Seeing the world through other eyes: Optimizing the visualization of sample composition by micro-XRF

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Introduction
Presenters

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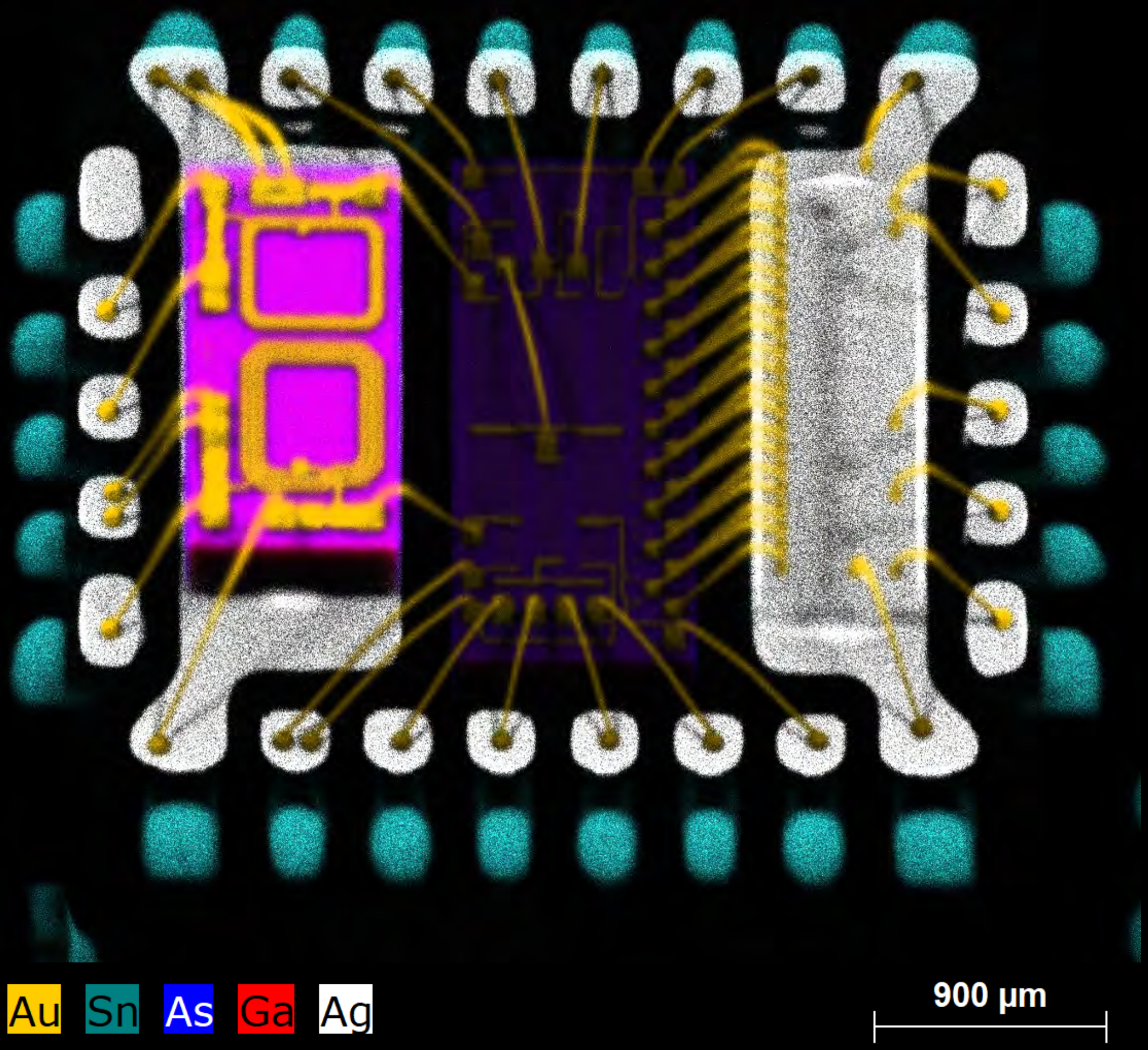
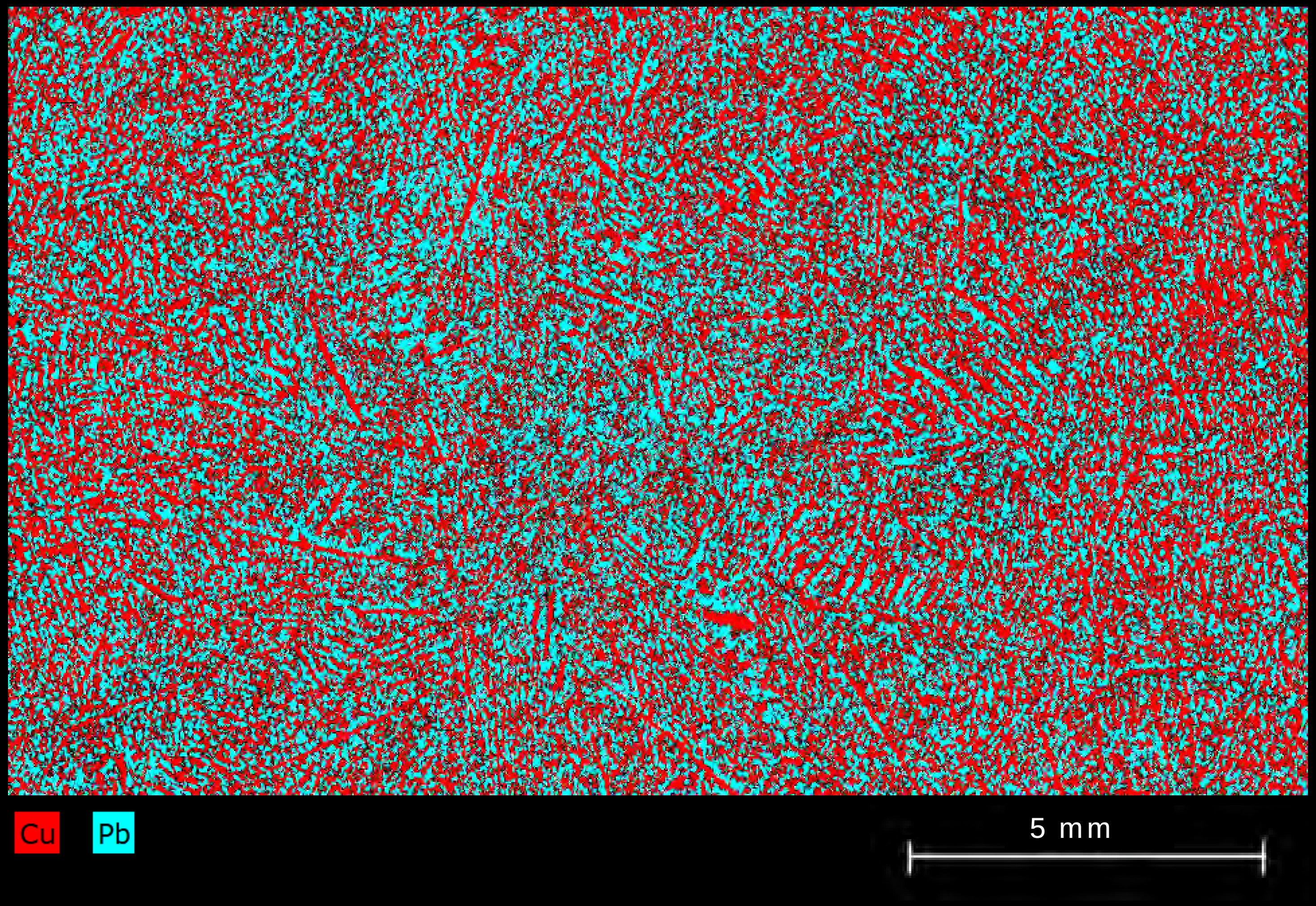
Freeze-dried potato

