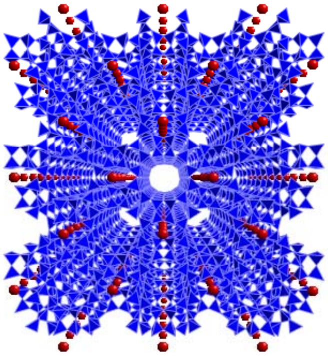
Earth and Planetary Materials

Spring 2013

Lecture 7
2013.01.30

Rock forming silicates



Silicates

- 27% of known minerals
- 40% of common minerals
- 90% of Earth's crust

- Rock-forming minerals
  - major components of a rock
  - Used for classification of rock types

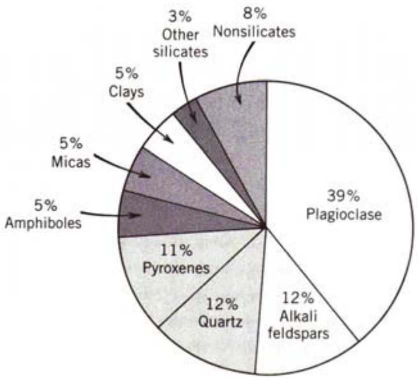
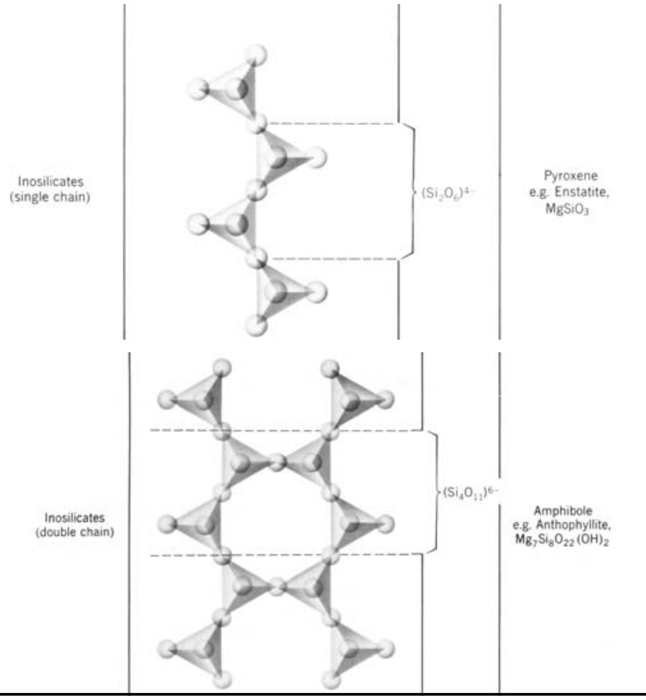
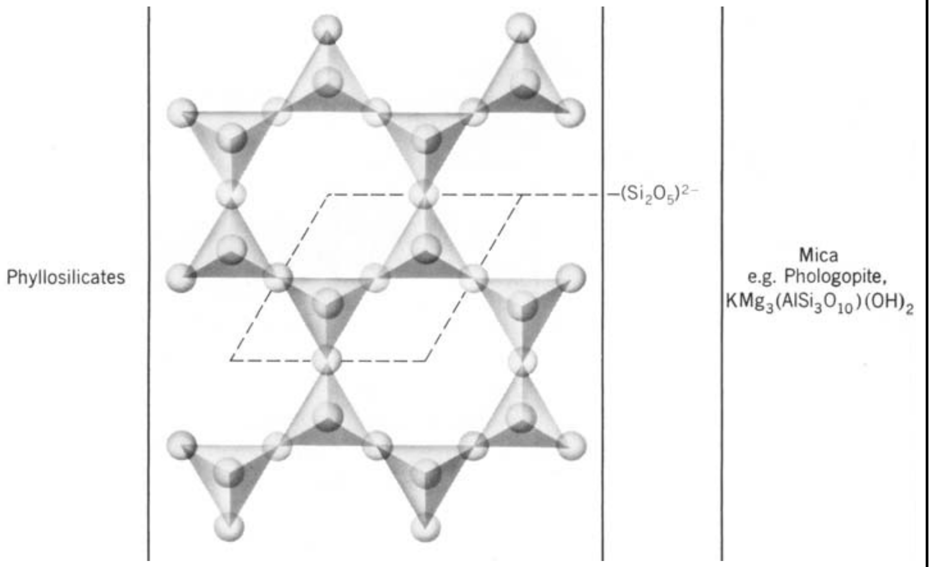
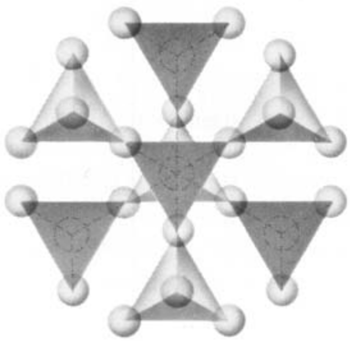


FIG. 18.1 Estimated volume percentages for the common minerals in the Earth's crust, inclusive of continental and oceanic crust. Ninety-two percent are silicates. (From Ronov, A. B. and A. A. Yaroshevsky. 1969. Chemical composition of the Earth's crust. American Geophysical Union Monograph no. 13, 50.)

Nesosilicates		$(SiO_4)^{4-}$	Olivine, $(Mg, Fe)_2SiO_4$
Sorosilicates		$(Si_2O_7)^{6-}$	Hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$
Cyclosilicates		$(Si_6O_{18})^{12-}$	Beryl, $Be_3Al_2Si_6O_{18}$


Inosilicates
(single chain)
$(Si_2O_6)^{4-}$
Pyroxene
e.g. Enstatite,
$MgSiO_3$
Inosilicates
(double chain)
$(Si_4O_{11})^{6-}$
Amphibole
e.g. Anthophyllite,
$Mg_7Si_8O_{22}(OH)_2$


Phyllosilicates
$-(Si_2O_5)^{2-}$
Mica
e.g. Phologopite,
$KMg_3(AlSi_3O_{10})(OH)_2$

