Marianne Liebi– Material Science at Large Scale Facilities

X-ray Fluorescence Spectroscopy (XRF) exercise

EPFL Master Course 2025 MSE435

case study

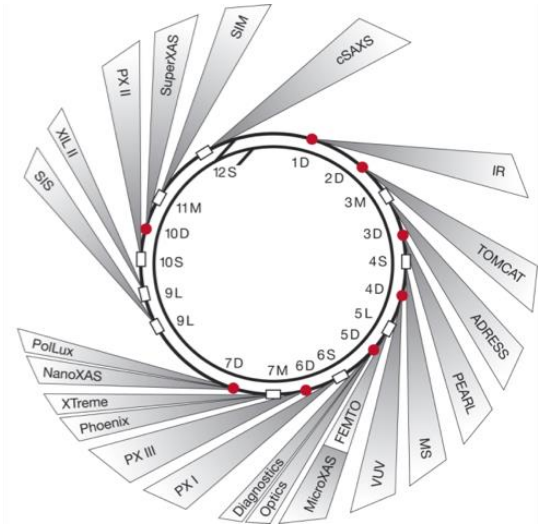
Thermal fatigue in micro-electronics	Antoine Georges Henri Fotius
Extracellular matrix (ECM)	Jean-Bernard Caron
Hip-implants: considerations for long term success	David Kerzel
?	Kevin Aaron Murphy

What beamline/endstation?

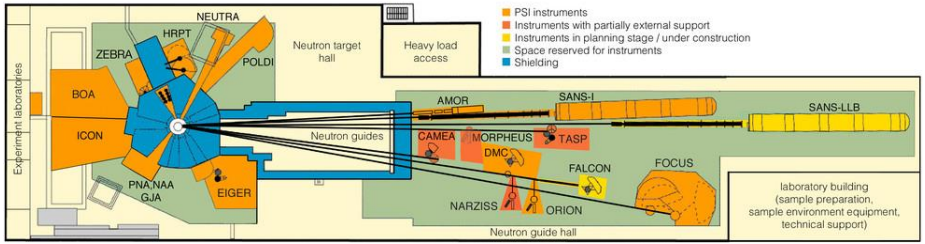
https://www.psi.ch/de/science/methods-and-scopes-of-the-large-research-facilities

43 endstations at PSI

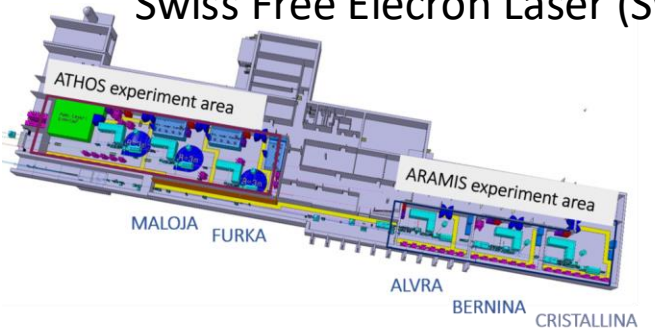
Swiss Light Source (SLS)



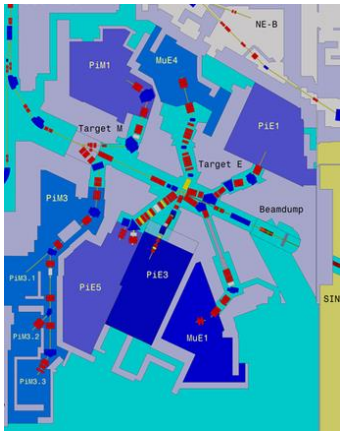
Swiss Spallation Neutron Source (SINQ)



Swiss Free Elecron Laser (SwissFEL)



Swiss Muon Source (SμS)



Case study grading scheme

A) Goal of experiment

max 4 points

B) Background

max 4 points

C) Experimental method

max 8 points

D) Results expected

max 8 points

E) Estimate and justification of the beamtime

Max 2 points

F) References relevant to the experiment description

Max 2 points

Case study grading scheme

CATEGORY	4	3	2	1
A) → Goal of experiment **max 4 points**	The main goal of the experiment is stated, together with eventual minor goals. How the goal will be achieved and why the experiment is interested is described concisely.	The main goal is stated together with a description of how it will be achieved.	The goal of the experiment is stated.	The goal of the experiment remains unclear.
B) → **Background** **max 4 points**	The background explains the concepts that are needed to understand the proposal. Previous research within the field is described as well as why this specific experiment is scientifically important.	The background explains the concepts that are needed to understand the proposal and describes what previous research has been performed in the field.	The background explains some of the concepts needed to follow the rest of the proposal.	The proposal cannot be understood based on the information in the background.
C) → **Experimental method** **max 8 points**	The experimental method is stated together with the requirements of the setup needed to perform the experiments (for example; energy of the beam, length scales and sample stages) with explanation It is explained how this experiment will be correlated to other techniques to obtain the goal stated.	The experimental method is stated together with the requirements of the setup needed to perform the experiments (for example; energy of the beam, length scales and sample stages) OR It is explained how this experiment will be correlated to other techniques to obtain the goal stated.	The experimental method is stated. Some requirements regarding the experimental setup is mentioned.	The experimental method is stated, but it remains unclear how the experiments will take place.
D) → **Results expected** **max 8 points**	The hypothesis /expected results of the proposed experiment are stated together with strong arguments and previous results. From other techniques specified in the experimental methods, the correlations between the different results from the different experiments are explained.	The hypothesis/expected results of the experiment are stated together with strong arguments and previous results OR The hypothesis/expected results are stated together with arguments. From other techniques specified in the experimental methods, the correlations between the different results from the different experiments are explained.	The hypothesis/expected results are stated together with arguments.	The hypothesis/expected results are stated without explanation.
E) → **Estimate and justification of the beamtime** **Max 2 points**	It is explained why the experiments should take place at a large-scale facility with the specified method. There are arguments for the choice of beamline and why it fits the proposed experiments.	It is explained why the experiments should take place at a large-scale facility with the specified method. Some properties of the beamlines are explained to justify the choice of the beamline.	It is explained why the experiments should take place at large-scale facilities with the specified method OR some properties of the beamlines are explained to justify the choice of the beamline.	It remains unclear why experiments at a large-scale facility would help the proposers to obtain their goal.
F) → **References relevant to the experiment description** **Max 2 points**	Appropriate citation of reference, work on multiple sources, including scientific articles.	Appropriate citation of references, work on multiple sources.	Use of more than one source. Some citations missing	Only one source used.

