

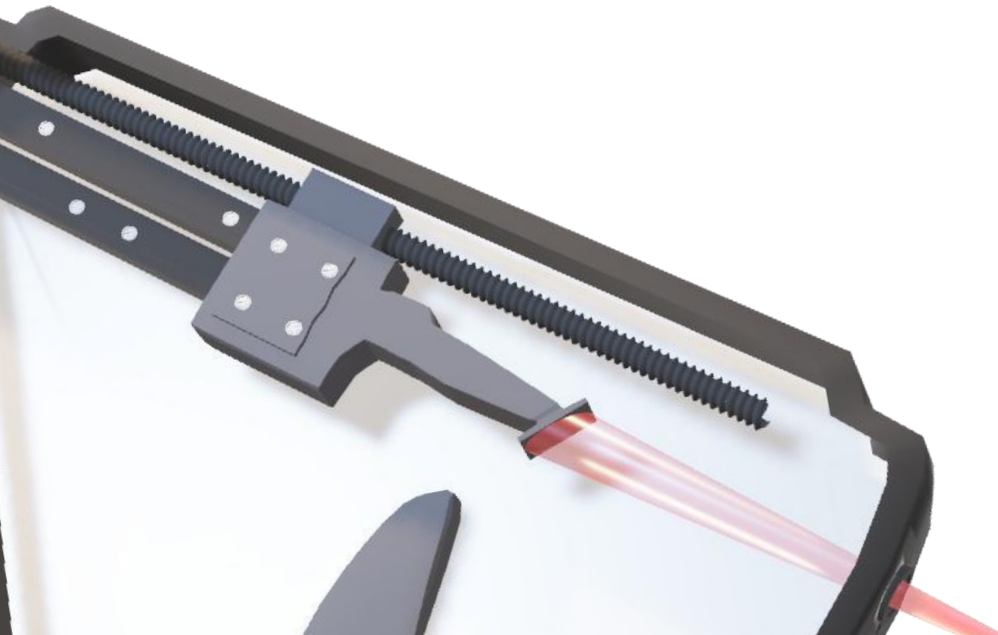
# Detection of Li K emission in different lithium compounds

Khalil HASSEBI

2<sup>nd</sup> year Ph.D. student

*LCPMR, Sorbonne University*

*Paris, France*



# Summary:



X-ray emission spectroscopy

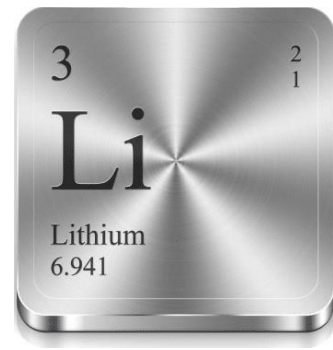


Experiment: EPMA, RZP



Results: Spectra of Li

# Lithium



## Batteries

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

Growing hybrid and electric-vehicle market is raising demand.



## Research

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



## Geology

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



## Medication

Used to treat bipolar disorders



## aeronautics

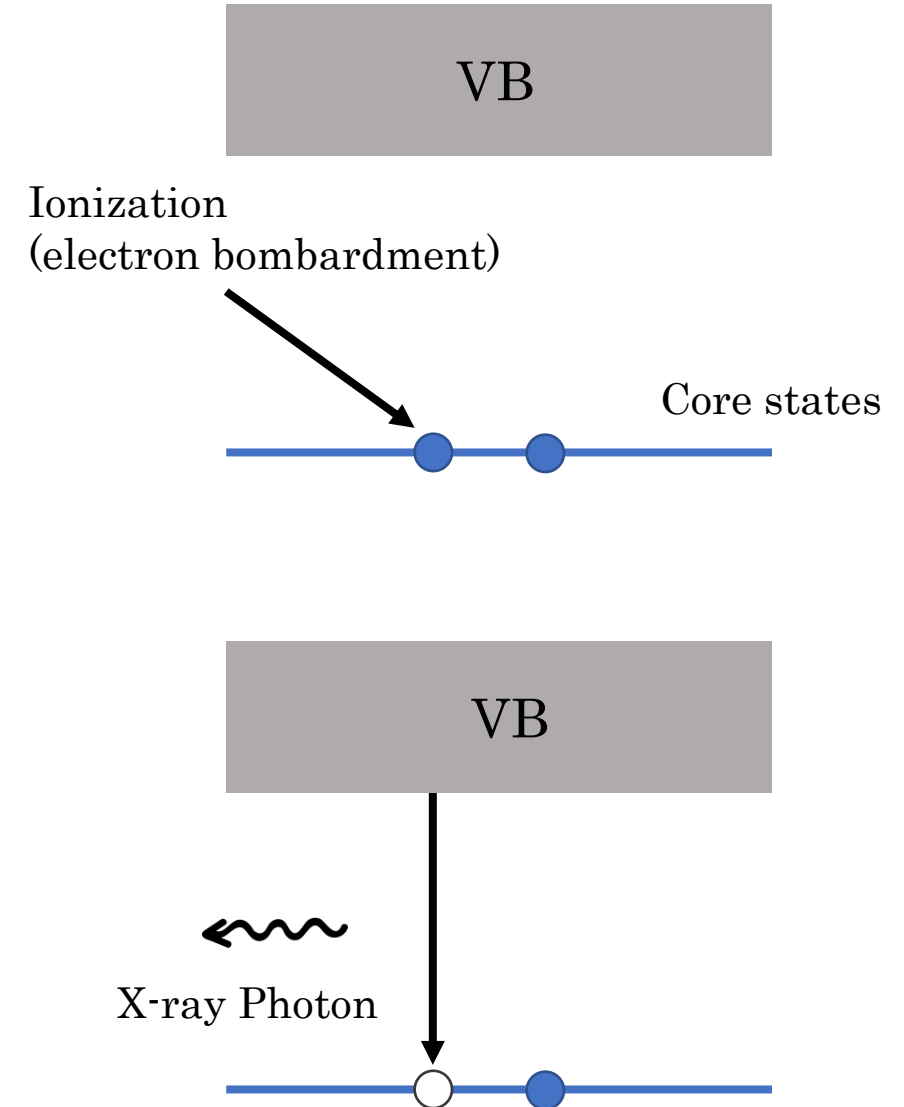
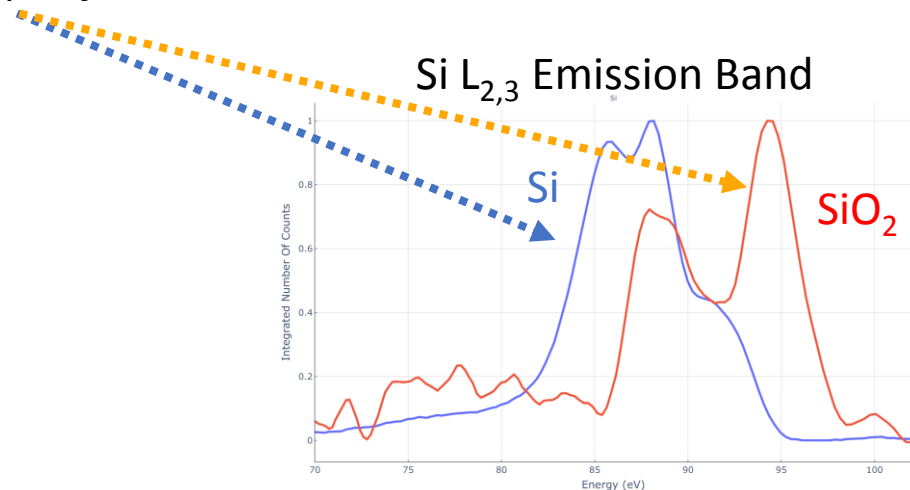
With light Al/Li alloys (wing Airbus A380...)

\*S.H. MOHR AND OTHERS, MINERALS 2012



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**.

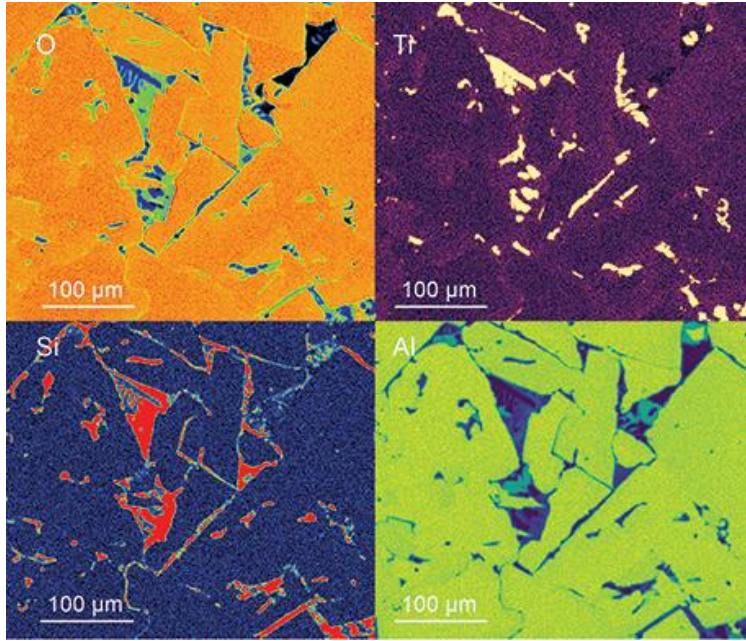
→ X-ray emission spectroscopy (XES) provides a means of **probing the partially occupied density of electronic states** → *element-specific* and *site-specific*.



# Electron Probe Microanalyzer (EPMA):

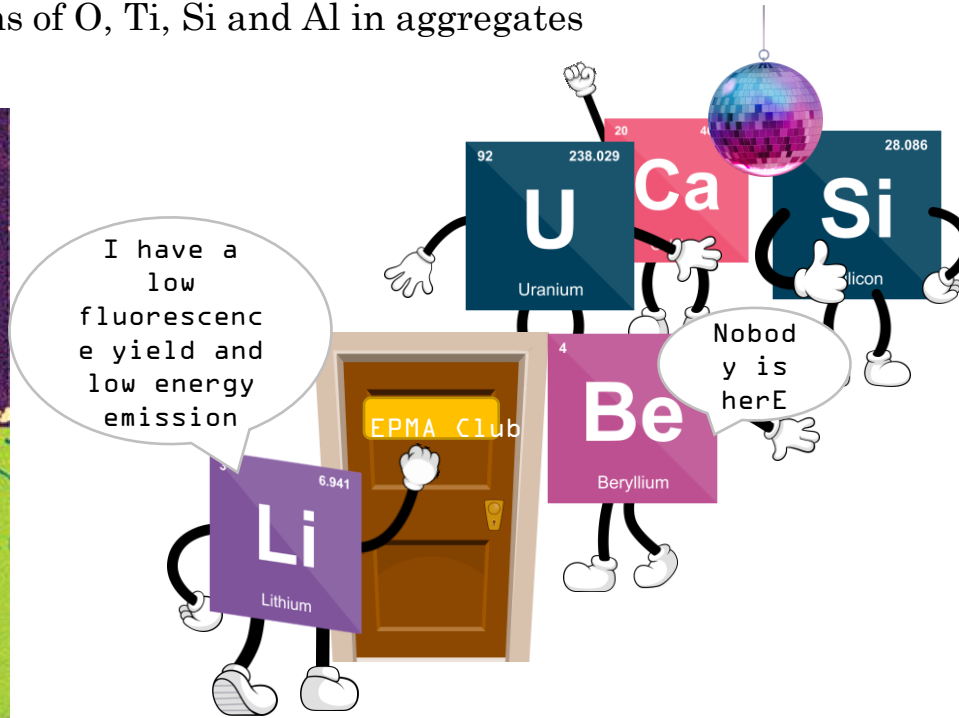


WDS X-ray maps showing the distributions of O, Ti, Si and Al in aggregates of hopper (skeletal).



