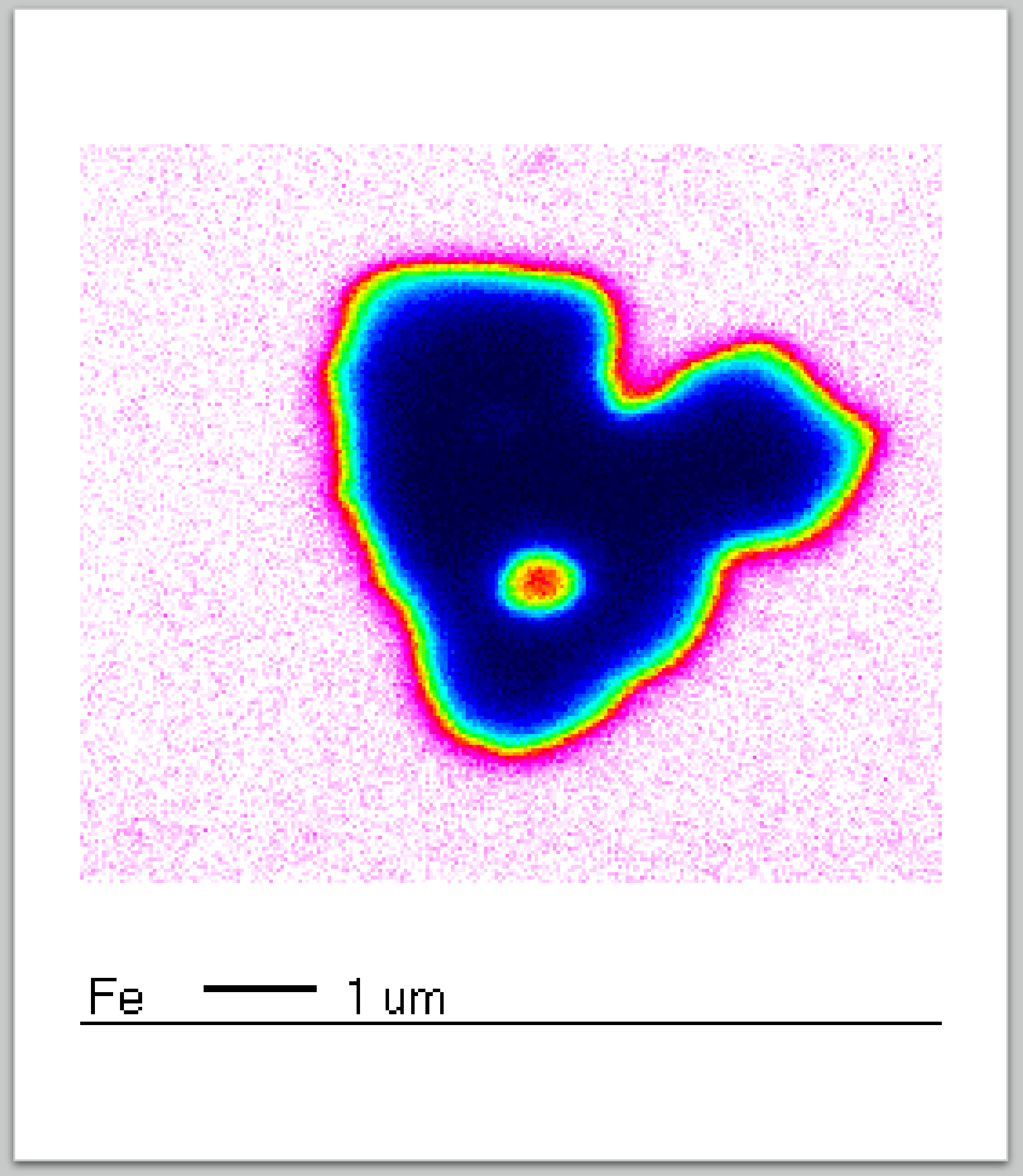
Electron Probe Micro Analysis

Annelies Malfliet

SIM²/MRC event

3 June 2022



Electron Probe Micro Analysis (EPMA)

- Principle of EPMA
- Applications and SWOT analysis
- Case study
- Information on how to get access

The principle of EPMA

No.	SiO2	MgO	Al2O3	CaO	Total
1	41.475	5.464	10.634	42.232	99.805
2	41.467	5.631	10.471	42.073	99.642
3	41.140	5.613	10.455	42.573	99.781
16	40.919	5.980	10.463	42.698	100.060
17	40.615	5.929	10.640	42.817	100.001
18	40.866	5.961	10.619	42.900	100.346
Minimum	40.398	5.421	10.455	42.073	99.104
Maximum	41.576	5.980	10.734	42.963	100.410
Average	40.996	5.750	10.587	42.563	99.896
Sigma	0.369	0.197	0.080	0.267	0.312
"No. of data"	18				

