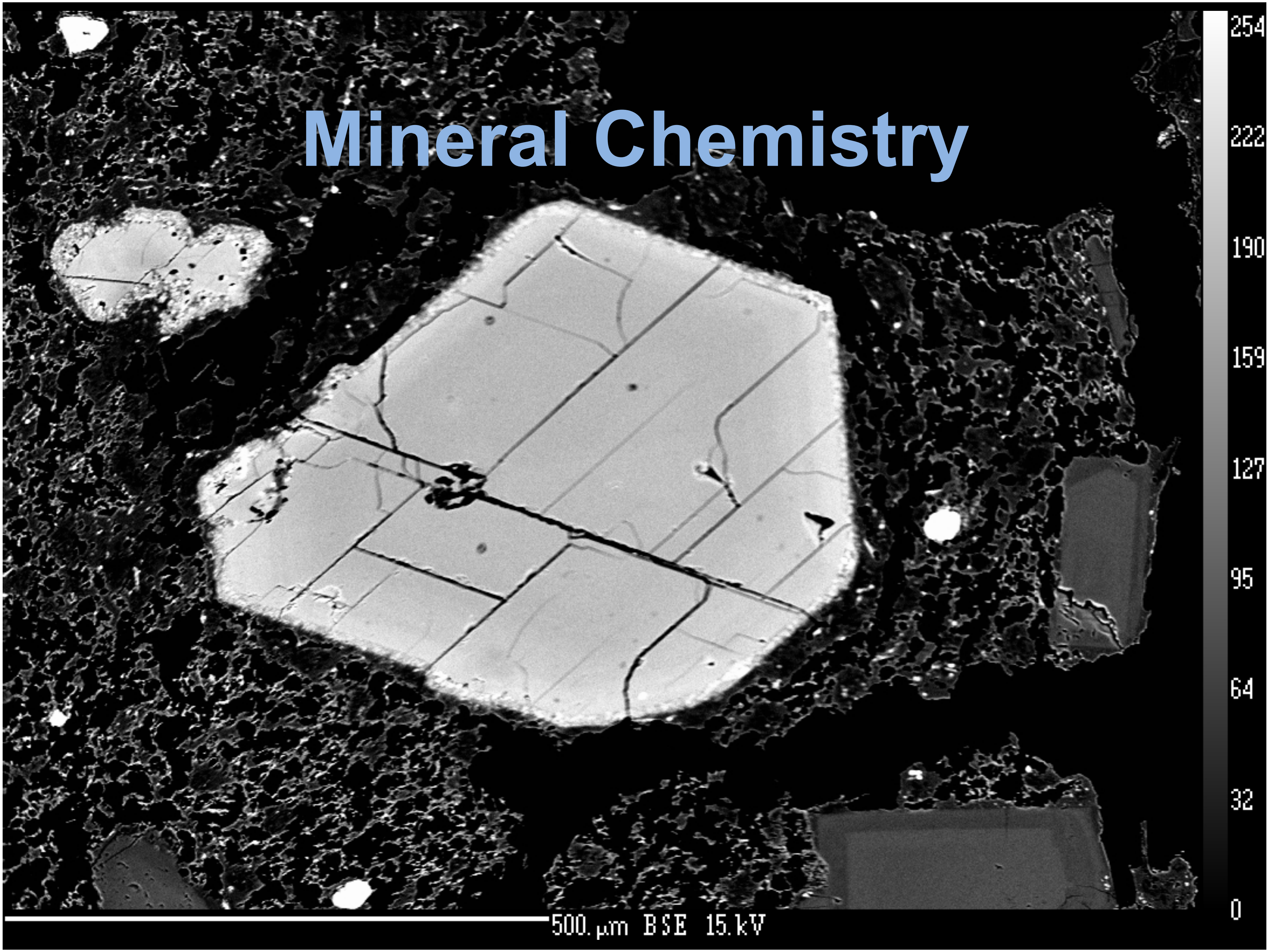
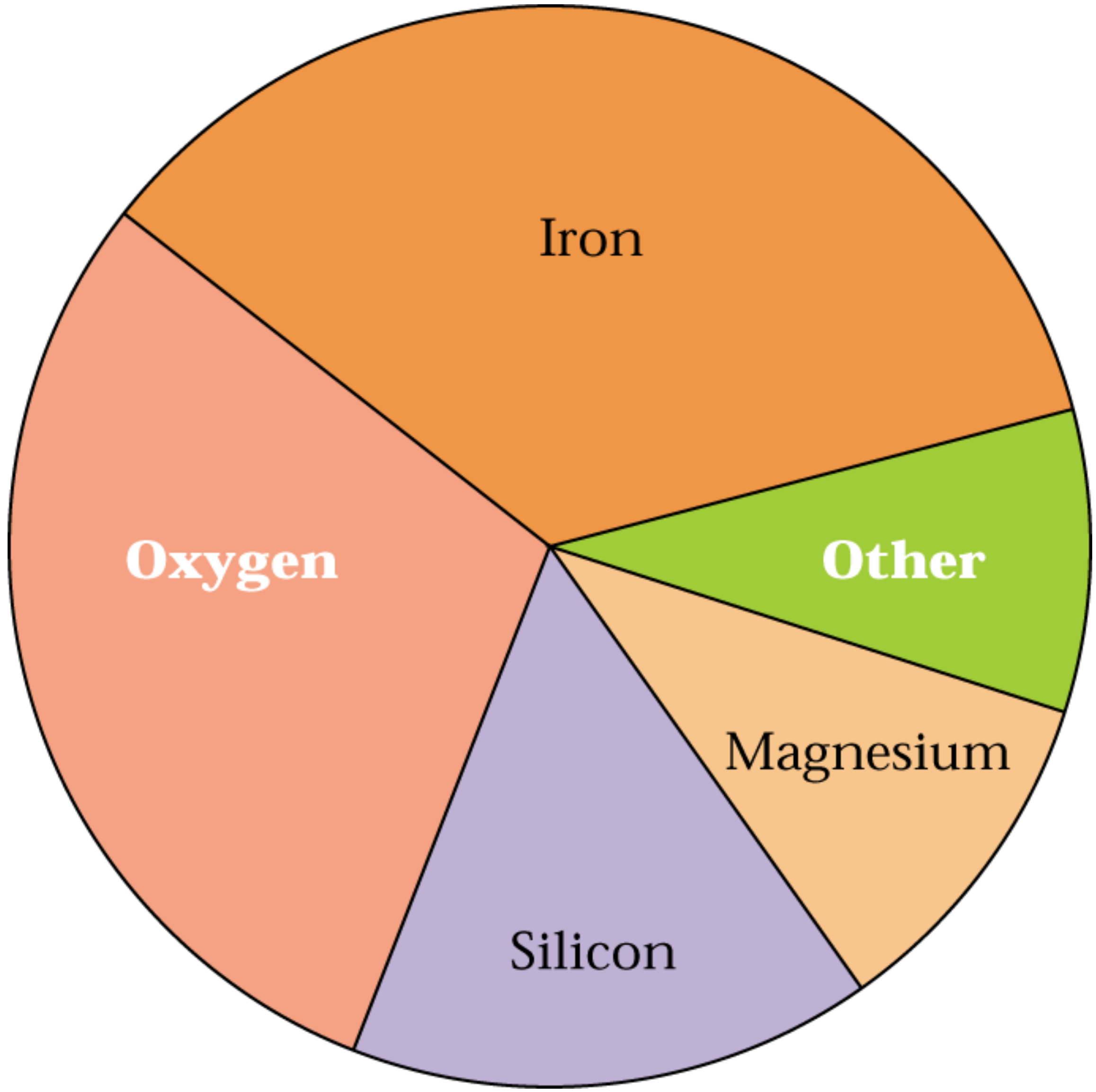
Mineral Chemistry

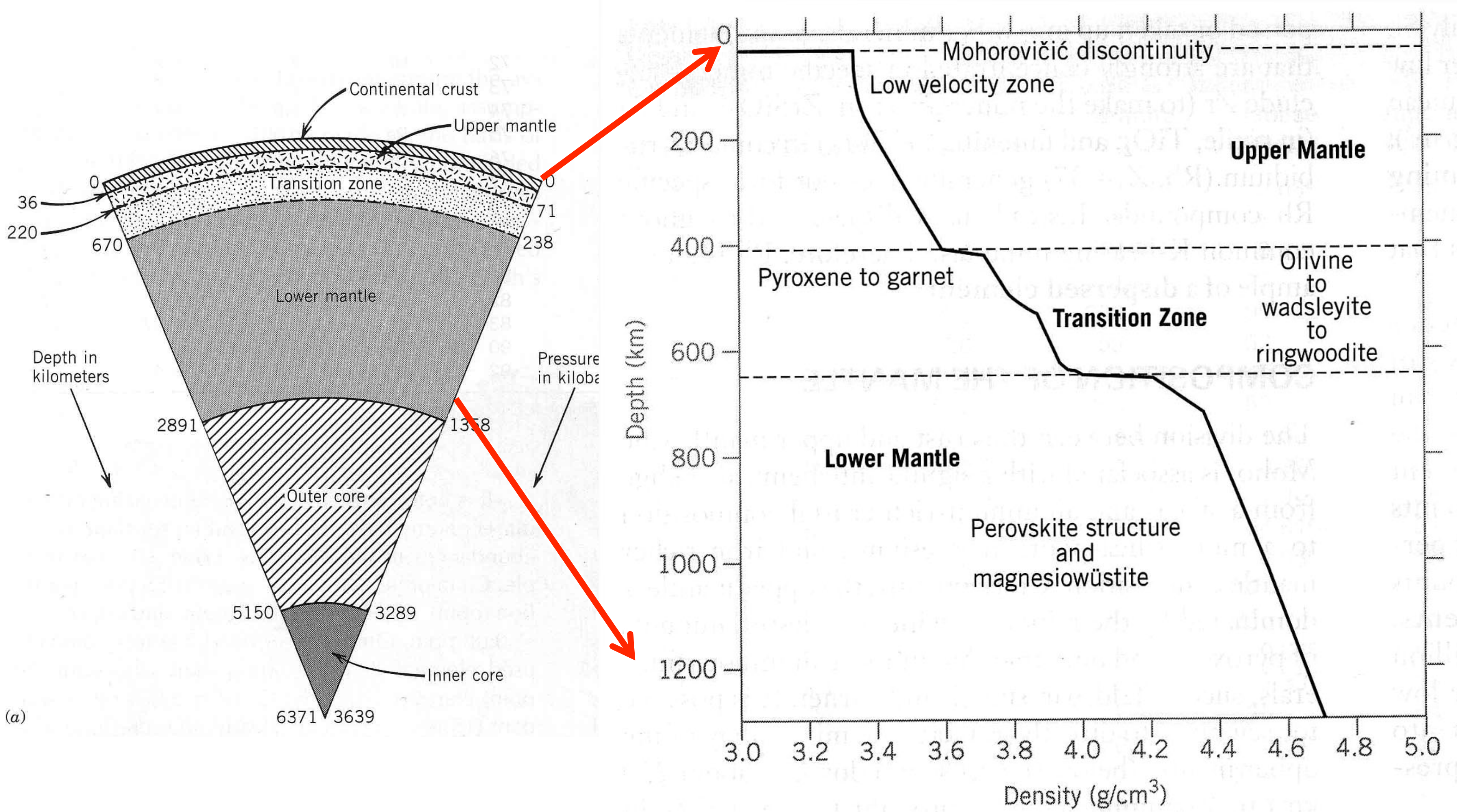


Chemical Composition of the Earth

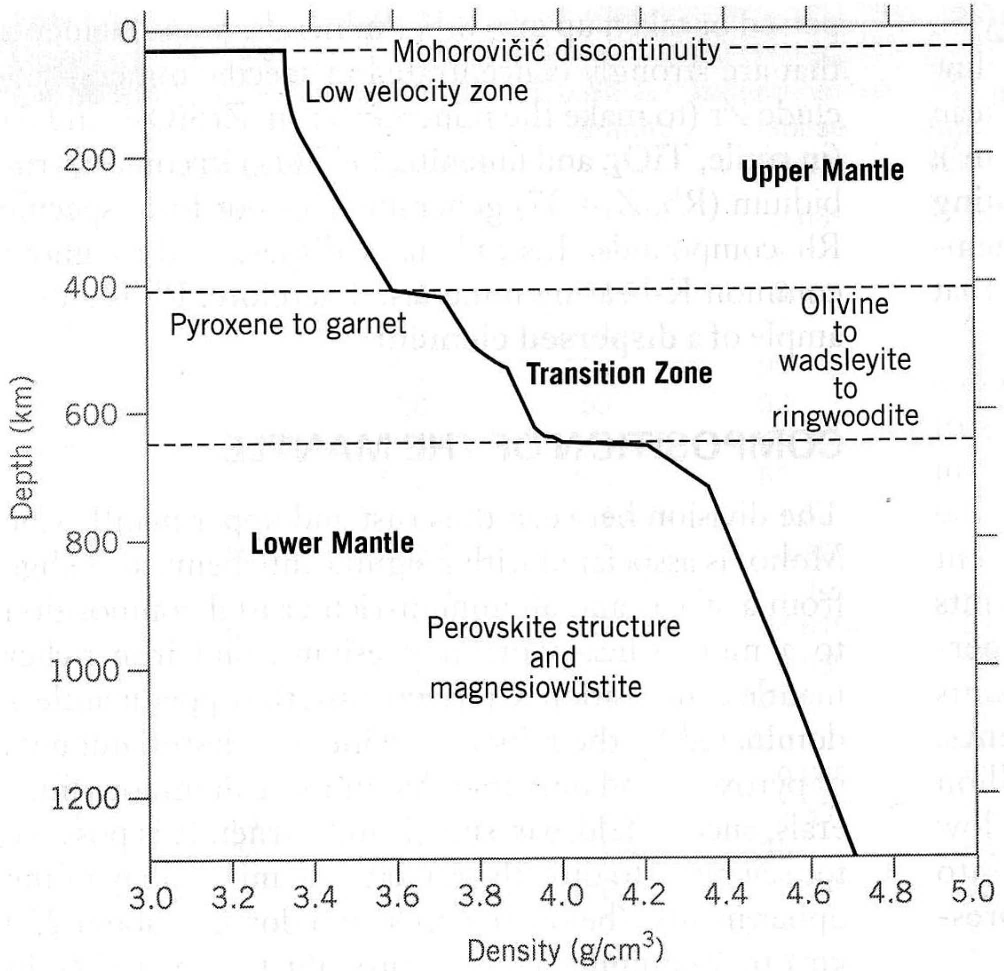
- **Whole Earth (wt. %)**
  - Fe 25%
  - O 30%
  - Si 15%
  - Mg 13%
  - Other 7%
- Explained by **olivine** composition and iron-rich core
- Note olivine structure changes with pressure!



