Understanding the economic importance and scientific significance of oceanic Fe-Mn crusts

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Geometallurgy Conference 2025

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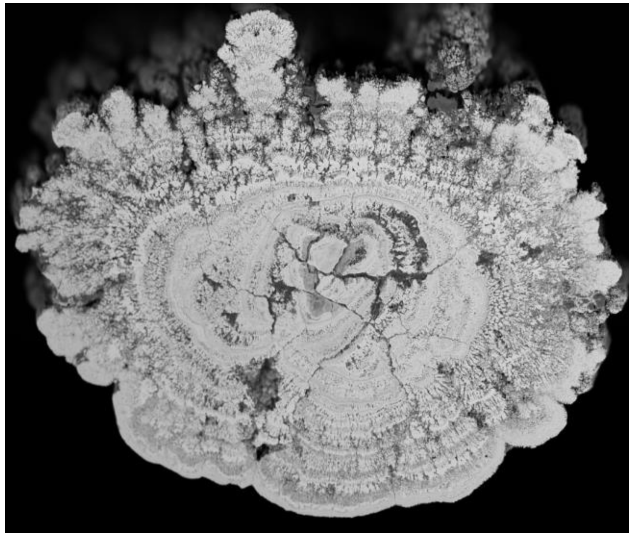
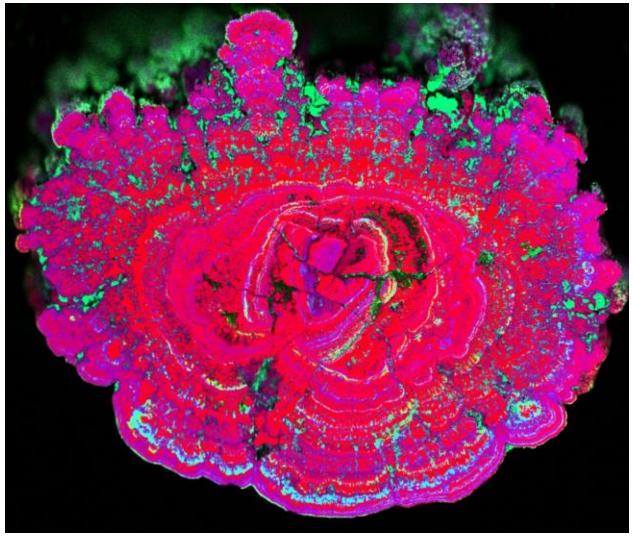
Ferromanganese (Fe-Mn) Crusts:
Supporting exploration with rapid mineralogy mapping

Fe-Mn crusts, or ferromanganese crusts, are marine sedimentary mineral deposits primarily composed of iron and manganese oxides.

These crusts are of both scientific and economic interest due to their unique chemical composition, which includes valuable metals like cobalt, nickel, copper, titanium, platinum, tellurium and rare earth elements.

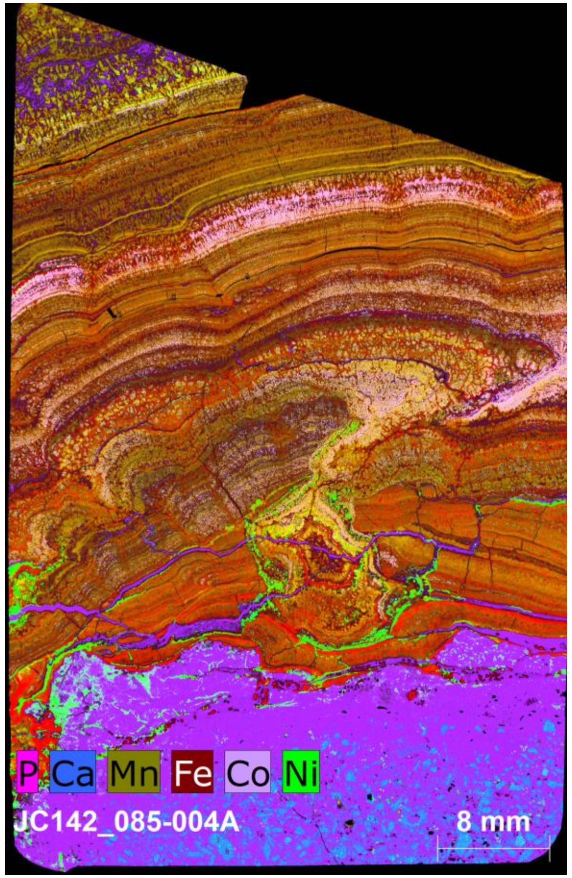
They form as thin layers on rock surfaces in the deep ocean ranging from 500 to 7,000 meters, particularly on seamounts, ridges, and plateaus, over millions of years through the direct precipitation of oxides from seawater and possible subsequent phosphatisation episodes.

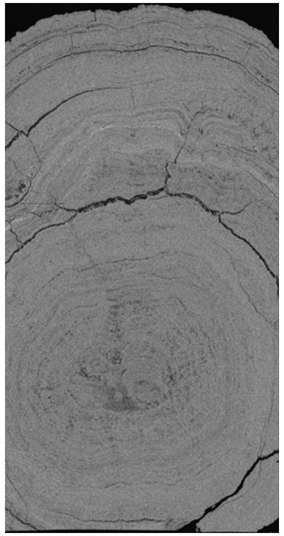


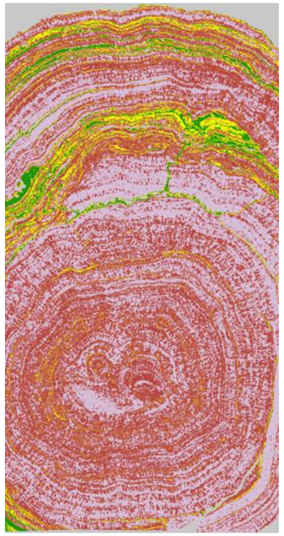


Ferromanganese (Fe-Mn) Crusts:
Supporting exploration with rapid mineralogy mapping

Firstly, Fe-Mn crusts are valuable for scientific research, as they act as an historical record of past ocean conditions. Their slow growth rate and ability to accumulate elements over long periods make them ideal for studying changes in the marine environment and the Earth's climate.



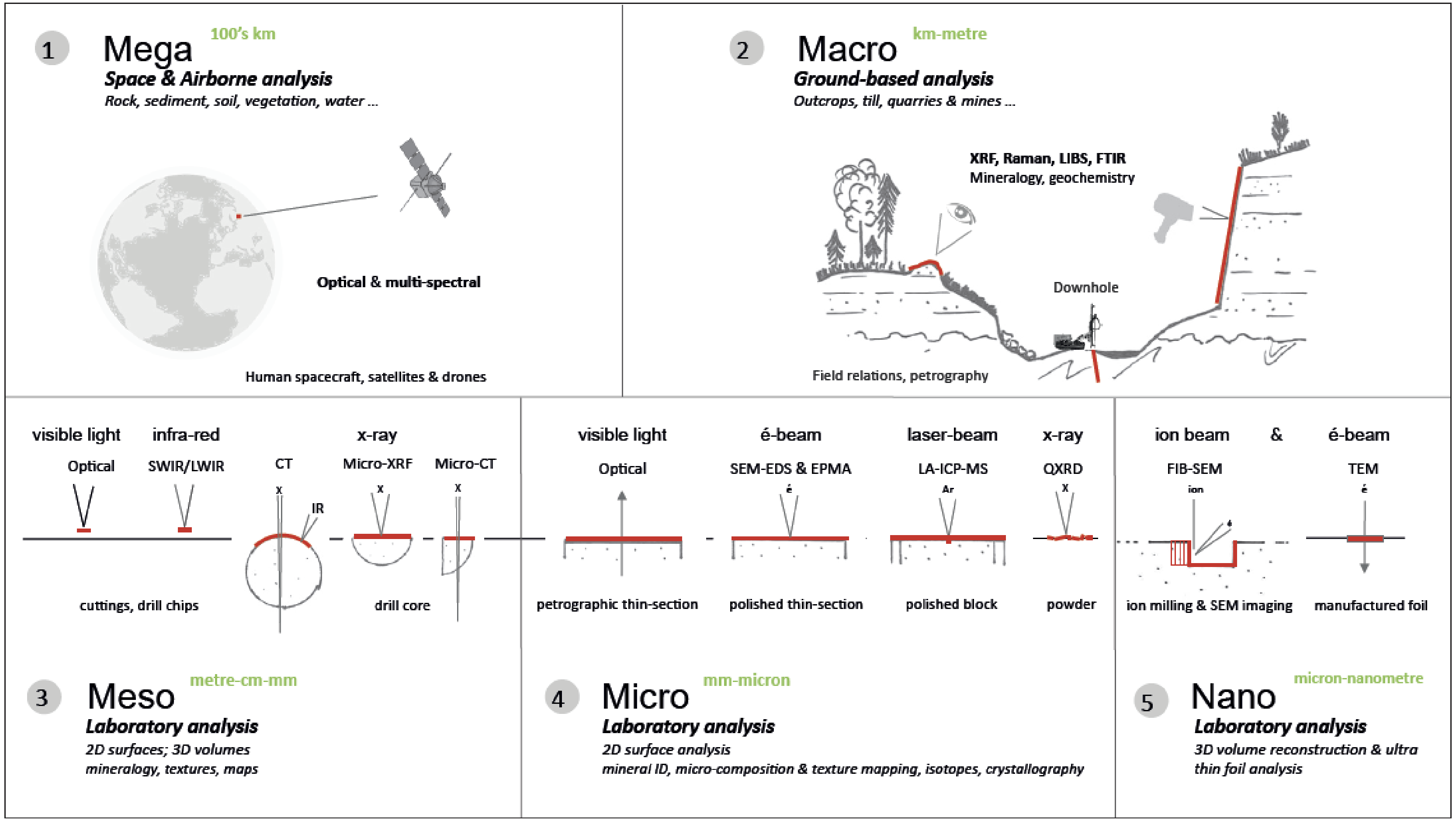


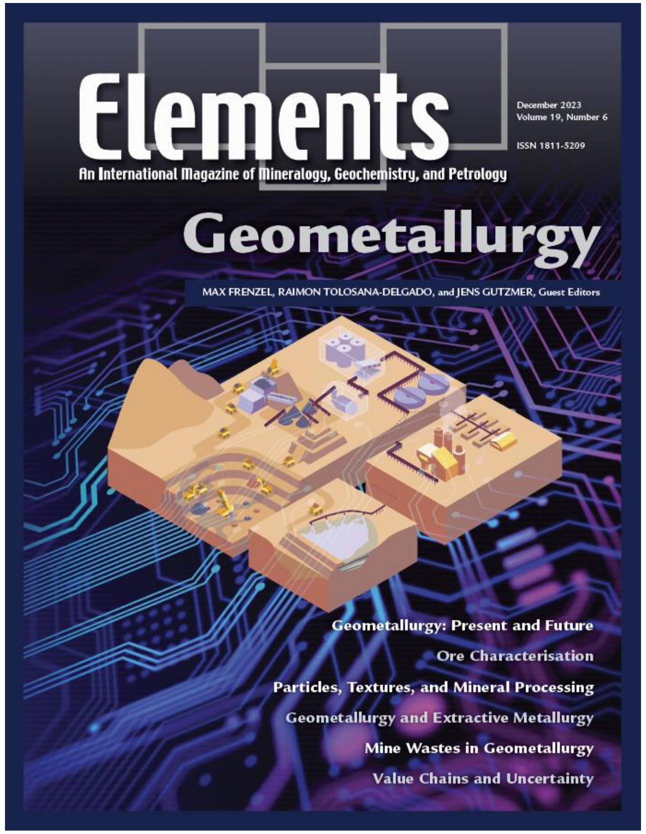


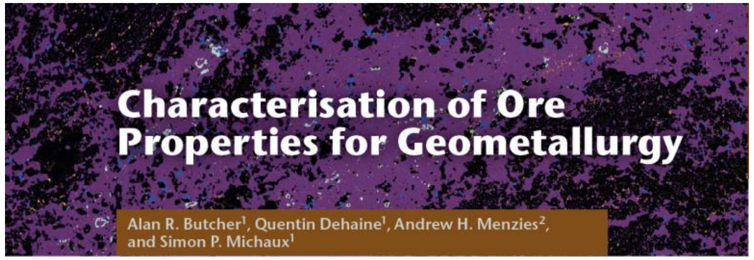
Secondly, Fe-Mn crusts are of growing interest as a potential source of valuable metals, particularly nickel and cobalt, which are essential for emerging technologies. The high concentrations of various metals in Fe-Mn crusts, compared to land-based deposits, make them attractive for potential future mining operations.

It should be noted that such potential, as described here, does not discuss the political nor environmental considerations, as this is a separate topic, albeit important and relevant.

Overview:
Characterization Workflow of a multiscale approach



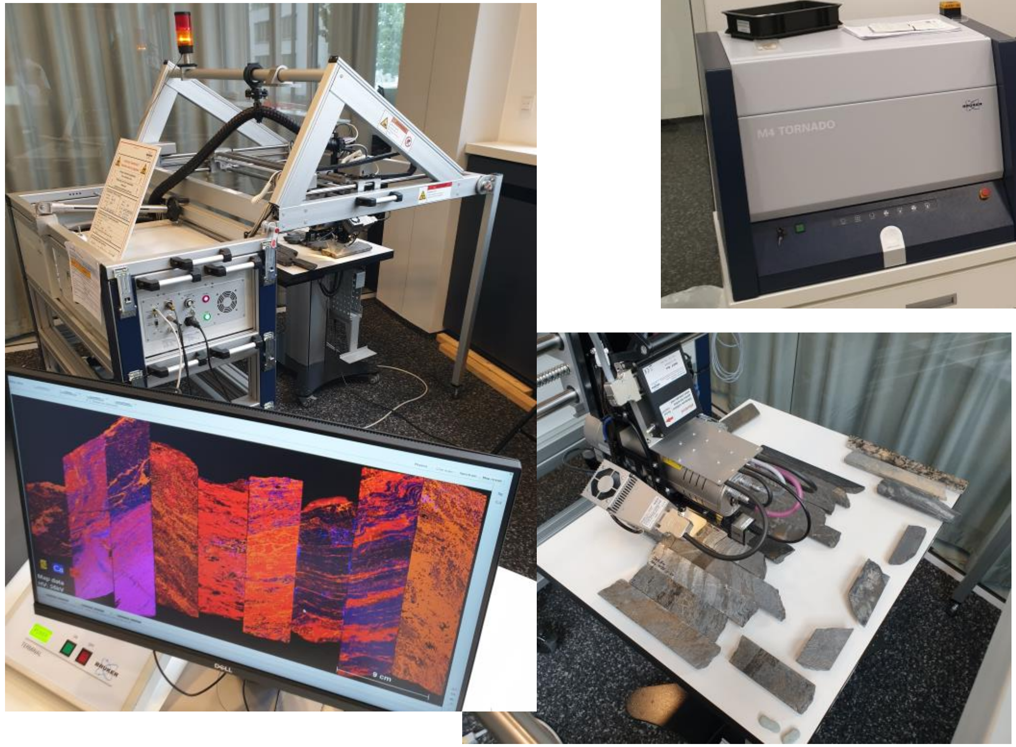


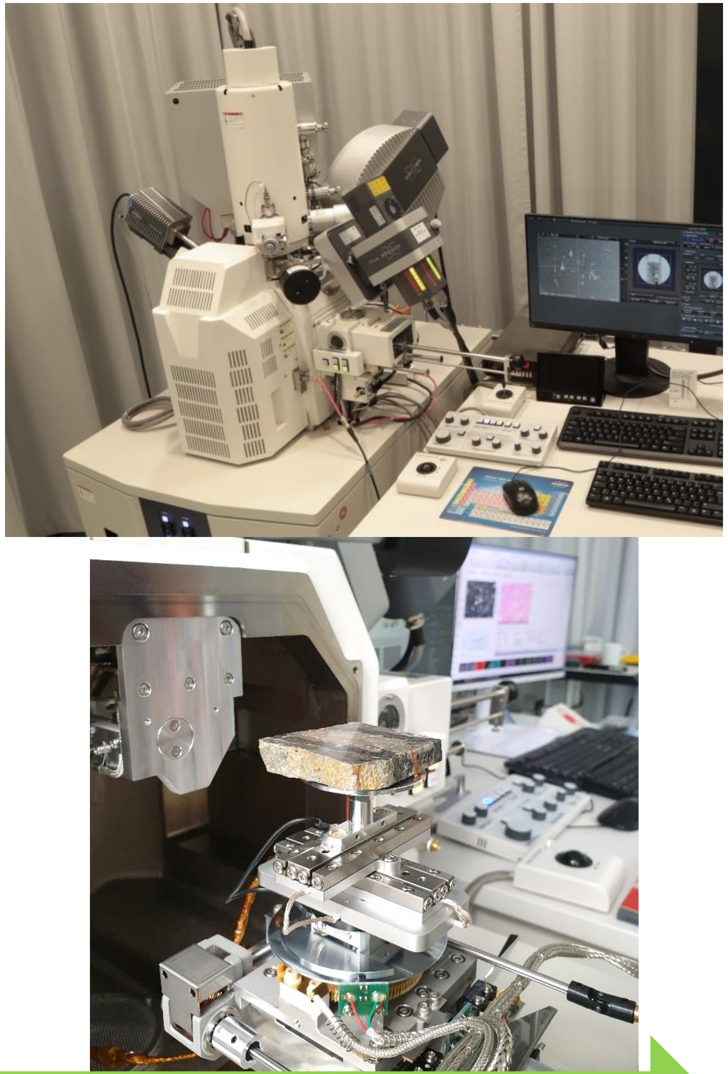


1811-5209/23/0019-0352$2.50 DOI: 10.2138/gselements.19.6.352

Alan R Butcher, Quentin Dehaine, Andrew H Menzies, and Simon P Michaux(2023) Characterisation of Ore Properties for Geometallurgy. *Elements* v19 num6

Measurements Across Scales





Automated Mineralogy: AMICS

Open Source MicroXRF

(M6 JETSTREAM)

Benchtop MicroXRF

(M4 TORNADO)

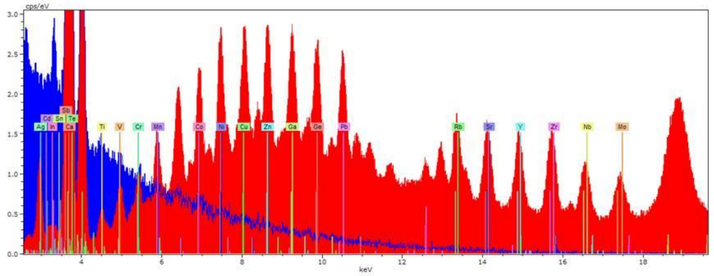
SEM-EDS

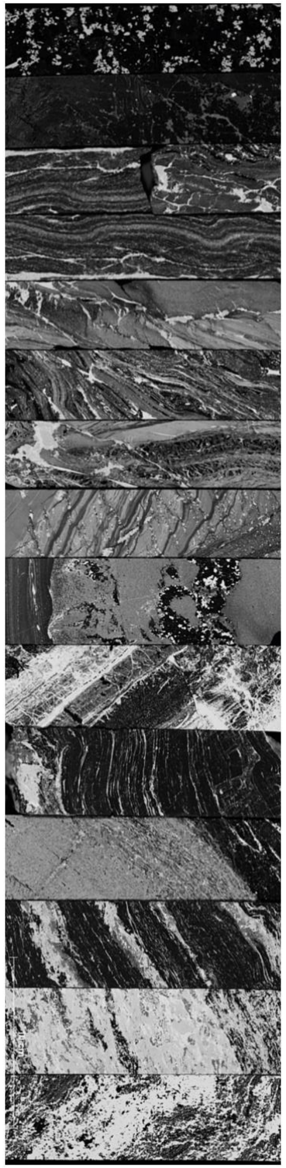
Hitachi SU5000

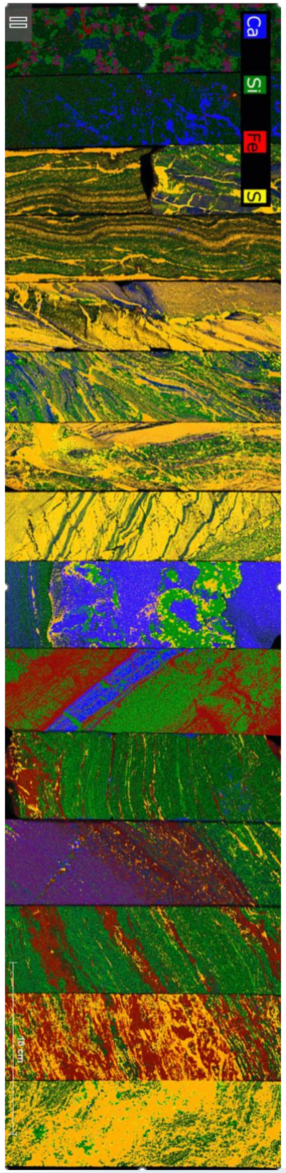
Micro-XRF Analysis: Introduction

Micro-XRF is used across a wide variety of applications, including geological sciences. Its advantages are due to the minimal sample preparation required, the ability to analyse large samples at a micro scale, as well as quick and non-destructive data acquisition, including down to the trace element level.