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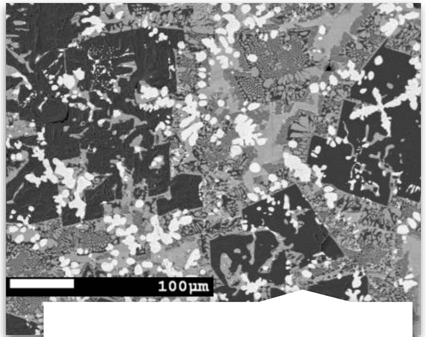
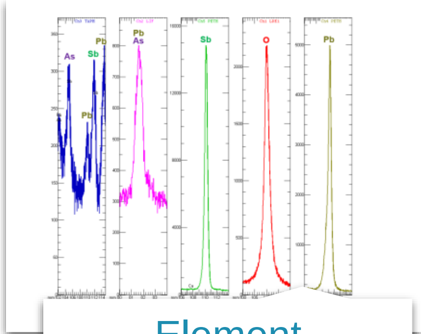
Electron Probe Micro Analyzer

Microarea and surface analysis instrument



Imaging



Element identification

No.	SiO2	MgO	Al2O3	CaO	Total
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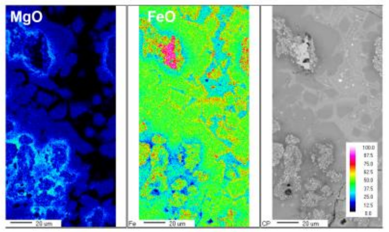
Quantitative elemental analysis



Element mapping

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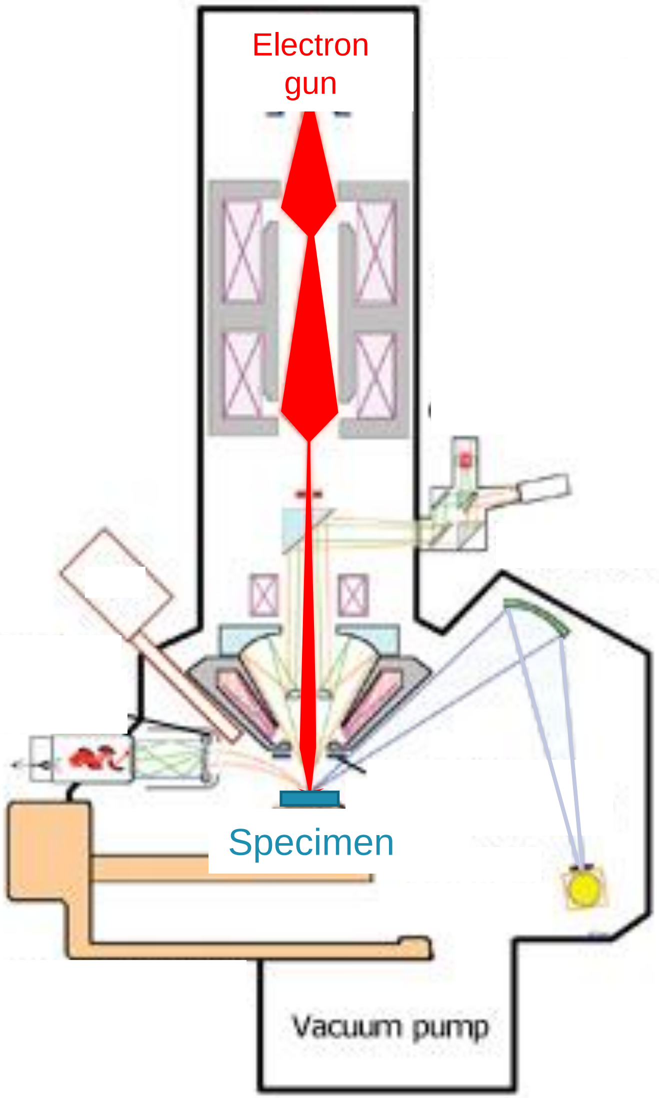
Electron Probe Micro Analyzer