Chemical Composition of the Earth



Chemical Composition of the Earth



$Mg_2^{[6]}Si^{[4]}O_4 \rightarrow$
olivine structure

($\rho = 3.22$ gm/cm^3)

$Mg_2^{[6]}Si^{[4]}O_4 \rightarrow$
spinel structure
(wadsleyite)
($\rho = 3.47$ gm/cm^3)

$Mg_2^{[6]}Si^{[4]}O_4 \rightarrow$
spinel structure
(ringwoodite)
($\rho = 3.55$ gm/cm^3)

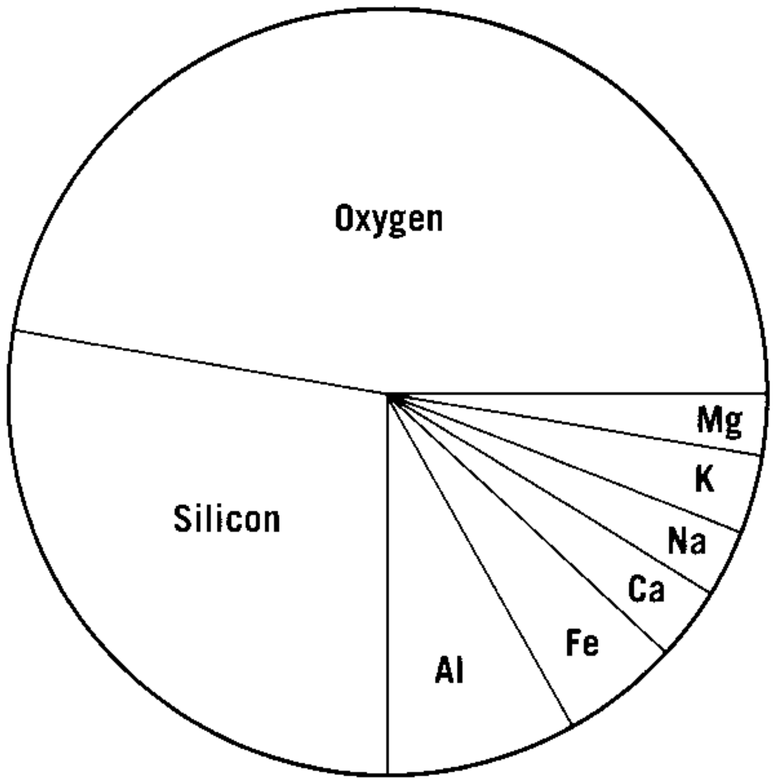
$Mg_2^{[8]}Si^{[6]}O_3$ $+ Mg^{[6]}O$
perovskite structure, halite structure

($\rho = 4.10$ gm/cm^3)

Chemical Composition of the Earth

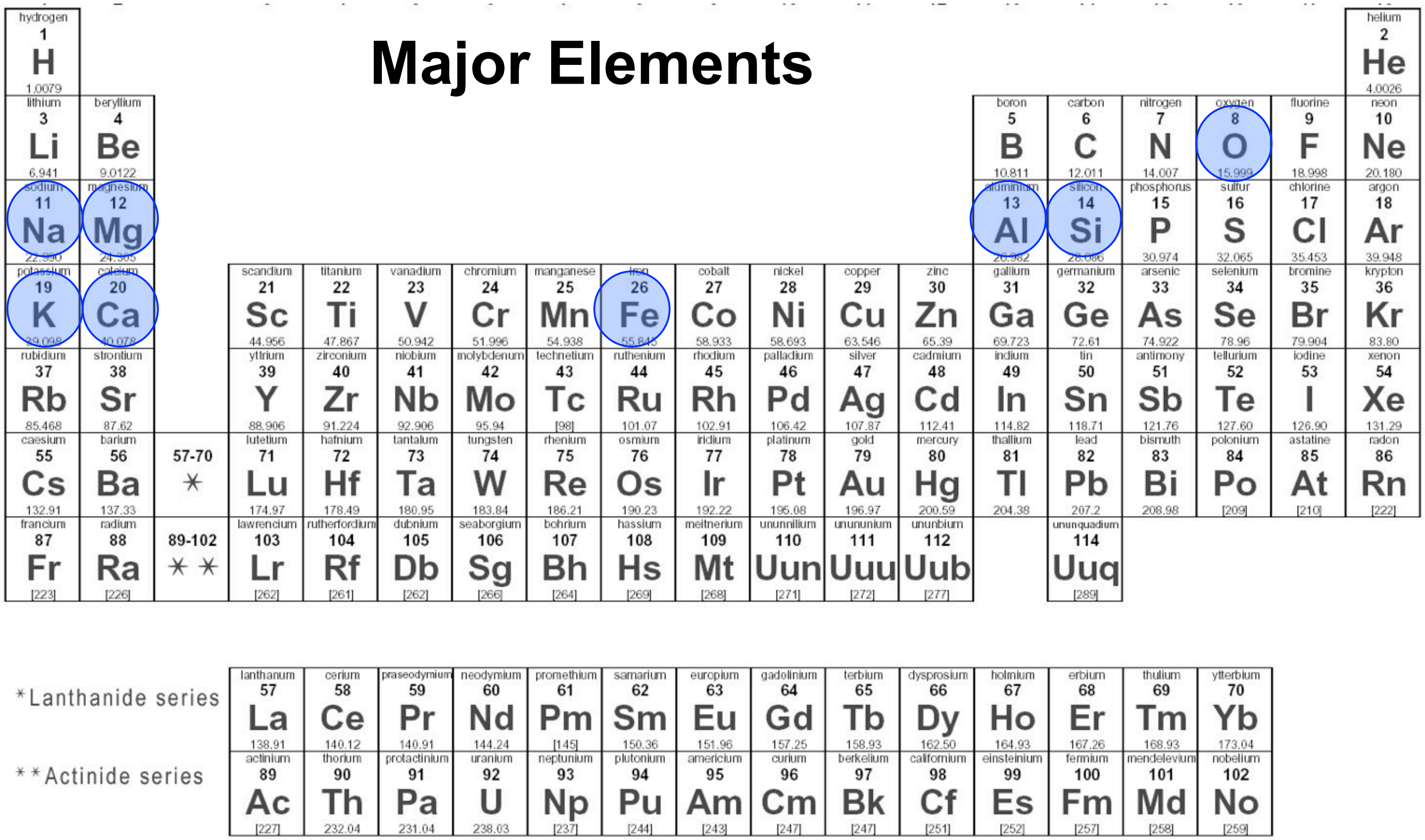
- **Average Crust**

	Weight percent*	Atom percent	Ionic+ radius (Å)	Volume percent
O	46.60	62.55	1.36	~ 94
Si	26.72	21.22	0.26 [4]	~ 6% in total
Al	8.13	6.47	0.39 [4]	
Fe	5.00	1.92	0.78 [6]	
Ca	3.63	1.94	1.00 [6]	
Na	2.83	2.64	1.02 [6]	
K	2.59	1.42	1.51 [8]	
Mg	2.09	1.84	0.72 [8]	
	98.59	100.00		



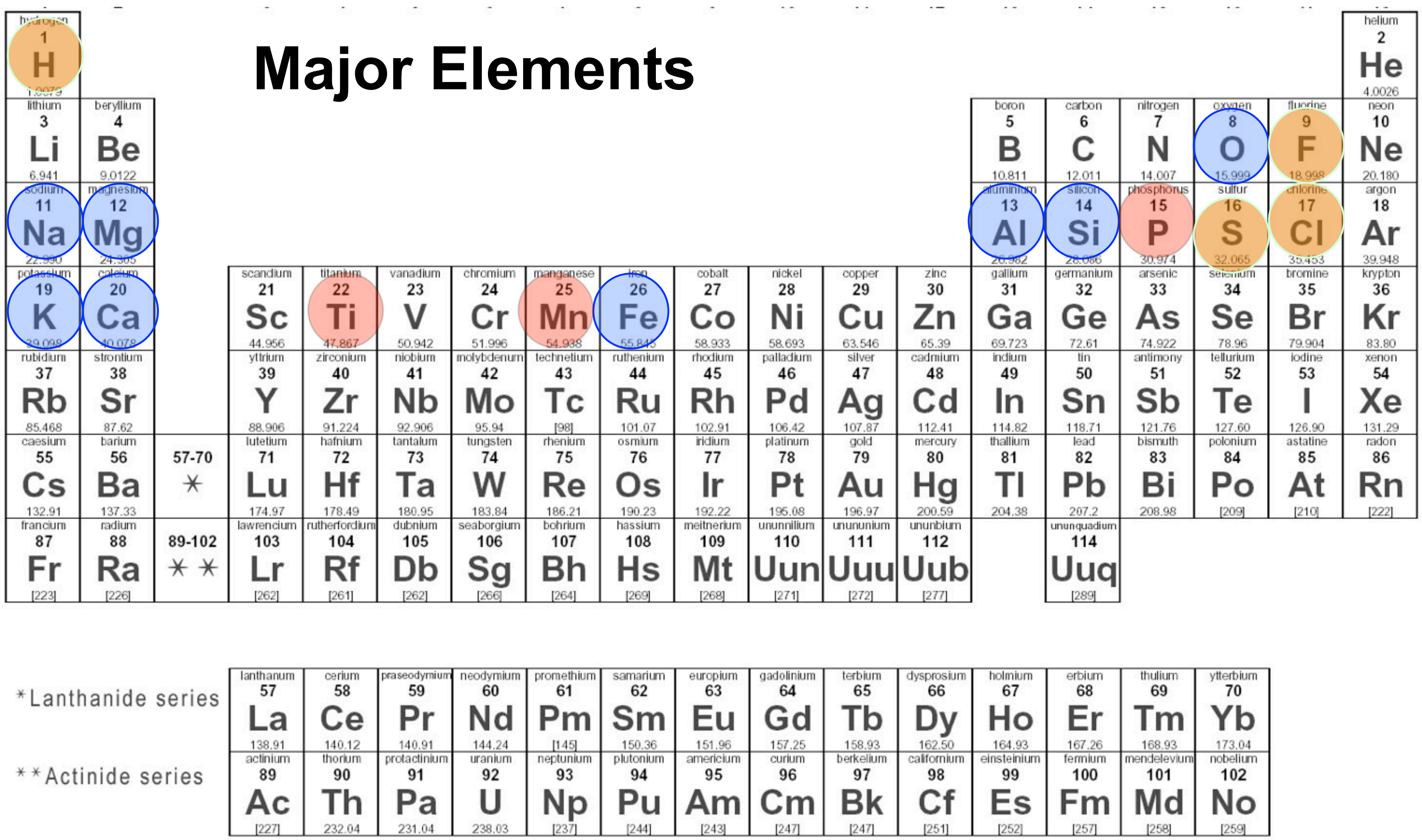
Weight percent

Chemical Composition of the Earth



- Major elements >1 wt%
  - – O, Si, Al, Fe, Ca, Na, K, Mg

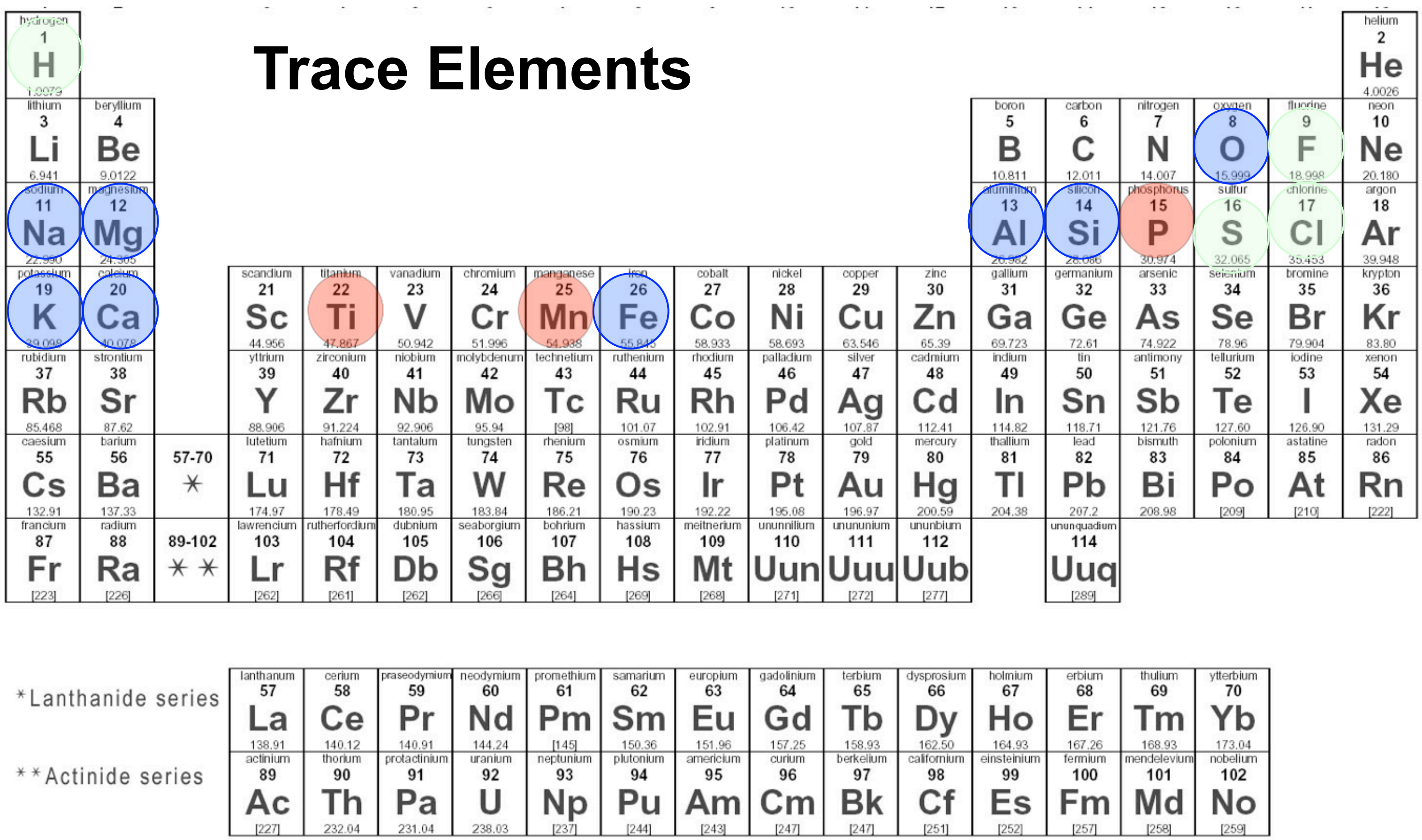
Chemical Composition of the Earth



Minor elements 0.1-1 wt.%: Ti, Mn, P

typically includes volatile elements too

Chemical Composition of the Earth



The rest--- Trace elements (<0.1wt.%)

reported in ppm or parts per million: 0.01 to 100,000 ppm

ppm→wt. %   ppm*10,000= wt.%

Mineral Formulas

- Multi-Step Process:
  1. Write out cations, followed by anions or anionic groups
  2. Make sure the charge is balanced
  3. Group cations by structural site (coordination!)

