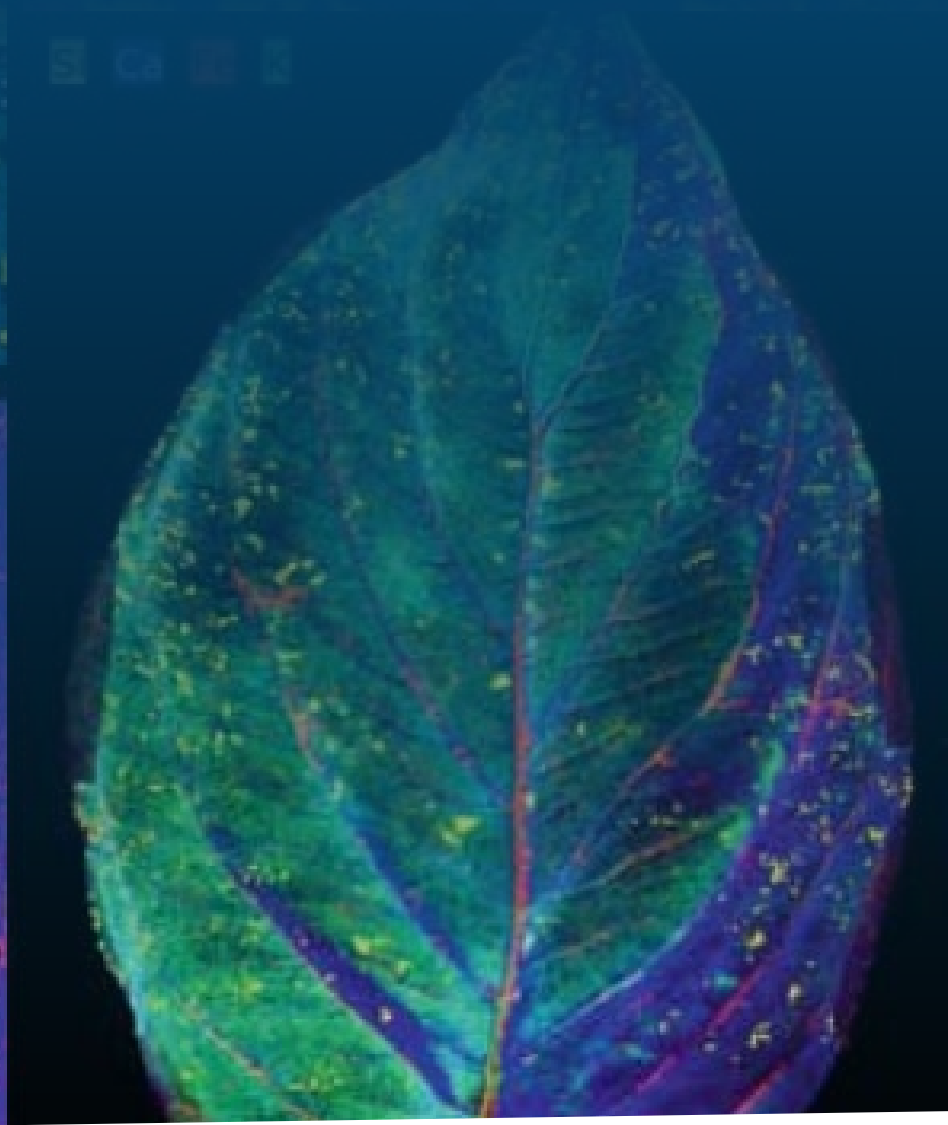


BRUKER NANO ANALYTICS PRESENTS

# Micro-XRF Back to the Roots – Part II

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Using micro-XRF for Qualitative Analysis



# The speakers

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- Falk Reinhardt
- Senior Application Scientist,  
Bruker Nano Analytics, Berlin, Germany



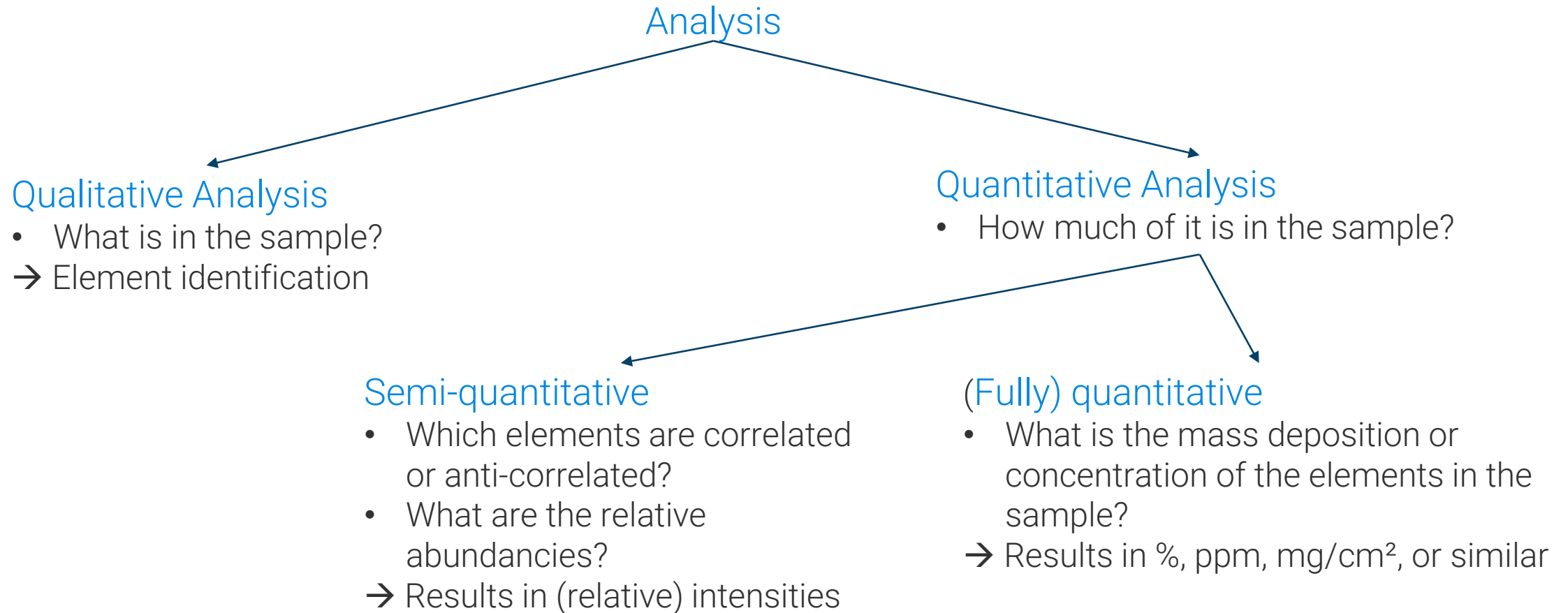
- Dr. Roald Tagle
- Head of XMP Application,  
Bruker Nano Analytics, Berlin, Germany

# Overview

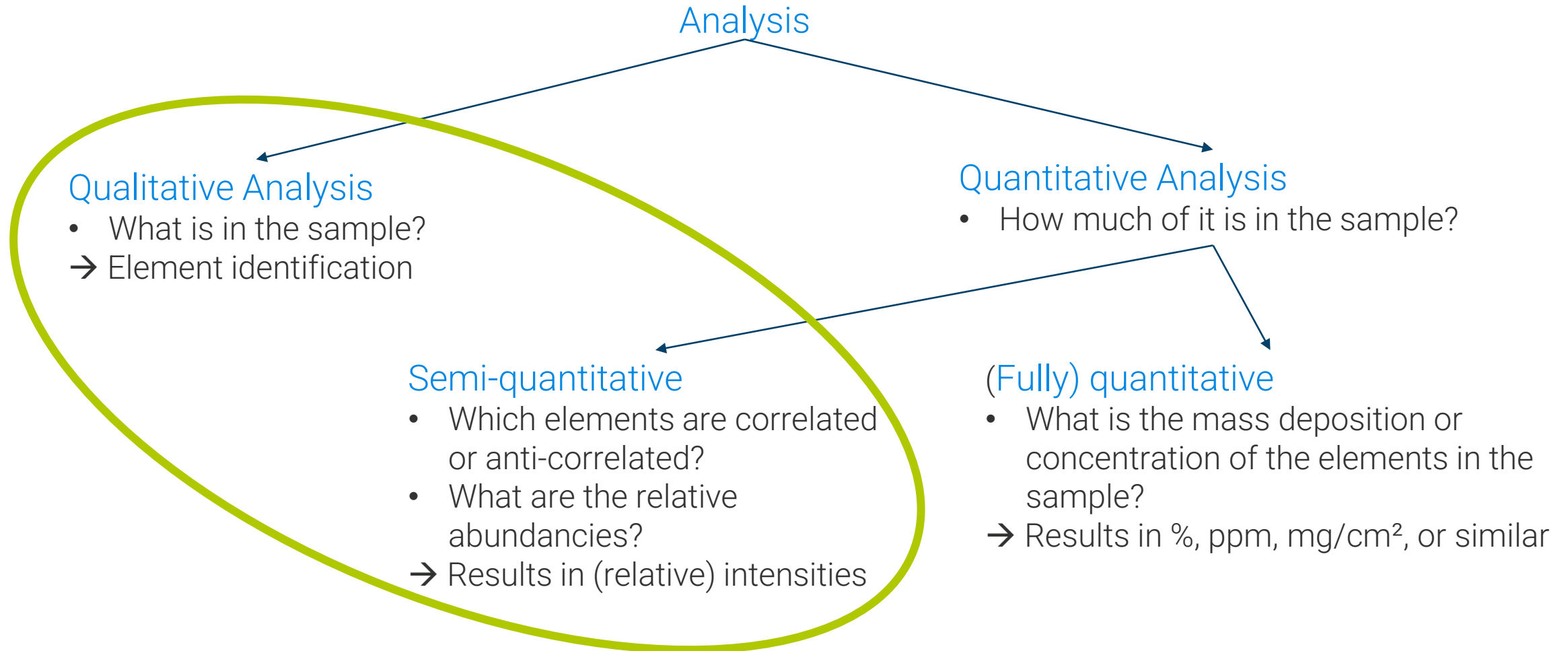
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- **Part I** of this series aimed to introduce micro-XRF as a technique and give an overview of the individual components of a micro-XRF instrument and why they are the way they are, today.
- **Part II** focuses on qualitative micro-XRF analysis.
- **Part III** will discuss quantitative XRF analysis and whether standards are a necessity or merely a support.
- So what do we mean with “qualitative analysis”?

