Explore Micro-XRF in the Geosciences

Bruker Nano Analytics, Berlin, Germany
Webinar, May 16, 2019

M4 TORNADO Webinar
Presenters / Moderators

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Introduction
The instrument – M4 TORNADO

30 W micro-focus Rh tube with polycapillary lens
for excitation spot sizes < 20 µm (for Mo-Kα)

Optional 40 W micro-focus W tube with collimator
for excitation of 'heavy' elements, embedded in lighter matrices

Up to two Silicon drift detectors (SDD)
with 30 or 60 mm² active area each
energy resolution < 145 eV
(for Mn-Kα @ 130 kcps throughput)
Optional light element window (LEW)

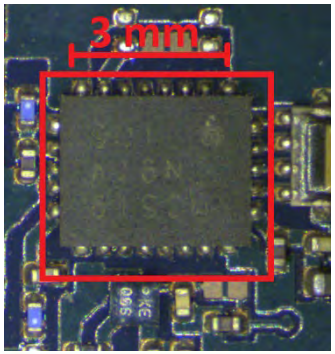
Sealed sample chamber with adjustable pressure between 1 mbar and atmospheric pressure for detecting elements down to Na (down to C with LEW)

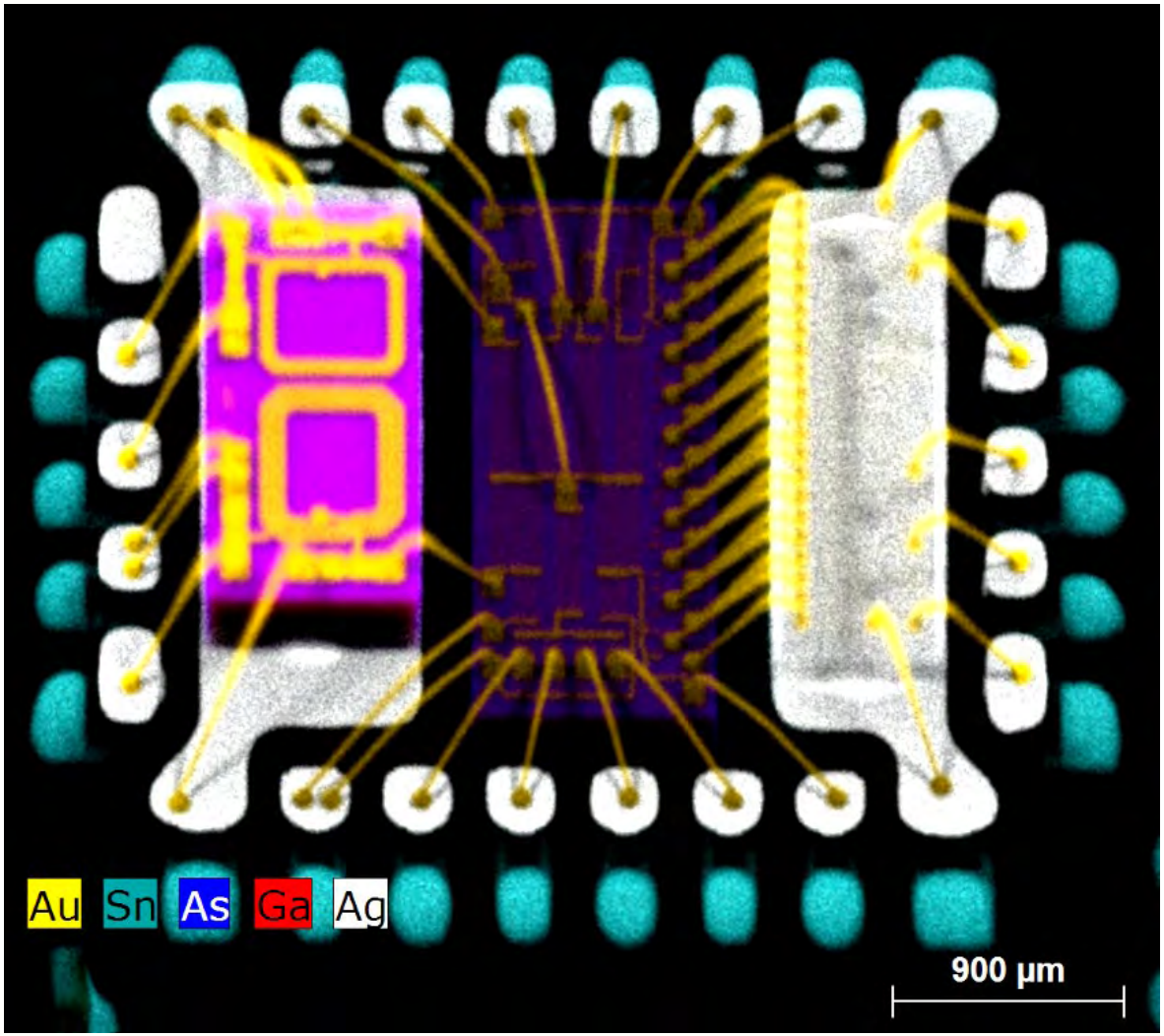
Sample stage with measureable area of 200 mm x 160 mm, maximum sample height 120 mm, maximum sample weight 7 kg, and sample stage speed up to 100 mm/s, minimum step size 4 µm

Introduction
The method – micro-XRF

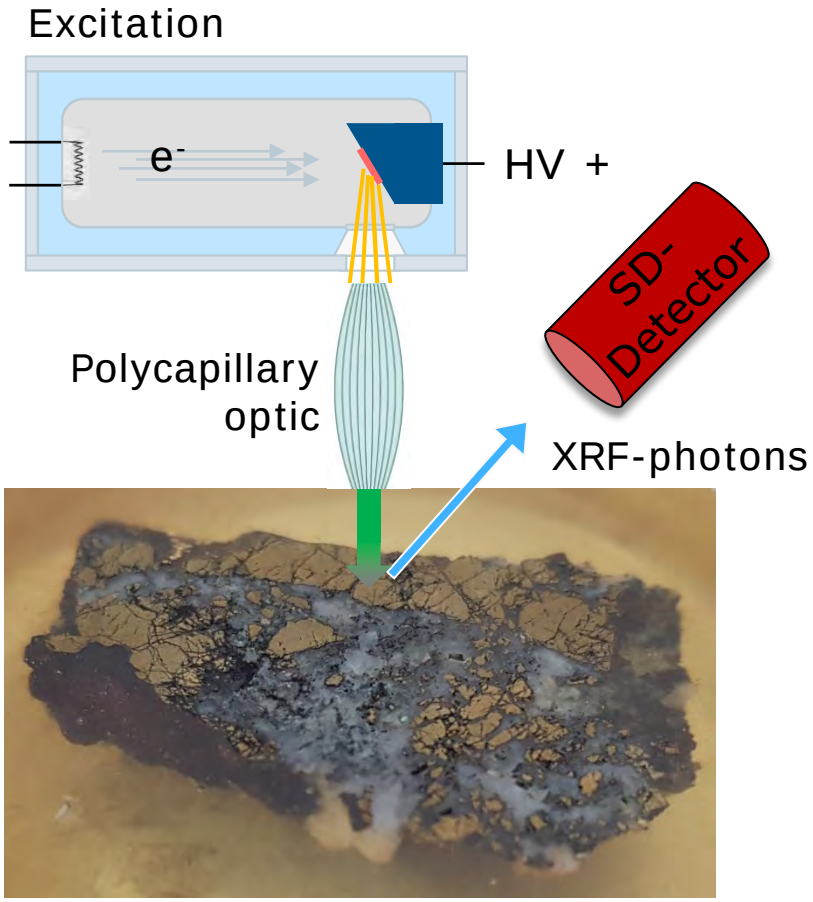
- Little to no sample preparation
- Non-destructive
- Elemental information
- Small spot analysis
- Information from within the sample

- Large-scale
- Quantification

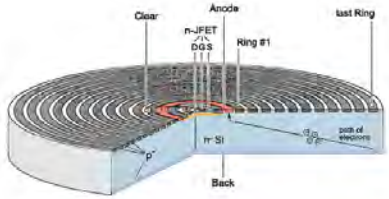




Introduction
The method applied to geology



XRF Detection



Silicon **D**rift **D**etector
with XFlash® Technology

- X-rays can be guided onto a small spot
- Spatially resolved element-specific signal
- Intensity ratios of observed elemental lines can be used for quantification

Overview

Purely qualitative Analysis

- Element distributions
- Element localization
- Element contrast
- Aperture management system → colorful pictures

Semi-quantitative analysis

- Where is what and is it more or less than anywhere else?

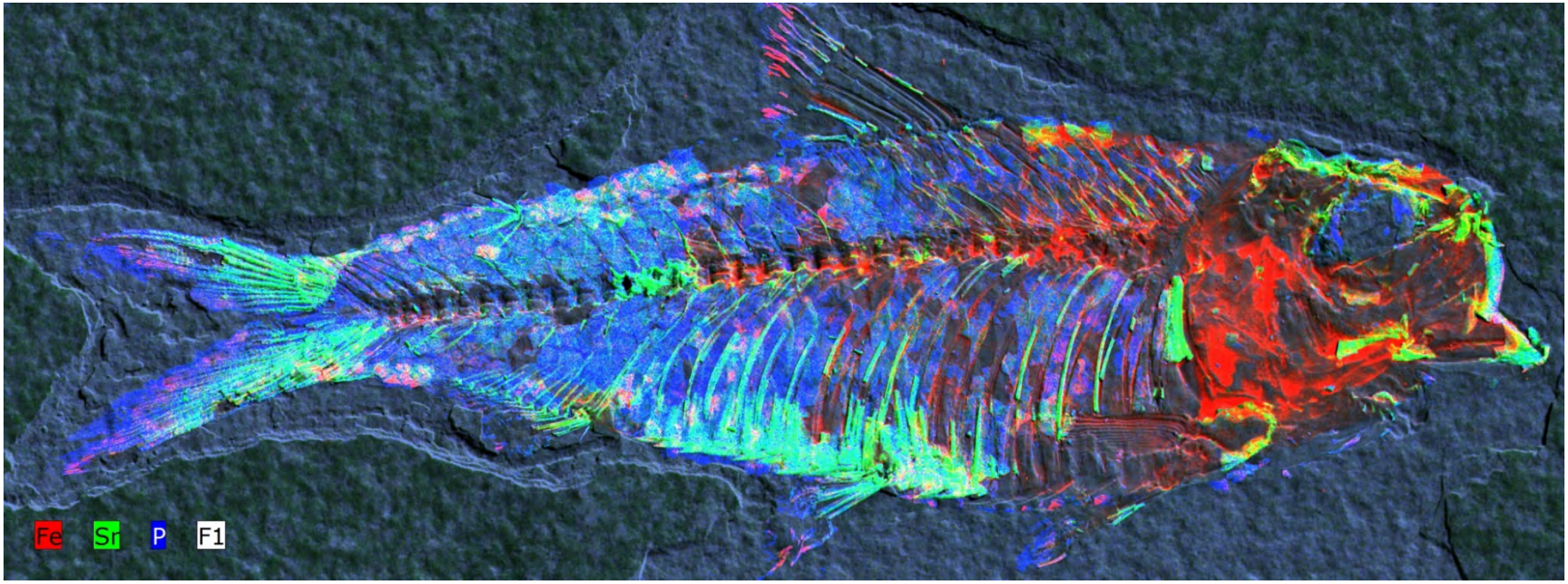
Quantitative analysis

- What to have in mind when quantifying geological samples
- Light elements
- Samples appropriate for calibration of micro-XRF
- Empirical trace element quantification examples
- FP major element quantification

