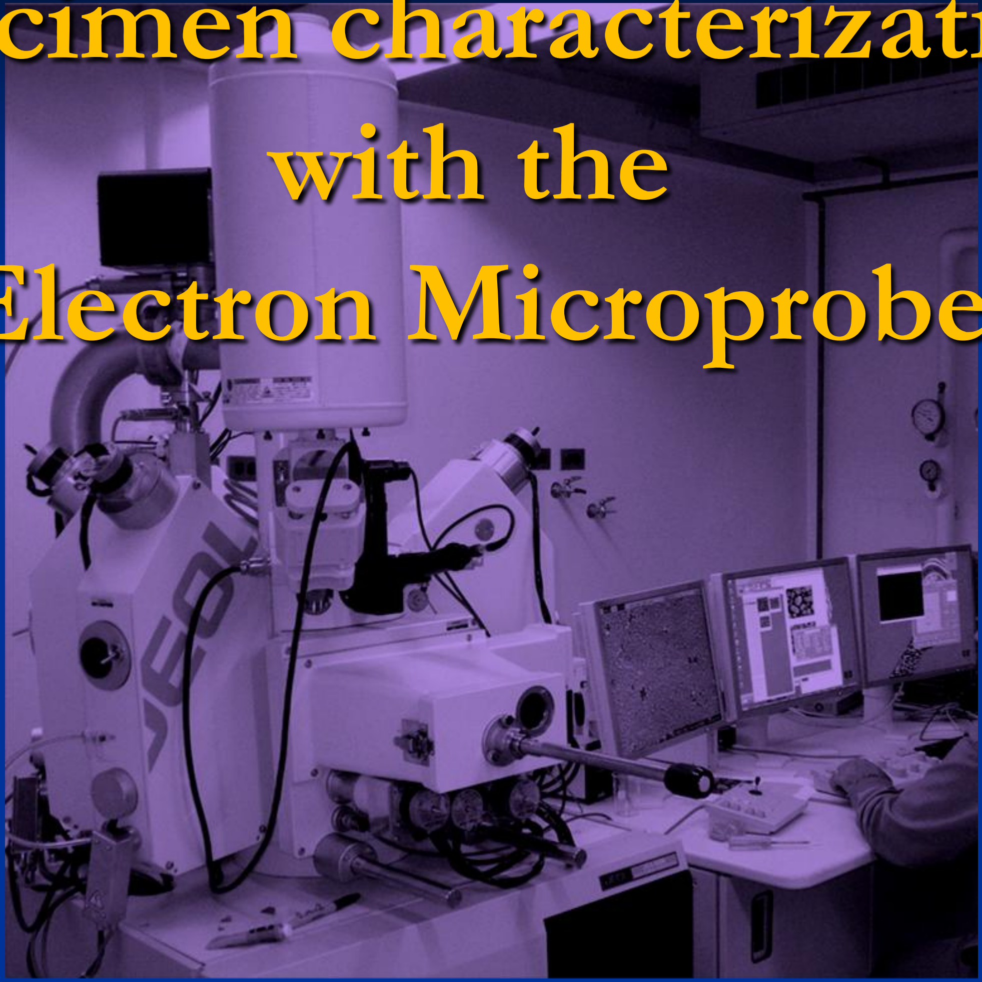
# Specimen characterization with the Electron Microprobe



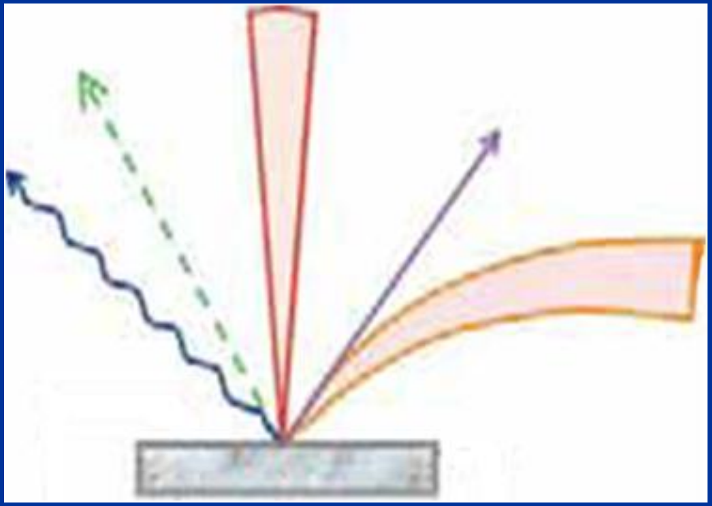
# Signals produced in the Electron Microprobe

***Electron beam***

Cathodoluminescence (CL)

Back-scattered electron (BSE)

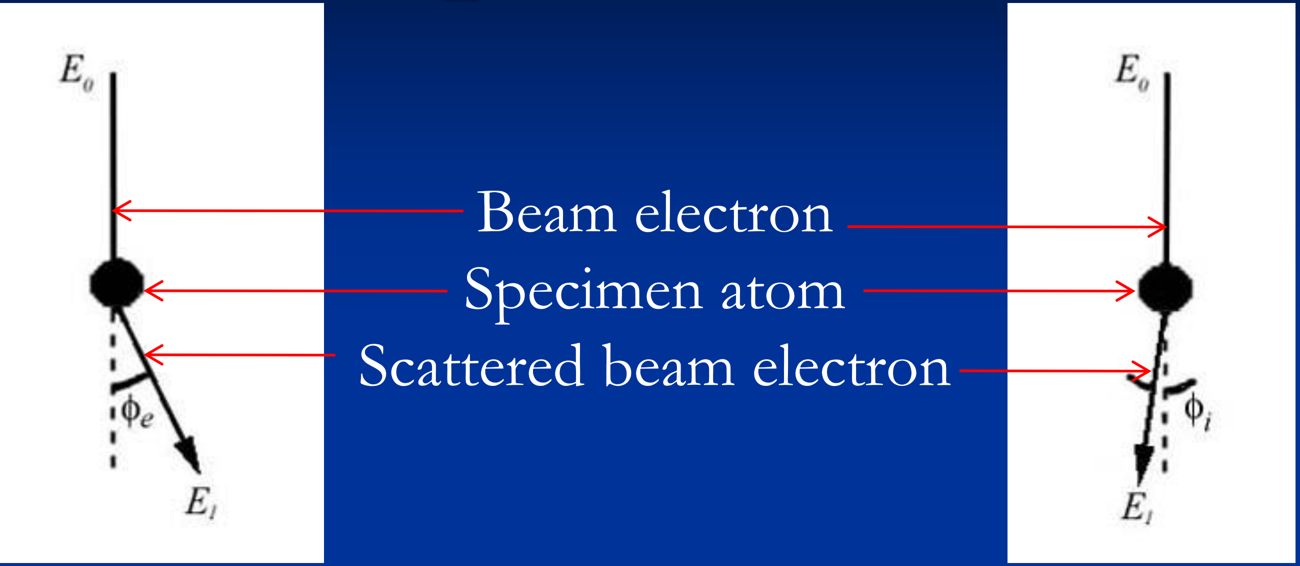
Characteristic X-ray



Secondary electron (SE)

***Specimen***

# Electron-specimen interactions




**Elastic Scattering**

$E_1 = E_0$, large $\phi_e$

**Inelastic Scattering**

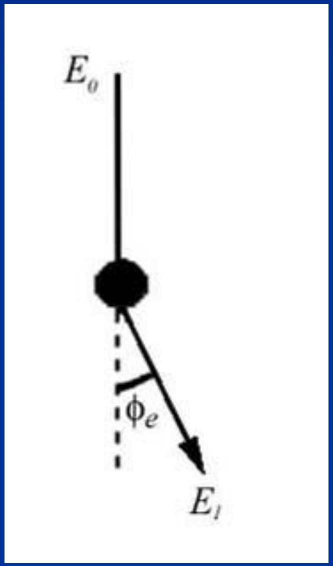
$E_1 < E_0$, small $\phi_i$

$(\phi_e >> \phi_i)$

- Back-scattered electron

- Characteristic X-rays
- Secondary electron
- Cathodoluminescence

# Elastic scattering cross-section




$E_1 = E_0$, large $\phi_e$

$$Q(>\phi_e) = 1.62\text{x}10^{-20}\ (Z^2/E^2)\cot^2(\phi_e/2)$$

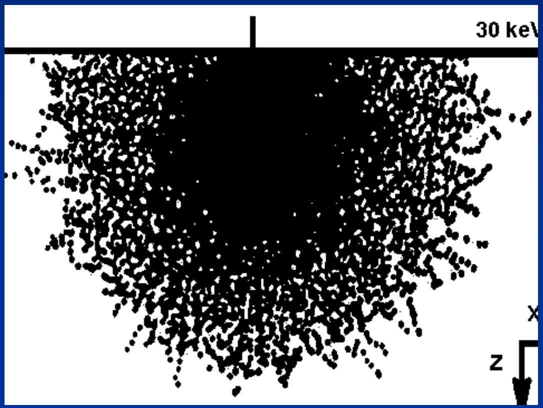
$Q$: cross section (events.cm$^2$/e$^-$.atom)

