TATA STEEL

TATA

When the dust settles: using particle mineralogy to pinpoint steelmaking contributions in dust deposits

James Small, Corrie van Hoek, Frank van der Does, Anne-Bart Seinen, Stefan Melzer, Elmira Moosavi, Katrin Schollbach, Sieger van der Laan

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Together we make the difference

Background – dust in the IJmond

- **Integrated steelmaking known to emit dust**
- **Dust emission from Tata Steel site in IJmuiden**
  - Nuisance to neighbours, public health concerns
- **RIVM reports in 2019, 2021 & 2022:**
  - **2019-2021: elevated loads of metals and PAH in IJmond, especially Wijk aan Zee**
    - Deposited dust and as suspended fine dust in air
    - Remains a major issue to solve
  - Based on bulk chemical analyses
  - Dust deposition:
    - Insufficient data for detailed, quantitative source apportionment
    - General increase in metal loads with proximity to site

Key questions to be addressed by dust characterisation

- What are the sources and their quantitative contributions to deposited dust?
- What are the sources of potentially toxic elements (PTE) / compounds in the dust?
- In which forms are PTE present (in which phases), with relevance for bioavailability?
- How can emissions be mitigated and monitored in the future?

- Not sufficient for us just to identify Tata Steel site as source of dust
- To address the dust emissions need to be much more specific:
  - Which materials:
    - raw materials, products and by-products of iron- and steelmaking processes
  - Emission points and events:
    - stack emissions, open storage, transport belts, slag handling

Philosophy of Tata Steel dust characterisation approach

- Dust deposits are:
  – particulate materials – dominated by ~10-100 µm diameter particles
  – reflecting contributions from multiple disparate sources
- Particles may have been modified greatly during emission, dispersal and post-deposition
  – e.g. chemical weathering, acquiring surface contamination, breakage, re-aggregation into composite particles

- Which means:
  – Every particle tells a story about its origin(s) and life history
  – A dust deposit needs to be viewed in terms of particle populations
  – Bulk chemical and mineralogical compositions of deposits reflect the ‘demographics’ of their constituent particles

➔ **Place individual particles at the centre of characterisation approach**

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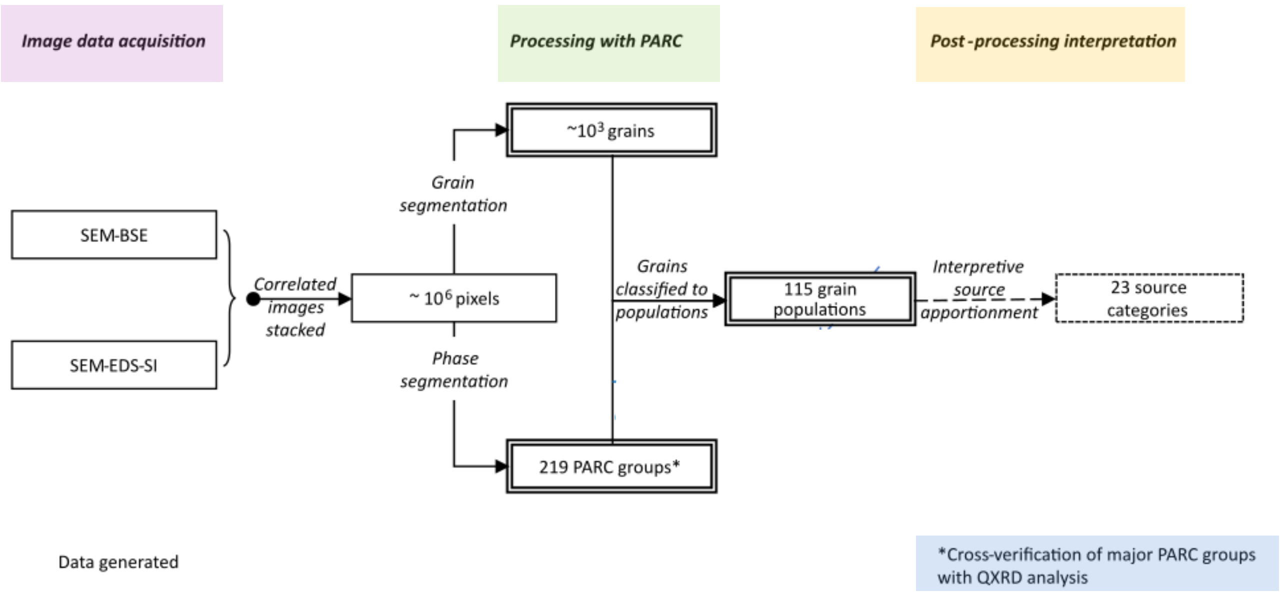
Particle mineralogy → source-diagnostic phase assemblages
Particle appearance → offers extra criteria where mineralogy not diagnostic

➔ **Place individual particles at the centre of characterisation approach**

* References:
Small et al., Environmental Sciences Europe 2020, 32(135)
Small et al., Minerals 2021, 11(9), 929

Outline of approach



Data generated

Per pixel

Raw –
SEM-BSE: greyscale;
SEM-EDS-SI: EDS spectrum;

Processed –
Label: PARC group;
Label: grain ID;
Label: grain population

Per grain

Total area & morphological parameters;
Number of sub-grains;
Sum-spectrum (all pixels);
PARC group areas, area %;
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Grain population assignment

Per grain population

Total area ;
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Interpretive assignment to source/material category

Per image (field)

PARC group areas, area %;
PARC group sum-spectra;
Area % of grain populations;
Area % of source/material categories

- Dust particles analysed by automated SEM-EDS spectral imaging (SI)
- Data processed with in-house **P**h**A**se **R**ecognition and **C**haracterisation (PARC) software
- **Particles classified to populations → source apportionment**
- Supported by independent quantitative X-ray diffraction (QXRD) analyses on bulk samples

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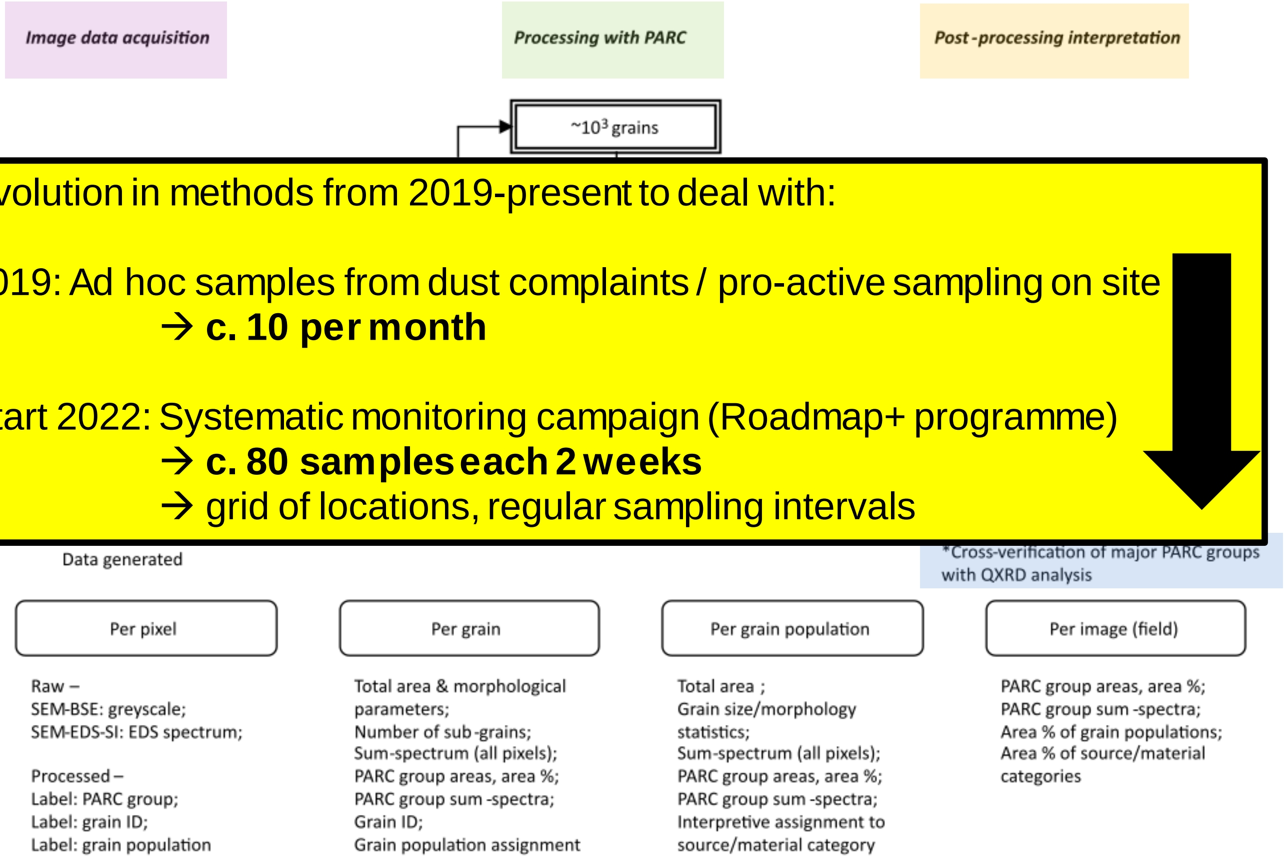

Evolution in methods from 2019-present to deal with:

2019: Ad hoc samples from dust complaints / pro-active sampling on site
→ **c. 10 per month**

Start 2022: Systematic monitoring campaign (Roadmap+ programme)
→ **c. 80 samples each 2 weeks**
→ grid of locations, regular sampling intervals