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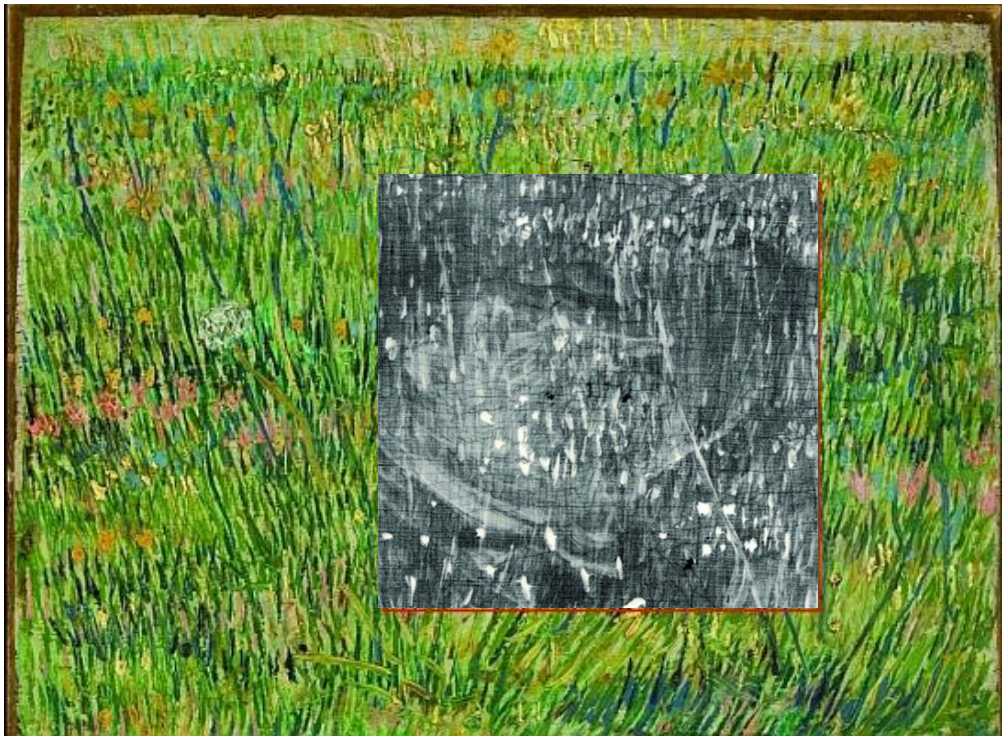
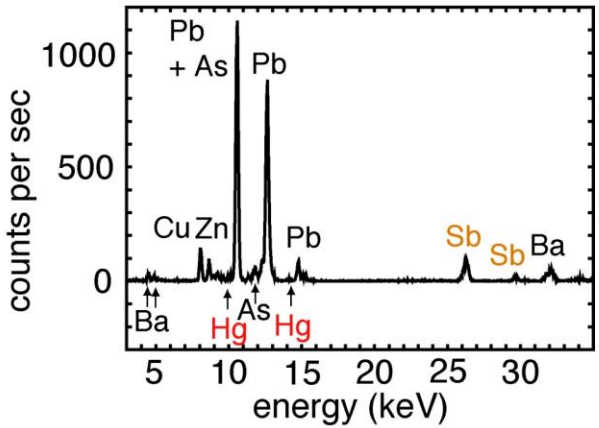
Goal of experiment	The main goal of the experiment is stated, together with eventual minor goals. How the goal will be achieved and why the experiment is interested is described concisely.
Background	The background explains the concepts that are needed to understand the proposal. Previous research within the field is described as well as why this specific experiment is scientifically important.
Experimental method	The experimental method is stated together with the requirements of the setup needed to perform the experiments (for example; energy of the beam, length scales and sample stages) with explanation It is explained how this experiment will be correlated to other techniques to obtain the goal stated.
Results expected	The hypothesis /expected results of the proposed experiment are stated together with strong arguments and previous results. From other techniques specified in the experimental methods, the correlations between the different results from the different experiments are explained.
Estimate and justification of the beamtime	It is explained why the experiments should take place at a large-scale facility with the specified method. There are arguments for the choice of beamline and why it fits the proposed experiments.
References relevant to the experiment description	Appropriate citation of reference, work on multiple sources, including scientific articles.

