Correlative Microscopy

13 December 2022

Sieger van der Laan

Together we make the difference

Introduction - Materials characterization

Starting point: Bulk analysis

- Chemical composition (XRF)
- Phase composition (QXRD)

Introduction - Materials characterization

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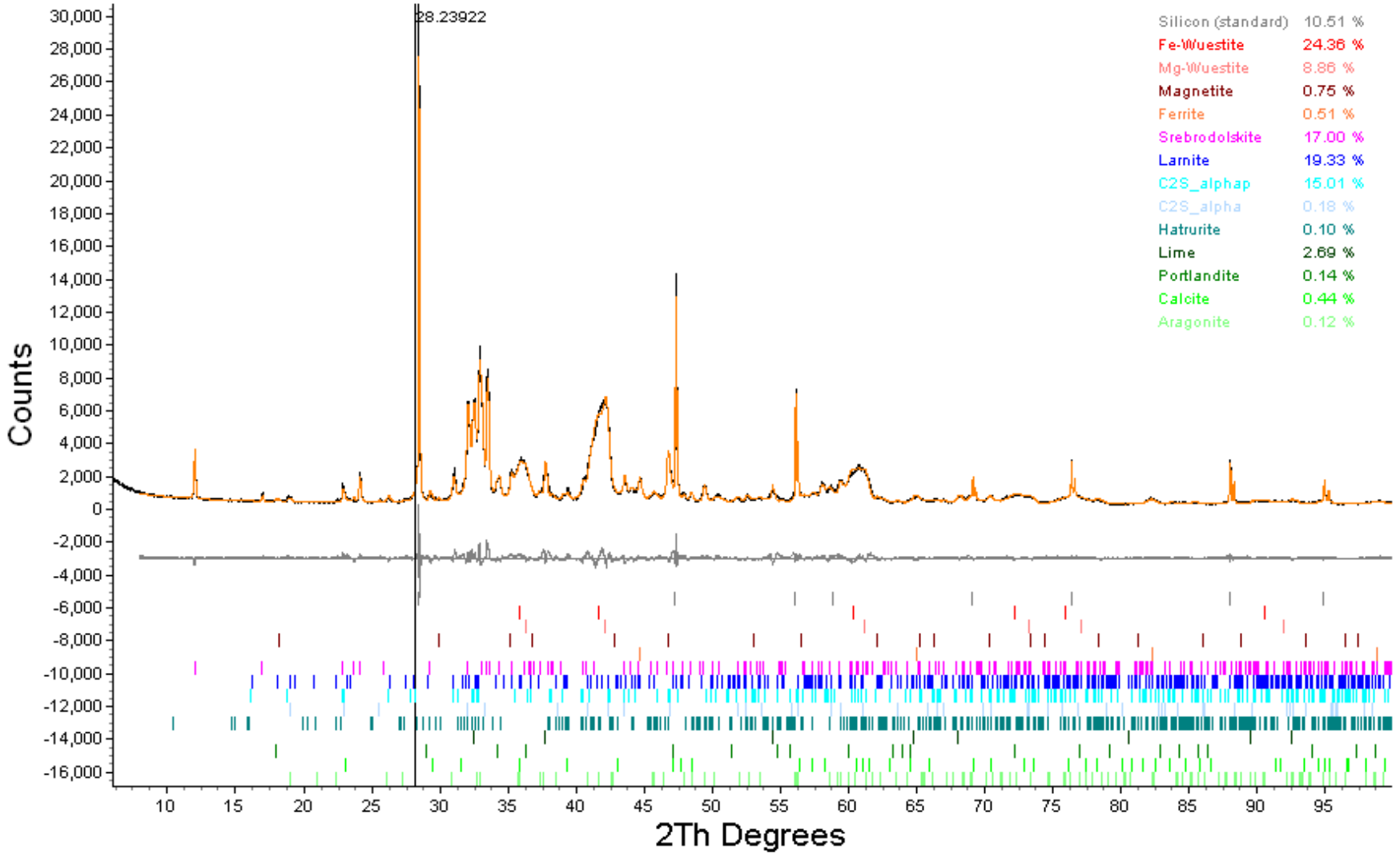
XRF

FeO	27.1	23.3
CaO	39.1	42.3
SiO2	12.3	14.9
MgO	9.5	8.9
MnO	4.1	4.1
Al2O3	1.1	1.0
P2O5	1.5	1.8
TiO2	1.0	0.9
V2O5	-	0.8
Cr2O3	-	0.2
total	98.0	99.4

QXRD

Fe-Wuestite Fe(Mg)O	25.7	35.9	24.1	30.8
Mg-Wuestite Mg(Fe)O	9.4		6.3	
Magnetite Fe3O4	0.8		0.4	
Iron met Fe	0.5		0.0	
Srebrodolskite Ca2Fe2O5	18.0	18.0	12.3	12.3
Hatrurite C3S	0.1		0.2	
Larnite beta C2S Ca2SiO4	20.4	36.5	45.2	50.4
alpha' C2S Ca2SiO4	15.9		4.8	
alpha C2S Ca2SiO4	0.2		0.4	
Lime CaO	2.8	3.2	4.5	4.7
Portlandite Ca(OH)2	0.1		0.1	
Calcite CaCO3	0.5		0.2	
Aragonite CaCO3	0.1		0.3	
Amorphous	5.4		1.2	



Sensitivity:

Introduction - Materials characterization

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TiO2	1.0	0.9
V2O5	-	0.8
Cr2O3	-	0.2
total	98.0	99.4

And then: Microscopic information

- How to relate microscopic information to bulk information?
- How to correlate observations from different microscopes?

QXRD

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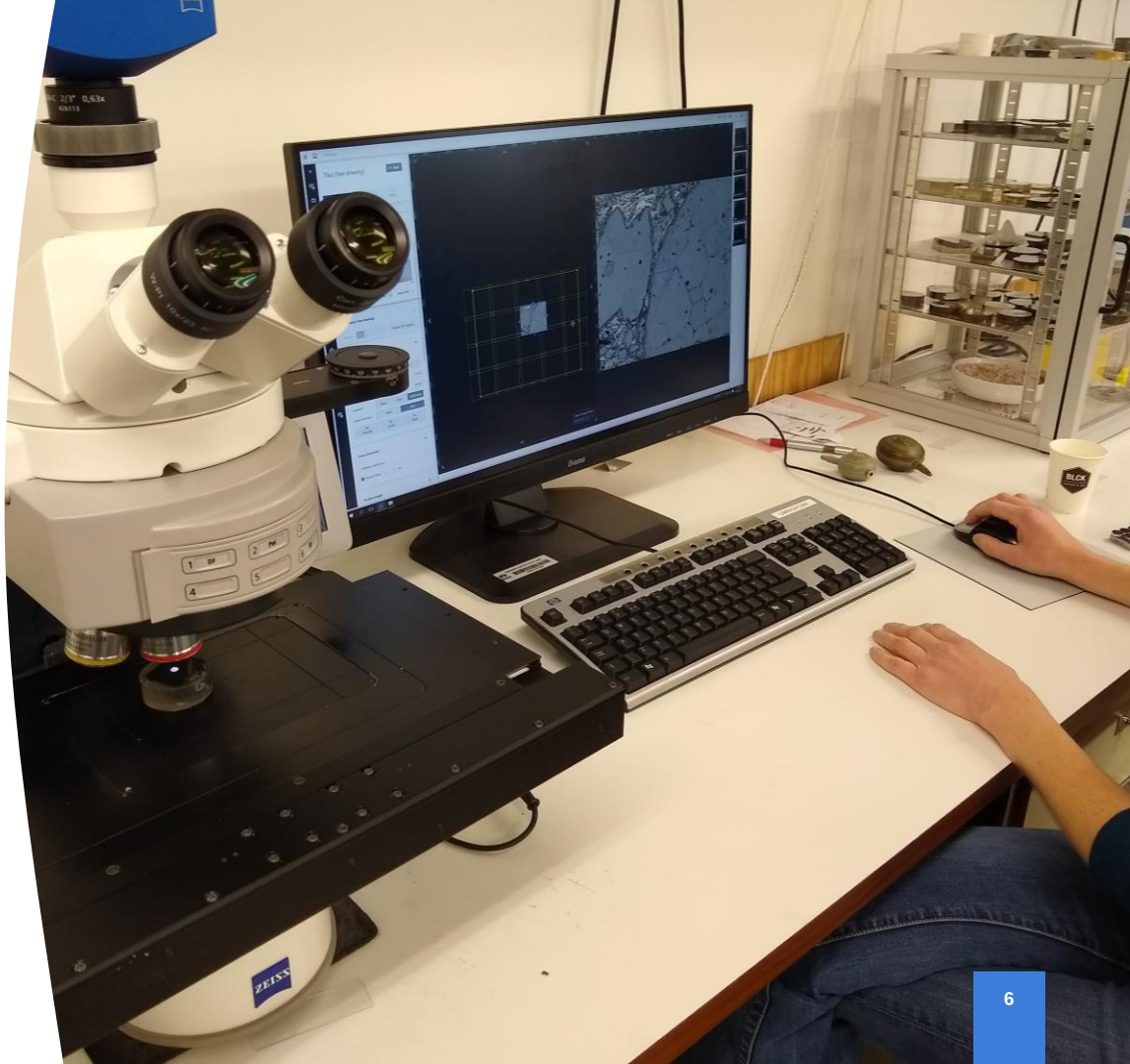
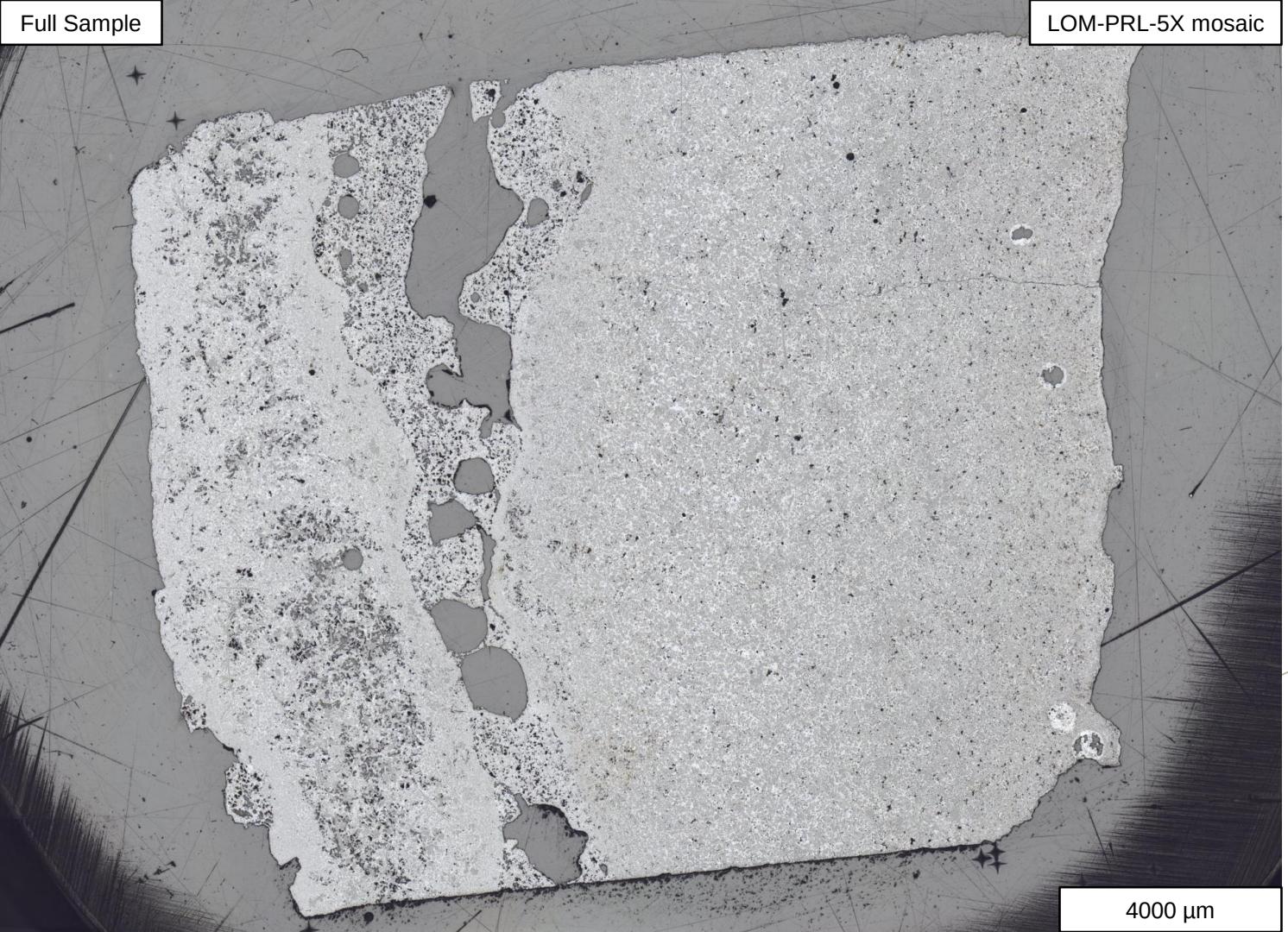
Light Optical Microscopy