T. Murphy et al. Electron Probe Microanalysis 2<sup>nd</sup> edition.

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



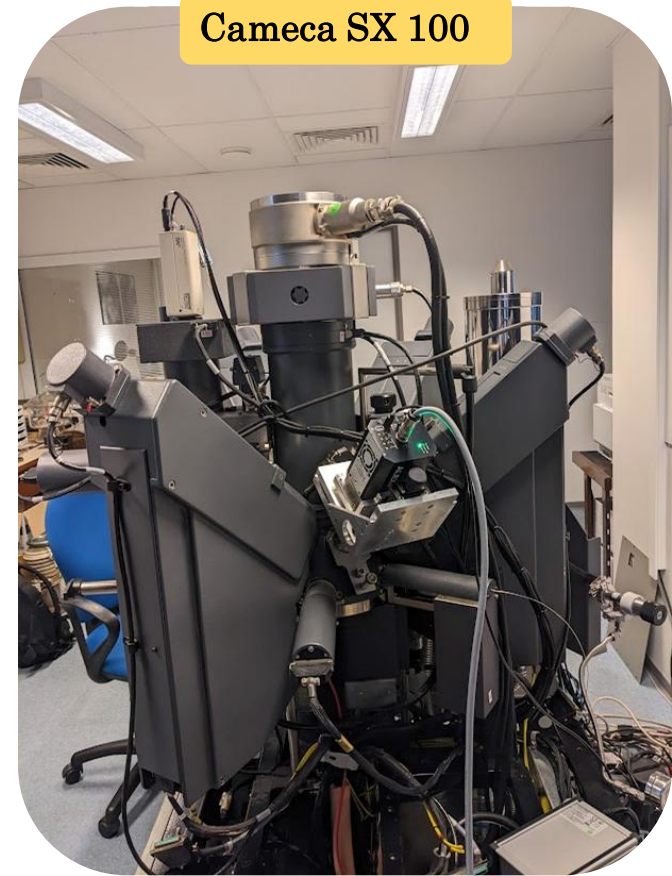
No accessible for Li!



- Low fluorescence yield  $1.6 \cdot 10^{-4}$
- Low energy ( $\sim 50$  eV) and high self absorption



Would it be possible to open this door for Li?

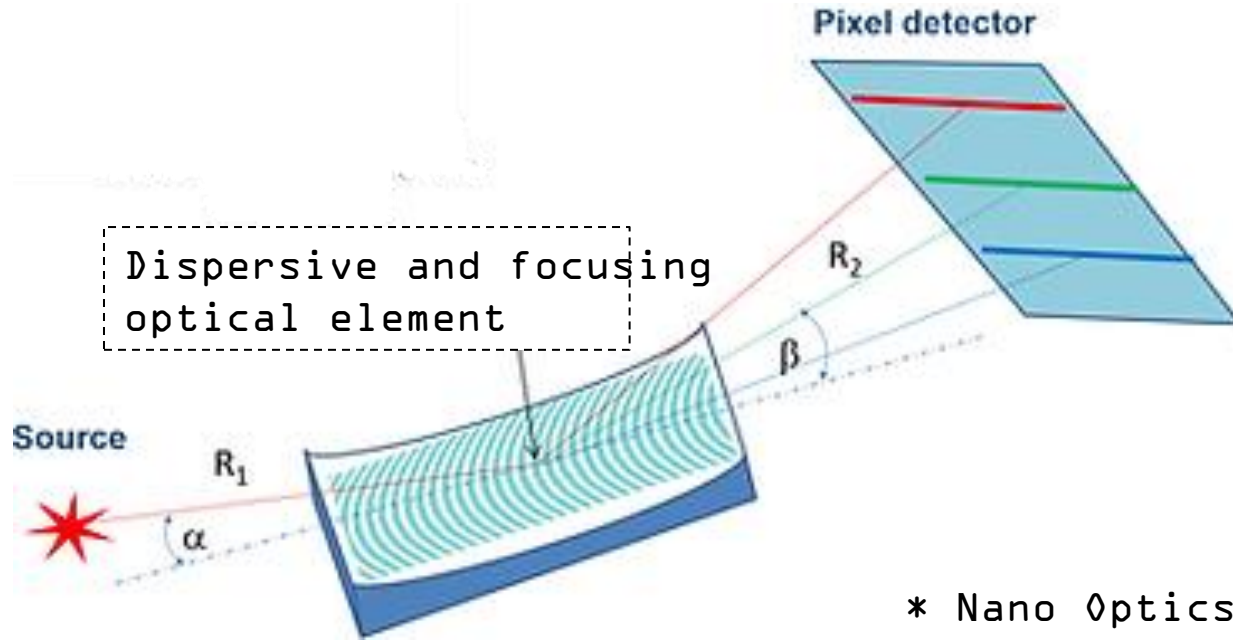


Cameca SX 100

# Reflection zone plates:



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

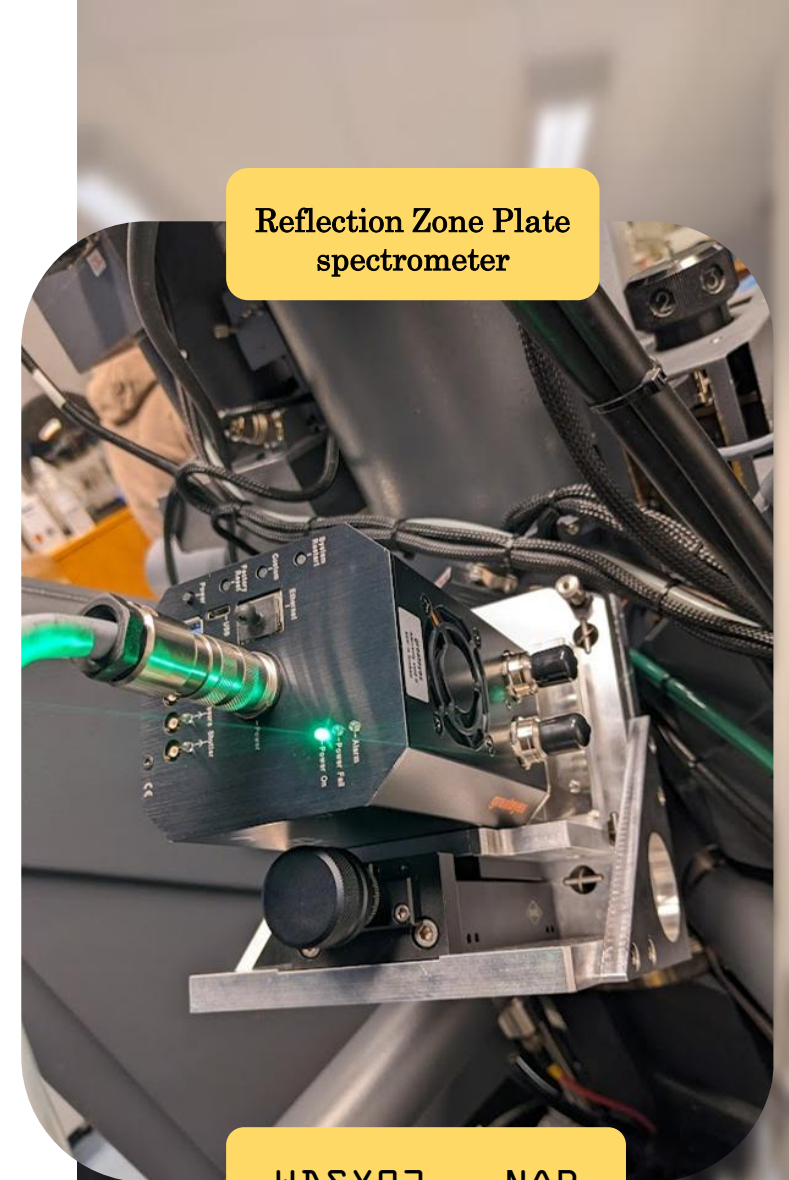


\* Nano Optics Berlin

**Grating formula:**

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

We have a spectral resolution:  
**0.5 eV at the Al L<sub>2,3</sub> edge**



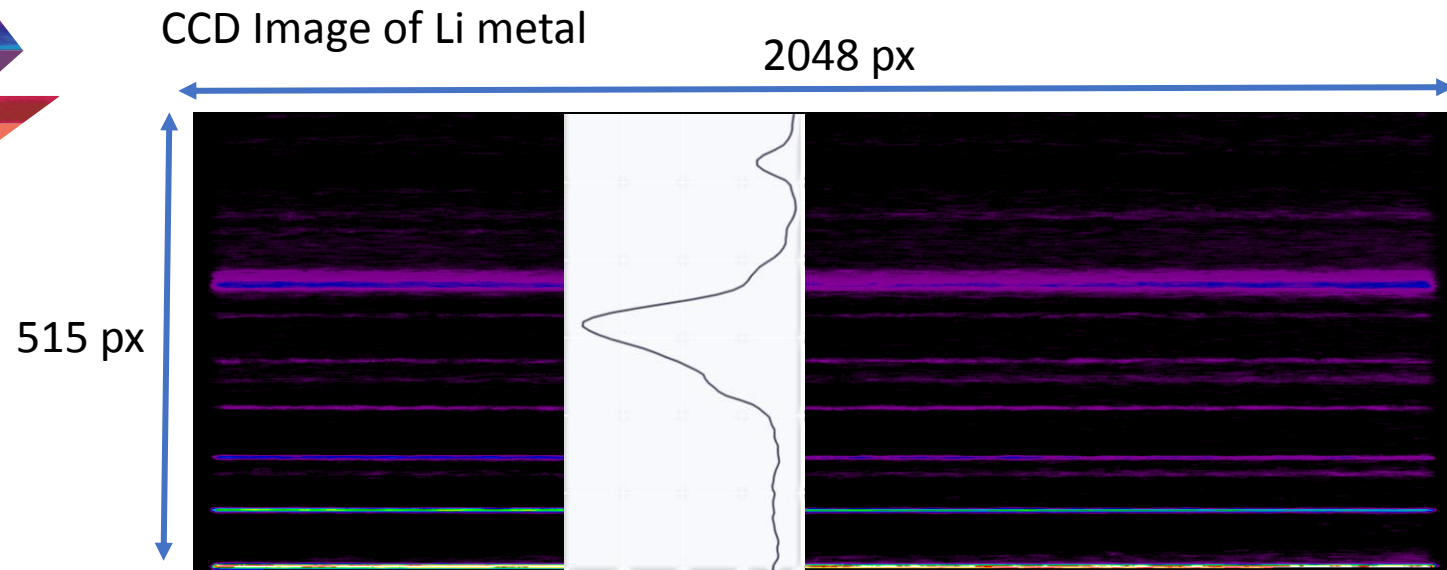
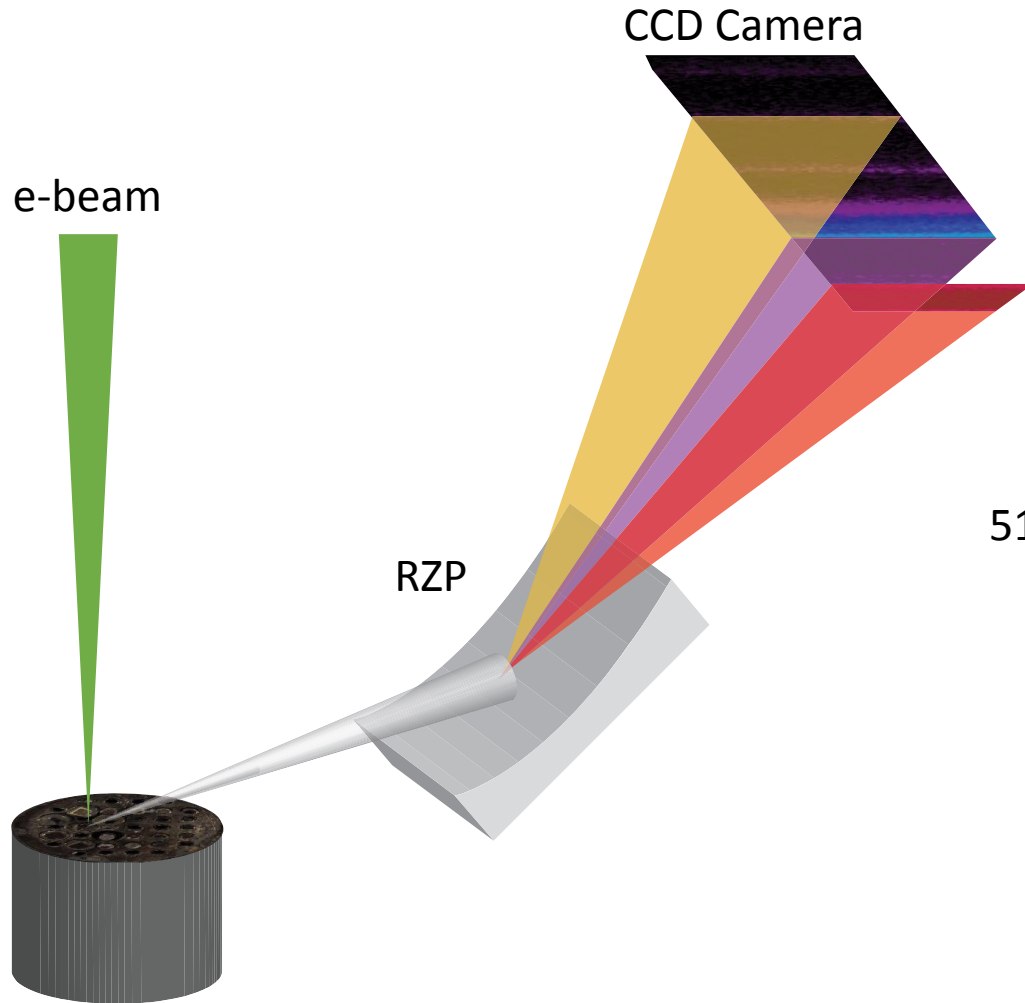
Reflection Zone Plate spectrometer