Tectosilicates		$(SiO_2)^0$	High cristobalite, SiO_2

A general formula for all silicates: $X_mY_n(Z_pO_q)W_r$

W: additional anionic groups, e.g. OH^-, F^-, Cl^-

X: large, weekly charged cations, CN ≥ 8

Y: medium sized, +2 to +4, CN = 6

Z: small, highly charged, CN = 4

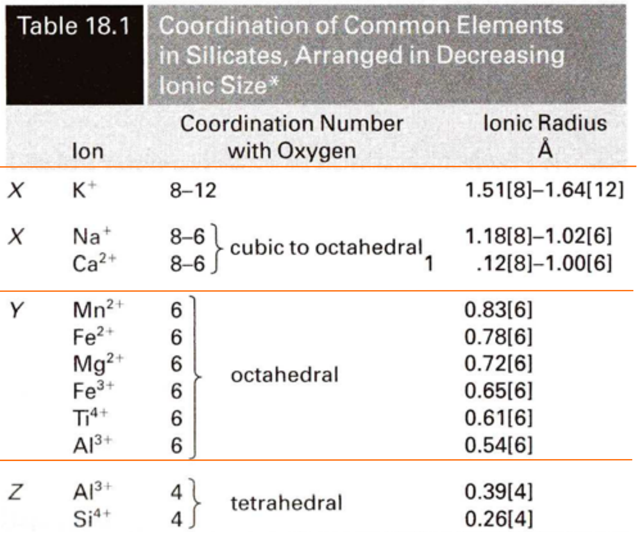
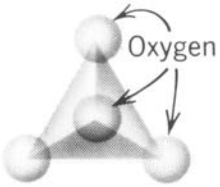


Table 18.1 Coordination of Common Elements in Silicates, Arranged in Decreasing Ionic Size*

	Ion	Coordination Number with Oxygen		Ionic Radius Å
X	K^+	8–12		1.51[8]–1.64[12]
X	Na^+	8–6	cubic to octahedral	1.18[8]–1.02[6]
	Ca^{2+}	8–6		.12[8]–1.00[6]
Y	Mn^{2+}	6	octahedral	0.83[6]
	Fe^{2+}	6		0.78[6]
	Mg^{2+}	6		0.72[6]
	Fe^{3+}	6		0.65[6]
	Ti^{4+}	6		0.61[6]
	Al^{3+}	6		0.54[6]
Z	Al^{3+}	4	tetrahedral	0.39[4]
	Si^{4+}	4		0.26[4]



Nesosilicates (orthosilicates)

Olivine $(Mg,Fe)_2SiO_4$
Garnet $A_3B_2Si_3O_{12}$
Zircon $ZrSiO_4$
Alumina silicate polymorphs Al_2SiO_5

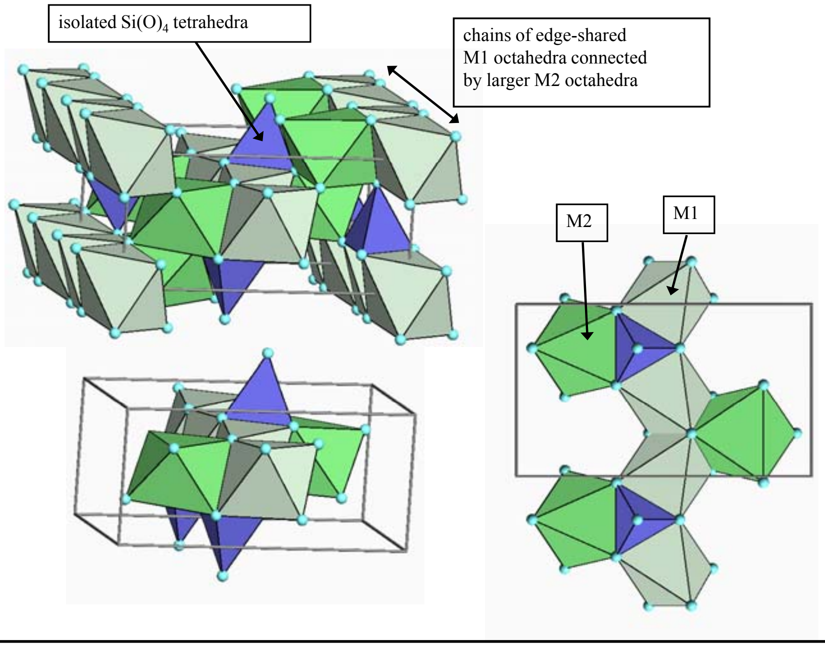
Nesosilicates

- Characterized by isolated SiO_4 tetrahedra that do not share polyhedral elements with other silicate tetrahedra
- Generally dense atomic packing → relatively high specific gravity and hardness
- This group includes some important rock forming minerals
  - Olivine $(Mg,Fe)_2SiO_4$
  - Zircon $ZrSiO_4$
  - Alumina silicate polymorphs Al_2SiO_5
  - Garnet $A_3B_2Si_3O_{12}$

Olivine $(Mg,Fe)_2SiO_4$

- Common in high-temperature igneous rocks
- Complete solid solution between forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4)
- Chains of edge-shared octahedra (M1) connected by larger (M2) octahedra (Fe and Mg occupy both sites with no preference)
- Octahedra cross linked by independent SiO_4 tetrahedra

Olivine Structure $(Mg,Fe)_2SiO_4$



isolated $Si(O)_4$ tetrahedra

chains of edge-shared M1 octahedra connected by larger M2 octahedra

Garnet $A_3B_2Si_3O_{12}$

- A cation: CN = 8
- B caion: CN = 6

Garnet $A_3B_2Si_3O_{12}$ – two composition series

- Pyralspite (A ≠ Ca, B = Al)

pyrope	$Mg_3Al_2Si_3O_{12}$
almandine	$Fe_3Al_2Si_3O_{12}$
spessartine	$Mn_3Al_2Si_3O_{12}$

Complete solid solutions

- Ugrandite (A = Ca)
  - uvarovite $Ca_3Cr_2Si_3O_{12}$
  - grossular $Ca_3Al_2Si_3O_{12}$
  - andradite $Ca_3Fe_2Si_3O_{12}$

Garnet $A_3B_2Si_3O_{12}$– structure

- Tetrahedra and octahedra share corners

- A cations are in a "twisted" cube, that shares edges with adjacent tetrahedra and octahedra

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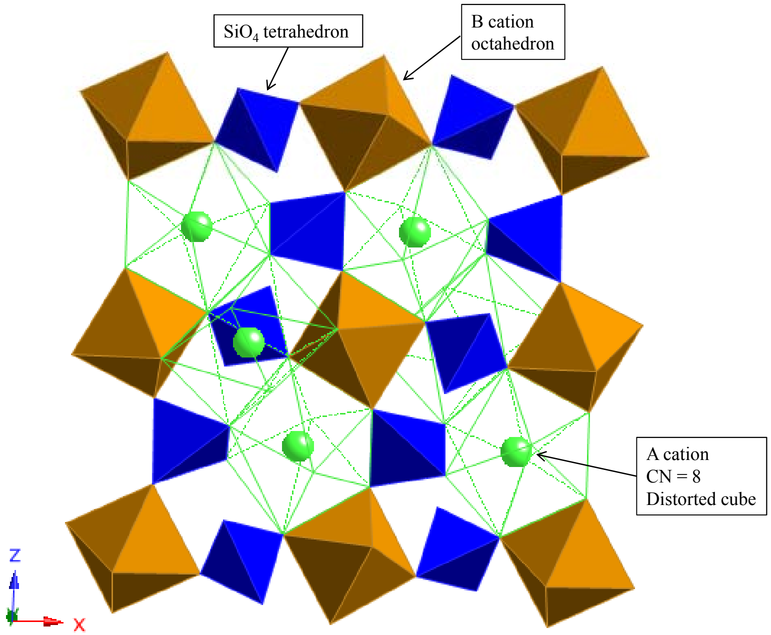
Garnet $A_3B_2Si_3O_{12}$ structure



