Detection of Li K emission in different lithium compounds

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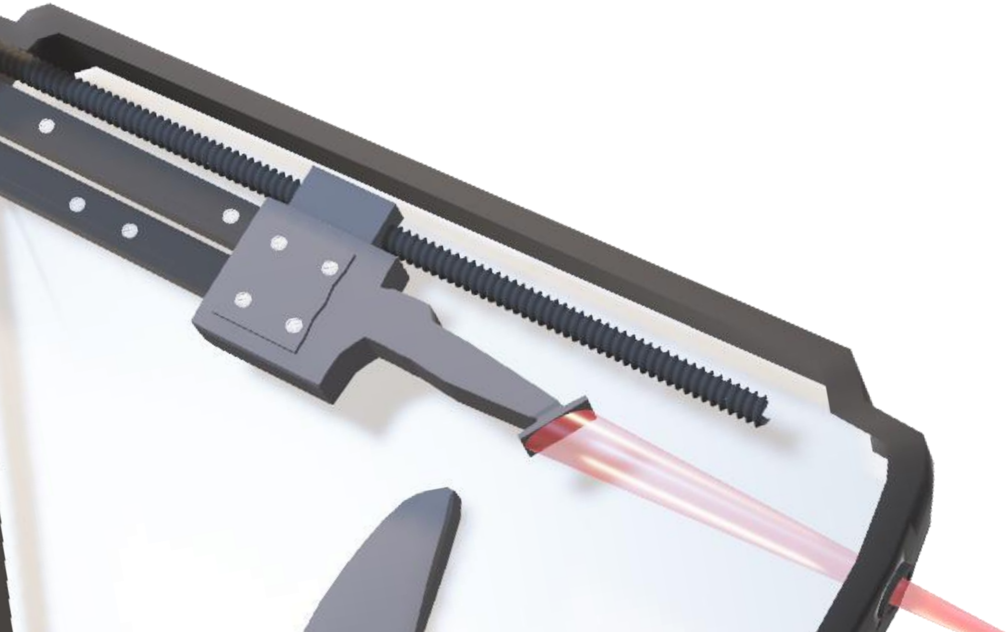
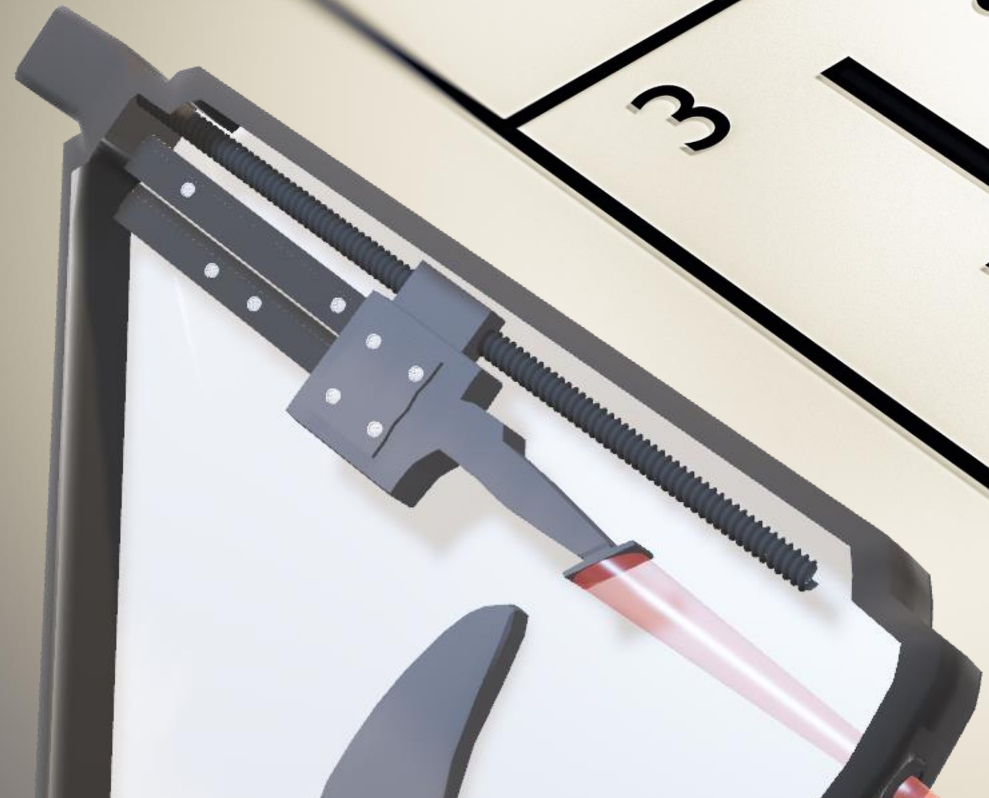
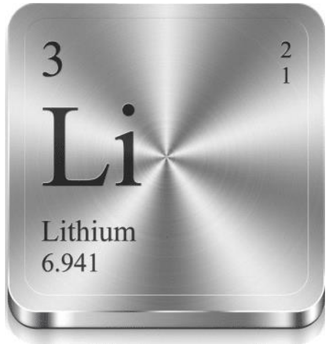


Summary:

- Theory
- Experiments
- Results



Lithium



Batteries

Rechargeable lithium-ion batteries (high energy density, wide operating voltage..)

Growing hybrid and electric-vehicle market is raising demand.

Geology

67% produced from hard-rock minerals (minerals presented)*

Medication

Used to treat bipolar disorders

Research

More than 21802 papers published in 2022 (Web Of Science)

aeronautics

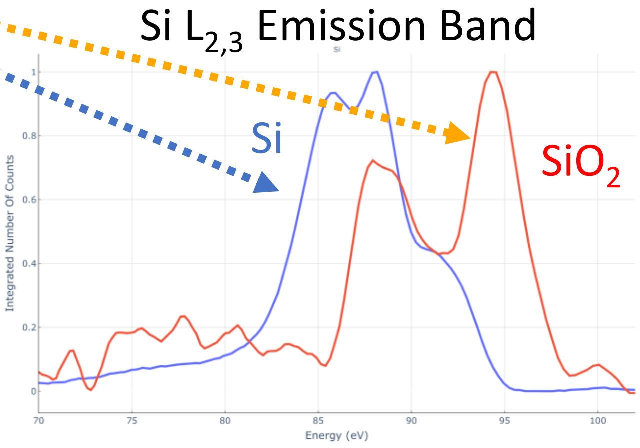
With light Al/Li alloys (wing Airbus A380…)

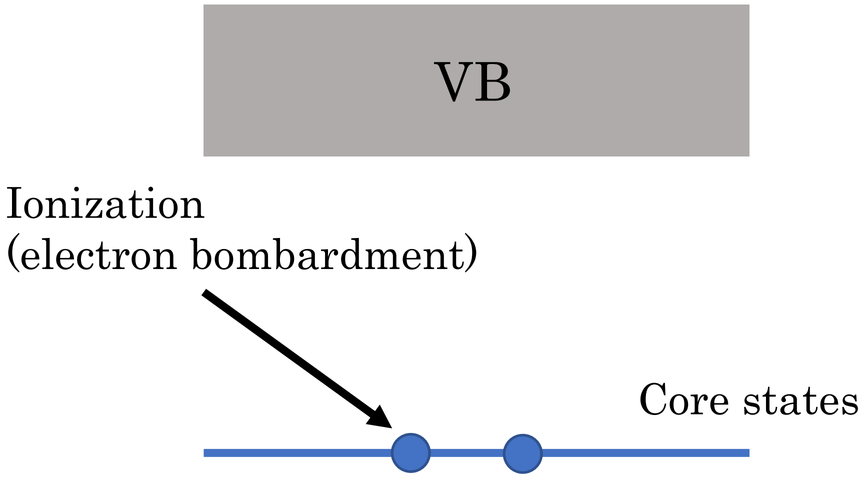
*S.H. MOHR AND OTHERS, MINERALS 2012

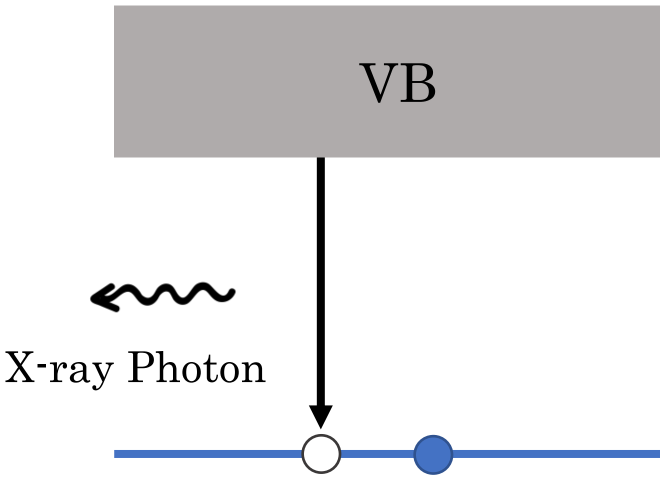
X-ray emission spectroscopy

1. The X-ray emission spectrum is generated by **bombarding** the sample with electrons or by absorption of a photon.
2. These X-rays **ionize inner-shell electrons**, which then decay by emitting X-ray photons.
3. These emitted X-rays have energies that correspond to the energy **differences between the two electronic states**.

→ X-ray emission spectroscopy (XES) provides a means of **probing the partially occupied density of electronic states** → *element-specific* and *site-specific.*



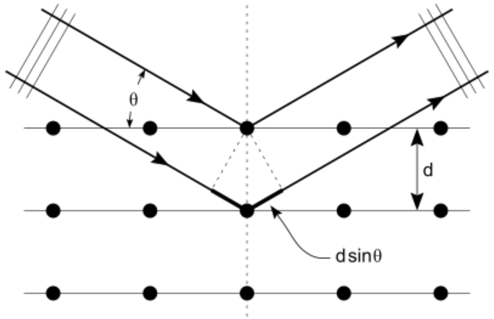




Wavelength Dispersive Spectrometer

WDS

Multilayers



$2d\sin(\theta) = n\lambda$

- Mechanical scanning (Rowland mount)
- High efficiency
- **Resolution:** few eV

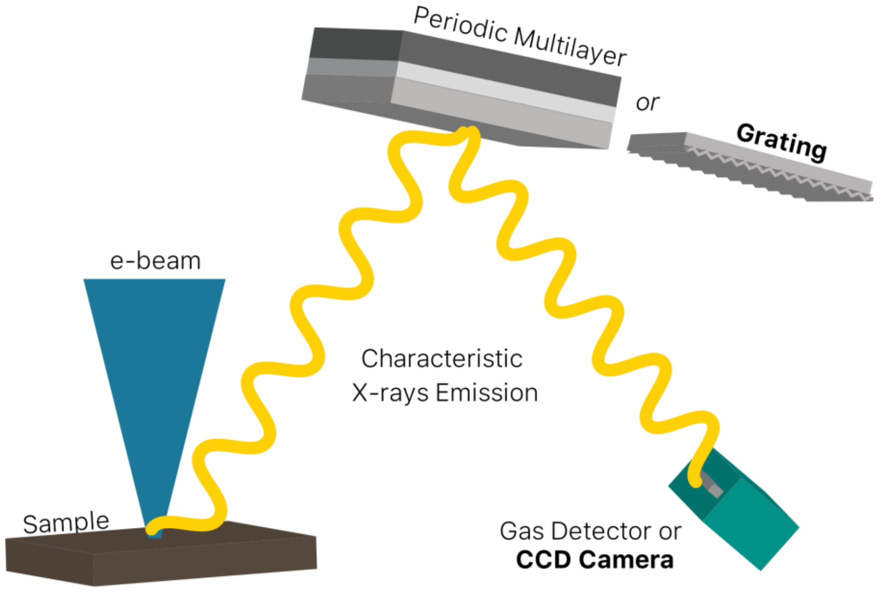
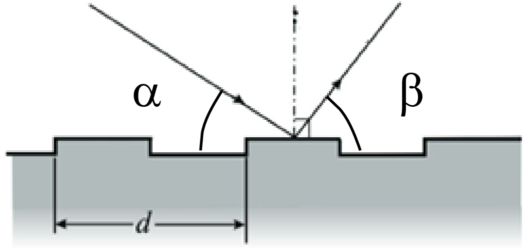


Figure: Wavelength dispersive spectroscopy (WDS) technique implemented inside the EPMA to acquire emission spectra

[Be (12.5 nm) / Si (2 nm) / Al (14.5 nm)]x20 / Si substrate
Period of the stack d = 29 nm
(V. Polkonikovet et al.)

Gratings

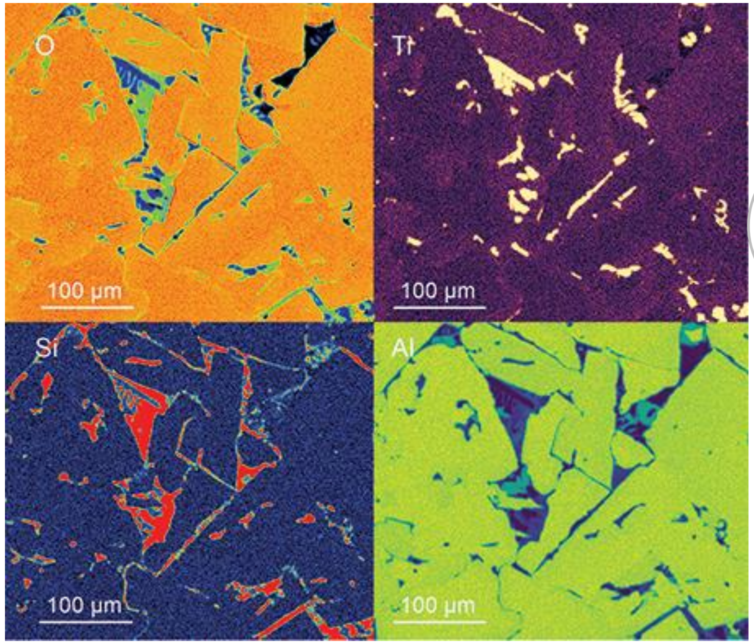


$d(\cos\alpha - \cos\beta) = n\lambda$

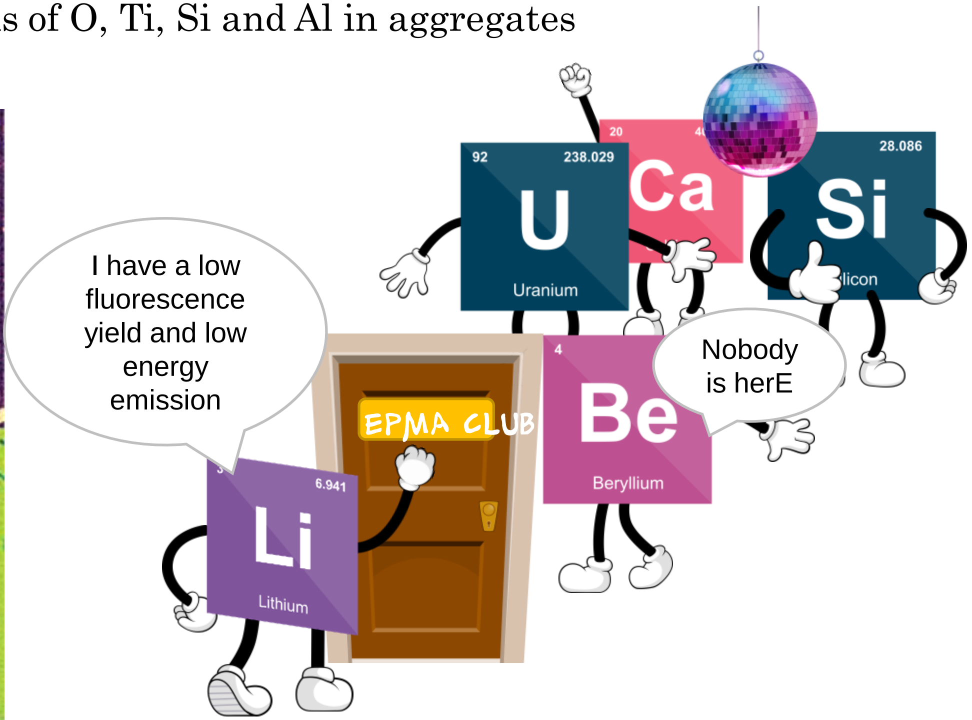
- Simultaneous (VLS)
- Low efficiency 10-25%
- **Resolution:** < 1 eV

