



Bruker Nano Analytics, Berlin, Germany Webinar



#### Presenters





Andrew Menzies, PhD

Sr. Applications Scientist Geology and Mining, Bruker Nano Analytics, Berlin, Germany



Roald Tagle, PhD

Sr. Applications Scientist, Bruker Nano Analytics, Berlin, Germany

#### Overview: Trace Elements and Mineralization



- The motivation and analytical challenge
- Short introduction to the analytical techniques applied in this work
- Advantages of combining analytical techniques
  - Case Study 1: Au (Gold)
  - Case Study 2: Co (Cobalt)
  - Sample size and analytical solution
  - Spectroscopical overlaps and analytical considerations
- Summary and Conclusion



#### The motivation and analytical challenge:

- In many economic deposits the element or mineral of interest is a trace component.
- The ability to identify or even extract these elements and minerals depends on how they
  occur.
- Such information is important to understand the genesis of the deposit as well as the mineral and metallurgical processes to yield the maximum recovery.
- The analytical questions and samples to be studied cover a wide range in terms of sample and relevant mineral sizes; in addition, occasional spectroscopical challenges such as element overlaps might hinder the evaluation.

The examples shown will highlight the difference between a trace element and trace mineral characterization as well as the multiple analytical tools for the ultimate project goal.

#### **Overview:** Analytical techniques

#### **Benchtop micro-XRF:**

Micro-XRF is spatially resolved X-ray fluorescence analysis. The high spatial resolution is achieved by using a focusing polycapillary x-ray optic. Generated fluorescent signal is analyzed using one or two SDDs.

#### Scanning electron microscope (SEM) and analytical add-on options

The SEM is a well-known analytical technique based on electron beam spatially resolved imaging and elemental composition analysis using Energy Dispersive Spectrometers (EDS). Additional options such as wavelength dispersive spectrometers (WDS) as well as focused X-ray beam sources have been added to complement the analytical capabilities.

#### Micro-XRF M4 TORNADO PLUS

#### SEM-EDS: QUANTAX Micro-XRF: XTrace SEM-WDS: XSense









### Overview: Micro-XRF as an analytical technique





#### No sample preparation

AusBr. Sn. recipie of the company of

Information from the depth of the sample

Trace element sensitive

Main analytical advantages of micro-XRF



Reference samples free and standard supported quantify-cation options

#### Micro-XRF M4 TORNADO PLUS



#### Micro-XRF: XTrace



# Analytical differences:

- M4 TORNADO PLUS as a benchtop instrument allows faster scan of lager samples and heavier sample (up to 30 cm and 7 kg) at higher resolution
- XTrace as and ad-on techniques allows to combine the advantages of micro-XRF with the associated SEM options (high spatial resolution of the E-Beam and resolution of the WDS)

### Overview: Scanning Electron Microscopy (SEM) and analytical options

#### Analytical advantages of SEM-EDS and SEM-WDS relevant for this work



**SEM-EDS-WDS:** Analysis based on the sample interaction with an electron beam source from the SEM and the resultant X-rays that are detected using either and SDD or and WDS.

\* For 121 eV for Mn Ka (equivalent to 73 eV for a Si Ka), \*\* for Si Ka

#### SEM-EDX: QUANTAX

BRUKER





SEM and analytical options: Electron and Photon Excitation for micro-XRF and EDS/WDS





