PAUL SCHERRER INSTITUT

PSI

EPFL

Marianne Liebi– Material Science at Large Scale Facilities

X-ray Fluorescence Spectroscopy (XRF) exercise

EPFL Master Course 2024 MSE435

case study groups

Caulier	Lucie Julia	Case study 5: GaN nanowires
Zanada	Vincent Jonathan Thomas	Case study 5: GaN nanowires
Malmasson	Charles Joseph	Case study 5: GaN nanowires
Filippo	Andrea Saverio	Case study 9: Pharmaceutical formulations
Bréas	Davide Raphaël	Case study 9: Pharmaceutical formulations
Greulich	Eric	Case study 9: Pharmaceutical formulations
Grosjacques	Noah	Case study 8: Nickel-based superalloys
Casagrande Kulcke	Maximilian	Case study 8: Nickel-based superalloys
Kulkarni	Pranav	Case study 8: Nickel-based superalloys
Micaleff	Arthur Baptiste	Case study 11: Li-ion batteries
Bonvin	Jérémie Florentin	Case study 11: Li-ion batteries
Rolle	Olivier Noé	Case study 11: Li-ion batteries
Hassanzadeh	Mohammadreza	Case study 12: Brain
Chen	Pin-Ying	Case study 12: Brain
Chen	Kuan-Yu	Case study 12: Brain
Ducommun	Léandre	Case study 7: Human bone
Bour	Thomas Louis Vincent	Case study 7: Human bone
Paratte	Noé	Case study 7: Human bone

Access to large scale facilities

Synchrotrons, FEL's and Neutron Sources have in general to access routes

- proprietary beamtime, mainly for industry
  - paid for
  - faster access, guarenteed time-slot
  - confidential: data results are protected and available only to the customer
  - most facilities offer "packages" including support for the measurement or data analysis in technology transfer center
  - no obligation to publish the results
- open access beamtime
  - open to both the national and the international user community
  - beamtime proposals are submitted at specific deadlines (typically 2 times a year)
  - beamtime allocation based on the recommondations of the external Scientific Committee
  - free of charge
  - publish scientific results in internationally accepted journals and give proper credit to the beamline scientists involved in the experiment and proper mention of the facilities (publication policiy)
  - written report has to be submitted within 6 months of the experiment

SLS Techno Trans AG

anaxam
analytics for advanced manufacturing

Total Beamtime

Title	Amount
User time	70%
Commissioning and in-house research time	25%
Directors time	5%

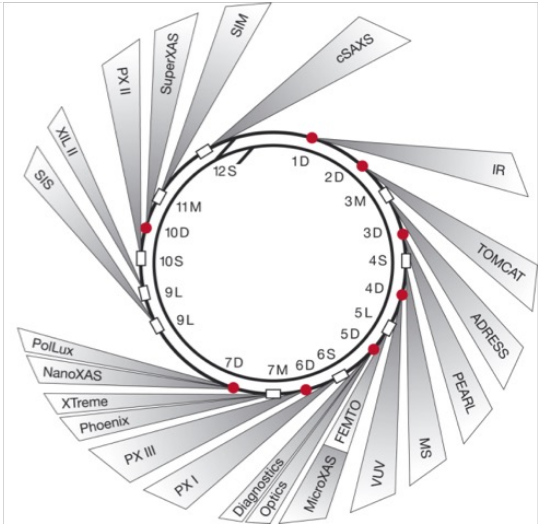
Comissioning and in-house research includes alignment of the beamline, new components, detector integration, method development and part of own research of the groups operating the beamline

What beamline/endstation?

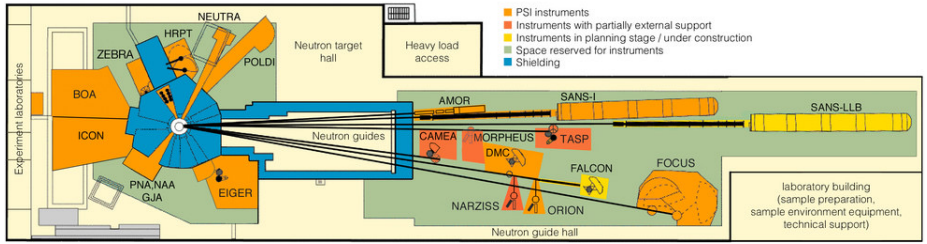
https://www.psi.ch/de/science/methods-and-scopes-of-the-large-research-facilities