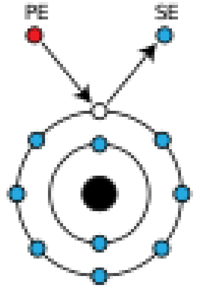


Electron Probe Micro Analyzer

Emission of different signals due to specimen-beam interaction

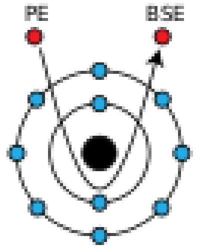
SE — Secondary Electrons

- Imaging with good spatial resolution
- Topography



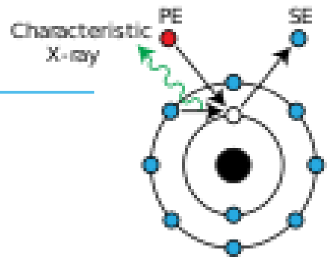
BSE — Back-Scattered Electrons

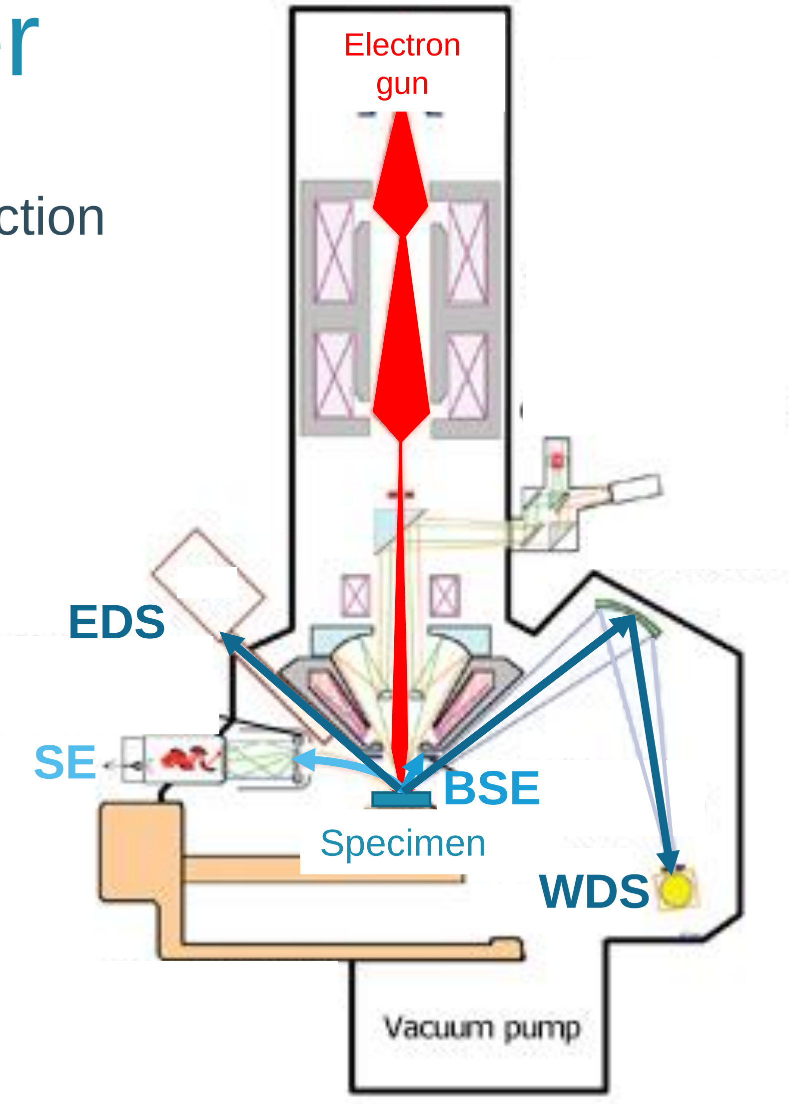
- Imaging with strong atomic number contrast
- Phase contrast



X-ray — Characteristic X-rays

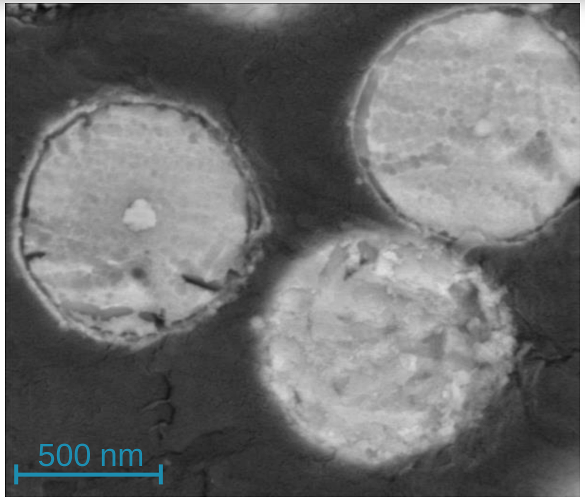
- Element information
- Energy Dispersive Spectrometer (EDS)
- Wavelength Dispersive Spectrometer (WDS)

