The Analysis of Rare Earth Elements in various sample types using SEM-XRF (XTrace)

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Presenters

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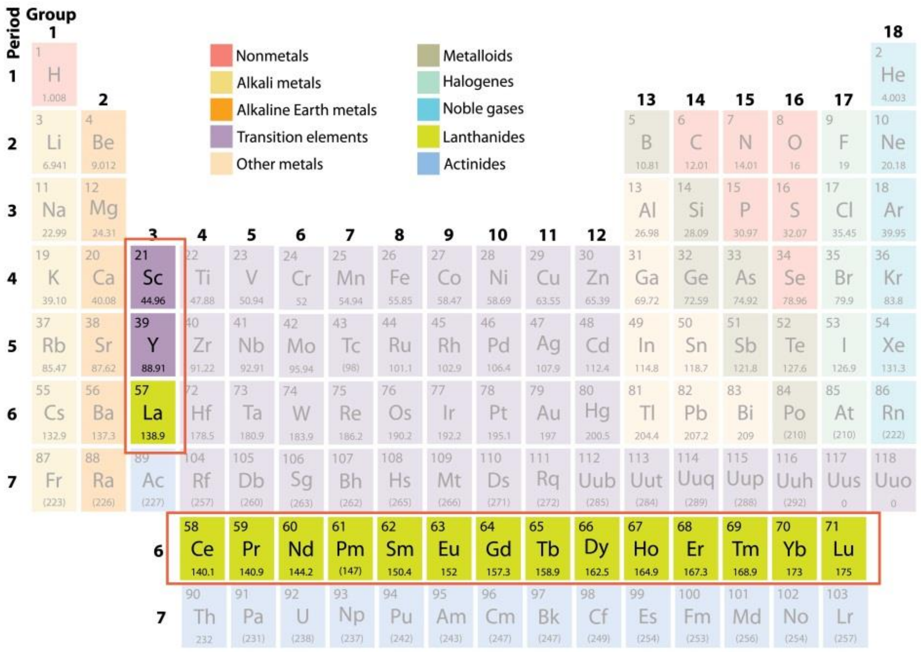
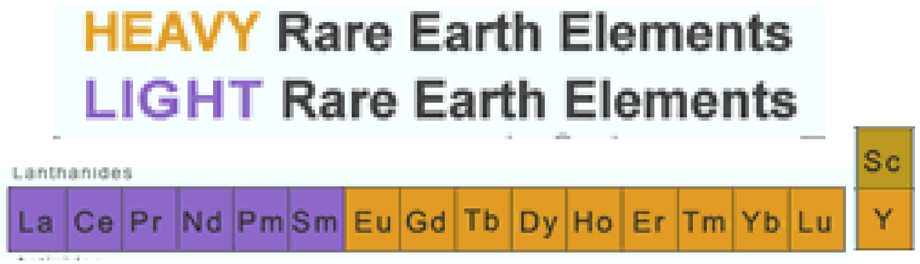
SEM-XRF Analysis of Rare Earth Elements (REE´s): Introduction

- Rare Earth Elements (REE´s) are extremely useful and used in many modern components. Consequently, they are classified as critical elements in many western countries, especially given the current dominant production levels from China.
- The identification and quantification of REE´s in various samples is thus crucial, whether it be for geological exploration and mining, or component quality control, or recycling for the future.
- Micro-XRF is ideal to analyse large sample areas on the micro-scale and is a powerful analytical tool for identifying both trace elements or minerals with minimal preparation.
- This is especially so for samples that are also electron beam sensitive, such as specialized glasses. The addition of a micro-XRF source to your SEM will augment your laboratories capabilities and the benefits and capabilities of SEM-XRF will be discussed in the context of REE analysis within various fields of study.

Rare Earth Elements (REE´s): Introduction

- Group of 17 chemically similar metallic elements, including the 15 lanthanides as well as scandium and yttrium.
- Chemically similar:
  - easily substitute for each other and often occur together within various minerals
- Earth’s crust abundance of < 10 ppm (Rudnick et al., 2003)
- Do NOT occur naturally as metallic elements, but
- Do occur in a wide range of mineral types, for example halides, carbonates, oxides, phosphates and silicates.





15 lanthanides
Lanthanum [La]
Cerium [Ce]
Praseodymium [Pr]
Neodymium [Nd]
Promethium [Pm]
Samarium [Sm]
Europium [Eu]
Gadolinium [Gd]
Terbium [Tb]
Dysprosium [Dy]
Holmium [Ho]
Erbium [Er]
Thulium [Tm]
Ytterbium [Yb]
Lutetium [Lu]
And
Scandium [Sc] and
Yttrium [Y]

Source: https://geology.com/articles/rare-earth-elements/

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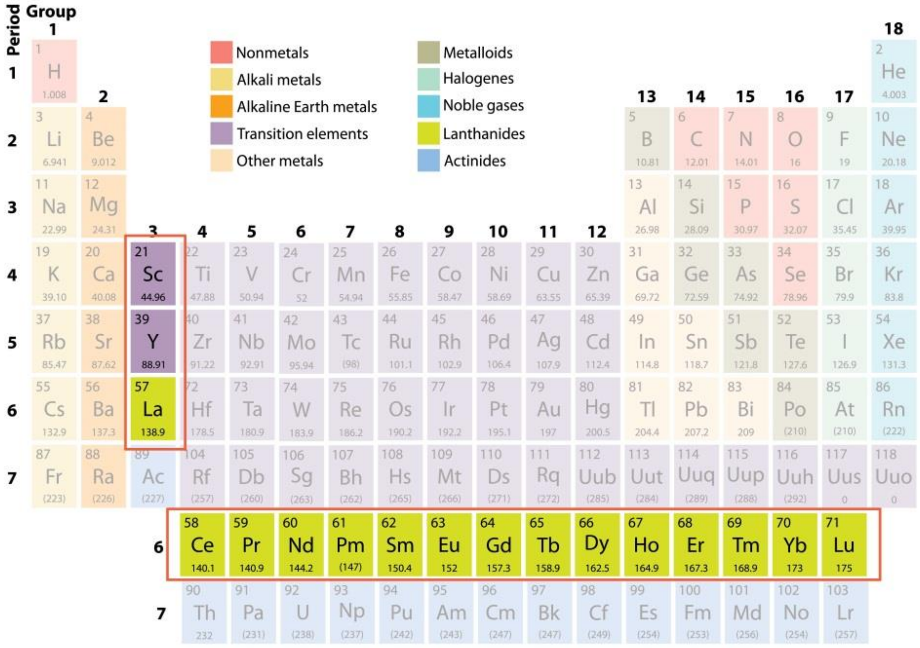
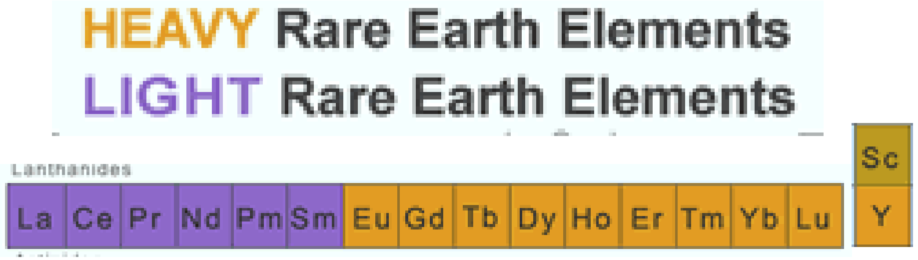


Composition of the Earth-comparison of different authors' data and levels of detail

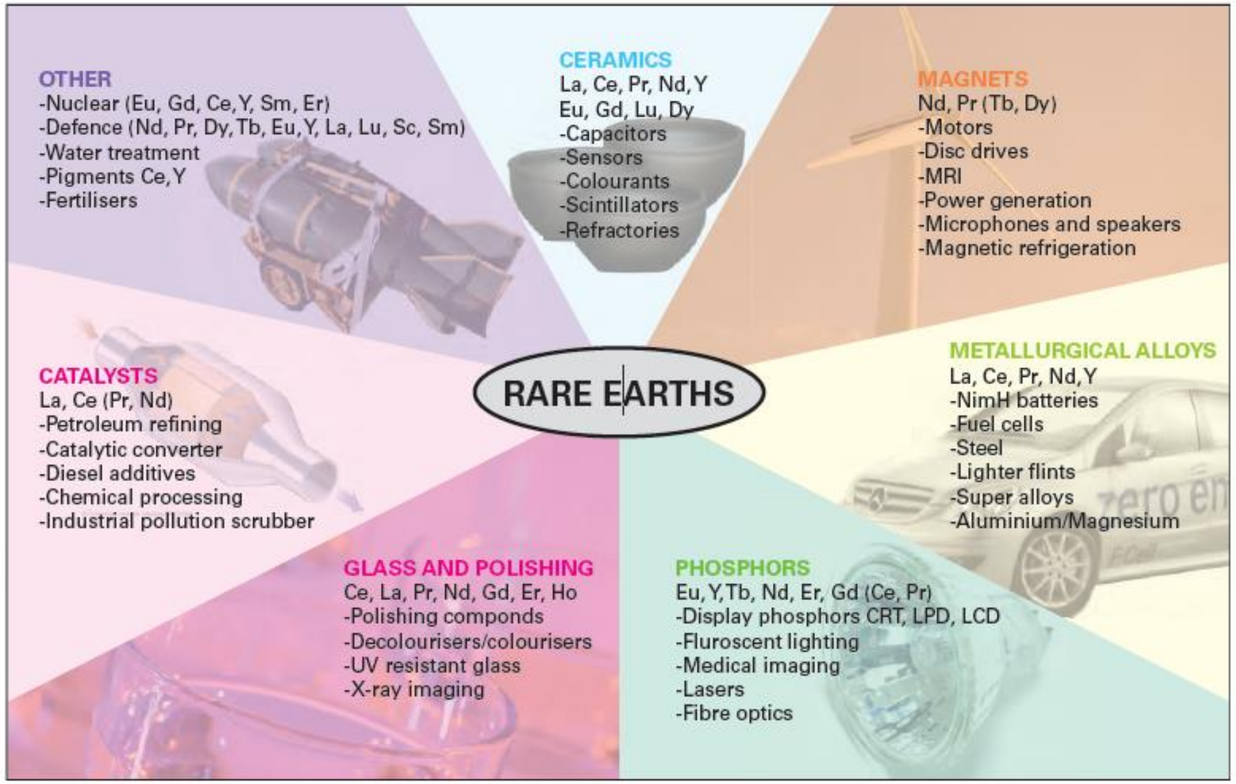
Element	Upper crust	Middle crust	Lower crust	Total crust	Composition of the Earth's crust	Bulk composition of the Earth
	Rudnick and Gao [9, p. 53f] ($\mu g\ g^{-1}$) ($\approx$ppm)				Binder [10, p.776f]	Allegre et al. ([6], p. 61)
Sc	14	19	31	21.9	20 ppm	10.1 ± 2 ppm
Y	21	20	16	19	31.5 ppm	2.4 ± 0.2 ppm
Cu	28	26	26	27	68 ppm	64.7 ± 5 ppm
La	31	24	8	20	35 ppm	415 ± 10 ppb
Ce	63	53	20	43	68 ppm	1088 ± 20 ppb
Pr	7.1	5.8	2.4	4.9	9.5 ppm	165 ± 5 ppb
Nd	27	25	11	20	40 ppm	814 ± 10 ppb
Sm	4.7	4.6	2.8	3.9	7.5 ppm	259 ± 3 ppb
Dy	3.9	3.8	3.1	3.6	6.2 ppm	424 ± 10 ppb
Tb	0.7	0.7	0.48	0.6	1.2 ppm	66.6 ± 5 ppb
Lu	0.31	0.4	0.25	0.3	0.81 ppm	42.5 ± 2 ppb
Pt	0.5	0.85	2.7	1.5	0.004 ppm	1562 ± 40 ppb
Au	1.5	0.66	1.6	1.3	0.0041 ppm	102 ± 20 ppb

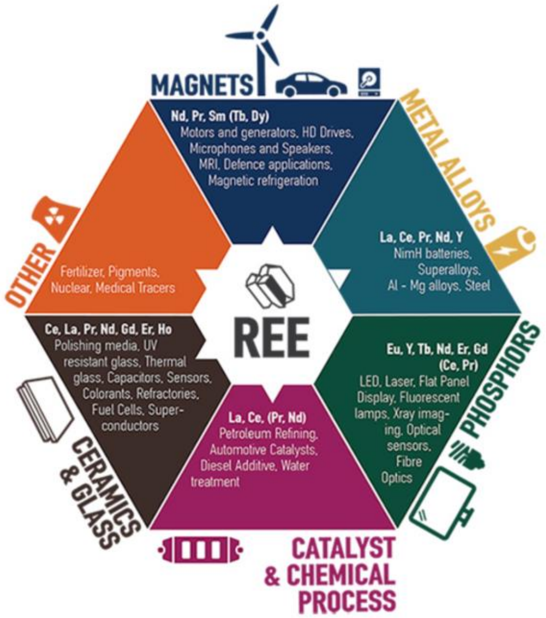
REE marked bold italic



Source: https://geology.com/articles/rare-earth-elements/

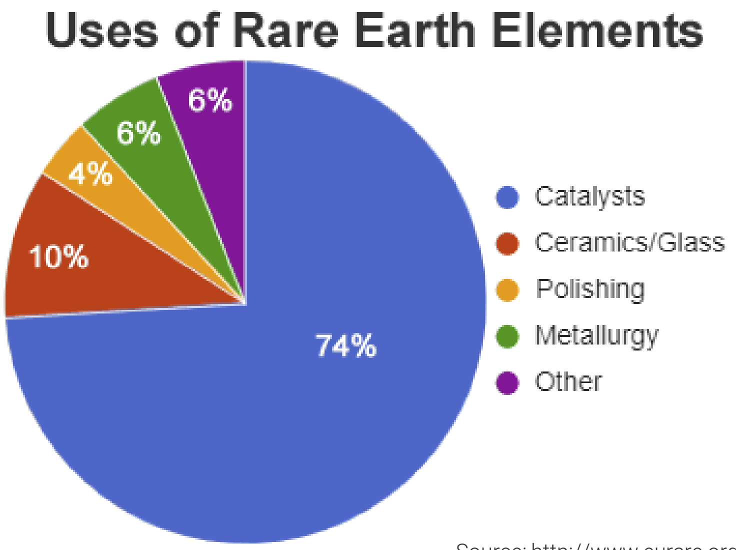
Rare Earth Elements (REE´s):
Essential to modern-day technologies





metallic state

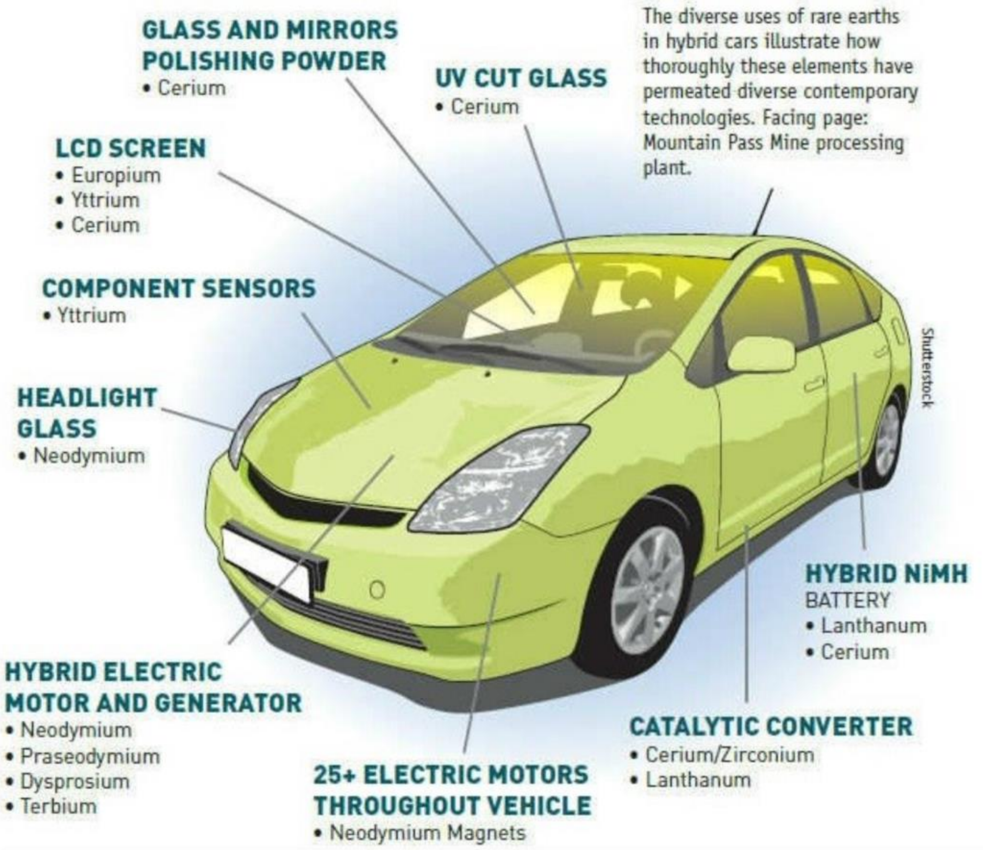
oxidized state



Source: http://www.eurare.org/RareEarthElements.html

Source: https://geology.com/articles/rare-earth-elements/

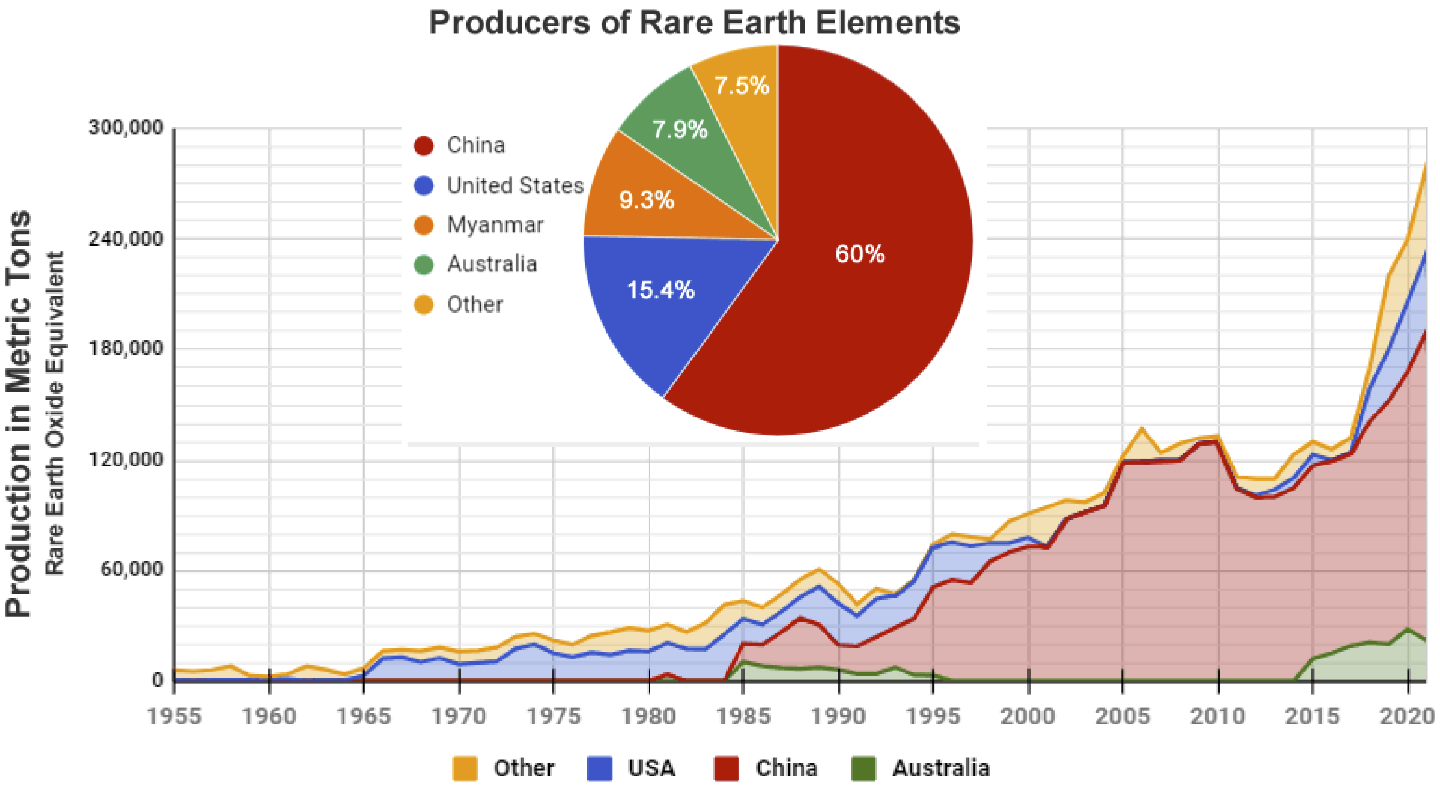
Rare Earth Elements (REE):
Essential to modern-day technologies