# What is qualitative analysis?



# What is qualitative analysis?

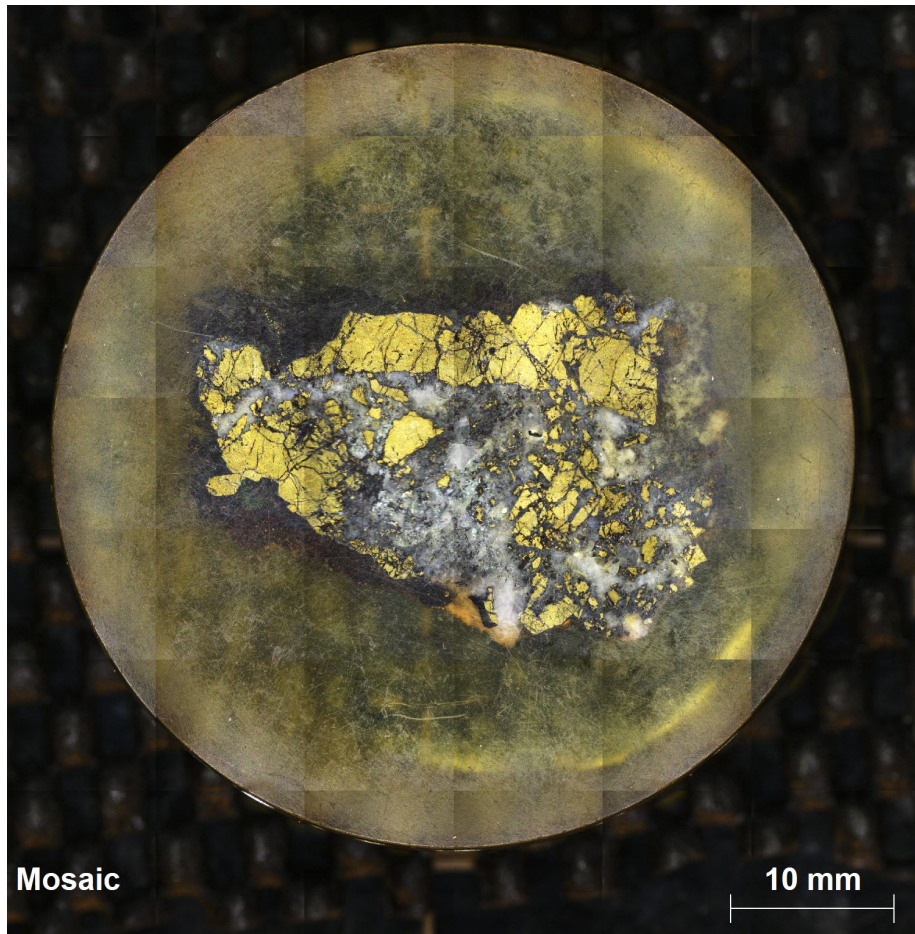


# What is qualitative analysis?

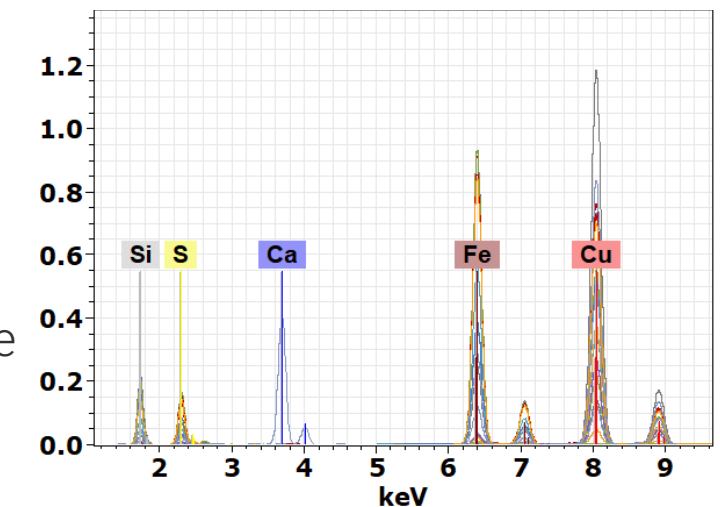
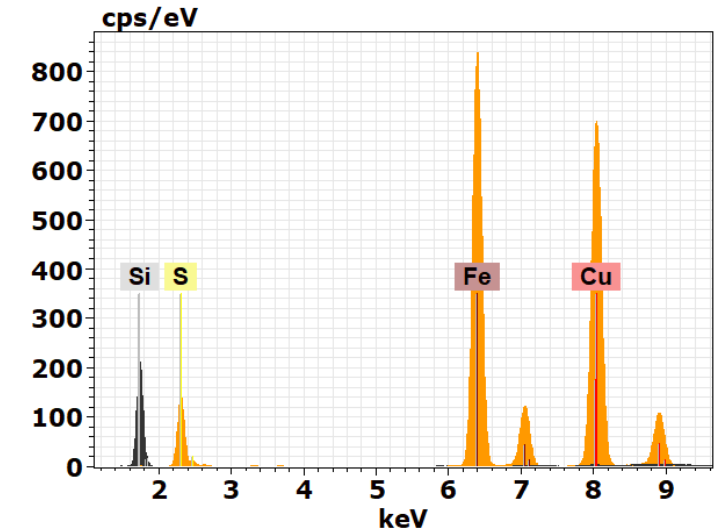
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- In micro-XRF it's more difficult to draw a line between qualitative and semi-quantitative analysis than between semi-quantitative and quantitative analysis.
- Purely qualitative analysis only works where elements are either there or not - as is the case in single-spot analysis.
- With a spatially resolving method any concentration gradient very quickly enters the realm of relative change and, thus, that of semi-quantitative analysis.

# How to understand a sample? Comparing single-point spectra



- To understand a sample like this, one could measure in the “golden” area and the bright “white” parts of the sample, to get a quick impression of the minerals.
- But what about the shades? The more positions you measure the more spectra you’ll end up that lie somewhere in between the “pure spectra”. How to evaluate that?





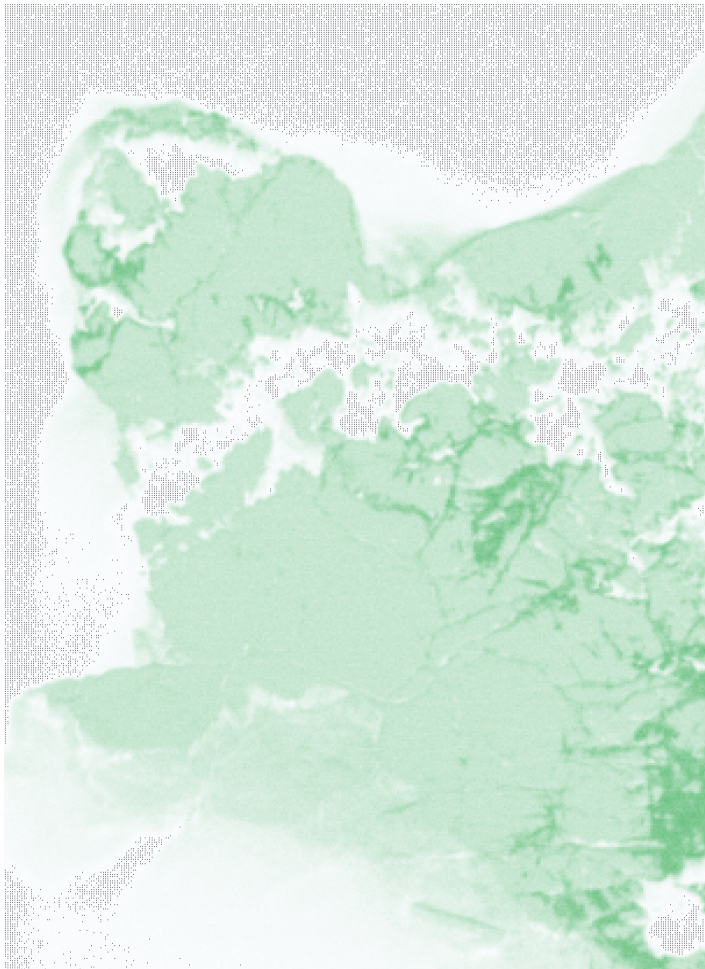




# How to understand a sample?

## Visualizing intensity changes over large areas

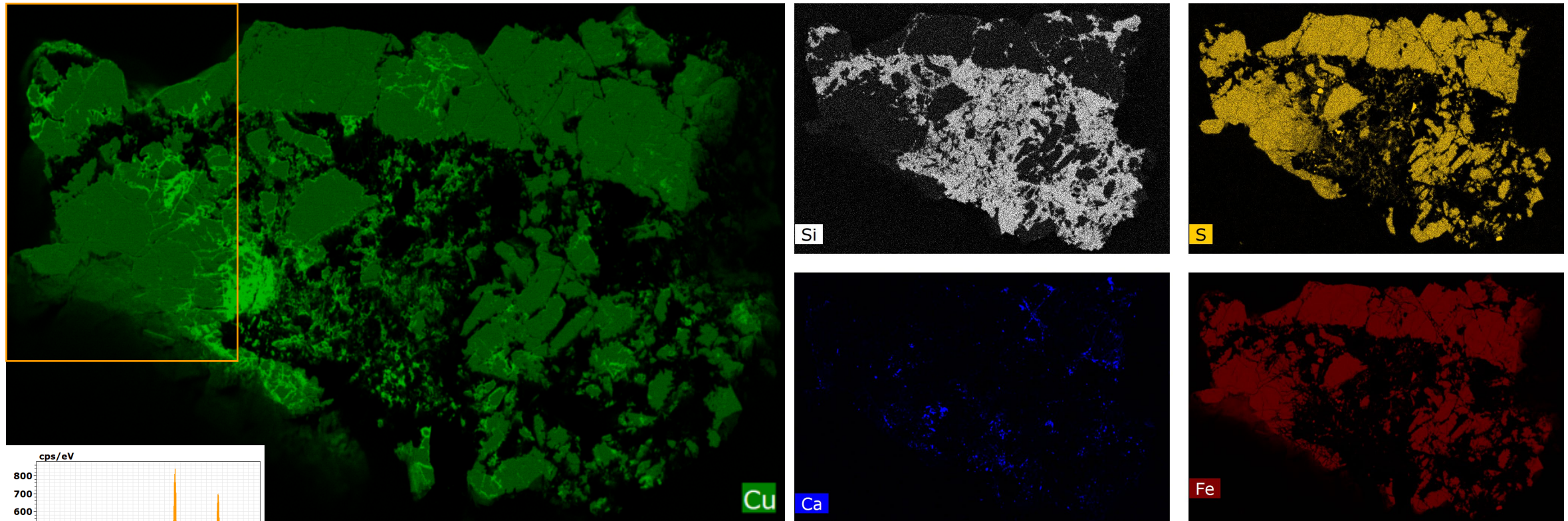
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- Same data but zoomed out:
  - By the color shade the human eye can easily discern between high-intensity areas, low-intensity areas and all the shades in between.
  - To quickly grasp relative intensity variations of many spectra (f.e. 1000x660 spectra) data is best presented in color scales.
- Important note: The assumption that intensities and concentrations have a strict correlation may prove to be a pitfall. Especially in layered samples.