#### Analytical Parameters and Conditions SEM-EDS vs. SEM-WDS vs. micro XRF



Demonstern	EDS: E-beam	WDS: E-beam	Micro-XRF	
Parameter	(SEM-EDS)	(SEM-WDS)	(SEM-XRF-EDS or benchtop)	
Ø: few µm		Ø: few µm	Ø: 15-30 μm	
Analyzed Volume	Information depth: µm;	Information depth: µm;	Information depth: µm to mm;	
	(depending primarily on electron energy)	(depending primarily on electron energy)	(depending on analysed element and matrix)	
Detectable Elements	Atomic number $Z \ge 4$ (beryllium)	Atomic number $Z \ge 4$ (beryllium)	Atomic number $Z \ge 6$ (carbon)	
Energy range	K- L –M – Lines ( up to 20 keV)	70 eV – 3.6 keV (L- M- Lines)	K- L –M – Lines ( up to 40 keV)	
Concentration Range	Down to 1000 ppm	Down to 100 ppm	Down to 5 ppm	
Quantification	Standard less and Standard based	Standard based	Standard less and standard based	
Data collection	Simultaneously	Sequentially	Simultaneously	
Sample Preparation	Sample needs to be electrically conductive (commonly carbon-coated), polishing required	Sample needs to be electrically conductive (commonly carbon-coated), polishing required	Electrical Conductivity not required, samples doesn 't need to be polished	
			5 to 10 cm (depends on SEM)	
Sample size / weight	Usually 5 to 10 cm (depends on SEM)	Usually 5 to 10 cm (depends on SEM)	up to 30 cm and 7 kg for benchtop instrument	
Spectroscopic resolution	Down to 121 eV for Mn Ka	~ 4 eV for Si Ka	better than 145 eV for Mn Ka (depending of detector even down to 121 eV)	

# Overview: Characterization Workflow of a multiscale approach





#### Micro-XRF M4 TORNADO PLUS



#### SEM-EDS-Micro-XRF-WDS



Butcher AR (2020) Upscaling of 2D mineralogical information to 3D volumes for geoscience applications using a multi-scale, multi-modal and multi-dimensional approach. *EMAS 2019*, *Conference Proceedings Volume, Trondheim*, 19-23 May 2019.

Trace Elements and Mineralization: Case Study 1 – Gold (Au)



#### Analyzing Large Samples: Drill Core (Micro-XRF)

#### Overview: Analysis for Gold

Gold can occur as a native element (mineral) or as high concentrations in a mineral (electrum, calaverite). Gold can also occur as a trace element in the structure of other minerals, for example **arsenopyrite**.

Electrum: Au = 70 to 95 wt%

#### Arsenopyrite: Au = 50 ppm (0.005 wt%)

For example: if a sample has 58 ppm

If the gold is in the form of Native Gold or Au-bearing mineral, then then elemental or mineralogical hyper-mapping (microXRF or SEM-EDS or AMICS) will detect the gold.

If the gold is included in arsenopyrite then it is unlikely that the gold will be detected.

Note: The arsenopyrite will be detected, however, point analysis with the microXRF would be required to determine if the arsenopyrite contains any gold.







# Case Study: Gold (Au) Drill Core/Rock Samples: Hyperspectral Datasets



In the following examples for different Au deposits we will show the ability to identify Gold-bearing minerals and to focus on obtaining the most information possible.



#### Micro-XRF images:

Top: optical mosaic, red box is the area of analysis (18 cm x 4 cm); Middle: combined elemental map of K (blue) and Au (orange) Bottom: AMICS mineralogy map



#### Case Study 1: Gold (Au) Analysis of Drill Core: Elemental Maps





#### Case Study 1: Gold (Au) Analysis of Drill Core: Elemental Maps





#### Case Study 1: Gold (Au) Analysis of Drill Core: Gold Identification





## Case Study 1: Gold (Au) Analysis of Drill Core: Gold Grains Identification





# Case Study 1: Gold (Au) Analysis of Drill Core: Gold Grains Analysis



Identified Elements in the "large" gold grain from Map 02

Grain Size: 300-400 µm

Showing the Au and Ag peaks.

Rh

Mineral → Electrum



# Case Study 1: Gold (Au) Gold Grains Analysis: Elemental Composition





Normalized FP		
quantification of the		
different gold grain in		
the sample.		