$\phi_e$: elastic scattering angle

$Z$: atomic number

$E$: beam energy

# Electron interaction volume



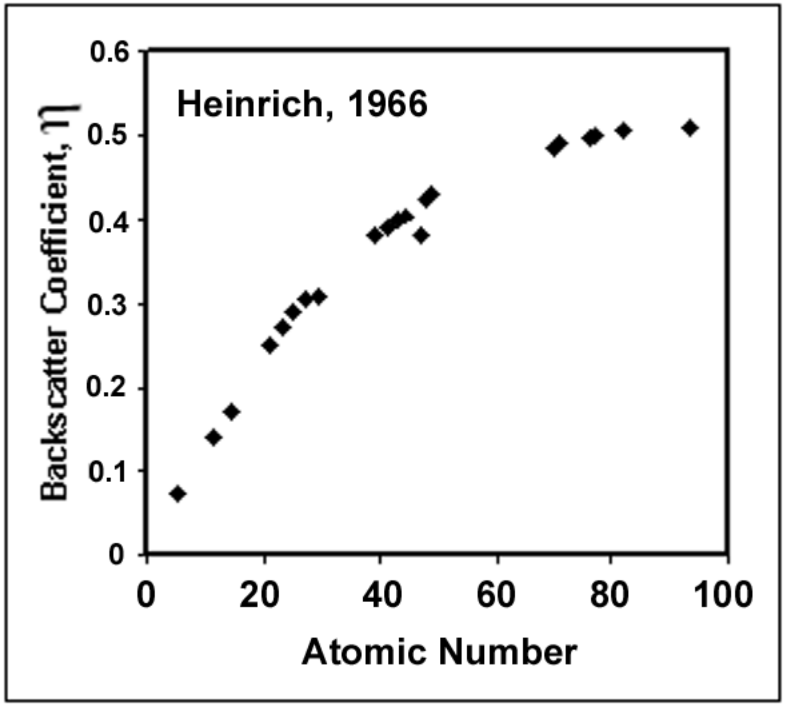

- *Increases with voltage (electron beam energy)*
- *Decreases with sample atomic number*

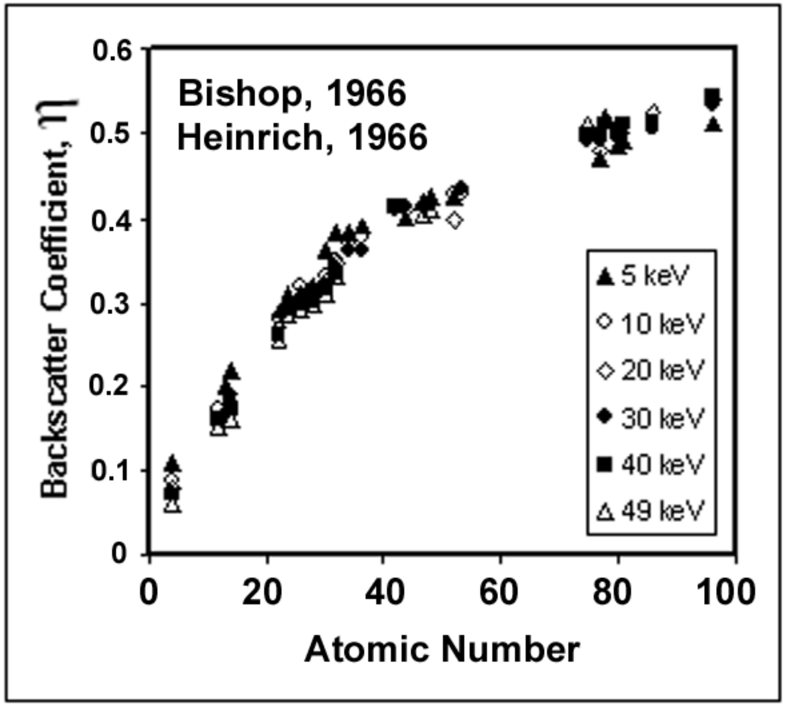
*Typical depths (*15 kV, *perpendicular beam):*

| | |
|---|---|
| **Carbon (C, At# 6)** | **1.8 µm** |
| **Iron (Fe, At# 26)** | **1.1 µm** |
| **Uranium (U, At#92)** | **0.8 µm** |

# Electron Back-scattering

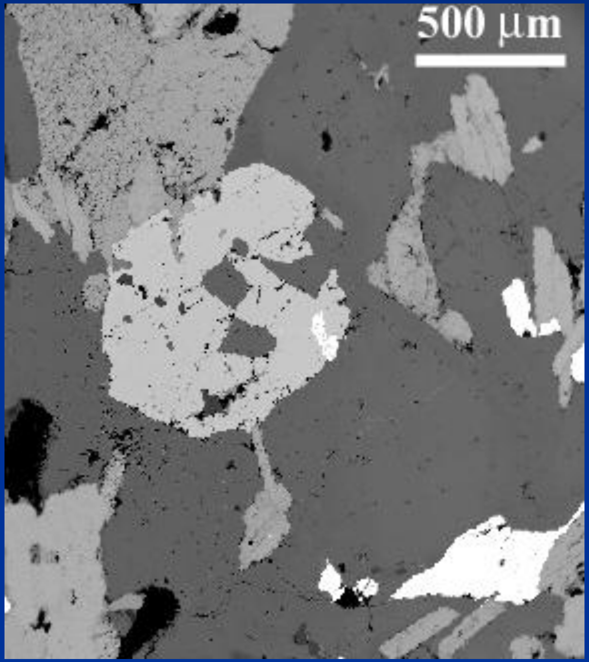
## (High angle elastic scattering)