  – Ex: diopside: $CaMgSi_2O_6$
    1. $Ca^{+2}Mg^{+2}Si_2^{+4}O_6^{-2}$ ✔
    2. $2 + 2 + (4*2) + (-2*6) = 0$ ✔
    3. $^{VIII}Ca^{VI}(Mg,Fe)^{IV}Si_2O_6$ ✔

Converting from Analysis

- Multi-Step Process:
  - Chemical data usually reported in wt.% oxide
    - wt. % from early chemical analyses by wet chemistry titrations
    - Modern equipment measures atomic proportions, but calibrates to wt.%
  - Must covert wt. % to molecular (or “atomic”)%
  - Simplify to relate to a chemical formula, typically normalize to a set number of “oxygens”

Converting from Analysis

- Multi-Step Process:
  1. Calculate moles of oxide = wt.% / molecular wt.
  2. ” moles of oxygen = moles oxide*oxygen stoichiometry
  3. ” moles of cation = moles oxide*cation stoichiometry
  4. Recalculate based on a set number of oxygen (or anions)

     a. Choose a desired amount of oxygen

     b. Divide amount of oxygen by the sum moles oxygen

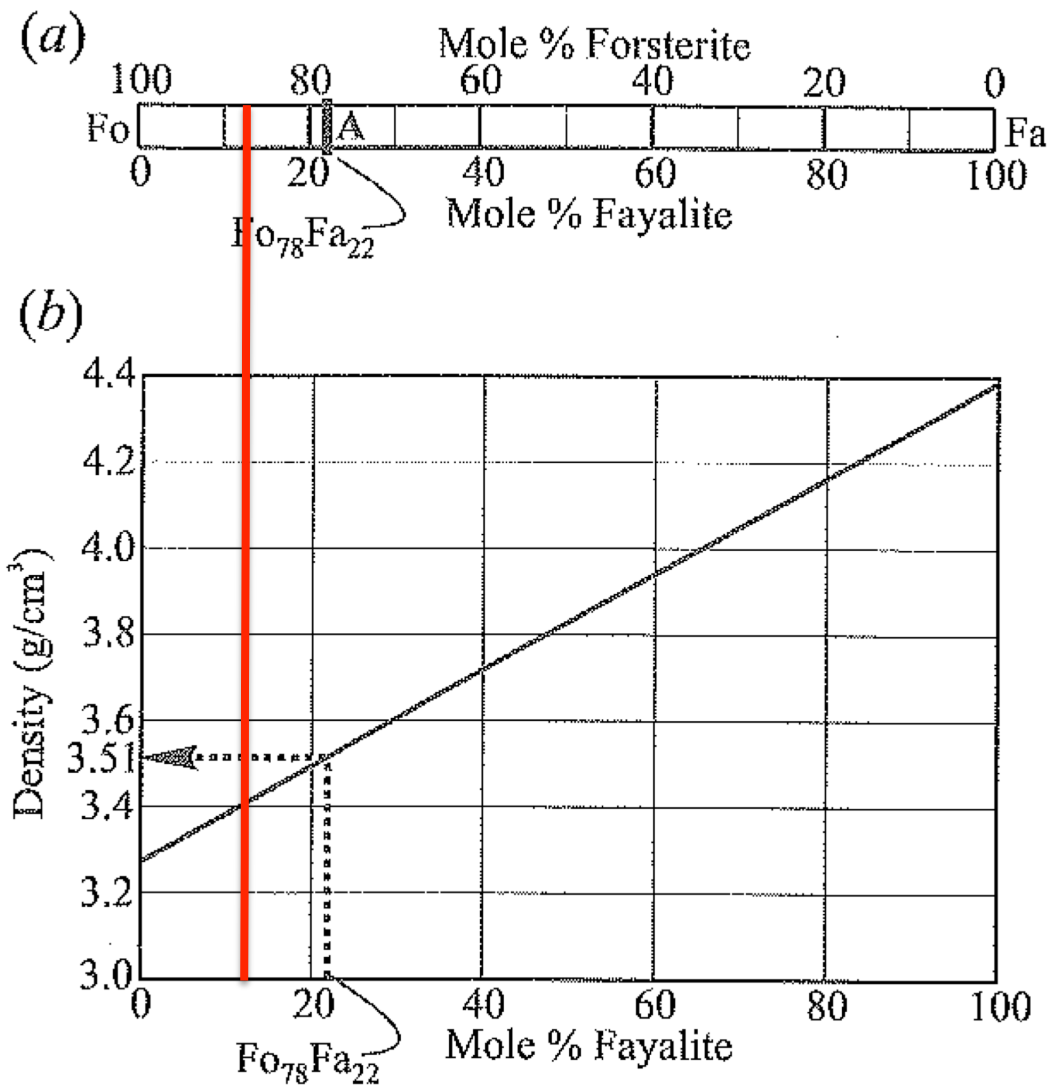
     c. Multiply this factor by each cation value
  5. Identify structural site for each cation

Converting from Analysis

			1	2	3	4	5	
	wt. %	molecular wt. (x/mol)	Moles Oxide	Moles Oxygen	Cation Moles	normailzed to Oxygen	Site	
SiO2	**39.80**	60.08	0.6625	1.325	0.6625	0.996	tet	
Al2O3	0.05							
K2O	-0.01							
MnO	0.20							
FeO	**12.04**	71.85	0.1676	0.167631176	0.1676	0.2521	oct	**Fo content**
NiO	0.40							**0.874**
Na2O	-0.02							
MgO	**47.04**	40.30	1.167	1.167	1.167166253	1.755	oct	
CaO	0.32							
TiO2	0.03							
Cr2O3	0.07							
Total	99.95			2.660		4	Oxygen Desired	
				1.504	=cation mult. Factor			

Plotting Compositions

Our olivine was **Fo$_{87}$**, so we can plot as 87% forsterite



We can use this to understand useful physical properties of the mineral, like denisty (right) and as we will see later, temperature!

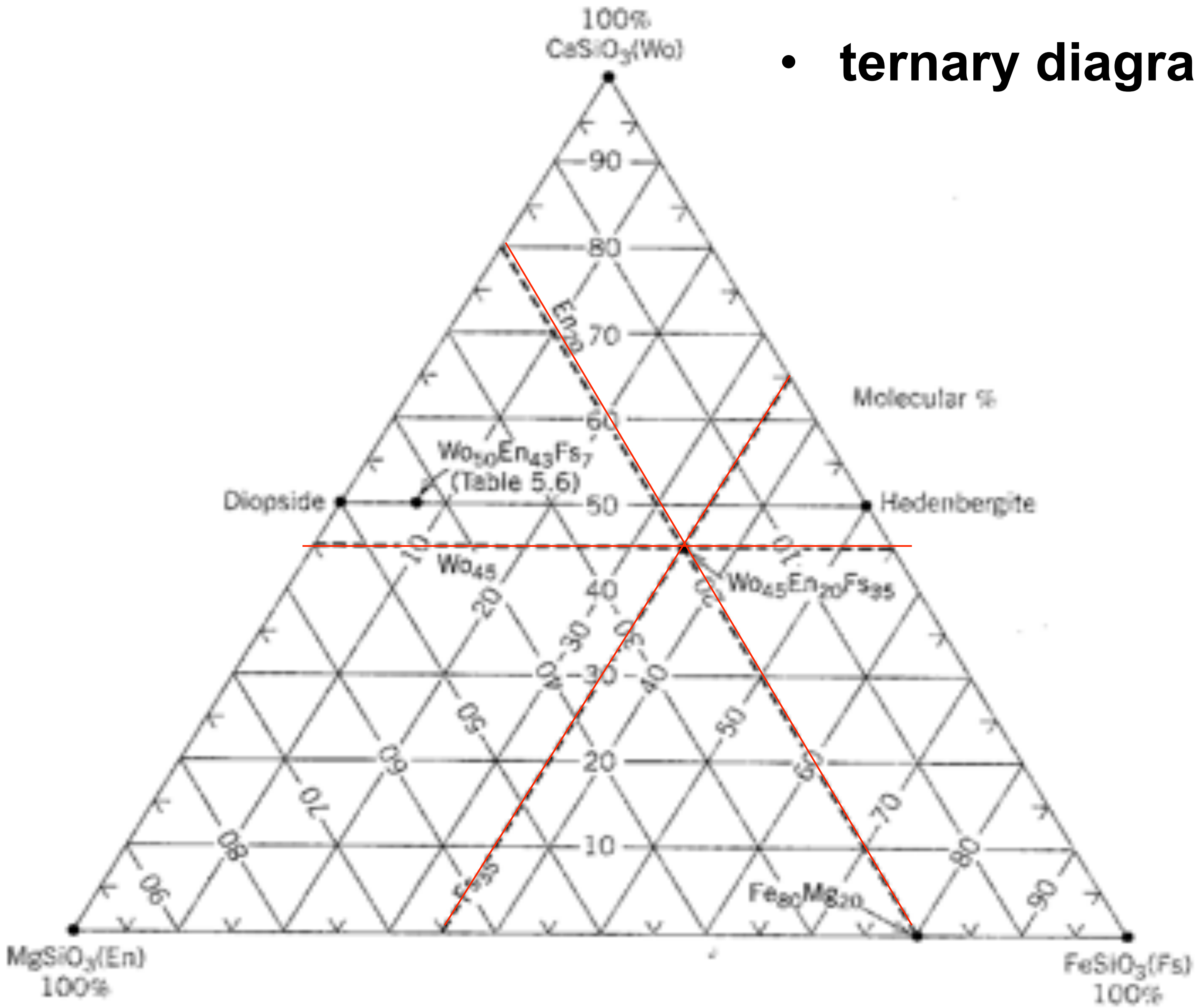
Fo$_{87}$ will have a density = 3.4 g/cm^3

Plotting Compositions

- If you have more than two variable elements, a **ternary diagram** can be useful!
  - *Pyroxenes*
  - Feldspars
  - Garnets (*2!)
- What if you have more than 3 variables?
  - Can plot a 3^{rd} dimension, ex: Spinel Prism

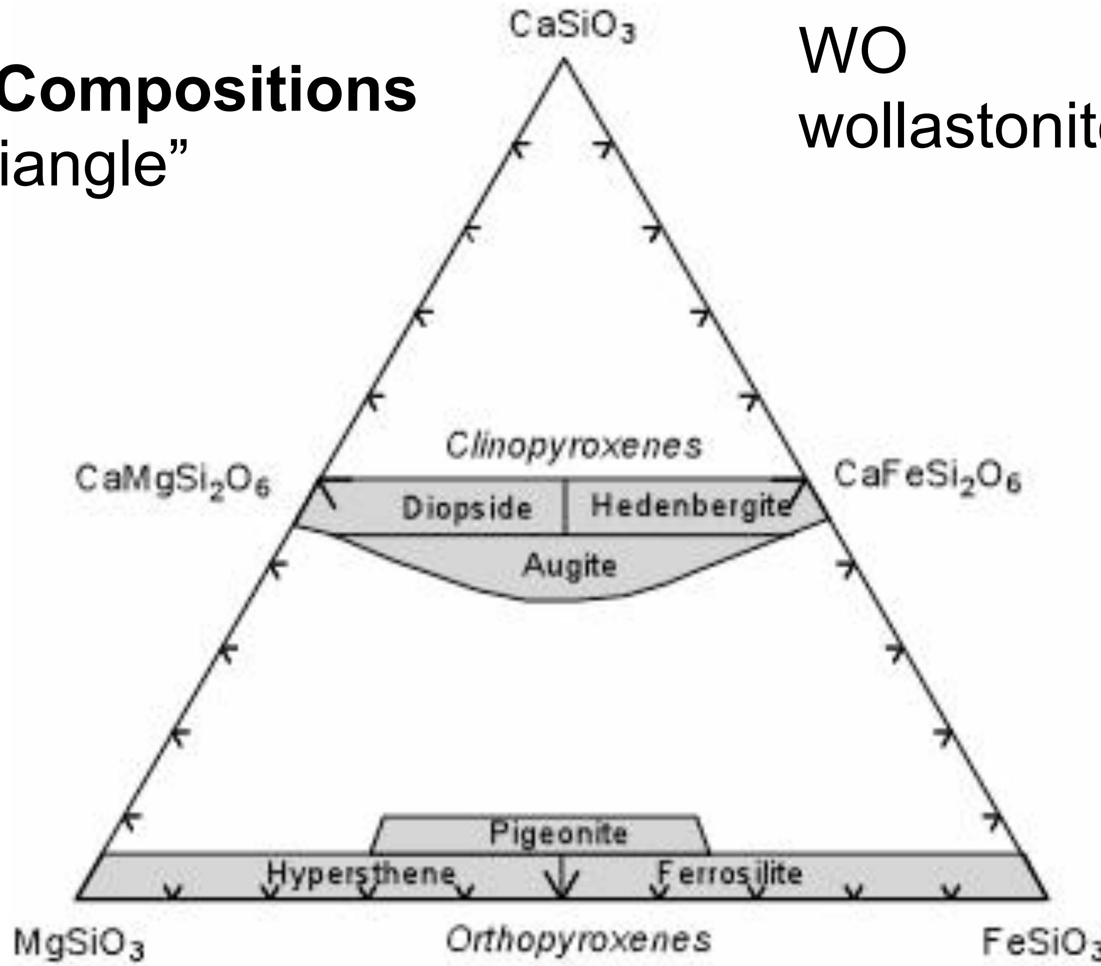
Plotting Compositions

- **ternary diagram** *Pyroxenes*



Classification Diagrams

Pyroxene Compositions
"Triangle"



