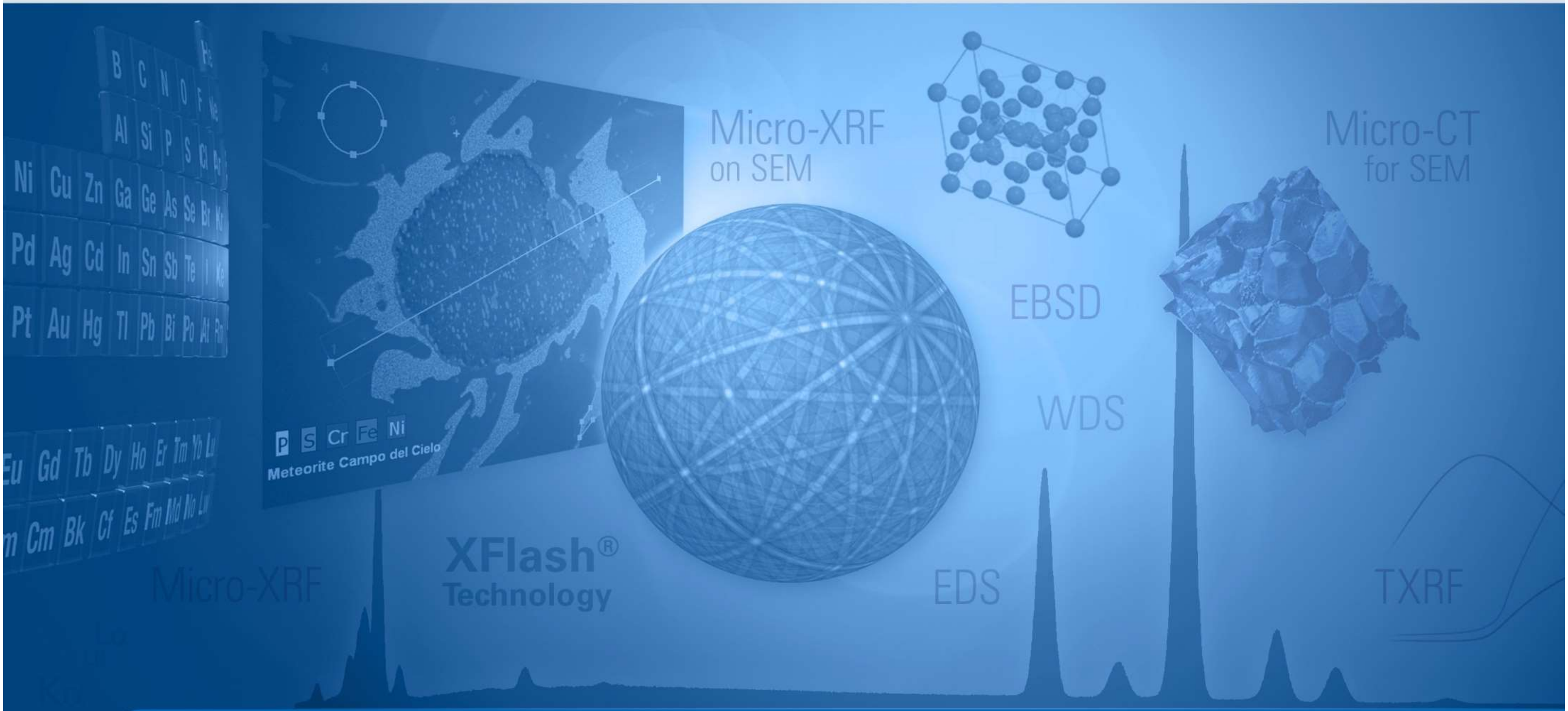
Analytical SEM Solutions for Geology

Exploring Microstructure and Chemistry in Minerals using EBSD and CL

Bruker Nano Analytics, Berlin, Germany

Webinar, September 10th, 2019



Innovation with Integrity

Presenters

- Toon Coenen, PhD

Product Manager,
DELMIC, Delft, NL

- Laurie Palasse, PhD

Senior Application Scientist,
Bruker Nano Analytics, Berlin, DE

- Sten Sturefelt

Application Specialist,
Hitachi High-Technologies Europe, Stockholm, SE

Analytical SEM Solutions for Geology

Overview of part 2

I – Cathodoluminescence for Geology

- CL process in rocks
- CL imaging of minerals

II – Advanced EBSD solution of mineralogical samples

- EBSD technique review
- Phase ID and discrimination with simultaneous EBSD/EDS measurement
- Advanced imaging with built-in ARGUS system

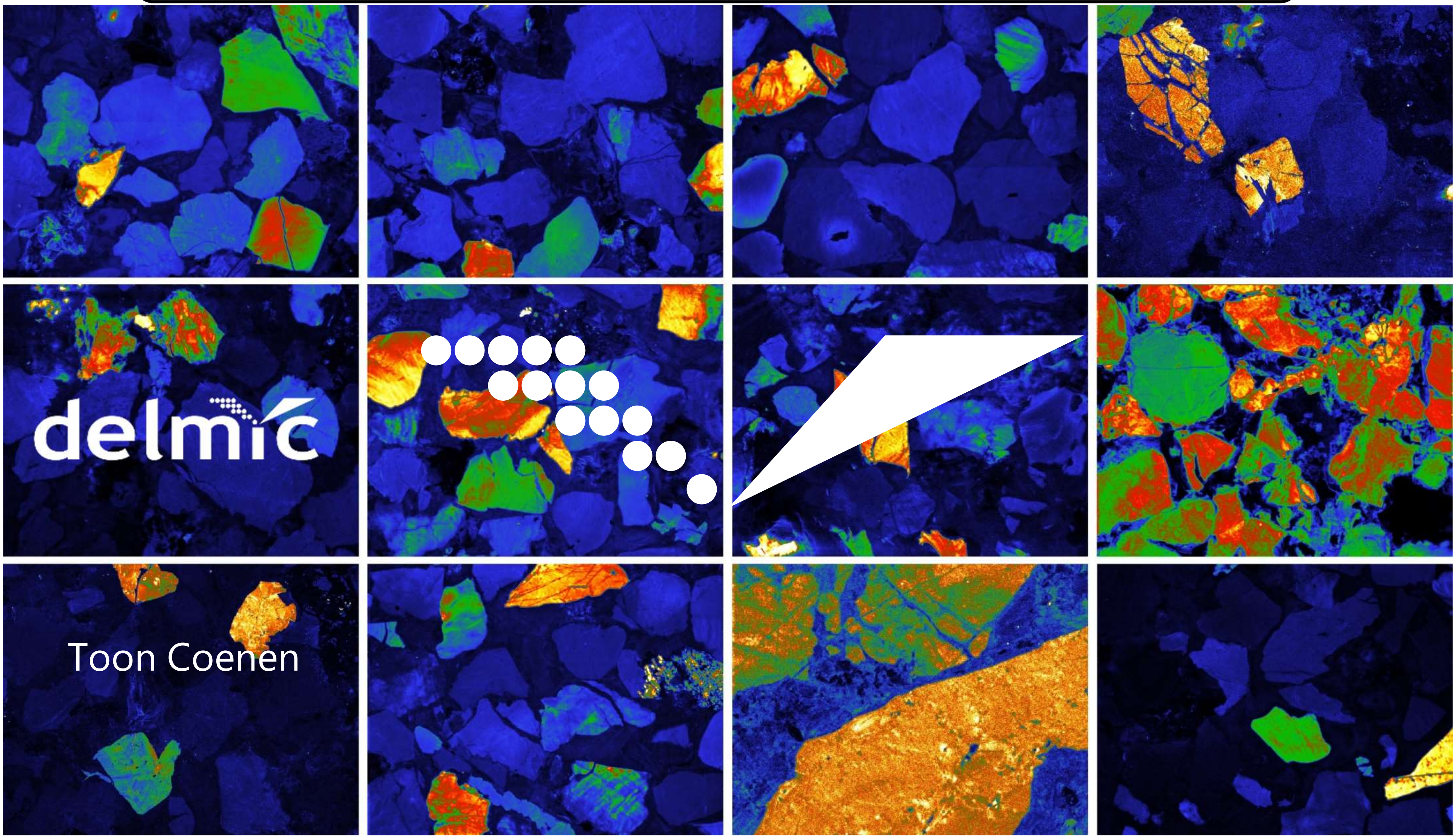
III – Sample preparation of minerals

- Broad Ion Beam Milling vs mechanical polishing
- Application examples

Q&A

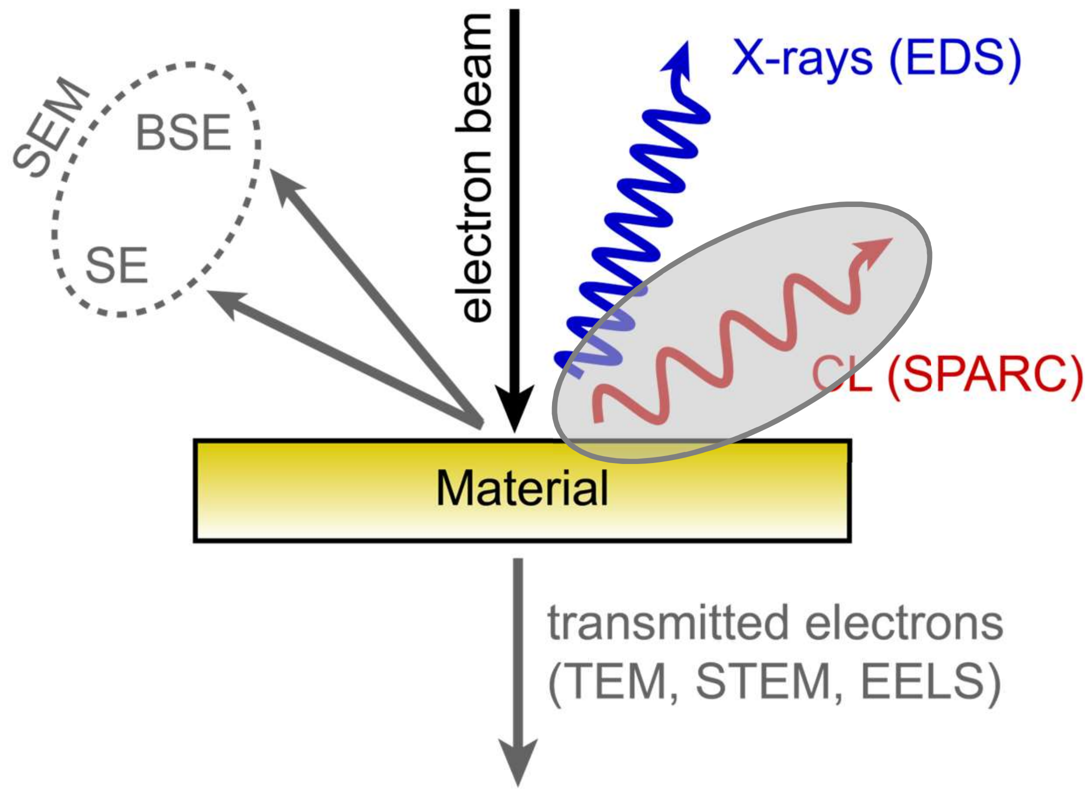
1 - Cathodoluminescence imaging for geology

Cathodoluminescence imaging for geology

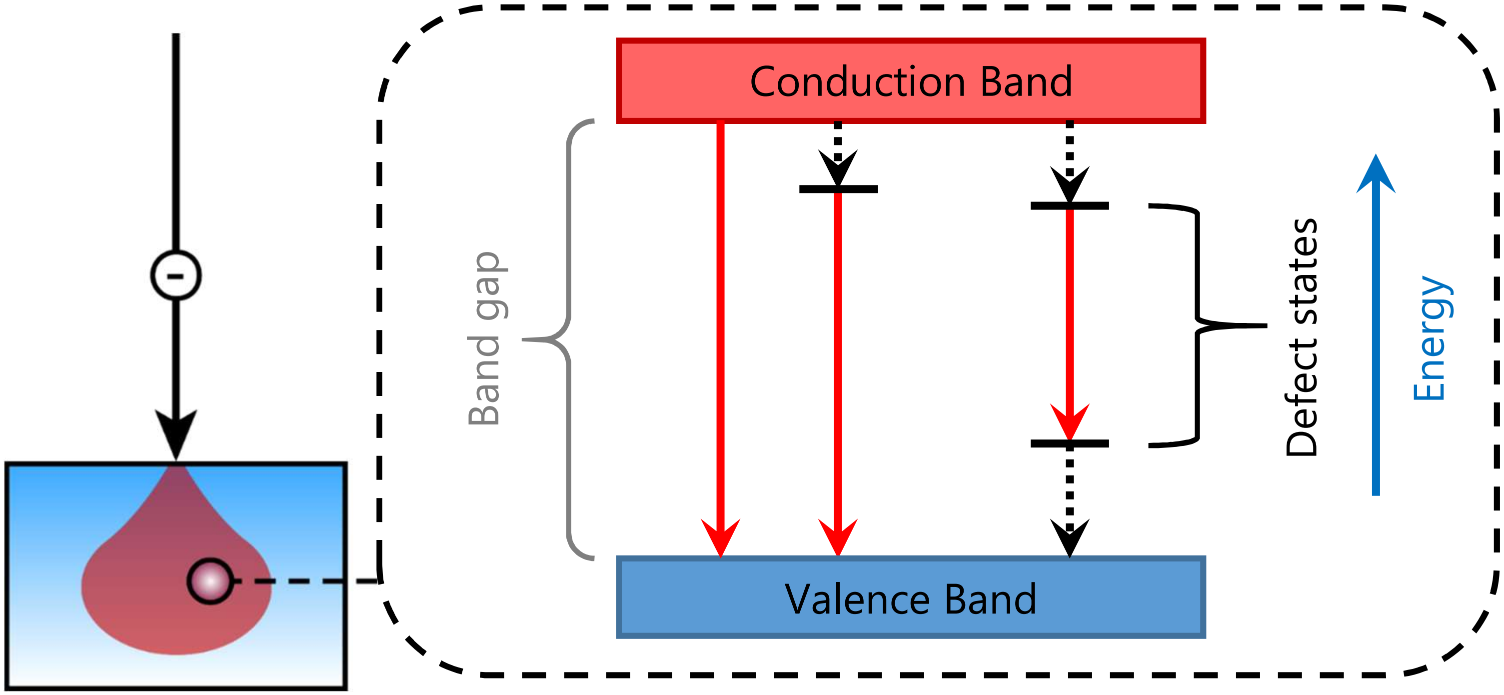


Electron beam excitation and light

Cathodoluminescence is the process whereby light (UV-VIS-IR) is generated when an electron beam hits a specimen.



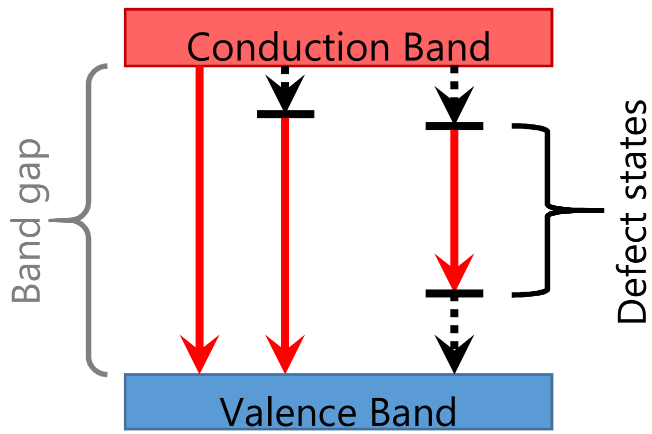
Cathodoluminescence process in rocks



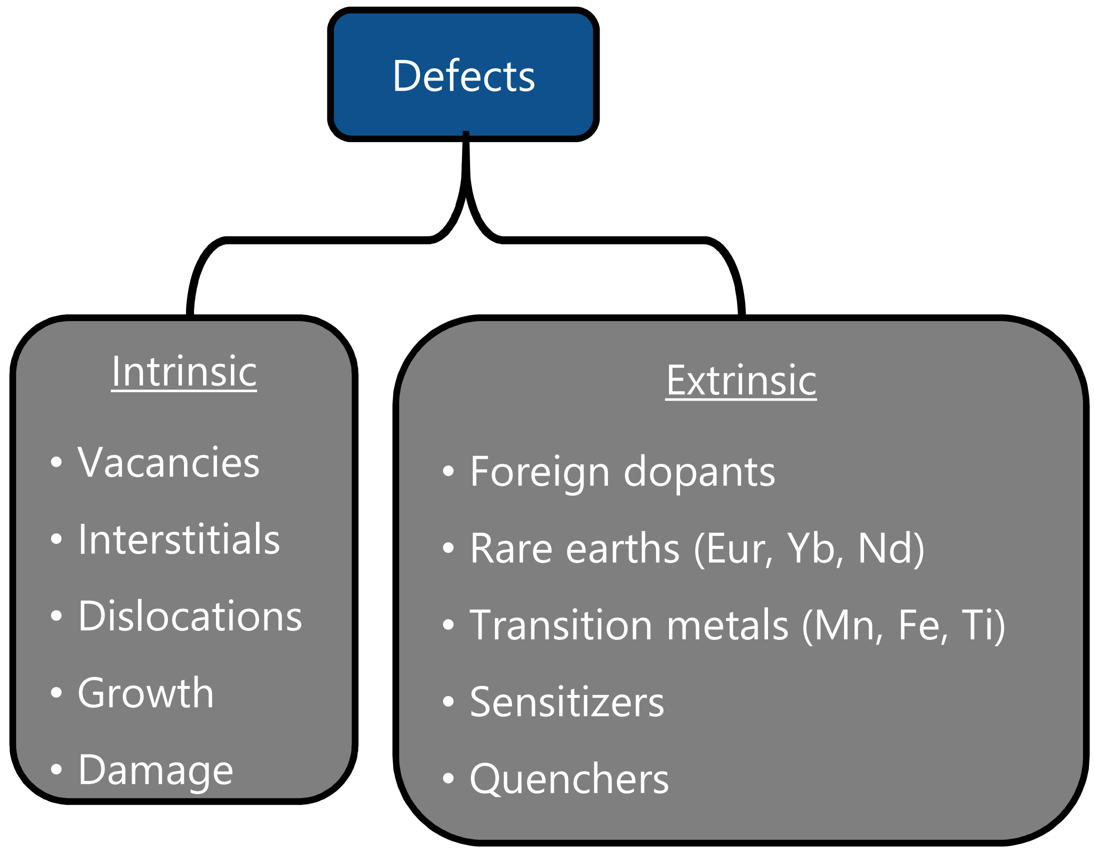
For a crystalline material, electrons in that material can only occupy certain energy states. Typically, (almost) all electrons reside in the valence band

- Rocks are typically insulators with wide band gaps between 5 - 15 eV (DUV-EUV)
- In CL we measure in the 0.8 – 6 eV range
- Defect states play an important role

Defect emission in CL



- There are many types of defects in rocks of which many have a distinct CL signature
- CL can be used to extract various types of information and gives a unique contrast, different from EM and X-ray images!



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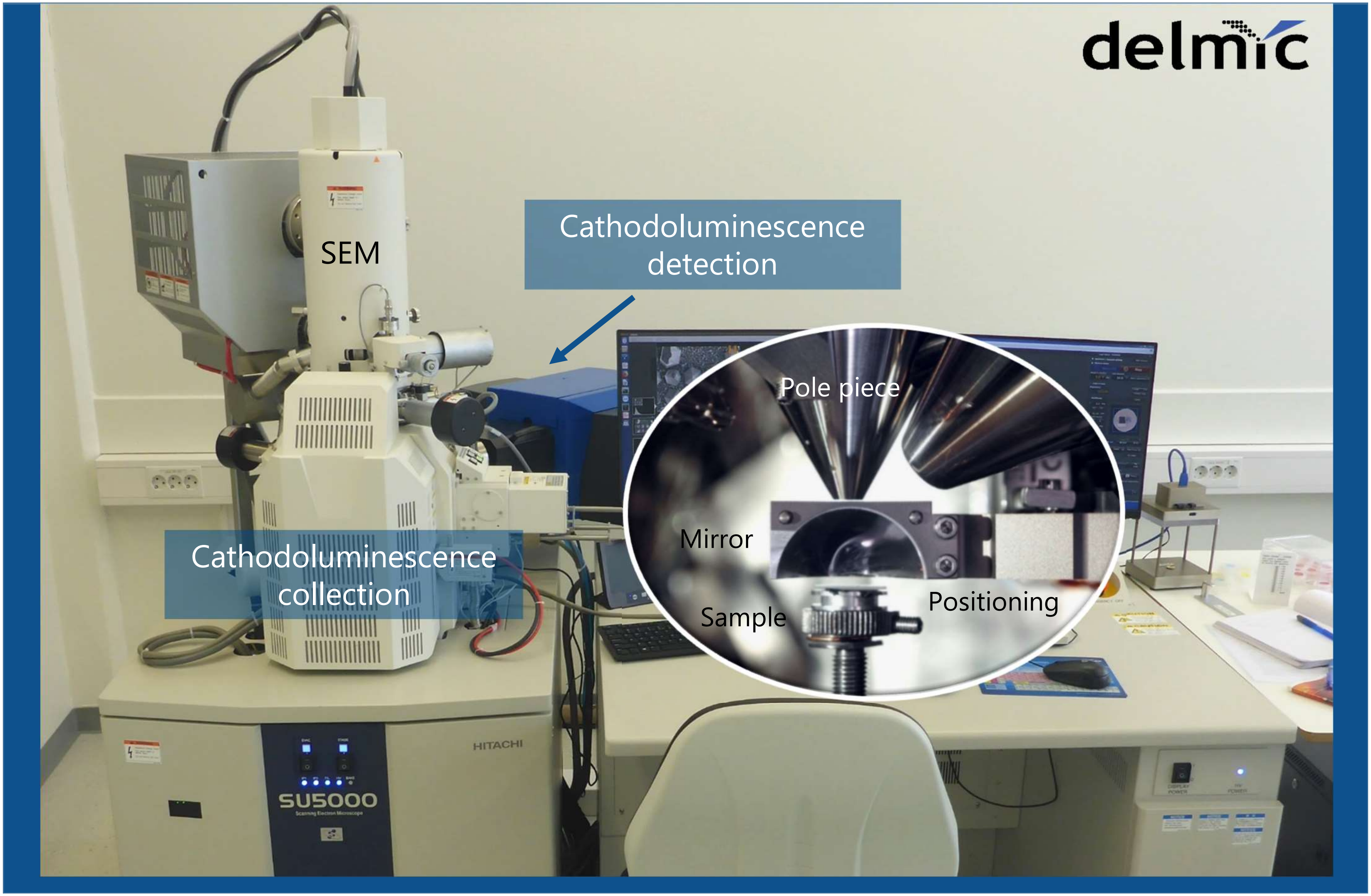
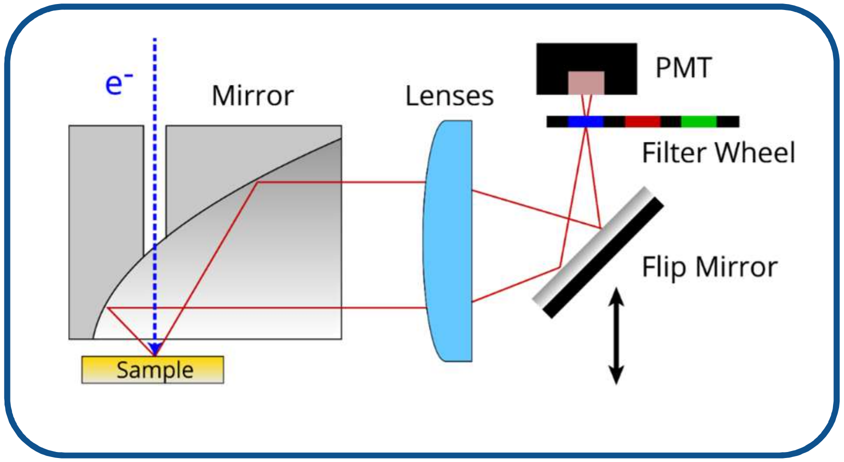
SPARC Cathodoluminescence system



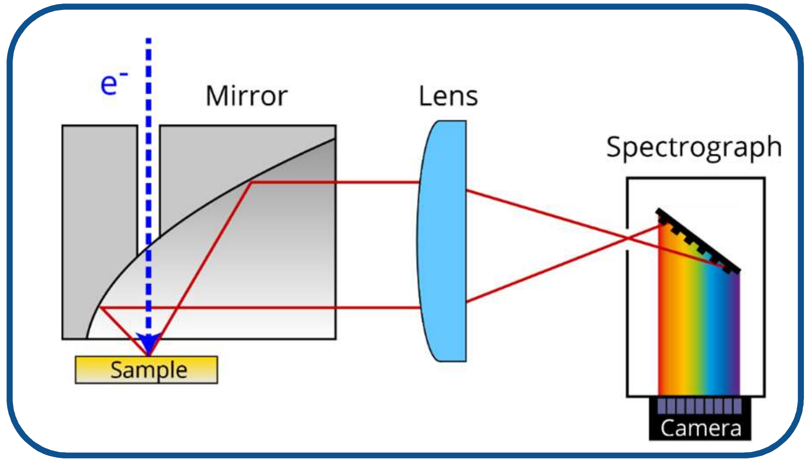
CL imaging modes

CL intensity mapping



- Measure CL intensity
- Short dwell times (10 - 100 µs) → video-rate imaging
- Coarse spectral filtering and RGB mapping

CL spectroscopy



- Measure CL spectrum
- Longer dwell times (10 - 1000 ms)
- Hyperspectral imaging with high spectral resolution

CL systems

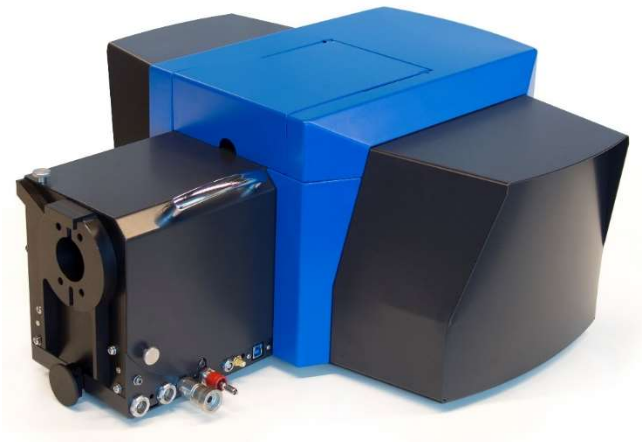
Jolt

Basic system for (RGB) intensity CL mapping

SPARC Compact

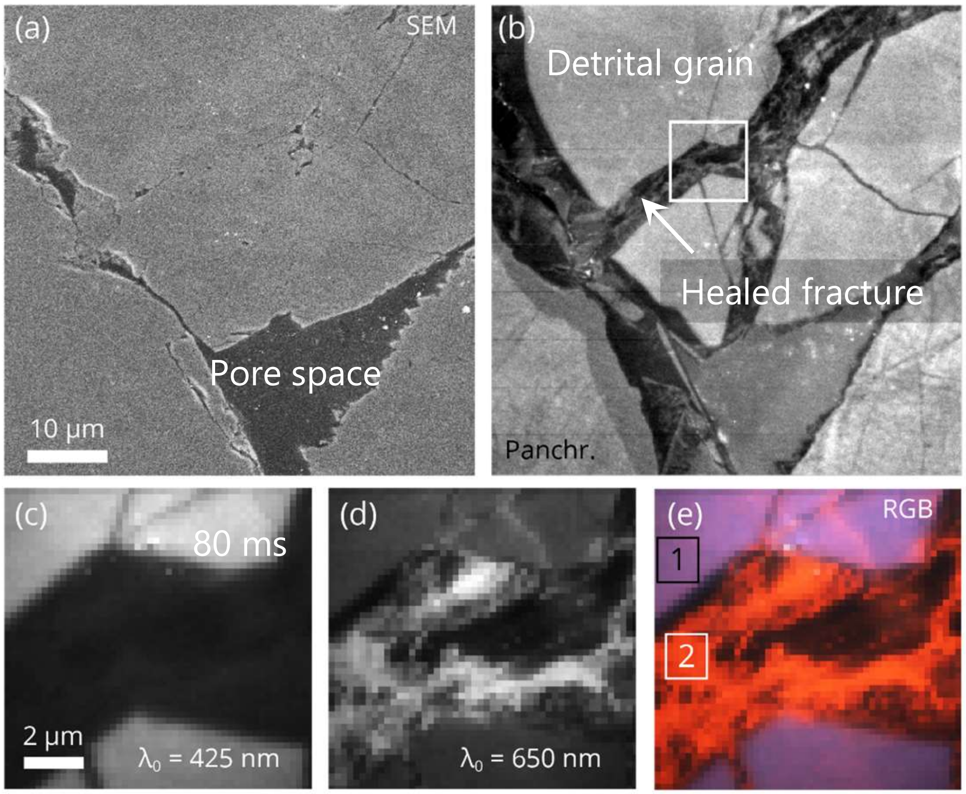
Compact CL system for high-performance (RGB) intensity CL mapping