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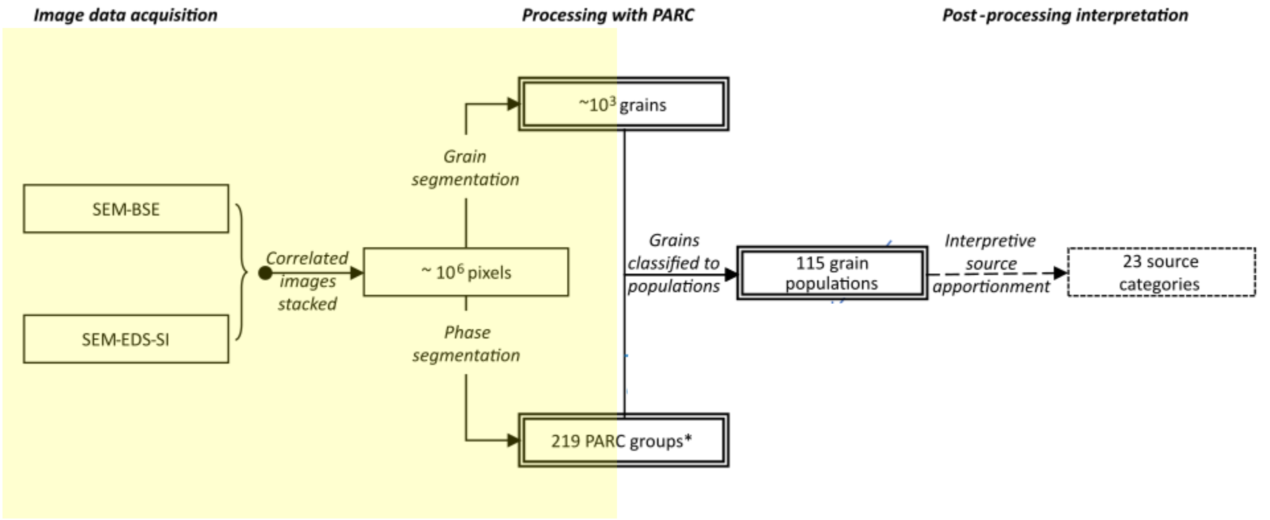
Spectral imaging → phase maps and grain segmentation



*Cross-verification of major PARC groups with QXRD analysis

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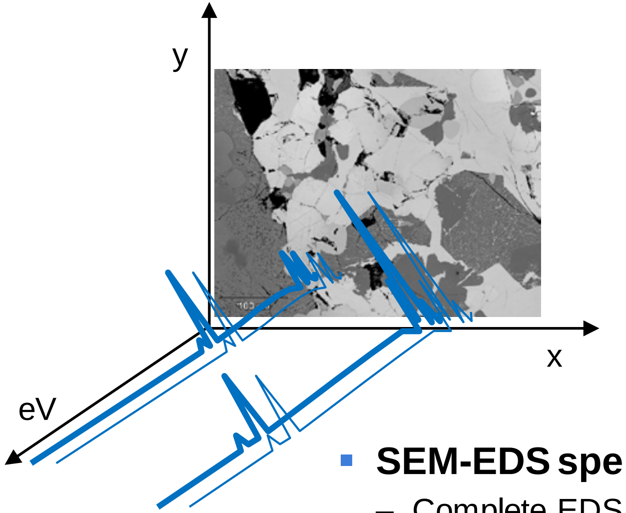
Basics of spectral imaging (SI) and PARC



- **SEM-EDS spectral imaging (SI) data cube:**
  - Complete EDS spectrum stored per SI pixel
  - Processing of SI data cubes varies widely, depending on application

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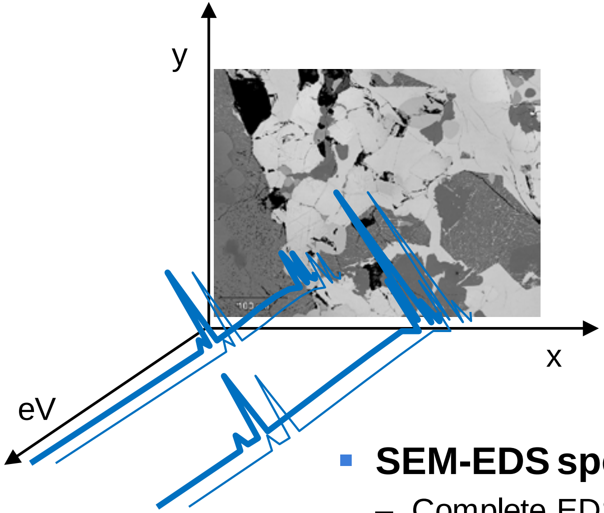

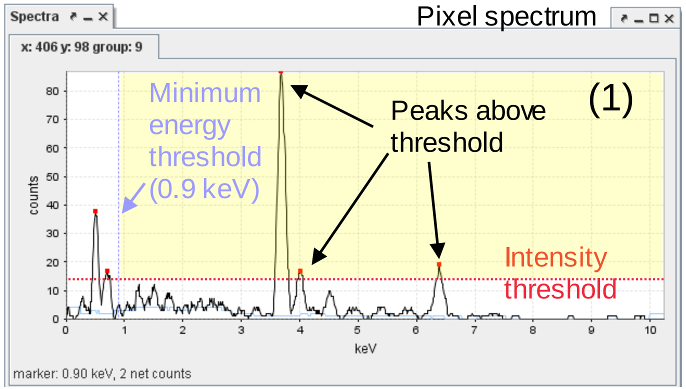

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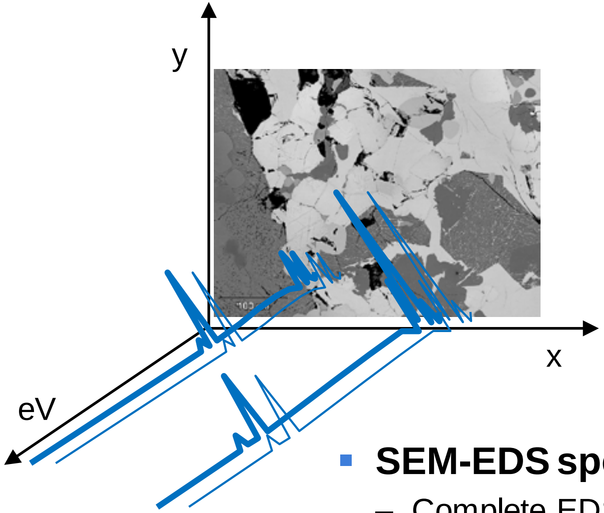

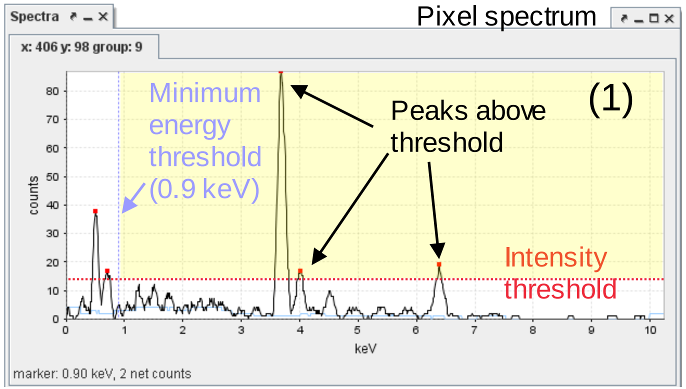

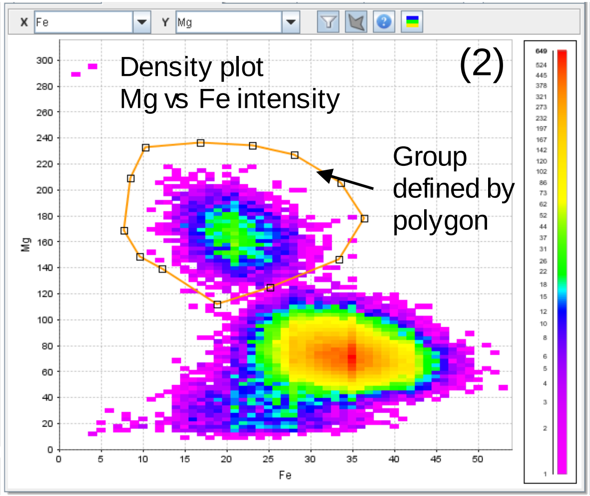

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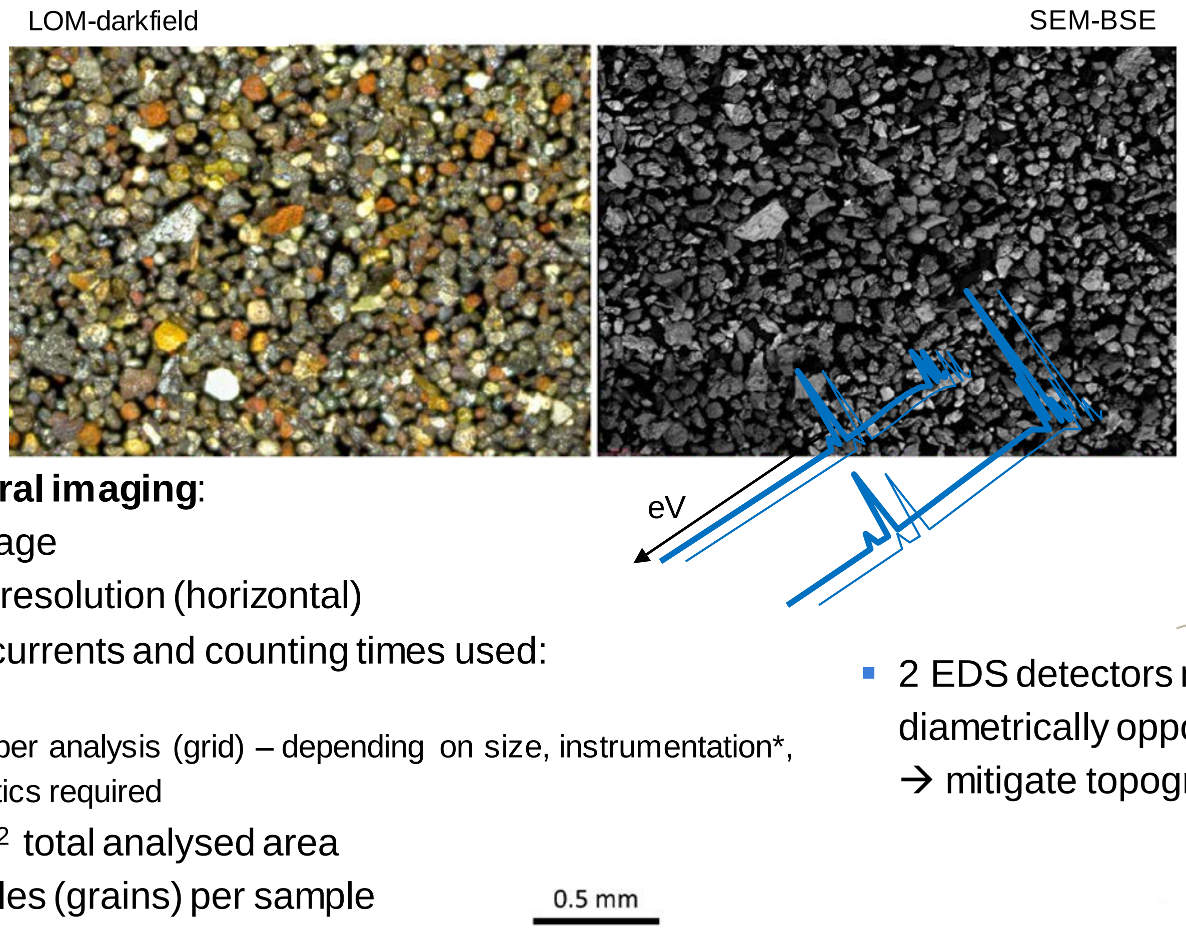
- **PARC processing:**
  - Pixels classified under (PARC-)groups by:
    - **1)** Combination of peaks above global threshold energy and intensity
    - **2)** More complex (branching-)filtering criteria – ‘density plot’ approach

