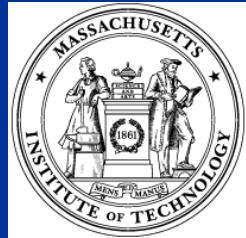
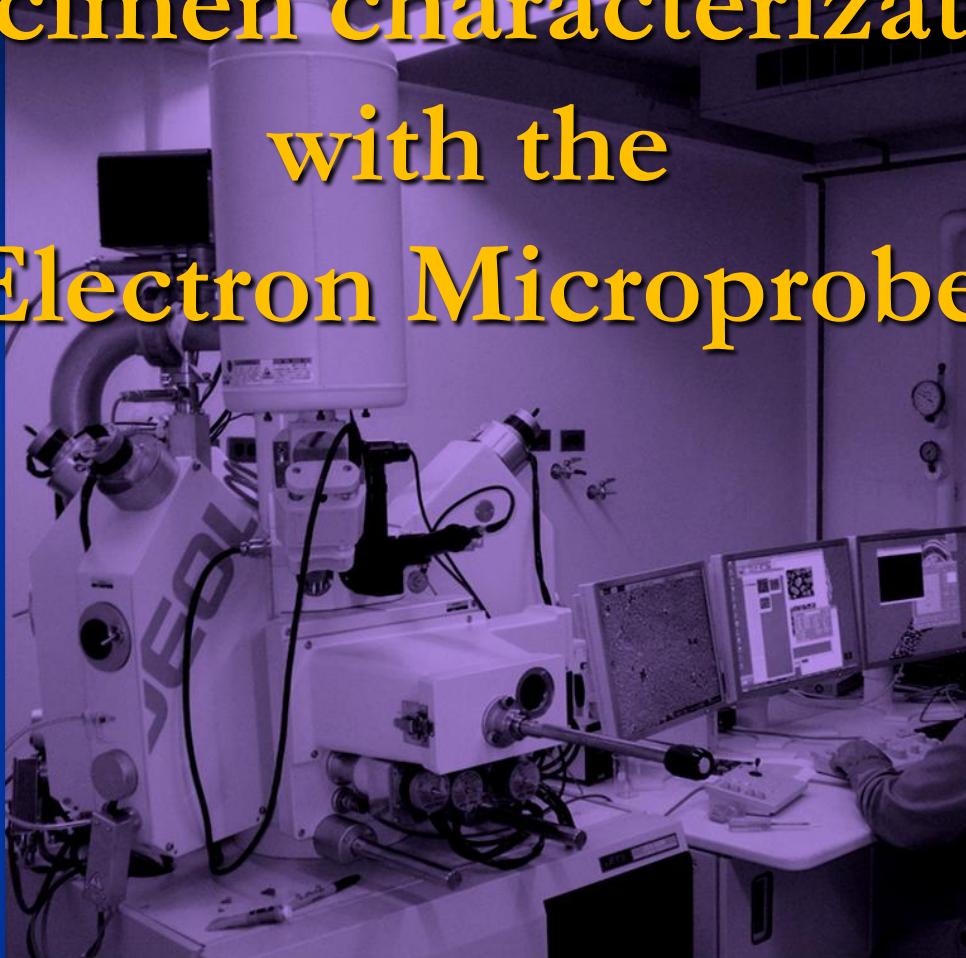
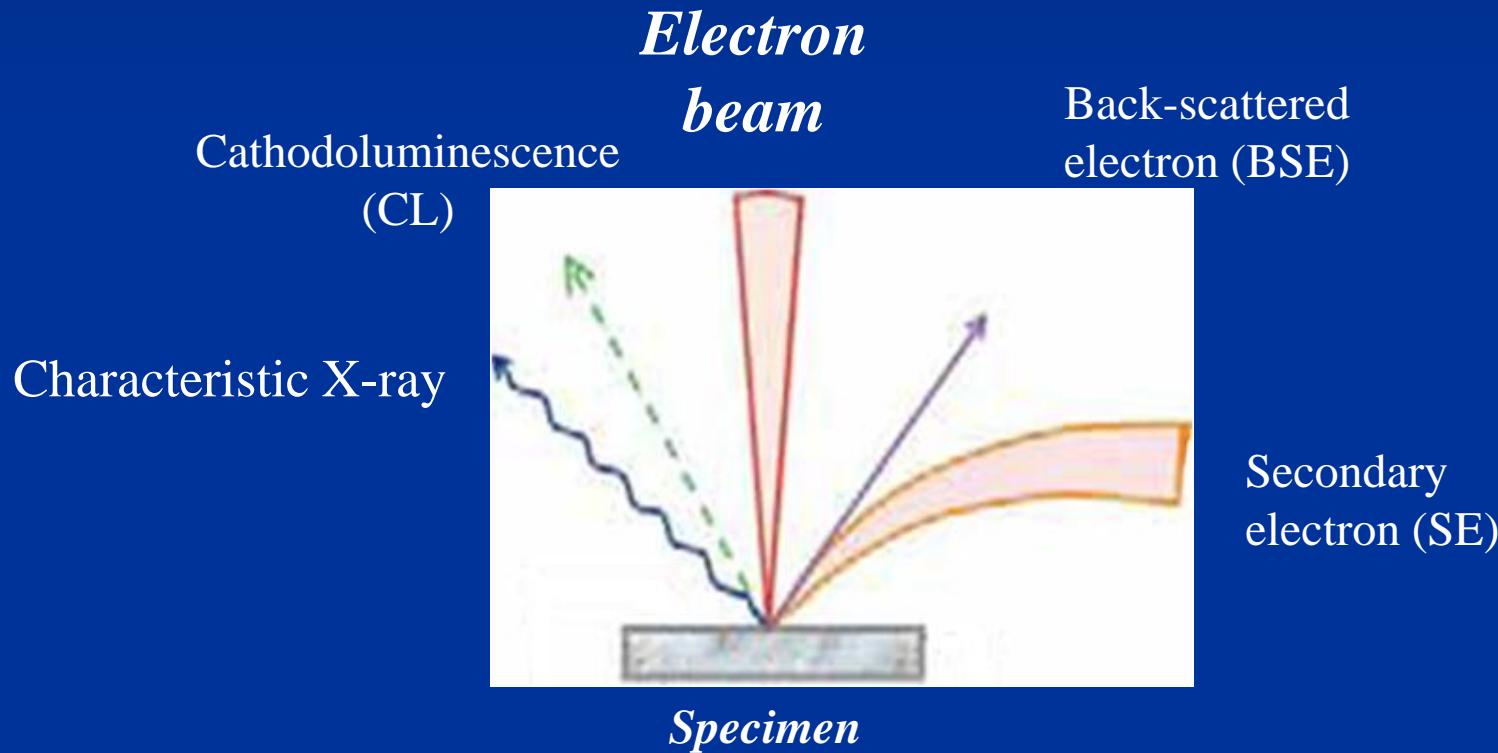


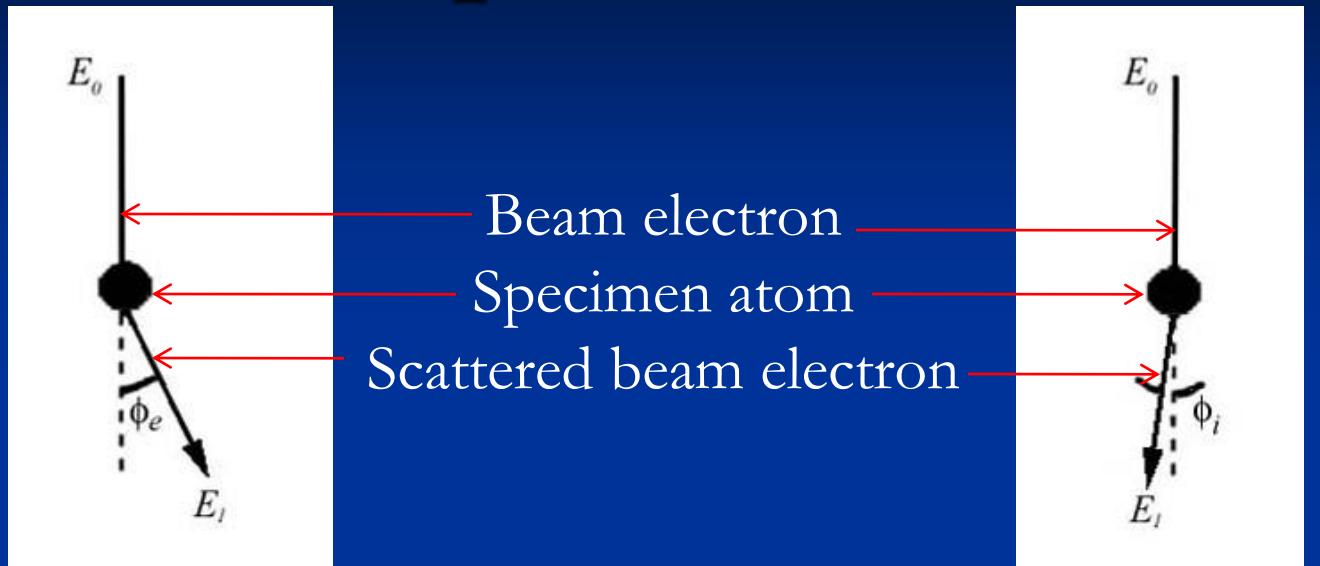
Specimen characterization with the Electron Microprobe