43 endstations at PSI

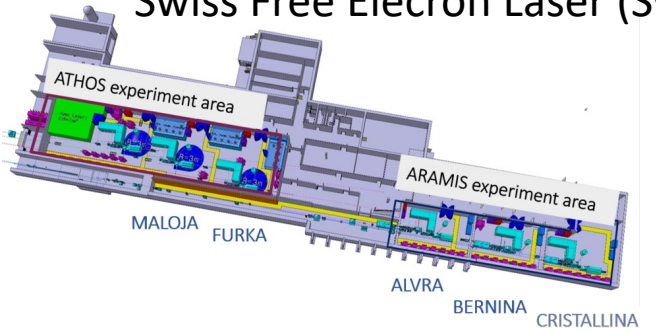
Swiss Light Source (SLS)



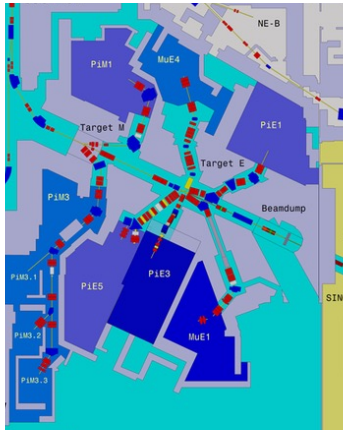
Swiss Spallation Neutron Source (SINQ)



Swiss Free Elecron Laser (SwissFEL)



Swiss Muon Source (SμS)



Beamtime proposals – general guidelines (SINQ)

- The proposals need a clear and precise definition of the proposed experiments and a well written scientific justification why these experiments should be performed.
- The aim of the experiment should clearly be stated and the proposal should be specific.
- A reasonable time estimate should be included. If necessary please contact the instrument responsible(s) in advance.
- The strategy/method of data treatment should be described.
- Previous/preliminary data should be shown if available.
- Please indicate on the proposal if the project is granted by a funding agency.
- New SINQ users should contact the respective instrument responsibles well in advance to discuss the feasibility of the proposed experiment.
- Please make use of the option to link **related previous proposals with their experimental reports** to the new one. A proper mention of previous results will provide a certain 'bonus' during the evaluation process. This new feature replaces the previous option to submit 'continuation proposals'. Please download the form here and submit the report via the Digital User Office DUO.
- Regular **submission deadlines: 15/05 and 15/11 (deviations possible, please always check here)**

Guidelines for entering the description as plain text

- Limit to the equivalent of 3 Pages A4
- Please adhere to the proposed structure
- Upload any figures separately within 'step 3' of the proposal submission.

A) Goal of the experiment

... insert text here ...

B) Background

... insert text here ...

C) Experimental method; specific requirements; need for SLS features

... insert text here ...

D) Results expected

... insert text here ...

E) Estimate and justification of the beamtime

... insert text here ...

F) References relevant to the experiment description

... insert text here ...

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

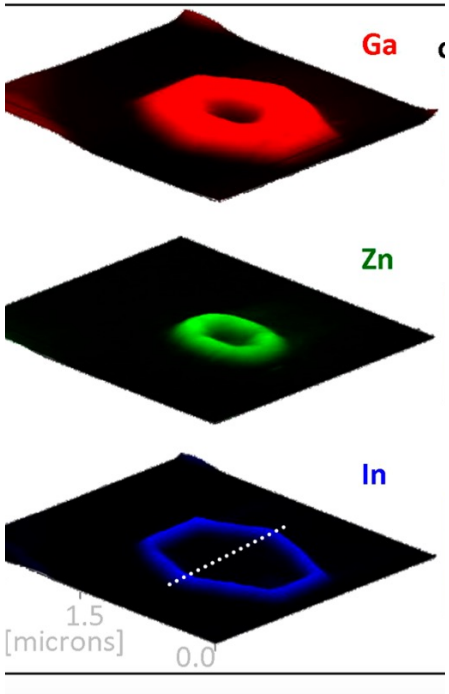
Max 2 points

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.

