

EMPA analyses and mineral formulae

GEO 2164: Analytical Methods
February 26th, 2007



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Electron Microprobe

All You Need to Know in 30
Minutes



Topics

- What is an Electron Microprobe?
- Why do we want to use it?
- How does it work?
- What can't we use it for?



What is an electron microprobe?

1. Chemical analysis of micron scale volumes (= numbers)
2. Chemical mapping of very small areas (= images)



Why do we want to use it

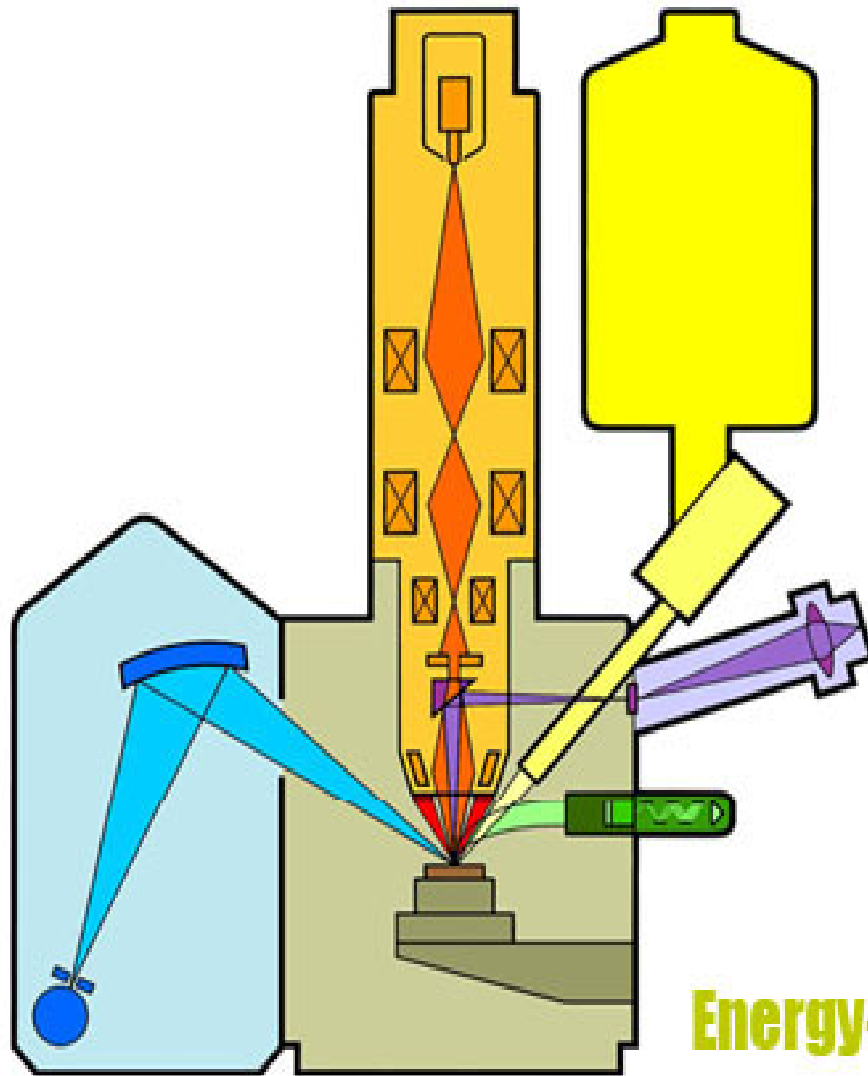
- No current technique which combines the sensitivity of the electron microprobe with its imaging and small volume capabilities
- Relatively non-destructive
- Rapid
- Easily understood data



How Does it work?