Spectral imaging acquisition



*

- *Jeol 7001*
  - *Thermo Fisher Scientific system*
  - *2 SDD/EDS detectors; 30mm2*
- *Zeiss Gemini 450*
  - *Oxford microanalysis system*
  - *2 SDD/EDS detectors; 170mm2*
- *Jeol 7001*
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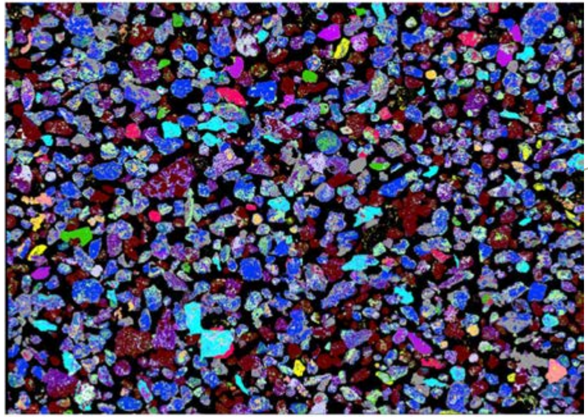
- **SEM-EDS spectral imaging**:
  - 15 kV acc. voltage
  - c. 1 um spatial resolution (horizontal)
  - Various beam currents and counting times used:
    - 10 - 25 nA
    - 0.5 to 5 hours per analysis (grid) – depending on size, instrumentation*, counting statistics required
  - c. 2.5 - 7.5 mm^2 total analysed area
  - 10^2 - 10^3 particles (grains) per sample

- 2 EDS detectors mounted diametrically opposite each other → mitigate topography effects

PARC groups → phase map

LOM-darkfield

SEM-BSE



0.5 mm

PARC groups

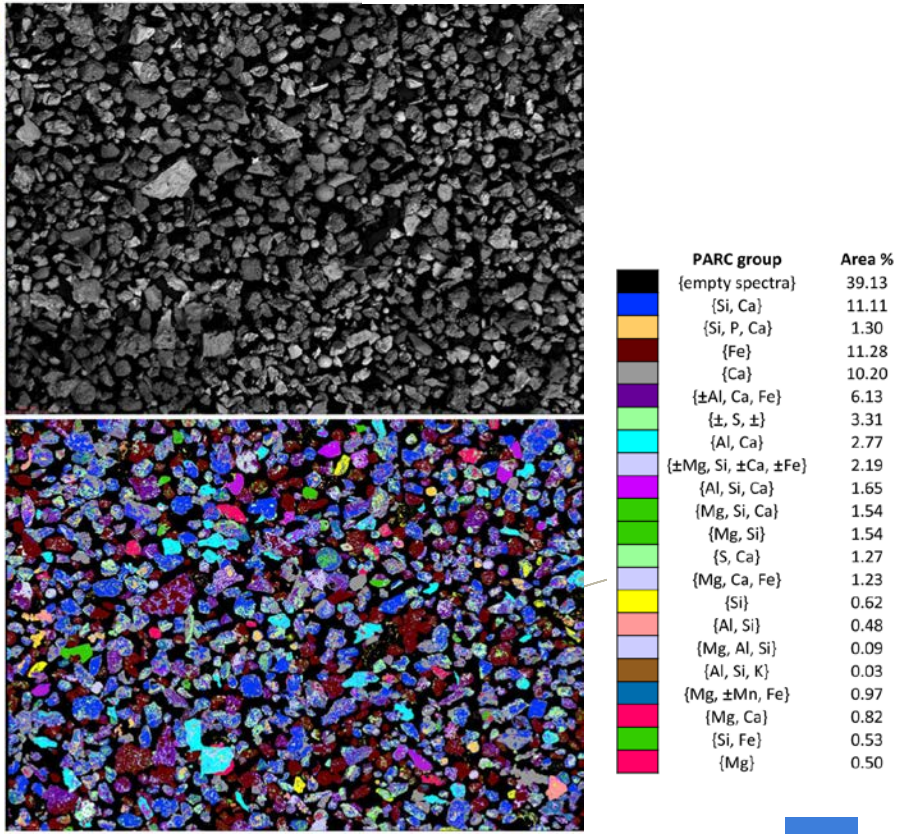
PARC group	Area %
{empty spectra}	39.13
{Si, Ca}	11.11
{Si, P, Ca}	1.30
{Fe}	11.28
{Ca}	10.20
{±Al, Ca, Fe}	6.13
{±, S, ±}	3.31
{Al, Ca}	2.77
{±Mg, Si, ±Ca, ±Fe}	2.19
{Al, Si, Ca}	1.65
{Mg, Si, Ca}	1.54
{Mg, Si}	1.54
{S, Ca}	1.27
{Mg, Ca, Fe}	1.23
{Si}	0.62
{Al, Si}	0.48
{Mg, Al, Si}	0.09
{Al, Si, K}	0.03
{Mg, ±Mn, Fe}	0.97
{Mg, Ca}	0.82
{Si, Fe}	0.53
{Mg}	0.50

- **SI data → PARC group segmentation**
  - > 200 groups
  - Limits of spatial & chemical resolution
    - ⇒Some degree of overlap/confusion between true phases
    - ⇒See as ‘pseudo’-phases
    - ⇒Sufficient for particle classification based on mineralogical criteria

Grain segmentation

LOM-darkfield

SEM-BSE

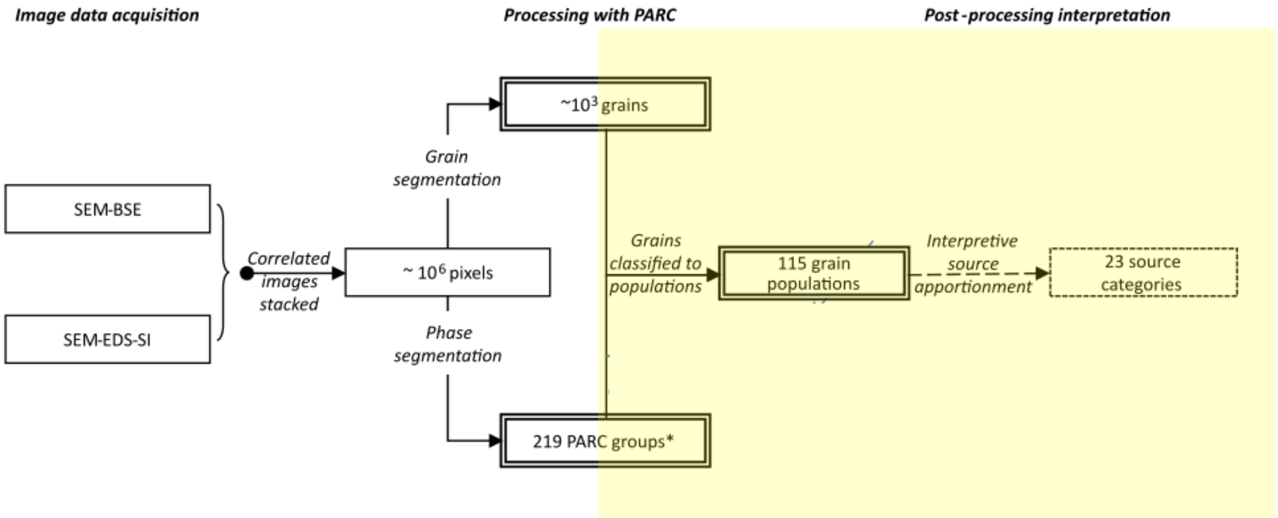


0.5 mm

PARC groups

- **Grain segmentation** currently based on SEM-BSE image
- Image split into individual grains
- Major challenge: avoiding spurious merging / splitting
- Work ongoing to utilise correlated light optical(LOM) and chemical (SI) information

Classifying grains under populations



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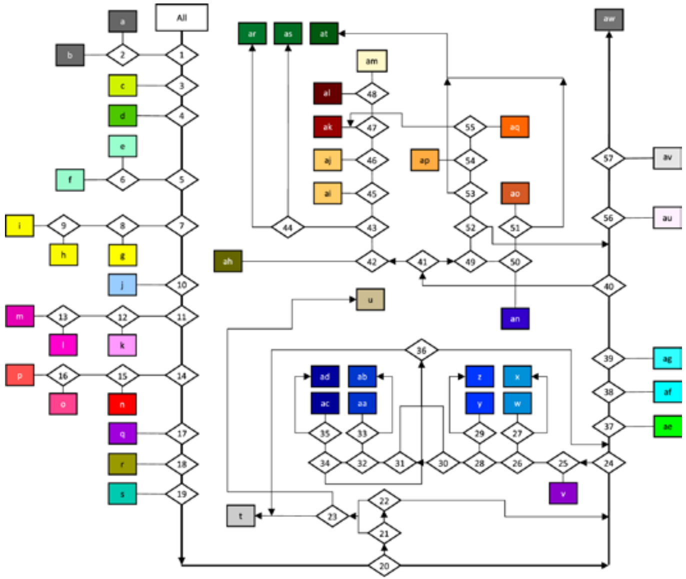
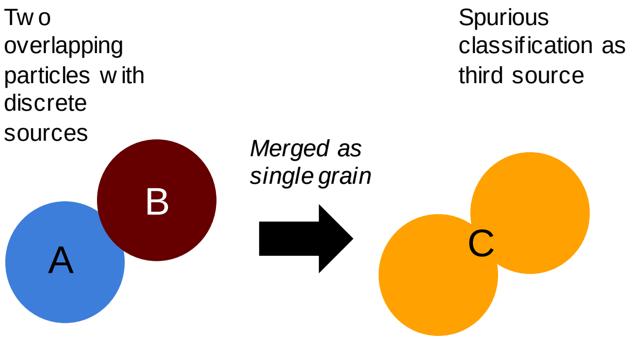


Population	Source / material
w	1. Converter
x	
y	
z	
aa	
ab	
ac	
ad	
an	
v	2. Slopping
q	
ao	3. Sinter
aq	
ai	4. Pellet
aj	
ap	
r	5. Ore/sinter/pellet
ah	
al	
ak	
am	6. Fe/FeOx + minor Zn
ar	7. Fe-metal rich
as	
at	