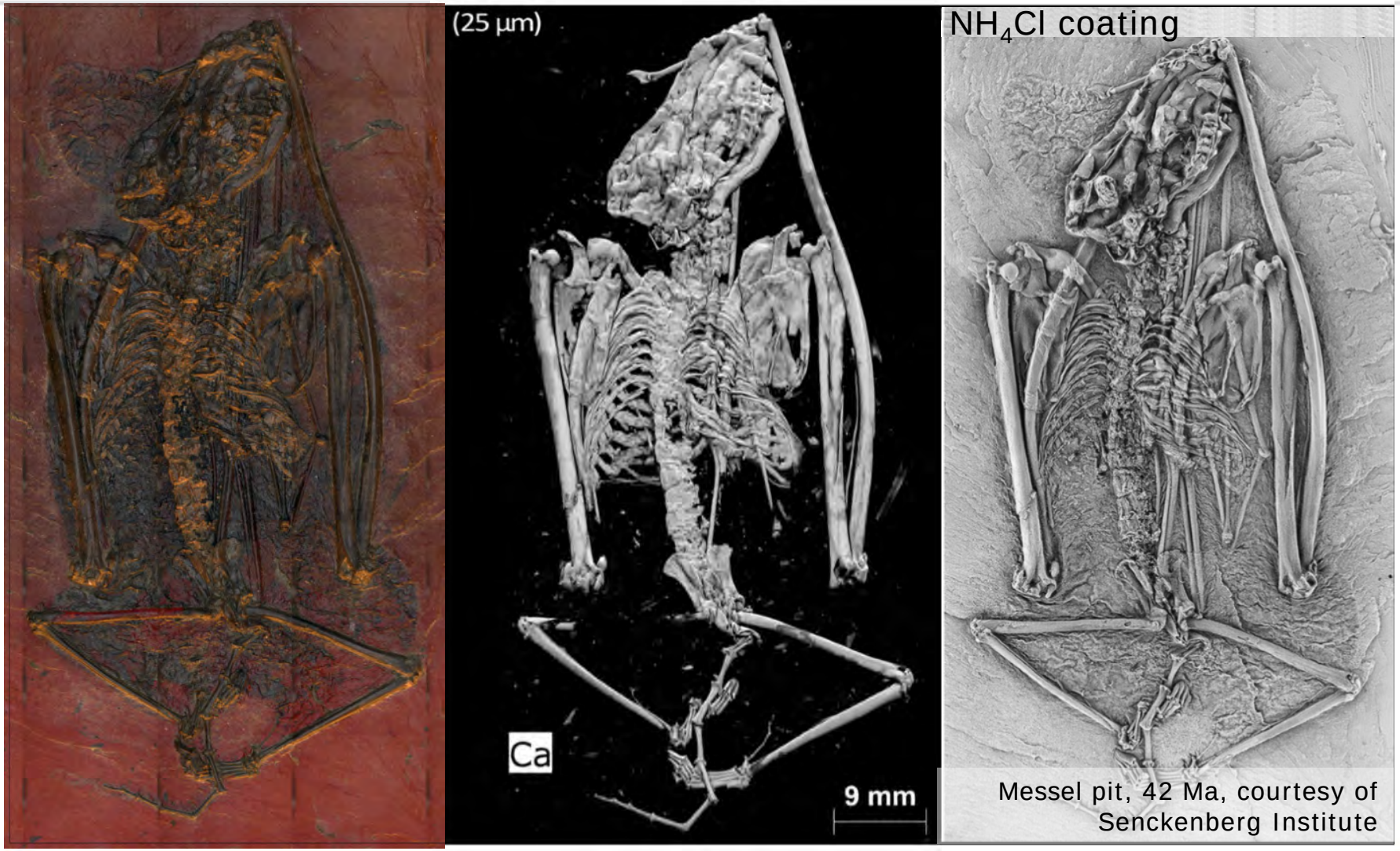
Qualitative analysis
Fish fossil – element distribution

Fossil fish, Green River Formation, Utah
≈ 50 Ma

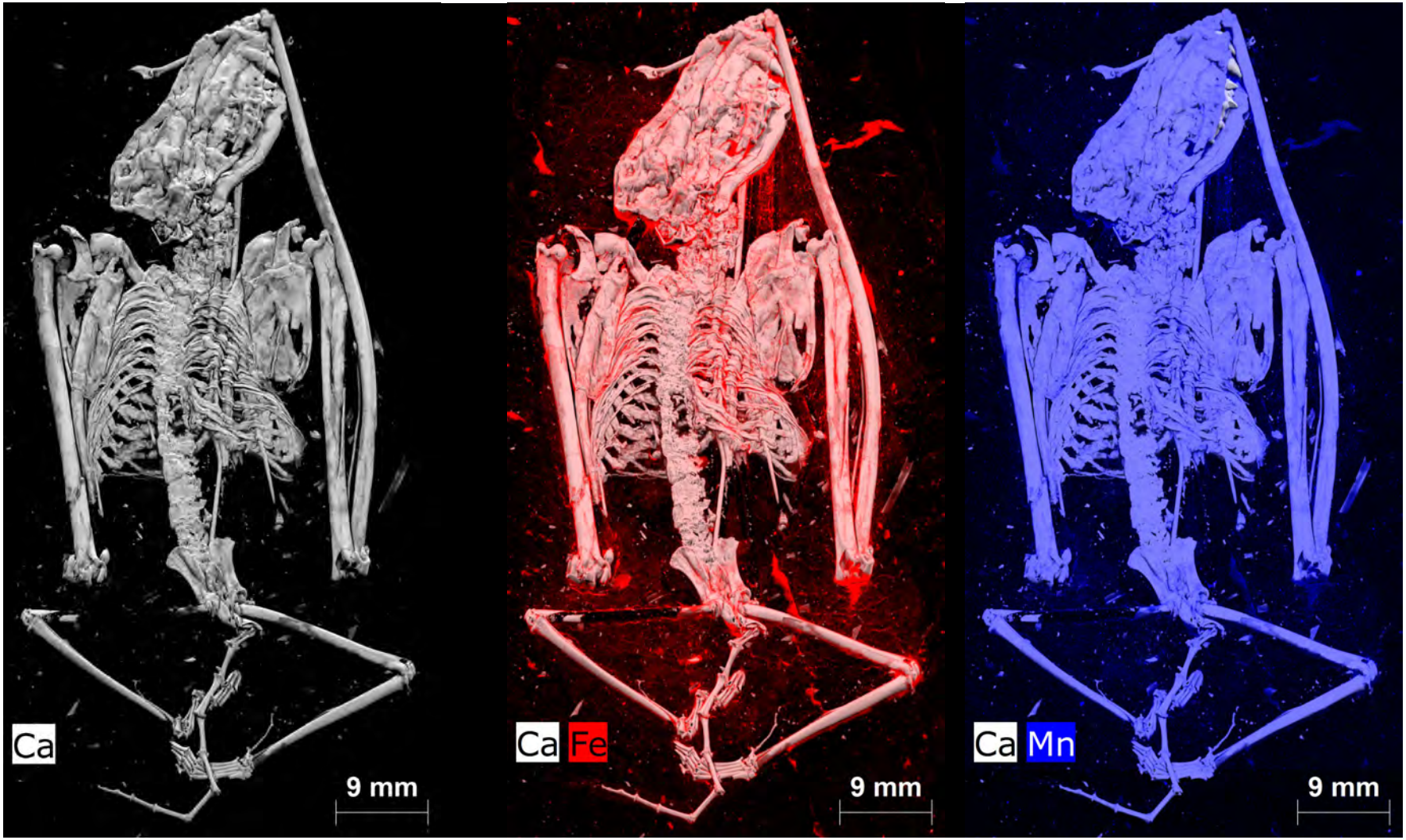
Width: 13 cm, pixel size: 40 µm
3300 pixel x 1200 pixel, 4 Mpixel (~ 8 h)



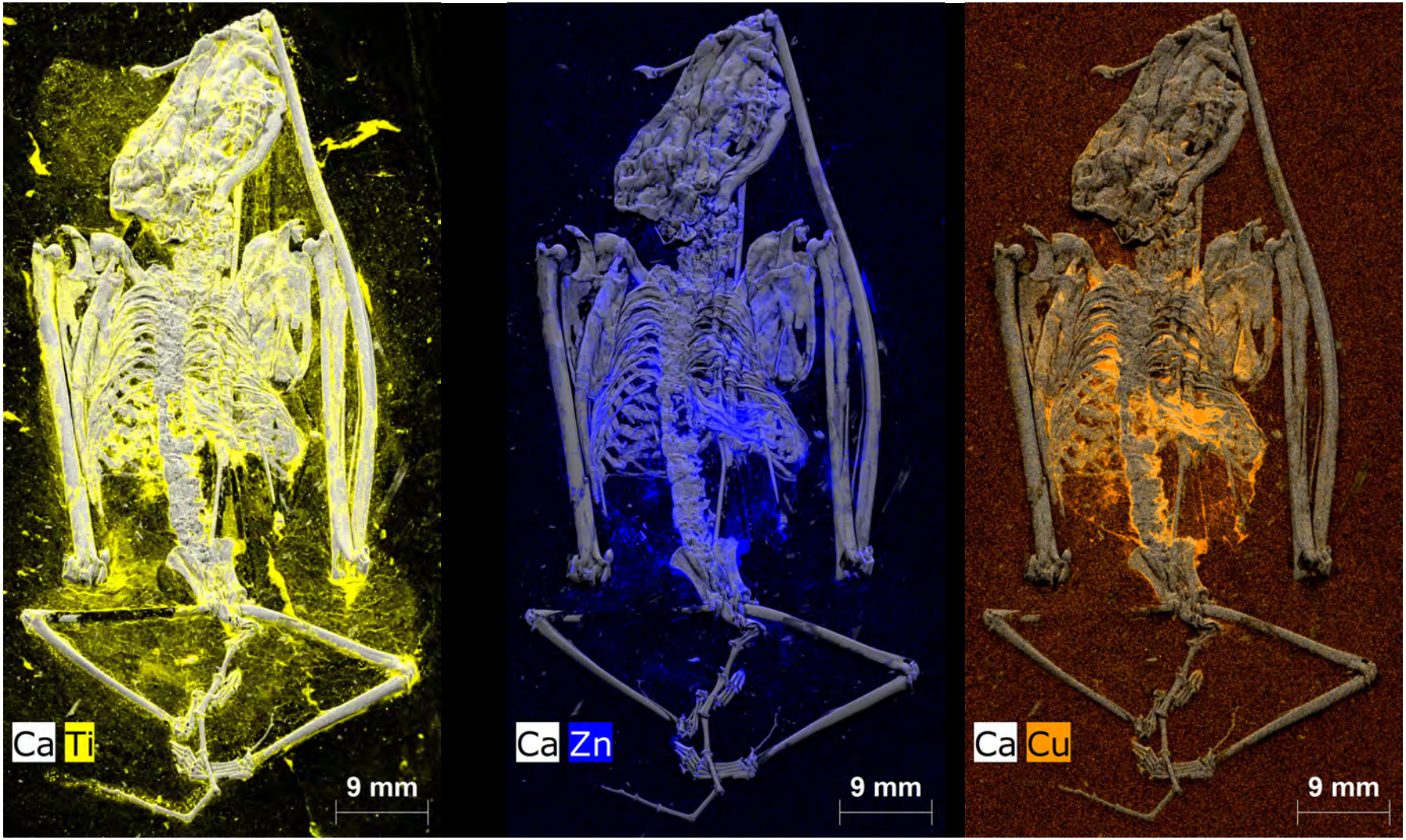
Qualitative analysis
Bat fossil – where are the bones?