- Two distinct sub-systems
 - Electron optical
 - X-ray Spectrometry





Electron Column

Sample Chamber

**Secondary
Electron Detector**

**Backscattered
Electron Detector**

**Wavelength-Dispersive
Spectrometers**

Visible-Light Microscope

Energy-Dispersive Spectrometer

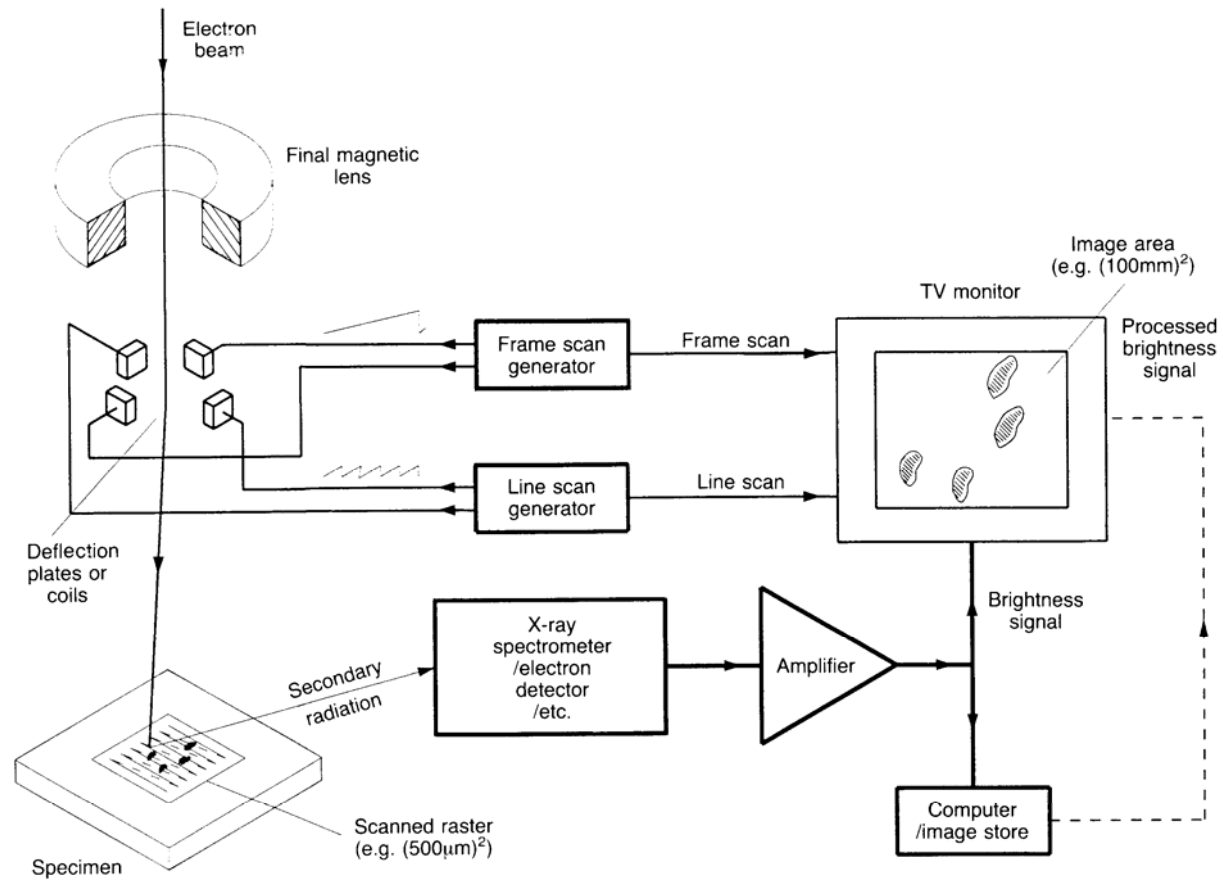


Figure 1.6 Schematic arrangement of an electron probe equipped with beam scanning.

Electron – Sample Interactions

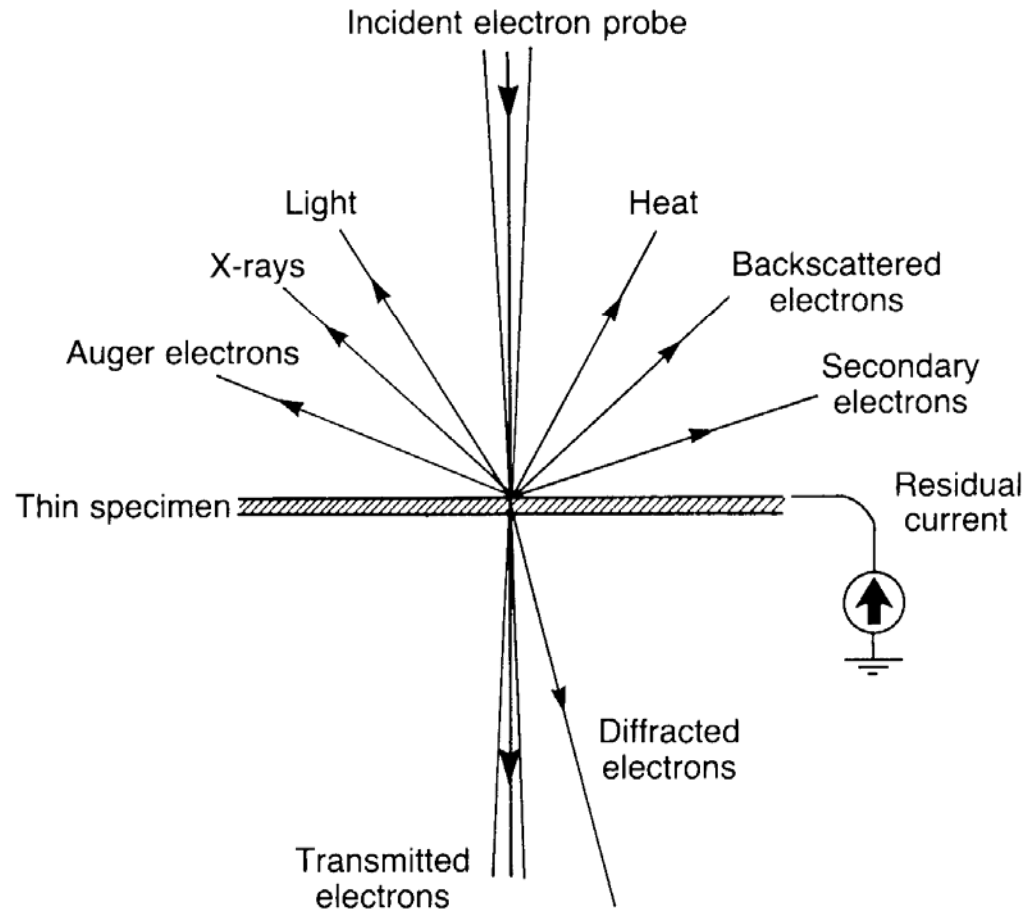


Figure 1.3 Schematic representation of processes resulting from electron bombardment.

Generation of X-rays

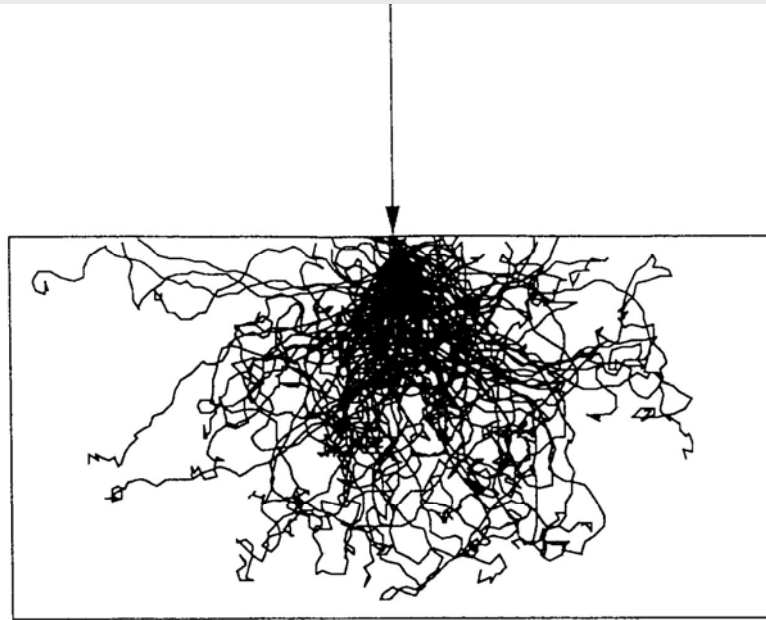


Figure 2.1 Simulated trajectories of electrons (initial energy 20 keV) in silicon (rectangle = $1 \times 2 \mu\text{m}$).