Population	Source / material
e	8. Zn-rich
f	
o	9. De-sulph
af	10. Ca-aluminate slag
ag	
n	11. Dolomite
p	12. MgO / residue after dolomite
l	13. Olivine flux
m	
k	14. Tundish gunning mass
ae	15. Alumina
s	16. Ca-Al-silicate
t	17. Lime / calcite
u	
j	18. Possible cement
d	19. Gypsum / anhydrite
au	20. TiO_2
av	21. Ti-rich paint
g	22. Quartz-clay-feldspar-mica
h	
i	
c	23. Chloride / salt (covering)
a	24. Coal & cokes min. estimate
b	25. Carbon rich other
aw	26. Unassigned, low-carbon

- Grain population model applied to classify grains
- **Manually defined set of branching filters**
  - Based on PARC group area proportions per grain and functions thereof
  - Numerous sub-compositions and mutual ratios between PARC groups used
- Overall structure and content of individual filters:
  - Conceived based on expert knowledge of source materials
  - Verified on reference materials wherever possible
- Indirect use made of statistical methods such as PCA and K-means clustering
  - Informs choice of filters and thresholds
- Data can be subjected to machine learning approaches

Classifying grains under populations: challenges

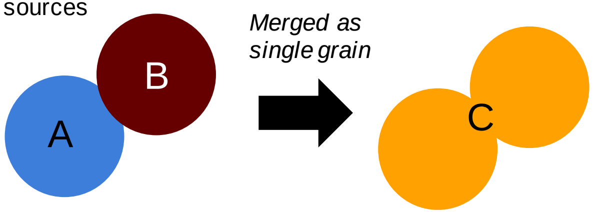


- Main challenges for both manual and machine learning approaches:
  - Grain segmentation artefacts (mixing)

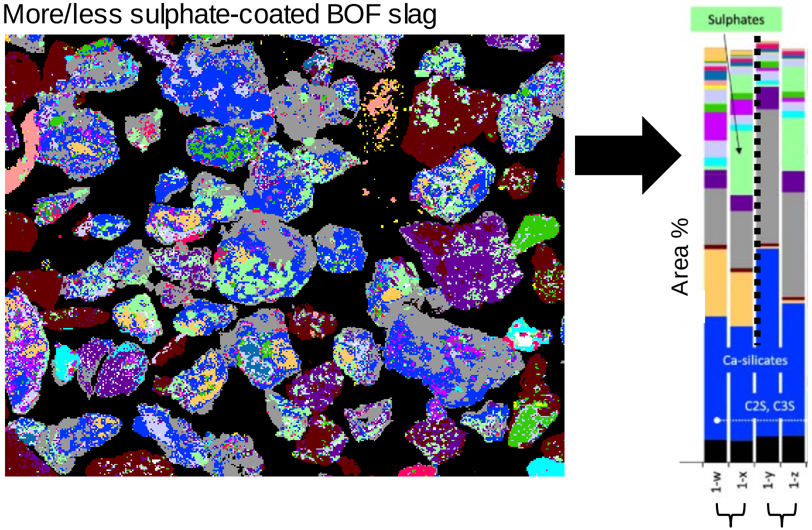
Classifying grains under populations: challenges

Two overlapping particles with discrete sources

Spurious classification as third source



Superficial sulphate layer – same substrate mineralogy
More/less sulphate-coated BOF slag



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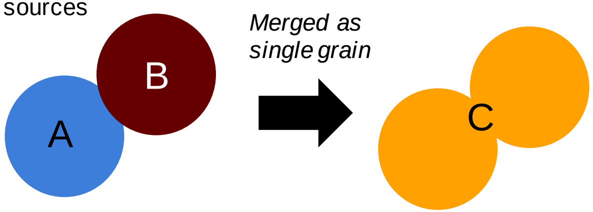
  - Grain segmentation artefacts (mixing)
  - Superficial layers obscuring substrate particle mineralogy → different sub-compositions need to be considered, not only raw area proportions

Classifying grains under populations: challenges

Two overlapping particles with discrete sources

Merged as single grain

Spurious classification as third source



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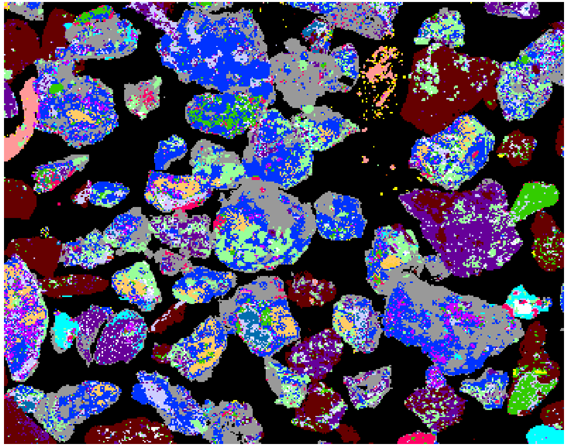
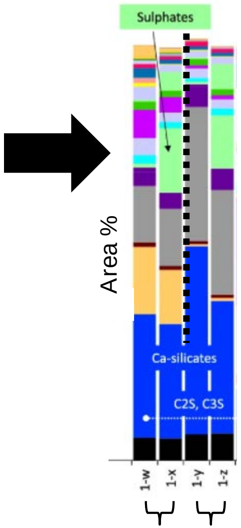




- Main challenges for both manual and machine learning approaches:
  - Grain segmentation artefacts (mixing)
  - Superficial layers obscuring substrate particle mineralogy → different sub-compositions need to be considered, not only raw area proportions
  - Overlapping mineralogy (PARC groups) of different materials → when mineralogy alone not diagnostic

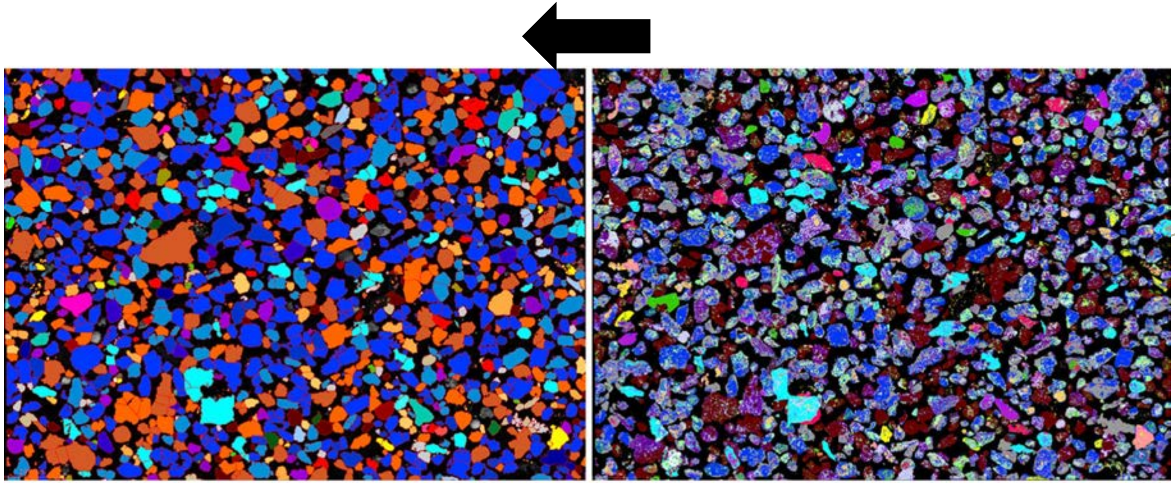
Classifying grains under populations: applied to image

- Grain population model applied
- Grains classified to populations
- Quantitative data yielded:
  - Area (→ volume) fractions of grain populations per sample → **dust provenance information**
  - PARC group makeup of grain populations → **mineralogical information**
  - Quantitative SEM-EDS analyses → **chemical information**

Population	Source / material	Area %
w	1	5.13
x		7.57
y		14.96
z		18.08
aa		3.84
ab		2.00
ac		0.61
ad		0.34
an		1.17
v	2	0.75
q		2.37
ao	3	14.58
aq		11.42
ai	4	0.93
aj		0.05
ap		2.59
r	5	0.22
al		2.51
ak		0.52
ar	7	0.16
at		0.23
f	8	0.00

Population	Source / material	Area %
o	9	0.05
af	10	4.84
ag		0.51
n	11	1.67
p	12	0.12
l	13	0.53
ae	15	0.06
s	16	1.27
t	17	1.40
u		0.59
j	18	0.54
d	19	0.17
av	21	0.01
g	22	0.09
i		0.59
a	24	0.42
b	25	0.84
aw	26	1.39

Classification



Grain populations

0.5 mm

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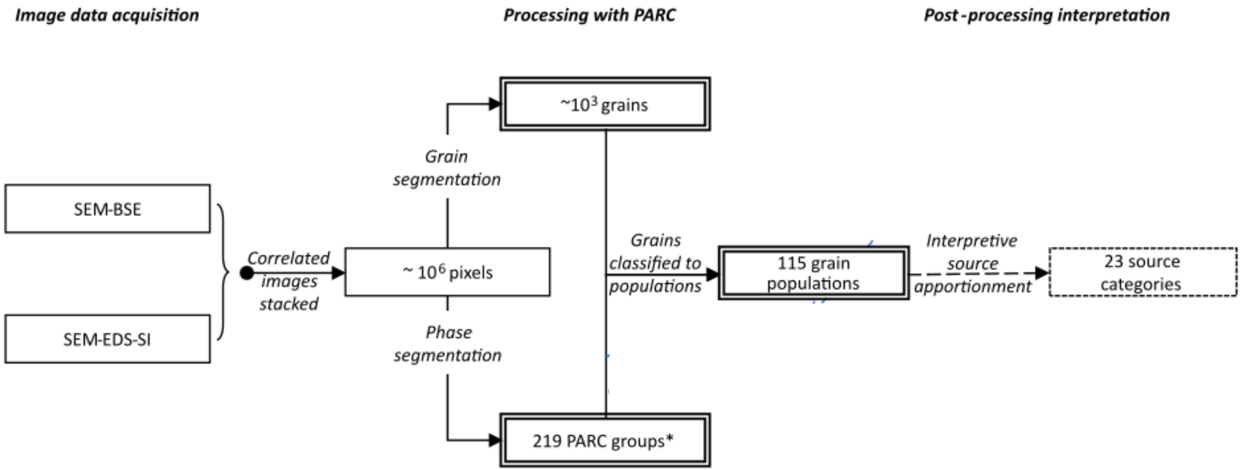
Supporting QXRD analyses