Signals produced in the Electron Microprobe



Electron-specimen interactions



Elastic Scattering

$$E_1 = E_0, \text{ large } \phi_e$$

$$(\phi_e \gg \phi_i)$$

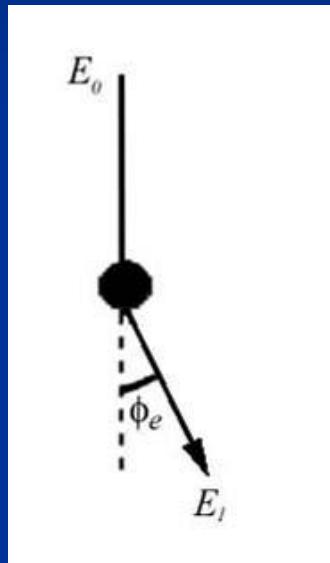
- Back-scattered electron

Inelastic Scattering

$$E_1 < E_0, \text{ small } \phi_i$$

- Characteristic X-rays
- Secondary electron
- Cathodoluminescence

Elastic scattering cross-section



$E_1 = E_0$, large ϕ_e

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

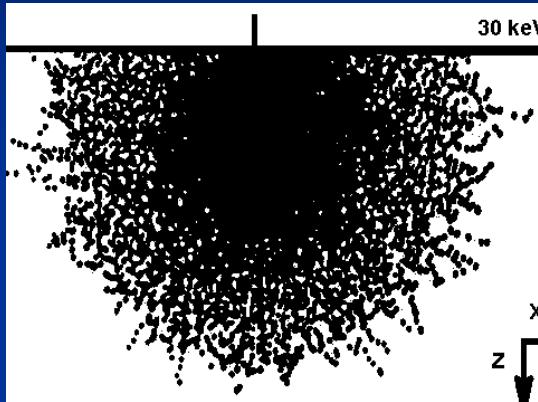
\mathcal{Q} : cross section (events.cm²/e⁻.atom)

ϕ_e : elastic scattering angle

Z : atomic number

E : beam energy

Electron interaction volume



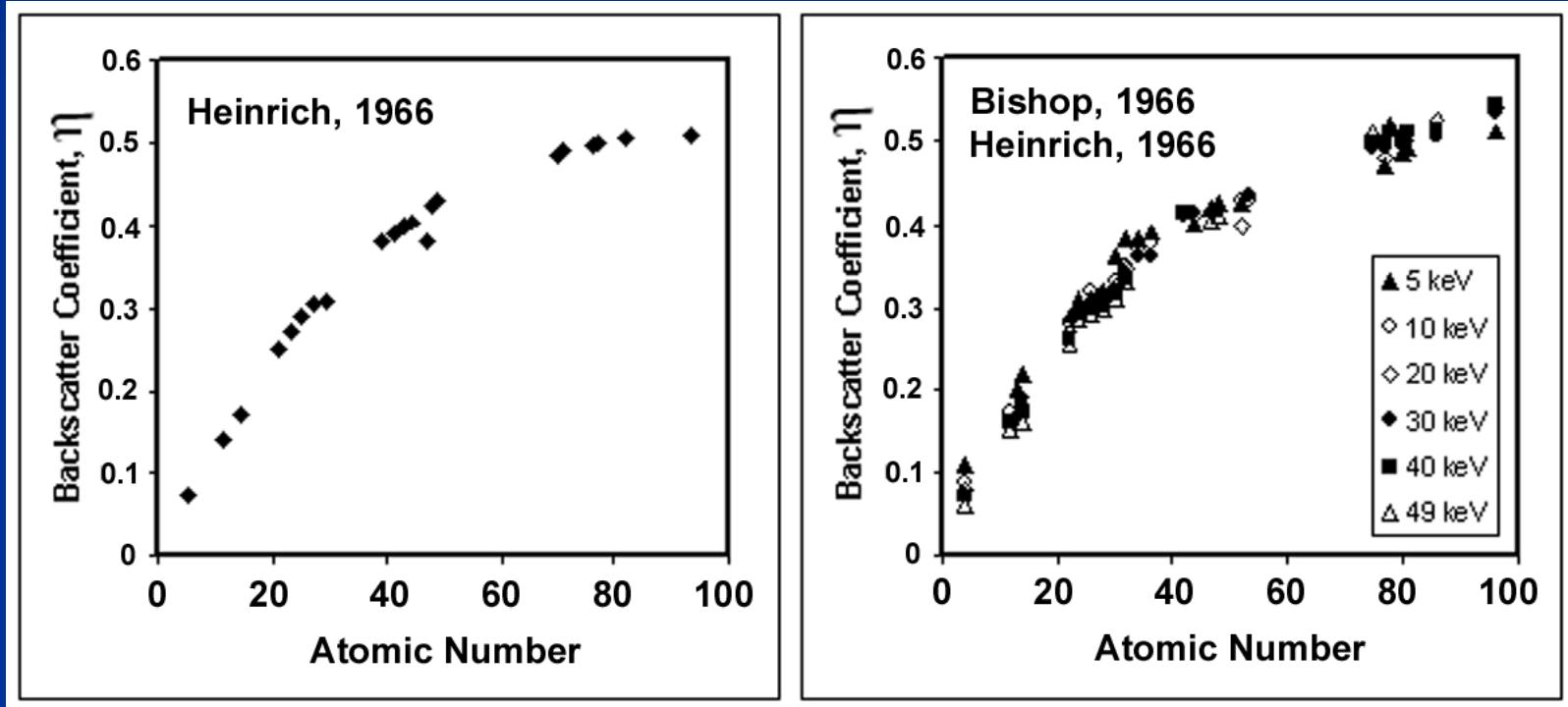
- Increases with voltage (electron beam energy)
- Decreases with sample atomic number

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

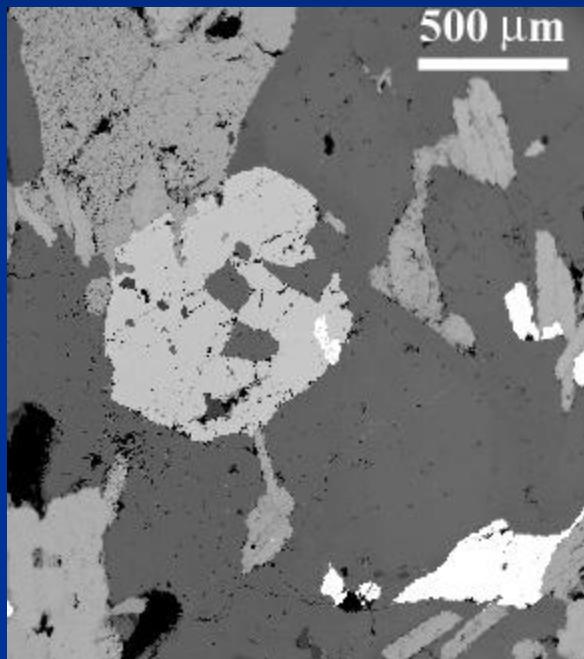
Electron Back-scattering

(High angle elastic scattering)