Bluetooth antenna

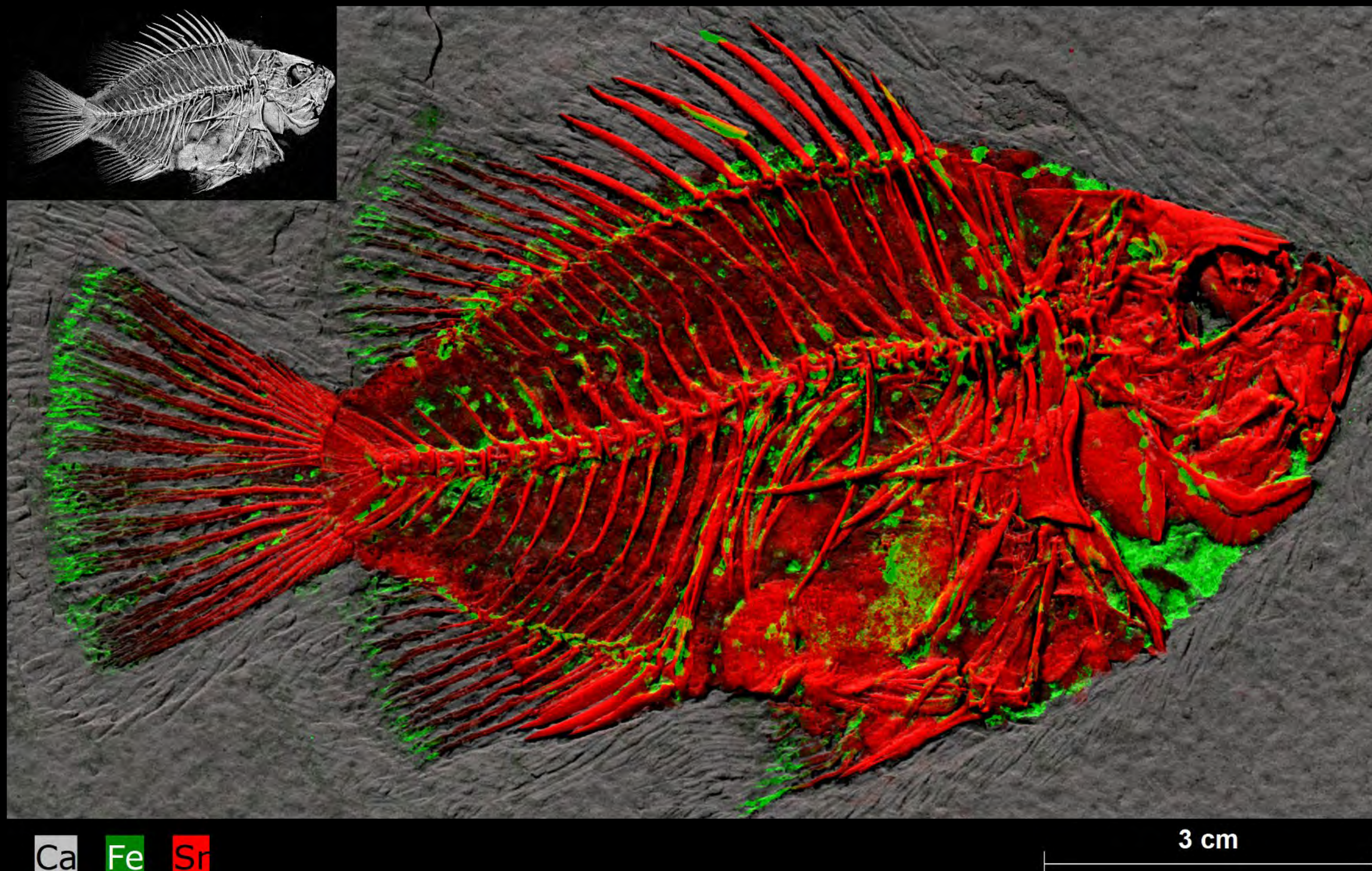


Copper alloy



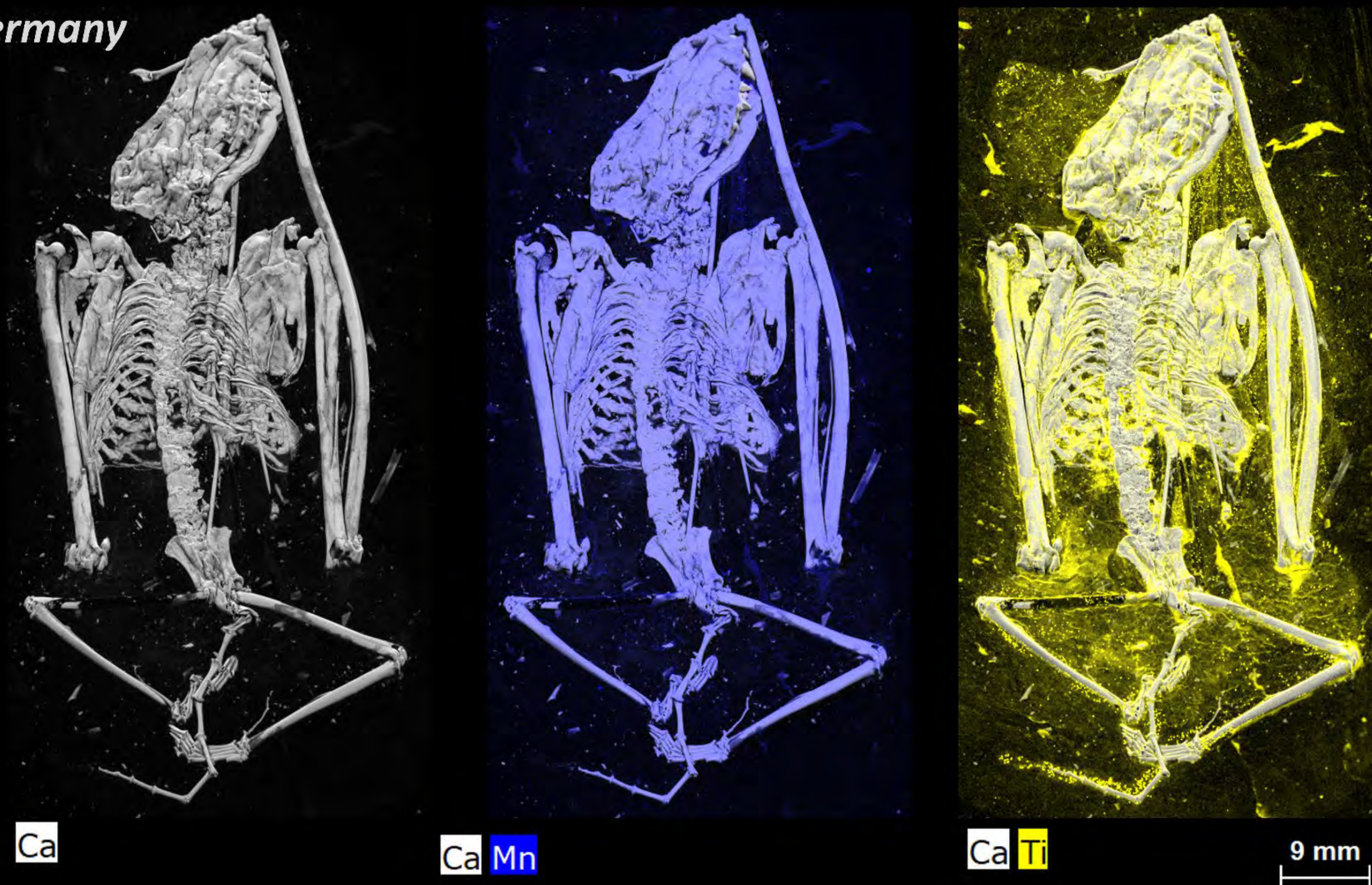
Fish fossil

Green River Fm



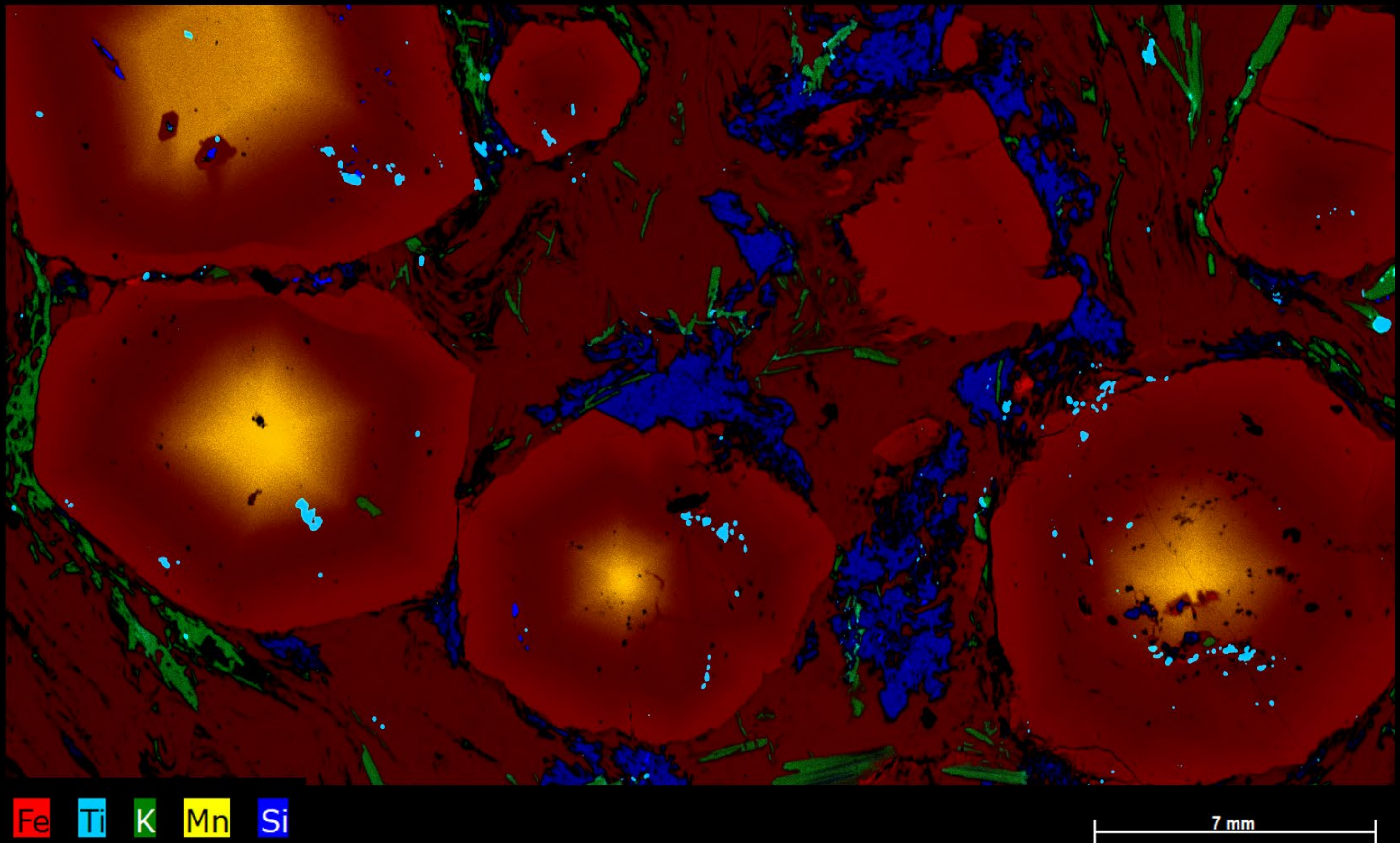
Fossil bats

Messel Pit, Germany



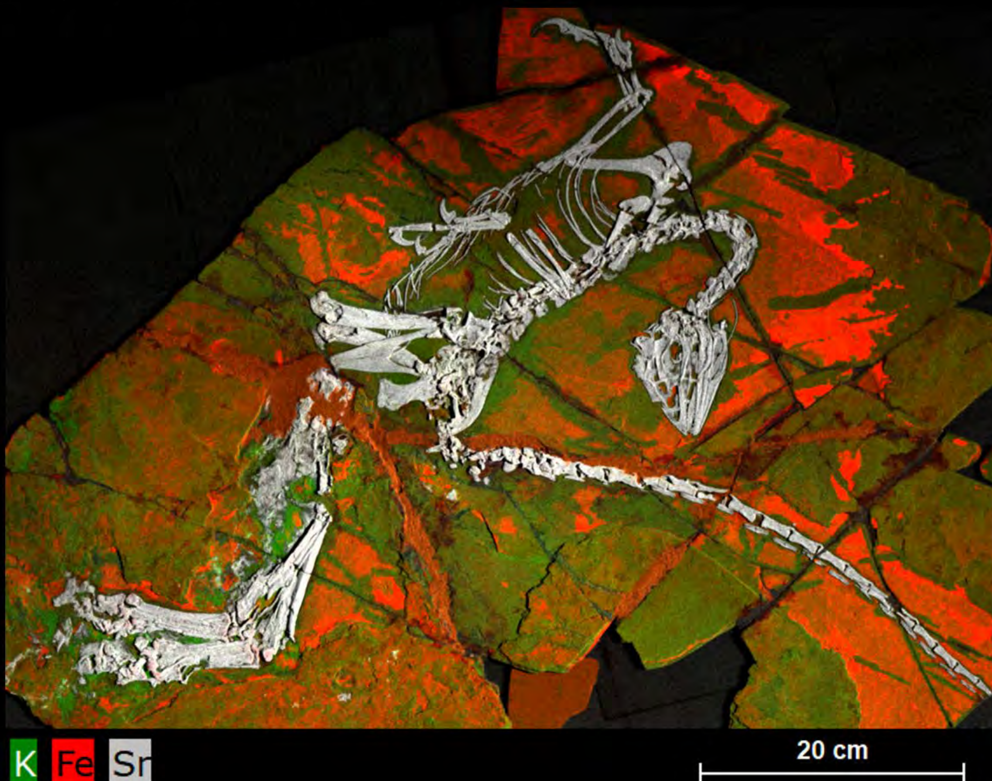
Garnets

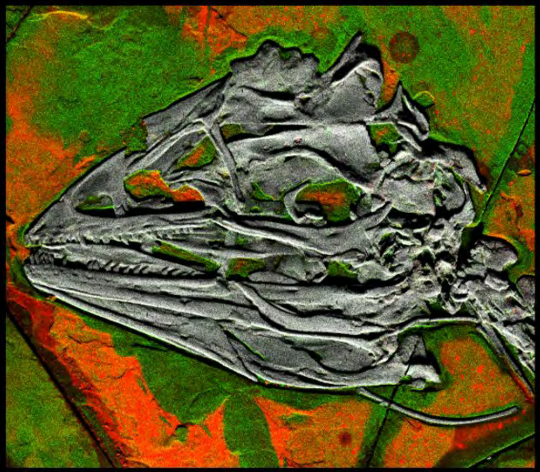
Zillertal, Austria



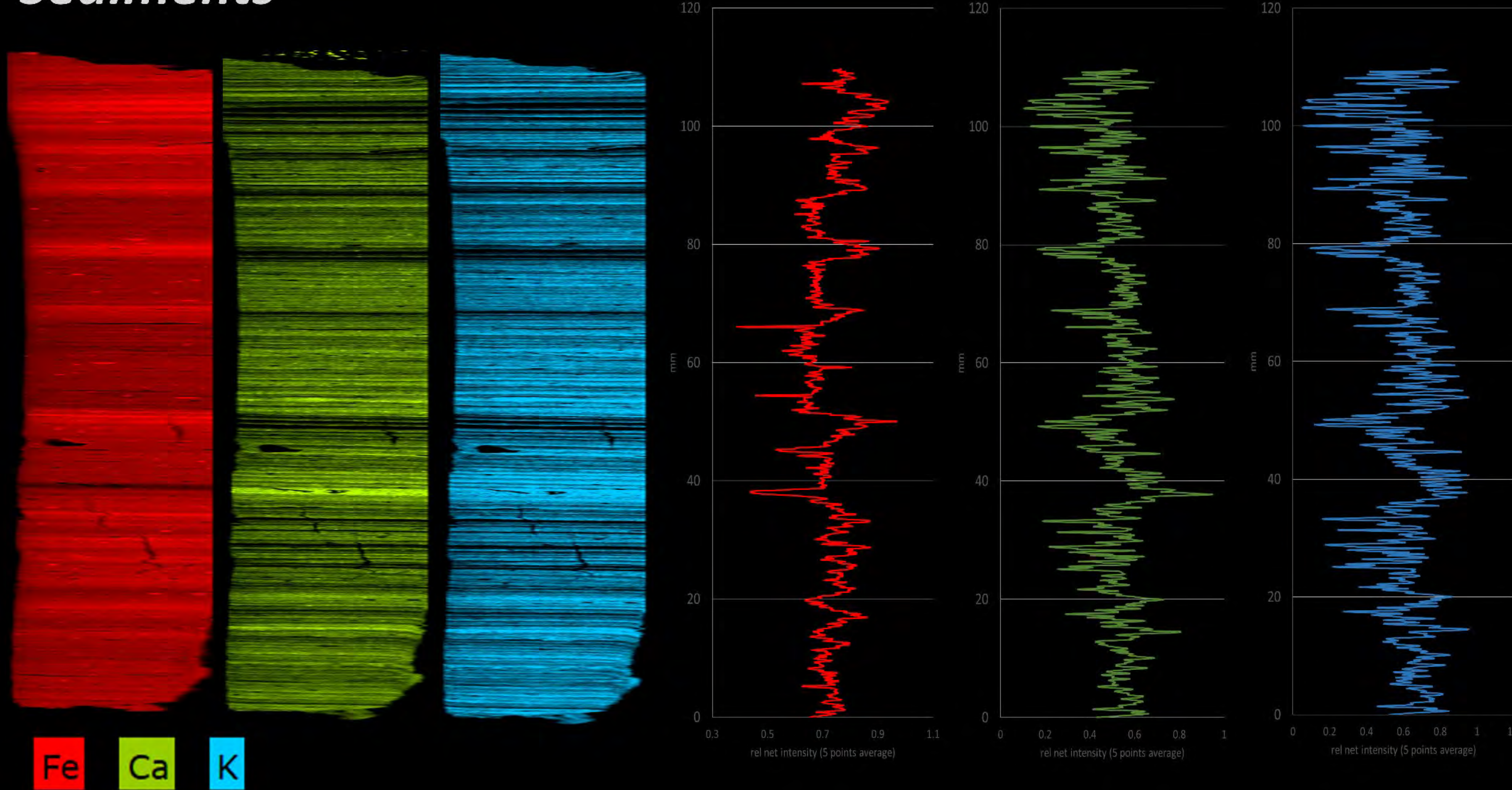
Jianianhualong

Early Cretaceous theropod, China





Sediments


Fe
Ca
K
120
100
80
60
40
20
0
mm
0.3
0.5
0.7
0.9
1.1
0
0.2
0.4
0.6
0.8
1
1.2
rel net intensity (5 points average)

Overview

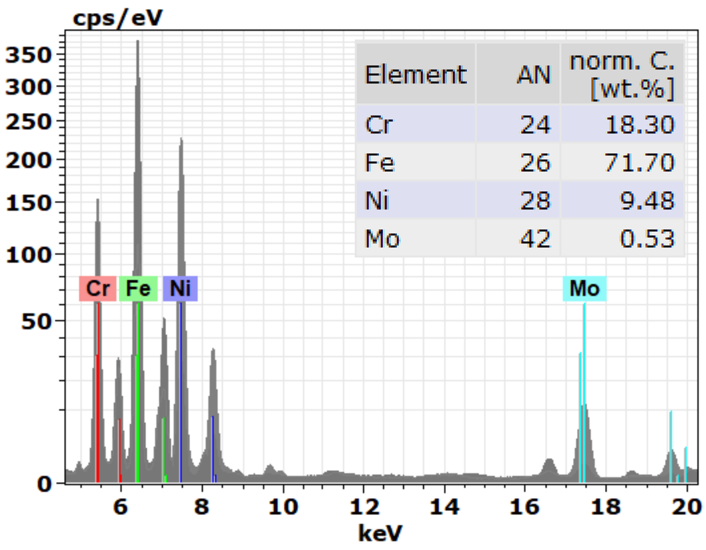
- Introduction
  - From **XRF** to **micro-XRF**
  - Measurement parameters and **the analytical question**
  - Hypermap (position-tagged spectroscopy)
- Optimizing measurement conditions
  - Pixel size and measurement time
  - Pixel size and grain size
  - Pixel size and spot size
  - Pixel size and sample structure
  - Additional measurement parameters
- Q&A session

XRF features and benefits
Conventional XRF

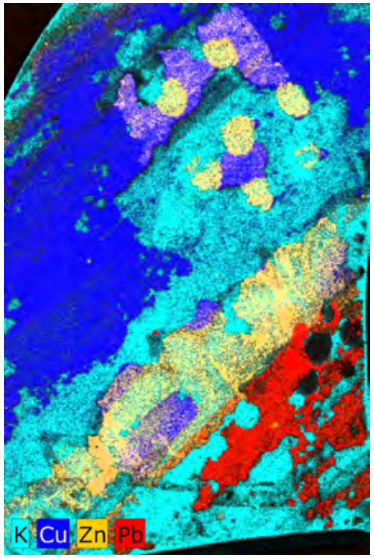
- **Conventional X-ray fluorescence analysis** (XRF) analytical tool for qualitative and quantitative material analysis
- Ideal as a **standardized task**
- XRF tells you **which** elements are in the sample and **how much** of each
- Usually sample needs a “**preparation**” includes **homogenization** and or **dilution** for matrix reduction

Information lost!

The compositional variations in a sample may be a crucial property of the material



Micro-XRF features and benefits
At a glance



- **Micro-XRF** is **XRF** with a small spot (M4 TORNADO <20 µm)

→ Micro-XRF reveals **where** the elements are

→ Micro-XRF is ideal for **non-homogeneous** samples

- It usually requires **minimal or no sample preparation**
- **Quantitative micro-XRF** is feasible for sufficiently homogeneous areas of a sample
- The measurement conditions are very **flexible** in order to address different analytical tasks or requirements posed by samples

→ A well-defined analytical question
is a key for optimal analytical conditions

Micro-XRF parameter options

Why an analytical question?

Multitude of measurable samples

- Solid/powder/liquid
- Metals/rocks/glass/tissue
- Unprepared/prepared
- Down to ~ 50 µm
- Up to 20x16x10 cm^3 and 7 kg

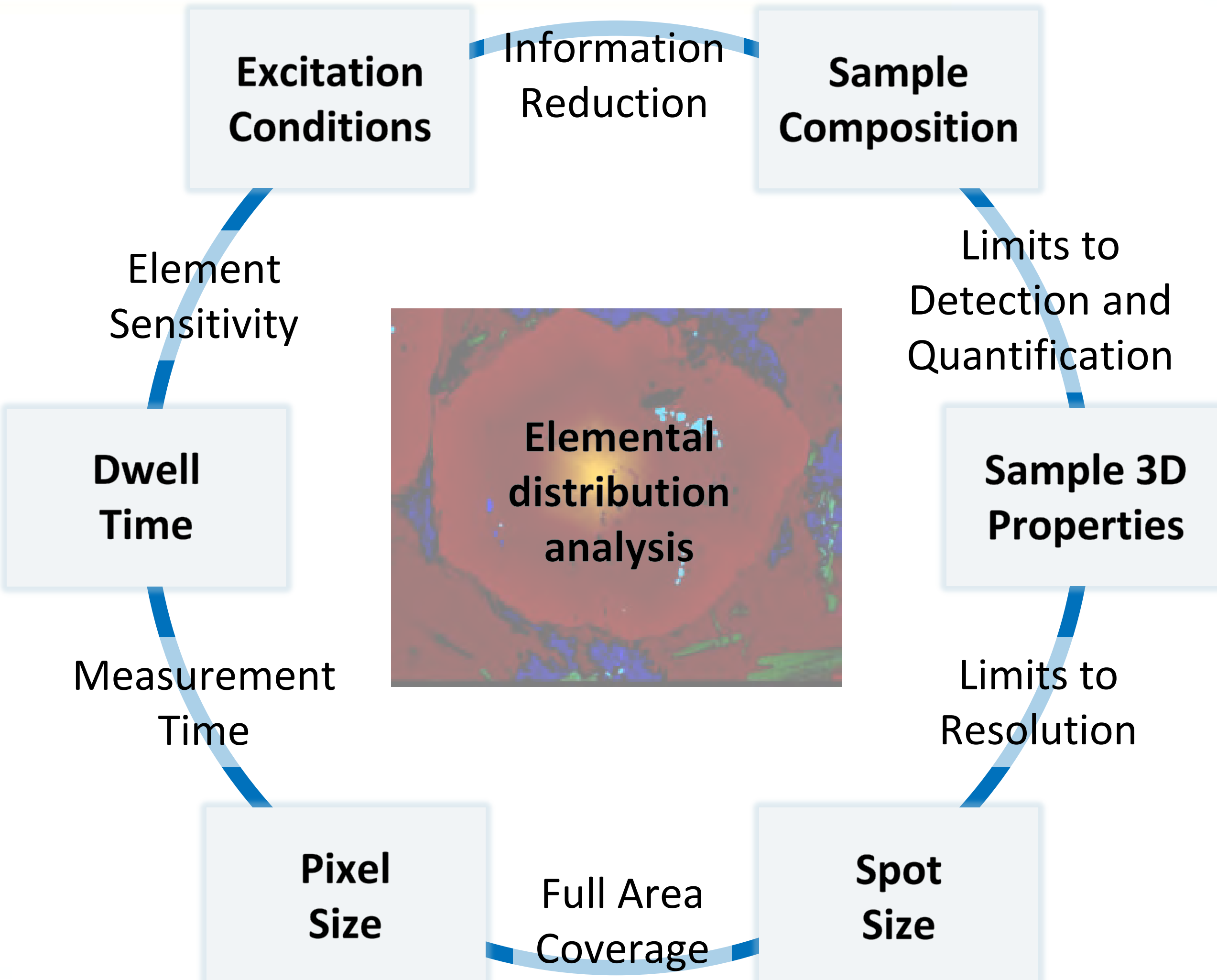
Flexible measurement conditions

- Point / line profile / full area
- Dwell time
- Pixel size
- Spot size
- Tube HV/current
- Filters
- Detectors
- Atmosphere and pressure
- Sample presentation

The **analytical question** helps to find the ideal set of measurement conditions for obtaining good results

Sample → **Analytical question** → Measurement conditions → Meaningful results

Micro-XRF parameter options
How are they interrelated?

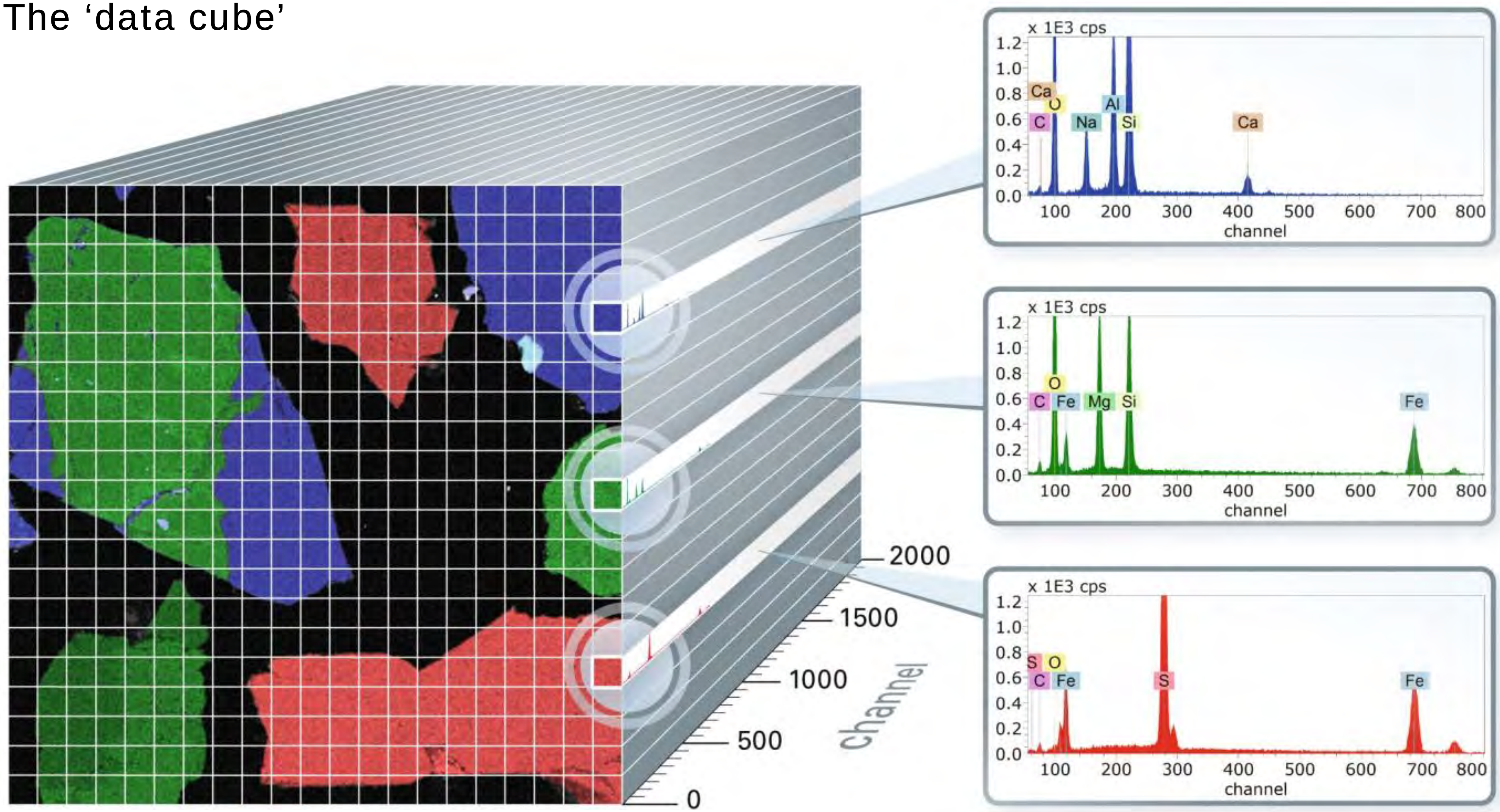


Micro-XRF and the data cube

PTS – Position Tagged Spectroscopy

All map data at hand

The 'data cube'



Pixel size

Distance over which the collected data is defined as a single spectrum during a sample scan.