WDSX02 - NOB

RZP:



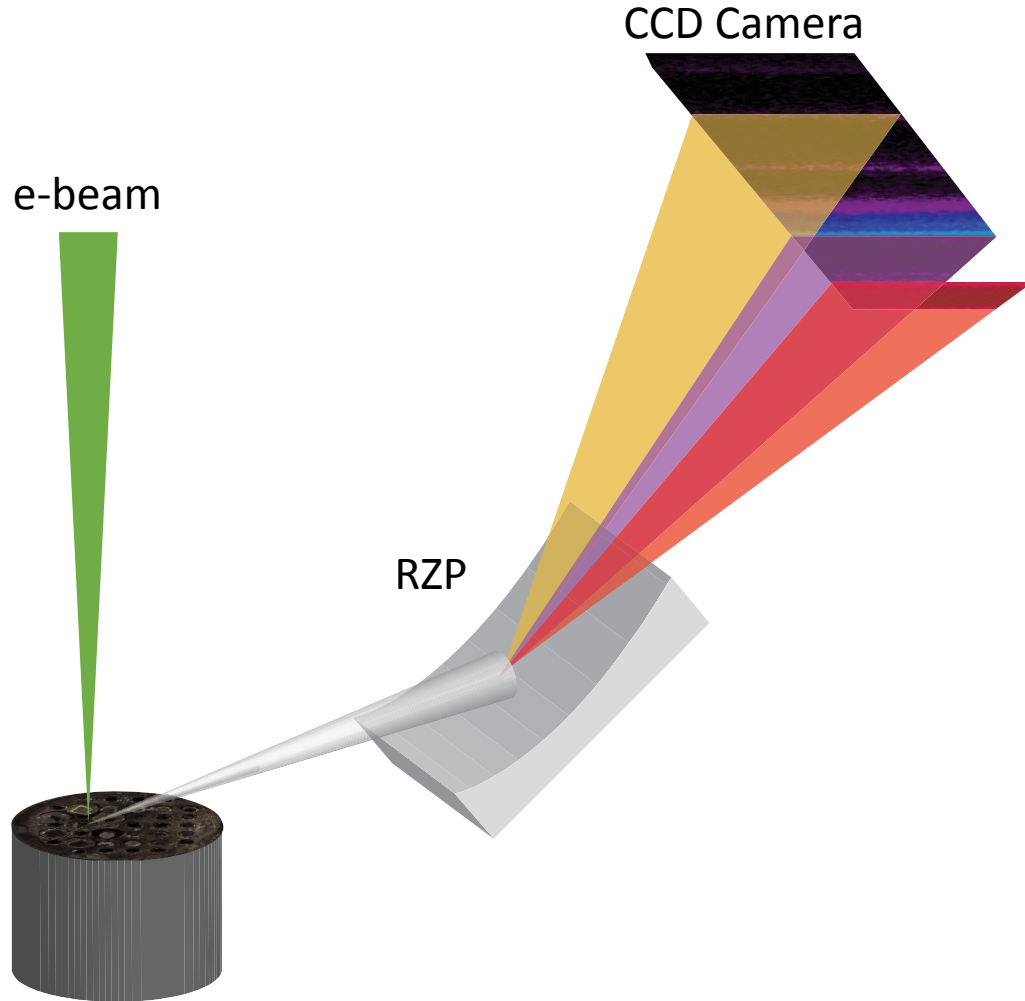
**HV: 5 kV, Current: 299 nA, Acquisition time: 300 s,**  
**Resolution: 0.5 eV**



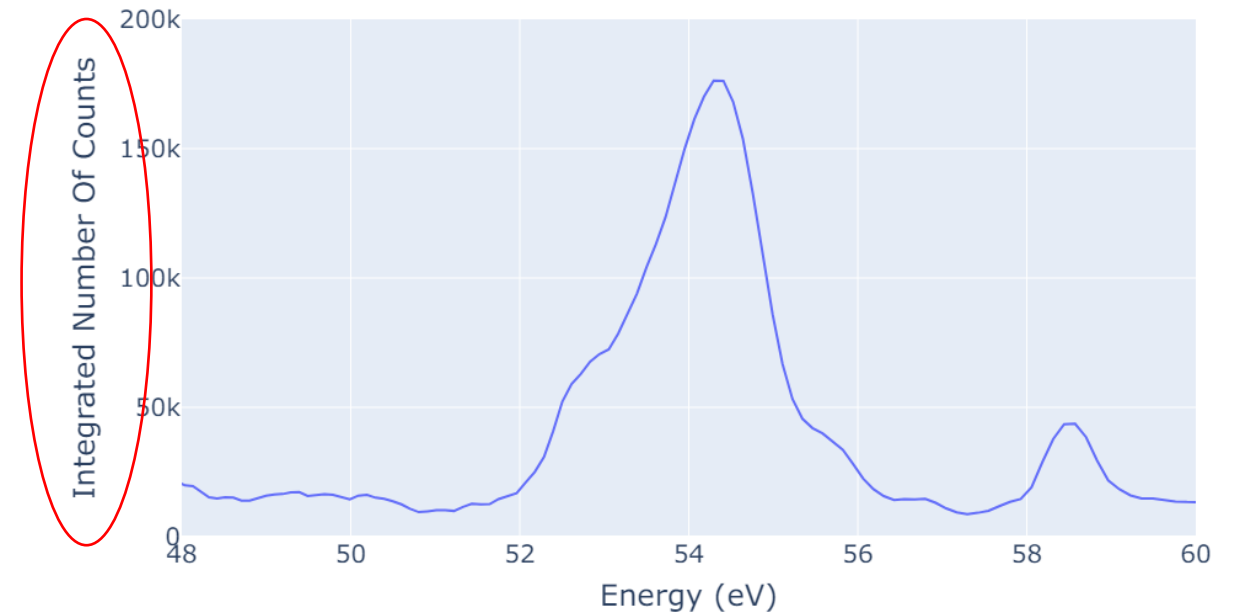
RZP:



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

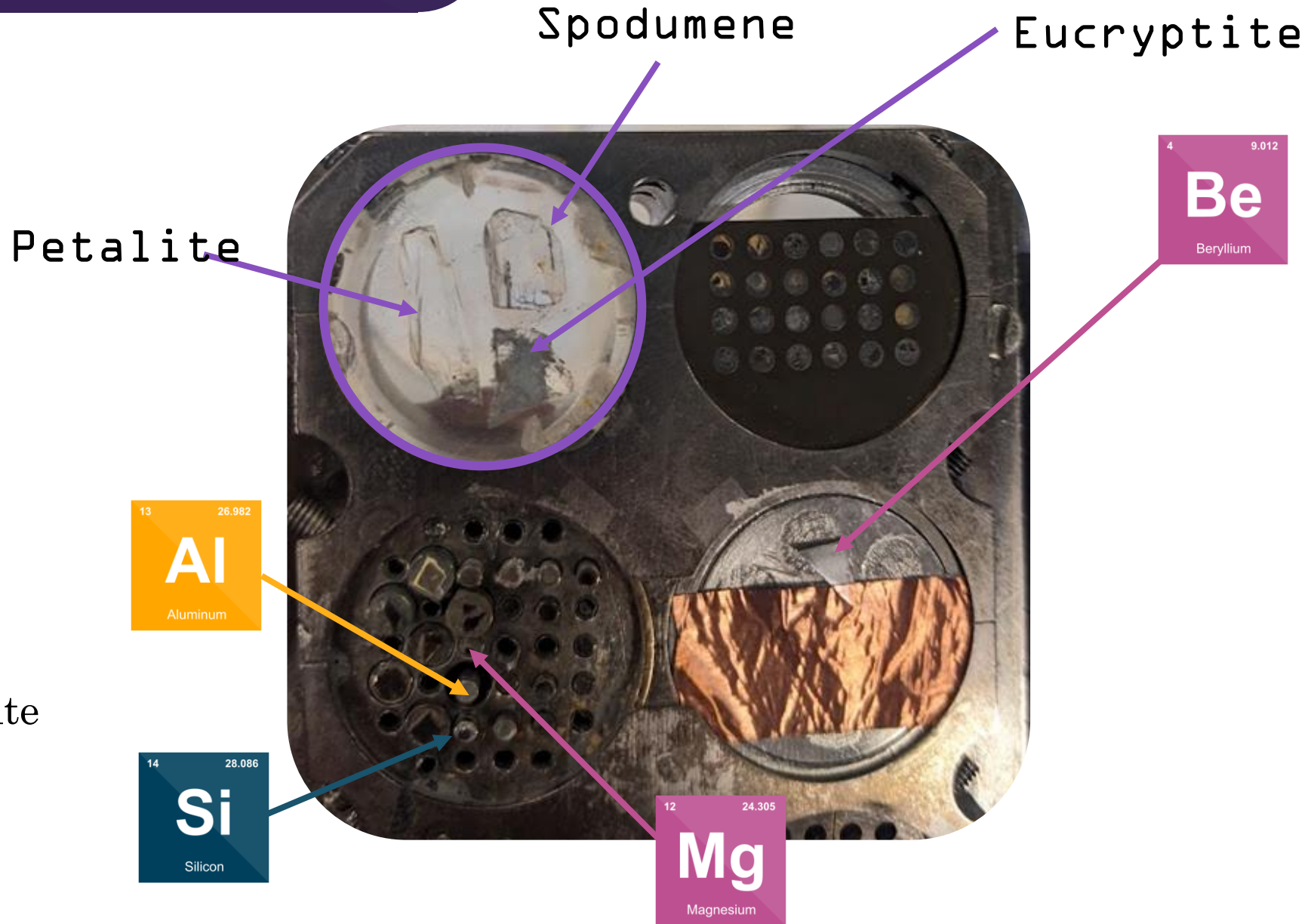


Spectrum of Li in lithium metal:



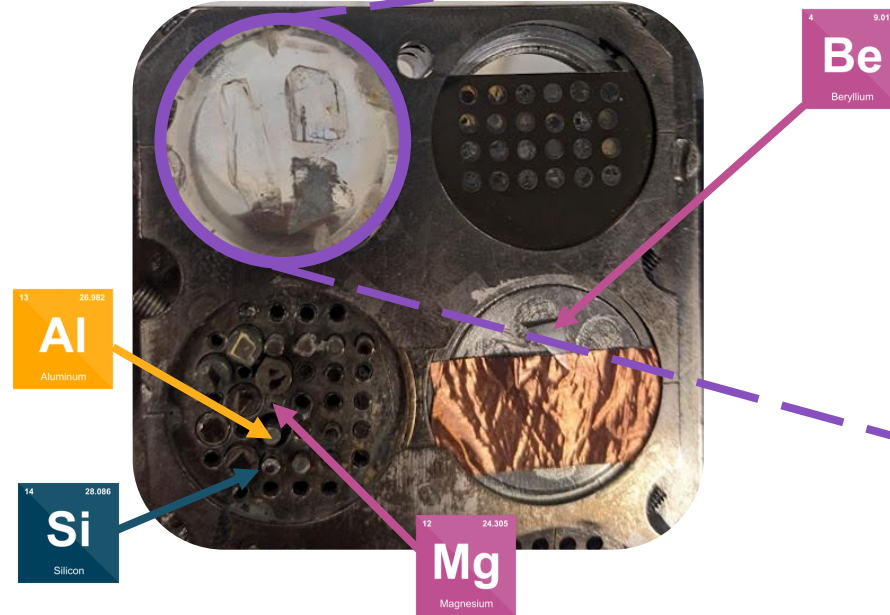


# Samples Analyzed:

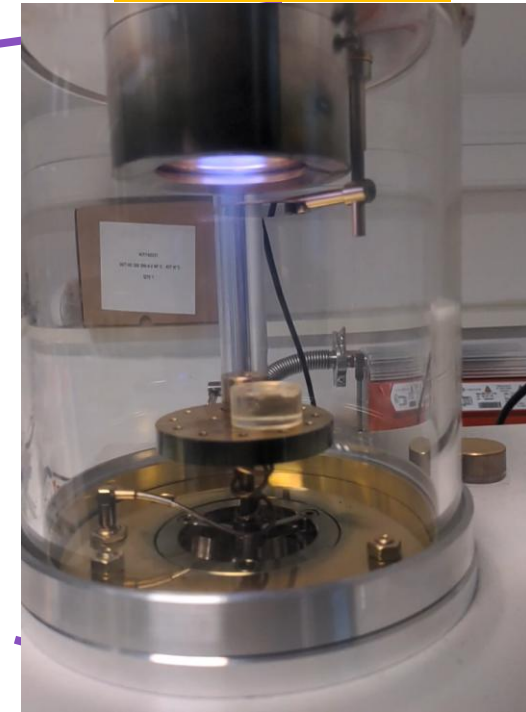


- Li metal
- LiF
- Bikitaite
- Lepidolite
- Amblygonite
- $\text{LiNbO}_3$
- $\text{LiTaO}_3$