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: Nanowires

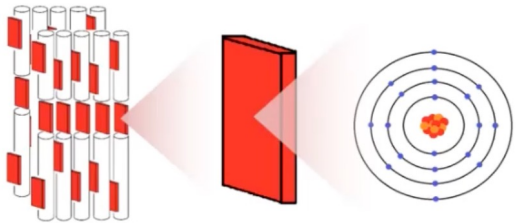


multi-shell single core nanowire

→ synchrotron XRF for high resolution

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

Application example bone

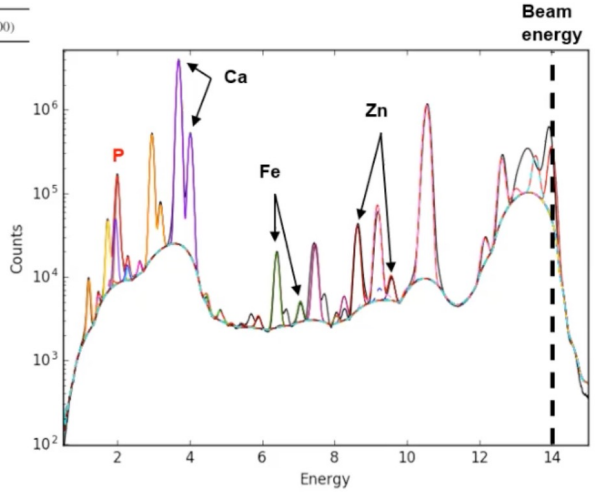


Interesting elements in bone:

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

Energy of K lines [1]

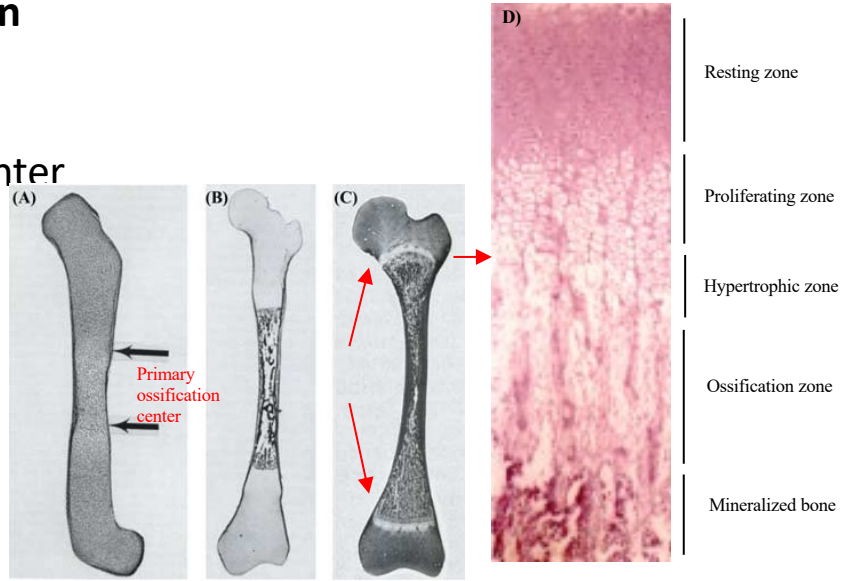
Z	Element	Kα1 (I = 100)	Z	Element	Kα1 (I = 100)
13	Al	1.49	38	Sr	14.16
14	Si	1.74	39	Y	14.96
15	P	2.01	40	Zr	15.77
16	S	2.31	42	Mo	17.48
17	Cl	2.62	44	Ru	19.28
18	A	2.96	46	Pd	21.17
19	K	3.31	47	Ag	22.16
20	Ca	3.69	48	Cd	23.17
22	Ti	4.51	50	Sn	25.27
24	Cr	5.41	51	Sb	26.36
25	Mn	5.90	53	I	28.61
26	Fe	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

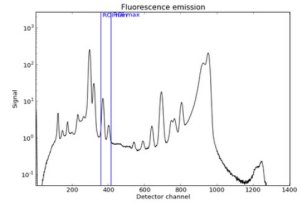
- Cartilage template
- Primary ossfication center
- Growth plates