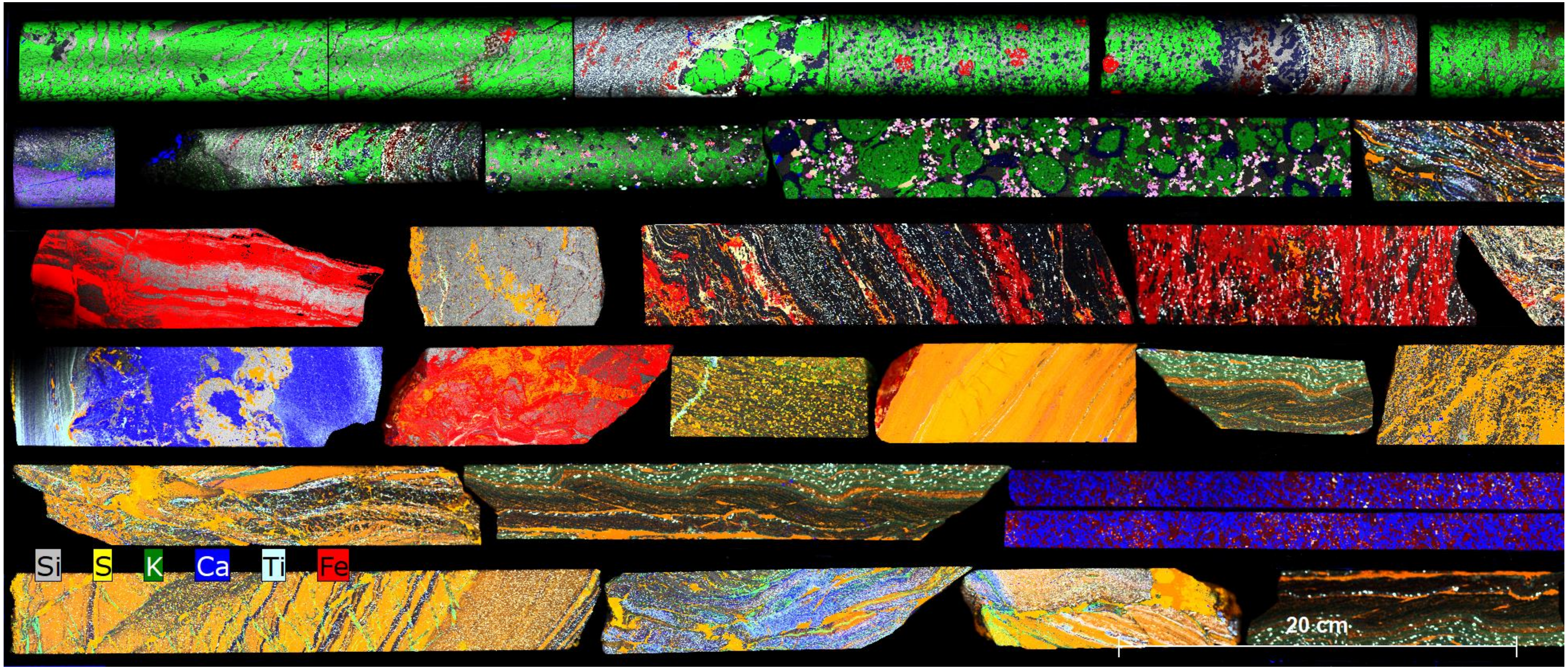
- Little to no sample preparation
- Non-destructive
- Elemental information (Major and Trace elements)
- Small spot analysis
- Information from within the sample
- Meso-scale samples : Micro-scale information
- Quantification (down to ppm levels)
- Mineralogy / Automated Mineralogy





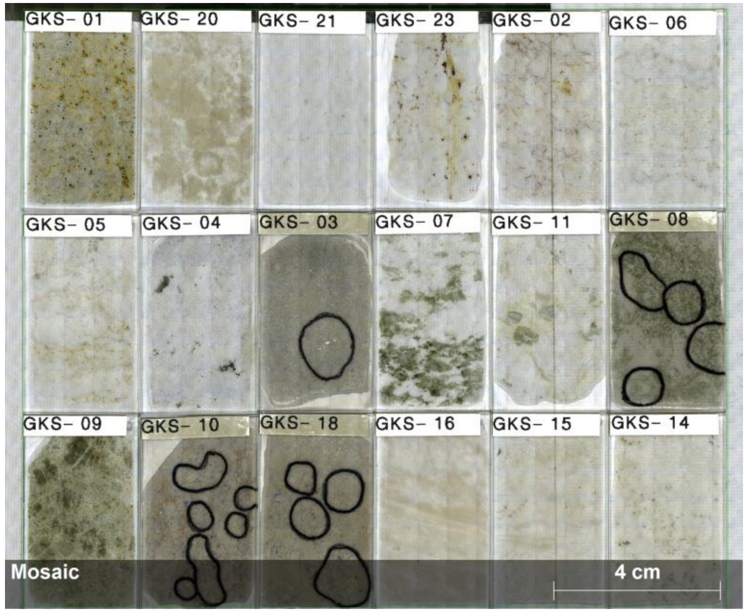


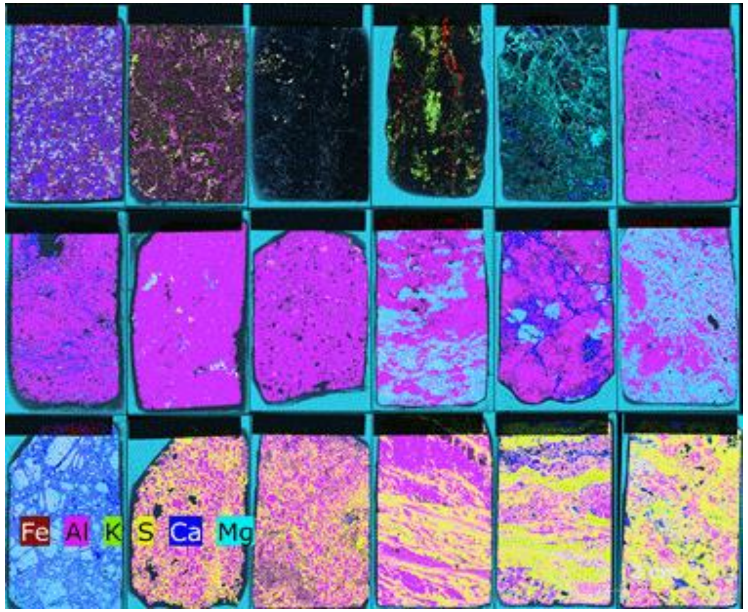
Examples:
Micro-XRF M6 JETSTREAM: Drill Core



Half Core vs Cylindrical Core

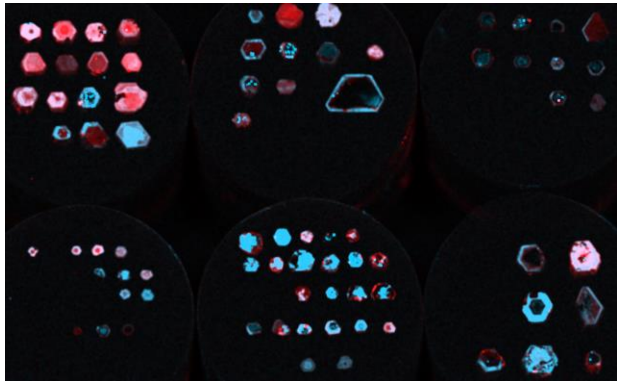
Overview:
Analytical Challenge – Multiple Samples of Different Sizes

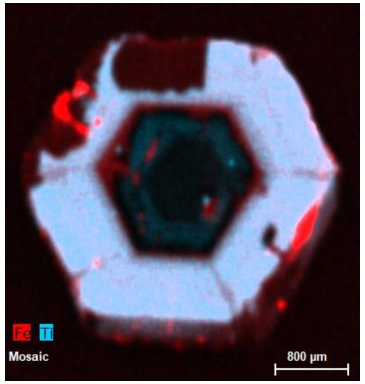


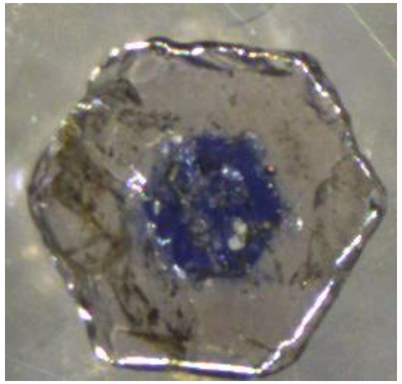


Micro-XRF (M4 Tornado) can analyse samples of different sizes:

Left: Field Rock Samples to
Top Right: Thin Sections to
Bottom Right: Individual Crystals







MicroXRF Applications Examples

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Mineralium Deposita
https://doi.org/10.1007/s00126-024-01315-x

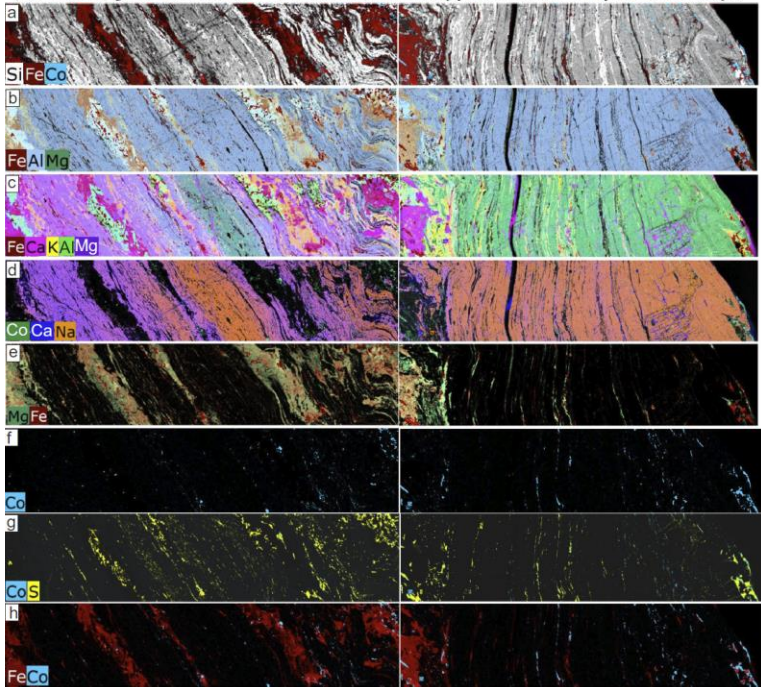
ARTICLE

Structural controls on cobalt mineralisation during regional metamorphism: an example from the Rajapalot area, Finland

Mohammad Sayab[1] · A. Menzies[2] · R. M. Palin[3] · A. R. Butcher[1,4] · N. Cook[5,6] · J. Kuva[1] · Q. Dehaine[1]

Received: 27 May 2024 / Accepted: 4 September 2024

Abstract
The Rajapalot area of Finnish Lapland hosts an unusually high-grade association of cobalt-only and gold–cobalt deposits (10.91 Mt @ 2.5 g/t Au + 0.44% Co total inferred resources) within multiply folded metasedimentary rocks of the Paleopro-



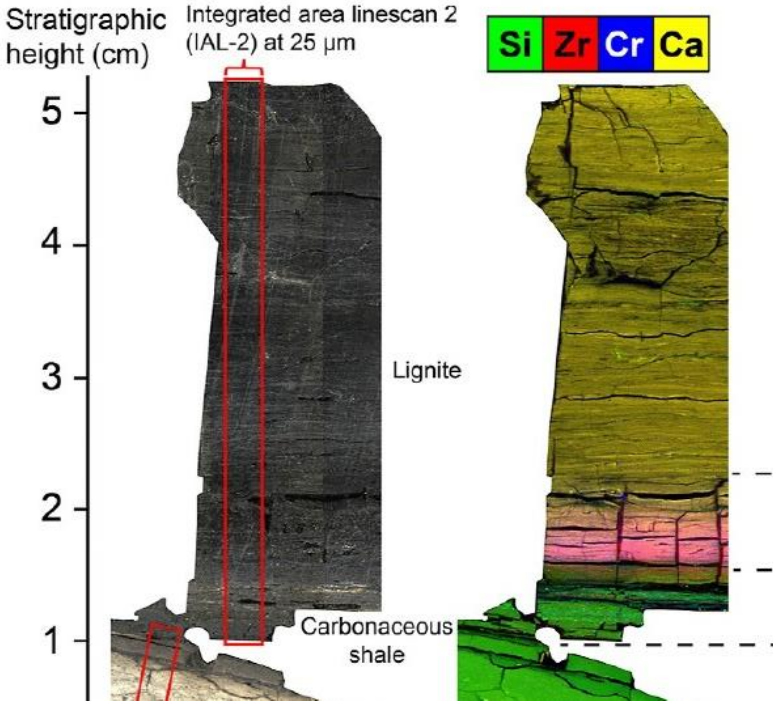
Geochemistry, Geophysics, Geosystems
AGU ADVANCING EARTH AND SPACE SCIENCES
RESEARCH ARTICLE
10.1029/2024GC012151

Key Points:
- Micro-X-ray fluorescence offers a well-suited high-resolution mapping tool for event deposits such as the Cretaceous-Paleogene boundary
- Geochemical profiles from the Raton Basin (USA) shed new light on ejecta dynamics in the first minutes to years

Disentangling Impact Ejecta Dynamics Using Micro–X-Ray Fluorescence (μ-XRF): A Case Study From the Terrestrial Cretaceous-Paleogene (K-Pg) Boundary

Pim Kaskes[1,2], Roald Tagle[3], Mariia Rey[1], Steven Goderis[1], Sophie Decrée[4], Jan Smit[5], and Philippe Claeys[1,6]

[1]Archaeology, Environmental Changes & Geo-Chemistry (AMGC), Vrije Universiteit Brussel, Brussels, Belgium, [2]Laboratoire G-Time, Université Libre de Bruxelles, Brussels, Belgium, [3]Nano Analytics GmbH, Berlin, Germany,



International Journal of Earth Sciences (2024) 113:635–656
https://doi.org/10.1007/s00531-024-02391-0

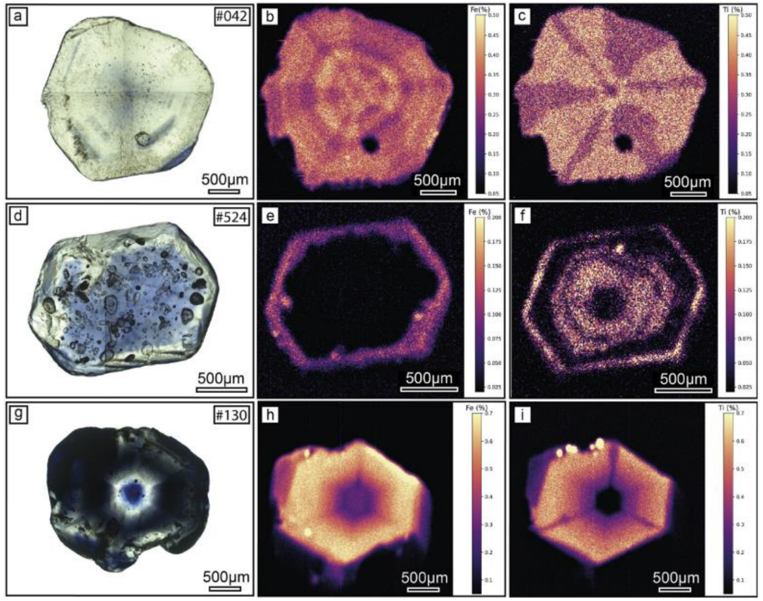
ORIGINAL PAPER

Mineralogy and geochemistry of multi-coloured sapphires at the Portezuelo de Pajas Blancas' deposits, northern Chile: revealing crystal growth processes