 $\overset{\frown}{\sim}$ 

Au 95.8	$\pm 0.7$ v	vt.	%
Ag 4.2	$\pm 0.7$ v	vt.	%

Spectrum	Ag	Au
Au-Map02-Grain01- 1.spx	4.3	95.7
Au-Map02-Grain01- 2.spx	4.2	95.8
Au-Map05-Grain01- 1.spx	3.3	96.7
Au-Map05-Grain01- 2.spx	2.2	97.8
Au-Map05-Grain02- 1.spx	3.8	96.2
Au-Map06-Grain01- 1.spx	4.3	95.7
Au-Map06-Grain01- 2.spx	4.7	95.3
Au-Map06-Grain02- 1.spx	3.8	96.2
Au-Map07-Grain01- 1.spx	4.9	95.1
Au-Map08-Grain01- 1.spx	4.7	95.3
Au-Map10-Grain01- 1.spx	4.6	95.4
Au-Map10-Grain02- 1.spx	4.7	95.3
Au-Map10-Grain03- 1.spx	4.3	95.7
Au-Map10-Grain04- 1.spx	4.5	95.5
Au-Map12-Grain01- 1.spx	4.1	95.9
Mean value:	4.2	95.8
Std. Abw.:	0.7	0.7
Std. Abw. rel. [%]:	16.5	0.7
Conf. interval:	0.2	0.2

#### Case Study 1: Gold (Au) Micro-XRF: High Resolution Map Area 02





Selected areas mapped at 5 micrometers pixel spacing



#### Automated Mineralogy (AMICS) Analysis of Drill Core











Trace Elements and Mineralization: Case Study 1 – Gold (Au)



#### Analyzing Large Samples: Rock Sample (Micro-XRF and SEM)

# Case Study 1: Gold (Au) Epithermal Gold



Mineral	Formula		
Native Gold	Au		
Native Silver	Ag		
<u>Sulphides</u>			
Pyrite	FeS <sub>2</sub>		
Chalcopyrite	CuFeS <sub>2</sub>		
Galena	PbS		
Sphalerite	ZnS		
Gangue Mineralogy			
Quartz	SiO <sub>2</sub>		
Adularia	KAISi <sub>3</sub> O <sub>8</sub>		





# SEM Micro-XRF Analysis: Epithermal Au Large Area Mapping



		and the second	<u>ينه المحمد المعمد المعمد المعمد المحمد ا</u>			Beam:	X-ray
	and the second			ata l	and the second second	High Voltage:	50 kV
State of the state	and the second	-11-1	1	+ 00 B	a free to	Anode Current:	600 μΑ
			Protocol and a second		- Carlos - A	Analytical Spacing:	100 µm
	and the second	Strate st				Dwell Time:	64000 µs (64 ms)
Contraction of the second of t			hen	i.a		Analytical Area:	4.5 x 4.5 cm
		war bet	an time			Total Analytical Time:	188 minutes
						Spot Size:	25 μm
	and the second	and the state			and the second	Interaction Depth:	10 – 100 µm
	and the second second	Al	Si	S	K	Host Rock Eler	ments: Al, Si, K
	And the second second	Fe	Cu	Zn	As	Mineralization:	S, Fe, Cu, Zn, As
		Se	Pb	Ag	Au	Economic Mine	eralization: Au, Ag, Se

Epithermal Gold-bearing rock sample from Karangahake, New Zealand

# Micro-XRF on SEM Identifying Gold (Au) in the Sample





Distinct and clear Au: Au-L<sub>β</sub> X-ray energy Lines.

Presence of Au in the sample is confirmed. But is it identified correctly?

#### Micro-XRF on SEM Identifying Gold (Au) in the Sample







Distinct and clear Au-La and Au-L $\beta$  X-ray energy Lines. Presence of Au in the sample confirmed.



### Micro-XRF on SEM (X-ray Beam) Identifying Gold (Au) in the Sample





Summed points within Grain – High Counts, clear and confirmed elemental peaks

#### Mining and Exploration Applications: Epithermal Gold



Micro-XRF hypermaps successfully identify the presence and location of Au Grains within the sample.

The sample can be analyzed with no carbon coat and at low vacuum.