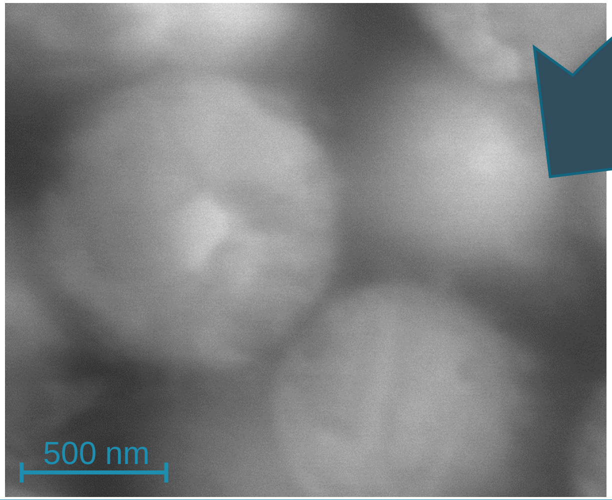




EPMA vs. SEM

Imaging with SE/BSE





Compared to SEM, imaging is not great in EPMA…

EPMA vs. SEM

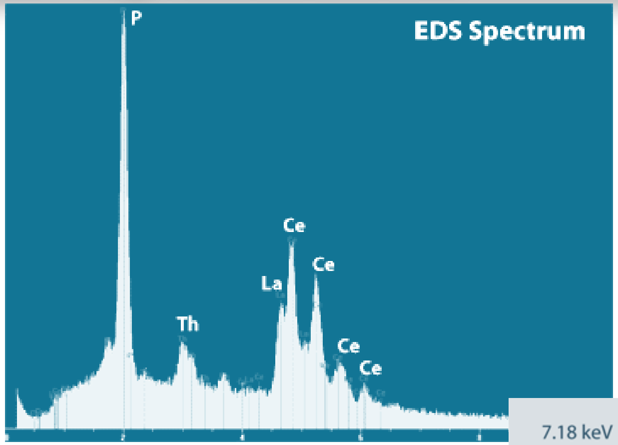
X-ray detection

Energy dispersive spectrometer (EDS)
→ Sorts X-rays based on energy

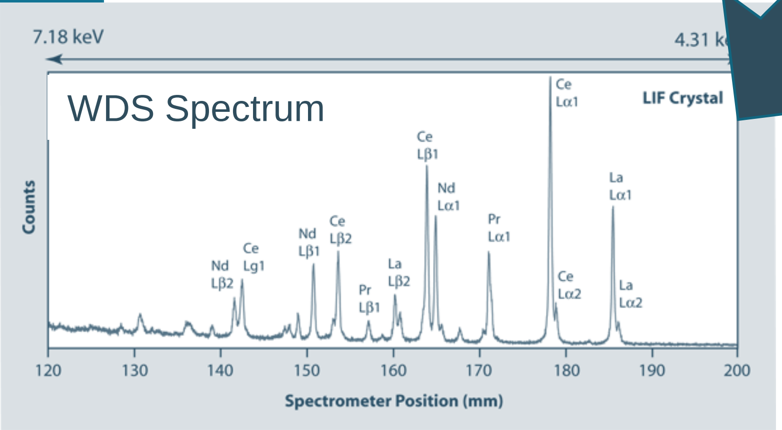
+ Wavelength dispersive spectrometers (WDS)
→ Sort X-rays based on wavelength

EPMA vs. SEM

X-ray detection



Element detection and quantification is great in EPMA!



- Higher spectral resolution
- Higher beam currents

  Higher precision

  Higher accuracy

  Lower detection limits

Spectra from: http://www.mcswiggen.com/TechNotes/Qual_Analysis.htm

From detection to quantification

Concentration of element i C_i is determined as:

$$C_i / C_{std} = k_i \ ZAFc$$

$$k = I_{unknown} / I_{standard}$$

Z = atomic number correction
A = absorption correction
F = secondary characteristic fluorescence correction
c = continuum fluorescence correction

$I_{standard}$ is measured on available standards

Several metal, mineral and other standards are available at MTM

Applications and SWOT analysis

Examples of application domains

High temperature metallurgical processing (slags, metals,…)

- Phase equilibria, reaction phenomena, diffusion profiles, …

Characterisation of process materials (slags, tailings, sludges, …)

- Quantification and distribution of minor and trace elements, …

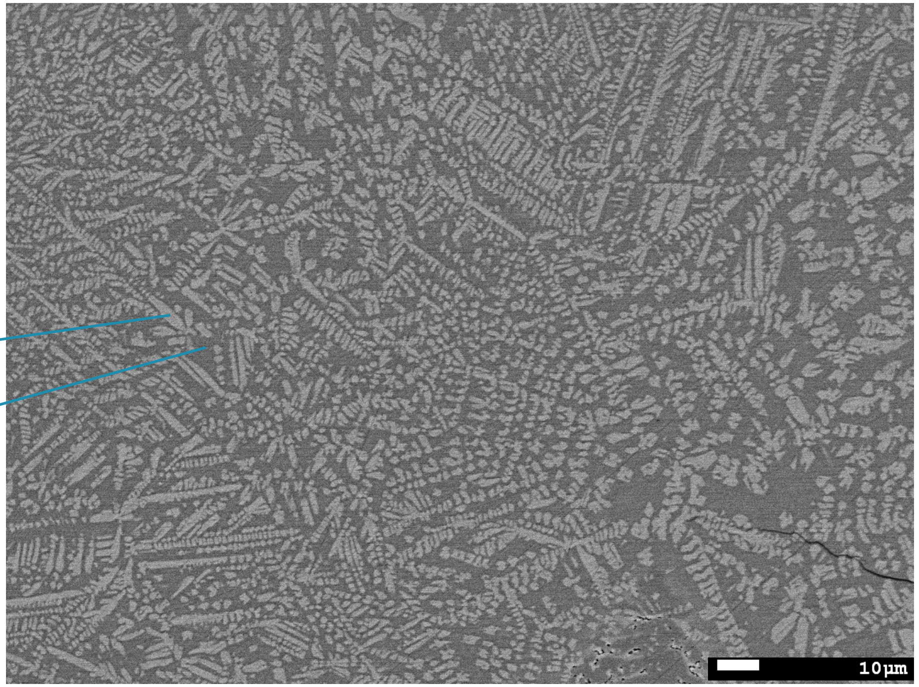
Geology (basalts, minerals, …)