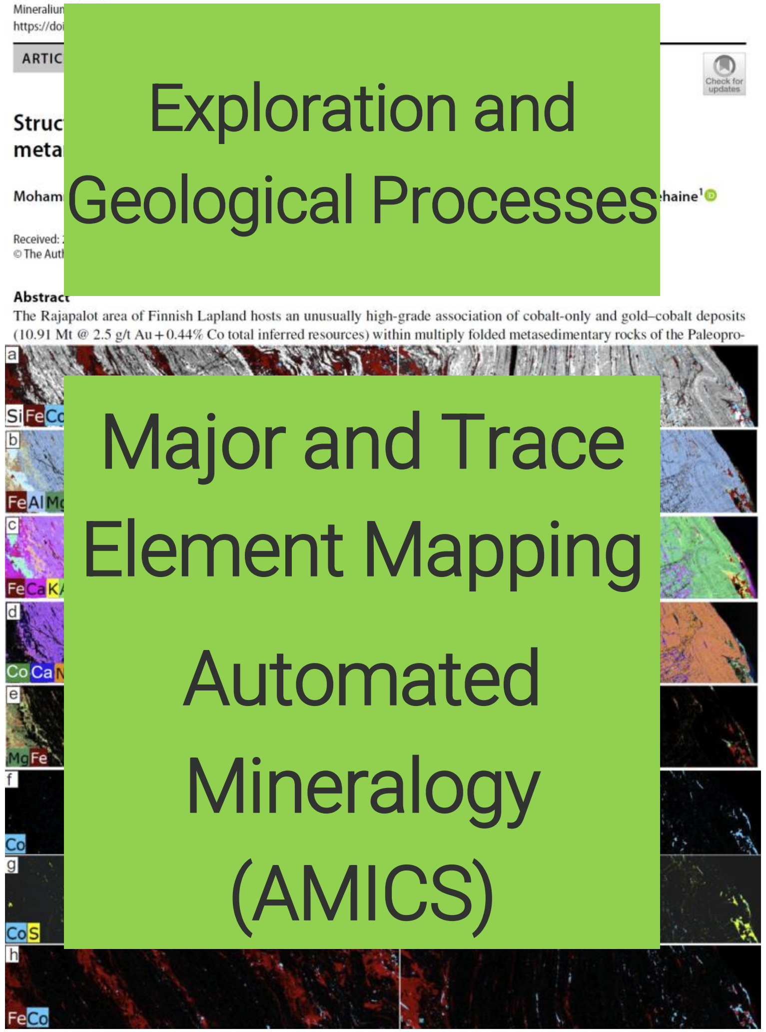
Gustavo Miranda-Díaz[1,2] · Andrew Menzies[3] · Karl Riveros-Jensen[2] · Gerhard Heide[1] · Lena Bußmann[4] · Birk Härtel[5] · Roald Tagle[3] · Eduardo Medina[6] · Wolfgang Griem[2]

Received: 12 June 2023 / Accepted: 23 January 2024 / Published online: 15 March 2024

Abstract
Portezuelo de Pajas Blancas' primary metasomatic deposits host sapphires that differ in size, colour, and colour distribution through different lithological units. The discovery of sapphire-bearing secondary aeolian placer deposits enabled a detailed analysis of sapphire types to determine the causes of this heterogeneity. Representative single sapphires from the primary and secondary deposits were analysed using various techniques, including SEM-CL, OM-CL, Micro-XRF, Raman



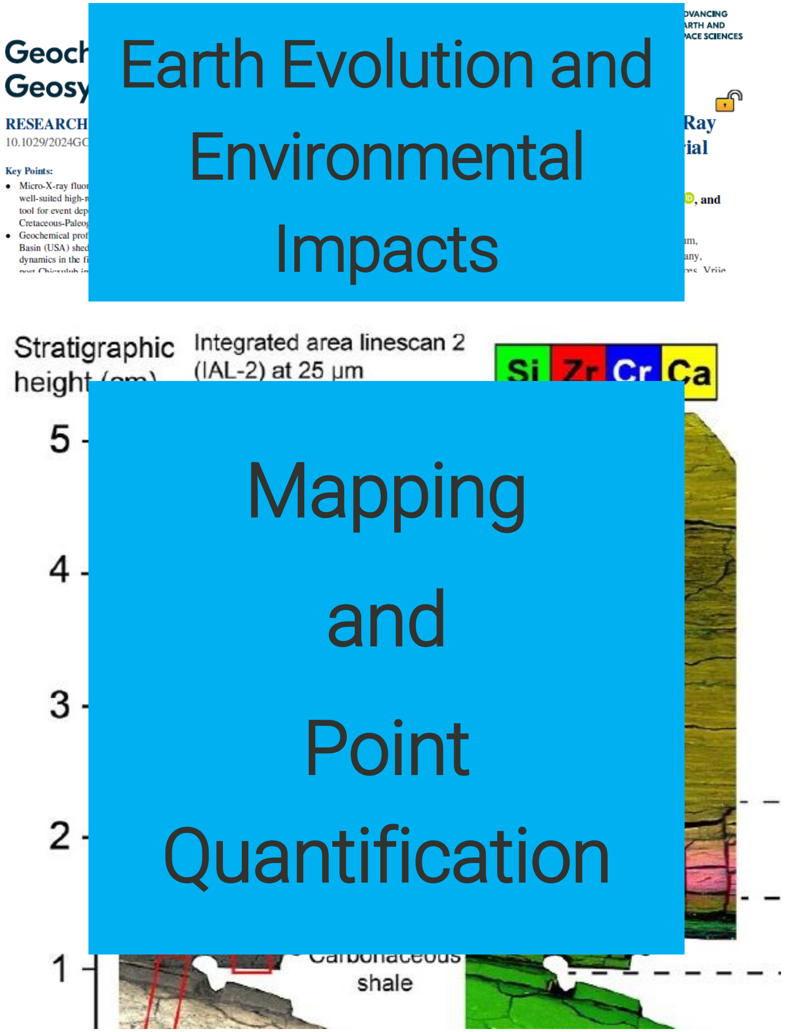
MicroXRF Applications
Examples



Exploration and Geological Processes

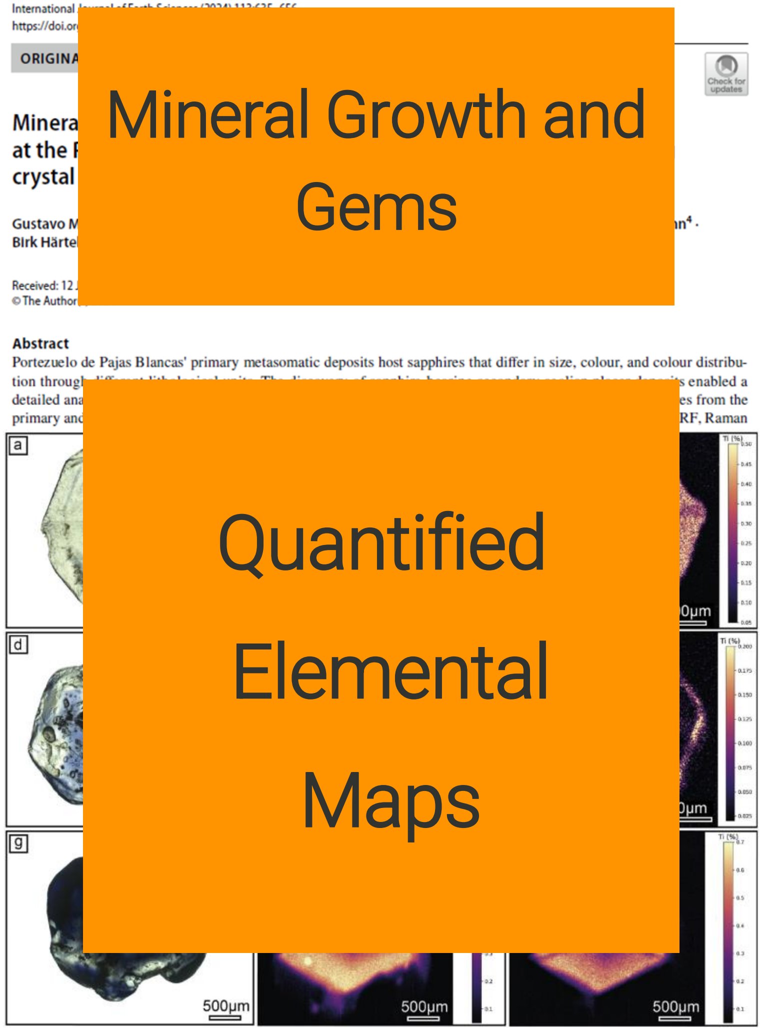
Major and Trace Element Mapping

Automated Mineralogy (AMICS)



Earth Evolution and Environmental Impacts

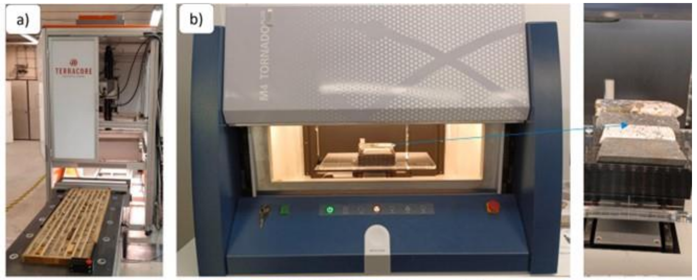
Mapping and Point Quantification

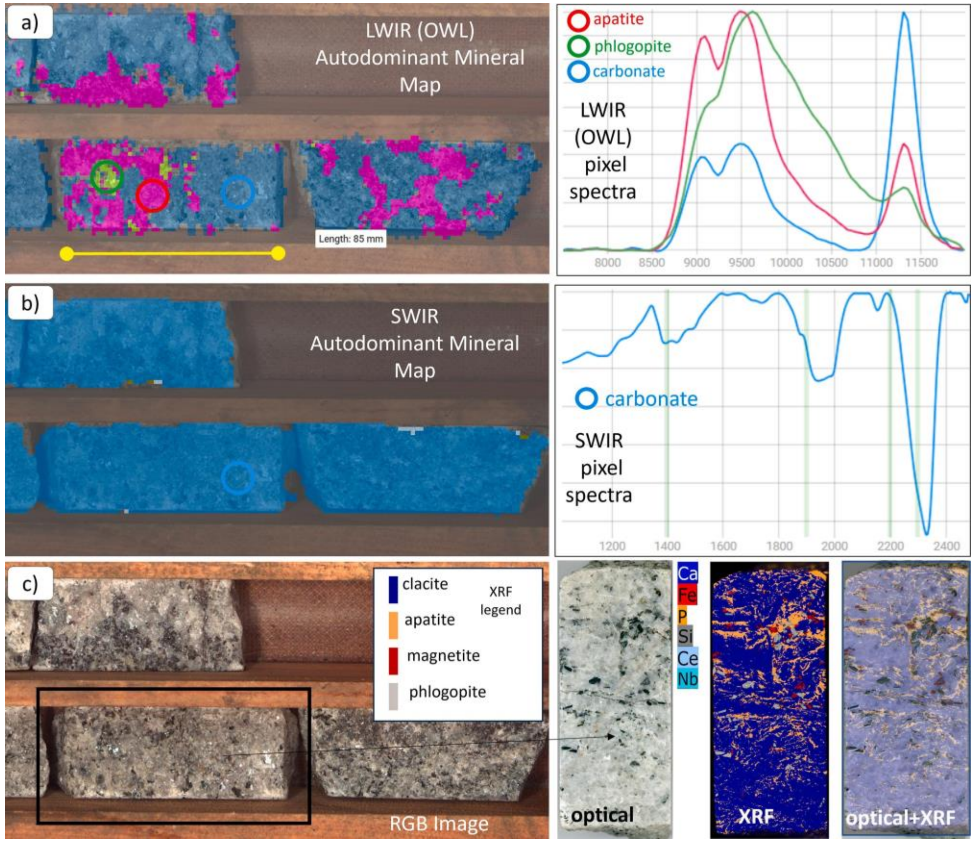


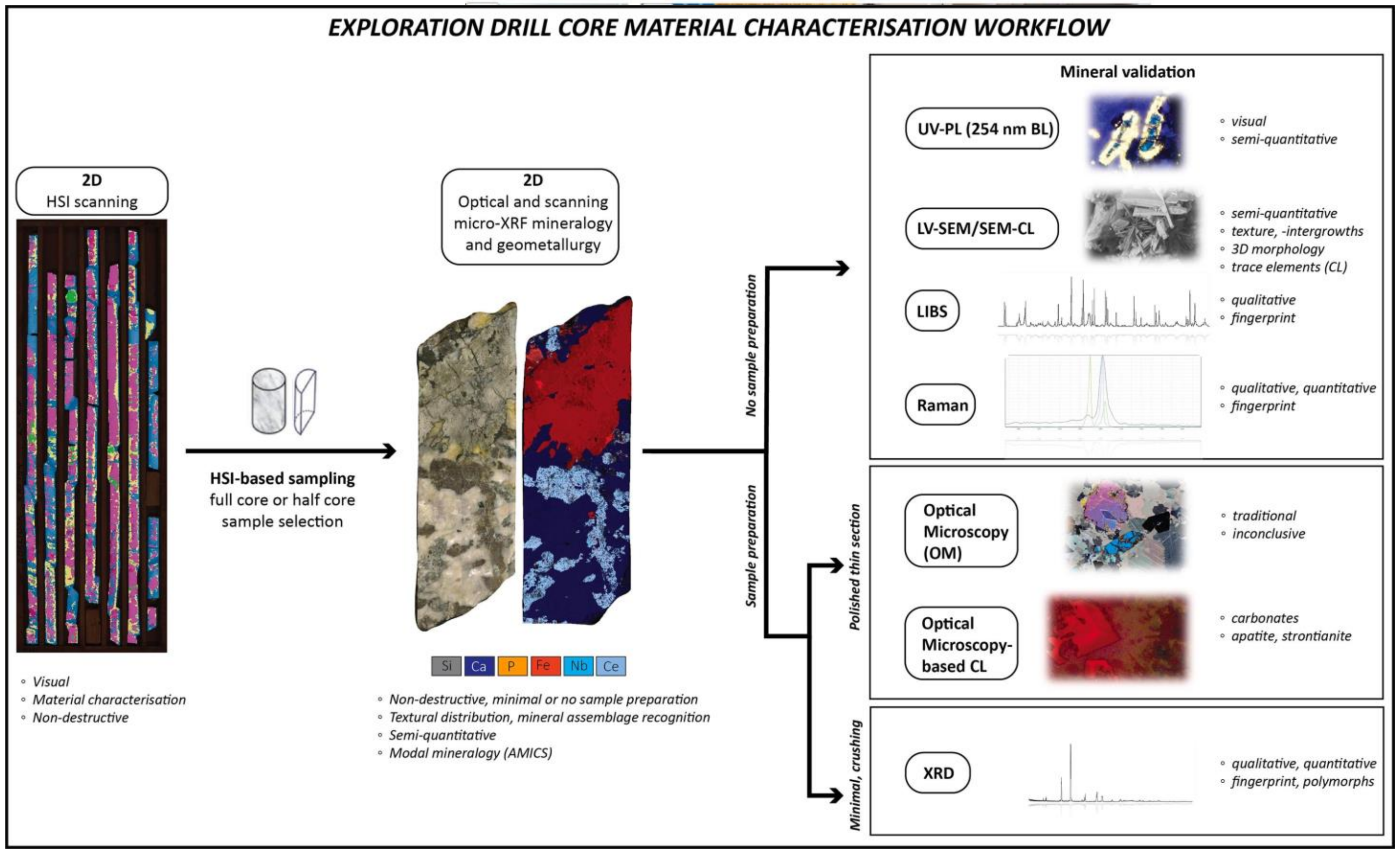
Mineral Growth and Gems

Quantified Elemental Maps

Workflow Considerations
Jolis et al. 2025







Ferromanganese (Fe-Mn) Crusts
Micro-XRF Analysis

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Late Cretaceous and Cenozoic paleoceanography from north-east Atlantic ferromanganese crust microstratigraphy

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[b] Camborne School of Mines, Tremough Campus, Penryn TR10 9EZ, UK
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Keywords:
FeMn crust
Atlantic
Paleoceanography
Geochemistry
Phosphatisation

ABSTRACT

Oceanic hydrogenetic ferromanganese (Fe-Mn) crusts precipitate directly from ambient seawater over millions of years. Their very slow growth rates and physio-chemical properties mean that they adsorb numerous elements from seawater. As such, they provide condensed records of seawater evolution through time that can be used for paleoceanographic reconstruction. Here, we present the results of a high-resolution, stratigraphic, textural and geochemical investigation of a core sample, obtained from a Fe-Mn crust pavement, located on the summit of Tropic Seamount in the tropical north-east Atlantic Ocean. A number of observations and interpretations are proposed, within the context of a well-constrained age model, spanning the last 75 ± 2 Myr. This core has textural stratigraphic coherence with Pacific Fe-Mn crusts formed since the Late Cretaceous, highlighting that global oceanic and climatic phenomena exert first-order controls on Fe-Mn crust development. All major hiatuses observed in the Fe-Mn crusts are contemporaneous with erosion events occurring throughout the Atlantic Ocean. High-resolution geochemical data indicate that there is variability in the composition of Fe-Mn crusts at the cm to µm scale. The dominant factors controlling this include major oceanographic events, mineral textures and micro-topography.

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Geochimica et Cosmochimica Acta 308 (2021) 60–74

Geochimica et Cosmochimica Acta

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Controls on metal enrichment in ferromanganese crusts: Temporal changes in oceanic metal flux or phosphatisation?