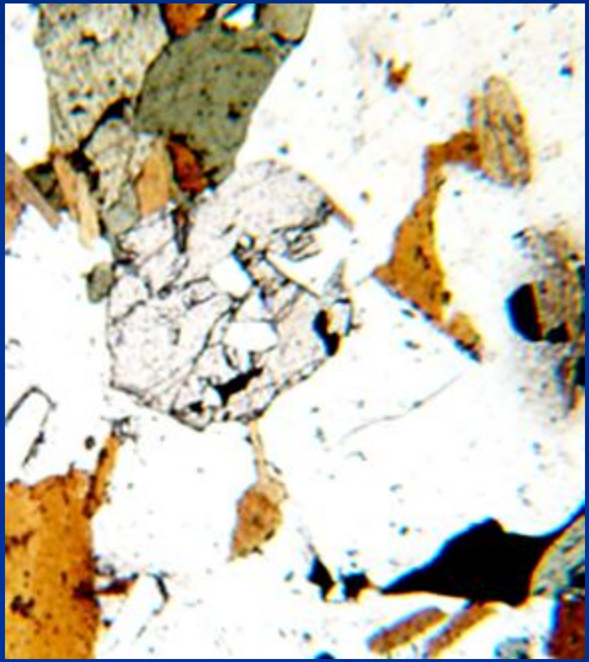
# Backscattered electron image

*Back-scattered electron*




Polished surface

*Plane polarized transmitted light*

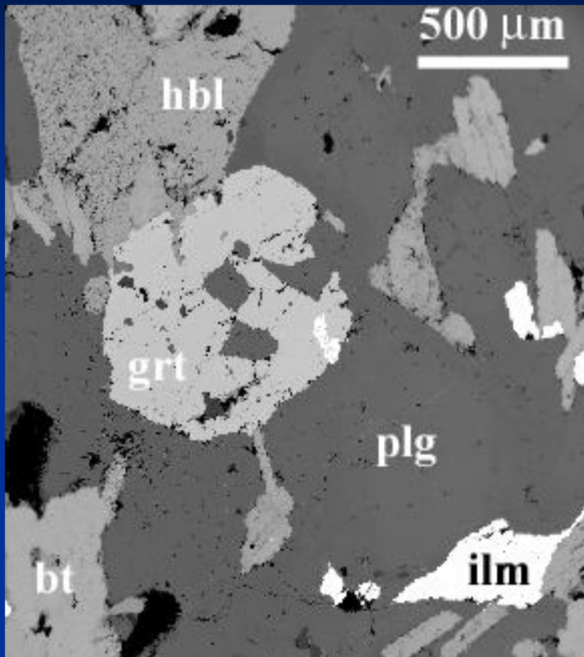


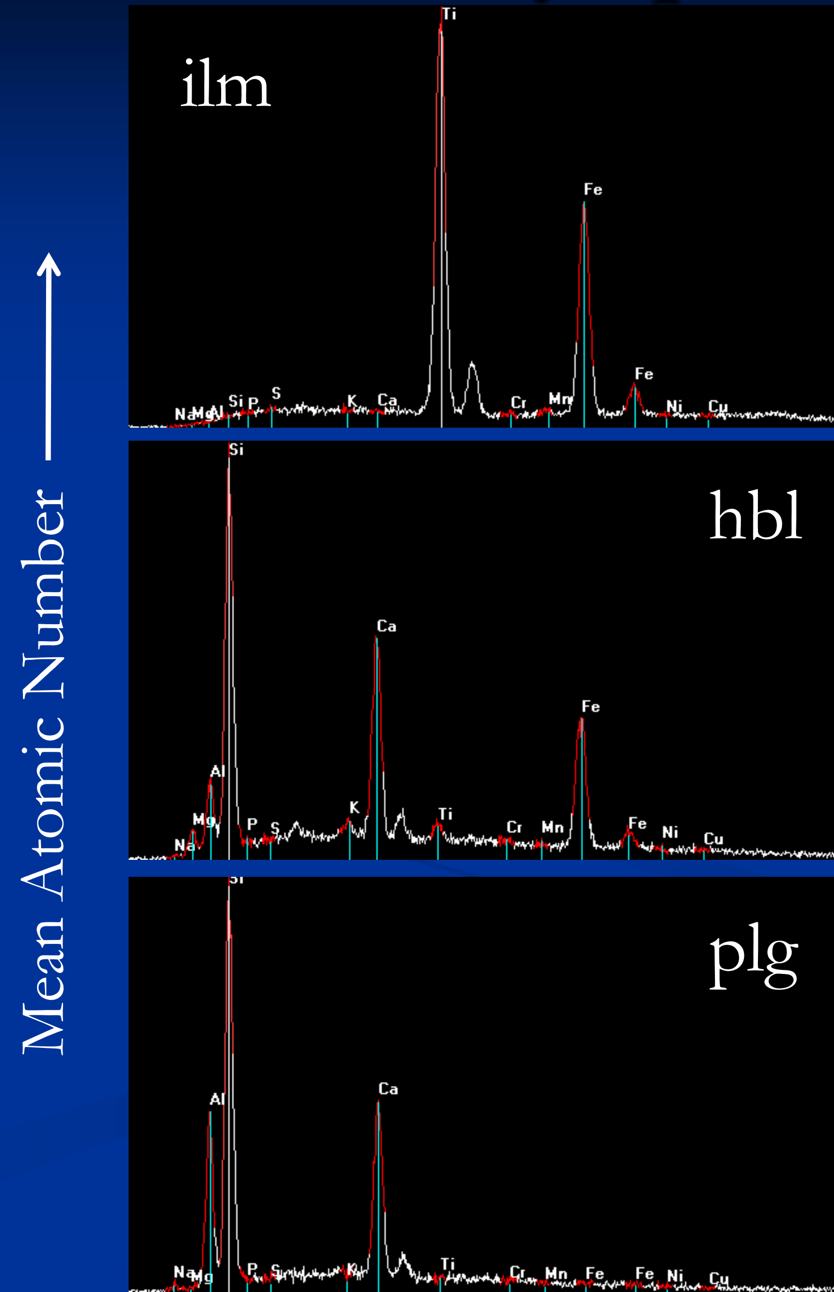
Thin section

Function of composition

Function of optical properties

# Phase identification: EDS X-ray spectra



# Understanding X-rays: Energy and Wavelength

$$E = h\nu$$

***h*** *: Planck's constant*

(**6.626x10$^{-34}$** Joule.sec

**or, 6.626x10$^{-34}$/1.6021x10$^{-16}$** keV.sec)

$\boldsymbol{\nu}$ *: frequency (=* $\boldsymbol{c/\lambda}$*)*

