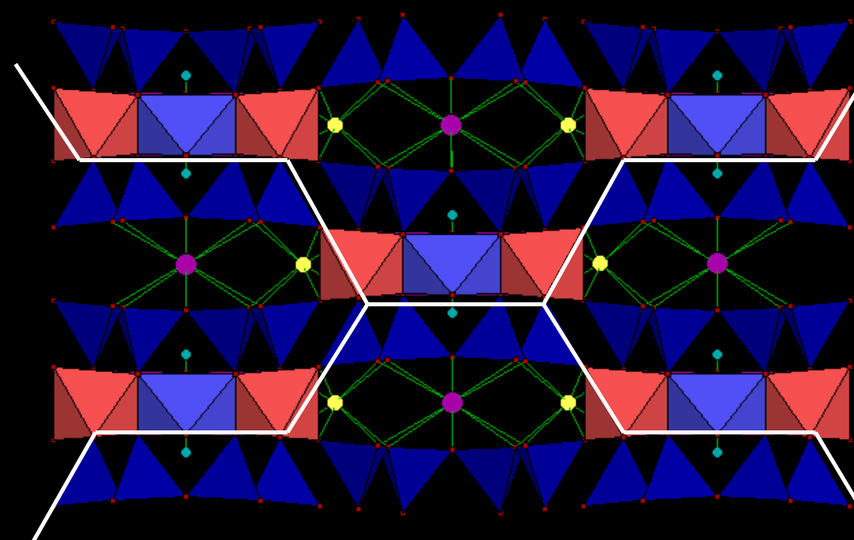
Cleavages in inosilicates

Pyroxenes:
2 cleavages at 88/92º

Amphiboles:
2 cleavages at 56/124







Amphibole Compositions (cont.)

Hornblende (the commonest amphibole) has Al in the tetrahedral site (Al can replace up to 2 of the 8 Si ions in the tetrahedral site)

Petrologists traditionally use the term "hornblende" as a catch-all term for practically any dark-colored amphibole. Compare with **tremolite**

□$Ca_2Mg_5Si_8O_{22}(OH)_2$ Tremolite

$NaCa_2 (Mg, Fe)_5 [AlSi_7] O_{22} (OH)_2$ Edenite--Ferroedenite (A site contains Na)

□$Ca_2 [(Mg, Fe)_3Al_2] [Al_2Si_6] O_{22} (OH)_2$ Tschermakite—Ferrotschermakite

$NaCa_2 [(Mg, Fe)_4Al)] [Al_2Si_6] O_{22} (OH)_2$ Pargasite--Ferropargasite

<u>Sodic amphiboles</u> (rich in alkali elements)

□$Ca_2Mg_5Si_8O_{22}(OH)_2$ Tremolite

Glaucophane: □Na_2 [Mg_3 Al_2] [Si_8O_{22}] $(OH)_2$

Riebeckite: □Na_2 [$Fe^{2+}{}_3$ $Fe^{3+}{}_2$] [Si_8O_{22}] $(OH)_2$

Some Fe^{2+} can substitute for Mg^{2+} in glaucophane and some Mg^{2+} can substitute for Fe^{2+} in riebeckite

Sodic amphiboles are commonly deeply colored In shades of blue or purple, and they are often called "blue amphiboles."

Amphibole Occurrences

<u>Hornblende</u> The complex solid solution called hornblende occurs in a wide variety of both igneous and metamorphic rocks, mostly intermediate to silicic.

<u>Glaucophane</u> <u>is a</u> metamorphic mineral and is characteristically formed at high pressure (relatively low T) in subduction-zone metamorphism where oceanic basalts are subducted to great depths. Glaucophane-bearing rocks are commonly called **"blueschist"** because of the abundance of glaucophane.

Riebeckite is rare but occurs in certain types of Na-rich granitic rocks, e.g., granites of the Golden Horn batholith on Hwy 20 contain euhedral riebeckite

Amphibole Occurrences

Tremolite (Ca-Mg) occurs in meta-carbonates (limestone/ dolostone protolith)

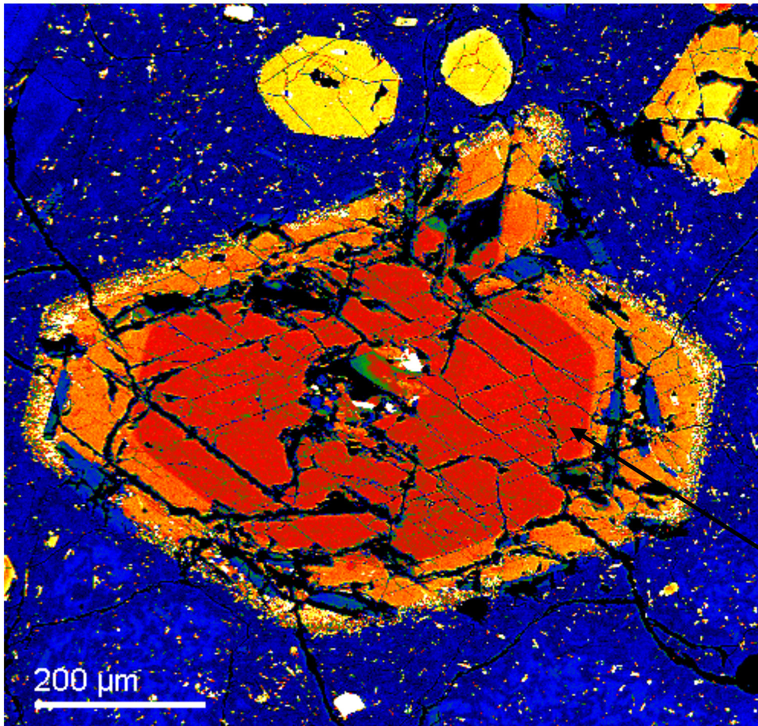
Actinolite occurs in medium-grade metamorphosed basic igneous rocks associated with chlorite and epidote (rocks are called greenstones)

Anthophyllite and **cummingtonite-grunerite** (Ca-free, Mg-Fe-rich amphiboles) are metamorphic and occur in meta-ultrabasic rocks and some meta-sediments. The Fe-rich grunerite occurs in meta-ironstones.

Anthophyllite

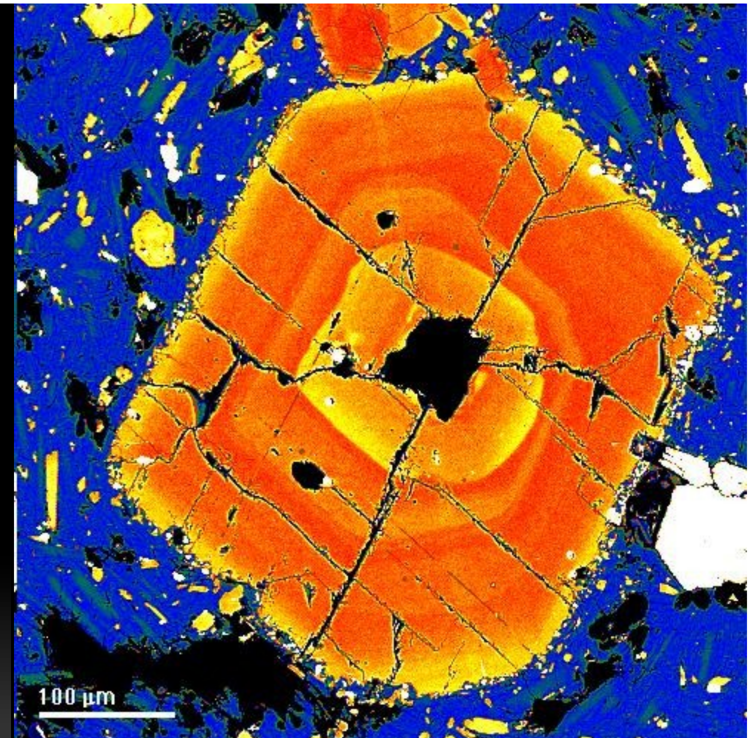
Amphiboles from Mt. Baker

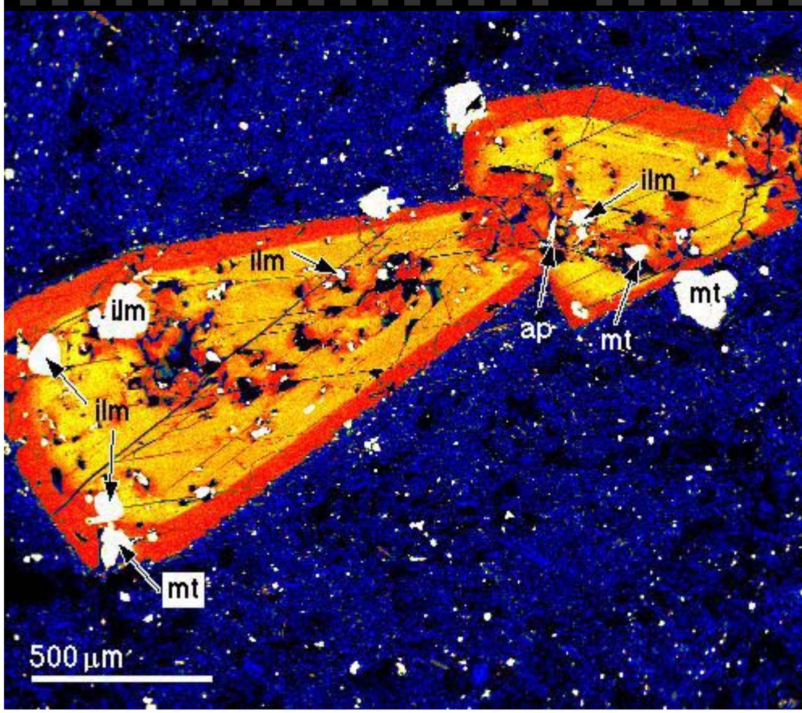
(courtesy of Emily Mullen)