SiO_4 tetrahedron

B cation
octahedron

A cation
CN = 8
Distorted cube

Zircon $ZrSiO_4$

- Widespread occurrence as an accessory mineral in igneous, metamorphic, sedimentary rocks.
- Very resistant to weathering → found as detrital grains in sediments and sedimentary rocks.
- U can substitute for the large Zr cation → U-Pb radiometric age determination (10's to 100's of millions of years)

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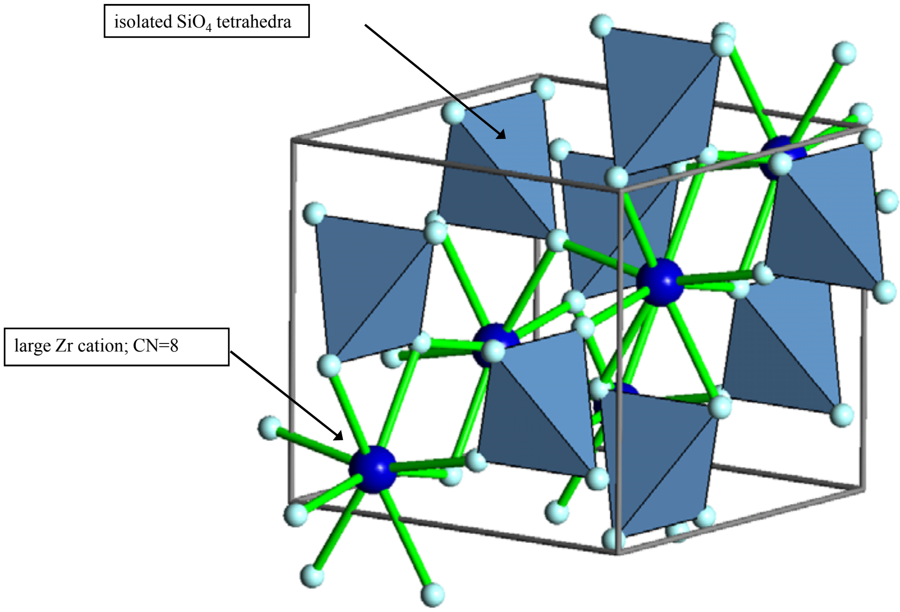
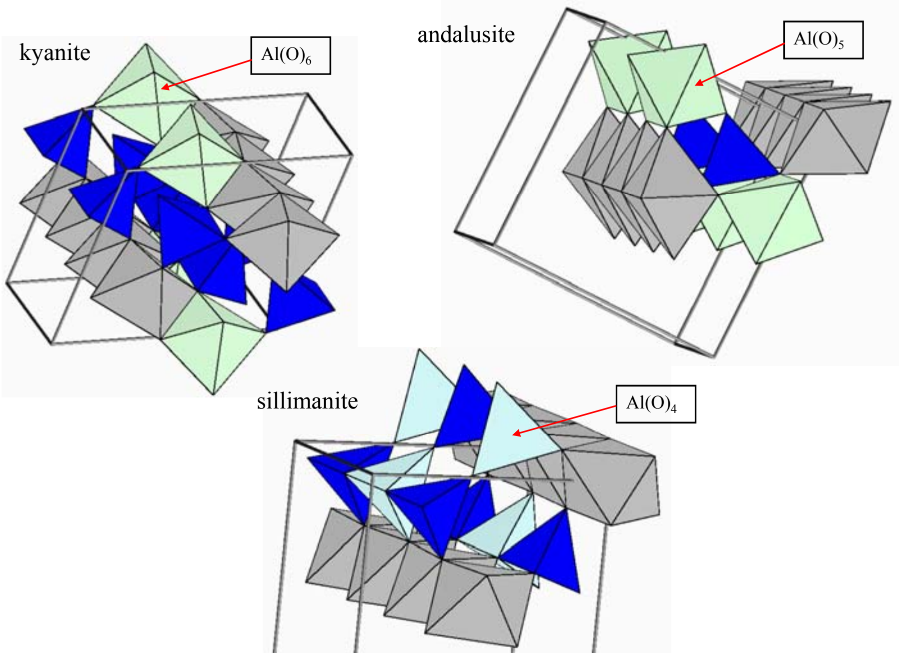
structure of zircon $ZrSiO_4$



The alumina silicate polymorphs Al_2SiO_5

- 3 polymorphs: kyanite, andalusite, sillimanite
- Similarity: all contain isolated silicate tetrahedra and one Al with CN = 6
- Difference: coordination of the second Al
  4 (sillimanite); 5 (andalusite); 6 (kyanite)

aluminum silicate minerals; Al_2SiO_5



The alumina silicate polymorphs Al_2SiO_5

- Each of these are stable under certain pressures and temperatures
- Common for higher coordination to be stable at high pressure (e.g., kyanite)

  ..... and for lower coordination to be stable at high temperature (e.g., sillimanite)

  - Comparison with CaCO3?

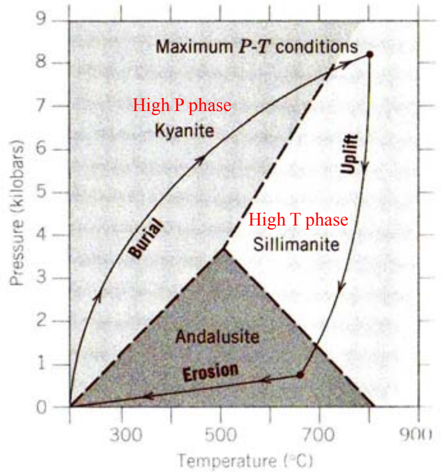


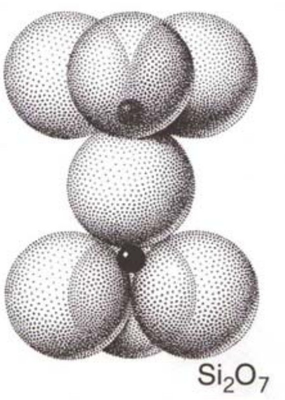
FIG. 11.5 The Al_2SiO_5 stability diagram with superimposed arrows showing the paths for various geologic processes. Material at the Earth's surface may originally have been buried to maximum *P–T* conditions of ~ 8 kb and 800°C. Subsequent to this, these metamorphic rocks may have been uplifted and eroded, returning the subducted material back to the Earth's surface. In addition to the evaluation of the textural reactions among the Al_2SiO_5 minerals, a geologist must assess the *P–T* conditions for other minerals in these same rocks, as well as the tectonic parameters of the region.