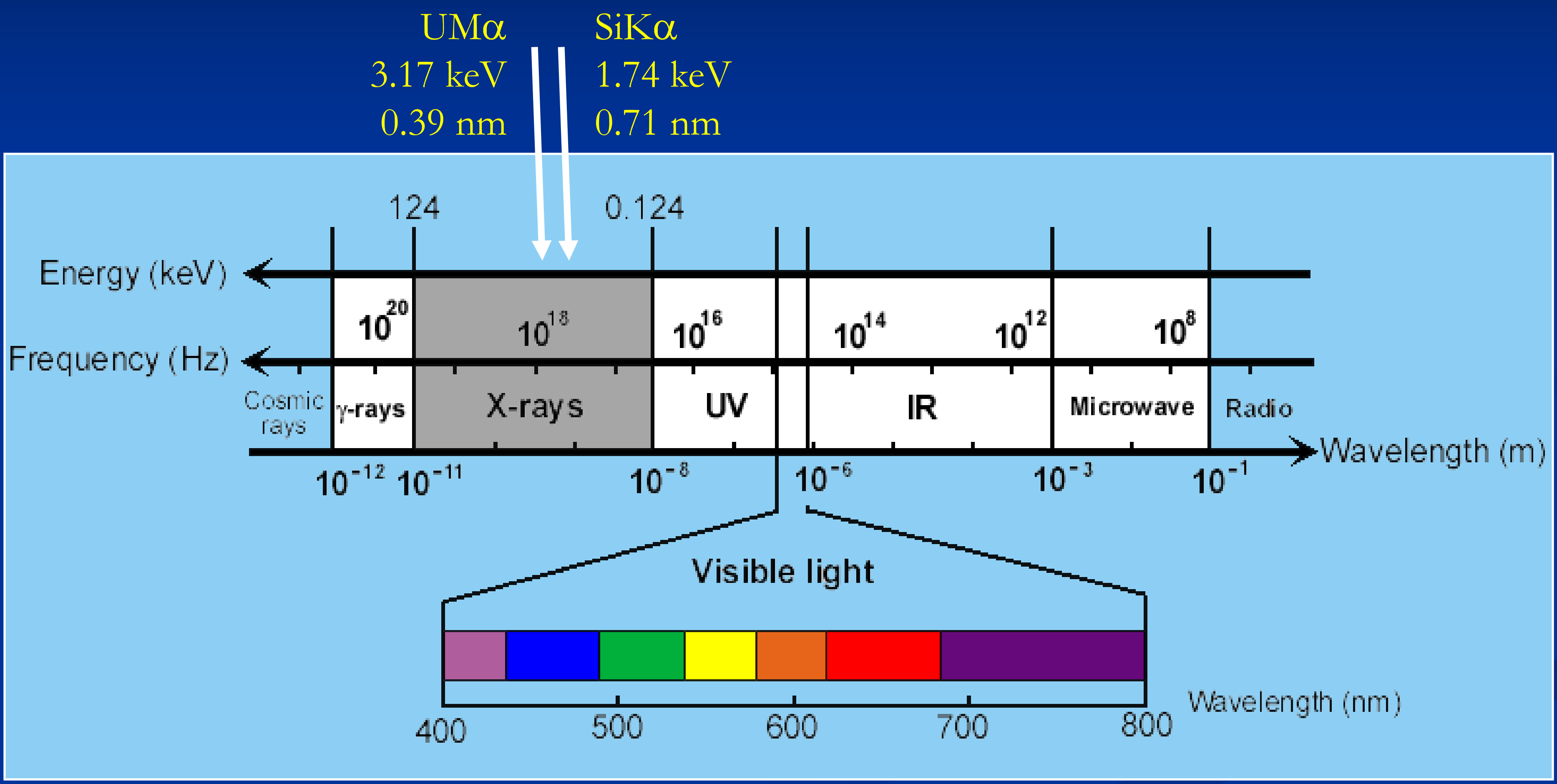
(***c*** *: speed of light in vacuum*

**= 2.99793x10$^{17}$** nm/sec

$\lambda$ *: wavelength)*

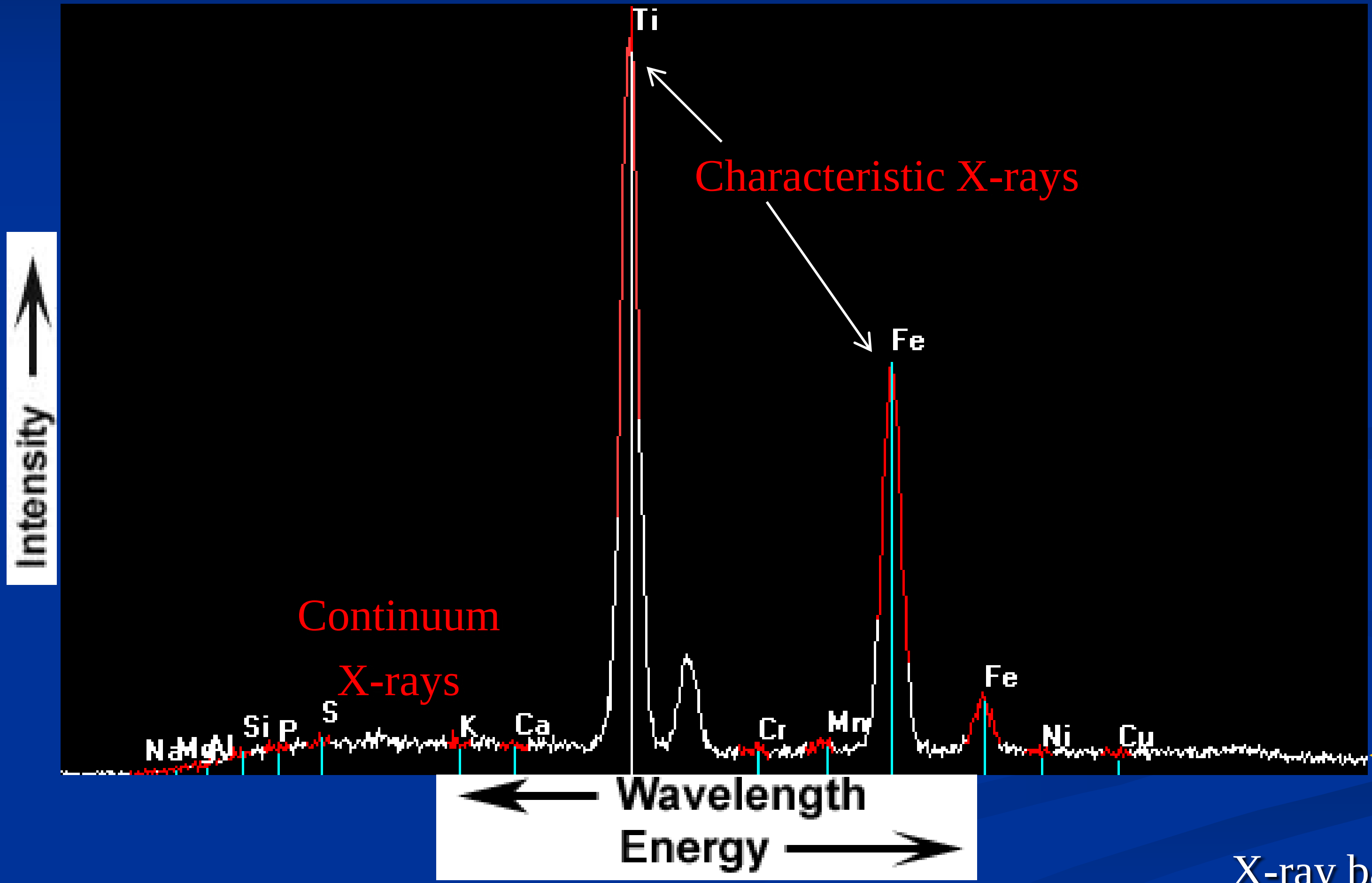
$$\lambda\ (\text{nm}) = c/\nu = hc/E = 1.2398/E\ (\text{keV})$$

# Understanding X-rays: The electromagnetic spectrum




$$\lambda\ (\mathrm{nm}) = 1.2398 / E\ (\mathrm{keV})$$

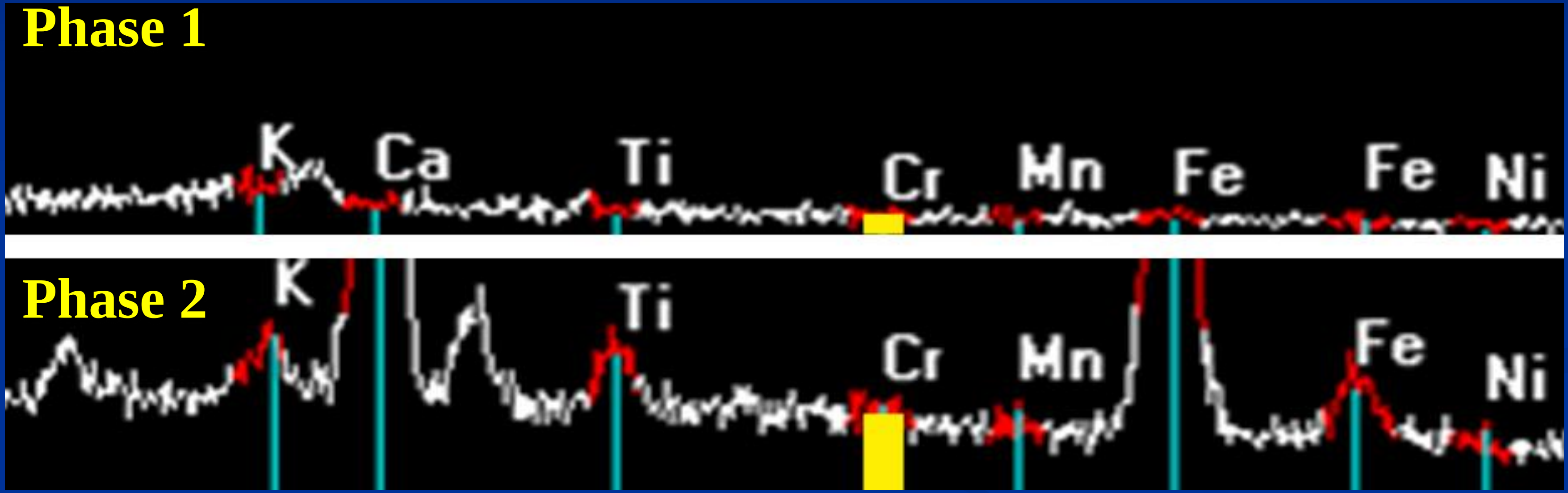
# The X-ray spectrum




X-ray background

(maximum energy = electron beam energy, $E_0$)