Back-scattered electron (BSE) images of zoned amphiboles

Note cleavages at 56/124º

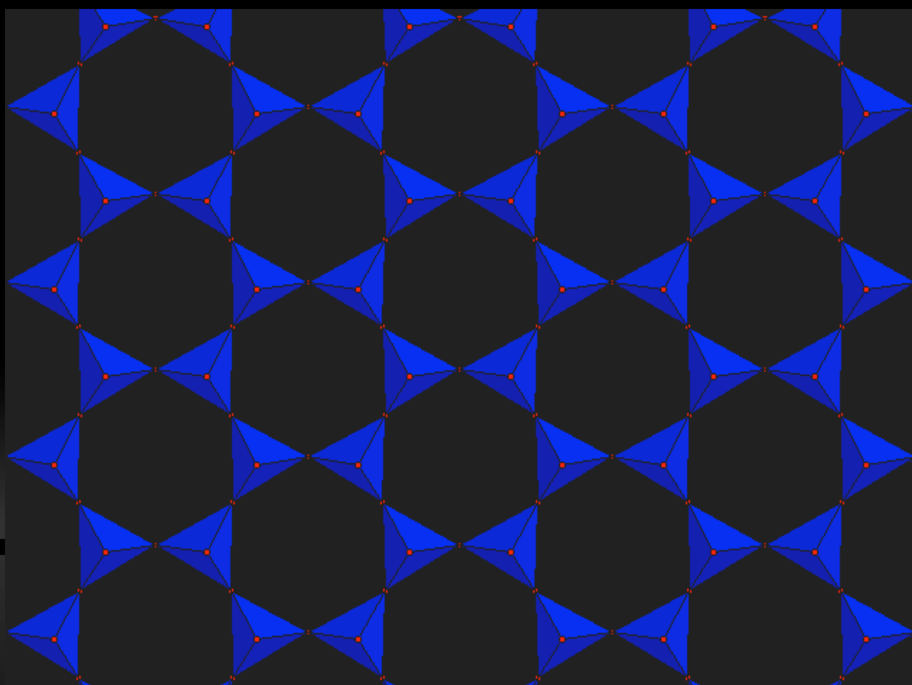




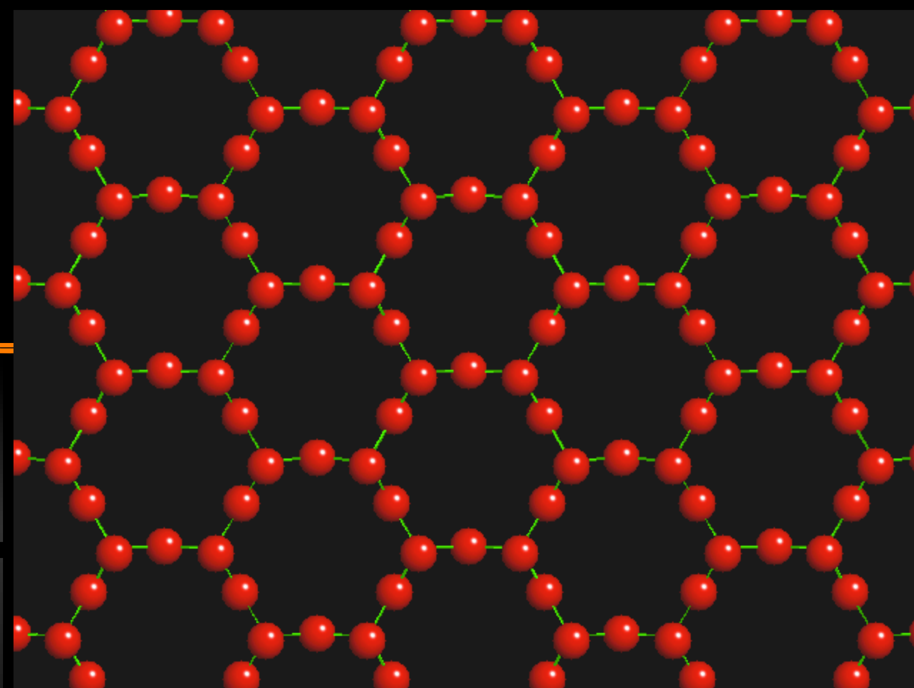
Phyllosilicates

Phyllosilicates

Polyhedral model



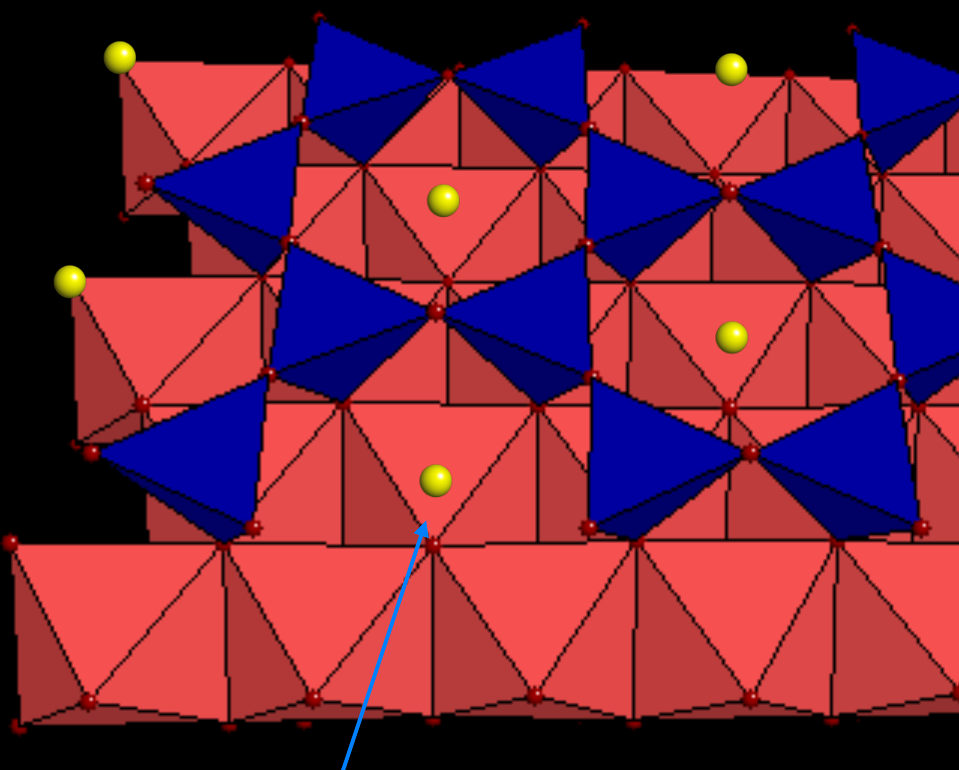
Ball and stick model

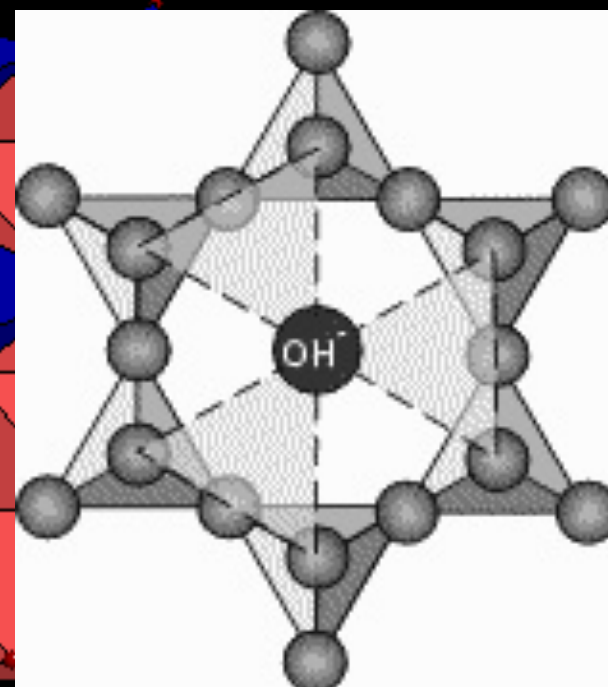


Sheets of tetrahedra extending infinitely in 2 dimensions;
each tetrahedron share 3 of its oxygens:
Basic compositional unit: $[Si_2O_5]^{2-}$ usually written as $[Si_4O_{10}]^{4-}$