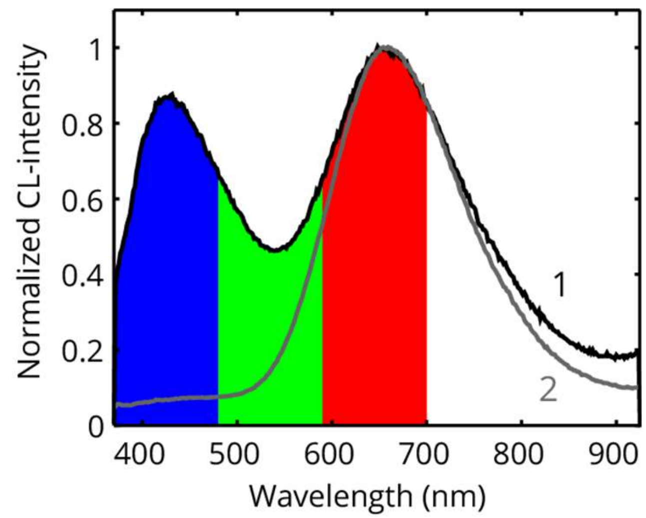
SPARC Spectral



High-performance intensity mapping and spectroscopy

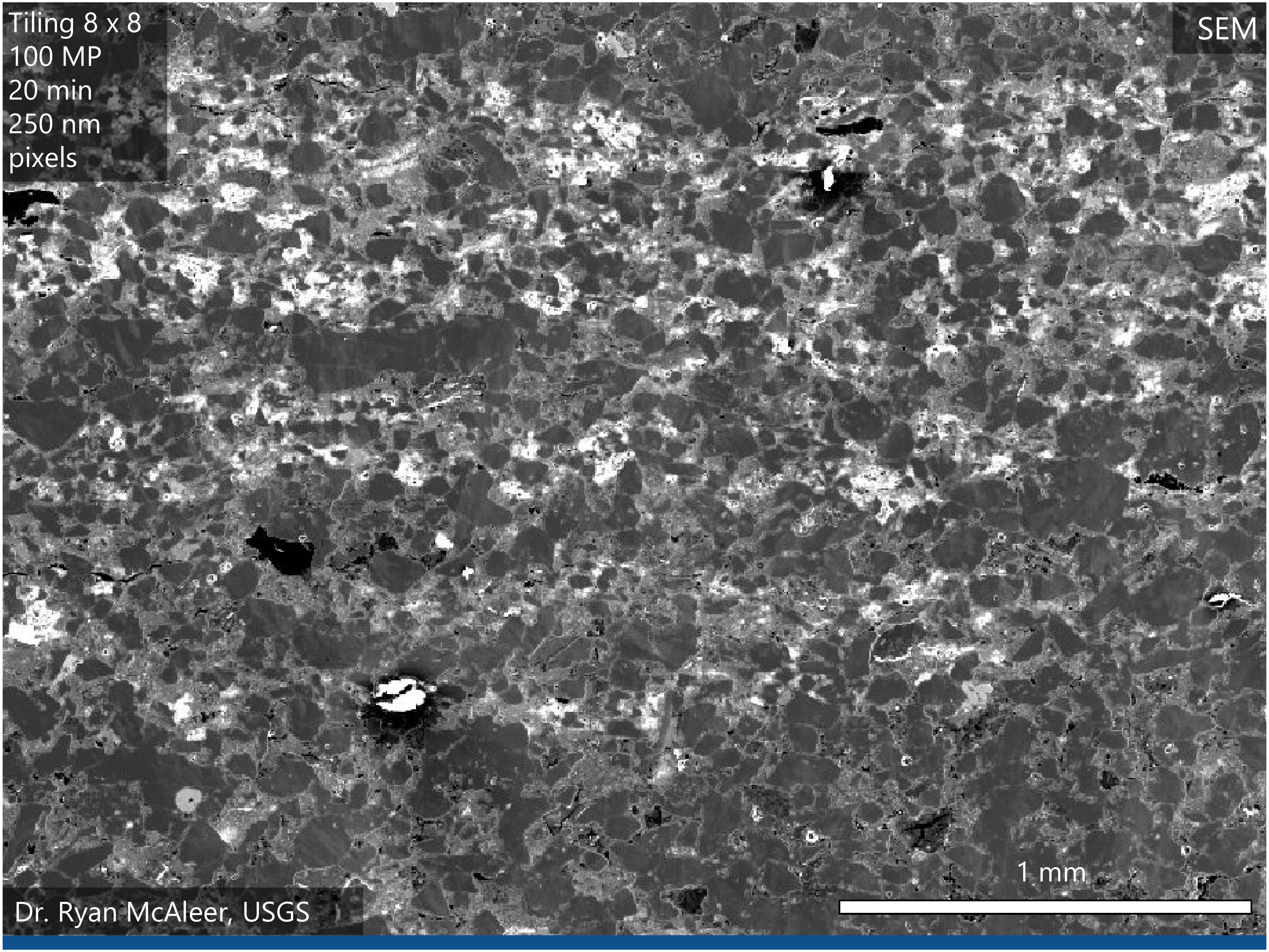
CL on quartz sandstone

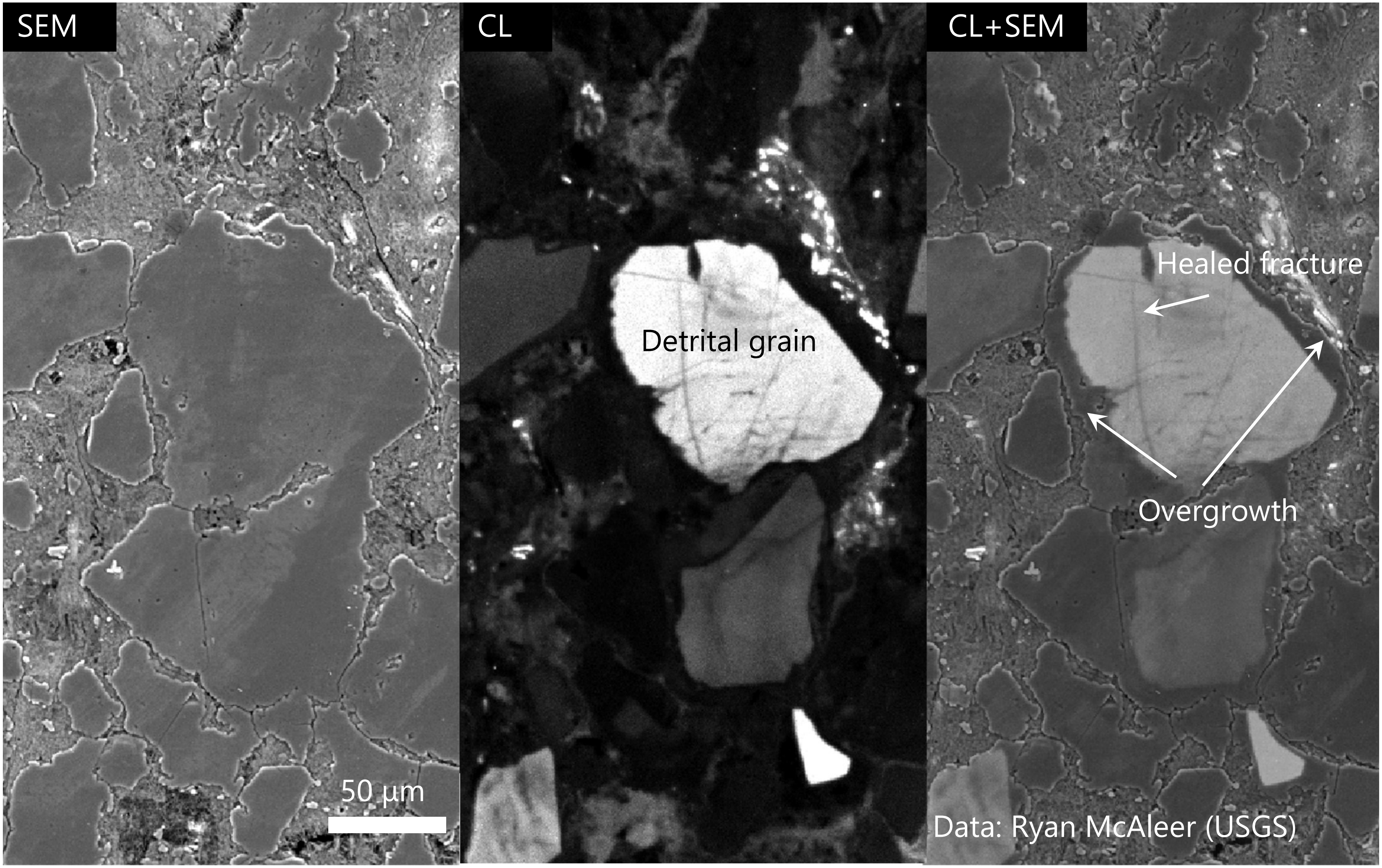




- Intrinsic defects dominate signal
- Hyperspectral imaging
- Cement versus detrital grain

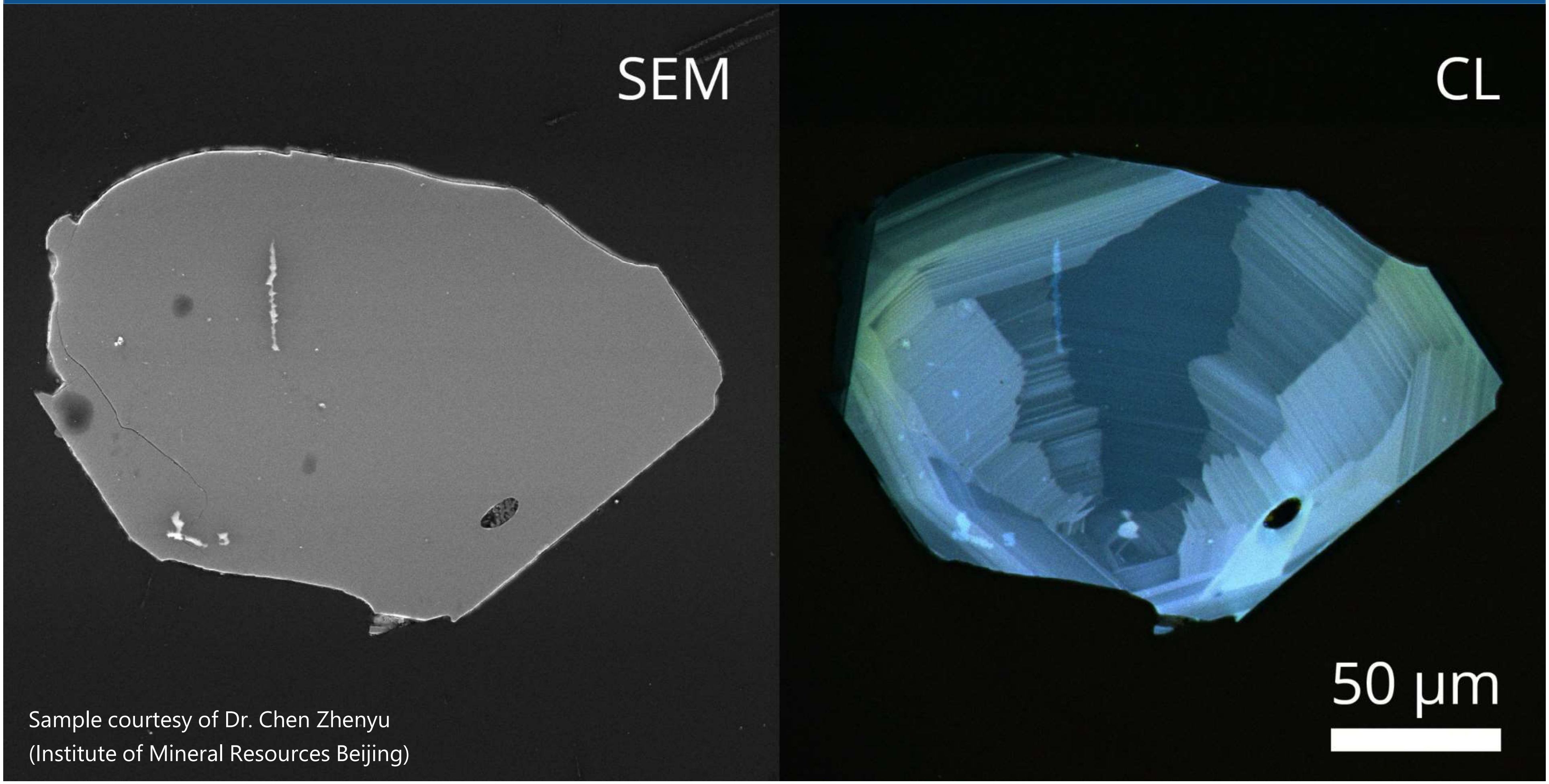
T. Coenen, whitepaper (2016)


Tiling 8 x 8
100 MP
20 min
250 nm
pixels
SEM
1 mm
Dr. Ryan McAleer, USGS



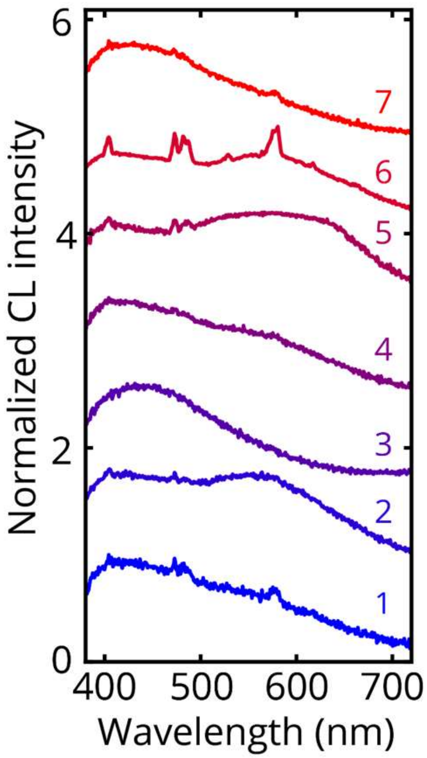
Combine CL and SEM data to reveal interesting sample features

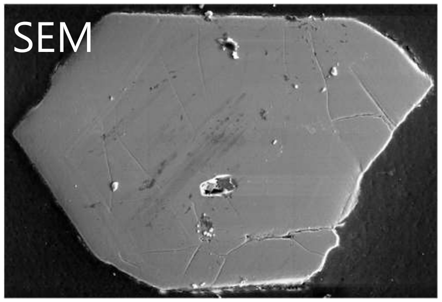
Microcharacterization of Zircons: Imaging zonation



Sample courtesy of Dr. Chen Zhenyu
(Institute of Mineral Resources Beijing)

Zircon spectroscopy





Sample: Dr. Changfu Fan
(Beijing Geonanalysis Co Ltd)

- Map spectral distribution over large crystal
- Observe spectral differences between bands
- REE and intrinsic defect emission

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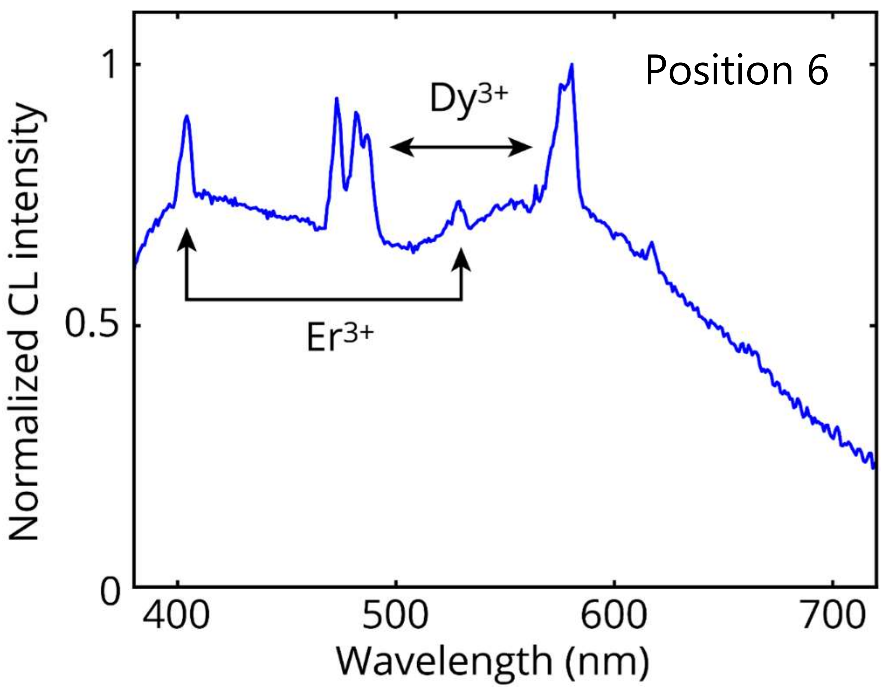
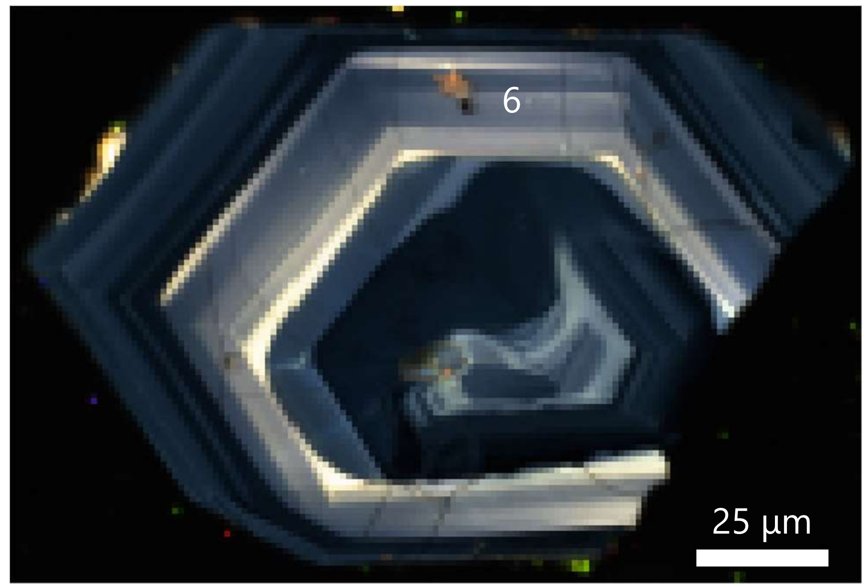
Zircon spectroscopy

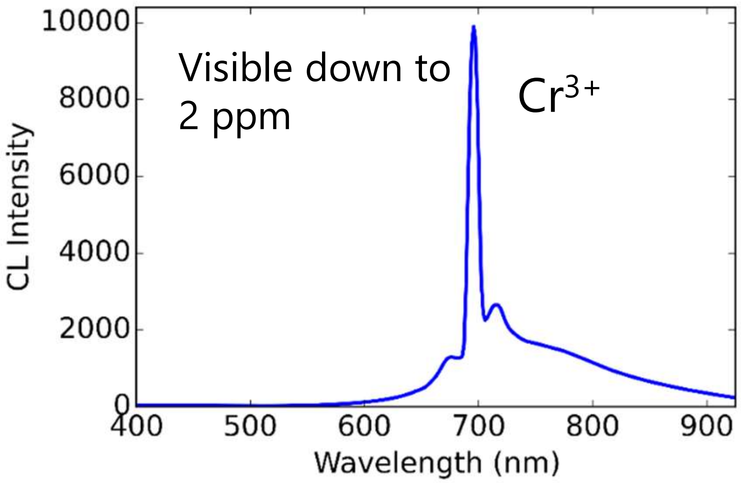


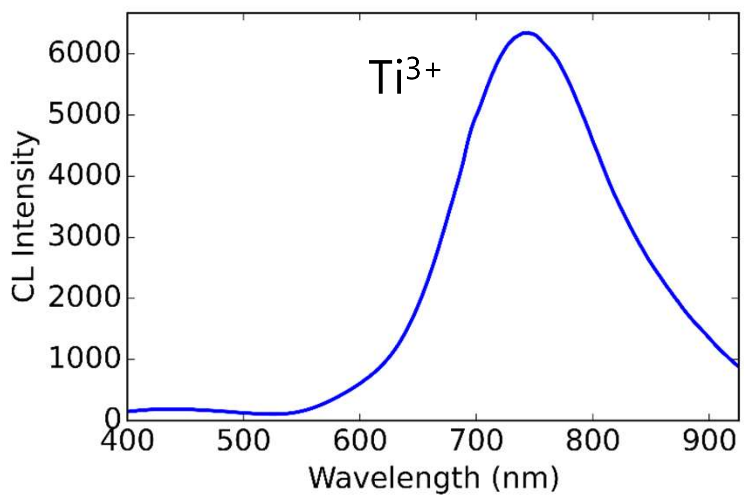


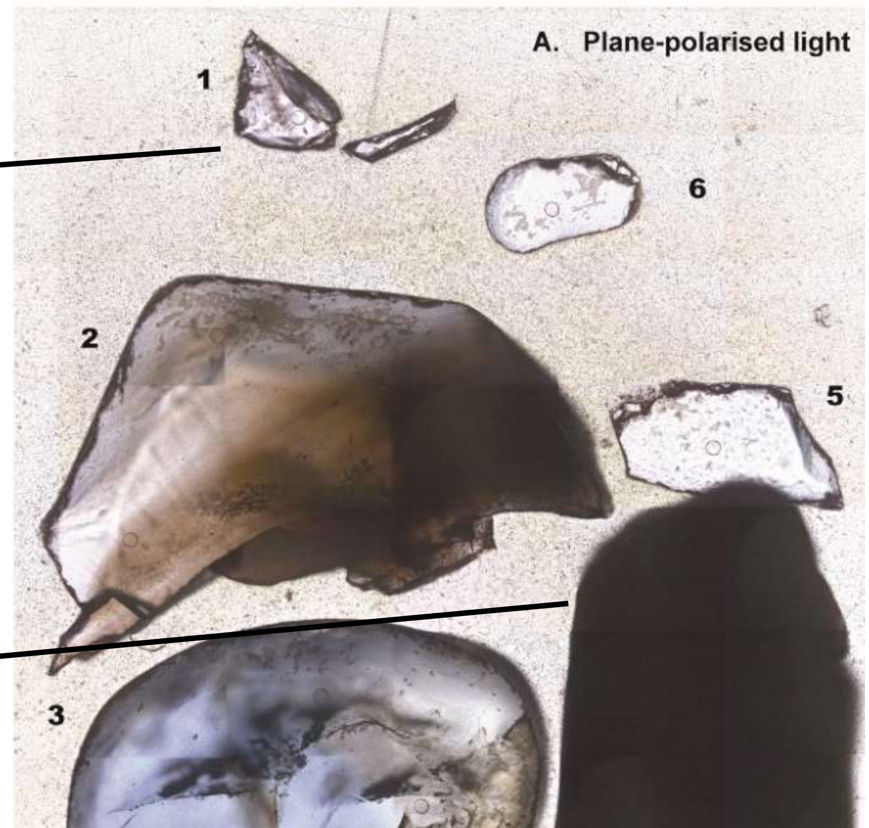
- Identify different REE species based on *4f* transition energies
- Very high sensitivity down to 10^{14} atoms/cm^3

➢ Carbonate
➢ Apatite
➢ Monazite

Sapphires





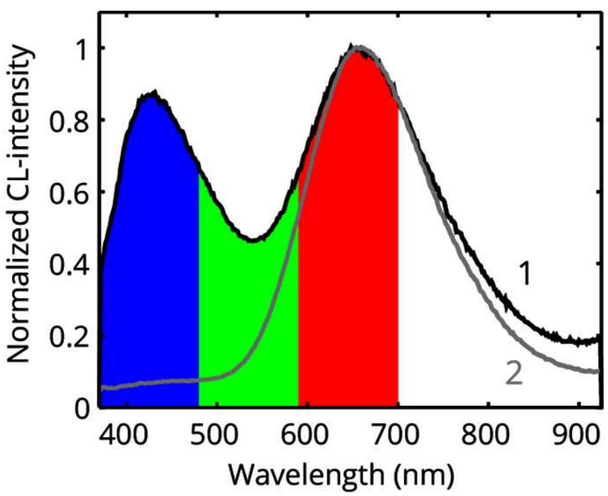


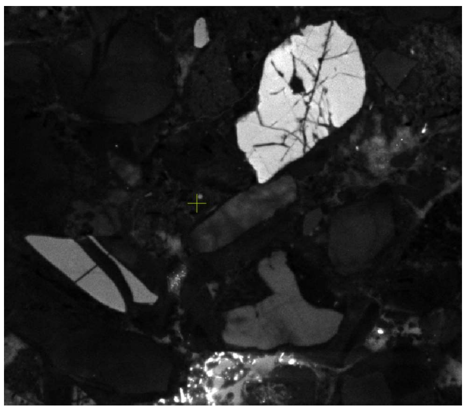
Sapphire luminescence is dominated by Cr (435 ppm) and Ti (3900 ppm) impurities as determined by LA-ICP-MS

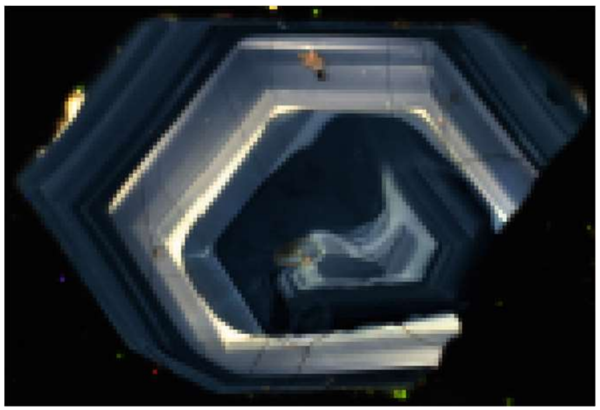
J. Wong *et al.* white paper (2018)

Conclusions

- CL presents a fast and powerful technique for microanalysis of rocks
- With current sensitivity and precision novel applications are within reach
- New CL approaches and techniques can broaden scope







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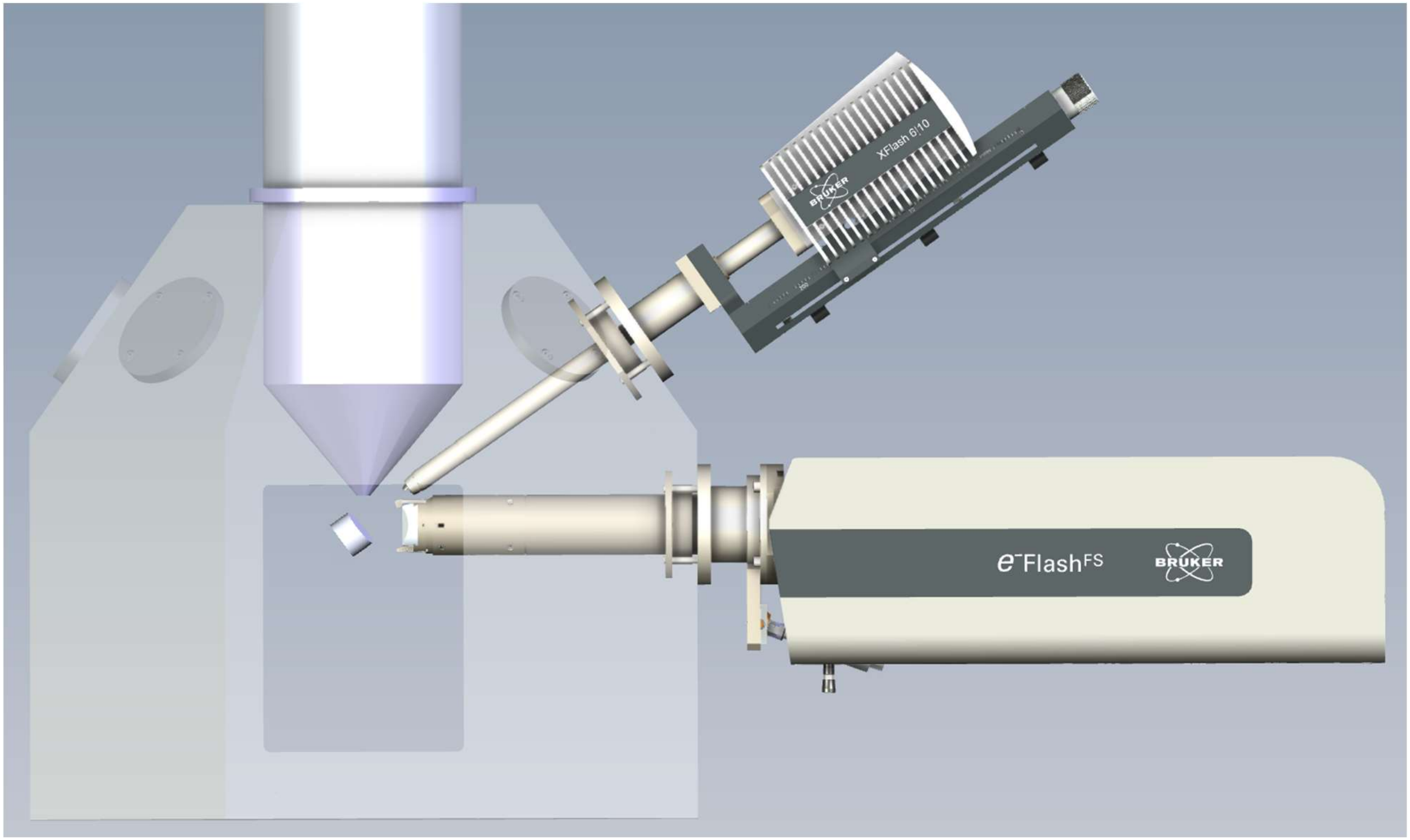
2 – Advanced EBSD solution for geology