Sometimes referred to as ‘step size’, even though this term is misleading for on-the-fly measurements.

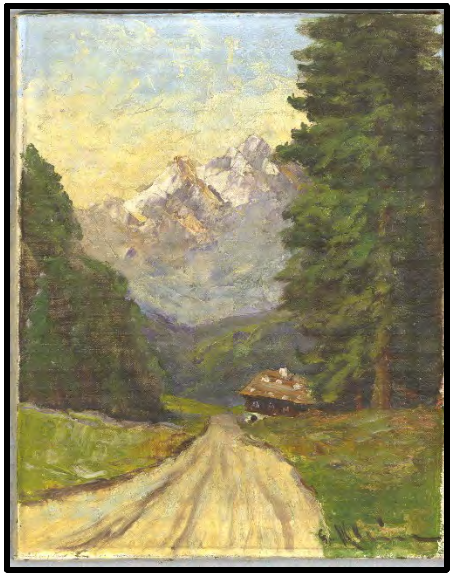
Dwell time

The **time** that the instrument spends collecting data per ‘pixel’ or spectrum.

With pixel size being a distance the value dwell time per pixel has the unit of **speed**. It is the speed of the X-ray beam relative to the sample surface (i.e. the speed of the measure head of the M6 JETSTREAM or the speed of the sample stage of the M4 TORNADO).

Introduction to pixel size and dwell time
What to consider? (M6 JETSTREAM)

Test painting



36 cm

46 cm

Variation of dwell time

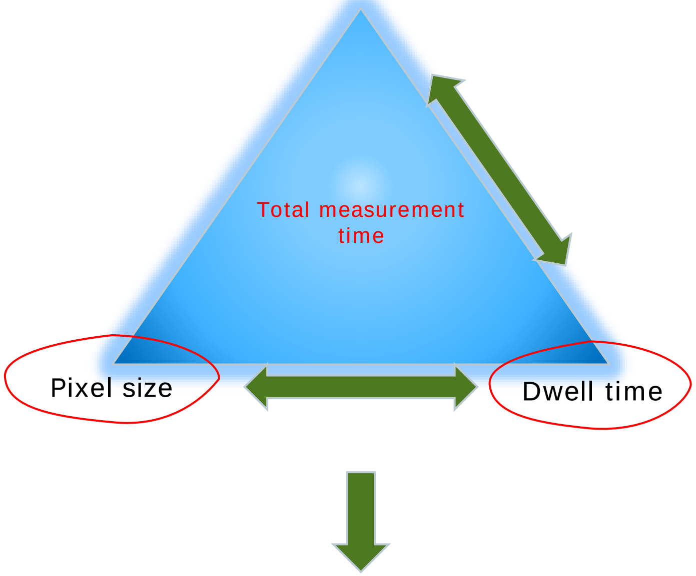
233 kpixel
800 µm / 8 ms

233 kpixel
800 µm / 800 ms

Variation of pixel size

233 Mpixel
800 µm / 8 ms

3.7 Mpixel
200 µm / 8 ms

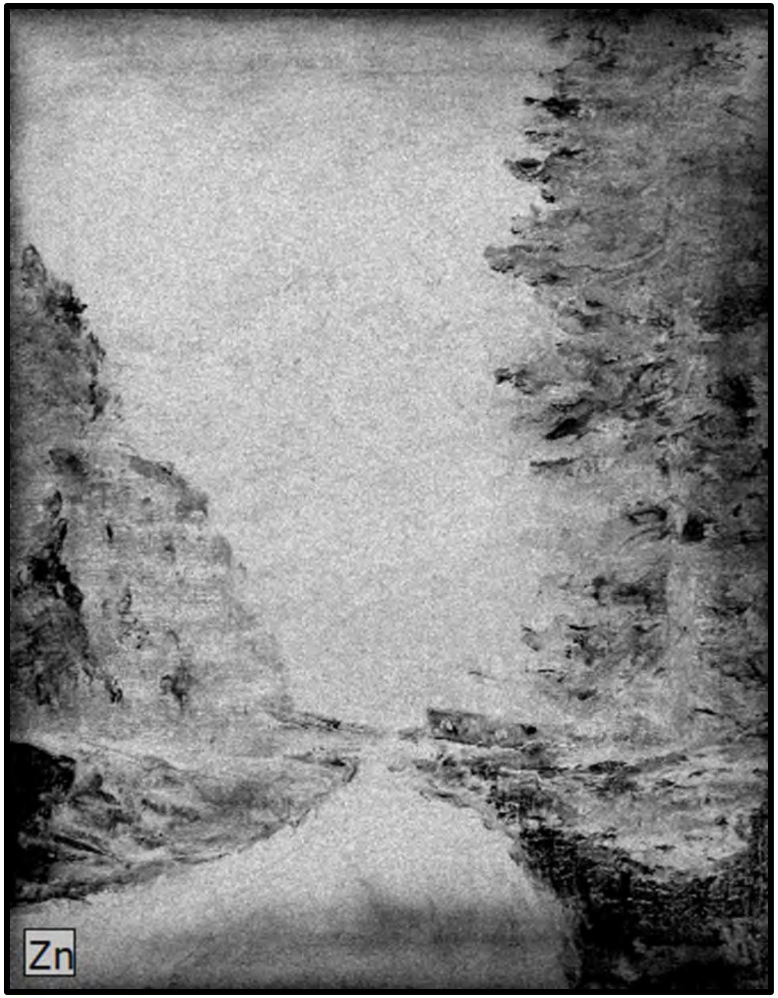


results

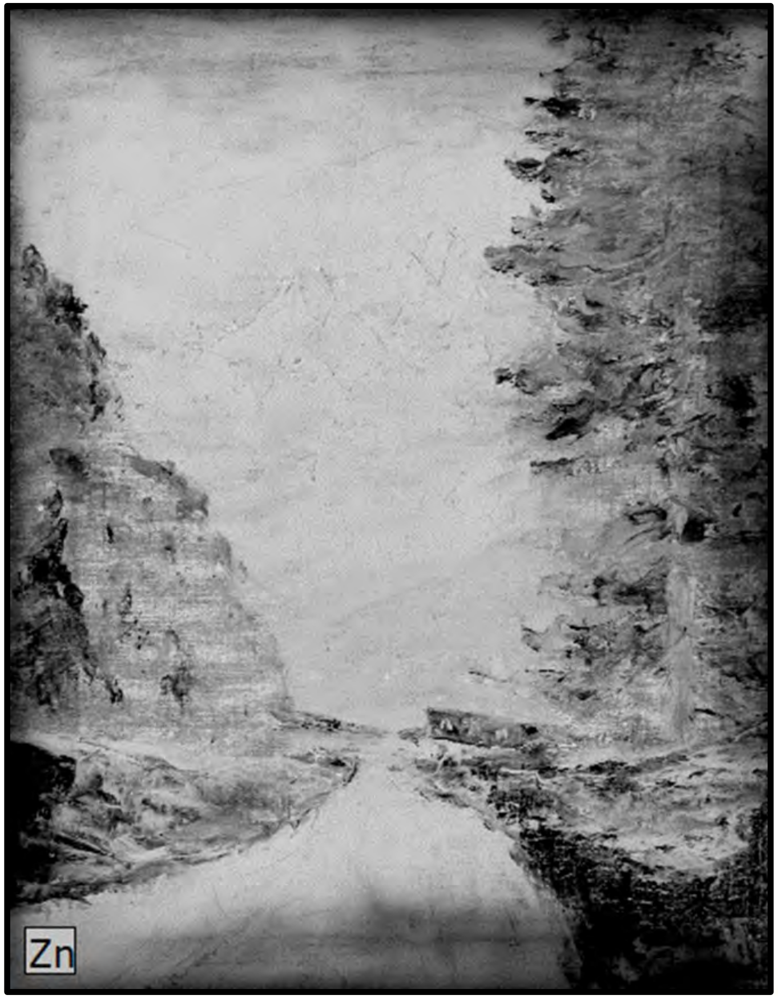
Introduction to dwell time

Effect on main elements (M6 JETSTREAM)

800 µm / 8 ms / 3 h

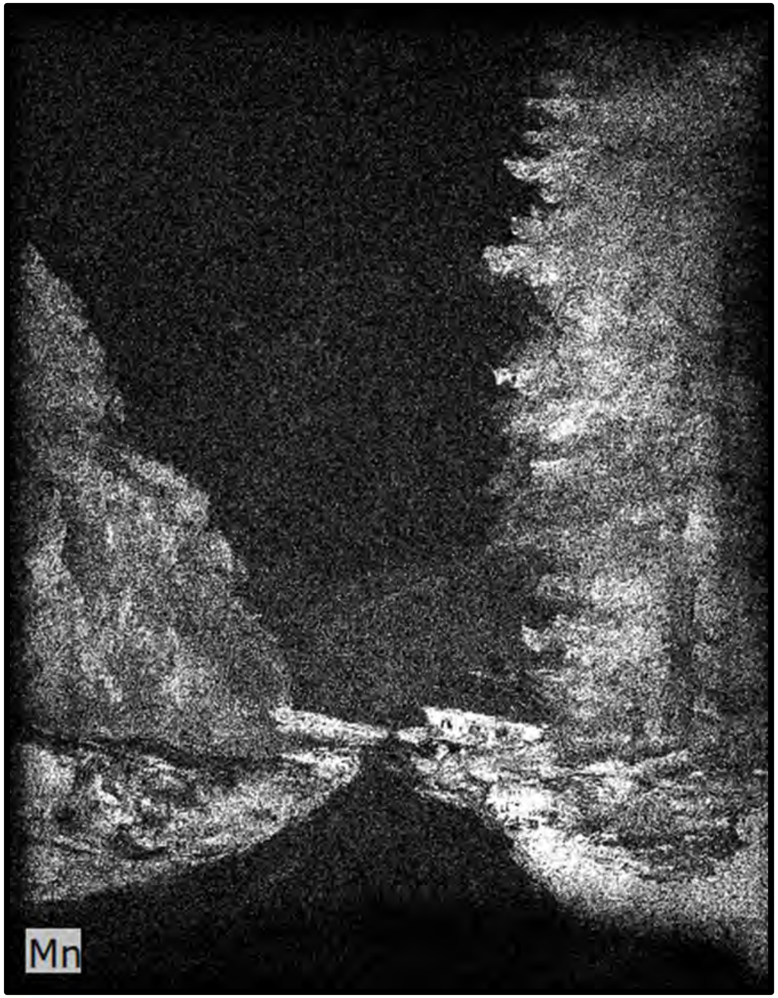


800 µm / 800 ms / 60 h



Introduction to dwell time
Effect on minor elements (M6 JETSTREAM)

800 µm / 8 ms / 3 h

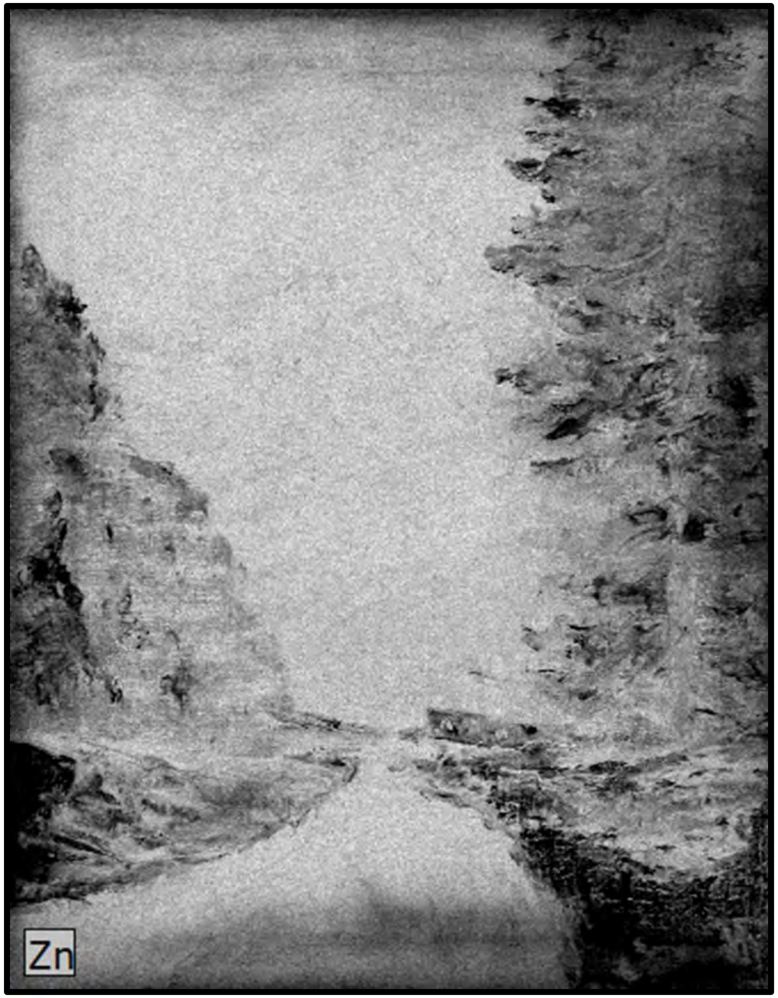


800 µm / 800 ms / 60 h

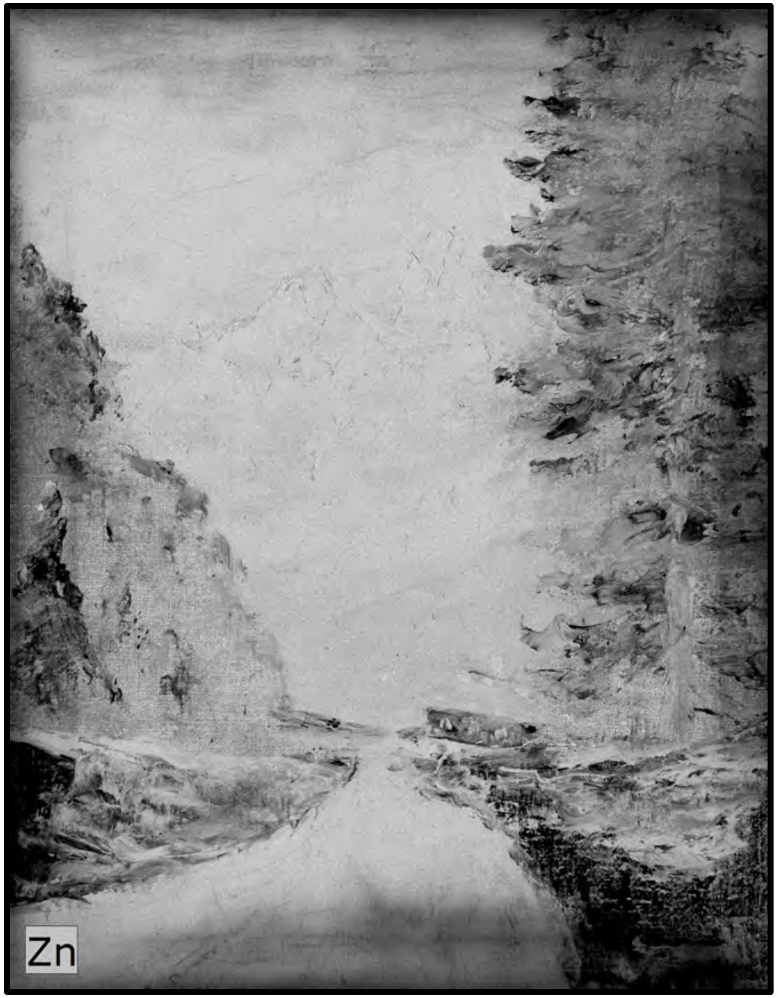
Introduction to pixel size

Effect on major elements (M6 JETSTREAM)