Phyllosilicates

- Tetrahedral layers are bonded to octahedral layers (sandwich)
- (OH) pairs are located in center of T rings

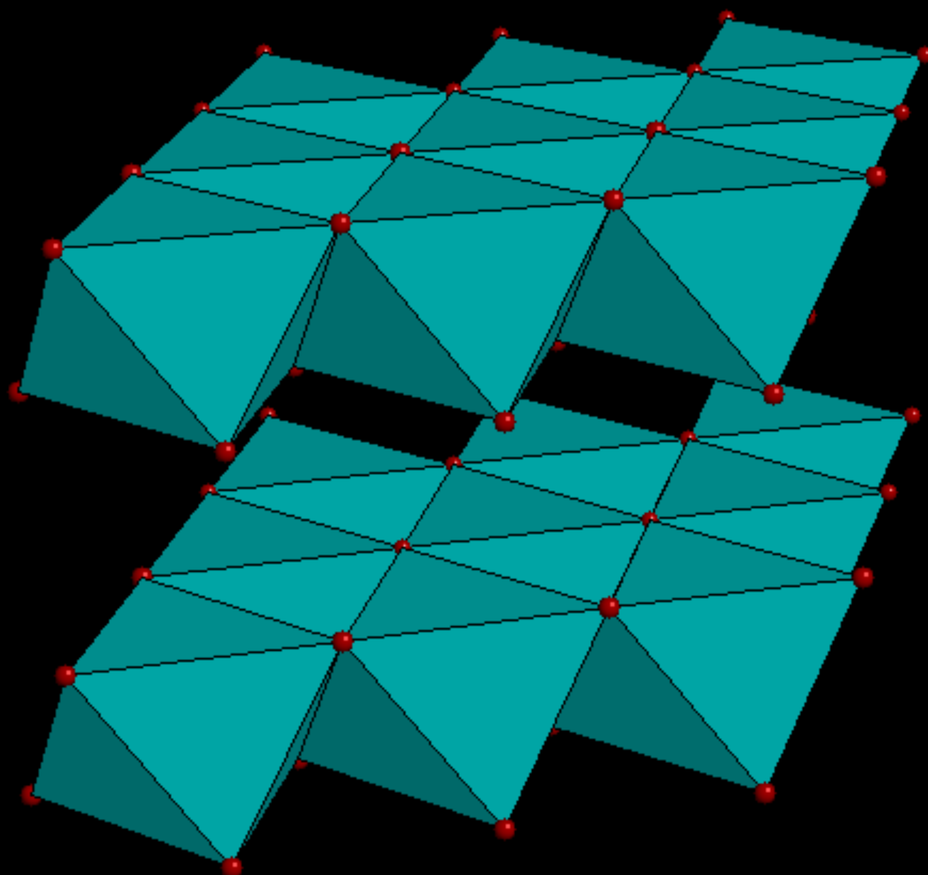




(OH)

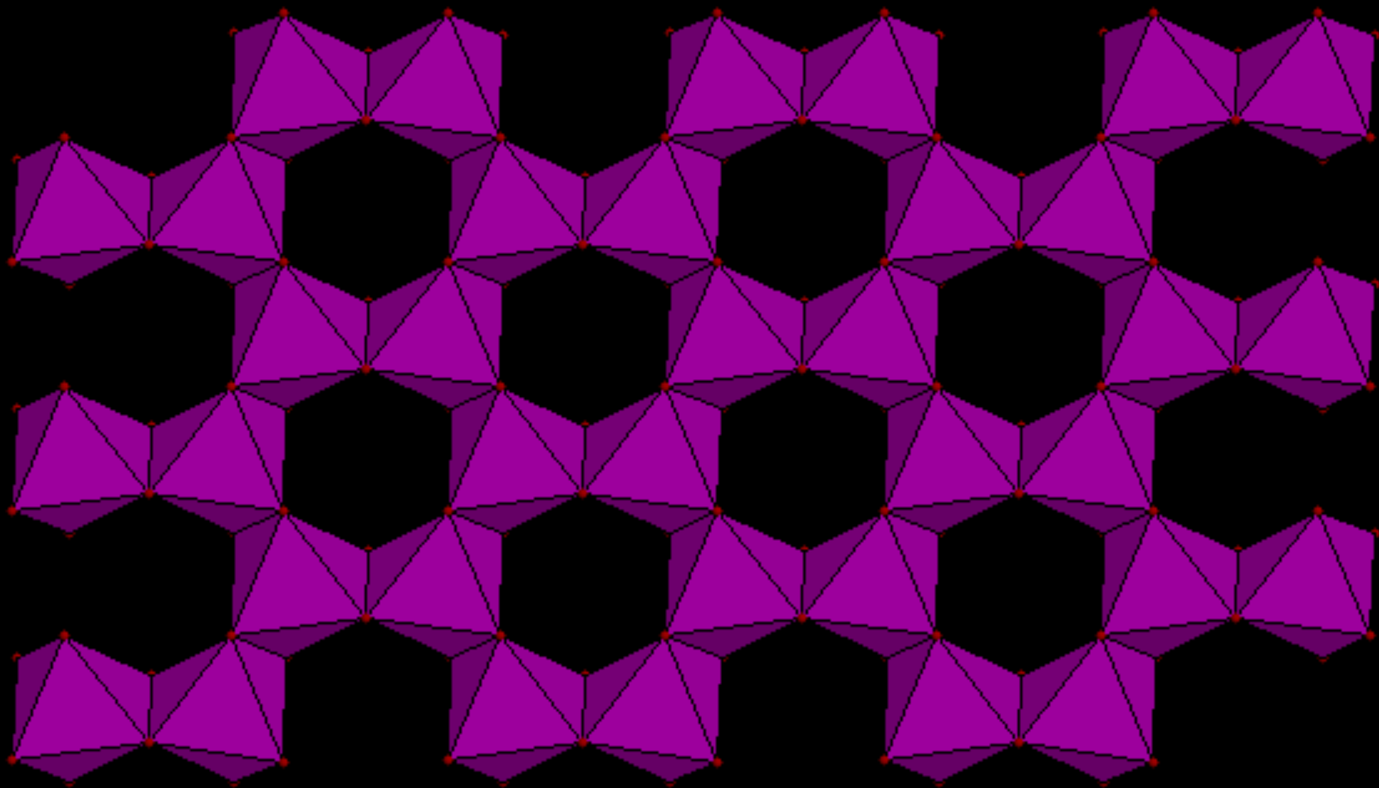
Octahedral layers of **two** types

Type 1 - Brucite layer



- Brucite: $Mg_3(OH)_6$
- Layers of Mg in octahedral coordination (6-fold) with (OH)
- Octahedra share edges
- All octahedra contain Mg

Phyllosilicates type 2- Gibbsite layer



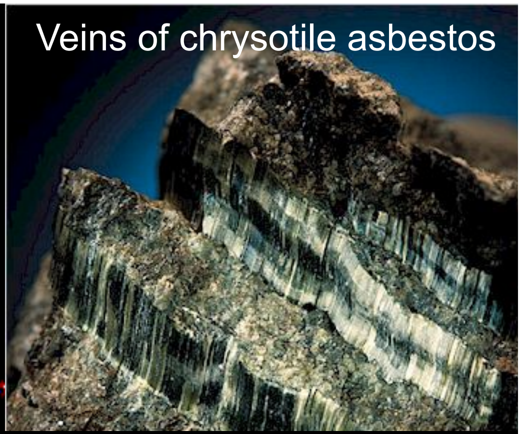
<u>Gibbsite:</u> $Al(OH)_3$ or $Al_2(OH)_6$