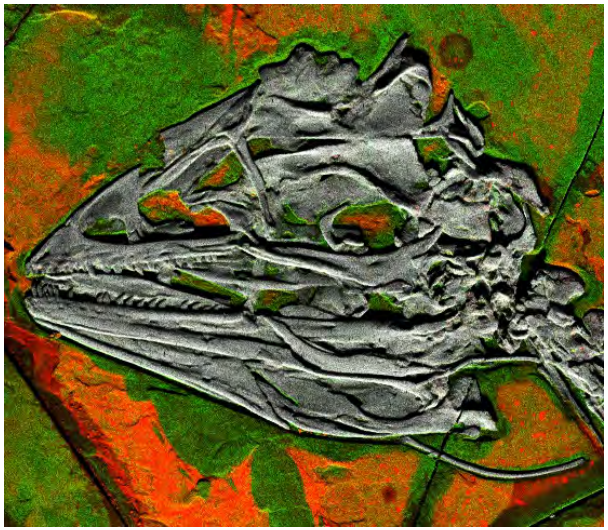
Qualitative analysis
Bat fossil – what else is there?

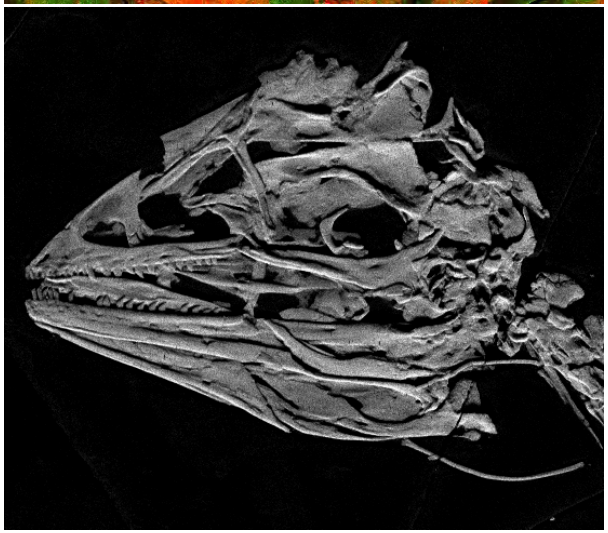


Qualitative analysis
Bat fossil – … and where?



Qualitative analysis
Dinosaur fossil –with M6 Jetstream



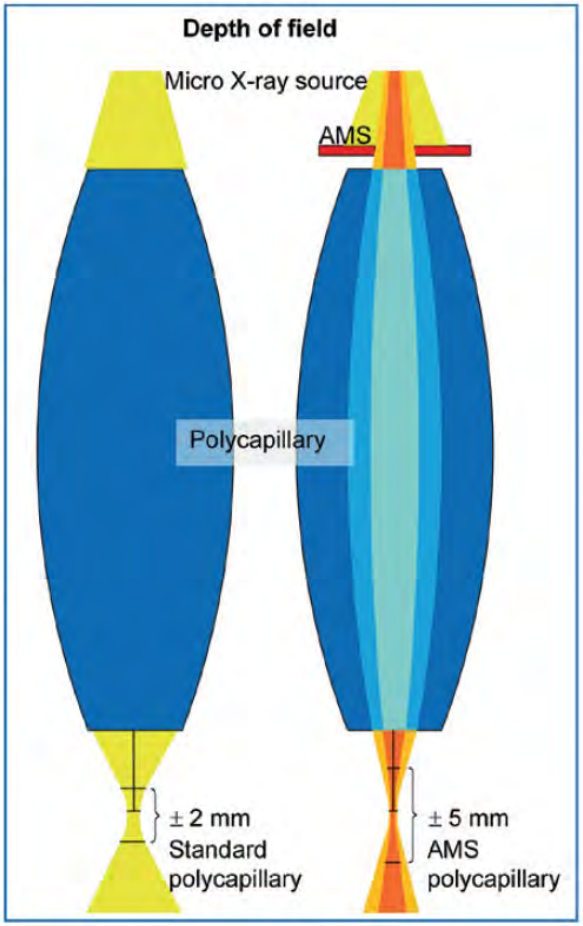


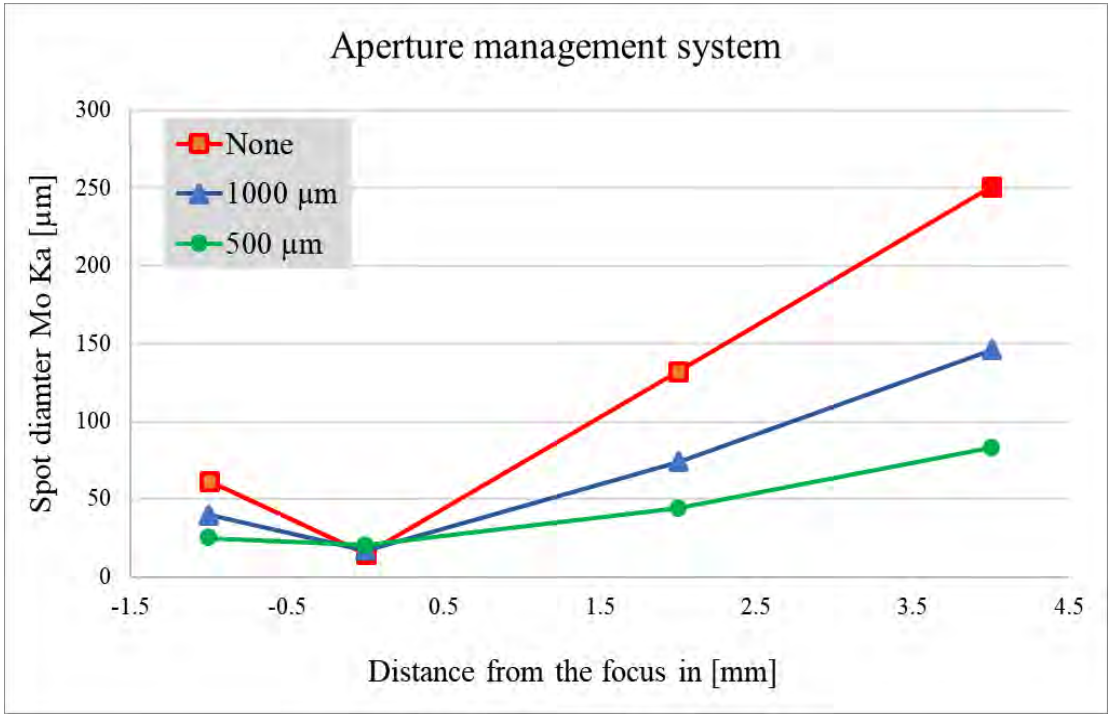
Jianianhualong, Early Cretaceous theropod, China, ~124 Ma old