XRF in cultural heritage



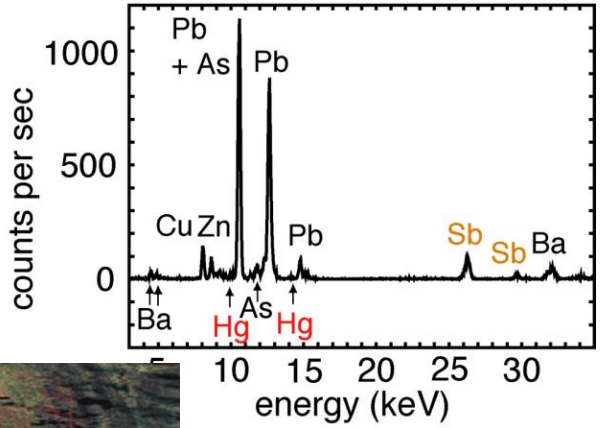


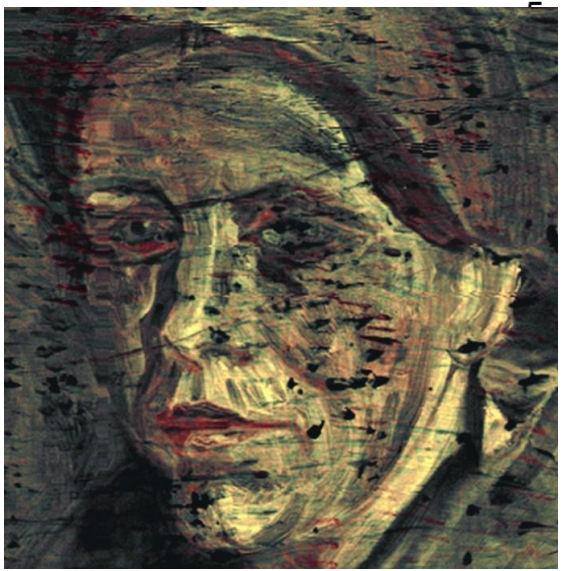
Vincent van Gogh, Patch of Grass, Paris, summer 1887, Kröller-Müller Museum, Otterlo.

Dik, J., Janssens, K., et al. *Analytical Chemistry*, *80*(16) 6436–6442.

XRF in cultural heritage

Vincent van Gogh, Patch of Grass, Paris, summer 1887, Kröller-Müller Museum, Otterlo.





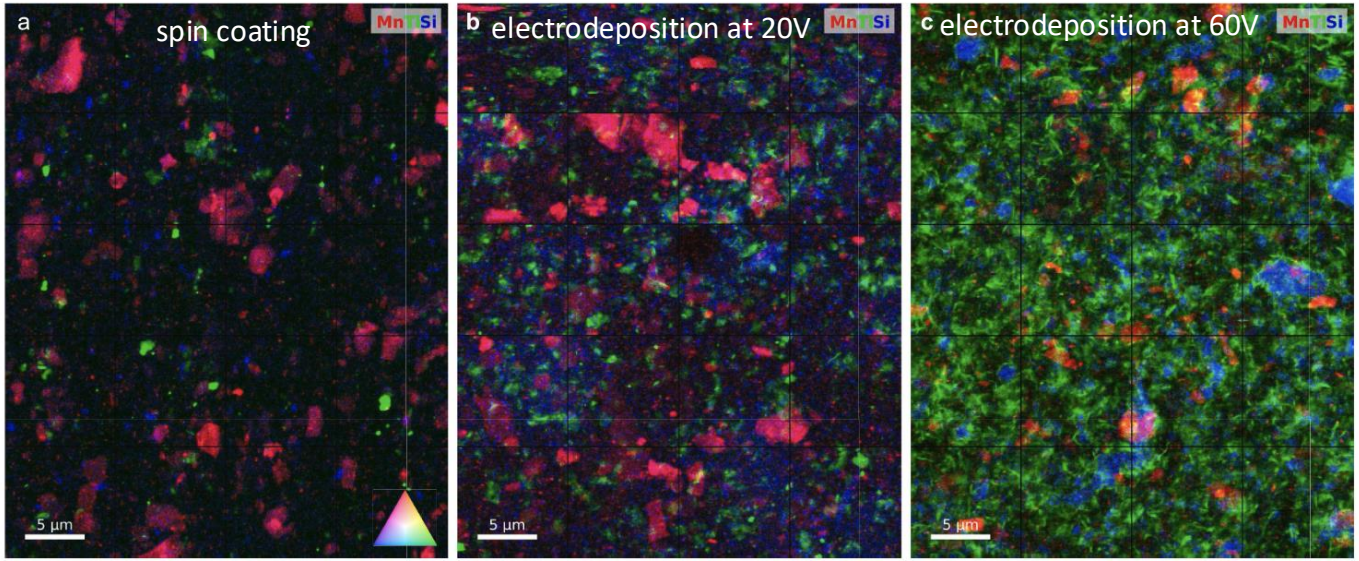
Bi-tonal colour reconstruction of Sb (pale yellow) and Hg (red)

Dik, J., Janssens, K., et al. *Analytical Chemistry*, *80*(16) 6436–6442.

XRF on electromagnetic compatibility coating

coatings shielding electromagnetic interference containing dispersed MXenes (synthetic inorganic 2D materials)

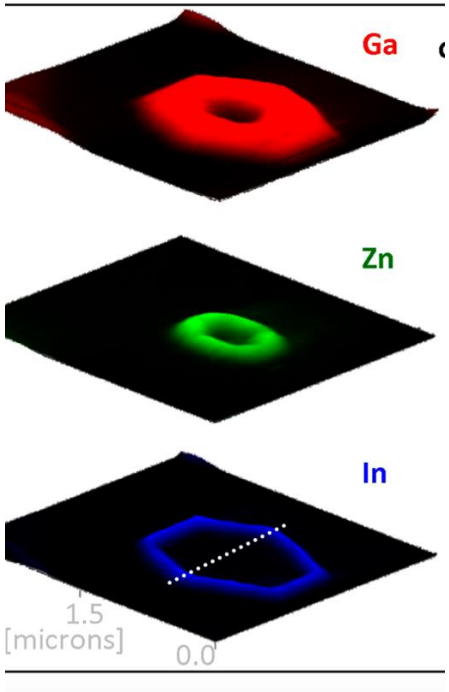
test 3 different coating procedures for distribution of Mxene (Ti_3C_2)