800 µm / 8 ms / 3 h



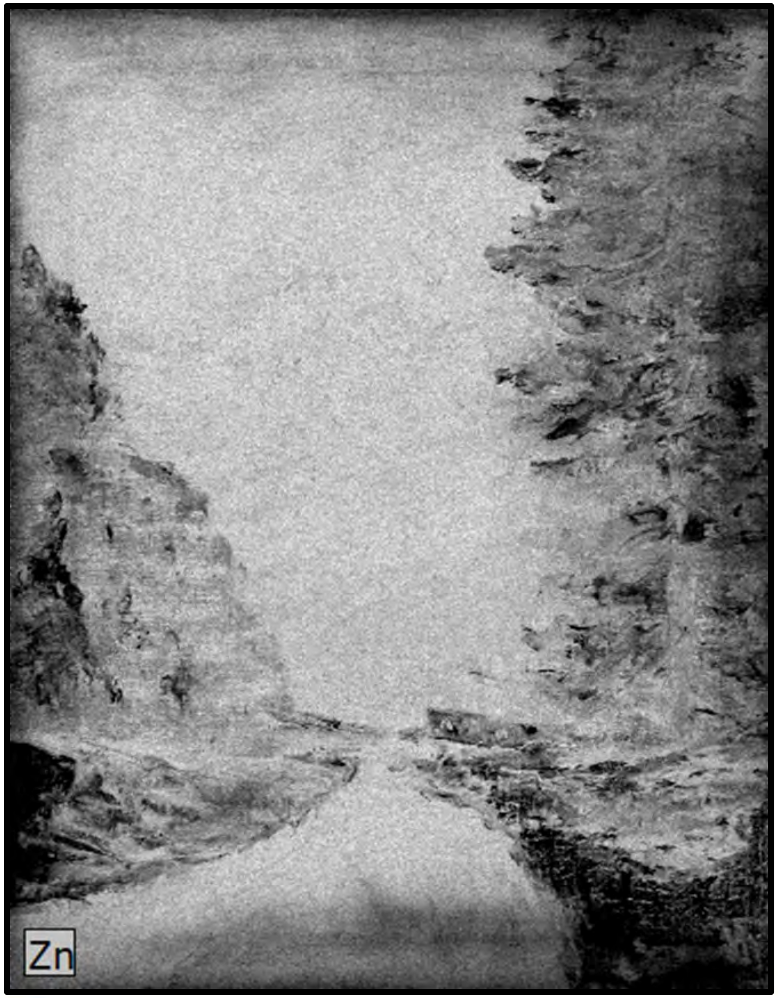
200 µm / 8 ms / 20 h



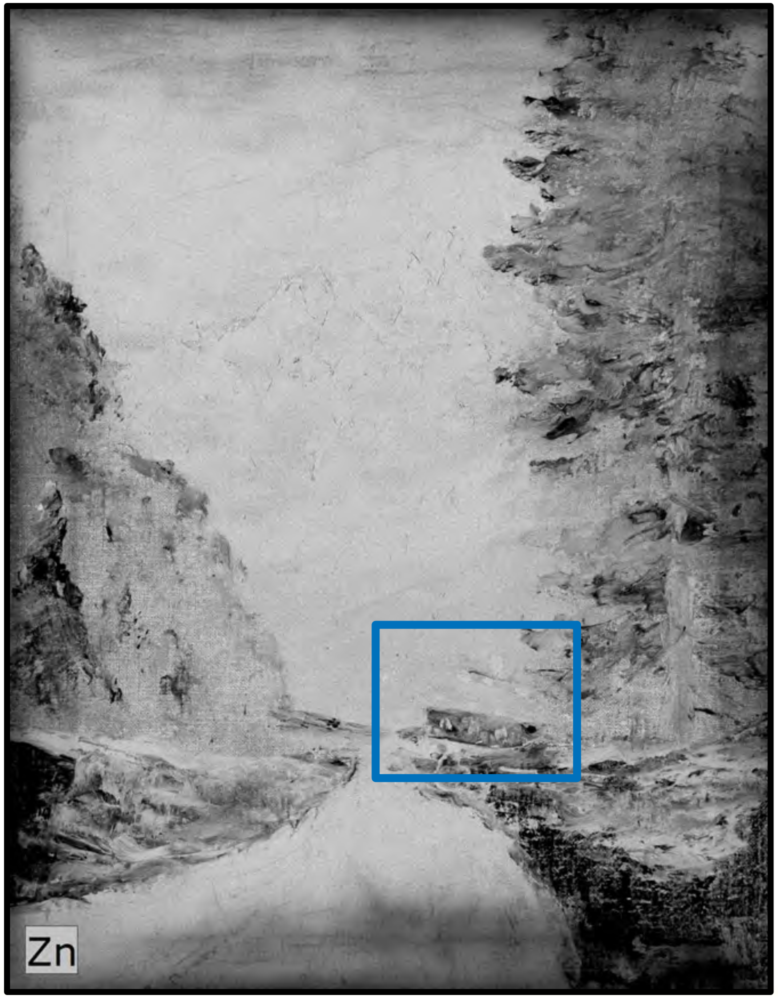
Introduction to pixel size

Effect on major elements (M6 JETSTREAM)

800 µm / 8 ms / 3 h

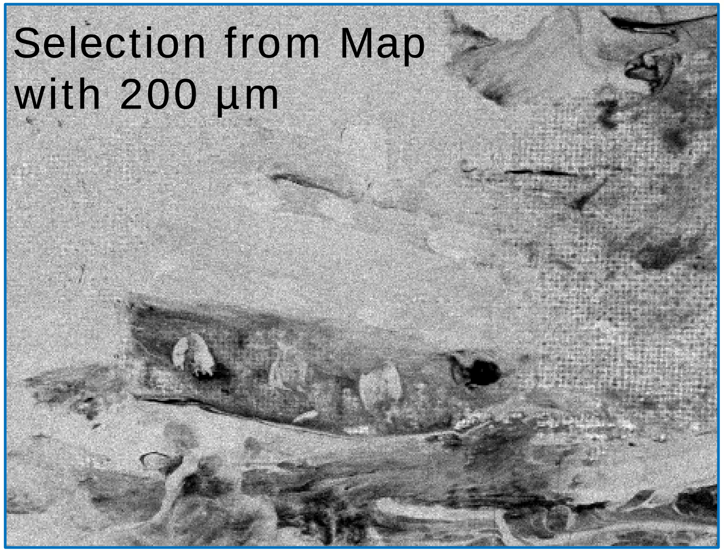


200 µm / 8 ms / 20 h

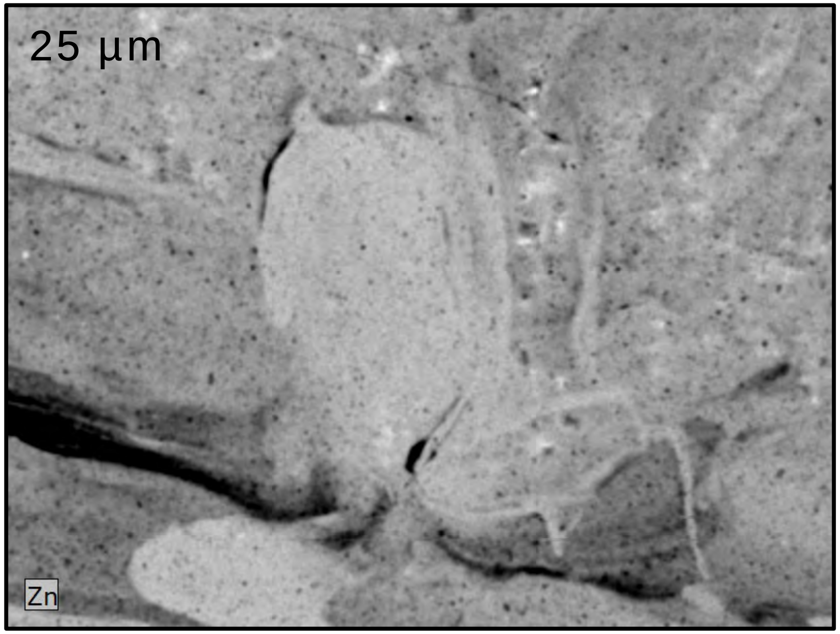


Introduction to pixel size

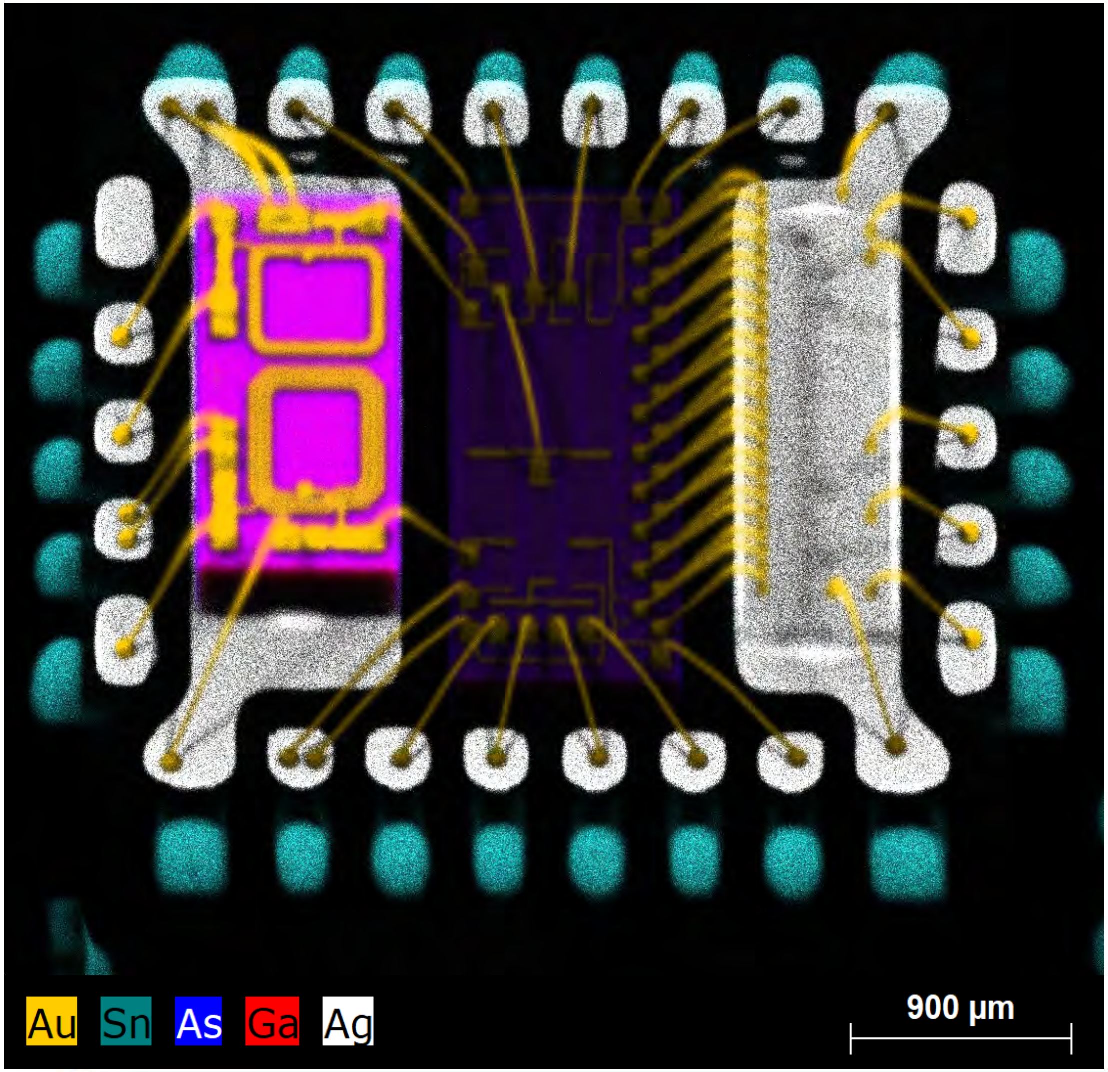
How to resolve small structures?



Pixel size should be adjusted to required resolution.



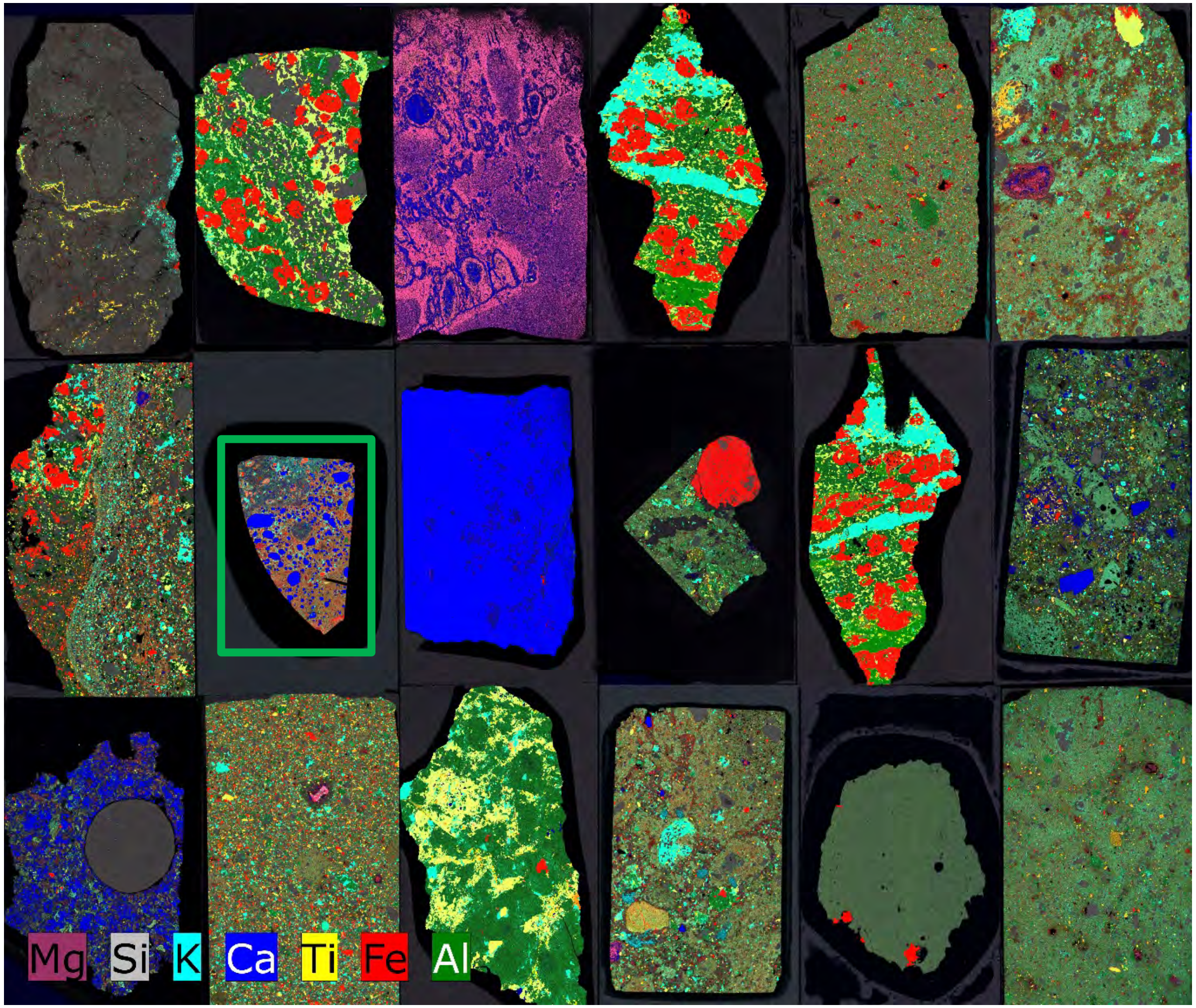
“Large” maps and pixel size
High resolution



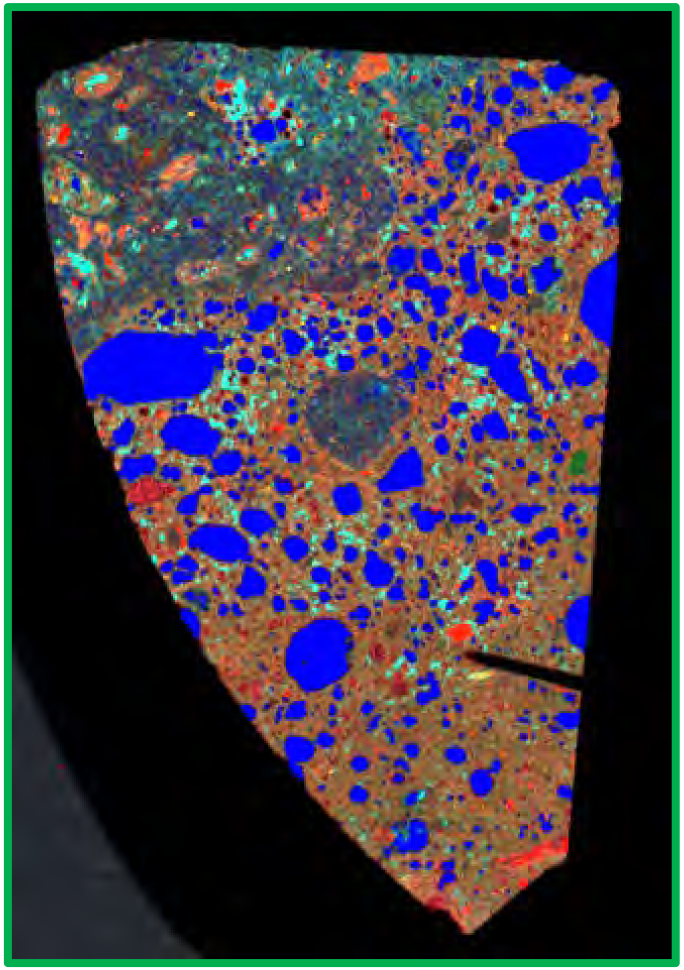
Mapping parameters		
Width:	1125	pixel
	4.5	mm
Height:	1000	pixel
	4	mm
Pixel Size:	4	µm
Total number of pixel:	1125000	pixel
Acquisition parameters		
Frame count:	10	
Pixel time:	4	ms/pixel
Measure time:	12:05 h	
Overall time:	16:46 h	
Stage speed:	1000	µm/s
Stage position (X,Y,Z):		
Tube parameter		
High voltage:	50	kV
Anode current:	600	µA
Filter:	Al630	
Optic:	Lens	