Sorosilicate

Epidote

Sorosilicates

- Characterized by isolated, double tetrahedral group Si_2O_7
- More than 70 minerals known – most are rare

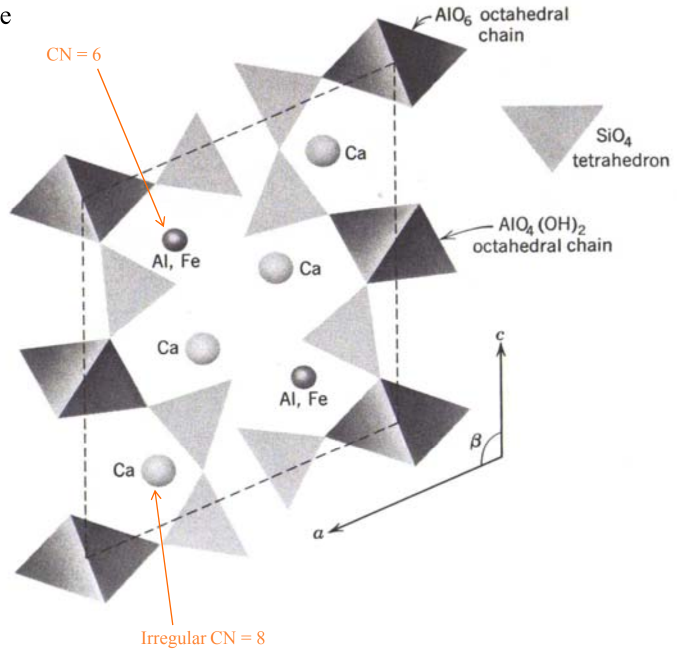


Epidote group

- Common in metamorphic rocks
- Structure contains both independent SiO_4 tetrahedra and Si_2O_7 groups

Epidote group	
Clinozoisite	$Ca_2Al_3O(SiO_4)(Si_2O_7)(OH)$
Epidote	$Ca_2(Fe^{3+},Al)Al_2O(SiO_4)(Si_2O_7)(OH)$
Allanite	$X_2Y_3O(SiO_4)(Si_2O_7)(OH)$
Vesuvianite	$Ca_{19}(Al,Fe,Mg)_{13}(Si_2O_7)_4(SiO_4)_{10}(O,OH,F)_{10}$

Epidote structure



CN = 6

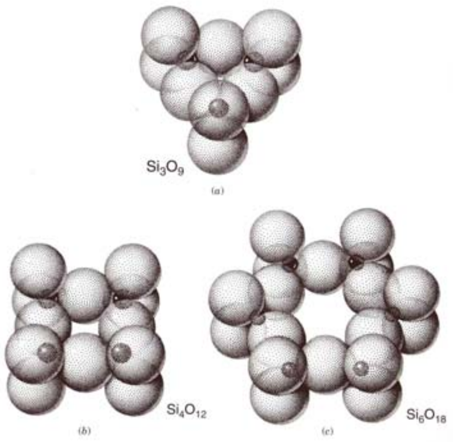
Irregular CN = 8

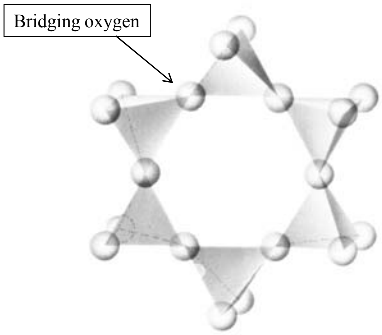
Cyclosilicates (ring silicates)

Beryl
Tourmaline

Cyclosilicates

- Rings of linked SiO_4 tetrahedra
- Si : O = 1 : 3

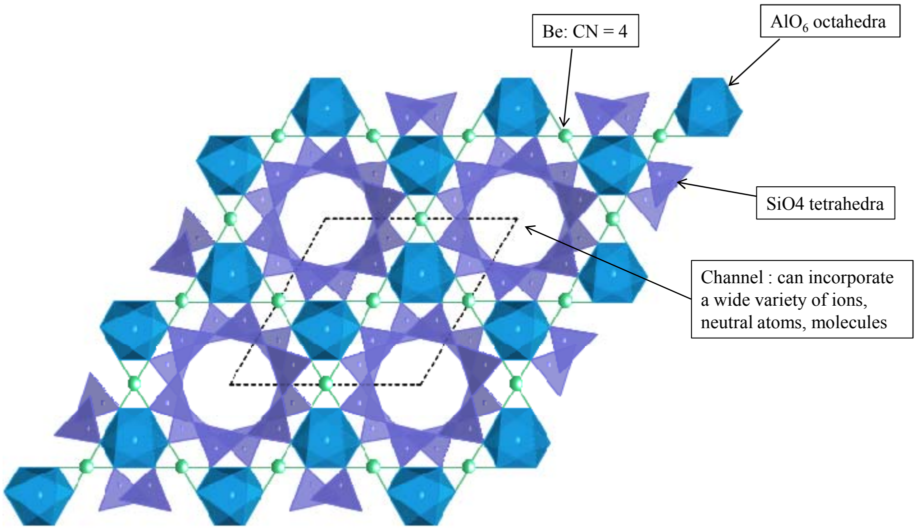




Beryl $Be_3Al_2Si_6O_{18}$

Goshenite Aquamarine Emerald Heliodor Red beryl Morganite

Beryl $Be_3Al_2Si_6O_{18}$



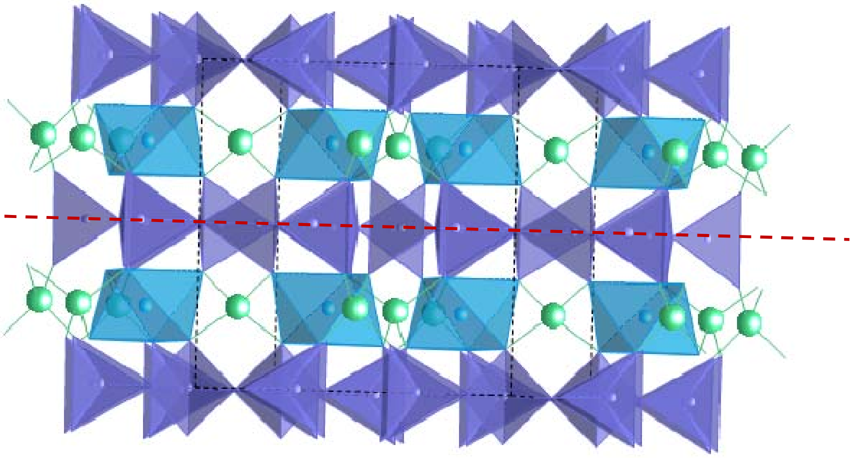
Be: CN = 4

AlO_6 octahedra

SiO4 tetrahedra

Channel : can incorporate a wide variety of ions, neutral atoms, molecules

Beryl $Be_3Al_2Si_6O_{18}$



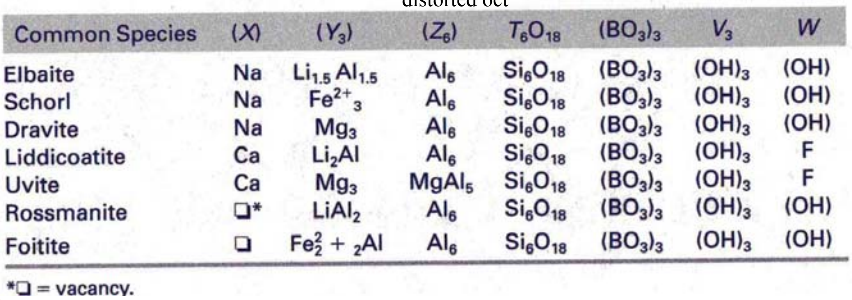
Tourmaline $XY_3Z_6(T_6O_{18})(BO_3)V_3W$