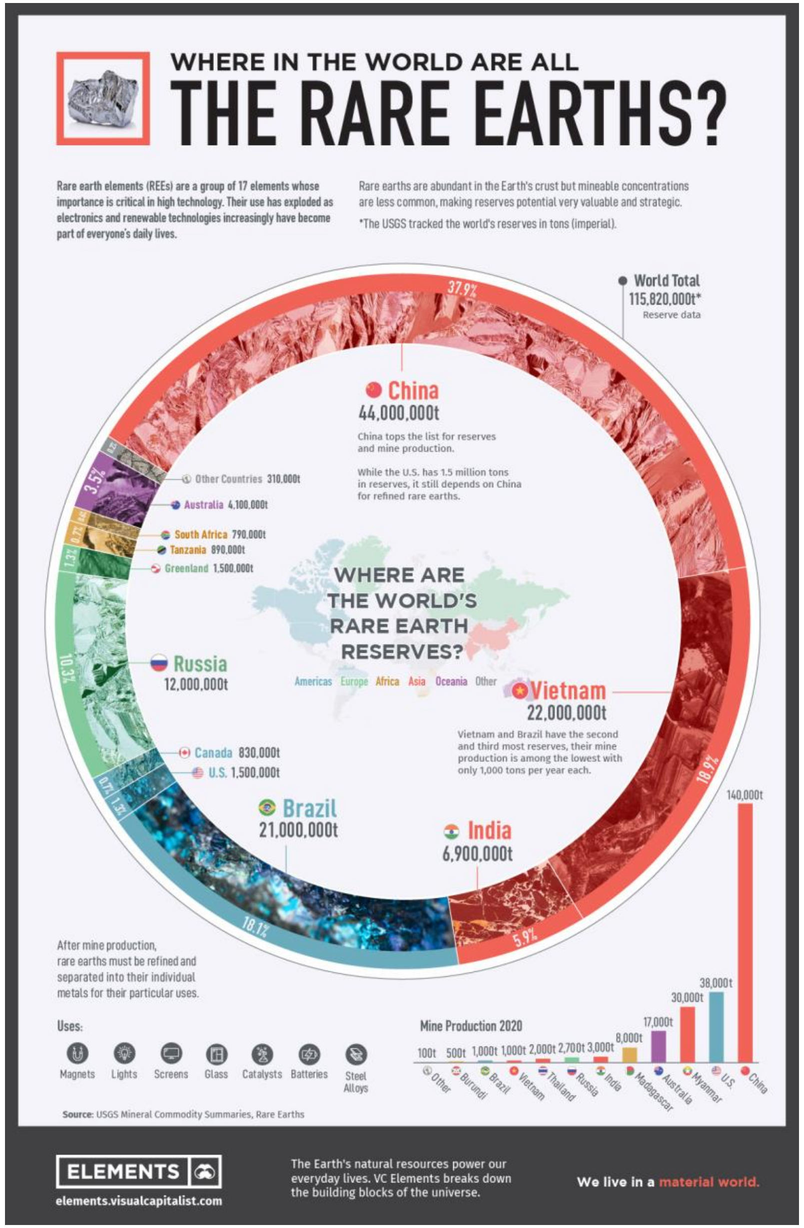


Source: https://etn-demeter.eu/what-are-rare-earth-elements-rees/

Rare Earth Elements (REE´s): World Production and Resources

The exploration for rare earth element deposits is currently experiencing a boom period due to their importance as a component within modern materials and technology devices.





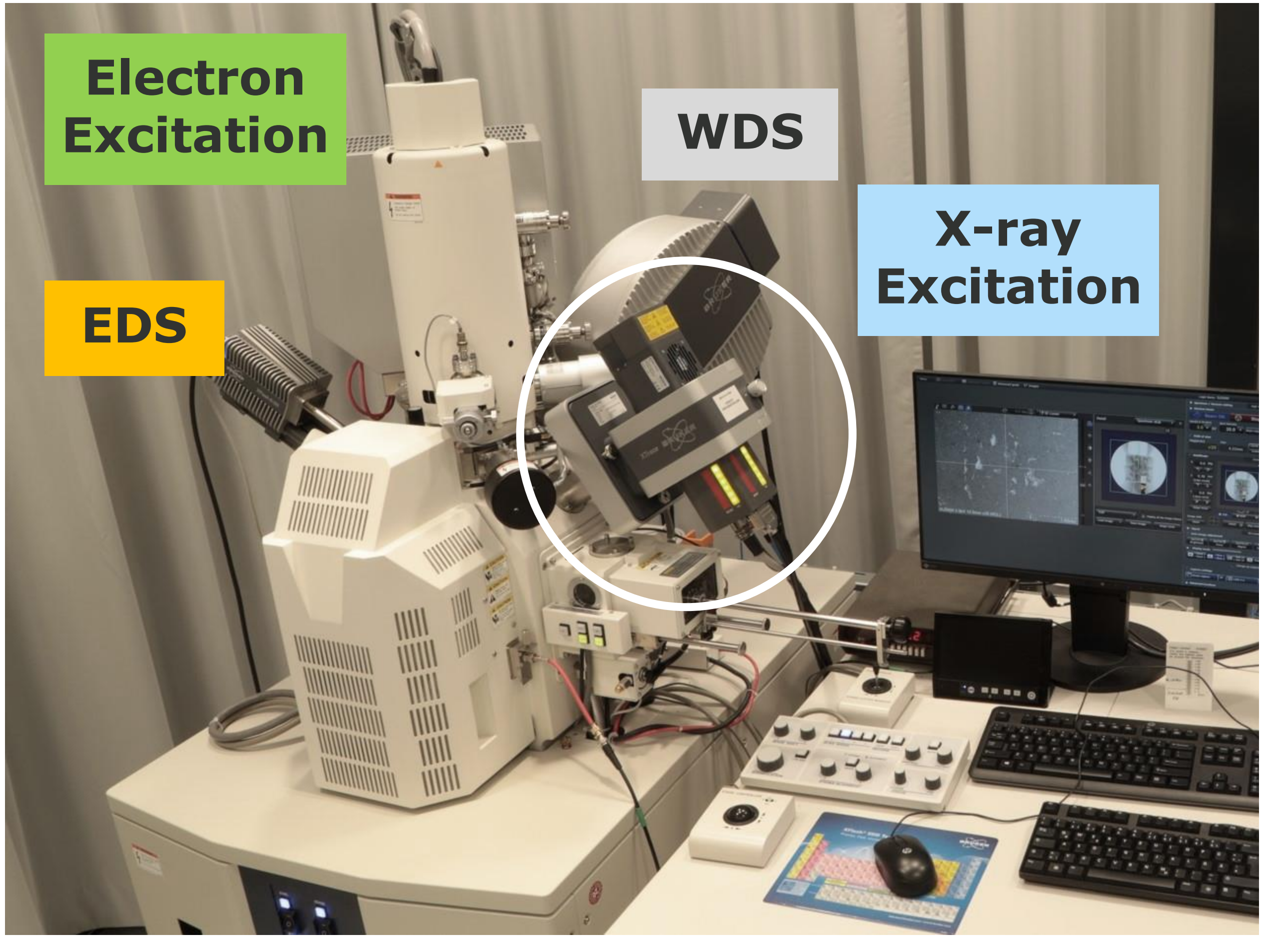
Source: http://www.elements.vialcapitalist.com

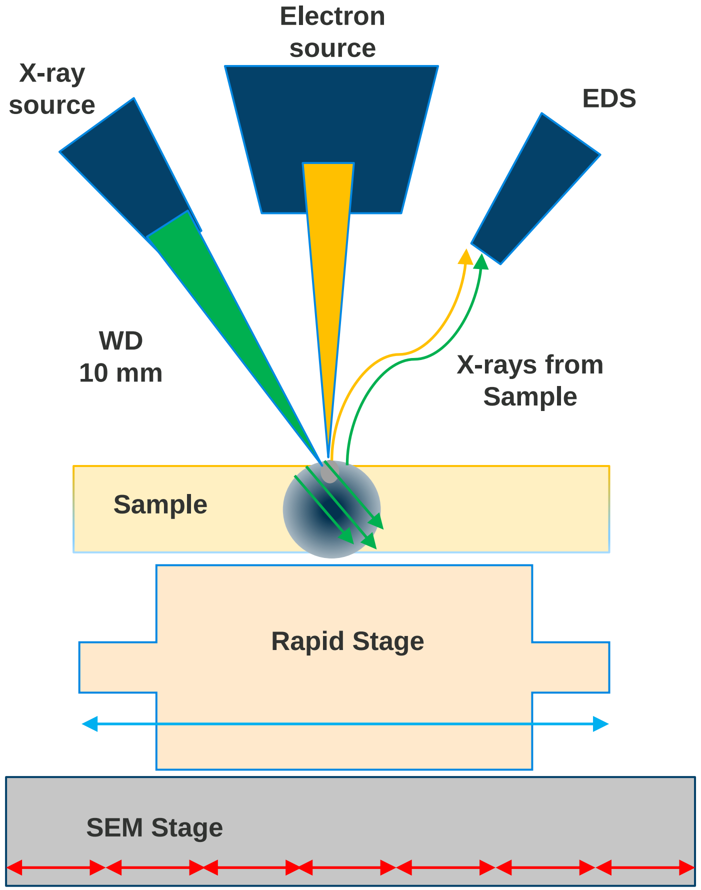
Source: https://geology.com/articles/rare-earth-elements/

The Analysis of Rare Earth Elements in various sample types using SEM-XRF (XTrace)

Introduction: SEM-XRF (XTrace)

SEM and analytical options:
Electron and Photon Excitation for micro-XRF and EDS/WDS





2 Excitation Sources:

Electron Beam (e-beam)

Micro-XRF (X-ray beam)

1 Detector:

Energy Dispersive

Spectrometer (EDS)

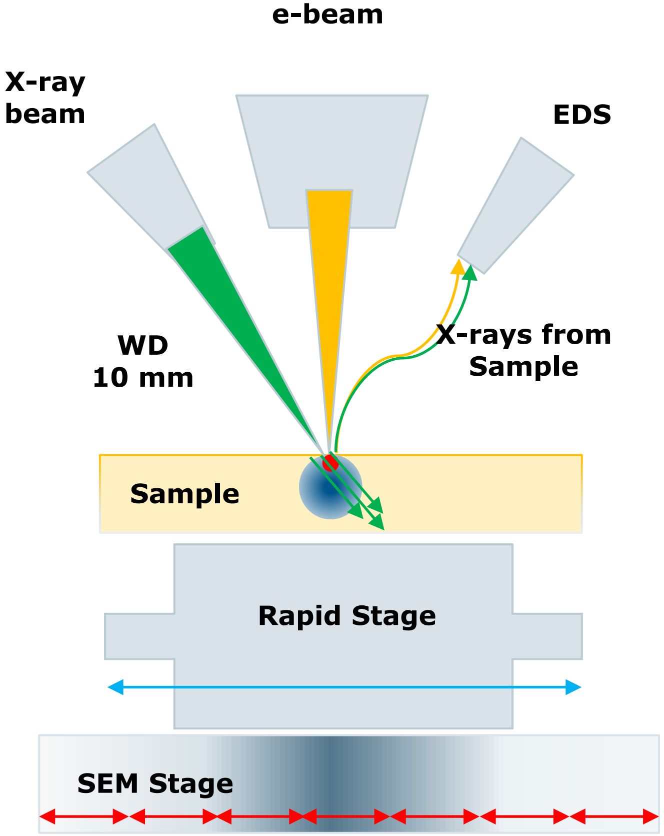
2 Stages:

SEM Stage

Rapid Stage

Analytical Parameters and Conditions
SEM-EDS vs SEM-XRF

Parameter	E-beam (SEM-EDS)	Micro-XRF (SEM-XRF-EDS)
Spatial Resolution & Analyzed Volume	Ø: few µm Information depth: µm; (depending primarily on electron energy)	Ø: 15-30 µm Information depth: µm to mm; (depending on analysed element and matrix)
Detectable Elements	Atomic number Z ≥ 4 (beryllium)	Atomic number Z ≥ 6 (carbon)
Energy range	K- L –M – Lines (up to 20 keV)	K- L –M – Lines (up to 40 keV)
Concentration Range	Down to 1000 ppm	Down to 5 ppm
Quantification	Standard less and Standard based	Standard less and standard based
Data collection	Simultaneously	Simultaneously
Sample Preparation	Sample needs to be electrically conductive (commonly carbon-coated), polishing required	Electrical Conductivity not required, samples doesn´t need to be polished
Sample stress	Heated due to absorbed electrons	minimal
Spectroscopic resolution	Down to 121 eV for Mn Ka	Down to 121 eV for Mn Ka
Distribution Measurements	By rastering e-beam	By continuously (Rapid) Stage movement since the X-ray optic is fixed in space



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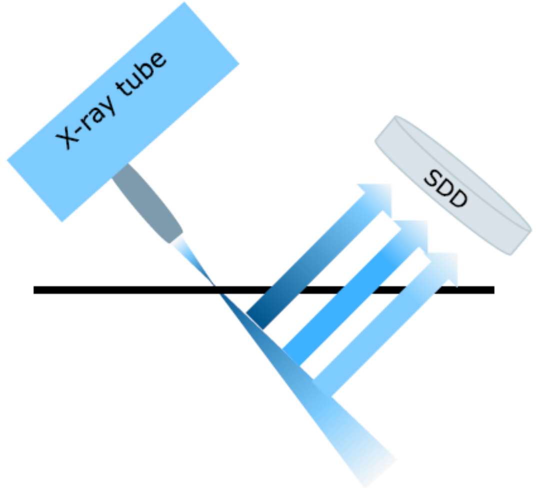
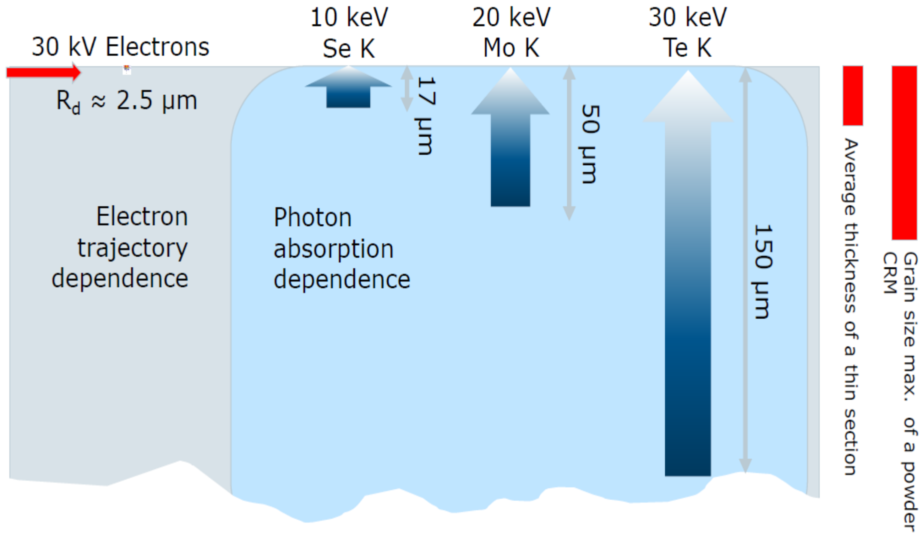
Spatial Resolution and Analyzed Volume:
Transmission and Attenuation



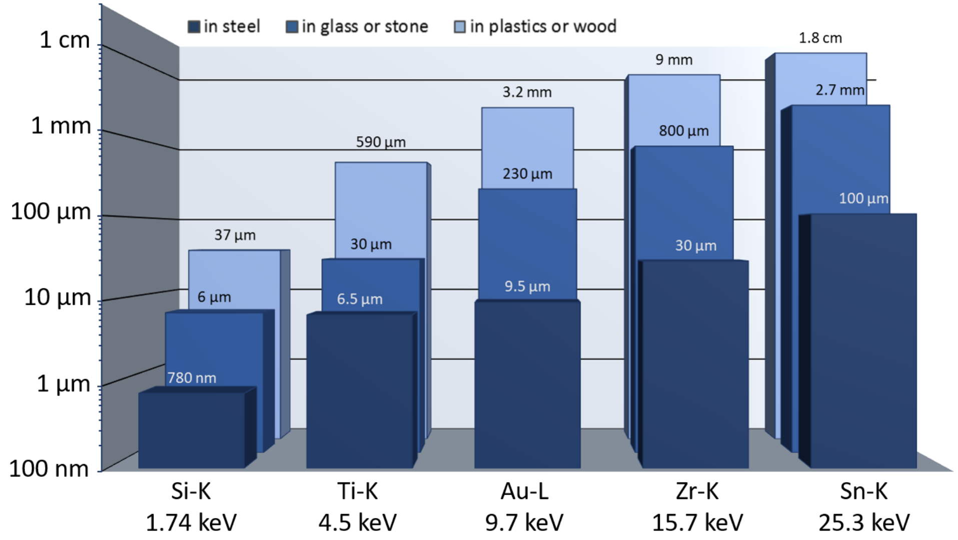
The transmission of X-rays is important for excitation of samples as well as for the fluorescence radiation.