Energy levels

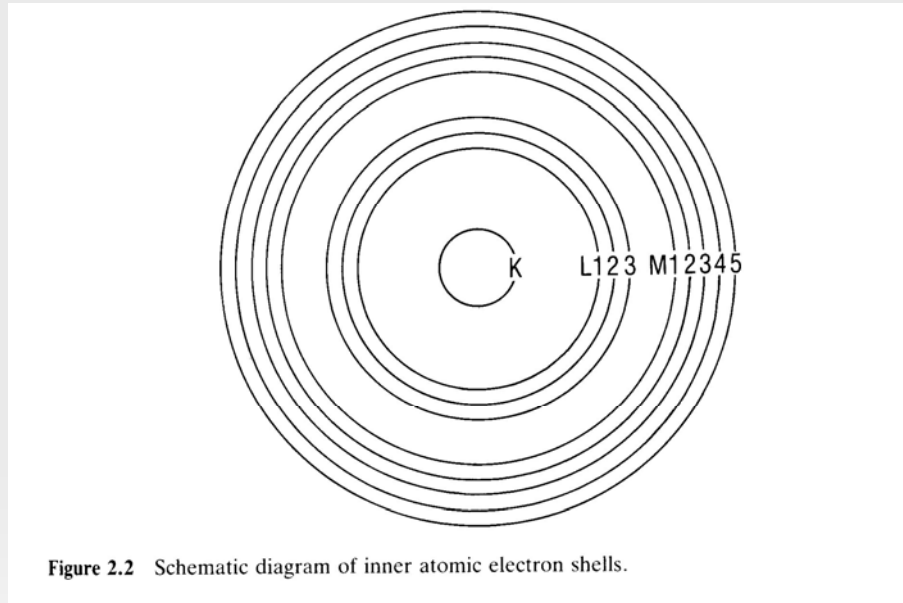
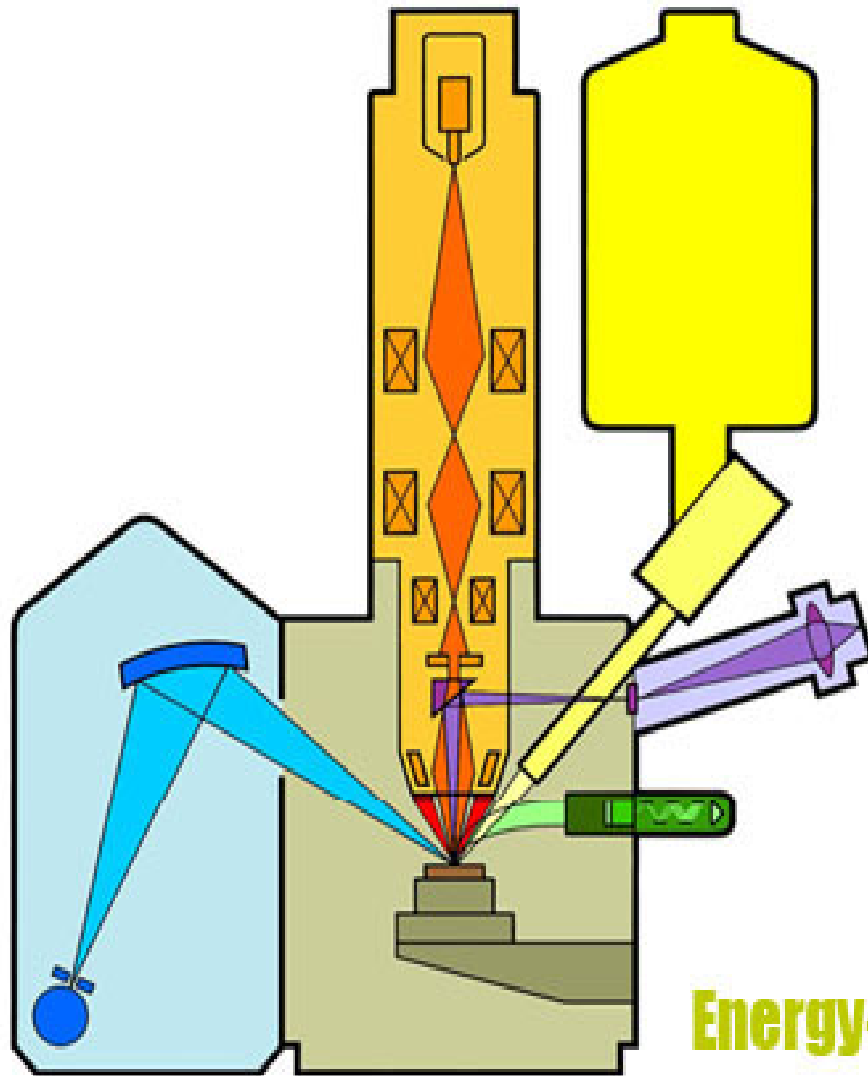


Figure 2.2 Schematic diagram of inner atomic electron shells.