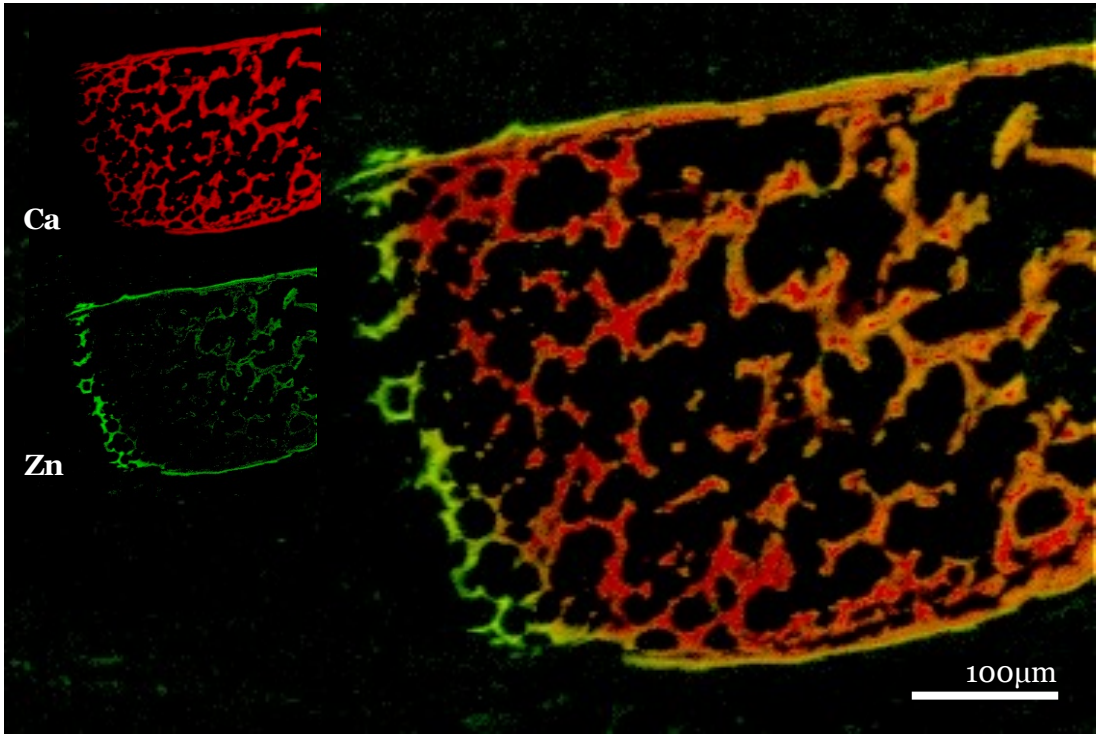
A), B), C) from *Nowlan et al. 2007, Annals of the New York Academy of Sciences*