Advanced characterization of mineralogical samples
outline

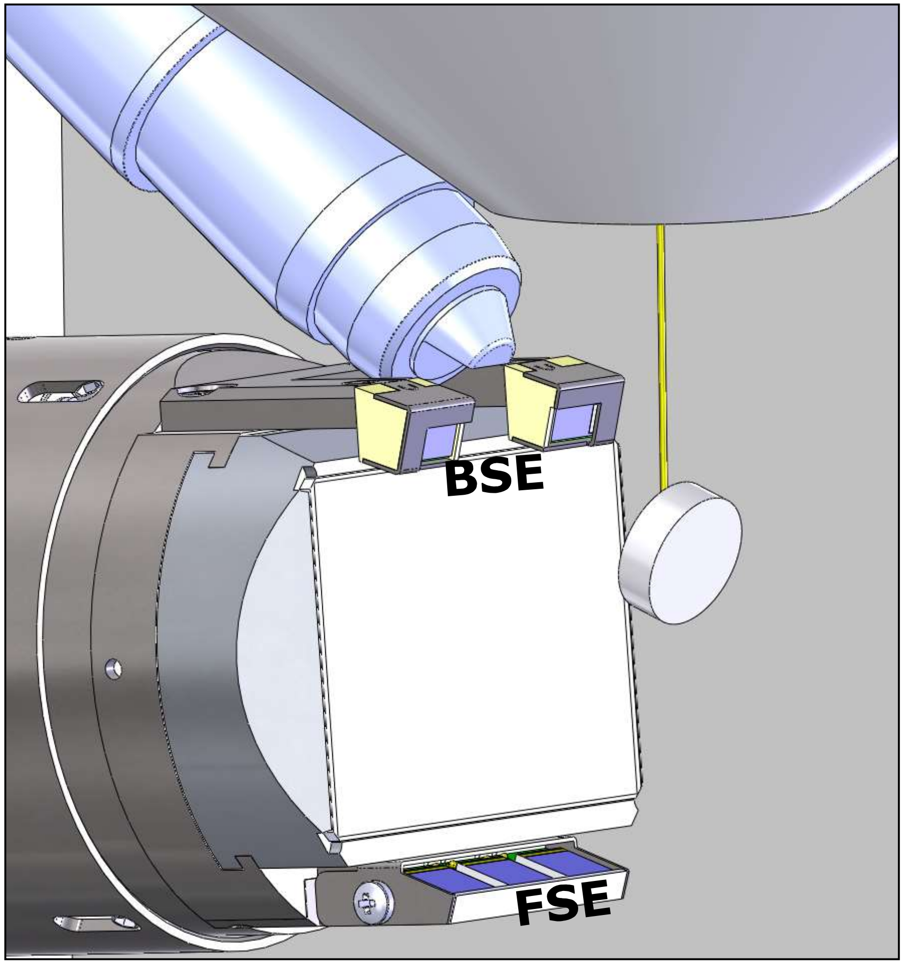
- EBSD setup
- Combined EBSD/EDS measurement
  - Advanced Phase Identification
  - Phase discrimination by EDS
- Advanced imaging with built-in ARGUS system
- Summary

Introduction
Experimental setup



Introduction

Combined EBSD/EDS measurement



Software features:

- One software platform to control both detectors and to perform all types of analysis possible
- Simultaneous EBSD/EDS acquisition of EBSP and full EDS spectrum
- Online/offline phase ID and discrimination between phases creating similar patterns

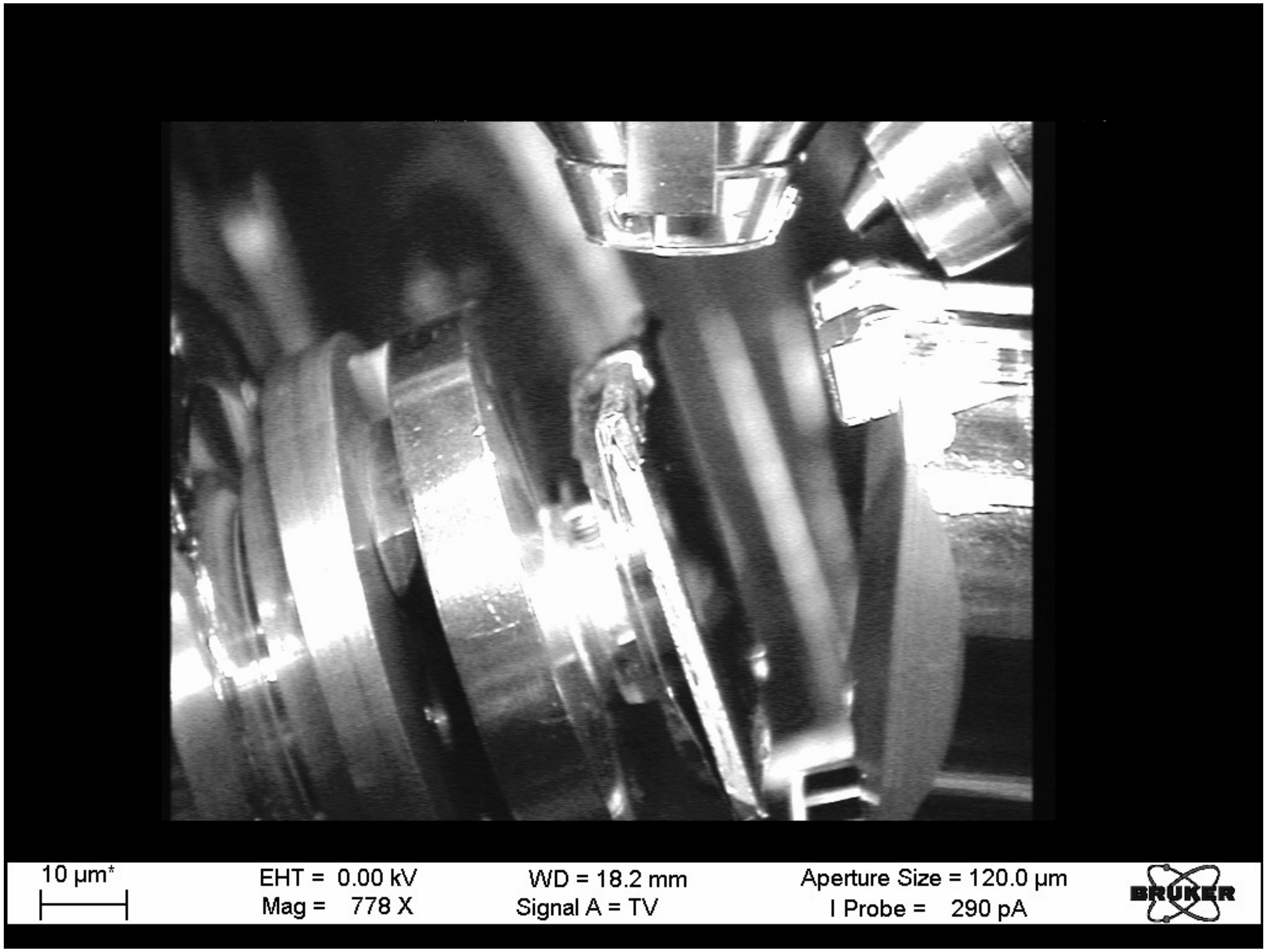
Hardware features:

Unique detector features for allowing data acquisition in optimized conditions:

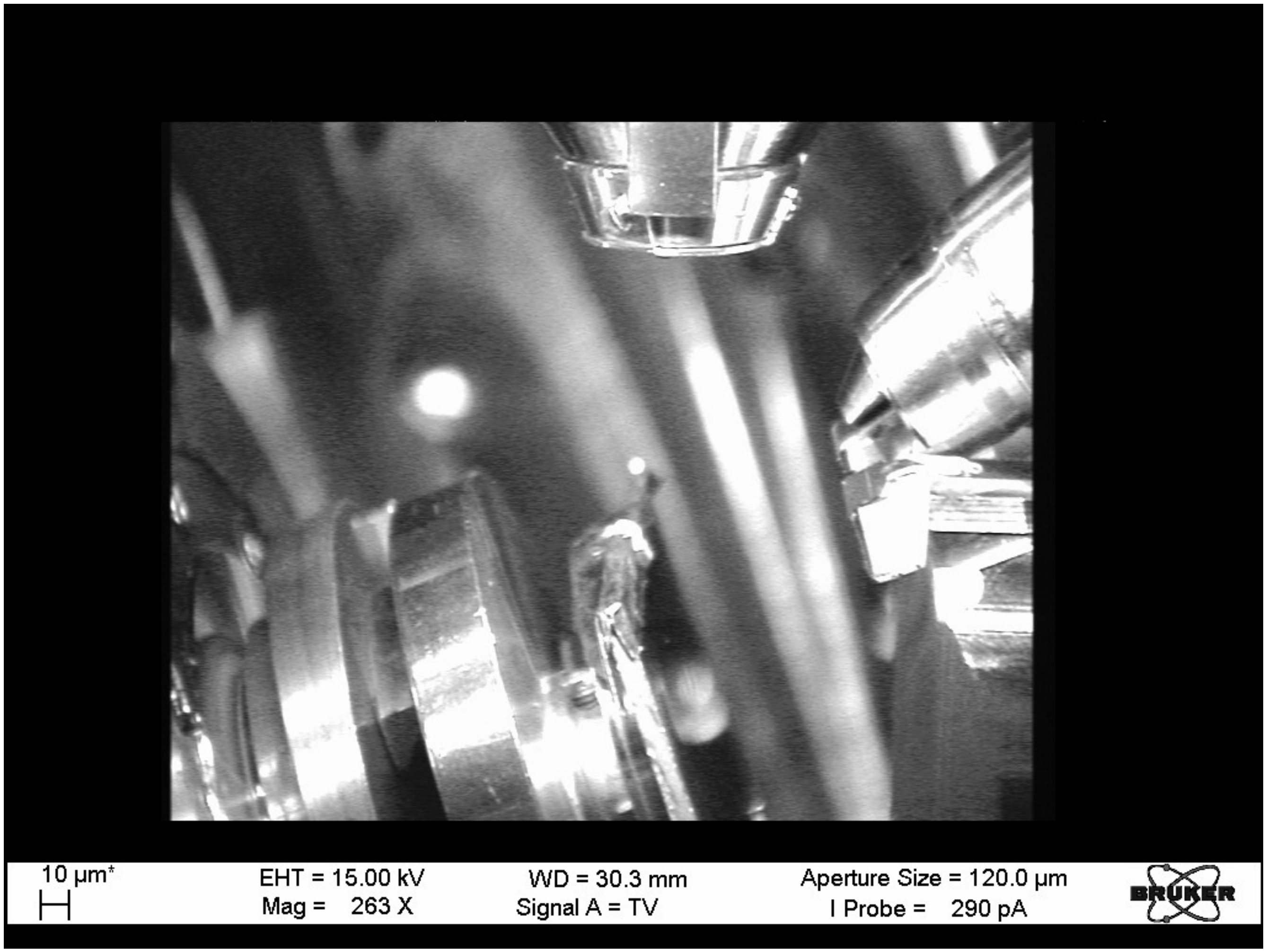
- In-situ EBSD detector tilt
- VZ-adapter for EDS detector tilt

Introduction

Measurement at short WD



Introduction
Measurement at long WD



Advanced characterization of mineralogical samples

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Phase identification

Conventional phase ID > *before launching measurement* ***keeps SEM busy***

- time consuming - manual setup
- inaccurate:

  based on BSE image – can miss phases

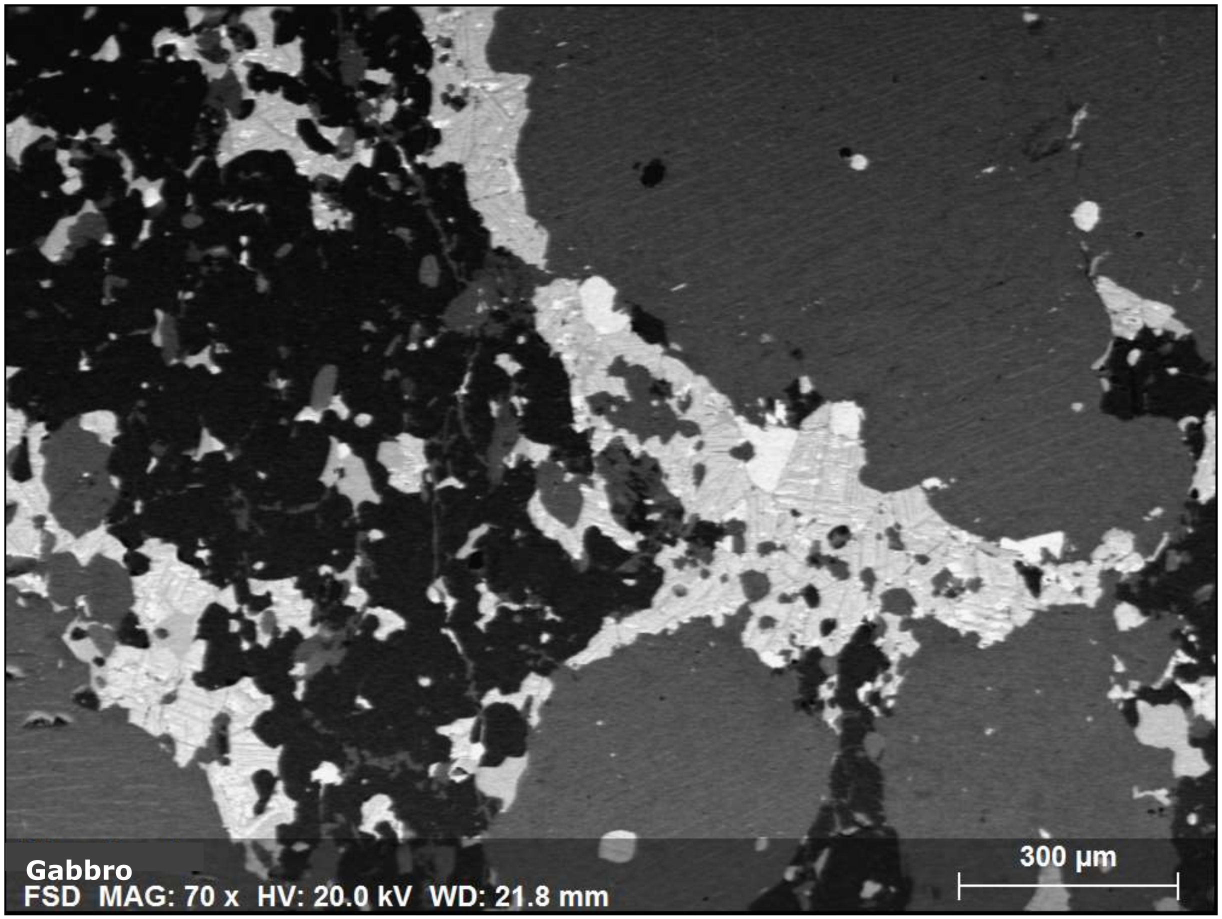
  using manually defined threshold – not best fitting phases

Advanced phase ID > *offline after measurement,* ***SEM is free***

- interactive (phase search, band detection, etc.)
- fast and automatic phase identification over thousands of candidates
- best fitting phase file is selected
- ultra fast reanalysis (>40 000 pps)

Advanced phase ID

Setup



Sample: oceanic gabbro from IODP 304/305

Measurement type: Simultaneous EBSD/EDS

EBSP resolution: 160x120 pixels

Map size: 1000x750 points

Pixel size: 1.66 microns

Acknowledgments to:

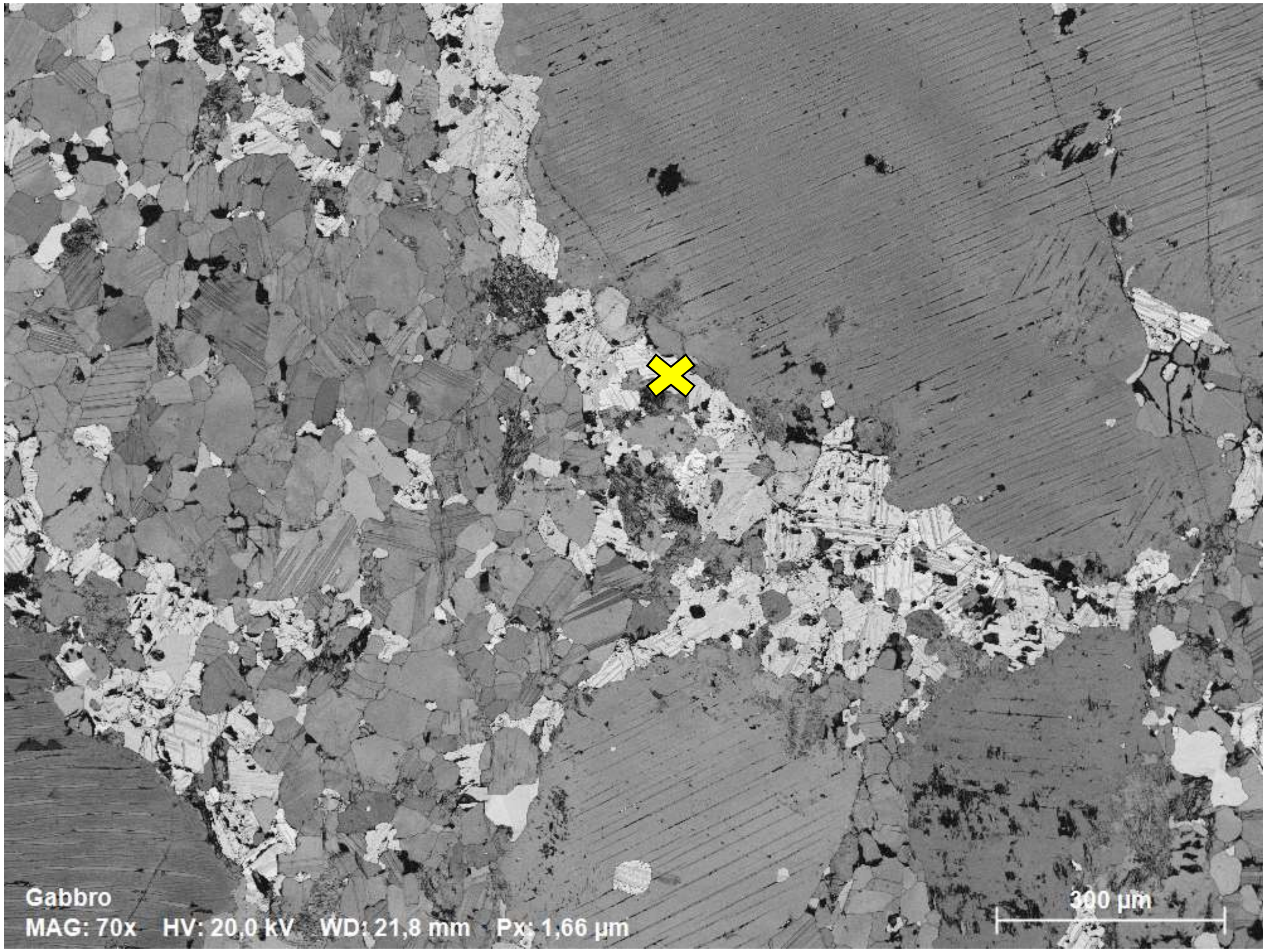
Dr. Angela Halfpenny*

Dr. Michael Verrall

CSIRO, Perth, Australia

*now at Central Washington University, WA, US

Advanced phase ID
How does it work?

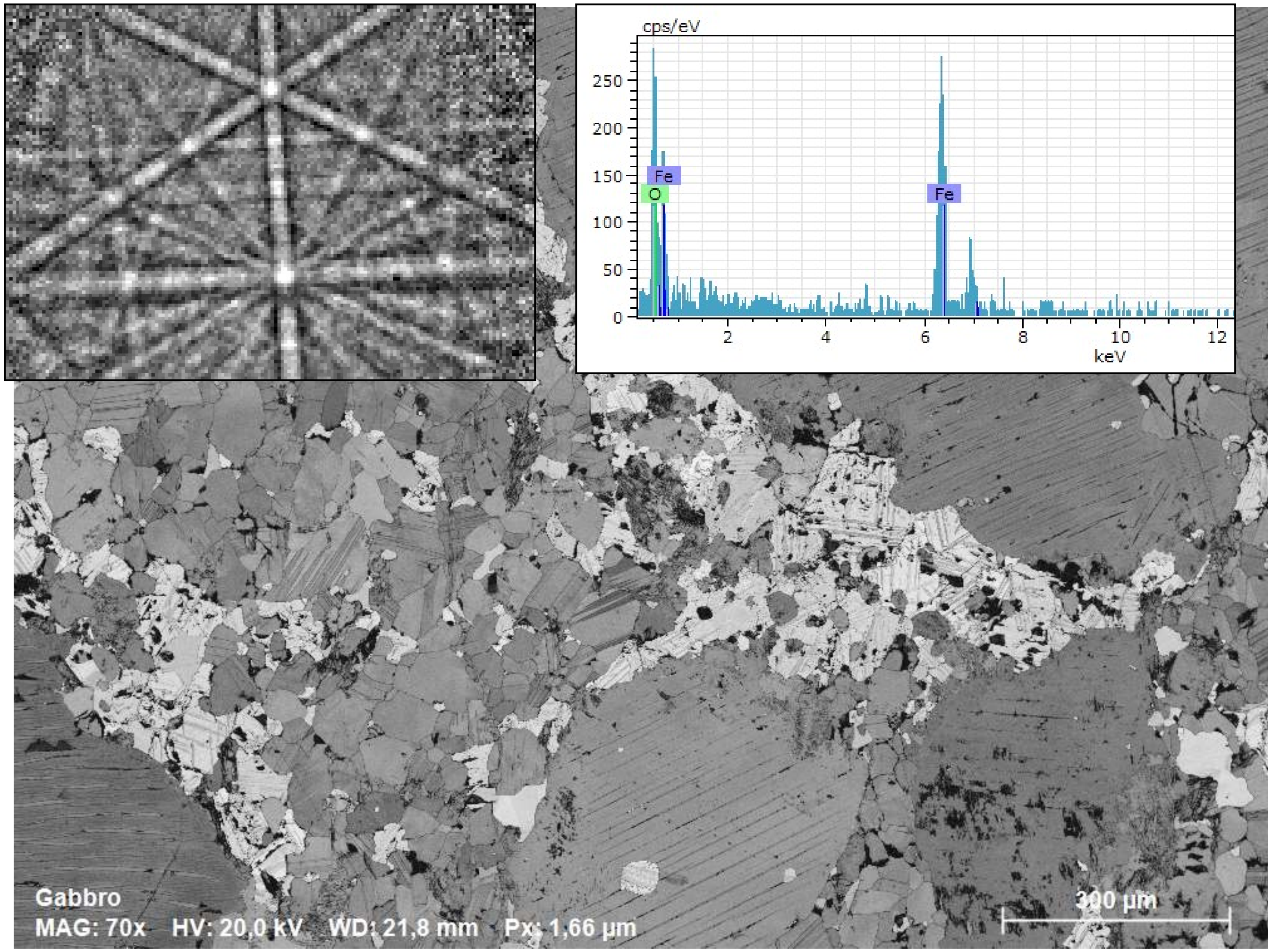


Advanced phase ID:
(Online)

1. Acquire EDS spectrum and EBSP on selected point

Advanced phase ID

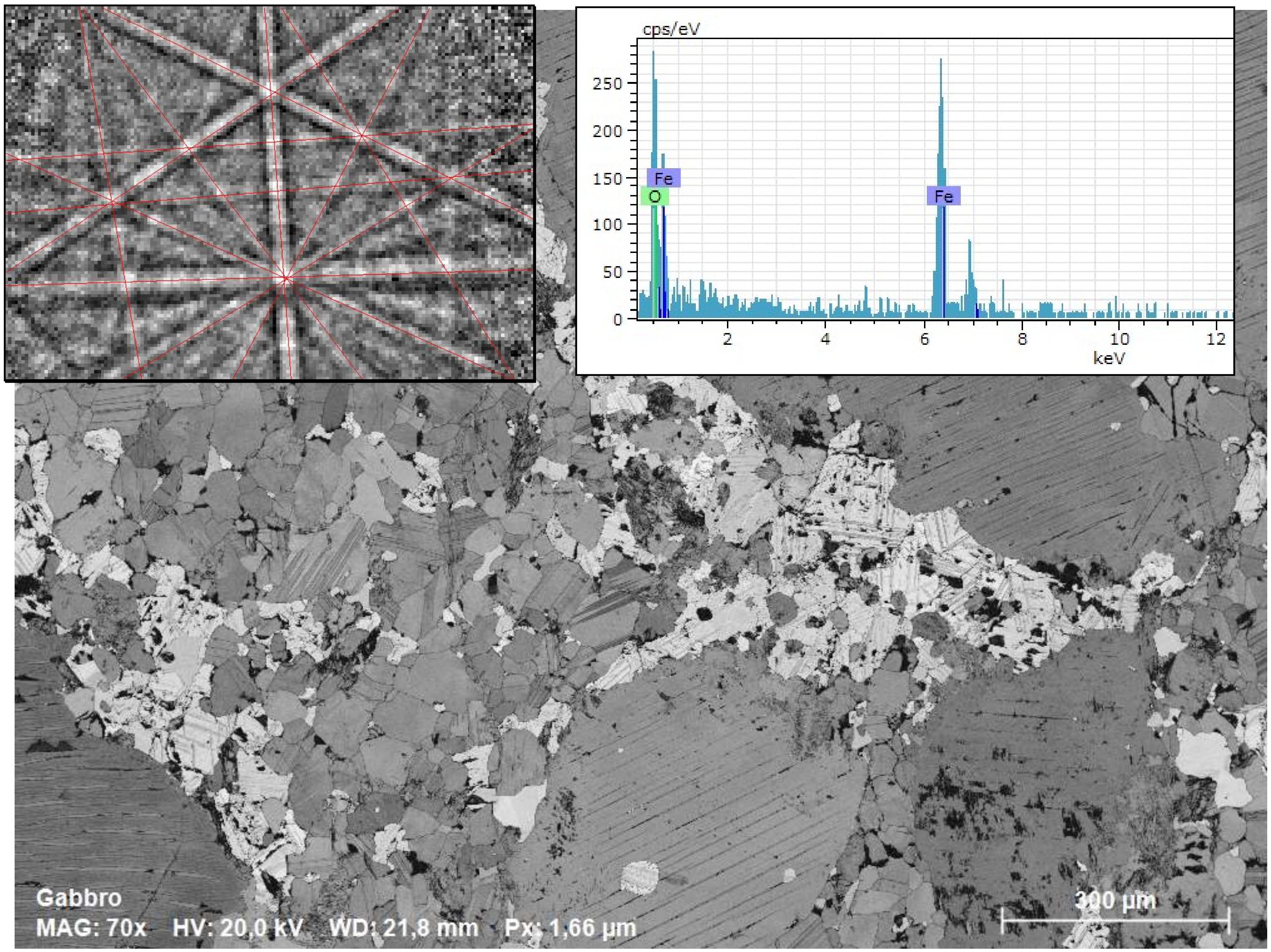
How does it work?



Advanced phase ID:
(Online)

1. Acquire EDS spectrum and EBSP

Advanced phase ID
How does it work?