Manganese and silicon contamination from the aluminum substrate

Sala, S., et al. (2025) *Radiation Physics and Chemistry*, *229*

XRF: Nanowires

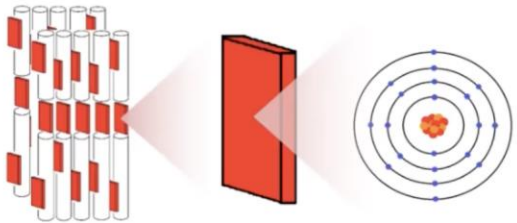


multi-shell single core nanowire

→ synchrotron XRF for high resolution

G. Martinez-Criado *et al*. Nano Lett. 2012 **12**, 5829-5834

Application example bone

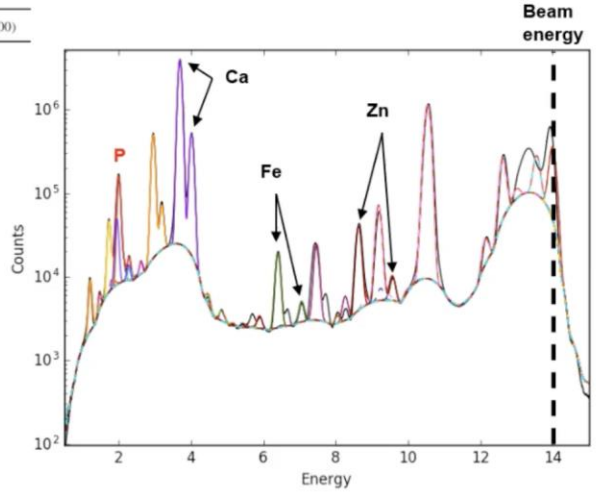


Interesting elements in bone:

- Main elements: Ca, P
- Trace elements: e.g. Mg, Fe, Ni, Zn, Sr, Ba

Energy of K lines [1]

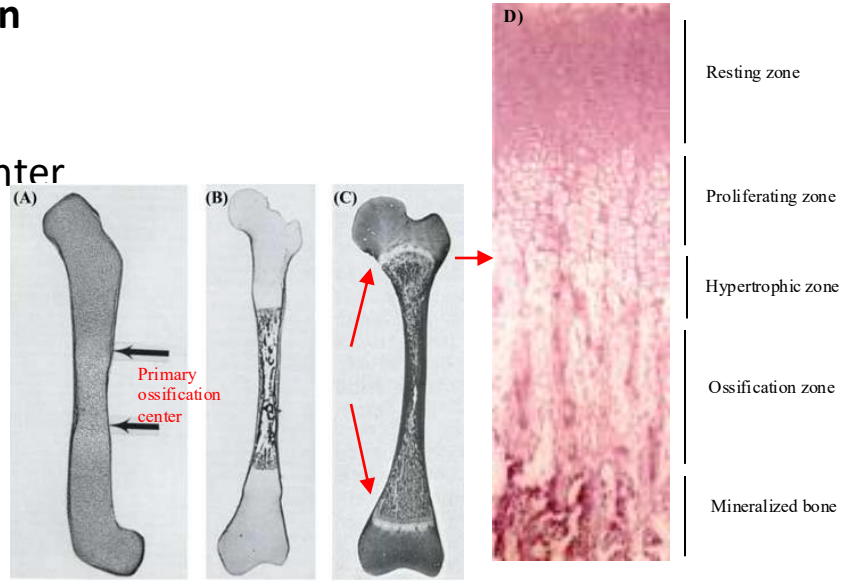
Z	Element	Kα1 (I = 100)	Z	Element	Kα1 (I = 100)
13	Al	1.49	38	Sr	14.16
14	Si	1.74	39	Y	14.96
15	P	2.01	40	Zr	15.77
16	S	2.31	42	Mo	17.48
17	Cl	2.62	44	Ru	19.28
18	A	2.96	46	Pd	21.17
19	K	3.31	47	Ag	22.16
20	Ca	3.69	48	Cd	23.17
22	Ti	4.51	50	Sn	25.27
24	Cr	5.41	51	Sb	26.36
25	Mn	5.90	53	I	28.61
26	Fe	6.40	56	Ba	32.19
27	Co	6.93	64	Gd	42.98
28	Ni	7.48	74	W	59.31
29	Cu	8.05	78	Pt	66.82
30	Zn	8.64	79	Au	68.79
31	Ga	9.25	80	Hg	70.82
32	Ge	9.88	82	Pb	74.96
33	As	10.54	92	U	98.43
34	Se	11.22			
35	Br	11.92			
37	Rb	13.39			



Long bone development

Endochondral ossification

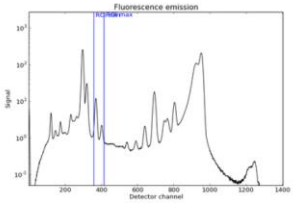
- Cartilage template
- Primary ossfication center
- Growth plates



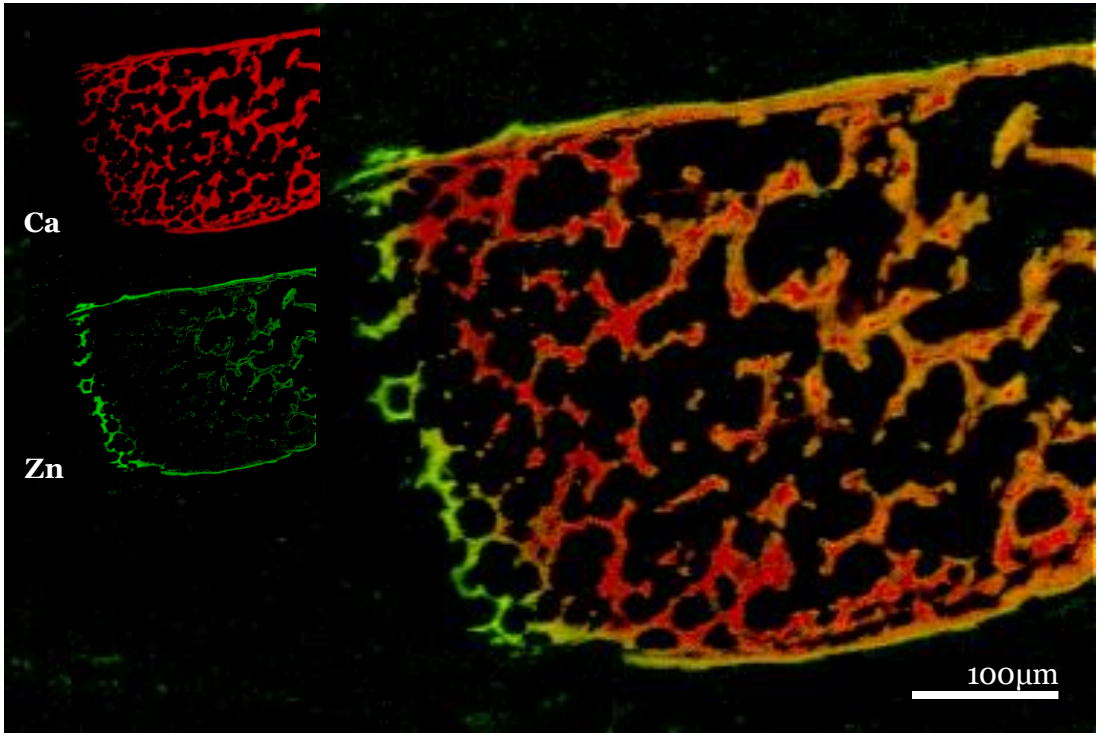
A), B), C) from *Nowlan et al. 2007, Annals of the New York Academy of Sciences*