 Follow-up analyses can be achieved by switching to e-beam SEM analyses (requires sample coating and high vacuum)

Or

• Selecting specific areas in the sample for further sample preparation prior to analyze

### Micro-XRF on SEM (X-ray Beam) Identifying Gold (Au) in the Sample





# SEM-EDS (e-beam) Identifying Gold (Au) in the Sample









Single Field 6 Large Gold Grain; Associated with Silver Other mineralization: Pyrite (FeS2),

Chalcopyrite (CuFeS2), Galena (PbS), Sphalerite (ZnS)

# SEM-EDS (e-beam) Identifying Gold (Au) in the Sample





Micro-XRF: Large Area Map





SEM-EDS: Detailed Small Area Maps

Single Field 5, 6 and 7 Large Gold (Au) Grains;

Associated with Silver – Mineralogy Electrum

Other mineralization: Pyrite (FeS2), Chalcopyrite (CuFeS2), Galena (PbS), Sphalerite (ZnS)





Trace Elements and Mineralization: Case Study 1 – Cobalt (Co)



Analyzing Large Samples: Drill Core (Micro-XRF)

# Case Study 2: Cobalt (Co) Battery Elements



#### In-situ non-destructive analysis Drill Core – 1 meter section



Centimeter-scale elemental mapping of cobalt mineralisation in drill hole PAL0163 by micro-XRF (directly onto a cut surface of a drill core), to reveal the spatial distribution of mineral species and their relationship to the micro-structural fabric.

#### Case Study 2: Cobalt (Co) Battery Relevant Elements



Ore mineralogy, petrogenesis and metallurgy

Centimeter-scale elemental mapping of cobalt mineralisation in drill hole PAL0163 by micro-XRF (directly onto a cut surface of a drill core), to reveal the spatial distribution of mineral species and their relationship to the microstructural fabric.



# Case Study 2: Cobalt (Co) Battery Elements



Identification of key elements of interest

Overlayed Mixed Element images can lead to mineral identification

High resolution scans can identify textures and associations



# Case Study 2: Cobalt (Co) Battery Elements



Identification of key elements of interest

Overlayed Mixed Element images can lead to mineral identification

High resolution scans can identify textures and associations



### Case Study 2: Cobalt (Co) Automated Mineralogy (AMICS)





Linnaeite (Co<sup>+2</sup>Co<sup>+3</sup><sub>2</sub>S<sub>4</sub>) Cobaltite (CoAsS)

# Case Study 2: Cobalt (Co) Automated Mineralogy (AMICS)





#### Case Study 2: Cobalt (Co) Grain Size Distribution - Linnaeite (Co<sub>3</sub>S<sub>4</sub>)





Cobaltite (CoAsS)



#### AMICS Mineralogy

### Case Study 2: Cobalt (Co) Grain Size Distribution - Linnaeite (Co<sub>3</sub>S<sub>4</sub>)





#### AMICS Mineralogy

# Case Study 2: Cobalt (Co) Co Concentration





#### Total Spectrum (Whole Rock)

Co concentration  $\rightarrow$  10400 ppm

Cobalt content at the depths of 417.6 - 418.6 m:

#### **Chemical assay**

```
Co concentration \rightarrow 9769.3 ppm
(reported by Mawson Oy)
```

Total Spectrum (Whole Rock) Micro XRF: Co 1.04 wt. %

## Case Study 2: Cobalt (Co) Identification of Co-in-pyrite











# Automated Mineralogy (AMICS): Micro-XRF vs SEM



**PAL0163** – 418.29m

418.29m 417.55m 418.05m Thin Section of Co-Ore showing Optical SEM **Micro-XRF** the Sulphide phases. Automated Mineralogy (AMICS) possible with both Micro-XRF and SEM. Principally Pyrrhotite and Cobaltite

### Automated Mineralogy (AMICS): Micro-XRF vs SEM





#### SEM-EDS Analysis: Co-in-Pyrite



Analysis of small (<100 μm) Co-bearing pyrite grain. Left: Individual Element intensity maps (BSE, Fe, S, and Co);



#### SEM-EDS Analysis: Co-in-Pyrite



Analysis of small (<100  $\mu$ m) Co-bearing pyrite grain.