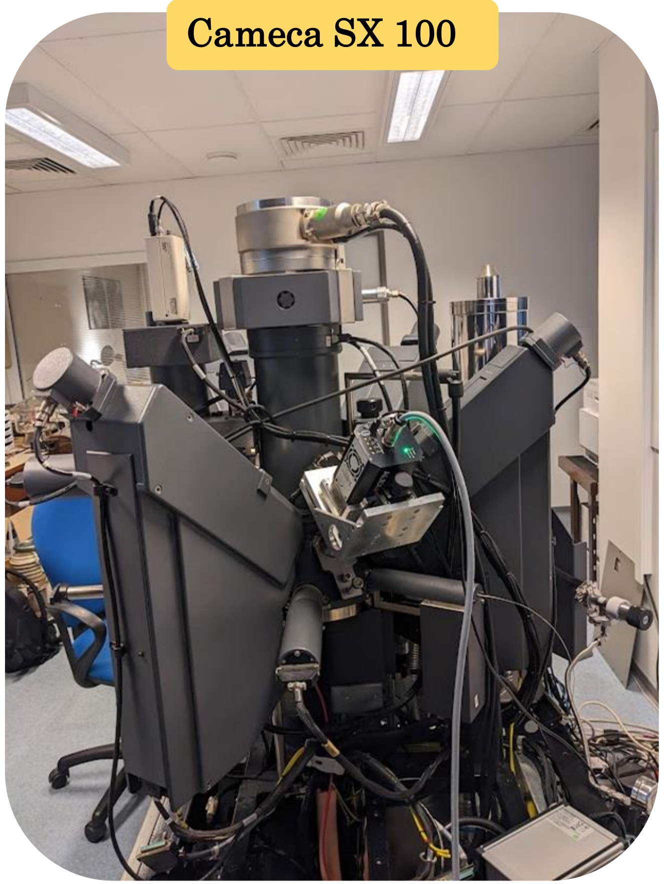
Electron Probe Microanalyzer (EPMA) :

WDS X-ray maps showing the distributions of O, Ti, Si and Al in aggregates of hopper (skeletal).



T. Murphy et al. Electron Probe Microanalysis 2nd edition.





- Determining the elemental composition of solid
- Produce maps - spatial distribution of elements over the surface in the submicron scale.

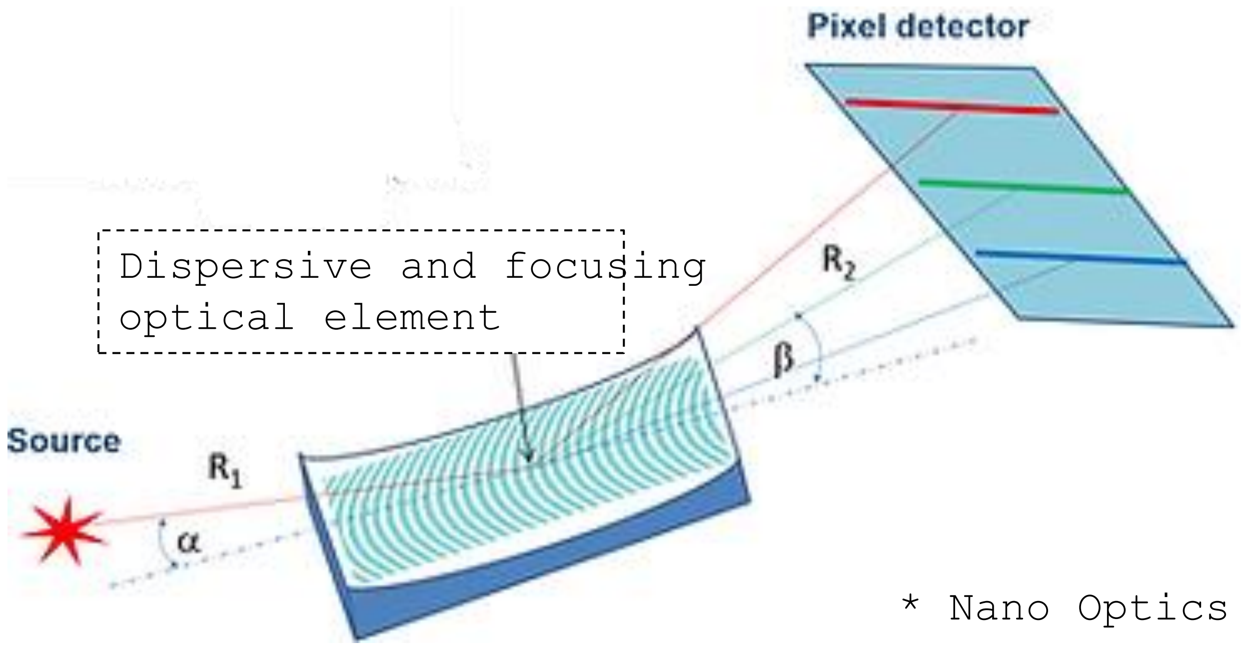
No accessible for Li!

- Low fluorescence yield 1.6 10^{-4}
- Low energy (~50 eV) and high self absorption

Would it be possible to open this door for Li?

Reflection zone plates:

Would it be possible to open this door for Li? YES!



Dispersive and focusing optical element

* Nano Optics Berlin

Flat-field spectrometer

Grating formula:

$d(\cos\alpha - \cos\beta) = n\lambda$

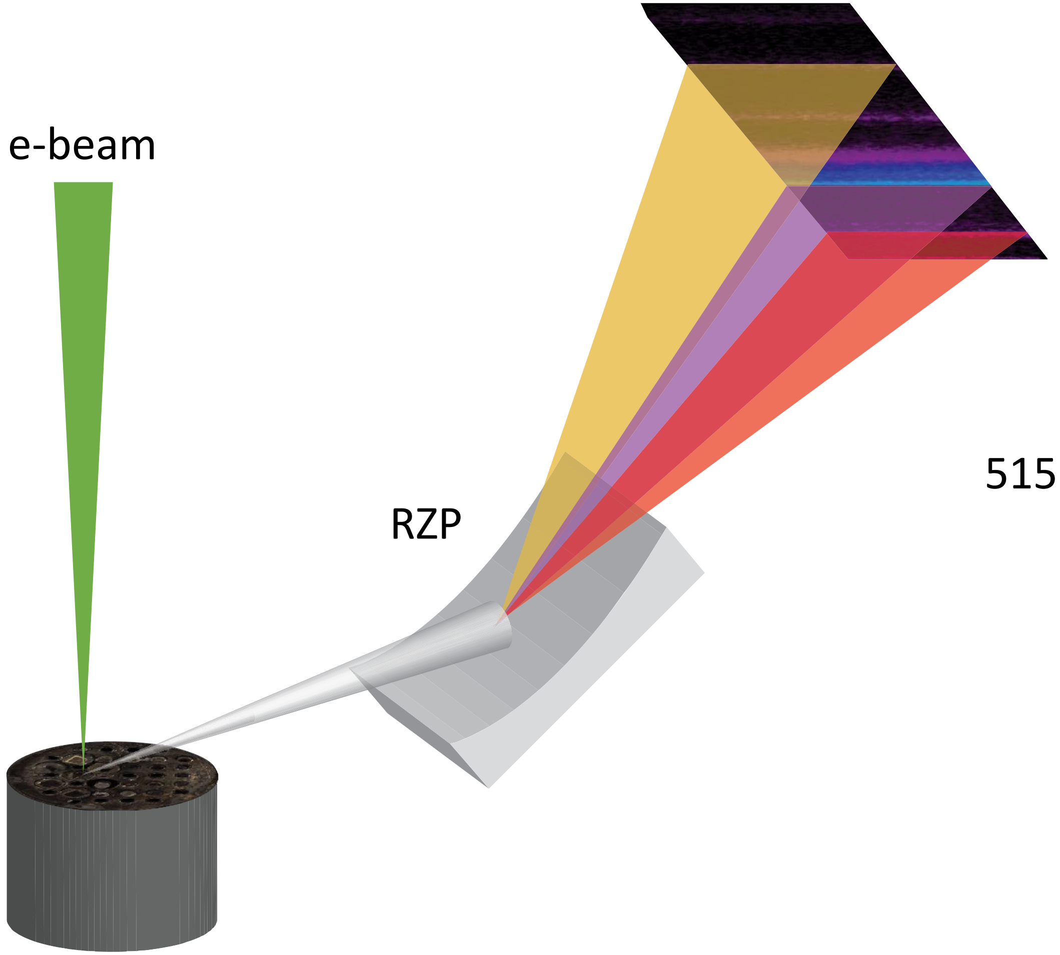
We have a spectral resolution: 0.5 eV at the Al L2,3 edge

Reflection Zone Plate spectrometer

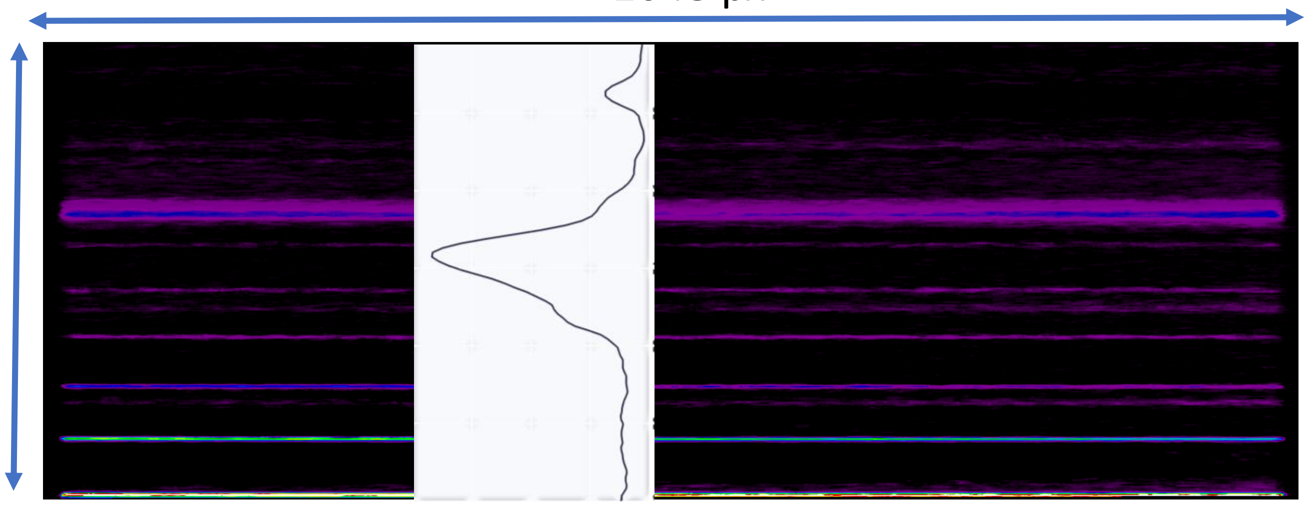
WDSX02 - NOB

RZP:

HV: 5 kV, **Current:** 299 nA, **Acquisition time:** 300 s, **Resolution:** 0.5 eV