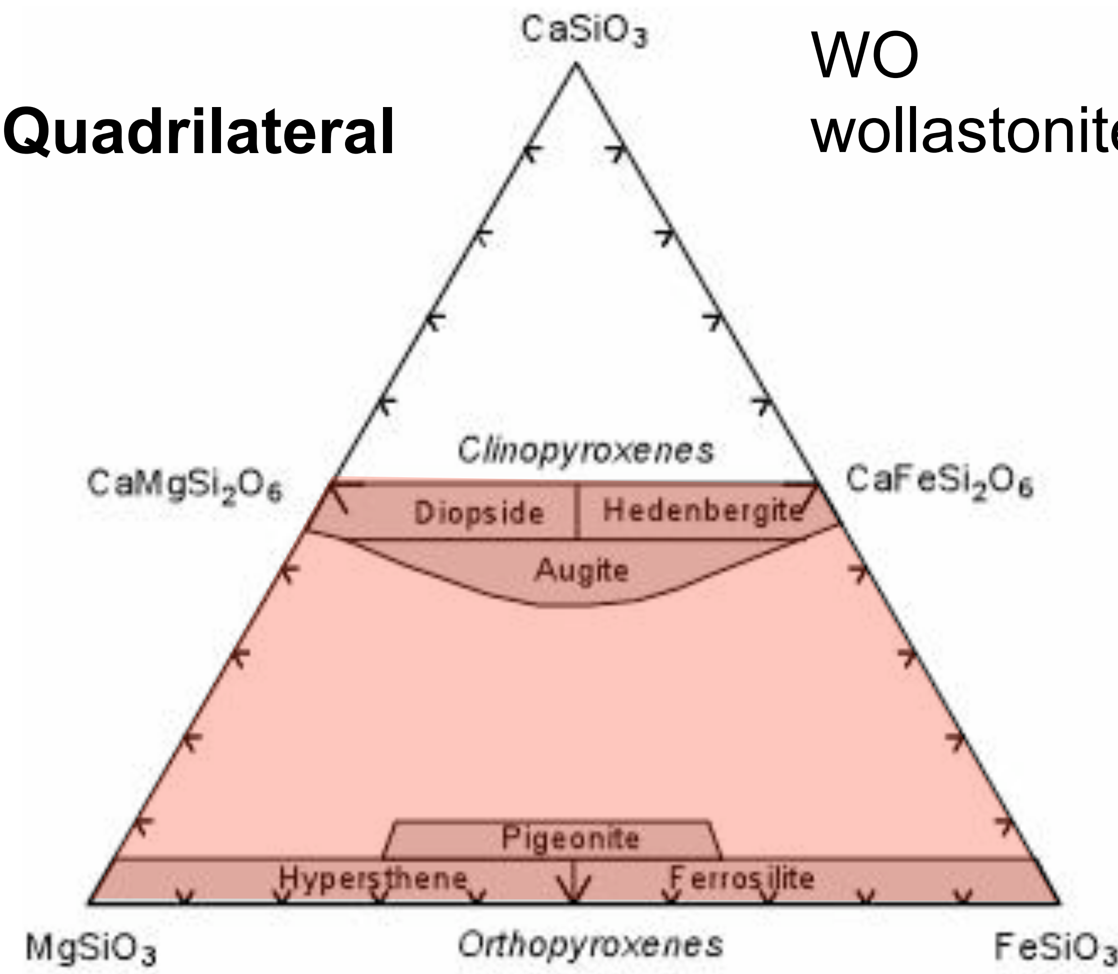
WO
wollastonite

EN
$Mg_2Si_2O_6$
Enstatite

FS
$Fe_2Si_2O_6$
Ferrosilite

Classification Diagrams

Pyroxene Quadrilateral



WO
wollastonite

EN
$Mg_2Si_2O_6$
Enstatite

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$Fe_2Si_2O_6$
Ferrosilite

Plotting Compositions

- If you have more than two variable elements, a **ternary diagram** can be useful!
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Before we examine these, let's think about solid solution more!

Solid Solution

- 3 Basic Types Solid Solution:
  1. **Substitution (Simple or Coupled)**
  2. **Omission**
  3. **Interstitial**

- Continuous (all proportions of elements can substitute)
- Discontinuous/Partial (restricted range of compositions)

Solid Solution

1. **<u>Substitution Solid Solution</u>**

- Similar elements can substitute into a structural vacancy following **Goldschmidt's Rules**:
  - Similar size (+/- 15%)
  - Electric neutrality is maintained (net charge of substitution equal)
  - Similar electronegativity (bond type)

- Other Factors include:
  - Availability of Ions
  - **Temperature and pressure** effects on mineral structure

Solid Solution

1a. Simple Substitution

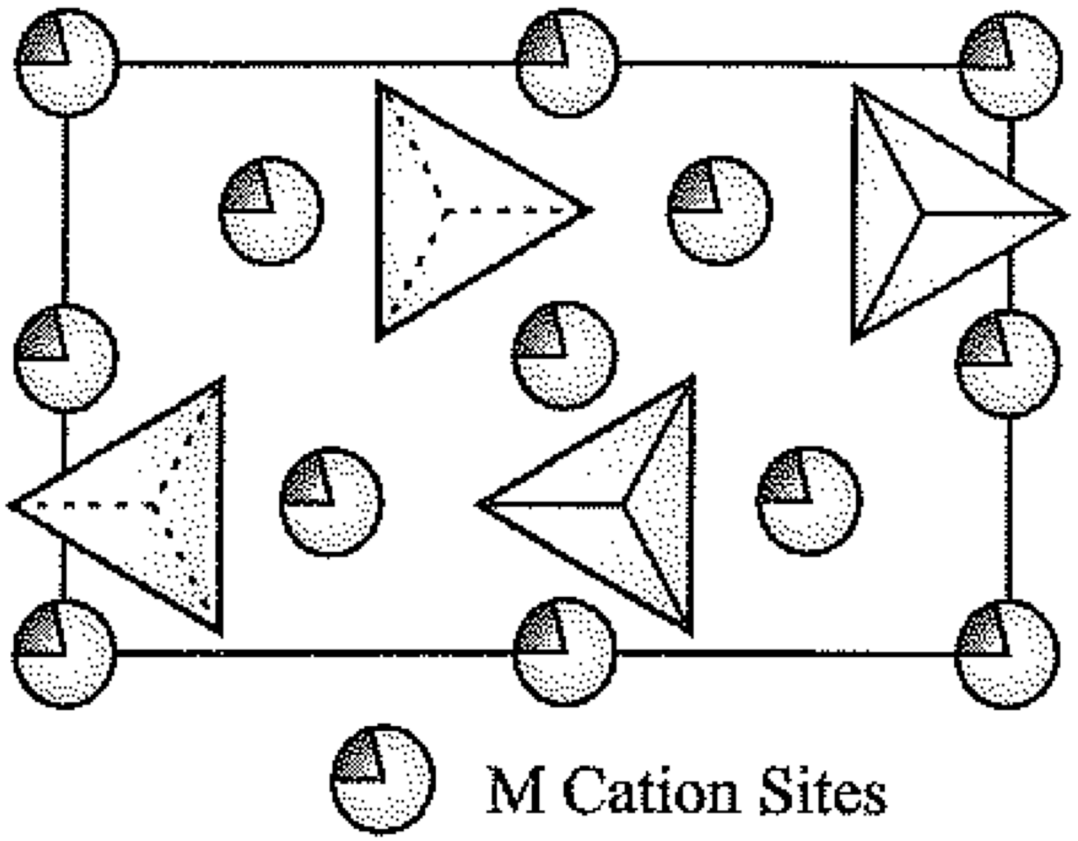
- Remember Pauling's First rule: coordination of structural sites dependent on Radius Ratio
- If **size difference <15%**, generally can accommodate substitution!
- Must be same charge!
- Increases in Temperature loosen structure, allowing larger size difference!**

  **decrease in temperature may cause *exsolution*

- Ex: **olivine** Fe-Mg; **pyroxenes** Fe-Mg, (Mg,Fe)-Ca; **alkali feldspar** Na-K