# Samples Preparation:



Gold Coating



## Insulating samples:

1



Polishing

To remove the surface contaminations

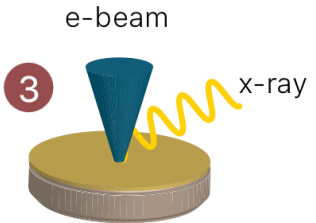
2



Coating

Sputter coating for non conducting samples

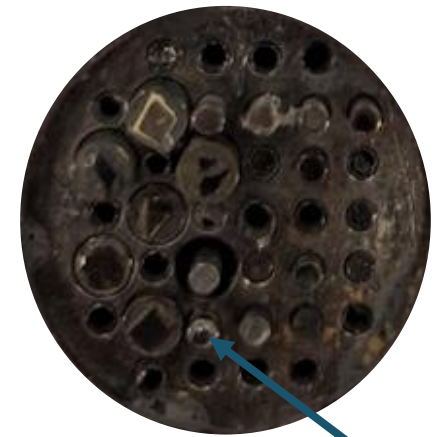
3



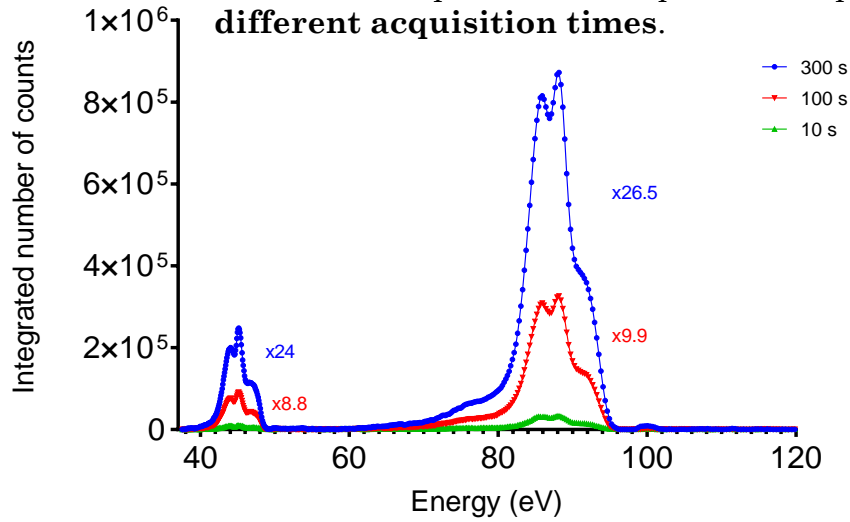
Analyzing

Introducing the sample into the microprobe

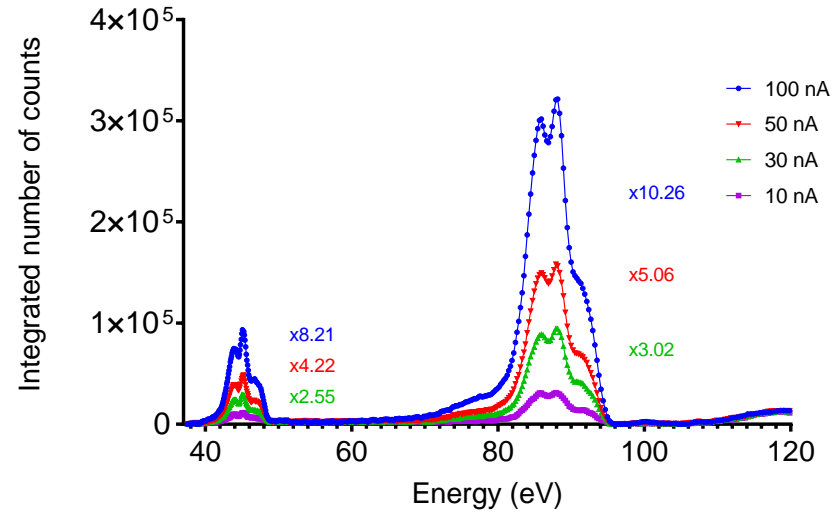
# Silicon:



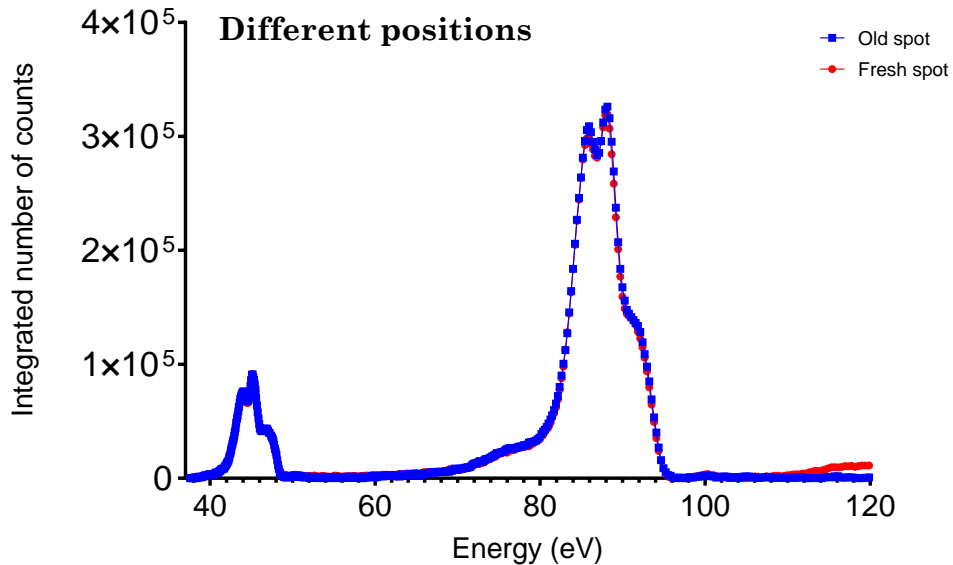
The emission spectrum of the pure Si sample with different acquisition times.



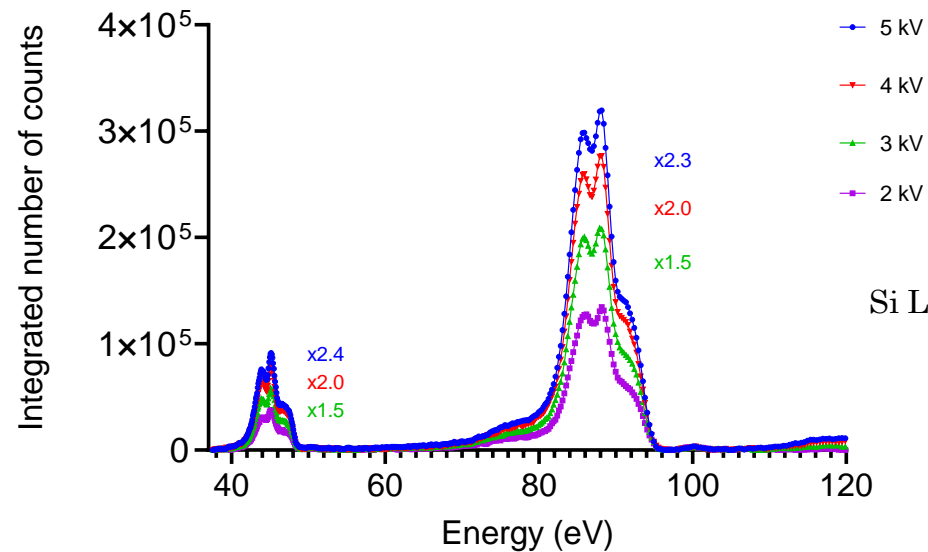
Si L2,3 with different Beam currents.



Different positions



Si L2,3 with acceleration voltages.

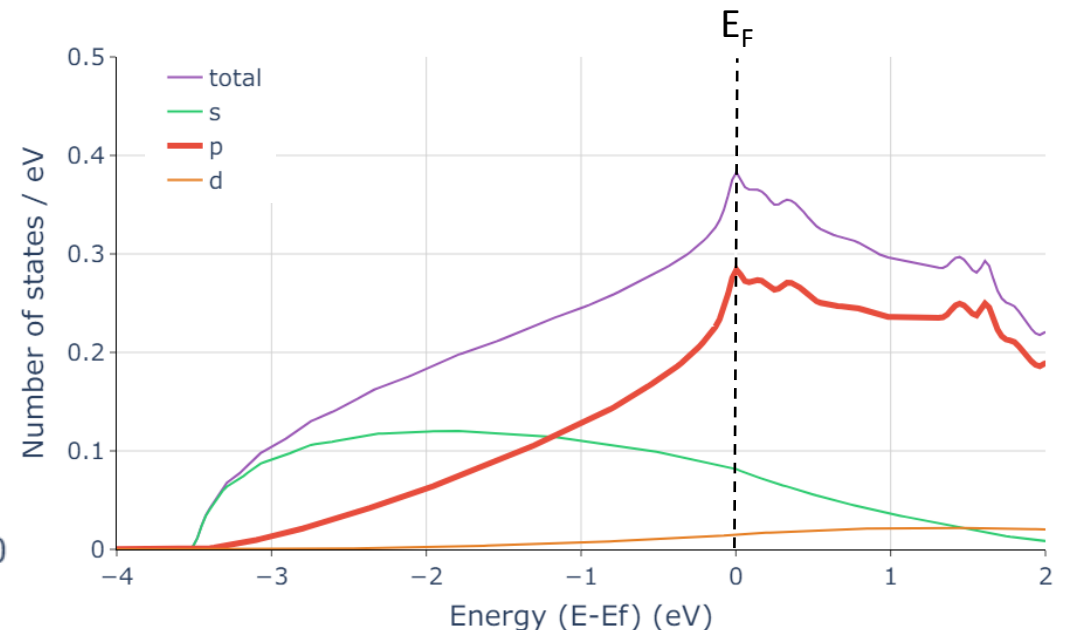
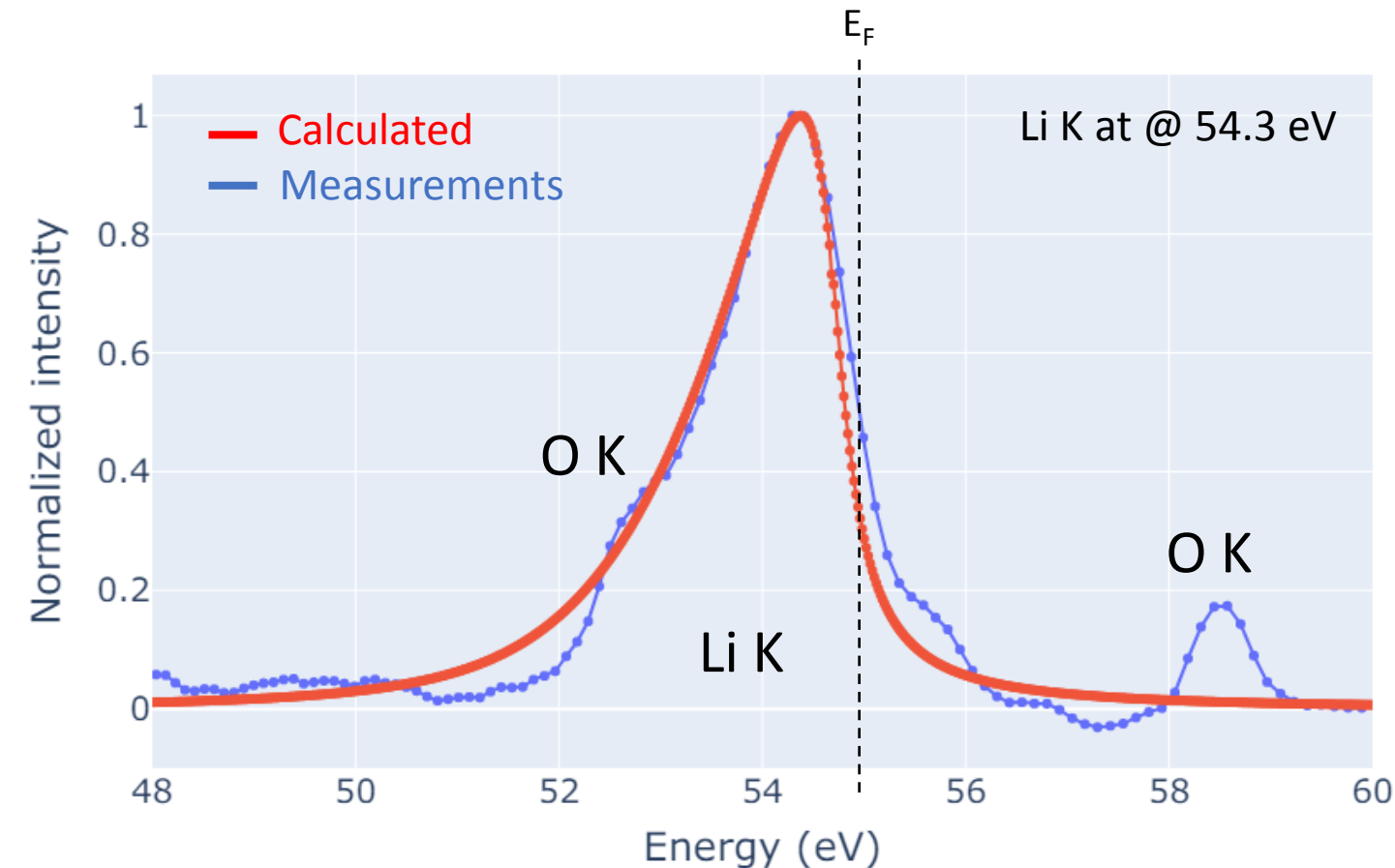