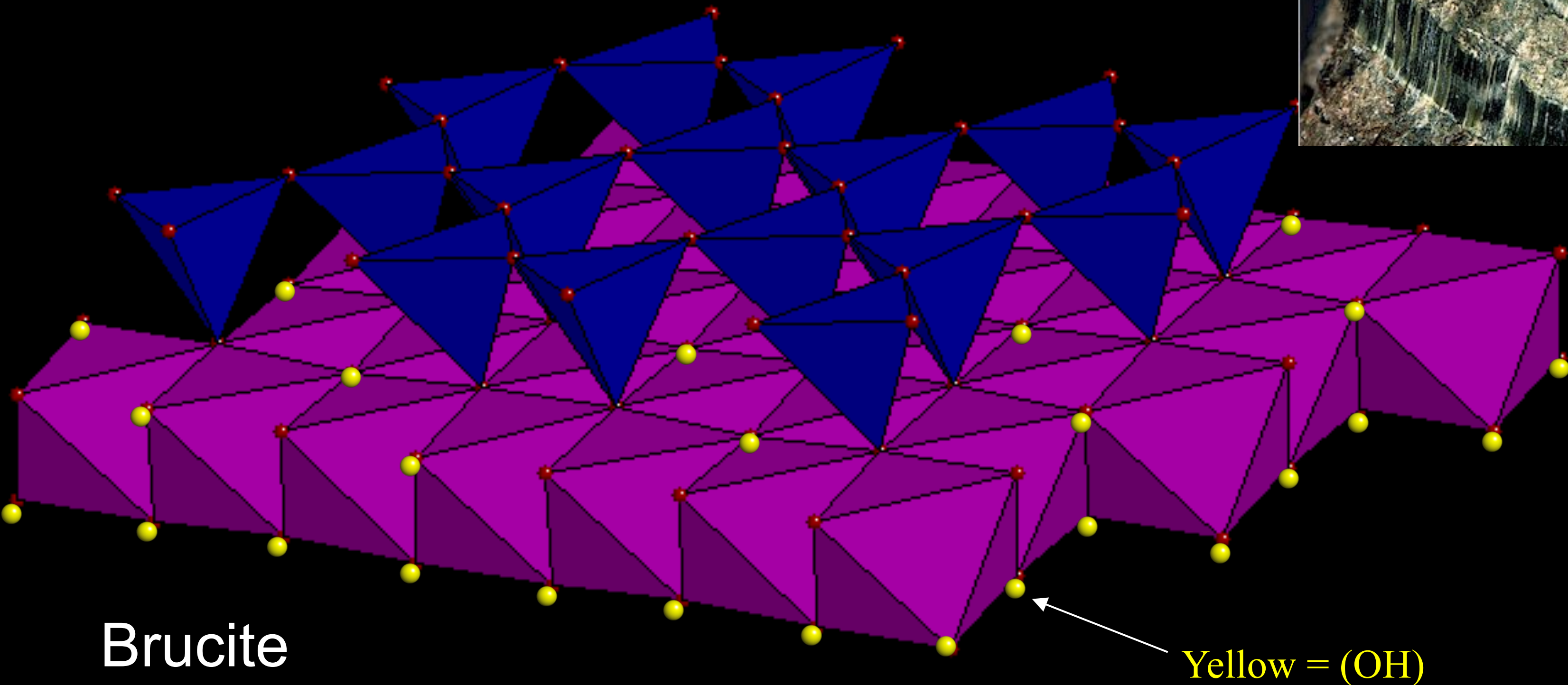
Layers of octahedrally coordinated Al with each Al coordinated to 6 (OH) units

Because Al is trivalent (Al^{3+}) charge balance dictates that only 2/3 of the octahedral sites may be occupied. The vacant sites cause the layer to be somewhat deformed compared to a brucite layer.

Brucite-type layers are called **<u>trioctahedral</u>** and gibbsite-type **<u>dioctahedral</u>**

Phyllosilicates





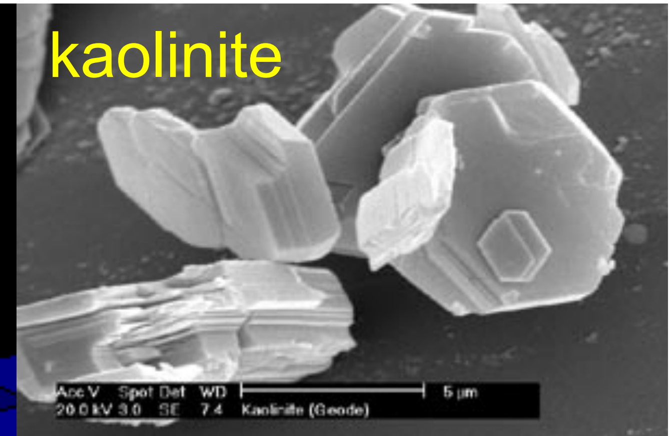
Serpentine: $Mg_3 [Si_2O_5] (OH)_4$: one $Mg_3(OH)_6$ layer and one $(Si_2O_5)^{2-}$ layer

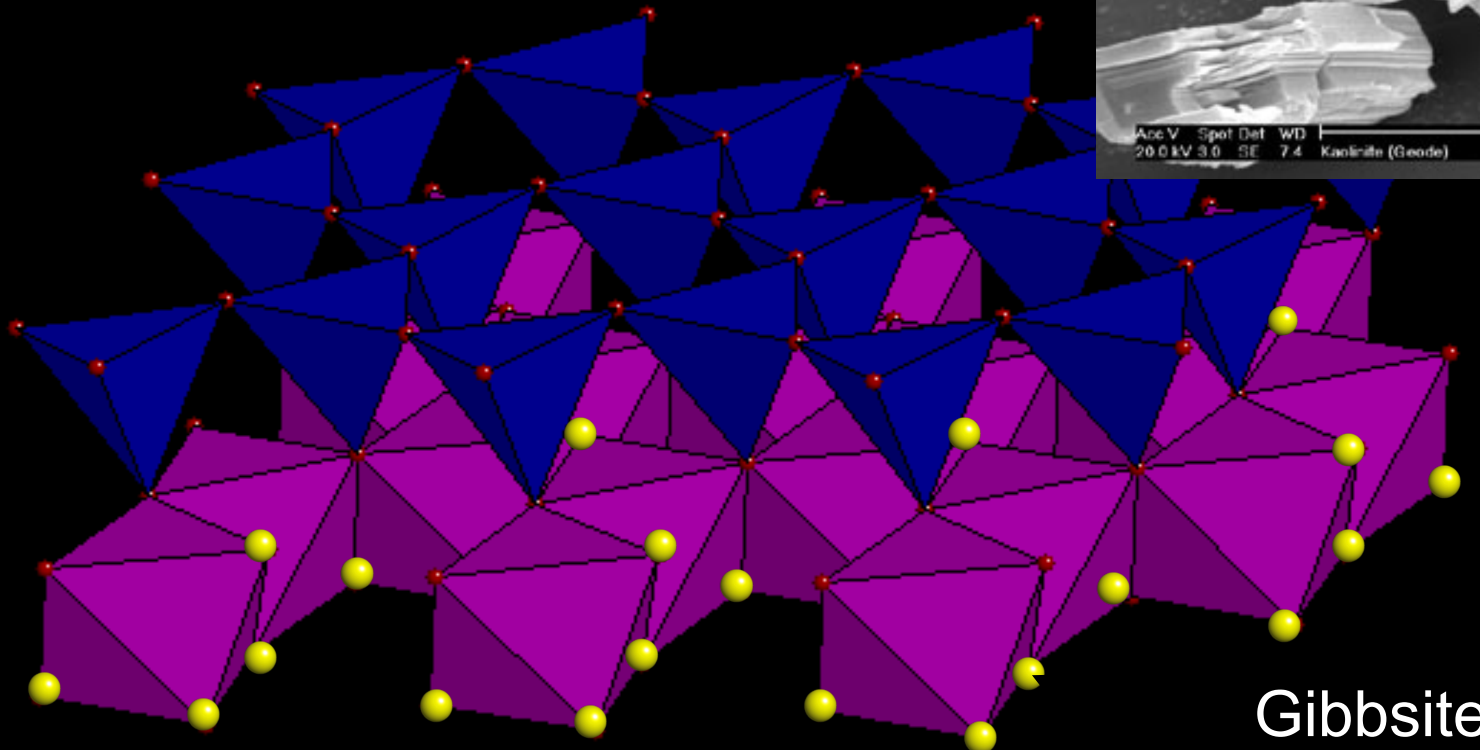
T-layers and **triocathedral** (Mg^{2+}) layers: open faced sandwich