- Large chemical variability
- Simple/coupled substitution

Most common: $Fe^{2+} \leftrightarrow Mn^{2+}$

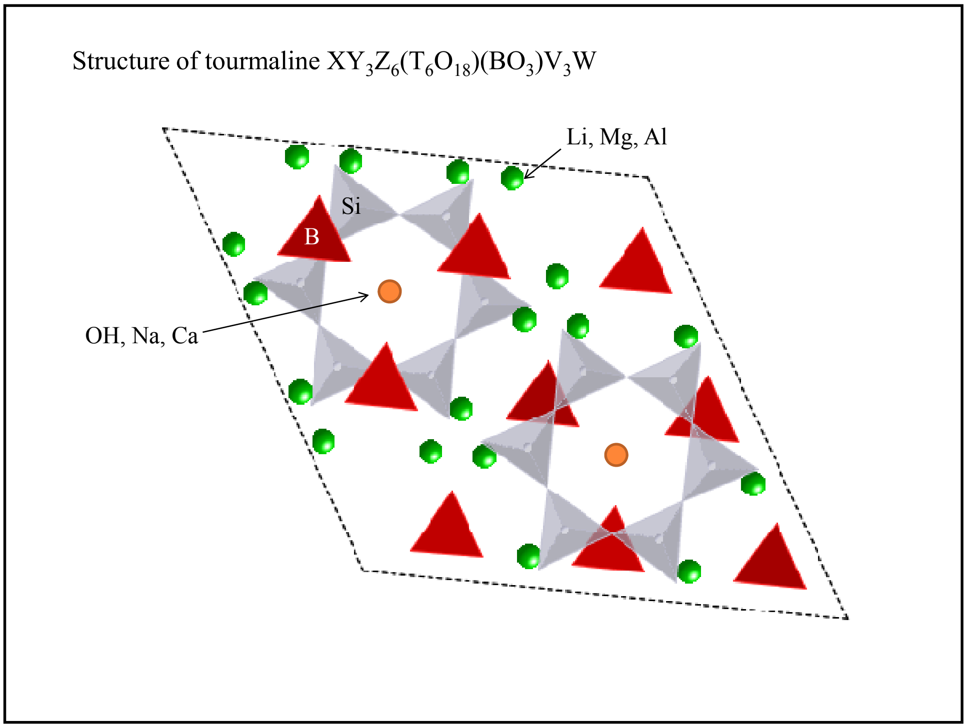
$Na^{+} + Al^{3+} \leftrightarrow Ca^{2+} + Mg^{2+}$

$Li^{+} + Al^{2+} \leftrightarrow 2Fe^{2+}$



	CN = 9	Regular oct	Relatively small ion, distorted oct				
Common Species	(X)	(Y_3)	(Z_6)	T_6O_{18}	$(BO_3)_3$	V_3	W
Elbaite	Na	$Li_{1.5}Al_{1.5}$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Schorl	Na	$Fe^{2+}{}_3$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Dravite	Na	Mg_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Liddicoatite	Ca	Li_2Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	F
Uvite	Ca	Mg_3	$MgAl_5$	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	F
Rossmanite	☐*	$LiAl_2$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Foitite	☐	$Fe_2^2 + {}_2Al$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)

*☐ = vacancy.



Structure of tourmaline $XY_3Z_6(T_6O_{18})(BO_3)V_3W$

Inosilicates (chain silicates)

Pyroxene group (single chain)
Amphibole group (double chains)

Inosilicates

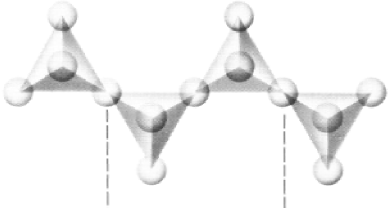
- Contain chains of corner shared silicate tetrahedra
- Two main groups:
  - pyroxenes (single chains)
  - amphiboles (double chains)

Pyroxenes XYZ_2O_6

- Anhydrous. Crystallize at higher T than amphibole analogues.
- Form early in a cooling igneous melt or high-T metamorphic rocks rich in Mg and Fe
- X @ M2 site: Na^+, Ca^{2+}, Mn^{2+}, Fe^{2+}, Mg^{2+}, Li^+
- Y @ M1 site: Mn^{2+}, Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Ti^{4+}
- Z @ tetrahedral sites of the chain: Si^{4+}, Al^{3+}

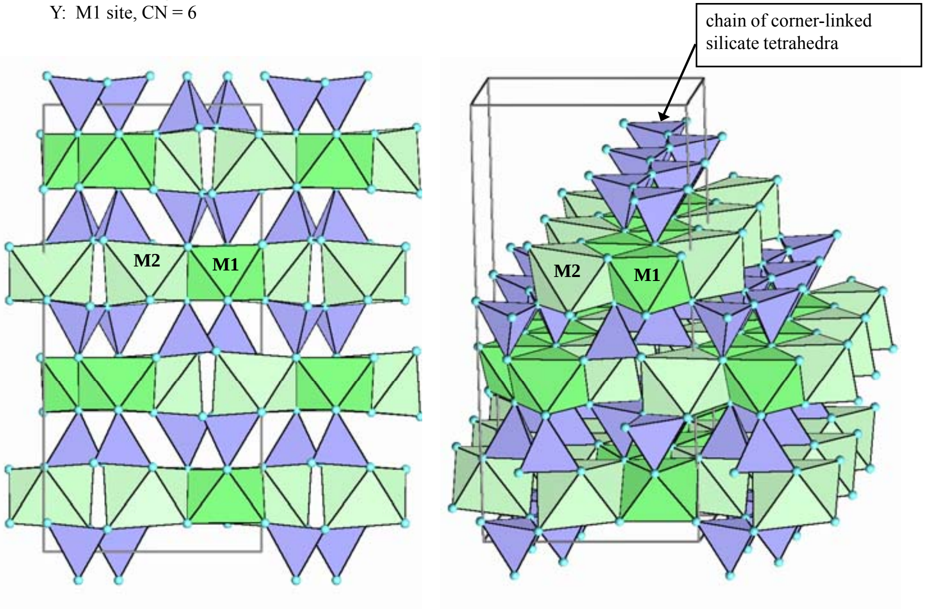
Pyroxenes XYZ_2O_6 – Structure

- Contain chains of corner-linked tetrahedra
- Chains are connected by their apices to a chain of edge shared octahedra, M1
- Chains of tetrahedra-octahedra-tetrahedra form T-O-T "I-beams"
- There are two types of octahedra: smaller M1, and larger M2 in a 1:1 ratio