D) from *Naski et al. 1998, Frontiers in Bioscience*

XRF: example embryonic bone development



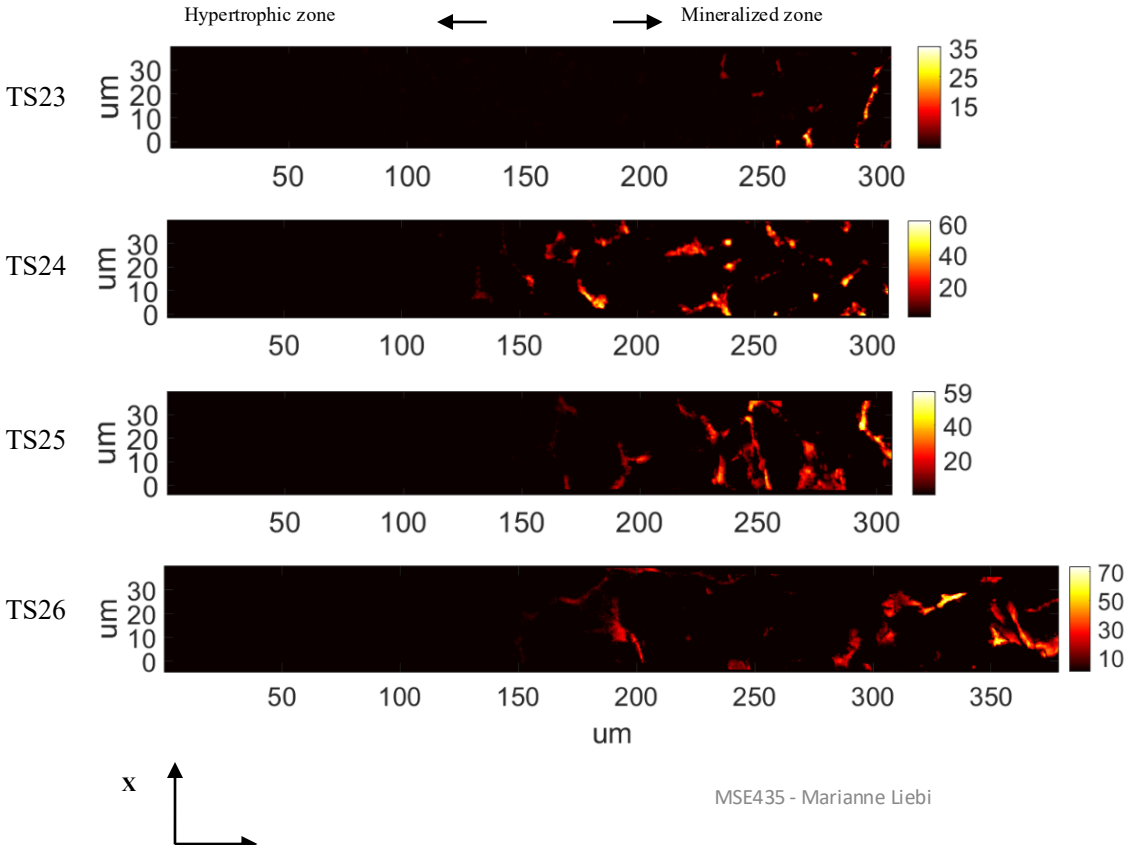
2µm beam @ID13 ESRF



multi-scale:
overview scan
high resolution

Silva Barreto, I., Le Cann, S., Ahmed, S., Sotiriou, V., Turunen, M.J. Johansson, U., Rodriguez Fernandez, A., Grünewald,T.A., Liebi, M., Nowlan, N., Isaksson, H. *Advanced Science 2020*