# Continuum X-rays: background in X-ray spectra

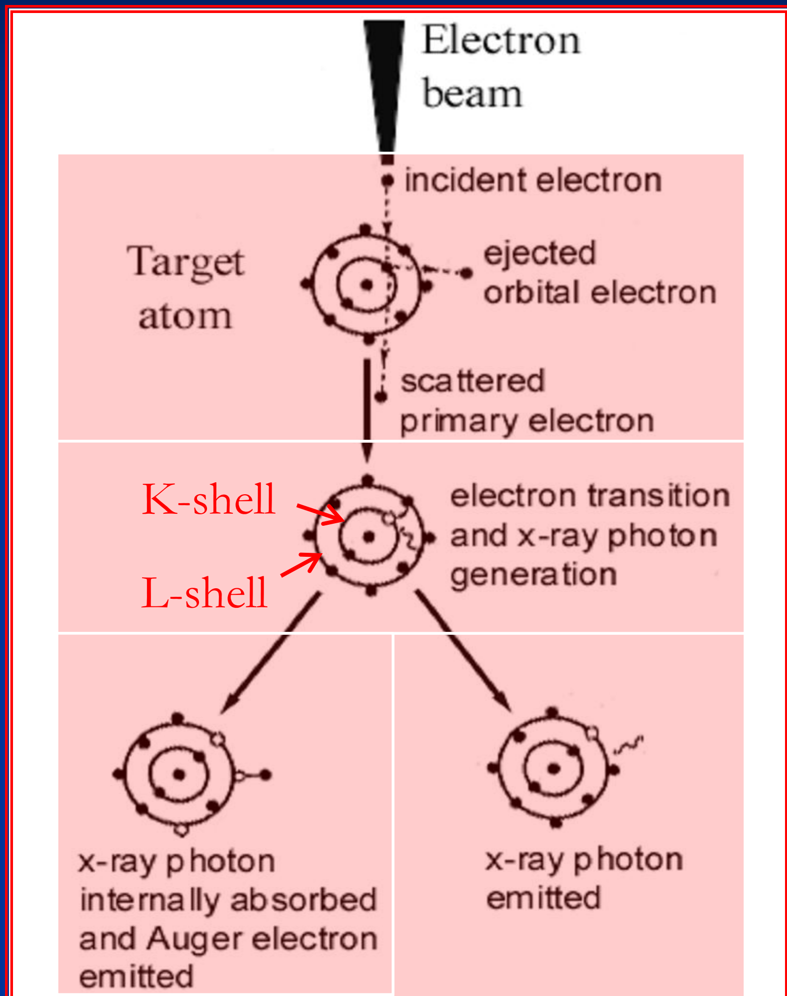



Neither phase contains Cr

But background counts at Cr :