# How to understand a sample?

## Visualizing intensity changes of multiple elements

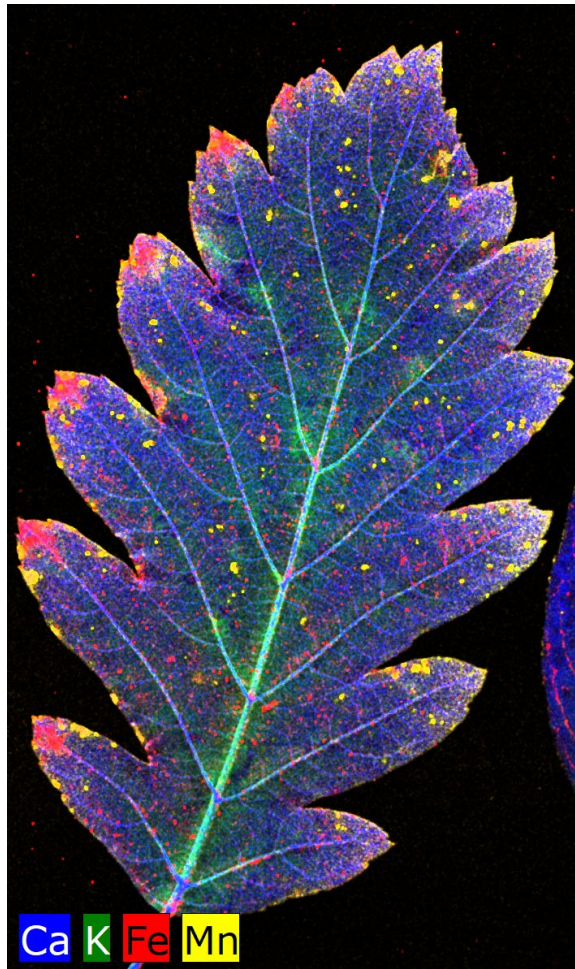


- Different colors for different elements allow to quickly overlay elements and, thus, see, where elements are mixed or not. ...in thousands of spectra at glance.

# How to understand a sample?

## What's the composition of a leaf?

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- Qualitative analysis can yield beautiful pictures, but that's not all
    - It helps to “get a feeling” for the sample.
    - It helps to identify areas of interest.
    - It already allows to identify correlations and anti-correlations.
  - It may already yield the revelation that quantification doesn't make much sense
    - If the sample is clearly too heterogeneous, or too thin, or adversely shaped, pressing the <quantify> button will still give numbers, but it will not be a good description of the sample properties.
- Bulk quantification is a valid approach, only if a sample is homogenous within the analytical volume!

# What's the color of a painting?

## Some simple examples

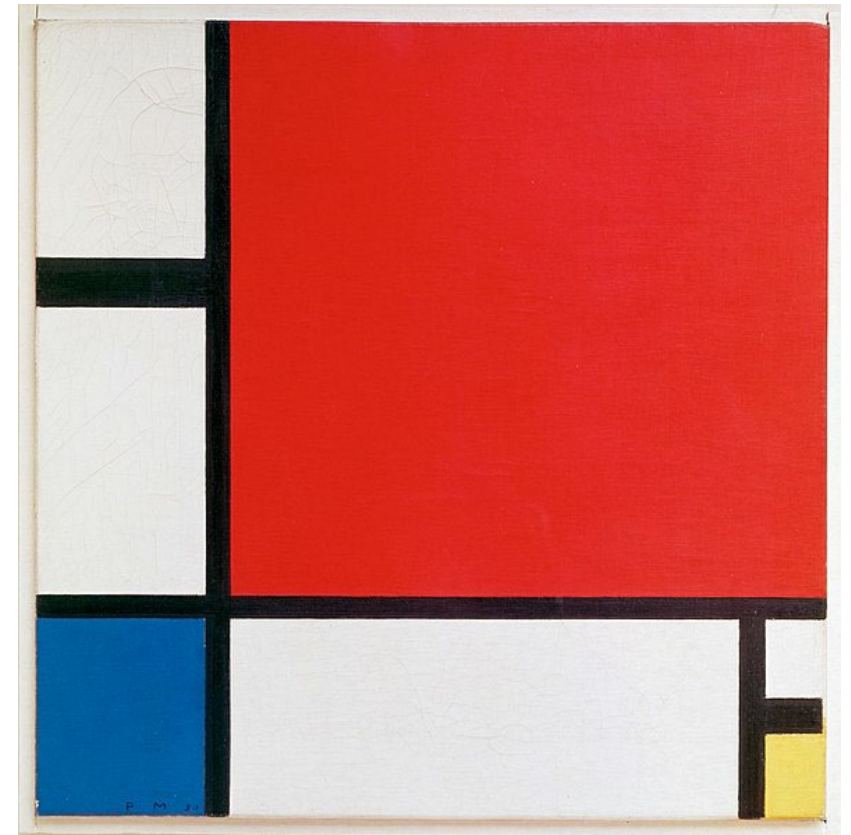
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Yves Klein, "Blue Monochrome"  
Photographed in MoMA, NY

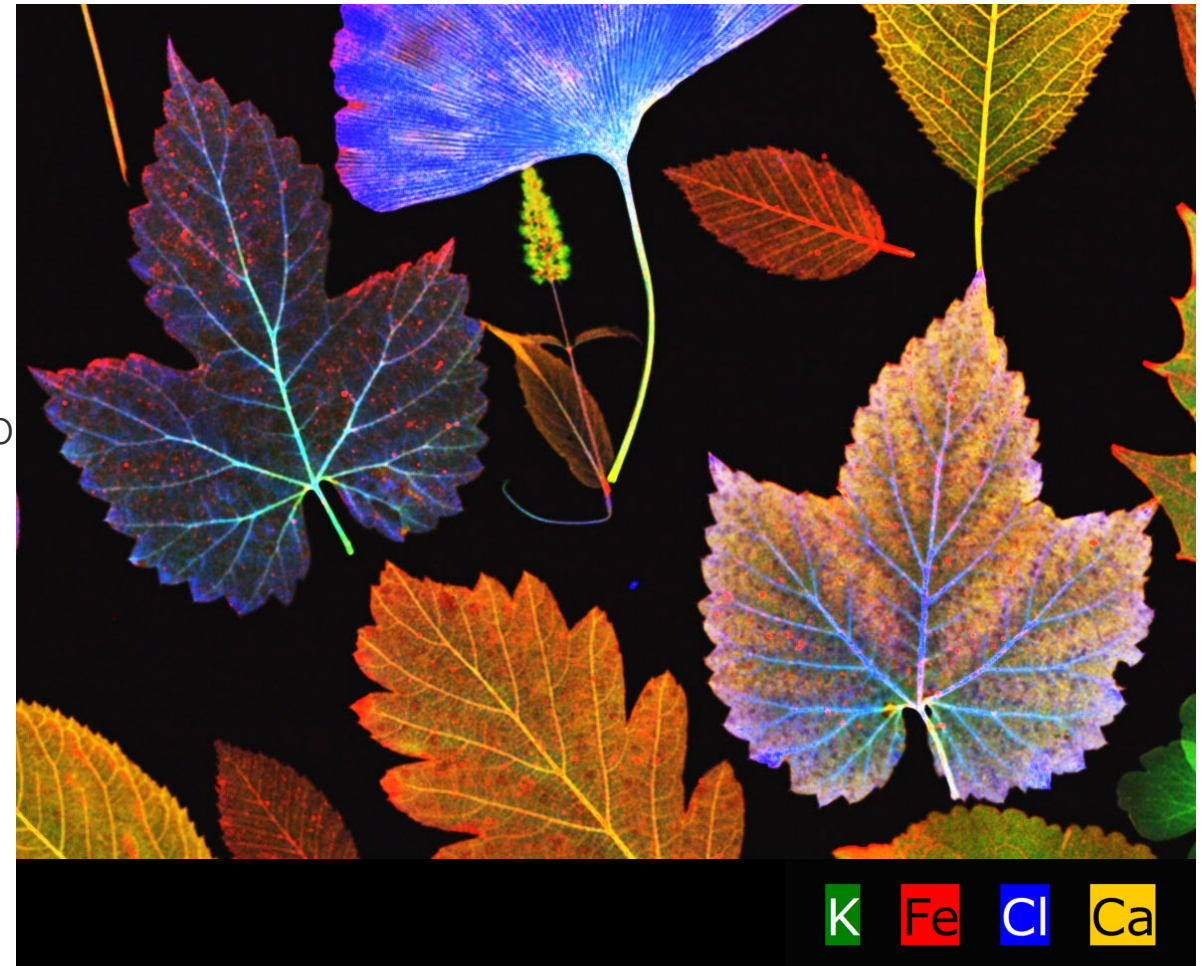
- Usually one wouldn't try to describe a picture by pointing out its color, but rather, the "distribution" of the colors.
- Still user try to describe an heterogeneous sample by a table of element concentrations.

*Piet Mondrian, "Composition with Red, Blue, and Yellow", Image from Wikipedia*



# Is qualitative analysis more than nice pictures? Information in a semi-quantitative analysis

- Some leaves, for example, have an upper and a lower side.
- They are thin enough that the X-rays shoot through, but still the qualitatively obtained signal looks very different.
- For many elements it would be quite futile to try to do quantitative analysis.
- There is quite a lot of samples that are similarly challenging, i.e. that are far from well-defined and, thus, hardly quantifiable.
- Does that mean, we cannot learn anything from our measurements?



# Where qualitative analysis is sufficient

## Fossilized bat

Optical image



Element distribution



Bone visualization



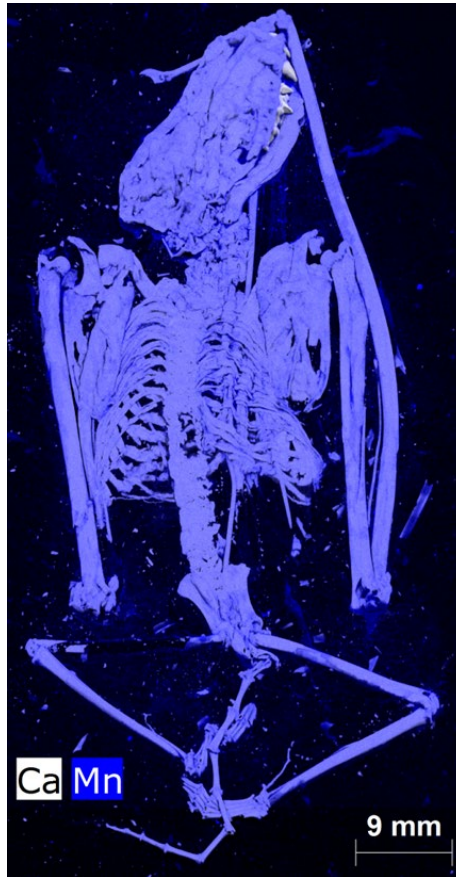
# Where qualitative analysis is sufficient