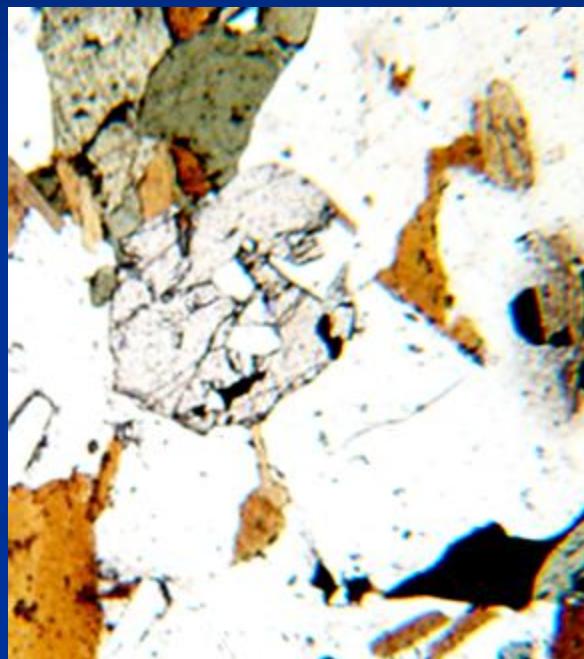
Backscattered electron image

Back-scattered electron



Polished surface

Plane polarized transmitted light

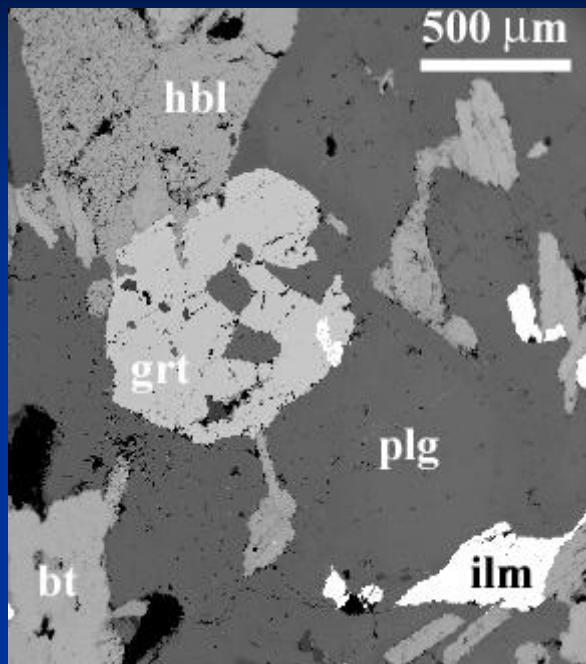


Thin section

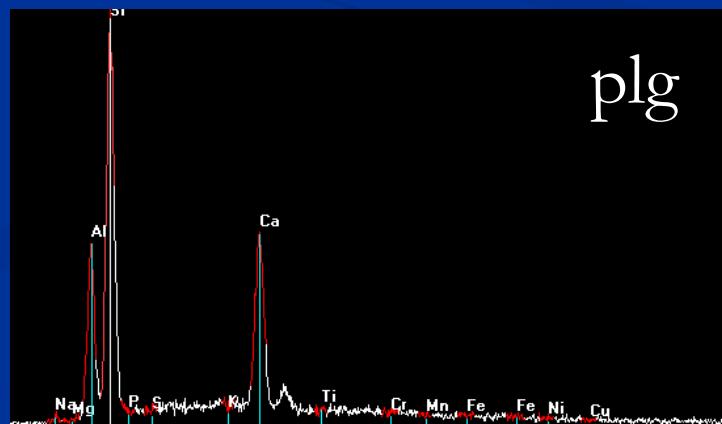
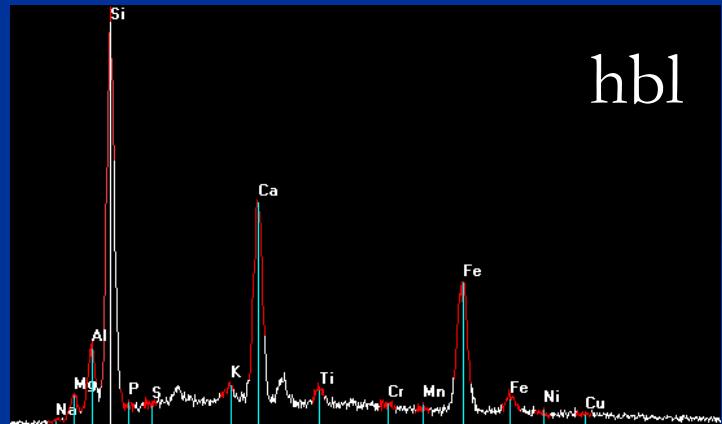
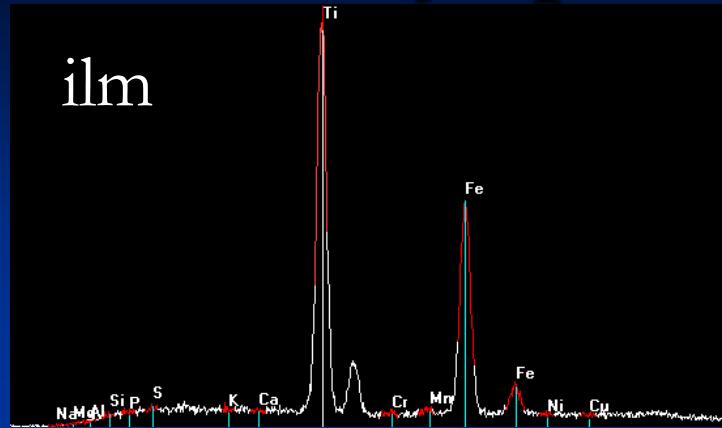
Function of
composition

Function of optical
properties

Phase identification: EDS X-ray spectra



Mean Atomic Number ↑



Understanding X-rays: Energy and Wavelength

$$E=h\nu$$

h : Planck's constant

(6.626×10^{-34} Joule.sec

or, $6.626 \times 10^{-34} / 1.6021 \times 10^{-16}$ keV.sec)

v : frequency (= c/λ)

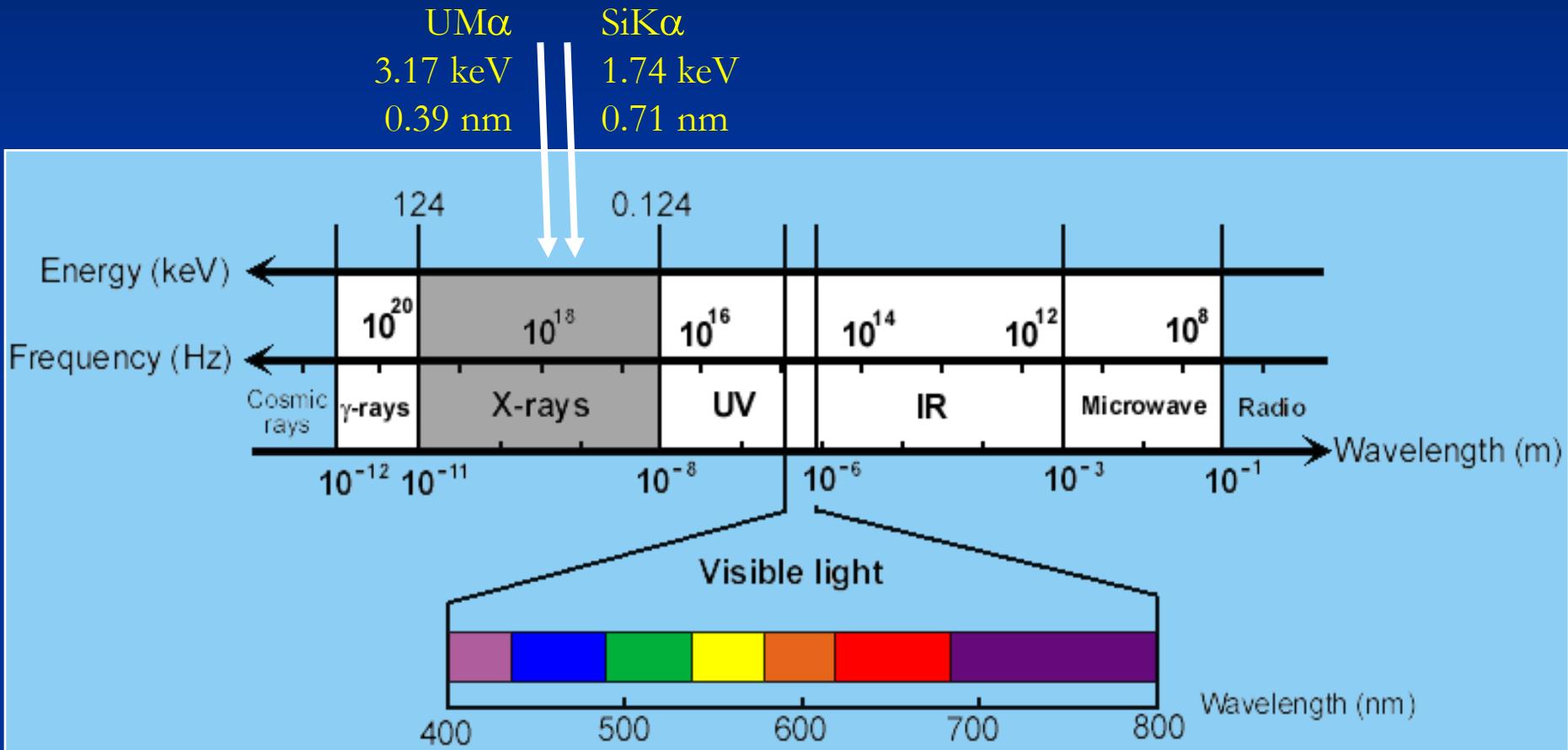
(*c : speed of light in vacuum*

= 2.99793×10^{17} nm/sec

λ : wavelength)