in 1 in 2

# Characteristic X-ray generation




Flowchart for
X-ray generation

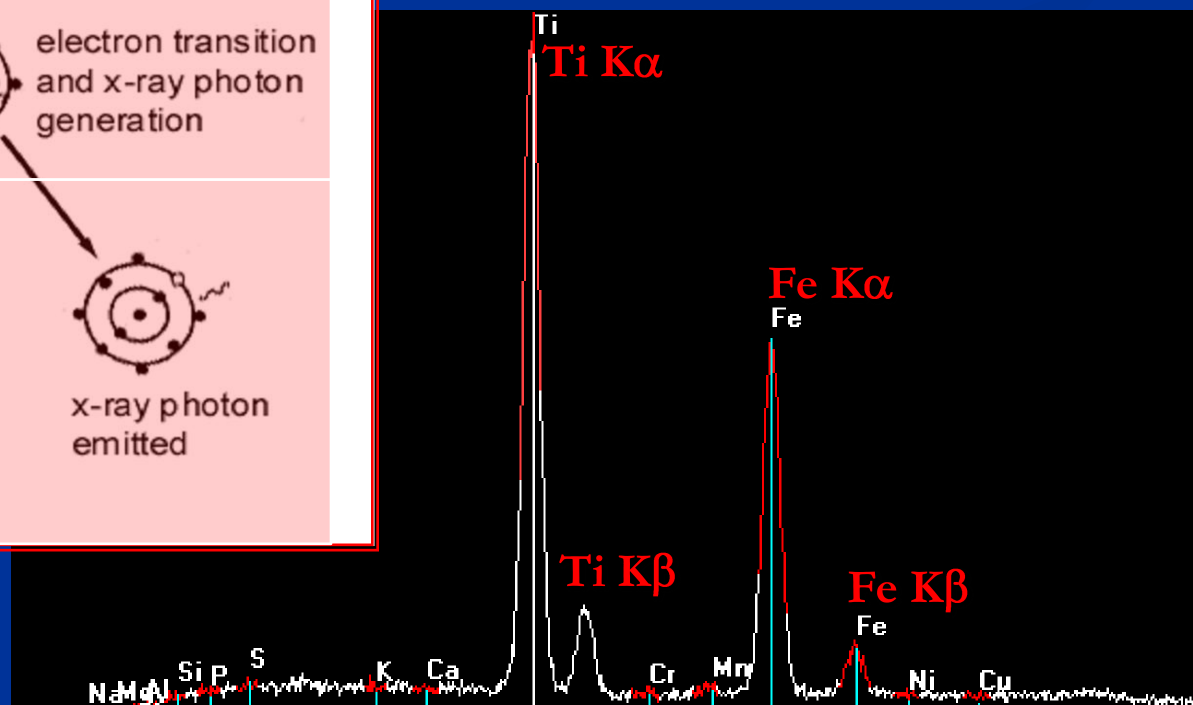
## Inner-shell ionization

<u>X-ray and electron transition</u>

**Kα:** *L to K-shell* **Kβ:** *M to K-shell*

**Lα:** *M to L-shell* **Lβ:** *N to L-shell*

**Mα:** *N to M-shell*



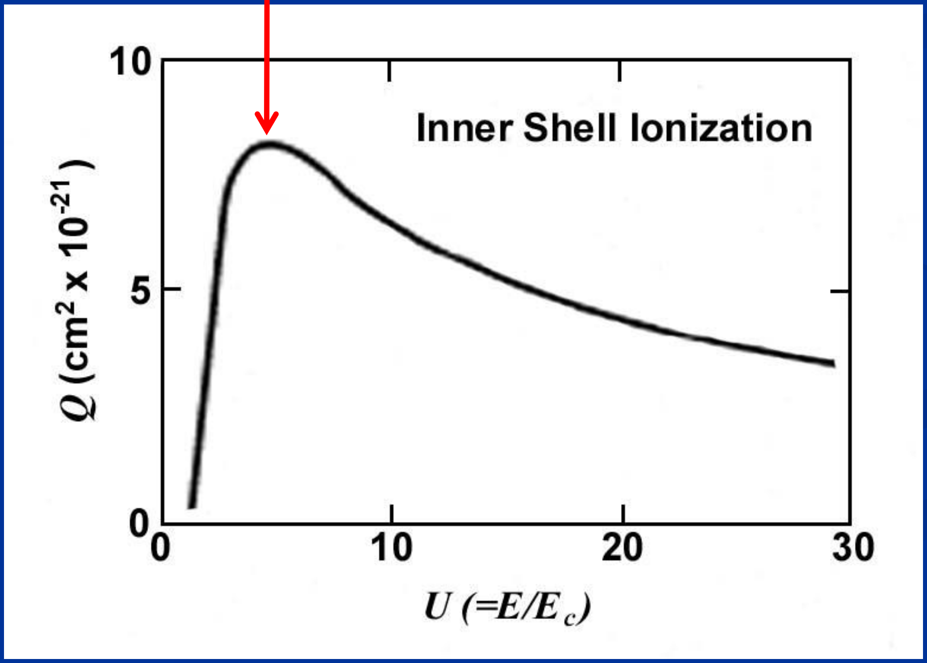
# Overvoltage

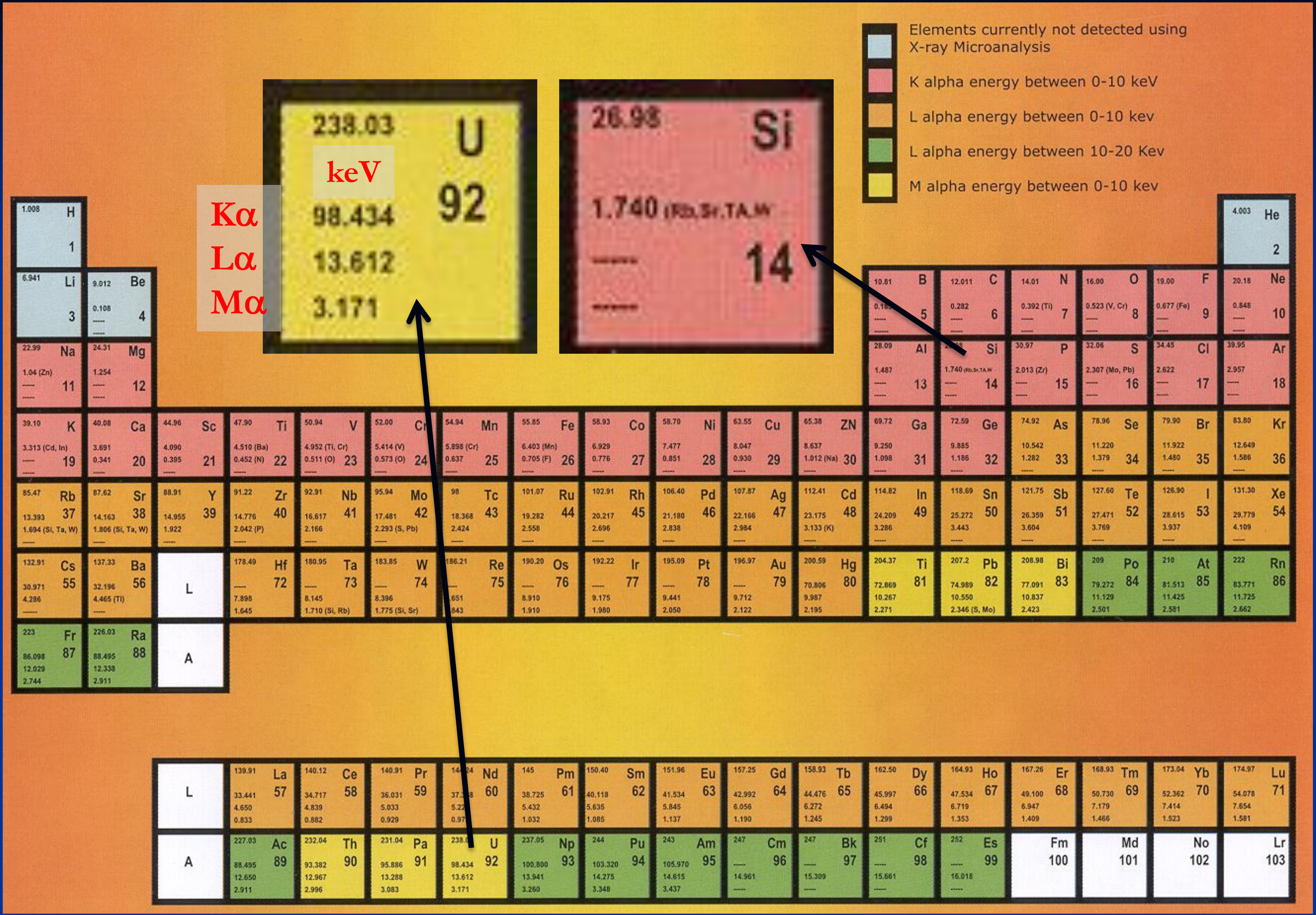
$$U = E_0/E_c$$

*where,* $E_0$ *is the electron beam energy (usually 10-25 keV)*

$E_c$ : critical excitation energy *for inner shell ionization*

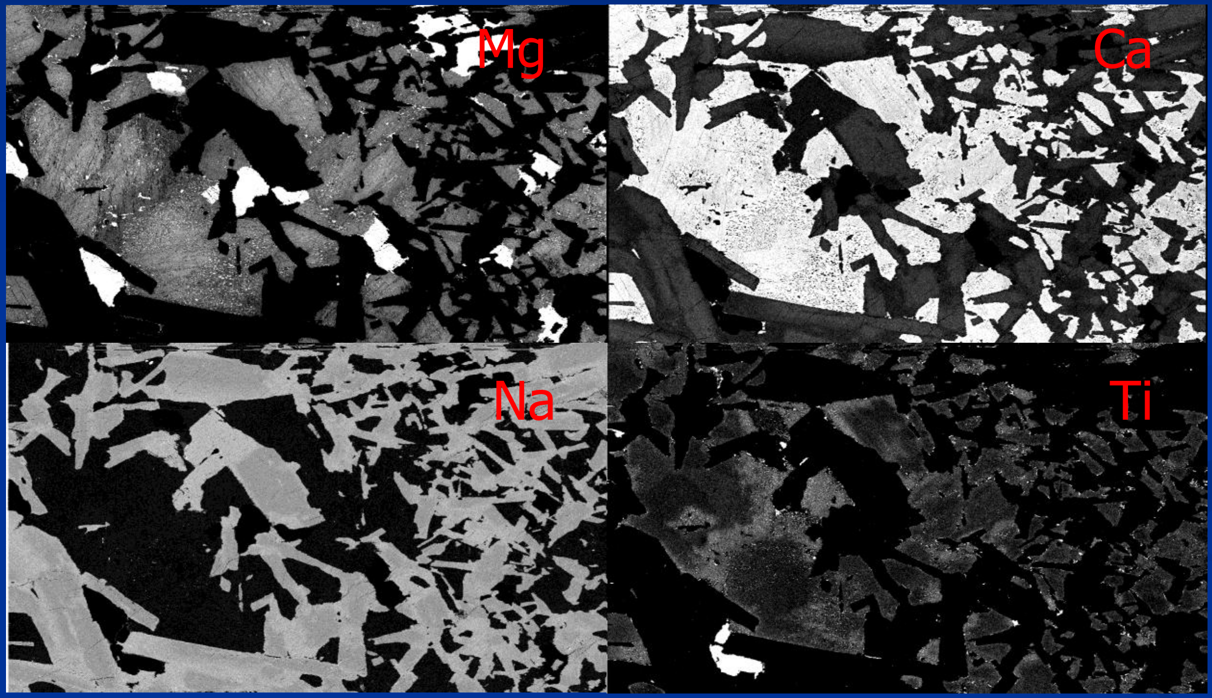
Best analytical condition, U≈5





Elements currently not detected using X-ray Microanalysis
K alpha energy between 0-10 keV
L alpha energy between 0-10 kev
L alpha energy between 10-20 Kev
M alpha energy between 0-10 kev
Kα
Lα
Mα
keV
238.03
U
92
98.434
13.612
3.171
26.98
Si
1.740 (Rb,Sr,TA,W
14

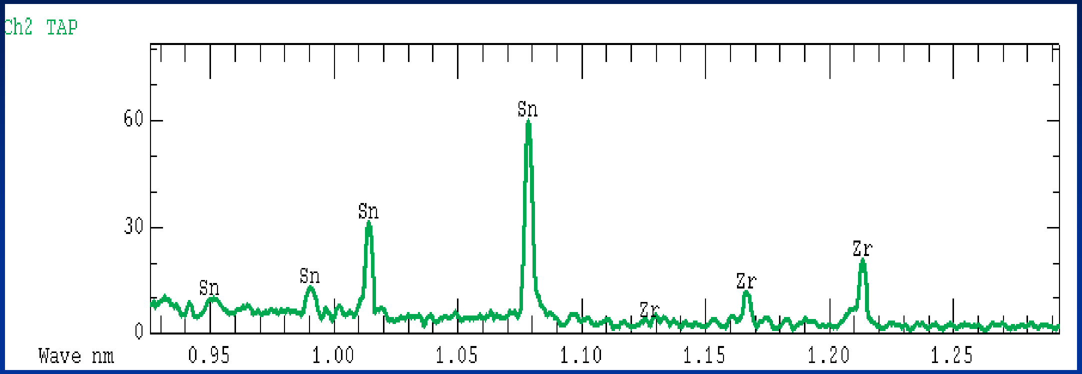
# Imaging with X-rays: compositional mapping




**Beam-rastered image:** *electron beam rasters over the area to be imaged*

**Stage-rastered image:** *electron beam is stationary, stage moves*

# EPMA: Quantitative analysis




***WDS spectrum:***

***Intensity is proportional to concentration***

$$\frac{C_i}{C_{(i)}} \propto \frac{I_i}{I_{(i)}} \qquad \text{where,} \qquad \frac{I_i}{I_{(i)}} = k_i$$

$$\frac{C_i}{C_{(i)}} = k_i \cdot [ZAF]_i$$

*$C_i$ and $C_{(i)}$: concentration of element 'i' in sample and standard*

*$I_i$ and $I_{(i)}$: measured X-ray intensities of element 'i' in sample and standard*