Electron Column

Sample Chamber

**Secondary
Electron Detector**

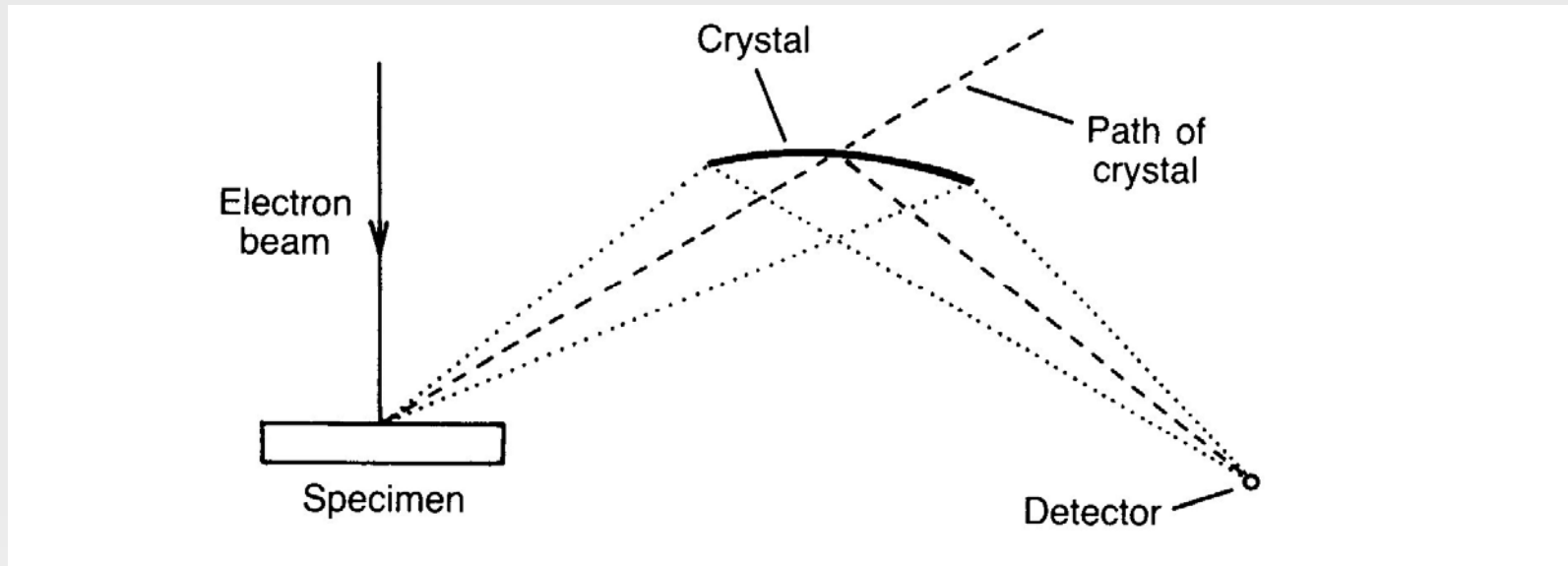
**Backscattered
Electron Detector**

**Wavelength-Dispersive
Spectrometers**

Visible-Light Microscope

Energy-Dispersive Spectrometer

WDS Spectrometer



➤ $n\lambda = 2d\sin\theta$

Proportional Counter

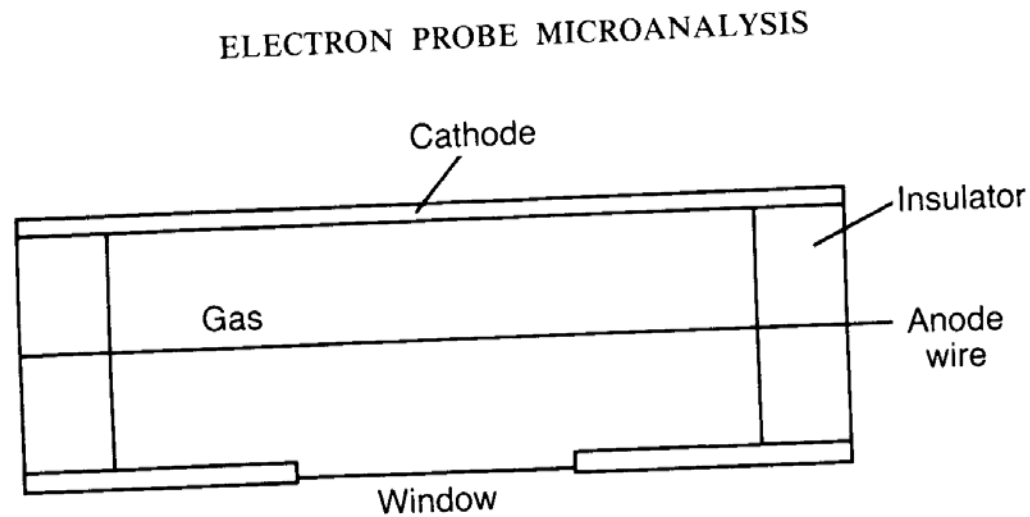
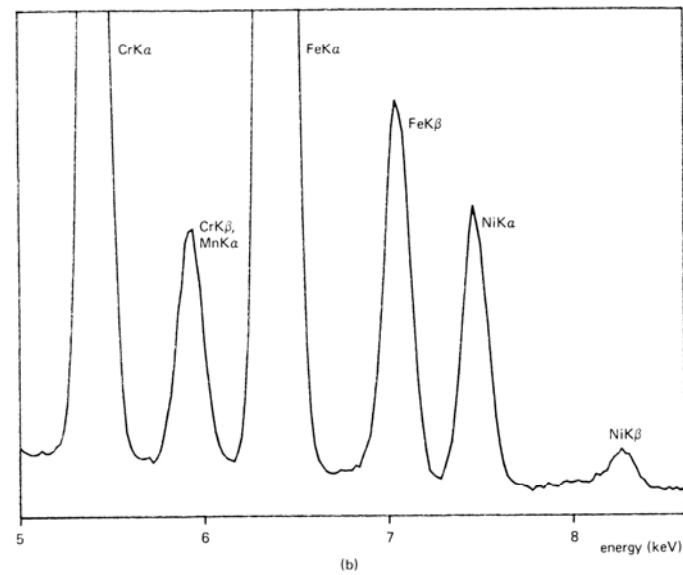
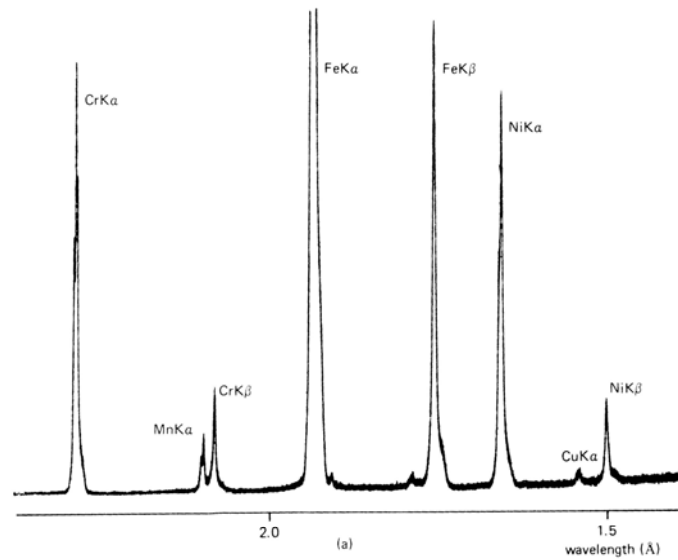


Figure 2.10 Proportional counter.