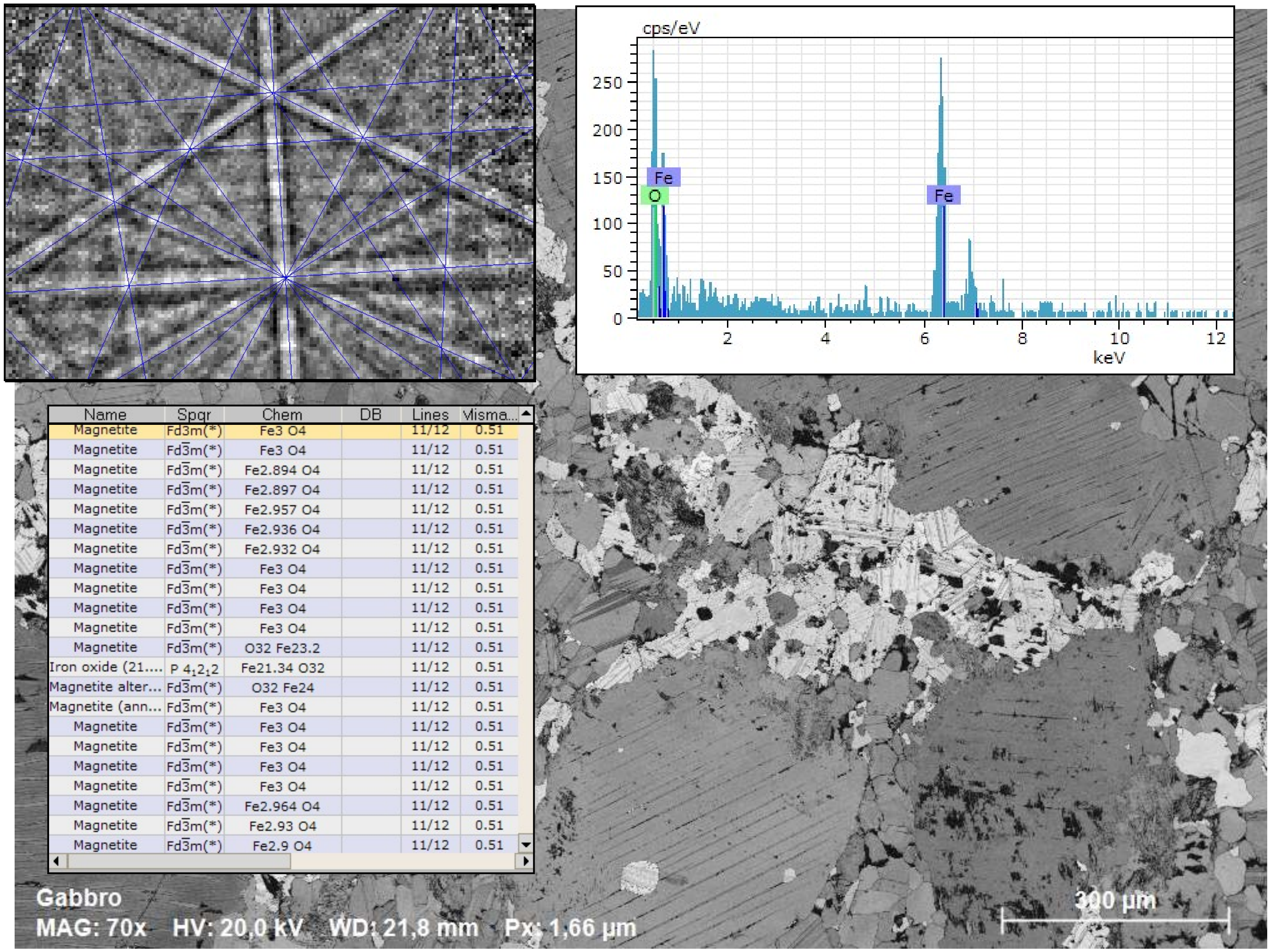


Advanced phase ID: (Online)

1. Acquire EDS spectrum and EBSP
2. Search in database for candidate phases (Fe, O) – 289 entries
3. Automatic/interactive band detection

Advanced phase ID

How does it work?

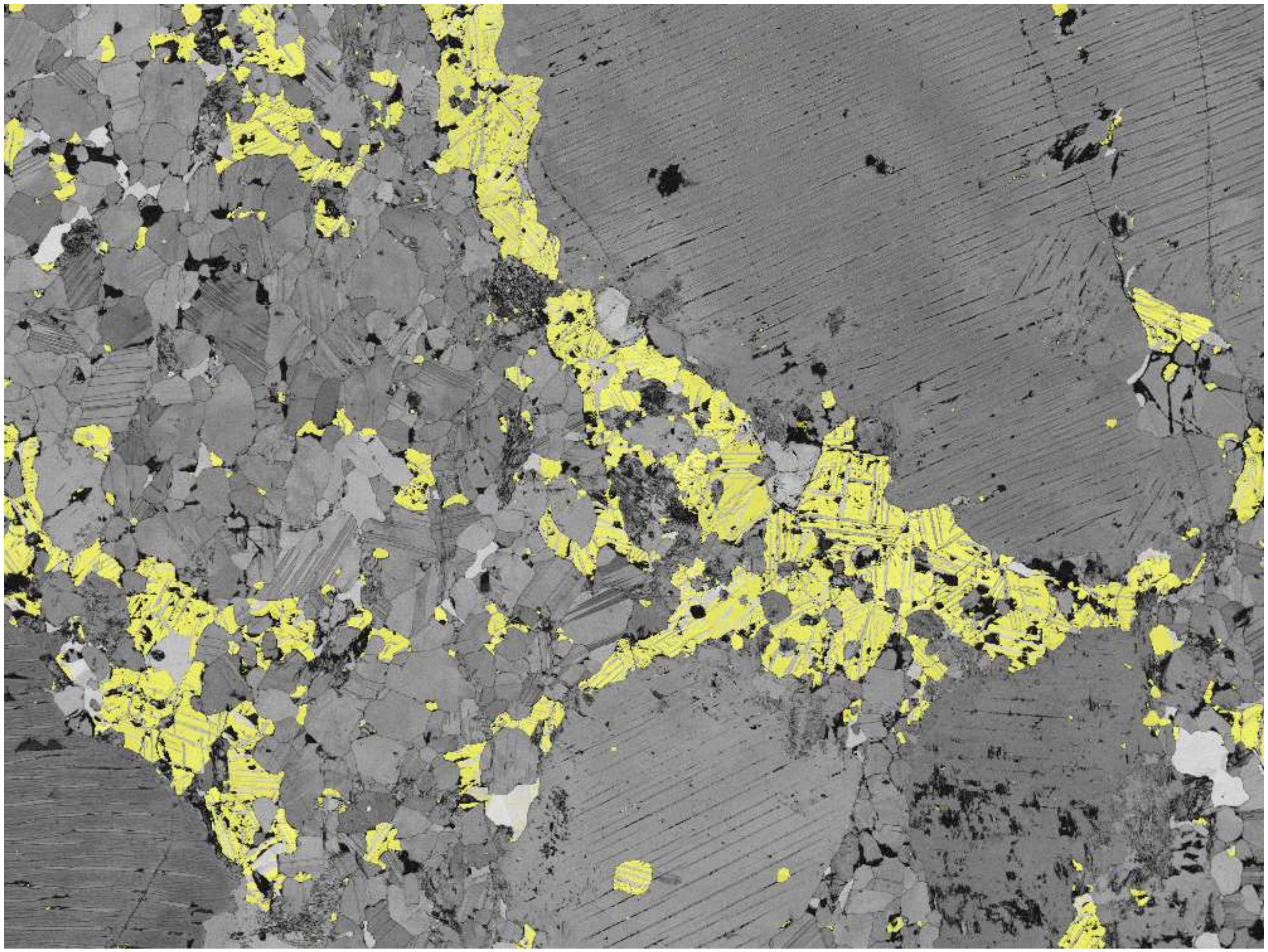


Name	Spgr	Chem	DB	Lines	Misma...
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe2.894 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe2.897 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe2.957 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe2.936 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe2.932 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	O32 Fe23.2		11/12	0.51
Iron oxide (21....	P 4_12_12	Fe21.34 O32		11/12	0.51
Magnetite alter...	$Fd\bar{3}m$(*)	O32 Fe24		11/12	0.51
Magnetite (ann...	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe3 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe2.964 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe2.93 O4		11/12	0.51
Magnetite	$Fd\bar{3}m$(*)	Fe2.9 O4		11/12	0.51

Advanced phase ID: (Online)

1. Acquire EDS spectrum and EBSP
2. Search in database for candidate phases (Fe, O) – 289 entries
3. Automatic/interactive band detection
4. Software tries all 289 entries in ~10 sec
5. Solutions are classified based on quality of fit
6. Best fitting phase file added to phase list
7. System ready for acquiring data

Advanced phase ID
How does it work?

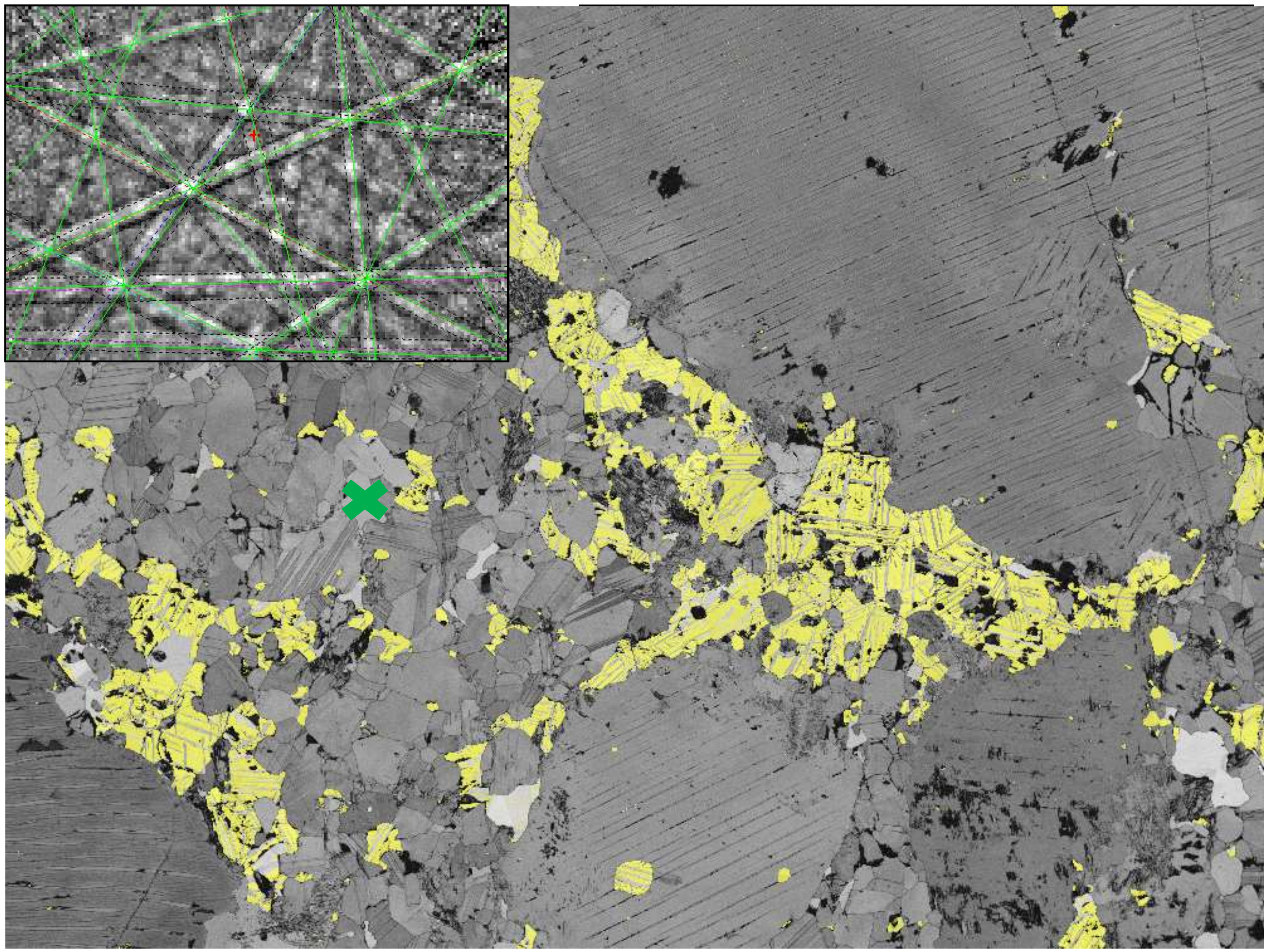


Advanced phase ID:
(**Offline**)

After data EBSD/EDS acquisition, repeat the same advanced phase ID procedure with the missing phases:

1. Select one point from the map
2. Perform advanced phase ID

Advanced phase ID
How does it work?



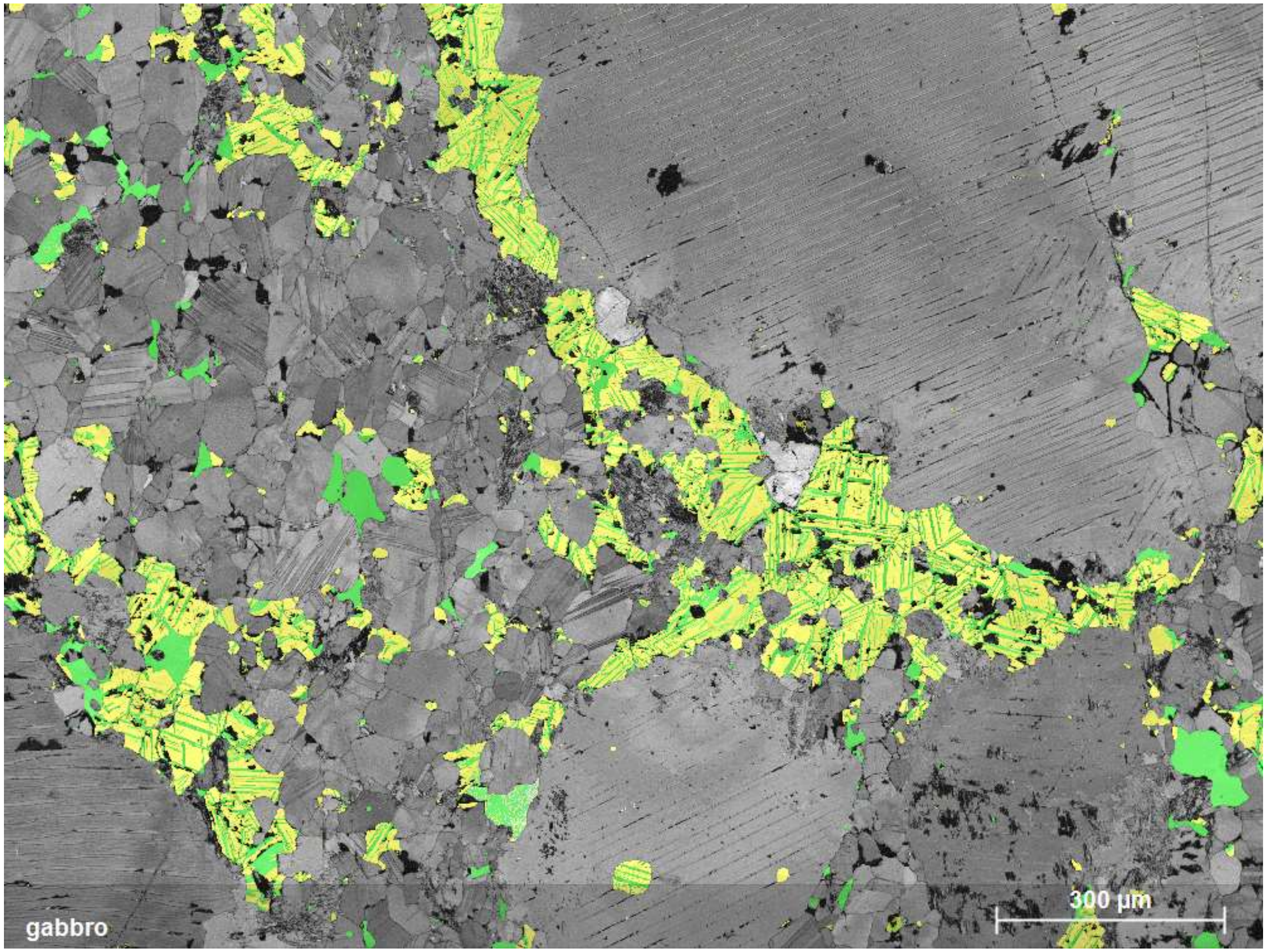
Advanced phase ID:
(**Offline**)

After data EBSD/EDS acquisition, repeat the same advanced phase ID procedure with the missing phases:

1. Select one point from the map
2. Perform advanced phase ID
3. Ilmenite: SG 148
4. Reindex map in 50 sec

Advanced phase ID

How does it work?

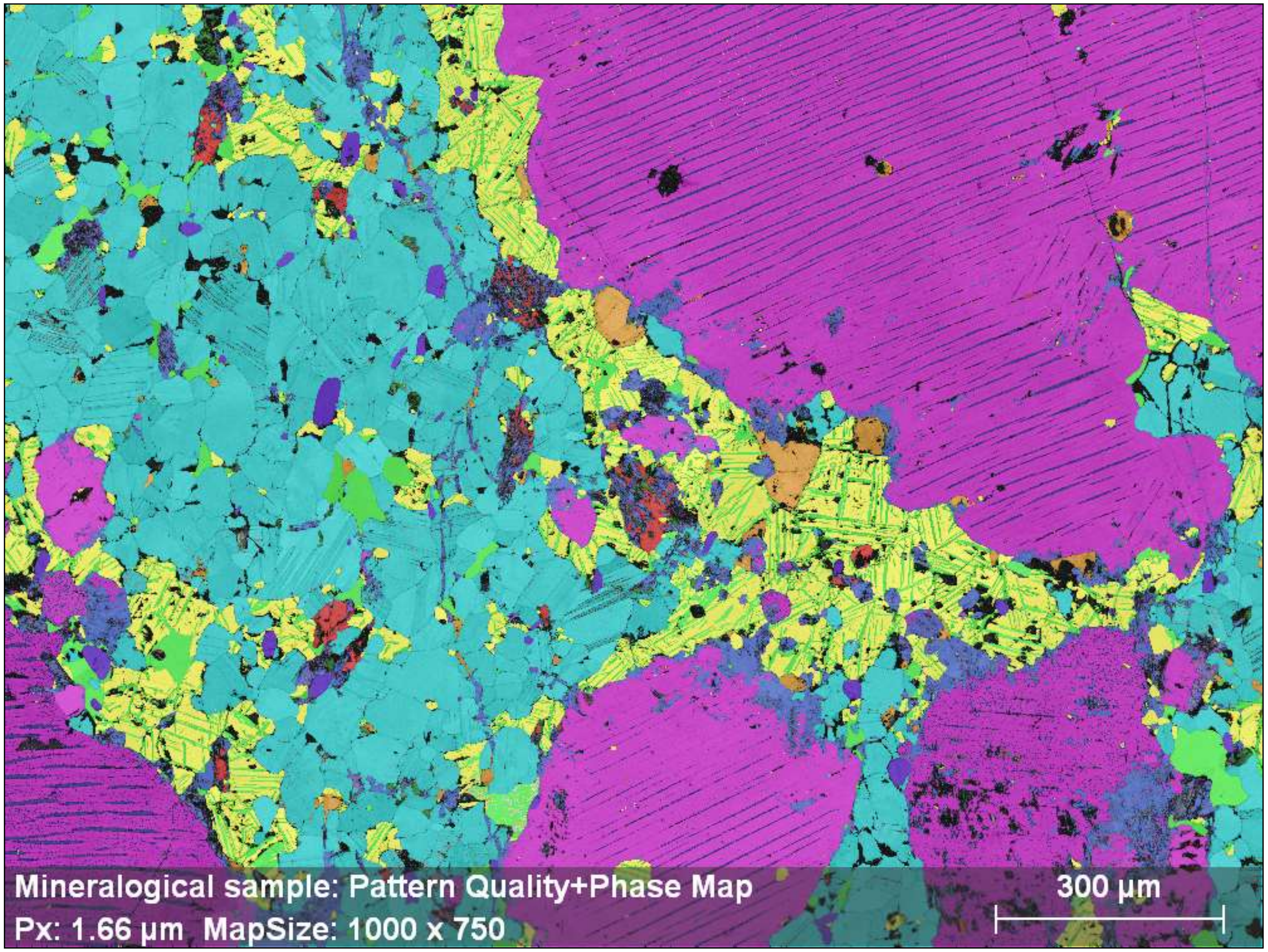


Advanced phase ID:
(**Offline**)

1. Magnetite: SG 227
2. Ilmenite: SG 148
3. Repeat procedure for the other unknown phases…

Advanced phase ID

How does it work?



Final EBSD data:

1. Magnetite: SG 227
2. Ilmenite: SG 148
3. Pyrrhotite: SG 194
4. Apatite: SG 176
5. Quartz: SG 152
6. Augite: SG 15
7. Anorthite (Na): SG 2
8. Hastingsite: SG 12
9. Clinohypersthene: SG 14
10. Clinochlore: SG 5

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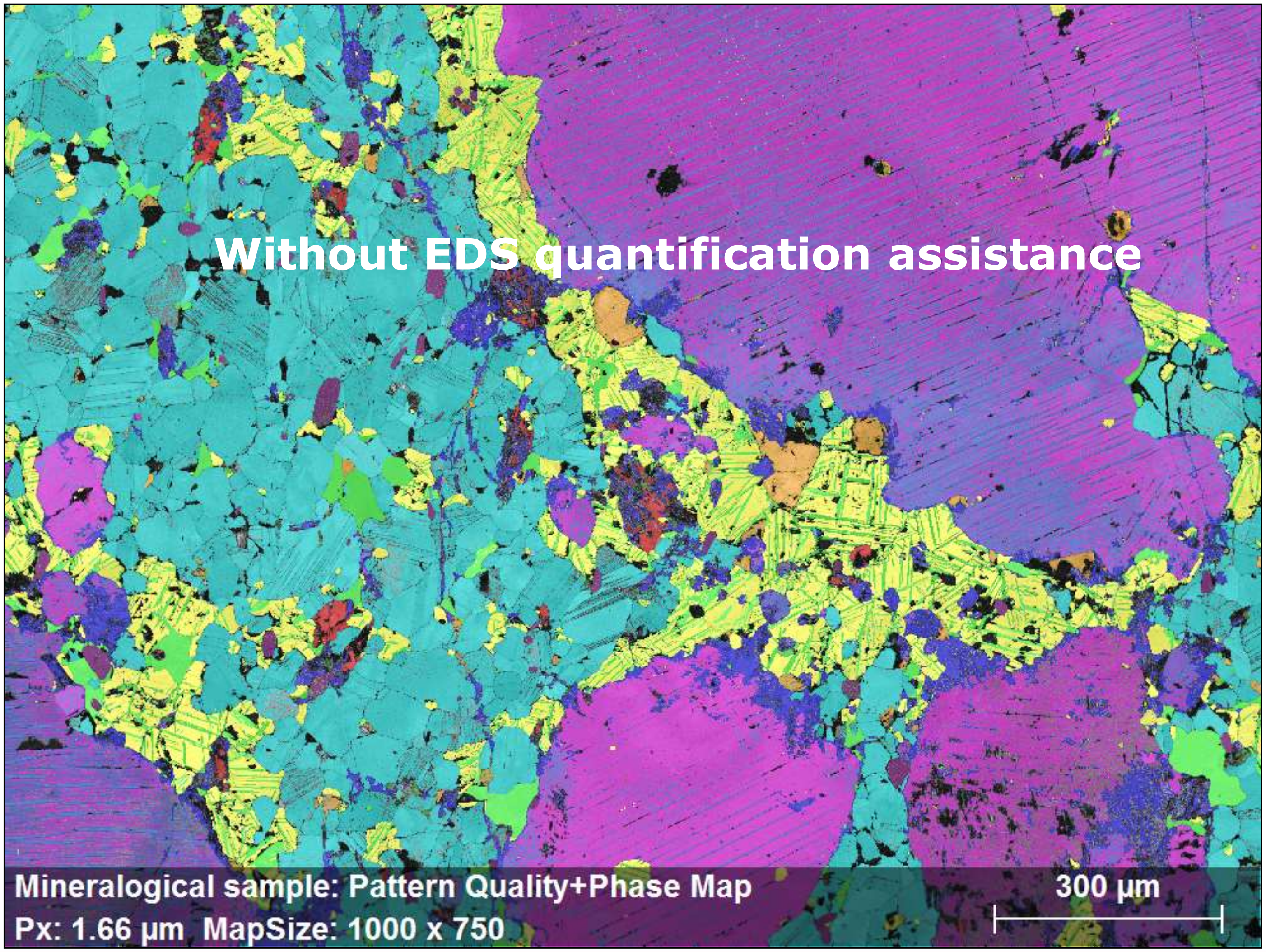
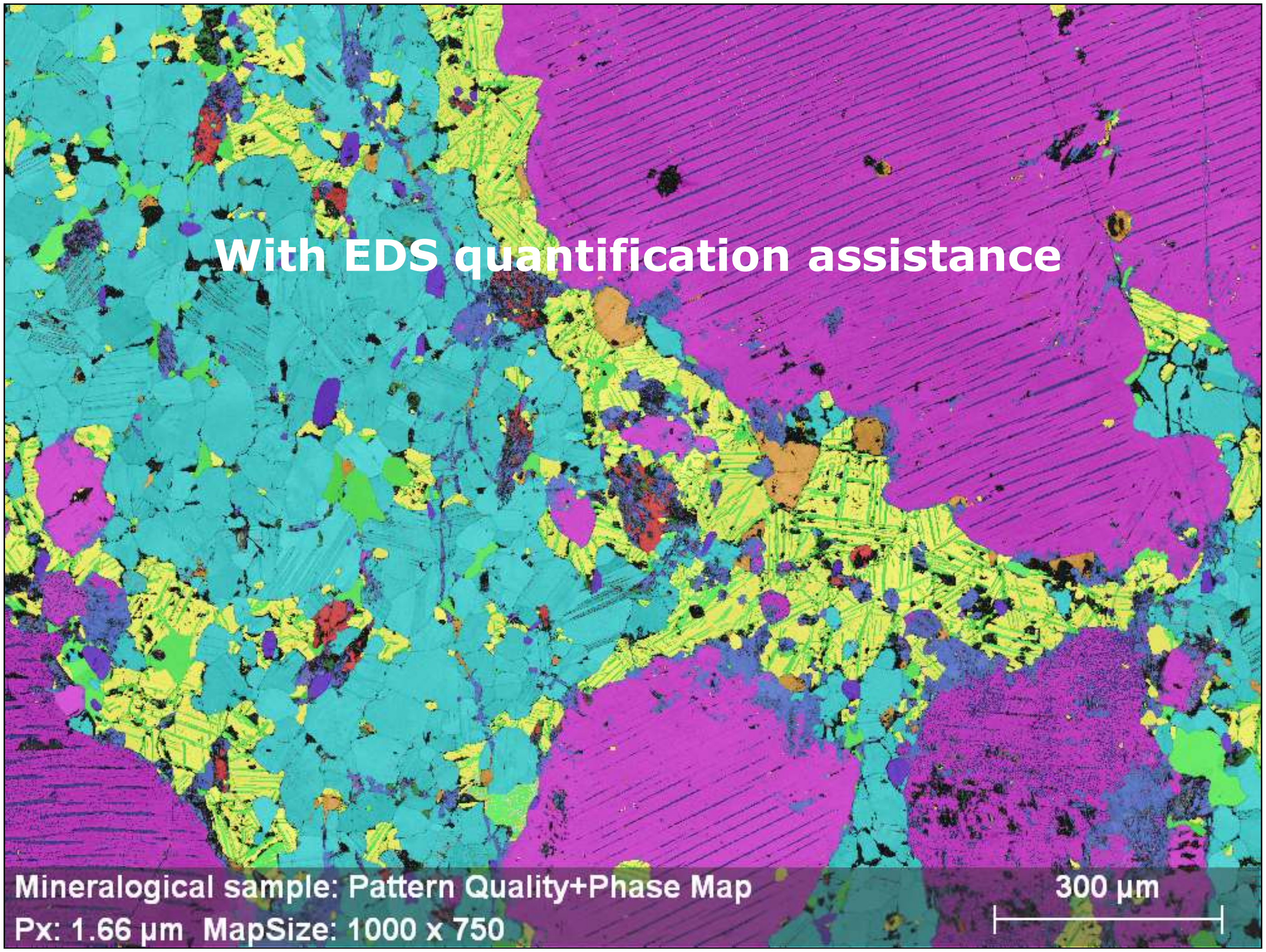
Phase discrimination by EDS
EBSD only