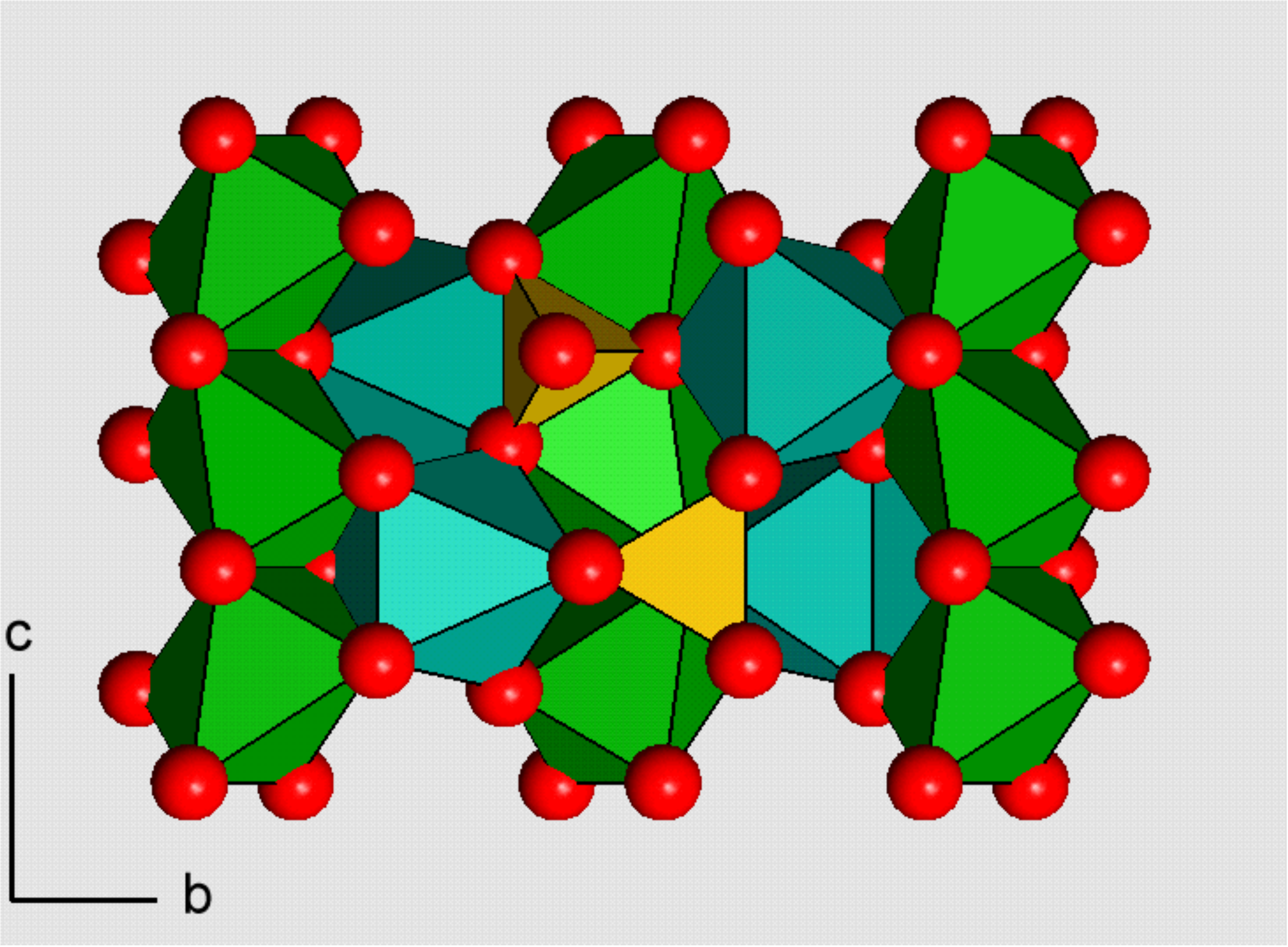
Solid Solution

Olivine solid soln*



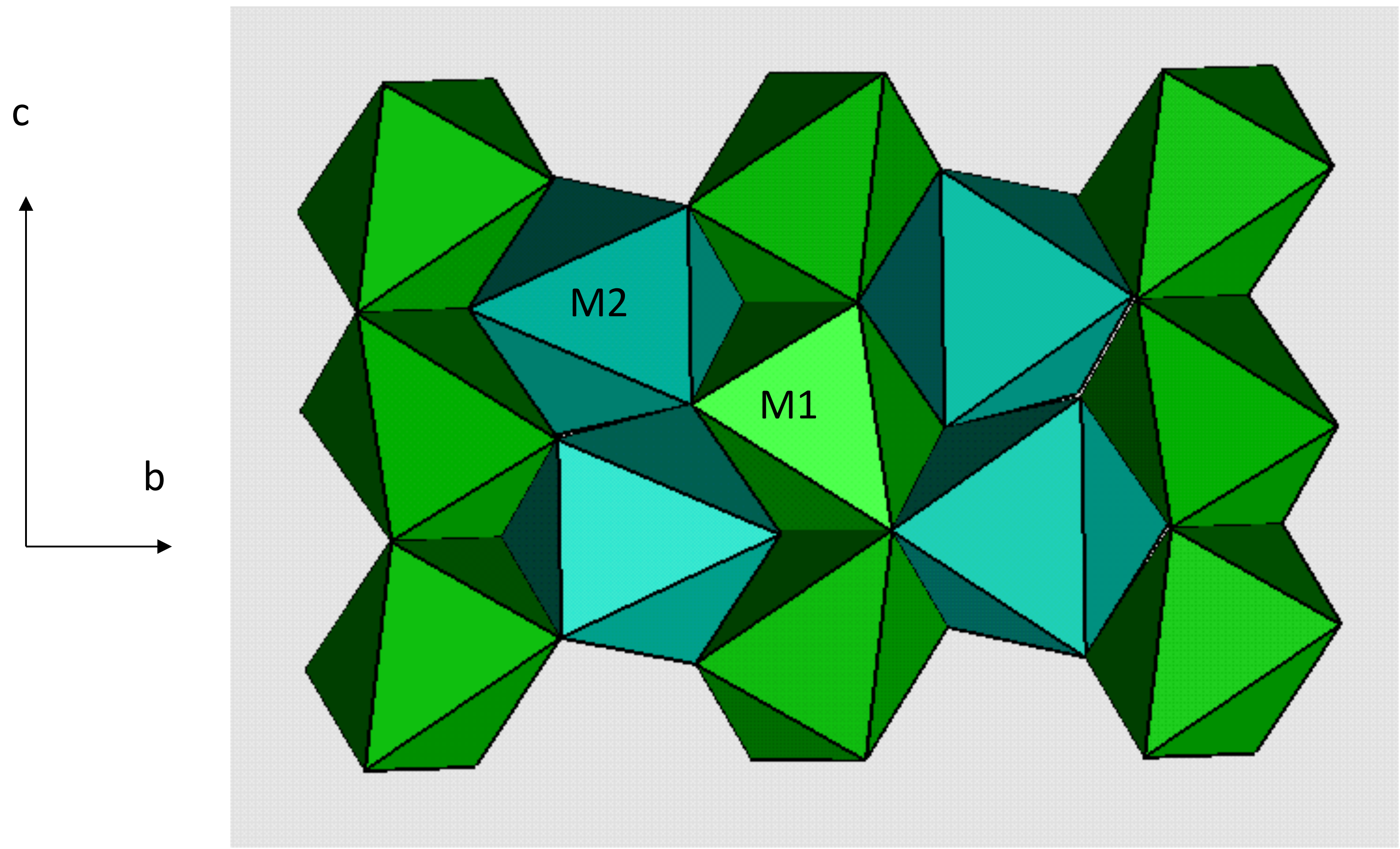
Solid Solution

Olivine solid soln



Solid Solution

note deformed octahedra= edge sharing!



Two octahedral cation (Mg^{2+}, Fe^{2+}) sites:

M1
M2

Solid Solution

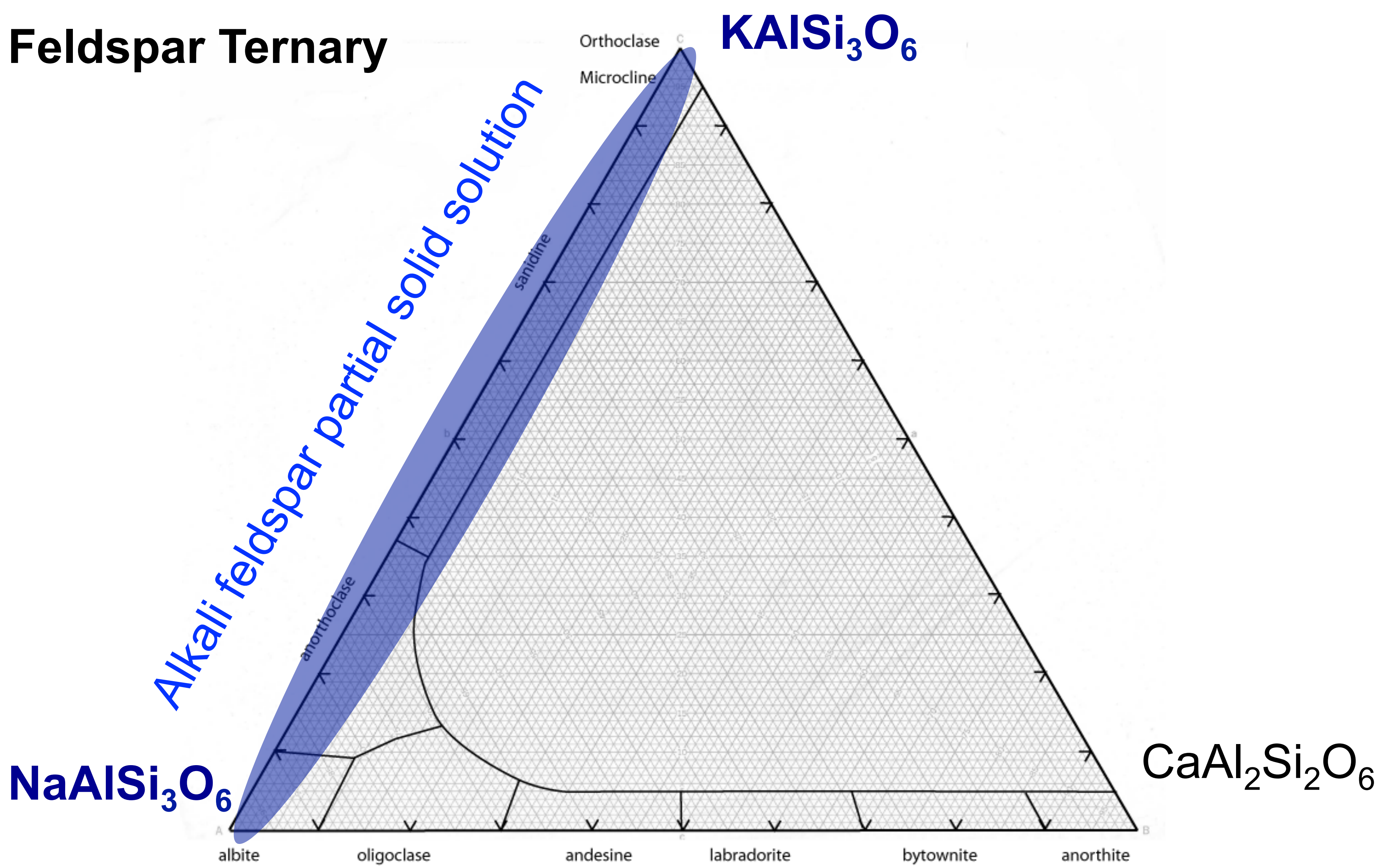
Compare cation sites, where does Mg and Fe go?

M1	M2
Distorted 6-coordination	More Distorted 6-coordination
<M-O> = 2.16 Å	<M-O> = 2.19 Å
Smaller site	Larger site

(recall: Mg^{2+} is smaller than Fe^{2+})

Solid Solution

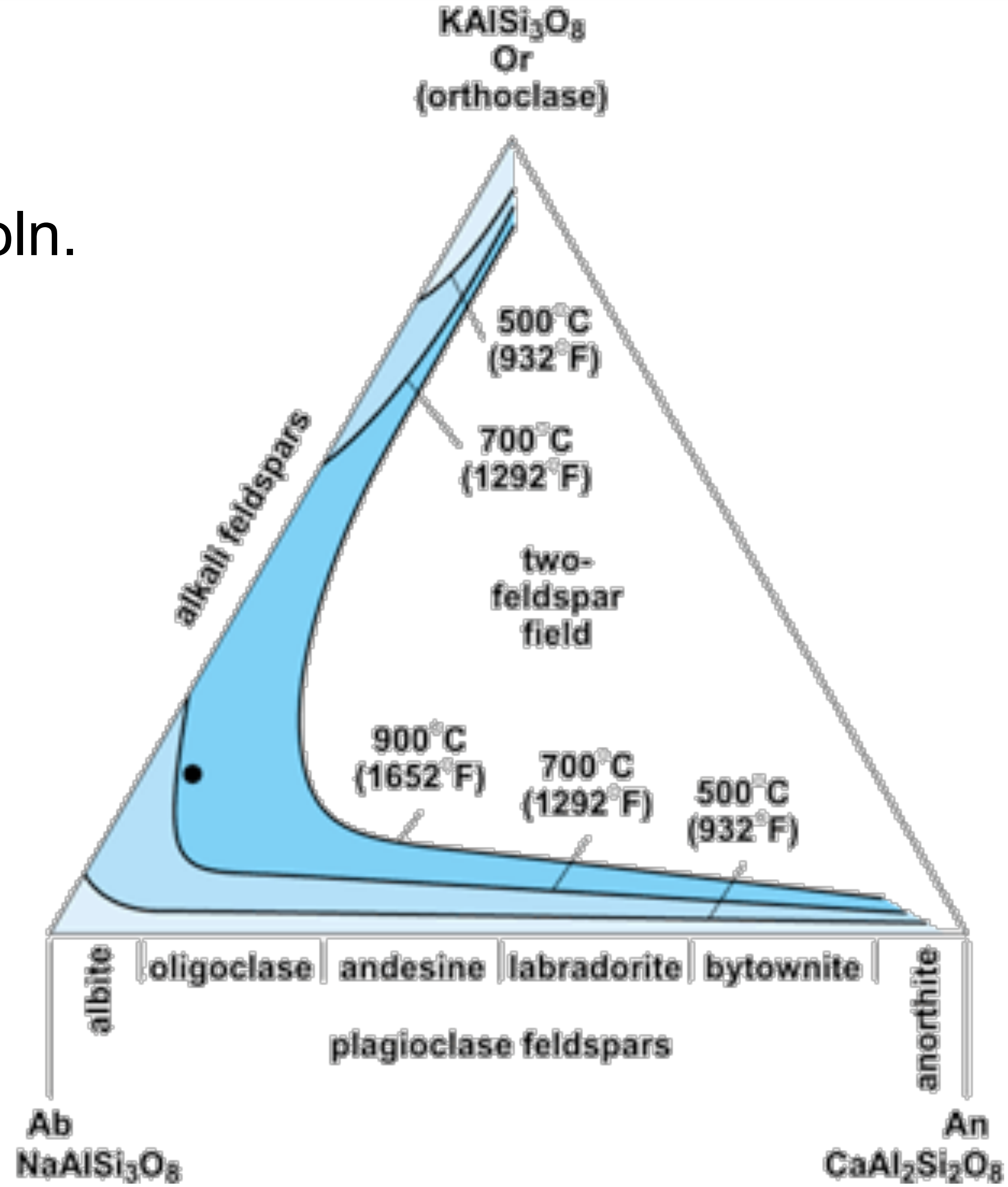
Feldspar Ternary



Solid Solution

Feldspar Ternary

High T expands solid soln.
of alkai fspars!