Pyroxene structure: $XYSi_2O_6$

X: M2 site, larger cation, CN = 6-8
Y: M1 site, CN = 6

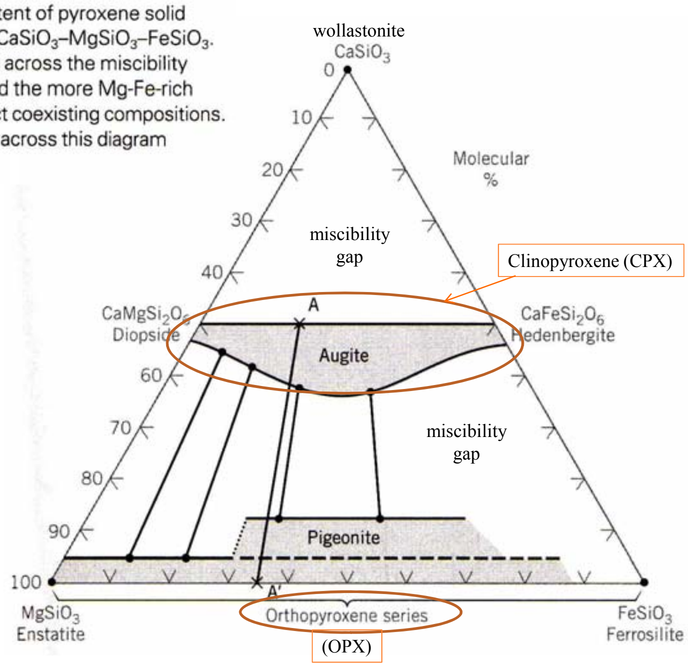


Pyroxenes XYZ_2O_6 – Chemistry

- Main compositions lie within the pyroxene ternary diagram

Wo	wollastonite	$CaSiO_3$ (a pyroxenenoid)
En	enstatite	$MgSiO_3$
Fs	ferrosilite	$FeSiO_3$

FIG. 11.11 (a)The extent of pyroxene solid solution in the system $CaSiO_3$–$MgSiO_3$–$FeSiO_3$. Representative tielines across the miscibility gap between augite and the more Mg-Fe-rich orthopyroxenes connect coexisting compositions. *AA′* locates the section across this diagram shown in Fig. 12.17.



Pyroxenes XYZ_2O_6 – Chemistry

- Solid solutions depend on temperature → miscibility gaps generally broaden with decreasing T (less solid solution)

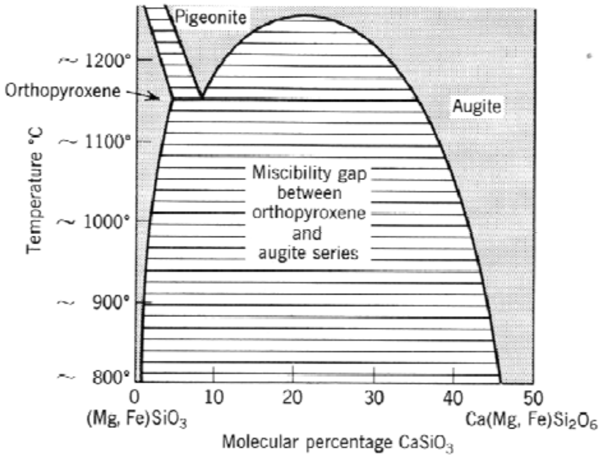


FIG. 10.42. Schematic *T*-composition section across the Wo-En-Fs diagram shown in Fig. 10.36. The section is at about En_{65} Fs_{35}.

Pyroxenes XYZ_2O_6 – Chemistry

- Clinopyroxene series at 50 mol% Wo:

  Ca fills the M2 sites, (Fe, Mg) solid solution on the M1 sites

- Orthopyroxene series at 0 mol% Wo: En to Fs.

  Term "hypersthene" is used by petrologists for intermediate compositions.

- Note miscibility gaps, where no compositions occur - Ca is too big for solid solution with (Fe, Mg) on M2 or M1.

- Augite contains other substitutions not present on this diagram (Na+, Fe3+, Al3+)

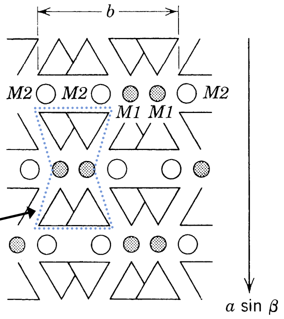
Pyroxenes XYZ_2O_6 – Physical properties

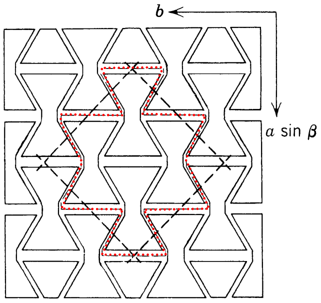
- A diagnostic characteristic of pyroxenes is their 2-directions of cleavage at approximately 90° .
- This property arises because it is easiest to break the structure between the T-O-T "I-beams", at the M2 sites

Relationship between structure and cleavage in pyroxenes.

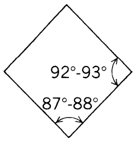
structure, viewed along the chains. The tetrahedra and M1 octahedra form relatively strong “I-beams” that are connected by weaker linkages to the M2 octahedra

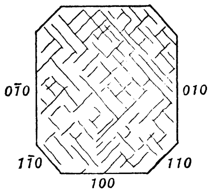
“I-beam”





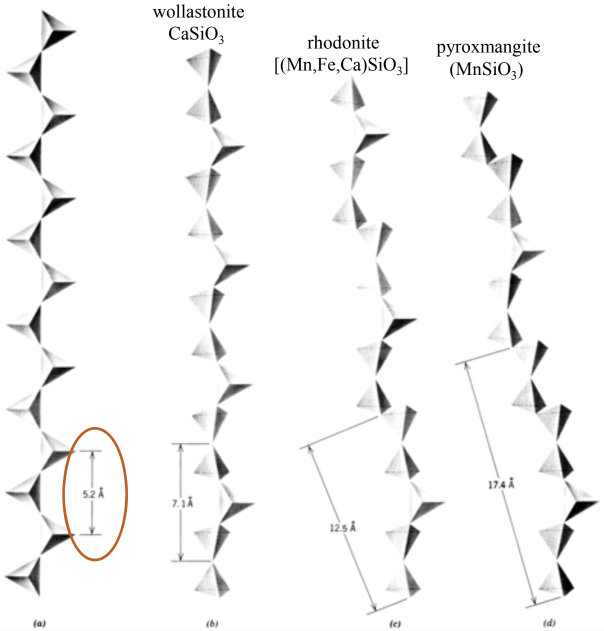
breaking the structure between the “I-beams” gives the two directions of cleavage at ~90°.