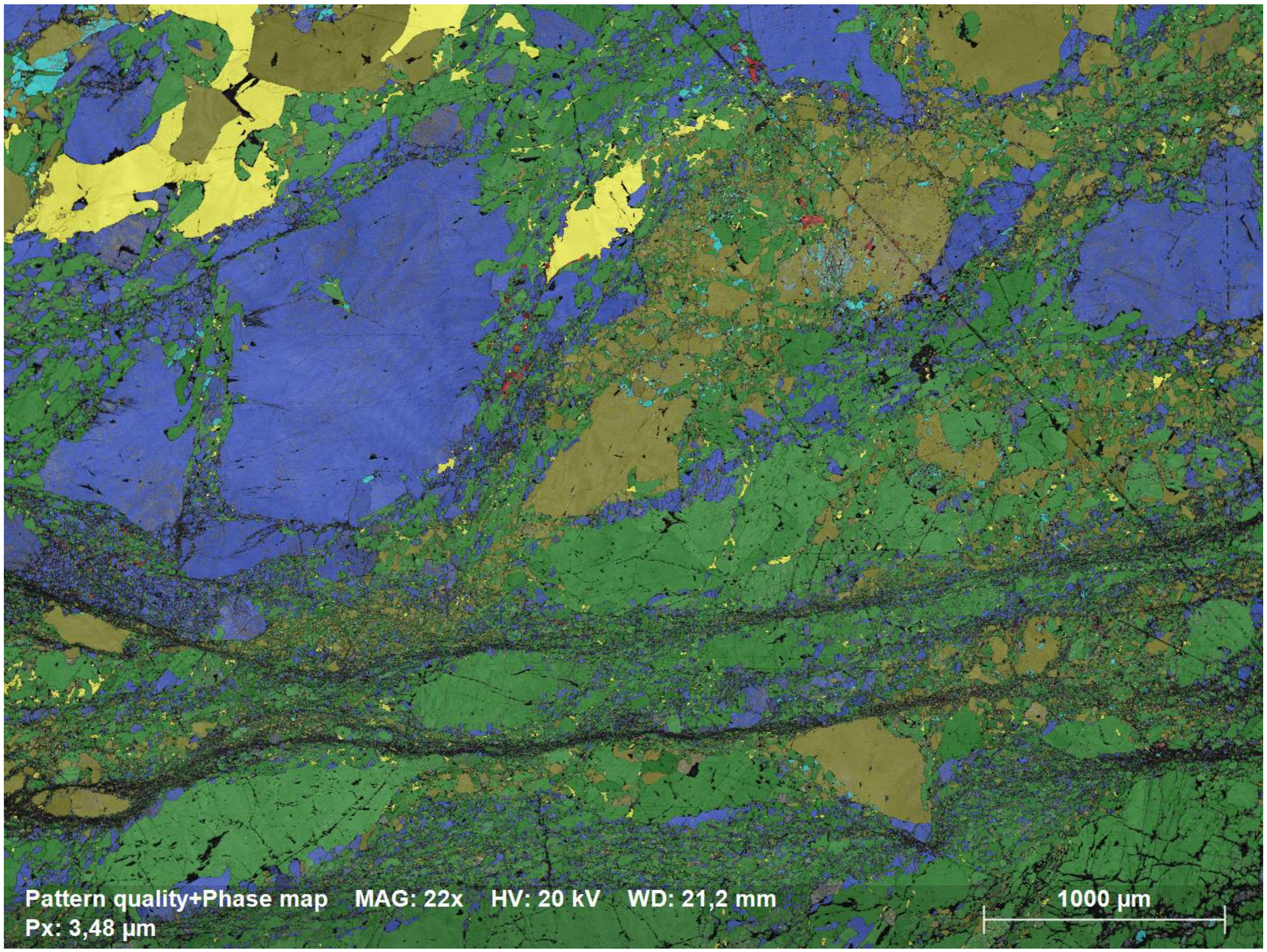


Phase discrimination by EDS
with EDS quantification assistance



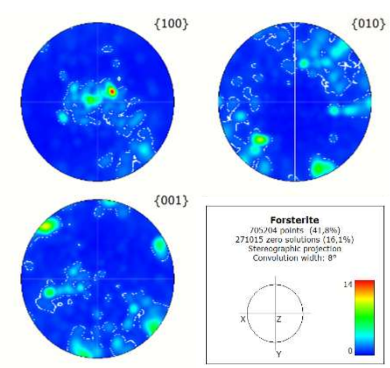
Mylonitic lherzolite (Lers, France)

EBSD Phase map

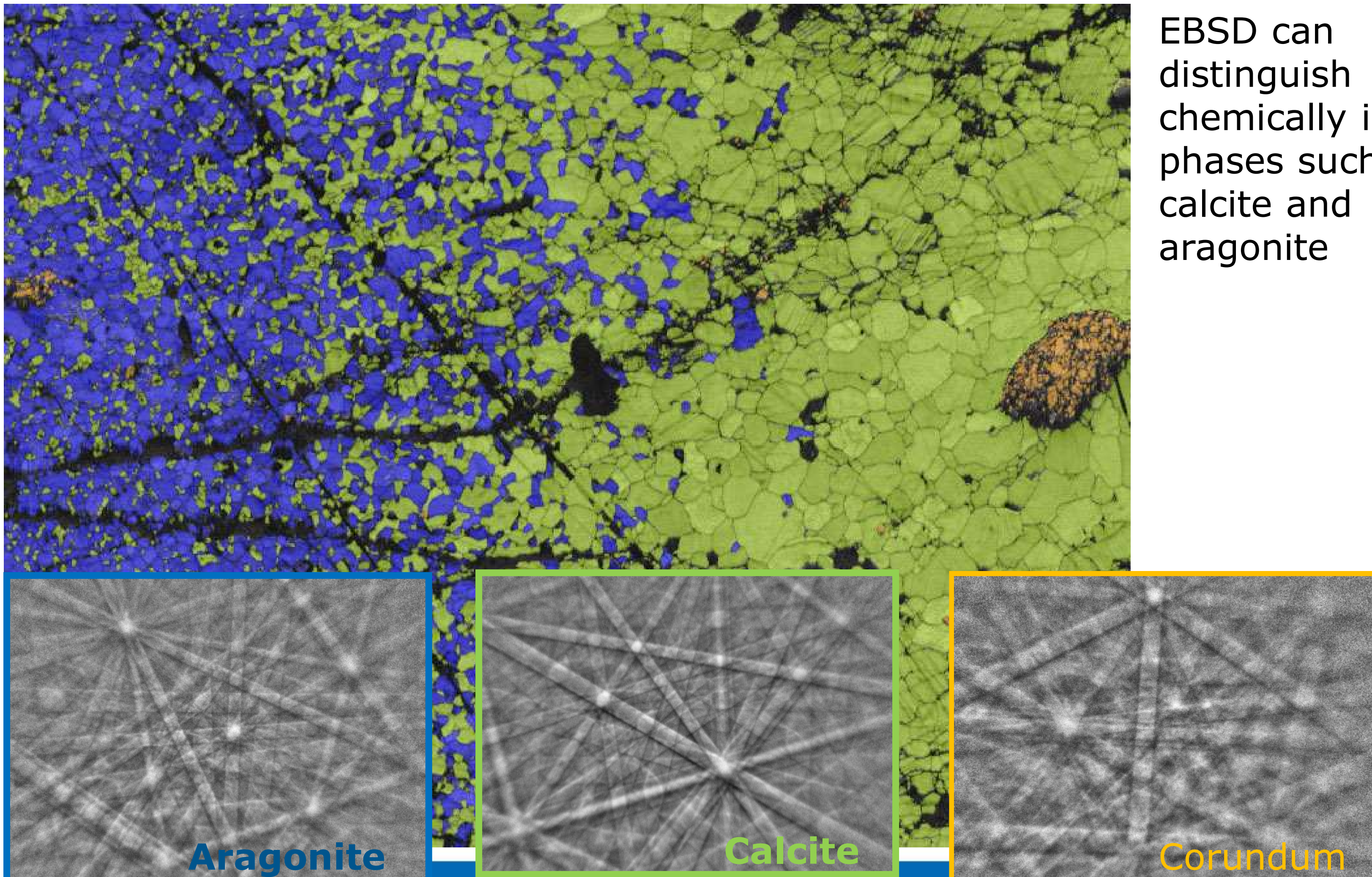


EBSD Phase map
Hit rate 85 %

Olivine
Opx
Cpx
Spinel
Amphibole!
Plagioclase!



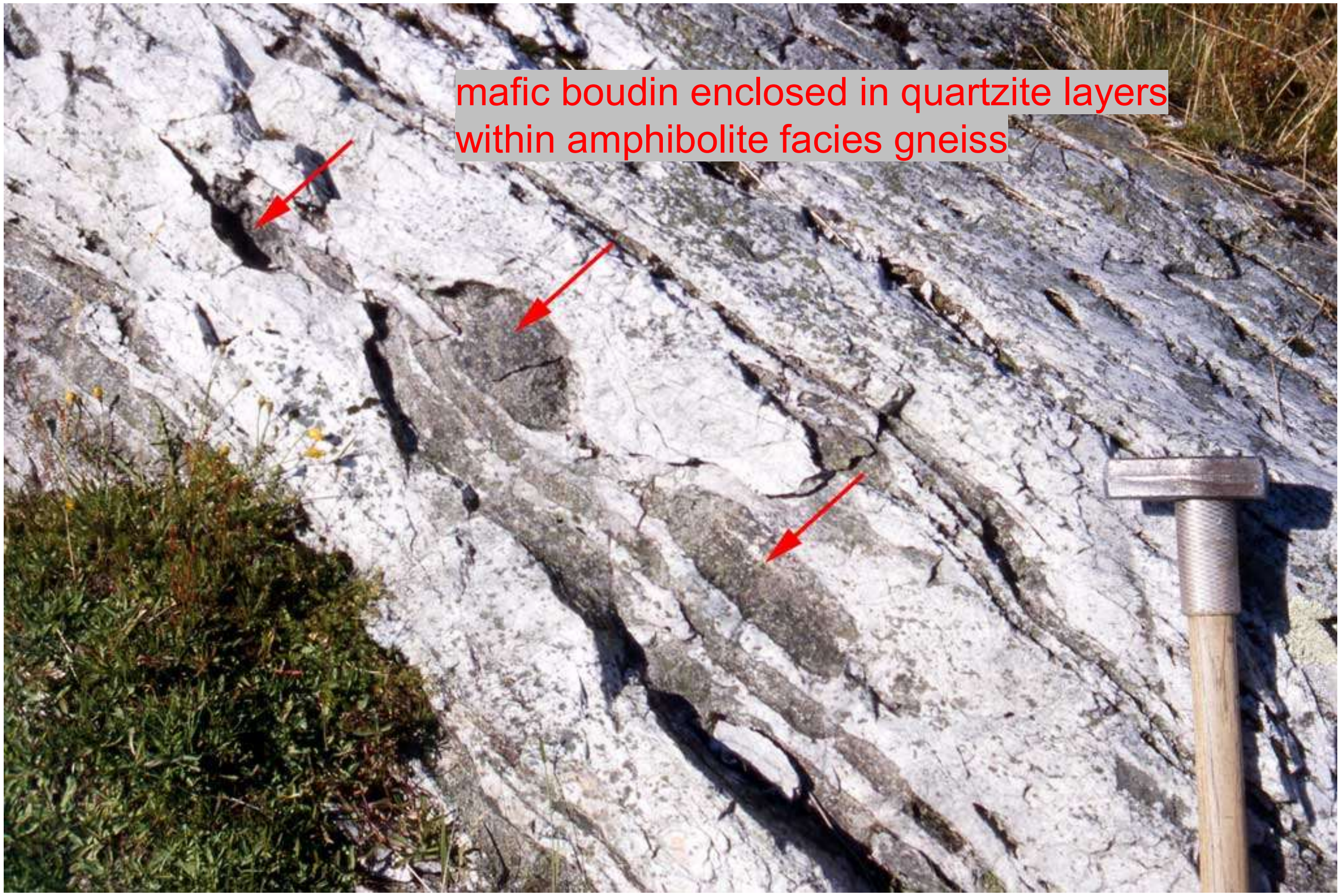
Calcium carbonates
Phase discrimination with EBSD/EDS



EBSD can distinguish chemically identical phases such as calcite and aragonite

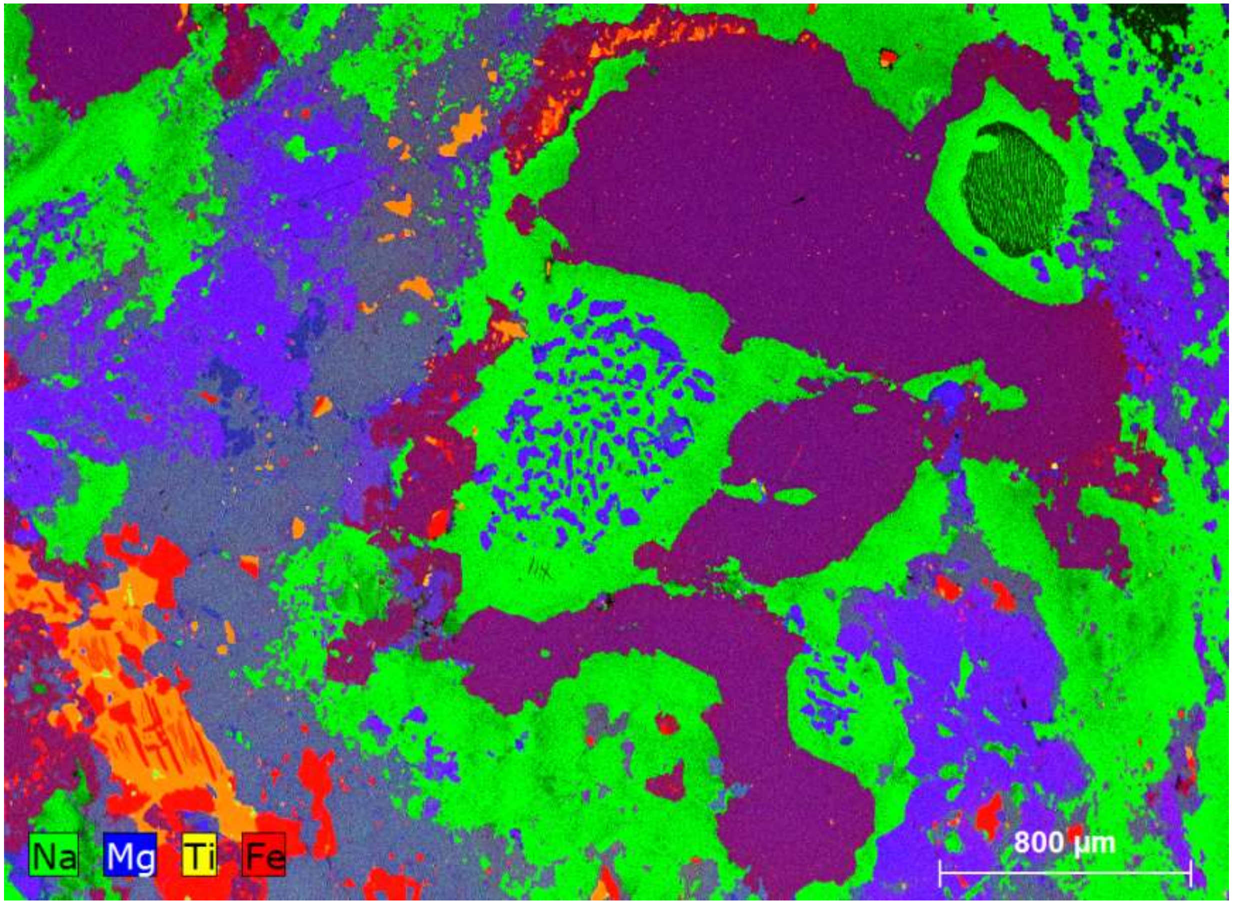
Investigating thermomechanical processes

Mafic boudins in granulite facies
Lindas Nappe, SW Norway

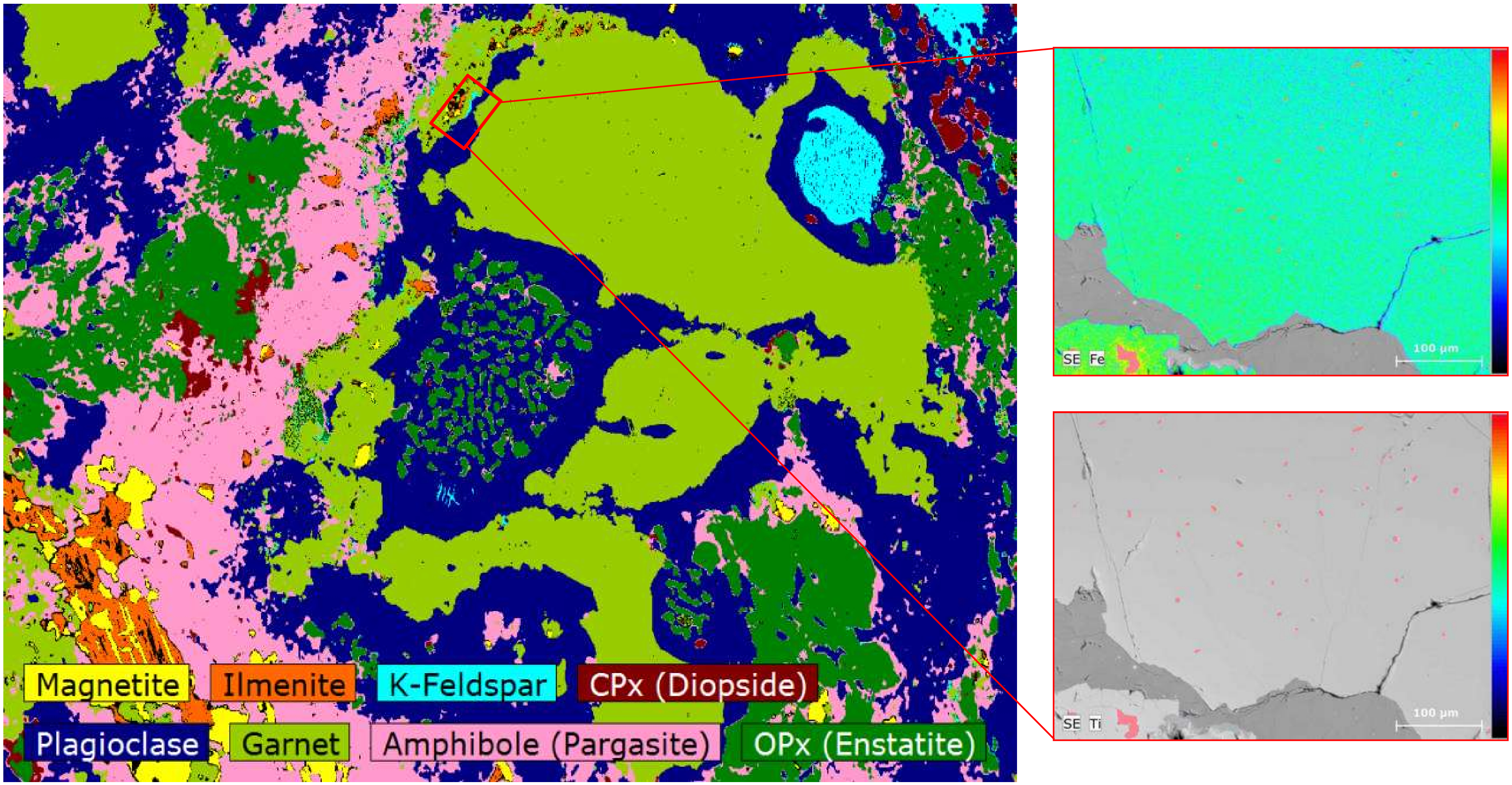


Sample courtesy and study: Dr. D.Spengler, Stuttgart University, Germany

Investigating thermomechanical processes
EDS mixed element map

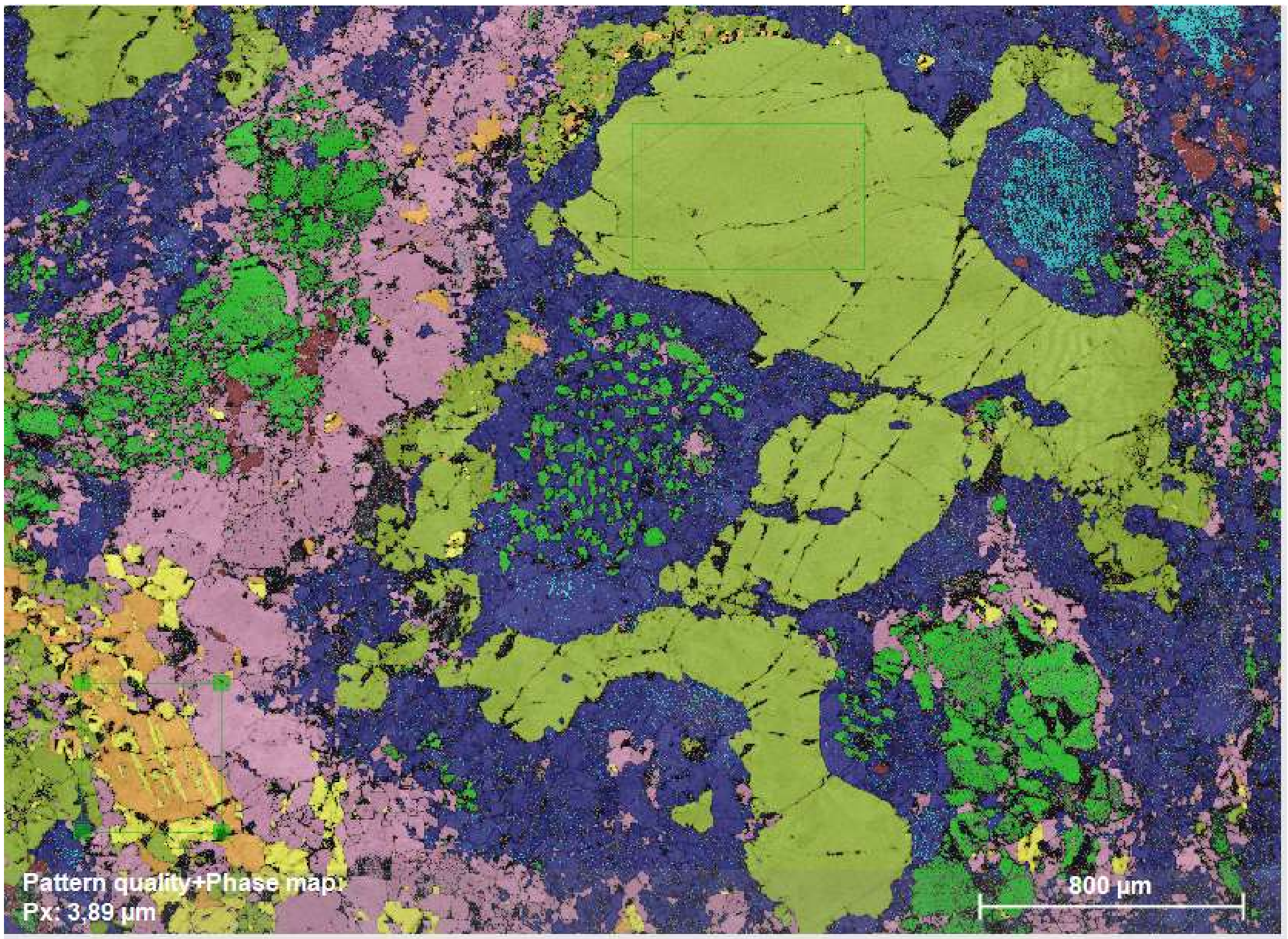


Investigating thermomechanical processes
EDS Autophase



Investigating thermomechanical processes

EBSD Phase map

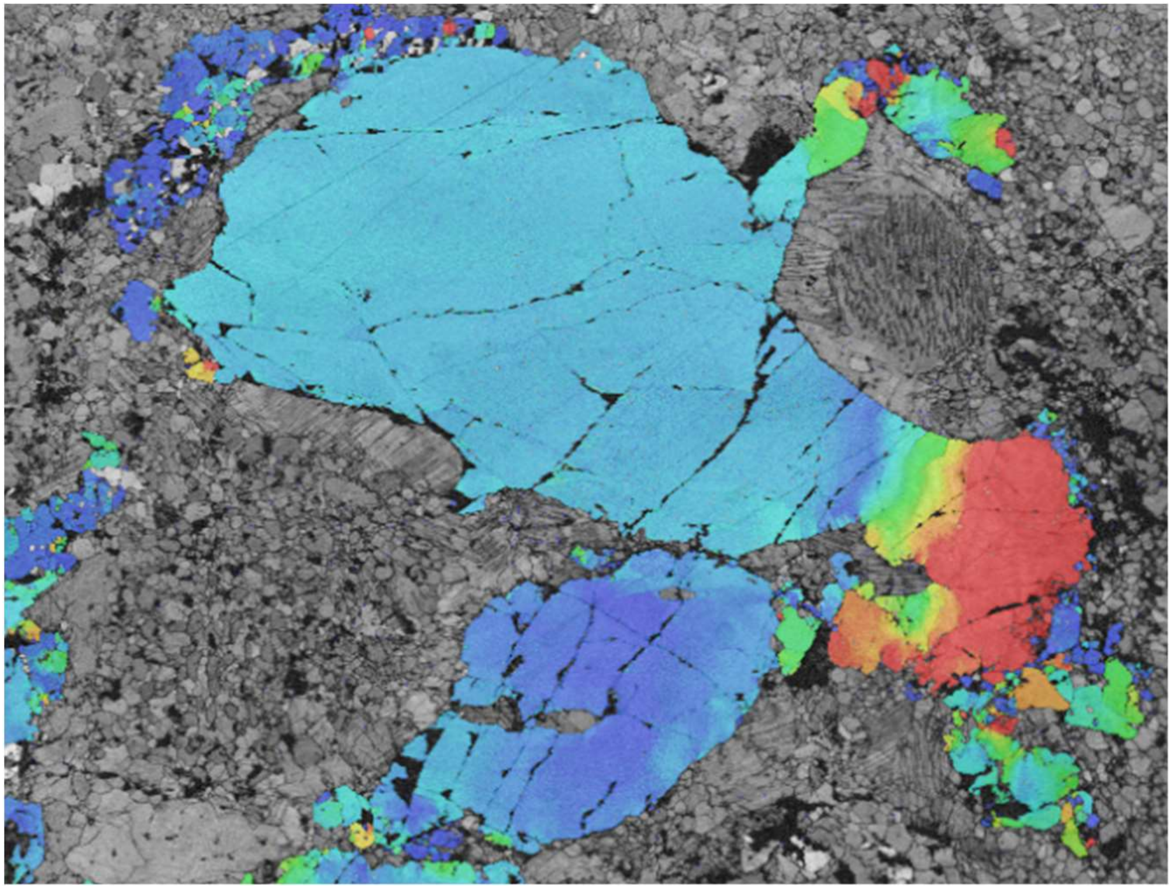


EBSD Phase map

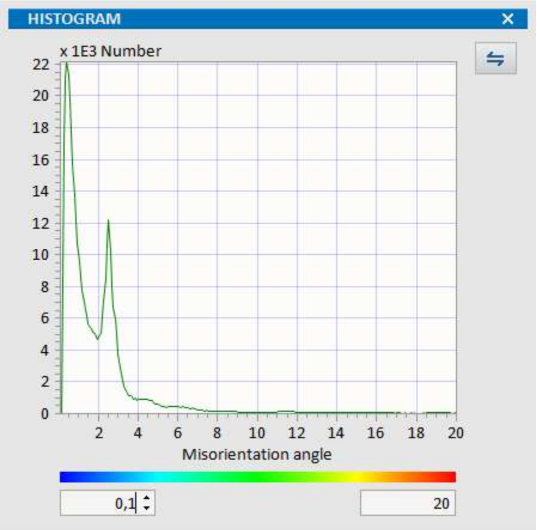
Magnetite
Ilmenite
K-Feldpsar
Plagioclase
Garnet
CPX
OPX
Amphibole

Investigating thermomechanical processes

Strain localisation map on garnet



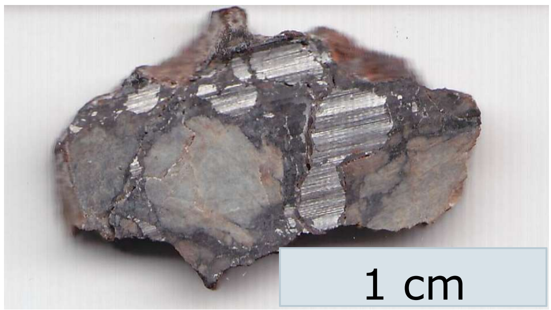
Misorientation map - porphyroclastic garnet