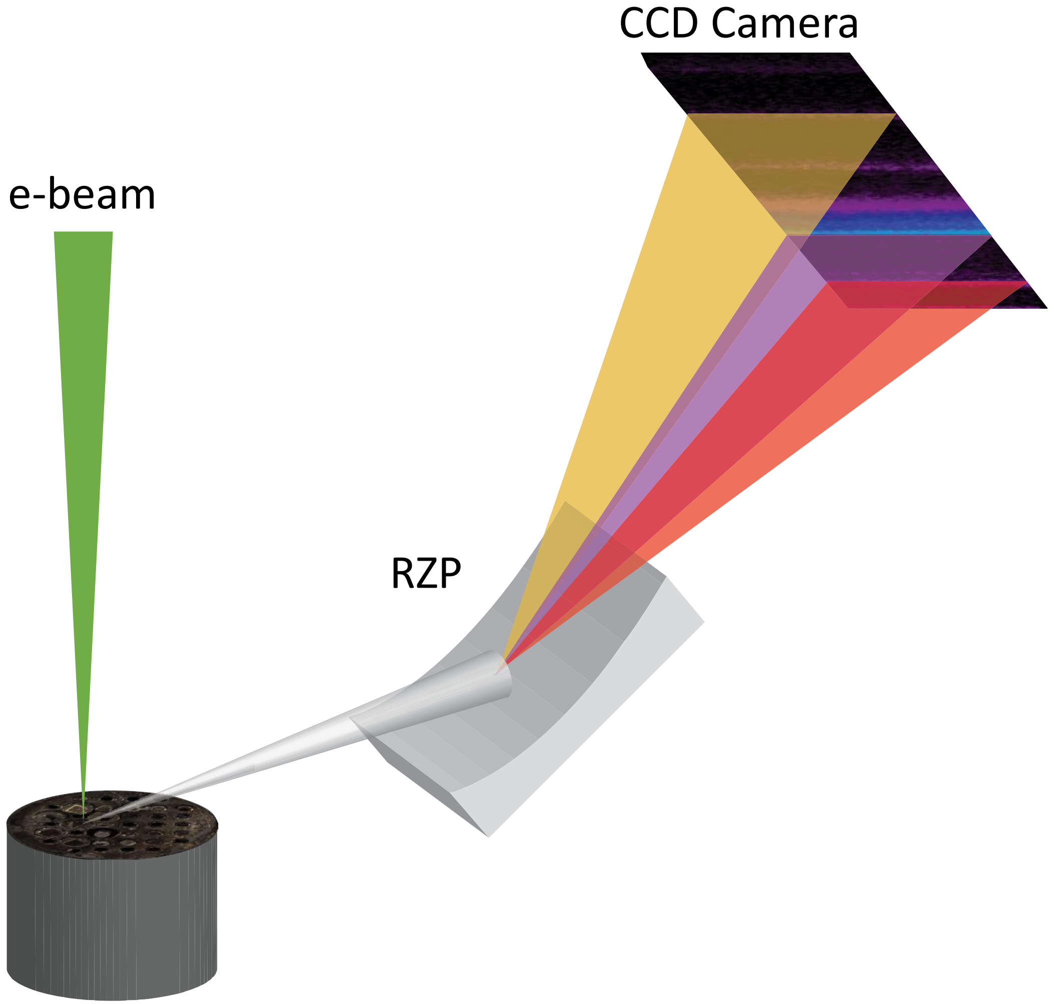


CCD Image of Li metal

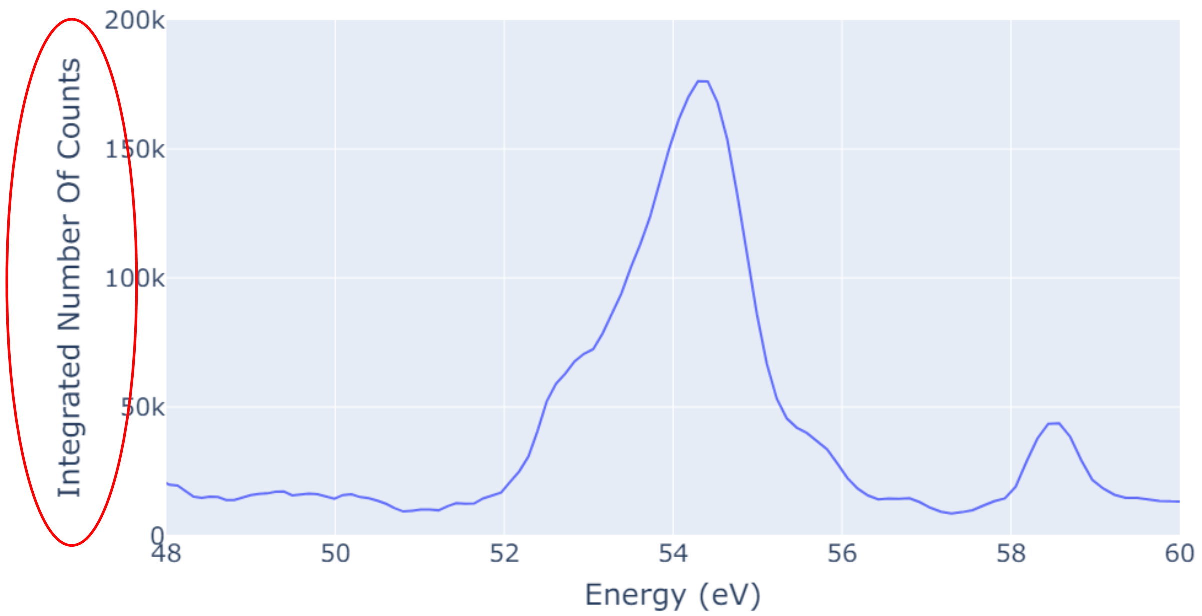


RZP:

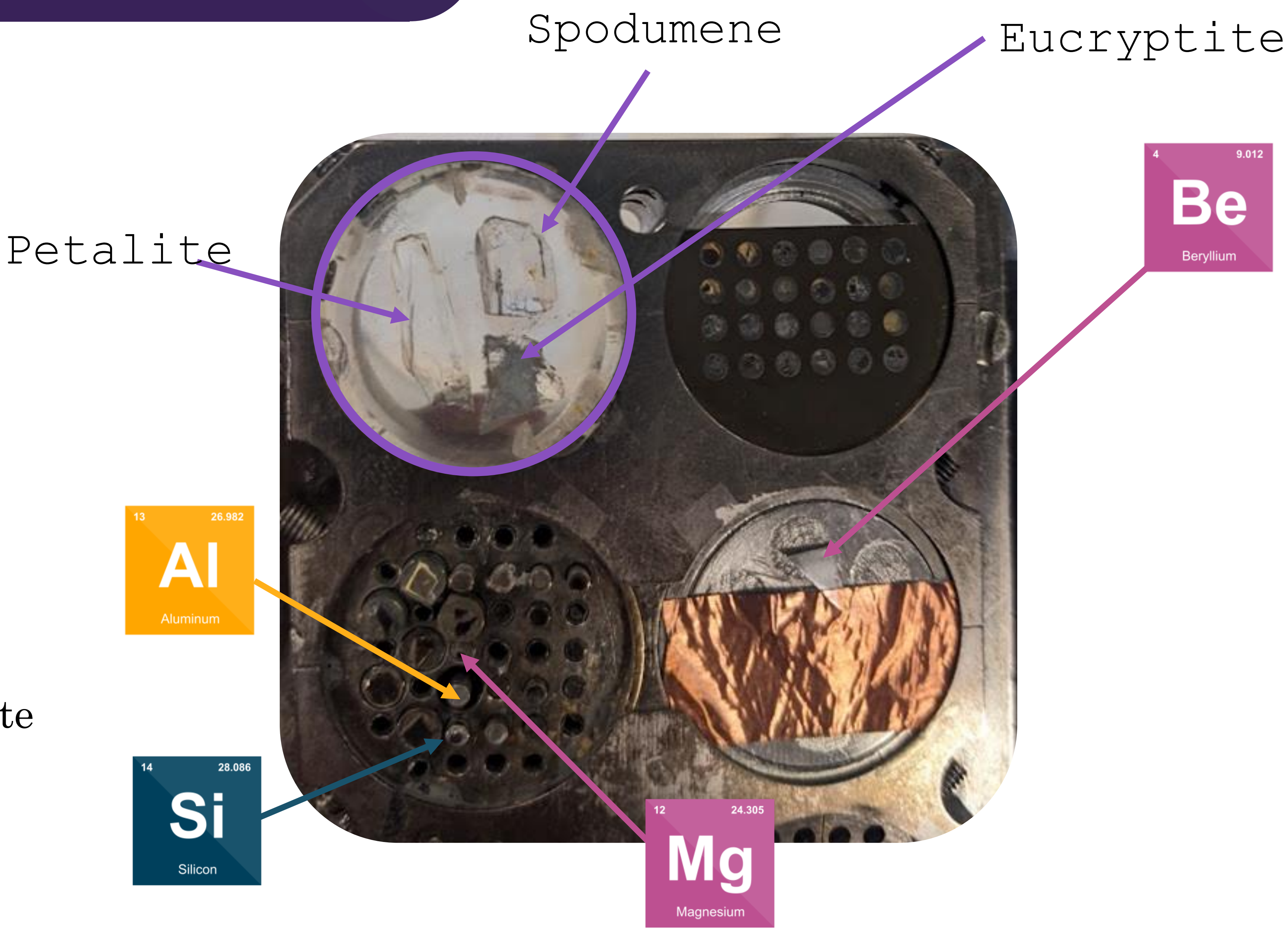
HV: 5 kV, **Current:** 299 nA, **Acquisition time:** 300 s, **Resolution:** 0.5 eV



Spectrum of Li in lithium metal:

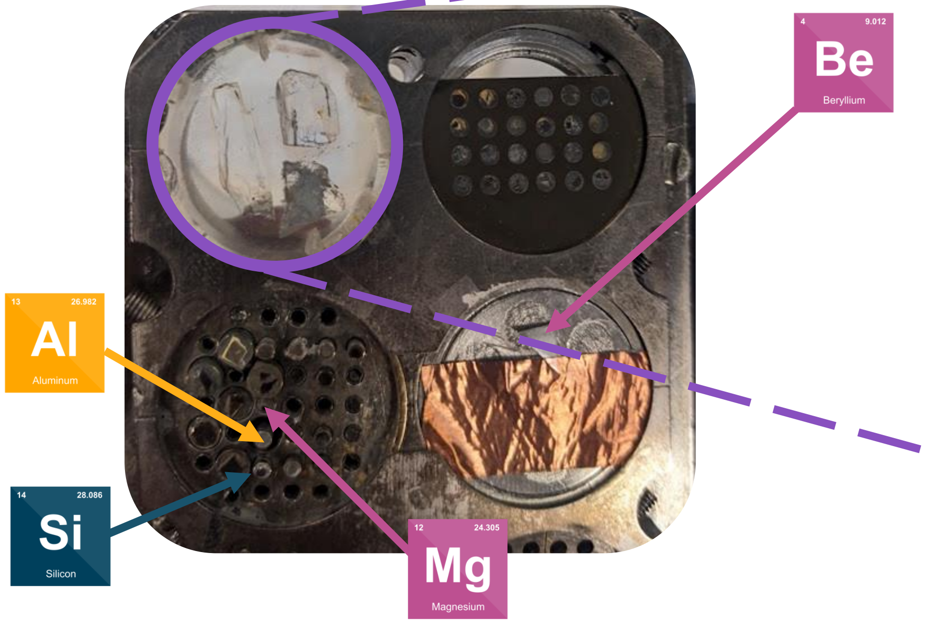


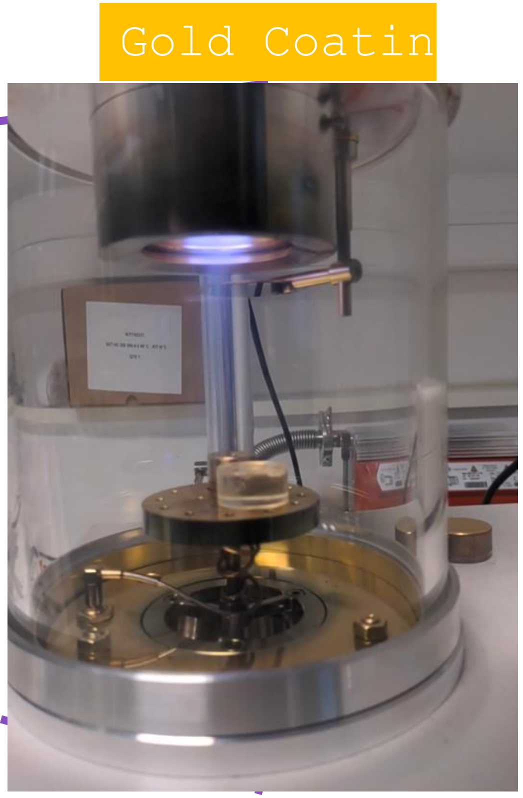
Samples Analyzed:



- Li metal
- LiF
- Bikitaite
- Lepidolite
- Amblygonite
- $LiNbO_3$
- $LiTaO_3$

Samples Preparation:

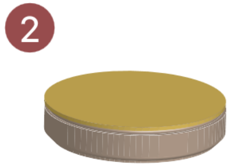




Insulating samples:

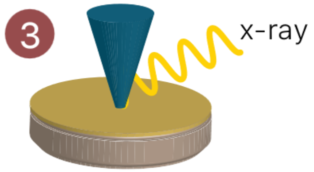
Polishing

To remove the surface contaminations



Coating

Sputter coating for non conducting samples

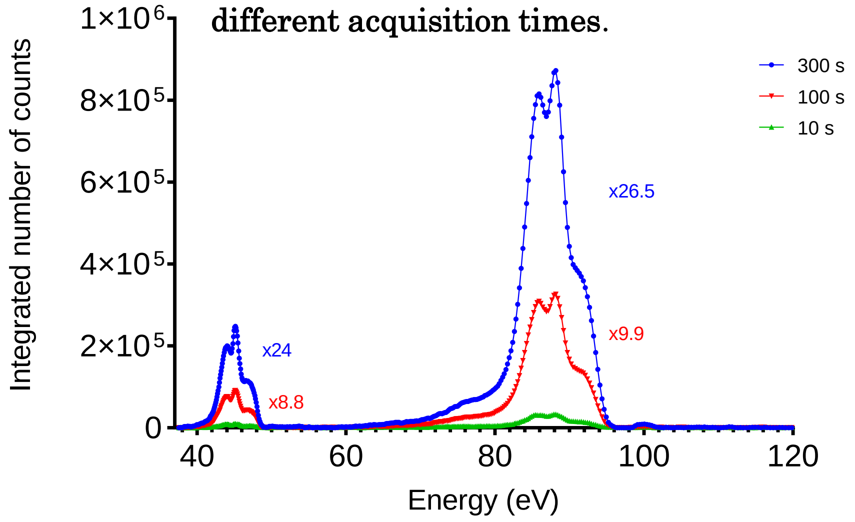


Analyzing

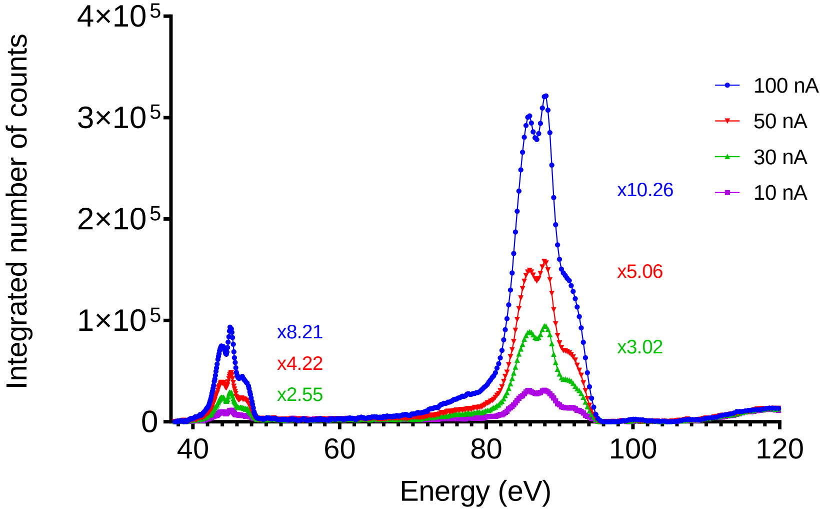
Introducing the sample into the microprobe

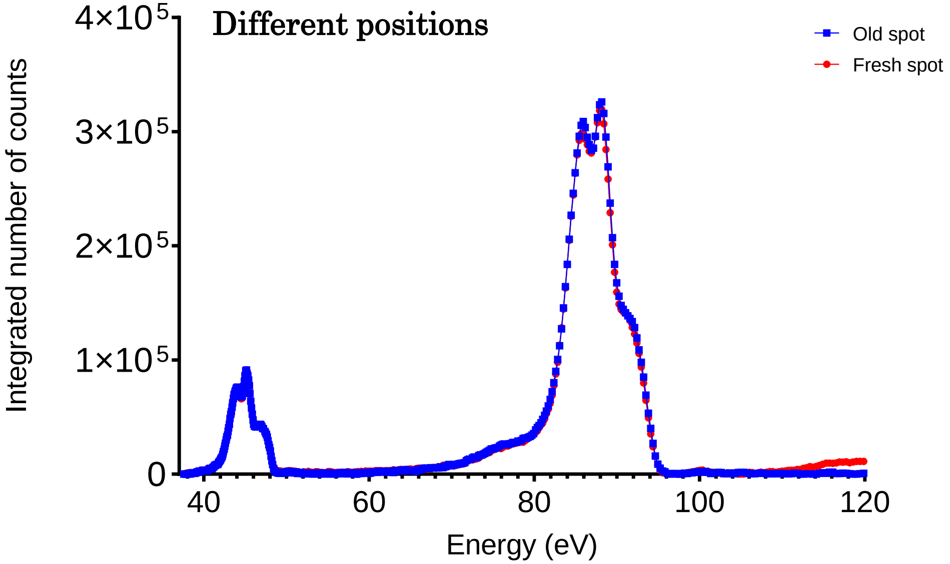
Silicon:

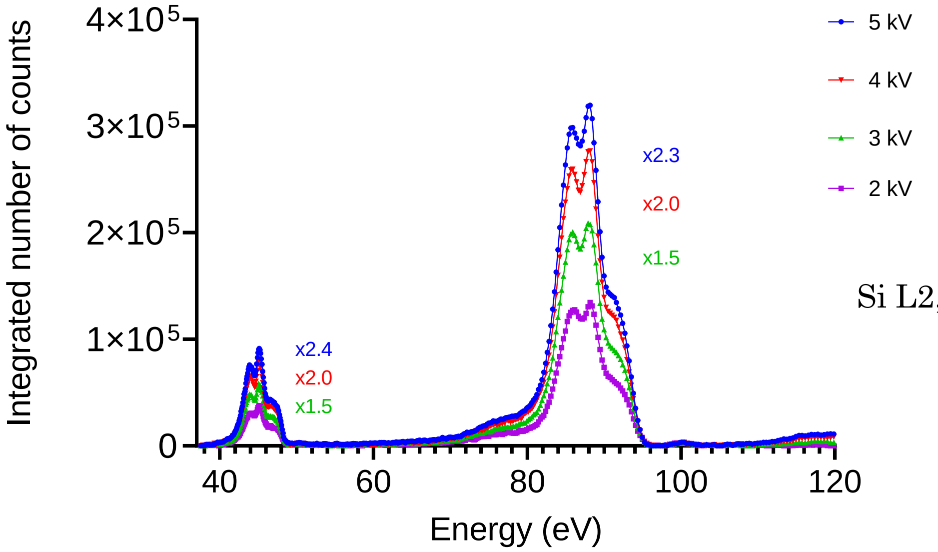
The emission spectrum of the pure Si sample with **different acquisition times**.



Si L2,3 with **different Beam currents**.

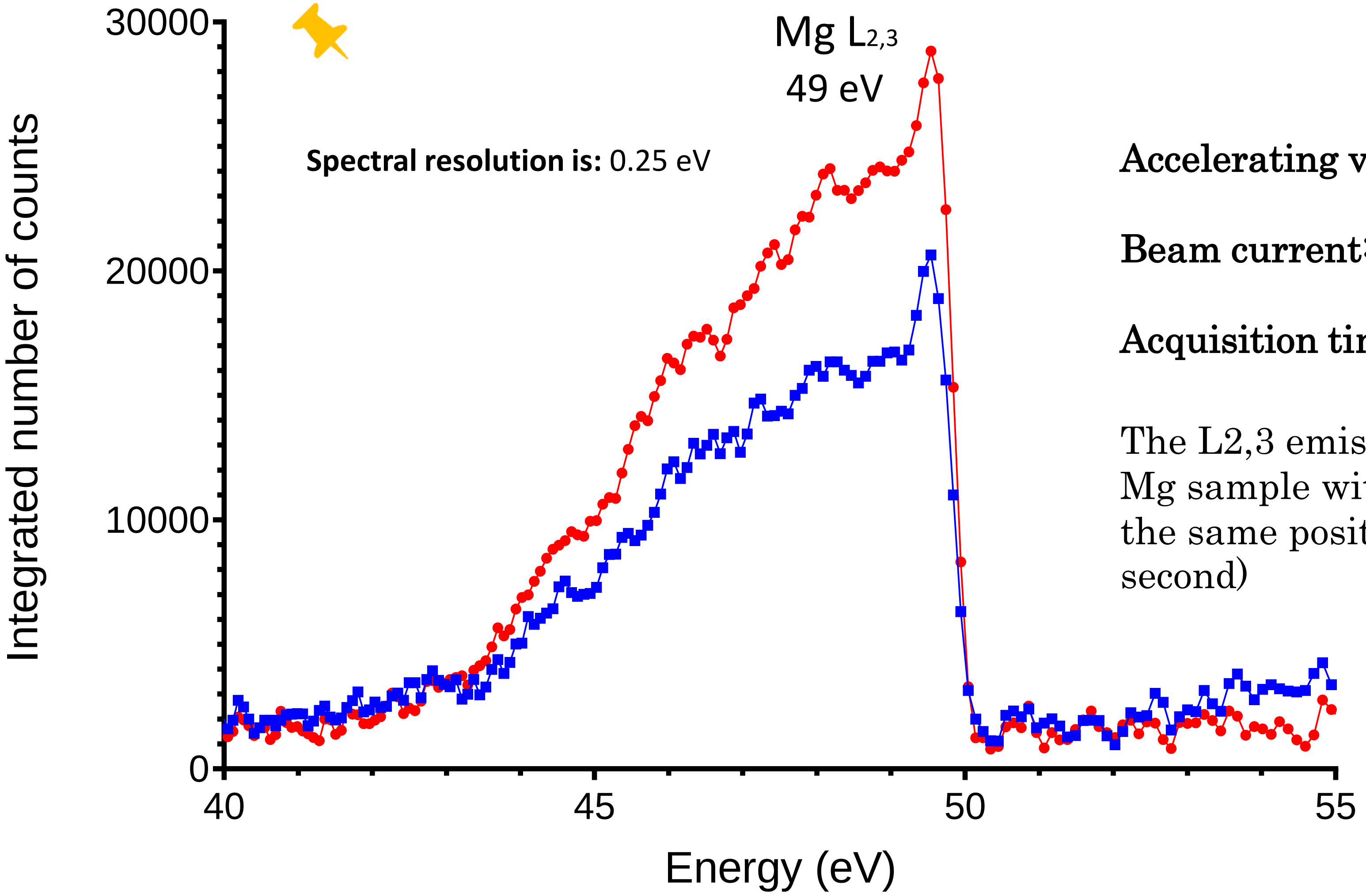


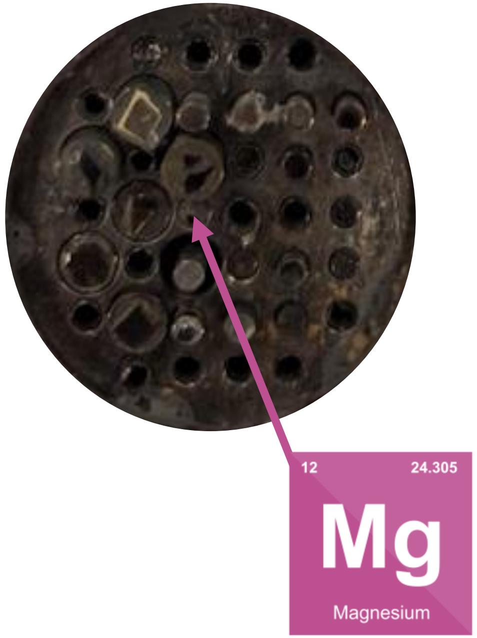




Si L2,3 with **acceleration voltages**.

Magnesium:





Accelerating voltage: 5 kV

Beam current: 100 nA

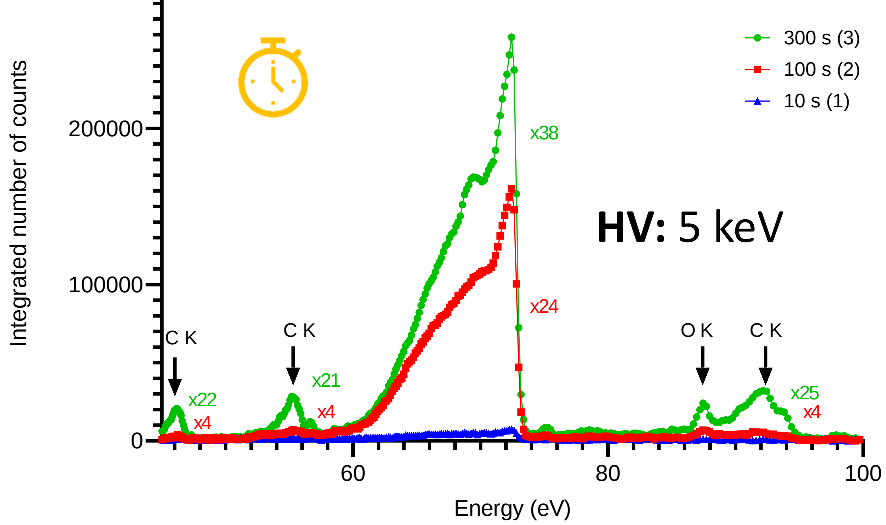
Acquisition time: 100 s

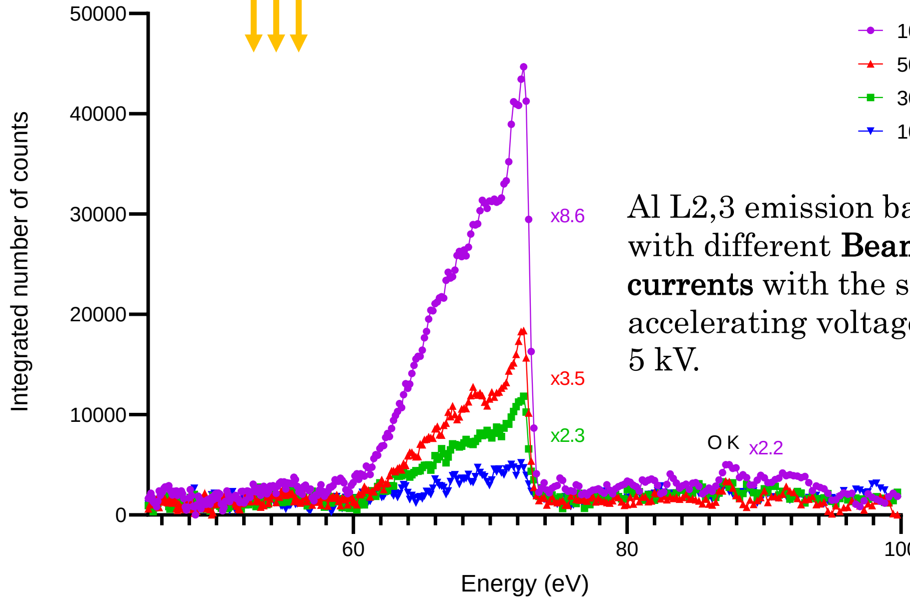
The L2,3 emission spectrum of the pure Mg sample with two measurements at the same position. (red first and blue second)

Aluminum:

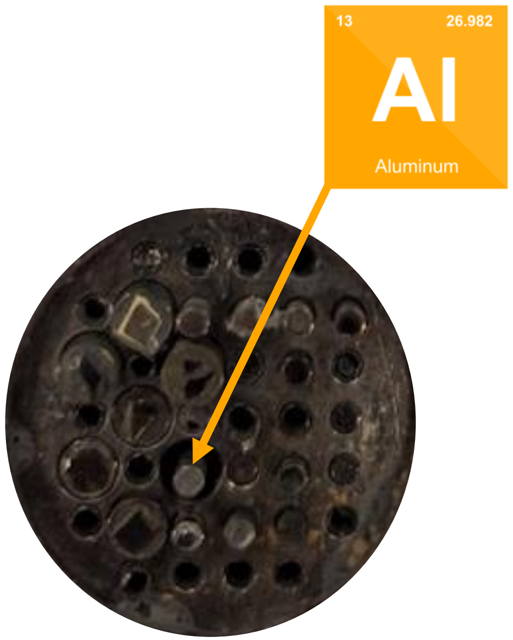
VB → 2p cores states

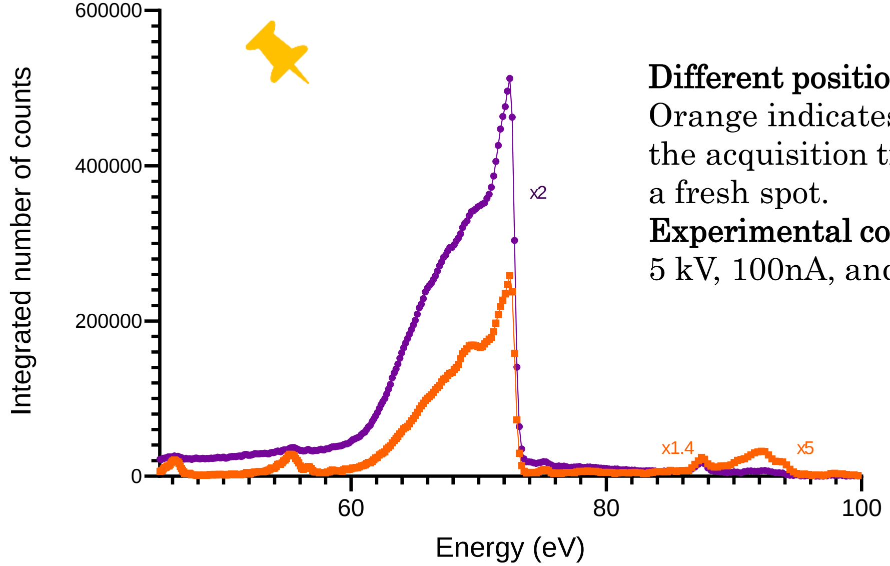
The emission spectrum of the pure Al sample with **different acquisition times**.





Al L2,3 emission band with different **Beam currents** with the same accelerating voltage of 5 kV.



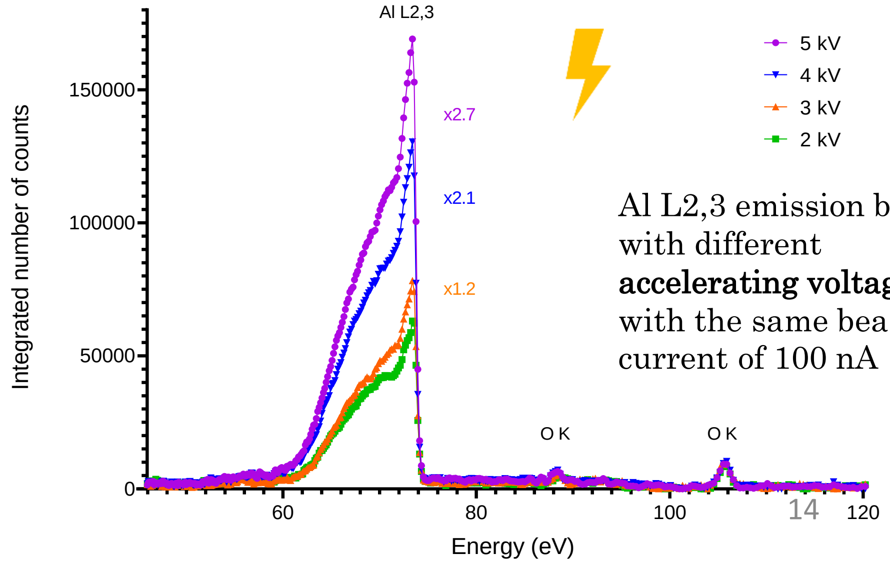


Different positions

Orange indicates the spot that was used during the acquisition time experiment and purple curve a fresh spot.