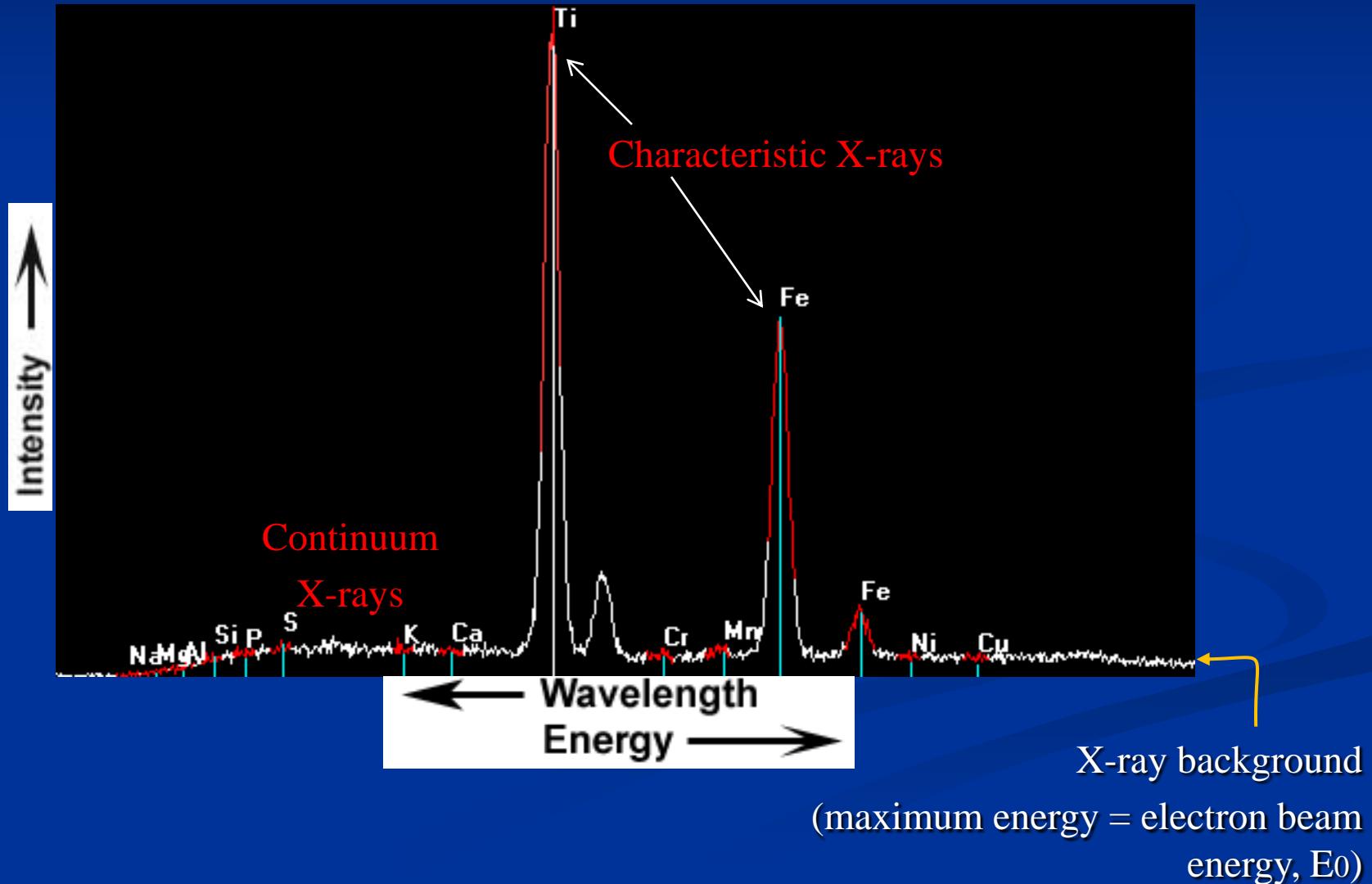
$$\lambda \text{ (nm)} = c/v = hc/E = 1.2398/E \text{ (keV)}$$