*$k_i$ : k-ratio of element 'i'* **ZAF** *: matrix corrections*

# Matrix (ZAF) corrections

**Z** : *atomic number correction*

**A** : *absorption correction*

**F** : *fluorescence correction*

# Atomic number (Z) correction

$$\mathbf{Z}_i \approx \frac{\dfrac{R_{(i)}}{S_{(i)}}}{\dfrac{R_i}{S_i}}$$

$R_i = \Sigma C_j R_{ij}$

*R = #X-rays generated / #X-rays if there were no electron backscattering*

$S_i = \Sigma C_j S_{ij}$

*S = -(1/ρ)(dE/ds), stopping power*

( ): standard

**a function of $E_0$ and composition (Duncumb and Reed)**

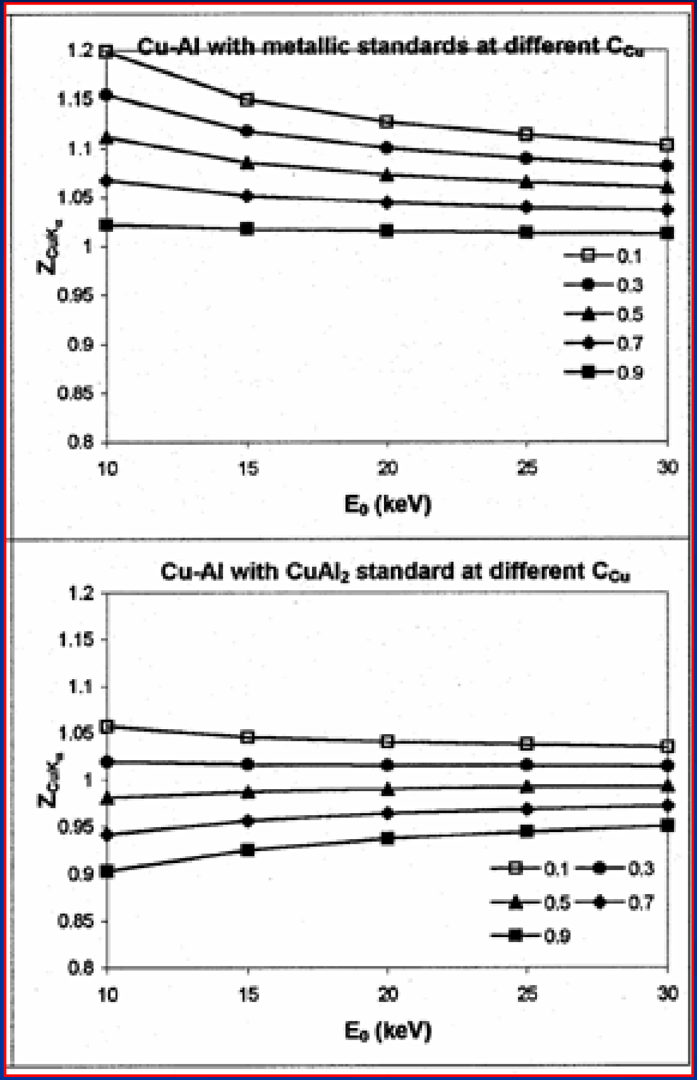
# Z, a function of $E_0$ and composition

Measuring Cu
in
Cu-Al alloy

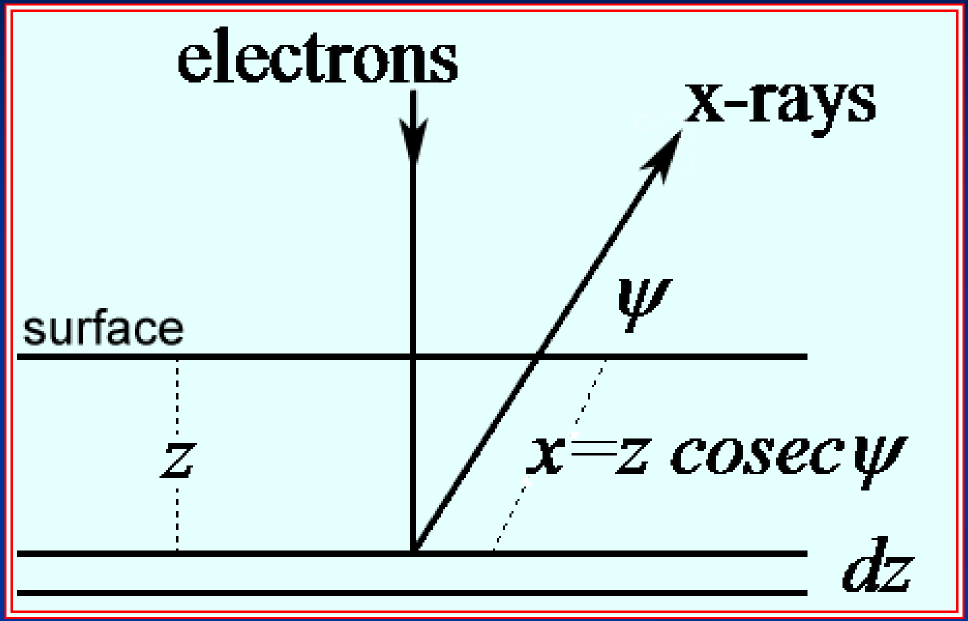
Pure Cu
standard

$CuAl_2$
standard

$Z_{CuK\alpha}$



# X-ray absorption



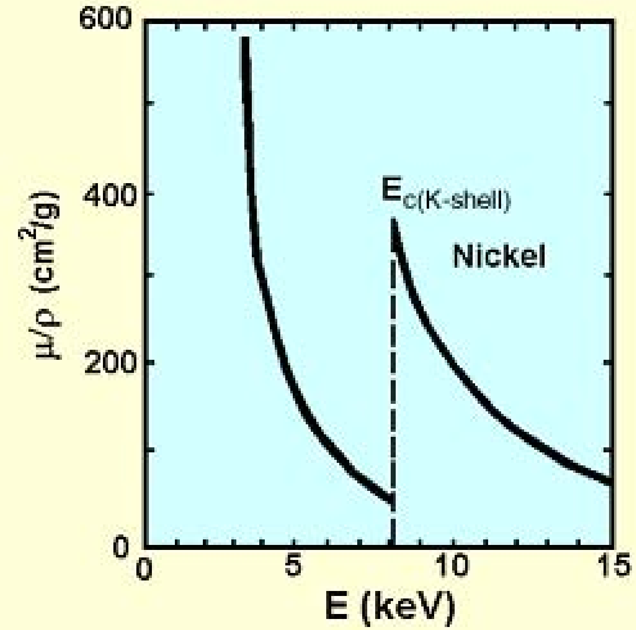

$$I = I_0 \exp^{-(\mu/\rho)(\rho x)} = I_0 \exp^{-(\mu/\rho)(\rho z \operatorname{cosec}\psi)}$$

*$I$: Intensity emitted; $I_0$: Intensity generated*

*$\mu/\rho$: mass absorption coefficient*

*$\rho$: density; $z$: depth; $\psi$: take-off angle*

# Mass absorption coefficient, $\left(\mu/\rho\right)^{energy}_{absorber}$




Plot of the mass absorption coefficient as a function of x-ray energy in Nickel

ZnKα is highly absorbed in Ni

| | Energy (keV) | $E_{c(K\text{-shell})}$ (keV) | $\left(\mu/\rho\right)^{energy}_{Ni}$ (cm$^2$/g) |
|---|---|---|---|
| CoKα | 6.925 | | 53 |
| **NiKα** | 7.472 | **8.331** | 60 |
| CuKα | 8.041 | | 49 |
| **ZnKα** | **8.632** | | **311** |

# Absorption (A) correction

$$\mathbf{A}_i = \frac{f(\chi_{(i)})}{f(\chi_i)}$$

*Absorption function,*

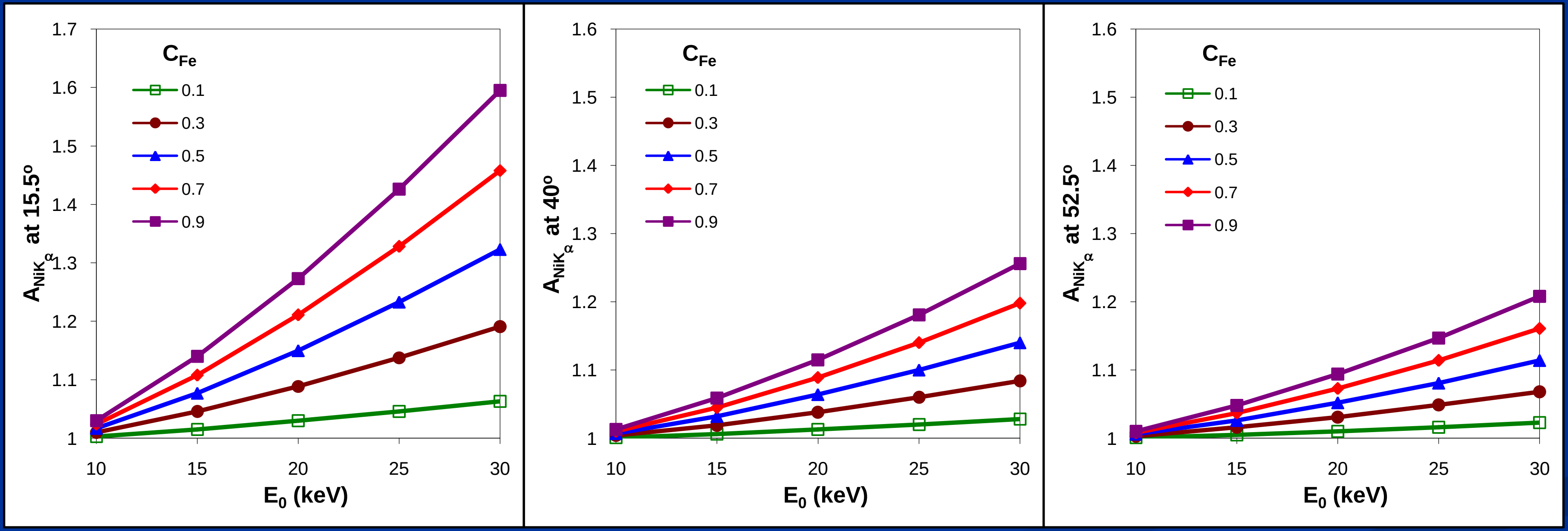
$f(\chi_i) = I_{i(emitted)}/I_{i(generated)}$