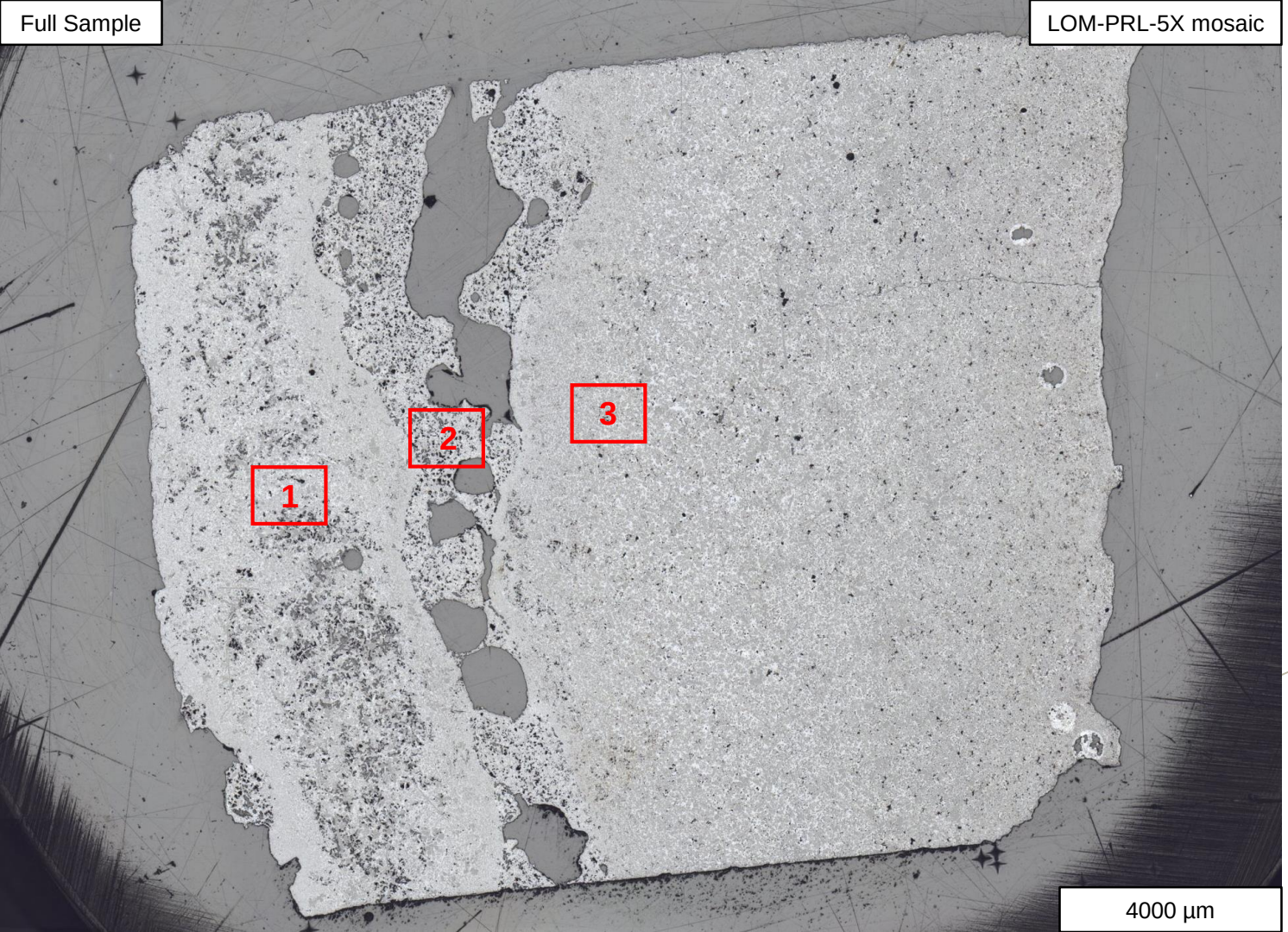
- ZEISS AxioImager Z1
- Automated X-Z stage
- Polarized Reflected Light imaging
- Polished sample mount
- Larger area imaging with stitching of individual fields ➔ mosaic





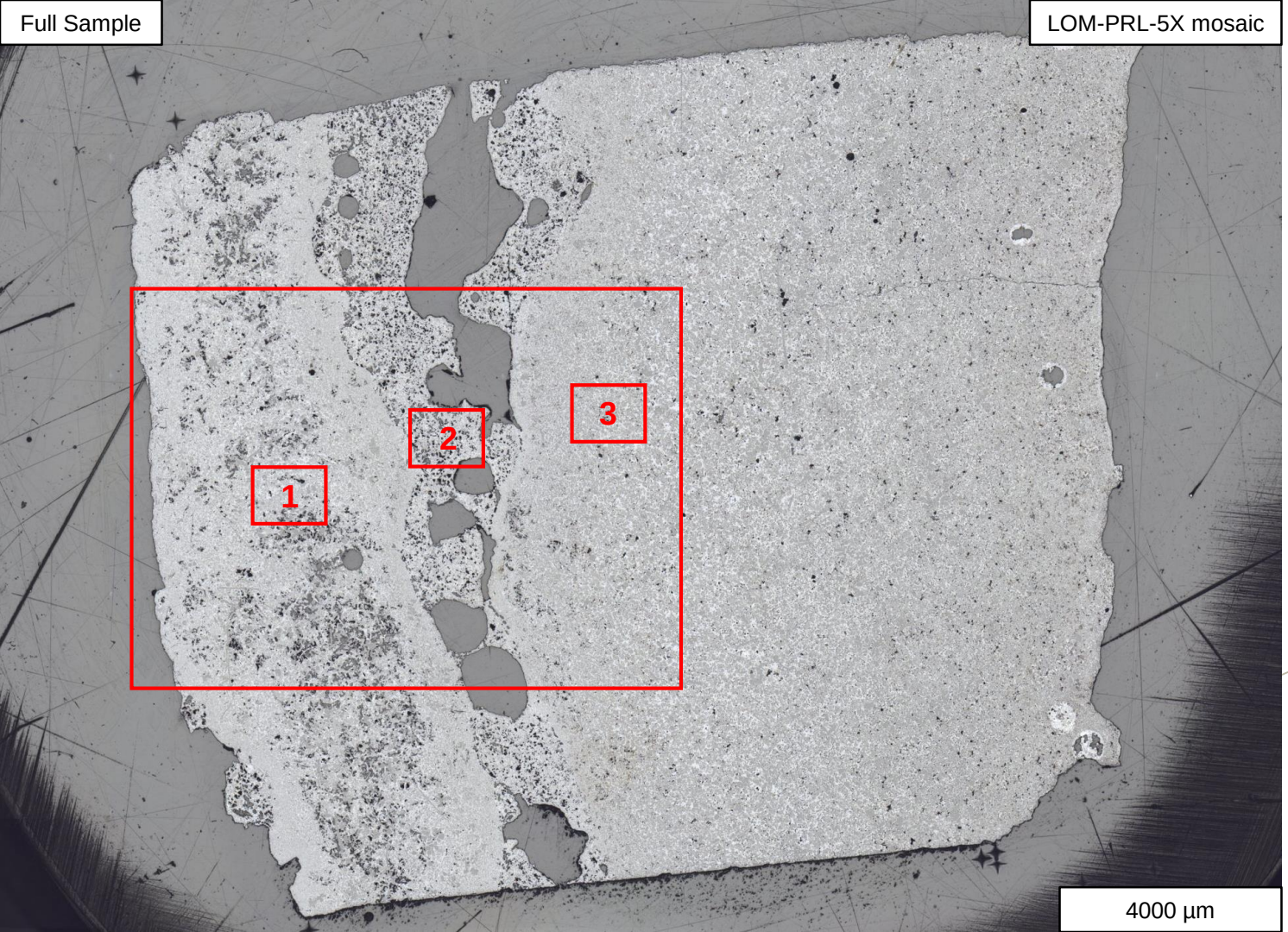
Optical Microscopy

- Full sample mosaic
- Zeiss Axio Imager Z1
- 5x objective
- Polarized reflected light
- Flat field correction
- White balance correction



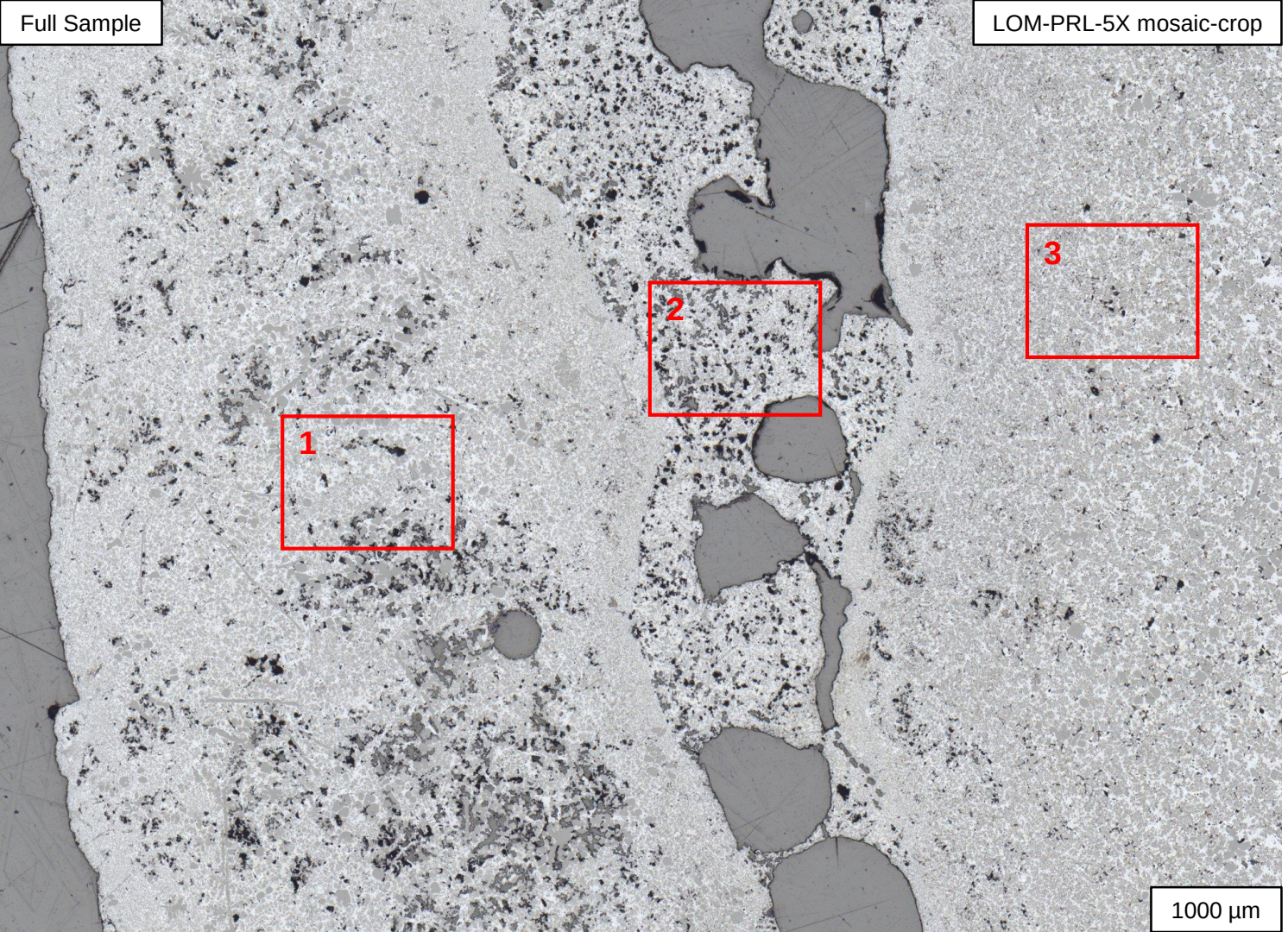
Regions of Interest

- Three regions selected for more in depth investigation



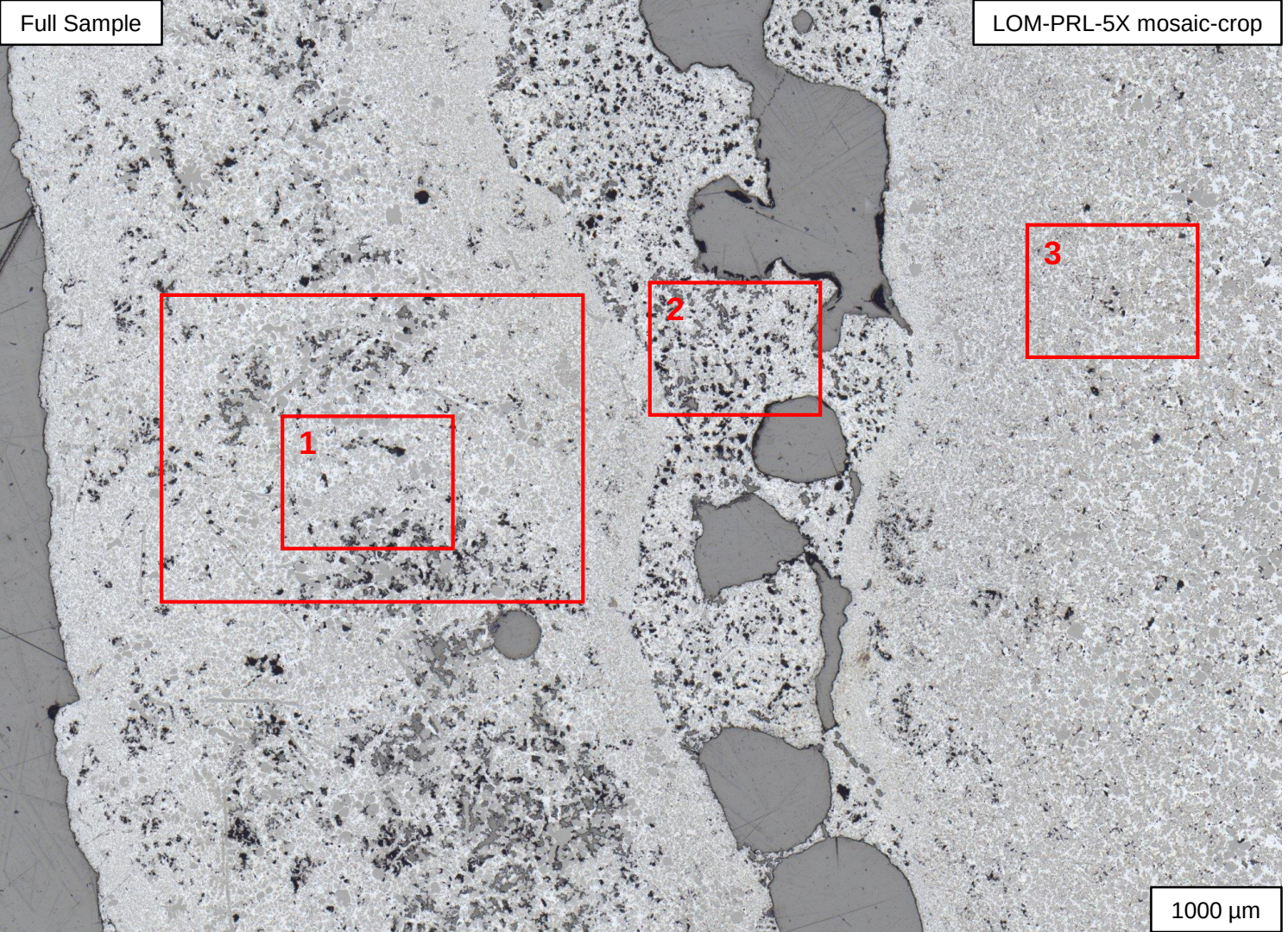
Regions of Interest

- Three regions selected for more in depth investigation
- Zooming in…



Regions of Interest

- Three regions selected for more in depth investigation
- Each region has differing textural and phase properties



Regions of Interest

- Three regions selected for more in depth investigation
- Each region has differing textural and phase properties
- Zooming in…