- Phase equilibria, (minor and trace) element partitioning and quantification, …

Other: ceramics, semiconductors, biology, medical and dental applications, …

Example of quantitative analysis

Wt.%	CaO	SiO_2	MgO	Al_2O_3	Total
Crystals	49.5 ± 0.2	37.4 ± 0.2	11.9 ± 0.1	0.3 ± 0.2	99.1 ± 0.3
Amorphous	37.9 ± 0.2	41.0 ± 0.5	5.0 ± 0.2	15.1 ± 0.4	99.1 ± 0.5



~1 min/spot
5 spots/phase

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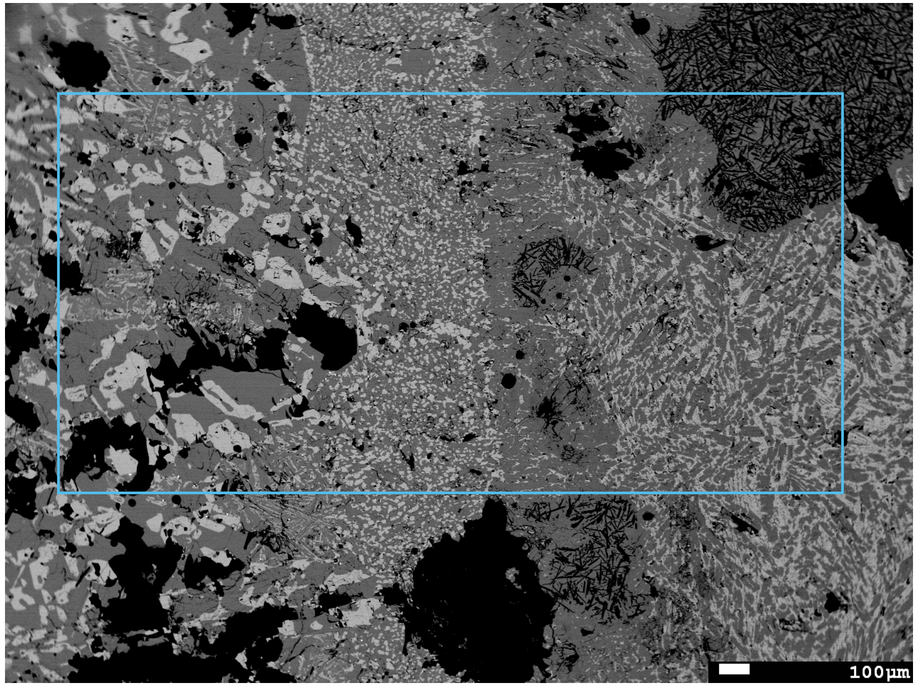
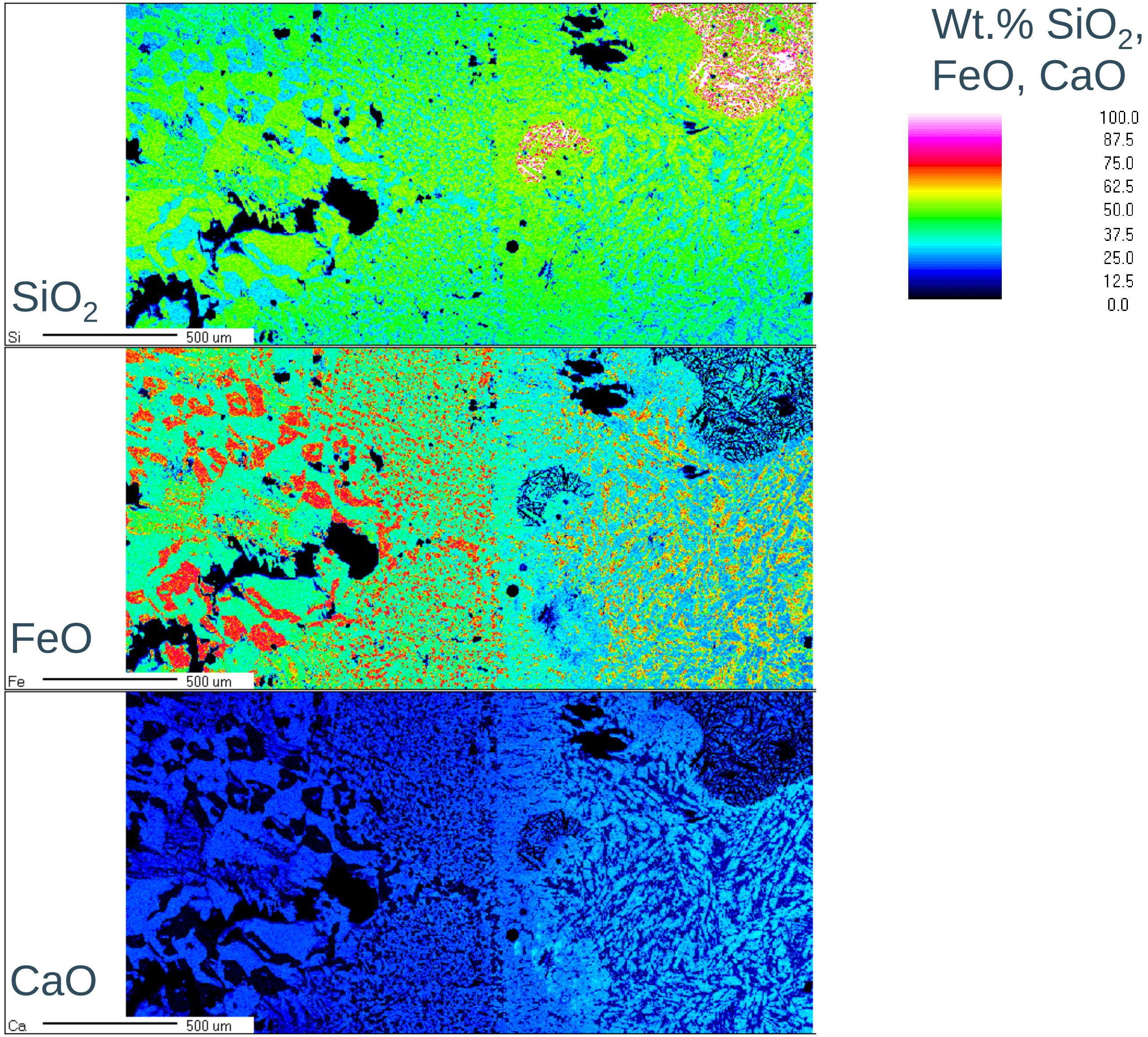
Example of mapping