Qualitative analysis
Dinosaur fossil – element contrasts

Bones in limestone …

Qualitative analysis
Topography and AMS



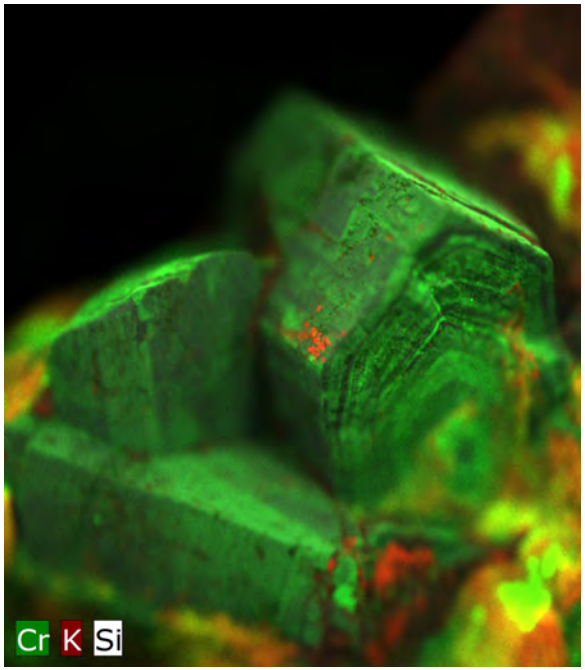


4 mm out of focal plane the spot size is reduced from 250 µm down to 80 µm

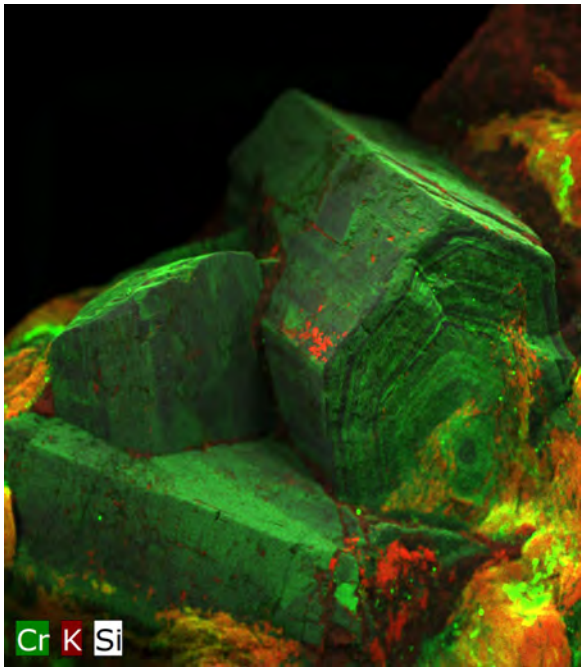
Aperture management – patent pending

Qualitative analysis
Topography and AMS

Emerald crystal, Brazil



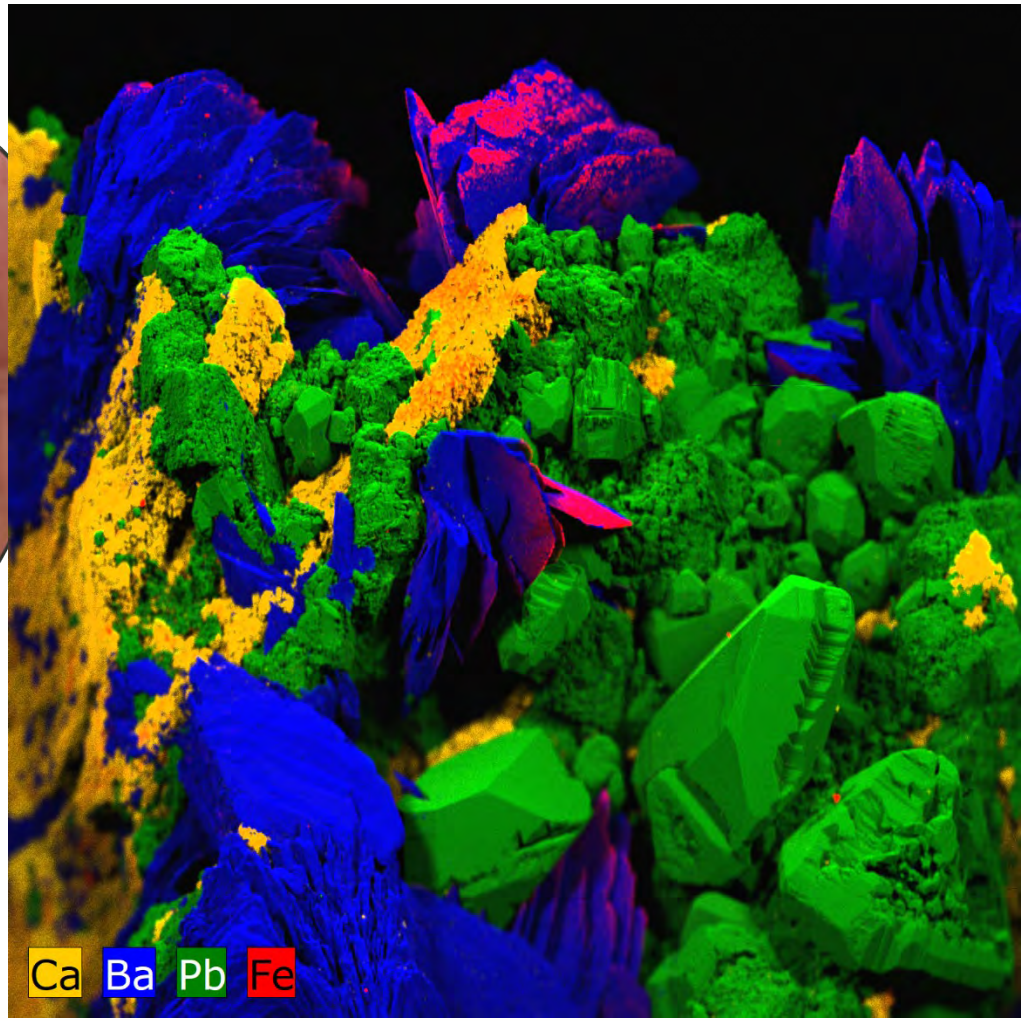
without AMS



with AMS

Qualitative analysis
Topography and AMS

Cerussite with bladed Barite on Galena, Morocco



Semi-quantitative analysis
Scan of the K-Pg boundary*

Chicxulub impact structure

- ~Ø 150 km, ~66 Ma
- Target rock:
  Silicate basement,
  3 km sediments
  (carbonates and anhydrites)