Pierre Josso [a,*], Paul Lusty [a], Simon Chenery [a], Bramley Murton [b]

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Abstract

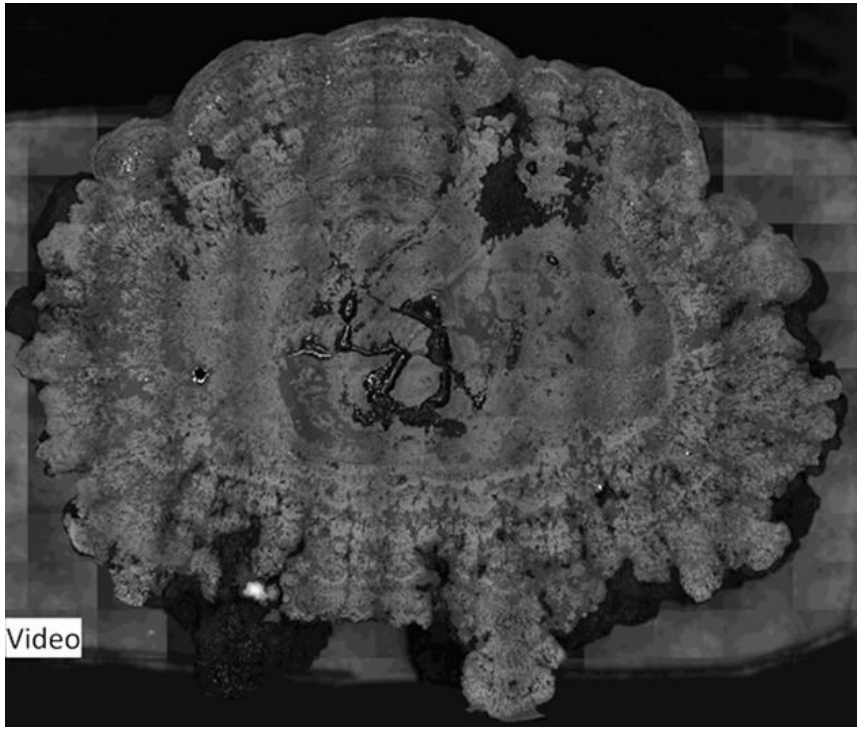
Oceanic hydrogenetic ferromanganese (Fe-Mn) crusts are a major repository for many metals, such as Co, Ni, Cu, Pt, Te and REE, which are essential for decarbonisation of transport and energy systems. Secondary mineralisation processes, occurring during phosphatisation episodes, commonly impregnate the shallower deposits with carbonate fluorapatite (CFA). The suboxic oceanic conditions during such events are frequently invoked to explain the lower Co content and unusually high Ni, Cu, Zn and Pt content of older phosphatised crusts. Here, the hypothesis of suboxic diagenetic recrystallization induced by phosphatisation episodes as a driving mechanism for Ni, Cu, Zn and Pt enrichment and Co depletion is evaluated. Accurately dated geochemical profiles, spanning 75 Ma of depositional history, for a shallow (1100 mbsl) phosphatised sample and a deeper (3100 mbsl) unphosphatised sample from Tropic Seamount in the north-east Atlantic, are compared. An isocon analysis, which allows to quantitively evaluate chemical gains and losses in mass transfer and therefore permits compensation for the dilution effect induced by the addition of CFA in the Fe-Mn crusts, demonstrates that no loss of Co has occurred in the phosphatised crust, whilst Pt, Te, Cu, Ni and Zn are enriched relative to younger, unphosphatised Fe-Mn crust. Both geochemical profiles show sympathetic trends and similar amplitudes of variation in concentration. This excludes phosphatisation as the driving mechanism for the metal enrichment and depletion. Systematic differences in metal content between the two samples, such as higher Cu and lower Co content in the deeper sample, are consistent with the depth profile of dissolved metal concentrations in the water column. The variability observed in the geochemical profiles is consistent with temporal changes in metal fluxes to the ocean, as a result of the evolving climate and oceanographic configuration of the north-east Atlantic Ocean through the Cenozoic. It is concluded that changing metal fluxes, rather than secondary mineralisation process associated with phosphatisation, is the dominant control on the primary metal content in Fe-Mn crust deposits at Tropic Seamount.

Keywords: Fe-Mn crusts; Phosphatisation; Isocon analysis; Metal fluxes; Critical metals

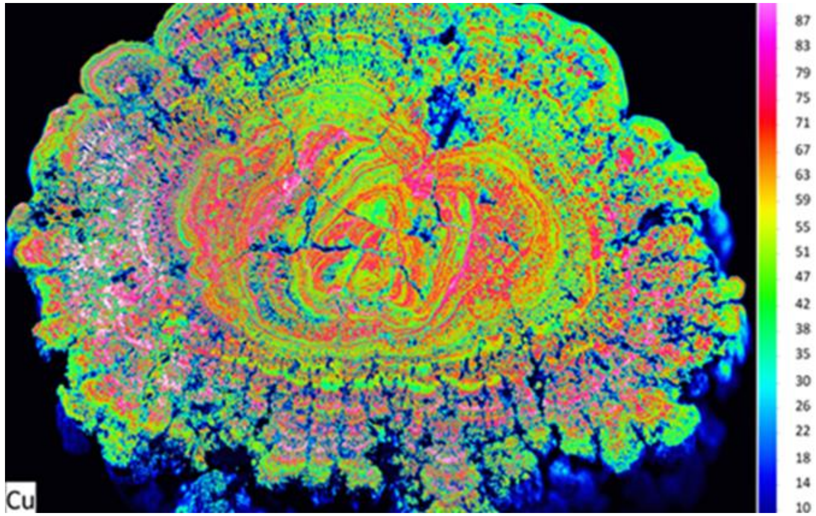
Ferromanganese (Fe-Mn) Crusts
Micro-XRF Analysis

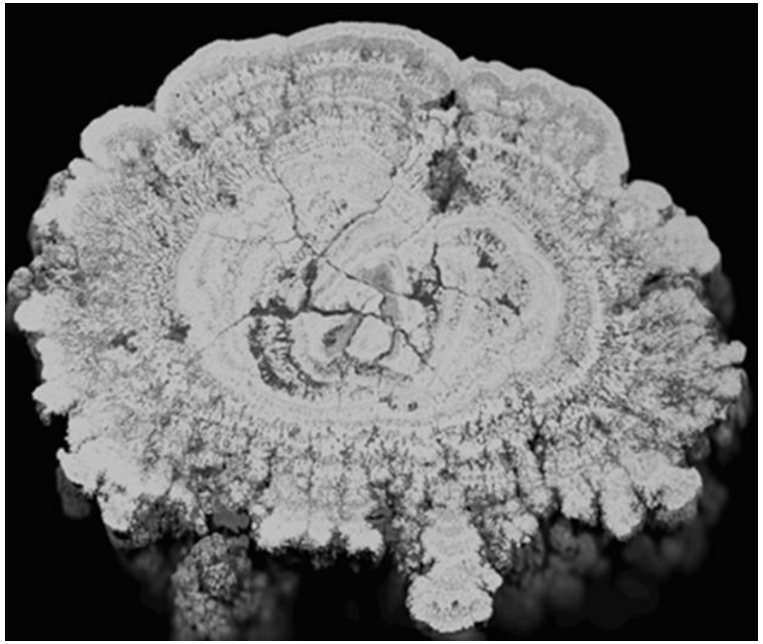
Samples from:

New England Seamount Chain, Hatton Bank, Walvis Ridge, and the Sierra Leone Rise.