Penetration depth: the depth that can still be excited

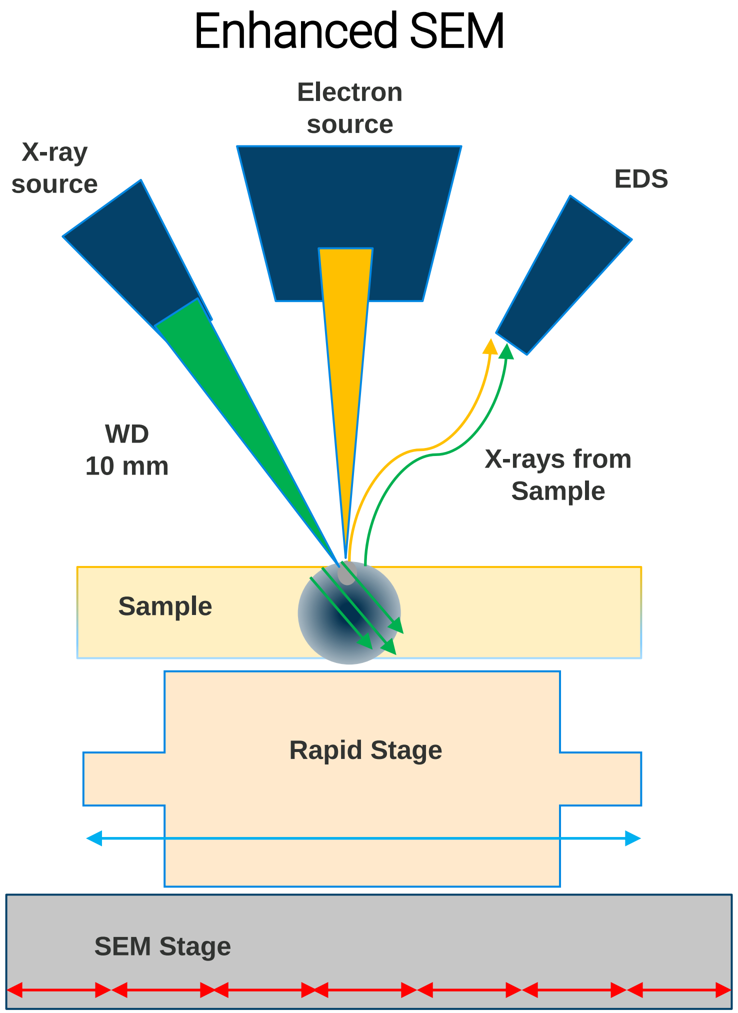
Information depth: the depth from which fluoresced X-rays can still reach the detector



Information depths of selected element fluorescence lines in different matrices

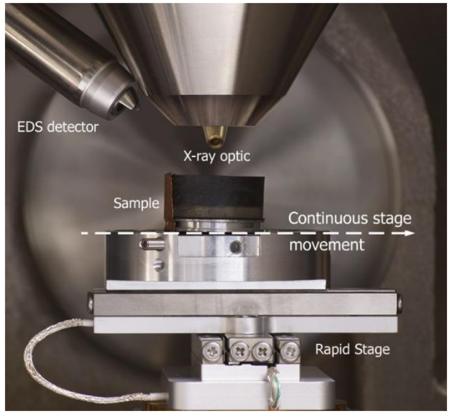


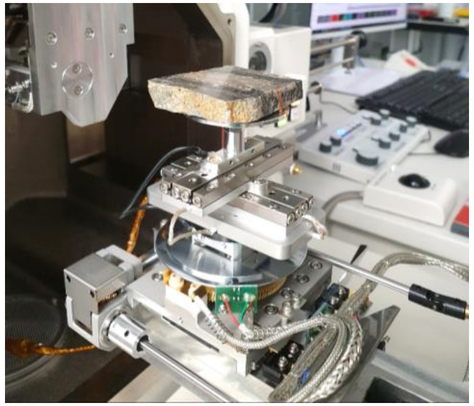
Introduction to Micro-XRF and Rapid Stage
Differences to Electron Beam Excitation



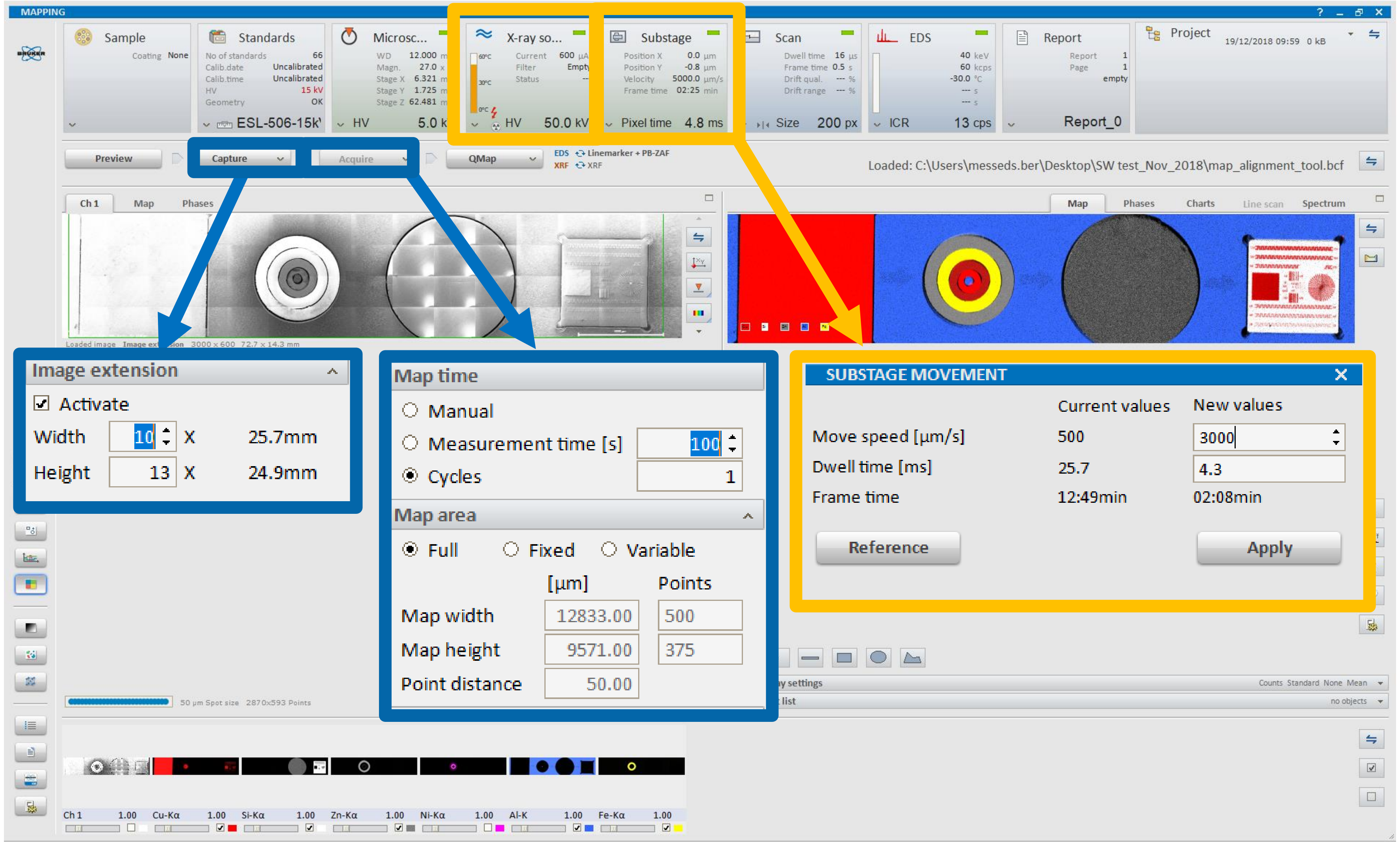
Micro-XRF Benefits:

- Non-destructive analytical technique
- No charging effects
- Minimal Sample Preparation Required
- Lower detection limits (down to 5 ppm)
- High Energy Lines Detection (Full Spectrum Range up to 40 keV)
- Ideal for Low kV or Beam sensitive samples
- Fast Large Area Mapping
- Micrometer scale measurement over cm

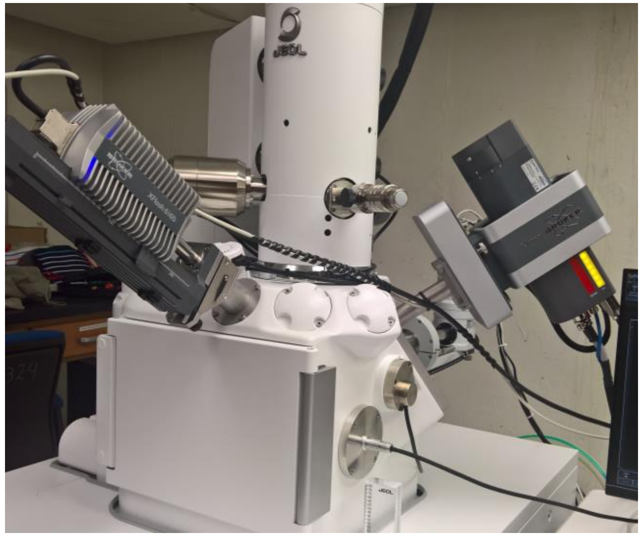




SEM-XRF and Rapid Stage
Integration in ESPRIT Software



Micro-XRF Installations:
Adaptable to Various SEM models



The Analysis of Rare Earth Elements in various sample types using SEM-XRF (XTrace)

Example: Geology and Mineralogy

Rare Earth Elements: X-ray Energies

Rare Earth Elements have a range of X-ray energies that are detectable by EDS:

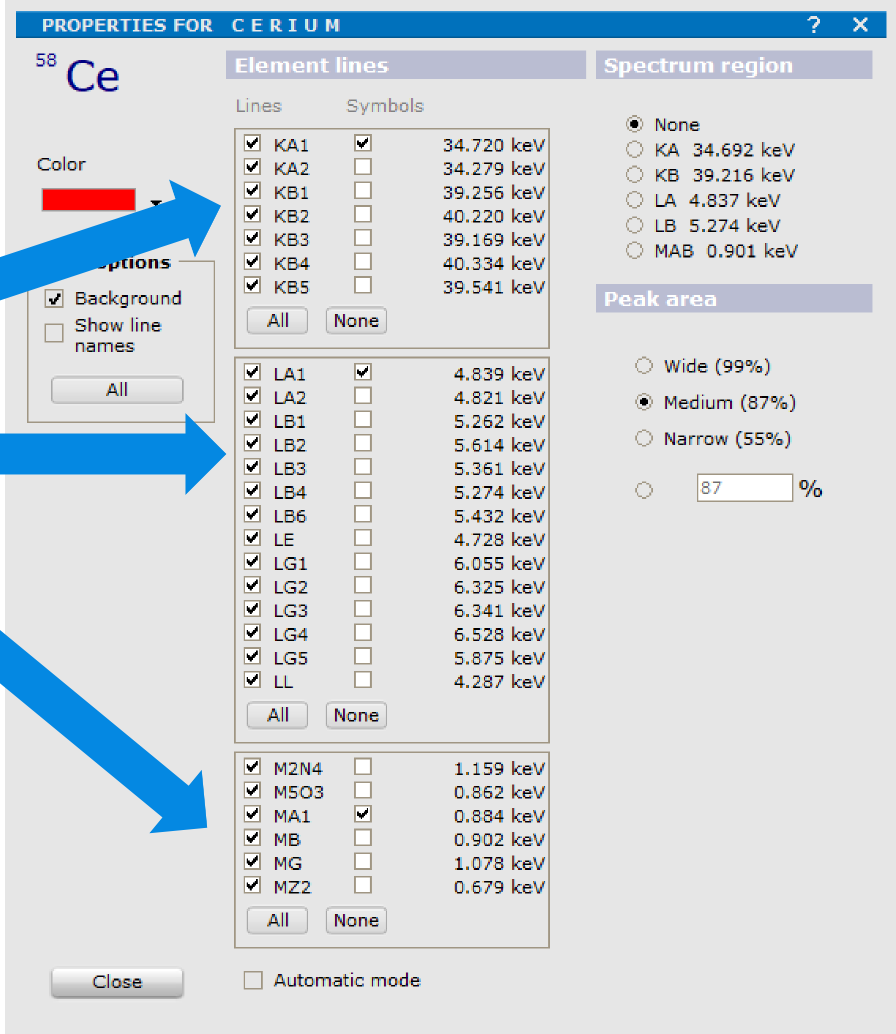
K-Series: 34 to 55 keV

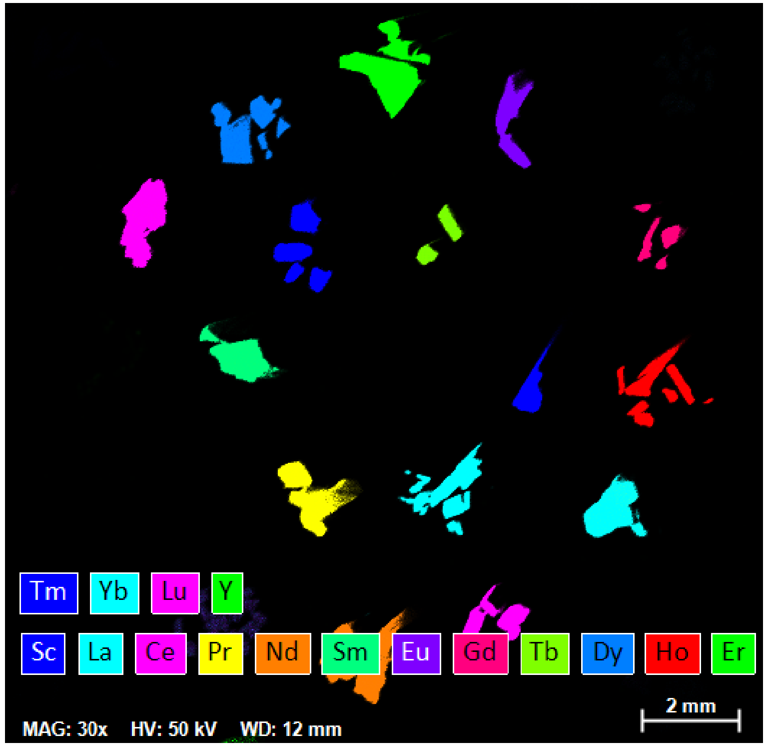
L-Series: 4 to 10 keV

M-Series: 0.5 to 1.5 keV

L-Series detectable with both electron and x-ray excitation source.

K-Series detectable with x-ray excitation source only.





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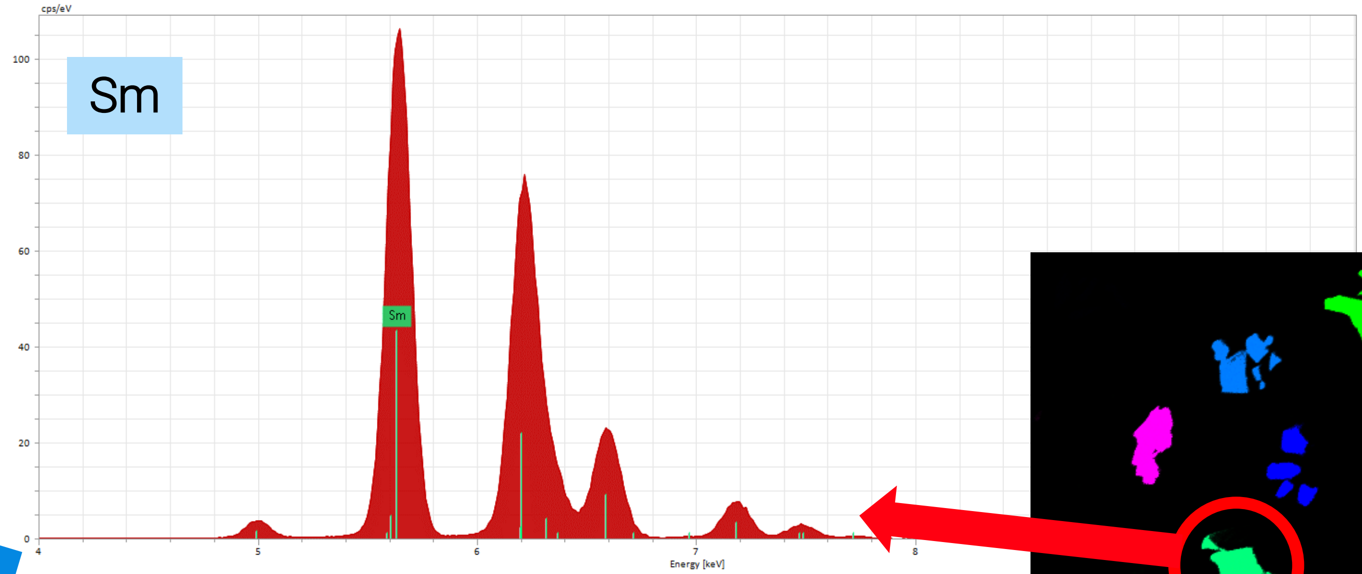

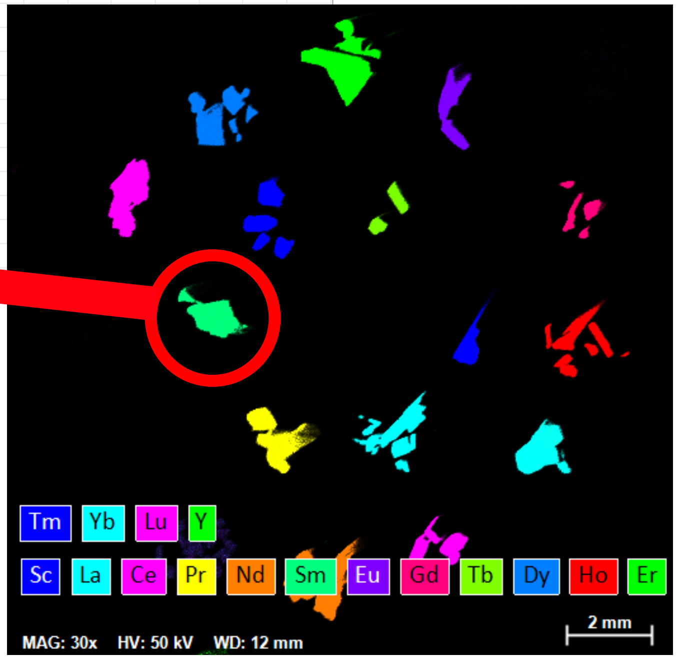

Jarosewich, E., and Boatner, L.A, 1991, Rare-Earth element reference samples for electron microprobe analysis, Geostandards Newsletter, Vol. 15, No. 2, p.397-399.