Understanding X-rays: The electromagnetic spectrum



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

The X-ray spectrum



Continuum X-rays: background in X-ray spectra

Phase 1



Phase 2



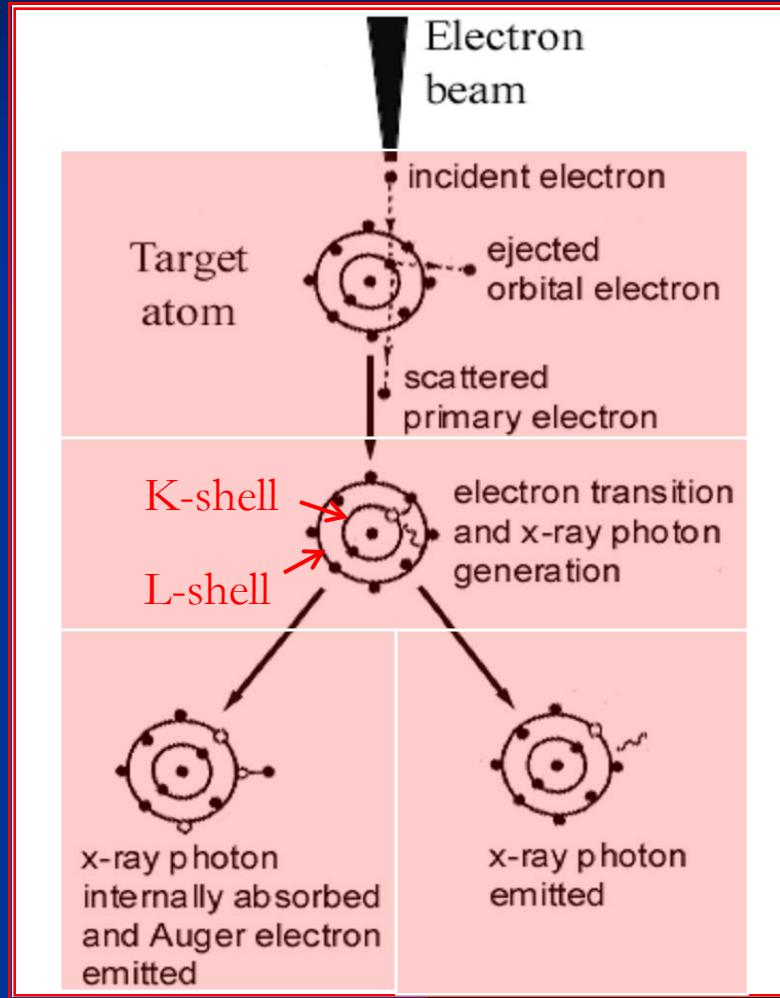
Neither phase contains Cr

But background counts at Cr : -



in 1 in 2

Characteristic X-ray generation



Flowchart for
X-ray generation

Inner-shell ionization

X-ray and electron transition

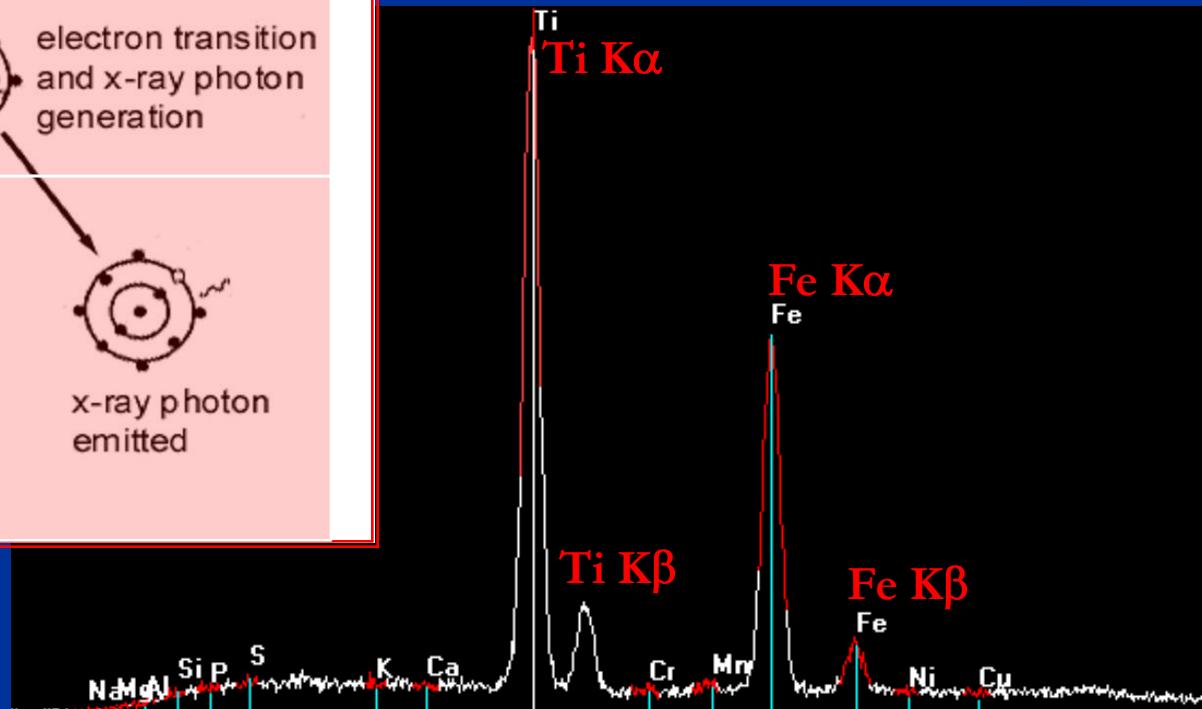
K α : L to K -shell

K β : M to K -shell

L α : M to L -shell

L β : N to L -shell

M α : N to M -shell

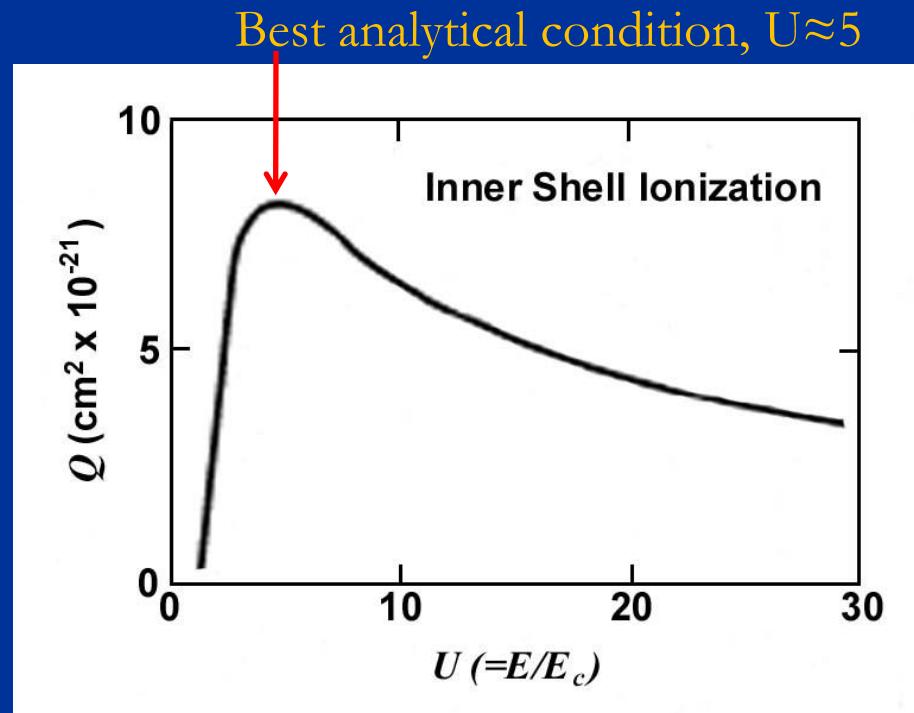


Overvoltage

$$U = E_0/E_c$$

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

E_c : critical excitation energy for inner shell ionization



Elements currently not detected using
X-ray Microanalysis

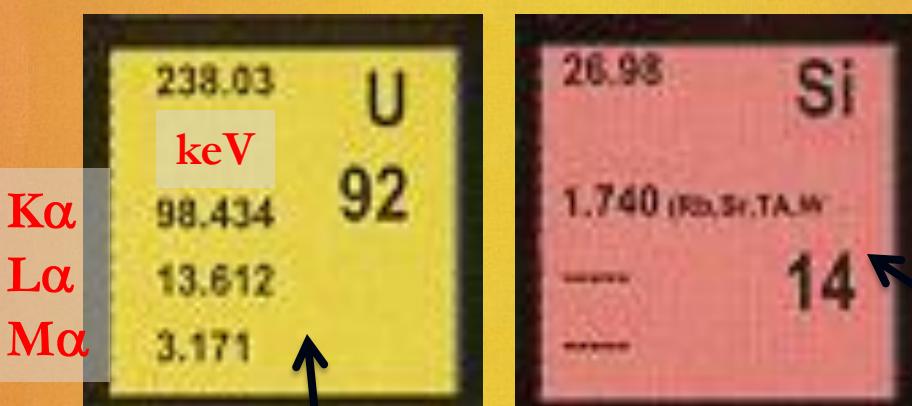
K alpha energy between 0-10 keV

L alpha energy between 0-10 keV

L alpha energy between 10-20 Kev

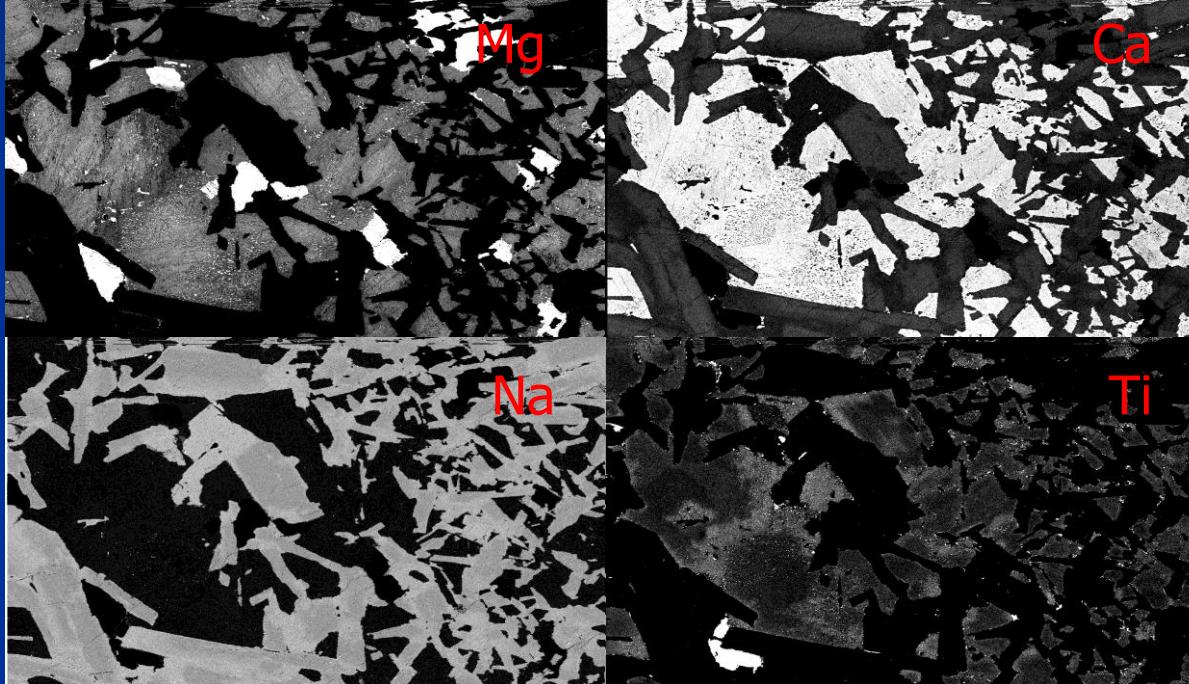
M alpha energy between 0-10 keV

1.008	H	
1		
6.941	Li	9.012 Be
3	0.108	4
—	—	—
22.99	Na	24.31 Mg
1.04 (Zn)	1.254	12
—	—	—
39.10	K	40.08 Ca
3.313 (Cd, In)	3.891	20
—	0.341	—
19	21	—
44.96	Sc	47.90 Ti
4.090	4.510 (Ba)	50.94 V
0.395	0.452 (N)	52.00 Cr
22	23	—
4.952 (Ti, Cr)	5.414 (V)	54.94 Mn
0.511 (O)	0.573 (O)	55.85 Fe
24	24	—
5.898 (Cr)	6.403 (Mn)	58.93 Co
0.637	0.705 (F)	58.70 Ni
25	26	—
6.929	7.477	63.55 Cu
0.776	0.851	65.38 ZN
27	28	—
8.047	8.637	69.72 Ga
0.930	1.012 (Na)	72.59 Ge
29	30	—
8.637	9.098	74.92 As
1.098	31	78.96 Se
31	32	—
9.250	9.885	79.99 Br
10.542	10.542	83.80 Kr
11.220	11.922	—
12.822	12.822	—
13.797	13.797	—
14.586	14.586	—
15.356	15.356	—
16.262	16.262	—
17.957	17.957	—
18.725	18.725	—
19.603	19.603	—
20.18	20.18	Ne
20.848	20.848	—
21.610	21.610	—
22.382	22.382	—
23.07	23.07 (Mo, Pb)	He
23.707	23.707	—
24.459	24.459	—
25.207	25.207	—
25.957	25.957	—
26.725	26.725	—
27.471	27.471	—
28.615	28.615	—
29.779	29.779	—
30.409	30.409	—
31.109	31.109	—
31.876	31.876	—
32.622	32.622	—
33.377	33.377	—
34.149	34.149	—
34.915	34.915	—
35.686	35.686	—
36.456	36.456	—
37.226	37.226	—
38.006	38.006	—
38.771	38.771	—
39.541	39.541	—
40.303	40.303	—
41.063	41.063	—
41.823	41.823	—
42.583	42.583	—
43.343	43.343	—
44.103	44.103	—
44.863	44.863	—
45.623	45.623	—
46.383	46.383	—
47.143	47.143	—
47.893	47.893	—
48.653	48.653	—
49.413	49.413	—
50.173	50.173	—
50.933	50.933	—
51.693	51.693	—
52.453	52.453	—
53.213	53.213	—
53.973	53.973	—
54.733	54.733	—
55.493	55.493	—
56.253	56.253	—
57.013	57.013	—
57.773	57.773	—
58.533	58.533	—
59.293	59.293	—
59.953	59.953	—
60.713	60.713	—
61.473	61.473	—
62.233	62.233	—
63.993	63.993	—
64.753	64.753	—
65.513	65.513	—
66.273	66.273	—
67.033	67.033	—
67.793	67.793	—
68.553	68.553	—
69.313	69.313	—
69.973	69.973	—
70.733	70.733	—
71.493	71.493	—
72.253	72.253	—
73.013	73.013	—
73.773	73.773	—
74.533	74.533	—
75.293	75.293	—
76.053	76.053	—
76.813	76.813	—
77.573	77.573	—
78.333	78.333	—
79.093	79.093	—
79.853	79.853	—
80.613	80.613	—
81.373	81.373	—
82.133	82.133	—
82.893	82.893	—
83.653	83.653	—
84.413	84.413	—
85.173	85.173	—
85.933	85.933	—
86.693	86.693	—
87.453	87.453	—
88.213	88.213	—
88.973	88.973	—
89.733	89.733	—
90.493	90.493	—
91.253	91.253	—
92.013	92.013	—
92.773	92.773	—
93.533	93.533	—
94.293	94.293	—
95.053	95.053	—
95.813	95.813	—
96.573	96.573	—
97.333	97.333	—
98.093	98.093	—
98.853	98.853	—
99.613	99.613	—
100.373	100.373	—
101.133	101.133	—
101.893	101.893	—
102.653	102.653	—
103.413	103.413	—