## Fossilized bat – showing its teeth

Optical image



Element distribution

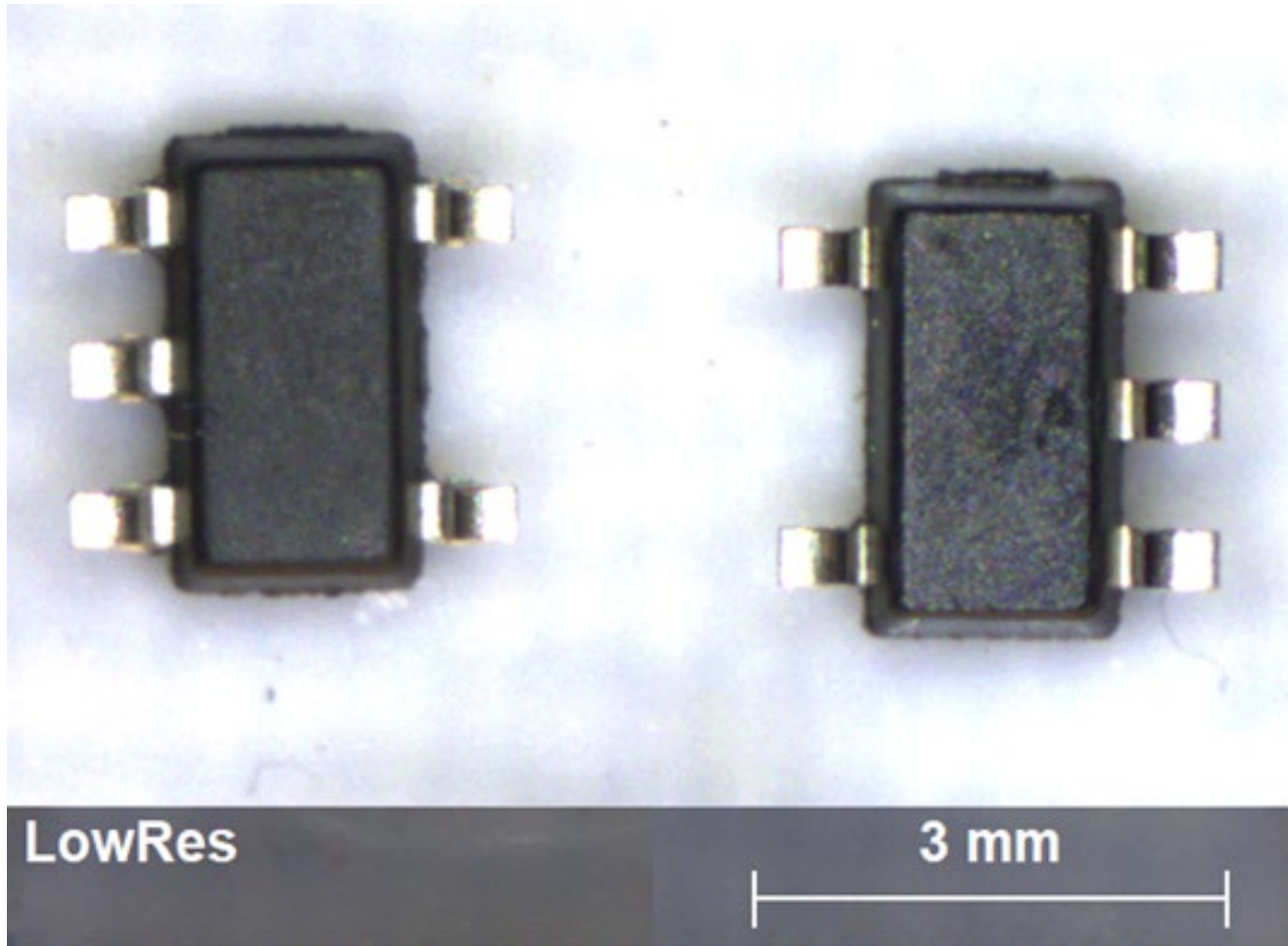


- Overlaying Ca and Mn information clearly reveals that Mn can be found in the bone material but not in the teeth.
- To tell bone fragments from teeth is actually a quite important piece of the puzzle for paleontologists...
- There is absolutely no quantification needed to answer this specific analytical question.



# Where qualitative analysis is sufficient

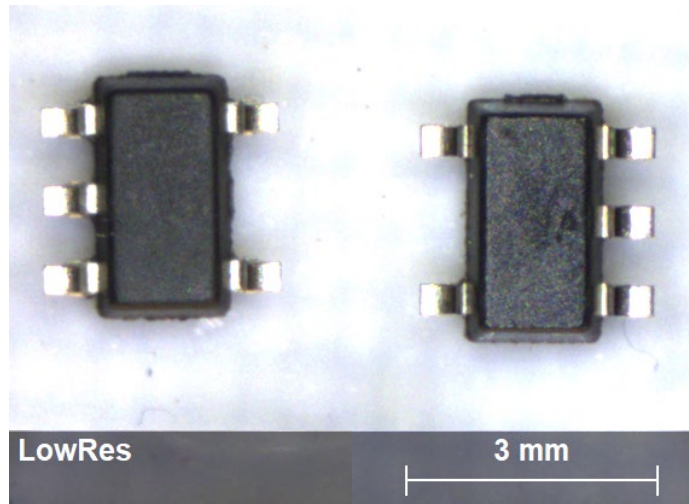
## Counterfeit security



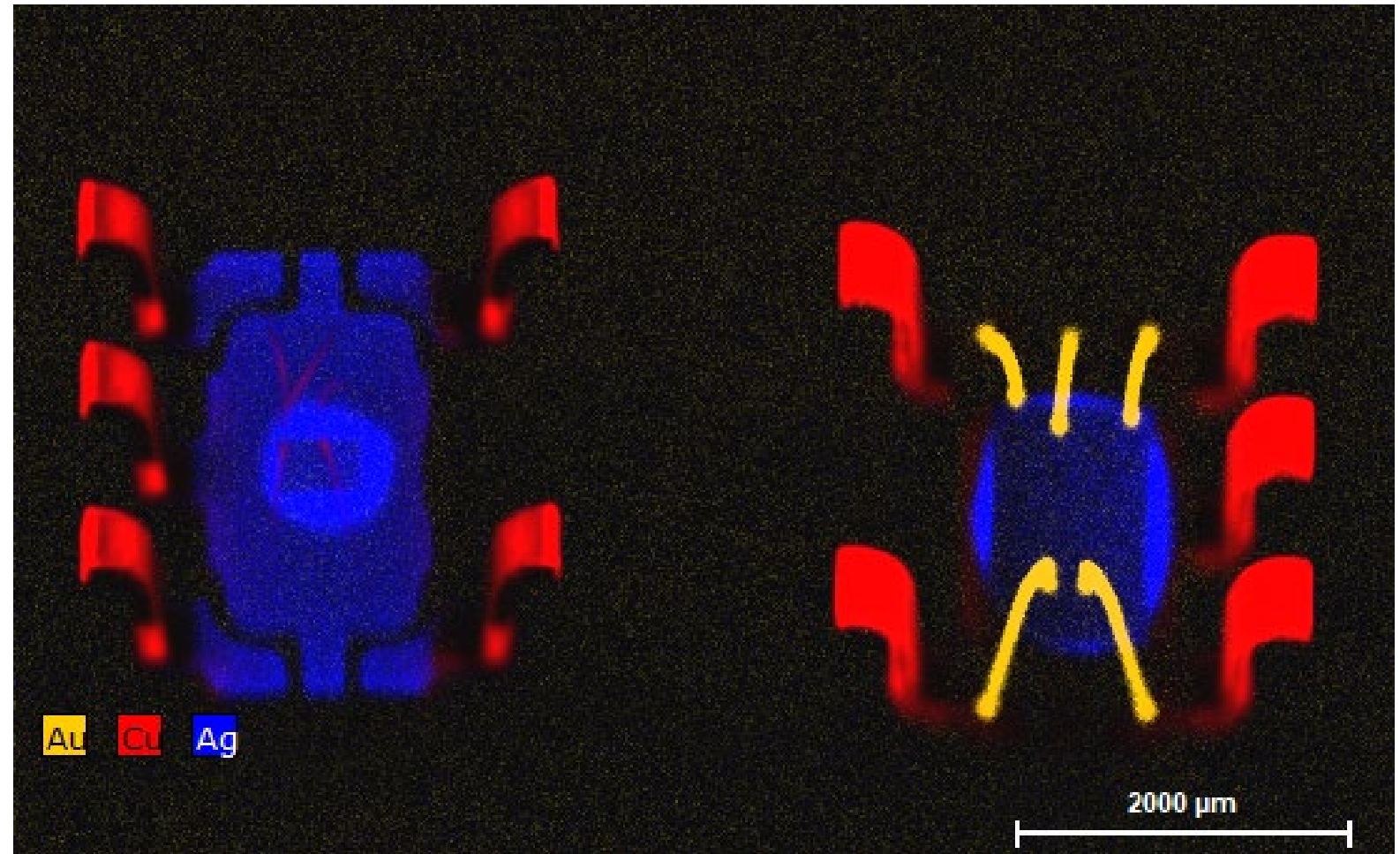
- Two chips from different supplier.
- They are supposedly the same but their price is remarkably different...
- Are they the same chip?

# Where qualitative analysis is sufficient

## Counterfeit security

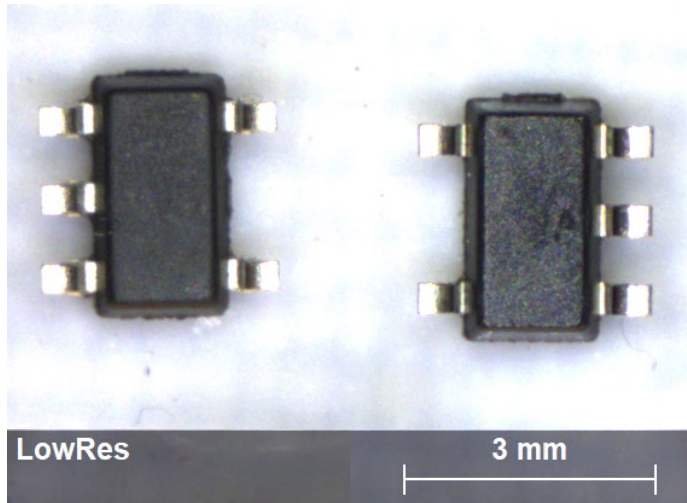


- The same?
- Purely qualitatively the answer is clear.
- Element intensities show different materials and different structure sizes.