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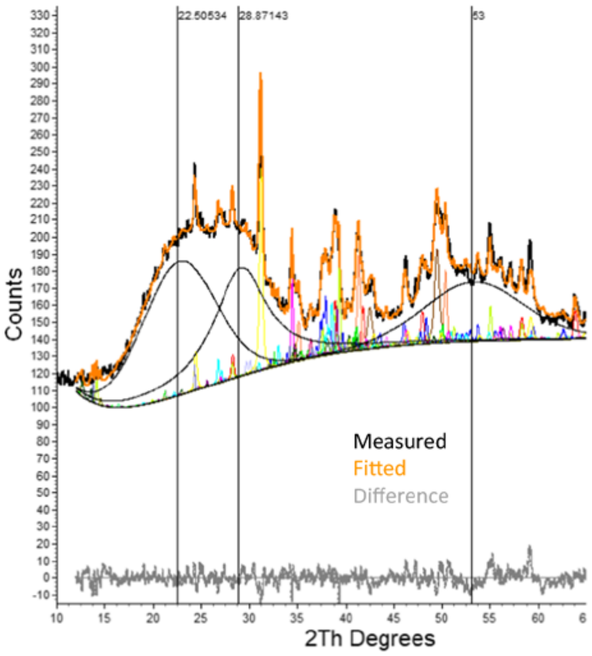


	wt%± 2σ	vol%
Hematite Fe_2O_3	37.1±2.0	30.5
Magnetite Fe_3O_4	14.0±1.2	12.0
Wuestite FeO	3.8±0.6	2.7
Goethite FeOOH	0.0±0.2	0.0
Iron metallic	0.0±0.2	0.0
SFCA $Ca_{2.3}Mg_{0.8}Al_{1.5}Fe_{8.3}Si_{1.1}O_{20}$	4.5±1.0	4.7
SFCA-I $Ca_{3.18}Fe_{15.48}Al_{1.34}O_{28}$	4.8±1.4	4.6
SFCA-II $Ca_{5.1}Al_{9.3}Fe3+_{18.7}Fe2+_{0.9}O_{48}$	2.7±0.2	2.8
CF2 $Ca_4Fe_{14}O_{25}$	1.2±0.8	1.2
α-CF_2 $Ca_2Fe_{16}O_{25}$	0.0±0.4	0.0
C2W4F9 $Ca_2Fe_{22}O_{33}$	1.3±0.6	1.1
CWF $CaFe_3O_5$	2.9±0.8	2.6
Brownmillerite $Ca_2Fe_2O_5$	6.3±1.0	7.2
Kirschsteinite $CaFeSiO_4$	0.0±0.2	0.0
β-C2S Larnite Ca_2SiO_4	4.0±1.2	5.4
a'-C2S Ca_2SiO_4	2.4±0.8	2.7
C3A $Ca_9Al_6O_{18}$	2.2±0.6	3.1
C12A7 Mayenite $Ca_{12}Al_{14}O_{33}$	0.2±0.4	0.3
CMAS Q-phase $Ca_{20}Al_{26}Mg_3Si_3O_{68}$	0.0±0.2	0.0
Katoite $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$	0.7±0.2	1.1
Gehlenite $Ca_2Al_2SiO_7$	0.7±0.6	1.0
Calcite $CaCO_3$	1.8±0.4	3.0
Lime CaO	0.1±0.2	0.1
Portlandite $Ca(OH)_2$	0.2±0.2	0.3
Dolomite $CaMg(CO_3)_2$	0.4±0.4	0.6
Graphite C	0.1±1.8	0.2
Anhydrite $CaSO_4$	1.2±0.4	1.7
Gypsum $CaSO_4*2H_2O$	0.7± 0.4	1.2
Quartz SiO_2	2.8±1.4	4.2
Kaolinite $Al_2Si_2O_5(OH)_4$	0.3±0.2	0.6
Mica $(K,Na)(Mg,Fe)(Al,Si)4O_{10}(OH)_2$	1.5±1.2	2.3
Feldspar $(Ca,Na,K)(Al,Si)_4O_8$	0.0±0.6	0.0
Amphibole $(Ca,Na,K)(Mg,Al,Fe)_5(Si,Al)_8O_{22}(OH)_2$	1.6±1.0	2.1
Clinopyroxene $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$	1.2±1.4	1.6
Halite NaCl	0.0±0.2	0.0

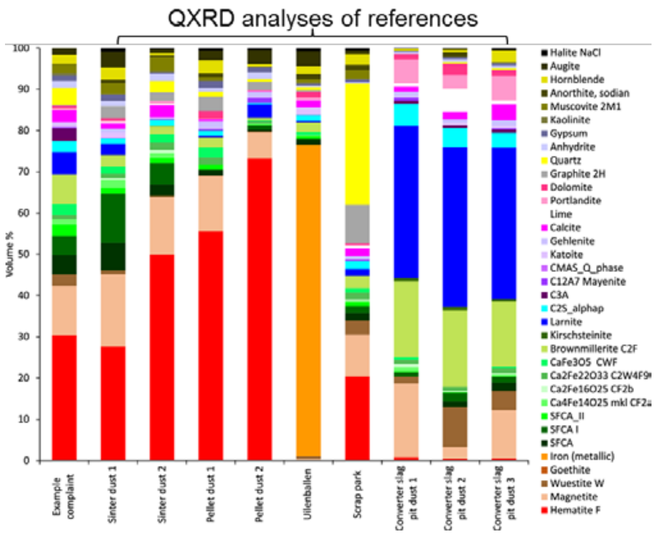
- Quantitative X-ray diffraction analysis
- Using Rietveld approach
- Quantify crystalline phase proportions **per sample**
- Supports interpretation of SEM-EDS-PARC analyses in terms of true mineralogical phases

- QXRD → crystallographic definitions
- SEM-EDS-PARC → chemical definitions

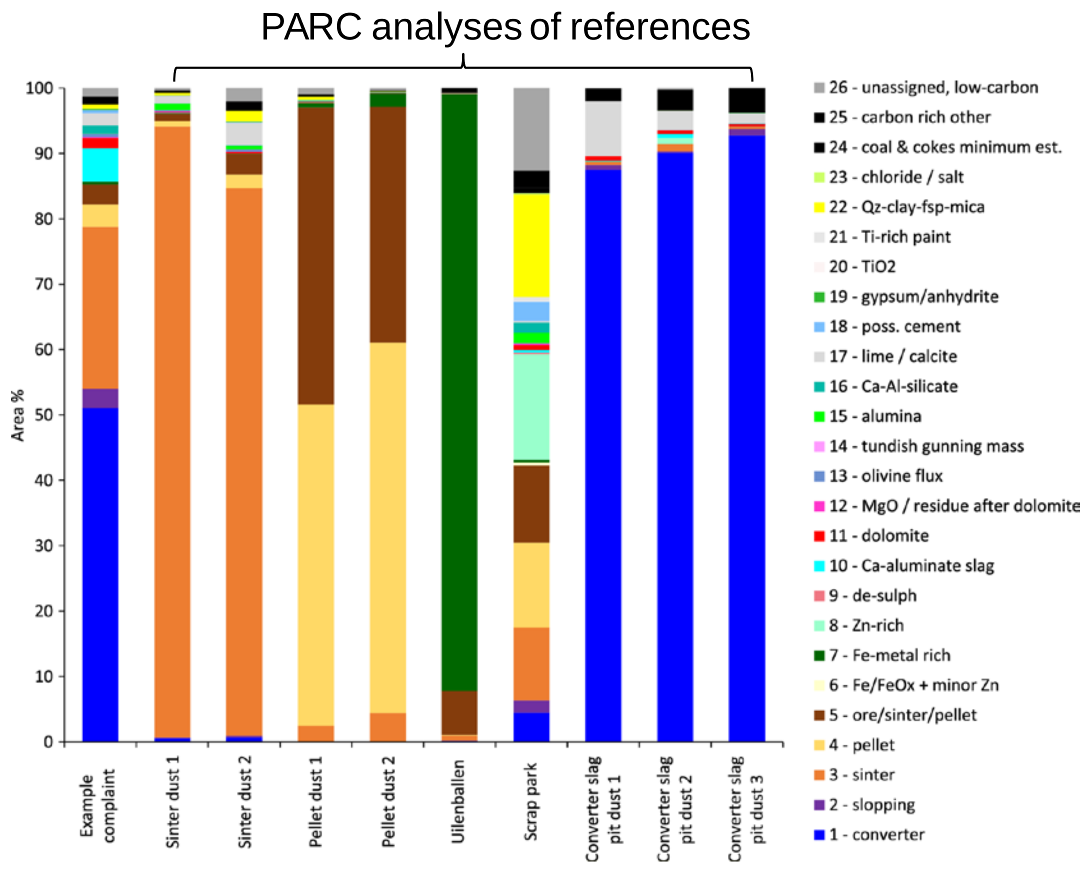
Verifying grain populations on reference materials

- **Key steelworks-related dust sources include:**
  - Iron ore, sinter and pellets
  - Slag material: e.g. from BOF converter process
  - Coal and coke

- **QXRD and PARC analyses of reference materials to help recognise them ‘in the wild’**



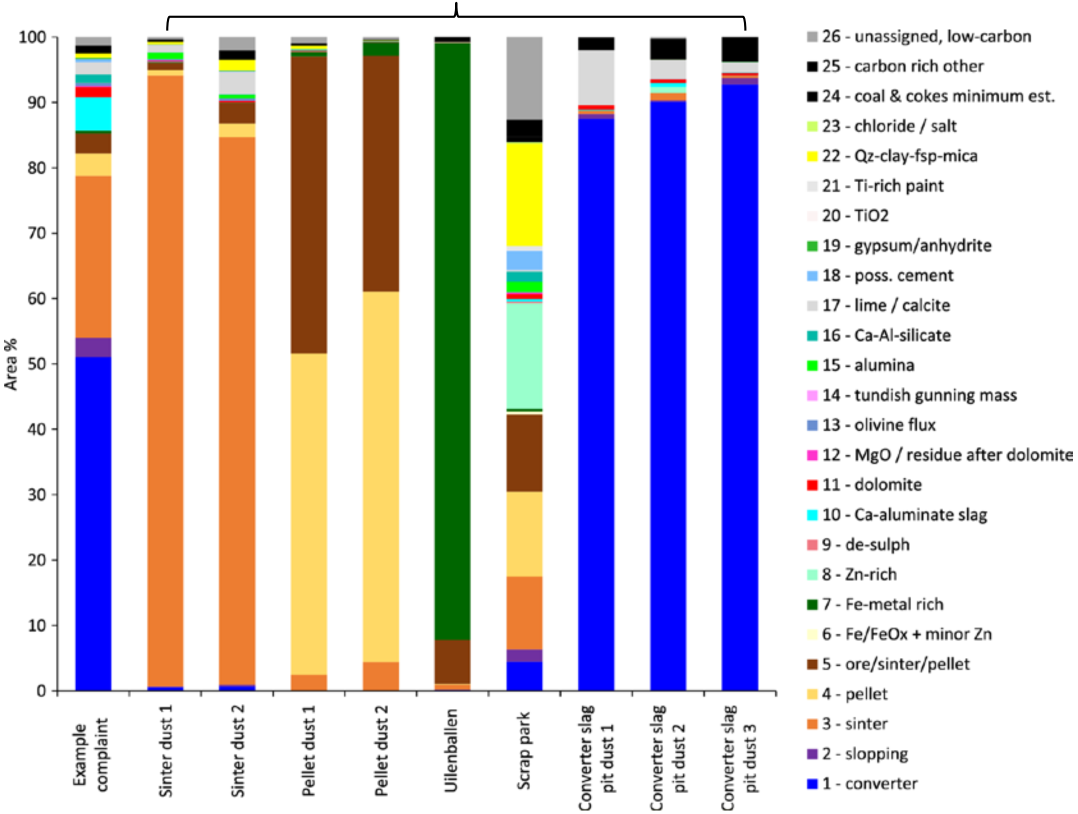
Verifying grain populations on reference materials