WDS vs EDS

- Speed
- Resolution
- Detection limit
- Precision
- Complexity and expense

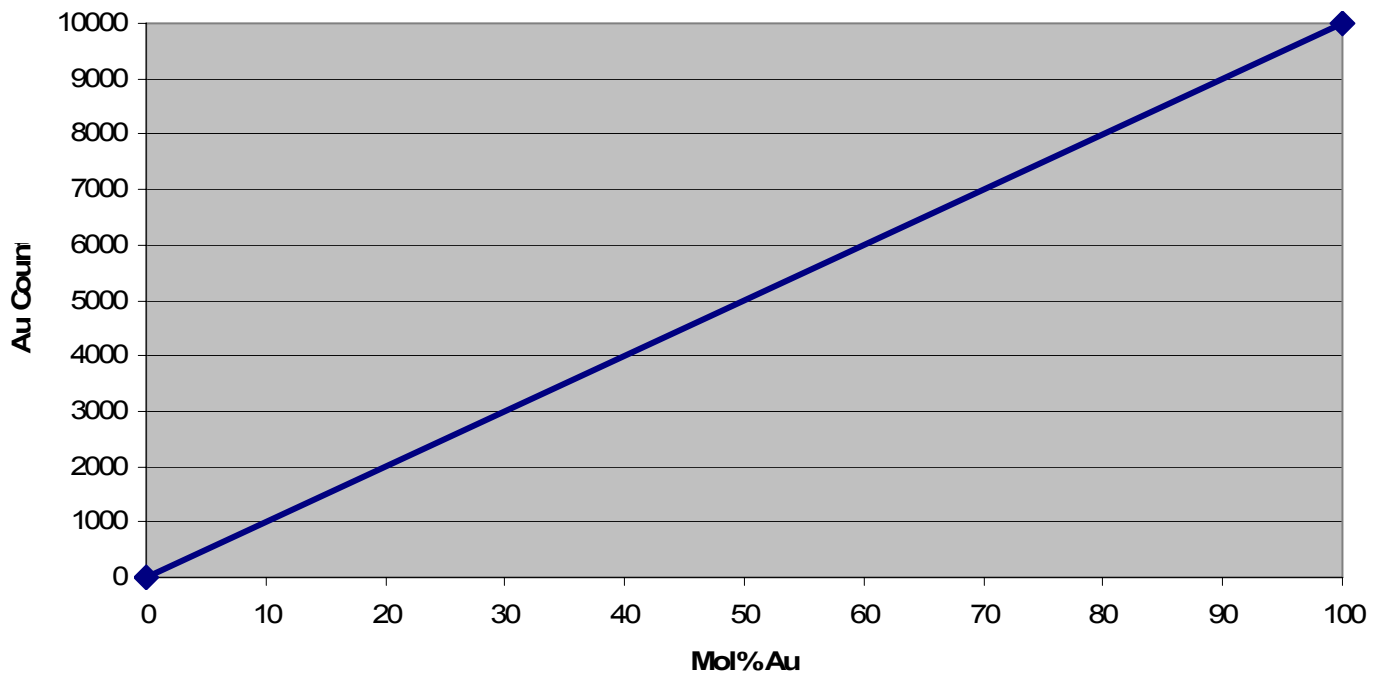


Where do the numbers come from?

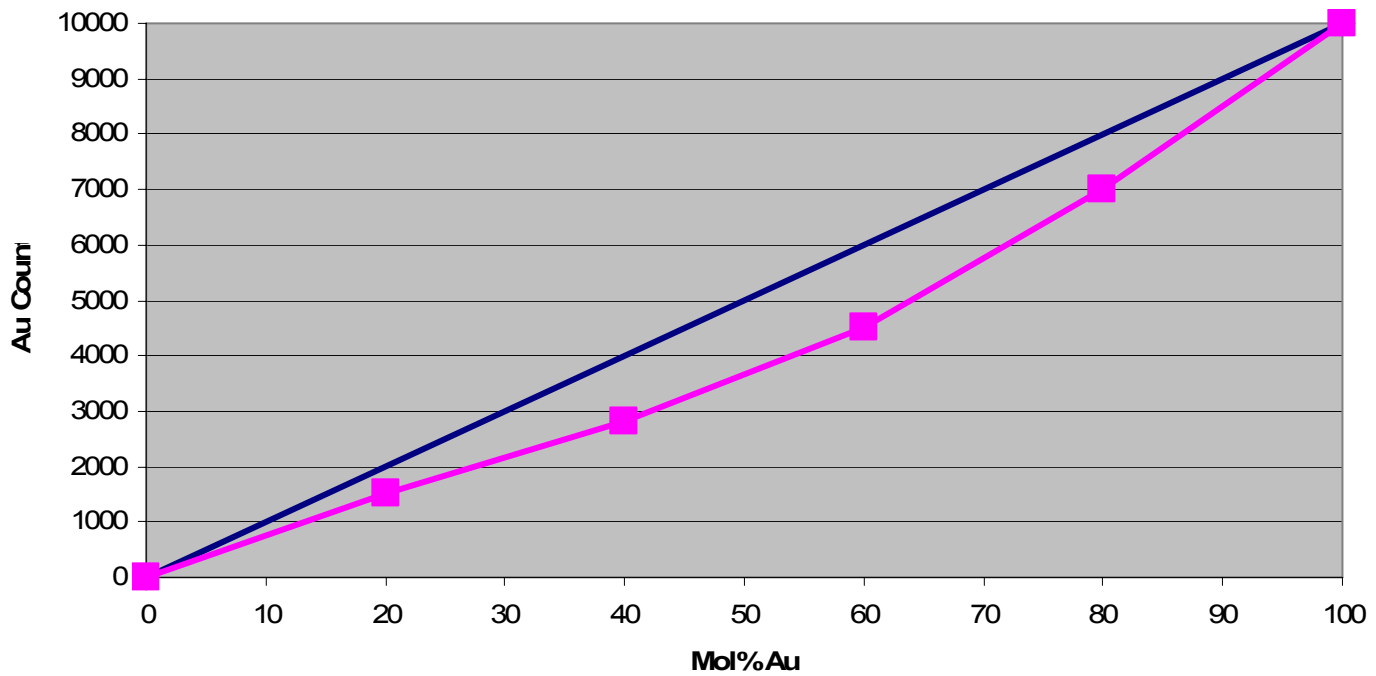
$$C_u \propto \frac{I_u}{I_s} \times C_s$$



X-Ray Intensity vs Composition



X-Ray Intensity vs Composition



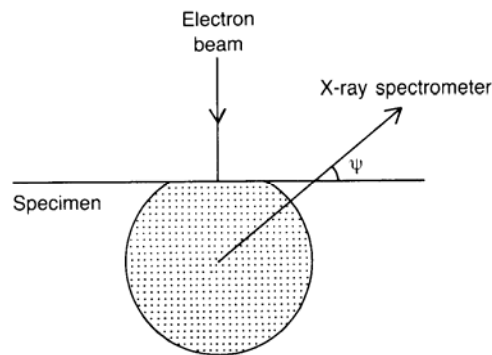
Matrix Corrections

- Allows use of standards which are different from unknowns
- ZAF, PAP, $\varphi\rho z$ (phi-rho-z)