(OH) at center of T-rings and fill base of VI layer

T
O
- vdw
T
O
- vdw
T
O

Phyllosilicates





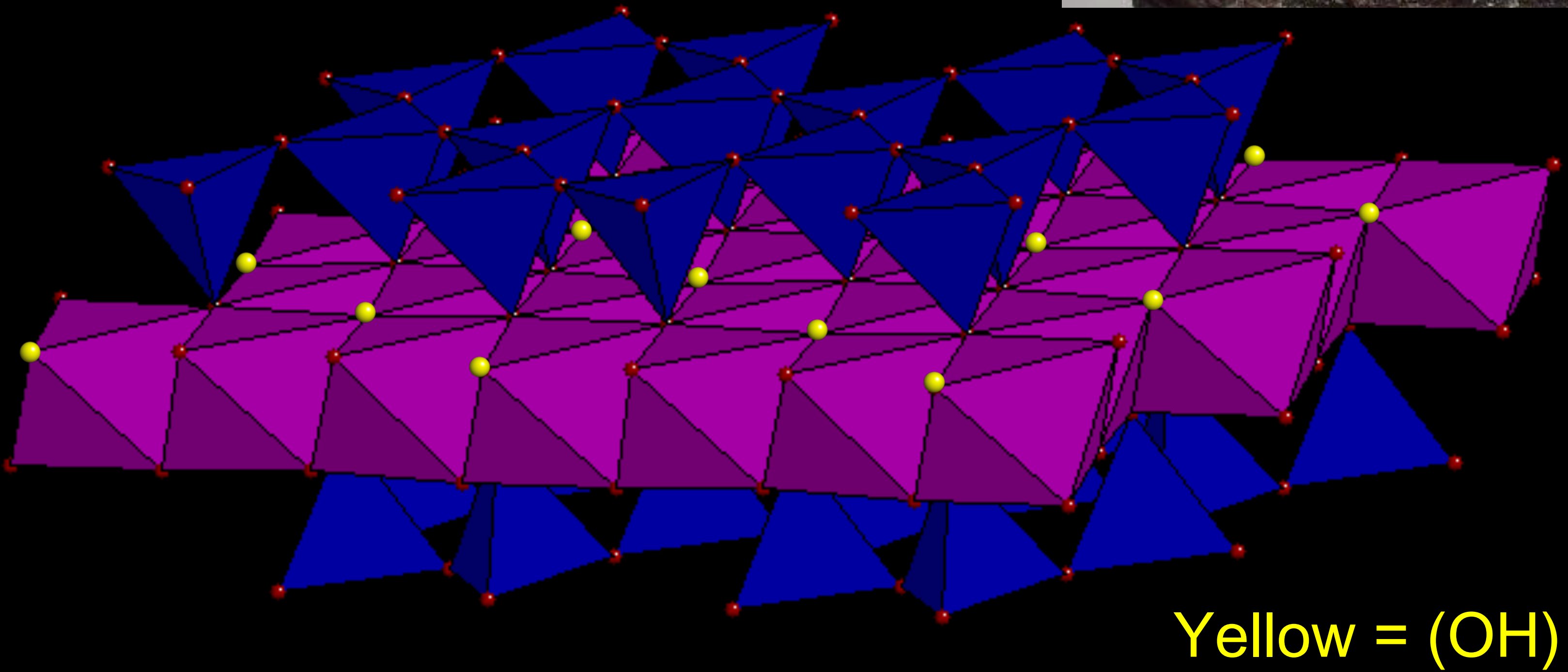
T
O
vdw
T
O
vdw
T
O

Kaolinite: $Al_2\ [Si_2O_5]\ (OH)_4$: one $Al_2(OH)_6$ layer and one $(Si_2O_5)^{2-}$ layer

Stacked tetrahedral layers and dioctahedral (Al^{3+}) layers (open faced sandwich)

(OH) at center of T-rings and fill base of VI layer

Phyllosilicates

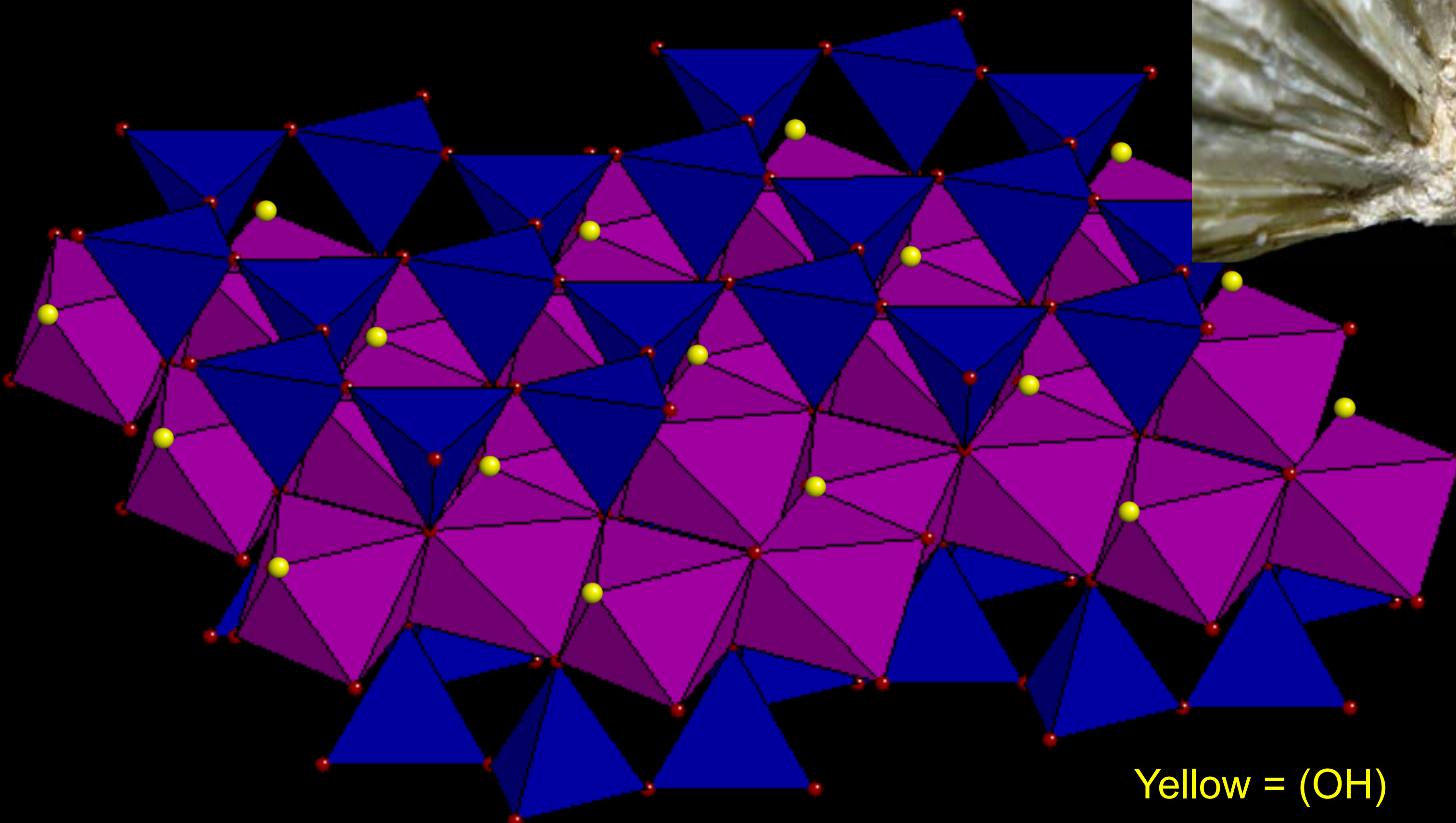


T
O
T
vdw
T
O
T
vdw
T
O
T

Talc: $Mg_3 [Si_4O_{10}] (OH)_2$: One $[Mg_3(OH)_6$ layer minus $4(OH)^-]$ and two $(Si_2O_5)^{2-}$ layers

Structure forms a sandwich of T layer--triocathedral (brucite) layer--T layer with weak van der Waal's bonds between T - O - T groups