10.81	B	12.011	C	14.01	N	16.00	O	19.00	F	20.18	Ne
0.183	5	0.282	6	0.392 (Ti)	7	0.523 (V, Cr)	8	0.677 (Fe)	9	0.848	10
—	—	—	—	—	—	—	—	—	—	—	—
10.89	Al	12.011	Si	13.01	P	14.00	S	15.00	Cl	16.95	Ar
1.487	13	1.740 (Rb,Sr,Ta,W)	14	2.013 (Zr)	15	2.307 (Mo, Pb)	16	2.622	17	2.957	18
—	—	—	—	—	—	—	—	—	—	—	—
11.75	Sb	12.75	Te	13.75	Pb	14.75	Bi	15.75	At	16.75	Rn
12.75	Sn	13.75	Te	14.75	Pb	15.75	Bi	16.75	At	17.75	Rn
13.75	Sn	14.75	Te	15.75	Pb	16.75	Bi	17.75	At	18.75	Rn
14.75	Sn	15.75	Te	16.75	Pb	17.75	Bi	18.75	At	19.75	Rn
15.75	Sn	16.75	Te	17.75	Pb	18.75	Bi	19.75	At	20.75	Rn
16.75	Sn	17.75	Te	18.75	Pb	19.75	Bi	20.75	At	21.75	Rn
17.75	Sn	18.75	Te	19.75	Pb	20.75	Bi	21.75	At	22.75	Rn
18.75	Sn	19.75	Te	20.75	Pb	21.75	Bi	22.75	At	23.75	Rn
19.75	Sn	20.75	Te	21.75	Pb	22.75	Bi	23.75	At	24.75	Rn
20.75	Sn	21.75	Te	22.75	Pb	23.75	Bi	24.75	At	25.75	Rn
21.75	Sn	22.75	Te	23.75	Pb	24.75	Bi	25.75	At	26.75	Rn
22.75	Sn	23.75	Te	24.75	Pb	25.75	Bi	26.75	At	27.75	Rn
23.75	Sn	24.75	Te	25.75	Pb	26.75	Bi	27.75	At	28.75	Rn
24.75	Sn	25.75	Te	26.75	Pb	27.75	Bi	28.75	At	29.75	Rn
25.75	Sn	26.75	Te	27.75	Pb	28.75	Bi	29.75	At	30.75	Rn
26.75	Sn	27.75	Te	28.75	Pb	29.75	Bi	30.75	At	31.75	Rn
27.75	Sn	28.75	Te	29.75	Pb	30.75	Bi	31.75	At	32.75	Rn
28.75	Sn	29.75	Te	30.75	Pb	31.75	Bi	32.75	At	33.75	Rn
29.75	Sn	30.75	Te	31.75	Pb	32.75	Bi	33.75	At	34.75	Rn
30.75	Sn	31.75	Te	32.75	Pb	33.75	Bi	34.75	At	35.75	Rn
31.75	Sn	32.75	Te	33.75	Pb	34.75	Bi	35.75	At	36.75	Rn
32.75	Sn	33.75	Te	34.75	Pb	35.75	Bi	36.75	At	37.75	Rn
33.75	Sn	34.75	Te	35.75	Pb	36.75	Bi	37.75	At	38.75	Rn
34.75	Sn	35.75	Te	36.75	Pb	37.75	Bi	38.75	At	39.75	Rn
35.75	Sn	36.75	Te	37.75	Pb	38.75	Bi	39.75	At	40.75	Rn
36.75	Sn	37.75	Te	38.75	Pb	39.75	Bi	40.75	At	41.75	Rn
37.75	Sn	38.75	Te	39.75	Pb	40.75	Bi	41.75	At	42.75	Rn
38.75	Sn	39.75	Te	40.75	Pb	41.75	Bi	42.75	At	43.75	Rn
39.75	Sn	40.75	Te	41.75	Pb	42.75	Bi	43.75	At	44.75	Rn
40.75	Sn	41.75	Te	42.75	Pb	43.75	Bi	44.75	At	45.75	Rn
41.75	Sn	42.75	Te	43.75	Pb	44.75	Bi	45.75	At	46.75	Rn
42.75	Sn	43.75	Te	44.75	Pb	45.75	Bi	46.75	At	47.75	Rn
43.75	Sn	44.75	Te	45.75	Pb	46.75	Bi	47.75	At	48.75	Rn
44.75	Sn	45.75	Te	46.75	Pb	47.75	Bi	48.75	At	49.75	Rn
45.75	Sn	46.75	Te	47.75	Pb	48.75	Bi	49.75	At	50.75	Rn
46.75	Sn	47.75	Te	48.75	Pb	49.75	Bi	50.75	At	51.75	Rn
47.75	Sn	48.75	Te	49.75	Pb	50.75	Bi	51.75	At	52.75	Rn
48.75	Sn	49.75	Te	50.75	Pb	51.75	Bi	52.75	At	53.75	Rn
49.75	Sn	50.75	Te	51.75	Pb	52.75	Bi	53.75	At	54.75	Rn
50.75	Sn	51.75	Te	52.75	Pb	53.75	Bi	54.75	At	55.75	Rn
51.75	Sn	52.75	Te	53.75	Pb	54.75	Bi	55.75	At	56.75	Rn
52.75	Sn	53.75	Te	54.75	Pb	55.75	Bi	56.75	At	57.75	Rn
53.75	Sn	54.75	Te	55.75	Pb	56.75	Bi	57.75	At	58.75	Rn
54.75	Sn	55.75	Te	56.75	Pb	57.75	Bi	58.75	At	59.75	Rn
55.75	Sn	56.75	Te	57.75	Pb	58.75	Bi	59.75	At	60.75	Rn
56.75	Sn	57.75	Te	58.75	Pb	59.75	Bi	60.75	At	61.75	Rn
57.75	Sn	58.75	Te	59.75	Pb	60.75	Bi	61.75	At	62.75	Rn
58.75	Sn	59.75	Te	60.75	Pb	61.75	Bi	62.75	At	63.75	Rn
59.75	Sn	60.75	Te	61.75	Pb	62.75	Bi	63.75	At	64.75	Rn
60.75	Sn	61.75	Te	62.75	Pb	63.75	Bi	64.75	At	65.75	Rn
61.75	Sn	62.75	Te	63.75	Pb	64.75	Bi	65.75	At	66.75	Rn
62.75	Sn	63.75	Te	64.75	Pb	65.75	Bi	66.75	At	67.75	Rn
63.75	Sn	64.75	Te	65.75	Pb	66.75	Bi	67.75	At	68.75	Rn
64.75	Sn	65.75	Te	66.75	Pb	67.75	Bi	68.75	At	69.75	Rn
65.75	Sn	66.75	Te	67.75	Pb	68.75	Bi	69.75	At	70.75	Rn
66.75	Sn	67.75	Te	68.75	Pb	69.75	Bi	70.75	At	71.75	Rn
67.75	Sn	68.75	Te	69.75	Pb	70.75	Bi	71.75	At	72.75	Rn
68.75	Sn	69.75	Te	70.75	Pb	71.75	Bi	72.75	At	73.75	Rn
69.75	Sn	70.75	Te	71.75	Pb	72.75	Bi	73.75	At	74.75	Rn
70.75	Sn	71.75	Te	72.7							