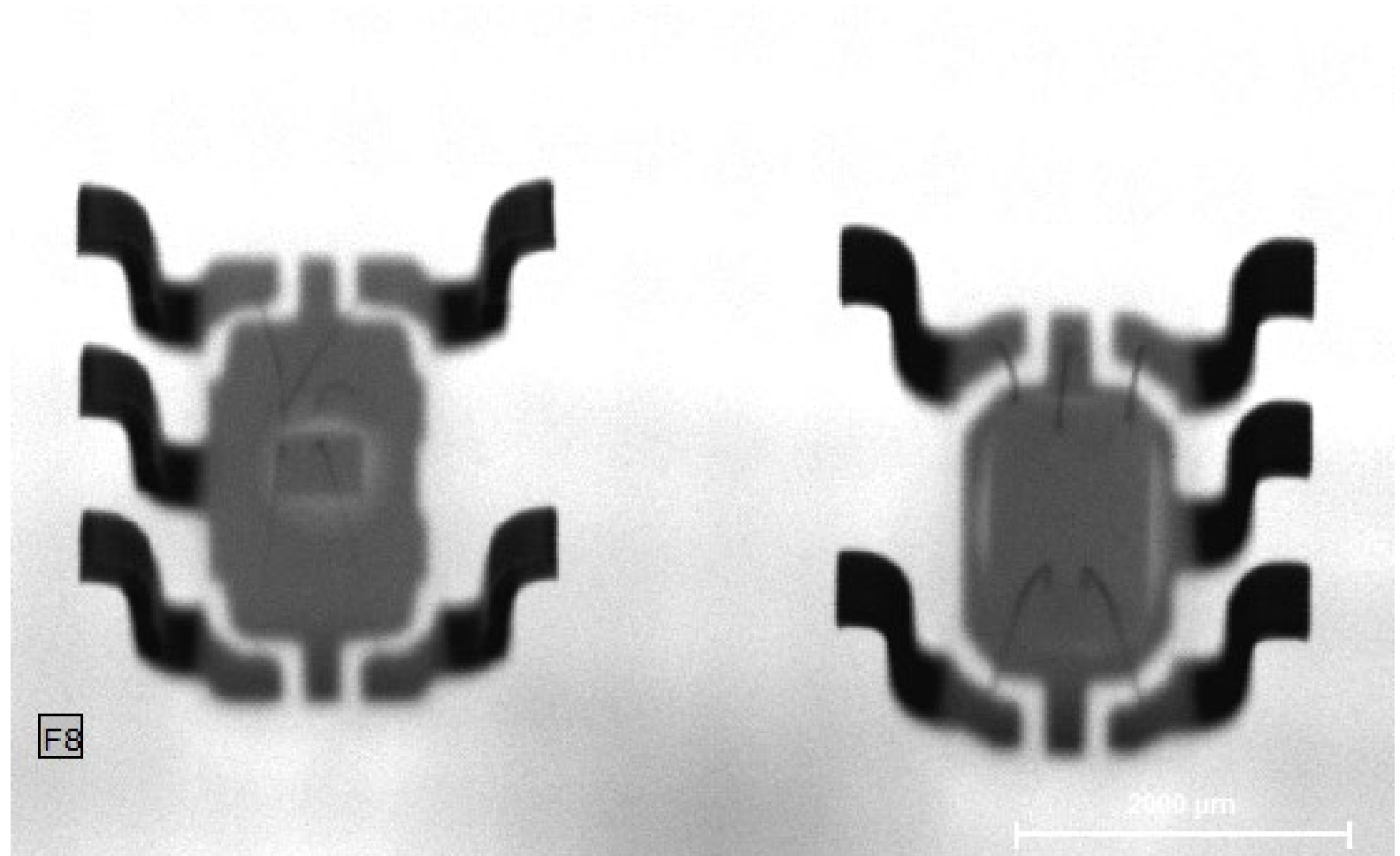


# Where qualitative analysis is sufficient

## Counterfeit security

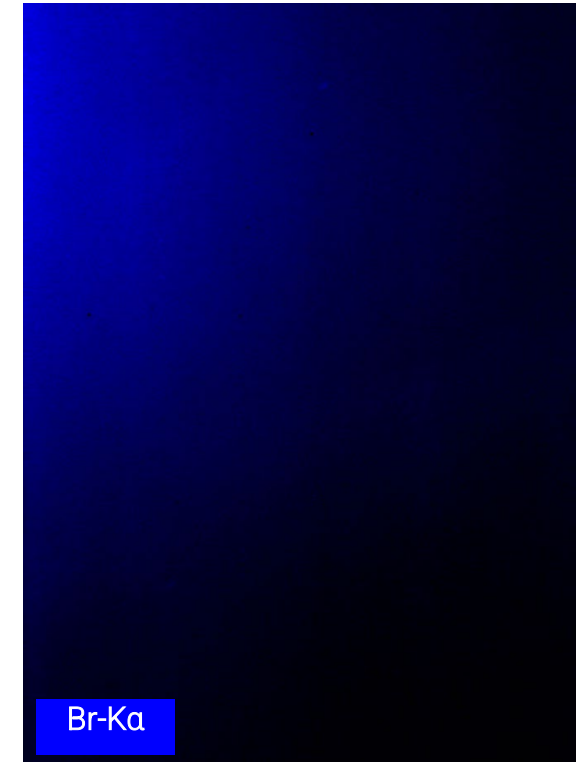


- The same?
- Even without direct element information the scattered high-energy radiation shows a difference.



# Where qualitative analysis is sufficient

## Recovering of photographic images

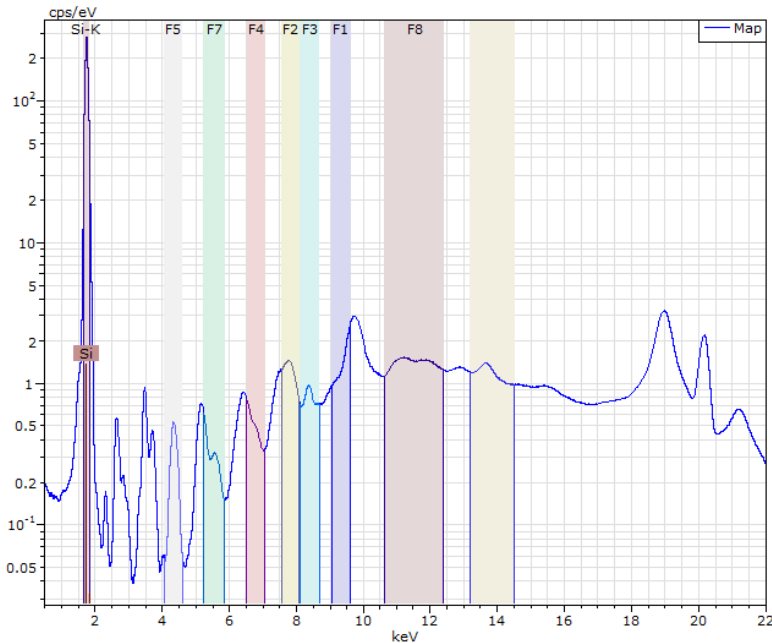


- Old, faded and partly damaged photograph of a kid.
- The Ag distribution reveals the original picture, and the presence of halides correlates with the damaged area.

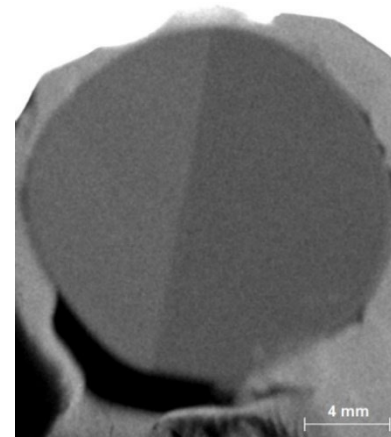
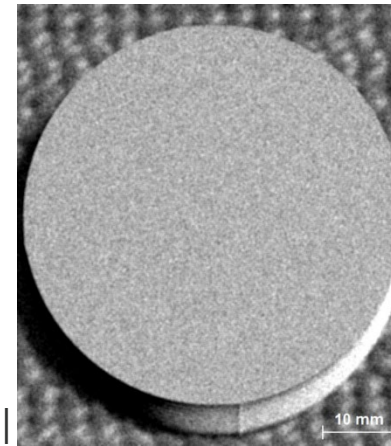
# Where qualitative analysis is sufficient

## Sample crystallinity

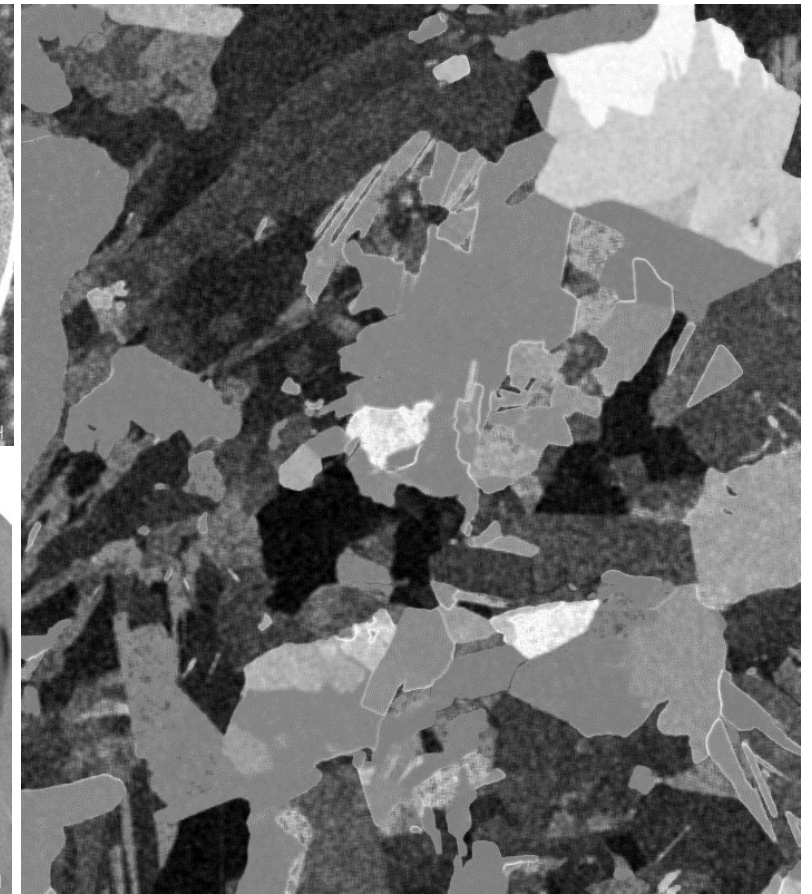
- A micro-XRF spectrum often features diffraction peaks in addition to fluorescence signals.
- Displaying the intensity distribution of individual Bragg peaks reveals information on sample crystallinity.