XRF: Ca-concentration

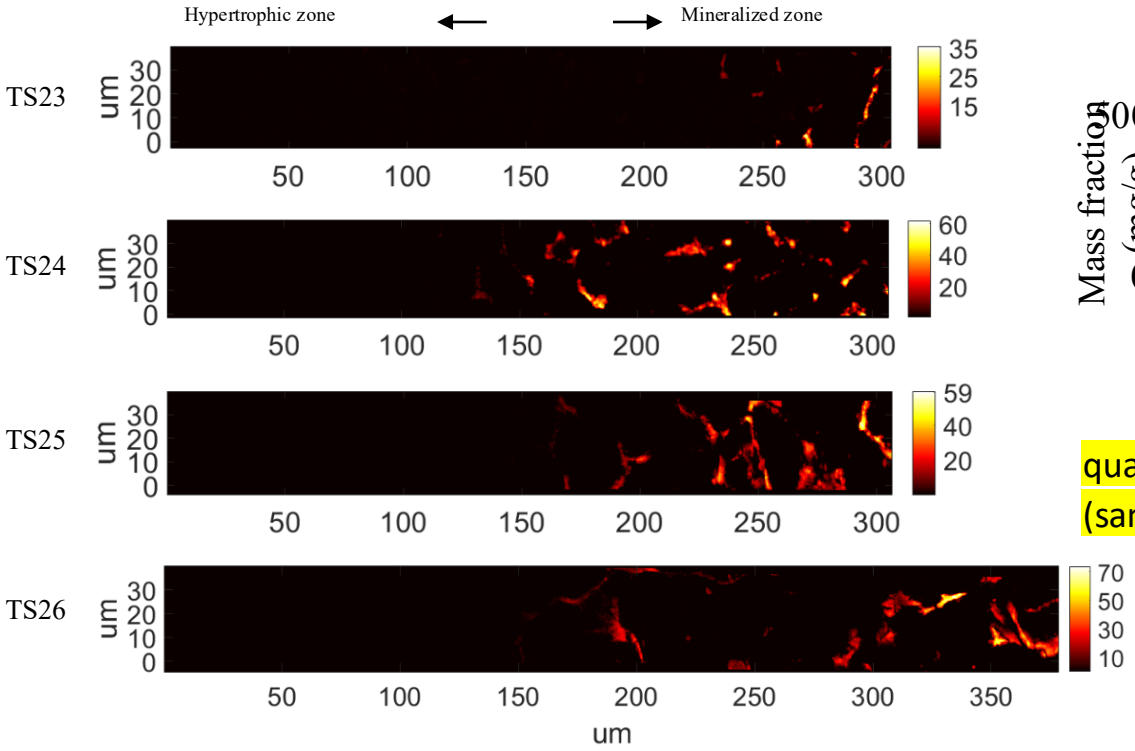


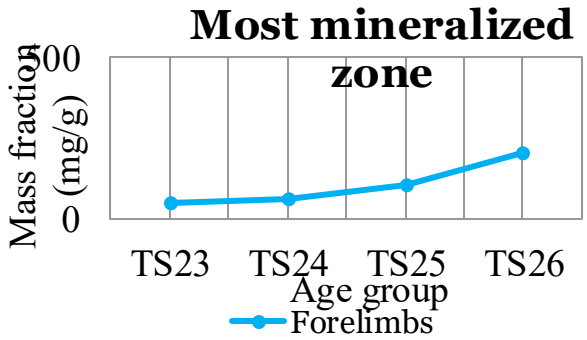
multi-scale:
overview scan
high resolution

XRF @NanoMAX

65-200 nm step size, 14 keV

XRF: Ca-concentration





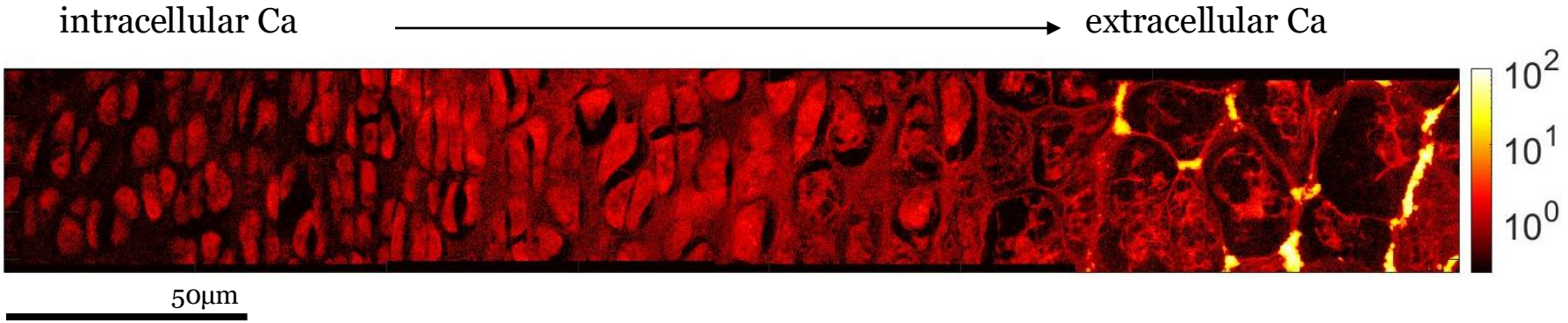
quantification between different samples (same thickness and conditions!)

XRF @NanoMAX

65-200 nm step size, 14 keV

XRF at synchrotron: high resolution and sensitivity!

→ high resolution and high sensitivity



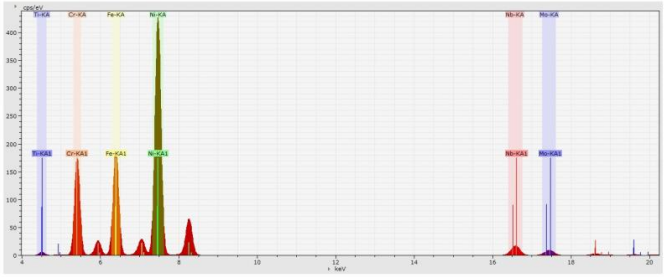
fluorescence Ca mapping

200 nm beam

embryonic bone @ NanoMAX MAXIV

Silva Barreto, I., Le Cann, S., Ahmed, S., Sotiriou, V., Turunen, M.J. Johansson, U., Rodriguez Fernandez, A., Grünewald,T.A., Liebi, M., Nowlan, N., Isaksson, H. *accepted in Advanced Science 2020*