1.1 M-Pixel on
4.5 x 4 mm area!

“Large” maps and pixel size
Large areas



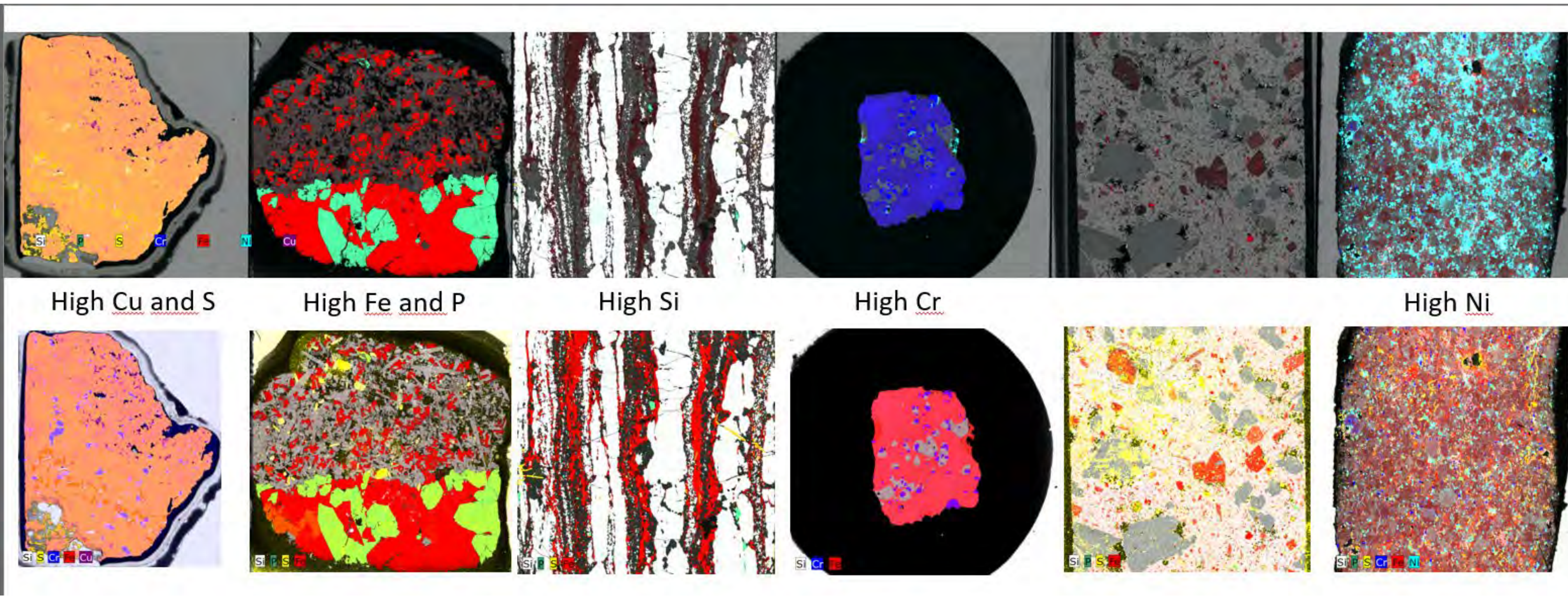
Zoom in



166 mm x 140 mm x 25 µm, 6640 x 5600 Pixel (37 MPixel), 2 ms/pixel , 26 h

“Large” maps and pixel size
Consistent data

6 samples of very different composition



Top Row: consistent dataset → dynamic range for relative element intensities

Bottom row: individual evaluation → independent color ranges impede the direct comparison of element abundancies

Pixel size and dwell time
The analytical question

Instrument options

Pixel size→ Small pixels for high resolution images (Megapixel range)
M4 TORNADO down to 4 µm, high resolution maps

M4 TORNADO has a flexible pixel size setting allowing to adjust value to the analytical task!

Dwell time→ Short dwell time sufficient for visualizing distribution of major elements. For trace elements longer dwell times required.

M4 TORNADO has a flexible dwell time setting and low speed scanning as well as multiple frame scan is possible for trace element detection

Understanding the role of the sample and analytical task to optimize measurement time

Pixel size and sample

Limits to attainable resolution

Ag-L line intensity distribution on a faded photograph

Pixel size 25 µm

50 µm

75 µm

100 µm

150 µm

200 µm

300 µm

600 µm

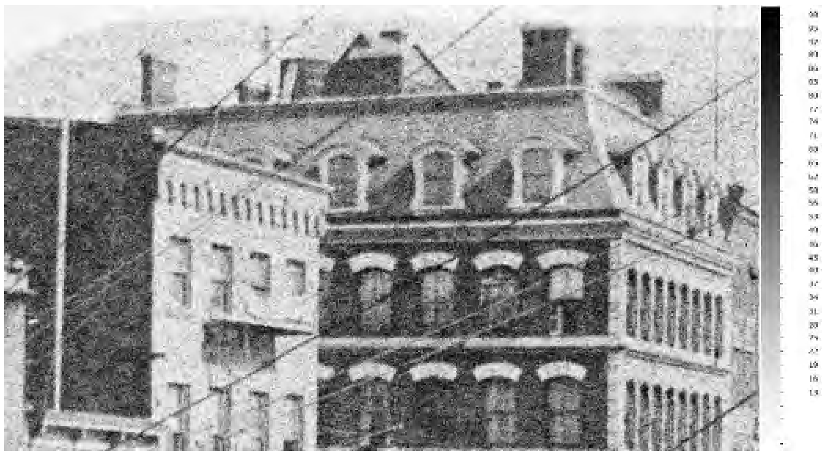
- Between 25 µm and 150 µm pixel size there is no significant difference in resolution, 200 µm appears to be “coarse”, at 300 µm it starts to get blurry, 600 µm even more so

Data presented in A&C Webinar 2020 pt.1

Pixel size and sample
Resolution comparison

Ag-L line intensity distribution on a faded photograph

Pixel size 25 µm



150 µm

The sample-inherent grain size does not reward a smaller pixel size

For the analytical question
Ag-L line distribution

A pixel size of 150 µm would gives here similar results
Note: same dwell time would reduce **total time 1/36!**

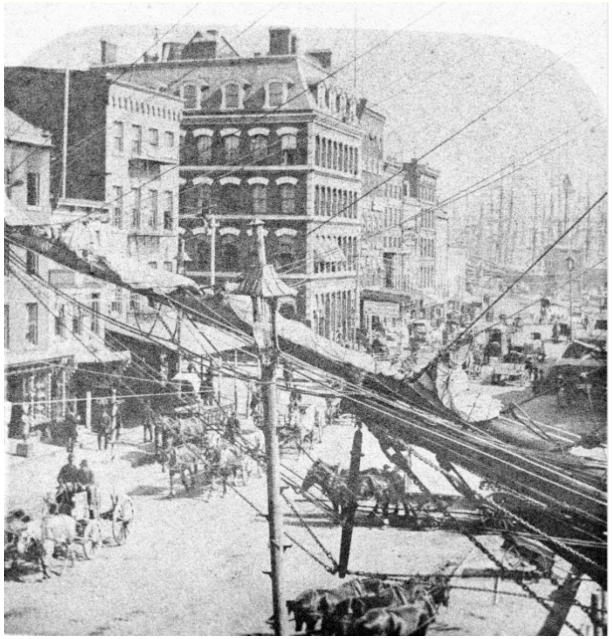
Data presented in A&C Webinar 2020 pt.1

Dwell time and sample

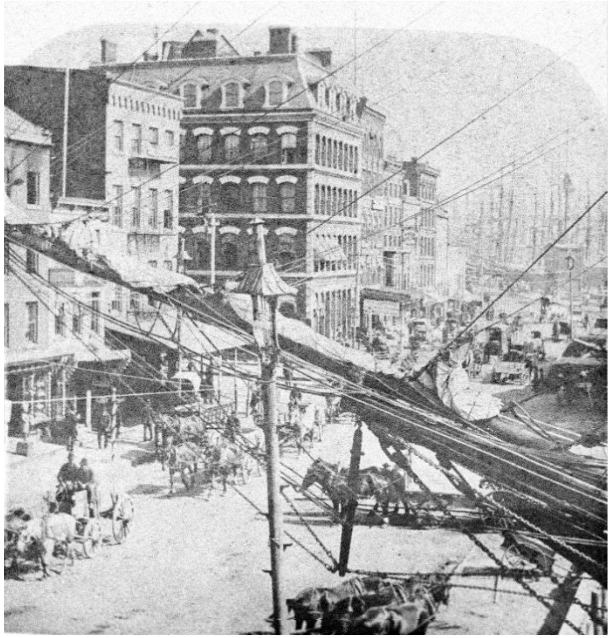
Time comparison – increasing dwell time

← Not much improvement from here

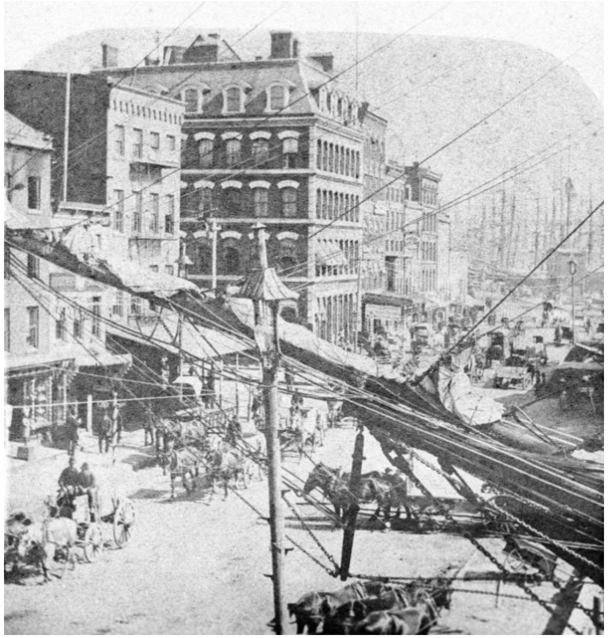
Conditions:
35 kV 800 µA
W-anode, vac 20 mbar
50 µm



50 ms, ~6 h



100 ms, ~ 12 h



830 ms, ~ 90 h

Only little difference for this object.
→ Measurement times around 50 ms are sufficient.

Pixel size and dwell time
The sample effect

Instrument options

Pixel size→ Smallest pixel might not allow better resolution for every sample.

M4 TORNADO has a flexible pixel size setting allowing to adjust value to the sample nature.

Dwell time→ There is a clear dependence between analytical task and sample nature.

M4 TORNADO has a flexible dwell time setting to adjust value to sample nature.

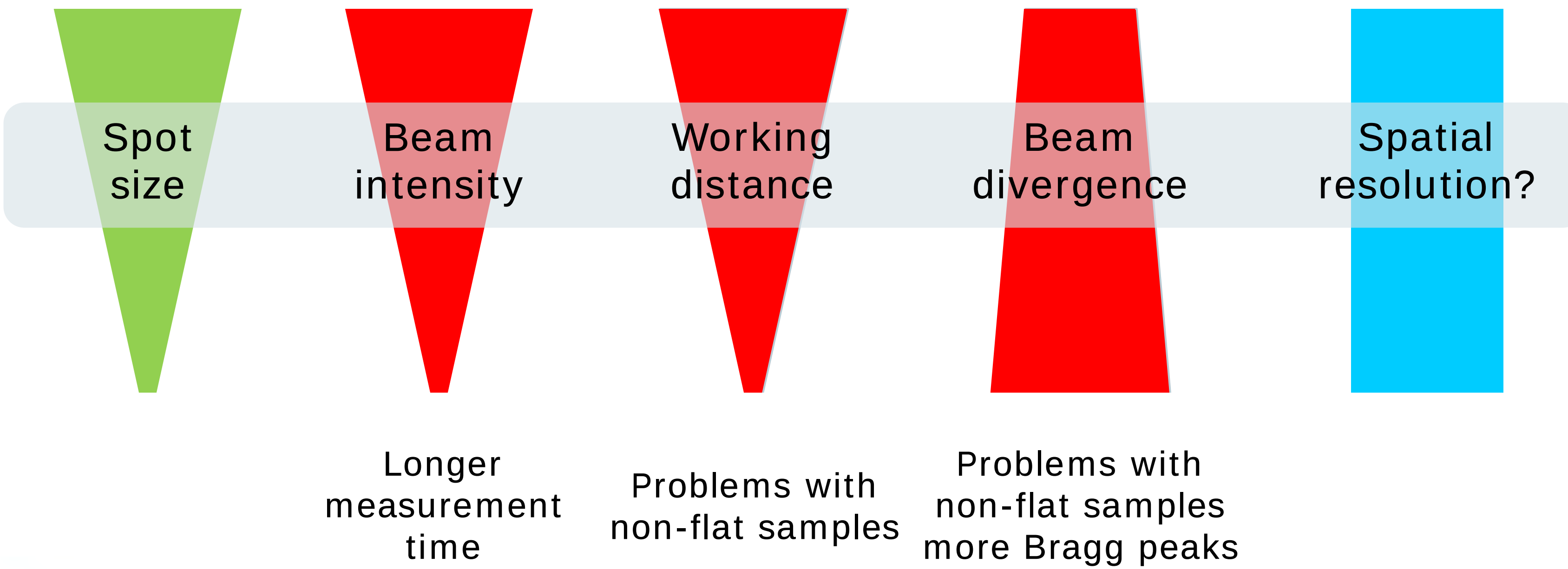
A measurement under optimal condition can achieve the best results in a fraction of the time!

Understanding the role of the X-ray beam focusing in micro-XRF advantages and disadvantages

Spatial resolution in Micro-XRF
Discussing relevant parameters

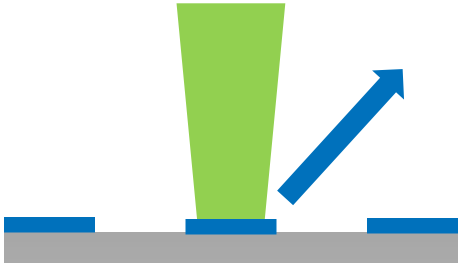
Known is that with decreasing sport size you give up intensity, you lose working distance and pay with higher beam divergency of the X-ray beam.

What is the gain in spatial resolution?
Does it pay off?



Spatial resolution in Micro-XRF

Sample and spatial resolution

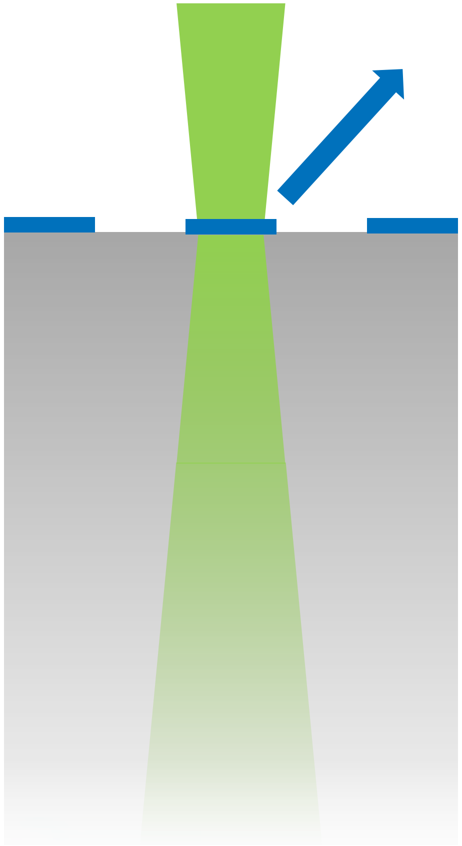


- A smaller beam spot size leads to higher spatial resolution

Spatial resolution in Micro-XRF
Sample and spatial resolution

- A smaller beam spot size leads to higher spatial resolution ... **at the surface**

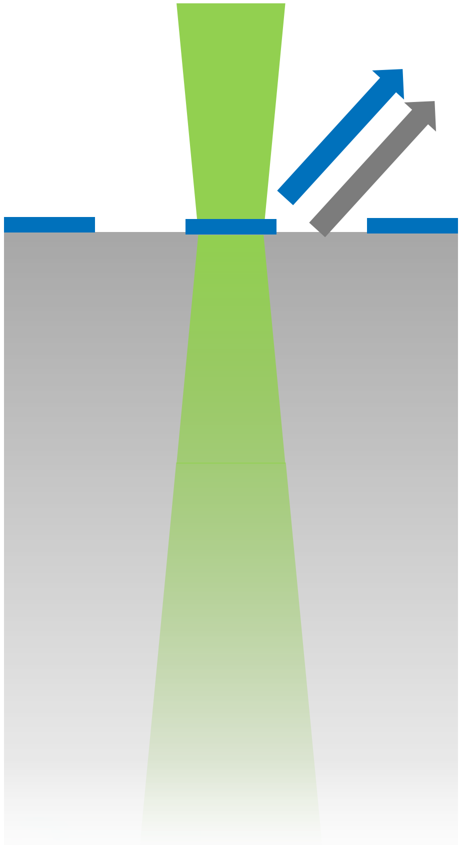
Spatial resolution in Micro-XRF
Sample and spatial resolution



- A smaller beam spot size leads to higher spatial resolution … **at the surface**
- Irrespective of the focal beam size the X-rays will travel the same depth into the material

Spatial resolution in Micro-XRF

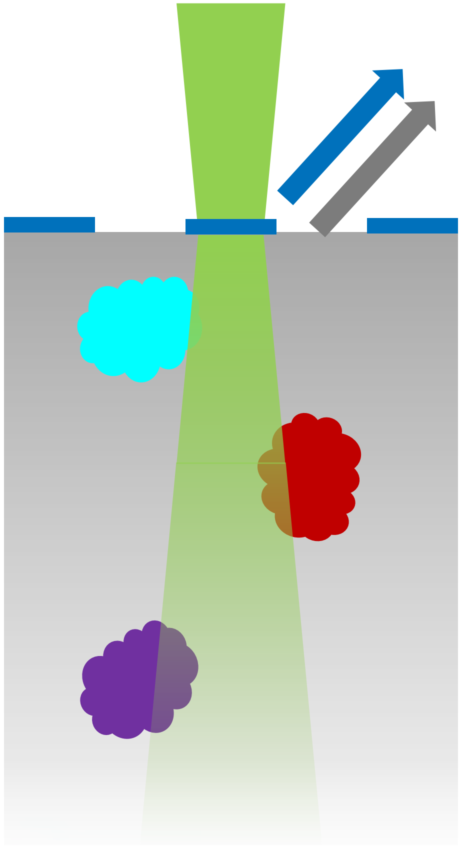
Sample and spatial resolution



- A smaller beam spot size leads to higher spatial resolution ... **at the surface**
- Irrespective of the focal beam size the X-rays will travel the same depth into the material ... **and produce fluorescence**