Area 1

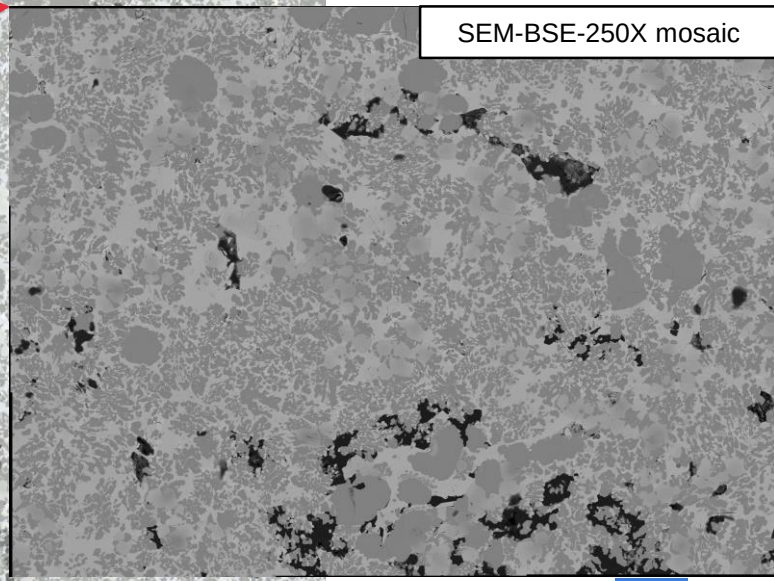
- ROI mosaic
- Zeiss Axio Imager Z1
- 20x objective
- Polarized reflected light
- Flat field correction
- Colour balance correction

Area 1

LOM-PRL-20X mosaic-crop

Electron Microscopy

- JEOL 7001F FEG-SEM
- 250x BSE mosaic
- Z contrast
- Needs correlation with optical image…



SEM-BSE-250X mosaic

500 µm

SEM-EDS Backscatter & Spectral Imaging

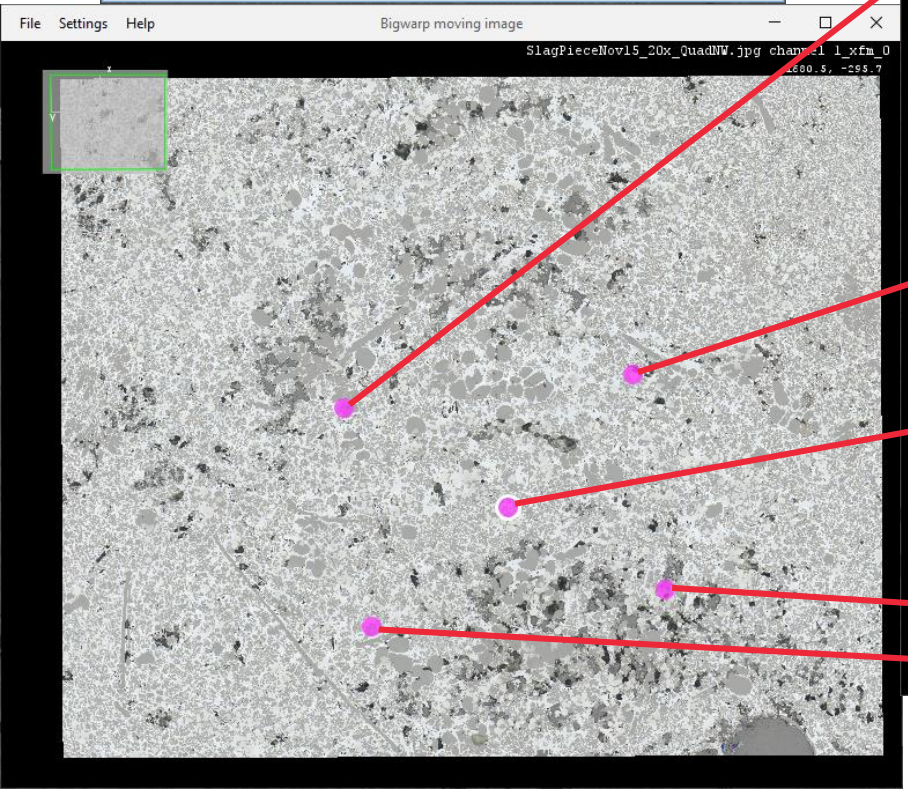
- JEOL 7001
- Dual OXFORD detectors (SDD 2x170mm)

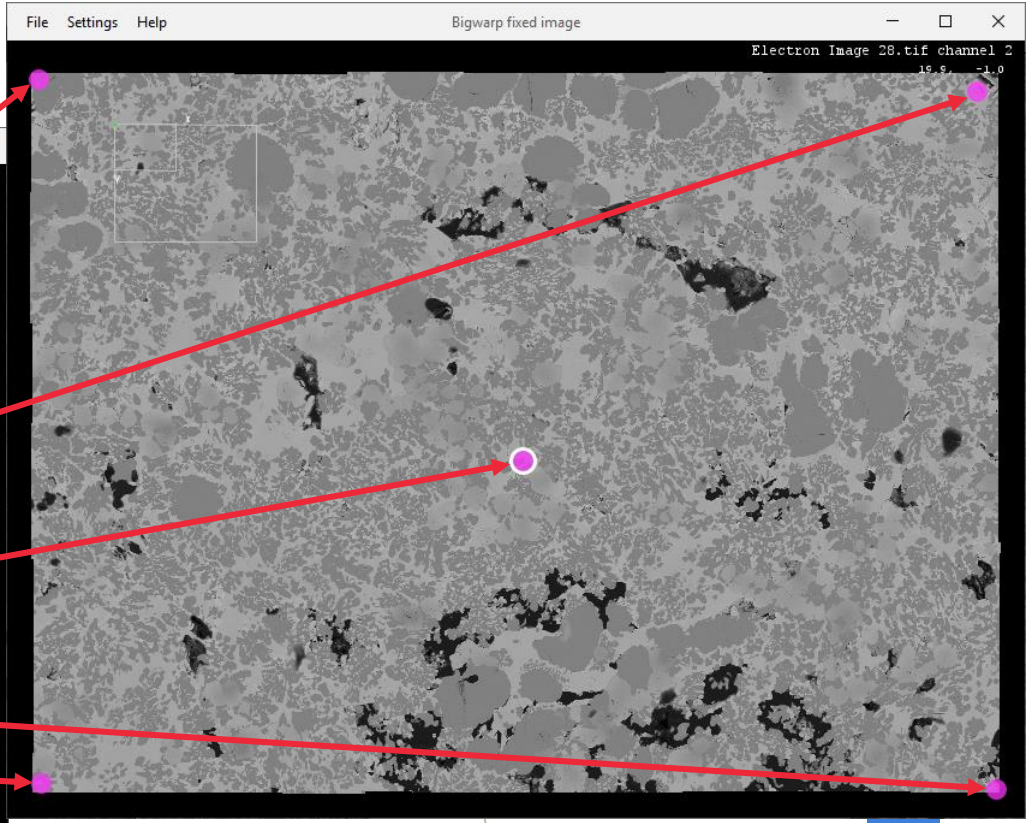
Optical Image-Electron Image Correlation

- ImageJ/FIJI & BigWarp plugin
- Set landmarks between images

File Landmarks — Landmarks

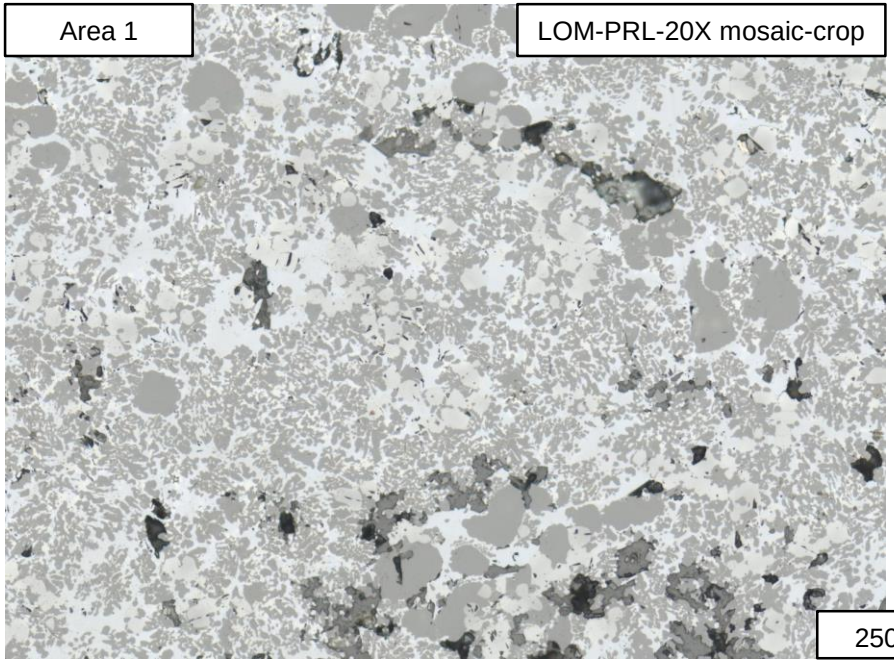
Name	Active	mvg-x	mvg-y	fix-x	fix-y
Pt-0	☑	2,369.027	2,773.293	0.258	0.322
Pt-1	☑	4,793.279	2,501.52	30.349	0.62
Pt-2	☑	5,065.928	4,311.15	31.038	22.932
Pt-3	☑	2,601.333	4,607.825	0.426	22.844
Pt-4	☑	3,742.562	3,612.053	15.853	12.498

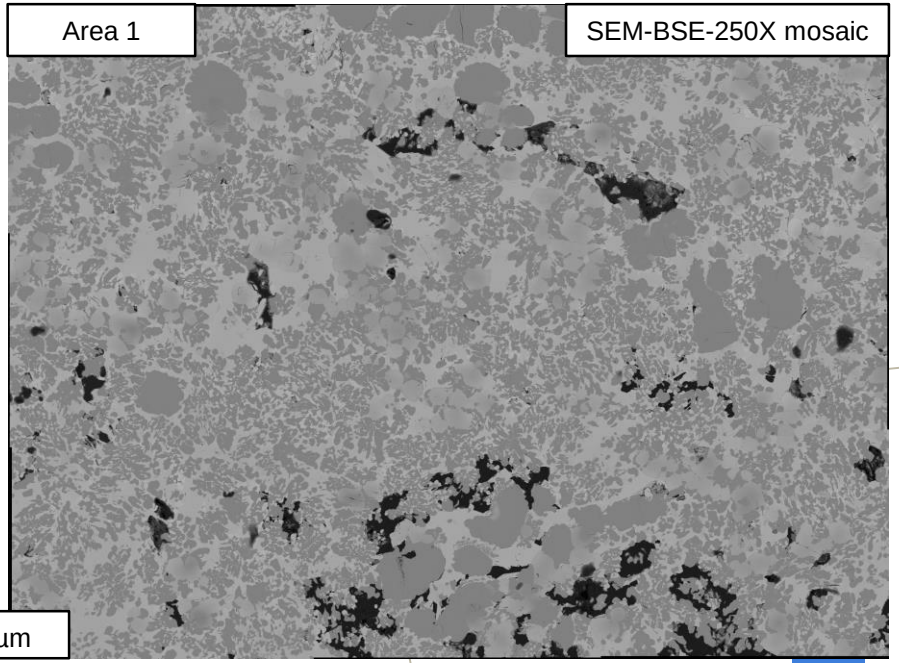




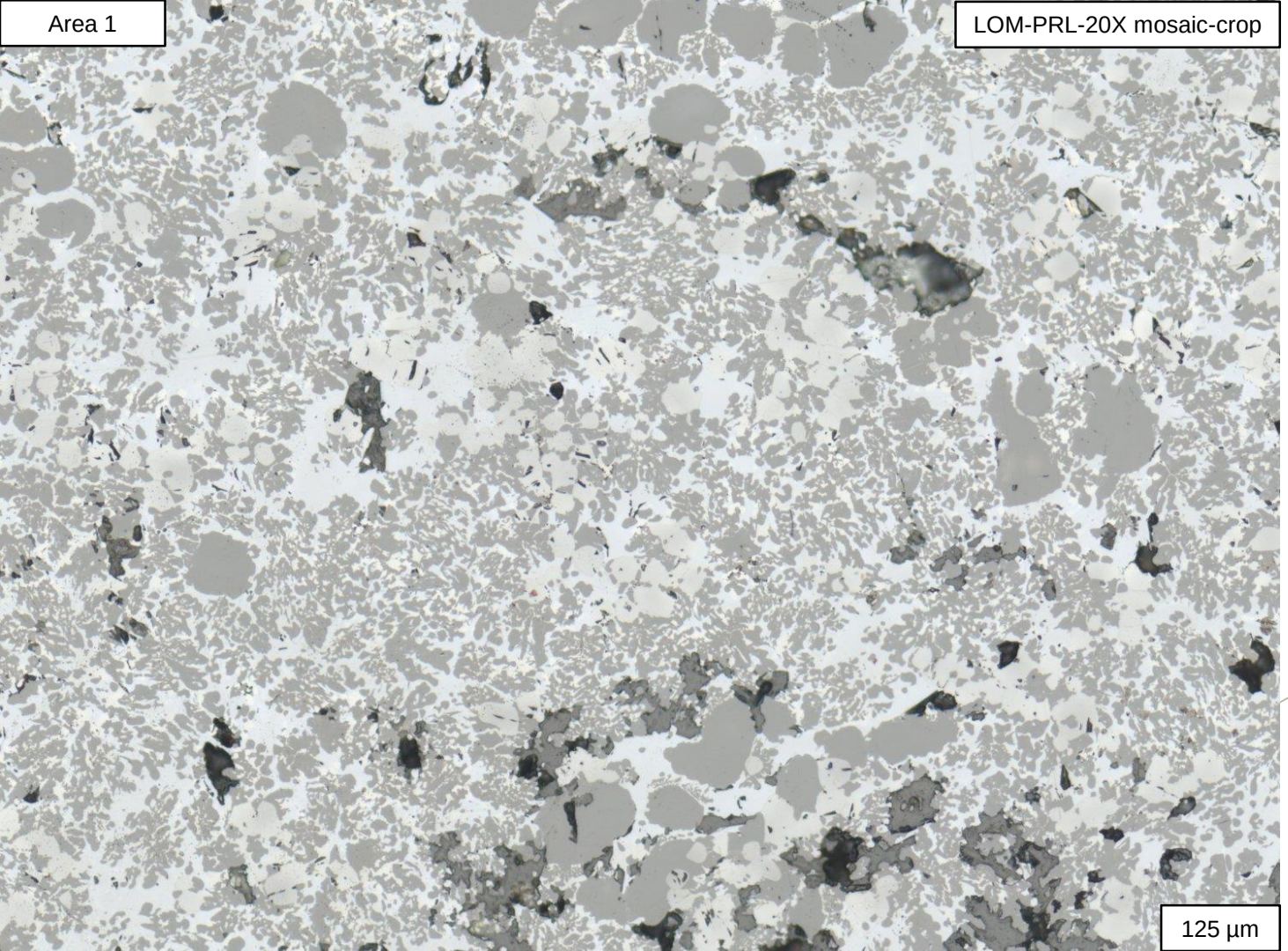
Optical Image-Electron Image Correlation