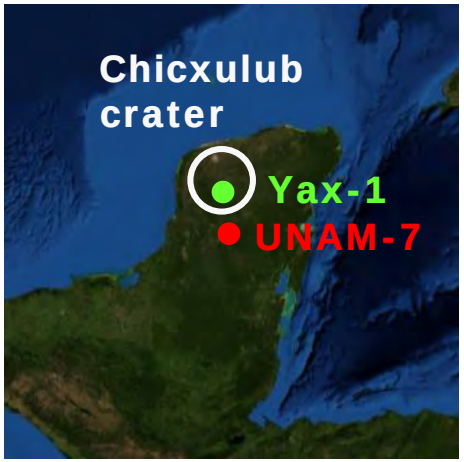


Image of NASA Worldwind

Raton Basin continental K-Pg sites

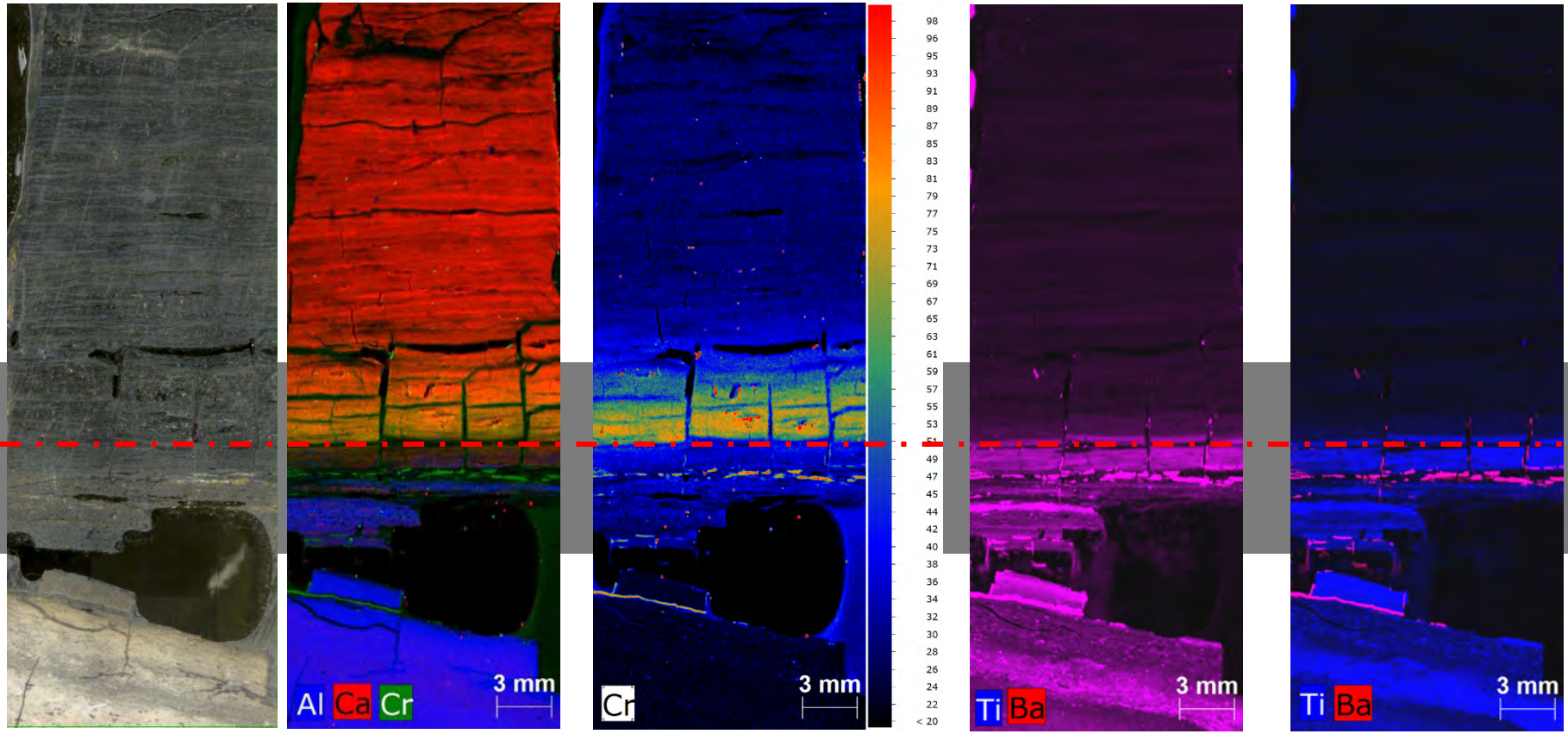
*Cretaceous–Tertiary (K-T) boundary

Semi-quantitative analysis
Scan of the K-Pg boundary*

Overview measurement
no filter

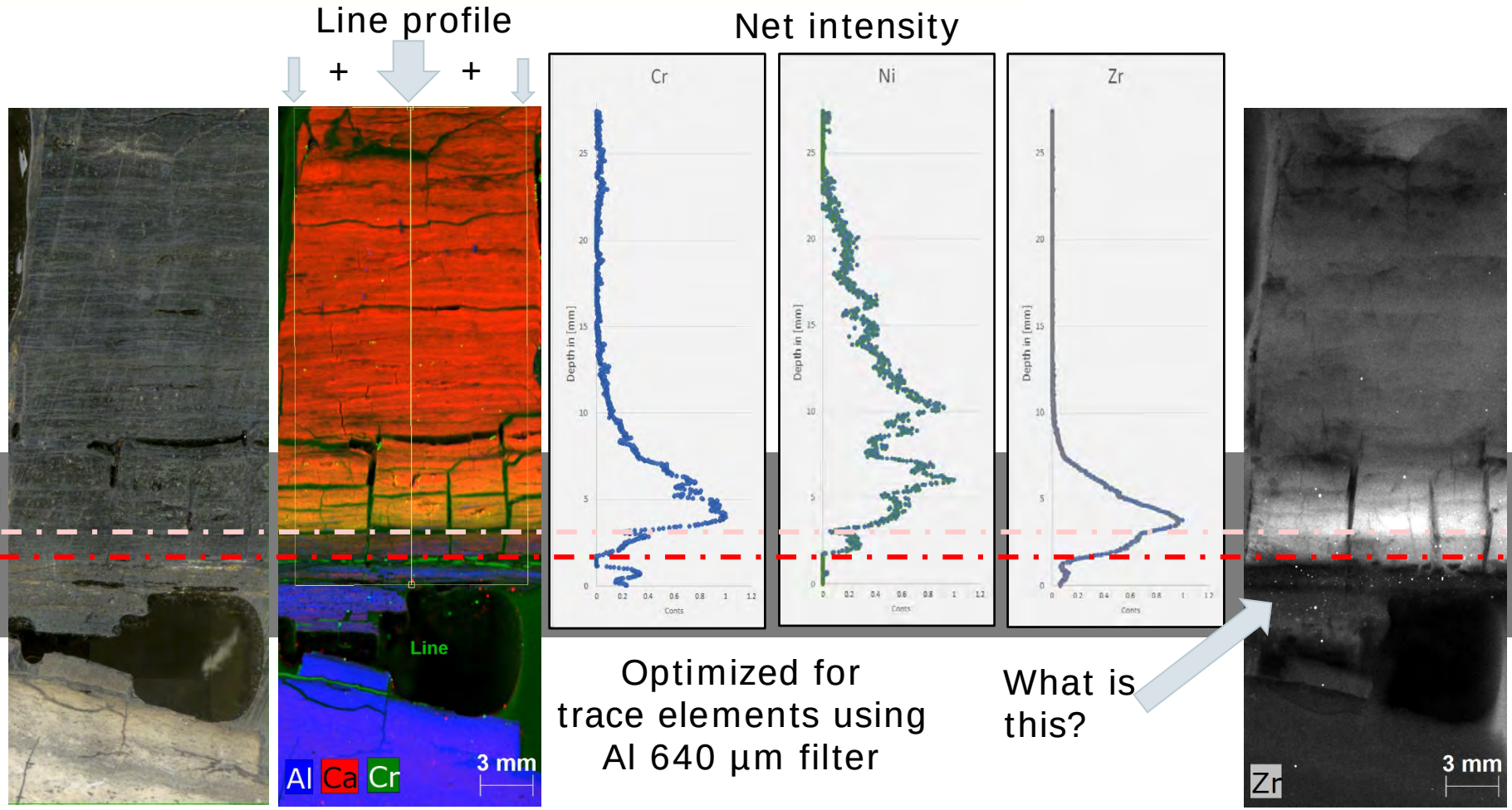
ROI

Deconvolution



*Cretaceous–Tertiary (K-T) boundary

Semi-quantitative analysis
Scan of the K-Pg boundary*

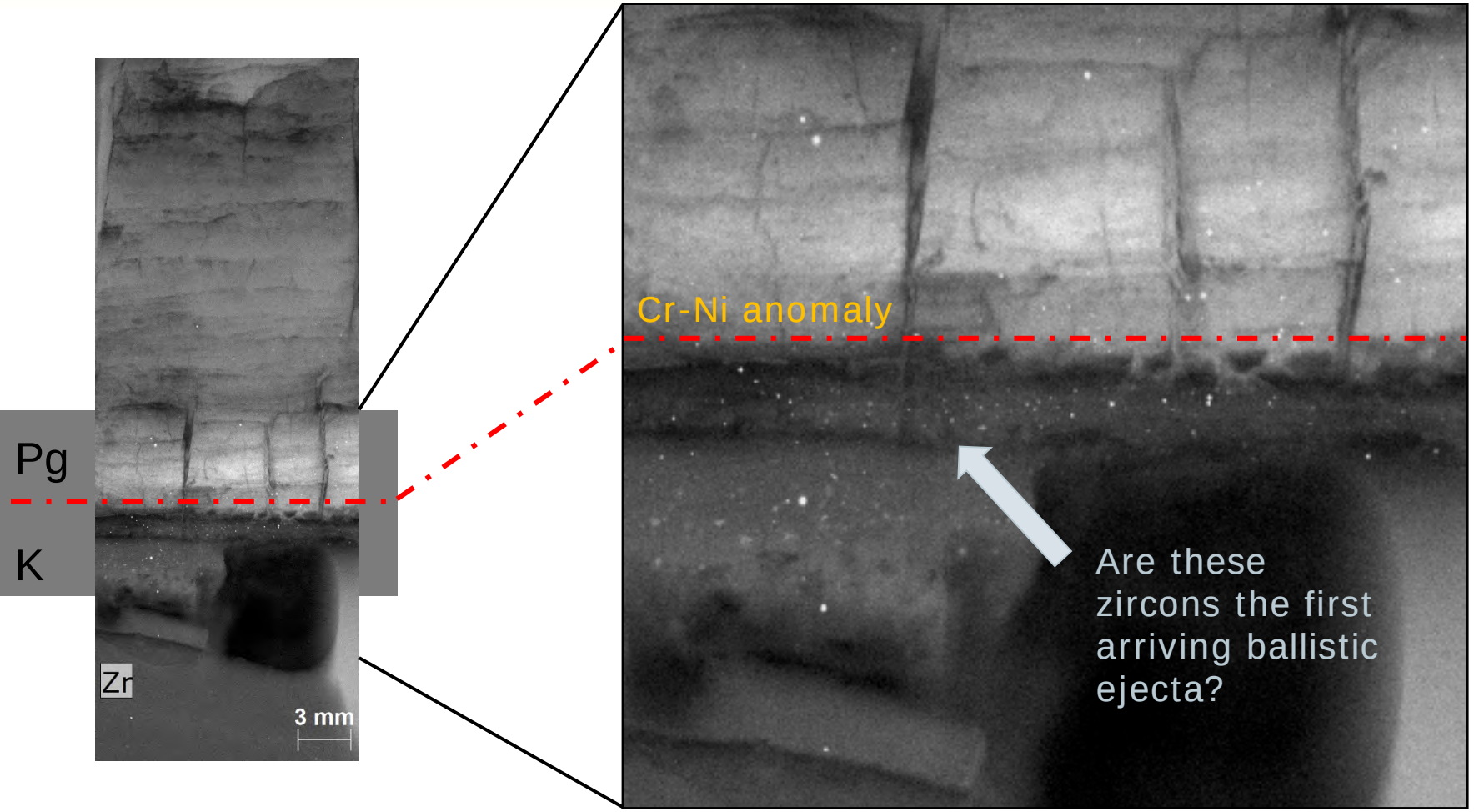


Optimized for trace elements using Al 640 µm filter

What is this?

*Cretaceous–Tertiary (K-T) boundary

Semi-quantitative analysis
Scan of the K-Pg boundary*



*Cretaceous–Tertiary (K-T) boundary

Quantitative analysis
Geology and micro-XRF

Quantitative XRF is for homogeneous samples!

Any sort if inhomogeneity will influence performance and requires additional assumptions and/or more complex interpretations.

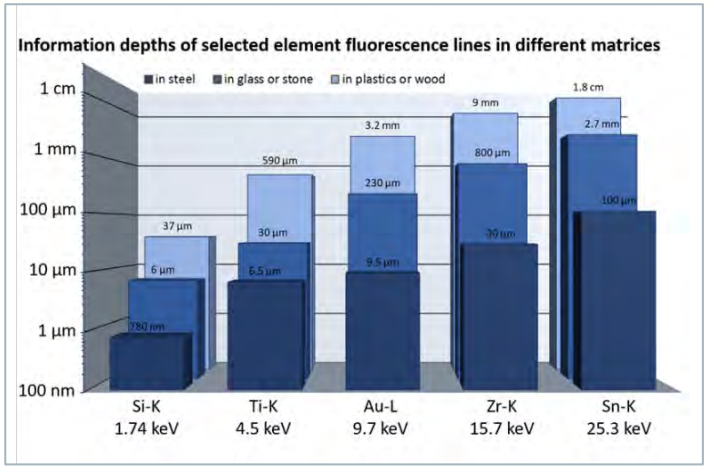
Benefits of (micro-)XRF in geology

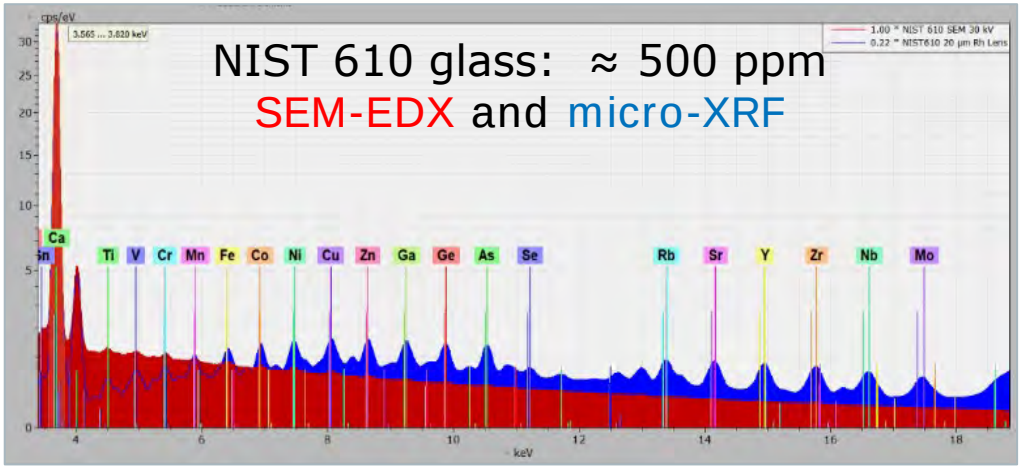
- Size of samples	millimeter to meter range
- Minimal sample preparation	quantifiability goes with preparation effort
- Relatively quick results	pre-screening within minutes
- Trace element sensitivity	medium to low ppm for most elements
- Spatial resolution	20 µm, usually below size of sample features

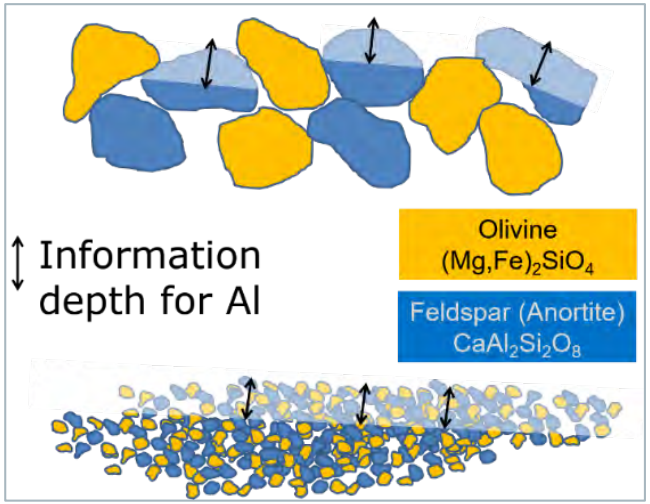
Challenging for (quantitative) analysis

- Information depth	often high and low-Z elements combined
- Grain (size) effects	surface and absorption effects rarely implemented in quantification algorithms

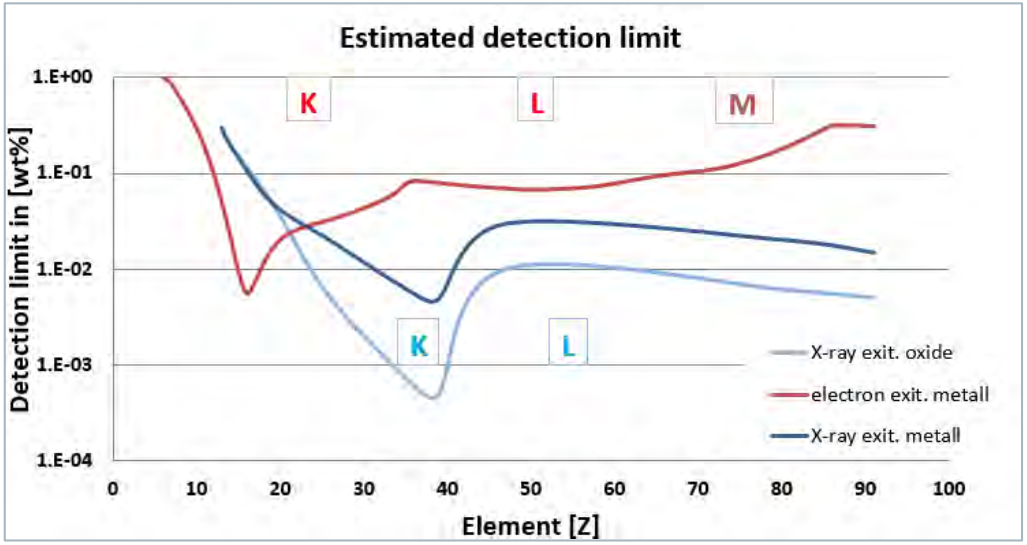
Quantitative analysis
Geology and micro-XRF







Mixture of mafic and felsic minerals

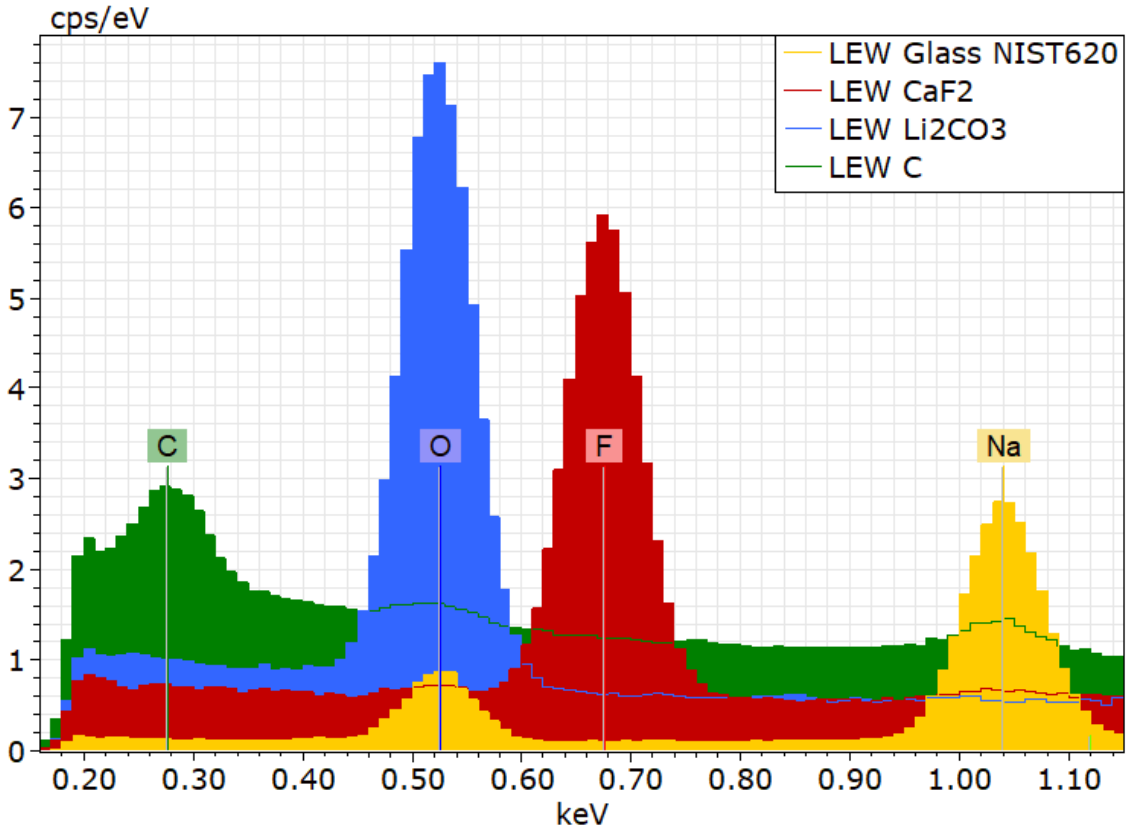


Quantitative analysis
Light element detection

M4 Tornado Plus features a light element window (LEW) SDD which extends the limit of detectable elements down to Carbon.