Spatial resolution in Micro-XRF

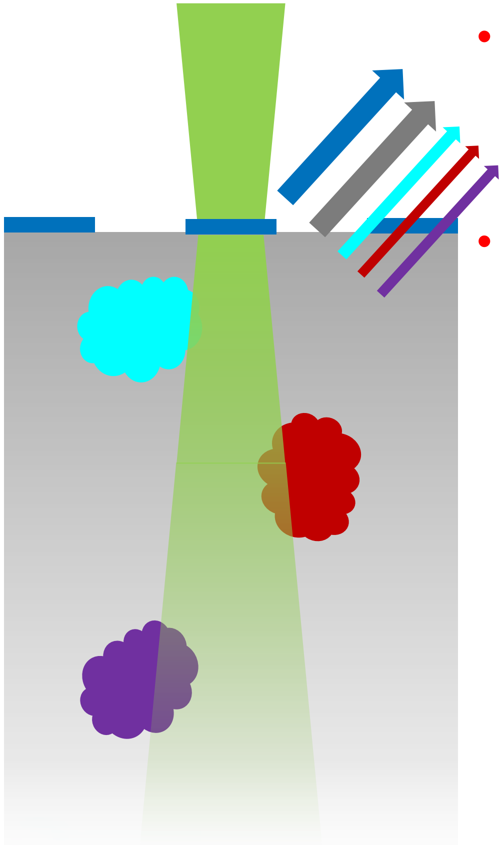
Sample and spatial resolution



- A smaller beam spot size leads to higher spatial resolution … **at the surface**
- Irrespective of the focal beam size the X-rays will travel the same depth into the material … **and produce fluorescence**
- In inhomogeneous samples structures may be hit which are further apart from each other than the focal beam size

Spatial resolution in Micro-XRF

Sample and spatial resolution



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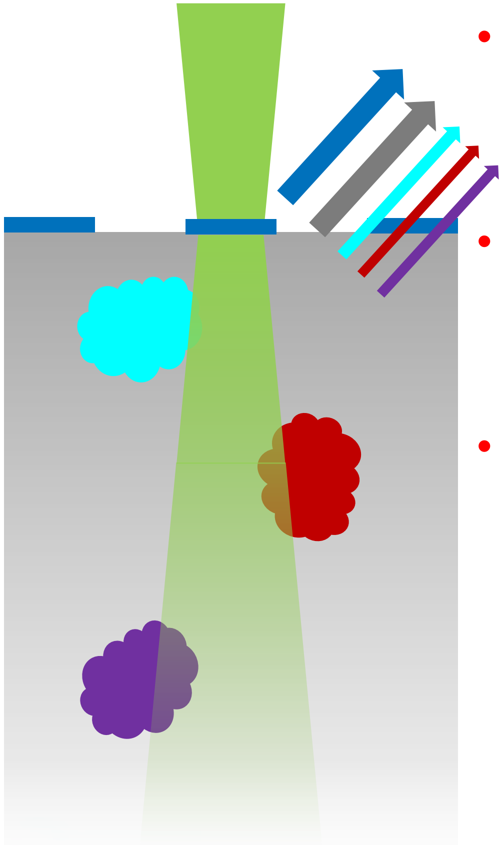
Spatial resolution in Micro-XRF
Sample and spatial resolution



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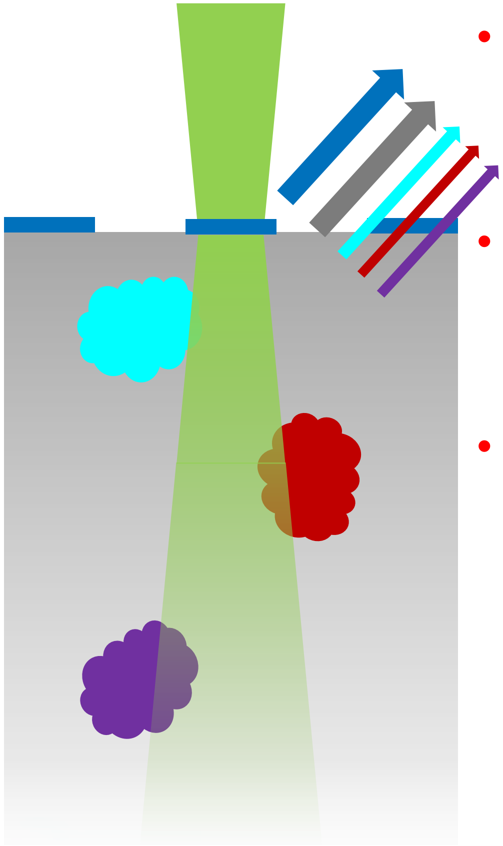
- In inhomogeneous samples structures may be hit which are further apart from each other than the focal beam size ... **and produce fluorescence**
- All this fluorescence radiation is detected at the same x-y-position.

Spatial resolution in Micro-XRF

Sample and spatial resolution



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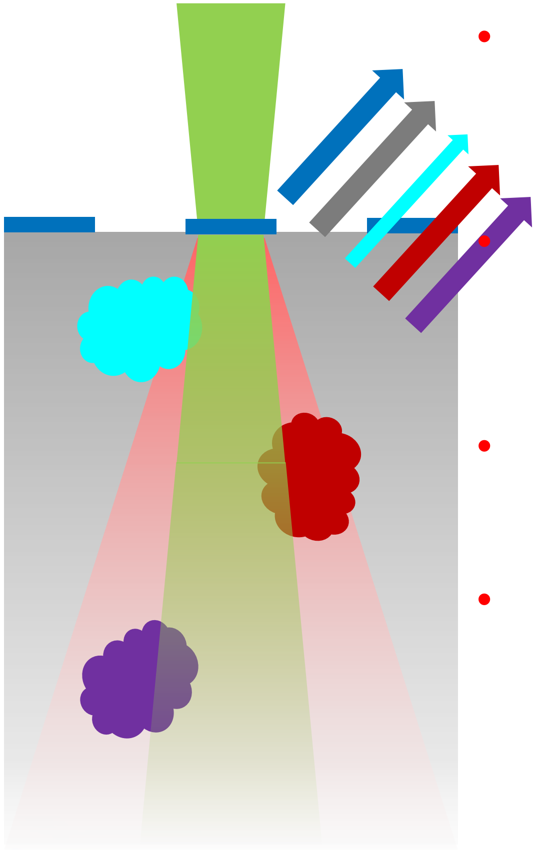
- All this fluorescence radiation is detected at the same x-y-position. …**and these are only first-order-effects**

Spatial resolution in Micro-XRF
Sample and spatial resolution



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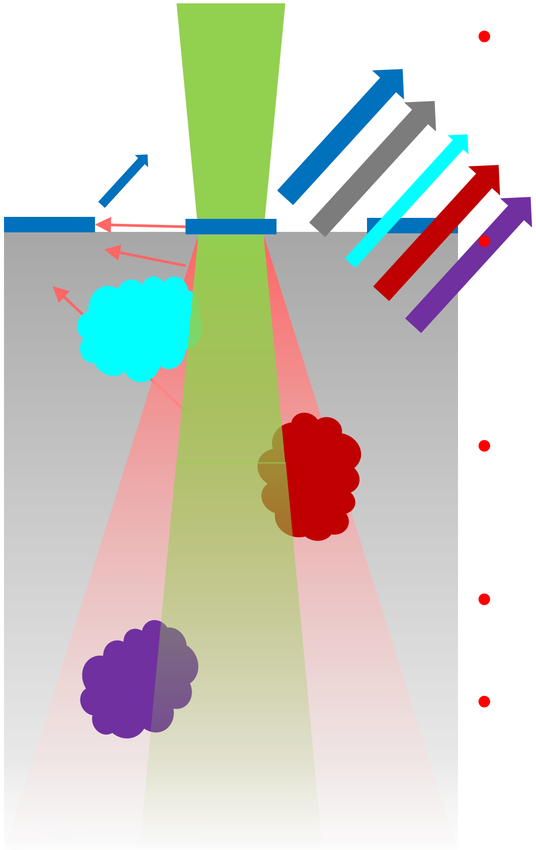
- All this fluorescence radiation is detected at the same x-y-position. …**and these are only first-order-effects**
- X-rays that have been scattered into a broader cone can still excite the sample

Spatial resolution in Micro-XRF
Sample and spatial resolution



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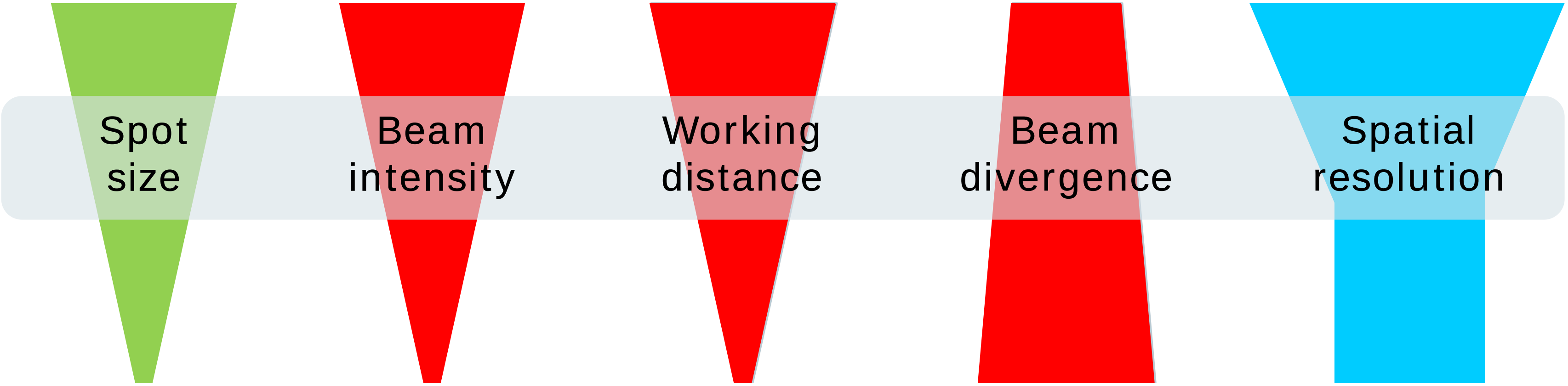
- Irrespective of the focal beam size the X-rays will travel the same depth into the material ... **and produce fluorescence**
- In inhomogeneous samples structures may be hit which are further apart from each other than the focal beam size ... **and produce fluorescence**
- All this fluorescence radiation is detected at the same x-y-position. ...**and these are only first-order-effects**
- X-rays that have been scattered into a broader cone can still excite the sample
- Even surface structures that are further away than the spot size can be excited

Spatial resolution in Micro-XRF
Sample and spatial resolution



This was a lot a theory... what does the praxis test say?

What do we gain in resolution?

Let's show the results of a small experiment....

Micro-XRF spatial resolution
Sample and spatial resolution

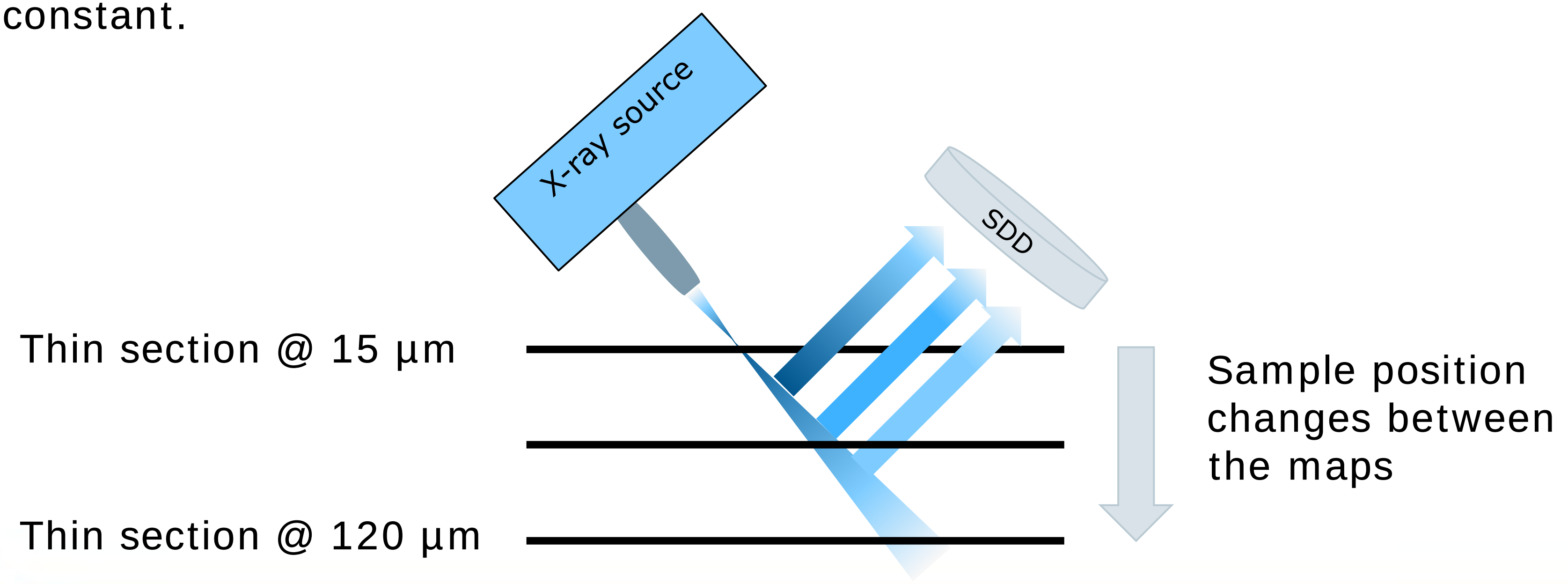
Experiment:

A thin section was measured multiple times on an M4 TORNADO PLUS.

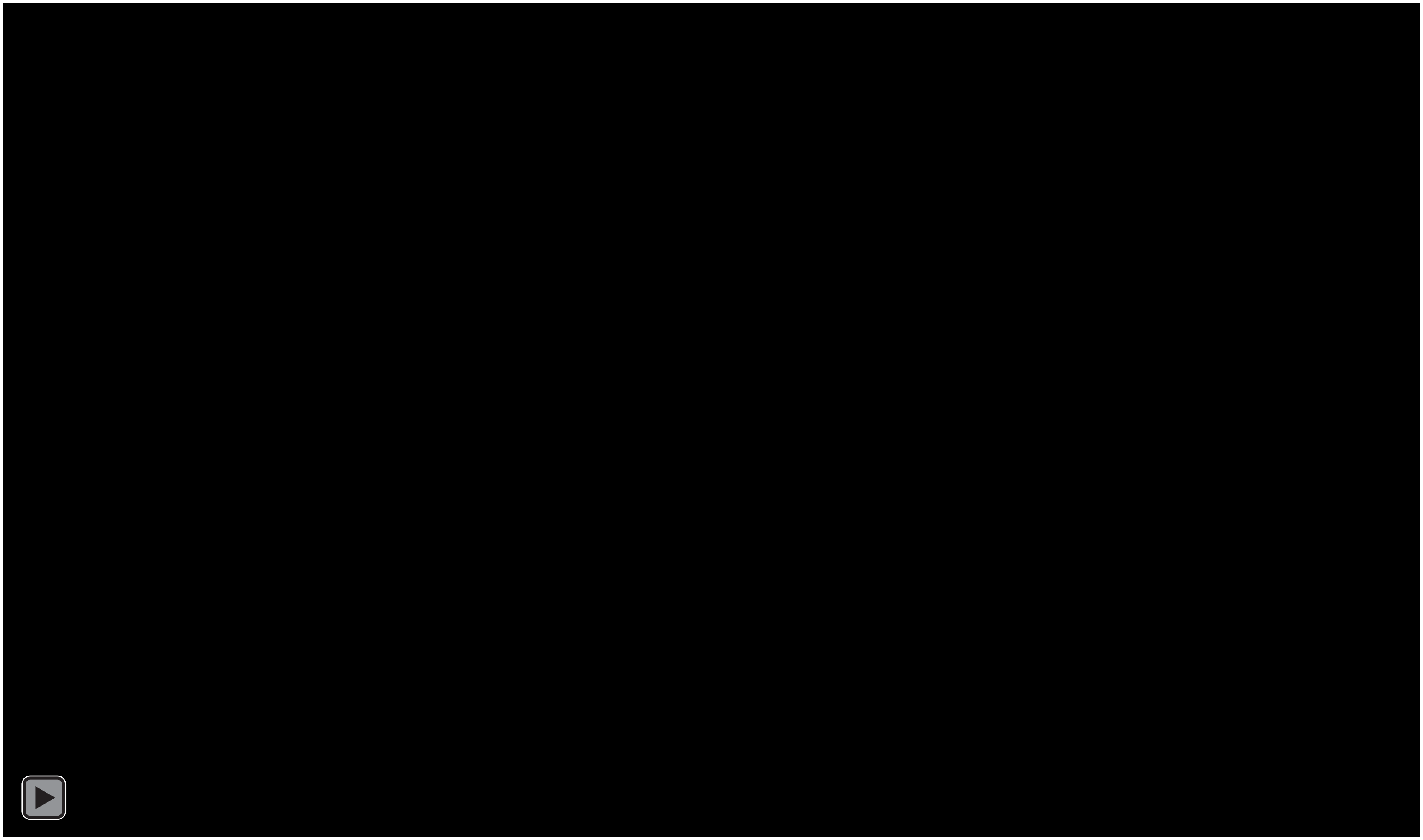
The working distance was increased between the measurements.

Due to beam divergence the **spot size increased** from 15 µm to 120 µm.

All other paraments (in particular dwell time and pixel size) where kept constant.