ZAF Correction

- Z – atomic number correction
- A – Absorption correction
- F – Fluorescence correction



$$C_u = ZAF \frac{I_u}{I_s} \times C_s$$



Analytical Nitty Gritty I

➤ Samples

- Polished
- Carbon coated (prevent charging)
- Solids
- Vacuum Stable



Analytical Nitty Gritty II

➤ Standards

- Homogeneous
- Well Characterized
- Similar to unknowns (*i.e.* silicate standards for analyses of silicates, sulphide standards for analysis of sulphides – not always possible)



Analytical Nitty Gritty III

- Analytical conditions
 - Accelerating Voltage
 - Beam Current
 - Counts are proportional to current
 - Spot size proportional to current
 - Beam damage
 - Beam Size



Chemical analysis of minerals

A. Olivine Analyses

	<u>OL1</u>	<u>OL2</u>	<u>OL3</u>	<u>OL4</u>	<u>OL5</u>
SiO ₂	40.94	40.24	39.57	40.70	39.75
TiO ₂	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.00
V ₂ O ₃	0.00	0.00	0.00	0.00	0.00
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00
FeO	8.19	8.36	9.87	7.48	8.80
MnO	0.00	0.13	0.00	0.15	0.17
MgO	49.75	50.11	49.41	50.63	50.13
NiO	0.42	0.39	0.30	0.35	0.35
CaO	0.00	0.00	0.08	0.00	0.00
Na ₂ O	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00
	-----	-----	-----	-----	-----
TOTAL	99.30	99.24	99.23	99.32	99.20

There are a number of ways to obtain **chemical** data on minerals:

EMPA (EDS, WDS)

X-ray fluorescence

Wet-chemistry

Mössbauer spectroscopy

Laser ablation ICP-MS

Nano-SIMS

Nuclear probes (NRA, PIXIE, proton)

Synchrotron microanalysis

Ion microprobe

Raman, FTIR

Calculation of mineral formulae

Analysis of minerals by the electron microprobe results in weight percent (wt.%) **oxide** data (e.g. SiO_2 , Fe_2O_3 , Al_2O_3 , etc.). You must convert this oxide data into **elemental or cation proportions** in order to develop a mineral formula. This can be done by hand or in a spreadsheet by following the steps below:

- 1) Divide each oxide constituent by the formula weight of the oxide. This gives you the **Molar Proportions of each oxide**.



Mineral formula calculation: olivine

Oxide	Wt.%	Mol. Wt. of oxide	Mol. Ratio		
SiO ₂	40.99	60.09	0.6821		
FeO	8.58	71.85	0.1194		
MnO	0.20	70.93	0.0028		
MgO	50.00	40.32	1.2400		
Total	99.77				

Molecular ratio: wt.% / molecular weight

Calculation of mineral formulae

- 1) Divide each oxide constituent by the formula weight of the oxide. This gives you the **Molar Proportions of each oxide**.
- 2) Multiply the molar proportions of each oxide by the number of cations in the oxide. This gives you **the cationic ratio**.
- 3) **Multiply** the molar proportions of each oxide by the number of oxygens in each. This gives you **anionic ratio** in your mineral.



Mineral formula calculation: olivine

Oxide	Wt. %	Mol. Wt. of oxide	Mol. Ratio	Anionic Ratio	Cationic Ratio
SiO ₂	40.99	60.09	0.6821	1.3642	0.6821
FeO	8.58	71.85	0.1194	0.1194	0.1194
MnO	0.20	70.93	0.0028	0.0028	0.0028
MgO	50.00	40.32	1.2400	1.2400	1.2400
Total	99.77			Σ = 2.7264	

Anionic ratio = molecular ratio x # of oxygens in oxide

Cationic ratio: = molecular ratio x # of cations in oxide

Calculation of mineral formulae

- 1) Divide each oxide constituent by the formula weight of the oxide. This gives you the **Molar Proportions of each oxide**.
- 2) Multiply the molar proportions of each oxide by the number of cations in the oxide. This gives you **the molar proportions of cations** in your mineral.
- 3) **Multiply** the molar proportions of each oxide by the number of oxygens in each. This gives you **the molar proportions of Oxygen** in your mineral.
- 4) **Sum the Molar proportions of Oxygen**, and divide this sum by the number of oxygens in the mineral's ideal chemical formula (i.e., 4 oxygens for olivine; 6 oxygens for pyroxene). The value you get is a normalization factor (a "fudge factor") that will allow you to obtain formula units.
- 5) Now, **divide the Molar Proportions of each Cation** by the **Correction Factor**. This will give you **the proportions of each cation with respect to oxygen (or the "Oxygen units" of each cation)** in your mineral. At this point, one can group your cations by valence and calculate the REAL mineral formula.

Mineral formula calculation: olivine

Oxide	Wt. %	Mol. Wt. of oxide	Mol. Ratio	Anionic Ratio	Cationic Ratio
SiO ₂	40.99	60.09	0.6821	1.3642	0.6821
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MgO	50.00	40.32	1.2400	1.2400	1.2400
Total	99.77			$\Sigma = 2.7264$	

F = fudge factor/normalization factor

F = ideal number of anions/anionic ratio sum = $4/2.7264 = \underline{1.4671}$

Mineral formula calculation: olivine

F = fudge factor/normalization factor

F = ideal number of anions/anionic ratio sum = $4/2.7264 = \underline{1.4671}$

F x Cationic Ratio = # of cations

1.4671×0.6821 (SiO₂) = 1.00 Si

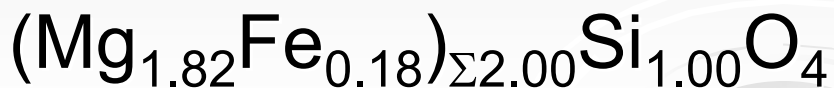
1.4671×0.1194 (FeO) = 0.18 Fe

1.4671×0.0028 (MnO) = 0.00 Mn

1.4671×1.2400 (MgO) = 1.82 Mg

Olivine general formula: XYO₄

CHEMICAL FORMULA:



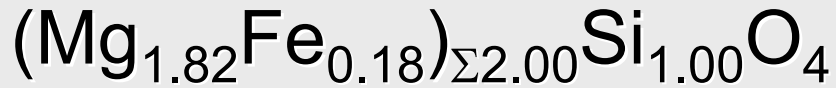
To determine the species:
 $\text{Mg}/(\text{Mg}+\text{Fe}) = 1.82/(1.82+0.18)$
 $= 0.91$

Fo₉₁Fa₉

Mineral formula calculation: olivine

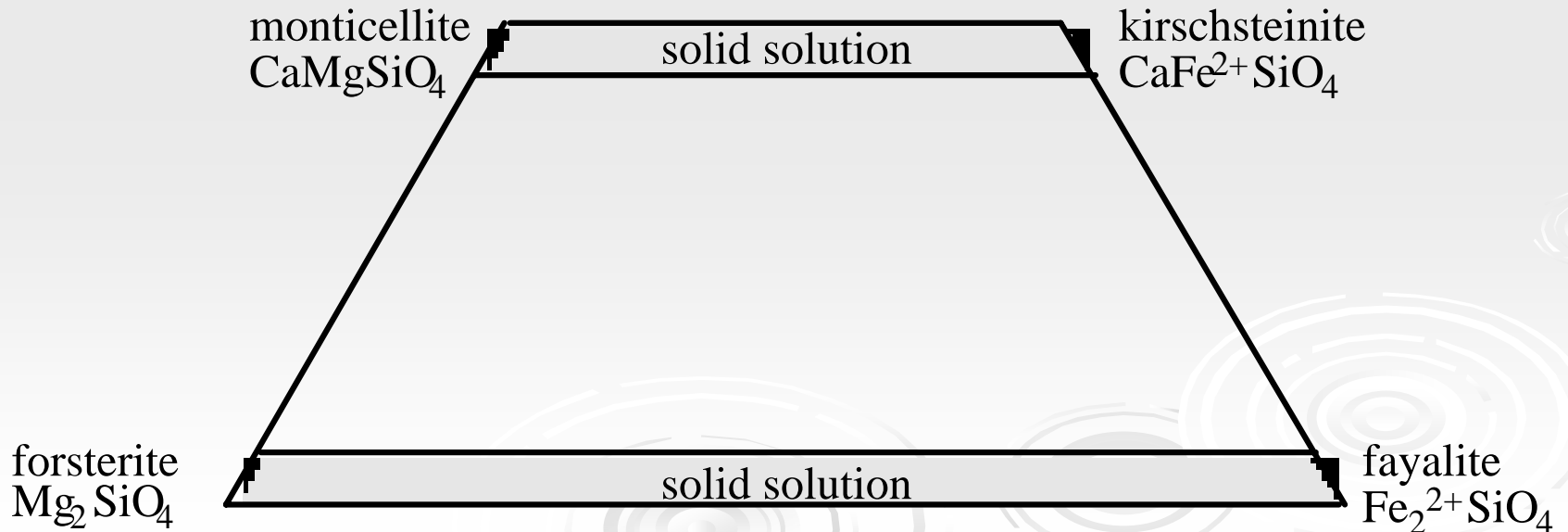
Olivine general formula: XYO_4

CHEMICAL FORMULA:



To determine the species:
 $\text{Mg}/(\text{Mg}+\text{Fe}) = 1.82/(1.82+0.18)$
 $= 0.91$

Fo₉₁Fa₉



Formula (© T.S. Ercit, 2006)

- uses EMPA oxide data to calculate mineral formulae

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data for empa lab

FORMULA

File

FORMULA 2000

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Vers. 06.1

Enter New Data
 Run Existing File

EXIT

Running

Garnet group compositions

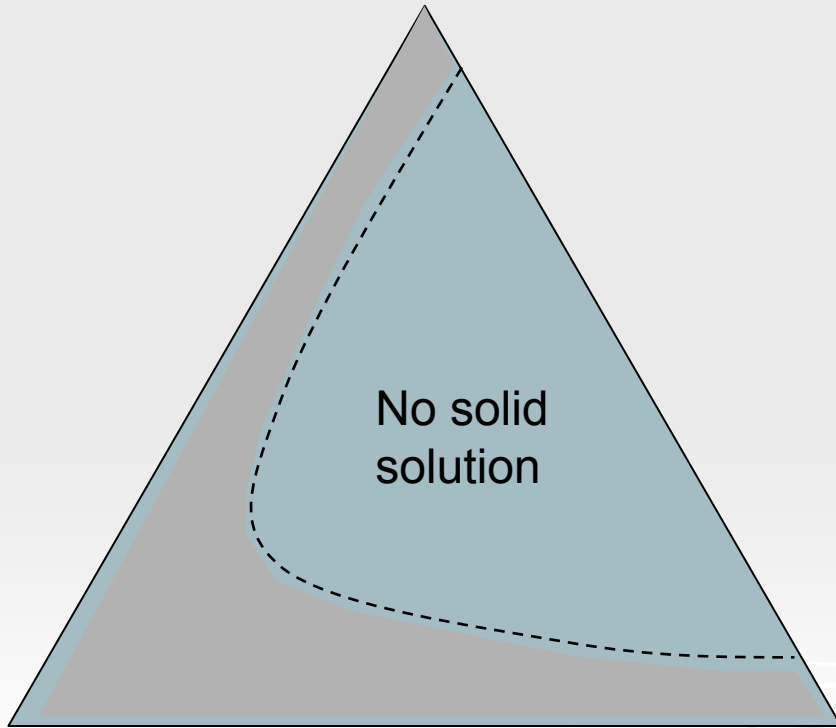
General formula: $X_3^{2+}Y_2^{3+}(\text{SiO}_4)_3$