Solid Solution

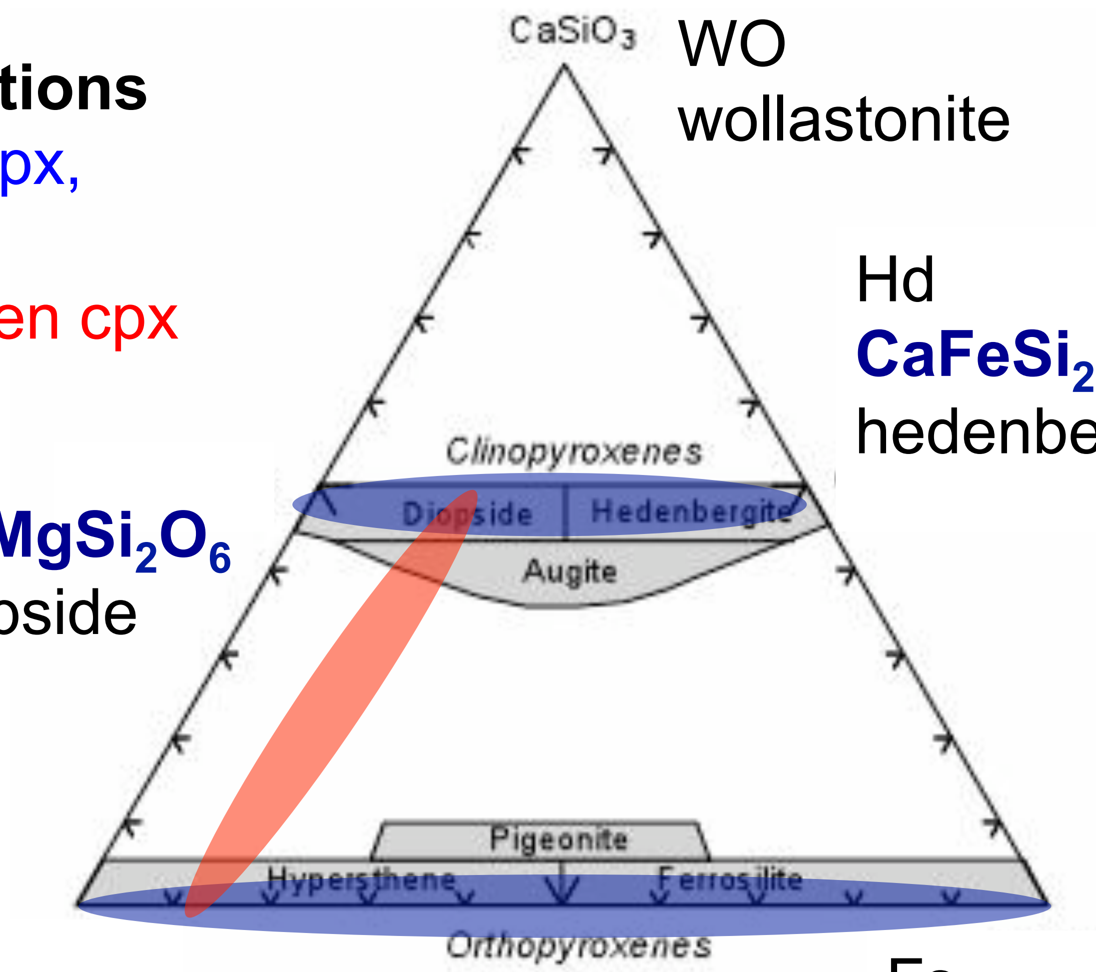
Pyroxene Compositions

- Complete within opx, some cpx
- Incomplete between cpx and opx

WO
wollastonite

Hd
$CaFeSi_2O_6$
hedenbergite

Di
$CaMgSi_2O_6$
diopside

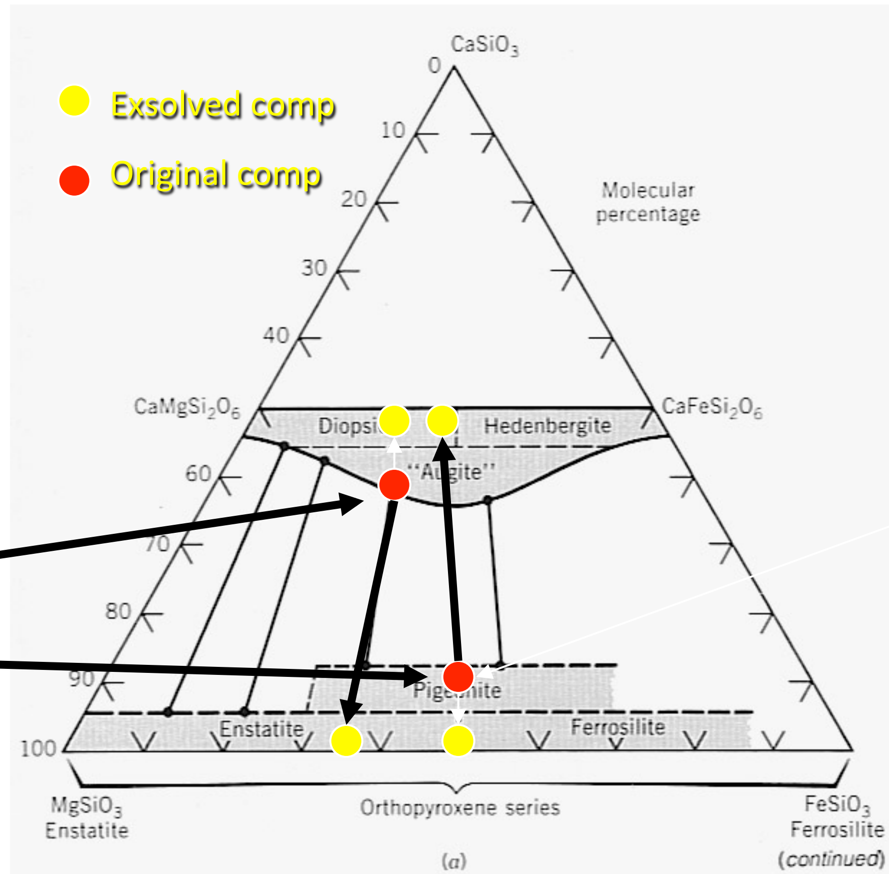


En
$Mg_2Si_2O_6$
Enstatite

Fs
$Fe_2Si_2O_6$
Ferrosilite

Solid Solution

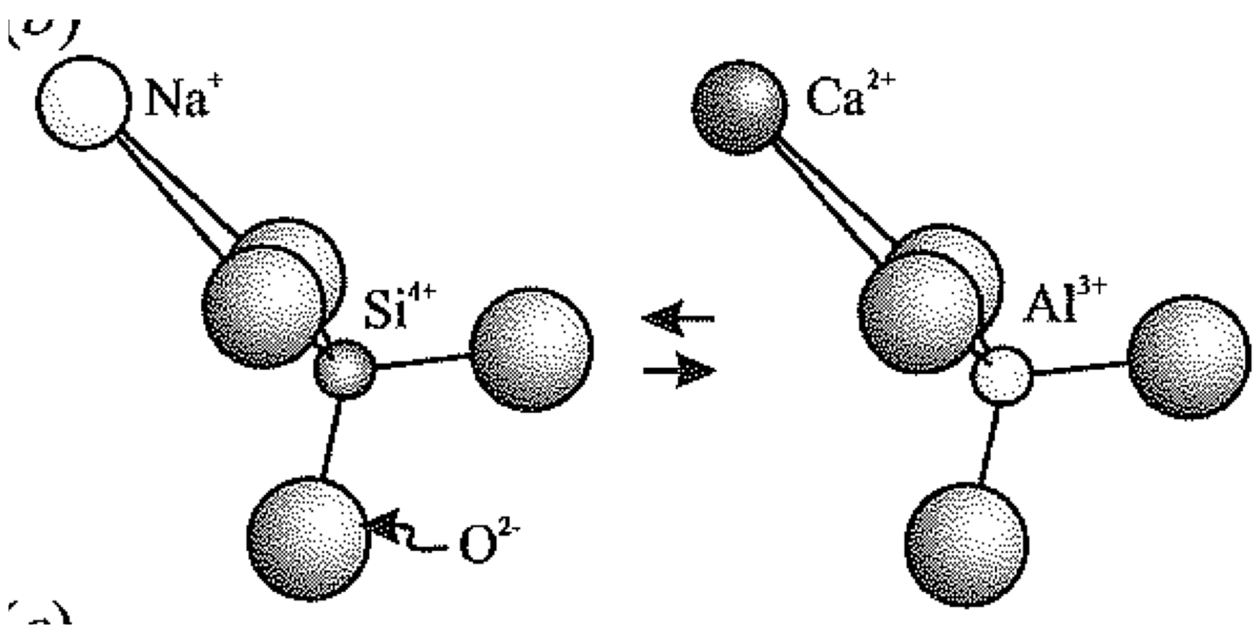
Pyroxene exsollution (opx and cpx)



Solid Solution

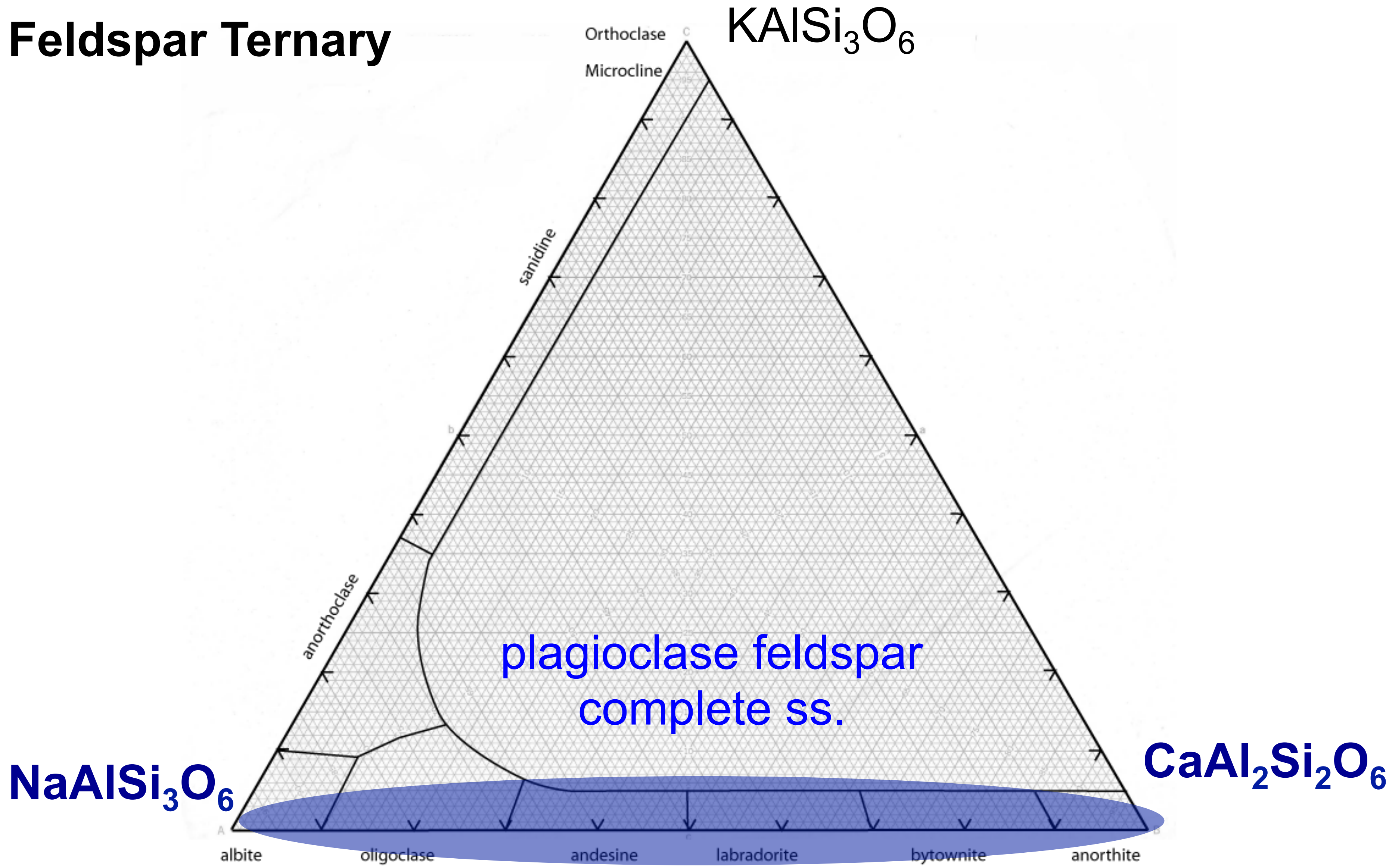
<u>1b. Coupled Substitution</u>

– Similar size, but *different charge*
– Elements pair up in exchange to maintain neutral charge
– Example: Albite-Anorthite



Solid Solution

Feldspar Ternary



Solid Solution

2. <u>Omission Solid Solution</u>

- Charge balance maintained by leaving a structural site unfilled
- Ex: pyrrhotite