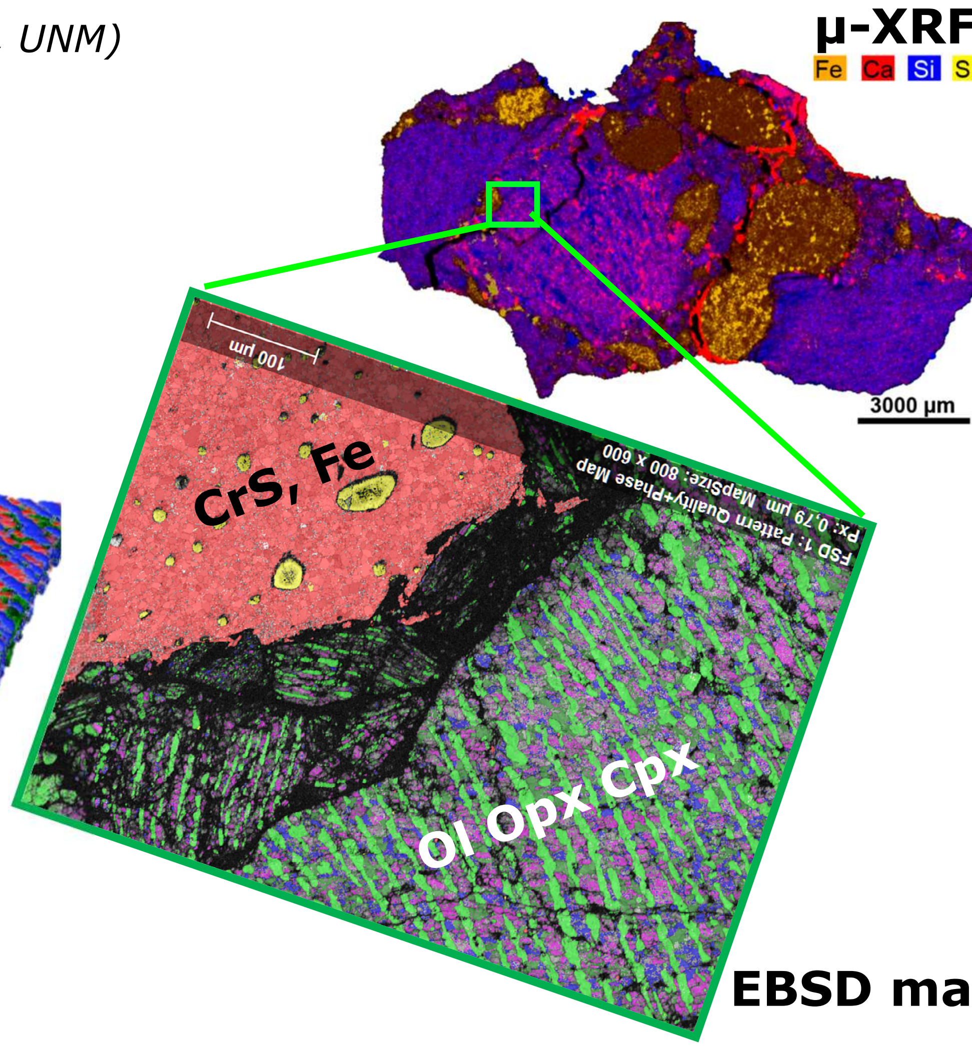


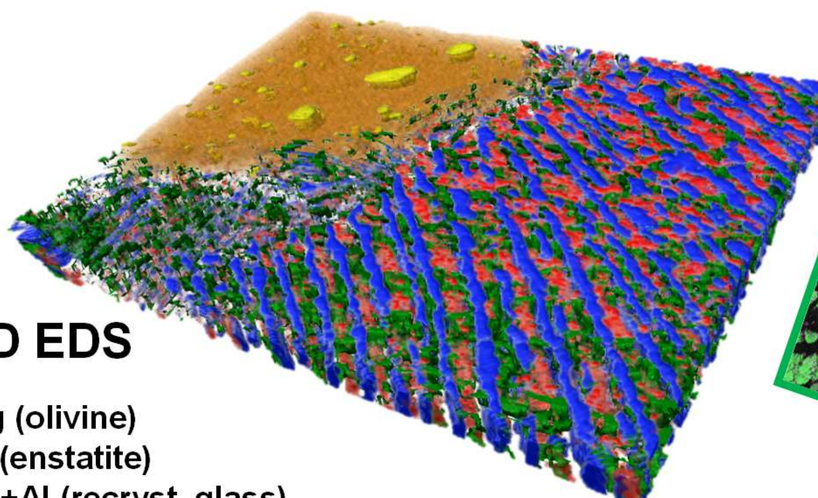
EBSD/EDS analysis on metals and minerals: CB carbonaceous chondrite Gujba

3D µ-XRF, 3D EDS & EBSD

Gujba sample *(courtesy of R. H. Jones, UNM)*





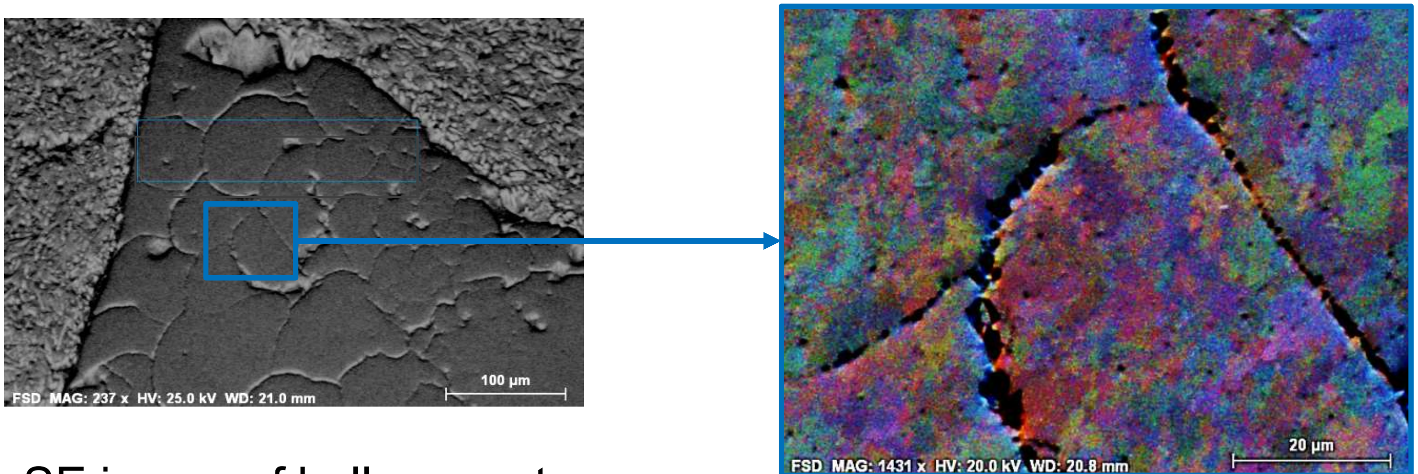


3D EDS

Mg (olivine)
Si (enstatite)
Ca+Al (recryst. glass)
Fe (Fe,Ni-metal)
S (Cr-bearing sulfide)

EBSD analysis of impactite
example on shocked quartz

Shocked quartz in impactite (Yaxcopoil sample)

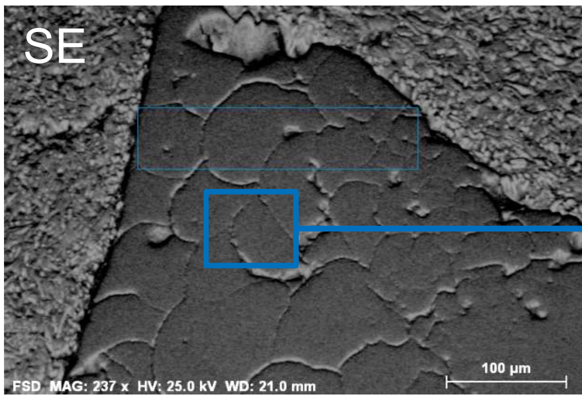


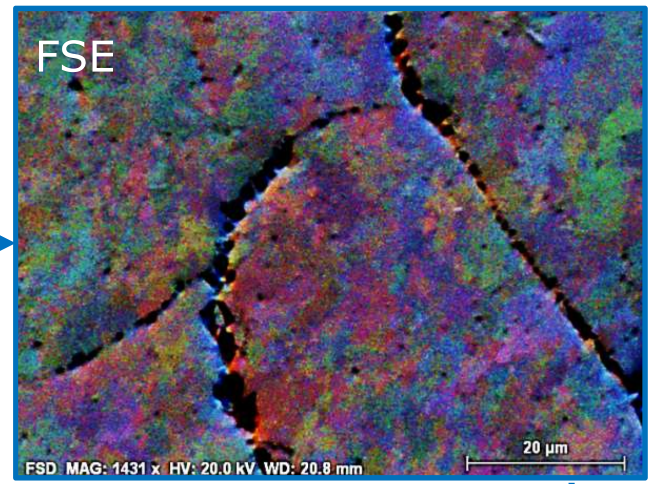
SE image of ballen quartz

Orientation contrast image (FSE)

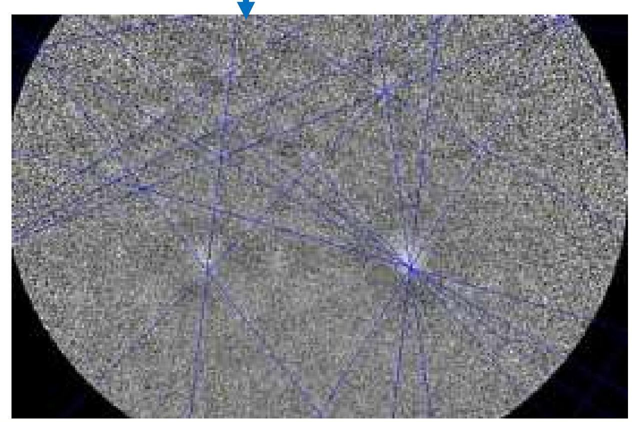
EBSD analysis of impactite
example on shocked quartz

Shocked quartz in impactite (Yaxcopoil sample)





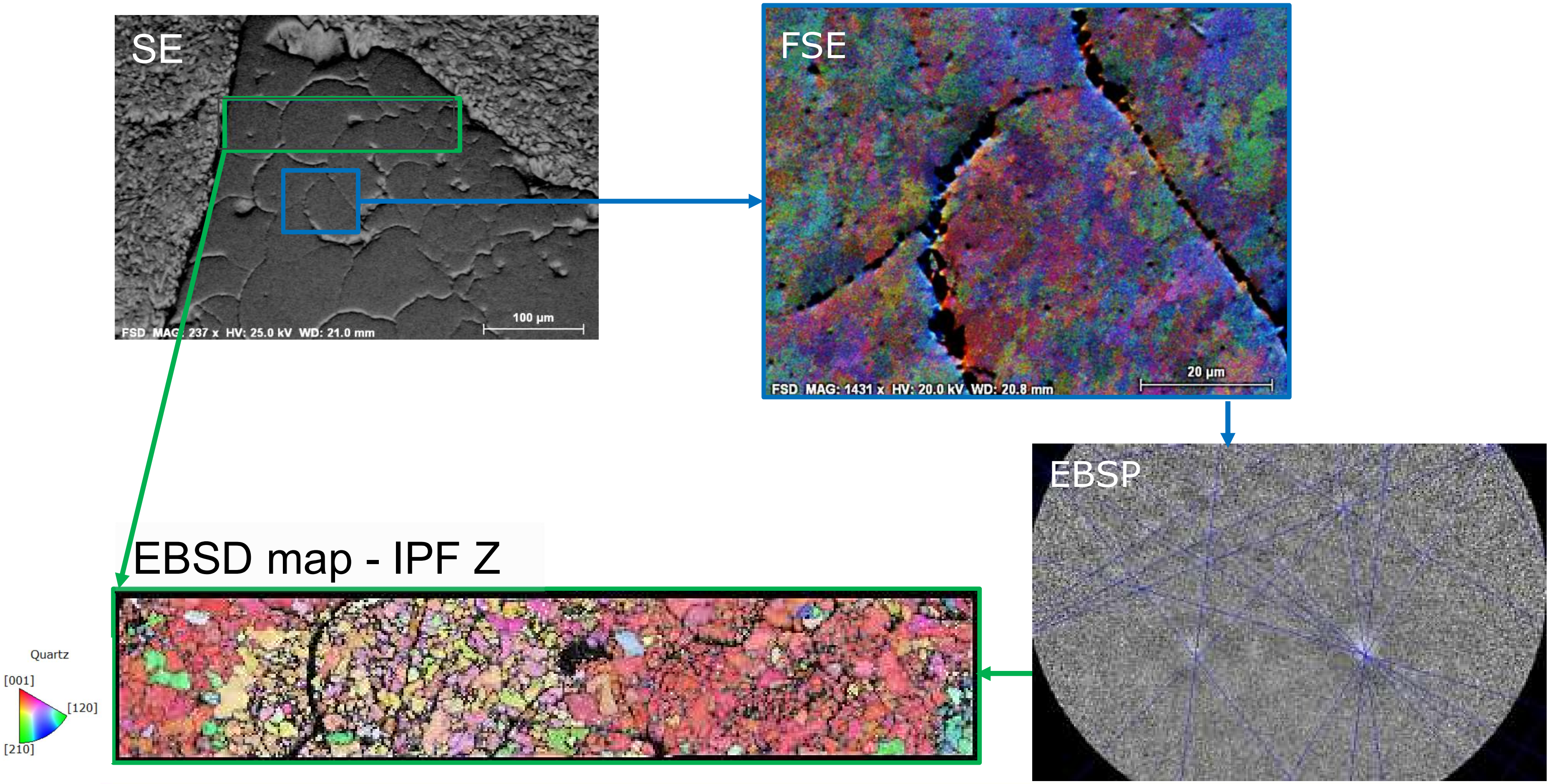
Diffraction pattern



EBSD analysis of impactite

example on shocked quartz

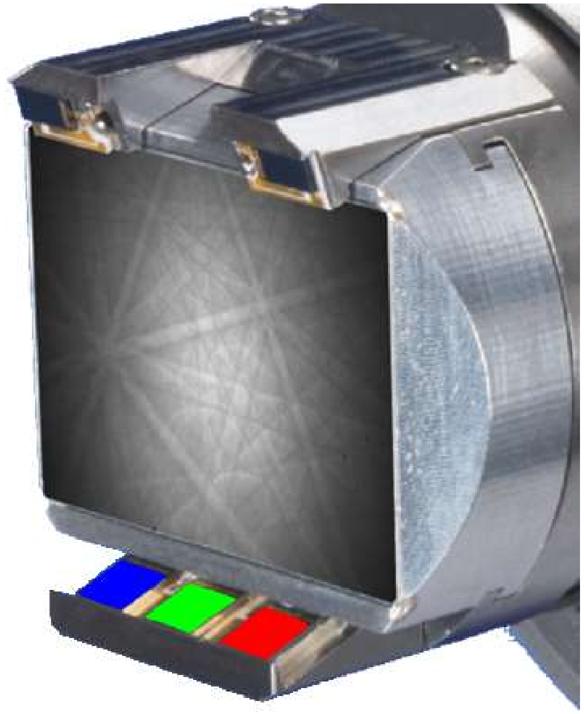
Shocked quartz in impactite (Yaxcopoil sample)



- EBSD setup
- Combined EBSD/EDS measurement
  - Advanced Phase Identification
  - Phase discrimination by EDS
- Advanced imaging with built-in ARGUS system
- Summary

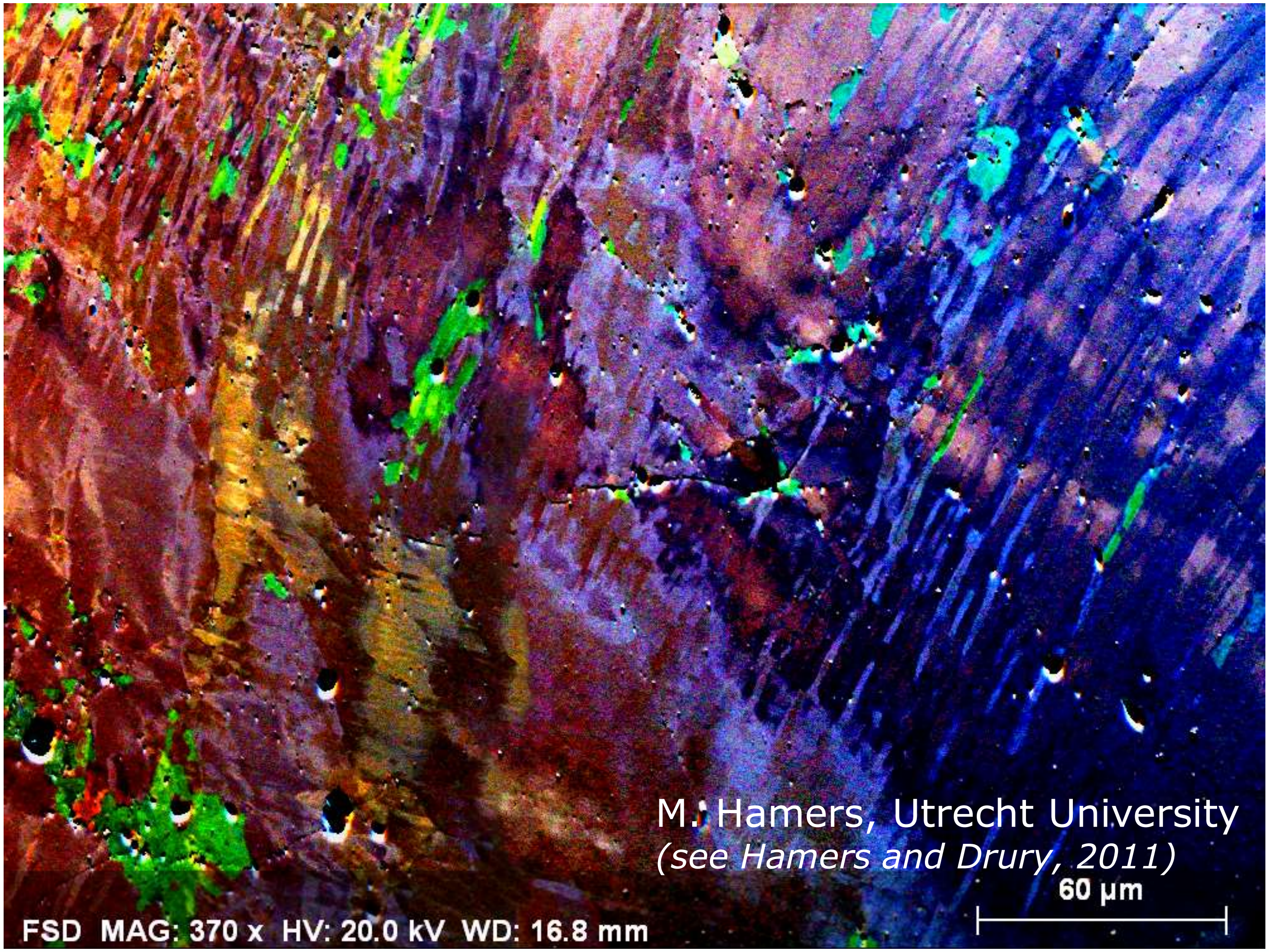
FSE/BSE imaging system
How does it work?

- ARGUS is a **build-in** BSE & FSE detector: no loss of signal, high signal/noise ratio
- Each diode captures a similar amount of noisy backscattered electrons and a different part of the diffracted backscattered electrons, i.e. EBSD signal.
- Signal (*e*$^-$ counts) is transferred using a separate channel for each diode. A color is assigned to each diode.
- When scanning, for each pixel the system will obtain three numbers which will be transformed into three RGB levels.
- Then the three signals/RGB levels are mixed



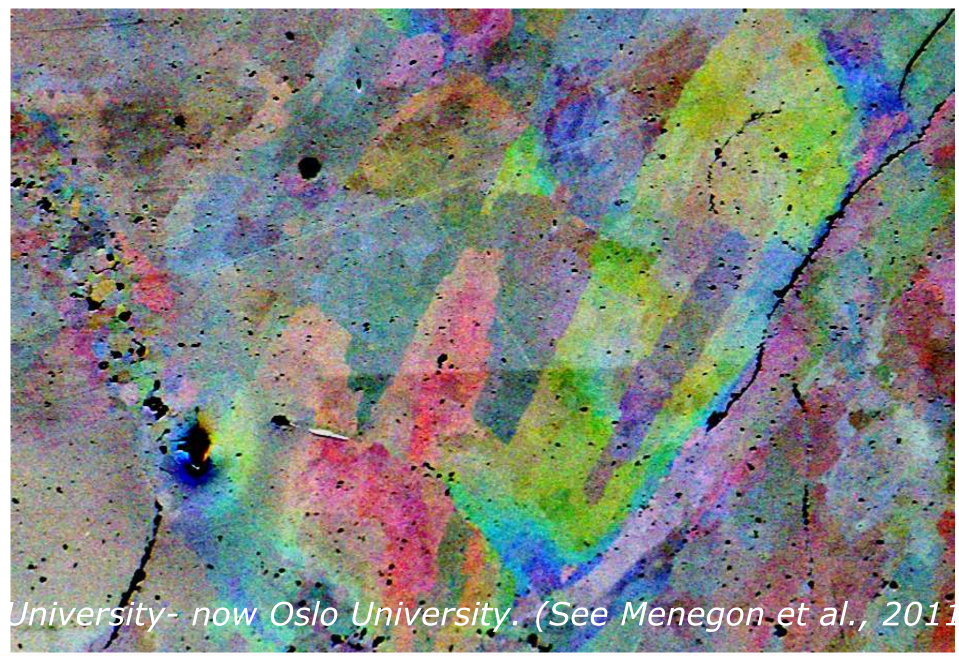
➢ **Following slides are examples of colour-coded FSE images on minerals**

Color-coded orientation contrast
Tectonically deformed Quartz



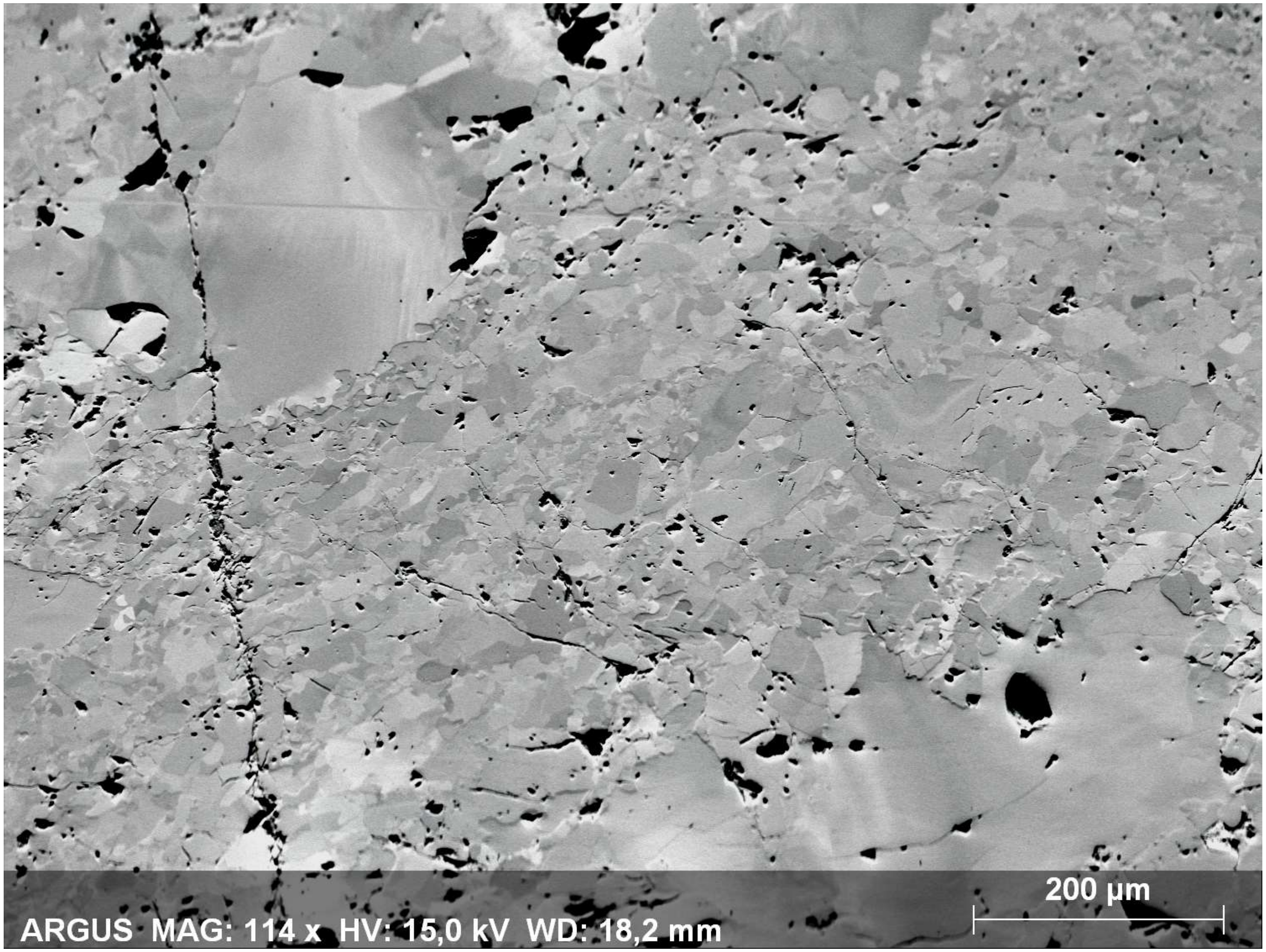
Color-coded orientation contrast
C-coated sample (quartz) and low vacuum mode examples

Sample courtesy (Prof. K. Stanek, Freiberg University)



Right: sample courtesy Dr L. Menegon, Tromso University- now Oslo University. (See Menegon et al., 2011

Grayscale orientation contrast
Protomylonitic lherzolite



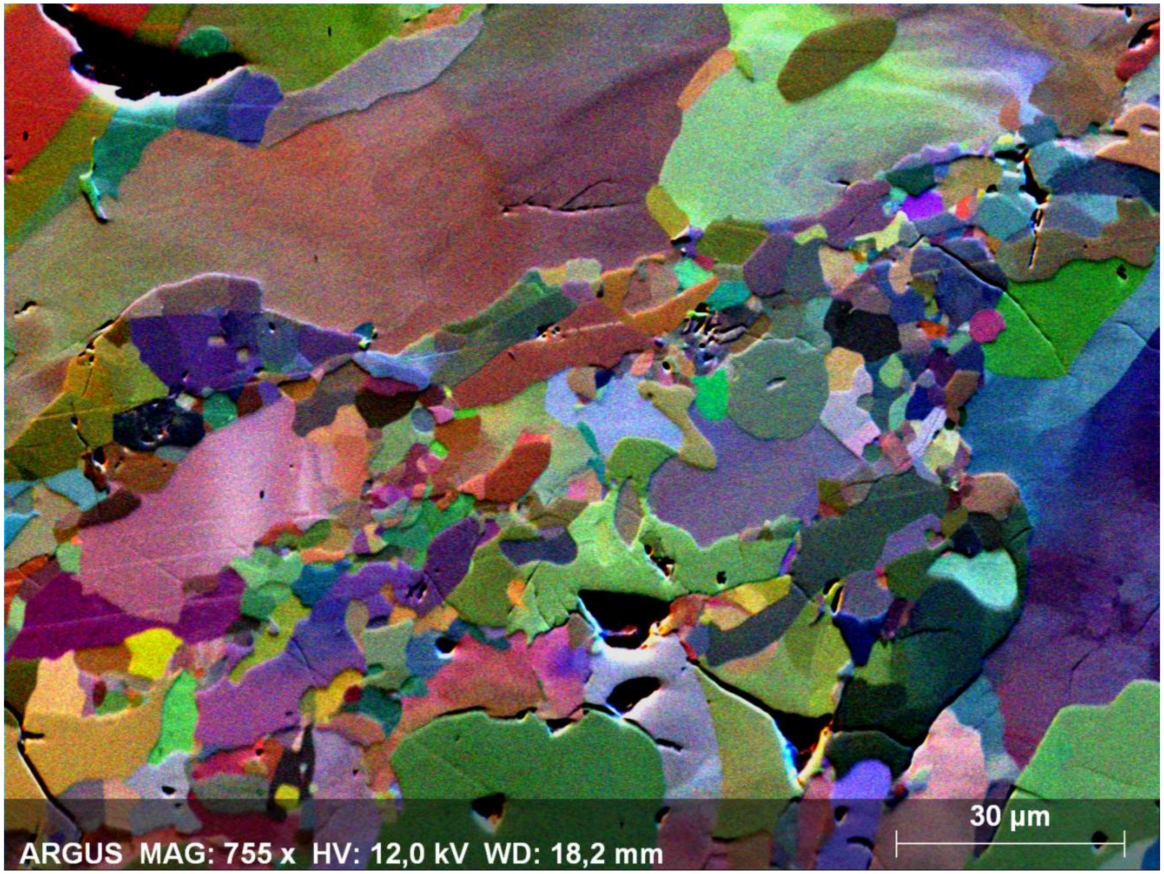
Color-coded orientation contrast
Protomylonitic lherzolite

Color-coded orientation contrast

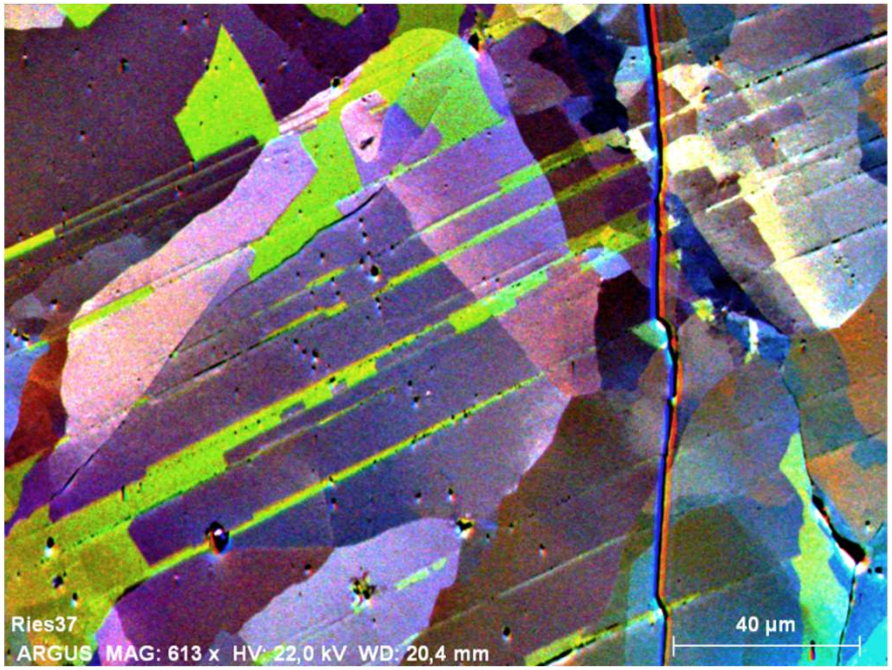
Protomylonitic lherzolite

Color-coded orientation contrast

Protomylonitic lherzolite – zoom on ultrafine grains



Colour-coded orientation imaging
shocked minerals - Quartz



grayscale orientation contrast imaging vs color-coded

Advanced characterization of mineralogical samples
Summary

- Unique hardware features

  - EBSD & EDS detector tilt and “slim” design for better data

  - built-in ARGUS™ FSE/BSE imaging system

- Optimized EBSD/EDS integration

  - Advanced phase ID offline & online

  - Phase discrimination by EDS quantification assistance during EBSD re-indexing

- Ultrafast re-indexing (optimizing SEM time)