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

XRF: example embryonic bone development



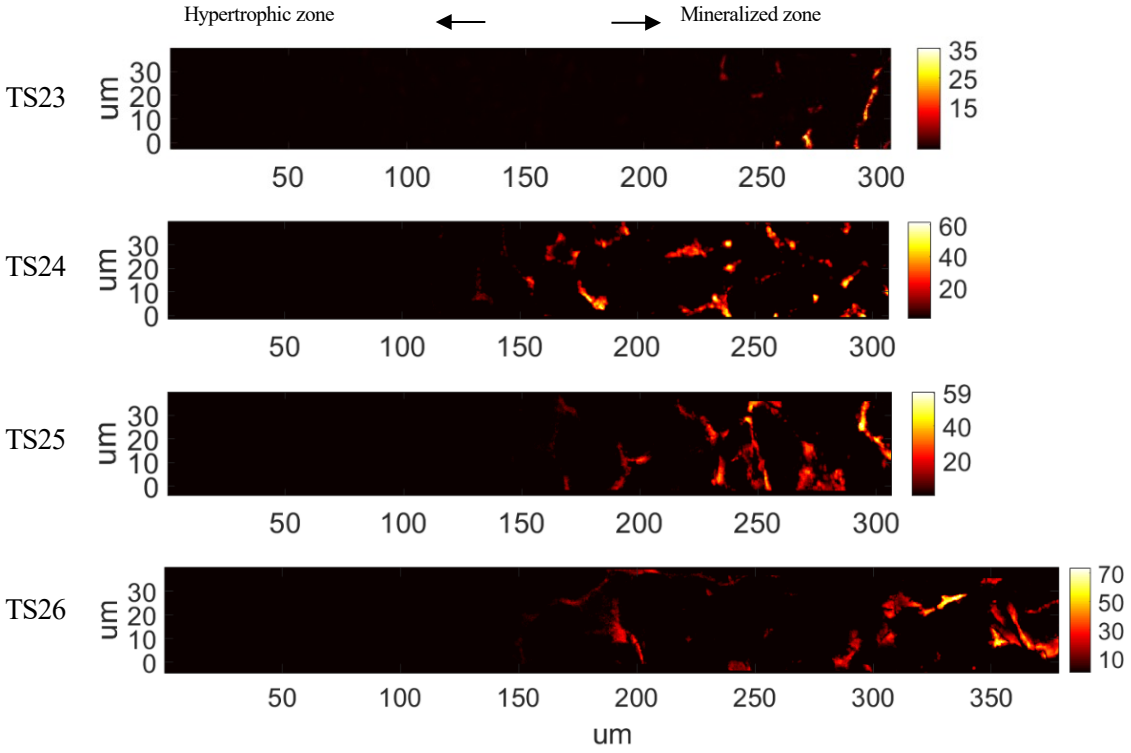
2µm beam @ID13 ESRF



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

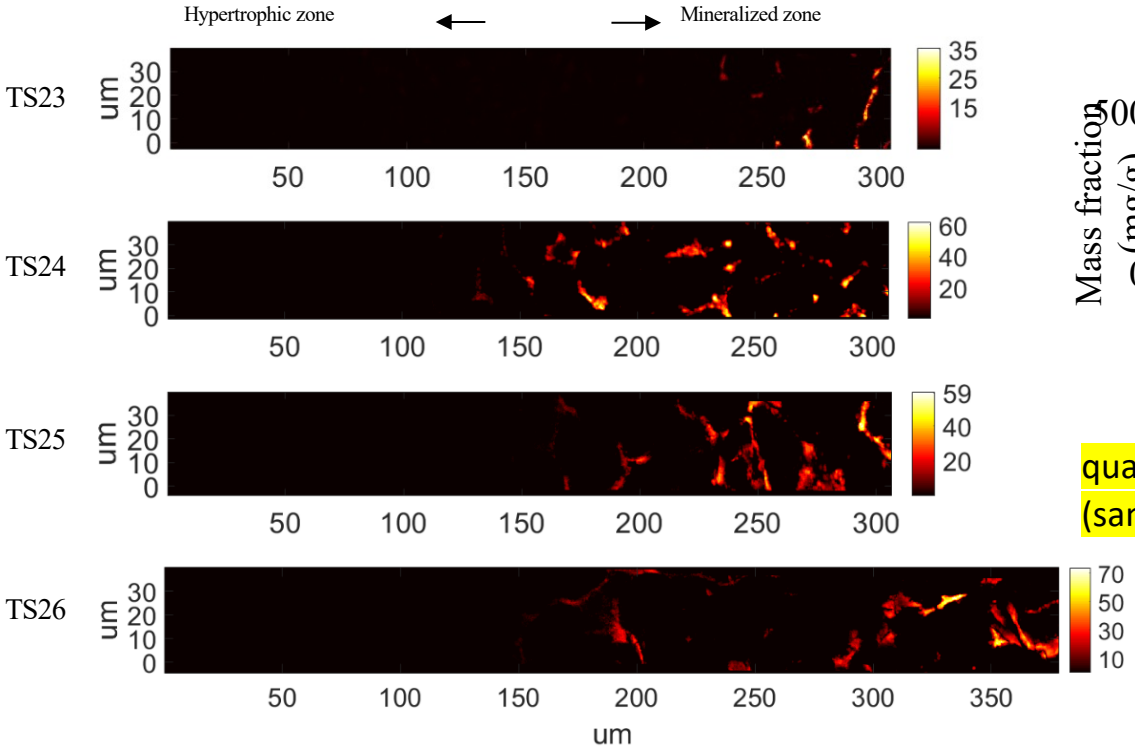


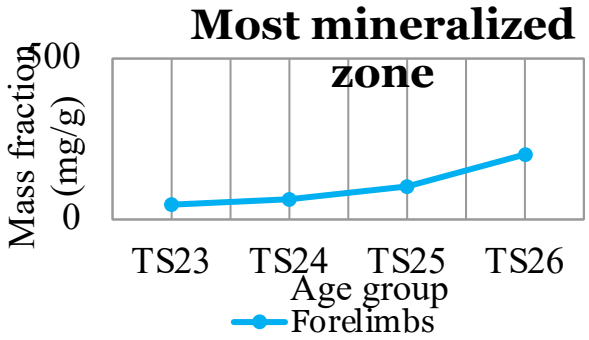
multi-scale:
overview scan
high resolution

XRF @NanoMAX

65-200 nm step size, 14 keV

XRF: Ca-concentration





quantification between different samples (same thickness and conditions!)