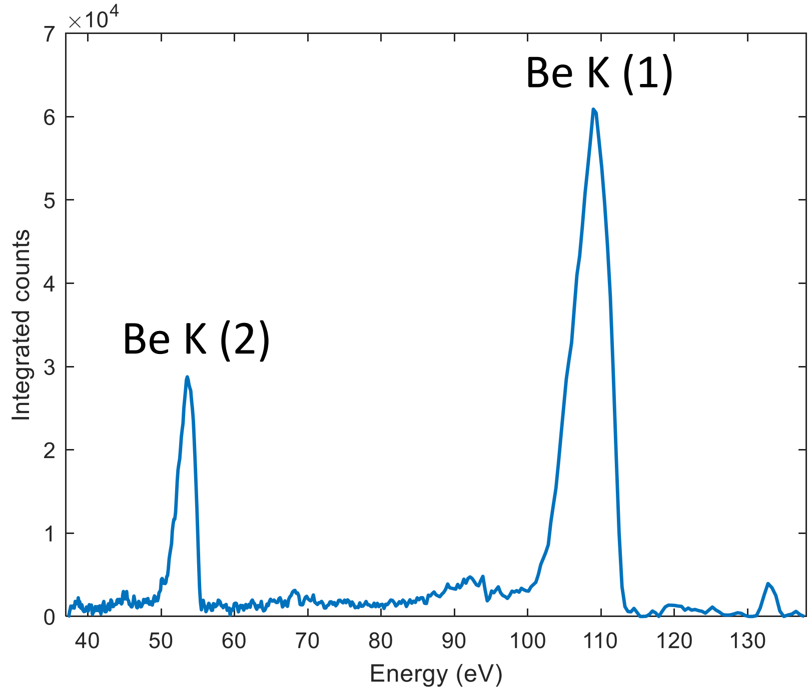
Experimental conditions:

5 kV, 100nA, and Acquisition time: 300s.



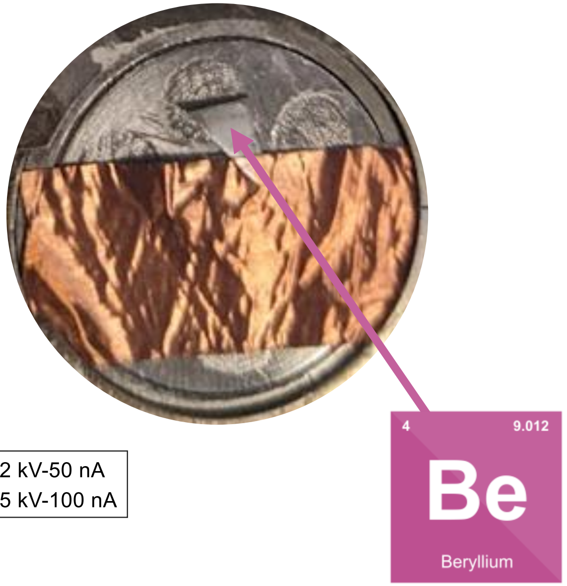
Al L2,3 emission band with different **accelerating voltages** with the same beam current of 100 nA

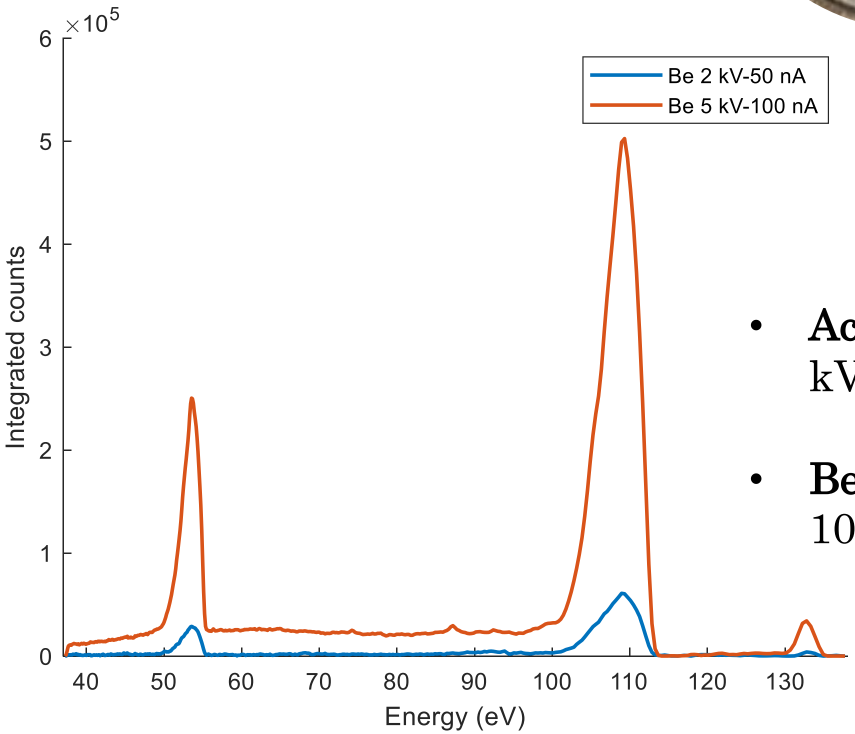
Beryllium:



- **Acceleration voltage:** 2 kV
- **Beam current** of 50 nA

- **Acquisition time:** 100s

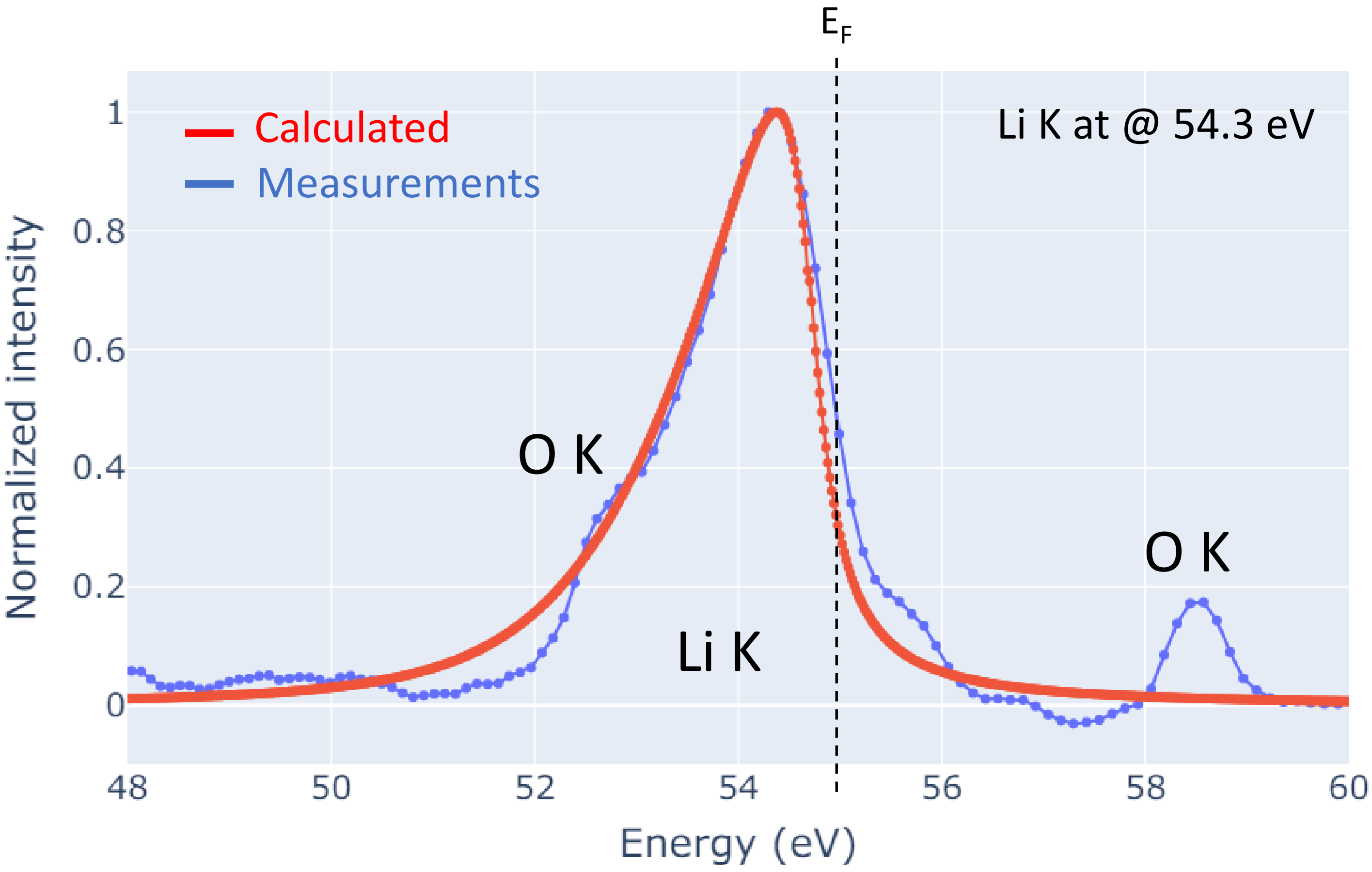




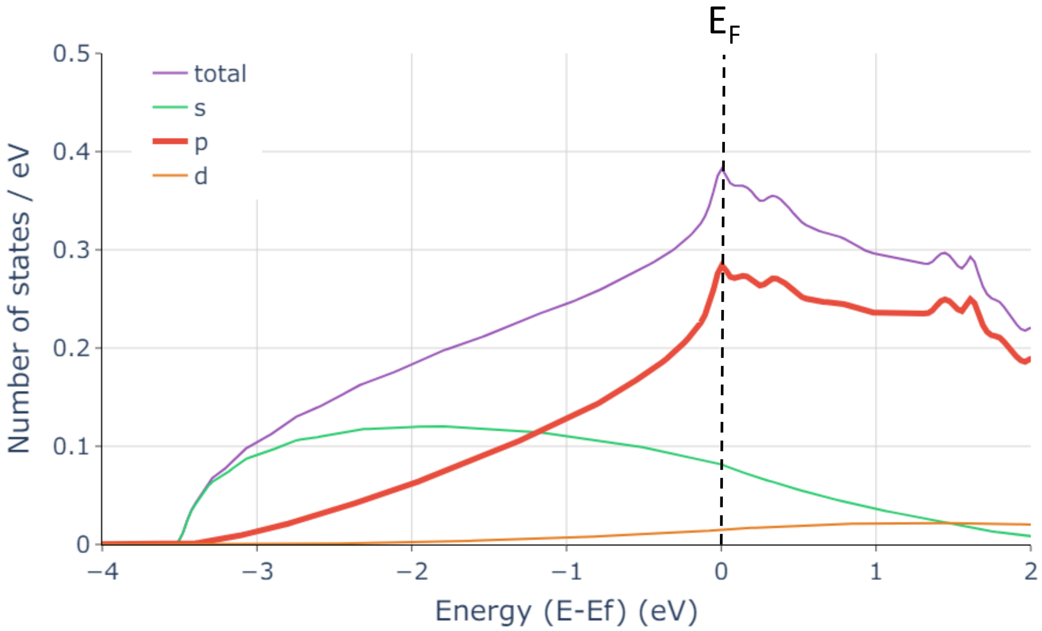
- **Acceleration voltage:** 2 kV, 5 kV
- **Beam current:** 50 nA, 100 nA

Li Metal:

The **shape** of the Li emission band is highly sensitive to the chemical state of the lithium atom.



***2p* valence states** transition to ***1s* core states** in lithium atoms and therefore the spectrum reflects the **distribution of the *p* states** within the valence band.

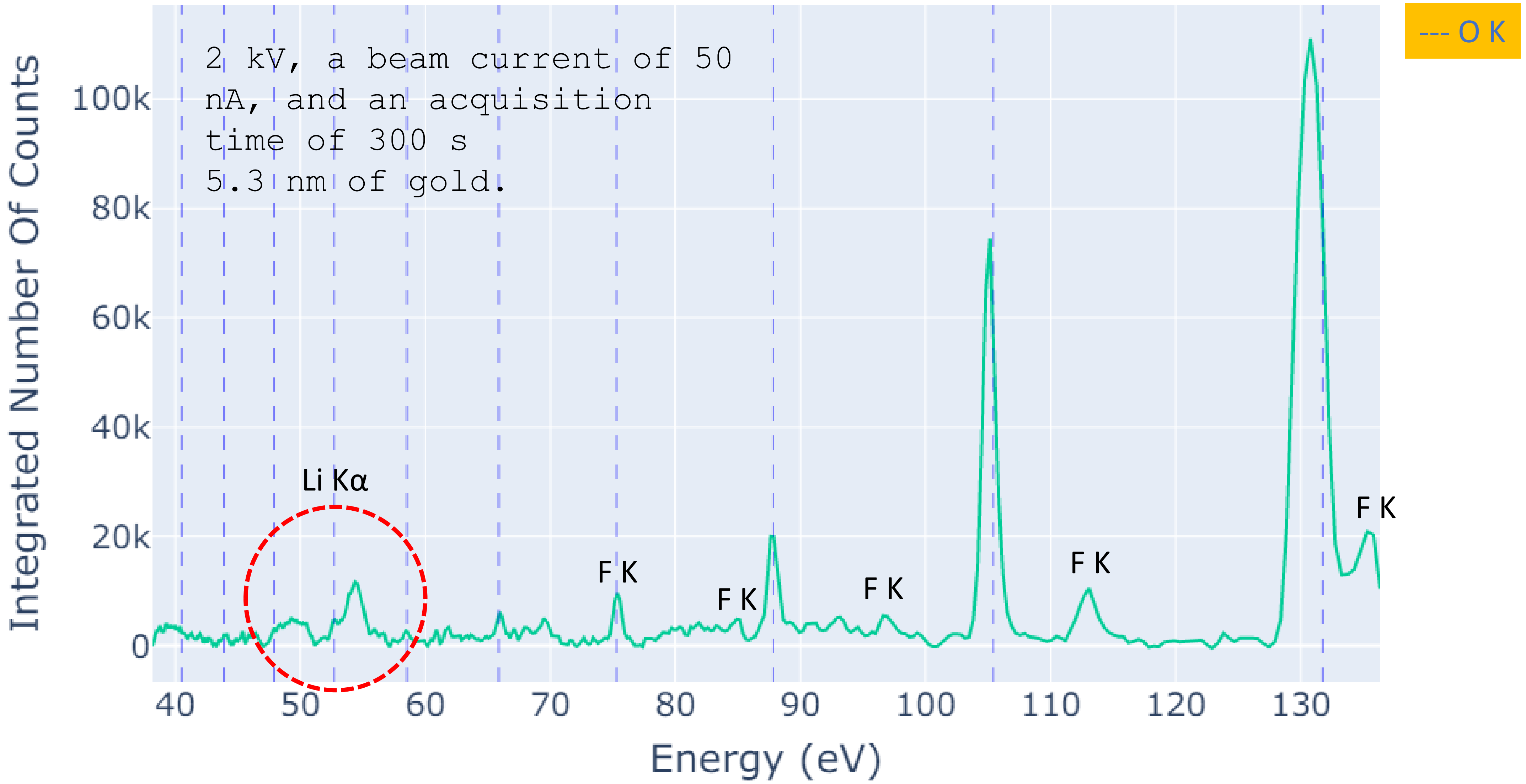


K. Hassebi, K. le Guen, N. Rividi, A. Verlaguet, and P. Jonnard, "Calculation of emission spectra of lithium compounds," *X-Ray Spectrometry*, vol. n/a, no. n/a, doi 10.1002/xrs.3329.