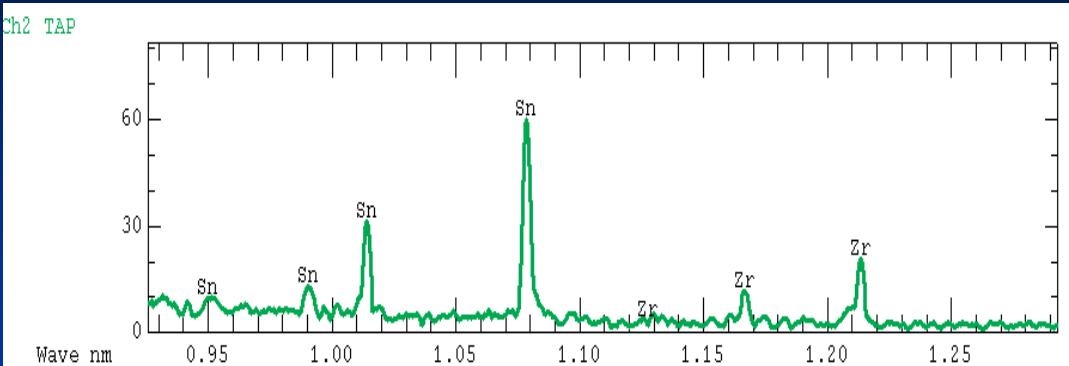
Imaging with X-rays: compositional mapping



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*

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

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

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

$$Z_i \approx \frac{\frac{R_{(i)}}{S_{(i)}}}{\frac{R_i}{S_i}}$$

$R_i = \sum C_j R_{ij}$
 $R = \#X\text{-rays generated} / \#X\text{-rays if}$
there were no electron backscattering

$S_i = \sum C_j S_{ij}$
 $S = -(1/\rho)(dE/ds), \text{stopping power}$

(): standard

a function of E_0 and composition
(Duncumb and Reed)

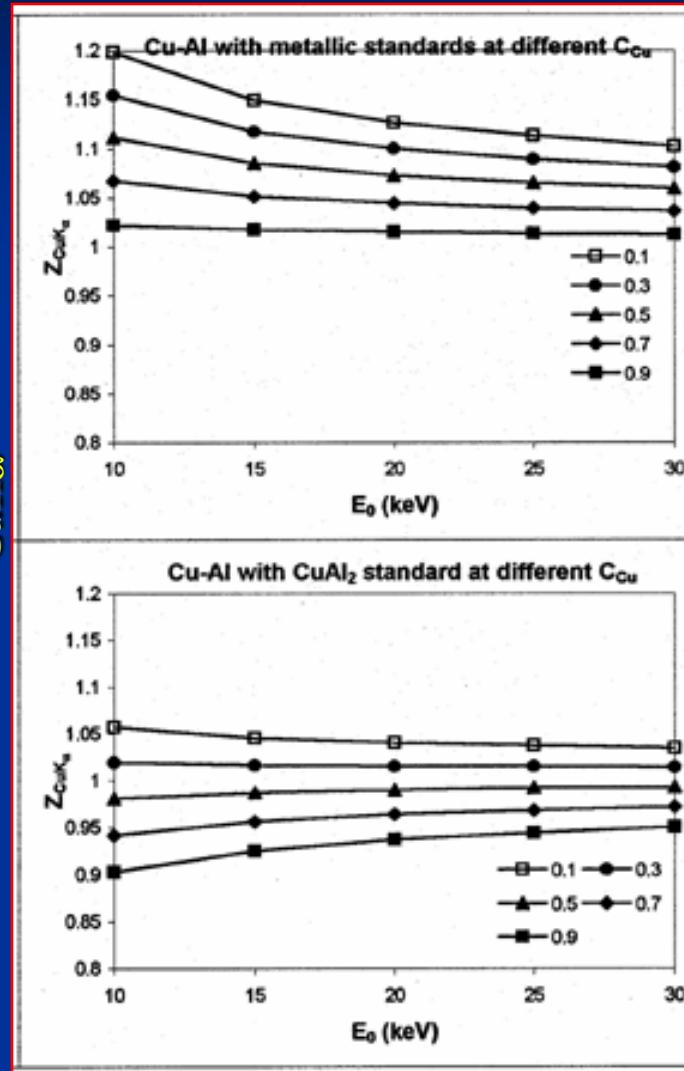
Z , a function of E_0 and composition

Measuring Cu
in
Cu-Al alloy

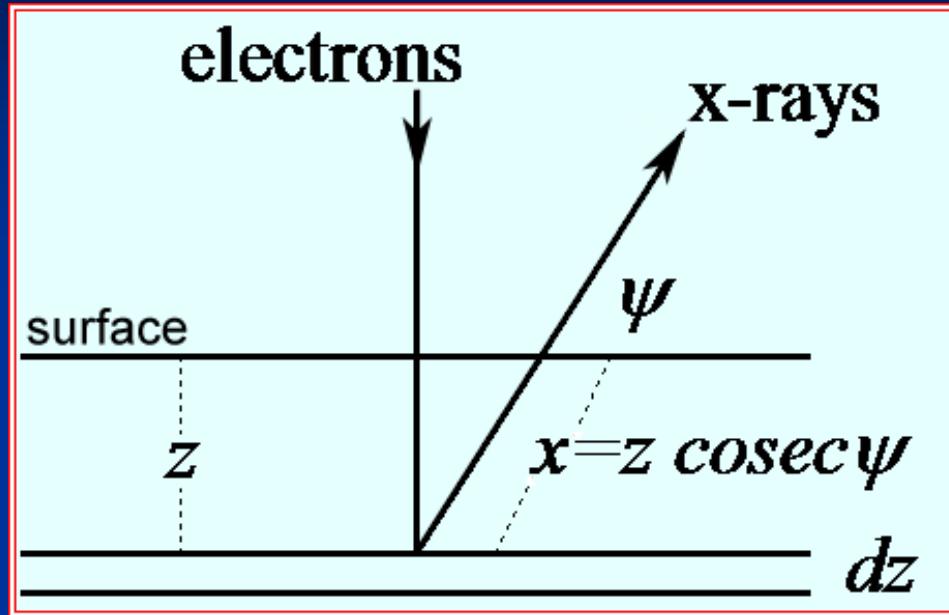
Pure Cu
standard

CuAl_2
standard

$Z_{\text{CuK}\alpha}$



X-ray absorption



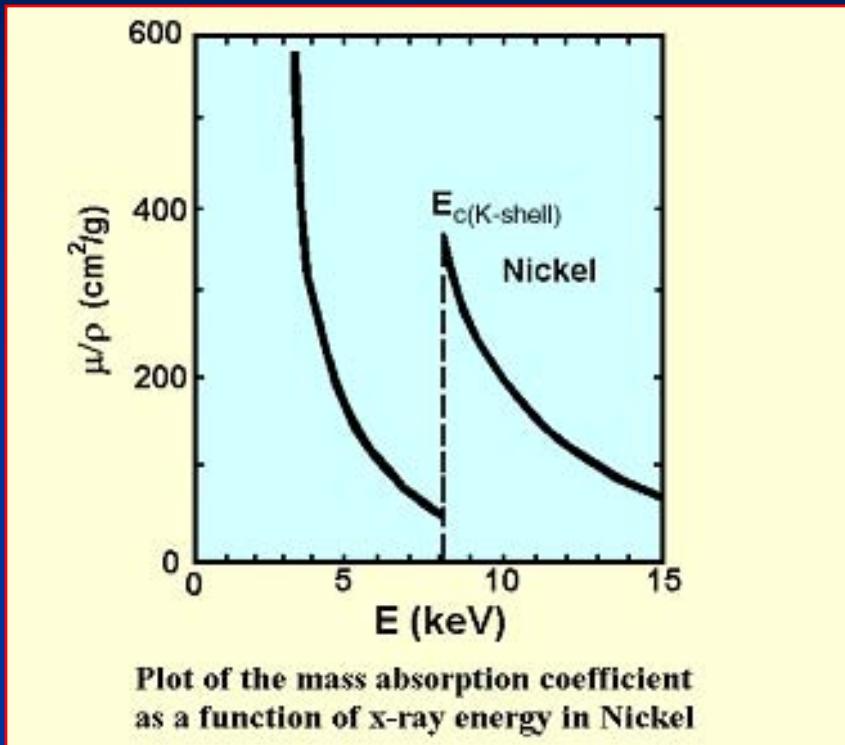
$$I = I_0 \exp^{-(\mu/\rho)(\rho x)} = I_0 \exp^{-(\mu/\rho)(\rho z \cosec \psi)}$$

I : Intensity emitted; I_0 : Intensity generated

μ/ρ : mass absorption coefficient

ρ : density; z : depth; ψ : take-off angle

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



ZnK α is highly
absorbed in Ni

Energy	$E_{c(\text{K-shell})}$	$(\mu/\rho)_{Ni}^{energy}$
(keV)	(keV)	(cm^2/g)
CoK α	6.925	53
NiK α	7.472	<u>8.331</u>
CuK α	8.041	49
ZnK α	<u>8.632</u>	<u>311</u>