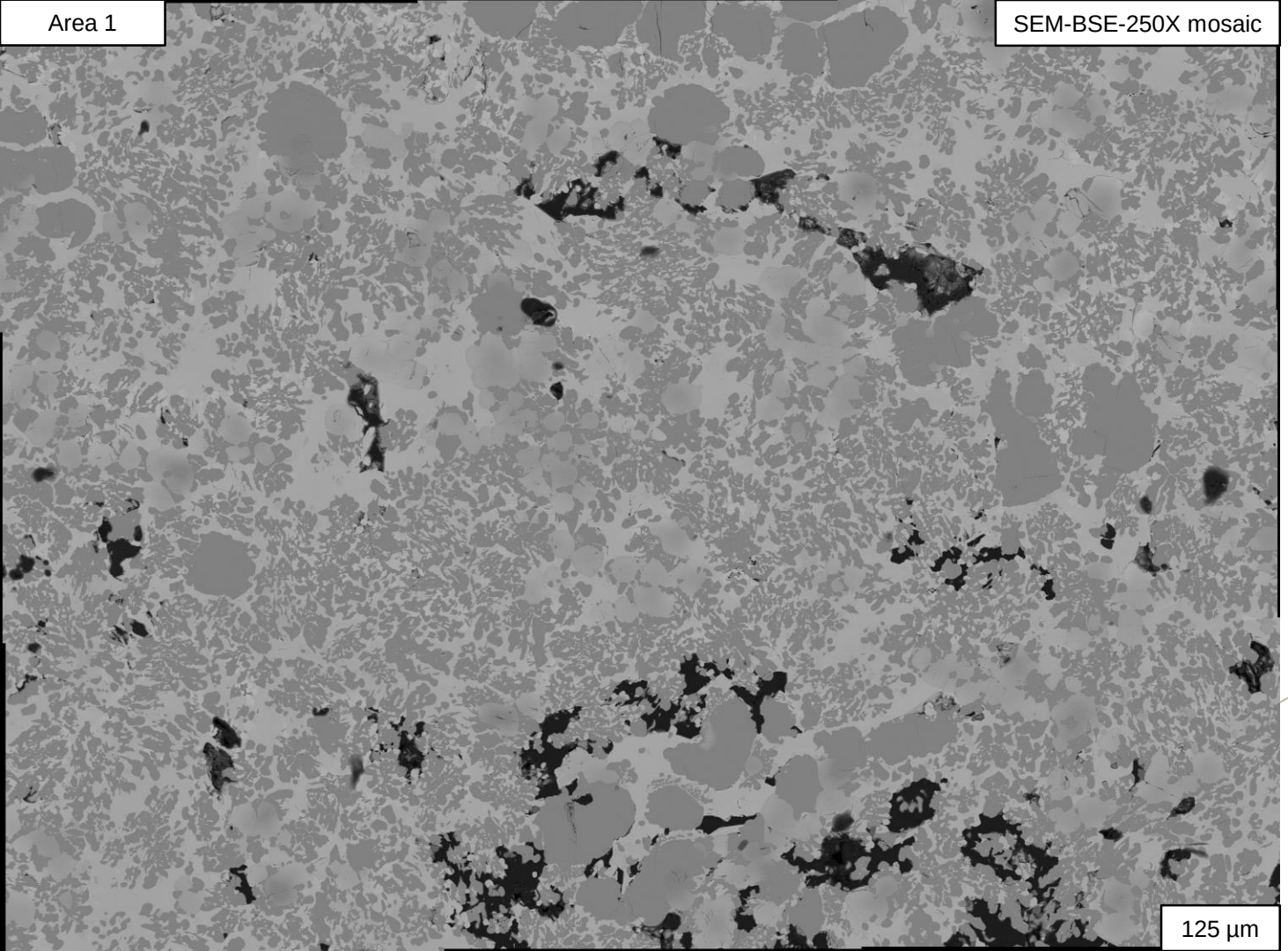
- ImageJ & BigWarp plugin
- Set landmarks between images
- Warp optical image to electron image
  - This is to align optical image, electron image, and X-ray chemical (EDS) data

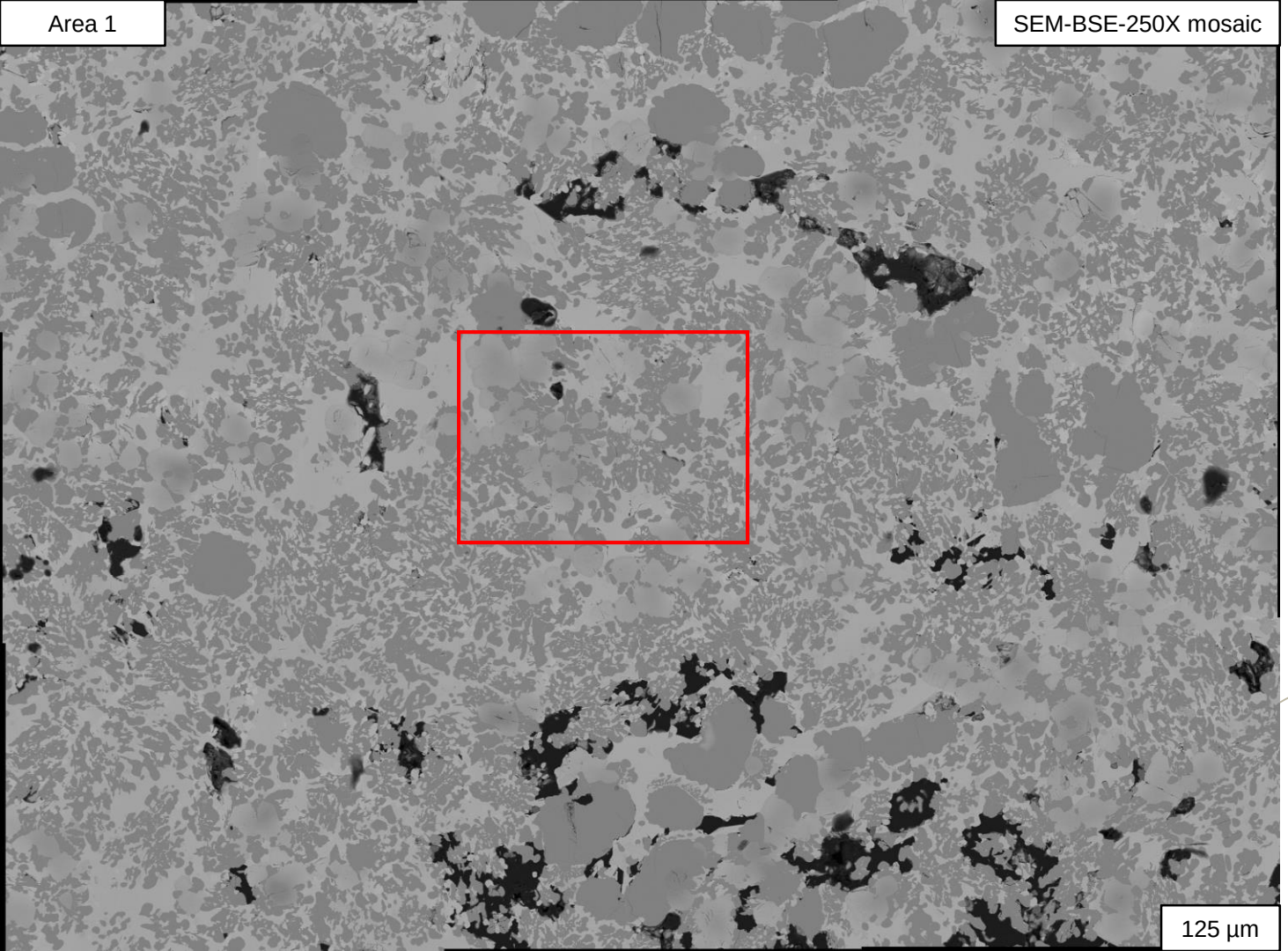




250 µm

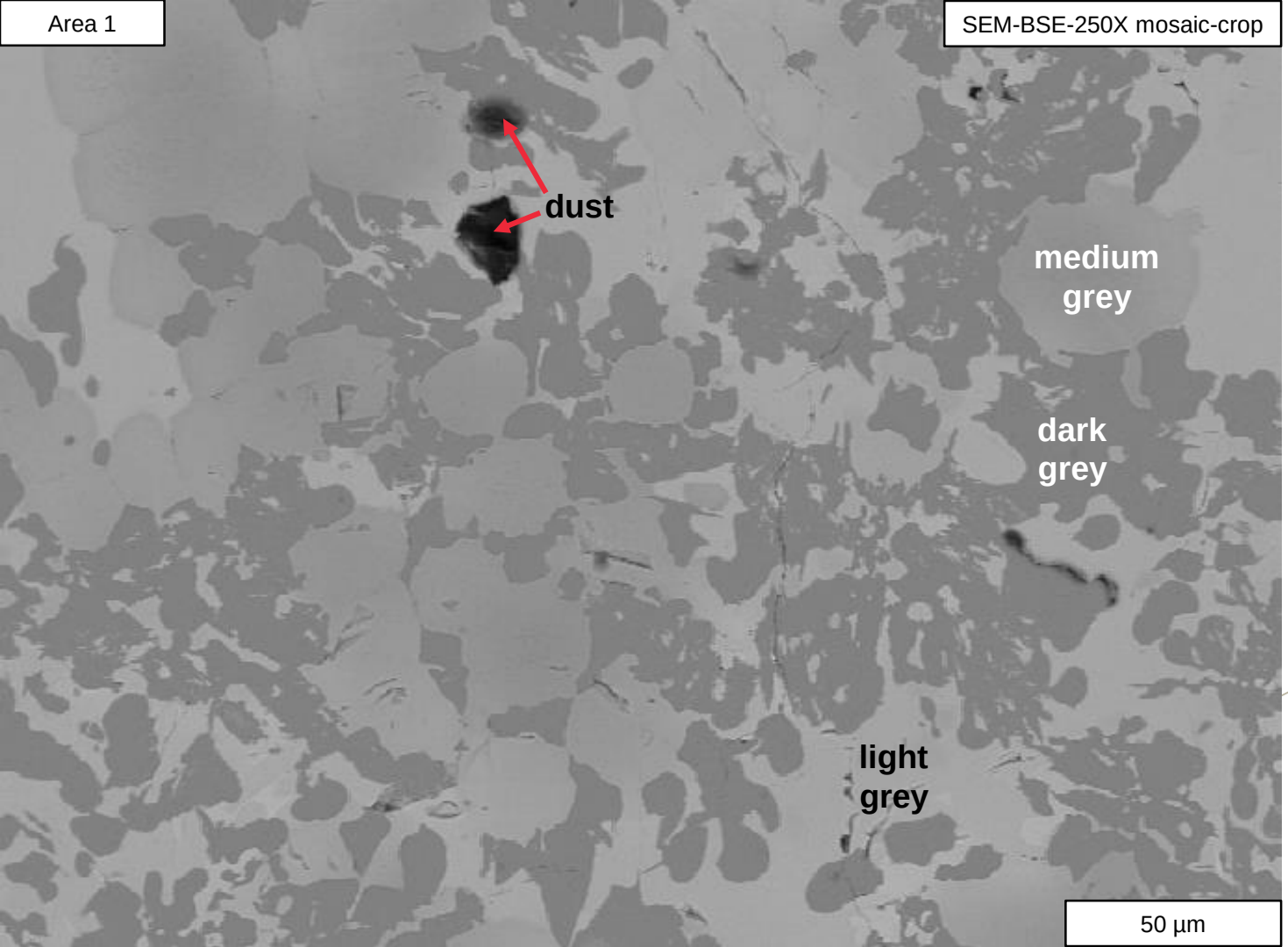

Area 1
LOM-PRL-20X mosaic-crop
125 µm


Area 1
SEM-BSE-250X mosaic
125 µm



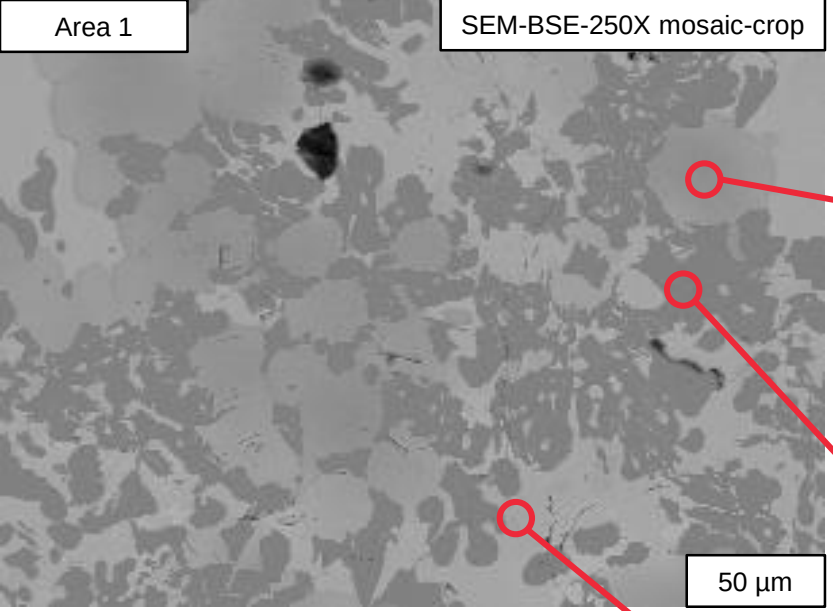
Phase Identification

- Understanding phases that are present
- Zooming in…

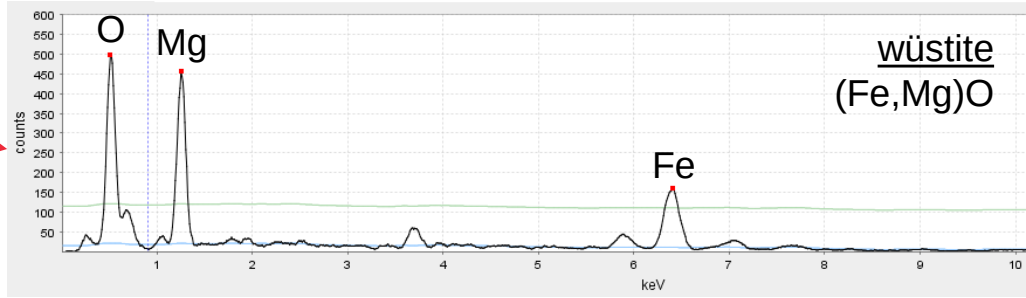


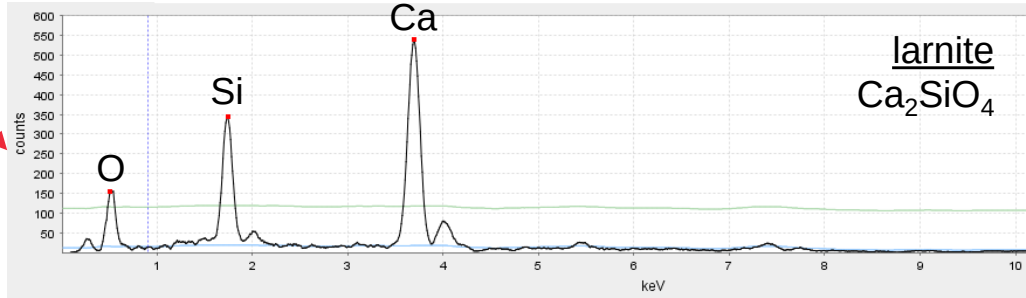
Phase Identification

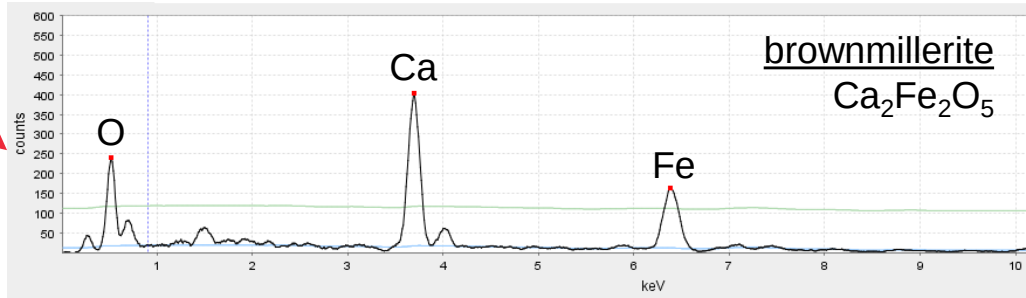
- Understanding phases that are present
- Z-contrast shows several phases:
  - Dark grey
  - Medium grey
  - Light grey
  - Black (dust, pores, cracks)
- What are they?