HV: 5 kV, Beam current: 100 nA, Acquisition time: 300 s

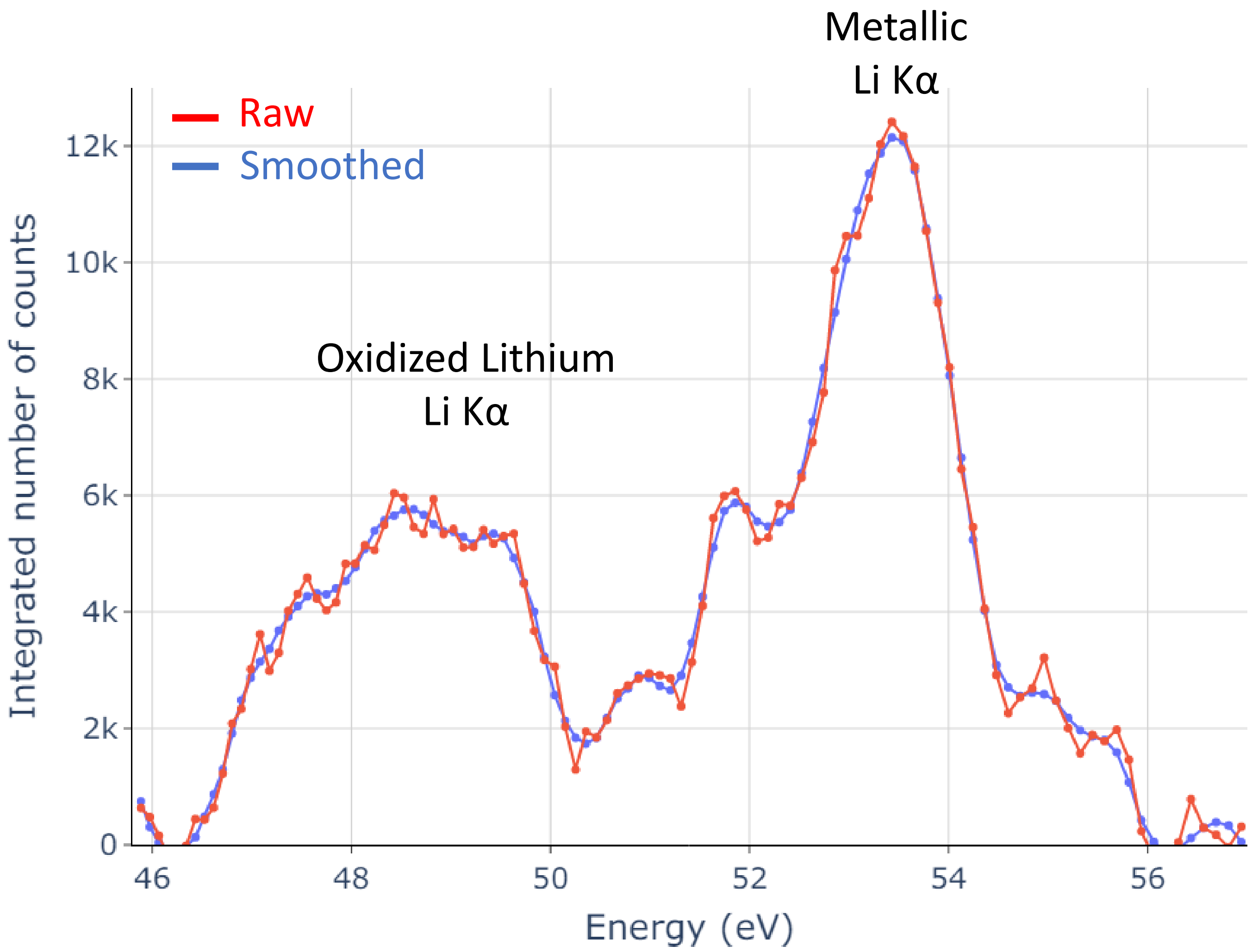
LiF:

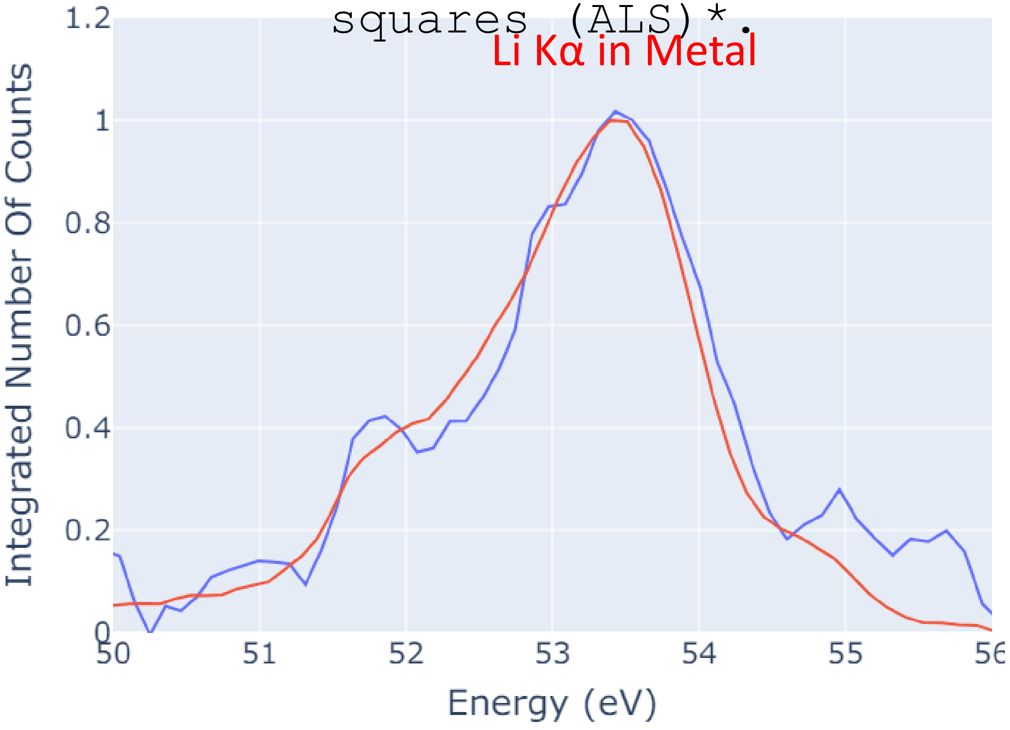
The fluorine is driven off the sample, leaving Li to accumulate in a layer on the surface.



LiF:

All spectra are smoothed by the **Savitzky-Golay** filter
The baseline was removed using Asymmetric least squares (ALS)*.

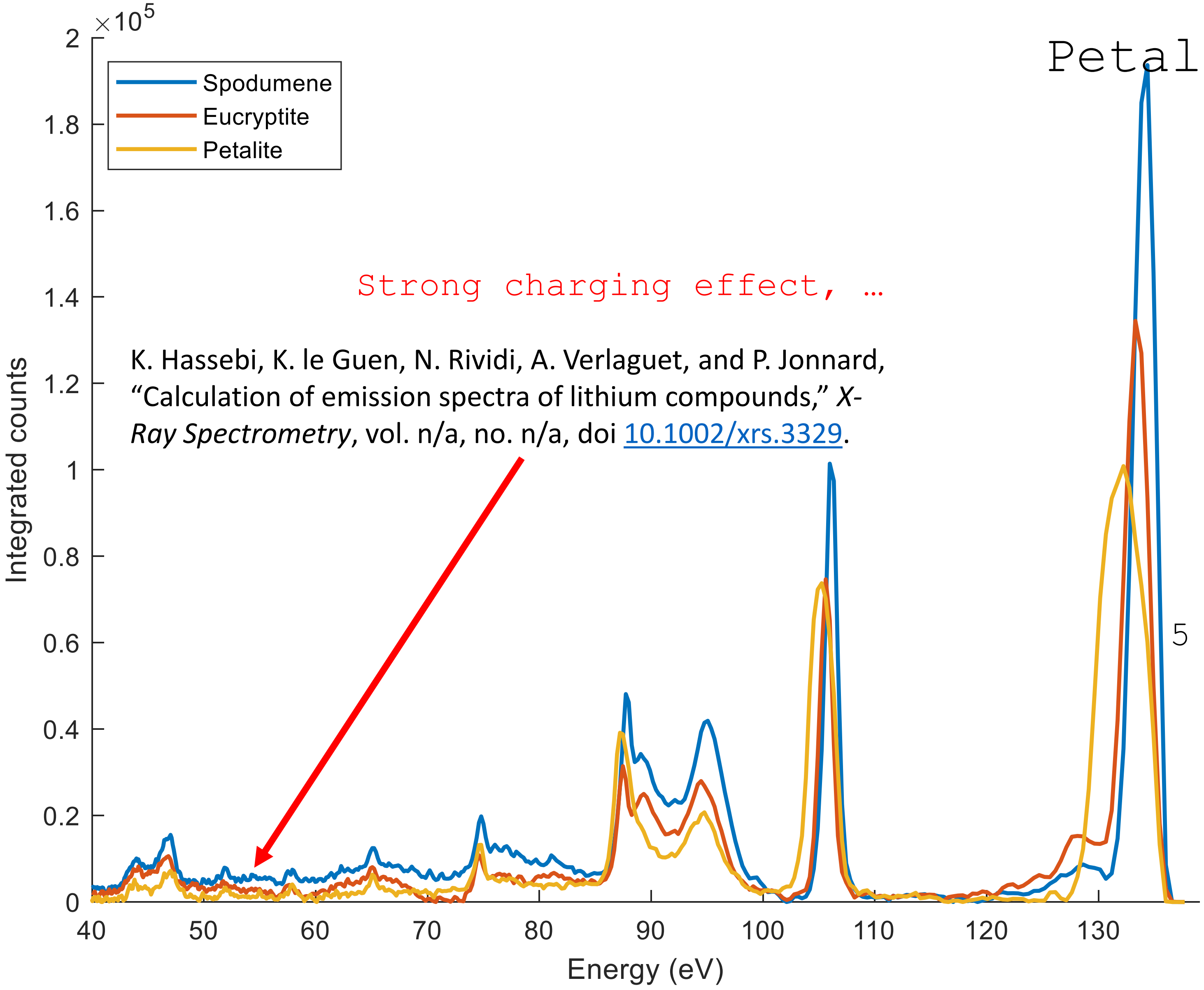


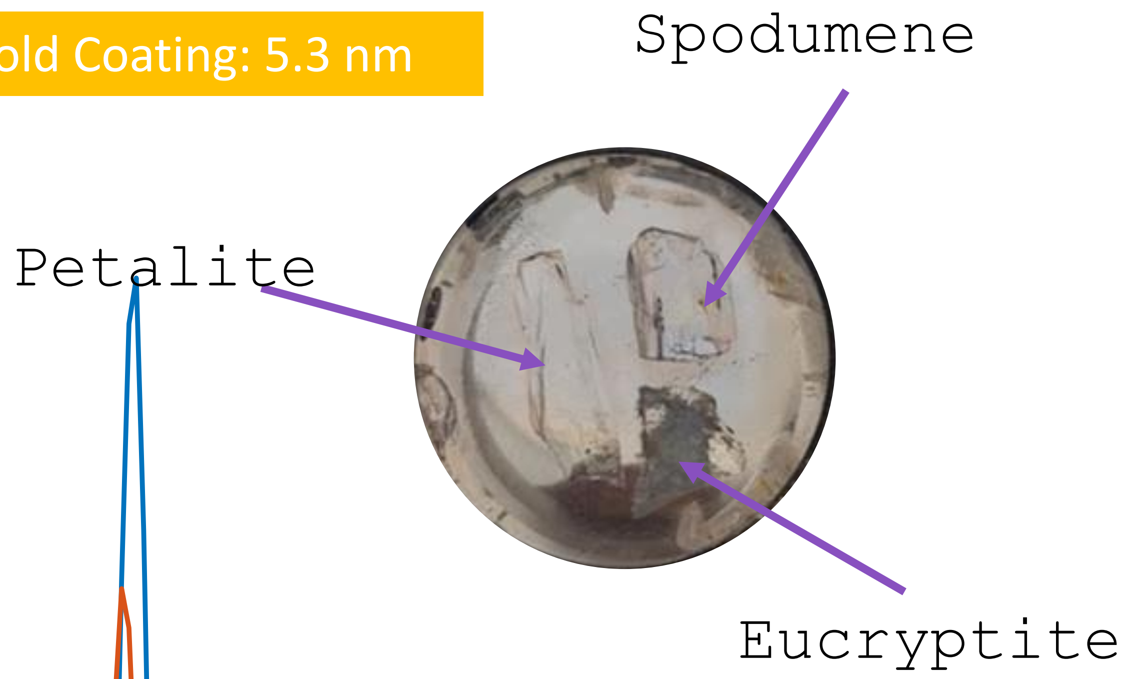


S.-J. Baek et al., *Analyst*, vol. 140, no. 1, pp. 250–257, 2015, doi: 10.1039/C4AN01061B.