# Li Metal:



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

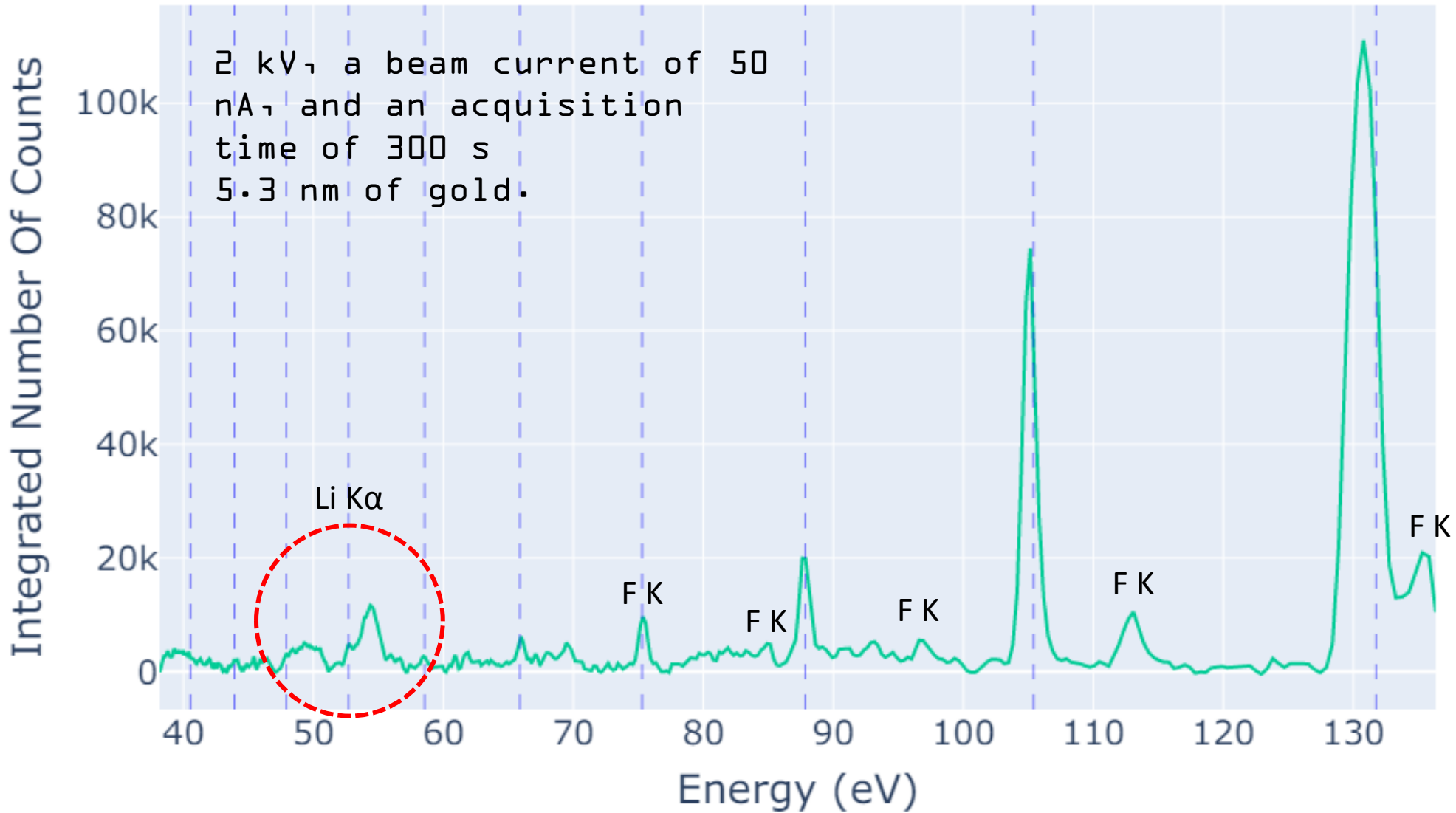
**2p valence states** transition to **1s core states** in lithium atoms and therefore the spectrum reflects the **distribution of the p states** within the valence band.

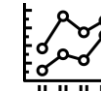


K. Hasebi, K. le Guen, N. Rividi, A. Verlaquet, and P. Jonnard, "Calculation of emission spectra of lithium compounds," *X-Ray Spectrometry*, vol. n/a, no. n/a, doi [10.1002/xrs.3329](https://doi.org/10.1002/xrs.3329).



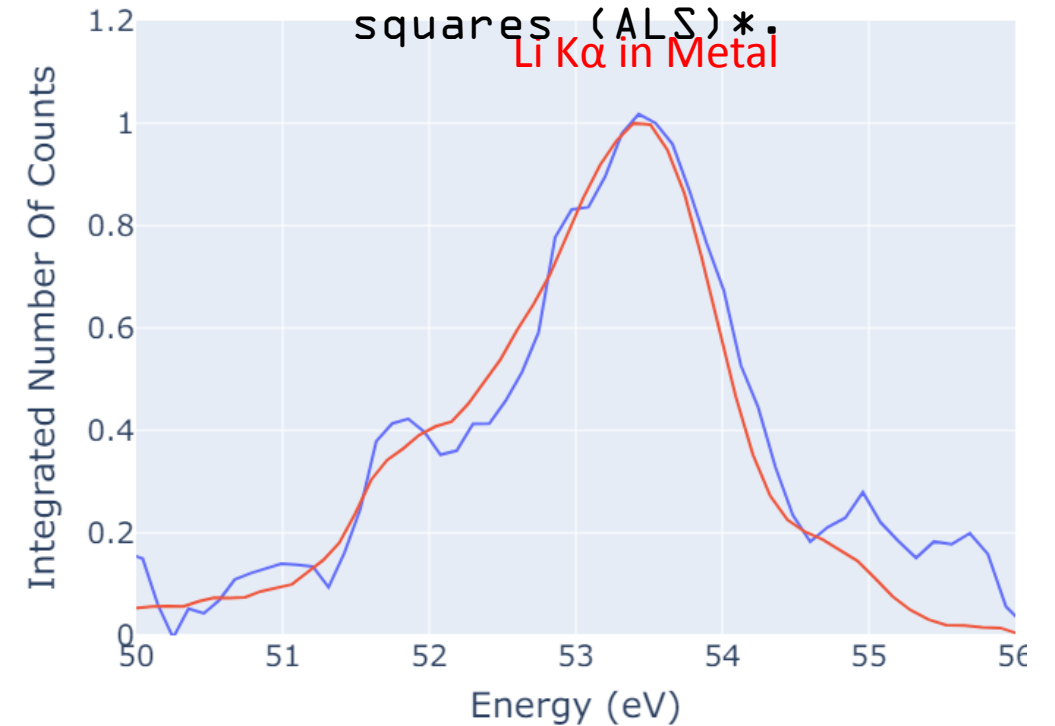
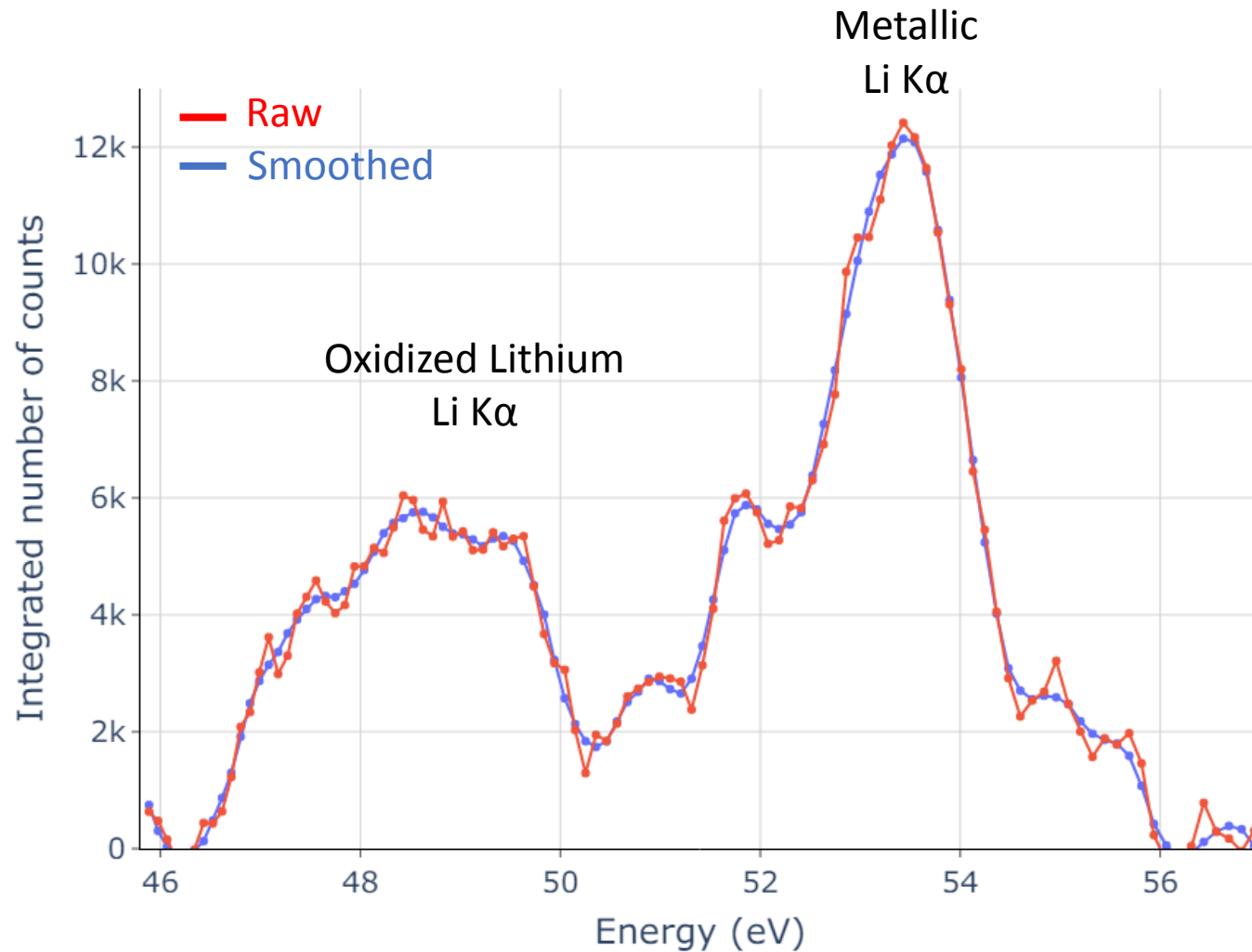
The fluorine is driven off the sample, leaving Li to accumulate in a layer on the surface.