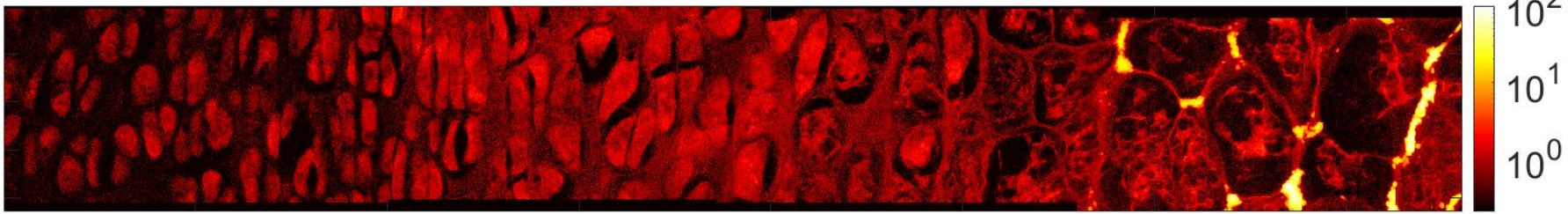
XRF @NanoMAX

65-200 nm step size, 14 keV

XRF at synchrotron: high resolution and sensitivity!

→ high resolution and high sensitivity

intracellular Ca → extracellular Ca



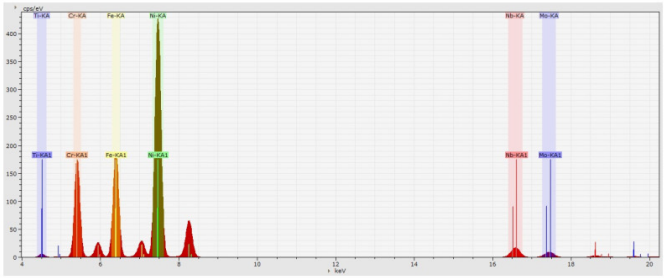
fluorescence Ca mapping

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



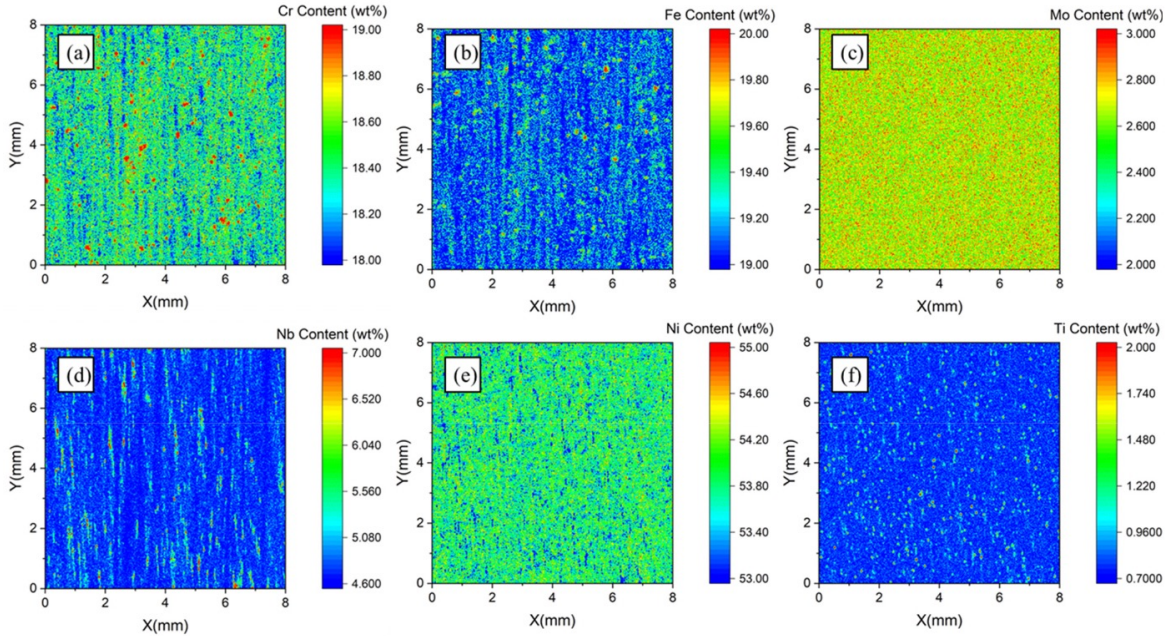


Figure 5. Quantitative distribution results of the S1 test area. (**a**) Cr, (**b**) Fe, (**c**) Mo, (**d**) Nb, (**e**) Ni, and (**f**) Ti.