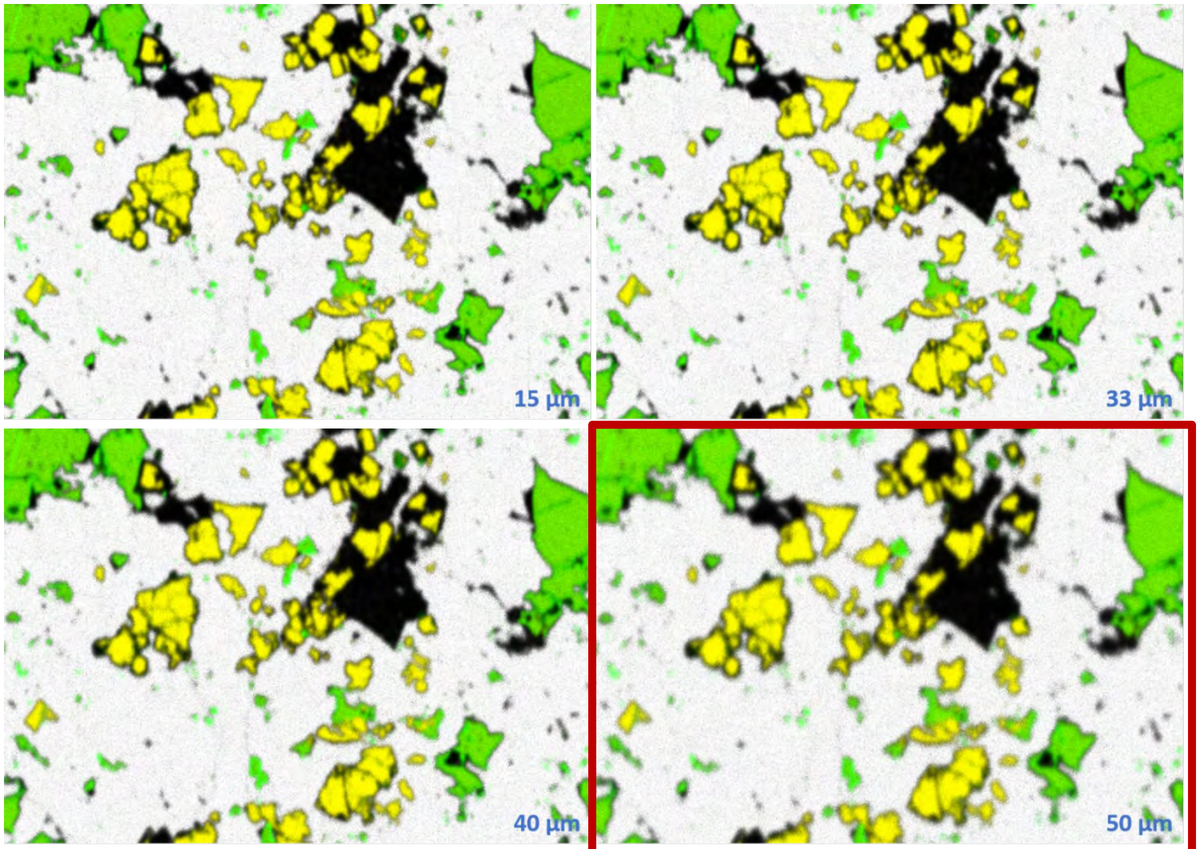


Micro-XRF spatial resolution
Sample and spatial resolution



Micro-XRF spatial resolution

Sample and spatial resolution



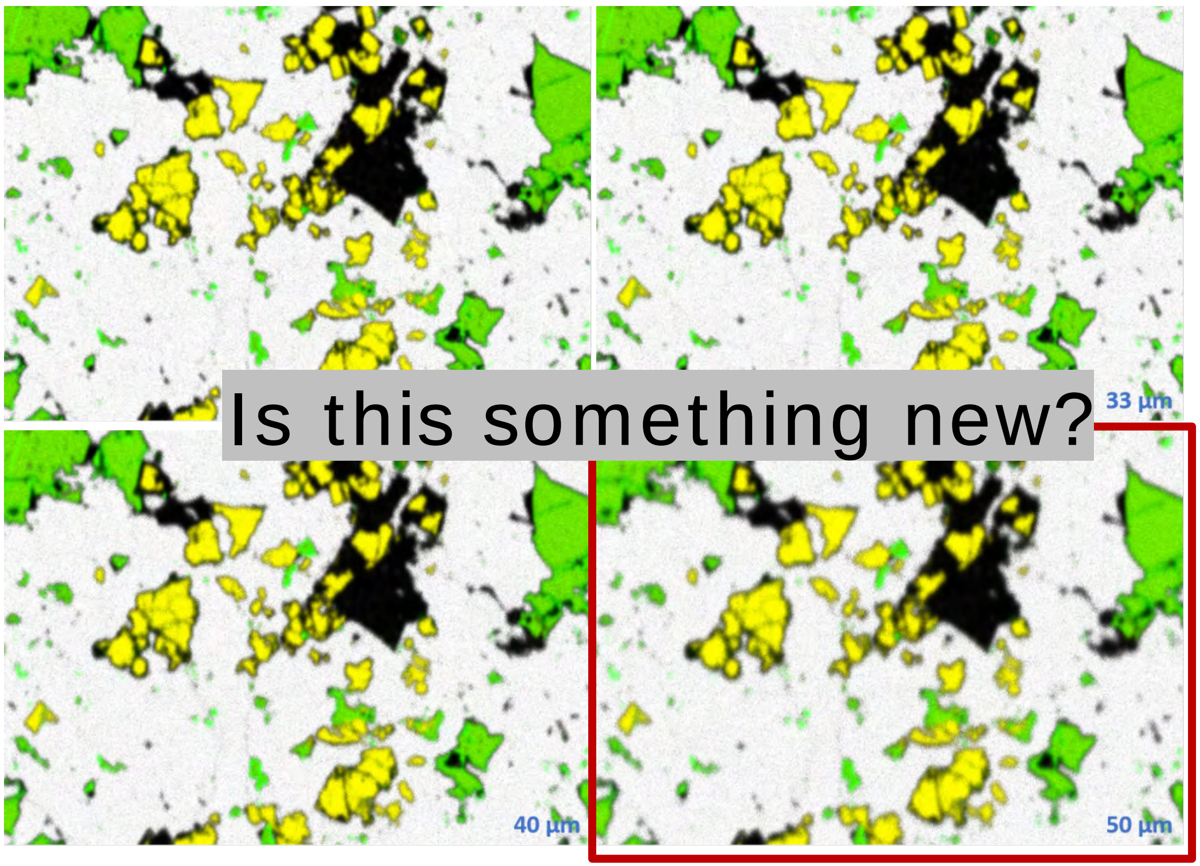
Thin section of ~ 25 µm thickness

Virtually **no difference** between a 15 µm spot and a 33 µm spot

A smaller X-ray spot would **not** help to increase the spatial resolution on this sample.

Micro-XRF spatial resolution

Sample and spatial resolution



Is this something new?

Virtually **no difference** between a 15 µm spot and a 33 µm spot

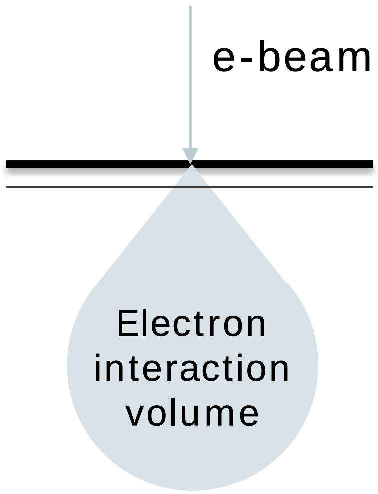
A smaller X-ray spot would **not** help to increase the spatial resolution on this sample.

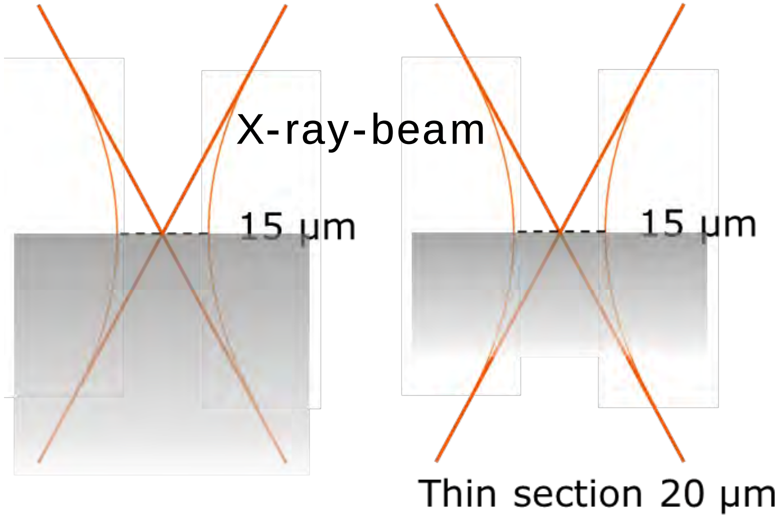
Thin section of ~ 25 µm thickness

Micro-XRF spatial resolution
Sample and spatial resolution

This effect is well-known from electron microscopy.

To achieve highest resolution not only the beam needs to be small but also the sample must be thinned down.
(see TEM samples).





Similar: the X-ray beam widens in the sample.
A thinner sample restricts the maximum width of the beam

Spot size and sample structure
Take home messages

- There is an '**effective spatial resolution**' which is only partly dependent on the focal spot size
- The nature of the sample (material density and thickness) plays a major role in determining the actual information volume
- Thinner samples and denser samples allows higher spatial resolution

Smaller spots do not necessarily come with a higher effective spatial resolution!

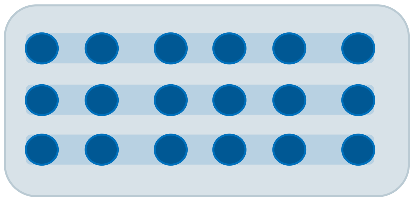
The M4 TORNADO and the M4 TORNADO PLUS

- High spatial resolution (< 20 µm)
- Large working distance (~ 4.5 mm to collision protection)
- High brilliance (intensity > 500.000 cps for Cu with a single 30 mm^2 SDD)

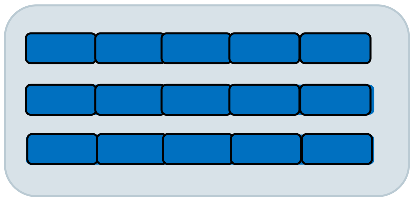
Spot size vs. Pixel size
Improving speed by considering sample structure

Spot size and pixel size
Covering the whole sample area?

Typical mode of scanning

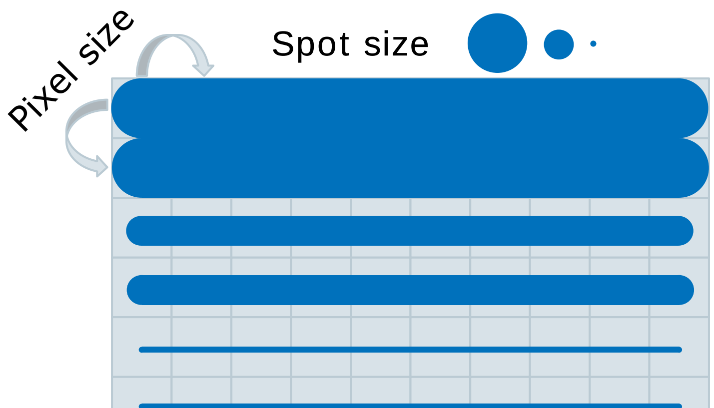


On-the-fly scanning



Map of 10x10 pixels²

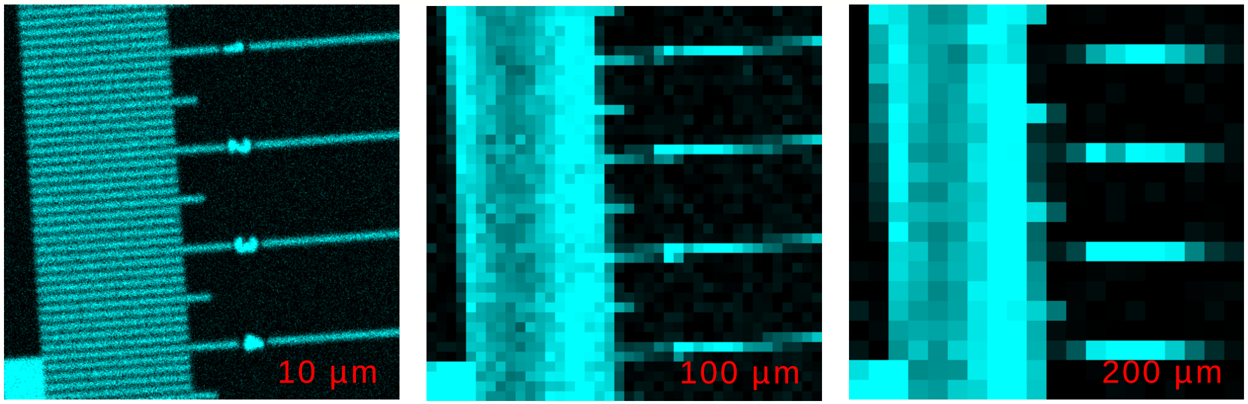
- Pixel size = spot size
  → Area fully covered
- Pixel size = 2x spot size
  → Only half the sample is mapped
- Pixel size = 10x spot size
  → 10 % of the sample are mapped



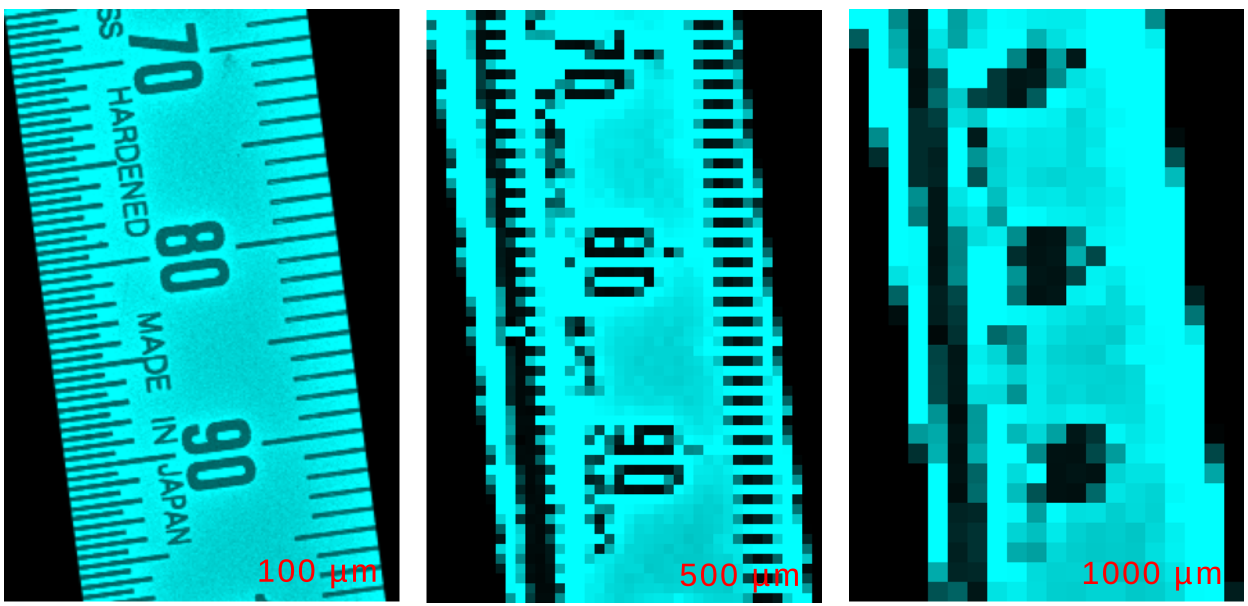
Do we have to measure the whole sample to see the whole sample?

→ Not necessarily

Spot size and pixel size
Measuring differently structured samples



Structures: 100 µm



Structures: 500 µm

Spot size and pixel size

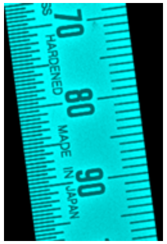
Seeing the whole sample

Instrument options

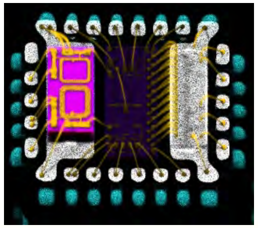
Spot size→ The spot size is a fixed value (or can be modified in few selected steps M6 JETSTREAM), whereas the structure size of the samples can span several orders of magnitude.

To see the whole sample consider:

Pixel size→ When sample structures are far larger than the spot size, the optimal pixel size is closer to the sample structures dimensions than to the spot size.



M4 TORNADO has a flexible pixel size setting to adjust value to sample nature. Pixel size can be adapted to the sample structure to optimize the overall measurement time.



Note: For very intricate structures (wire bond in ICs, or similar), 'oversampling', i.e. smaller pixels than spot size, may improve results

Improving performance:
Other options in micro-XRF
for material analysis

Additional measurement parameters
What else?