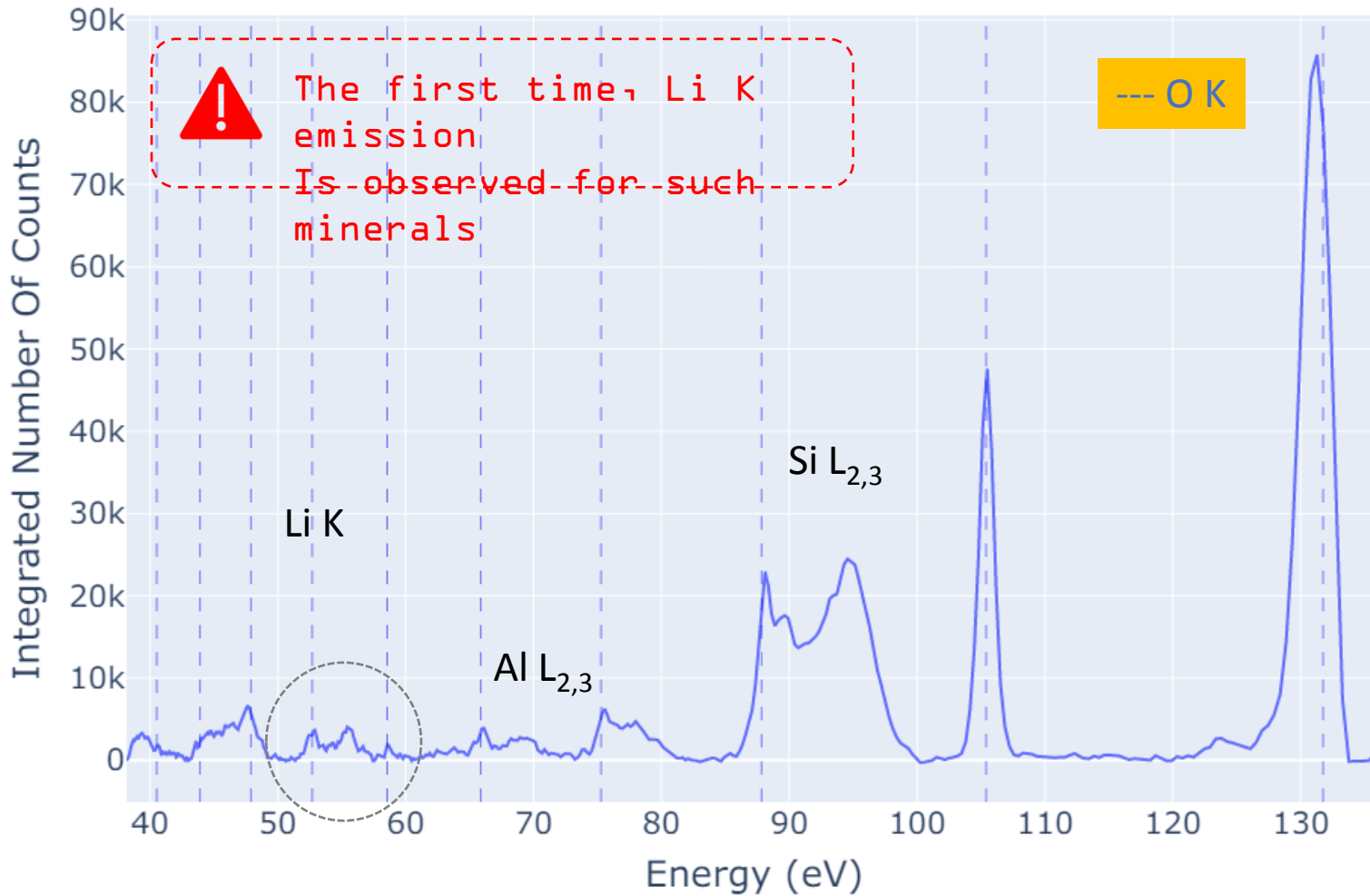
All spectra are smoothed by the **Savitzky-Golay** filter  
The baseline was removed using **Asymmetric least squares (ALS)\***.

Li K $\alpha$  in Metal



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

# Lepidolite - spectrum:



**i** It is the most abundant lithium-bearing mineral  $K(Li,Al)_3(Si_7Al)_4O_{10}(F,OH)_2$

- Solid-state electrolytes:

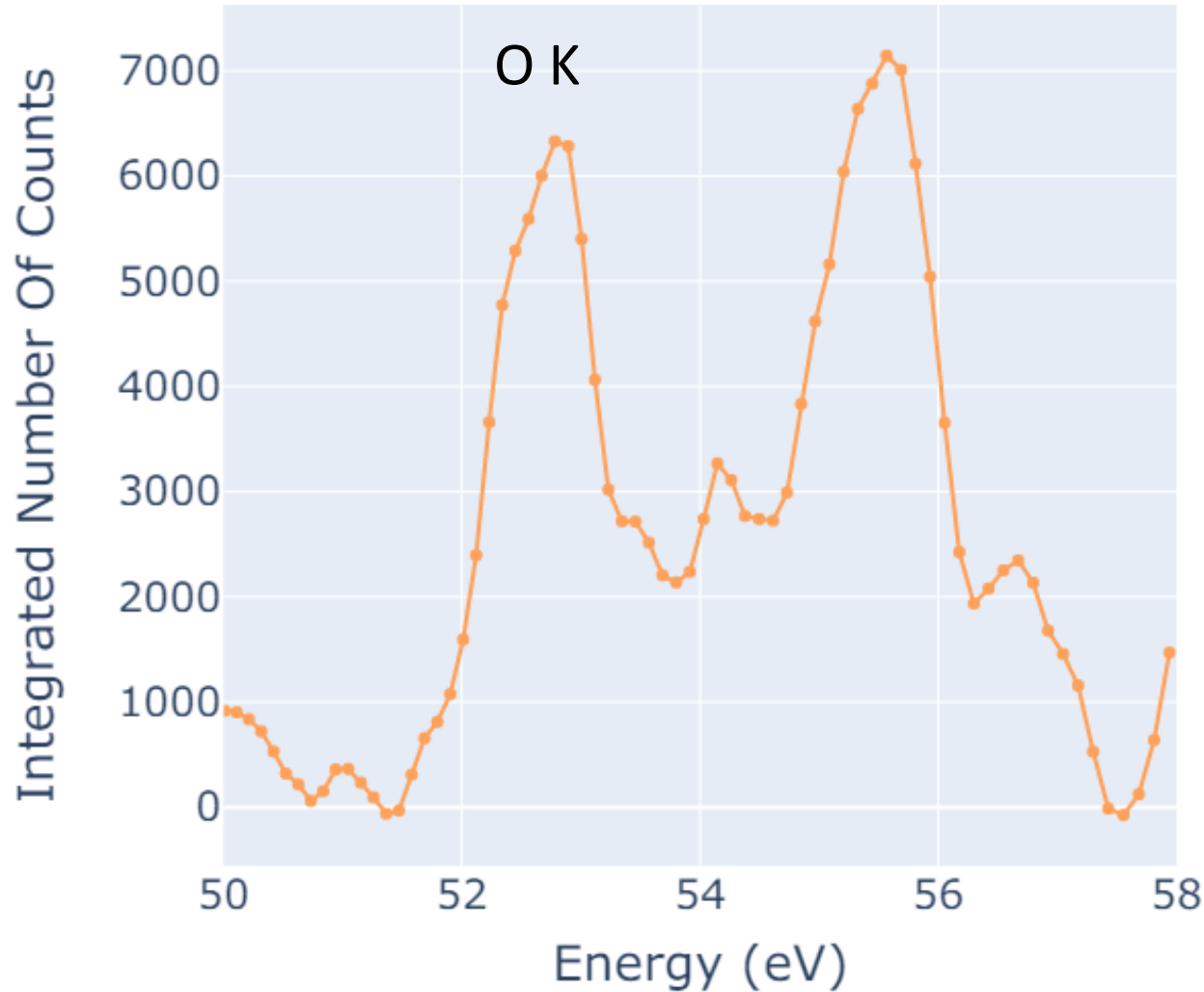
B. Wang *et al.* *ACS Appl. Energy Mater.*, 2019, [10.1021/acsaem.9b01046](https://doi.org/10.1021/acsaem.9b01046).

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

# 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<sub>1</sub> beam current of 100 nA, and an acquisition time of 300 s



# Amblygonite:

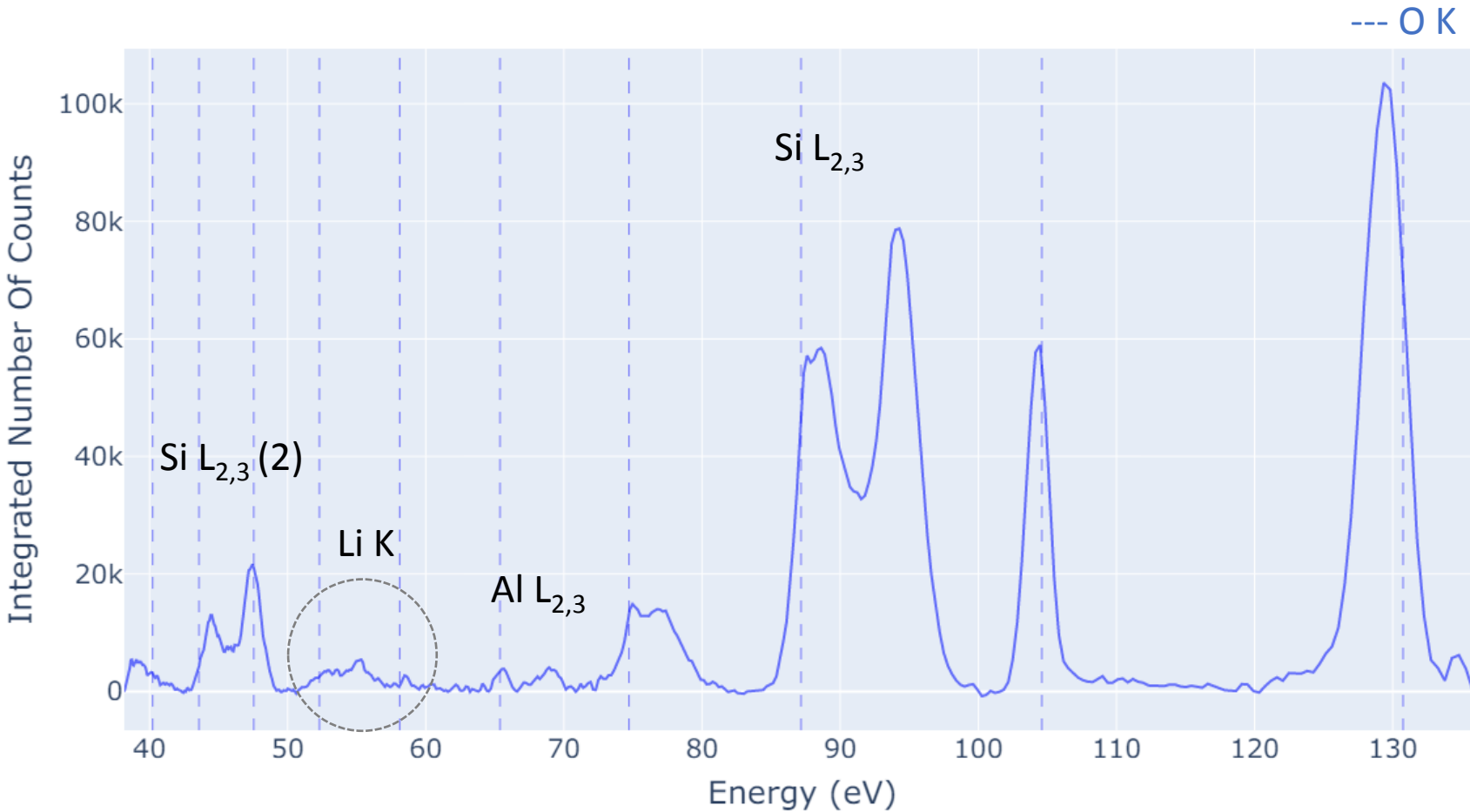


Contains about 10% lithium, used as a source of lithium.