Optical Image

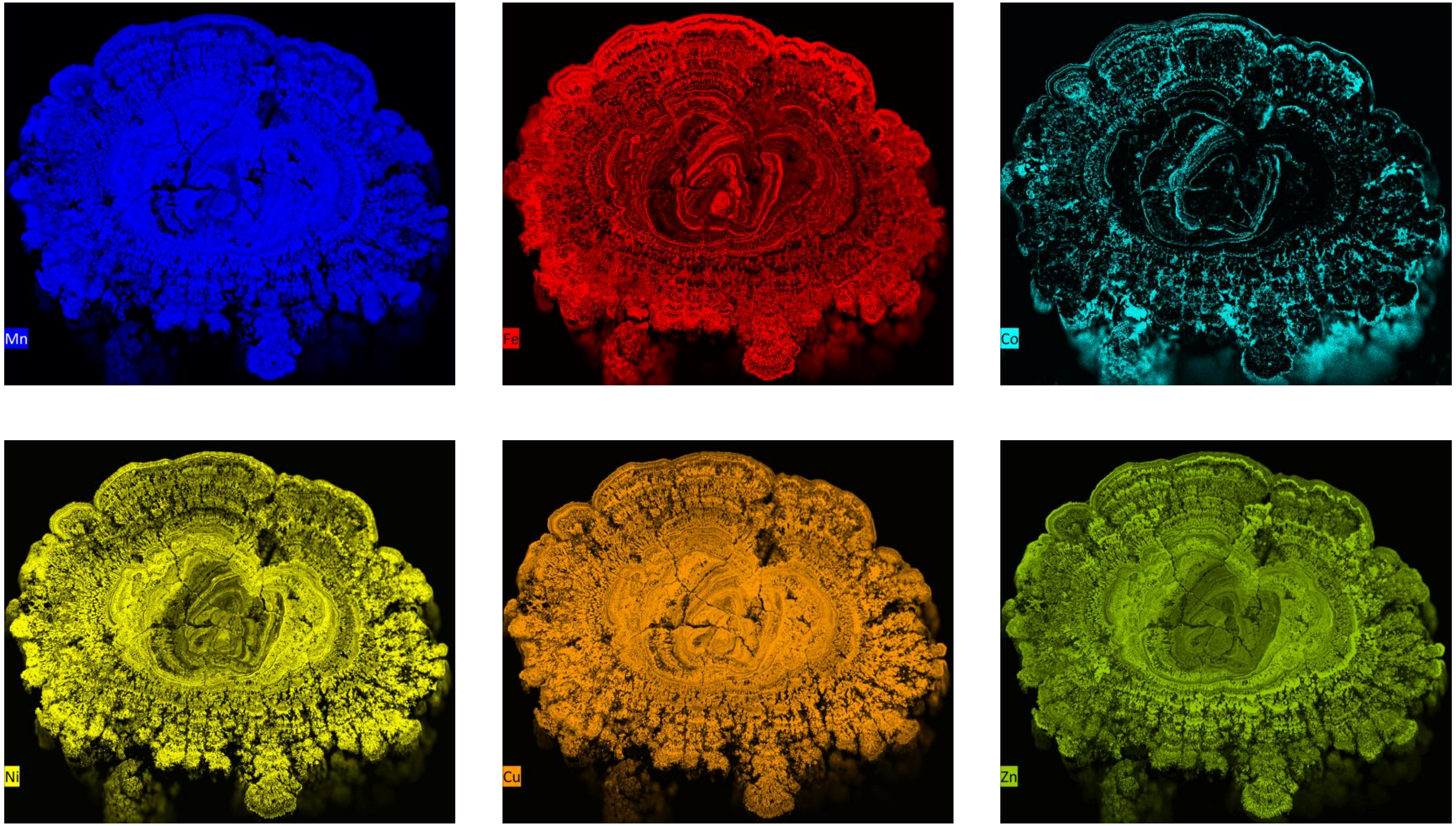




Total X-ray Intensity Map

Ferromanganese (Fe-Mn) Crusts:
AMICS: Mineralogy

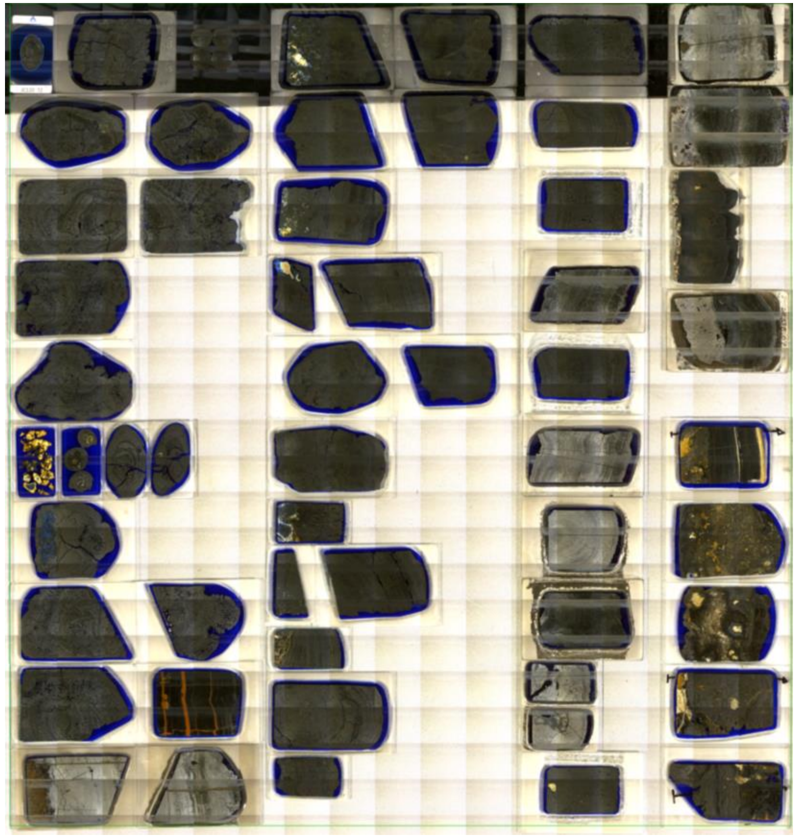
Sample Fe-Mn Nodule from Atlantic Ocean



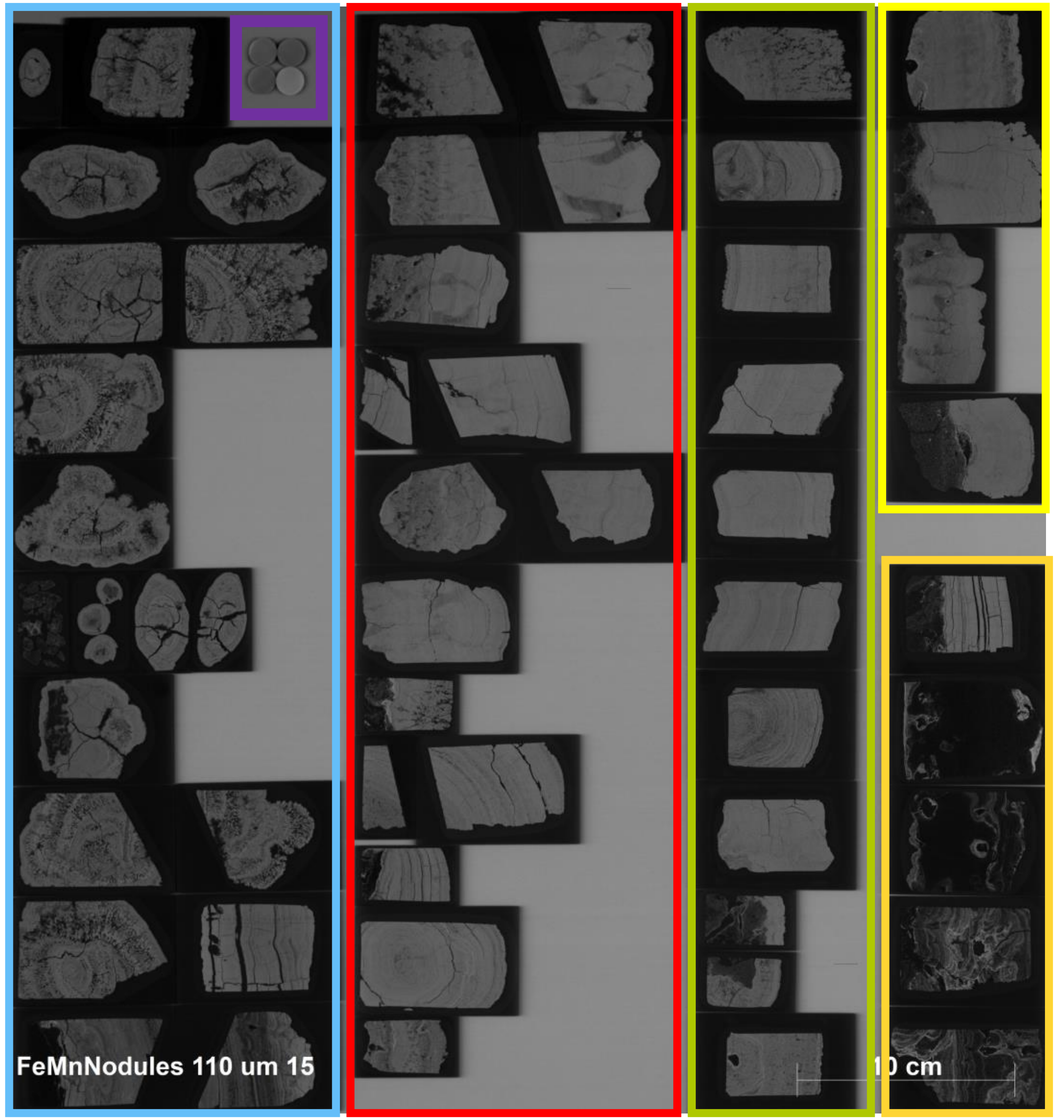
Total X-ray Intensity Map

Ferromanganese (Fe-Mn) Crusts
Micro-XRF Analysis

Analytical Area 800 x 600 mm



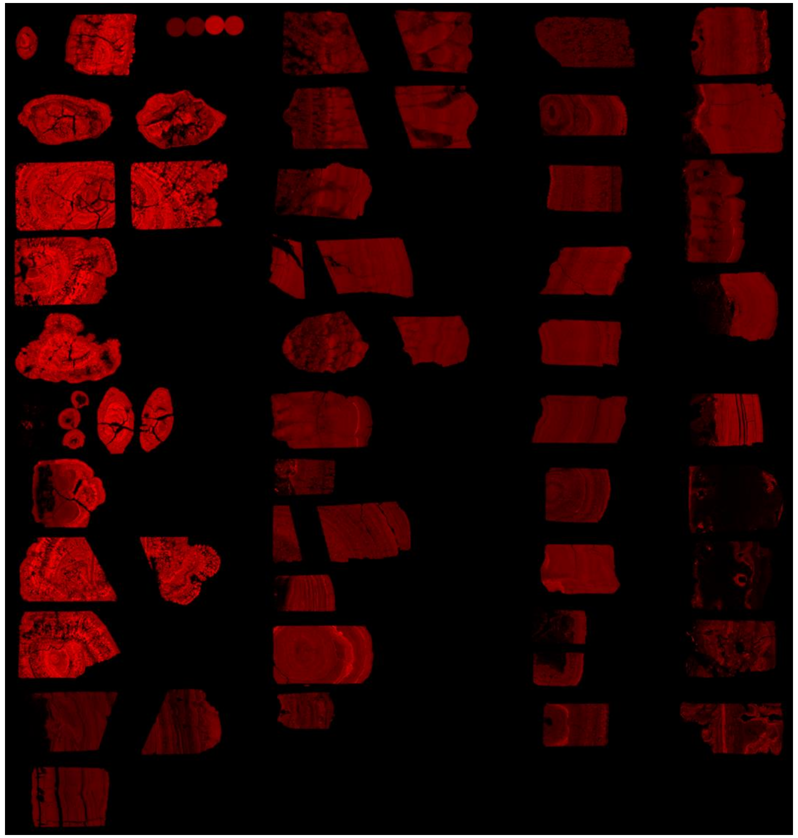
Optical Image



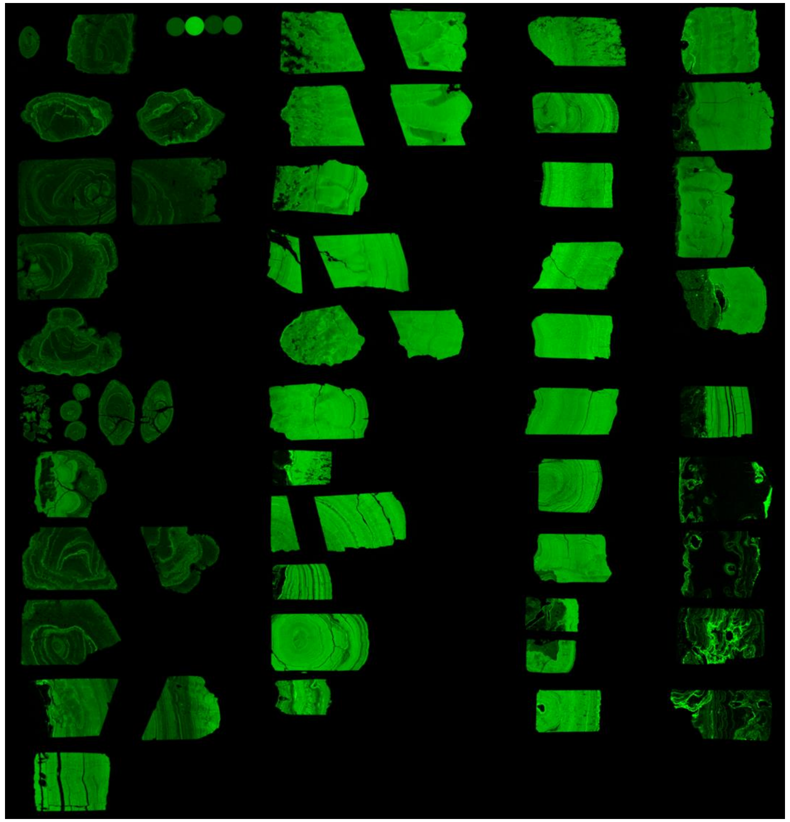
Total X-ray Intensity Map

Ferromanganese (Fe-Mn) Crusts
Micro-XRF Analysis

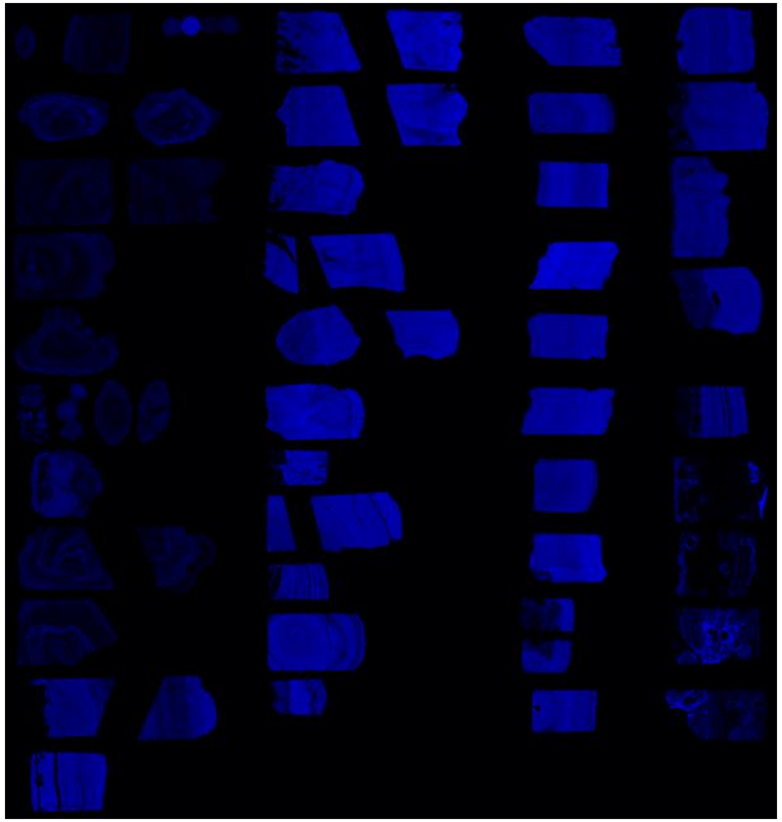
Analytical Area 800 x 600 mm



Mn



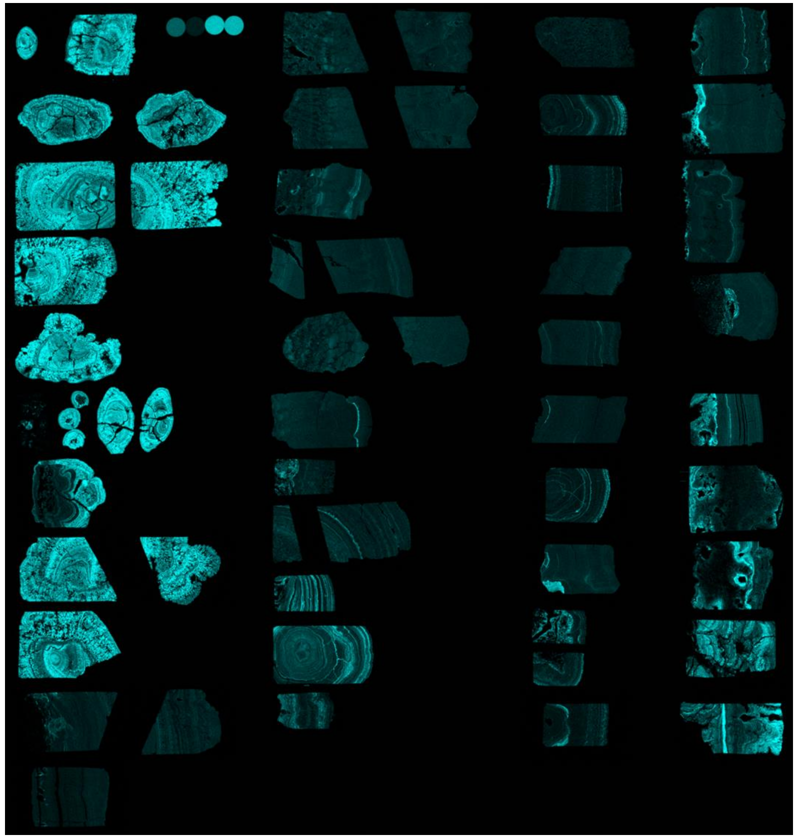
Fe



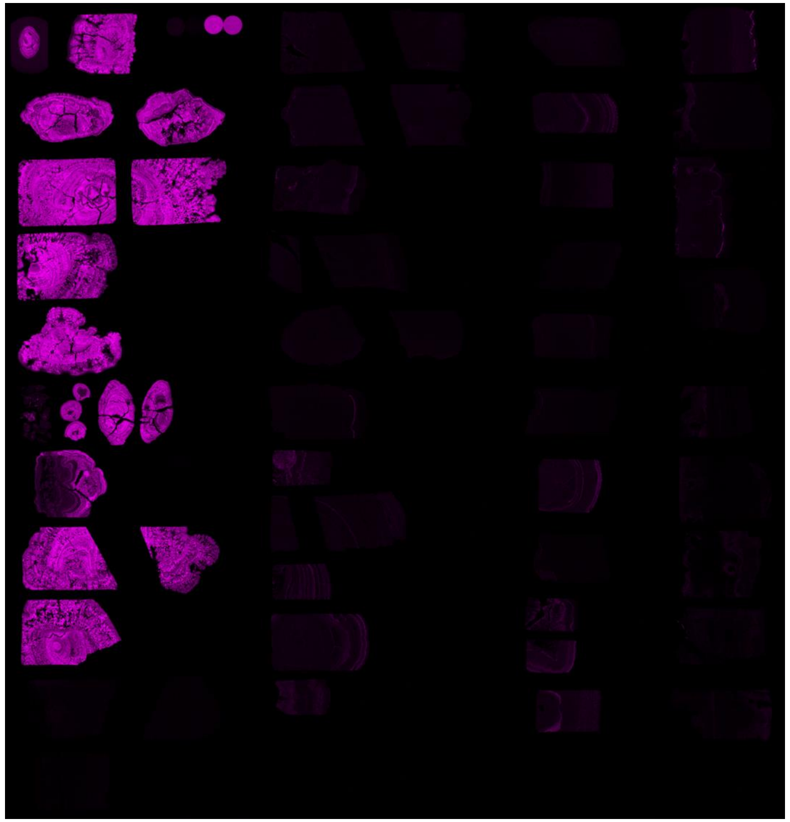
Co

Ferromanganese (Fe-Mn) Crusts
Micro-XRF Analysis

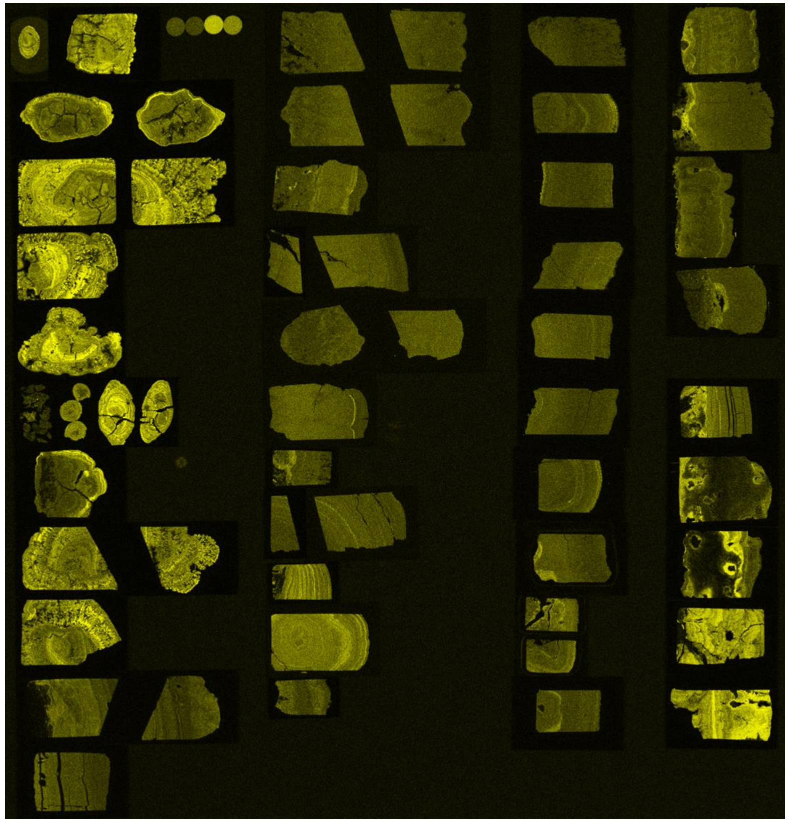
Analytical Area 800 x 600 mm



Ni



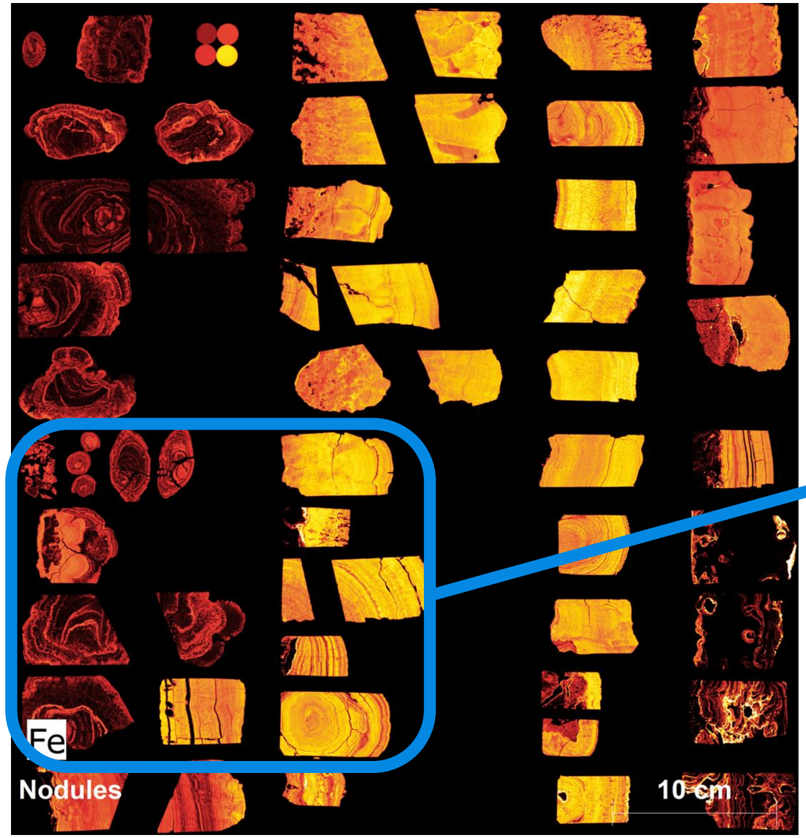
Cu

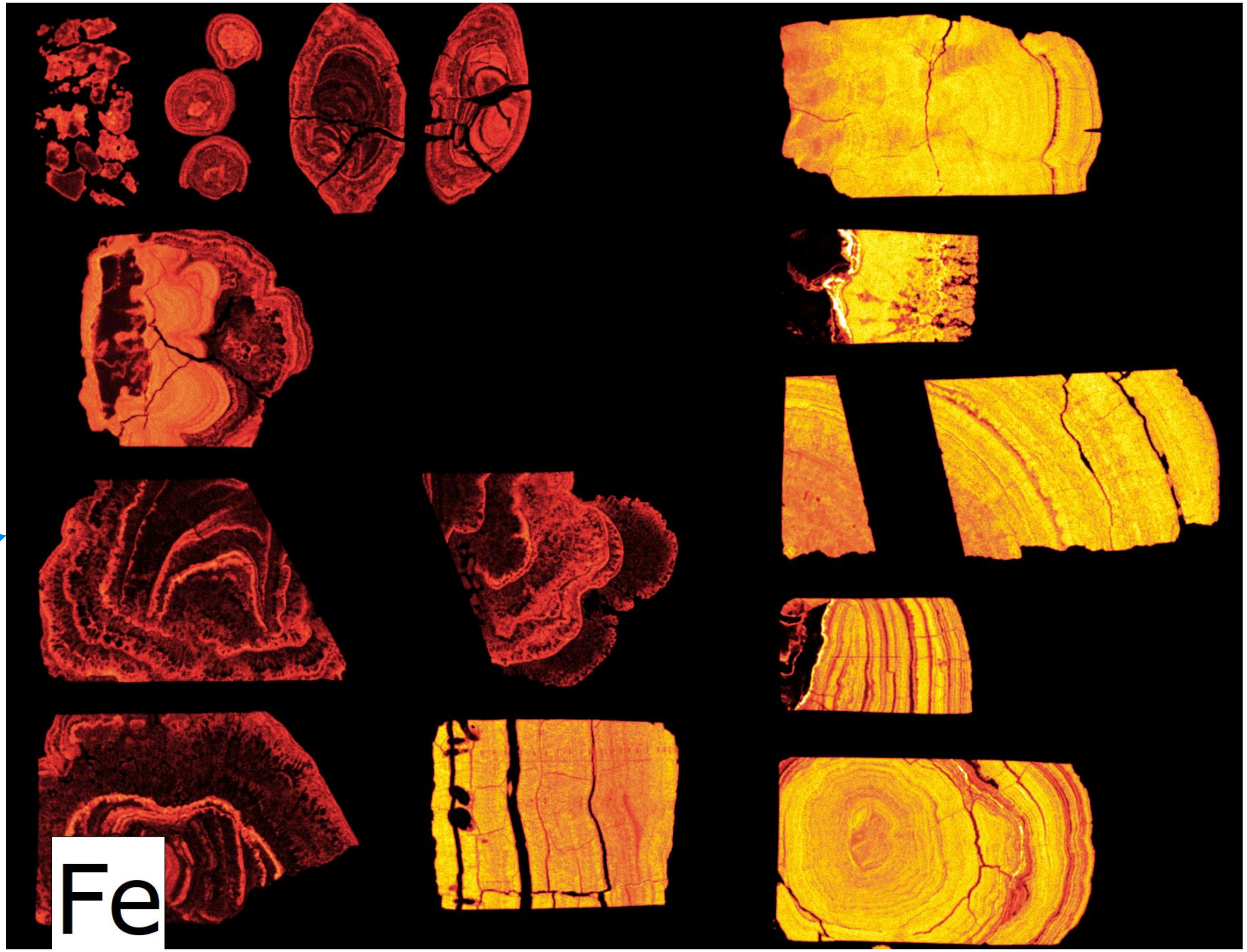


Zn

Ferromanganese (Fe-Mn) Crusts
Micro-XRF Analysis

Analytical Area 800 x 600 mm