C: in pure diamond
O: 65 wt.% in Li_2CO_3
F: 49 wt.% in CaF_2

(O in glass: 45 wt.%)



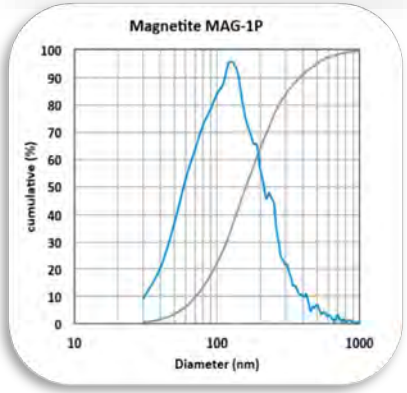
Note: with lower Z matrix the scattering background increases.

Coming soon: Webinar on M4 Tornado^{Plus}

Quantitative analysis
Geo reference materials for micro-XRF

Nano-milled powder pressed to pellets (no binder)

Particle size distribution



Elements Analyzed	Concentration Range
Rb	6- 390 ppm
Sr	3- 246 ppm
Y	17- 75 (184*) ppm
Zr	48- 780 ppm
Nb	9- 110 ppm
Pb	5- 45 ppm
Th	5- 87 ppm
U	2- 18 ppm

Reference samples utilized:

GH
JR-2
AC-E
RGM-1
JA-2
JB-2
BHVO-2
SARM-1
NIST 620

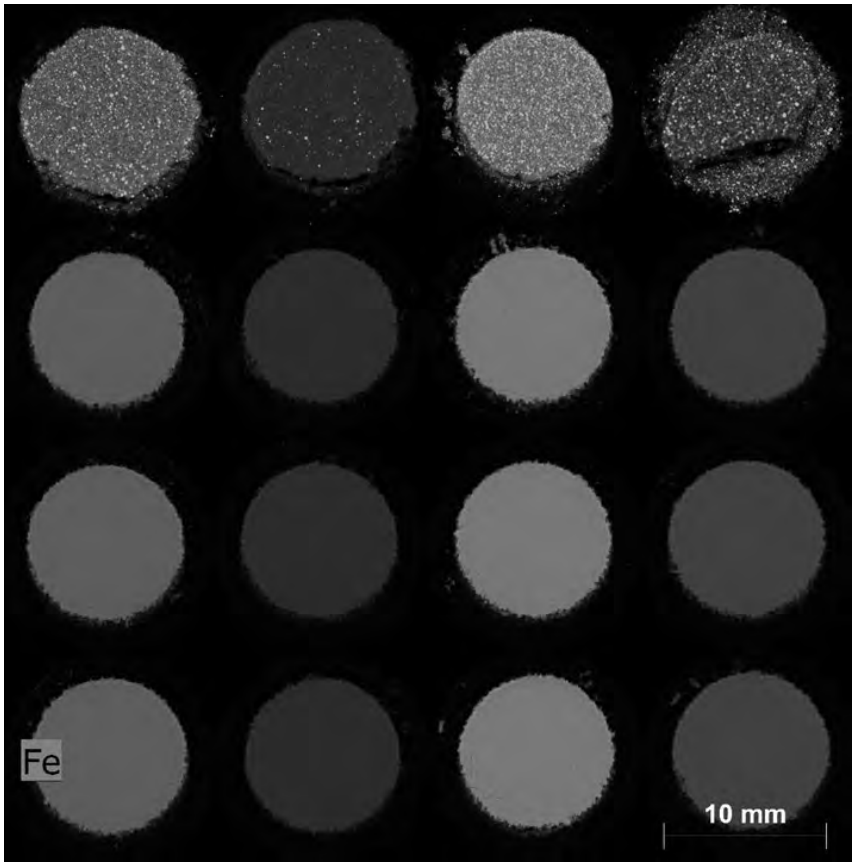
Values from GEOREM data base

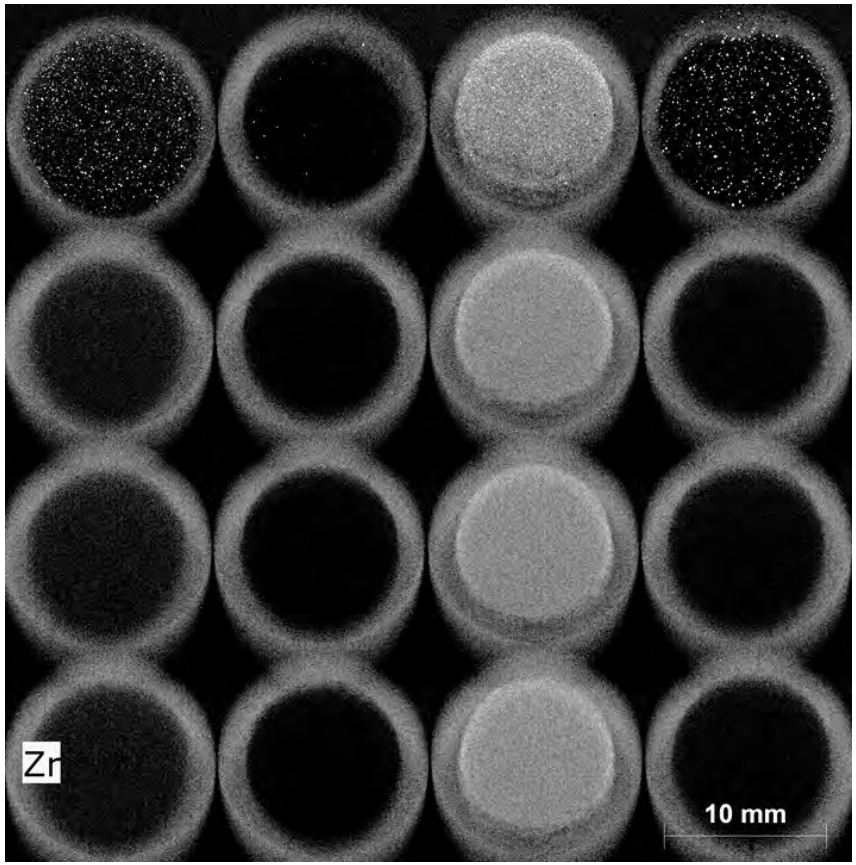
http://georem.mpch-mainz.gwdg.de/sample_query.asp

XRF analysis is very sensitive for the elements analyzed here; they also exhibit negligible inter-elements effects.

More information in the proceedings to EMAS 2019 conference

Quantitative analysis
Geo reference materials for micro-XRF

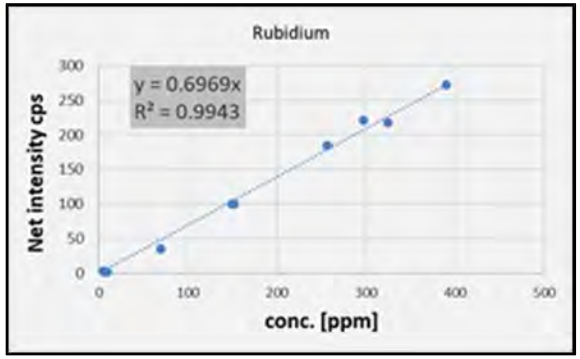


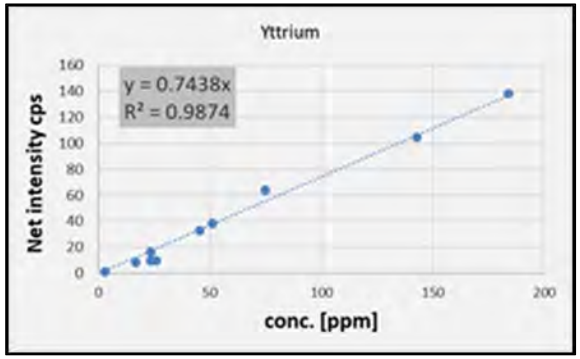


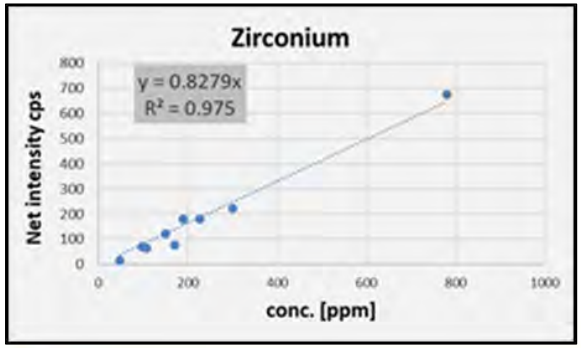
Top row: normal-sized pressed powder. Inhomogeneous on micrometer-scale.