$$\mathbf{Fe_{1\text{-}x}S}\ (x=0\text{-}0.2)$$

$$\mathbf{Fe^{2+}_{1\text{-}3x}Fe^{3+}_{2x}\,\square_{x}S}$$

  – Vacant sites (□) are occasionally filled with Fe^{3+} to balance charge

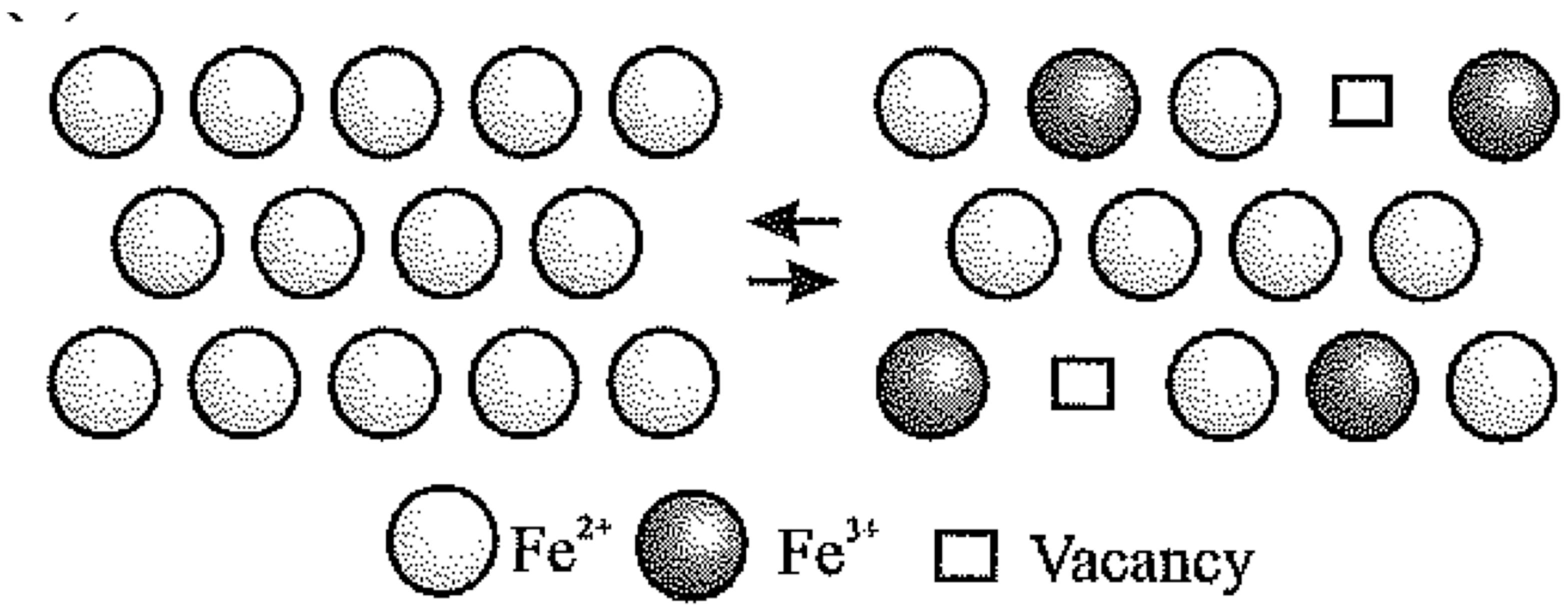
Solid Solution

2. Omission Solid Solution

- Ex: pyrrhotite

$$\mathbf{Fe_{1-x}S}\ (x=0\text{-}0.2)$$

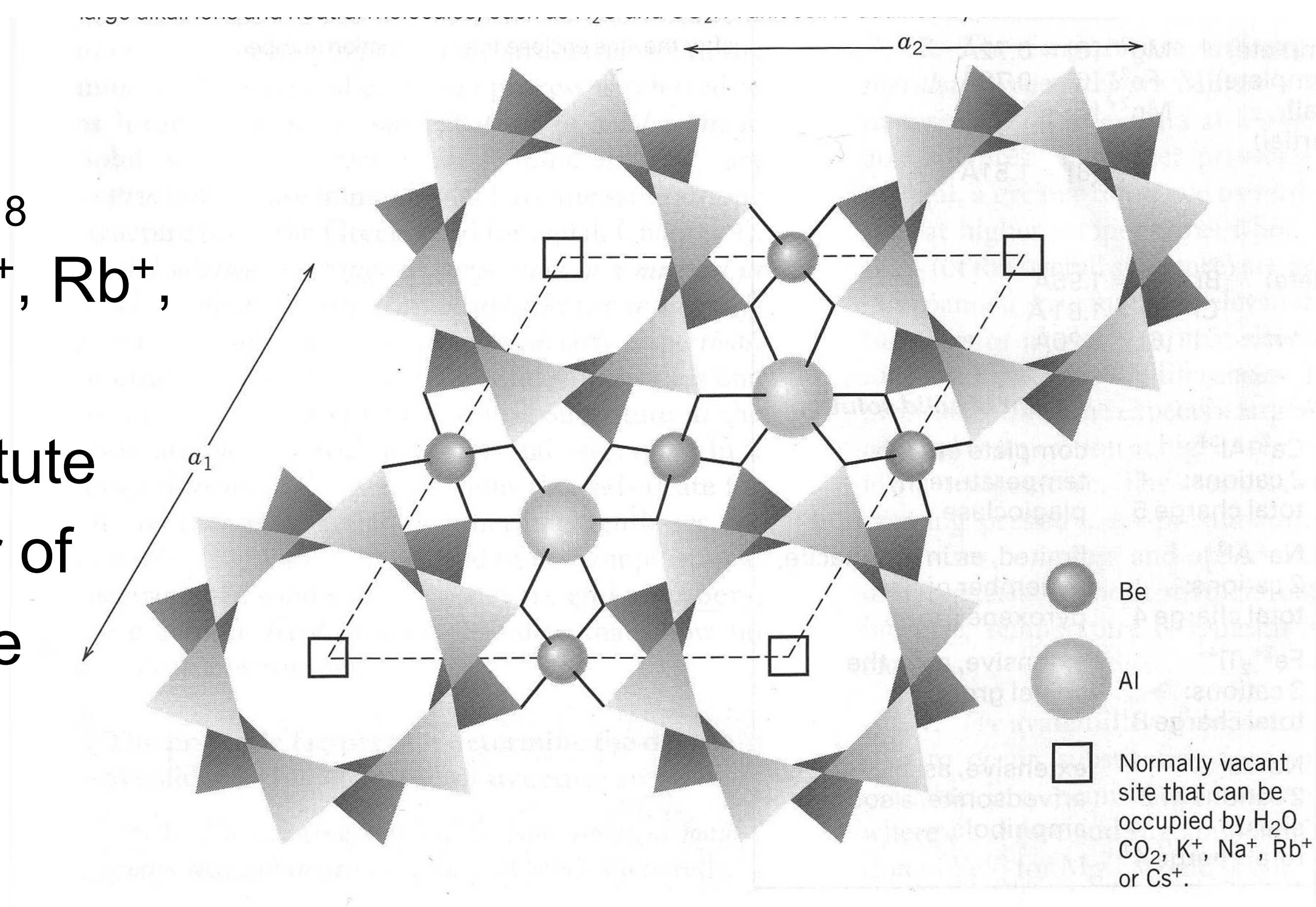
$$\mathbf{Fe^{2+}_{1-3x}Fe^{3+}_{2x}\,\square_{x}S}$$



Solid Solution

3. **<u>Interstitial Solid Solution</u>**

- Charge balance maintained by filling a normally unfilled structural site
- Ex: beryl
  - $Al_2Be_3Si_6O_{18}$
  - K^+, Na^+, Cs^+, Rb^+, H_2O, CO_2 can substitute into center of sorosilicate ring



Solid Solution

3. **Interstitial Solid Solution**

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  - $Al_2Be_3Si_6O_{18}$
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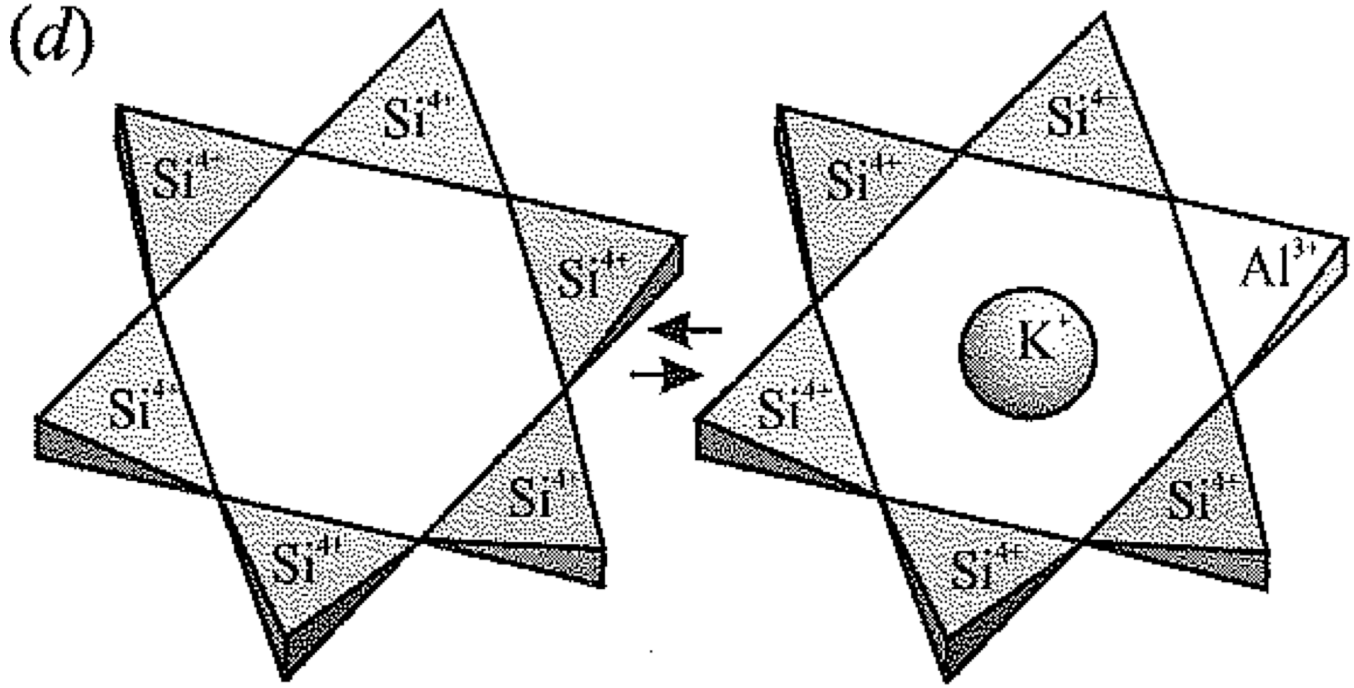


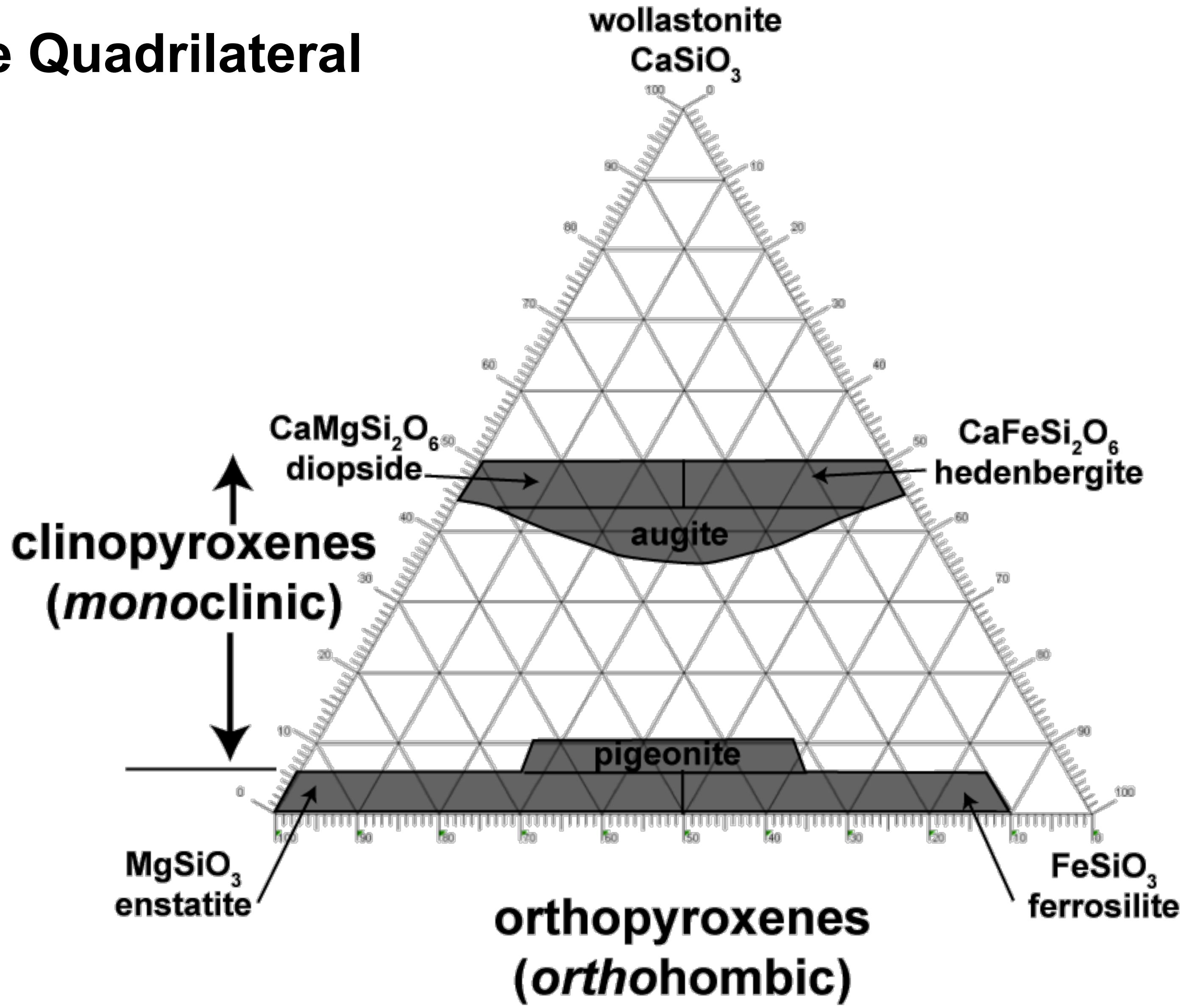
Classification Diagrams

- If you have more than two variable elements, a **ternary diagram** can be useful!
  - Pyroxenes
  - Feldspars
  - Garnets (*2!)

- What if you have more than 3 variables?
  - Can plot a 3^{rd} dimension, ex: Spinel Prism