X – Ca^{2+} , Mg^{2+} , Fe^{2+} or Mn^{2+}

Y – Al^{3+} , Fe^{3+} or Cr^{3+}

Pyralspite Group

Pyrope
 $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

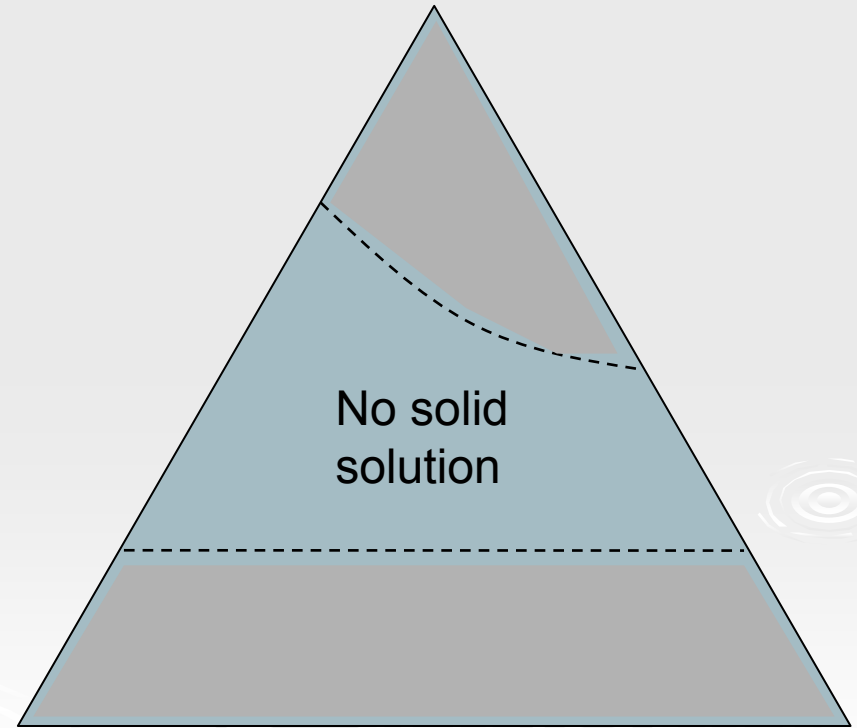


Almandine
 $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

Spessartine
 $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

Ugrandite Group

"Pyralspite"
 $(\text{Mg,Fe,Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}$



Grossular
 $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$

Andradite
 $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$

Pyroxene compositions – general formula



Three main groups:

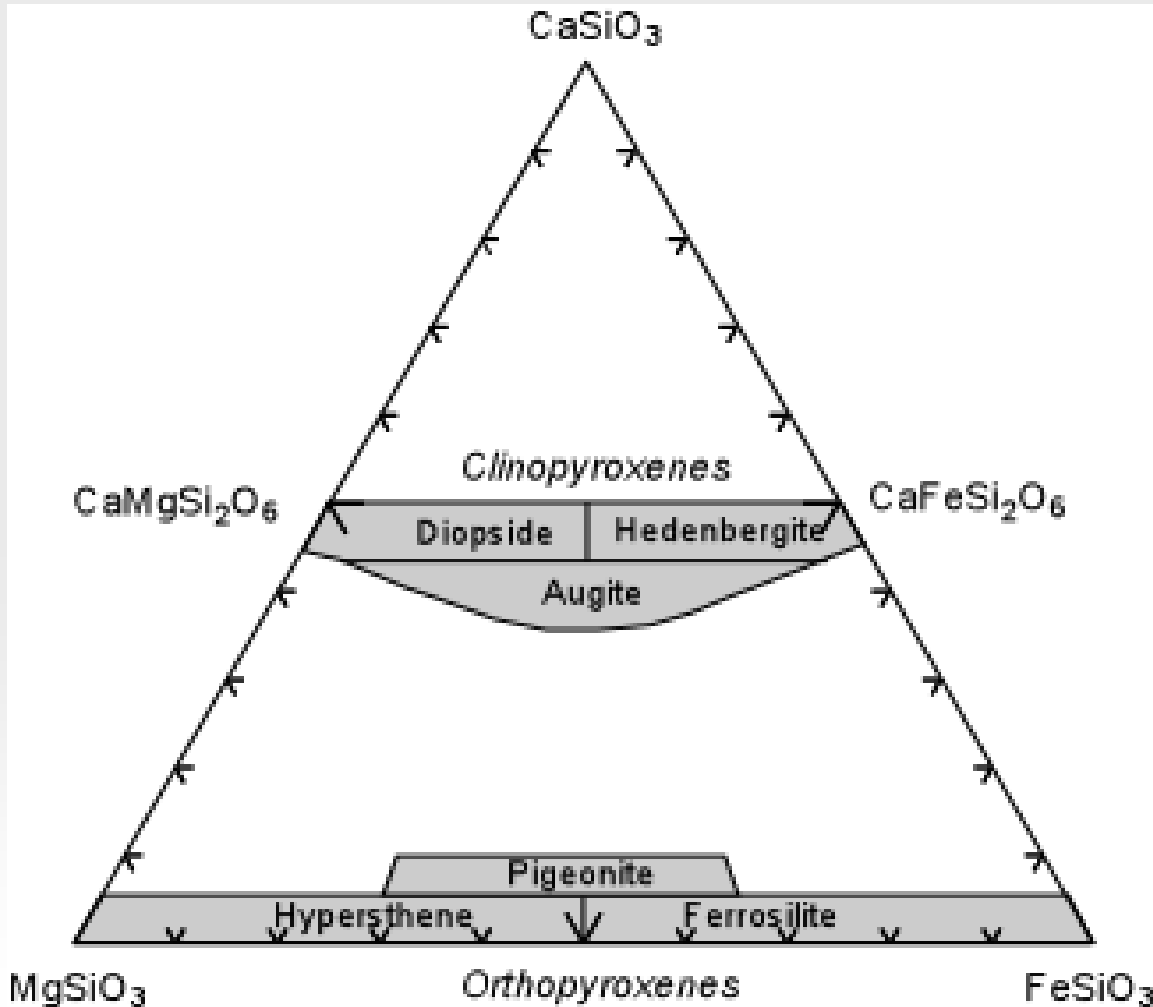
1. Fe-Mg pyroxenes > 90% of M1+M2 = Fe+Mg
2. Calcic pyroxenes: M2 = Ca > 2/3
3. Sodic pyroxenes: M2 = Na > 2/3

[4] Si & Al

M(1) – [6]
Mg, Fe, Al, Ti, Cr,
V, Zr, Zn

M(2) – distorted [6]-[8]
Ca, Na, Li, Mn, Fe, Mg

Pyroxene Quadrilateral



To calculate the proportions:

$\text{Ca}/(\text{Ca}+\text{Fe}+\text{Mg})$

$\text{Fe}/(\text{Ca}+\text{Fe}+\text{Mg})$

$\text{Mg}/(\text{Ca}+\text{Fe}+\text{Mg})$