Phyllosilicates

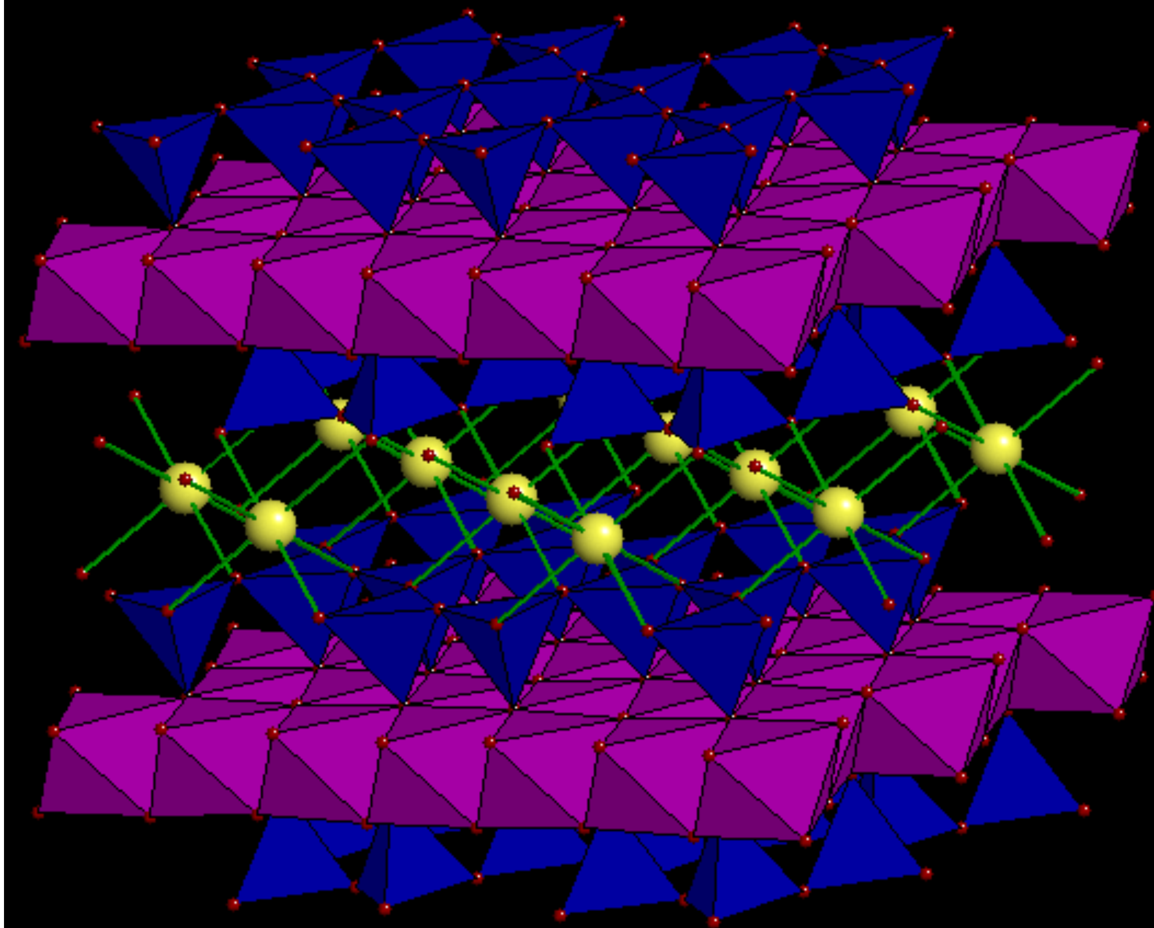


Pyrophyllite: $Al_2[Si_4O_{10}](OH)_2$: One $[Al_2(OH)_6$ minus $4(OH)^-]$ layer + two $(Si_2O_5)^{2-}$ layers

Structure forms a sandwich of T layer--**di**octahedral (gibbsite) layer—T layer with weak van der Waal's bonds between adjacent $(Si_2O_5)^{2-}$ layers

T
O
T
vdw
T
O
T
vdw
T
O
T

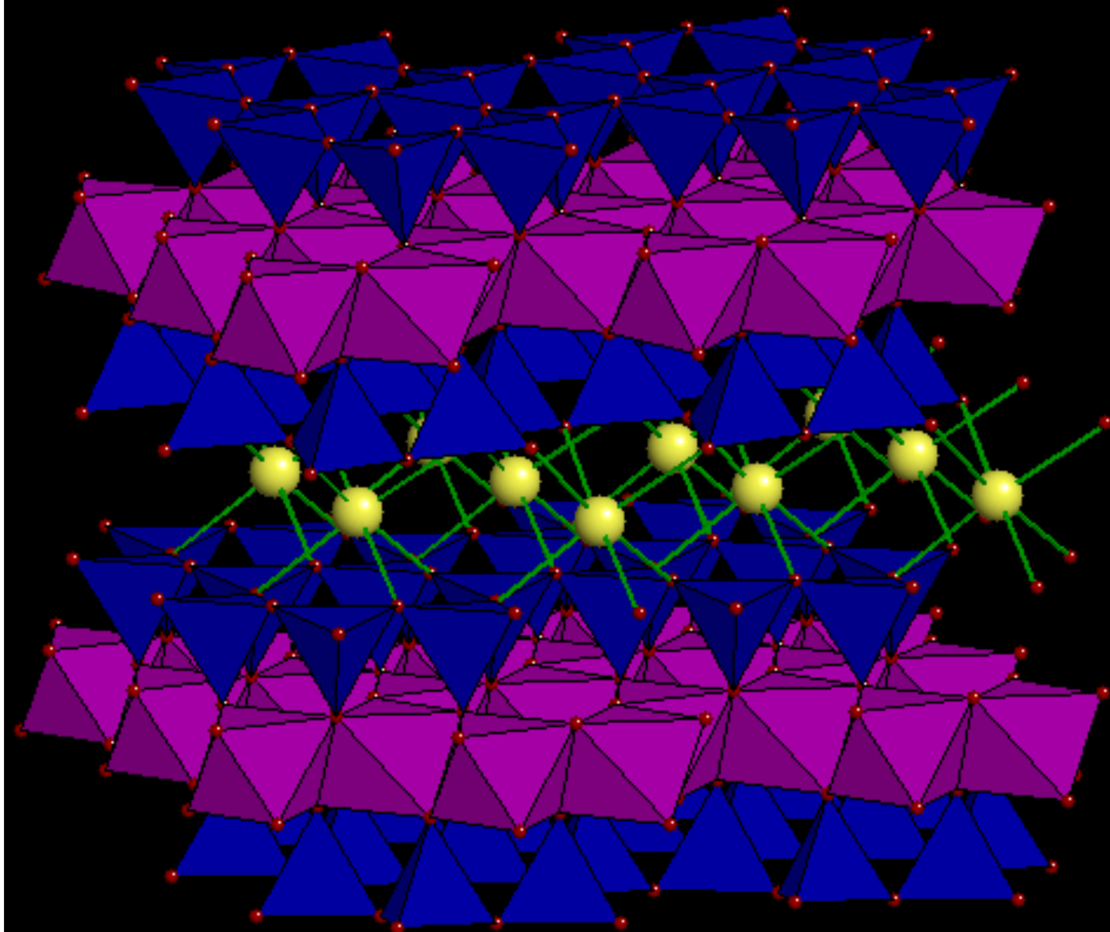
Phyllosilicates



Phlogopite: K Mg_3 $[AlSi_3O_{10}]$ $(OH)_2$ Talc structure but with every fourth Si ion replaced by Al. To balance the charge, K^+ is located in the large 12-coordinated site between layers. Mg^{2+} can be replaced by Fe^{2+} in solid solution to form the common micas called **biotite**