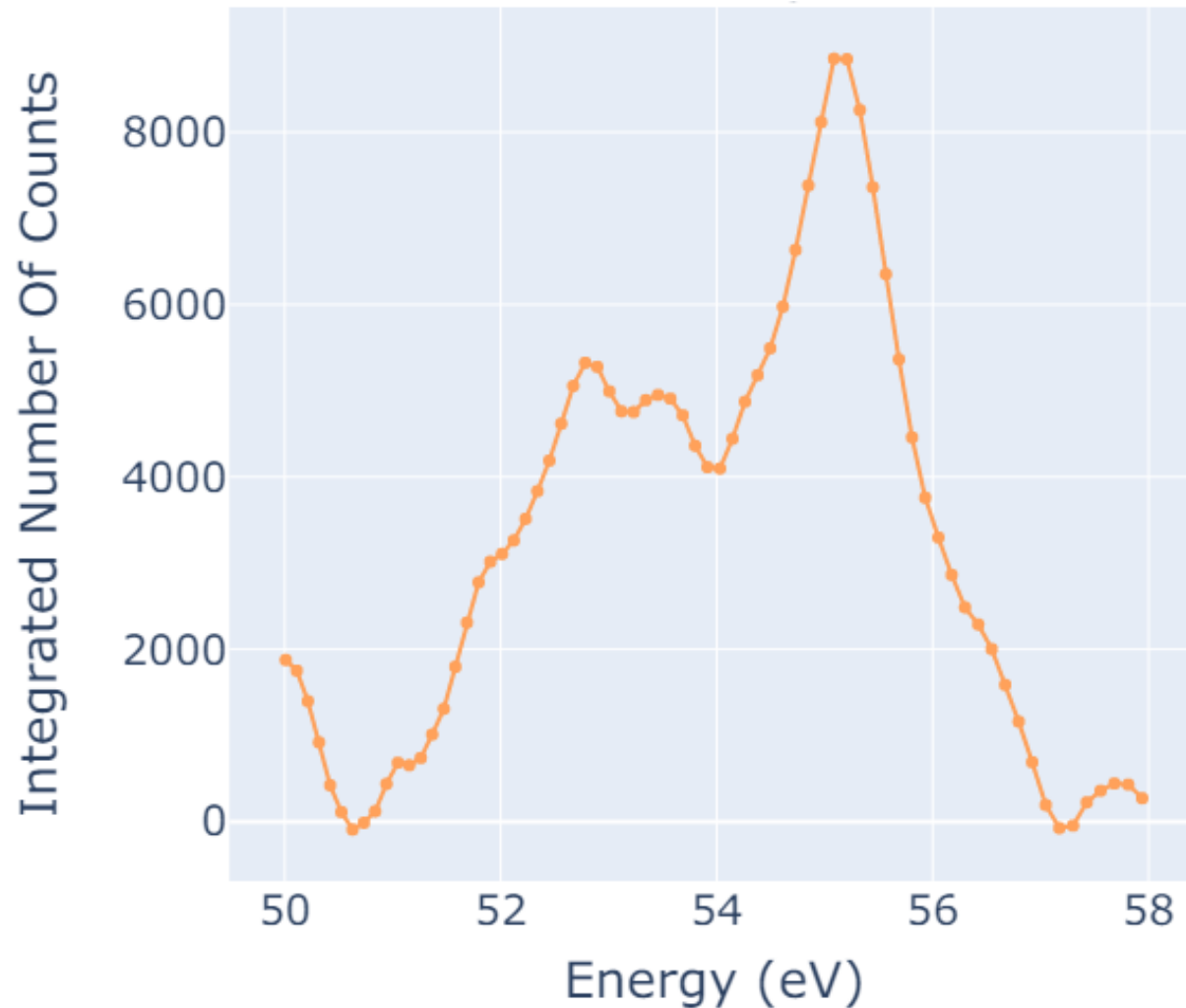


The first time, Li K emission is observed for such minerals

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)



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

# Bikitaite:



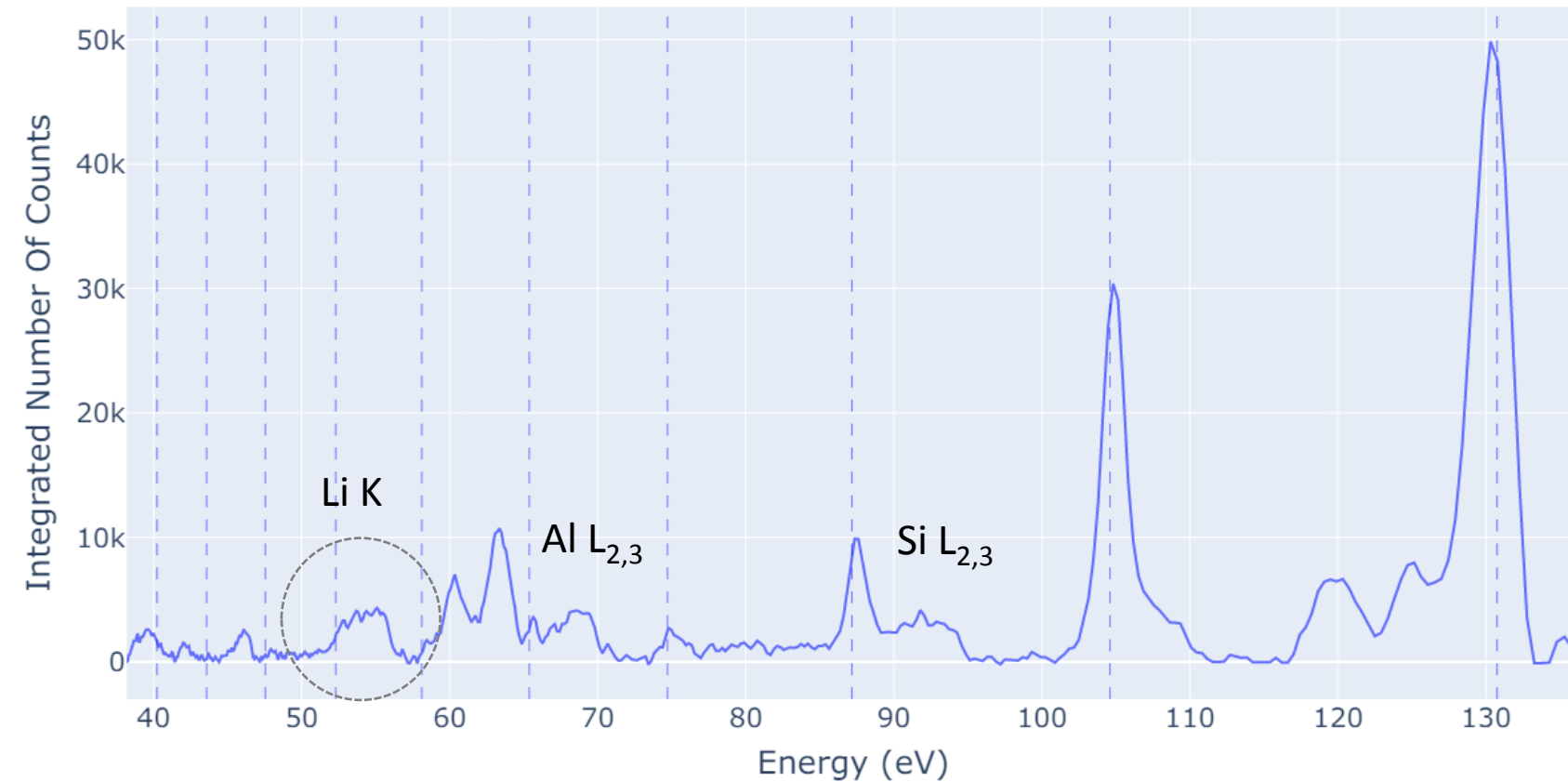
Lithium aluminum  
silicate



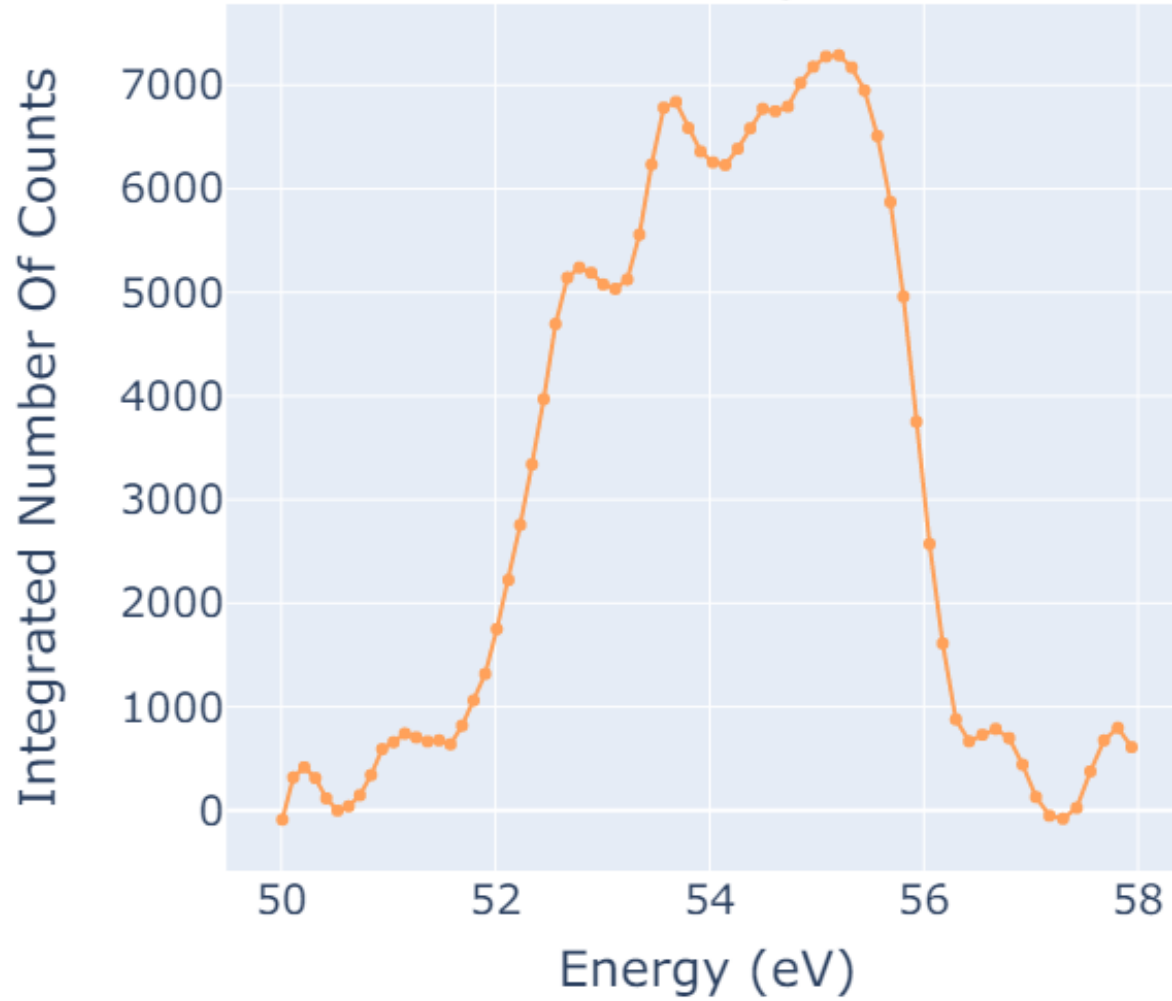
The first time, Li K  
emission

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



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)

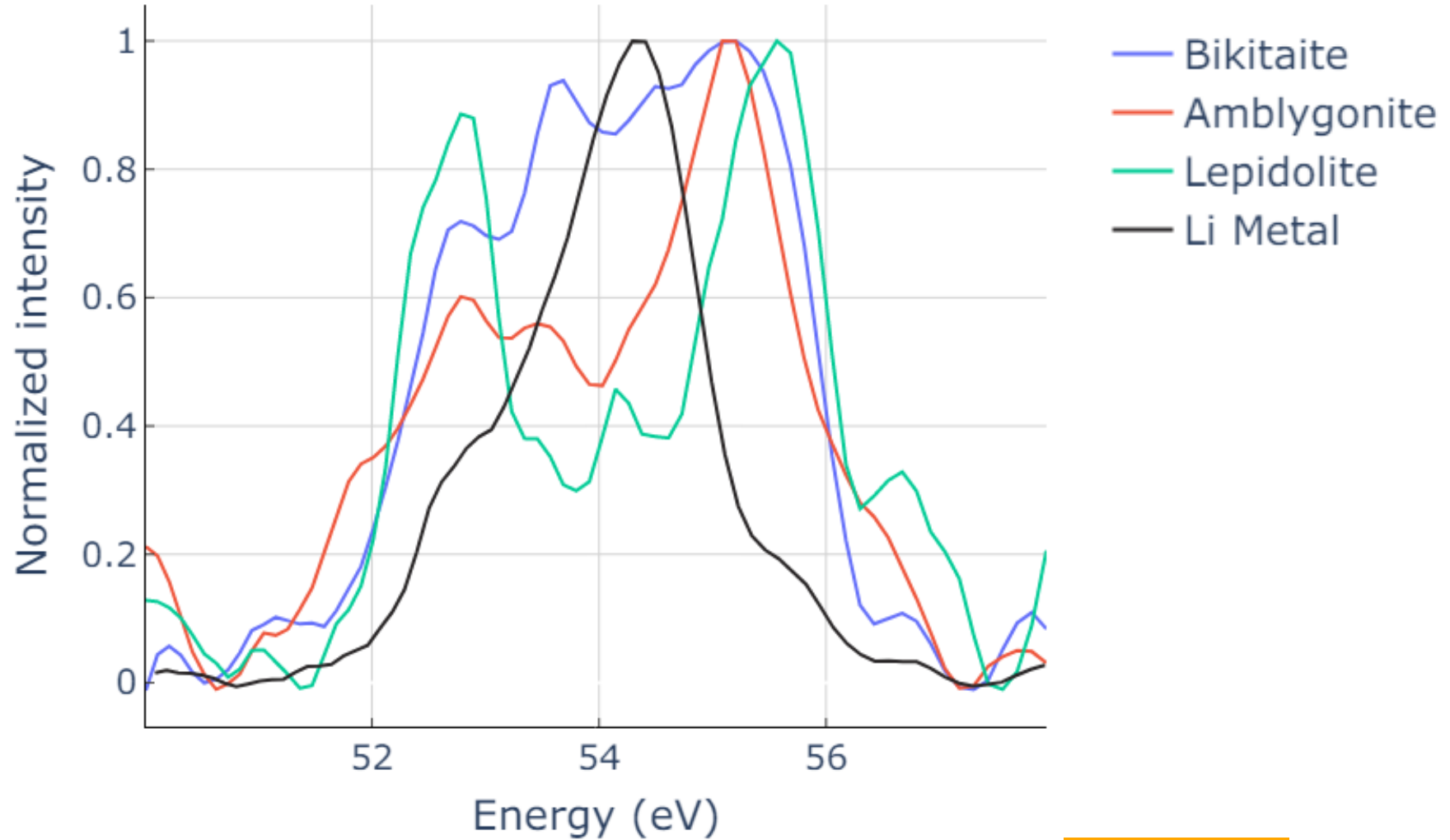


Figure: Comparison of Li K emission in the three minerals Bikitaite, Amblygonite, and Lepidolite

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).