( ): standard

**a function of $E_0$, ψ and composition (Philibert)**

# A, a function of $E_0$, ψ and composition

## $A_{NiK\alpha}$ in Fe-Ni alloy

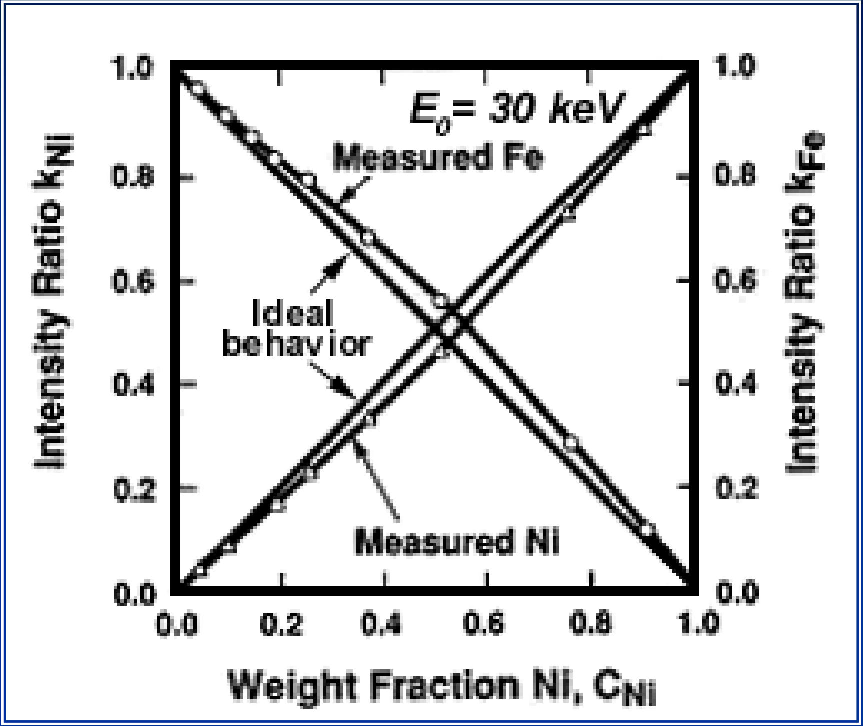


# X-ray fluorescence

*A consequence of X-ray absorption when*

$$E_{absorbed\ X\text{-}ray} > E_{c(absorber\ shell)}$$

# Absorption-Fluorescence in Fe-Ni alloy




NiKα *is absorbed in* Fe, *and* Fe *is fluoresced*

K-*shell excitation energy of Fe* = 7.111 keV; NiKα *energy* = 7.478 keV

$$\left(\mu/\rho\right)_{\text{Fe}}^{\text{NiK}\alpha} = 379.6\ \text{cm}^2/\text{g}$$

# Characteristic fluorescence (F) correction

$$\mathbf{F}_i = \frac{\left(1+\sum I\left\{{}^{f}_{(ij)}\middle/ I_{(i)}\right\}\right)}{\left(1+\sum\left\{I^{f}_{ij}\middle/ I_i\right\}\right)}$$

*$I^f$ : fluoresced intensity*

*$I$ : e-beam generated intensity*

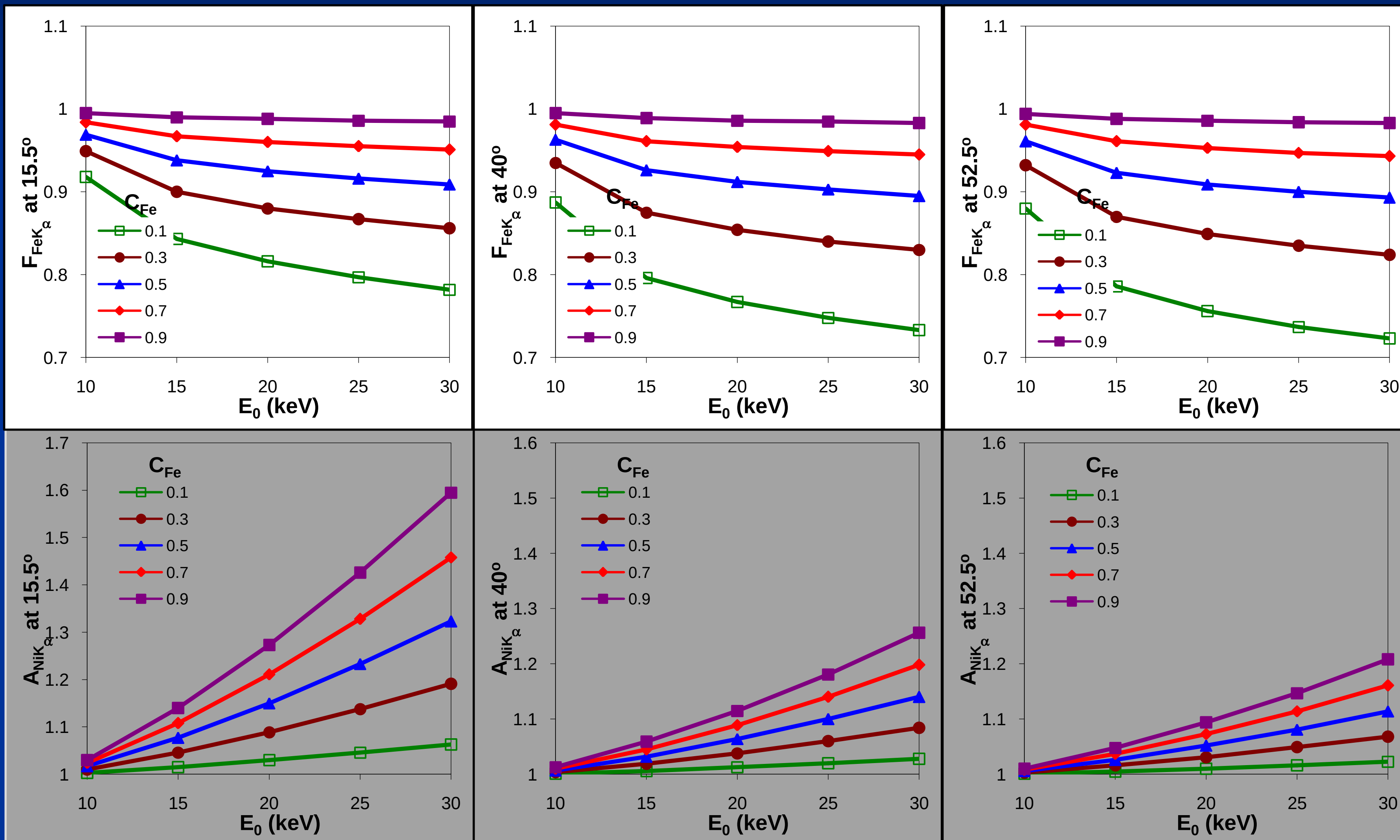
( ): standard

Fluorescence correction for an element includes the summation of fluoresced intensities by other elements in the compound

**a function of $E_0$ and composition (Castaing-Reed)**

# F, a function of $E_0$ and composition

## $F_{FeK\alpha}$ in Fe-Ni alloy




## $A_{NiK\alpha}$ in Fe-Ni alloy