Minerals:

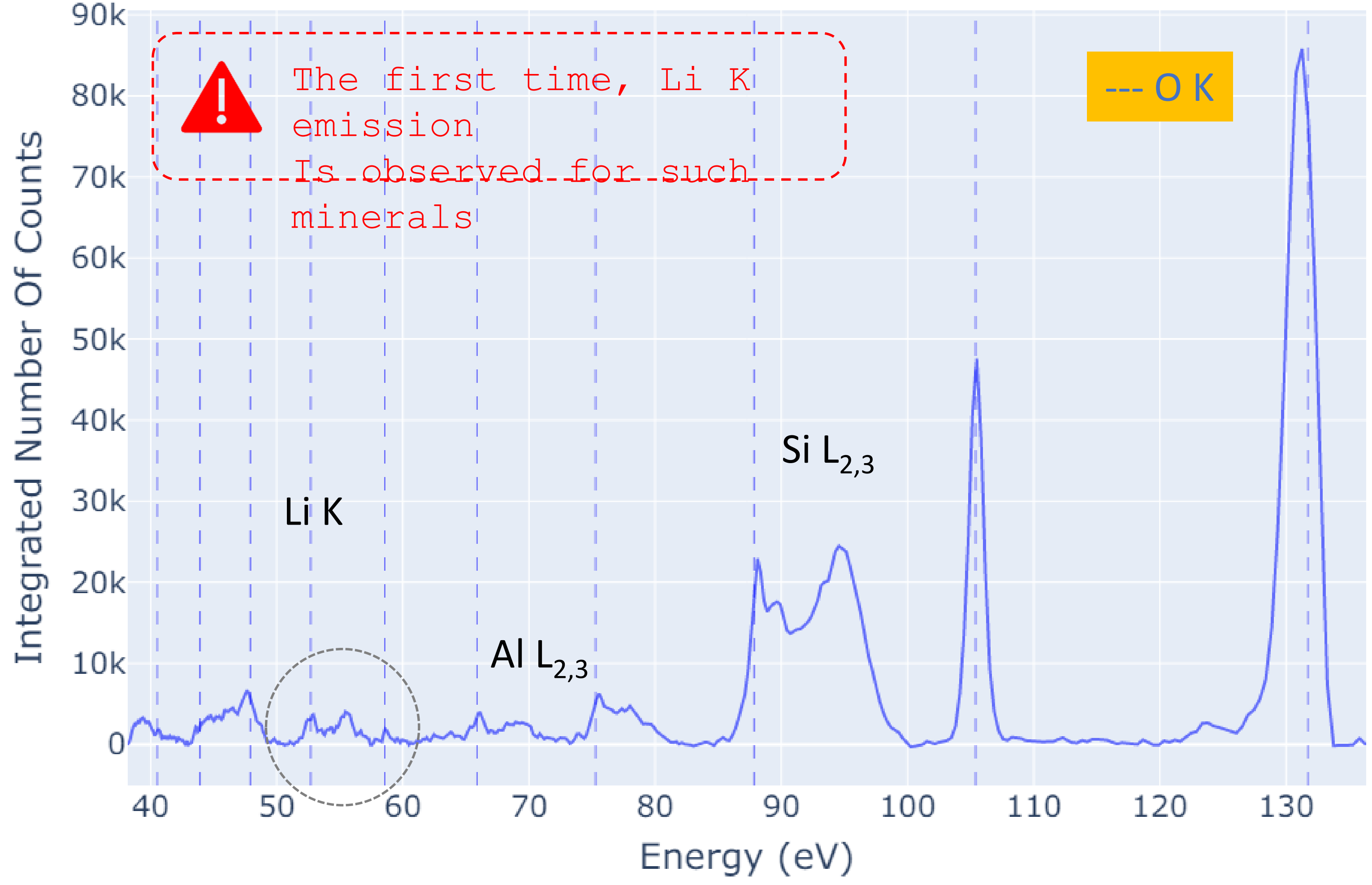
Gold Coating: 5.3 nm





5 kV, a beam current of 100 nA, and an acquisition time of 100 s

Lepidolite - spectrum:



2 kV, beam current of 100 nA, and an acquisition time of 300 s

It is the most abundant lithium-bearing mineral

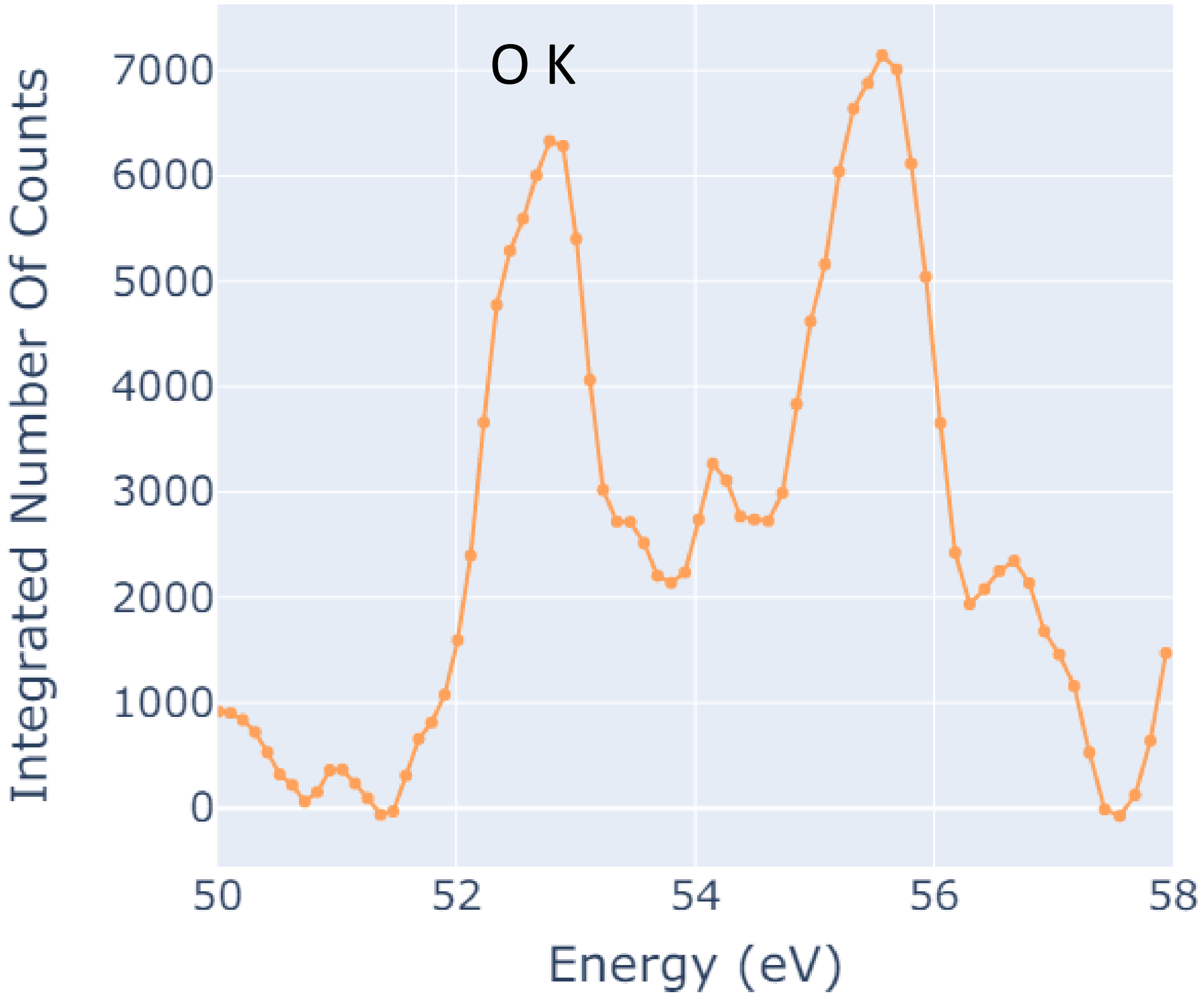
$K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$

- Solid-state electrolytes:

B. Wang *et al. ACS Appl. Energy Mater.* ,2019, [10.1021/acsaem.9b01046](https://doi.org/10.1021/acsaem.9b01046).

Lepidolite- Li K emission band:

A lower energy shoulder that is not present in the Li metal



Li K emission band in Lepidolite @ 55.4 eV (1.1 eV to Li metal)

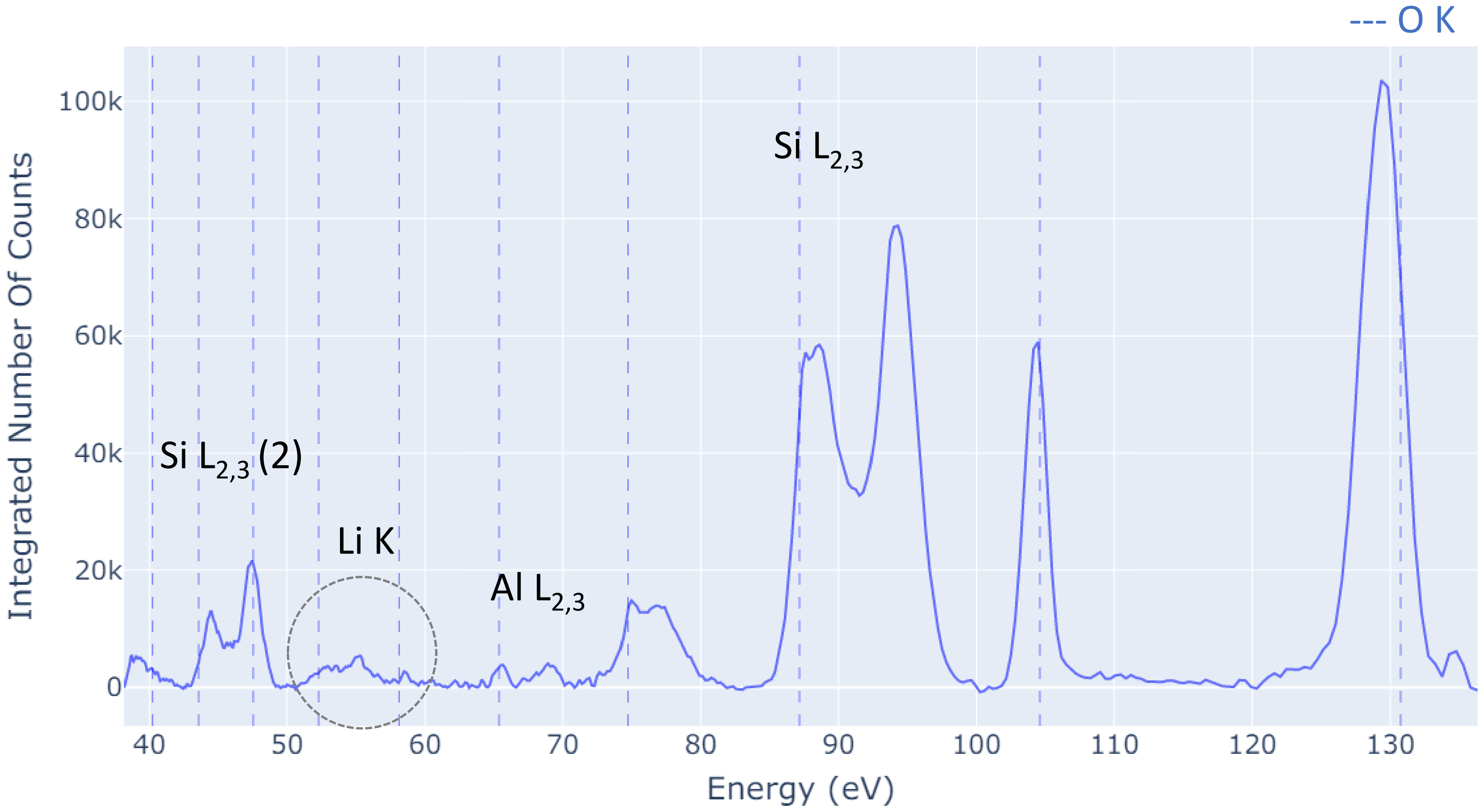
The first time, Li K emission
Is observed for such minerals

V, beam current of 100 nA, and an acquisition time of 300 s

Amblygonite:

Contains about 10% lithium, used as a source of lithium.

(Li,Na)$AlPO_4$(F,OH)

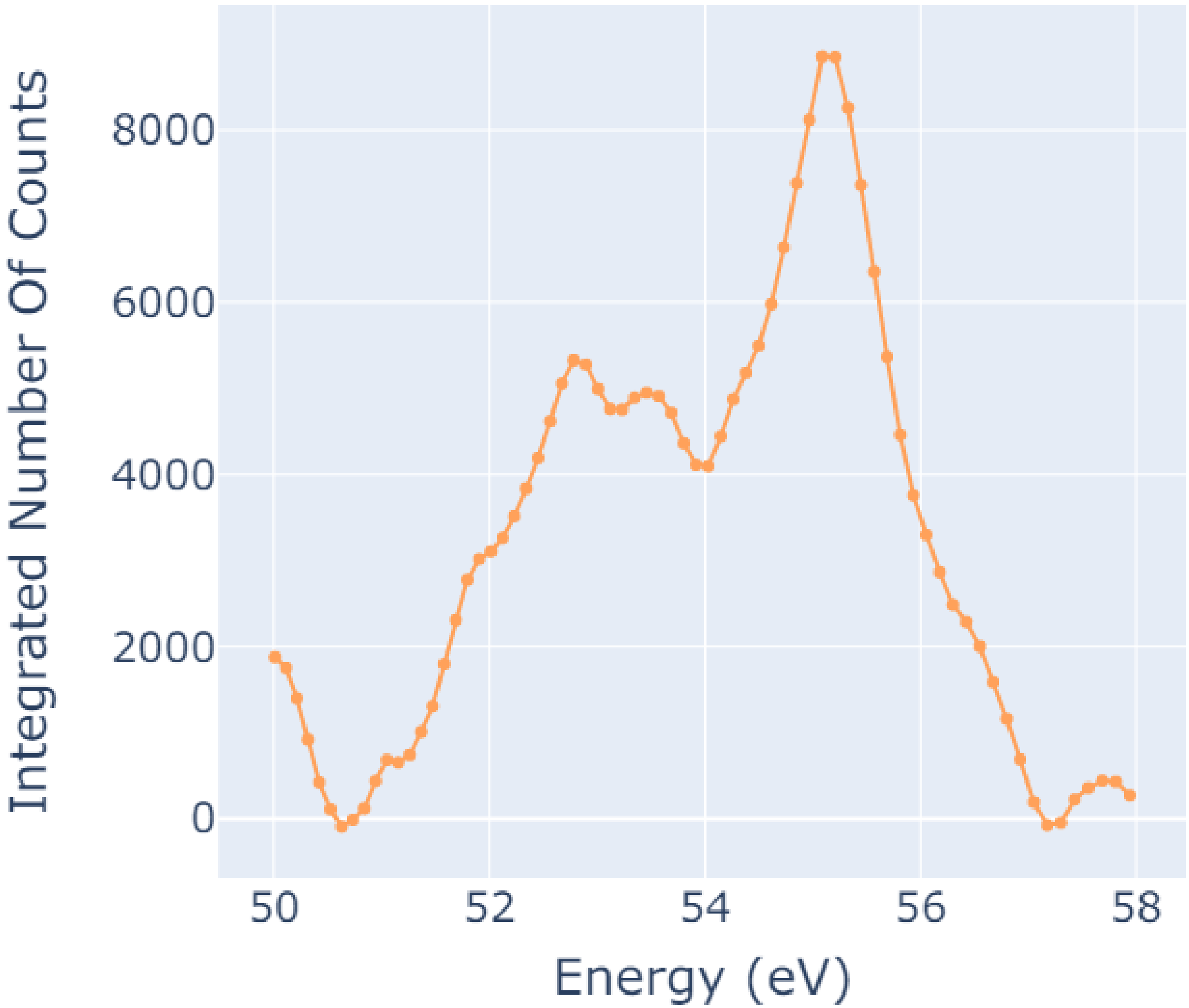


The first time, Li K emission Is observed for such minerals

Li K emission band in Amblygonite @ 55.2 eV (0.9 eV to Li Metal)