Energy Dispersive X-ray (EDS) Spectra

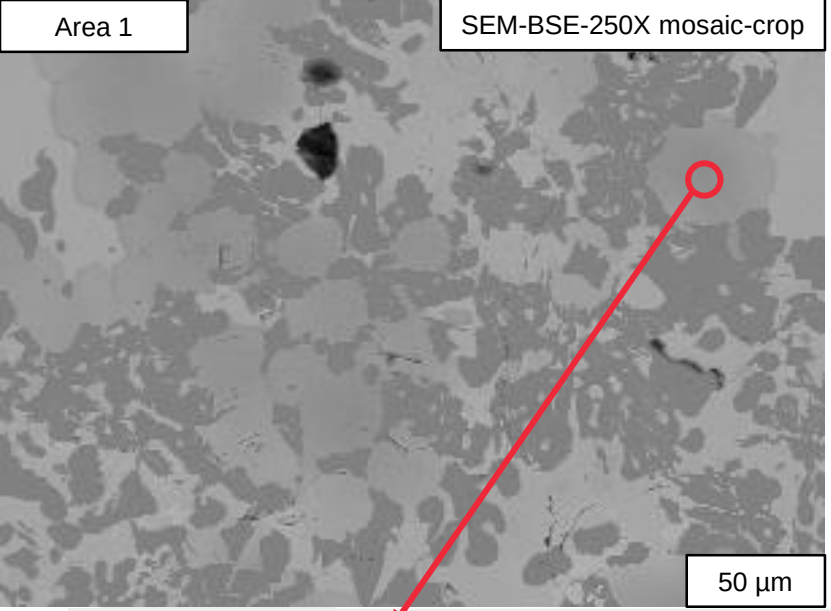


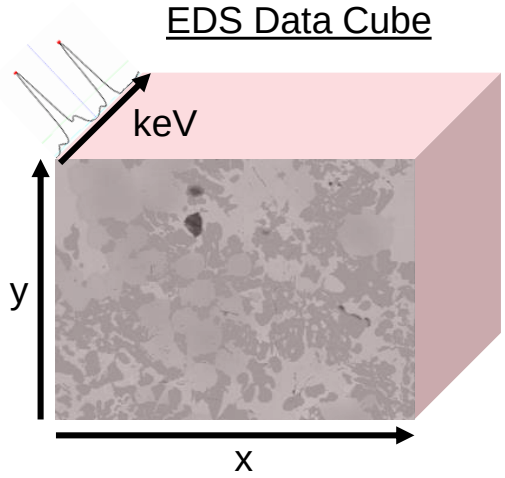




Phase Identification

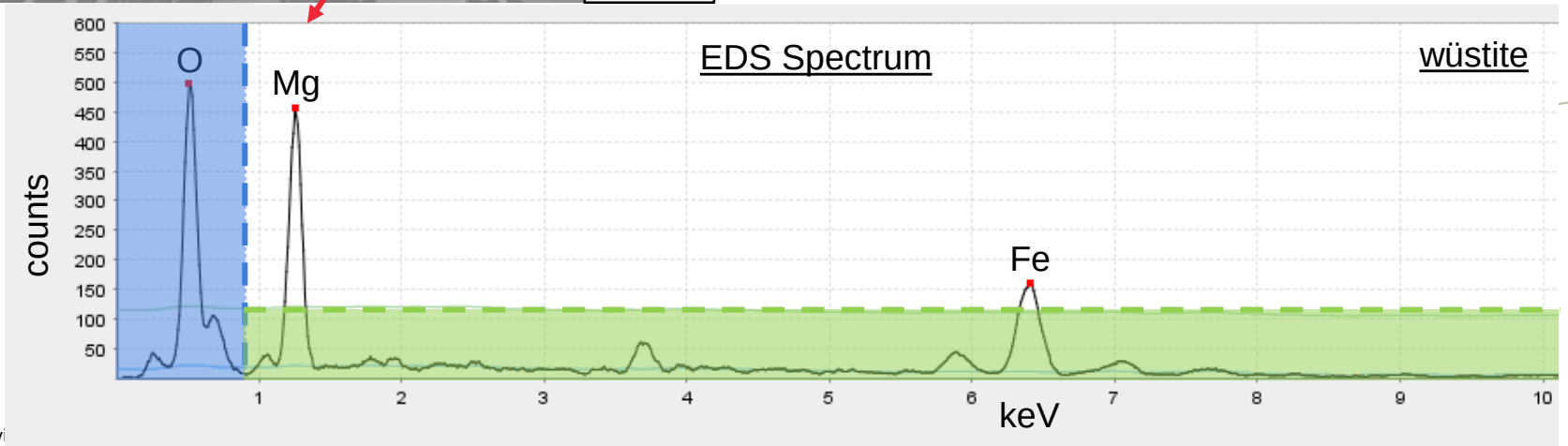
- EDS spectroscopy
- Characteristic X-ray peaks
- Peak height proportional to elemental abundance

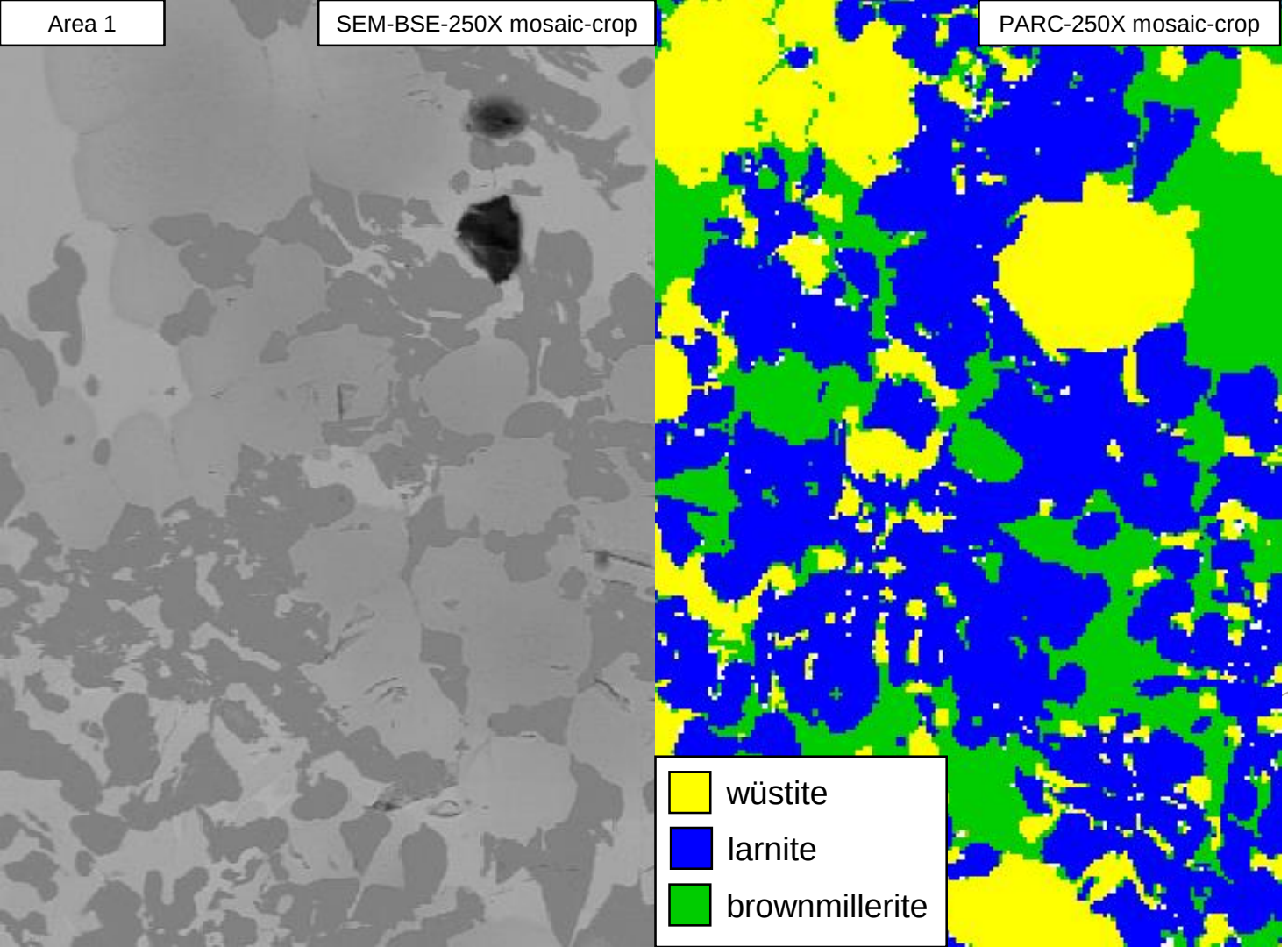




Phase Assignment

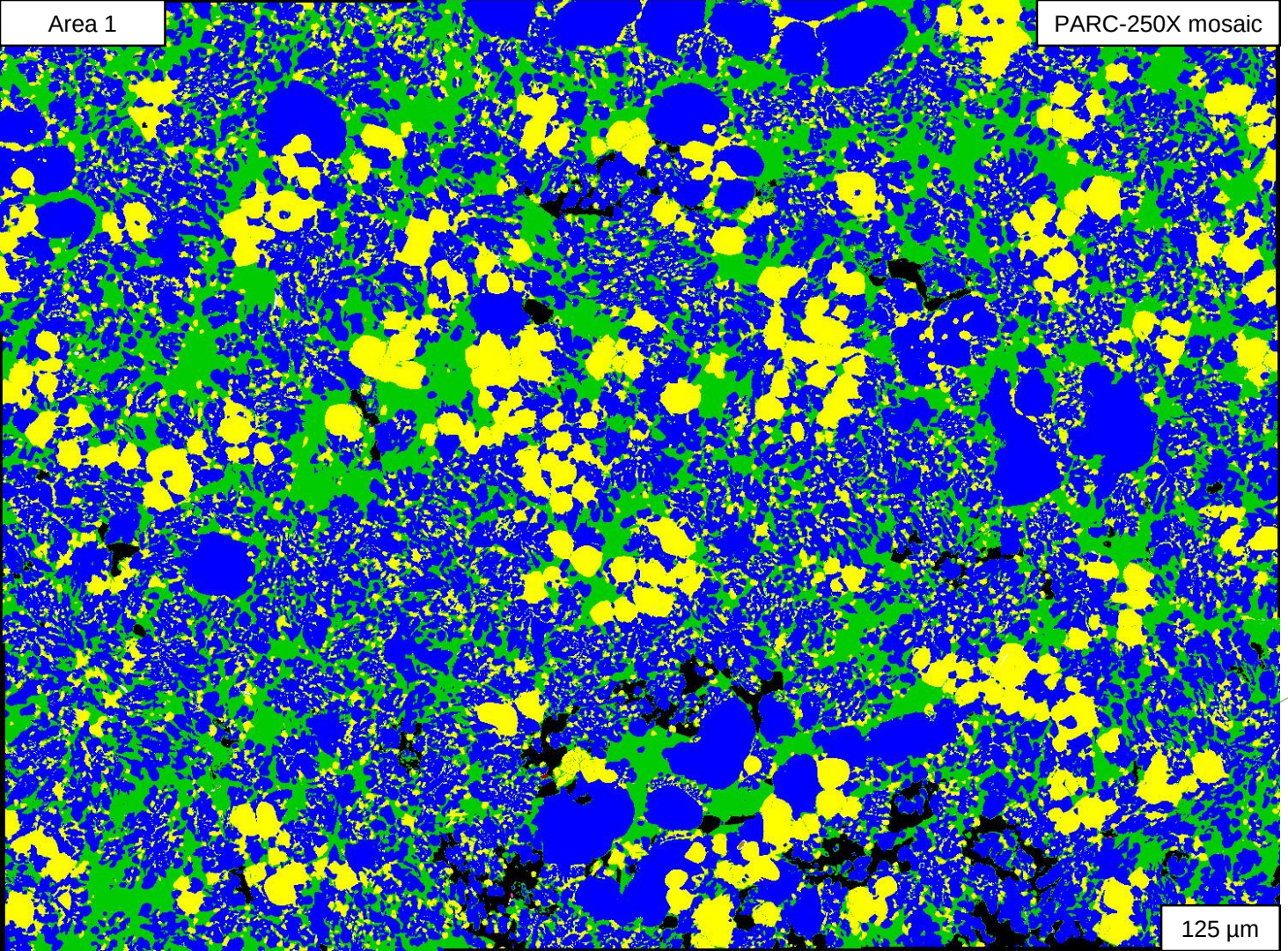
- EDS data cube can be used to map
- Phases can be identified by characteristic peaks
- Peak combinations above threshold are assigned to groups





Phase Mapping

- PARC—PhAse Recognition and Classification
- Simple phase mapping with 3 phases
- EDS data simplified into pixels with similar characteristics