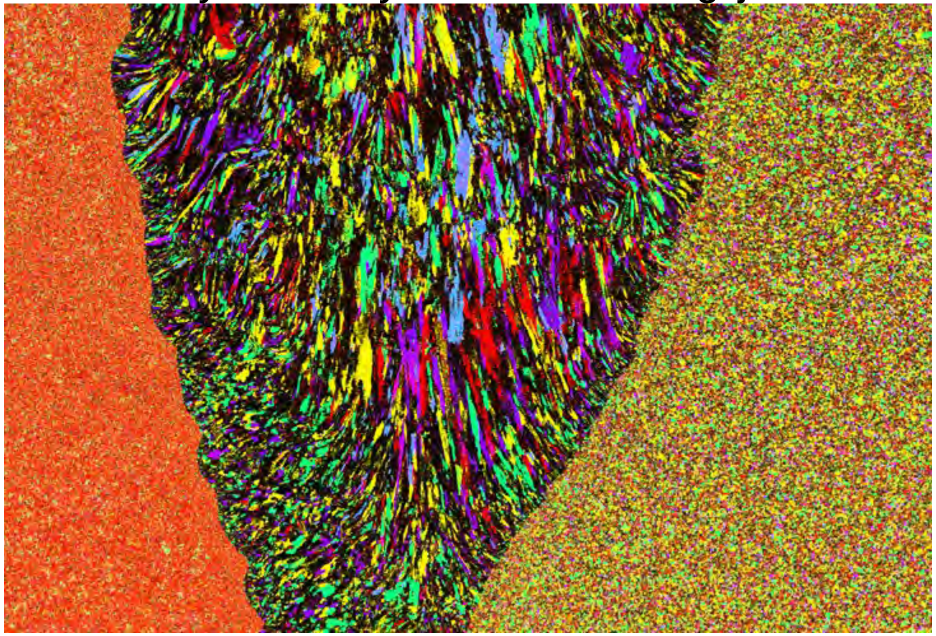
There are many additional parameters that may affect the result's quality

- Tube HV and current
- Atmosphere and pressure
- Use of filters *
- Beam divergence * (AMS)
- Selected detectors *
- Energy range and maximum pulse throughput of the detectors
- Sample presentation *
  - Horizontal alignment
  - Raw/cut/polished
  - Powders: as a heap or in a cup, pressed or loose

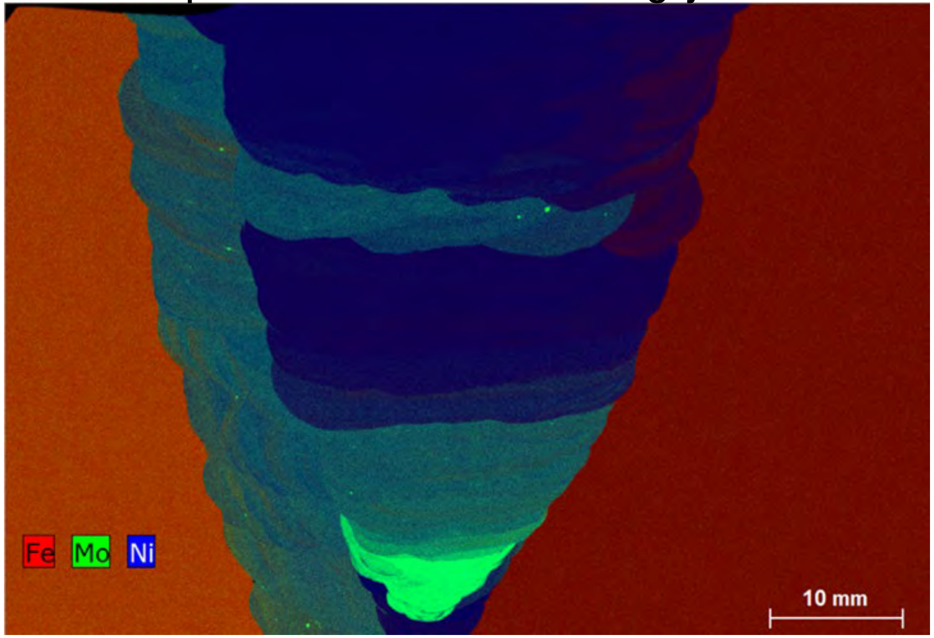
* some examples on the following slides

Additional measurement parameters
Optimal use of filters

Crystallinity of the welding joint

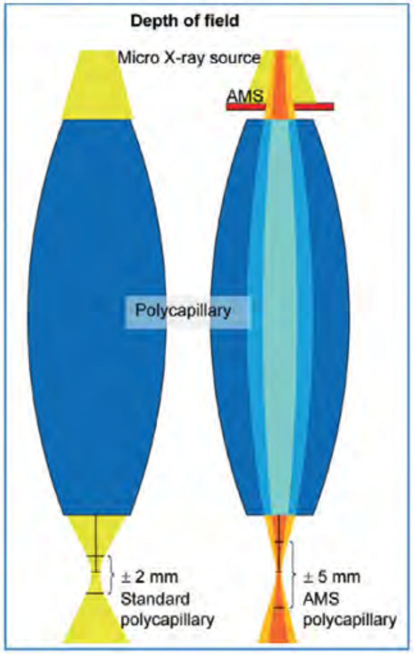


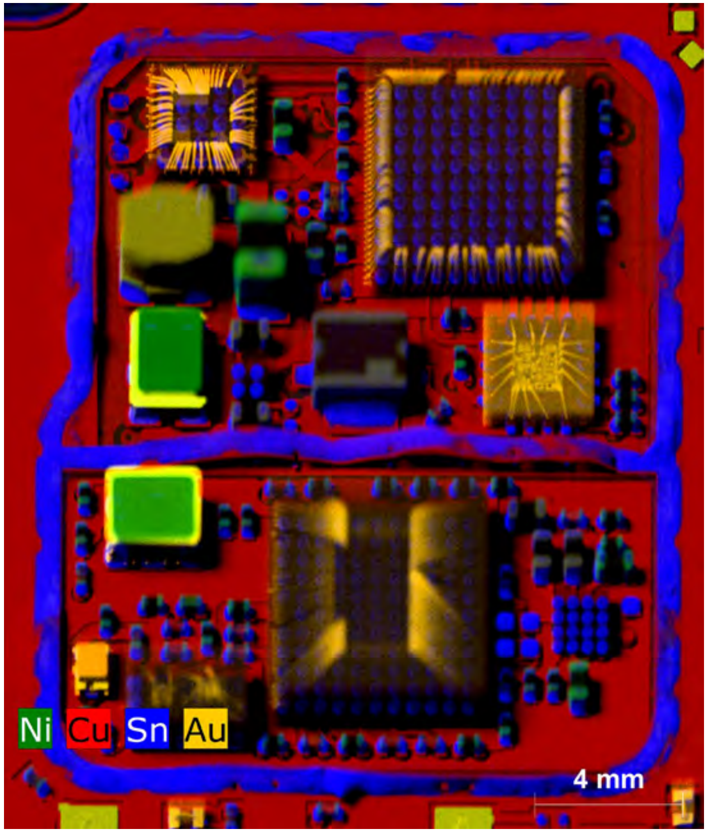
Composition of the welding joint

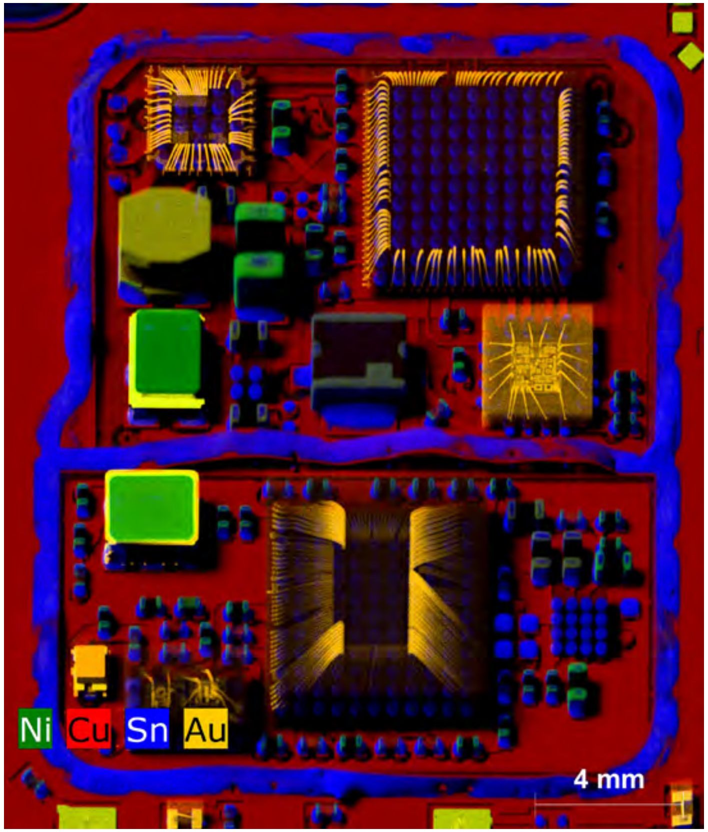


- Diffraction peaks are very common in metal samples
- These peaks are usually considered an artifact, because they impede the detection and evaluation of minor and trace elements
- ...on the other hand, detection of diffraction peaks may yield interesting information on material properties, i.e. crystallinity

Additional measurement parameters
Beam divergence





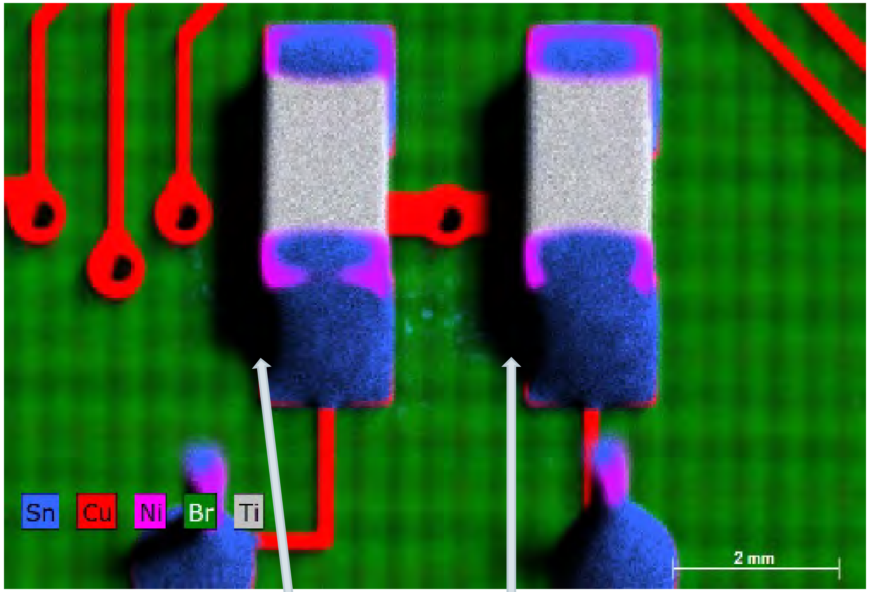


The focal plane of this measurement was on the PCB.
Left: The bond wires and SMD parts are out of focal plane and due to beam divergence appear blurry
Right: The aperture management system allows to adapt the beam divergence

Additional measurement parameters
Choice of Detector – Detection shadow

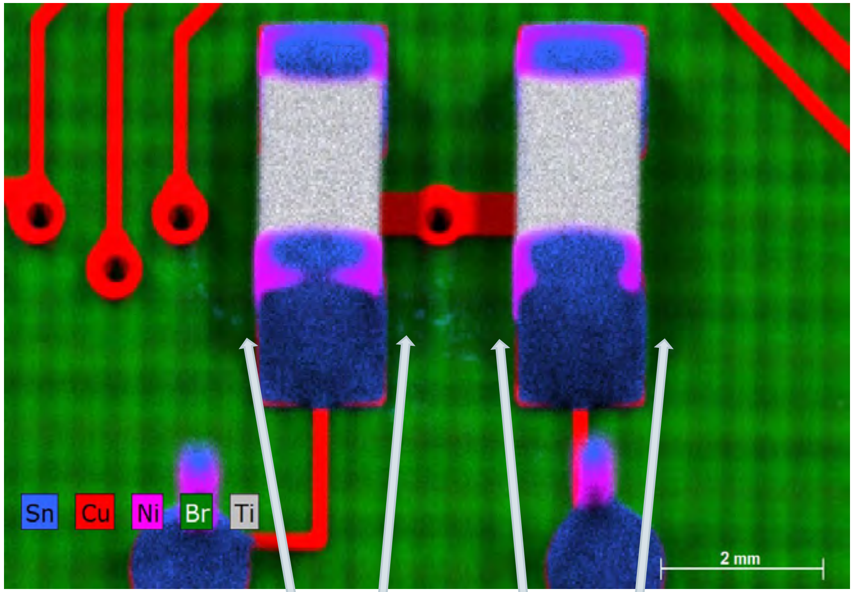
Contrary to popular belief, the shadow in a micro-XRF map originates from **non-coaxial detection**. → multiple detectors reduce the effect

Single detector
"looking" from the right



Full detection shadow

Double detector
"looking" from both sides



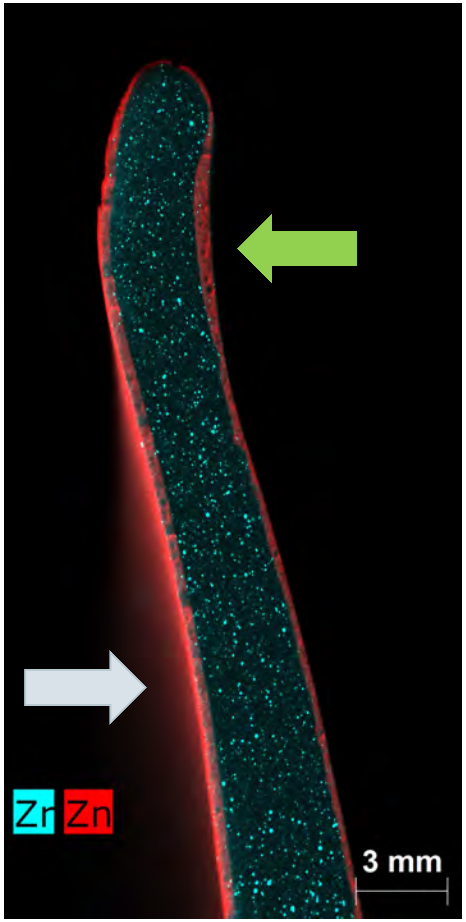
Half detection shadows

Additional measurement parameters
Choice of Detector – Detection direction

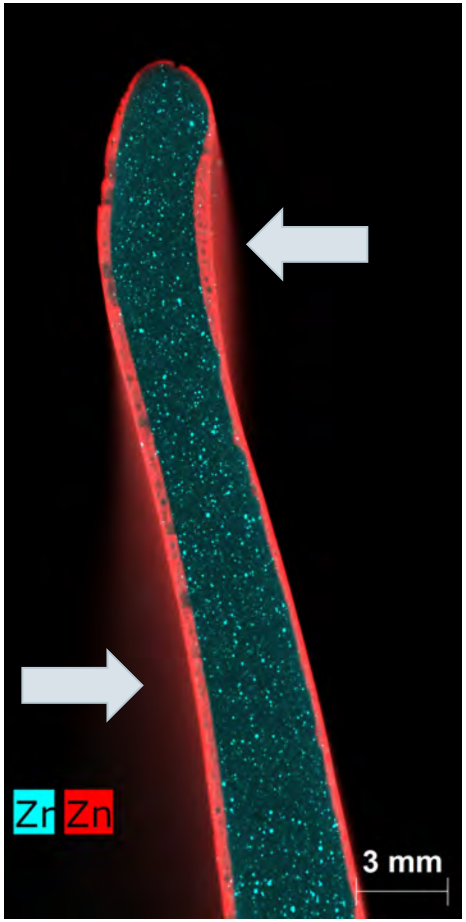
The polished edge of a ceramic sample placed vertically.

Choice of detector enables “cleaner” edges

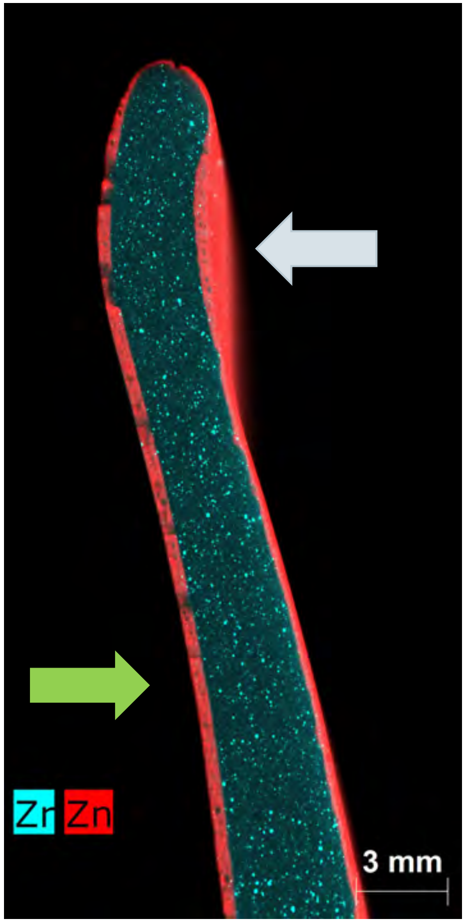
Left detector



Both detectors

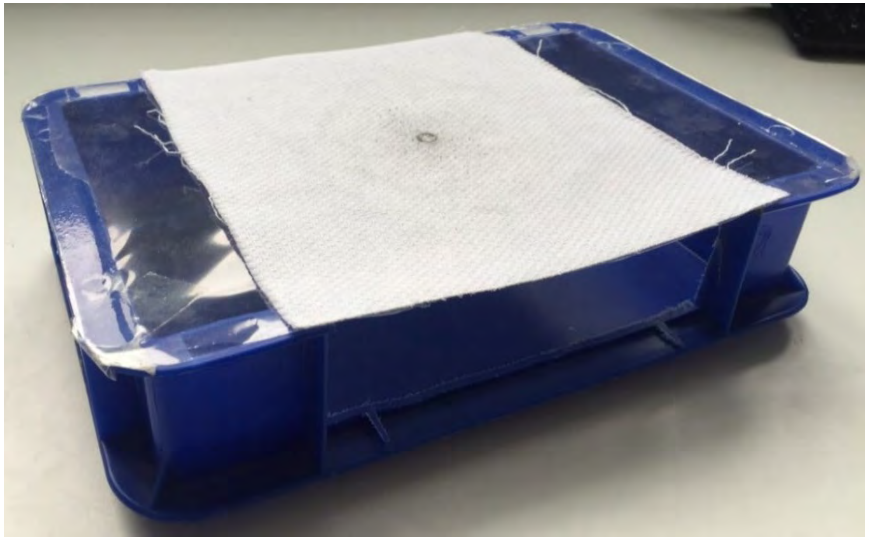


Right detector



Additional measurement parameters
Sample placement

- X-ray penetrate deep into a sample
- If the sample is very thin or has a low density, the X-ray will pass through it and produces (lots of) scattering in the sample table
- Scatter impedes detection limits and unnecessarily increases detector dead time
- It is suggested to try and minimize this scatter background



Spot size and pixel size
Take home messages

- Micro-XRF is an analytical technique applicable to a wide variety of samples
- Flexible hardware and software settings are required to ensure an optimal analytical performance
- Out of the many possible measurement settings the optimal setting is defined by the sample and the according analytical question
- Important features for micro-XRF are
  - An X-ray optic ensuring high excitation intensity in a small spot at a convenient working distance
  - Flexible software with access to key parameters, such as pixel size, dwell time, and scan area

- Any limitations to the versatility of the instrument (and software) would compromise the analytical performance of micro-XRF

Questions, Thoughts or Comments?

If you have questions or want to contact us during the Webinar, please **type your questions**, thoughts, or comments in the **Q&A box** and **press Submit**.

We ask for your understanding if we do not have time to discuss all comments and questions within the session.

Any unanswered questions or comments will be answered and discussed by e-mail or in another Webex session.