Rare Earth Elements: X-ray Energies

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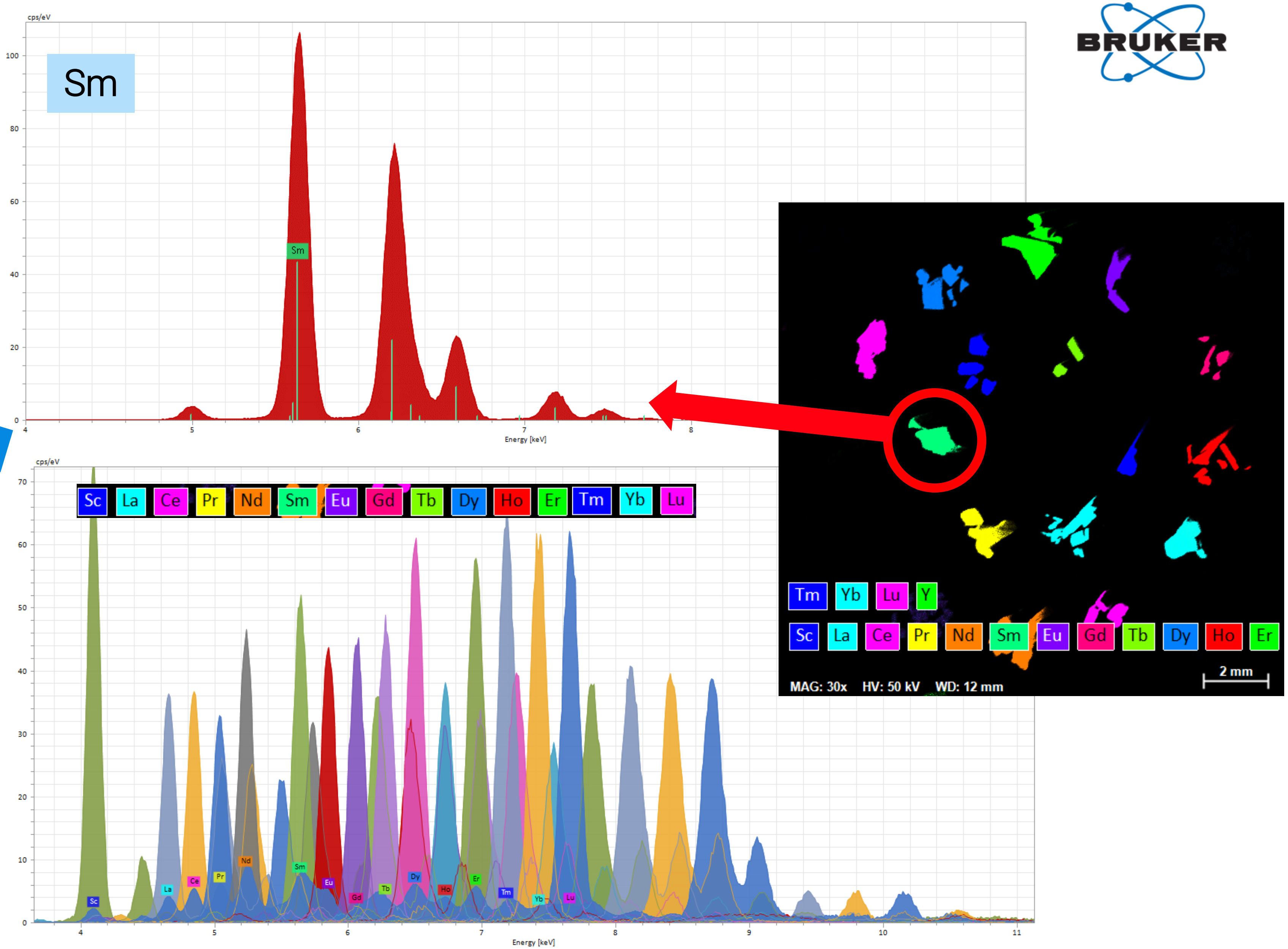
L-Series:	4 to 10 keV
M-Series:	0.5 to 1.5 keV

L-Series detectable with both electron and x-ray excitation source.

K-Series detectable with x-ray excitation source only.



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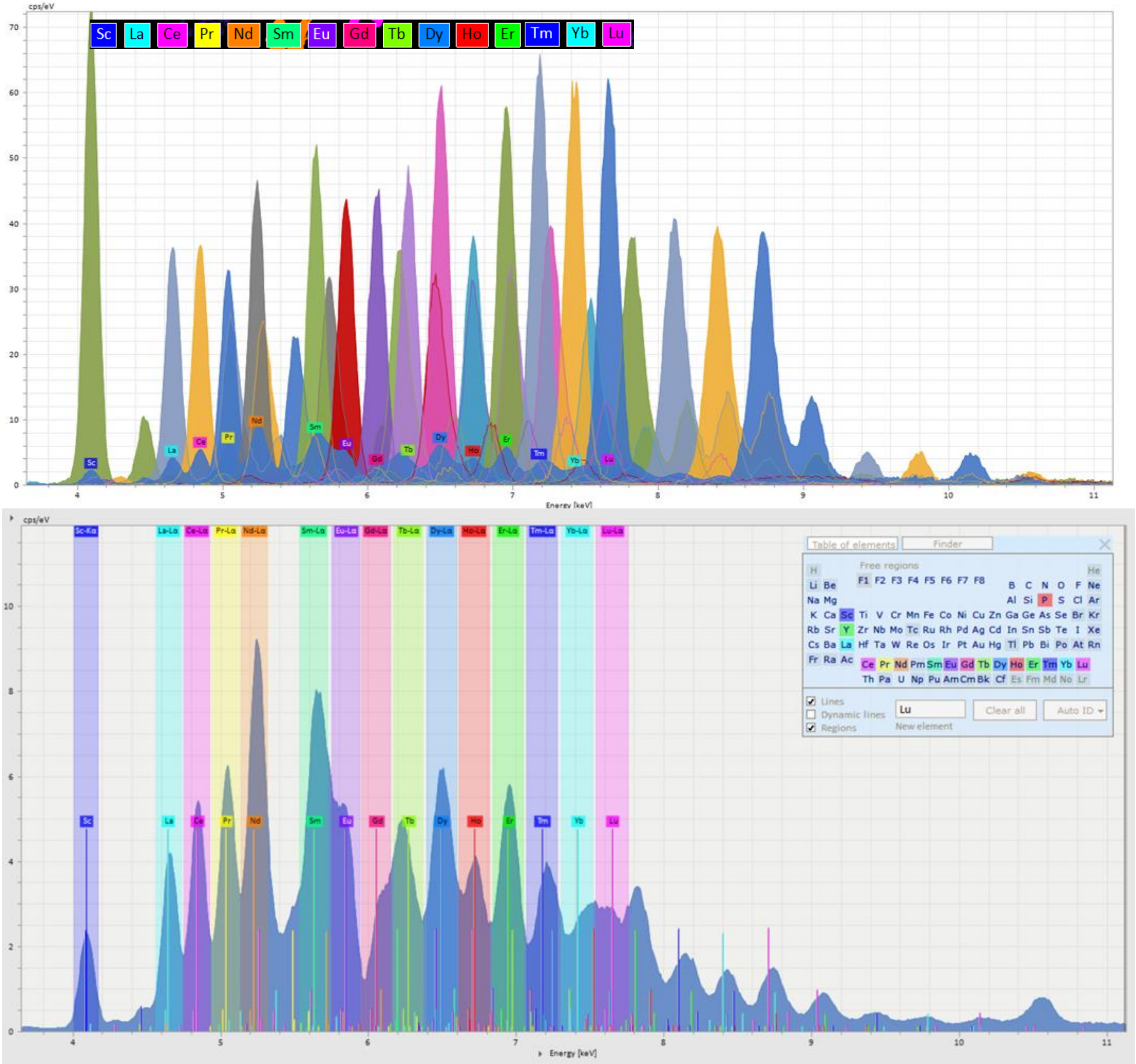

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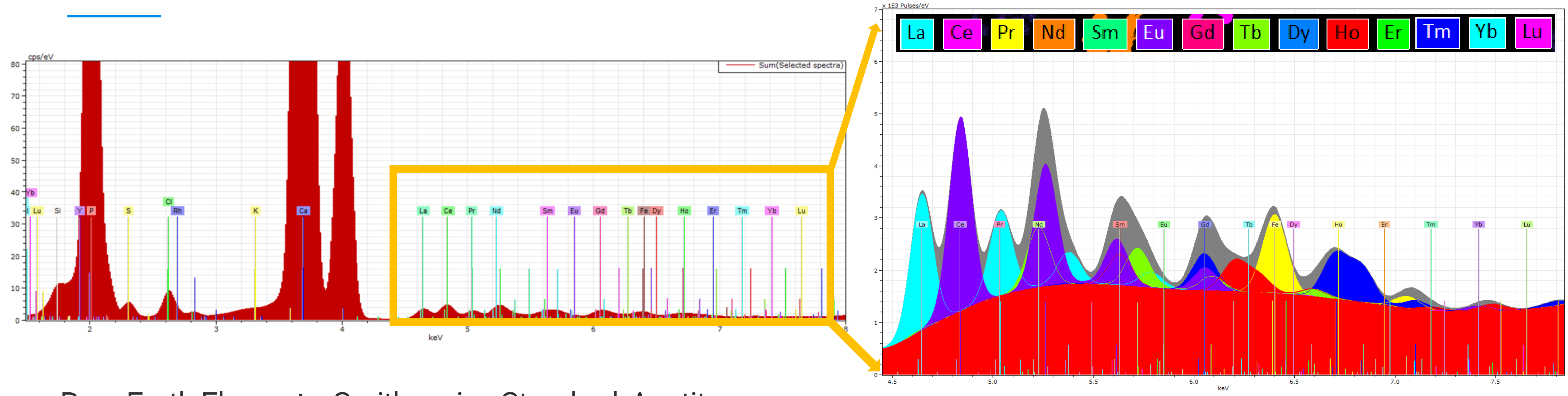
Rare Earth Elements:
Apatite – Low concentrations



Rare Earth Elements: Smithsonian Standard: Apatite
Total REEs approx. 1.43 wt%

La2O3	Ce2O3	Pr2O3	Nd2O3	Sm2O3	EuO	Gd2O3	Tb2O3	Dy2O3	Ho2O3	Er2O3	Tm2O3	Yb2O3	Lu2O3	Sum
0.509	0.655	0.000	0.165	0.073	0.000	0.081	0.000	0.001	0.000	0.001	0.000	0.008	0.000	1.493

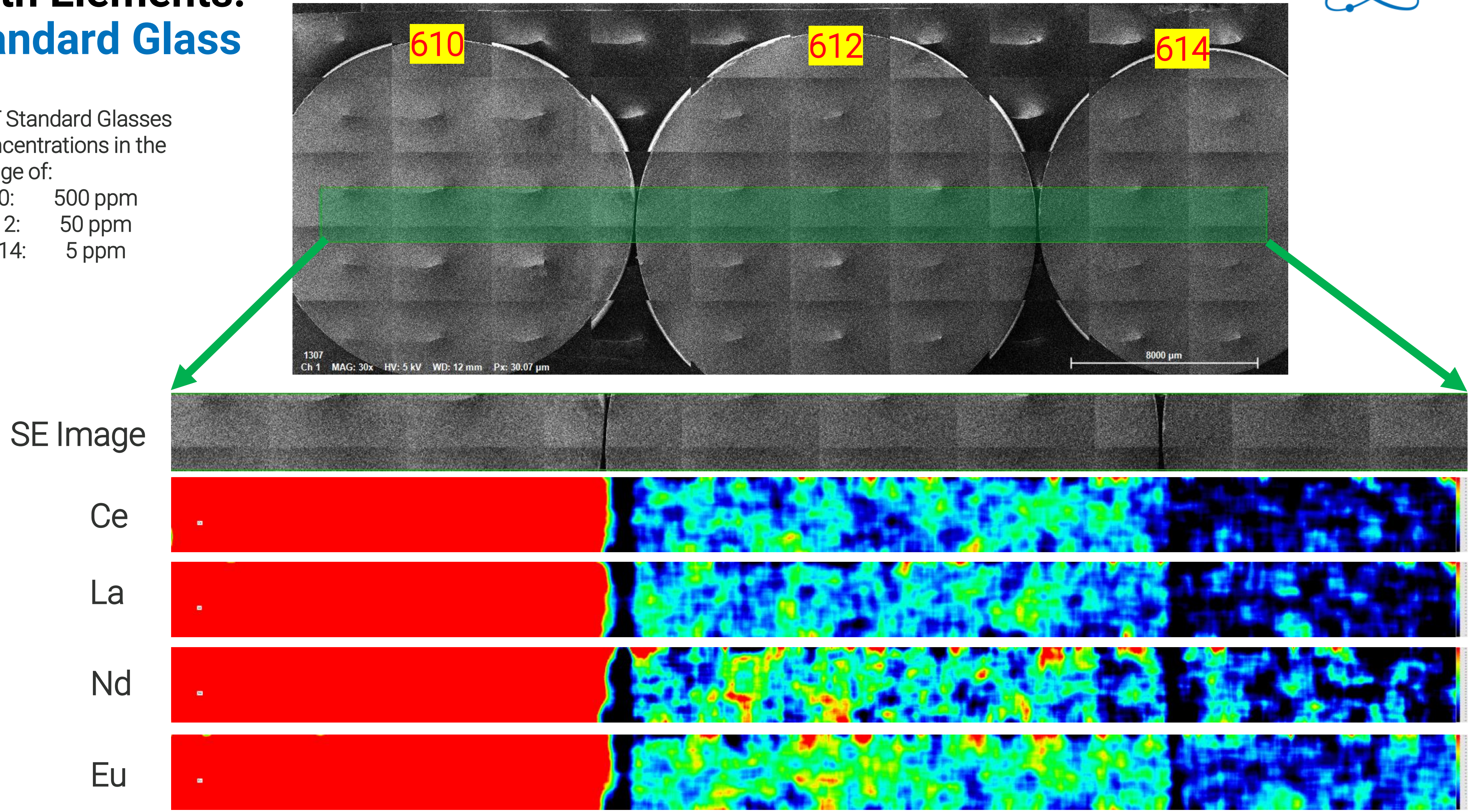
Jarosewich, E., Gooley, R., and Husler, J. 1987. Chromium Augite – A new microprobe reference sample, Geostandards Newsletter, Vol. 11., No. 2, p197-198.

Rare Earth Elements: NIST Standard Glass

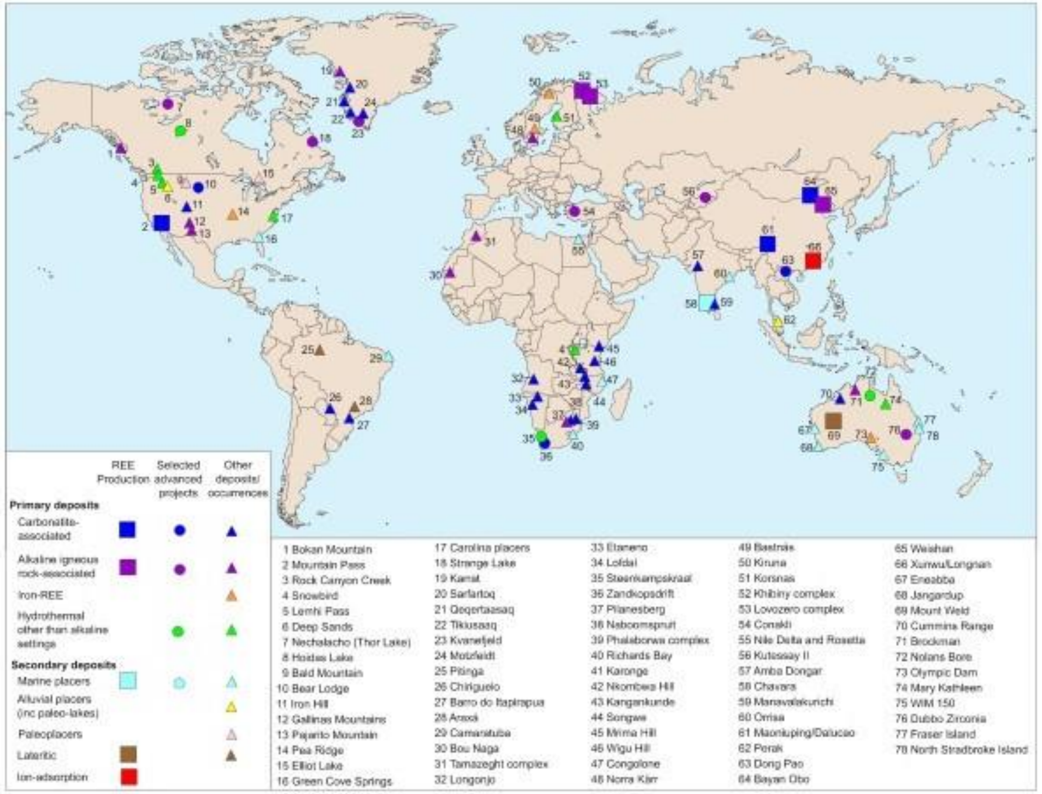
Analysis of NIST Standard Glasses with dopped concentrations in the approximate range of:

NIST 610:	500 ppm
NIST 612:	50 ppm
NIST 614:	5 ppm

NIST Glass Standards



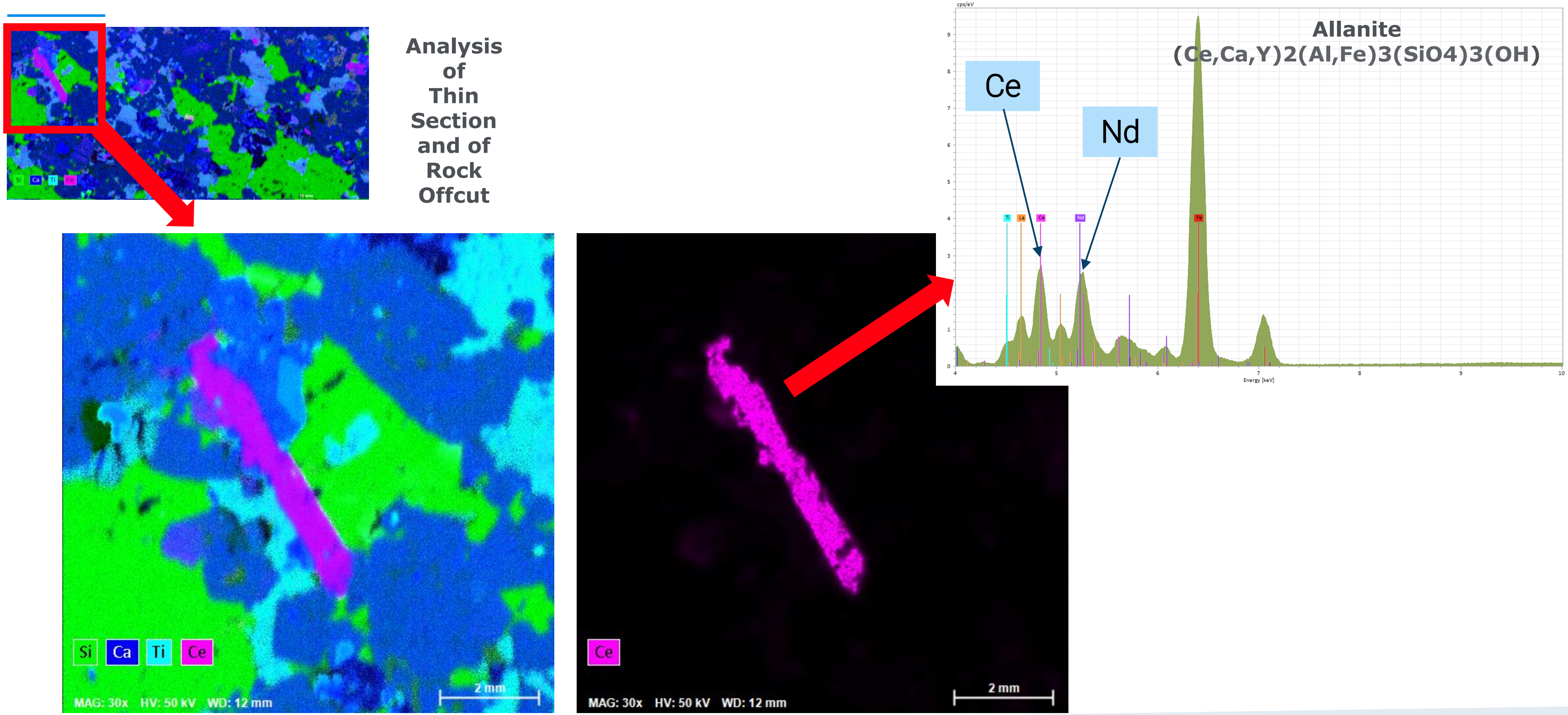
Rare Earth Elements:
Geology – major deposits