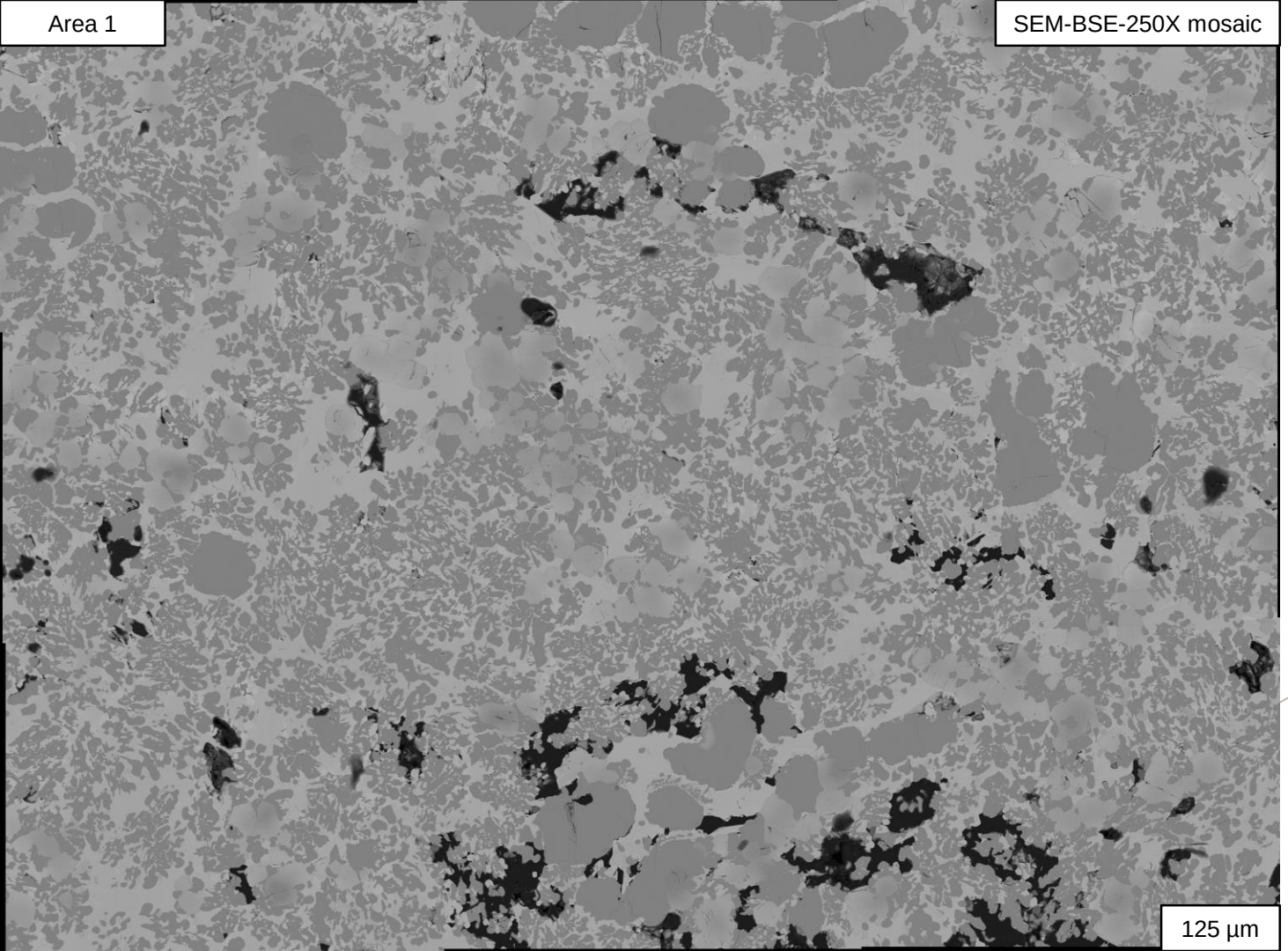


Phase Mapping

- Useful for both qualitative and quantitative analysis
- Relationships between chemistry and structure
- Relationships between phases and chemical variation
- Phase abundances

	area %
wüstite	19.1
larnite	54.2
brownmillerite	26.7

wüstite
larnite
brownmillerite



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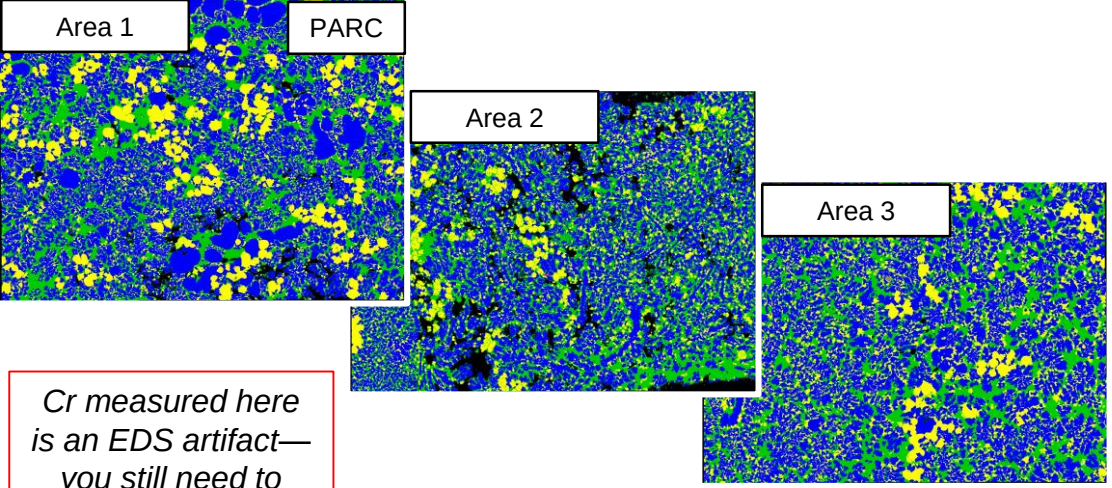


Cr measured here is an EDS artifact—you still need to know your sample!

(Semi-)Quantitative Chemical Composition

- Internally standardized EDS quantification using DTSA-II
- Spectra summed from phase interiors
  - Omits edge pixels for higher quality
- Bulk composition from phase abundances, compositions, and densities (assumed or measured)

major phase composition by area

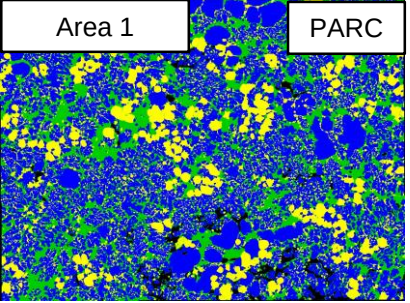
	Area 1			Area 2			Area 3		
	wüstite	larnite	brownmillerite	wüstite	larnite	brownmillerite	wüstite	larnite	brownmillerite
(wt.%) P_2O_5	0.0	3.9	0.0	0.0	3.8	0.0	0.0	3.9	0.0
V_2O_5	0.0	1.2	1.2	0.0	1.1	1.2	0.0	1.1	1.5
SiO_2	0.9	27.3	1.4	0.7	26.8	1.5	0.0	27.1	1.3
TiO_2	0.0	0.9	3.6	0.0	0.8	3.2	0.0	0.8	3.4
Al_2O_3	1.5	1.1	4.7	1.2	1.2	4.1	1.1	1.1	5.3
Cr_2O_3	0.0	*3.8*	0.7	0.0	*3.7*	0.6	0.0	*3.8*	0.0
FeO_T	47.6	2.4	41.6	53.6	3.5	42.1	57.0	2.8	39.6
MgO	32.5	0.0	0.9	25.8	0.0	1.0	23.4	0.0	0.9
CaO	2.7	59.4	44.4	1.3	59.0	44.6	4.4	59.4	46.2
MnO	14.7	0.0	1.6	17.3	0.0	1.8	14.1	0.0	1.7
area %	19.1	54.2	26.7	15.4	51.3	33.3	17.4	53.7	28.9
density (g/cm³)	5.3	2.9	3.7	5.3	2.9	3.7	5.3	2.9	3.7
mass %	28.2	44.1	27.7	22.9	42.2	34.9	25.9	44.0	30.1

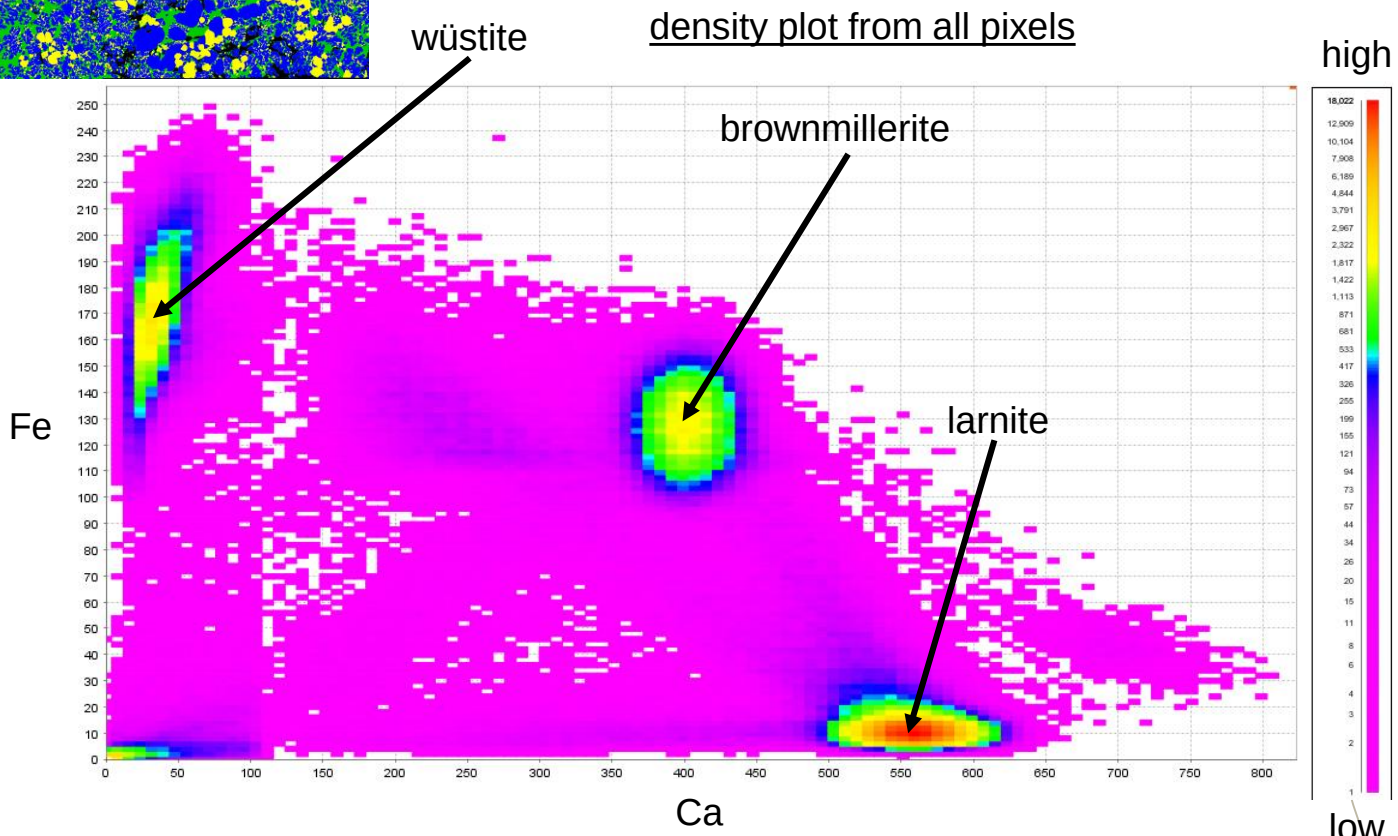
bulk composition (compared to XRF)

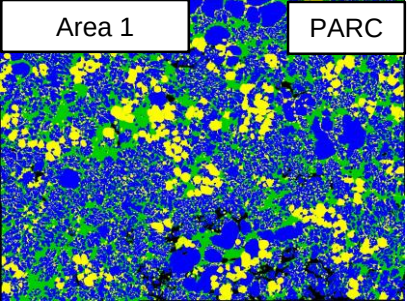
	Area 1	Area 2	Area 3	XRF
P_2O_5	1.7	1.6	1.7	1.6
V_2O_5	0.8	0.9	0.9	0.8
SiO_2	12.7	12.0	12.3	12.5
TiO_2	1.4	1.5	1.4	1.0
Al_2O_3	2.2	2.2	2.4	1.1
Cr_2O_3	*1.9*	*1.8*	*1.7*	0.2
FeO_T	26.0	28.4	27.9	30.5
MgO	9.4	6.3	6.3	9.6
CaO	39.3	40.8	41.2	39.6
MnO	4.6	4.6	4.2	4.2

Compositional Space

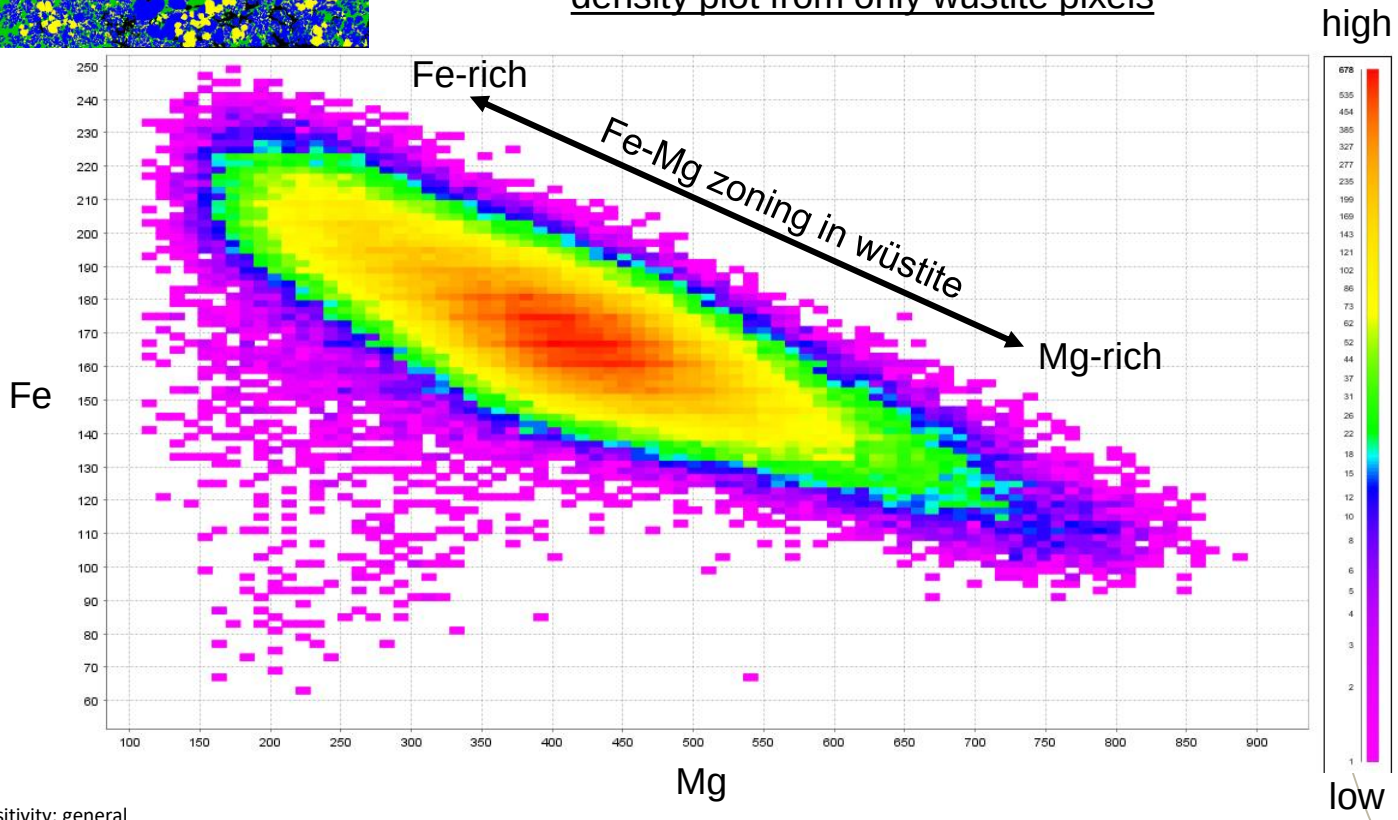
- Element density plots help illustrate compositional domains/phases