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

Nickel-based super alloy

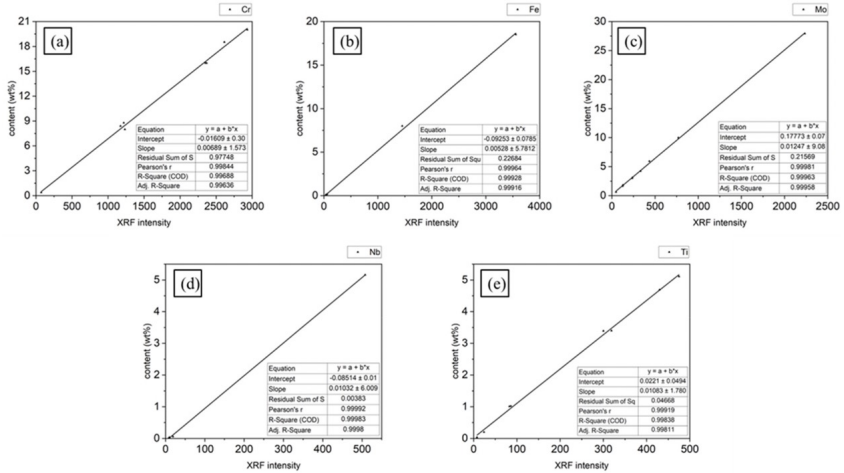


Figure 4. Calibration curves of X-ray fluorescence intensity and reference concentration of nickel-based alloy. (**a**) Cr, (**b**) Fe, (**c**) Mo, (**d**) Nb, and (**e**) Ti.

calibration for quantitative measurements!

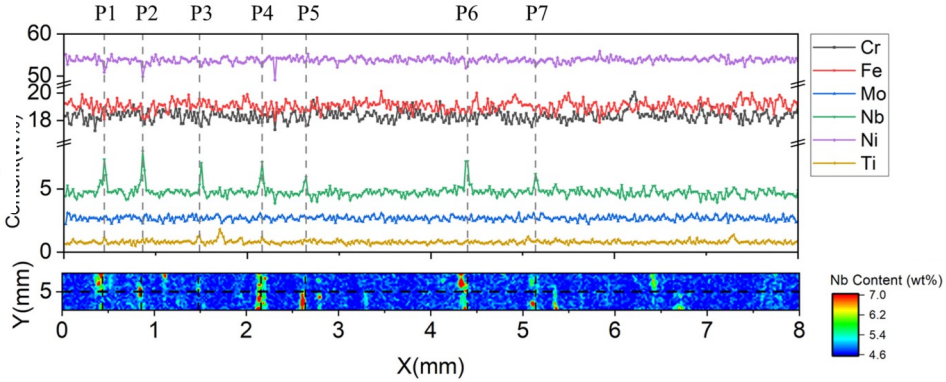
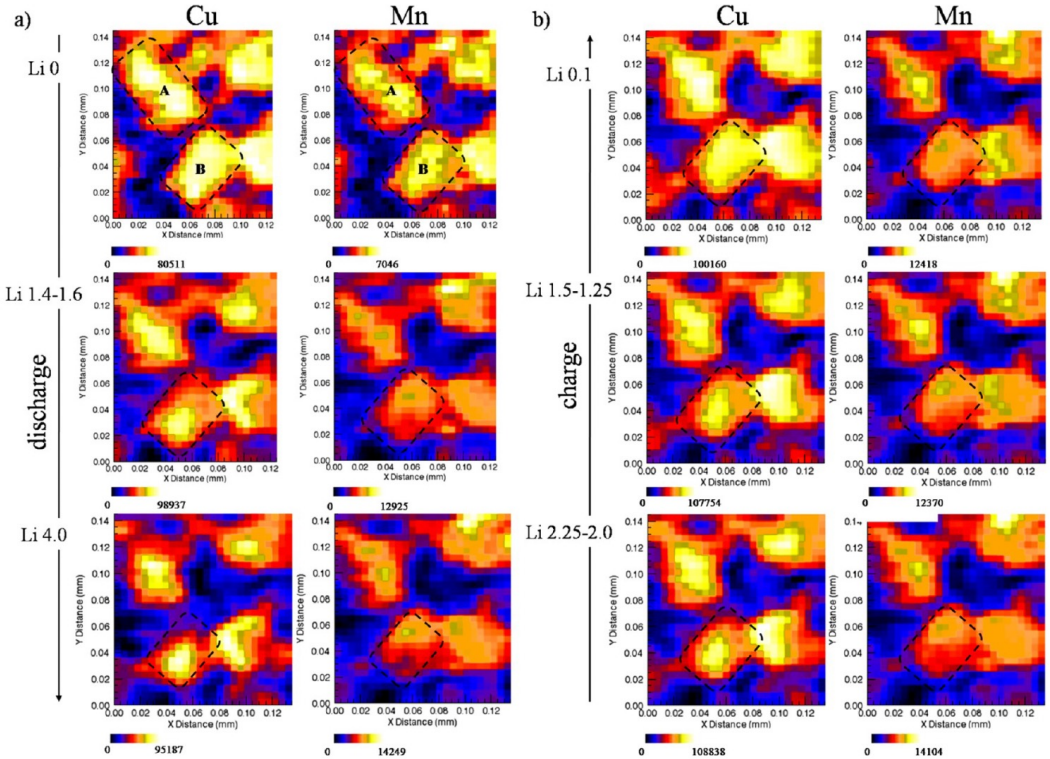