Mineral	Formula	Approximate REO %
Aeschynite-(Ce)	$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$.	32
Allanite-(Ce)	$(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3OH$.	38
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	19
Bastnäsite-(Ce)	$(Ce,La)(CO_3)F$	75
Brannerite	$(U,Ca,Y,Ce)(Ti,Fe)_2O_6$	9
Britholite-(Ce)	$(Ce,Ca)_5(SiO_4,PO_4)_3(OH,F)$	32
Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$(?).	9
Euxenite-(Y)	$(Y.Ca.Ce,U,Th)(Nb,Ta,Ti)_2O_6$	24
Fergusonite-(Ce)	$(Ce,La,Nd)NbO_4$	53
Gadolinite-(Ce)	$(Ce,La,Nd,Y)_2Fe^{2+}Be_2Si_2O_{10}$.	60
Kainosite-(Y)	$Ca_2(Y,Ce)_2Si_4O_{12}CO_3.H_2O$.	38
Loparite	$(Ce,La,Na,Ca,Sr)(Ti,Nb)O_3$	30
Monazite-(Ce)	$(Ce,La,Nd,Th)PO_4$	65
Parisite-(Ce)	$Ca(Ce,La)_2(CO_3)_3F_2$.	61
Xenotime	YPO_4.	61
Yttrocerite	$(Ca,Ce,Y,La)F_3.nH_2O$.	53
Huanghoite-(Ce)	$BaCe(CO_3)_2F$.	39
Cebaite-(Ce)	$Ba_3Ce_2(CO_3)_5F_2$.	32
Florencite-(Ce)	$CeAl_3(PO_4)_2(OH)_6$.	32
Synchysite-(Ce)	$Ca(Ce,LA)(CO_3)_2F$.	51
Samarskite-(Y)	$(Y,Ce,U,Fe^{3+})_3(Nb,Ta,Ti)_5O_{16}$.	24
Knopite	$(CaTi,Ce_2)O_3$	na

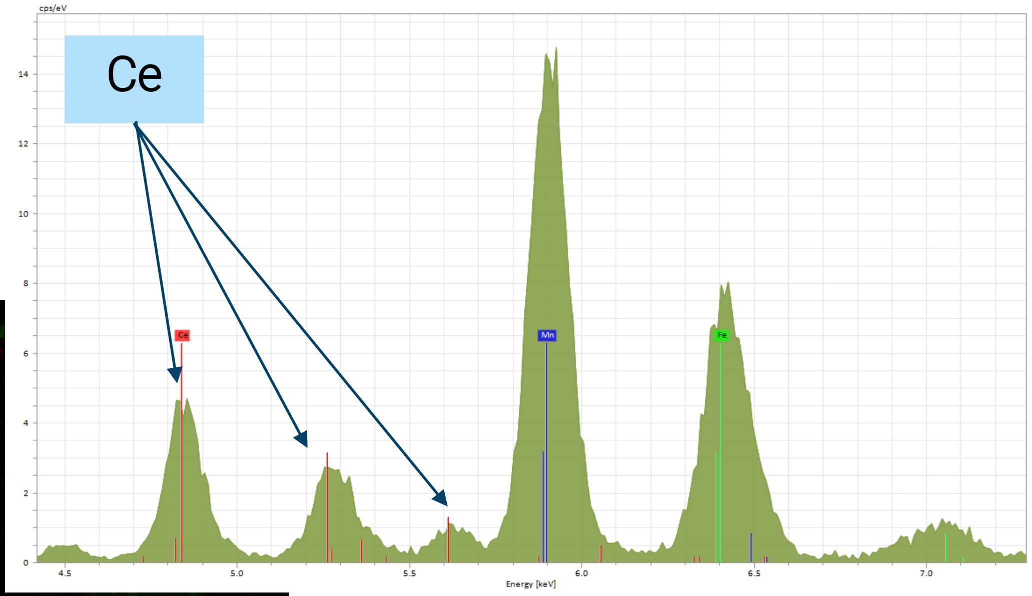
REE Minerals occur as:
silicates,
carbonates,
oxides,
phosphates…

SEM-XRF Analysis of Rare Earth Elements (REE´s): Applications – Granite with Allanite

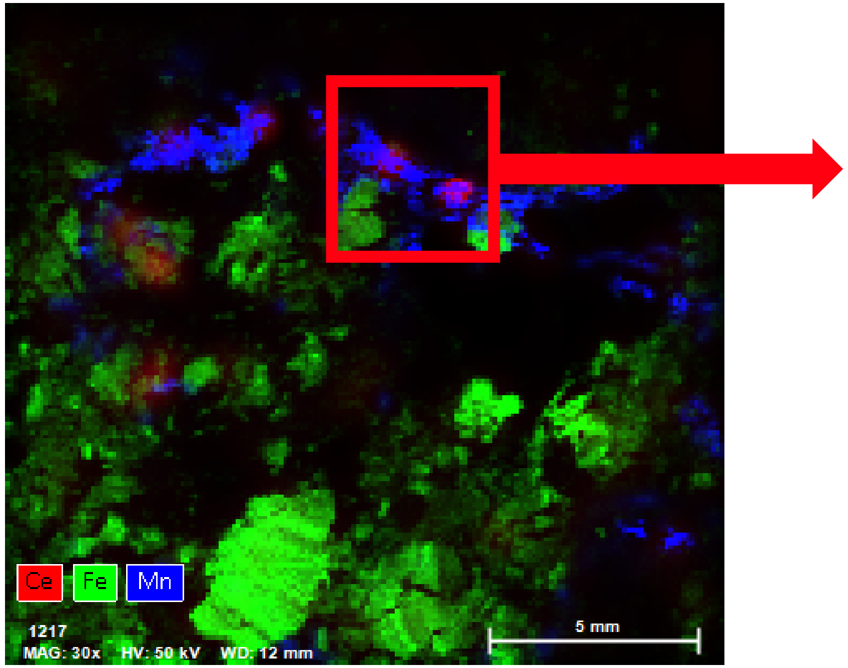


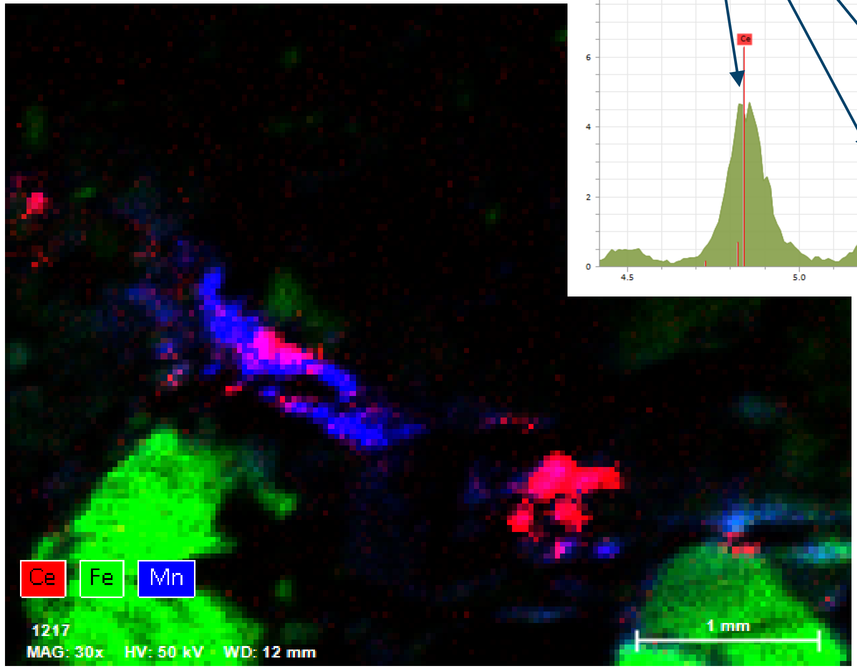
Analysis of Thin Section and of Rock Offcut

SEM-XRF Analysis of Rare Earth Elements (REE´s):
Saprolite with REE ´s

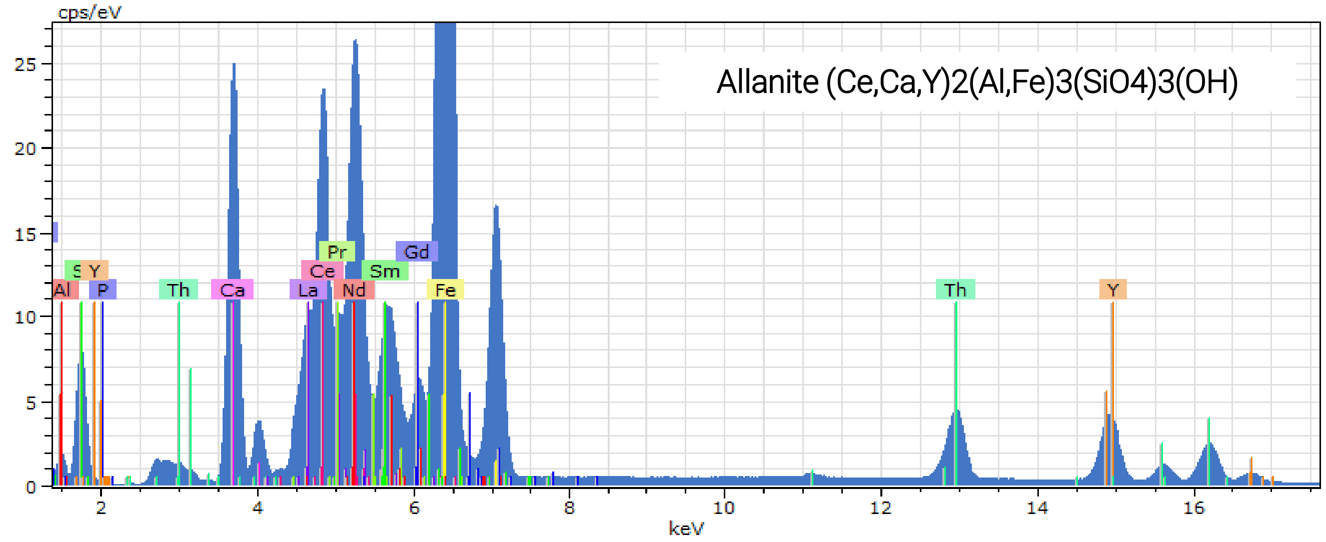


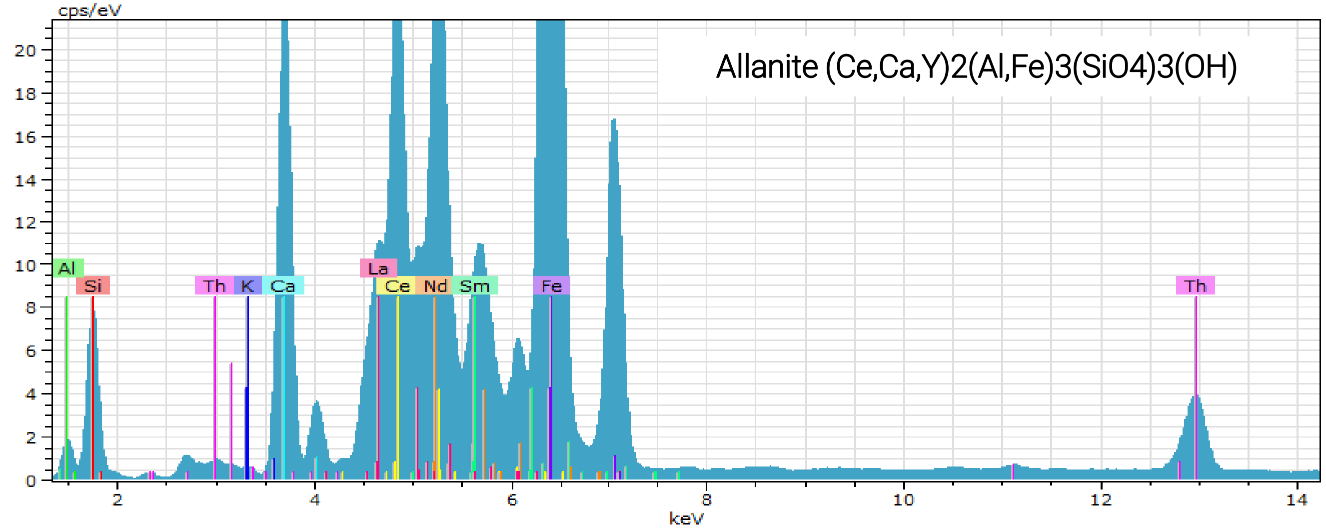
Analysis of Thin Section



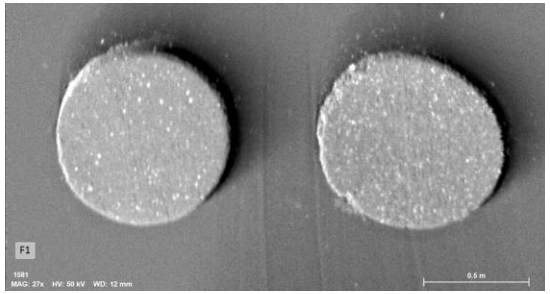


SEM-XRF Analysis of Rare Earth Elements (REE´s):
Individual Mineral Grains

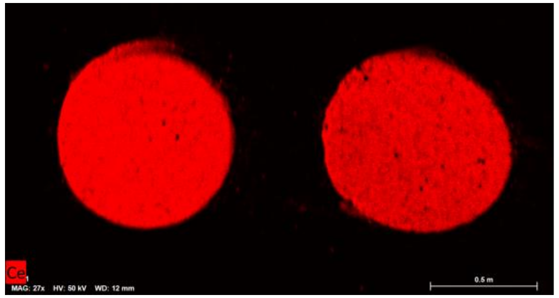


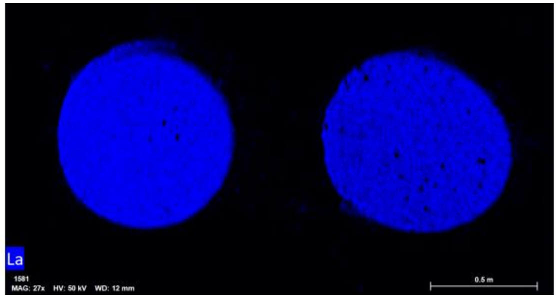


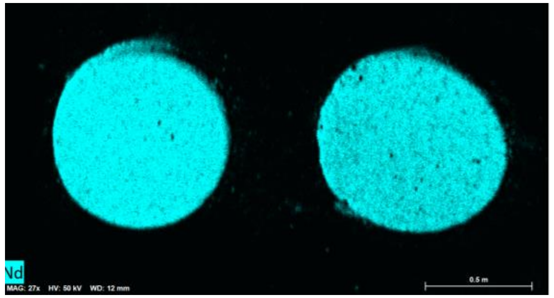
SEM-XRF Analysis of Rare Earth Elements (REE´s):
Crushed Monazite Powder

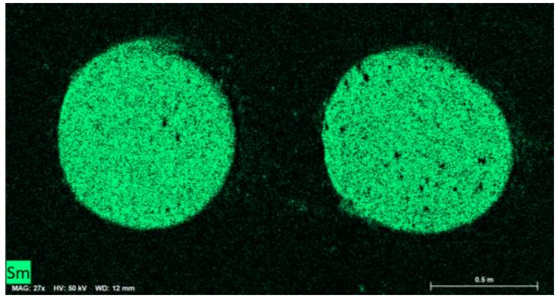


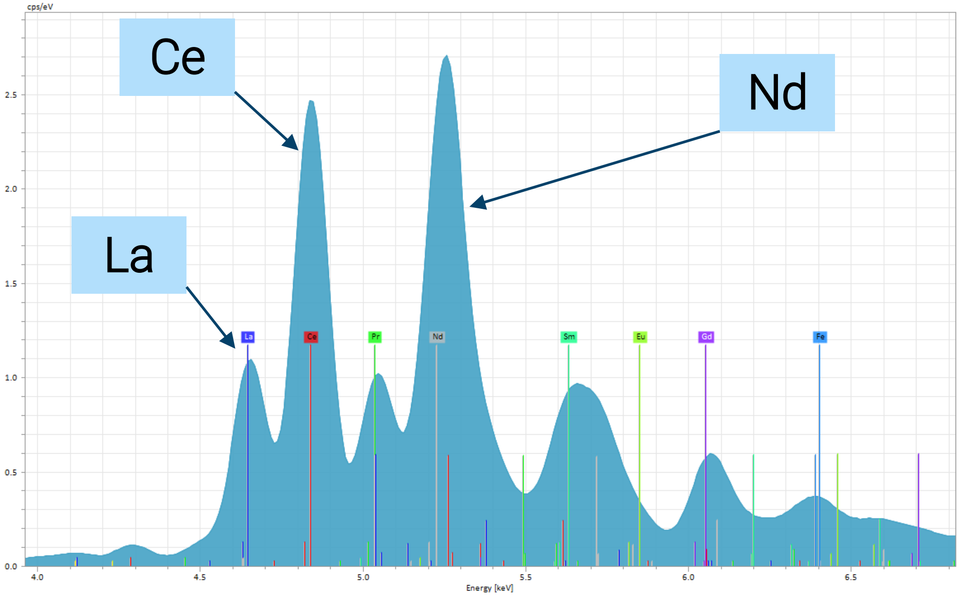
Analysis of Crushed Monazite Samples: pressed pellet, no carbon coating

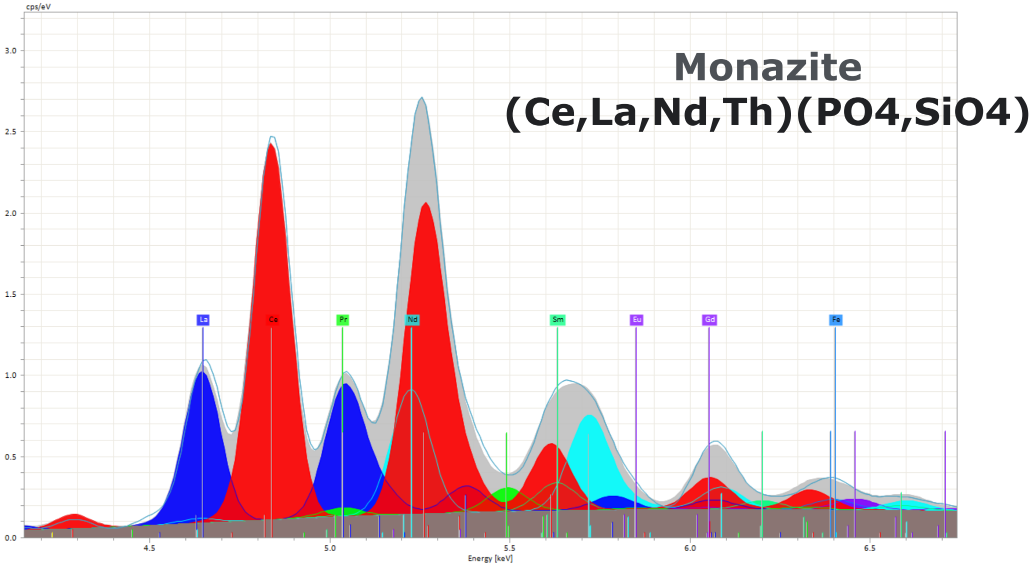












The Analysis of Rare Earth Elements in various sample types using SEM-XRF (XTrace)