Chapter 3 – Sample preparation for SEM & EBSD

Advanced Sample Preparation for SEM & EBSD

Sten Sturefelt, Hitachi High-Technologies
Webinar, 10th of September 2019

Broad Ion Beam Milling

Creating a clean and flat sample surface for SEM and EBSD studies

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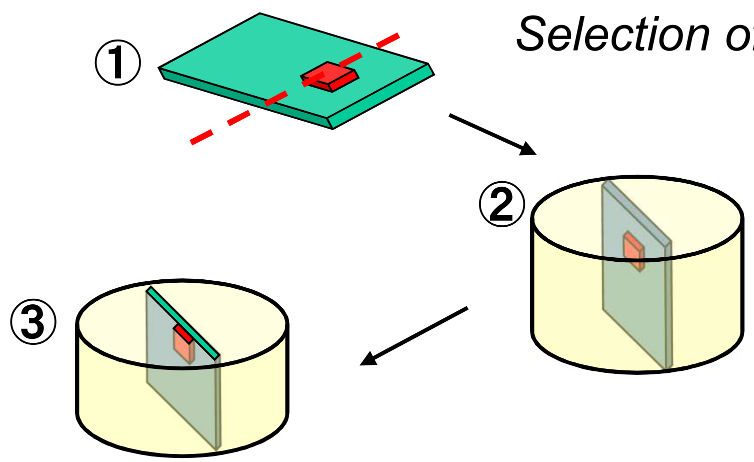
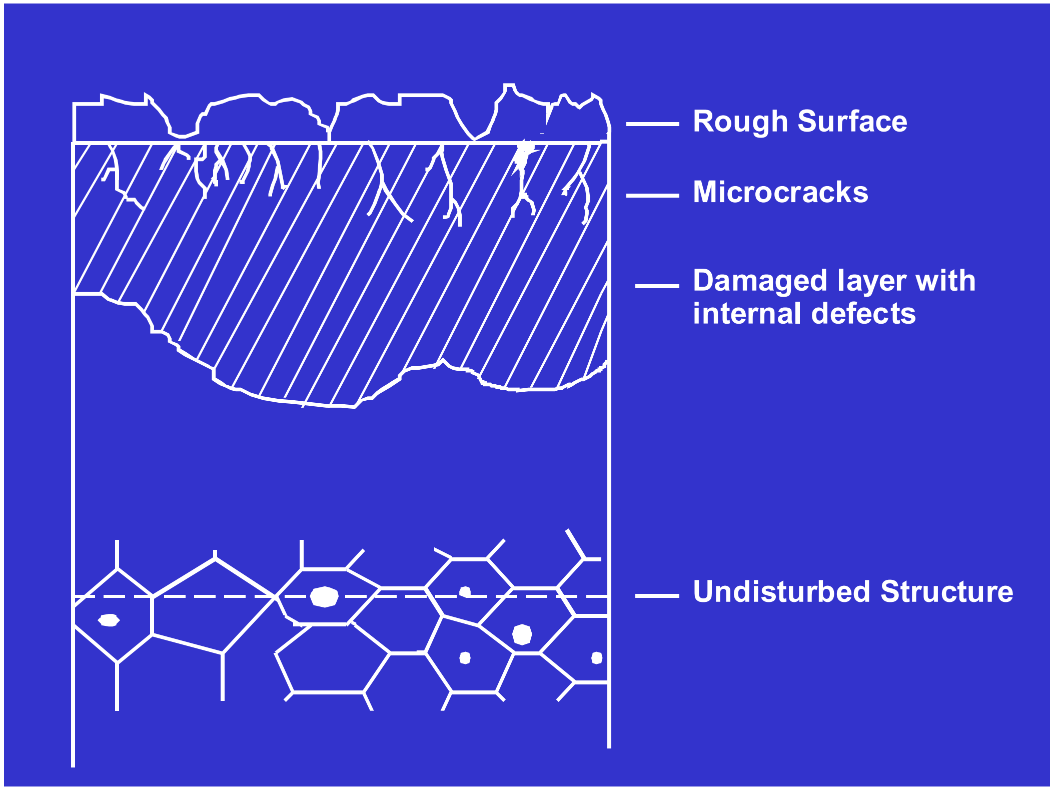
Embedding, Cutting, Polishing & Milling

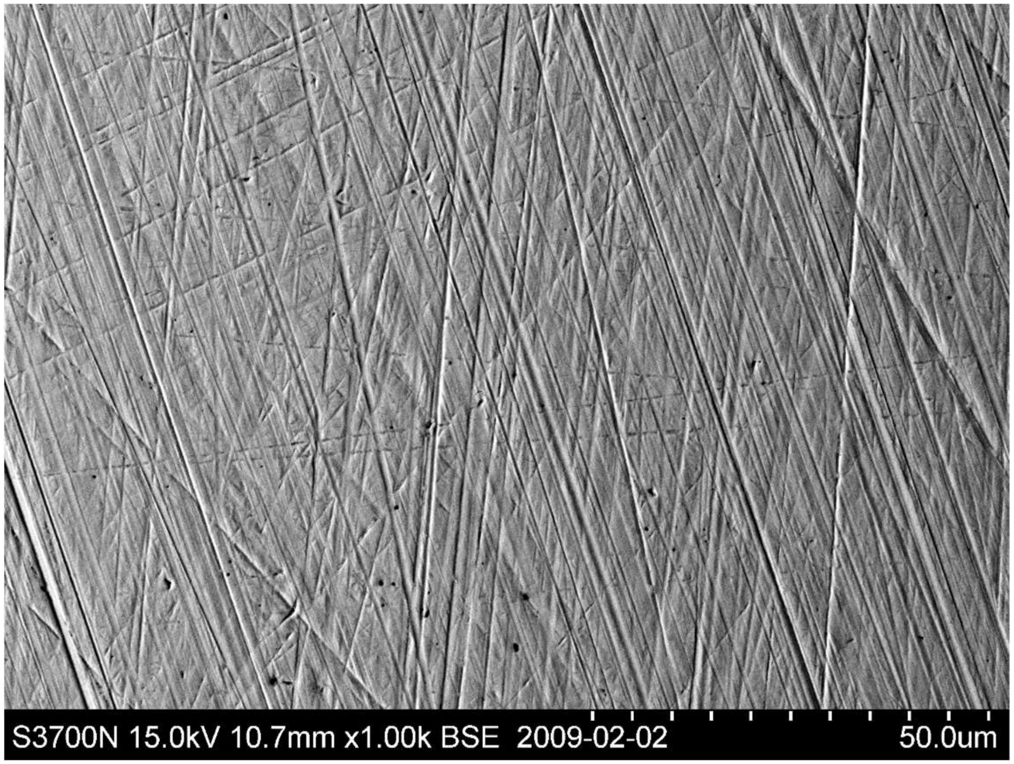


Is it ready for high resolution studies?

Damages from Cutting and Polishing

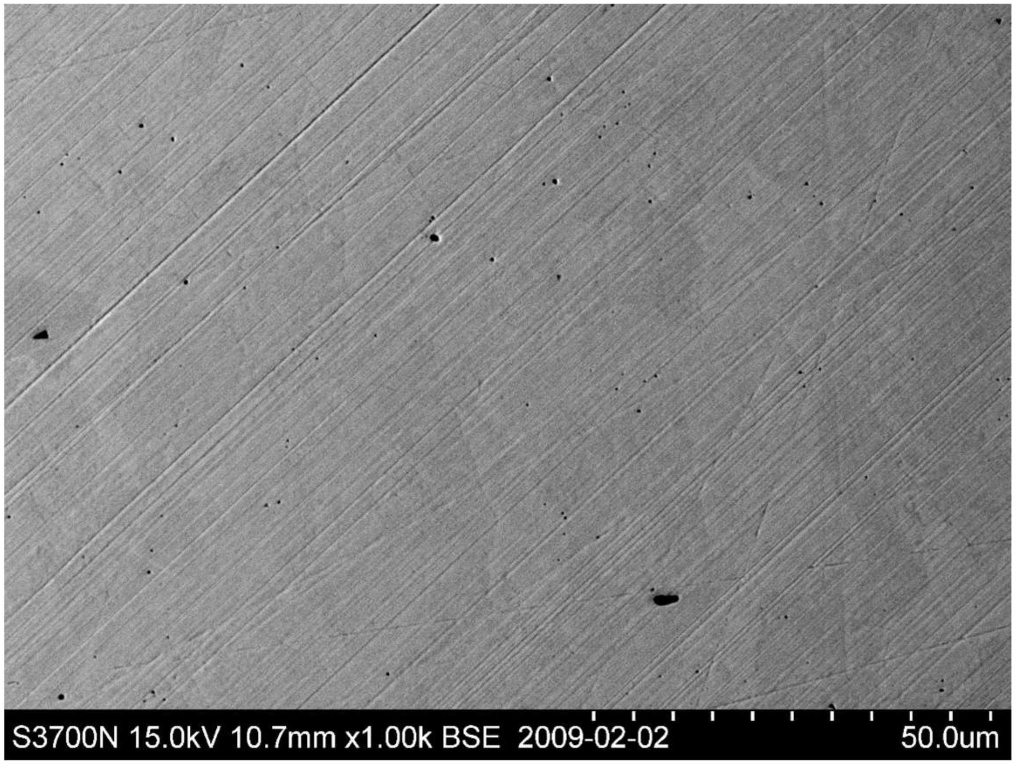


Damages from Polishing - Example



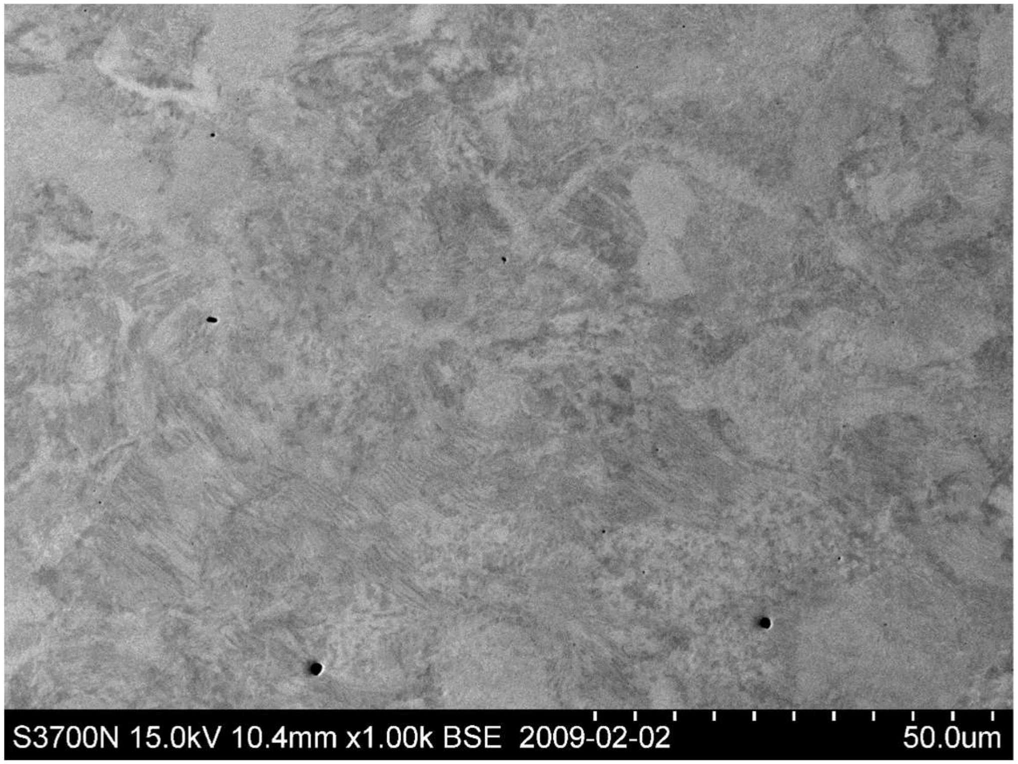
Steel polished with
9 µm diamond

Damages from Polishing - Example



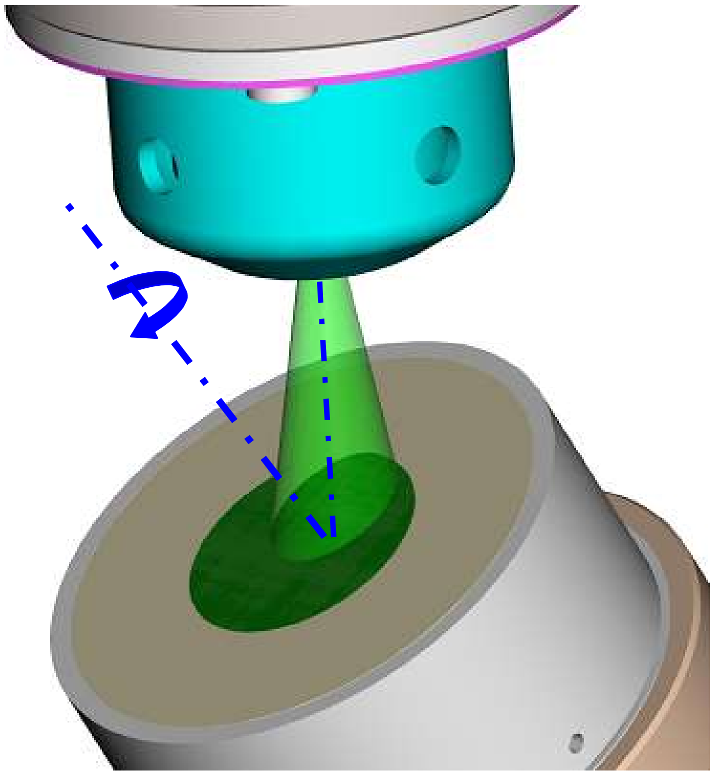
Steel polished with
3 µm diamond

Damages from Polishing - Example



Steel polished with
1 µm diamond

Broad Ion Beam Milling (BIB)



BIB ≠ FIB

Ablation via momentum transfer from Argon Ions

Broad Ion Beam Milling – Reasons Why

- Traditional polishing or cutting techniques of hard or ductile, soft and composite materials introduce significant lateral sheer forces
- The result is scratches, smearing, delamination or other damage
- Ion Milling eliminates oxide films or contamination and will enhance crystal orientation contrast
- Ion Milling removes artifacts resulting in a smooth, polished surface ideal for EDX and EBSD analysis
- Prepare a “stress-free” cross-section of complex compound materials

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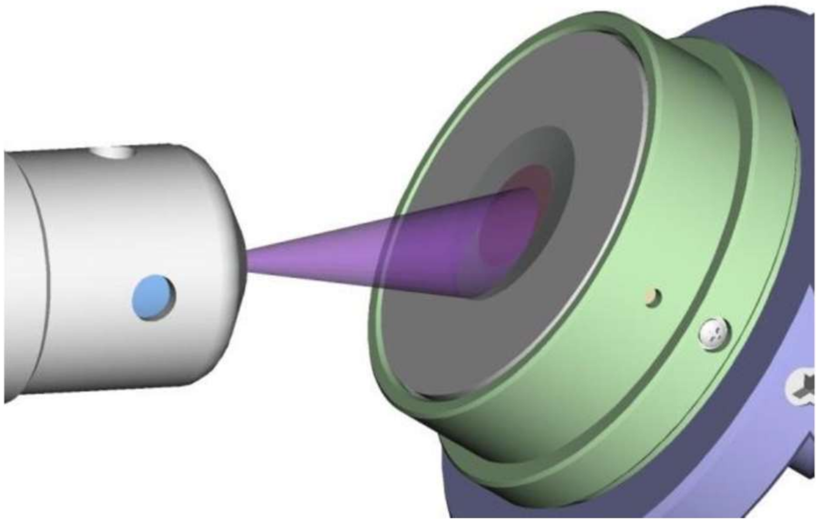
Broad Ion Beam Milling – Flat Milling & Cross-sections

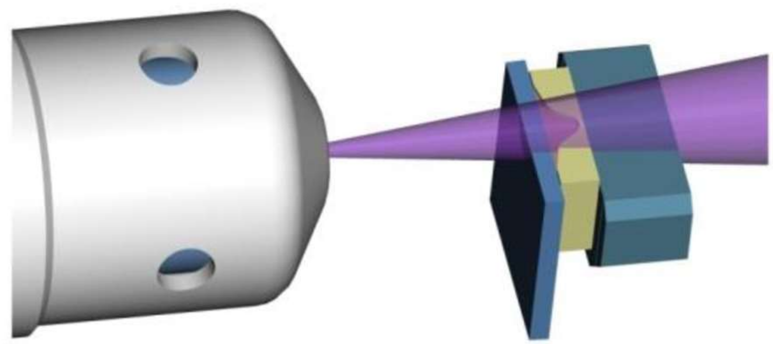
Hitachi IM4000+

Hitachi IM5000 (ArBlade)

Broad Ion Beam Milling – Flat Milling & Cross-sections

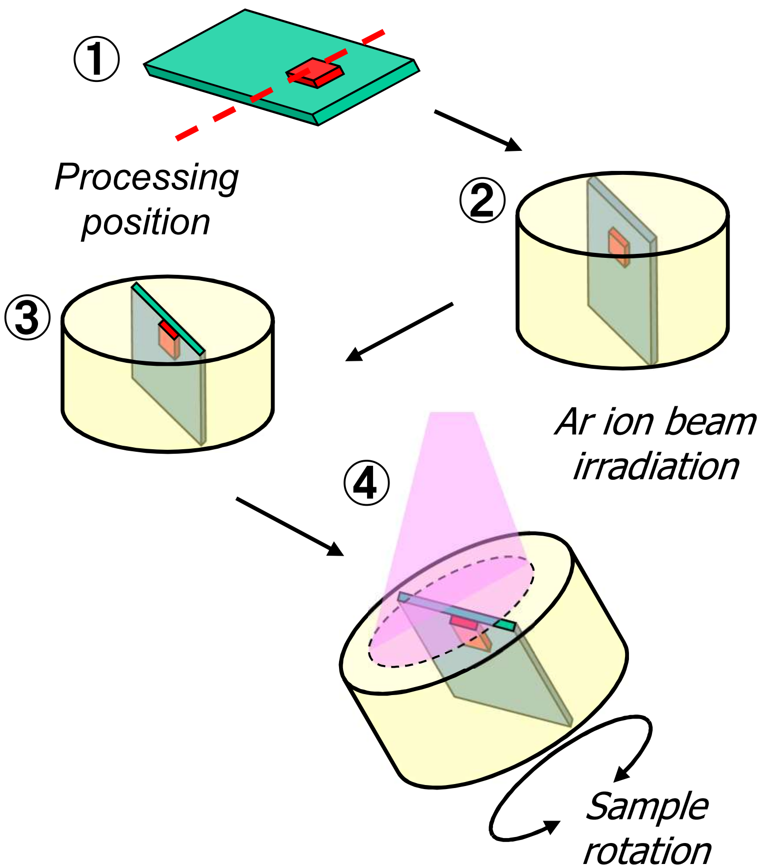


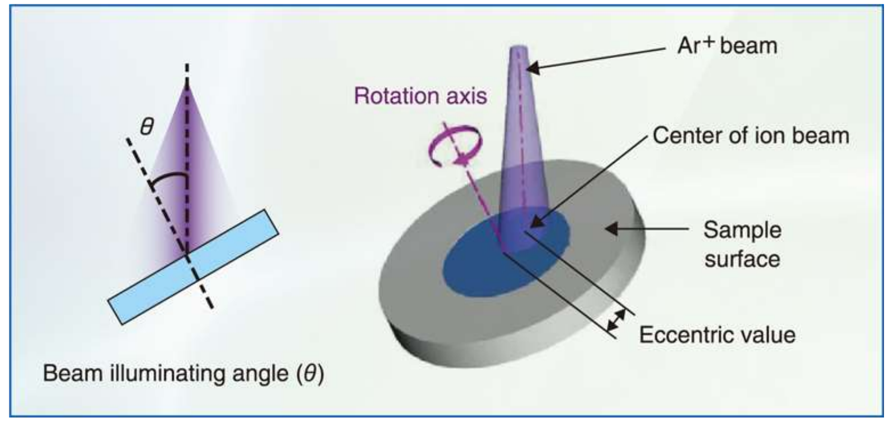
Flat Milling Set-up



Cross-section Set-up

Ion Milling of Flat Surfaces





Flat milling method: Shifts the beam over the surface to uniformly sputter-etch the sample with Argon ions

The milling angle strongly influences the result

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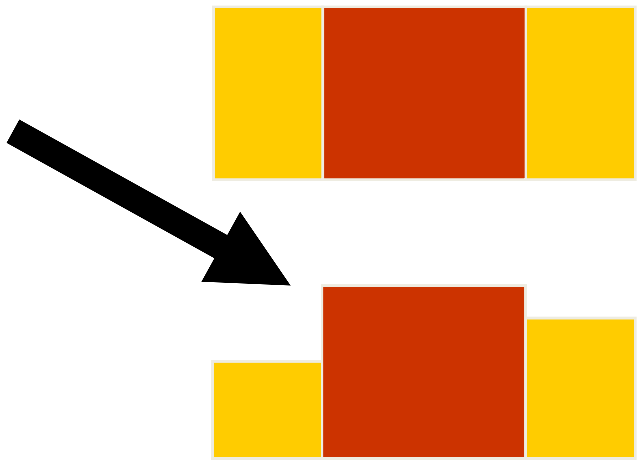
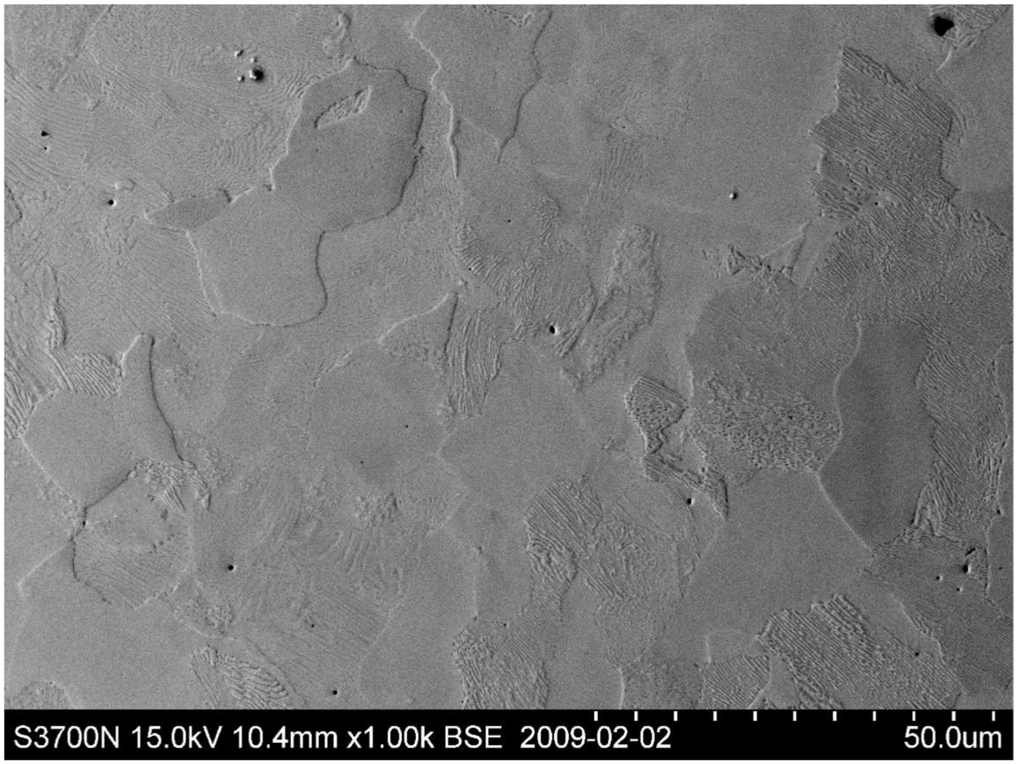
Ion Beam Milling and Incidents Angles – Flat Milling



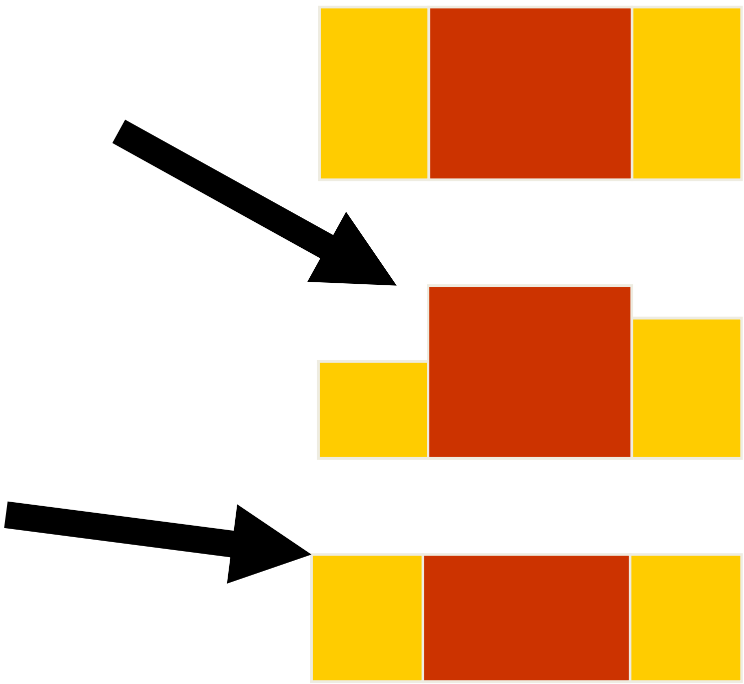
Angles >15º ⇨ Selective etching (chemistry, orientation)

Ion Beam Milling and Incidents Angles – Flat Milling



Steel polished with 1 um diamond.
Ion polished at 60 degrees at 6 kV during 10 minutes.