Figure 7. Concentration distributions of different elements at $Y = 5$ mm on the scanning area.

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).

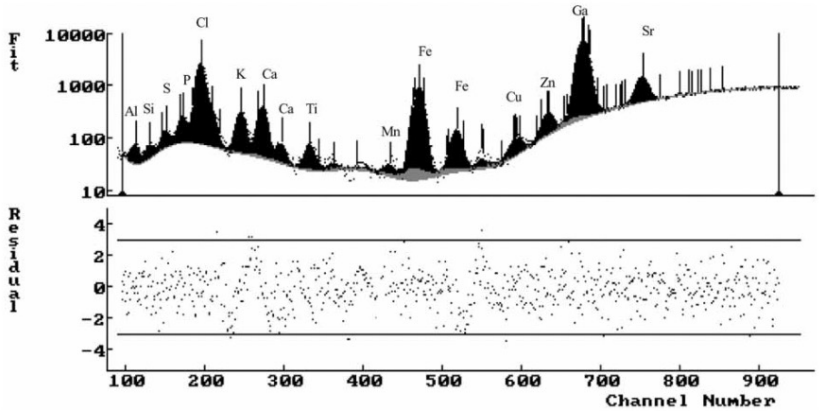


Figure 3. XRF spectrum of covered tablet (sample L11).

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

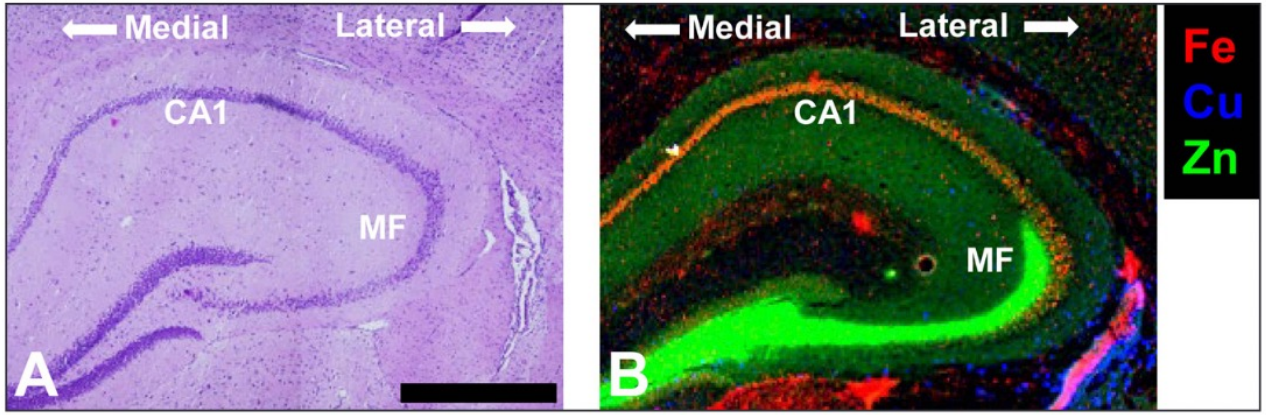


Figure 1. (A) Haematoxylin and eosin histology of the hippocampus showing the characteristic organisation of brain cells (purple dots). (B) XRF elemental maps highlighting two key sub-regions of the hippocampus, the Fe-enriched neuron layer Corpus Ammonis 1 (CA1) and the Zn enriched mossy fibre region (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