1024 x 512 pixels
20 ms/pixel
~3h

Sample from Gaëlle Butin
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SWOT analysis of EPMA-WDS

Main goal:
Accurate and reproducible quantification of concentration of elements on the microscale

Strengths

- From B to U
- High spectral resolution
- High spatial resolution (~1 µm)
- High count rates
- High reproducibility
- Low detection limit (< 100 ppm)

Weaknesses

- Requires solid, not beam-sensitive samples with flat and polished surface
- Need to measure standards
- More time consuming than EDS
- Not suitable for bulk analysis of heterogeneous materials
- Not suitable for ppb level detection

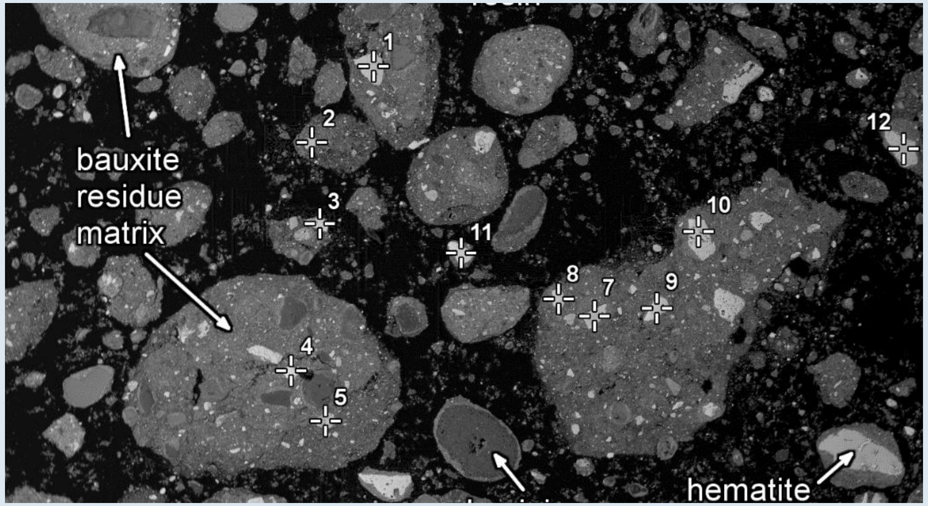
Opportunities

- Trace element analysis (high peak-to-background ratio)
- Quantification of light elements
- Able to distinguish elements with overlapping peaks in EDS

Threats

- Requires operator skills
- Pre-knowledge about the materials may be required

Case study



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Characterization of REE minerals in bauxite residue