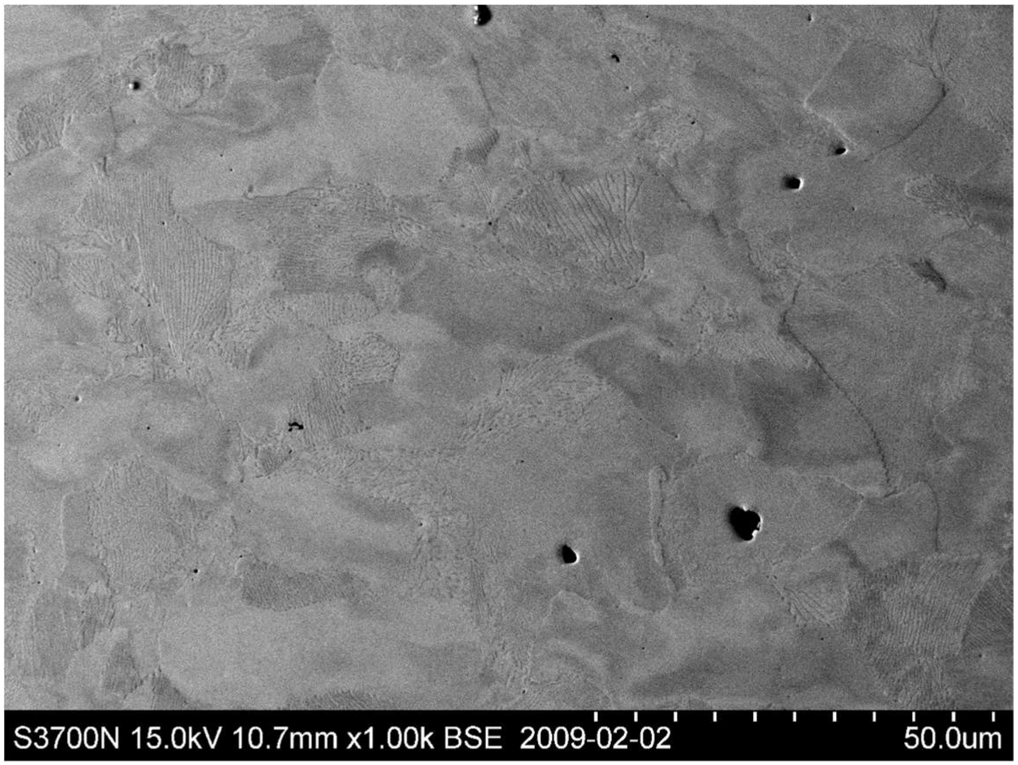
Ion Beam Milling and Incidents Angles – Flat Milling



Angles >15º ⇨ Selective etching (chemistry, orientation)

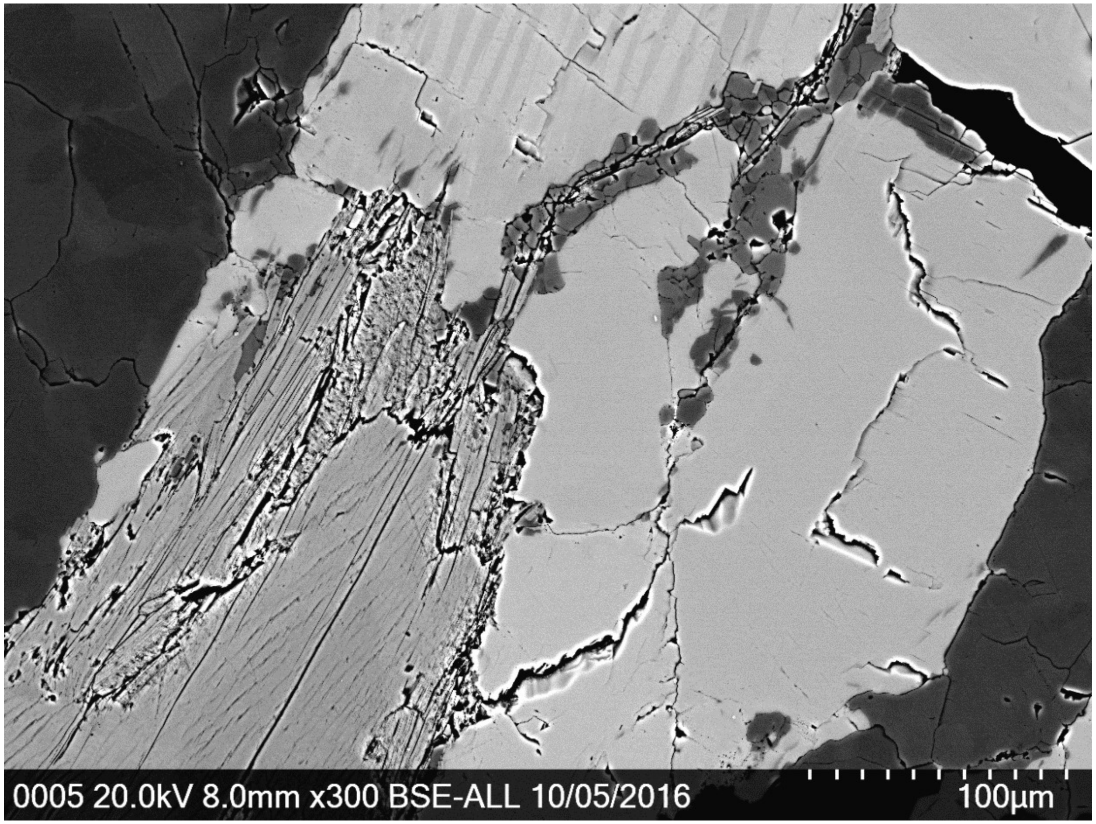
Angles <10º ⇨ Reduces topography

Ion Beam Milling and Incidents Angles – Flat Milling



Steel polished with 1 um diamond.
Ion polished at 10 degrees at 6 kV during 10 minutes.

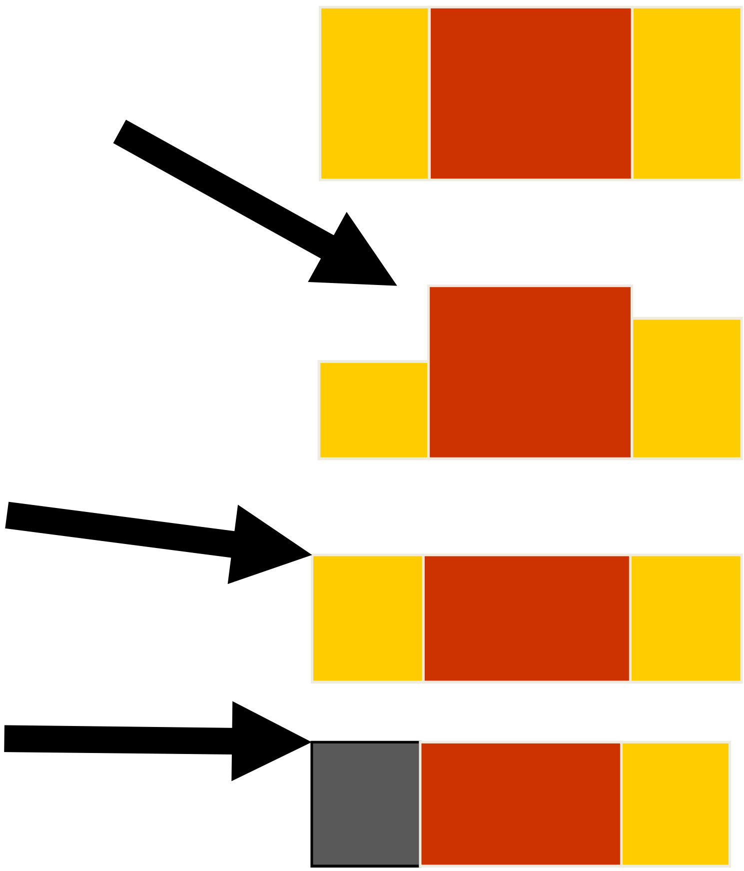
Flat Milling - Geological Application



Pegmatit after
Flat Milling

Sample courtesy of Prof. Claudia Trepmann, Ludwig Maximilian University, Munich

Ion Beam Milling and Incidents Angles – Cross-sections

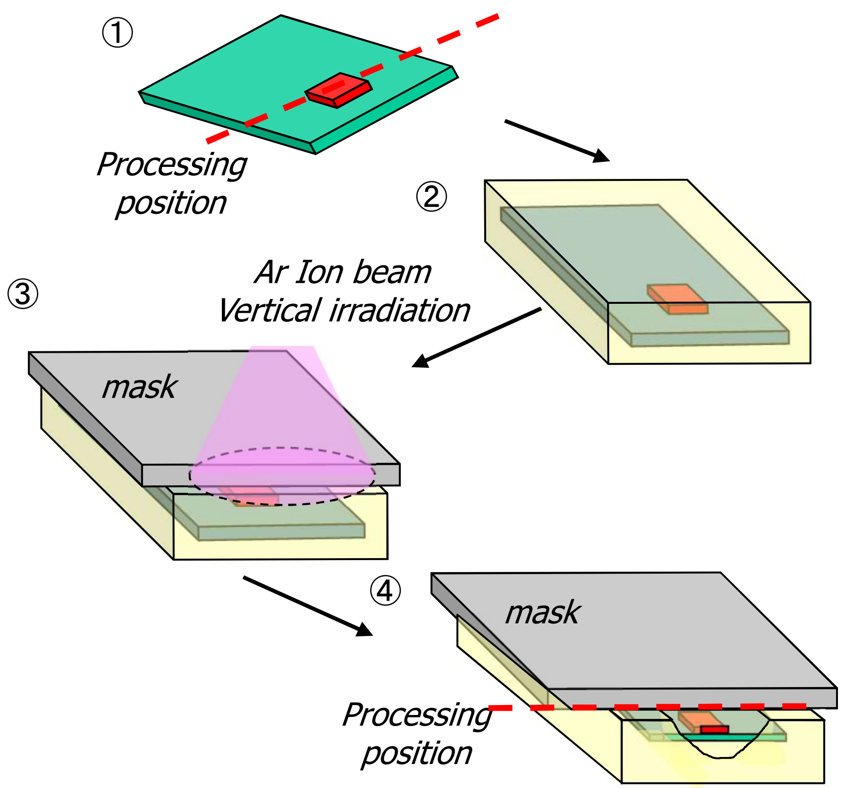


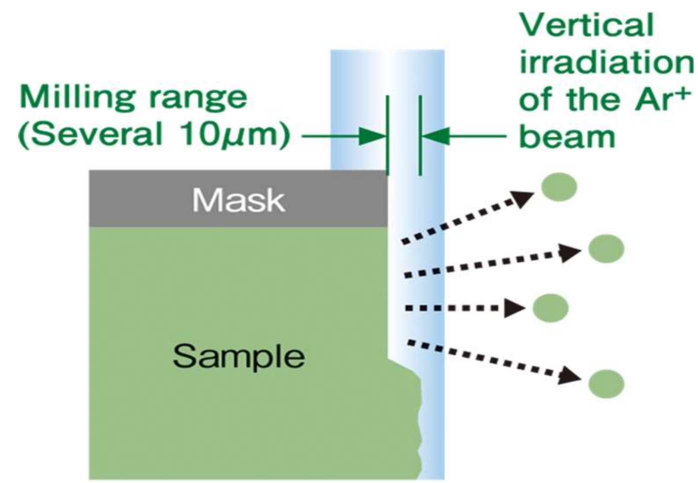
Angles >15º ⇨ Selective etching (chemistry, orientation)

Angles <10º ⇨ Reduces topography

At 0º using a mask ⇨ Cross-section

Ion Milling Cross-sections





Cross-section Milling: Sputter-etch the sample with Ar ions partly covered with a mask to gradually produce a sharp edge

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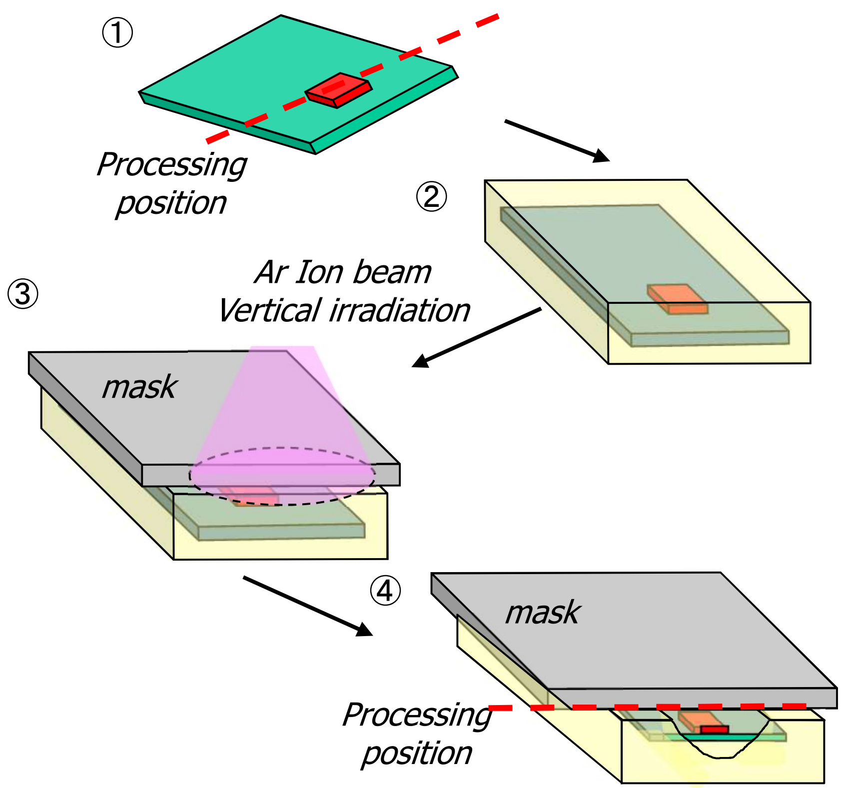
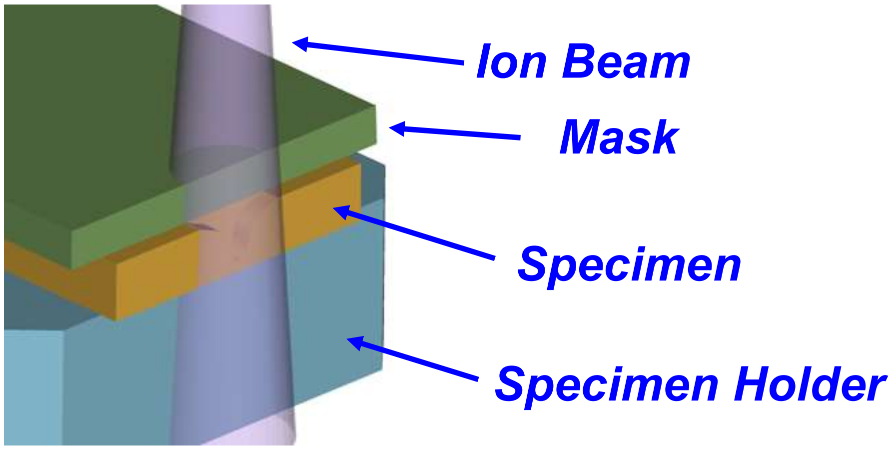
Ion Milling Cross-sections

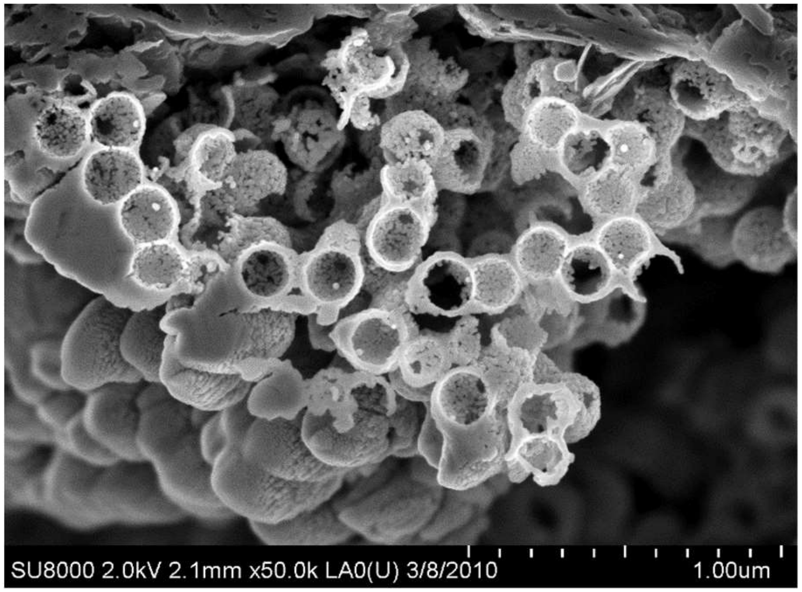


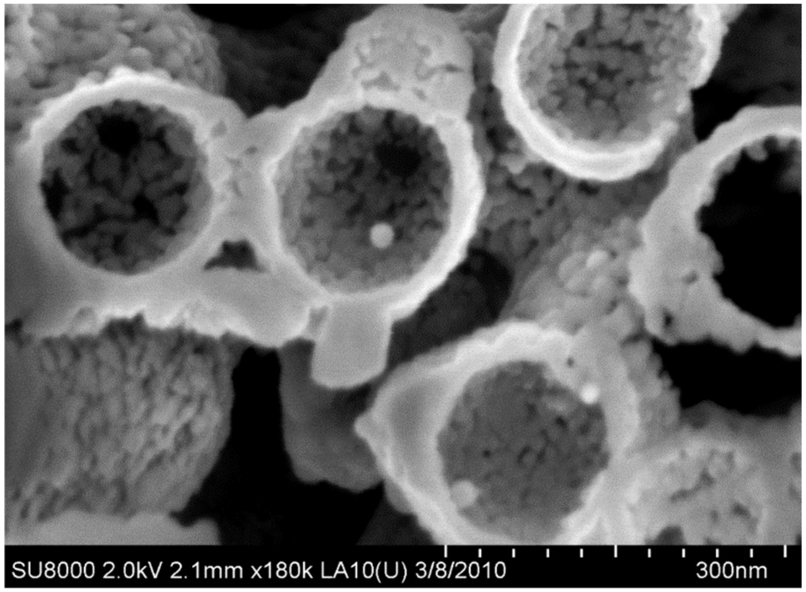


Resin embedding can be omitted,
carbon glue can be used instead.
No pre-polishing needed.

Ion Milling Cross-sections - Application Example

Ion milled section

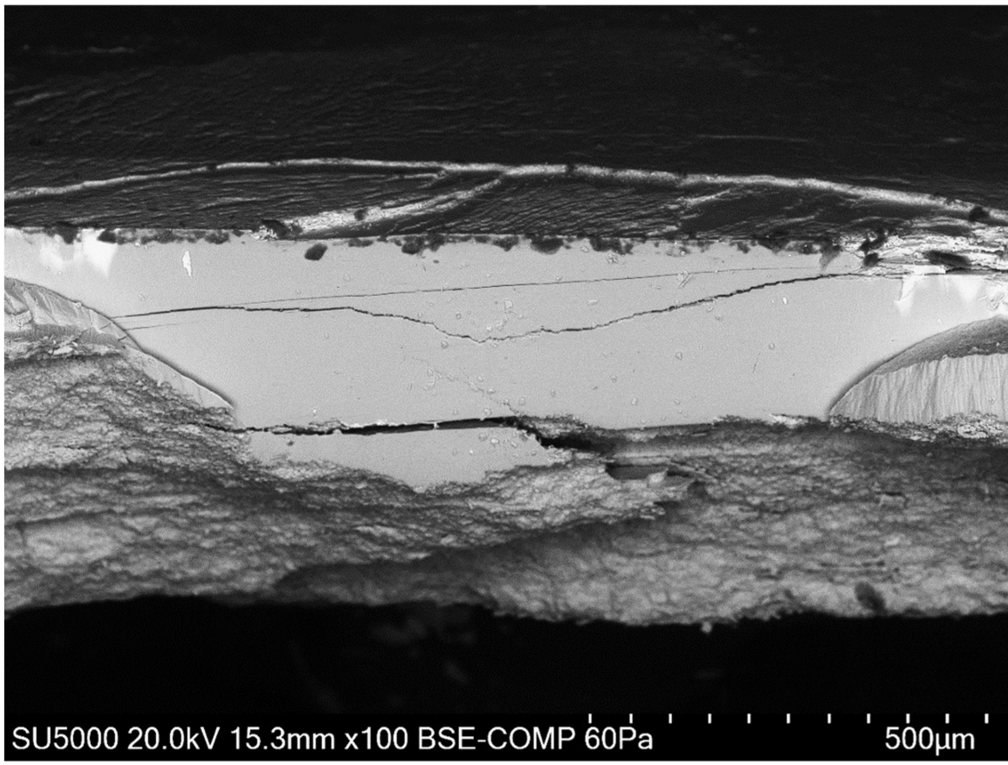




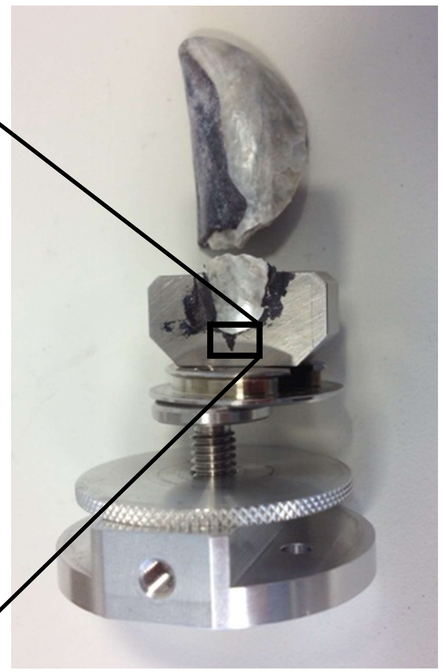
Porous Zirkonium shell with active catalyst particle

Milling condition: Ion beam voltage 6 kV, time 1-2 hours

Ion Milling Cross-sections – Application Example

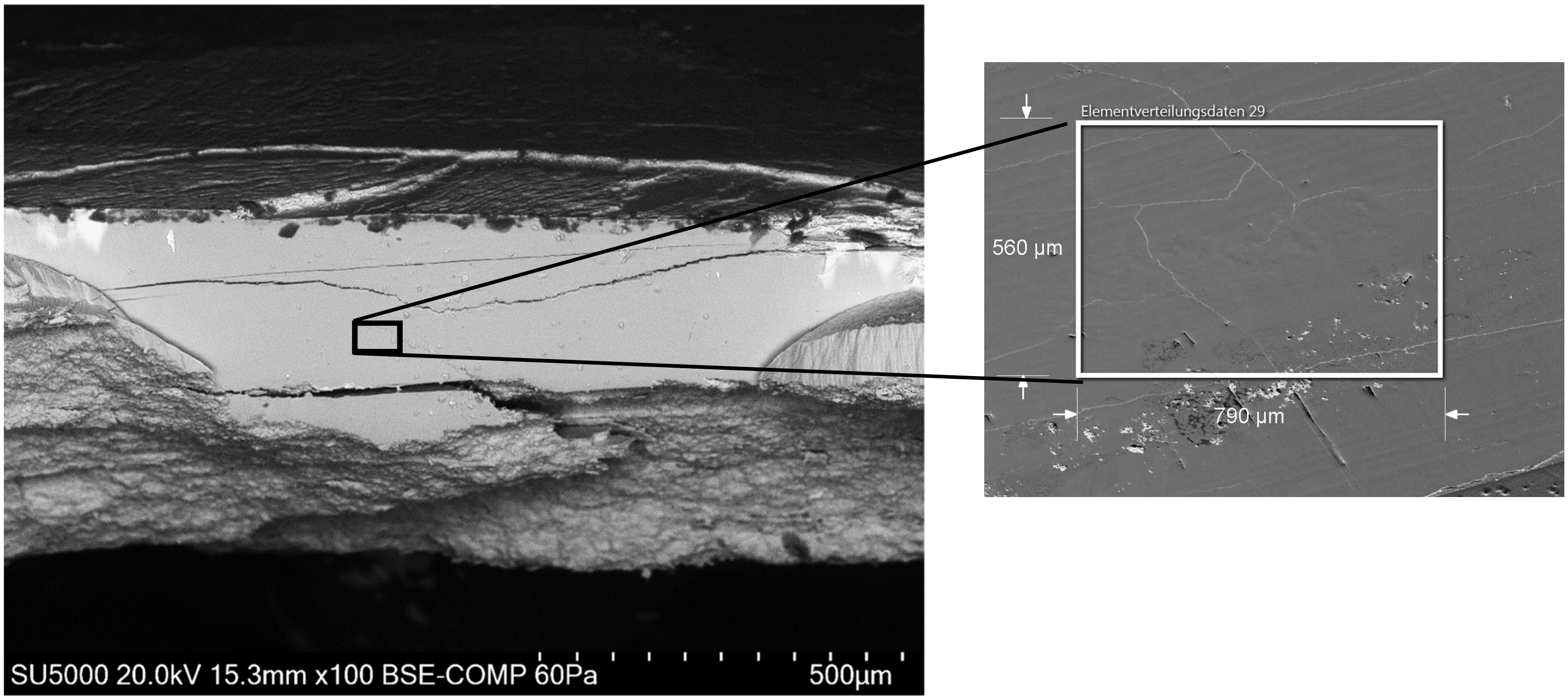


Shell from the North Sea



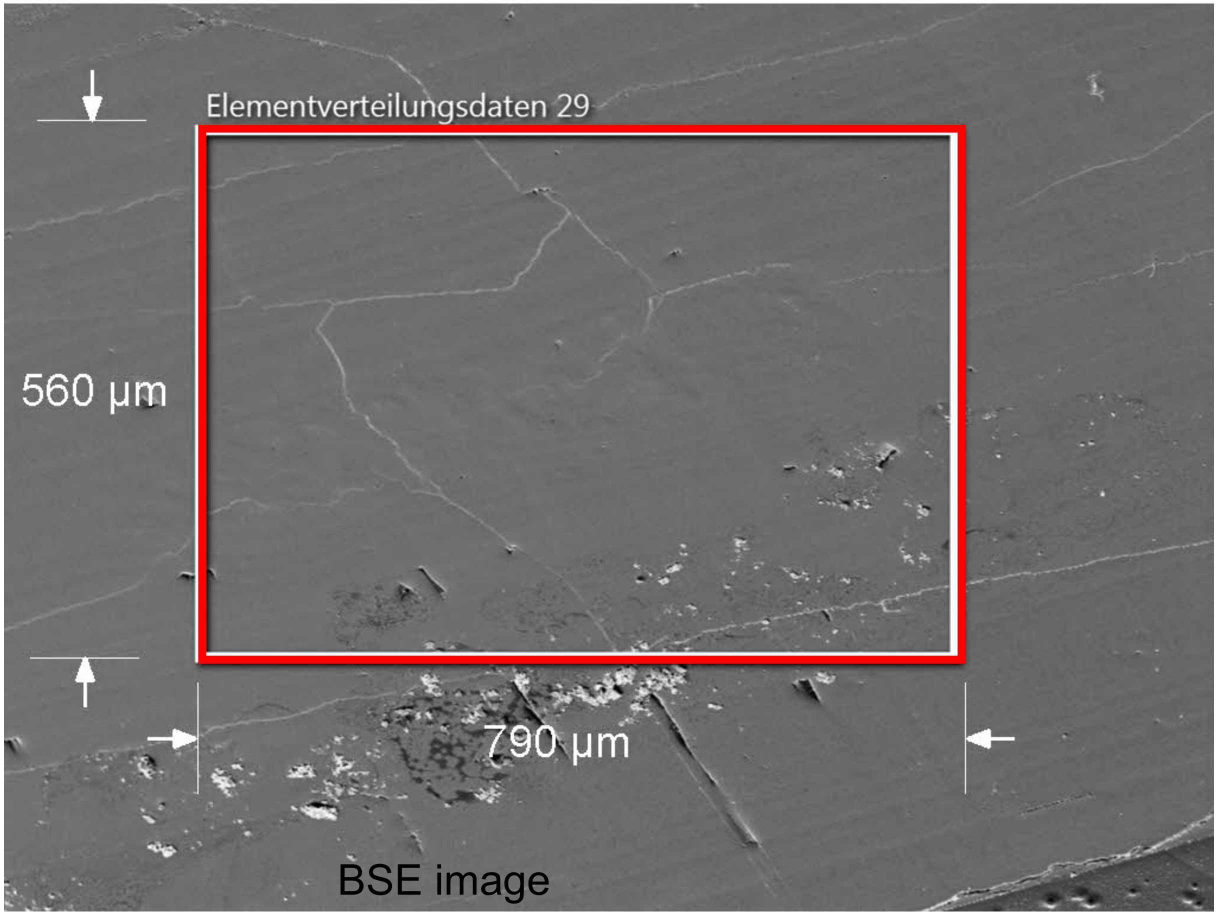
Cross-section of a Drill Core

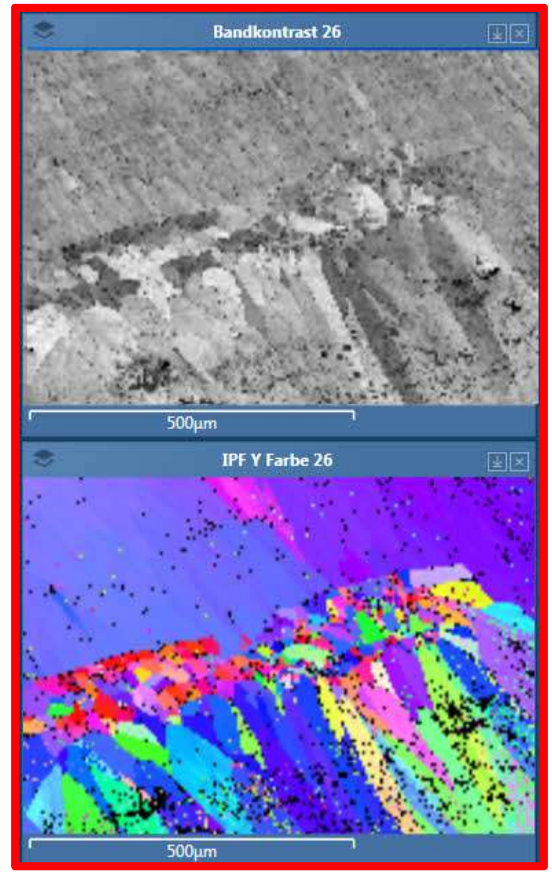
Ion Milling Cross-sections – Application Example



Shell from the North Sea (calcite)

EBSD of biominerals without coating





Right: diffraction band contrast image and IPF Y map (calcite)

Summary

- Broad Ion Beam (BIB) Milling is ideal for creating a flat and smooth sample surface for both EDX and EBSD analysis in high resolution.
- BIB also eliminates oxide films or contamination and will enhance crystal orientation contrast.
- BIB can be used on hard, soft and composite materials.
- Flat Milling is a quick method for embedded samples and can be adjusted for selective etching.
- Cross-section Milling is ideal for flat samples and thin layer studies. No resin embedding or pre-polishing needed.

Q&A

Are There Any Questions?

Please type in the questions you might have

in the Q&A box and press *Send*.

More Information

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Innovation with Integrity