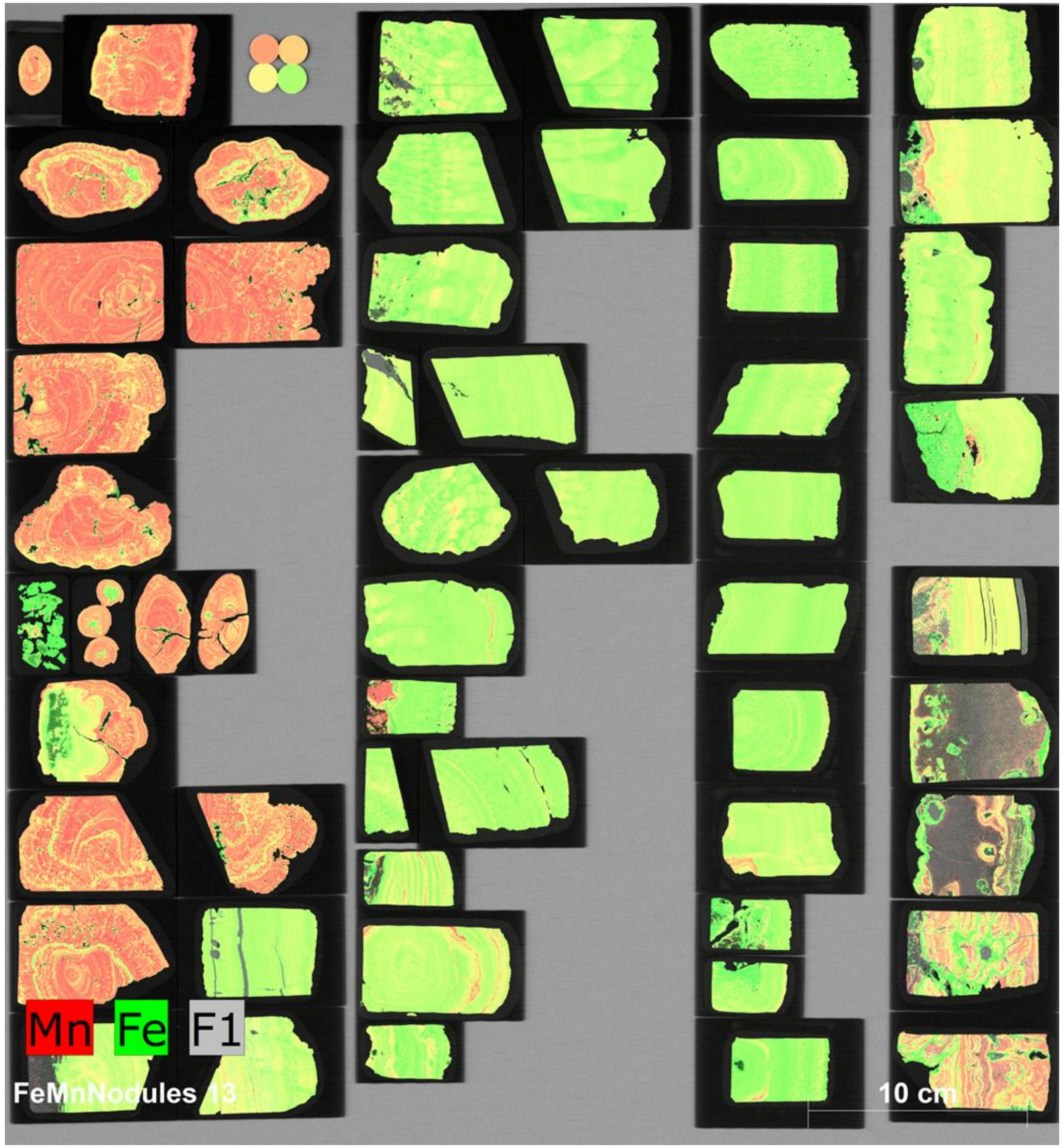




Ferromanganese (Fe-Mn) Crusts
Micro-XRF Analysis

Analytical Area 800 x 600 mm

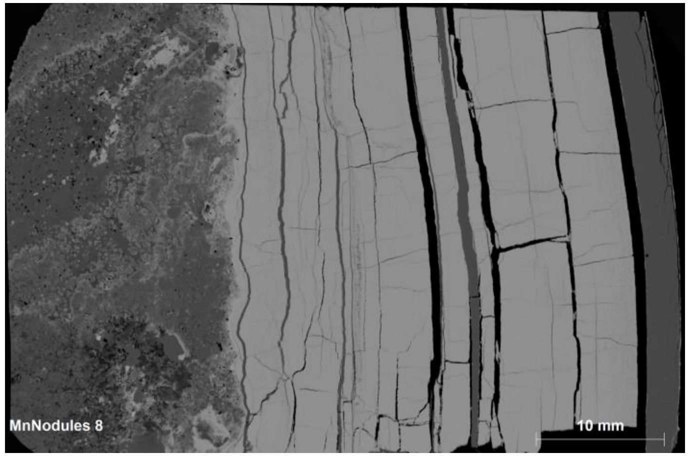
Total X-ray Intensity



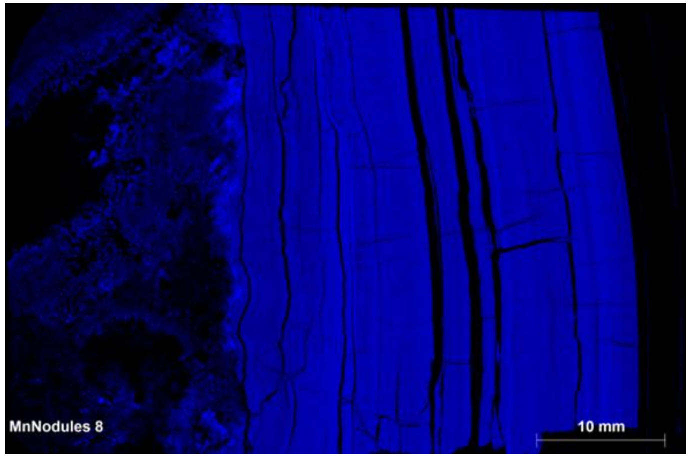
Mn + Fe

Ferromanganese (Fe-Mn) Crusts:
Thin section mapping

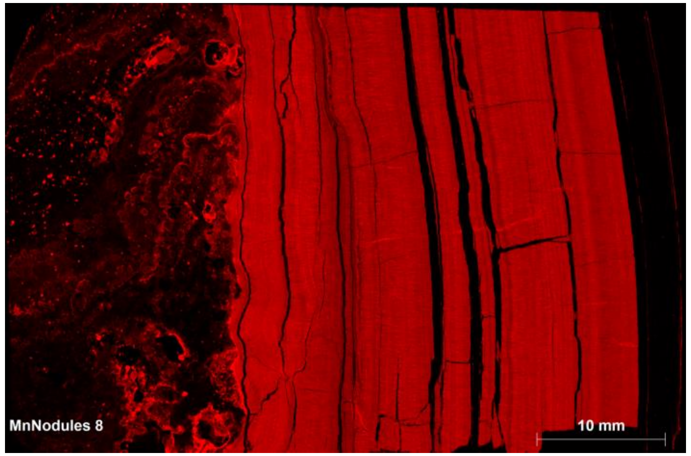
Total X-ray Intensity

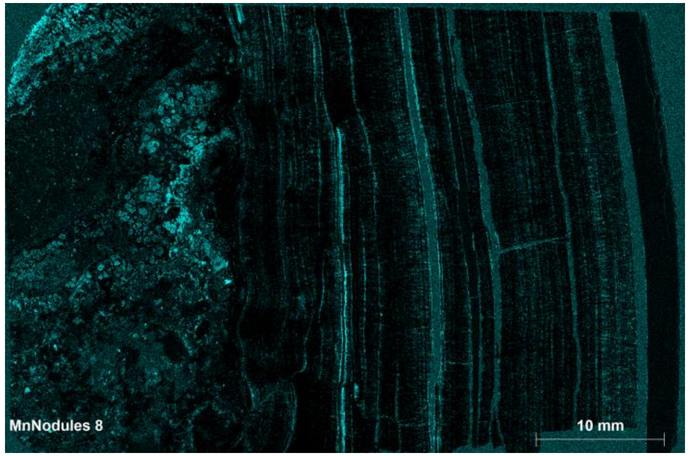


Mn

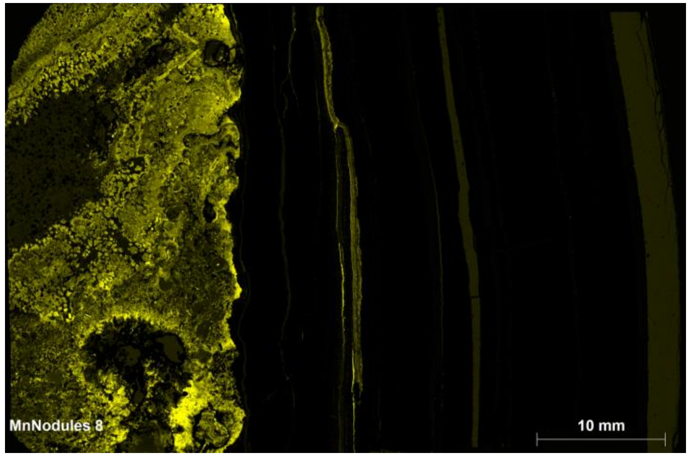


Fe

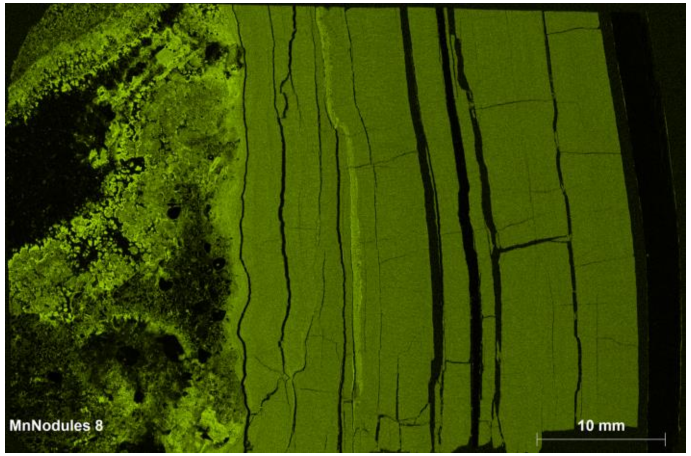




Co

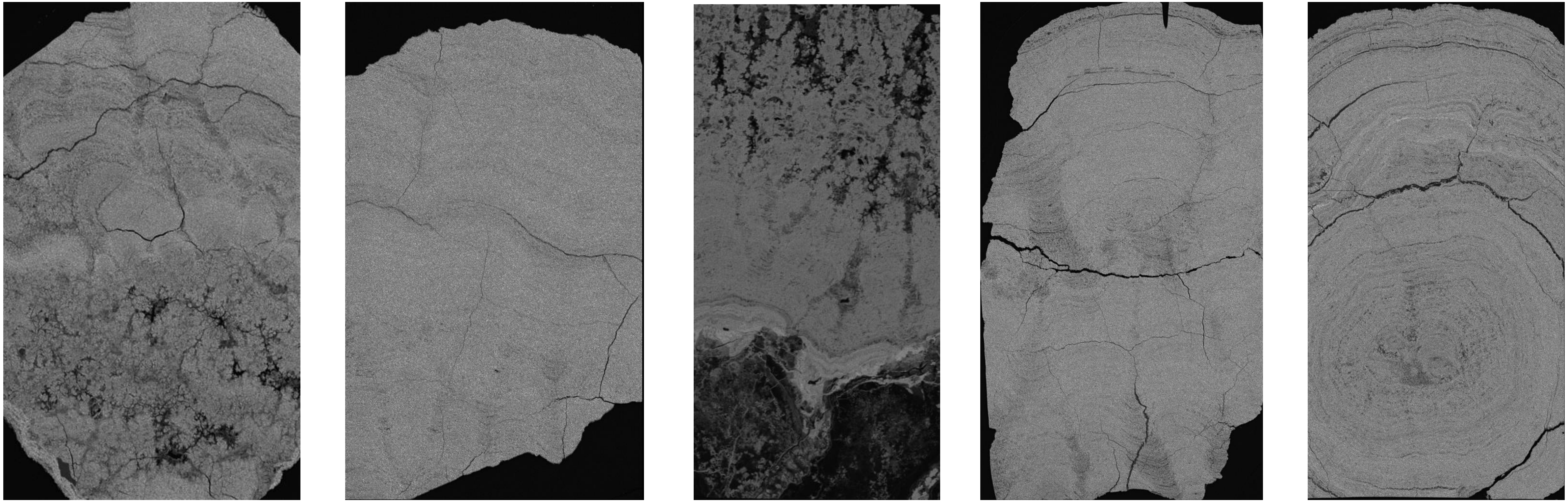


Ni

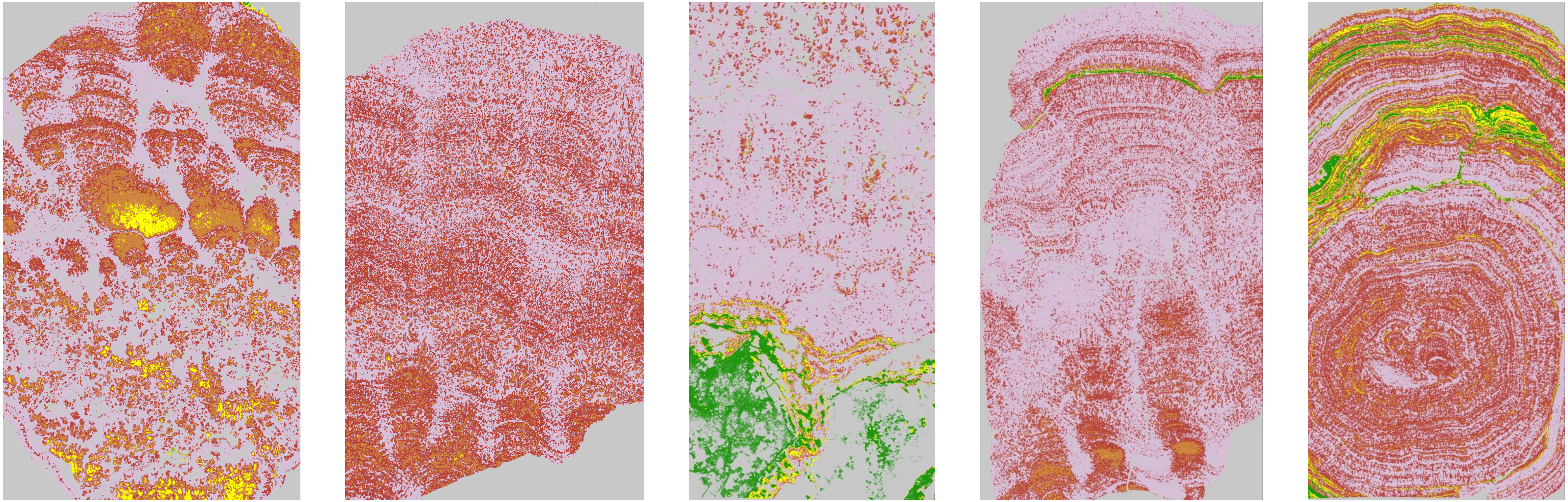


Zn

Ferromanganese (Fe-Mn) Crusts:
Total X-ray Intensity



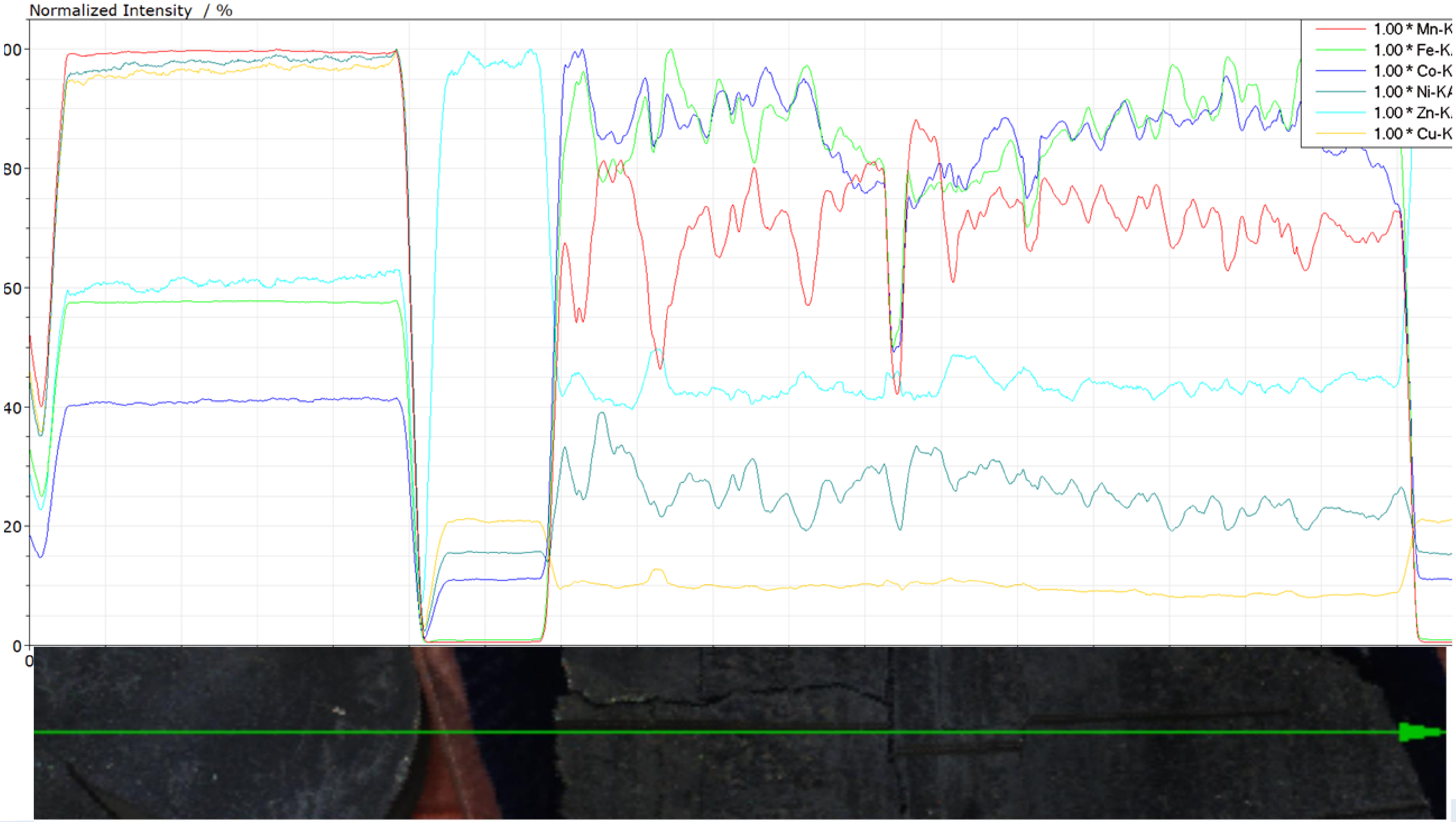
Ferromanganese (Fe-Mn) Crusts:
AMICS: Mineralogy



AMICS Automated Mineralogy

Ferromanganese (Fe-Mn) Crusts
Line Scan Analysis and Quantification

Ferromanganese (Fe-Mn) Crusts
Line Scan Analysis and Quantification



Analytical Workflow:
Multi-scale in situ non-destructive scanning micro-XRF analysis