T layer--trioctahedral (brucite) layer--T-layer—K. Interlayer bonds are stronger

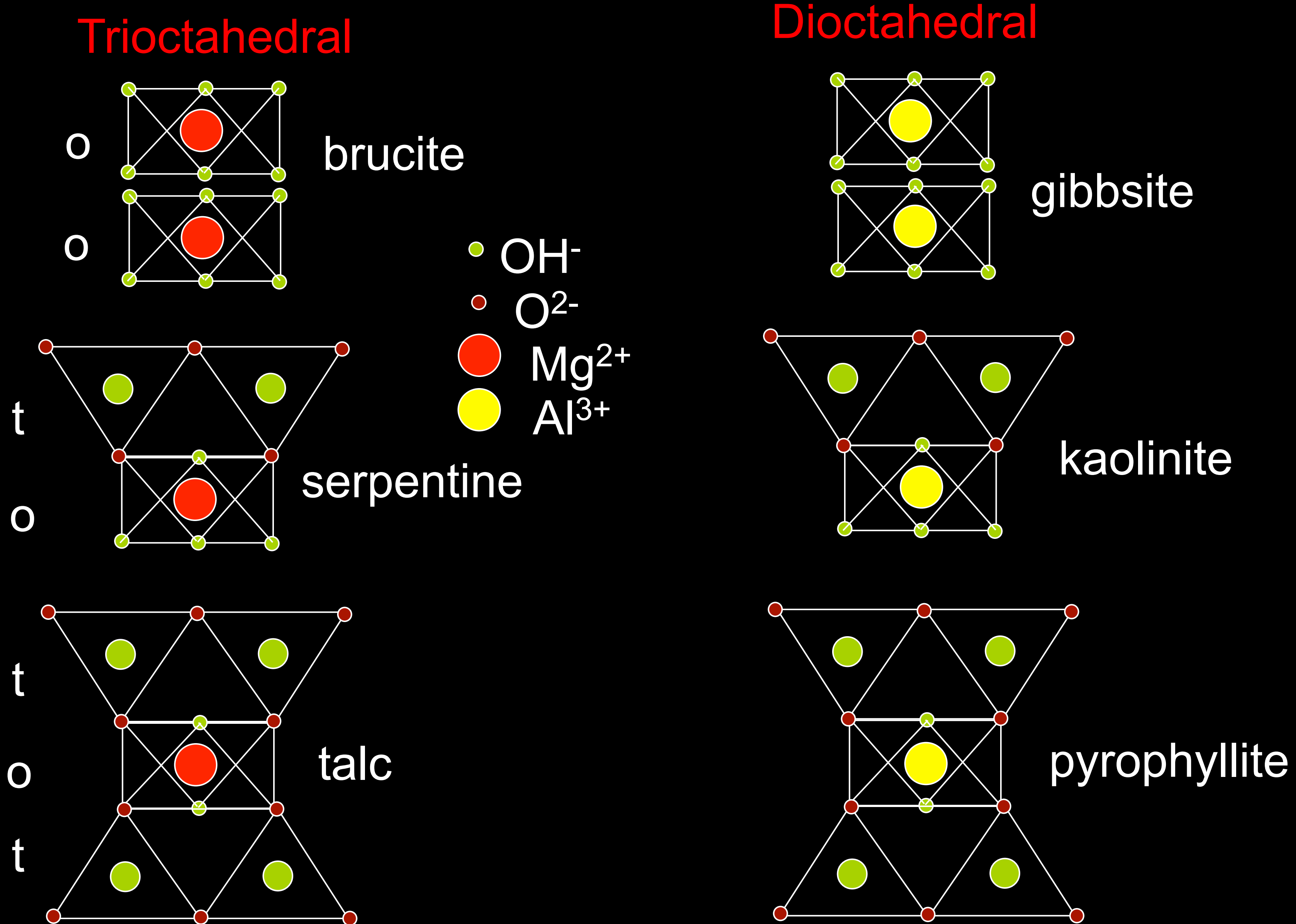
Phyllosilicates



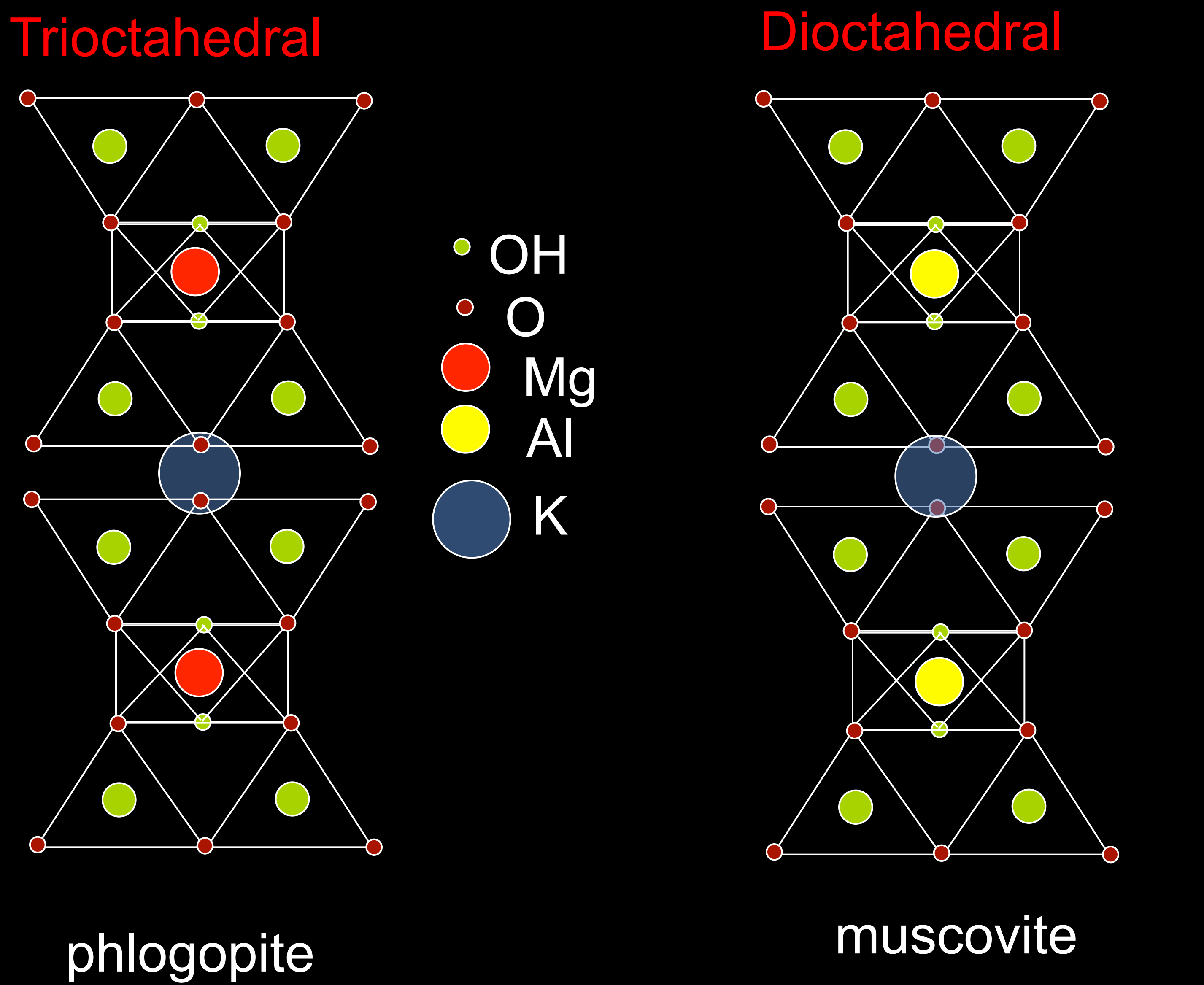
T
O
T
K
T
O
T
K
T
O
T

Muscovite: K Al_2 [$AlSi_3O_{10}$] $(OH)_2$ Pyrophyllite structure but with every fourth Si ion in T site replaced by Al. To balance the charge, K^+ is located in the large 12-coordinated site between layers.

A schematic summary of Phyllosilicate Structures



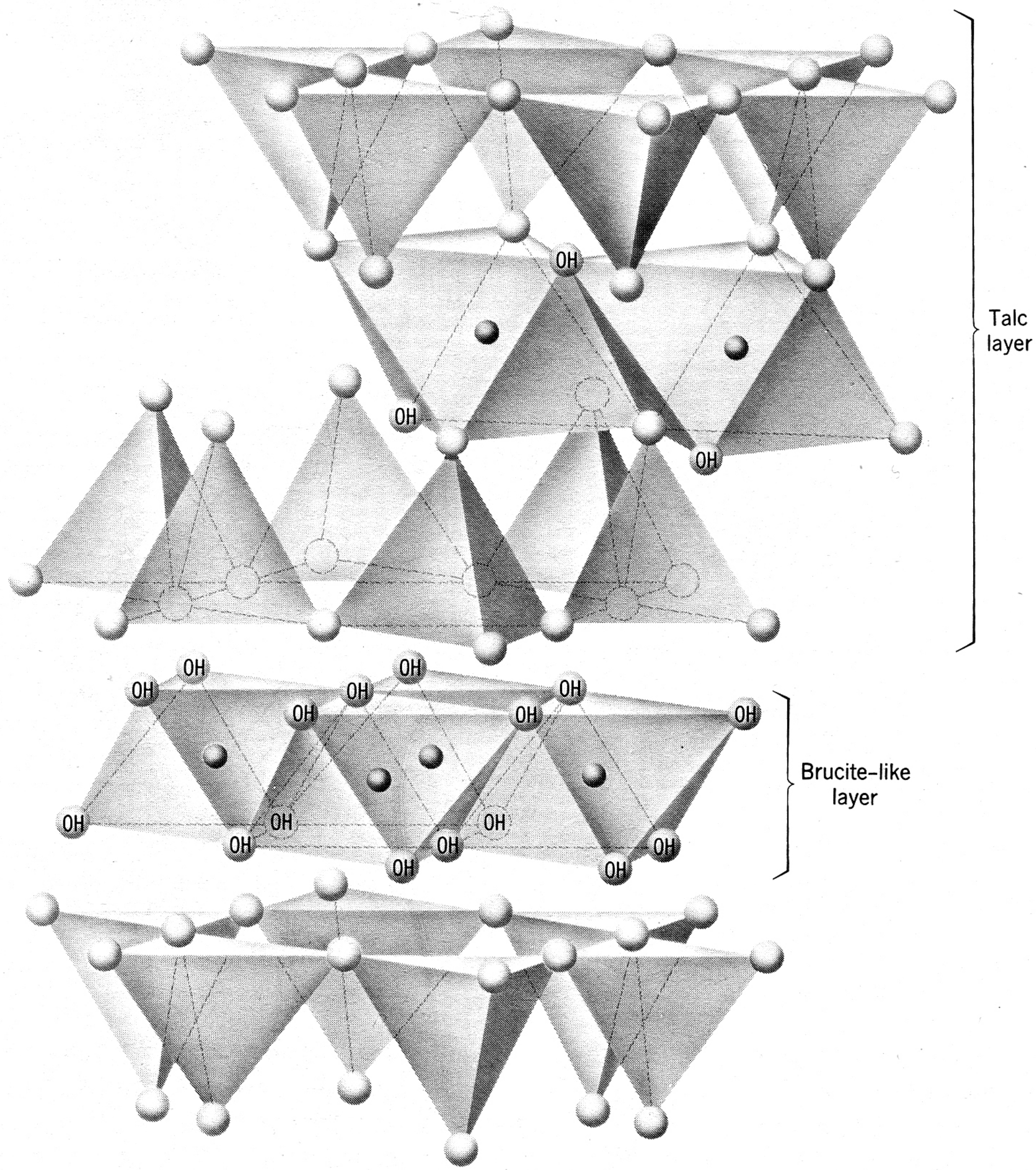
A schematic summary of Phyllosilicate Structures