- Reference samples of candidate dust sources
- Used for defining grain populations
- Establish discrimination performance
- Thereafter, verifying analyses in case of (enforced) changes in instrumentation / measurement conditions

Verifying grain populations on reference materials

PARC analyses of references



- Model performs very well when applied to reference materials
  - → Low degree of confusion
- More challenging in dust deposit samples:
  - Alteration of particles vs original reference characteristics
  - Mixing of disparate materials
    - Genuine composite particles
    - Imperfect grain segmentation in image analysis step
    - => mimicry and incorrect classification

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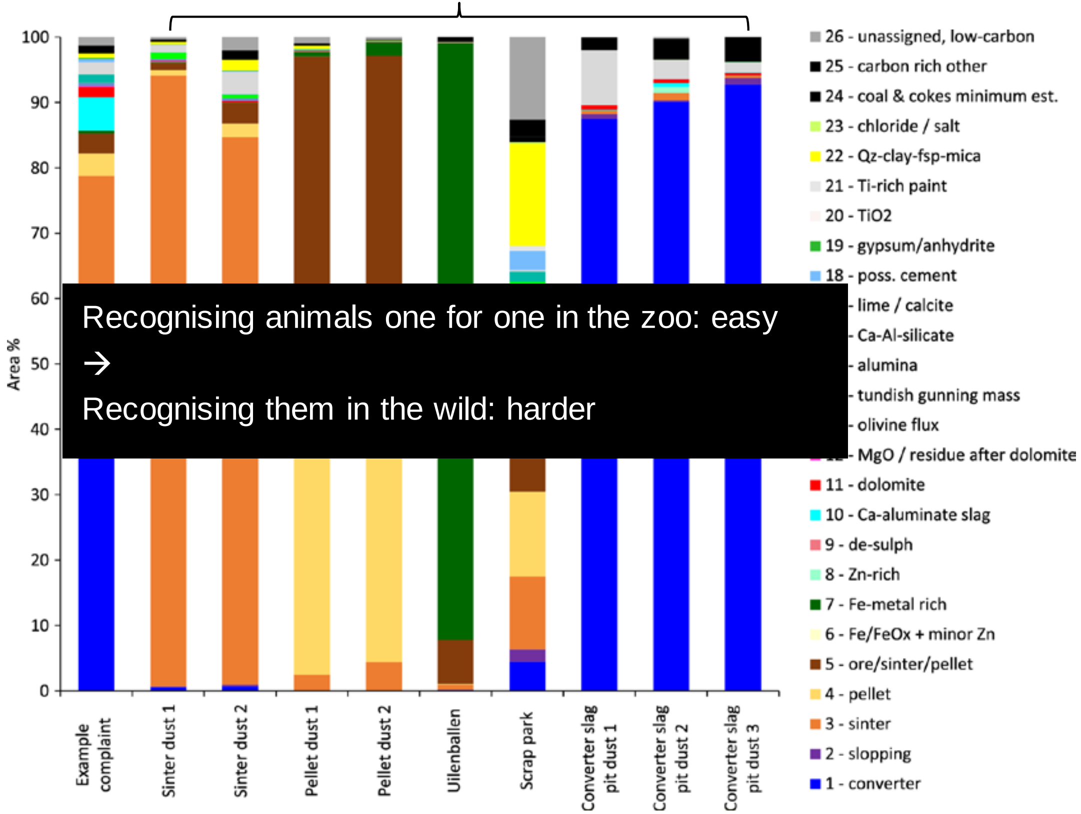
PARC analyses of references



Recognising animals one for one in the zoo: easy
→
Recognising them in the wild: harder

- Model performs very well when applied to reference materials
  - → Low degree of confusion
- More challenging in dust deposit samples:
  - Alteration of particles vs original reference characteristics
  - Mixing of disparate materials
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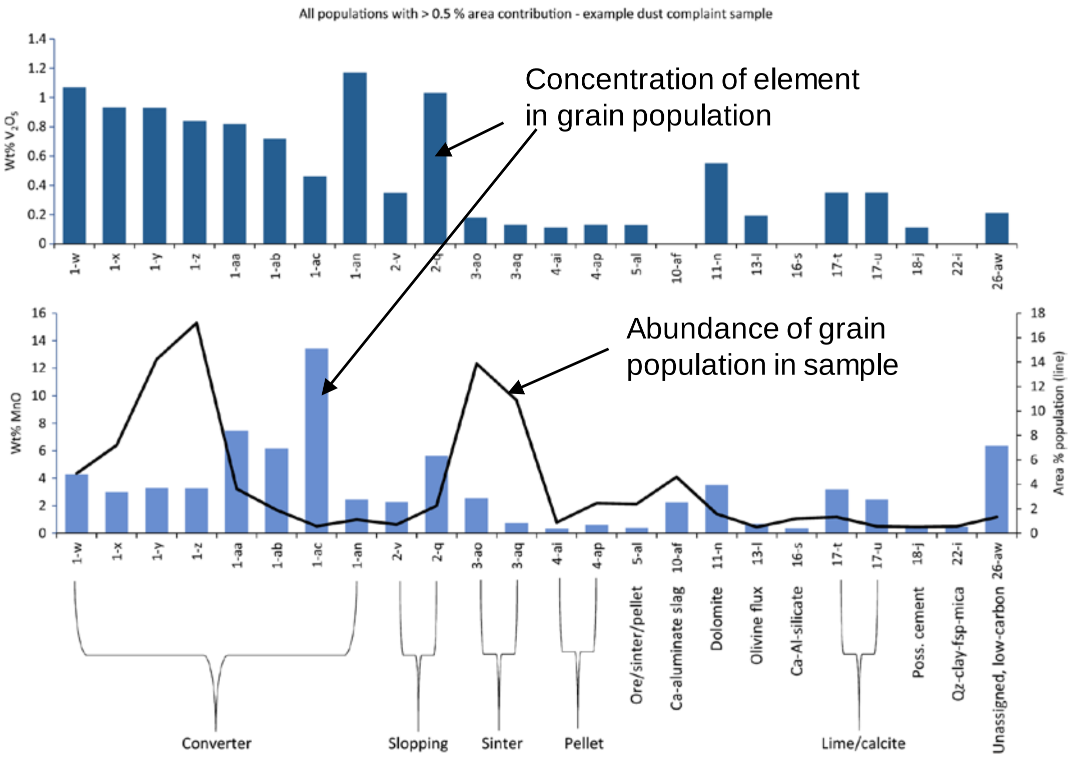
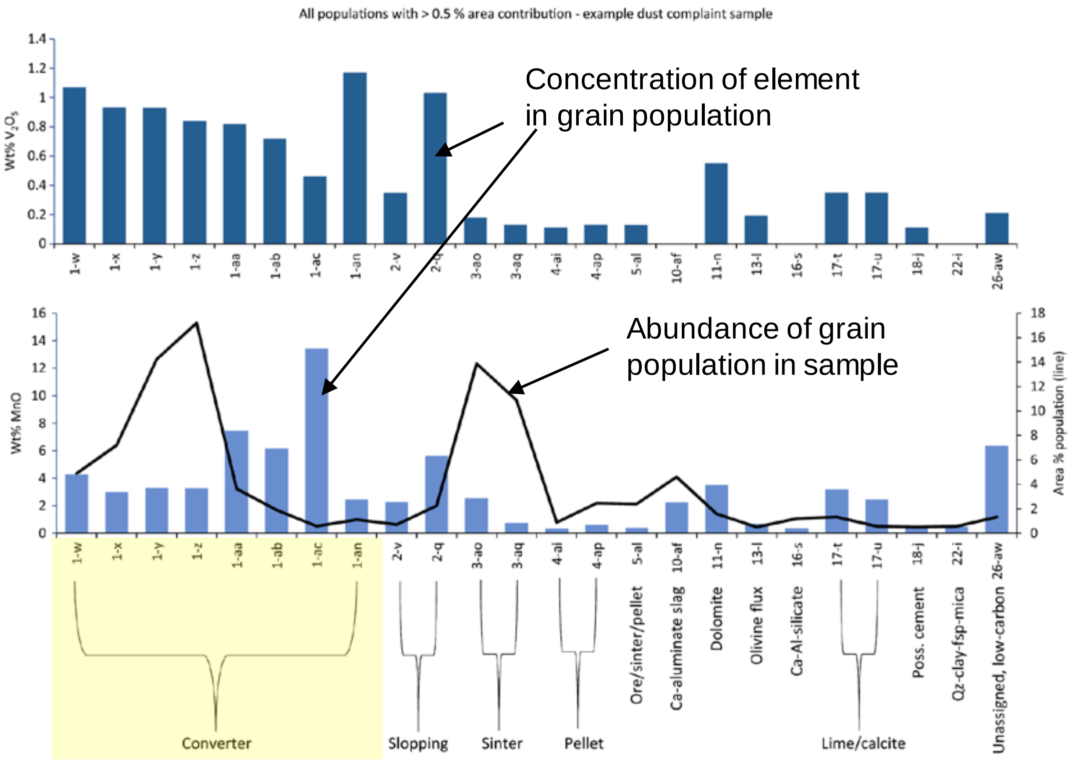
Pinpointing sources of V and Mn in dust deposits



- Use quantitative EDS analyses of grains, grain populations and PARC groups (pseudo-phases)
- Locate the main source materials and carrier phases of potentially toxic elements

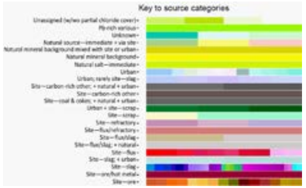
Pinpointing sources of V and Mn in dust deposits