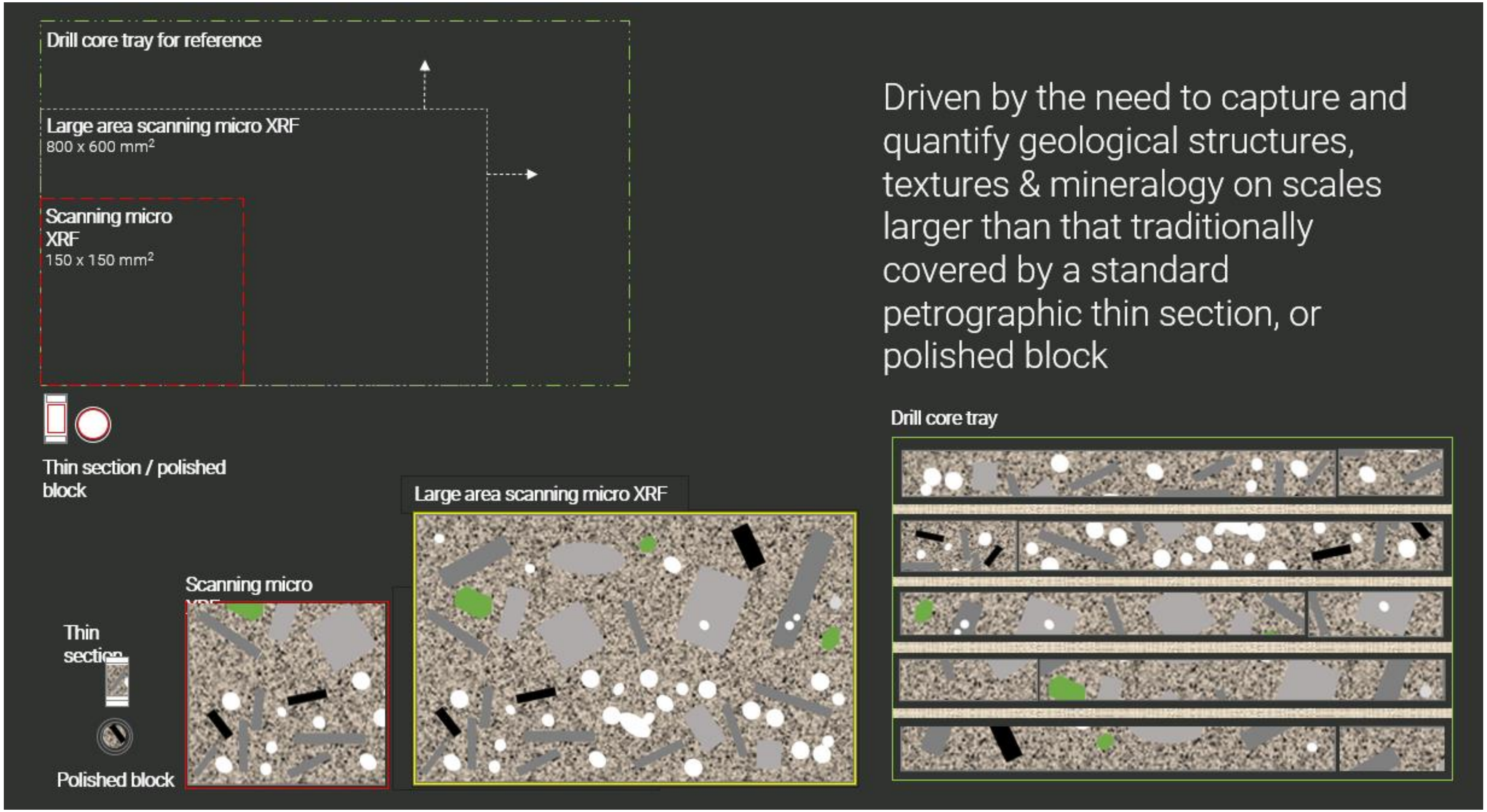


Image from Alan Butcher

Summary and Conclusions: Analytical Benefits

Micro-XRF Benefits:

- Lower detection limits (down to 10 ppm)
- Detection of High Energy X-ray Lines (Full Spectrum Range up to 40 kV)
- Micrometer scale measurement over large areas (Hand Specimens and Drill Cores)
- Ideal for Low kV or Beam Sensitive samples
- Minimal Sample Preparation Required, No charging effects
- Fast elemental X-ray mapping over large areas

Results:

- Elemental and Mineralogical
- Point, Line Scan, and Mapping
- Automated Mineralogy outputs: Modal Mineralogy, Grain Size, Associations etc

Summary and Conclusions:
Analytical Results

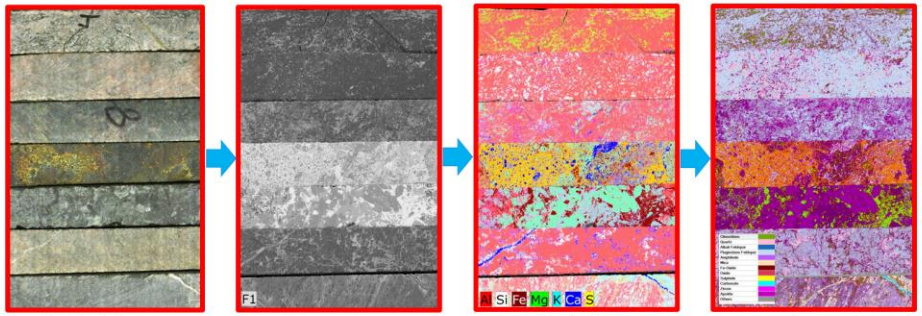
Micro-XRF and AMICS software

- ***Esprit / Micro-XRF***:
  - Elemental Quantification
- ***AMICS***:
  - Mineralogy Quantification

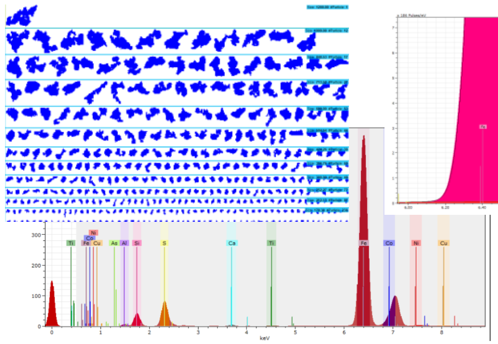
Automated analysis of multiple samples.

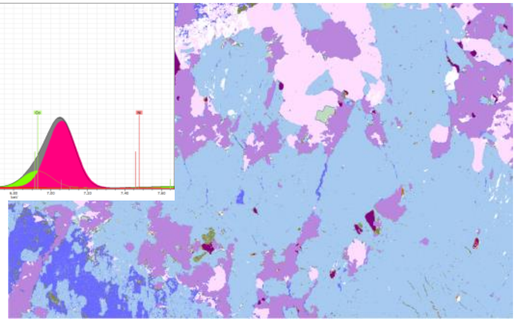
Compare Between Samples:

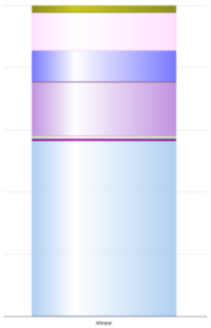
- Whole Rock Composition
- Individual Mineral Composition and Zonation
- Modal Mineralogy
- Mineral Size Distribution
- Mineral Shape
- Mineral Associations / Inclusions



Optical Image | Total X-ray Intensity Map | Overlaid Element X-ray Map | Mineralogical Map







Name	Wt%
Albite	56.0
Amblygonite	0.6
Kyanite	1.1
Lepidolite	17.2
Other	0.0
Perhamite	0.1
Petalite	10.1
Quartz	12.1
Spodumene	2.7

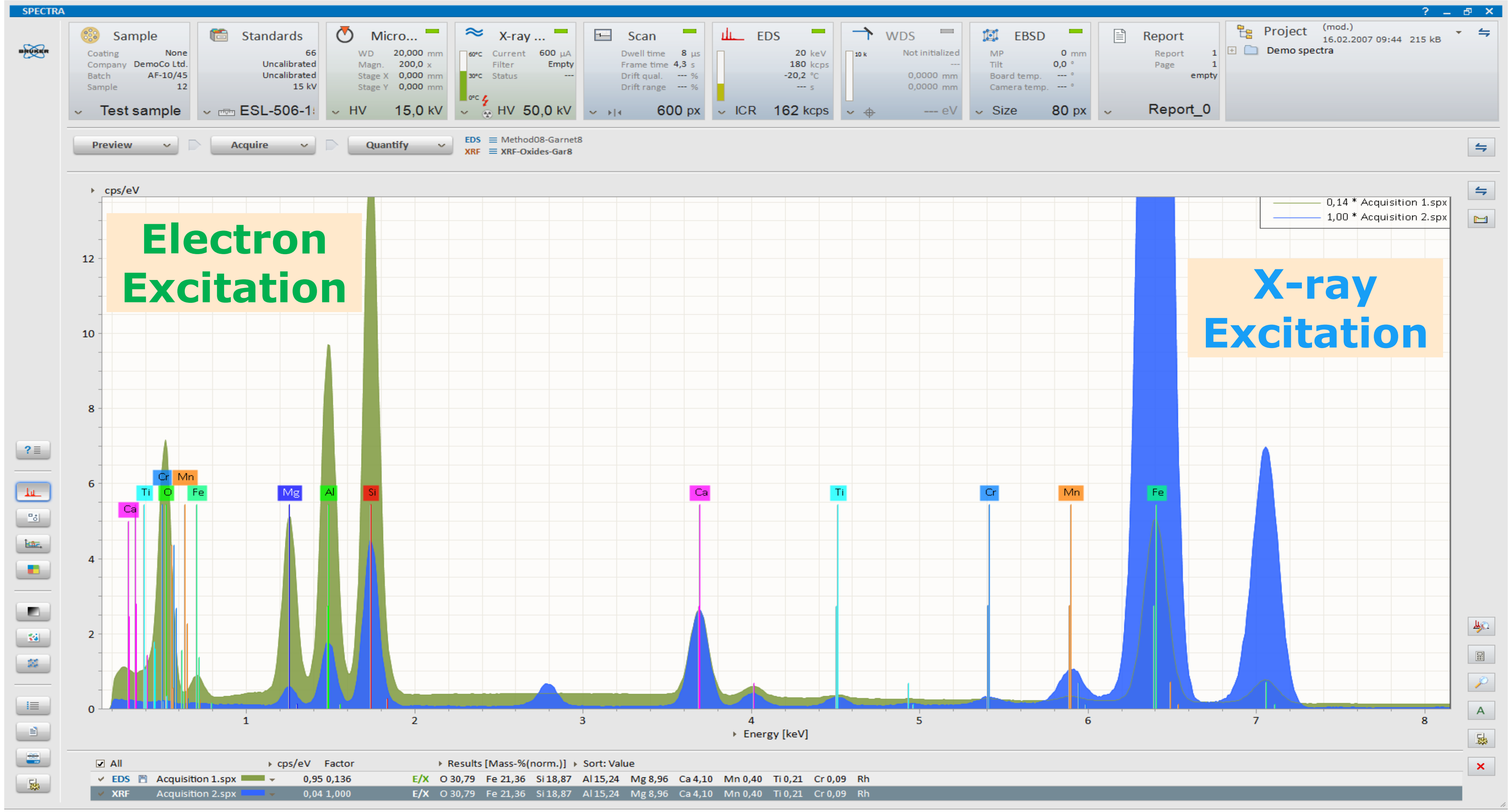
Thank you for your time.

Any Questions?

BRUKER

Innovation with Integrity

Energy Dispersive Spectra
Comparison: Electron vs. X-ray Excitation

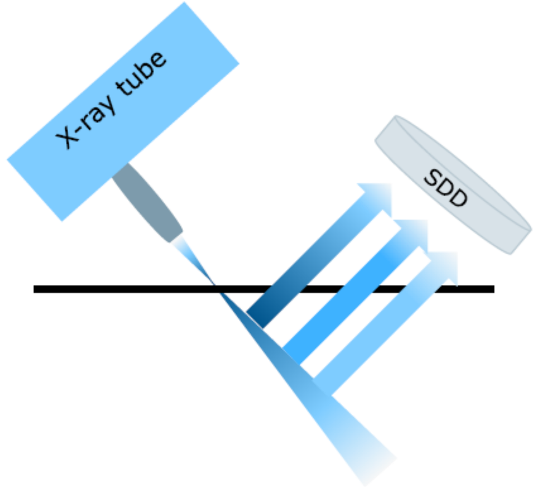


The garnet has:
40 wt% SiO_2 and
20 wt% FeO.

The different spectrum profiles are obvious.
For example, the e-beam spectra (in green) the lighter elements are more intense.

Whereas for the heavier elements the X-ray spectrum (in blue) has a significantly more intense signal.

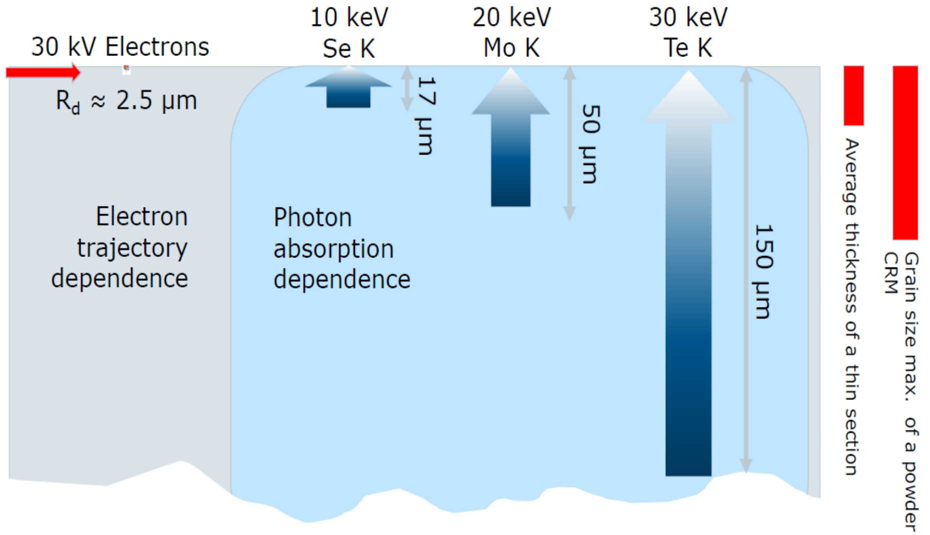
Spatial Resolution and Analyzed Volume: Transmission and Attenuation



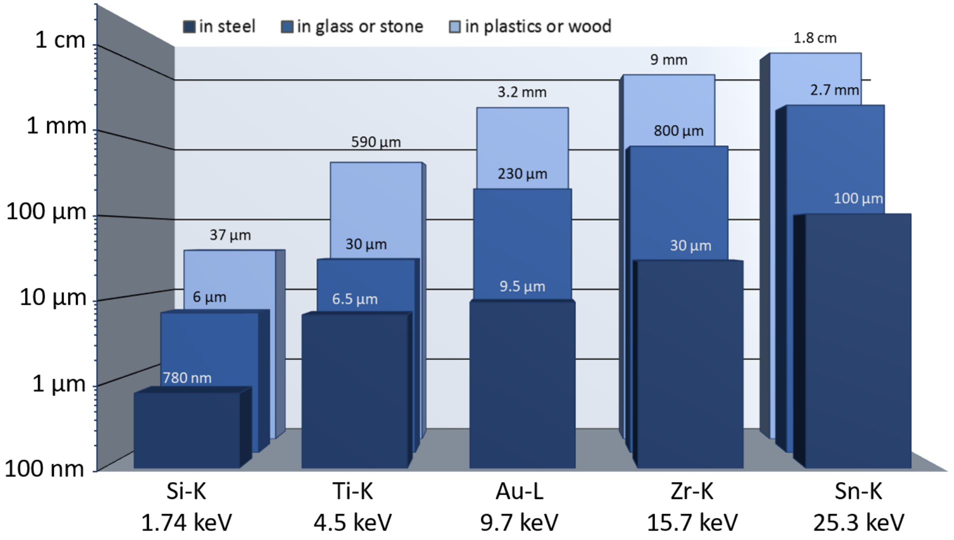
The transmission of X-rays is important for excitation of samples as well as for the fluorescence radiation.

Penetration depth: the depth that can still be excited

Information depth: the depth from which fluorescence X-rays can still reach the detector



Information depths of selected element fluorescence lines in different matrices



Automated Mineralogy (AMICS): Micro-XRF vs SEM

PAL0163 – 418.29m

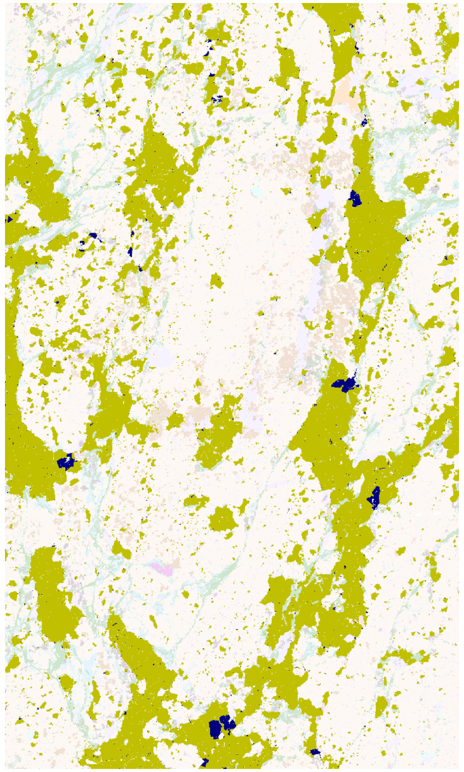
Thin Section of Co-Ore showing the Sulphide phases.

Automated Mineralogy (AMICS) possible with both Micro-XRF and SEM.