Nickel-based super alloy



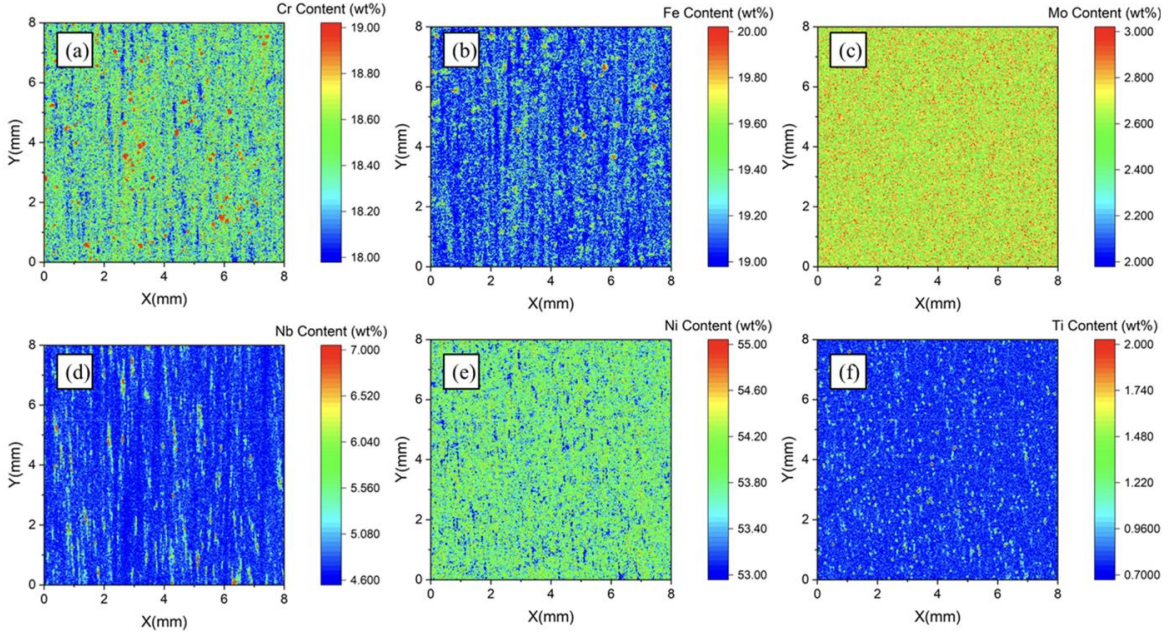


Figure 5. Quantitative distribution results of the S1 test area. (**a**) Cr, (**b**) Fe, (**c**) Mo, (**d**) Nb, (**e**) Ni, and (**f**) Ti.

Zhou X. *et al. Materials* **2023**, *16*, 7163

Nickel-based super alloy

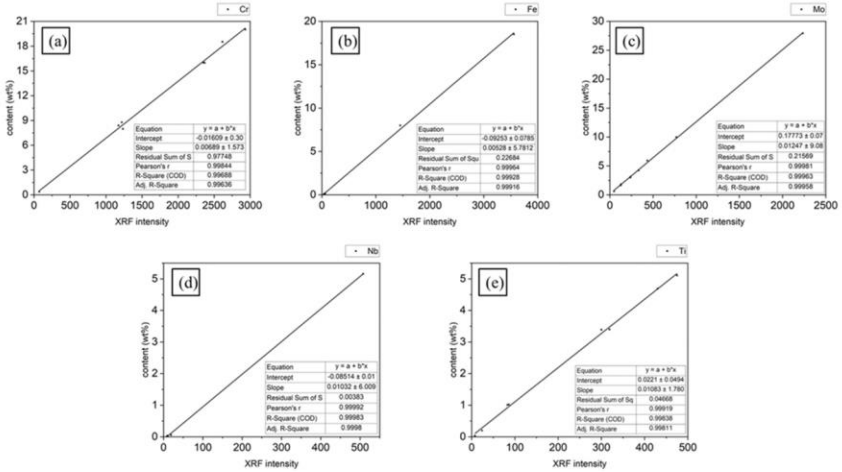


Figure 4. Calibration curves of X-ray fluorescence intensity and reference concentration of nickel-based alloy. (**a**) Cr, (**b**) Fe, (**c**) Mo, (**d**) Nb, and (**e**) Ti.

calibration for quantitative measurements!

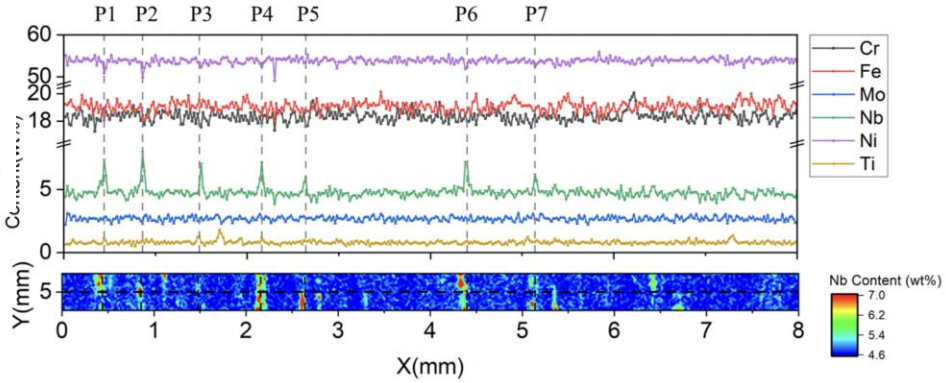
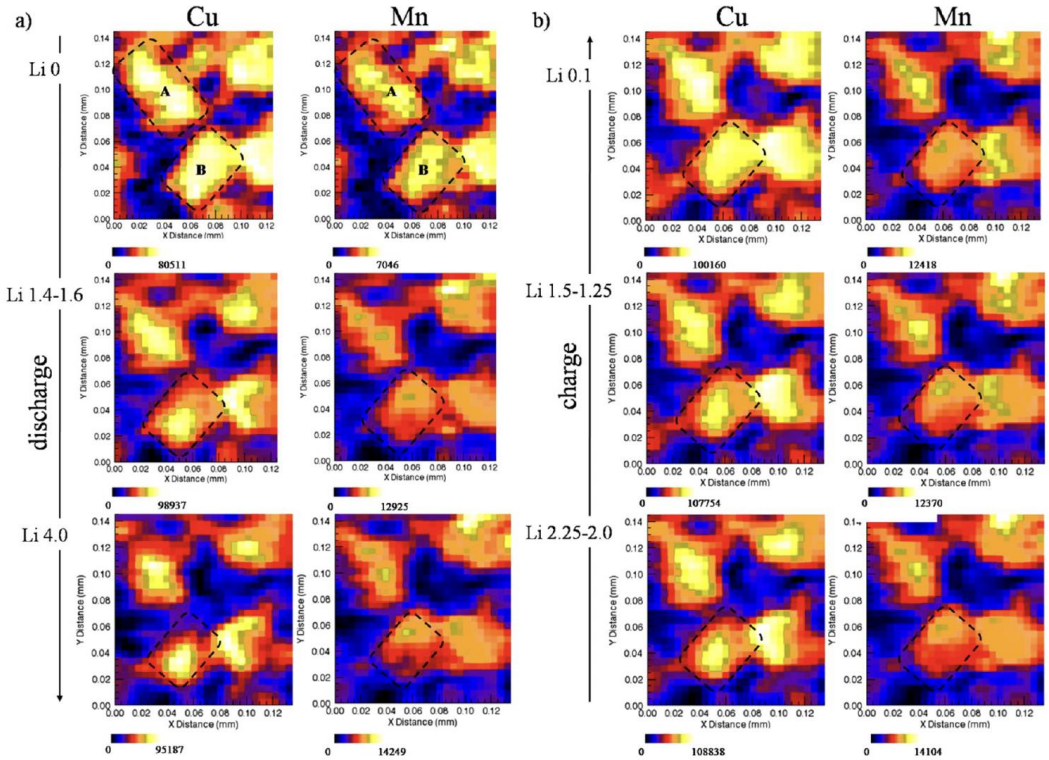