Single crystal



NdGaO<sub>3</sub> twin

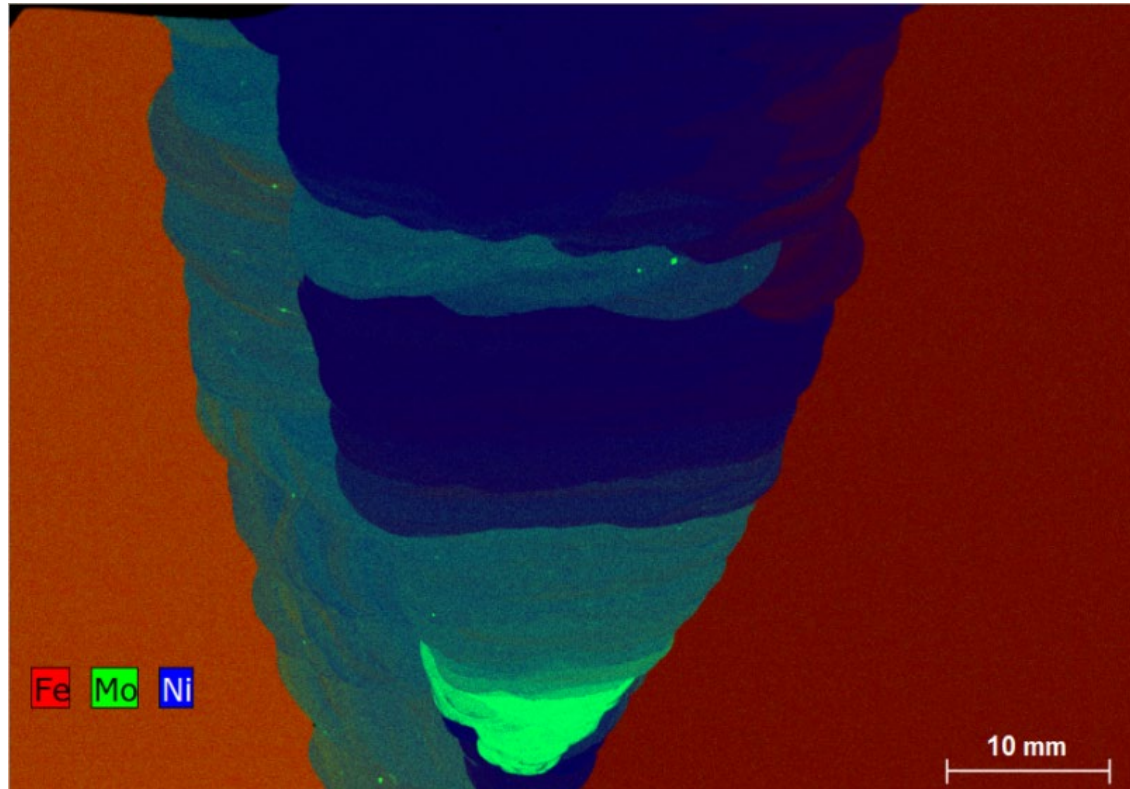


Multi-crystalline sample

# Where qualitative analysis is sufficient

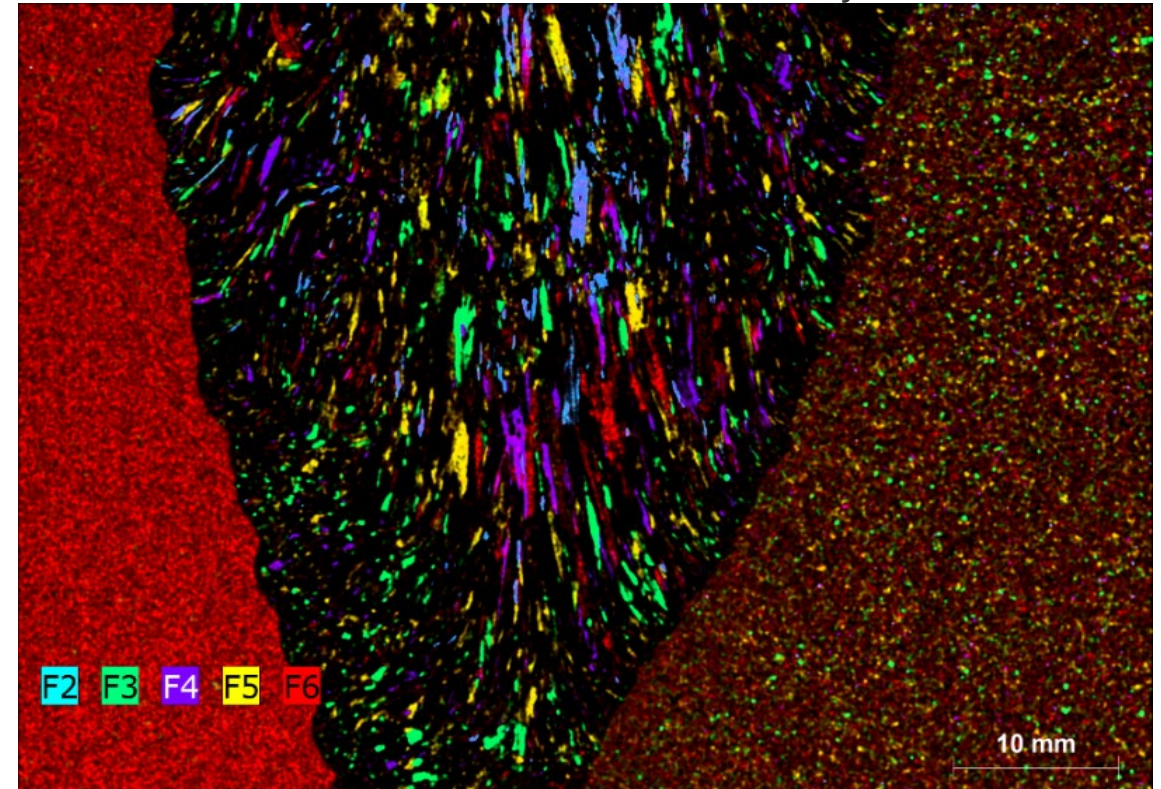
## Visualizing sample crystallinity

Composition



Al100/Ti50/Cu25 [ $\mu\text{m}$ ], 50 kV 600  $\mu\text{A}$   
15  $\mu\text{m}$ , 3 ms, time 14 h

Crystal domains

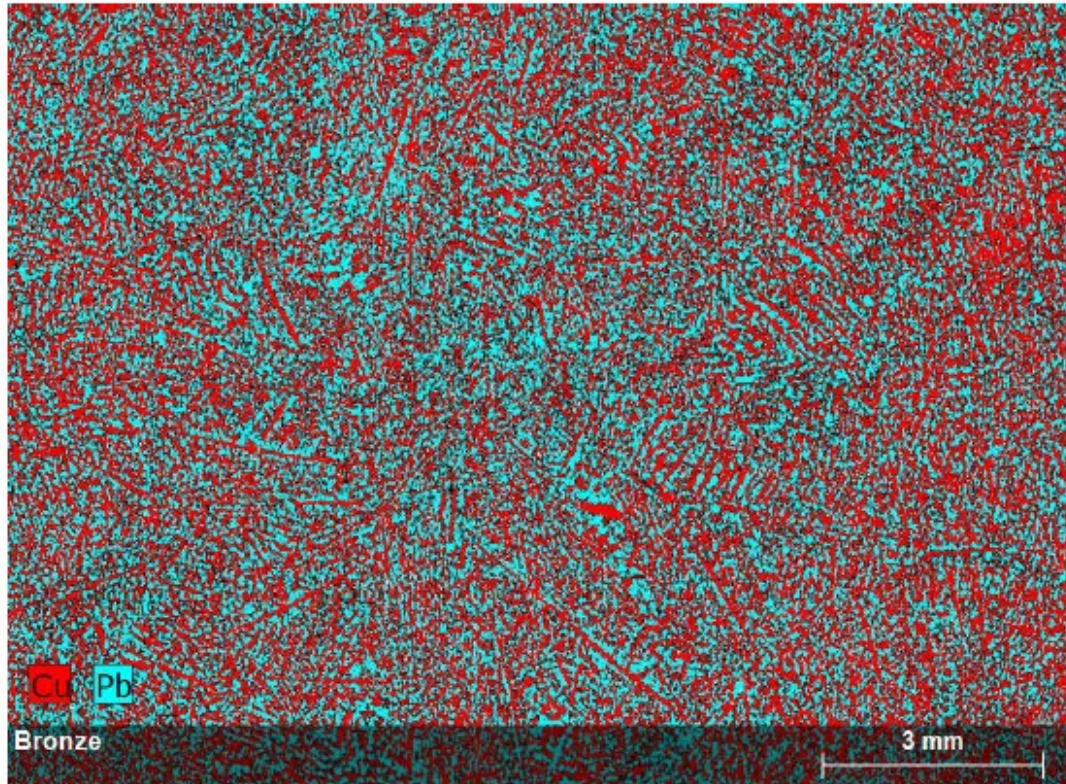


Without filter, 50 kV 100  $\mu\text{A}$ ,  
20  $\mu\text{m}$ , 3 ms, time 8 h

# Where qualitative analysis is sufficient

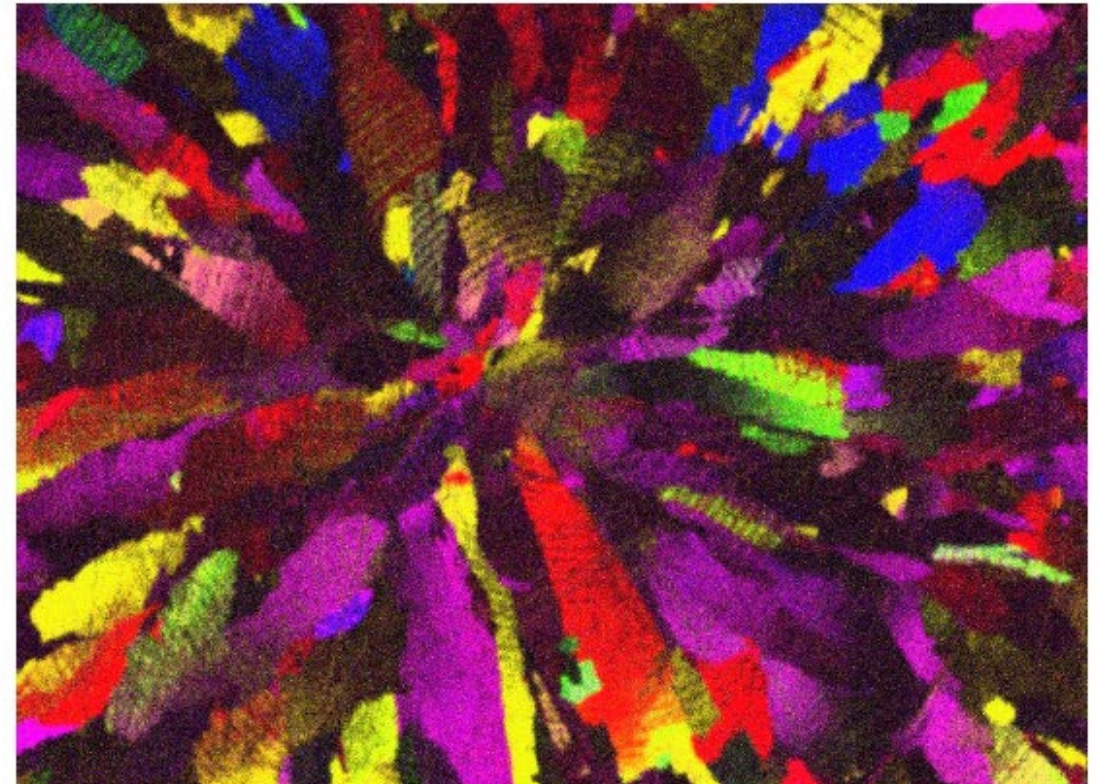
## Visualizing sample crystallinity

Composition



Al630 [ $\mu\text{m}$ ], 50 kV 200  $\mu\text{A}$   
15  $\mu\text{m}$ , 10 ms, time 2 h 25 min