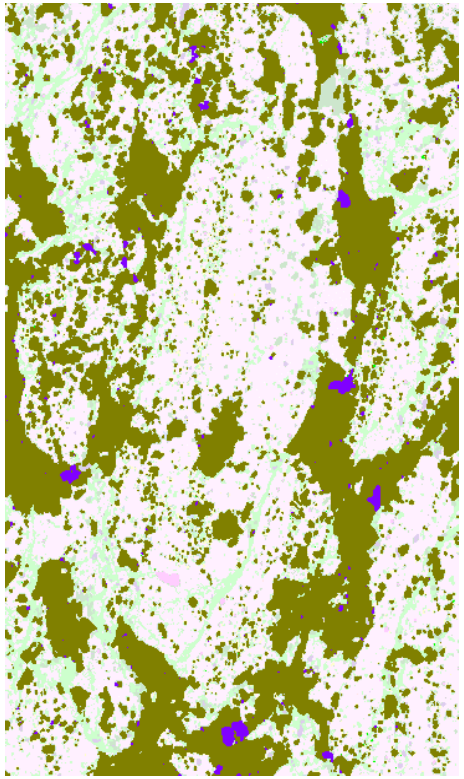
Principally Pyrrhotite and Cobaltite

Optical

SEM



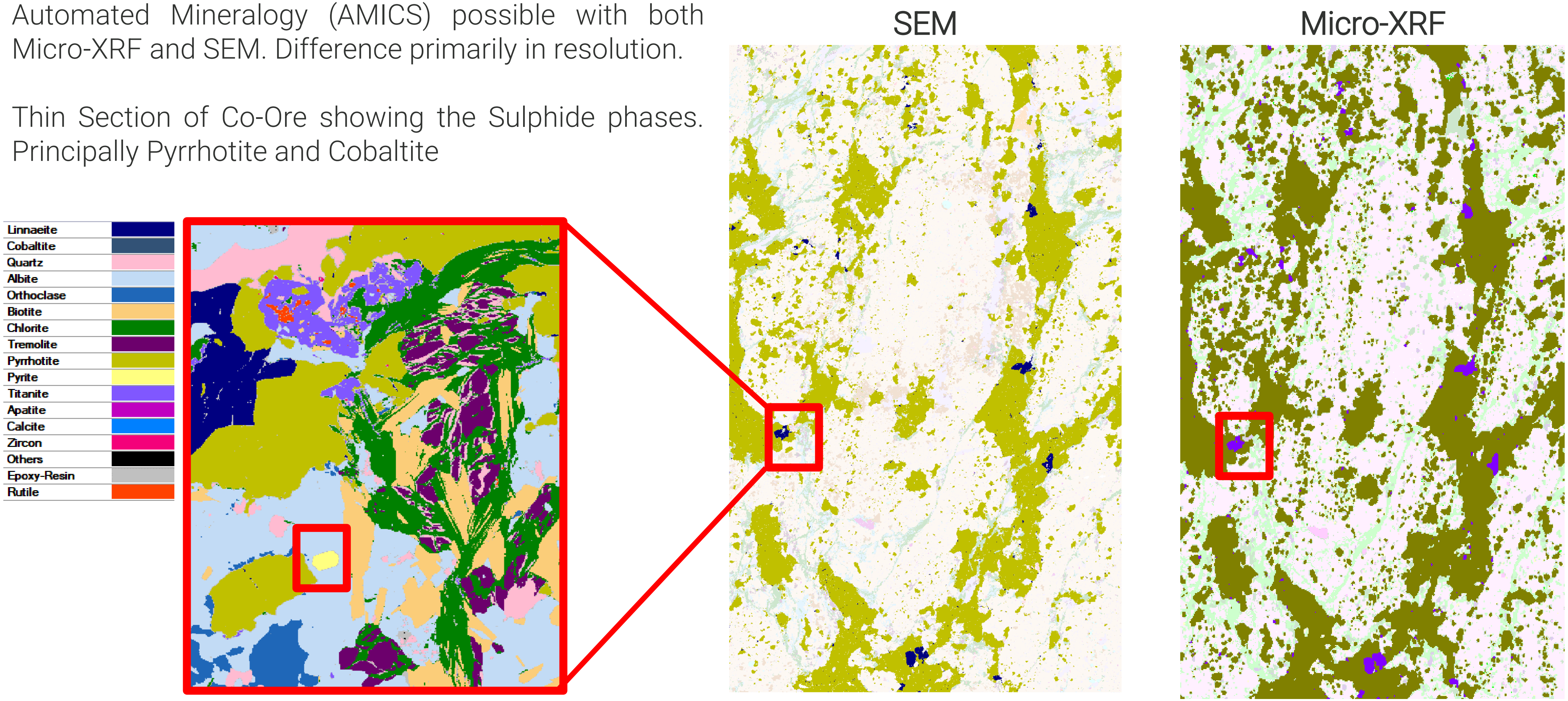
Micro-XRF



Automated Mineralogy (AMICS): Micro-XRF vs SEM

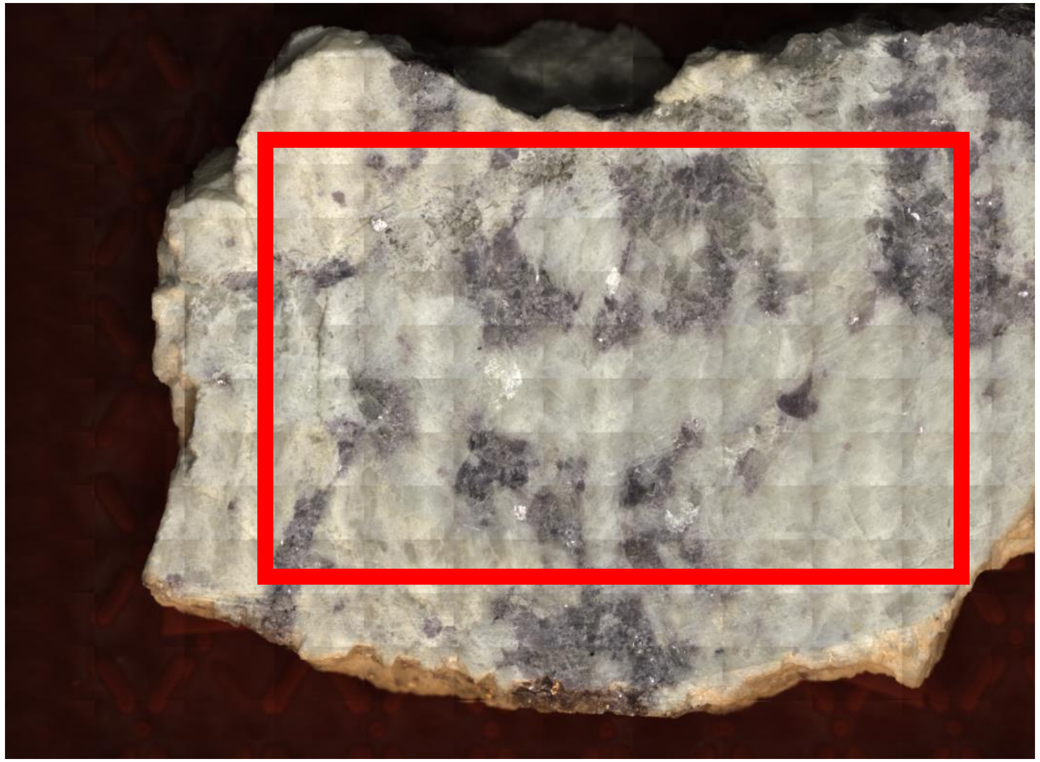
Automated Mineralogy (AMICS) possible with both Micro-XRF and SEM. Difference primarily in resolution.

Thin Section of Co-Ore showing the Sulphide phases. Principally Pyrrhotite and Cobaltite



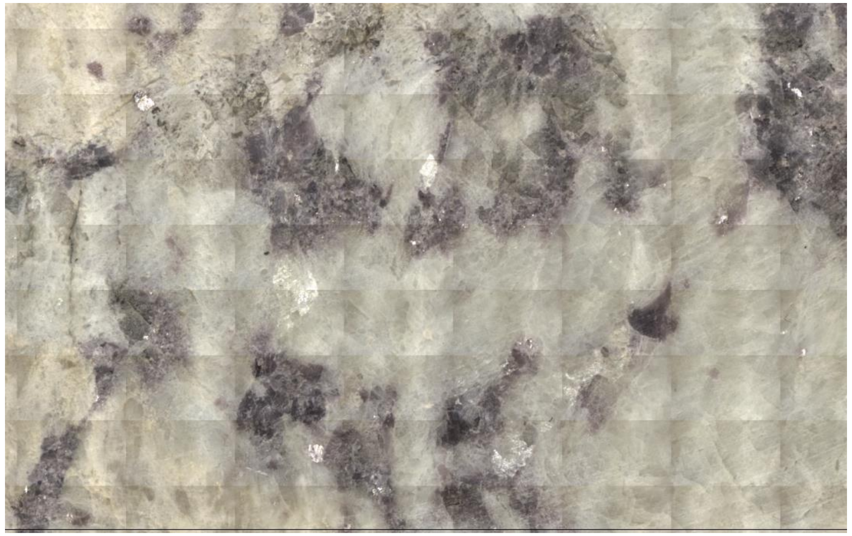
Li-Pegmatite from Portugal:
AMICS: Mineralogy

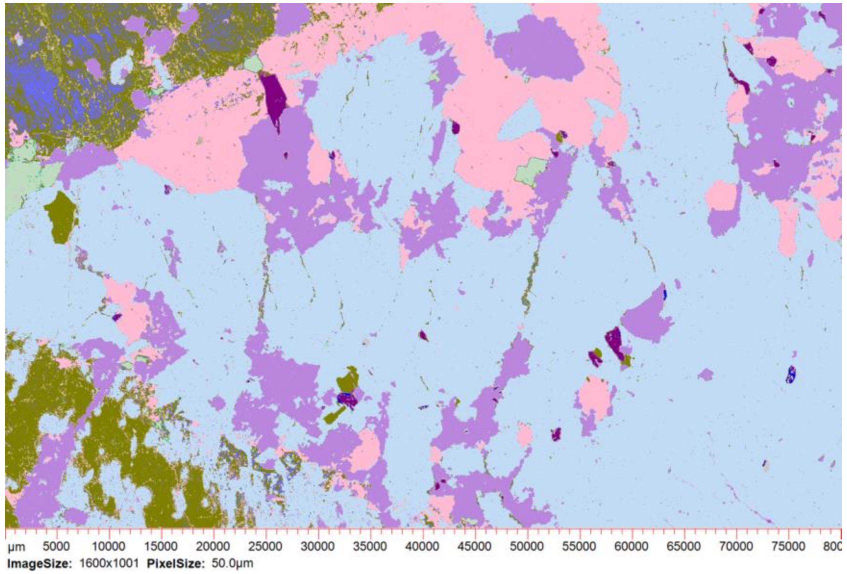
Sample Description: Pegmatite from Portugal



- Eucryptite
- Spodumene
- Petalite
- Lepidolite
- Zinnwaldite
- Amblygonite
- Montbrasite
- Ferrisicklerite
- Lithiophilite
- Muscovite
- Sanidine
- Albite
- Apatite
- Quartz
- Zircon
- Perhamite
- Topaz
- Others

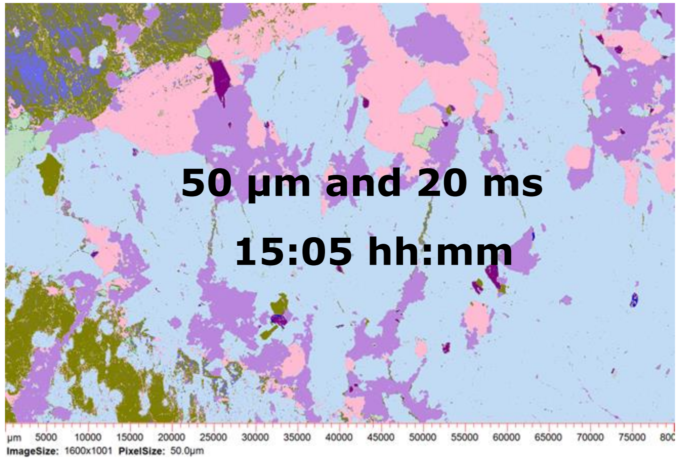
Optical Image

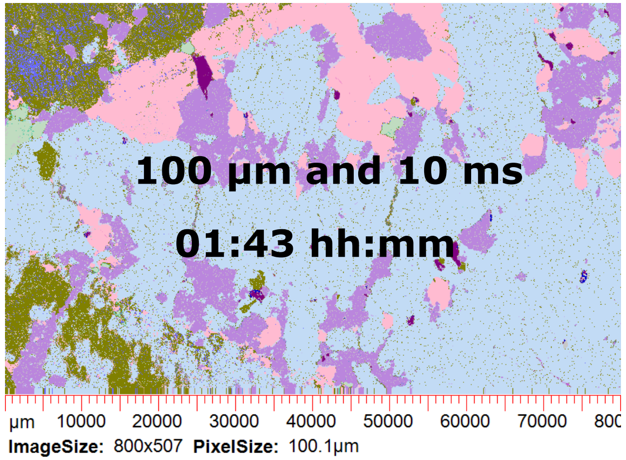


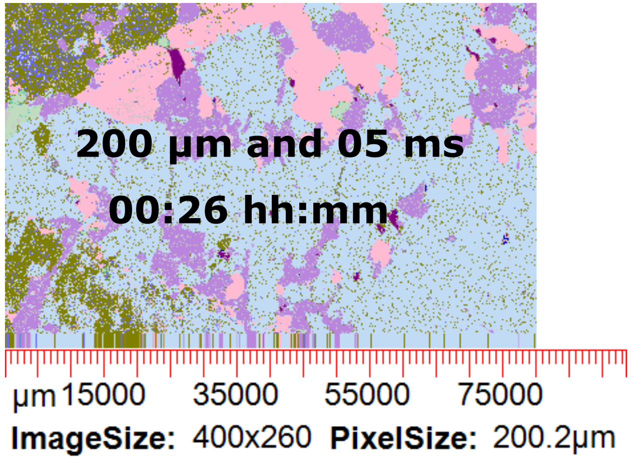


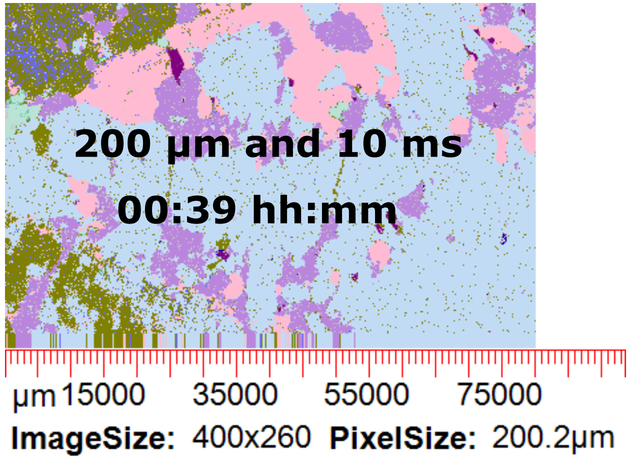
Total X-ray Intensity Map

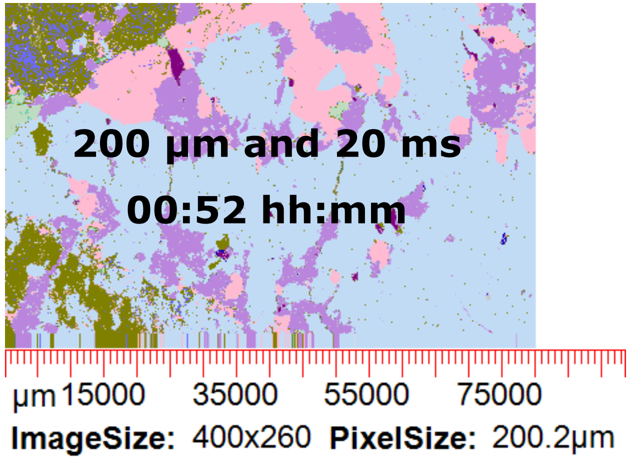
Li-Pegmatite from Portugal
AMICS: Modal Mineralogy Comparison











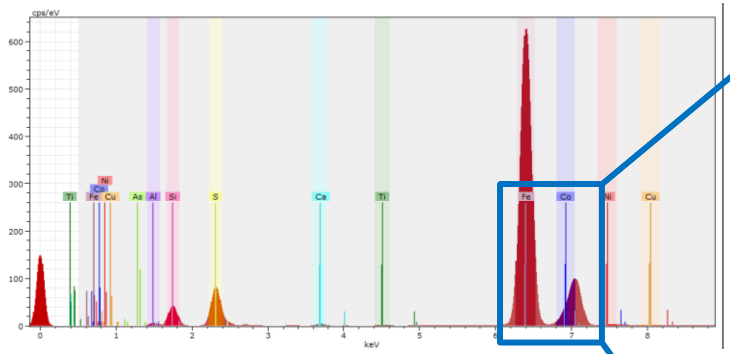
Ferromanganese (Fe-Mn) Crusts:
AMICS: Modal Mineralogy Comparison

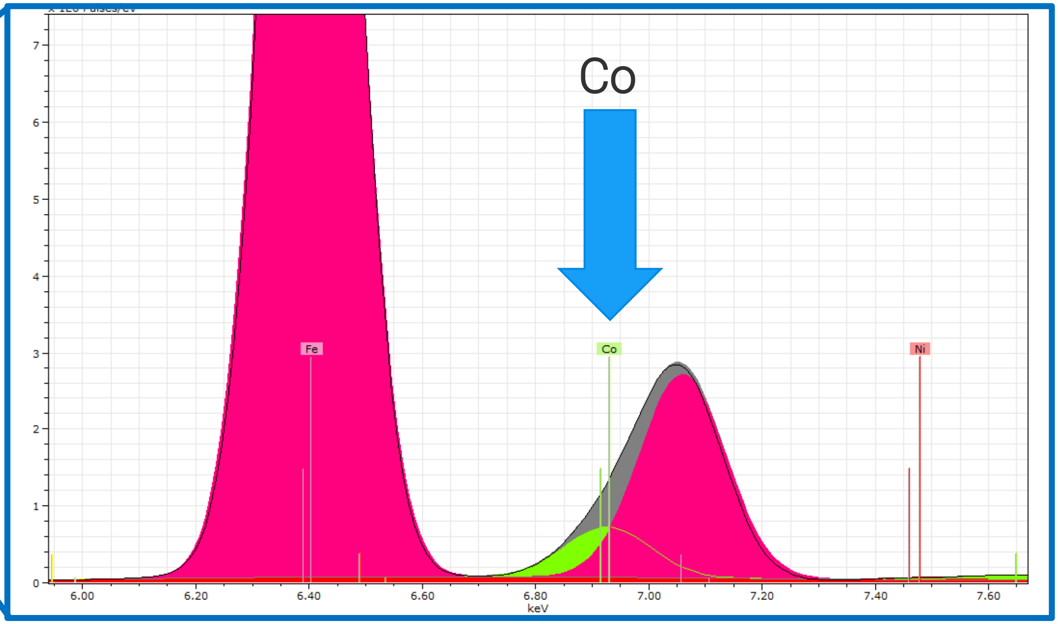
Pixel Size (um)	50	100	200	200	200
Dwell Time (ms)	20	10	20	10	5
Measurement Time (hh:mm)	15:05	01:43	00:52	00:39	00:26

Mineral	Wt%	Wt%	Wt%	Wt%	Wt%
Eucryptite	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
Spodumene	**10.1**	**10.5**	**10.6**	**10.5**	**9.5**
Petalite	**2.0**	**1.7**	**1.5**	**1.7**	**1.8**
Lepidolite	**15.6**	**14.5**	**14.4**	**14.2**	**13.4**
Amblygonite	**0.6**	**0.6**	**0.6**	**0.6**	**0.6**
Sanidine	0.1	0.2	0.2	0.2	0.2
Albite	57.9	59.3	59.4	59.7	61.5
Apatite	0.0	0.0	0.0	0.0	0.0
Quartz	12.7	12.3	12.3	12.3	12.2
Perhamite	0.0	0.0	0.0	0.0	0.0
Topaz	0.9	0.9	0.9	0.9	0.8
Others	0.0	0.0	0.0	0.0	0.0

Case Study 3 – Battery Elements: Cobalt (Co)
Co Concentration

Assay
Calculations
Comparison





Cobalt content at the depths of 417.55 - 418.05 m

Back Calculated (Mineralogical)

Co concentration → 9340 ppm

Total Spectrum (Whole Rock)

Co concentration → 10400 ppm

Cobalt content at the depths of 417.6 - 418.6 m:

Chemical assay

Co concentration → 9769.3 ppm

(reported by Mawson Oy)

Total Spectrum (Whole Rock)

Micro XRF: Co 1.04 wt. %