- V and Mn as example in a dust deposit sample rich in steelworks-derived materials
- BOF converter slag emerges as main source of V and Mn
- Carrier phases:
  - V:
    - Dicalcium silicate (C2S)
    - Brownmillerite (C2(A,F))
    - Weathering products after these
  - Mn:
    - Magnesio-wustite and oxidation products thereof
    - Scarce Mn-Fe-oxide

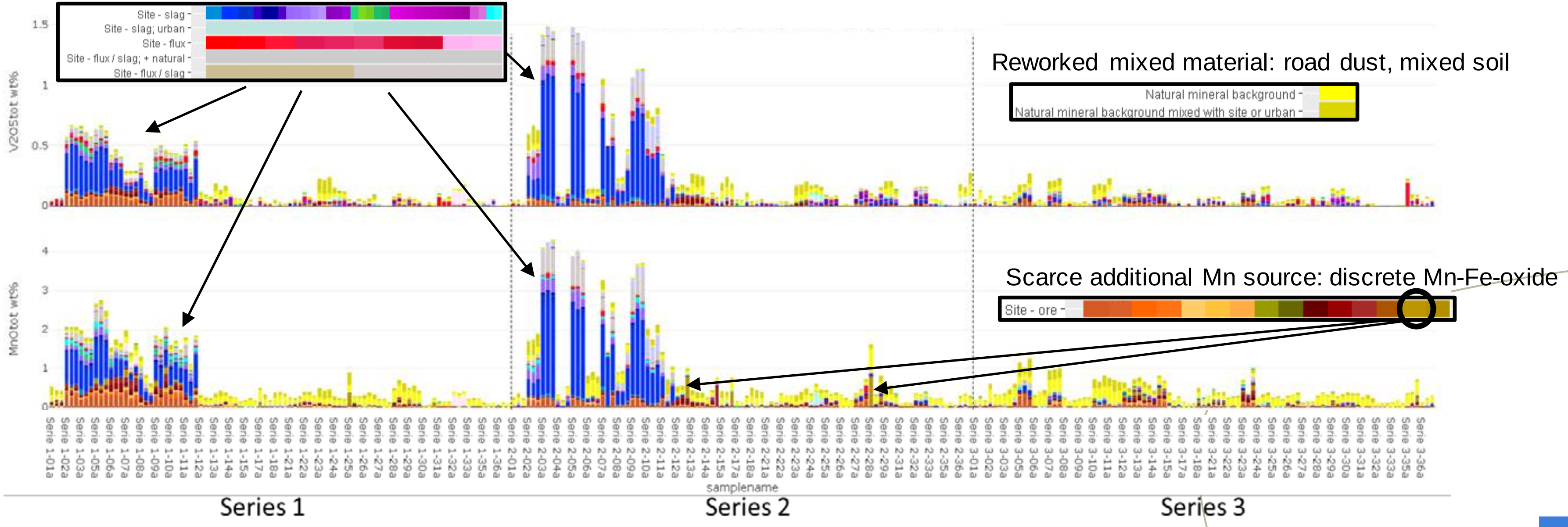
Pinpointing sources of V and Mn in dust deposits

- Confirmation of distribution of V and Mn (and Fe) across large sample set in joint study with TNO



Calculated bulk-sample wt% contributions of grain populations (C-free basis)

Steelmaking BOF slag related



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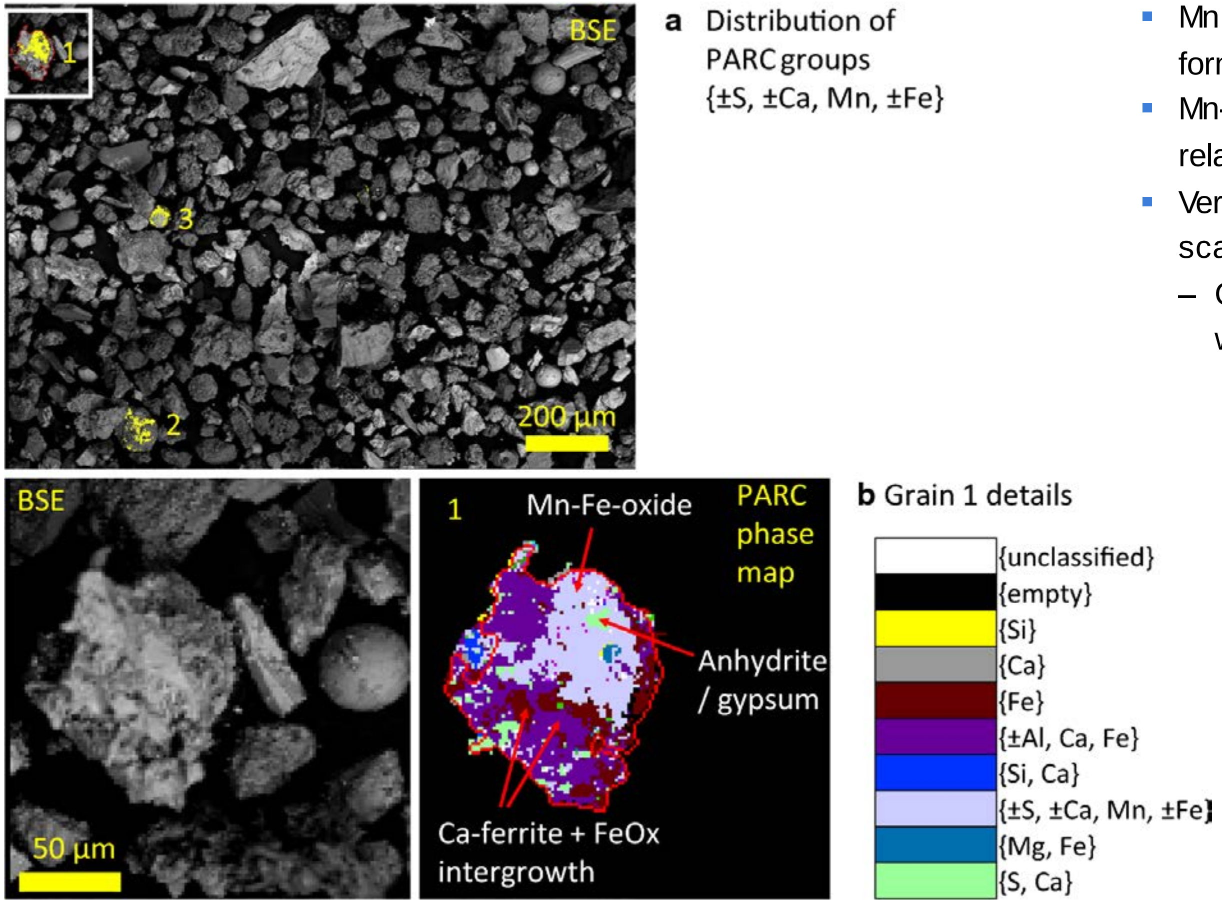
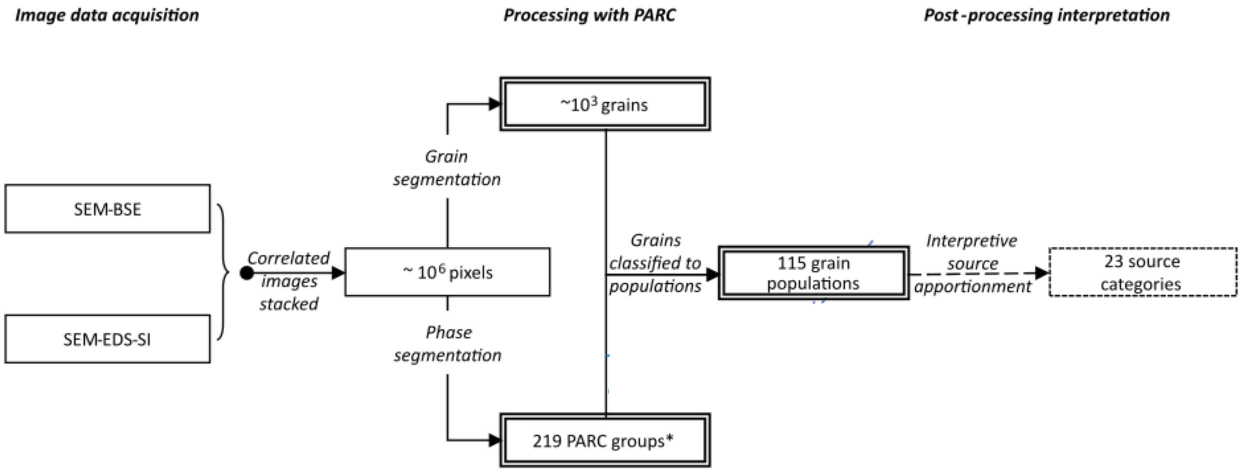


- Mn also occurs more rarely in concentrated form
- Mn-Fe-oxide phase found in/on particles related to iron ore preparation
- Very low abundance and concentrated in scarce particles
  - Only detectable with PARC approach, not with bulk sample QXRD

Detecting Pb-rich phase occurrence



*Cross-verification of major PARC groups with QXRD analysis

Data generated

Per pixel

Raw –
SEM-BSE: greyscale;
SEM-EDS-SI: EDS spectrum;

Processed –
Label: PARC group;
Label: grain ID;
Label: grain population

Per grain

Total area & morphological parameters;
Number of sub-grains;
Sum-spectrum (all pixels);
PARC group areas, area %;
PARC group sum-spectra;
Grain ID;
Grain population assignment

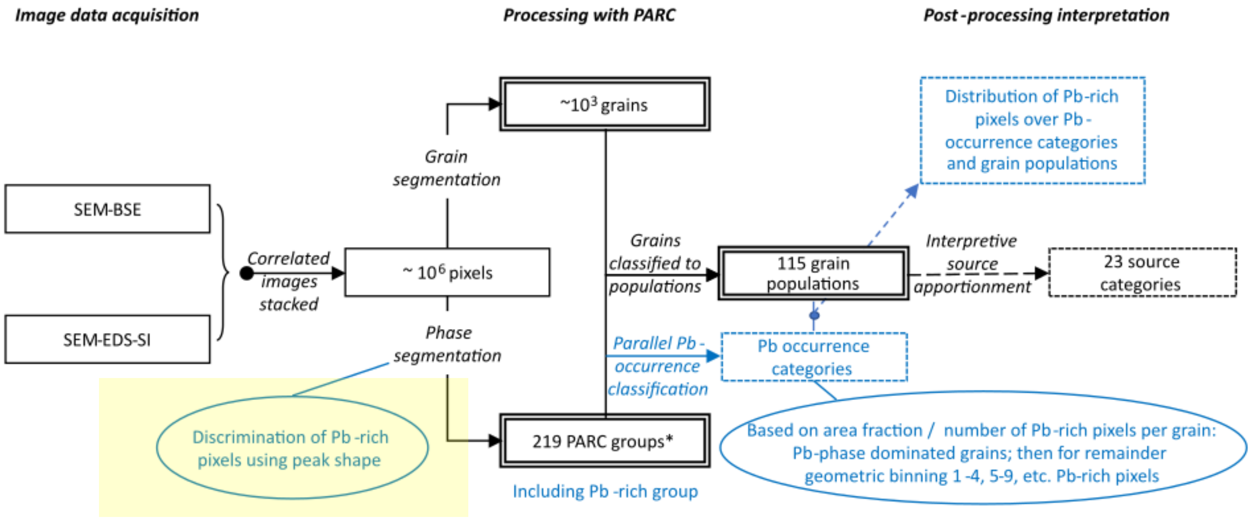
Per grain population

Total area ;
Grain size/morphology statistics;
Sum-spectrum (all pixels);
PARC group areas, area %;
PARC group sum-spectra;
Interpretive assignment to source/material category