Crystal domains



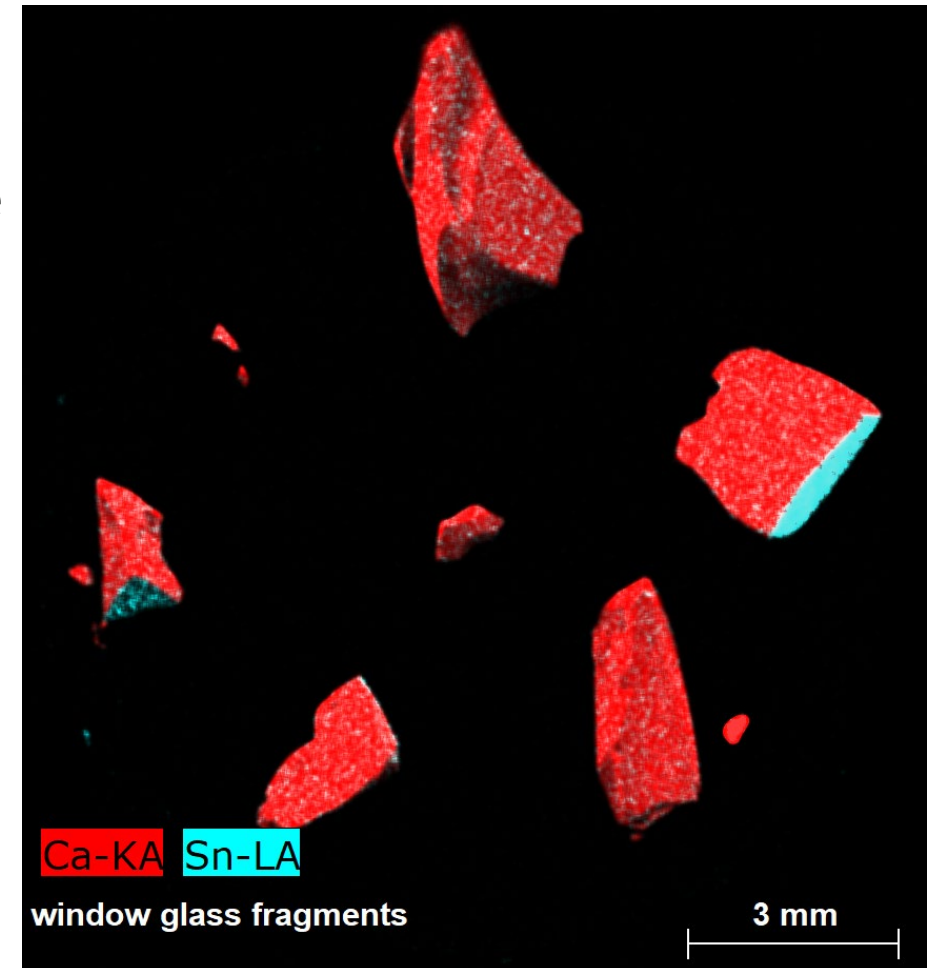
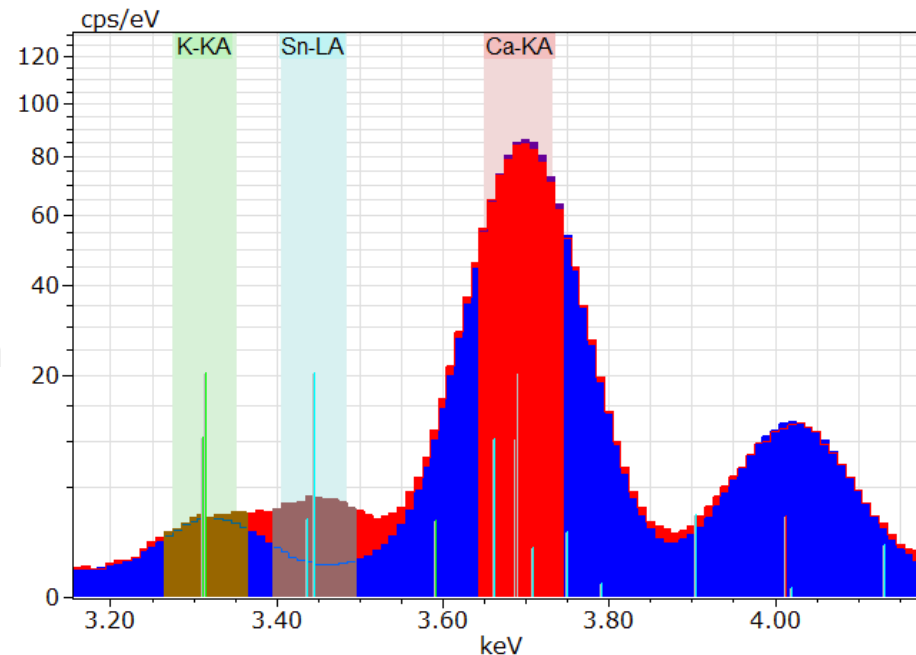
Without filter, 50 kV 200  $\mu\text{A}$ ,  
15  $\mu\text{m}$ , 20 ms, 4 frames, time 19 h

# Where qualitative analysis is sufficient

## Identification of relevant sample areas

- In forensics glasses are classified based on element intensity ratios.
- BEFORE doing the classification, the user needs to make sure, the glass is not measured on its float side (because there is overlap with Ca and K)

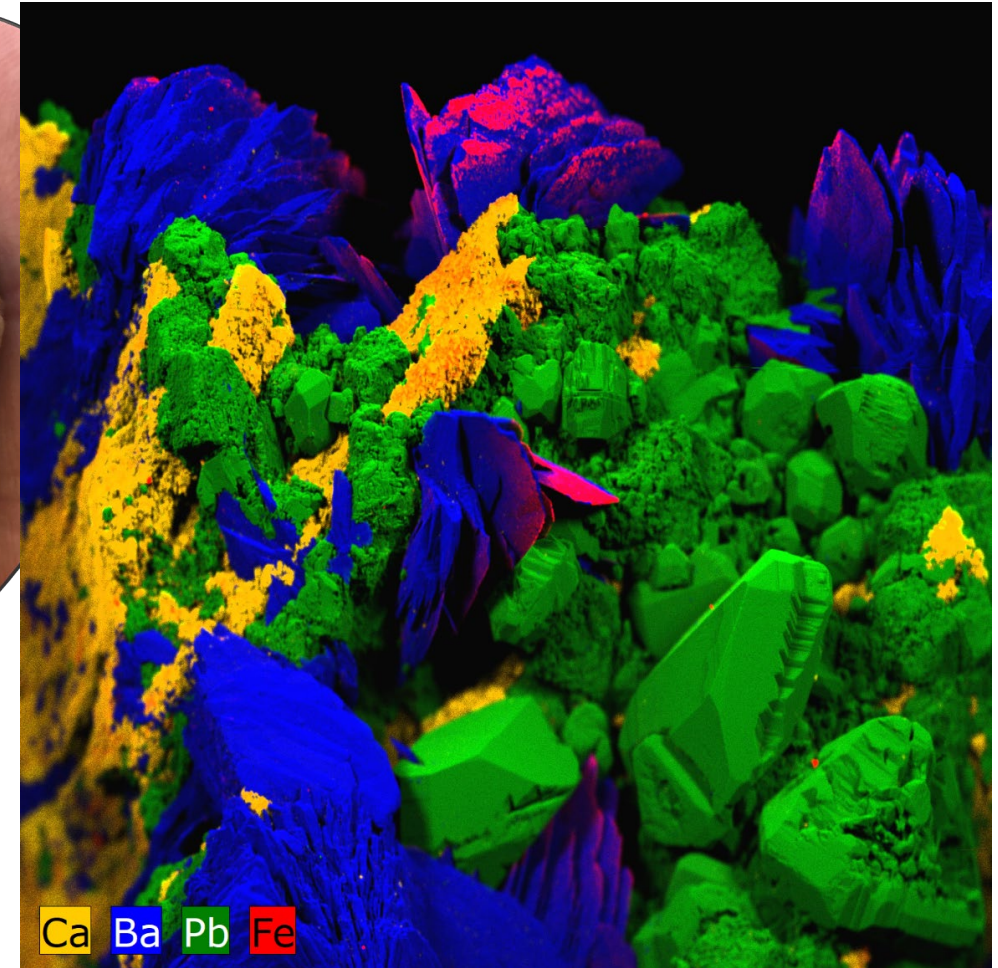
- Qualitative analysis before doing some sort of quantification





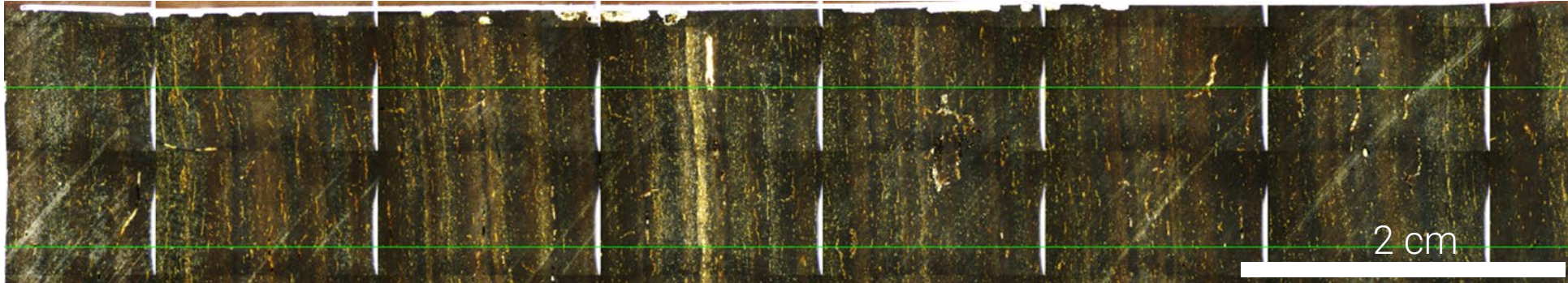
# Where qualitative analysis is sufficient ...and quantification not possible

- Besides homogeneity there is one special parameter required for a quantification – a defined geometry
- The angle of the sample surface to incoming and outgoing radiation must be known for a quantification
- Ideal samples are flat to the incoming and outgoing radiation
- A sample such as the one presented here does not meet this requirement.  
→ results must be “semi-quantitative”