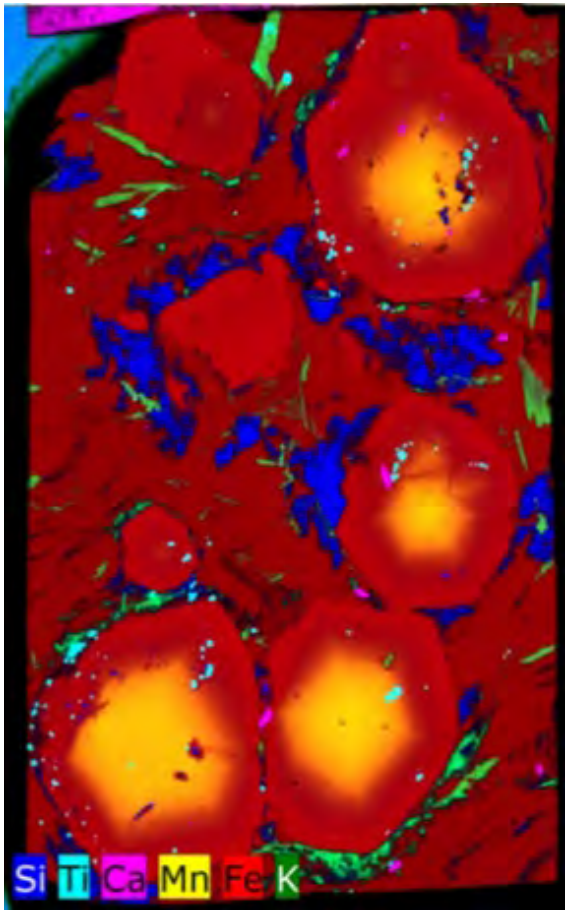
Rows 2-4: nano-milled samples. Homogeneous to micro-XRF

Quantitative analysis
Trace element quantification



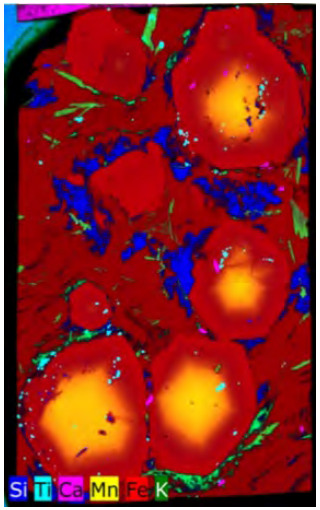




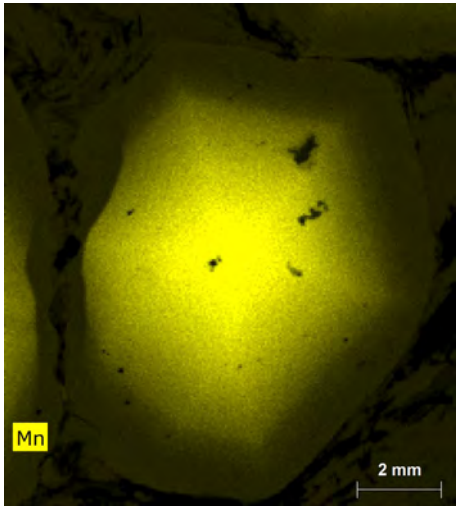


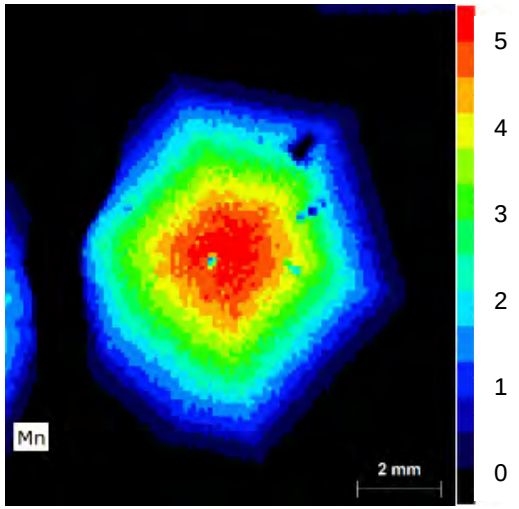
Webinar recording:
https://www.bruker.com/events/webinars/different-approaches-to-bulk-quantification.html

Quantitative analysis
Trace element quantification

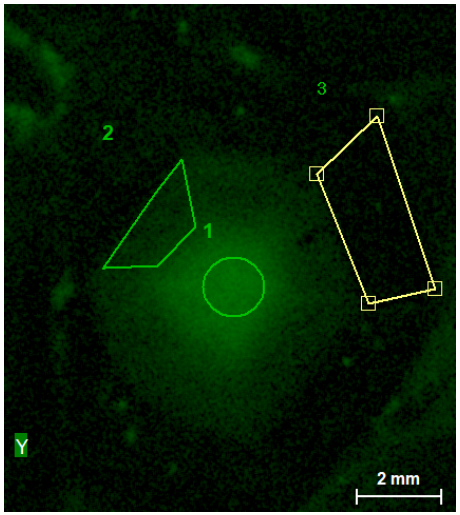


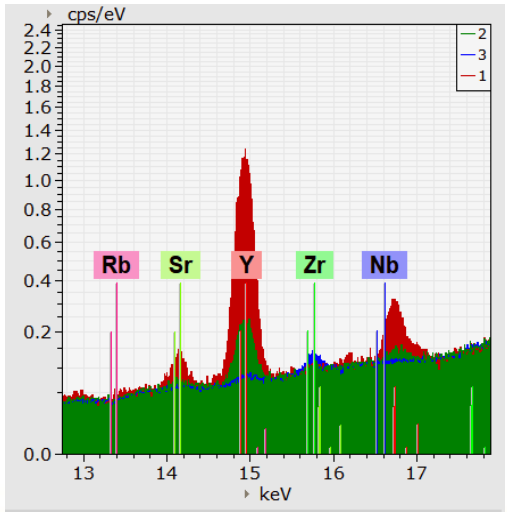
Mn concentration gradient from inside to outside.





The Y concentration found in the garnet changes from 400 ppm in the center to 60 ppm in the region 2 and down to 3 ppm on the rim.

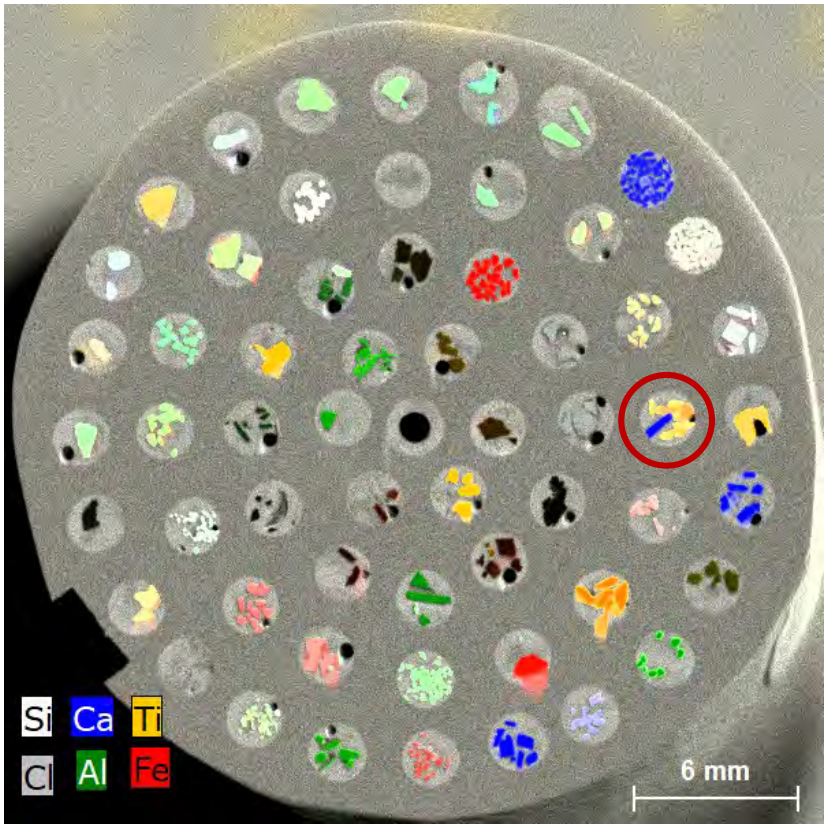




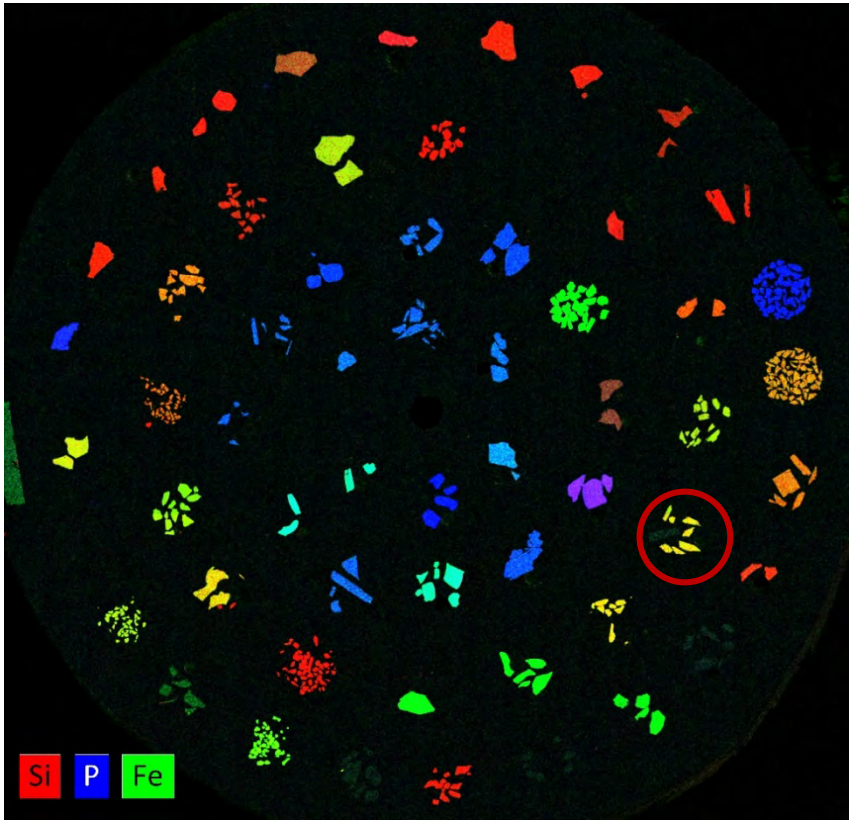
Webinar recording:
https://www.bruker.com/events/webinars/different-approaches-to-bulk-quantification.html

Quantitative analysis
Mayor elements quantification using FP

Micro-XRF Map of the same sample block (slightly rotated)



SEM-EDX Maps of a set of Smithsonian reference materials

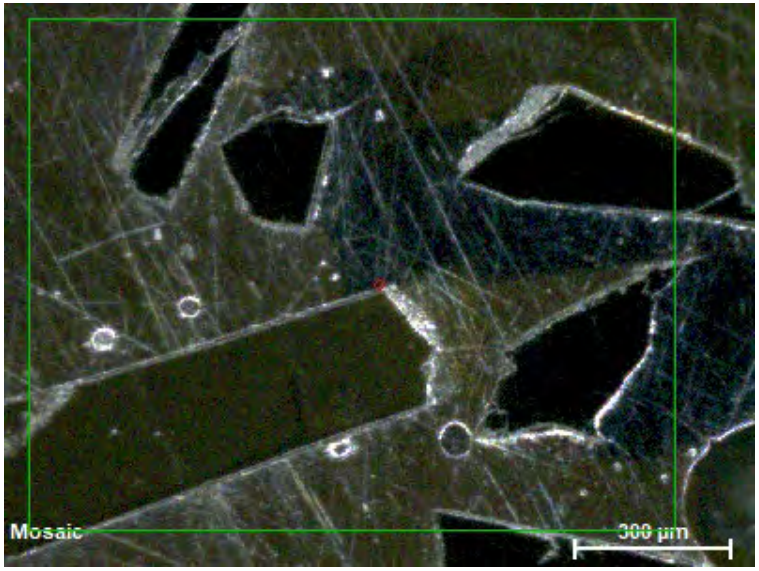


https://www.bruker.com/events/webinars.html?technologies=816&cHash=bb71002f6187ec96f37b2e74ad7698d3