Example: Glass

SEM-XRF Analysis of Rare Earth Elements (REE´s):
Comparison with SEM-EDS

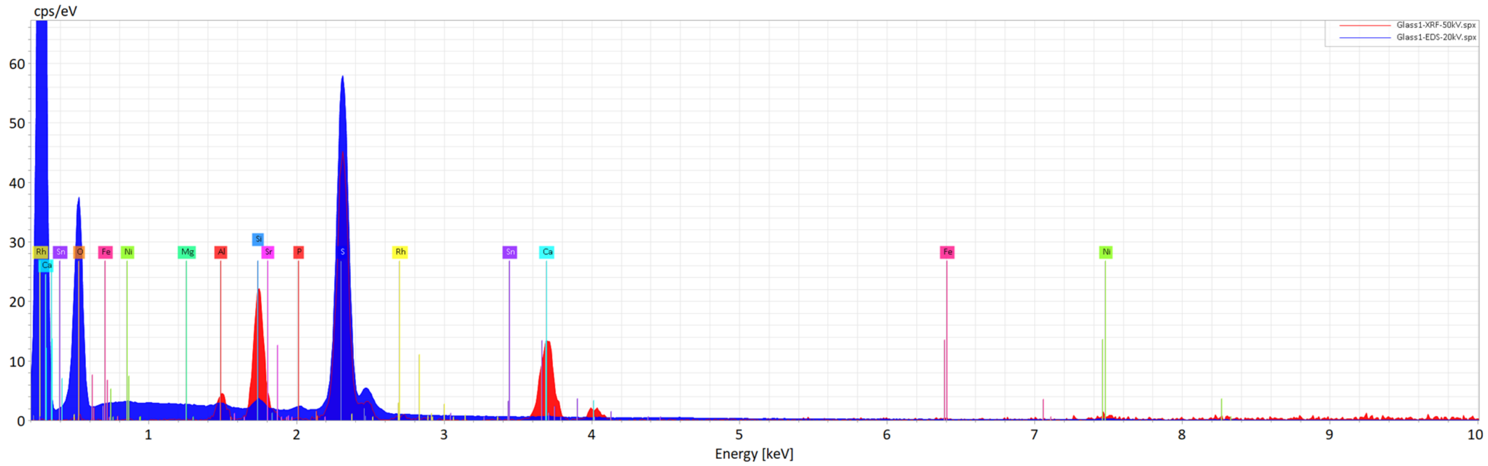
SEM-EDS is better for low energy lines

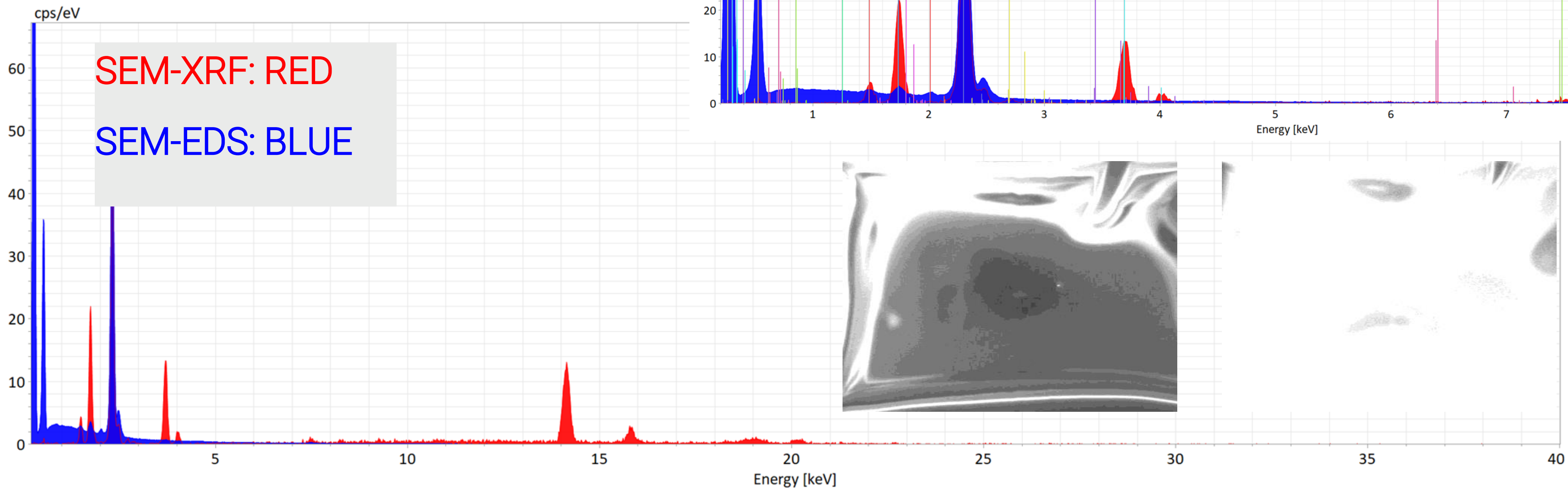
SEM-XRF is better for high energy lines

Glass Spectrum: SEM (20 kV), XRF (50 kV)

Bottom: 0 to 40 keV

Right: 0 to 10 keV





SEM Image showing charging under e-beam:

5 kV (left) and

20 kV (right)

SEM-XRF Analysis of Rare Earth Elements (REE´s):
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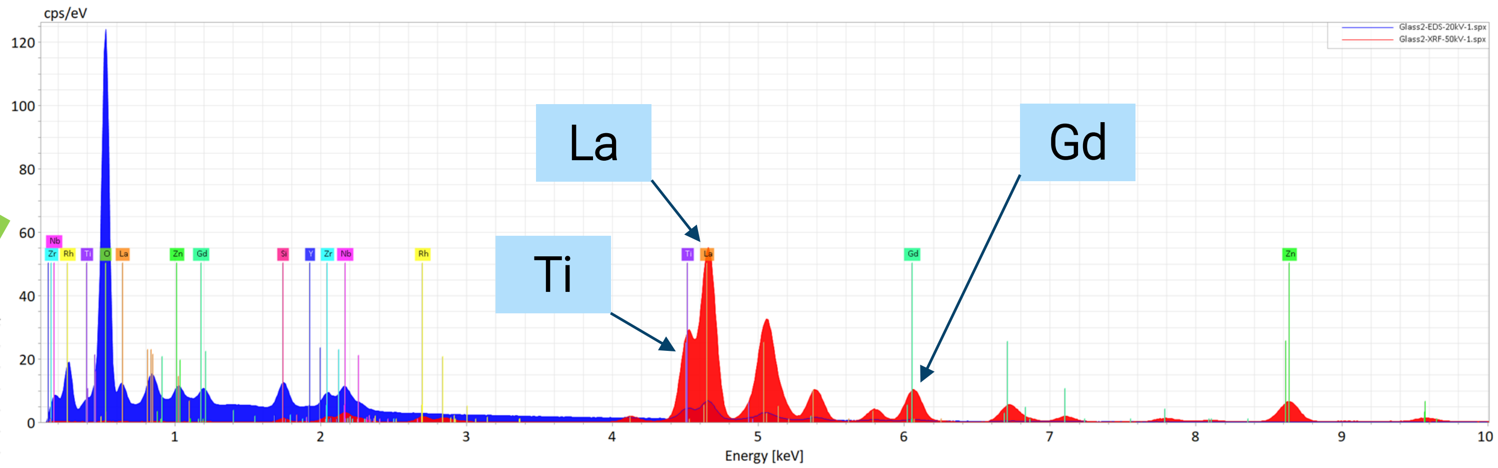
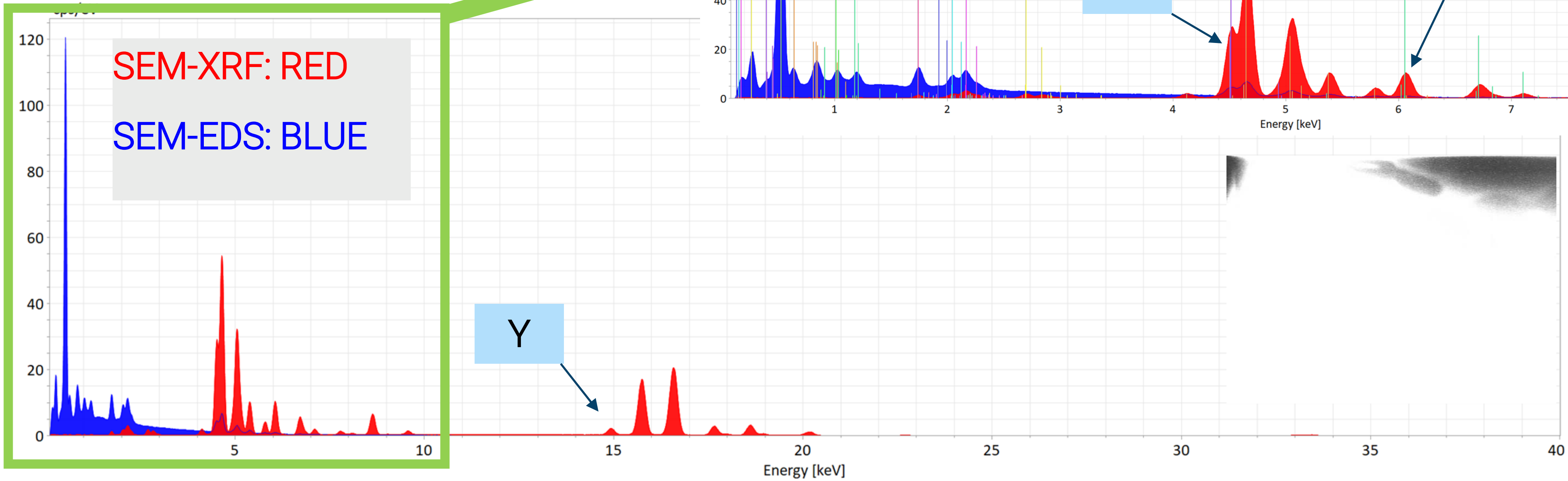




SEM Image showing charging under e-beam:

20 kV

SEM-XRF Analysis of Rare Earth Elements (REE´s): Applications – High Index Glass

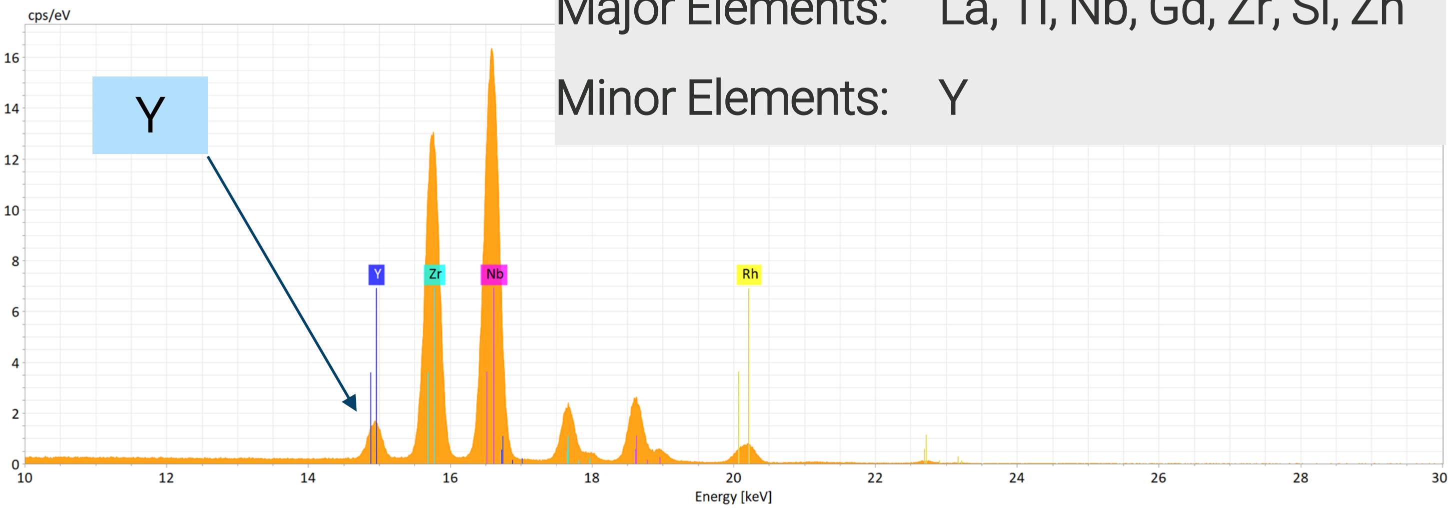
Major Elements: La, Ti, Nb, Gd, Zr, Si, Zn

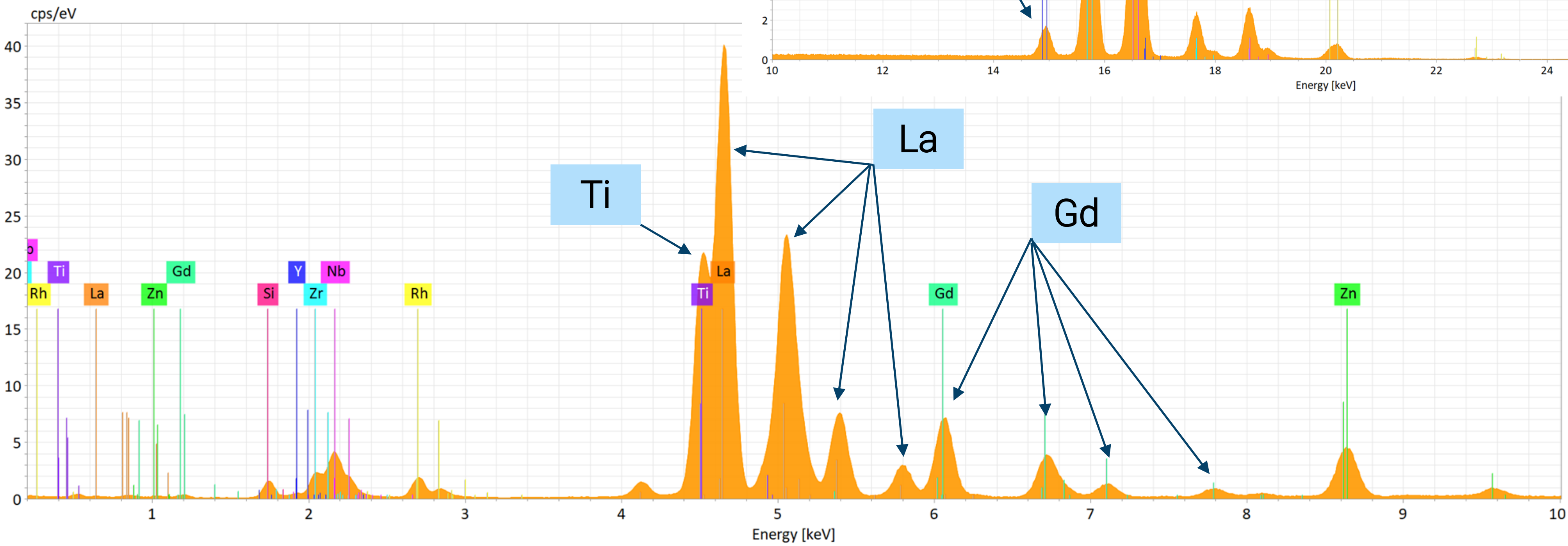
Minor Elements: Y

Spectrum X-axis Range:

Bottom: 0 to 10 keV

Right: 10 to 30 keV





SEM-XRF Analysis of Rare Earth Elements (REE´s):
Applications – High Index Glass

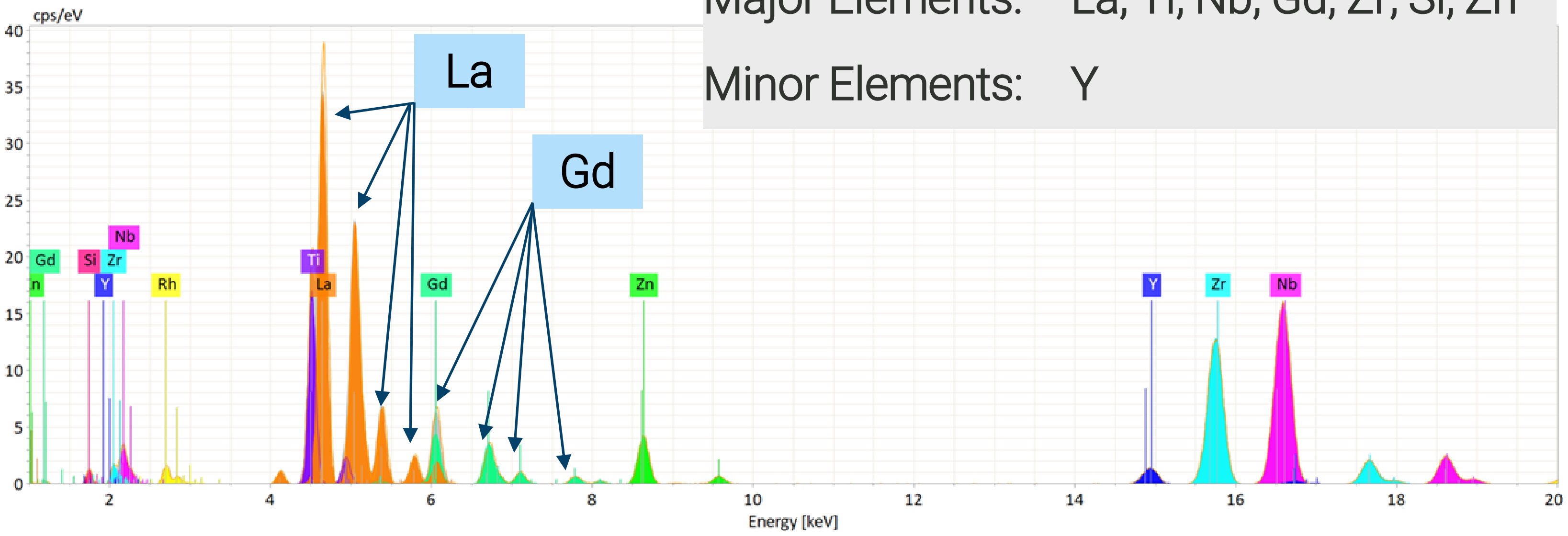
Spectrum X-axis Range:

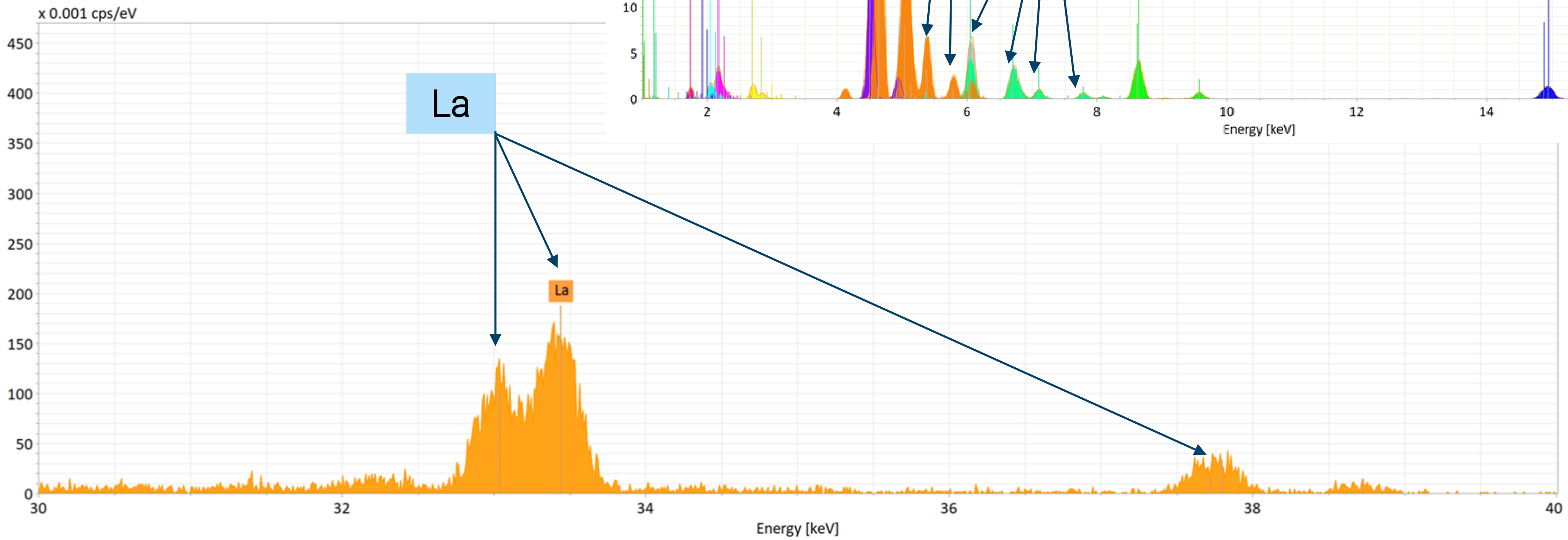
Bottom: 30 to 40 keV

Right: 1 to 20 keV (Deconvolution)

Major Elements: La, Ti, Nb, Gd, Zr, Si, Zn

Minor Elements: Y





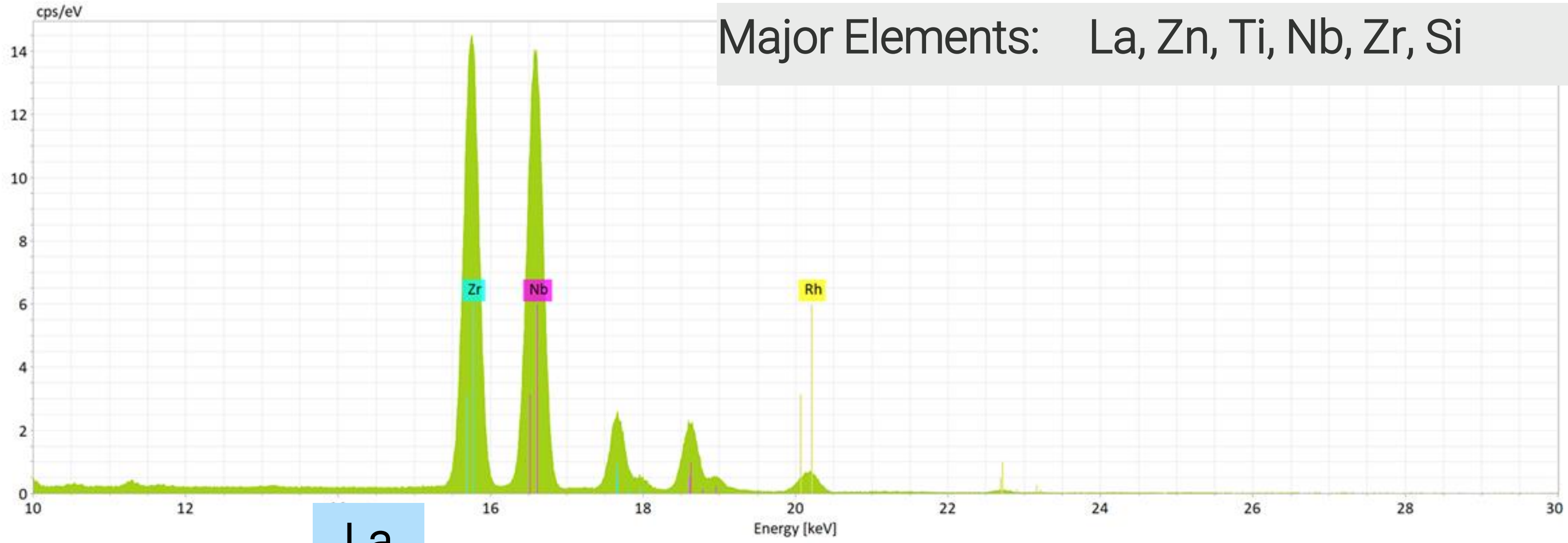
SEM-XRF Analysis of Rare Earth Elements (REE´s): Applications – High Index Glass

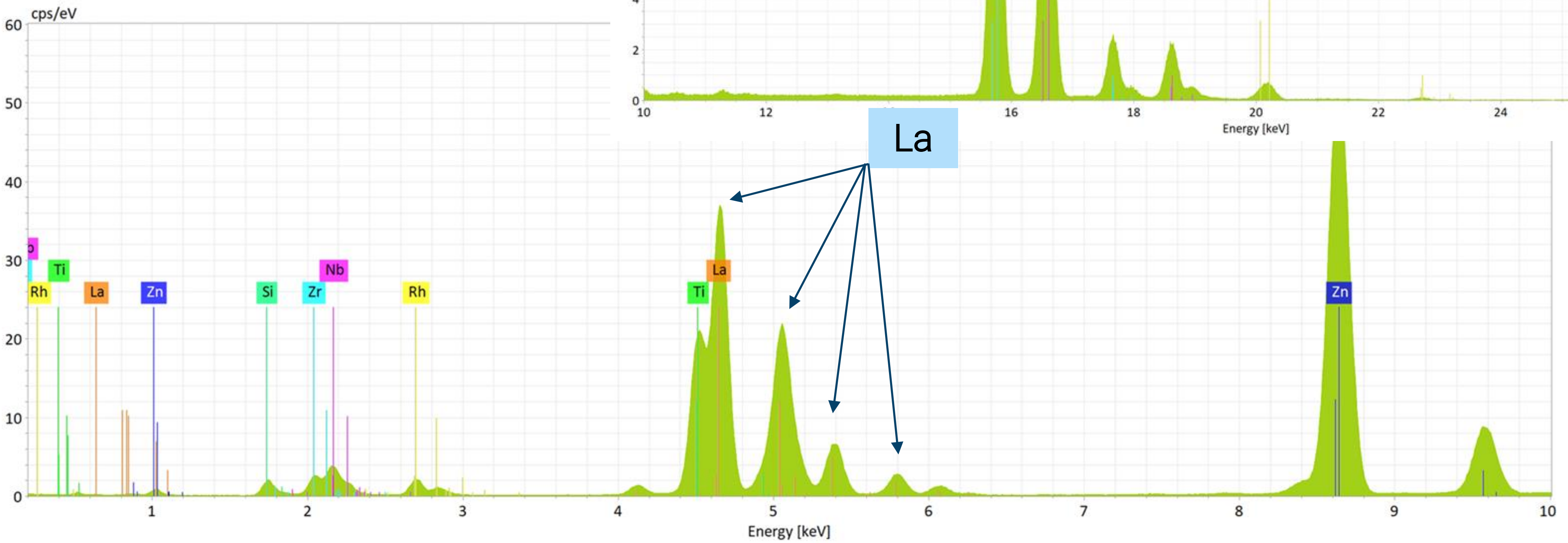
Major Elements: La, Zn, Ti, Nb, Zr, Si

Spectrum X-axis Range:

Bottom: 0 to 10 keV

Right: 10 to 30 keV





SEM-XRF Analysis of Rare Earth Elements (REE´s):
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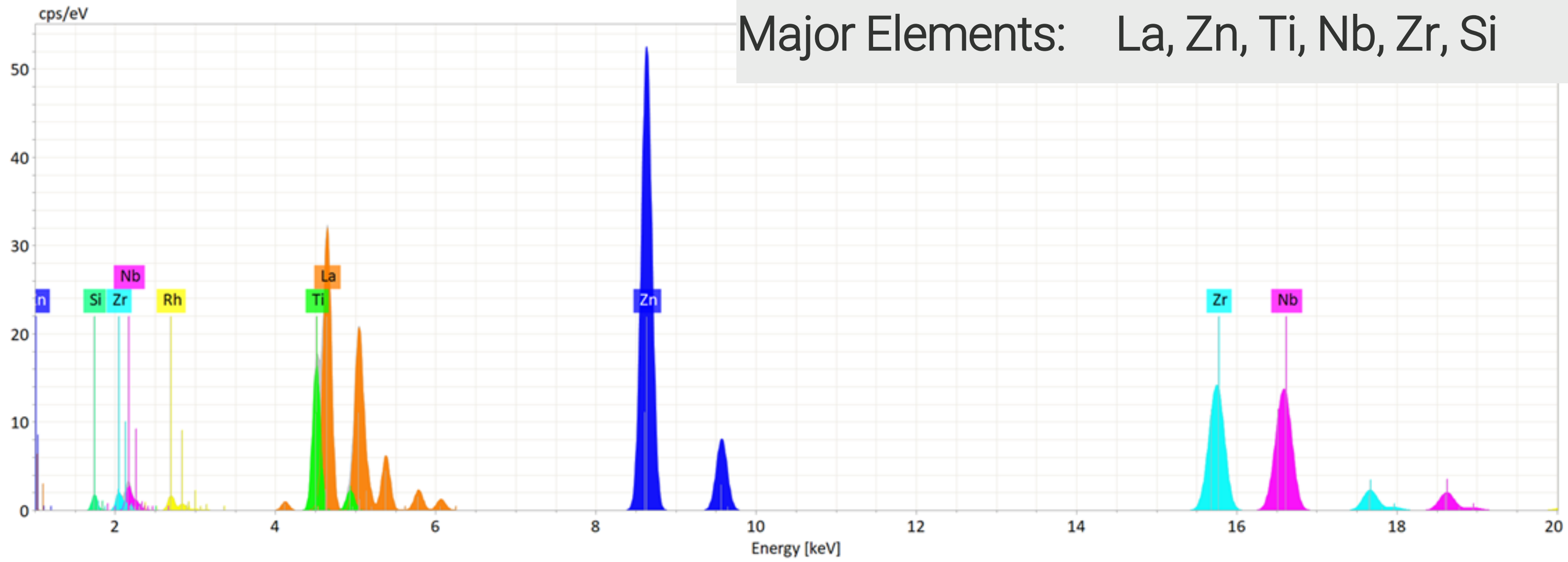
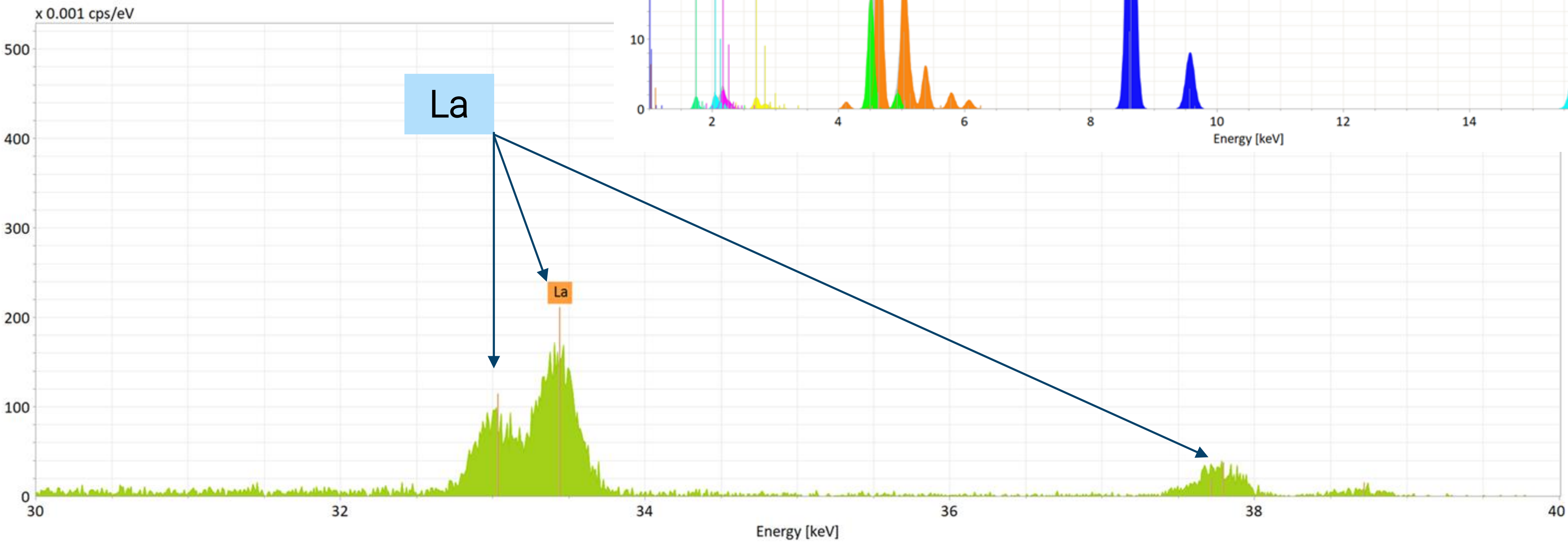
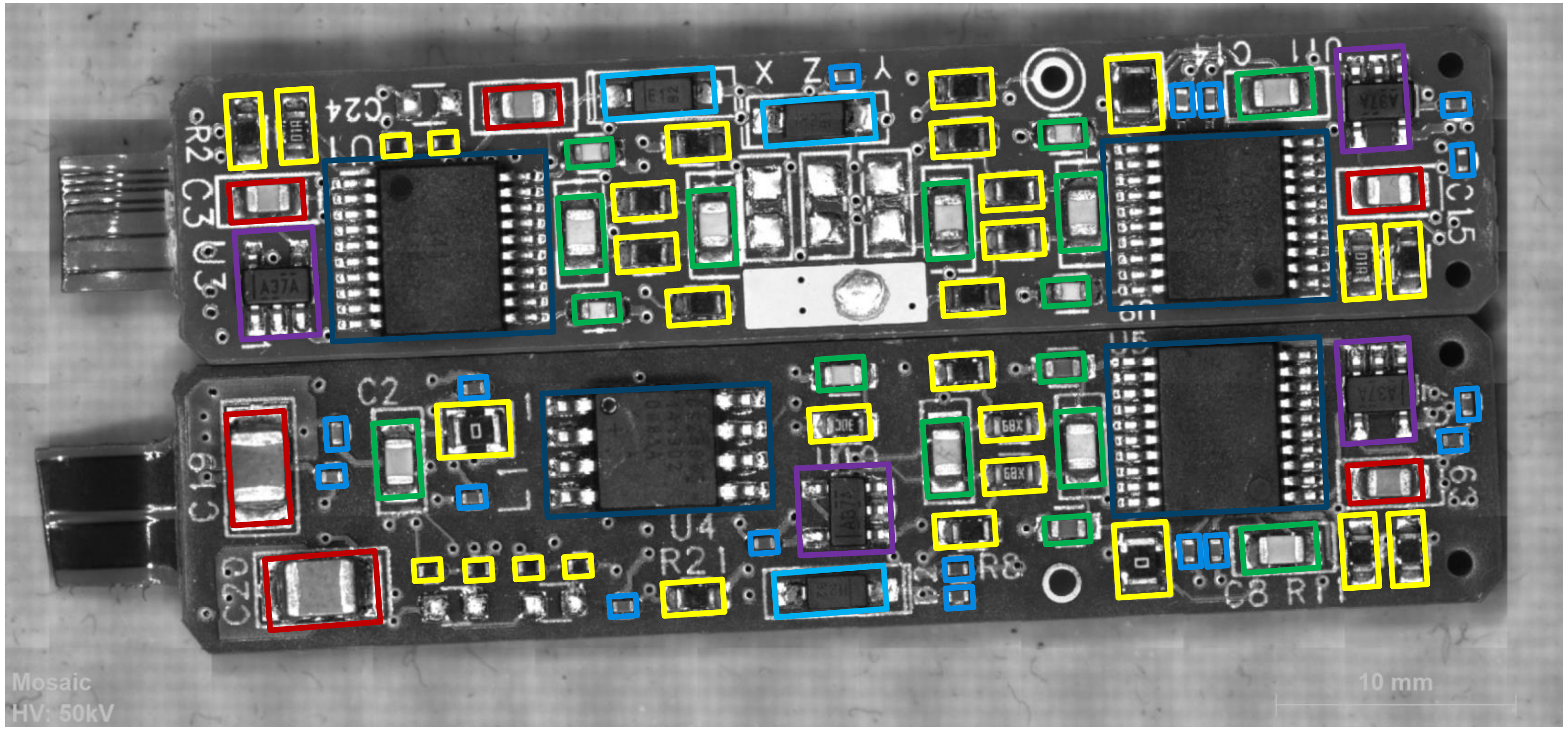




The Analysis of Rare Earth Elements in various sample types using SEM-XRF (XTrace)

Example: Electronics

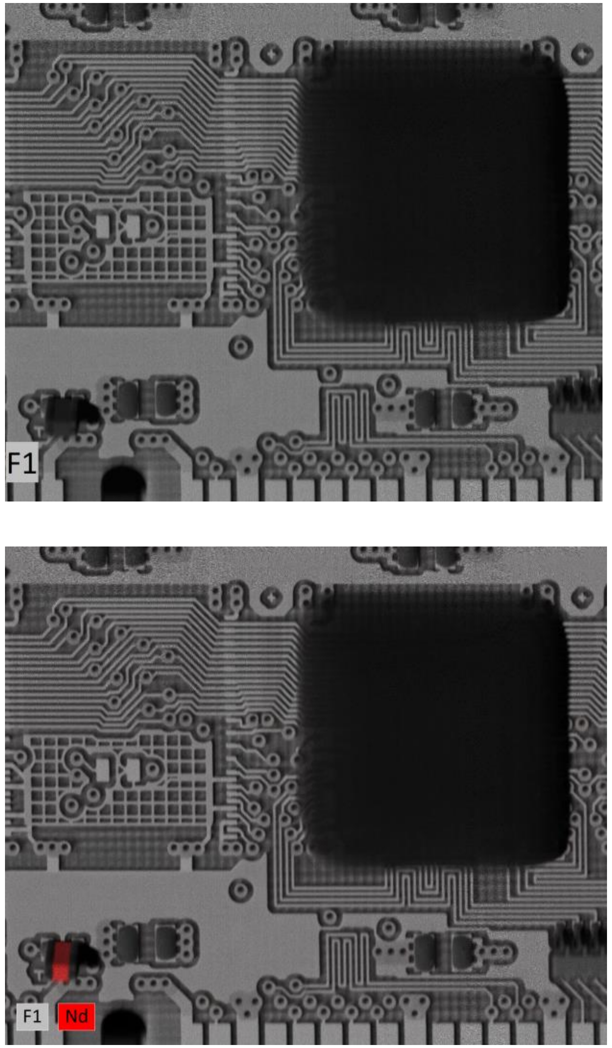
SEM-XRF Analysis of Rare Earth Elements (REE´s):
Applications – Electronics