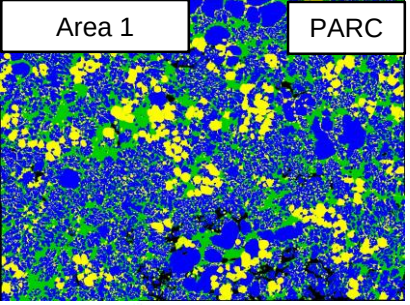


density plot from only wüstite pixels



Compositional Space

- Element density plots help illustrate compositional domains/phases
- And variation within a single compositional domain/phase



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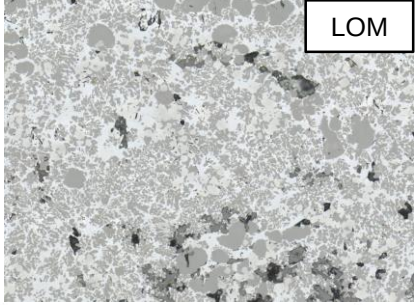
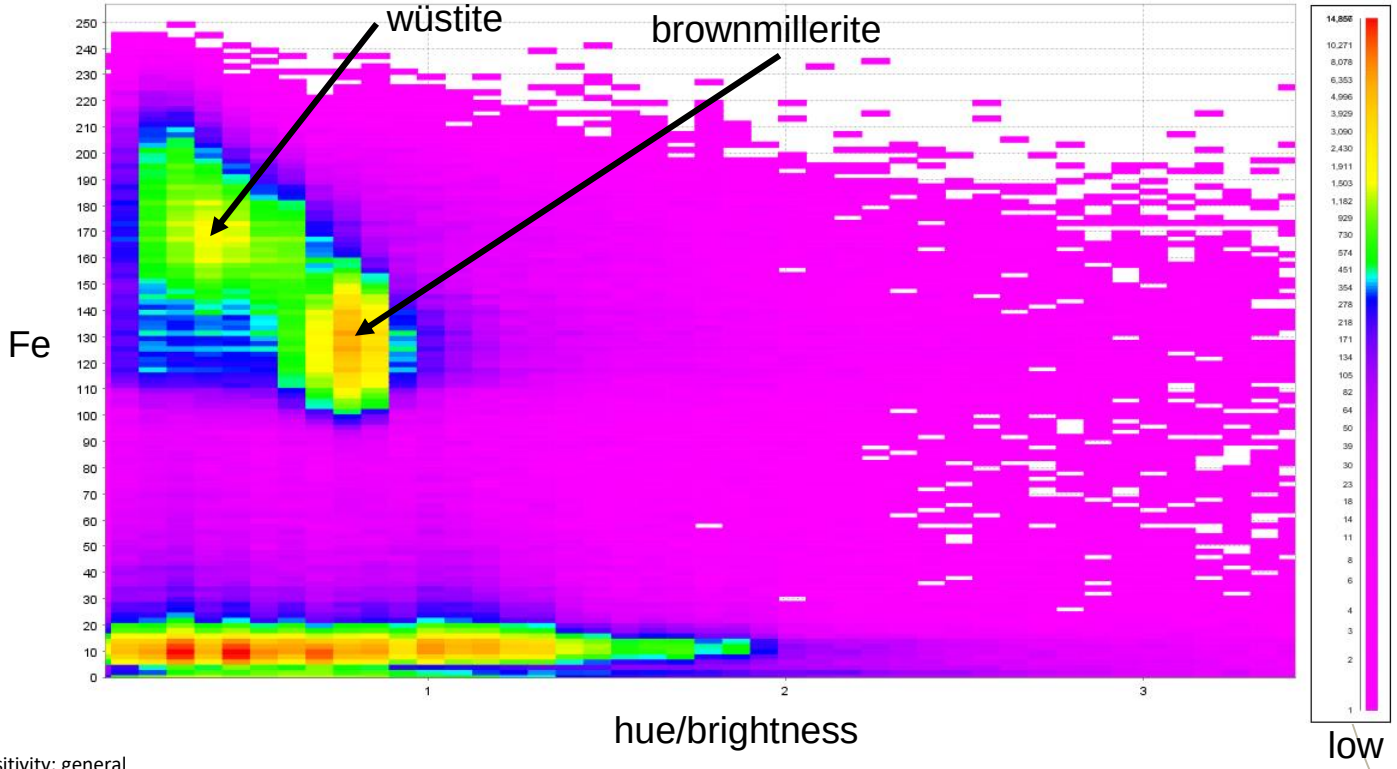


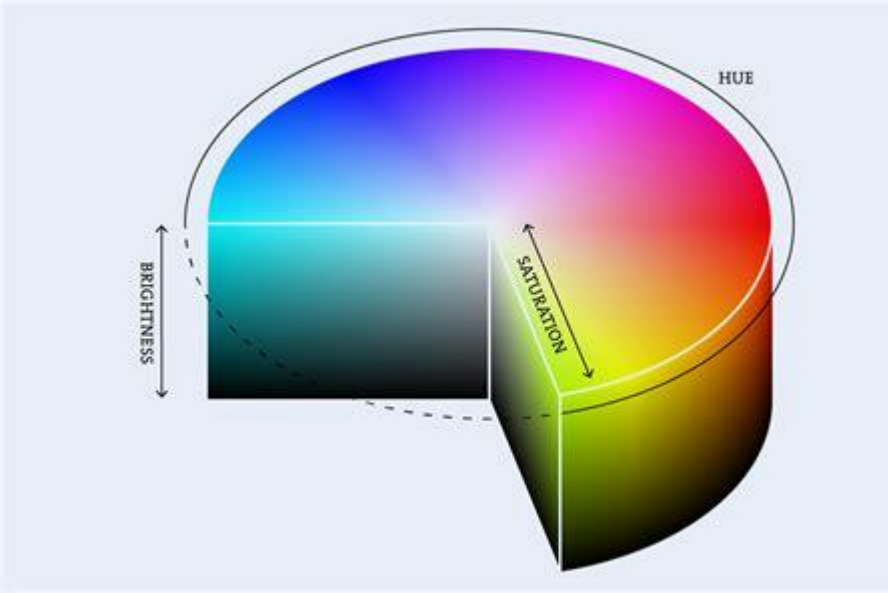
density plot from all pixels

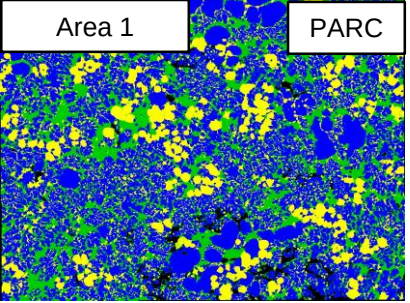


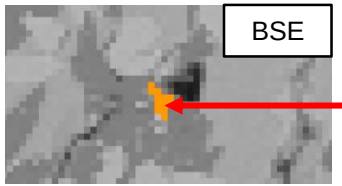
Compositional Space

- Element density plots help illustrate compositional domains/phases
- And variation within a single compositional domain/phase
- Colour LOM image can also be combined with EDS data to further discriminate phases

Hue, saturation and brightness







V-rich phase

larnite

brownmillerite

density plot from all pixels

V-rich pixels

high

low

Ca

V

Minor/Trace Components

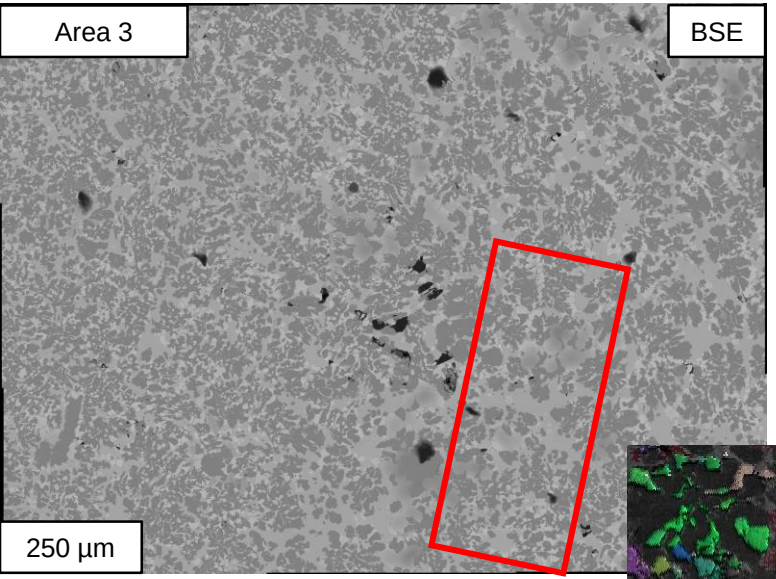
- V is mostly hosted in larnite and brownmillerite
- Selecting only very V-rich pixels shows V is also hosted in another phase
- Complex composition, possibly a glass

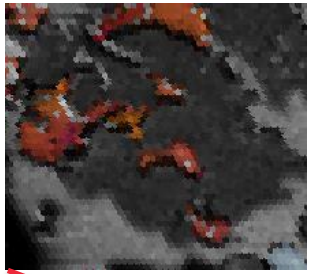
V-rich phase (wt.%)

P_2O_5	15.63
V_2O_5	9.58
SiO_2	10.72
TiO_2	0.00
Al_2O_3	0.00
Cr_2O_3	1.18
FeO_T	6.42
MgO	0.73
CaO	52.38
MnO	0.00
ZnO	1.86
Cl	0.56
S	0.94

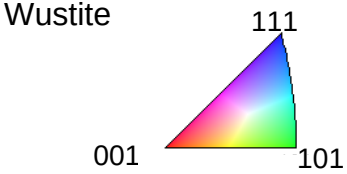
EBSD

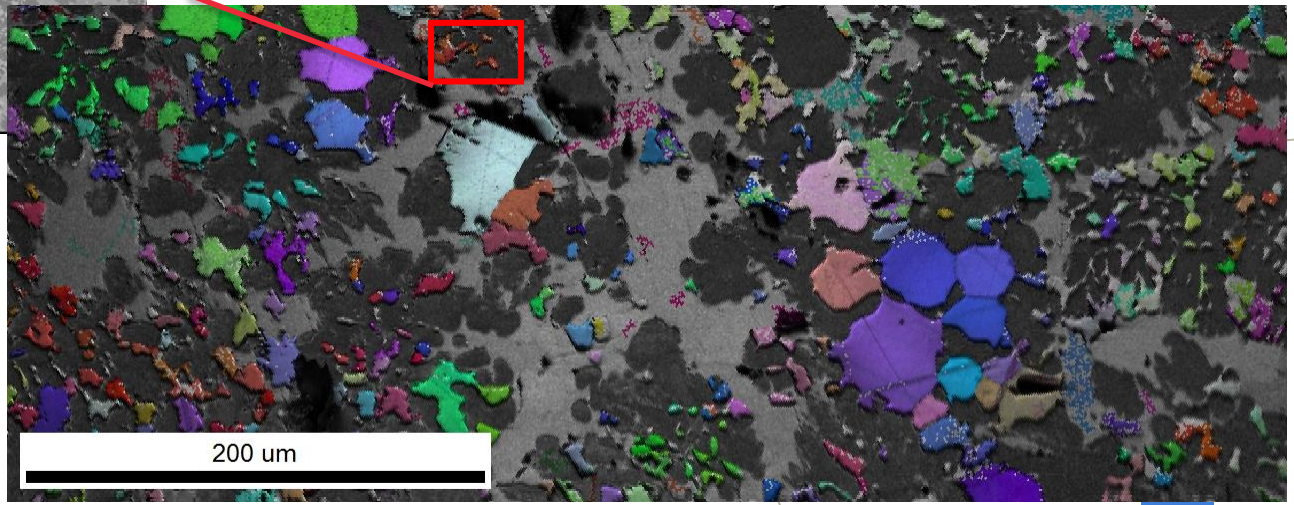
- Zeiss Ultra 55 (25 kV, 15nA), OIM
- Image quality + orientation map
- Image quality: the contrast between kikuchi bands and the background. Dark: no bands