Quantitative analysis
Mayor elements quantification using FP

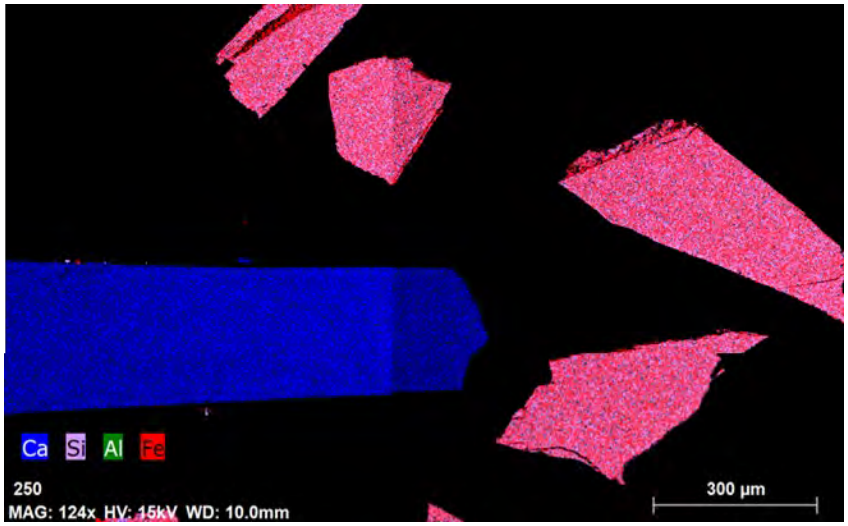
Smithsonian sample
#28 Hornblende

Micro-XRF



Video image

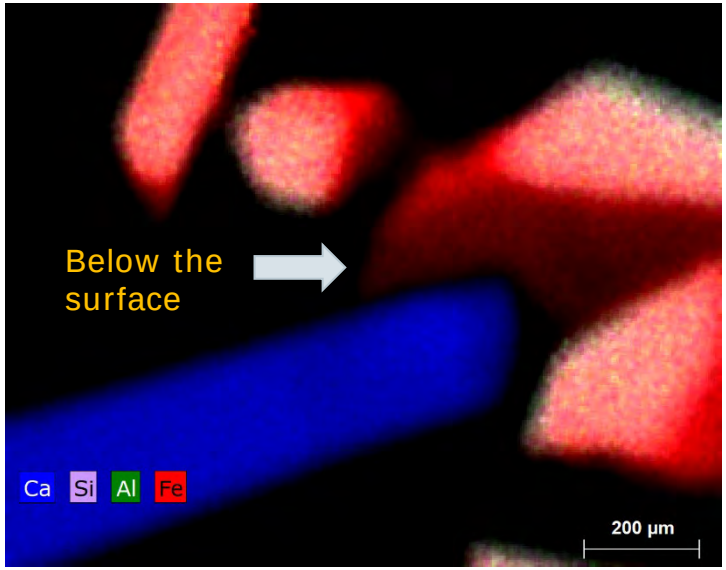
SEM-EDX



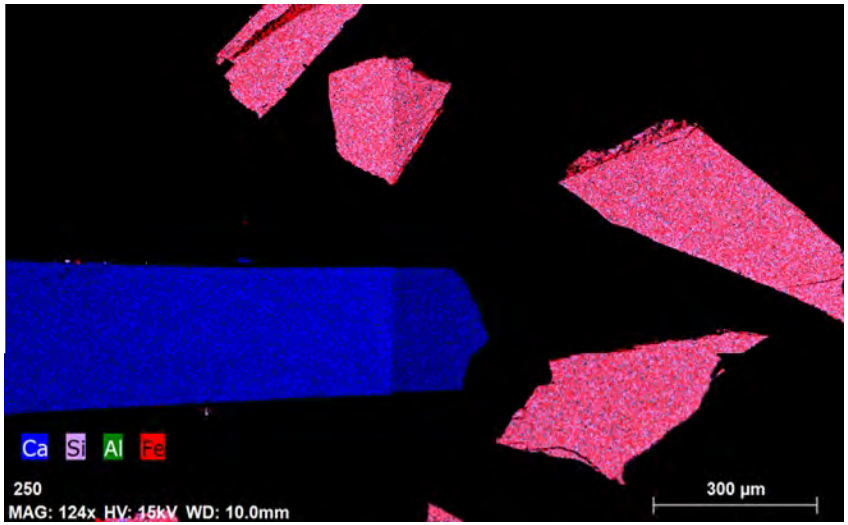
Quantitative analysis
Mayor elements quantification using FP

Smithsonian sample
#28 Hornblende

Micro-XRF



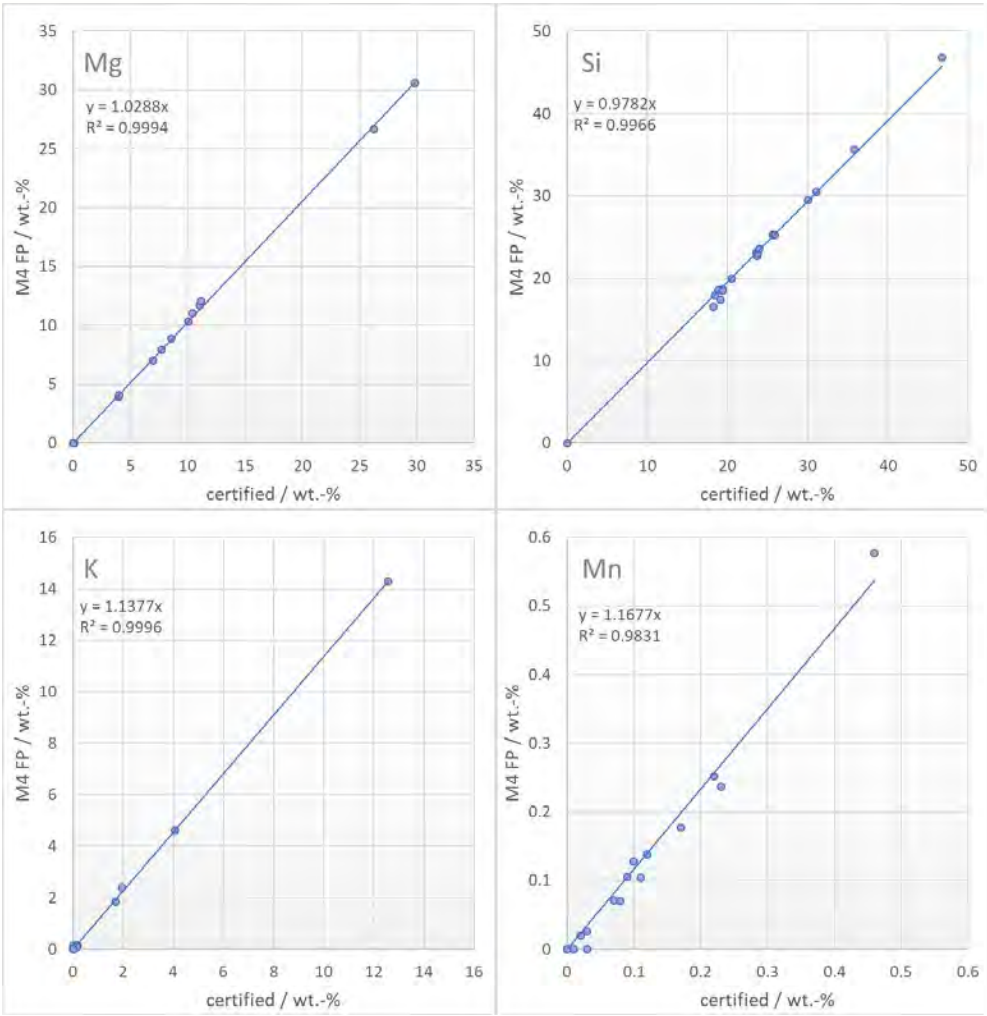
SEM-EDX



Even lower resolution due to scattering of the X-ray in the epoxy where the samples are embedded.

Quantitative analysis
Mayor elements using FP

Pos	Mineral	Pos	Mineral
1	Anorthite	31	Magnetite
2	Anorthoclase	32	Microcline
3	Apatite (Fluroapatite)	33	Olivine
4	Augite	34	Olivine
5	Chromium Augite	35	Omphacite
6	Benitoite	36	Osumilite
7	Calcite	37	Plagioclase (Labradorite)
8	Chromite	38	Pyrope
9	Corundum	39	Quartz
10	Diopside	40	Scapolite (Meionite)
11	Dolomite	41	Siderite
12	Fayalite	42	Strontianite
13	Gahnite	43	Zircon
14	Garnet	44	$CePO_4$
15	Garnet	45	$DyPO_4$
16	Glass	46	$ErPO_4$
17	YPO_4	47	$EuPO_4$
18	Glass	48	$GaPO_4$
19	Glass	49	$HoPO_4$
20	Glass	50	$LaPO_4$
21	Glass	51	$LuPO_4$
22	Glass	52	$NdPO_4$
23	Glass	53	$PrPO_4$
24	Glass	54	$SmPO_4$
25	Glass	55	$ScPO_4$
26	Glass	56	$TbPO_4$
27	Hornblende	57	$TmPO_4$
28	Hornblende	58	$YbPO_4$
29	Hypersthene	59	Faraday Cup
30	Ilmenite		



Quantitative analysis
live part

Summary

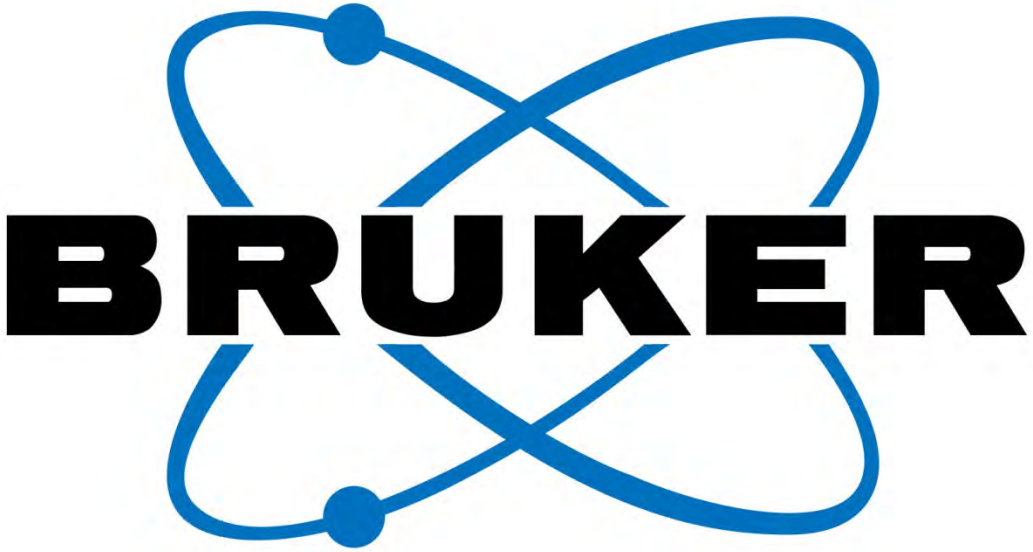
- The specific characteristics of micro-XRF make the method extremely applicable in the field geological science
  - Sample size
  - Element range
  - Minimal sample preparation
- Qualitative analysis
  - Identification of regions with relative enrichment or depletion
  - Mineral identification element distribution
- Quantitative analysis
  - Major and trace elements
  - Standard-free and standards-supported

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.



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