pyroxene

Pyroxenoids:
chains are kinked with longer repeat distance



Amphiboles $W_{0\text{-}1}X_2Y_5Z_8O_{22}(OH,F)_2$

- W @ A site
  - Na^+ and K^+
- X @ M4 site
  - Ca^{2+}, Na^+, Mn^{2+}, Fe^{2+}, Mg^{2+}, Li^+
- Y @ M1, M2, M3 sites:
  - Mn^{2+}, Fe^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Ti^{4+}
- Z @ tetrahedral sites:
  - Si^{4+}, Al^{3+}

Amphiboles $W_{0-1}X_2Y_5Z_8O_{22}(OH,F)_2$ – Structure

- Contains double chains of corner-linked tetrahedra
- These chains are connected by their apices to a wide chain of edge shared octahedra, M1,M2,M3
- Three types of small octahedra M1, M2, and M3 in a ratio 2:2:1
- The ratio of sites gives rise to the amphibole formula:

  2 large sites (M4); 5 octahedral sites (M1+M2+M3); 2 double chains: $2*(Si_4O_{11})$
- Chains of tetrahedra-octahedra-tetrahedra form T-O-T "I-beams"

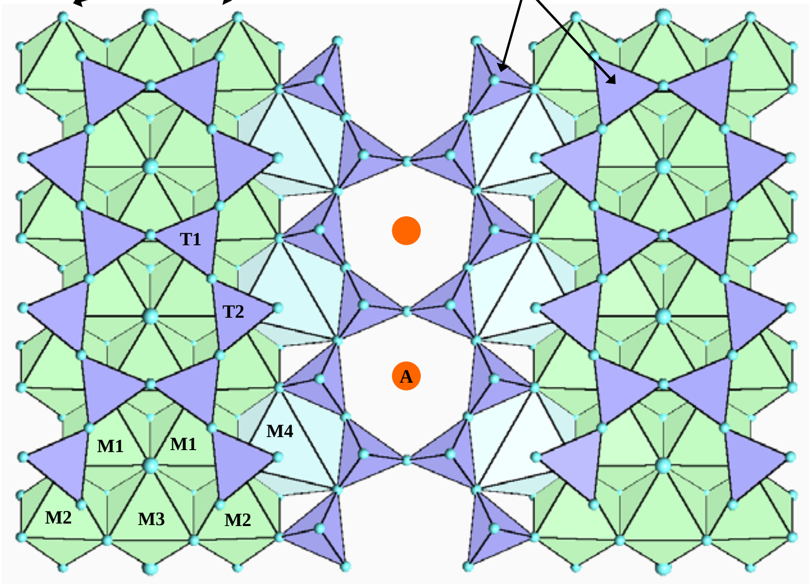
Amphiboles $W_{0-1}X_2Y_5Z_8O_{22}(OH,F)_2$ – Structure

- Larger M4 polyhedra (CN = 6 or 8) lie between the T-O-T "I-beams"
- Another large "A" site (CN = 9 to 12) lies between the base of two tetrahedral chains; not always occupied

Amphibole structure; “top view”

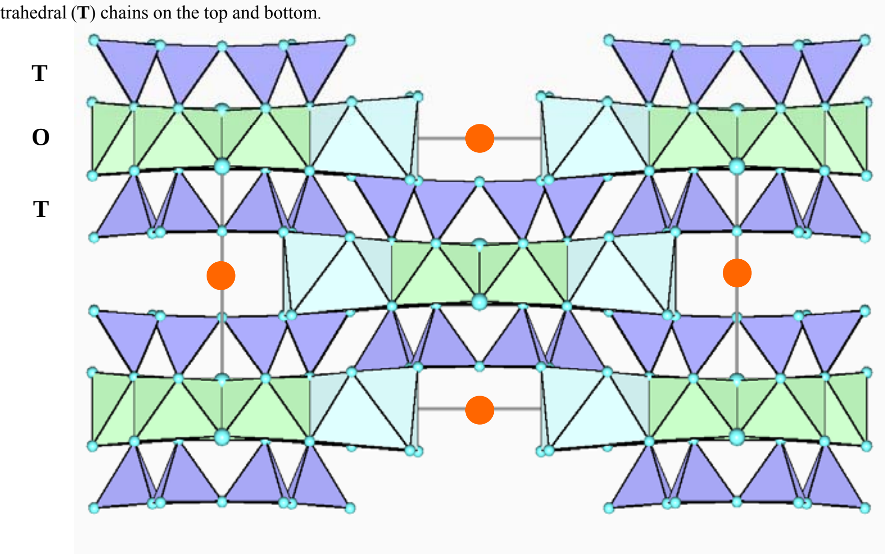
thick chain of edge-linked M1, M2, M3 octahedra

double-chains of corner-linked silicate tetrahedra



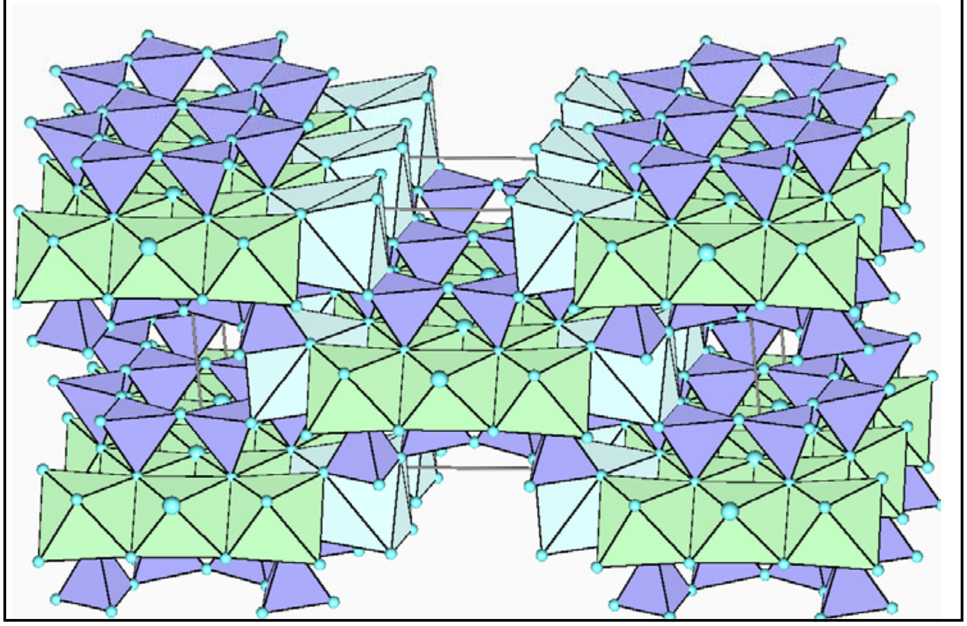
Amphibole structure; “side view”

Octahedral (**O**) chains “sandwiched” between tetrahedral (**T**) chains on the top and bottom.