Research within MSCA-ETN Redmud project

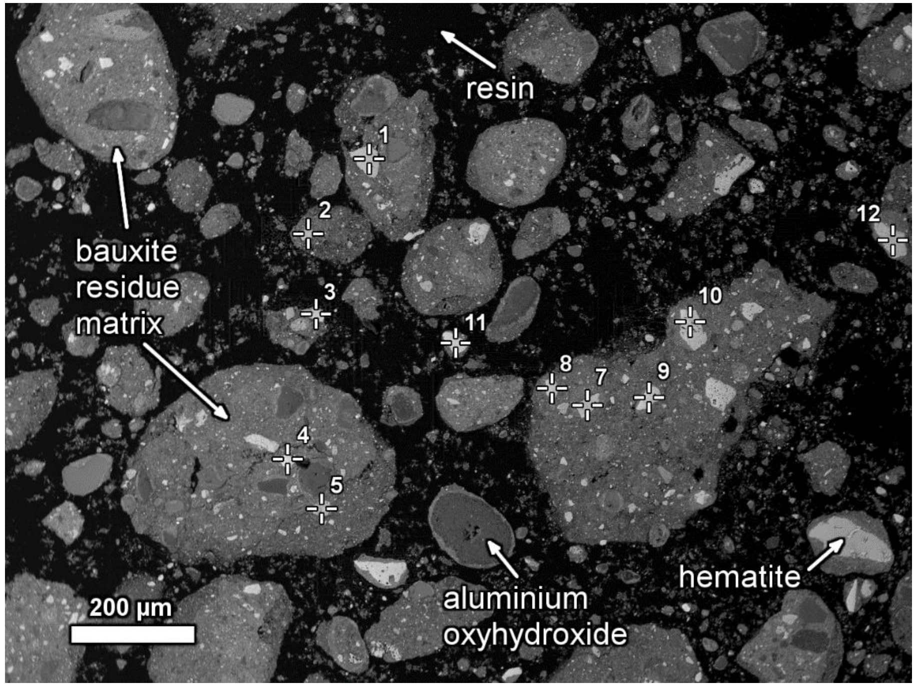
- Combined EPMA, HRTEM, LA-ICP-MS, µ-raman spectroscopy study of mineral phases in bauxite residue

- EPMA in particular useful for:
  - Trace element analysis
  - Analysis of LREE, considering overlap in LREE peaks with EDS

Vind J. et al. (2018). Rare Earth Element Phases in Bauxite Residue. MINERALS, 8 (2), 77

Vind J. et al. (2018). Modes of occurrences of scandium in Greek bauxite and bauxite residue. MINERALS ENGINEERING, 123, 35-48

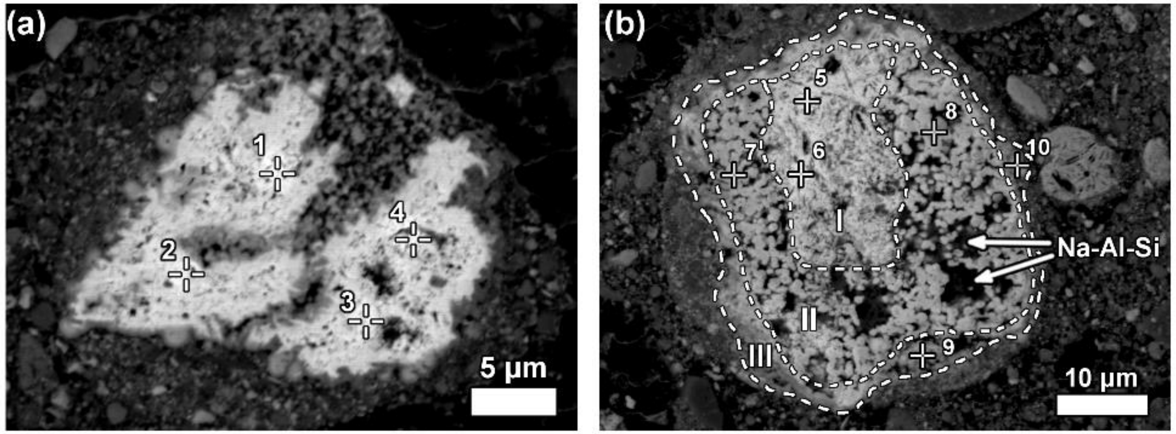
Quantitative analysis of Sc-containing hematite