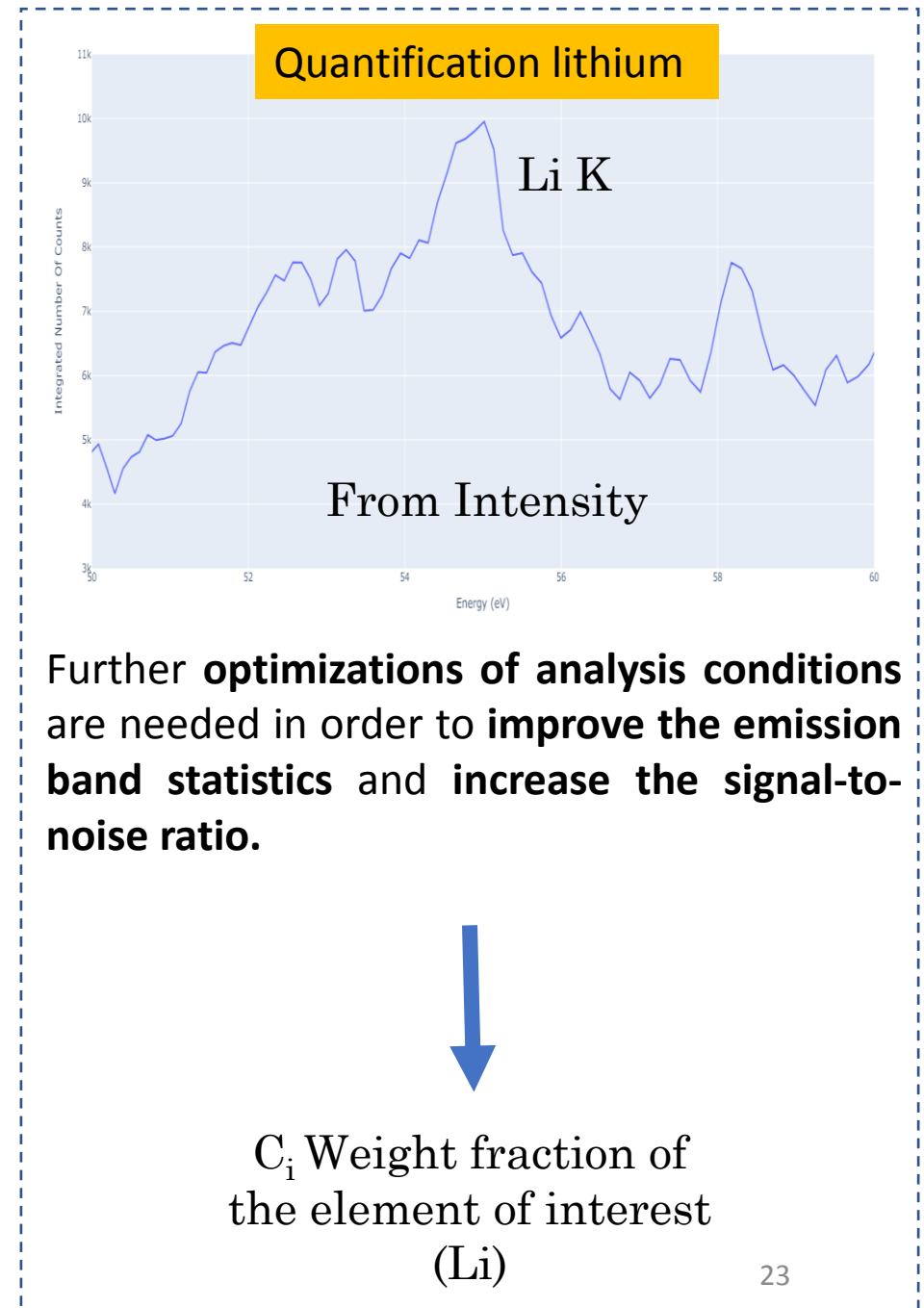
Detection



Standards



Quantification



$C_i$  Weight fraction of the element of interest (Li)



SQ<sup>3</sup>LiX

anr<sup>®</sup>



Under the supervision of:

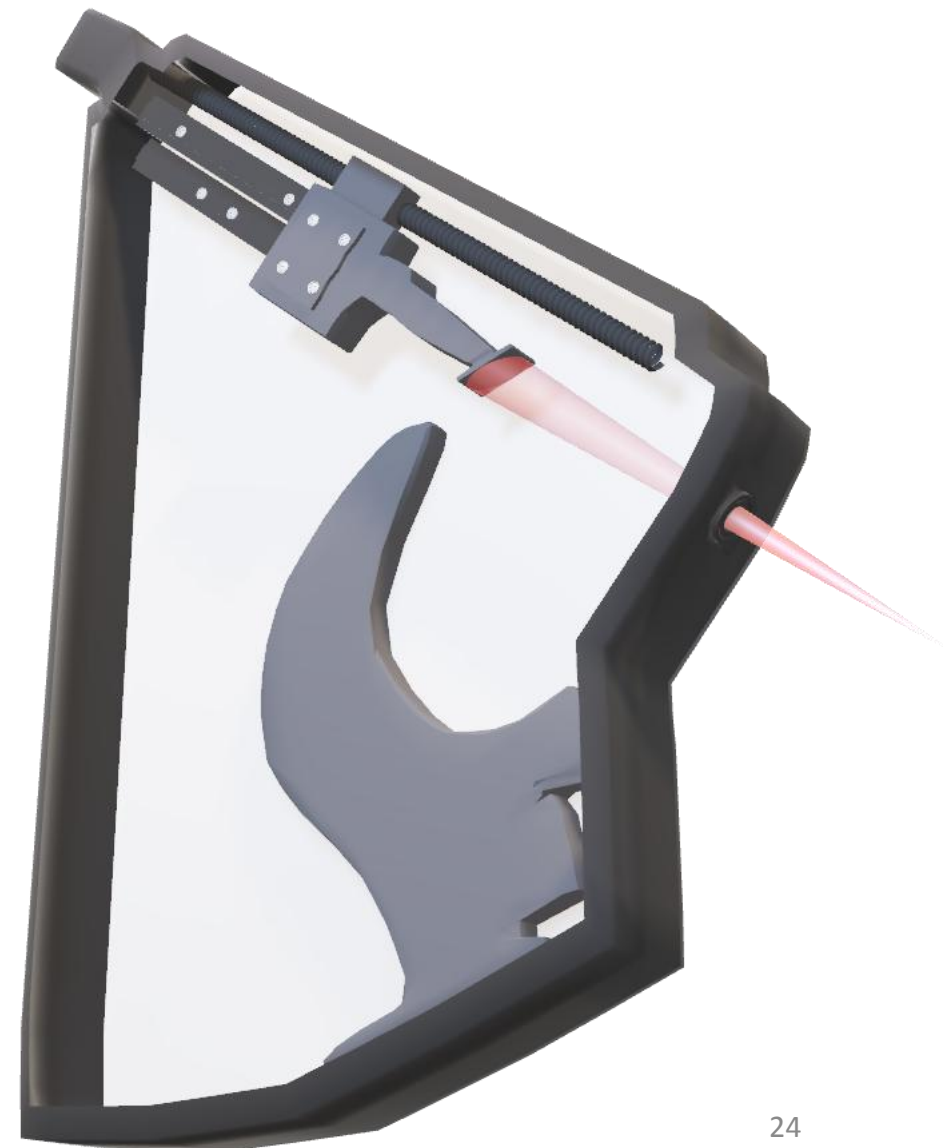
Dr. Philippe JONNARD

Dr. Nicolas RIVIDI

Dr. Anne VERLAGUET

Special thanks to all S<sup>Q</sup>LX  
team:

- Régis Vacheresse
- Rabah Benbalagh
- Karine Le Guen
- Vita Ilakovac
- Marie Christine Lepy
- Michel Fialin



**REFLECTION ZONE PLATE SPECTROMETER FOR LI K EMISSION DETECTION IN LITHIUM COMPOUNDS**

Khalil Hassebi<sup>1</sup>, Nicolas Rividi<sup>2</sup>, Anne Verlaquet<sup>3</sup>, Alexei Erko<sup>4,5</sup>,  
Juergen Probst<sup>6</sup>, Heike Loechel<sup>6</sup>, Thomas Krist<sup>6</sup>, Karine Le Guen<sup>6</sup>, Philippe Jonnard<sup>1</sup>

**Motivation:**

**The challenge:**

- Low fluorescence yield
- Low energy emission and strong self-absorption

Meet the detector with a non-destructive technique on unpolished base.

**How?**

- Probing the fine electronic structure of the valence band using soft x-ray emission spectroscopy technique (XES) integrated in EPMA
- Tracking the changes in the chemical environment and emission spectrum (intensity, shape, shift, band width...)

**Can we detect lithium and study its electronic structure in complex materials?** Yes!

**Results:**

The Li K emission occurs when a 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 (Z). The Li K emission of lithium in LiF, Lepidolite (LiAlSi<sub>3</sub>PO<sub>8</sub>), BL (Li<sub>2</sub>O<sub>2</sub>(CH<sub>3</sub>)), Bixite (LiAlSi<sub>2</sub>O<sub>6</sub>(OH)), and Amblygonite (LiNaAl<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)) is presented below.

Figure 1: The Li K emission in LiF series, presenting the emission band of Li in the LiF series.

**X-ray emission spectra of minerals**

Figure 2: The x-ray emission spectra of Lepidolite and Amblygonite in the full range of the spectrometer.

**Li K emission reported for the first time in minerals**

Figure 3: The Li K emission in the minerals Lepidolite, Amblygonite, and Bixite.

**Methods:**

**The x-ray emission process:**

- Excitation: The sample is being bombarded with an accelerated beam of charged particles (electrons).
- Ionization: The interaction of the beam of electrons with matter leads to the ionization of the core states.
- Deexcitation: The vacancy is filled with an electron from an outer shell, resulting in the emission of an x-ray photon that corresponds to the energy difference between the two states.

Figure 4: Illustration of the X-ray emission process.

**Why RZP instead of Multibayer?**

- No scanning mechanism
- Higher resolution (~0.5 eV at Al L2,3 edge and ~0.25 eV at Mg L2,3 edge)
- Cover wider energy range

**Sample is ready in three easy steps:**

- Polishing: To remove the surface contamination.
- Coating: Sputter coating for non-conducting samples.
- Analyzing: Developing the sample in the microscope.

**Conclusion:**

We demonstrate the possibility to spectroscopically analyze Li K emissions in different compounds using a non-destructive and accessible technique. We also report for the first time the Li K emission bands in minerals. Our results unlocked potential for various applications to study in details the fine structure of valence band of lithium.

**References:**

[1] A. Erko et al., Opt. Express, vol. 22, no. 14, p. 18887, Jul. 2014, doi: 10.1364/OE.22.018887.  
[2] K. Hassebi et al., X-Ray Spectrometry, doi: 10.1002/xrs.3229

# Reflection zone plate spectrometer for Li K emission detection in lithium compounds

18:30 - 20:00 POSTER session  
Room 102-106