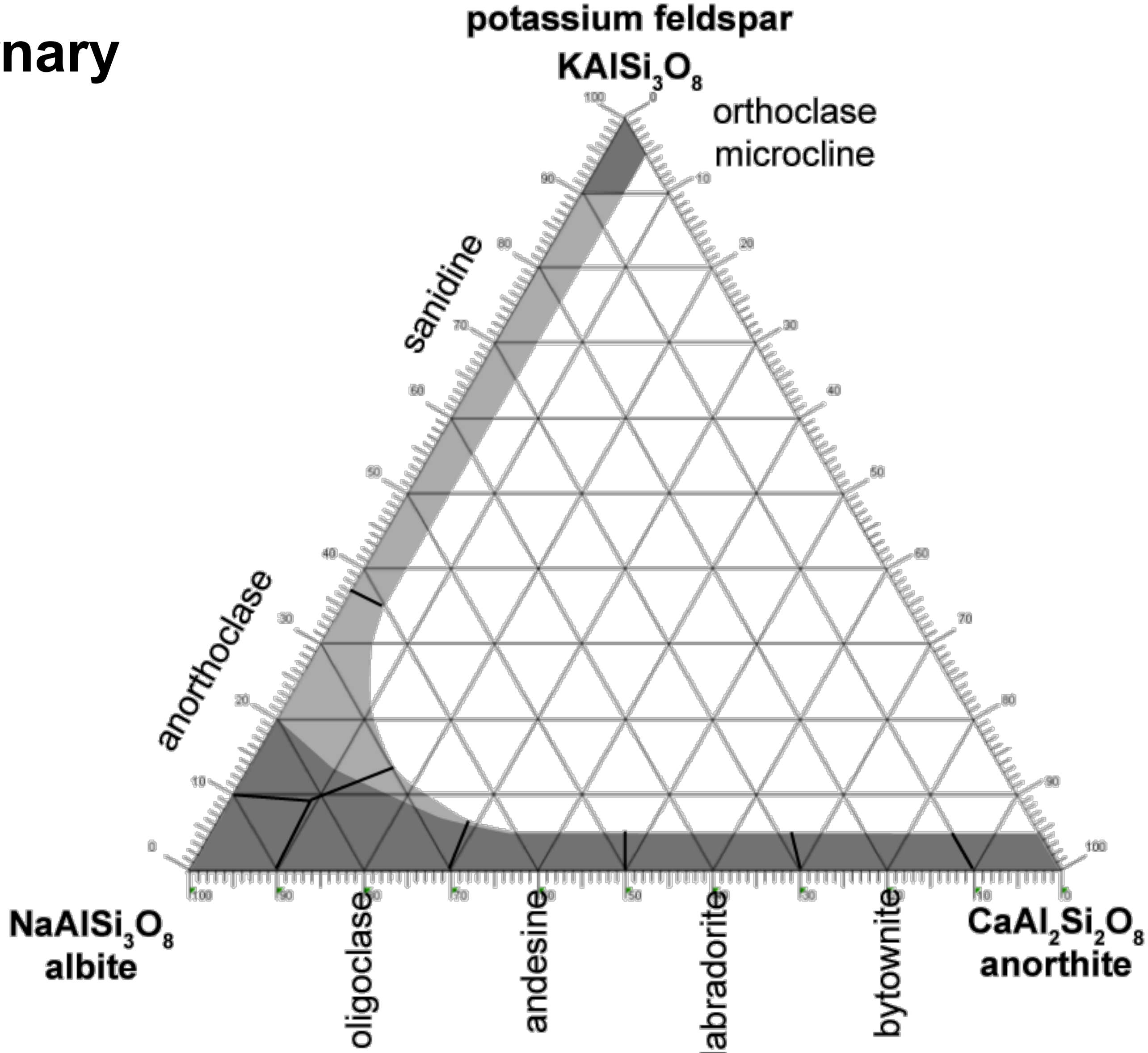
Classification Diagrams

Pyroxene Quadrilateral



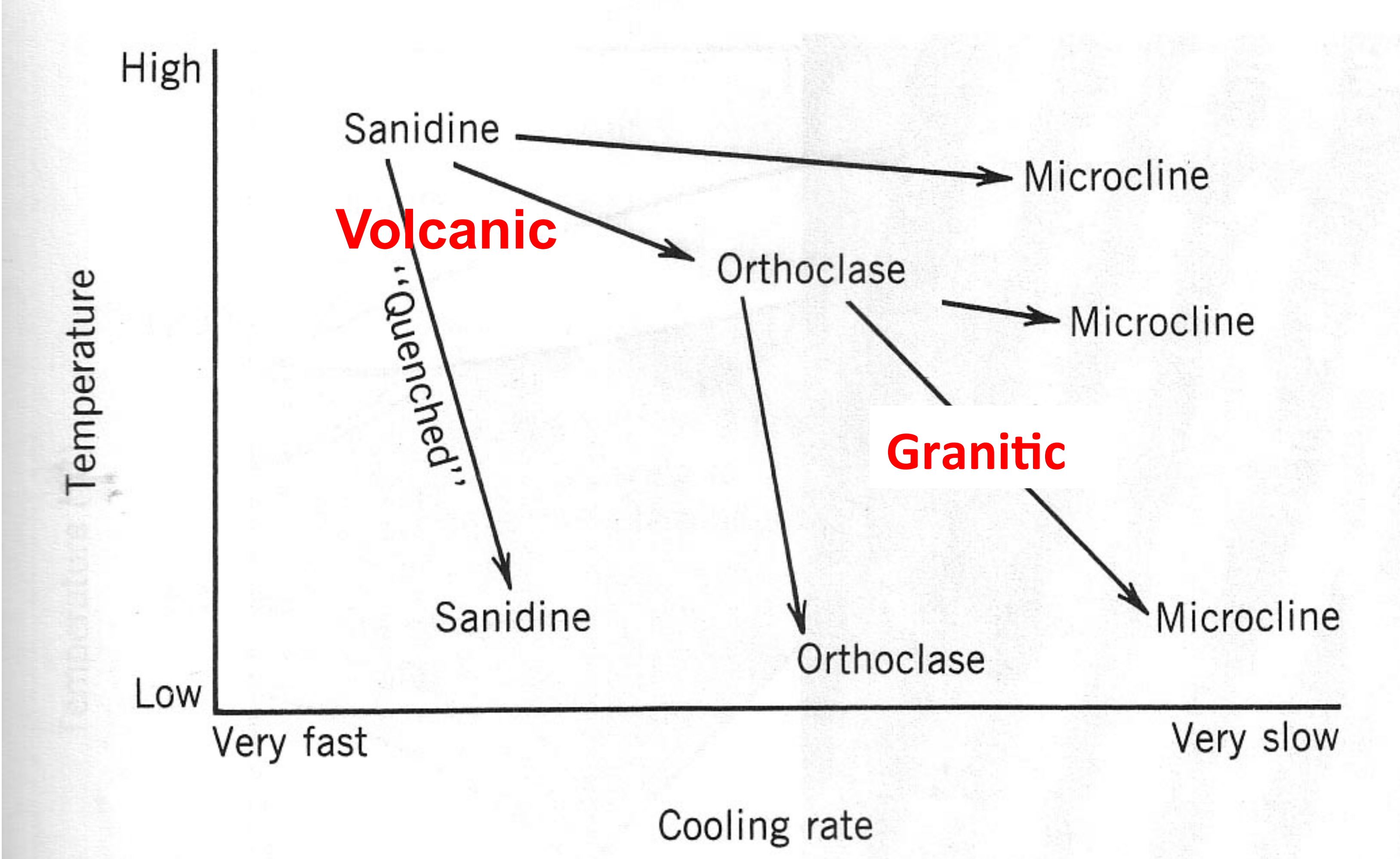
Classification Diagrams

Feldspar Ternary



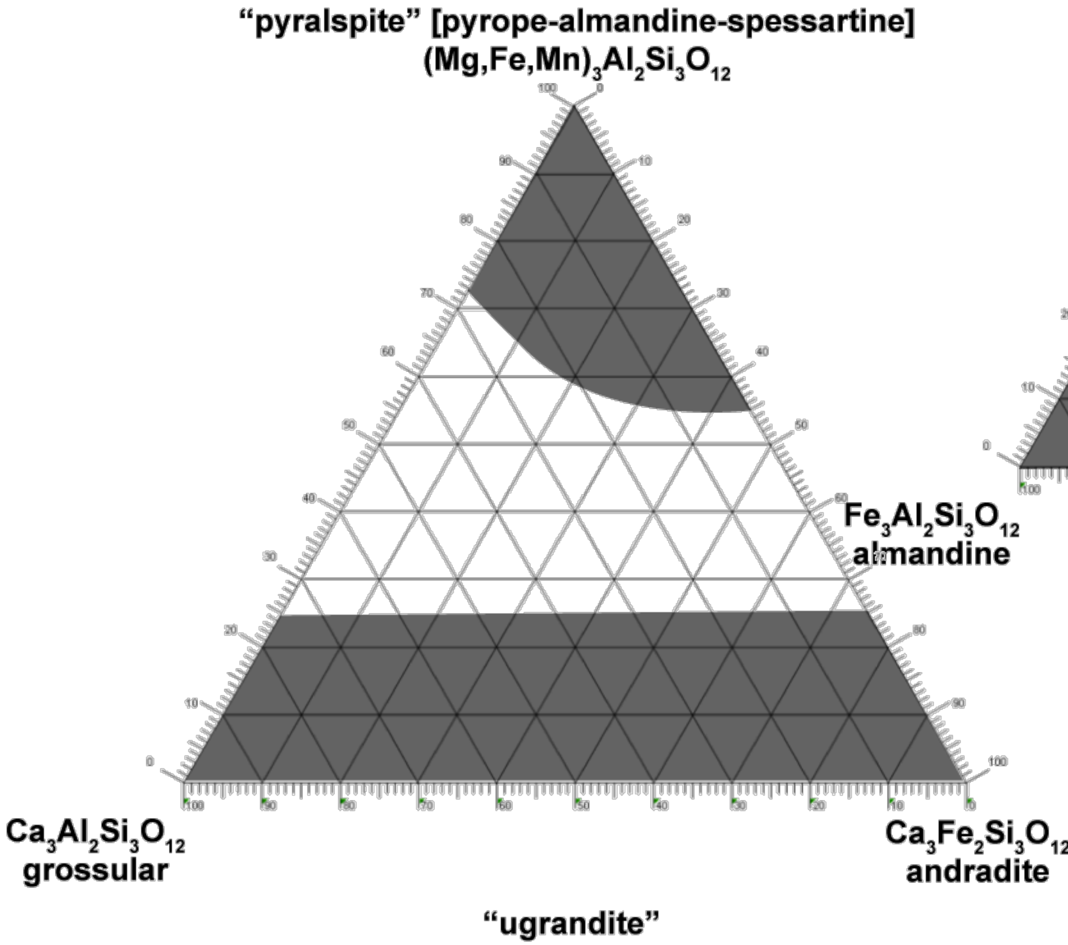
Classification Diagrams

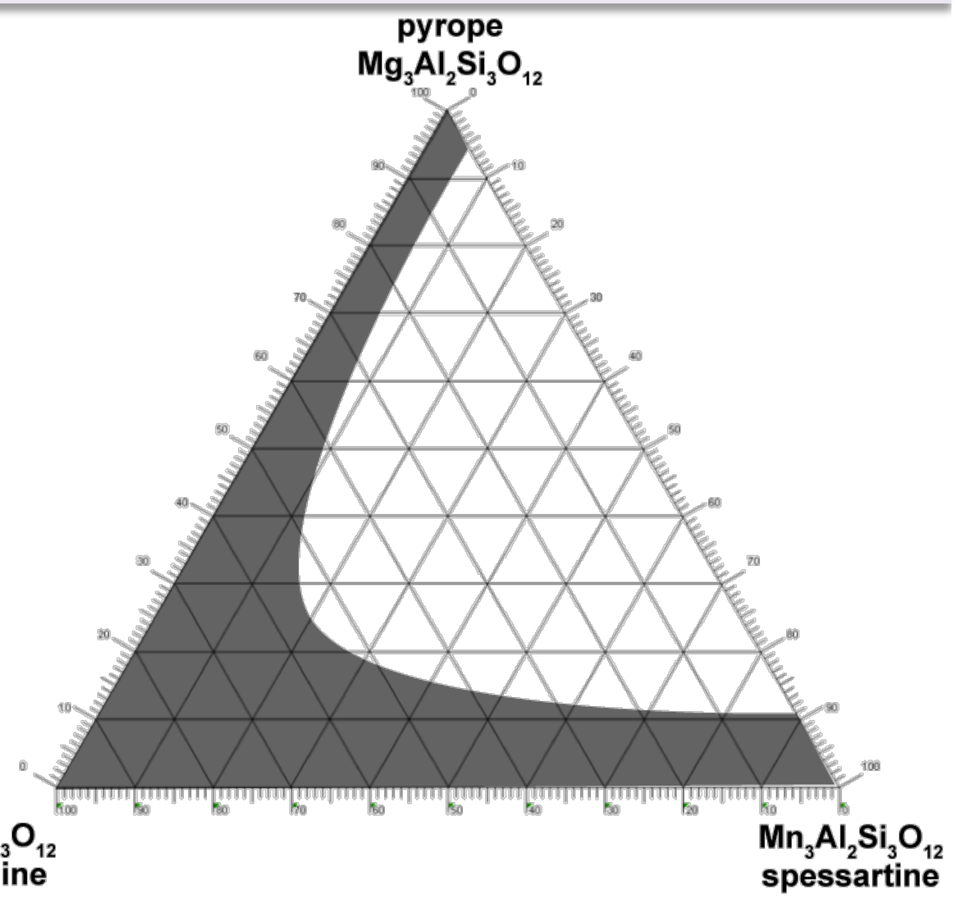
Potassium Feldspars



Classification Diagrams

Garnets

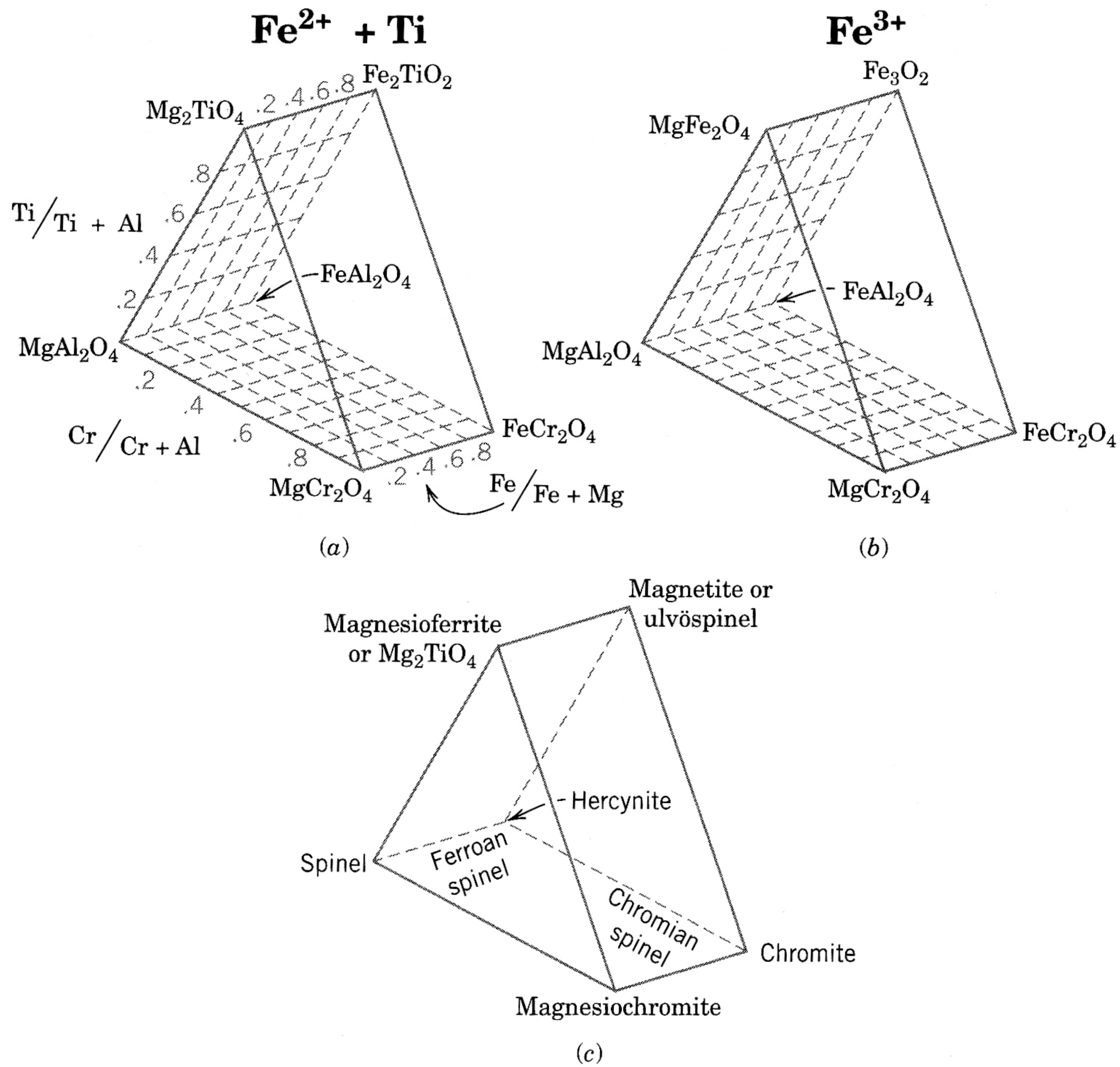




Classification Diagrams

Spinel Prism

YIKES!



Plotting Compositions

- **Classification Diagrams:**
  - **Know pyroxene quadrilateral (p. 259)**
  - **Know feldspar ternary diagram (p. 471) and differences between Kspar types (p. 474)**
  - **Know the two garnet ternary diagrams (p. 490)**
  - **Know spinel prism (p. 384)**
- Phase Diagrams (next week)
  - Know calcite-aragonite stability diagram (p. 402)
  - Know SiO2 phase diagram (p. 470)
  - Know the olivine (Fo-Fa) phase diagram (p. 485)
  - Know plagioclase (Ab-An) phase diagram (p. 253)
  - Know kyanite-andalusite-sillimanite phase diagram (p. 491)