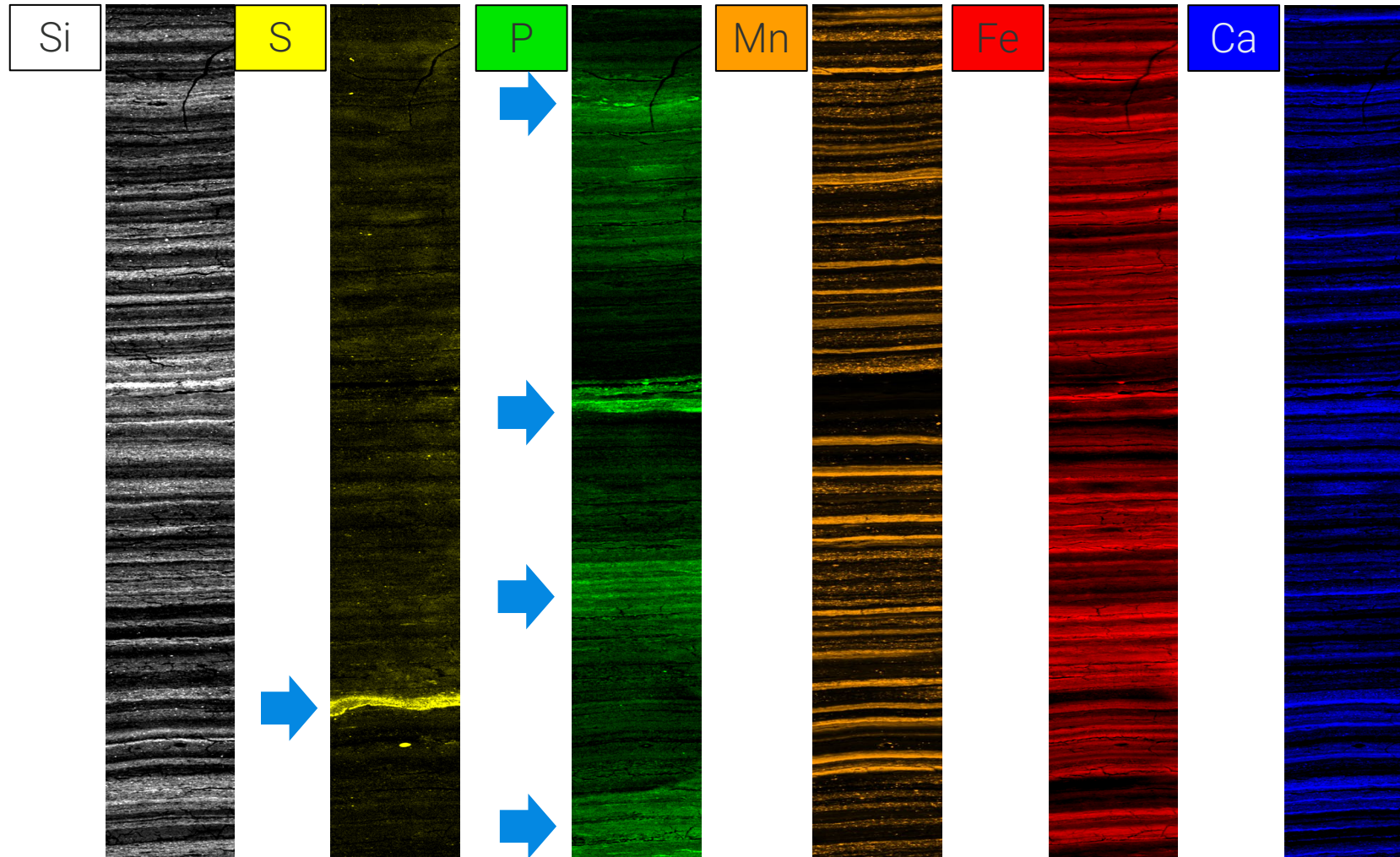
# Where qualitative analysis is sufficient ...and quantification might not even be needed

Epoxy embedded lake sediments



- Lake sediments are unique climate archives recording changes over time from within as well as around the lake and the sedimentary environment.
- Composition changes in the sediment core are correlated to changes in the lake region.
- These changes are mostly seasonal, but climate changes or catastrophic events like floods or volcano eruptions are logged, as well as human activity, such as farming.
- Interestingly some information is recorded in the relative change but not necessary in the absolute numbers.

# Where qualitative analysis is sufficient ...and quantification might not even be needed



- Each Fe or Ca horizon represents one vegetation period or year
- We can identify specific “events” such as the S-enrichment or the several P-enrichment, some apparently anti-correlating to Fe
- Each element and its relative variation records, in a different way, what is happening in and at the lake
- The absolute amounts might at a specific location only reflect the sedimentary conditions.

# Summary and outlook

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- Micro-XRF offers basically the opportunity to study **any** sample in at least a qualitative way.
- Whereas “semi-quantitative” is often used to describe “low quality” quantitative analysis, it is in many cases the ideal way to describe a sample and to report meaningful information.
- Sometimes, it is even the *only* information that can be obtained from a sample study as the samples themselves might not even have a **defined composition within the analytical volume**.
- Understanding the sample and the **analytical question** in combination with the basics of X-ray analysis (“Back to the Root webinar I) can provide a idea of the infinite number of application that can be addressed by means of micro-XRF
- In the next webinar of the “Back to the Root” series we will start presenting **quantitative analysis**.

*Leaves*  
*Berlin, Germany*

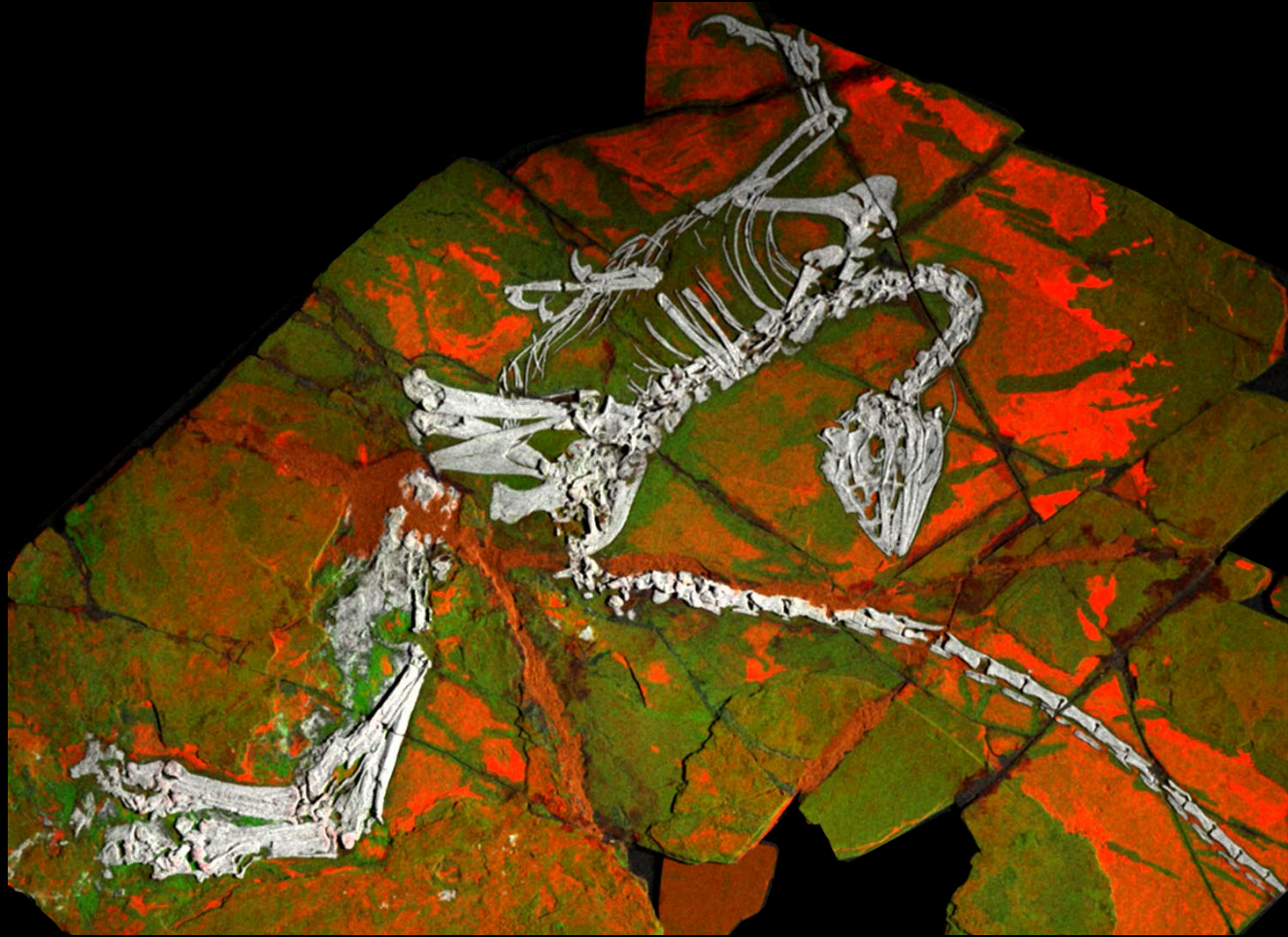


K Fe Cl Ca

20 cm

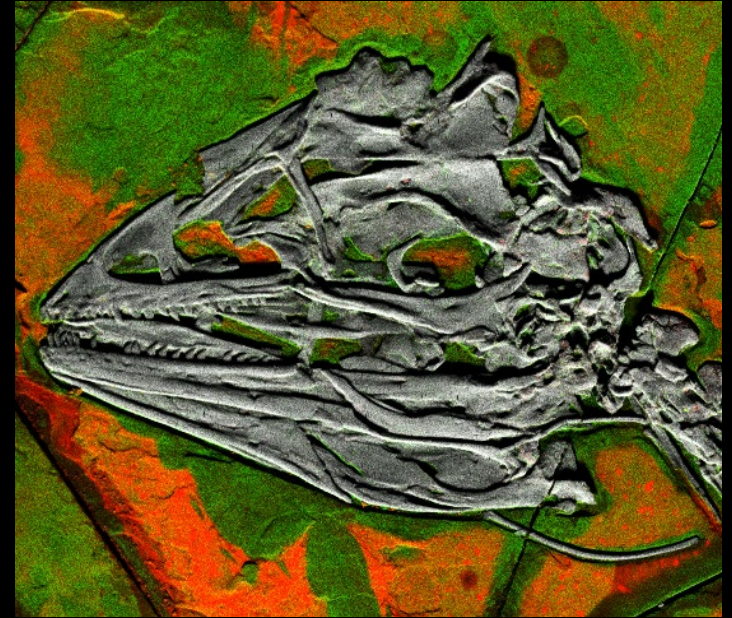
# *Jianianhualong*

*Early Cretaceous theropod, China*



K Fe Sr

20 cm



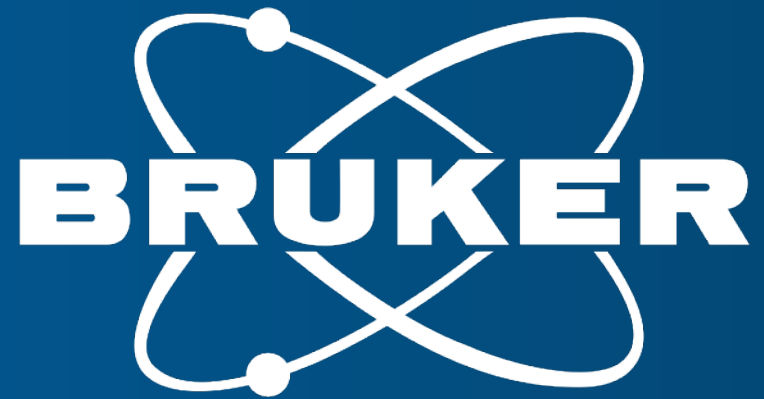


# Thank you!

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