Figure 7. Concentration distributions of different elements at $Y = 5$ mm on the scanning area.

Zhou X. *et al. Materials* **2023**, *16*, 7163

Li-Ion battery

Lithium Insertion into Copper Based Oxysulfides for Li-Ion Batteries



in-situ measurement
during charge and discharge

Robert R. *et al. Chem. Mater.* **2012**, *24*, 2684−2691

pharmaceutical formulations

presence of impurities, in particular trace metals, in pharmaceutical formulations in different labs and batches for quality control

limit of detections LOD:

$$LOD_i = 3 \cdot \sqrt{\frac{IBG_i}{t}} \cdot \frac{C_{Ga}}{I_{Ga} \cdot S_i'} \qquad (3)$$

where IBG_i is the background intensity for the element i (cps); I_{Ga} the internal standard (Ga) intensity (cps), C_{Ga} the internal standard (Ga) concentration ($\mu g \cdot mL^{-1}$), S_i' the relative sensitivity for the element I, and t the measuring time (s).

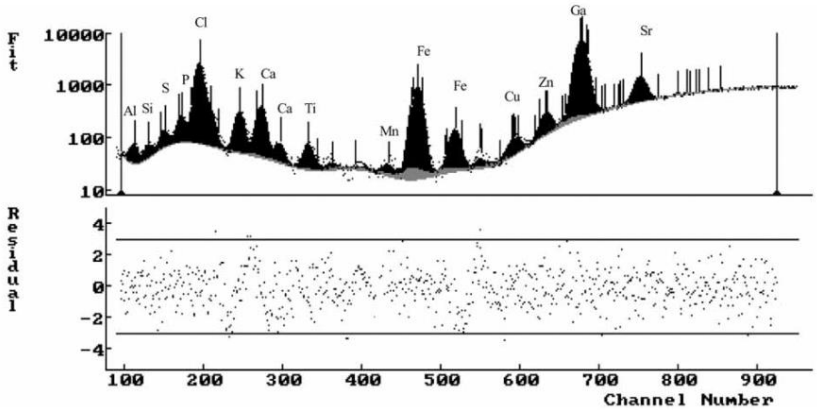


Figure 3. XRF spectrum of covered tablet (sample L11).

synchrotron XRF (measured in total reflection) –> high sensitivity, quantitative

Zucchi, O. L. A. D., et al . (2005). *Instrumentation Science & Technology*, *33*(2), 215–227.

brain

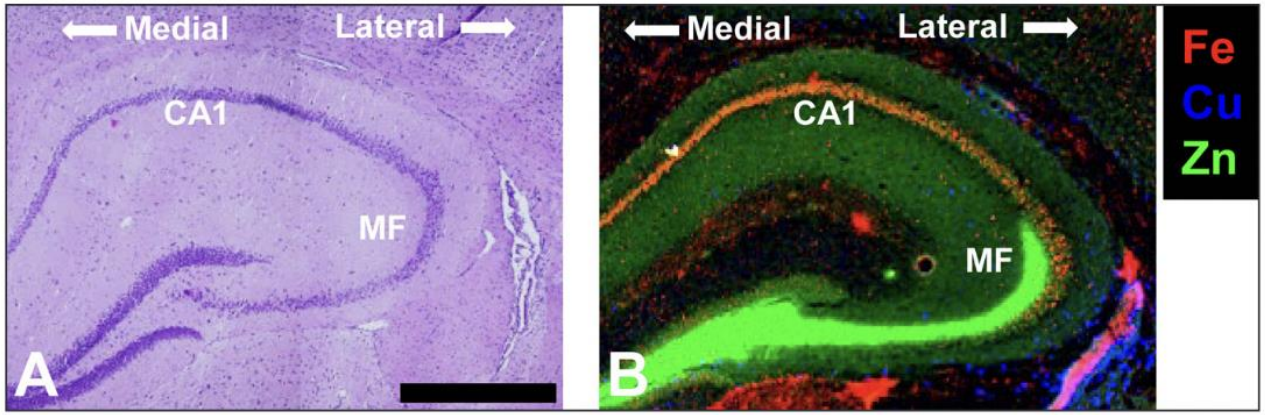


Figure 1. (A) Haematoxylin and eosin histology of the hippocampus showing the characteristic organisation of brain cells (purple dots). (B) XRF elemental maps highlighting two key sub-regions of the hippocampus, the Fe-enriched neuron layer Corpus Ammonis 1 (CA1) and the Zn enriched mossy fibre region (MF) that contains numerous neuron–neuron connections (synapses). The medial to lateral orientation of the tissue is shown. Scale bar = 500 µm. Data was collected at the X-ray fluorescence microscopy beamline at the Australian Synchrotron, and is adapted with permission from Reference 12.

Hollings and Hackett, *Spectroscopy Europe/World* 2022, 34, 4