Chlorite

- = talc with an extra **brucite** layer in the sandwich
- Clinochlore: $(Mg_5Al)(AlSi_3)O_{10}(OH)_8$
- Chamosite: $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$
- Nimite: $(Ni_5Al)(AlSi_3)O_{10}(OH)_8$
- Pennantite: $(Mn,Al)_6(Si,Al)_4O_{10}(OH)_8$

Chlorite structure



Occurrence and uses of phyllosilicates

- Serpentine
  - Low grade metamorphism of ultramafic rocks.
  - Forms primarily by hydration of olivine: $2Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$
  - Main player in subduction zones (lubrification, water storage)
  - Polished serpentinite used a ornamental stone and building facades

Olivine + water + CO2 = Serpentine +?

- *Olivine + water + carbonic acid → serpentine + magnetite + methane*
- $(Fe,Mg)_2SiO_4 + H_2O + CO_2 \rightarrow Mg_3Si_2O_5(OH)_4 + Fe_3O_4 + CH_4$
- Abiogenic methane!! life?

Olivine + water + CO2 = Serpentine +?

- *Olivine + water + carbonic acid → serpentine + magnetite + magnesite + silica*
- $(Fe,Mg)_2SiO_4 + nH_2O + CO_2 \rightarrow Mg_3Si_2O_5(OH)_4 + Fe_3O_4 + MgCO_3 + SiO_2$
- Carbon sequestration

Asbestos

- Chrysotile variety—main source of asbestos (95%).

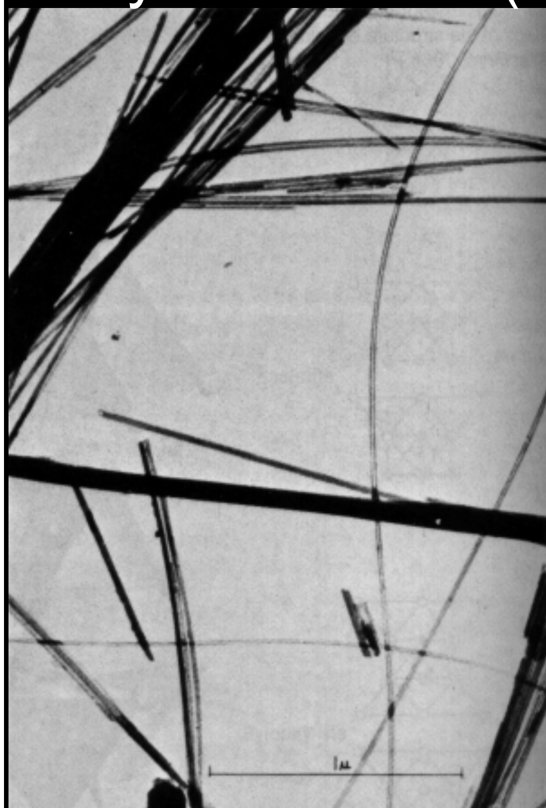
Serpentine polymorphs

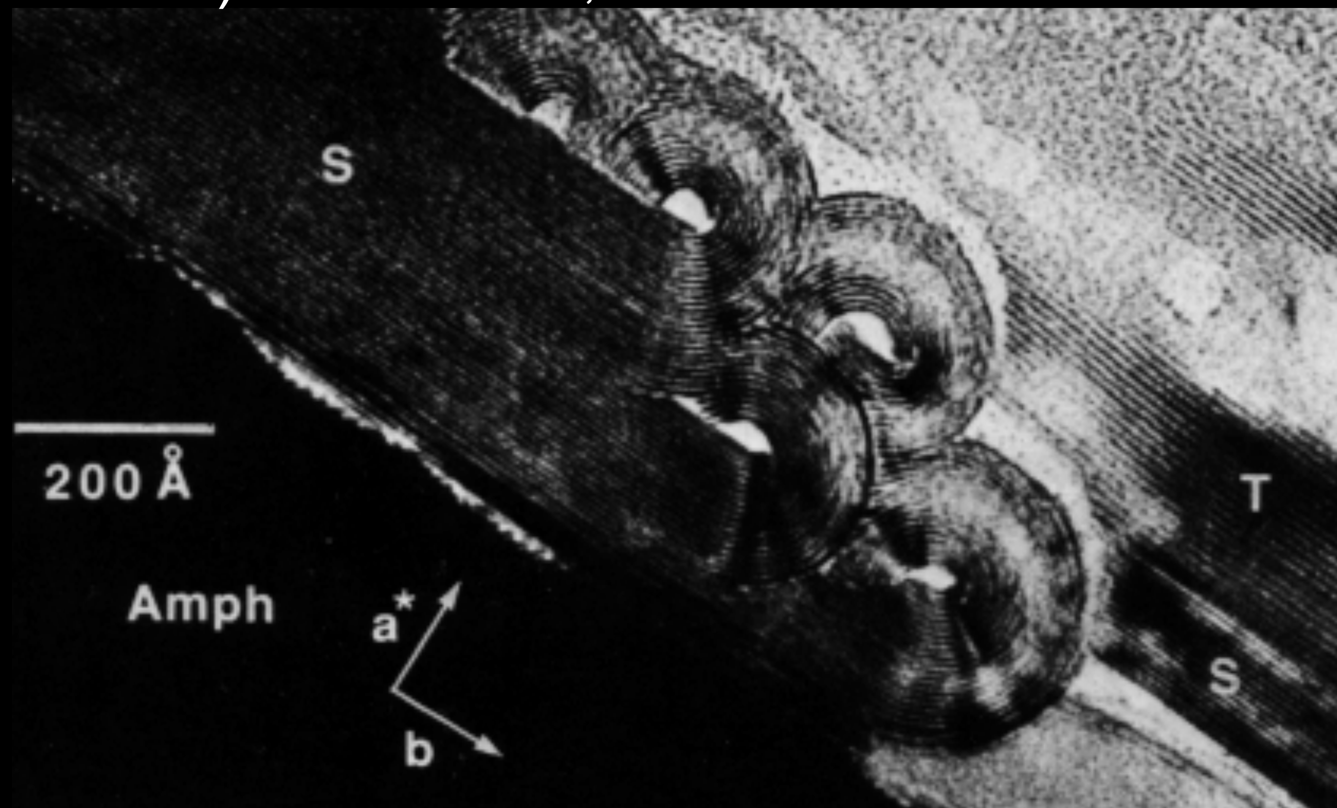
- Paradox: Serpentine is a phyllosilicate (sheets) but it forms BOTH fibers and masses - laths.
  - Antigorite and Lizardite = massive and fine-grained
  - Chrysotile = fibrous (Asbestiform)

Chrysotile

Veblen and Busek, 1979, Science 206, 1398-1400.

Chrysotile fibers (tube-like)





Transmission Electron Microscope (TEM) image of serpentine (S) forming within talc layers (T)

Serpentine polymorphs

- Antigorite: metamorphism of wet ultramafic rocks and is stable at the highest temperatures (> 600 ° C at depths of 60 km)
- Lizardite and Chrysotile : typically form near the Earth's surface and break down at relatively low temperatures (<400 °C)