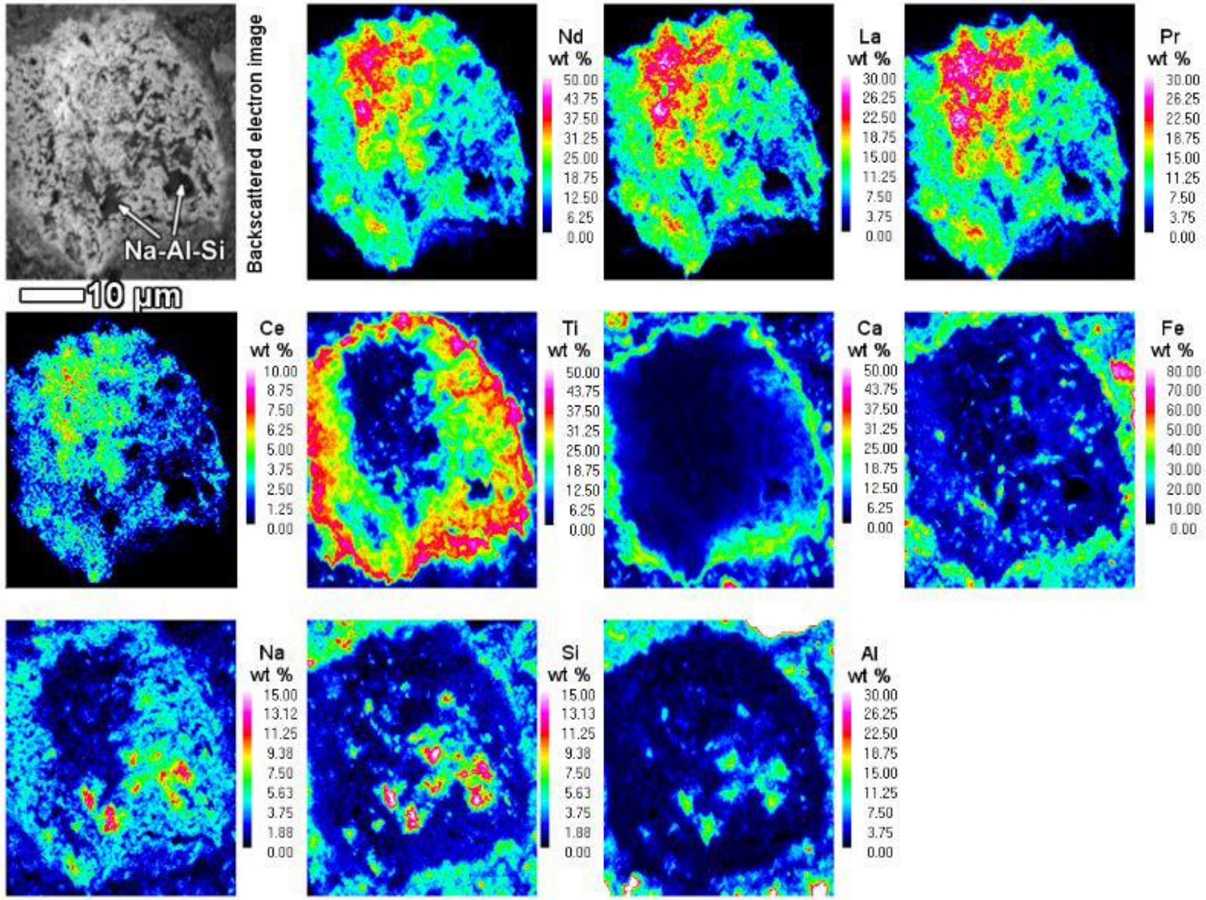
	Sc-hosting hematite (n = 24)		Sc-depleted hematite (n = 32)	
	Average	S.D.	Average	S.D.
Fe_2O_3 (wt%)	92.02	4.06	93.81	3.49
TiO_2 (wt%)	3.98	2.17	1.02	0.82
Al_2O_3 (wt%)	1.79	0.60	1.91	1.47
SiO_2 (wt%)	0.71	0.60	1.11	0.68
Na_2O (wt%)	0.29	0.26	0.43	0.27
CaO (wt%)	0.49	0.32	0.44	0.17
Cr_2O_3 (wt%)	0.24	0.12	0.05	0.05
V_2O_3 (wt%)	0.17	0.11	0.07	0.12
Sc (mg/kg)	190	70	30	20
Total (wt%)	99.74	3.39	98.99	2.28

Vind J. et al. (2018). Modes of occurrences of scandium in Greek bauxite and bauxite residue. MINERALS ENGINEERING, 123, 35-48

Quantification and mapping of Nd-La predominant particles



No.	1	2	3	4	5	6	7	8	9	10
La_2O_3	23.21	24.93	25.99	25.49	23.89	23.89	10.25	13.87	1.06	7.41
Ce_2O_3	7.87	8.87	10.57	10.47	5.99	5.46	2.71	3.49	0.58	1.29
Pr_2O_3	21.91	20.56	20.79	21.90	22.02	20.78	9.41	8.45	1.03	5.60
Nd_2O_3	35.10	33.73	33.59	34.02	34.92	34.19	14.37	17.22	1.71	8.53
TiO_2	3.87	5.85	0.83	3.08	1.44	2.03	27.48	24.13	32.60	40.35
Fe_2O_3	2.61	2.35	2.20	3.27	6.67	4.07	10.71	12.21	42.44	12.26
CaO	2.11	3.07	1.93	2.56	1.46	1.12	4.42	5.64	17.92	14.16
MgO	0.00	0.00	0.01	0.00	0.11	0.08	0.99	0.02	0.03	0.03
SiO_2	0.16	0.29	0.17	0.20	0.38	0.54	2.93	1.25	1.57	2.30
Na_2O	0.16	0.62	0.00	0.14	0.00	0.00	5.65	4.46	2.87	6.93
Al_2O_3	0.28	0.34	0.33	0.25	0.66	0.88	3.21	1.36	1.07	2.13
ThO_2	0.00	0.00	0.00	0.00	0.09	0.07	0.05	0.02	0.01	0.04
Total	97.28	100.62	96.40	101.37	97.62	93.11	92.17	92.12	102.89	101.02



Vind J. et al. (2018). Rare Earth Element Phases in Bauxite Residue. MINERALS, 8 (2), 77

How to get access to EPMA

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Access

Annelies Malfliet:
annelies.malfliet@kuleuven.be

Pieter L'hoëst:
pieter.lhoest@kuleuven.be

- €350 per weekday or weekend + €55/h for operator assistance
- €2100 for a training

(Prices for KU Leuven)

- What do you want to measure?
- Is EPMA suitable and best technique?
- How to prepare your sample?
- …

- Available timeslot+operator can take up to 2-4 weeks

Thank you for your attention!

Questions?