**Left**: Individual Element intensity maps (BSE, Fe, S, and Co)



**Middle**: Combined elemental maps: Fe, S, and Co



#### Right: Quantified Co Map



#### SEM-EDS Analysis: Co-in-Pyrite



**Left**: Position of Line Scan on combined elemental maps: Fe, S, and Co





Benefits: Understanding crystal growth and compositional changes and thus petrological implications and mineralization.

Bottom Right: Zoom of Line Scan of Fe and Co

# SEM-EDS Analysis: Automated Mineralogy (AMICS)



Left: BSE Image



Pyrite-HighCo	
Pyrite-MedCo	
Pyrite-LowCo	
Pyrrhotite	
Other	

**Middle**: AMICS mineralogical map showing the different pyrite classifications based on Co concentrations



Benefits: Ability to add accurate Co deportment to metallurgical calculations

Pyrite-HighCo Area%: 21.44 #Particle: 1618

**Right**: Individual zones of pyrite grain based on Co-concentrations.

# SEM-EDS Analysis: Automated Mineralogy (AMICS)



**Left**: AMICS mineralogical map showing general mineral classifications. Note that Pyrite has a single classification.

Linnaeite Cobaltite Quartz Albite Orthoclase Biotite Chlorite Tremolite Pyrrhotite Pyrite Titanite Apatite Calcite Zircon Others Epoxy-Resin Rutile Pyrite-HighCo Pyrite-MedCo Pyrite-LowCo Pyrrhotite Other

**Right**: AMICS mineralogical map showing the different pyrite classifications based on Co concentrations.

Benefits: Ability to add accurate Co deportment to metallurgical calculations

# **SEM-WDS Analysis:** Trace Element Distribution in Pyrite





WDS allows to improve EDS Co identification, especially in Fe-bearing Better assessment of Co contained in



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





The garnet has: 40 wt% SiO2 and 20 wt% FeO.

The different spectrum profiles are obvious. For example, the ebeam 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.

# Introduction Terminology











**SEM-EDS:** Analysis based on the sample interaction with an electron beam source from the SEM and the resultant X-rays that are detected using an EDS (simultaneous element detection)

- SEM-WDS: Analysis based on the sample interaction with an electron beam source from the SEM and the resultant X-rays that are detected using a WDS (sequential element detection)
- SEM-XRF-EDS: Micro-XRF on SEM (XTrace): Analysis based on the sample interaction with an X-ray beam source from the Micro XRF attached to the SEM and the resultant X-rays that are detected using an EDS (simultaneous element detection)

#### Exiting with electrons



#### 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



+ ray tube



#### In-situ non-destructive Micro-XRF analysis: **Analytical Conditions**





50 micron pixel scan

Less than 9 hours total measurement

**Demonstration of** variable resolution

### In-situ non-destructive Micro-XRF analysis: Analytical Conditions: Pixel Spacing







# 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 area
- Ideal for Low kV or Beam Sensitive samples
- Minimal Sample Preparation Required, No charging effects
- Fast elemental X-ray mapping over large areas

#### **SEM-EDS-WDS Benefits:**

- Higher Beam Resolution
- Smaller sample interaction area
- Improved element resolution when using WDS

# Summary and Conclusions: Applications



- In many applications, e.g., geology and mining, the element or mineral of interest is a trace component. Thus, the ability to analytically identify them can be important but challenging.
- Combining micro-XRF and SEM analytical information (either as two sperate systems or as one combined system) greatly enhances the sample information, specifically in relation to sample size, analytical resolution, element detection, and sample preparation.
- Accordingly, the benefits of each system can be applied to relevant samples, improving analytical and project workflows.
- This includes both elemental and mineralogical information through the relevant software (ESPRIT, M4, or AMICS).

#### Acknowledgements







Tagle, R. Buegler, M. Reinhardt, F.

Dehaine, Q. Cook, N. Kuva, J. Sayab, M. Sorjonen-Ward, P. Raič, S. Molnar, F. Michaux, S.

Botha, P. Rollinson, G. Sardisco, L. Jones, S.

Lundström, M.

**Questions and Answers** 



#### **Are There Any Questions?**

Please type in the questions you might have in the Q&A box and press *Send*.



Innovation with Integrity