Absorption (A) correction

$$A_i = \frac{f(\chi_{(i)})}{f(\chi_i)}$$

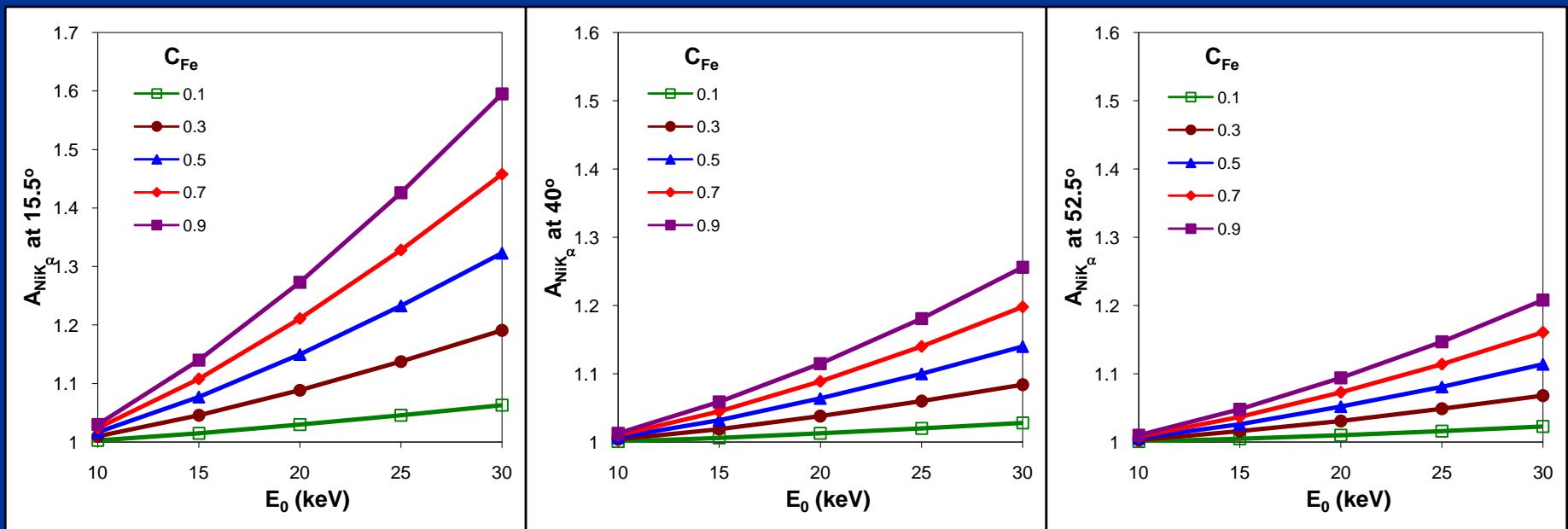
Absorption function,
 $f(\chi_i) =$
 $I_{i(emitted)} / I_{i(generated)}$

(): standard

a function of E_0 , Ψ and composition
(Philibert)

A, a function of E_0 , ψ and composition

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

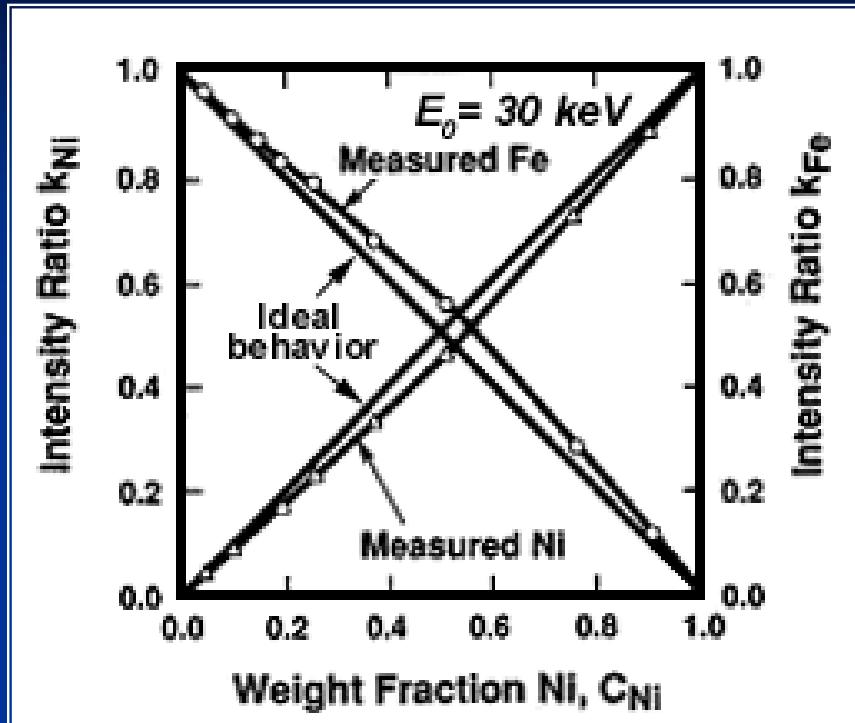


X-ray fluorescence

*A consequence of X-ray absorption
when*

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

Absorption-Fluorescence in Fe-Ni alloy



NiK α is absorbed in Fe, and Fe is fluoresced

K-shell excitation energy of Fe = 7.111 keV; NiK α energy = 7.478 keV

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

Characteristic fluorescence (F) correction

$$F_i = \frac{\left(1 + \sum I_{(ij)}^f / I_{(i)} \right)}{\left(1 + \sum I_{ij}^f / I_i \right)}$$

I^f : fluoresced intensity

I : e-beam generated intensity

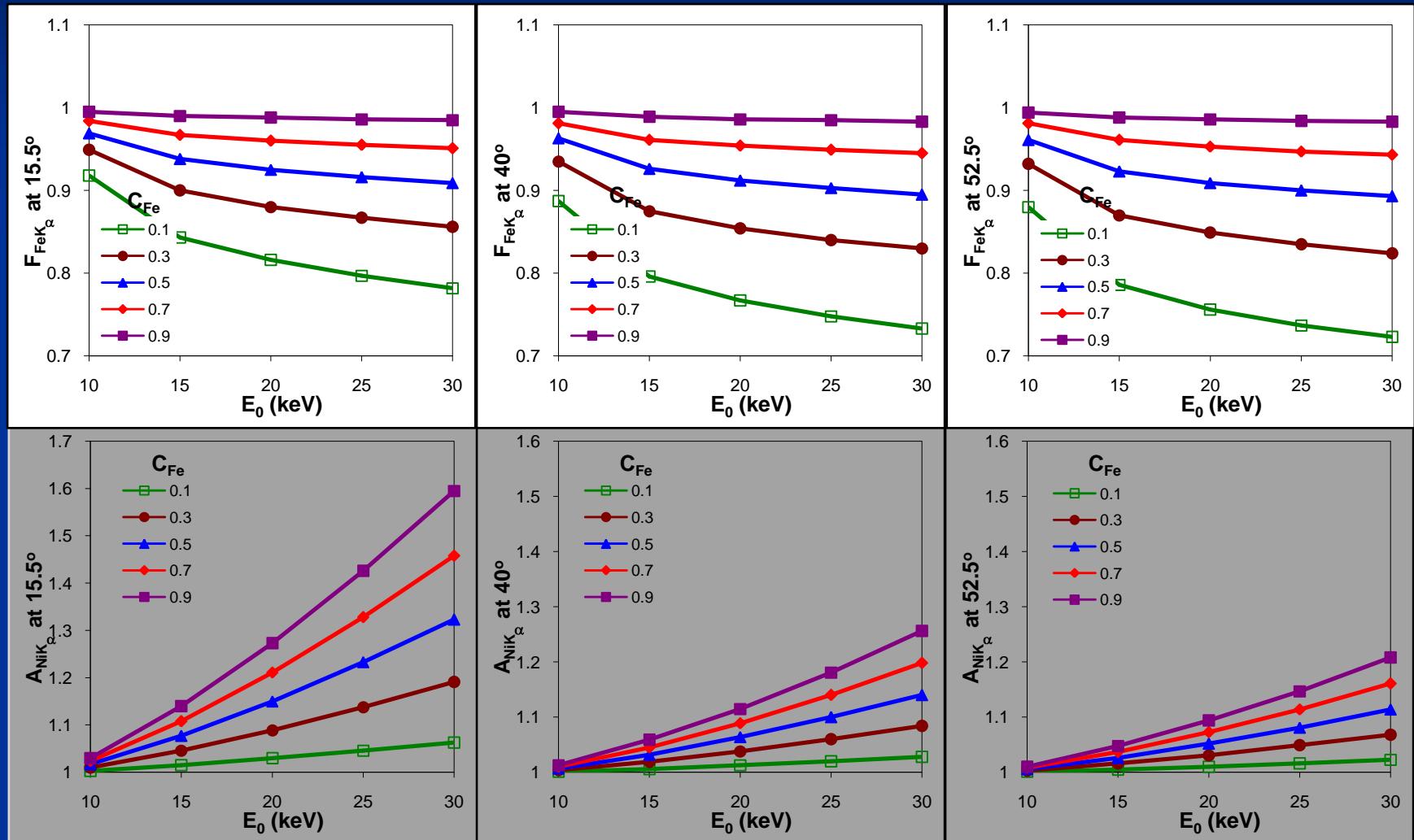
(): standard

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

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