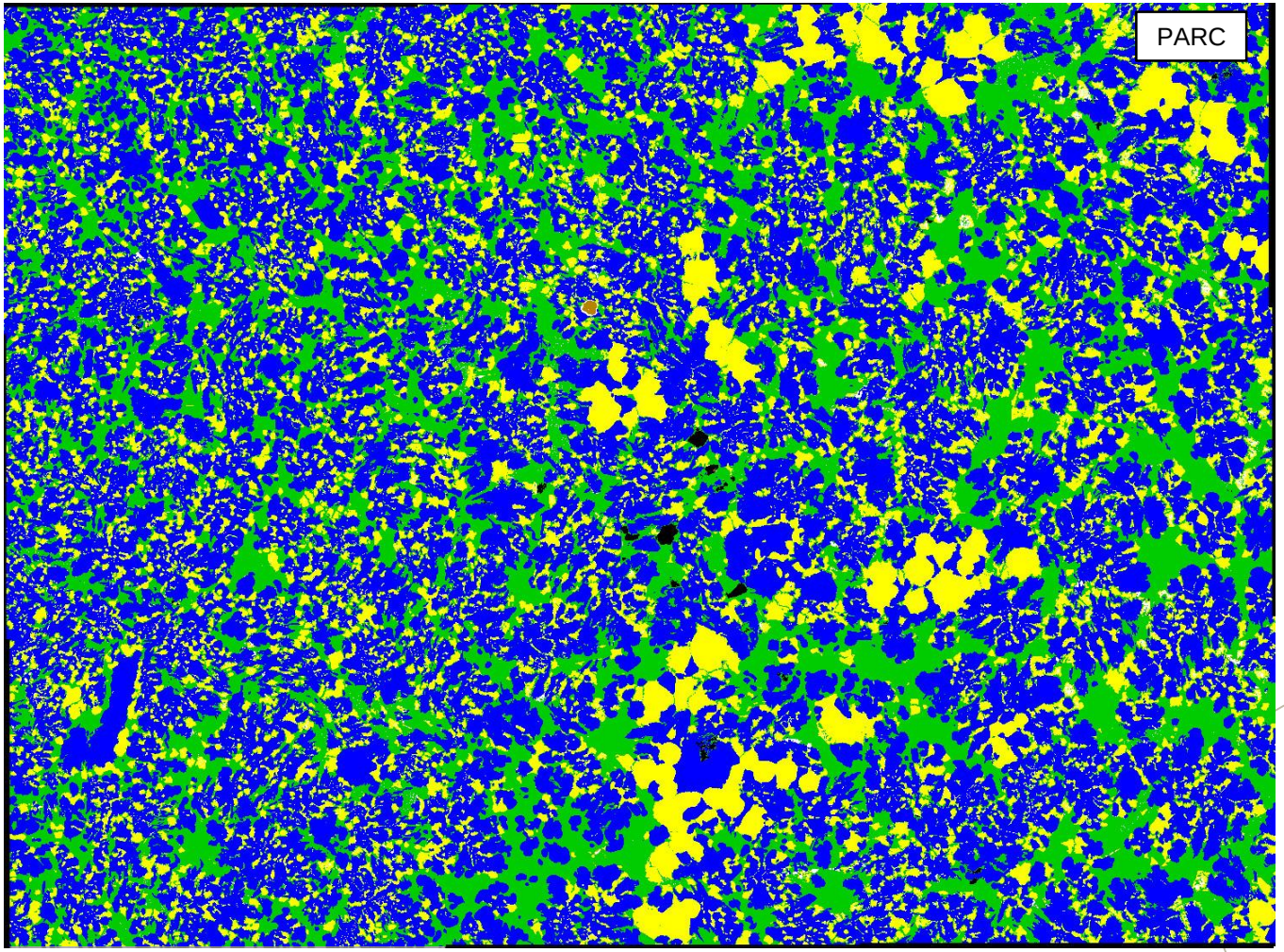




Multiple grains with similar orientations



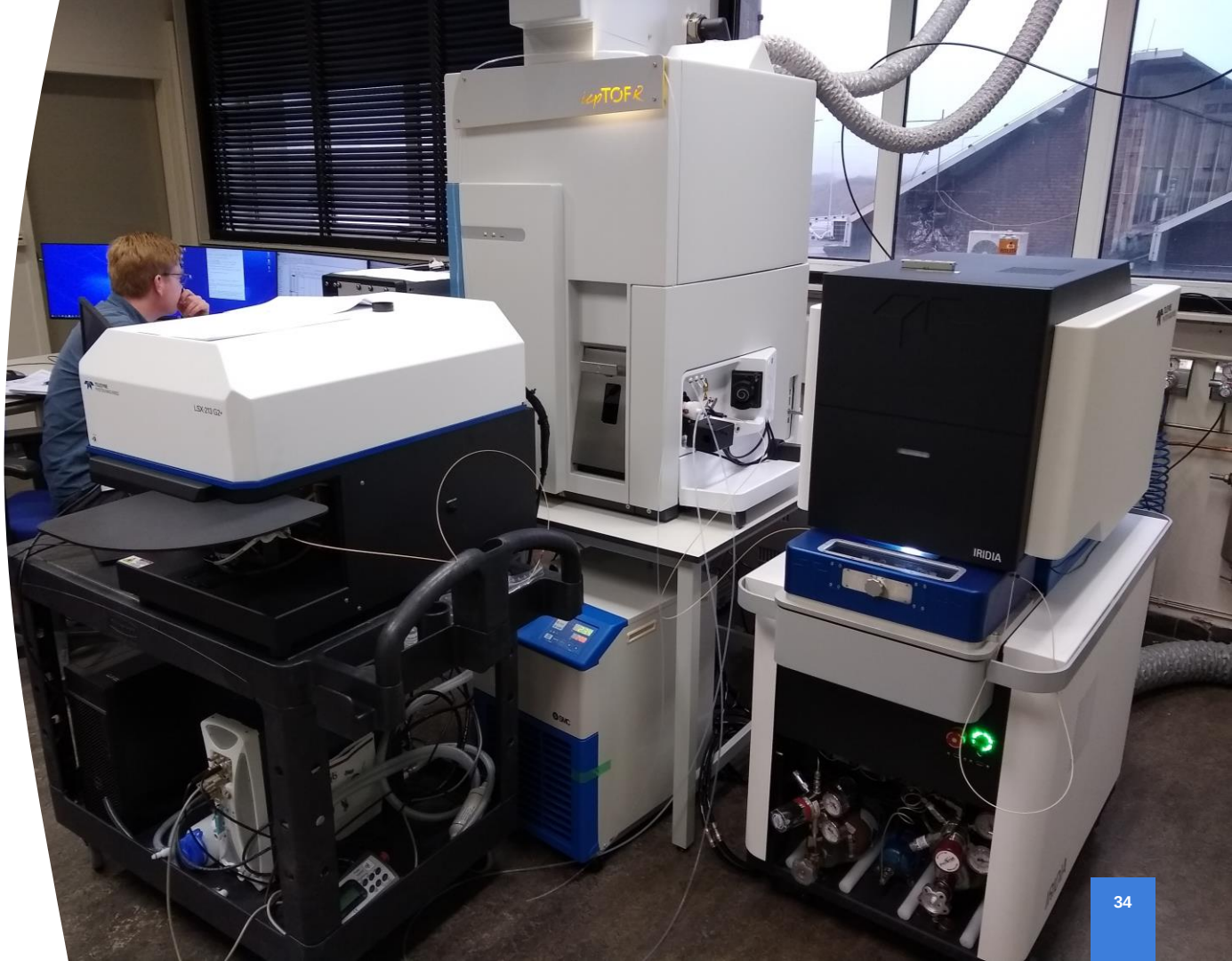


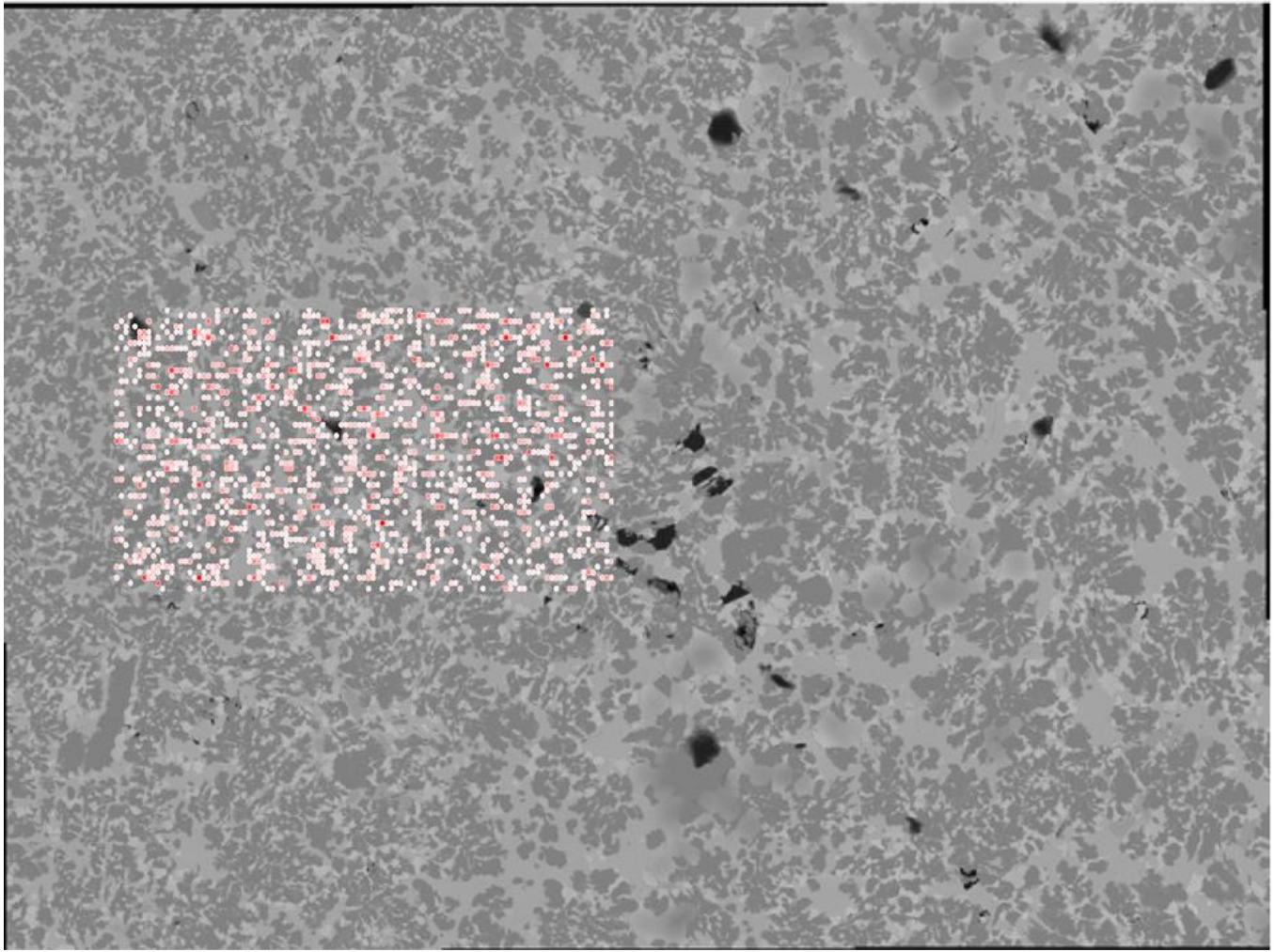


Area 3

Laser Ablation ICP-TOFMS

- Time-of-Flight Mass-Spectrometer for trace element analysis with solid sampling by:
- 213 nm Nd-YAG laser spotsize 4-250µm
- 193 nm Excimer laser spotsize 5µm with 500 Hz sampling rate
- Detection at: 50ppb Th, U, Pb, Bi, and at 10ppm Na, Mg, Al



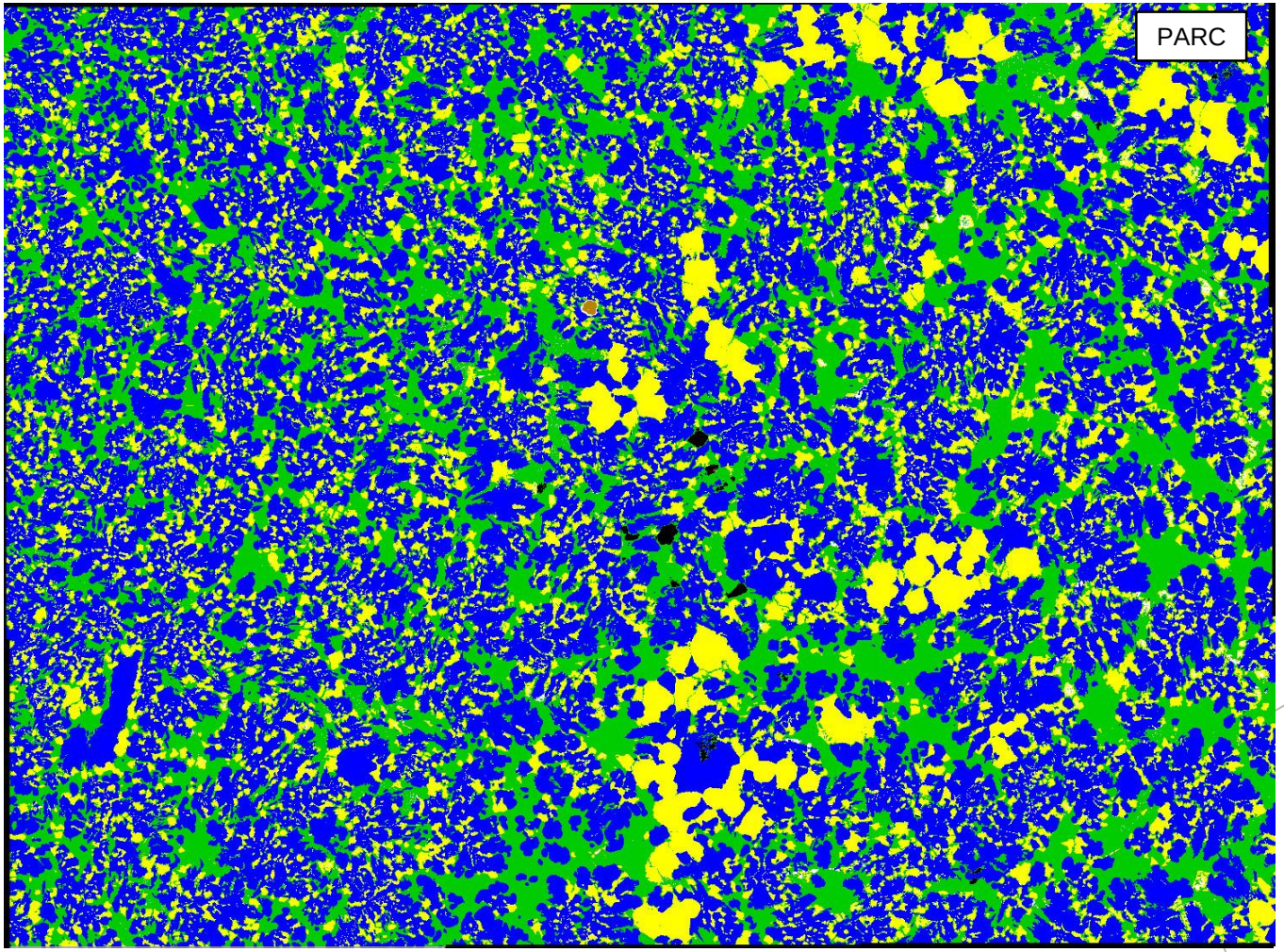


Ytterbium (Yb) Element map

- Correlated with BSE image
- Qualitative map

Red – high
White – low
Transparent – < d.l.

- Precision ~1-2% at ppm level of concentration



Area 3

Summary and Conclusions

Correlative microscopy

- Images from different microscope systems can be correlated with excellent spatial accuracy (within 0.1 µm) using routines in ImageJ/FIJI (shareware)

As demonstrated:

- Light optical microscopy serves to document large sample areas
- Detail areas can be analysed with Scanning Electron Microscopy and correlated with the LOM image
- Most useful are SEM Backscatter Electron, and Spectral Imaging (EDS)
- Spectral Images can be converted to phase distributions (using PARC)
- Electron Diffraction (EBSD) provides crystal-size and orientation
- Full area chemical information from microscopy is consistent with bulk chemical and phase analysis

Future:

- Trace element distribution correlated with microstructure
- FTIR & Raman microscopy
-

Do you have any questions?

Tata Steel R&D

Knowledge group: Microstructure and Surface Characterization

www.tatasteeleurope.com