2 kV, beam current of 100 nA, and an acquisition time of 600 s (More acquisition time)

Amblygonite:



Li K emission band in Amblygonite @ 55.2 eV (0.9 eV to Li Metal)

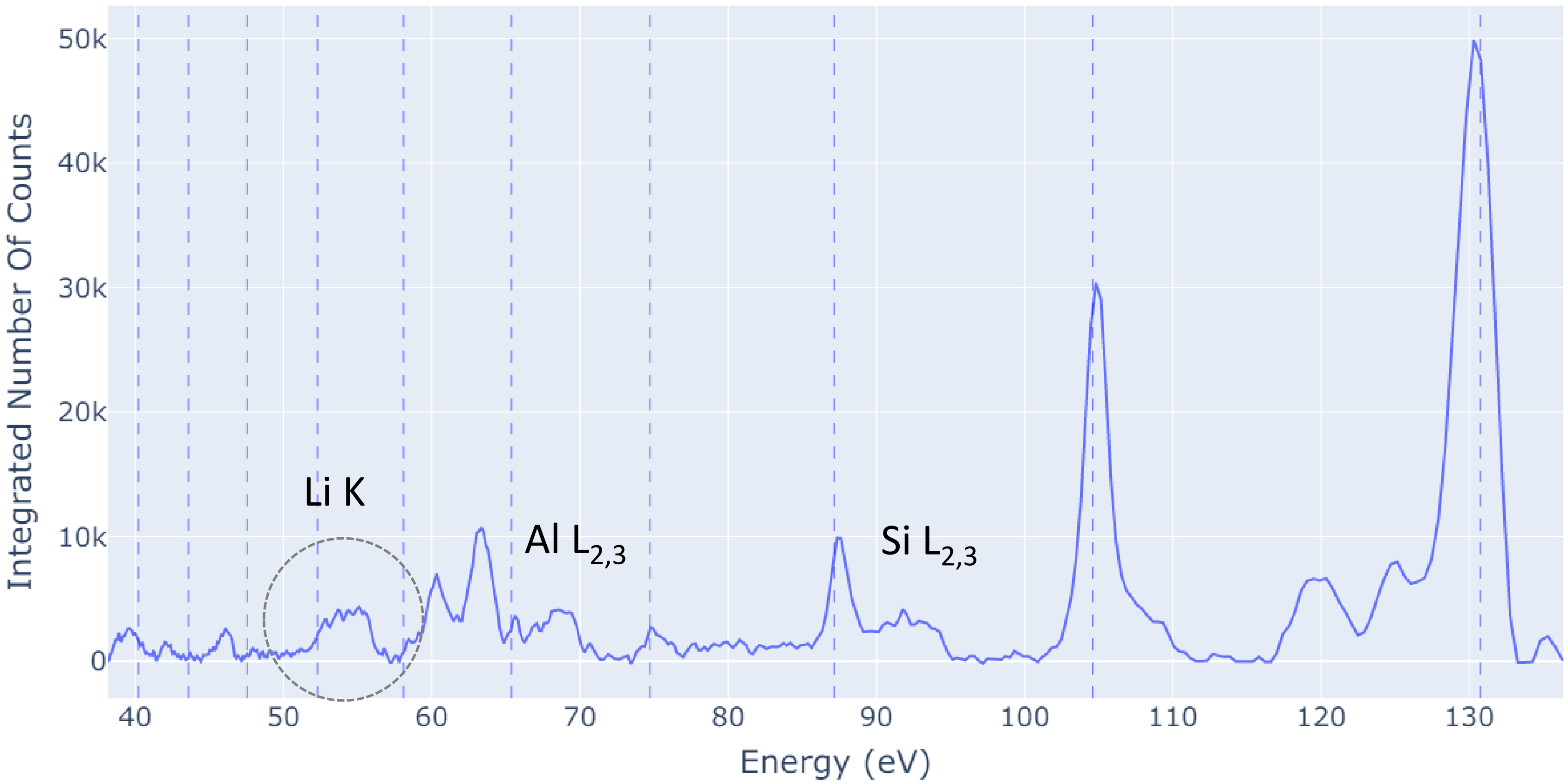
The first time, Li K emission Is observed for such minerals

beam current of 100 nA, and an acquisition time of 600 s

Bikitaite:

Lithium aluminum silicate

|Li(H_2O)| [$AlSi_2O_6$]

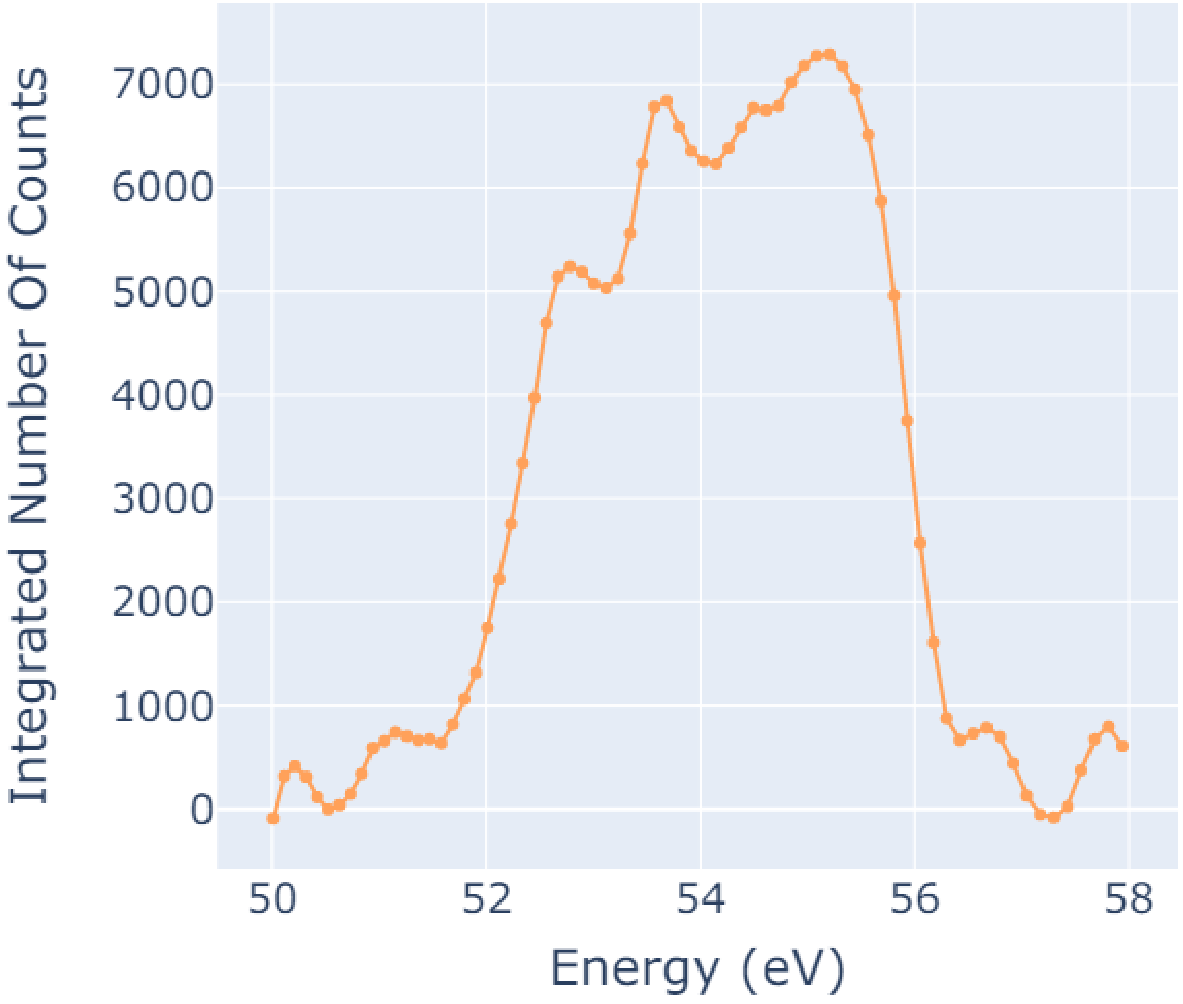


The first time, Li K emission
Is observed for such minerals

Li K emission band in Bikitaite
@ 55.2 eV (0.9 eV to Li metal)

3 kV, beam current of 200 nA, and an acquisition time of 200 s

Bikitaite:



Li K emission band in Bikitaite
@ 55.2 eV (0.9 eV to Li metal)

Li K emission bands:

Lepidolite @ 55.4 eV (1.1 eV to Li metal)

Amblygonite @ 55.2 eV (0.9 eV to Li Metal)

Bikitaite @ 55.2 eV (0.9 eV to Li metal)

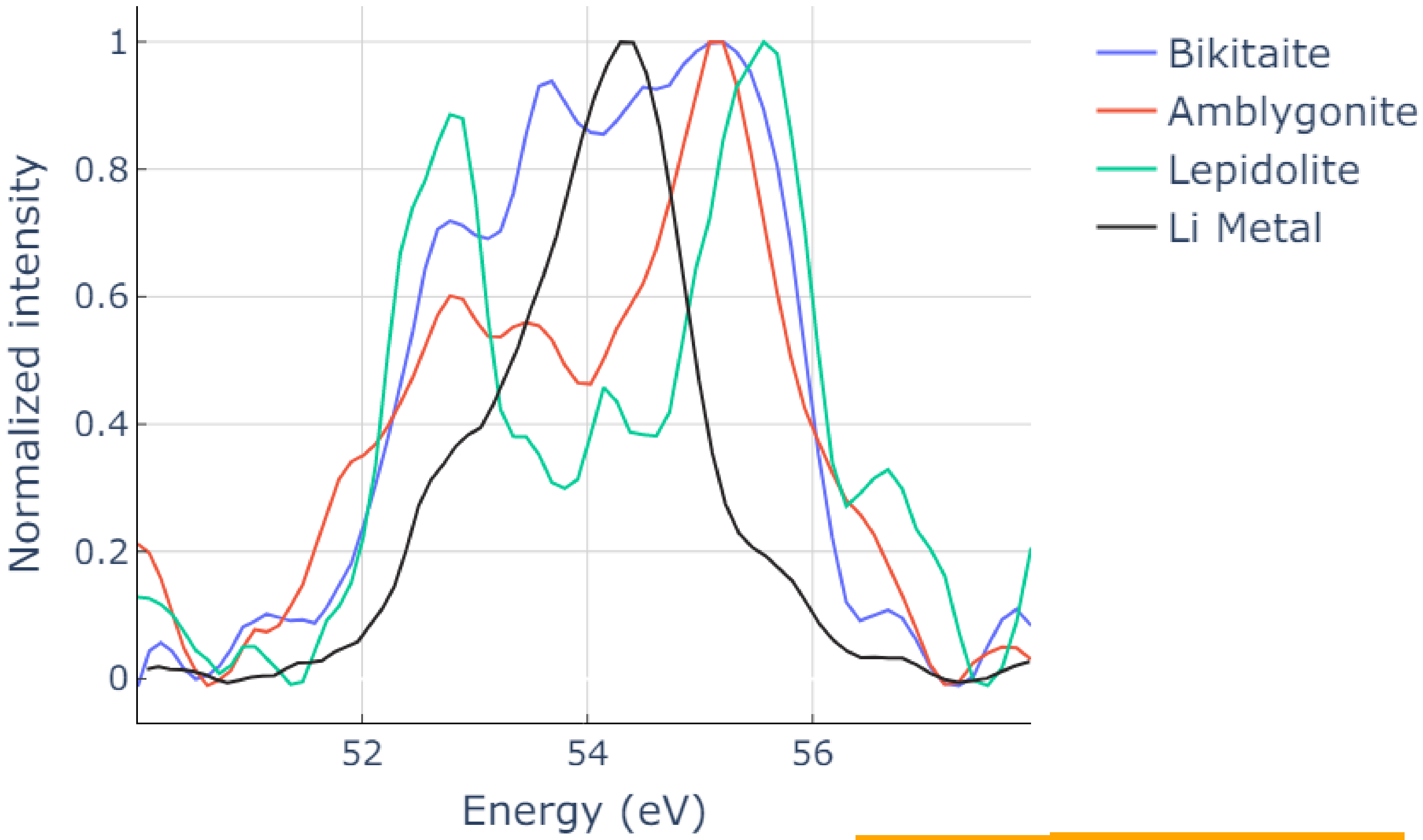


Figure: Comparison of Li K emission in the three minerals Bikitaite, Amblygonite, and Lepidolite

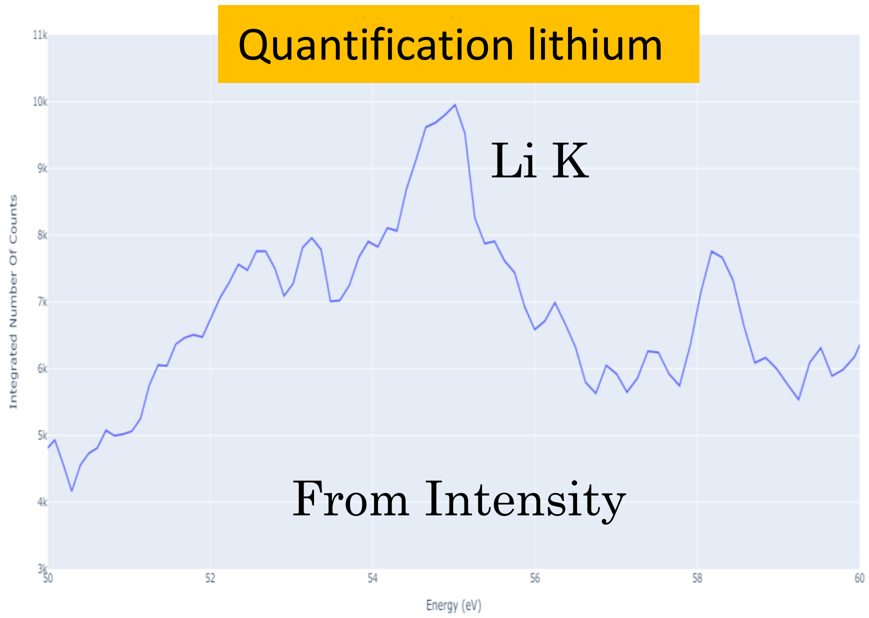
Li K sensitive to the chemical state of Li atoms

Conclusion:

⇒The first time that Li K is being reported in minerals

⇒X-ray **microanalysis is not yet applied** to the study of Lithium due to the hardship to detect lithium emission, especially in minerals!

⇒Quantifying lithium (To be achieved we need to develop and validate the quantification model on standard samples with known composition).



Further **optimizations of analysis conditions** are needed in order to **improve the emission band statistics** and **increase the signal-to-noise ratio.**

↓

C_i Weight fraction of the element of interest (Li)

Acknowledgement:

Under the supervision of:

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Dr. Nicolas **RIVIDI**

Dr. Anne **VERLAGUET**

Special thanks to all SQLX team:

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- Vita **Ilakovac**
- Marie **Christine Lepy**
- Michel **Fialin**