Amphibole structure; “oblique view”

note large, irregular M4 polyhedra

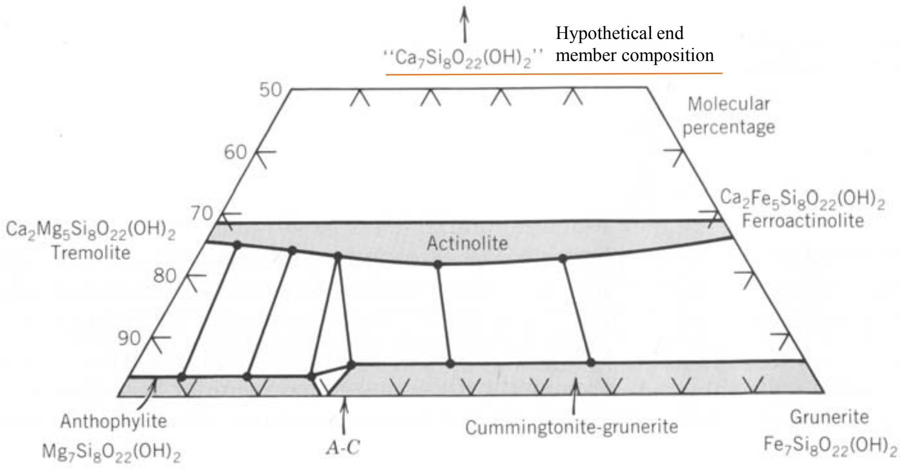


Amphiboles $W_{0-1}X_2Y_5Z_8O_{22}(OH,F)_2$ – Chemistry

Amphibole quadrilatrial:

- Tremolite - ferroactinolite series
  - 2*Ca in the M4 sites; 5*(Mg,Fe) in the M1+M2+M3
- Anthophyllite (near Mg-endmember)
  - 2*(Mg,Fe) in M4 and 5*Mg in M1+M2+M3
- Cumingtonite-grunerite series
  - 2*Fe in M4; 5*(Mg,Fe) in M1+M2+M3
- Hornblende (most common)
  - Tremolite-ferroactinolite type composition with additional partial substitution: Na^+ at A and M4 sites, Mn^{2+}, Fe^{3+}, Ti^{4+} for Y sites, Al for Si in the T sites

Amphibole composition in the system
$Mg_7Si_8O_{22}(OH)_2$ – $Fe_7Si_8O_{22}(OH)_2$ – “$Ca_7Si_8O_{22}(OH)_2$”

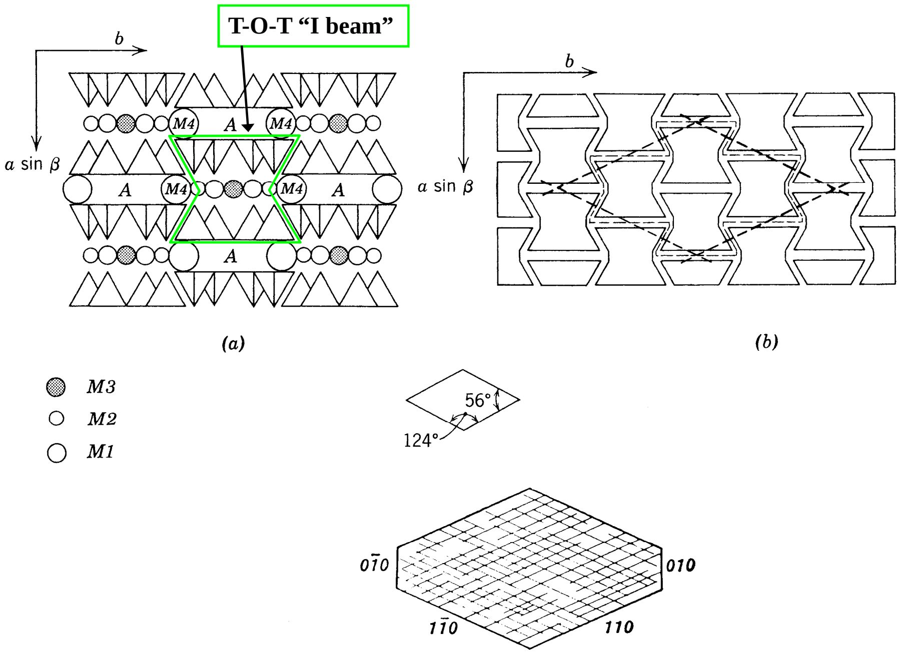


Klein p452

Amphiboles $W_{0-1}X_2Y_5Z_8O_{22}(OH,F)_2$ – Physical properties

- A diagnostic characteristic of amphiboles is their 2-directions of cleavage at approximately 60° and 120°
- Similar explanation as for the pyroxenes, but the T-O-T "I-beams" are twice as wide in amphiboles

Relationship between structure and cleavage in amphiboles.



Comparison between pyroxenes and amphiboles

Similar in physical and chemical properties

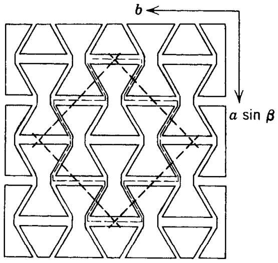
- Amphiboles are characterized by the presence of OH (lacking in pyroxenes)
- Pyroxenes form early in a cooling igneous melt or high-T metamorphic rocks rich in Mg and Fe
- Early formed pyroxene + water at low T → amphiboles

Structure:

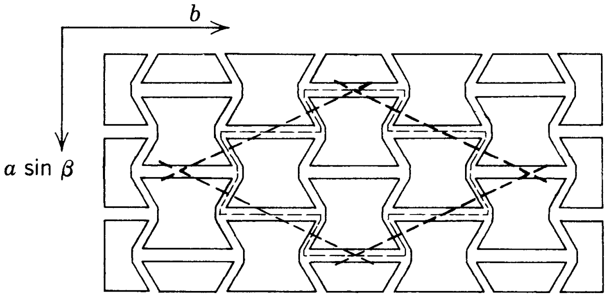
- I-beams are the same height, but different width

Comparison of structure and cleavage in pyroxenes and amphiboles.

pyroxene



amphibole



T-O-T “I-beams” are the **same height** for both,
but the amphibole chains are twice as wide.
This causes the difference in cleavage angle.