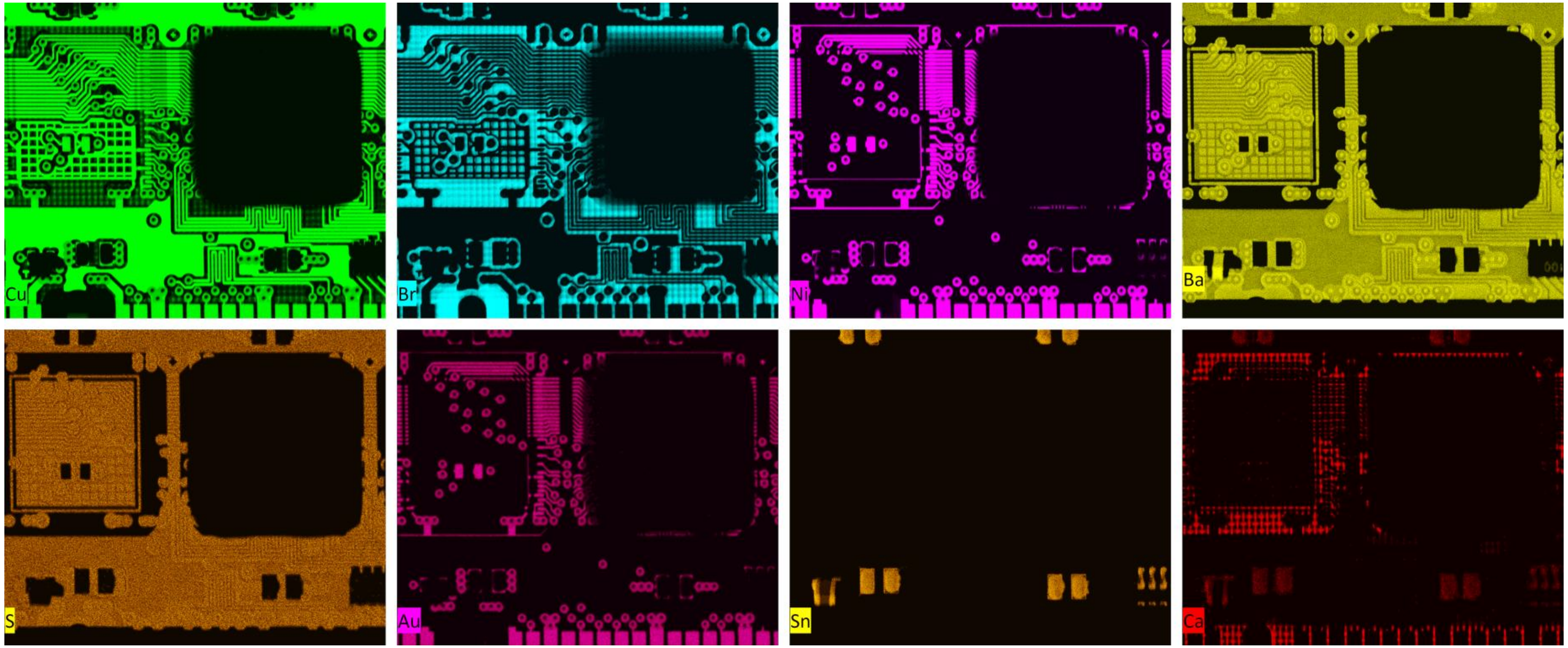


Diode | Integrated circuit | Small IC | White Capacitor | Resistors | Small EC | Brown Capacitor

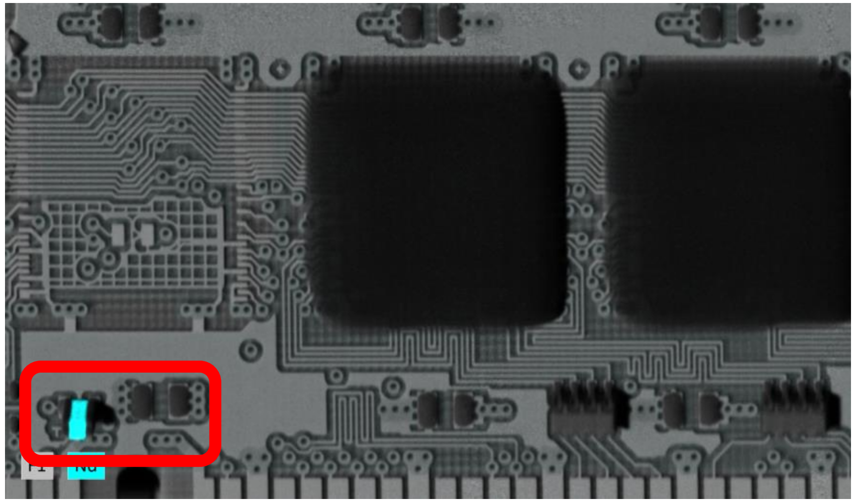
Image courtesy of Benjamin Monneron-Enaud, TU Bergakademie Freiberg, Germany.

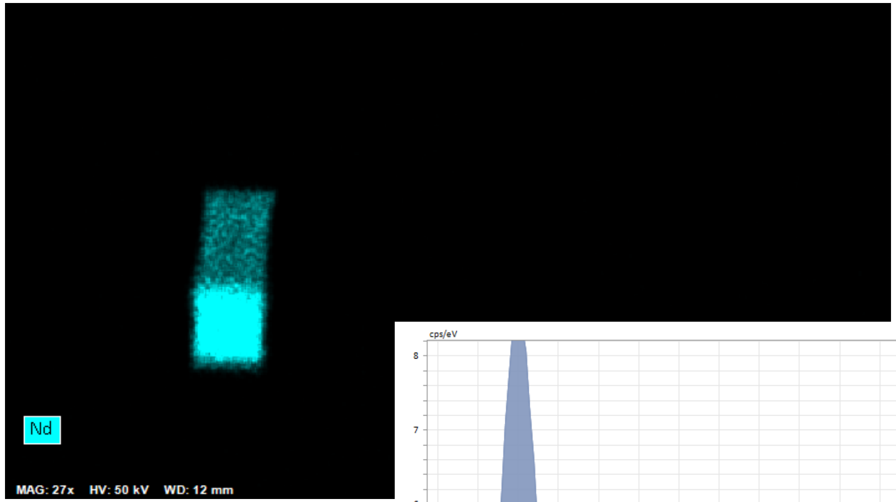
SEM-XRF Analysis of Rare Earth Elements (REE´s): Applications – Electronics

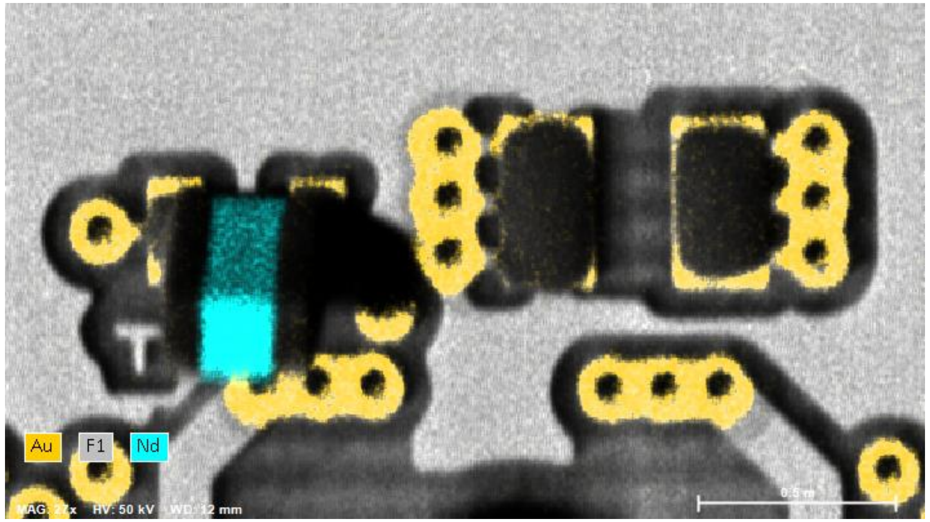


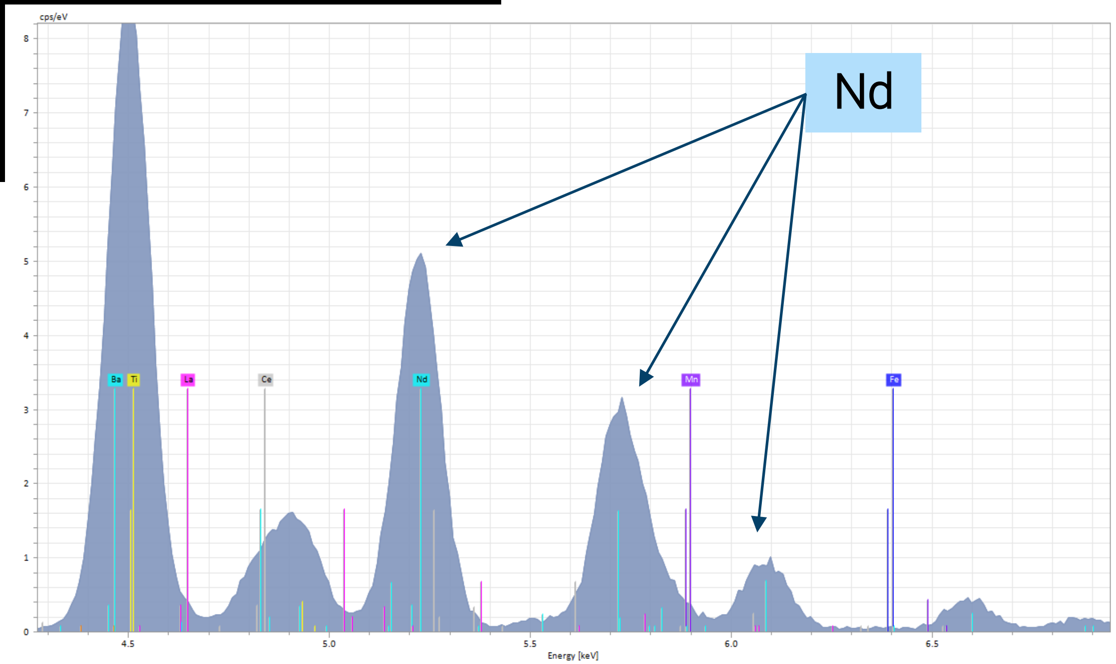


REEs Example:
Applications – Electronics









Summary and Conclusions: Micro-XRF on SEM

2 Excitation Sources:

Electron Beam (e-beam)

Micro-XRF (X-ray beam)

1 Detector:

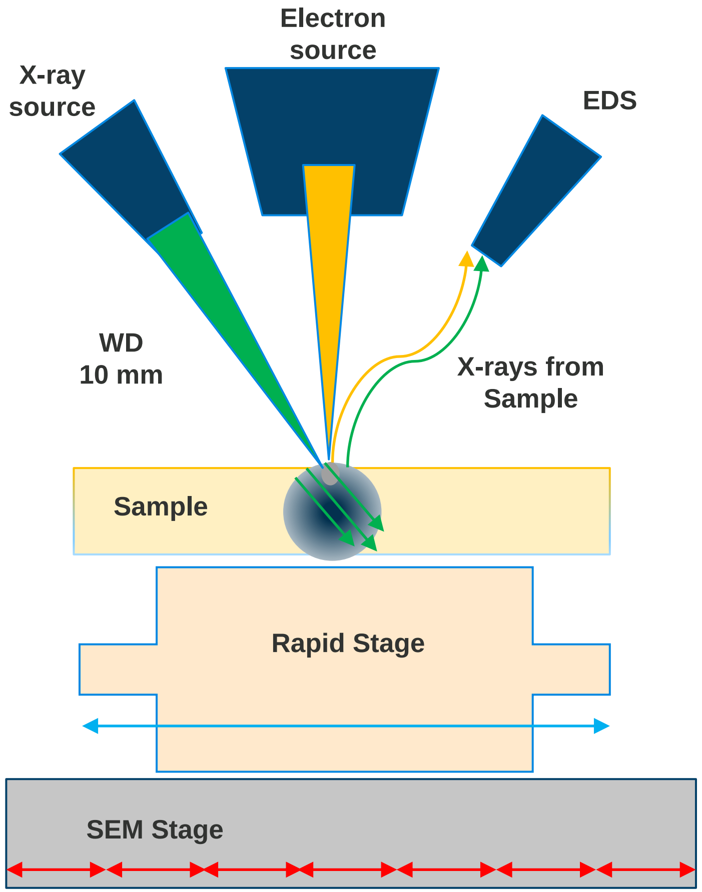
Energy Dispersive

Spectrometer (EDS)

2 Stages:

SEM Stage

Rapid Stage



Micro-XRF Benefits:

- Non-destructive analytical technique
- No charging effects
- Minimal Sample Preparation Required
- Lower detection limits (down to 5 ppm)
- High Energy Lines Detection (Full Spectrum Range up to 40 keV)
- Ideal for Low kV or Beam sensitive samples
- Fast Large Area Mapping
- Micrometer scale measurement over cm

Summary and Conclusions: Micro-XRF on SEM

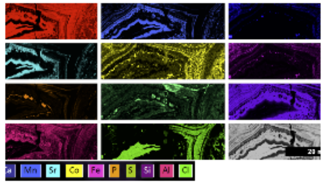
- The analysis of samples at micrometres (µm) scale over centimetres (cm) scale on a standard SEM.
- Able to perform large area maps on a variety of samples
  - Geological, Glass, Electronics, Powders…
- Sample Preparation Minimal for Micro-XRF
  - No carbon-coating, No polishing, Directly into the SEM
- Able to detect and resolve minor and trace elements, e.g. REE´s
- Identification of high energy X-Ray lines
- Can work in combination with SEM e-beam
  - Commonly Low-KV due to charging and sample interaction

WEBINAR: SEM-XRF (XTRACE)

Micro-XRF on SEM (XTrace): Further Information

https://www.bruker.com/

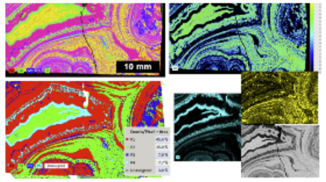
Search for:
QUANTAX Micro-XRF



Large Area Mapping of Mineralogical Samples

The new Rapid Stage is specifically designed for SEMs to enable large area mapping over millimeter (mm) to centimeter (cm) scales. This will eliminate potential SEM X-ray intensity variation artifacts associated with low magnification mapping and thus enhance elemental and mineralogical information in a timeous manor that was previously not possible.

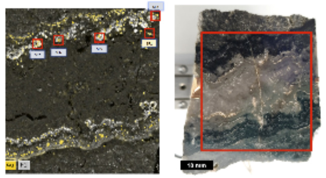
→ READ MORE



Elemental and Mineral distribution in Exotic-Cu Deposits

The ability to observe elemental changes within samples is important to understand geological processes and ore deposit genesis. The dual source system which incorporates a micro-XRF on a SEM enables elemental X-ray mapping over large areas, which shows major, minor and also trace elements on the ppm scale.

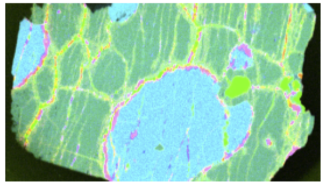
→ READ MORE



Dual Source Applications for Exploration and Mining: Au-bearing Epithermal Samples

The combination of micro-XRF with SEM enables the potential to analyze samples at multiple scales, from centimeters (cm) to millimeters (mm) to micrometers (µm) and below within a solitary system. Thus, by adding the micro-XRF to an SEM you convert your SEM to a dual source system, meaning that there are 2 excitations sources, the e-beam and photon beam. Either source can be used individually, or simultaneously, to generate sample X-rays that will be measured using the same EDS detector.

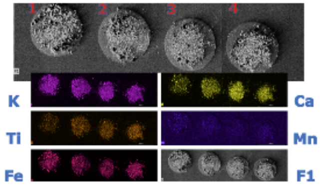
→ READ MORE



Mantle Petrology and the Source of Diamonds

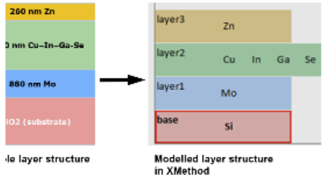
We present a SEM-XRF element map of a mantle garnet-spinel peridotite from the diamond-bearing Newlands kimberlite (South Africa, Kaapvaal Craton). The intensity of the various elements indicates certain minerals that are present in the sample.

→ READ MORE



Identification of Contaminants and Toxins in Soils

Large Area Mapping (Hypermaps) using SEM-XRF can be performed on samples with topography. That is, minimal sample preparation is required and the sample can be analyzed directly without any degradation. This is particularly relevant in the analysis of soils, where any form of sample preparation, such as mounting and polishing or carbon coating, may alter the specimen.

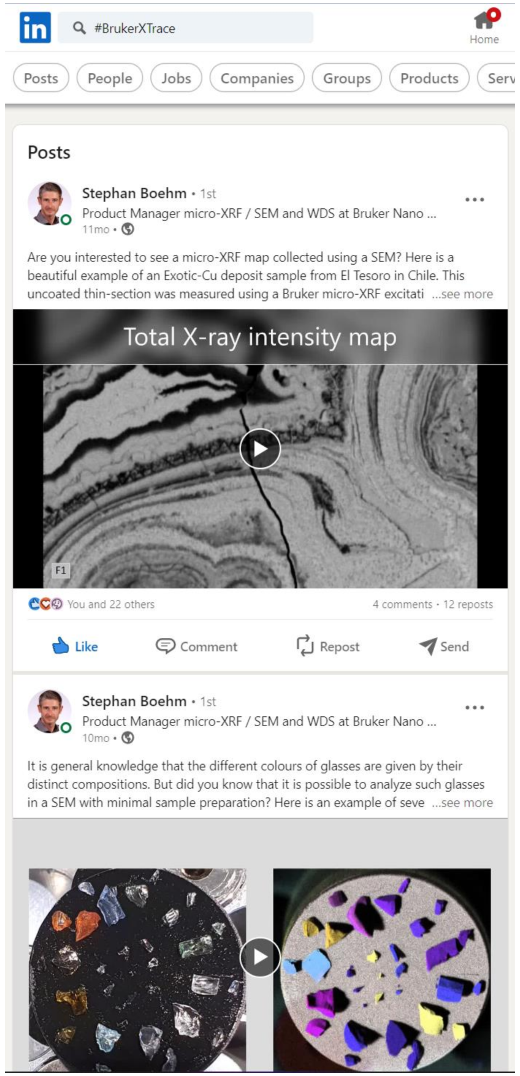


Thin Film Analysis with SEM micro-XRF

As X-rays may pass through matter, X-ray Fluorescence (XRF) allows the determination of layer thickness. Using micro-XRF on SEM, the layer analysis (thickness and composition) is rendered feasible with spatial resolution at the micrometer scale. Layer analysis is strongly based on quantification using atomic fundamental parameter (FP).

→ READ MORE

LinkedIn Posts: #BrukerXTrace



More Information

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Thank you for your time.

Any Questions?

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