Per image (field)

PARC group areas, area %;
PARC group sum-spectra;
Area % of grain populations;
Area % of source/material categories

Detecting Pb-rich phase occurrence



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Per pixel	Per grain	Per grain population	Per image (field)
Raw – SEM-BSE: greyscale; SEM-EDS-SI: EDS spectrum; Processed – Label: PARC group; Label: grain ID; Label: grain population	Total area & morphological parameters; Number of sub-grains; Sum-spectrum (all pixels); PARC group areas, area %; PARC group sum-spectra; Grain ID; Grain population assignment	Total area; Grain size/morphology statistics; Sum-spectrum (all pixels); PARC group areas, area %; PARC group sum-spectra; Interpretive assignment to source/material category	PARC group areas, area %; PARC group sum-spectra; Area % of grain populations; Area % of source/material categories

Crux of the methodology: discriminating Pb from S signal

Analyses performed at 15 kV → necessary spatial resolution
=> Need to distinguish Pb-M from S-K lines

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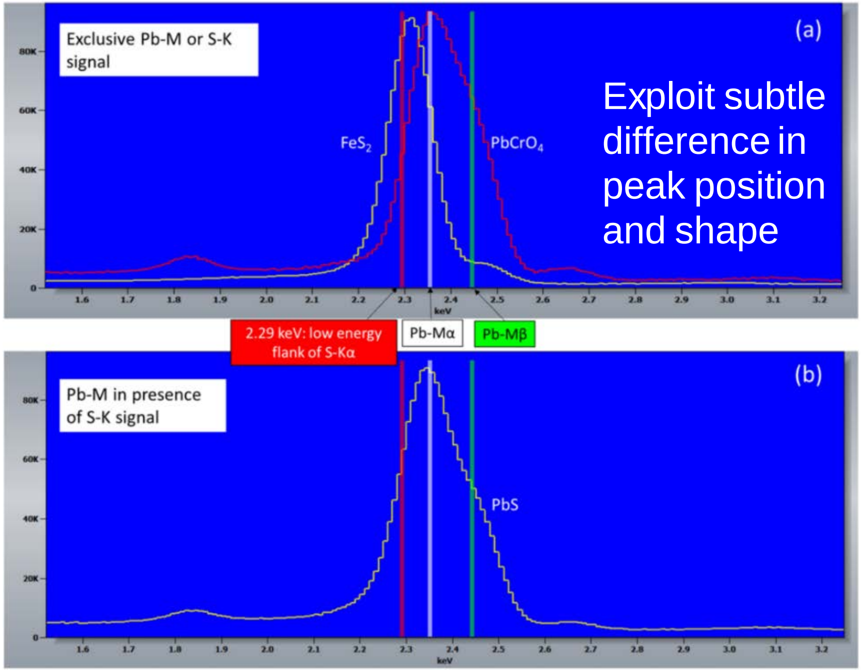

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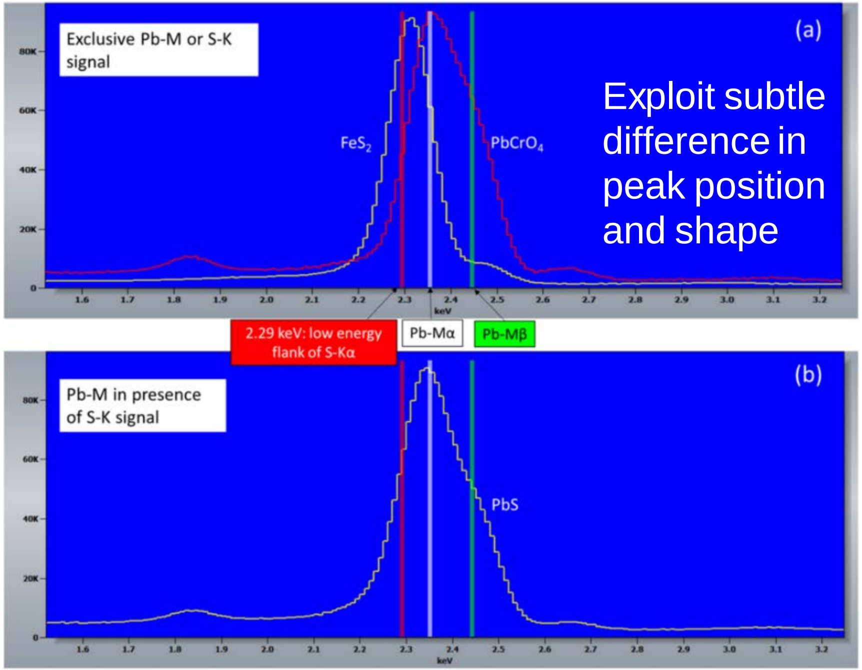


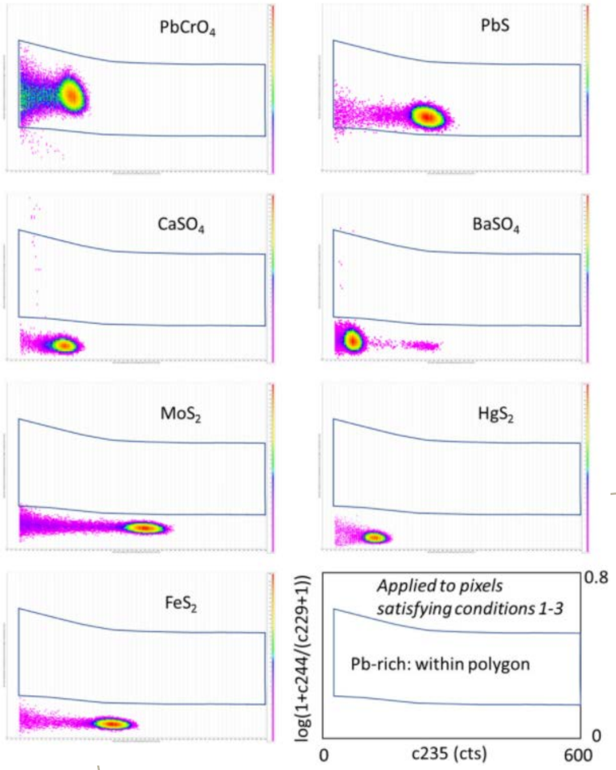
Use standard reference compounds (polished)

Calibrate discrimination of SI pixels:

Pb-rich

vs

S-rich, Pb-free



c235 = SI channel 235 → 2.35 eV

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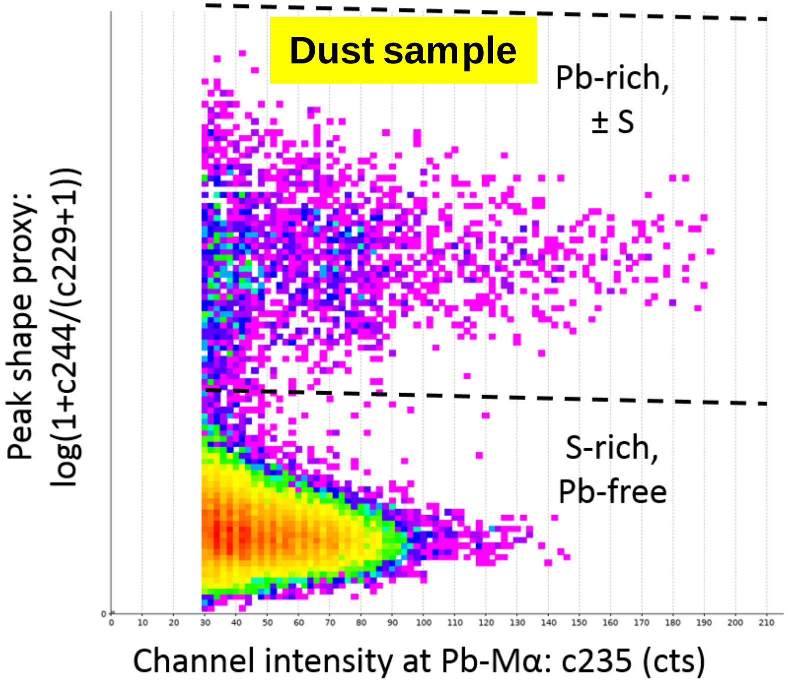

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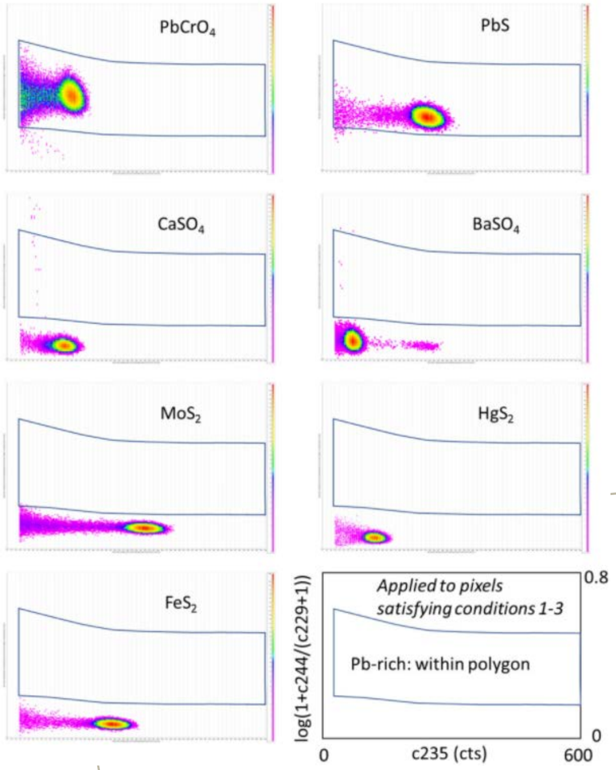

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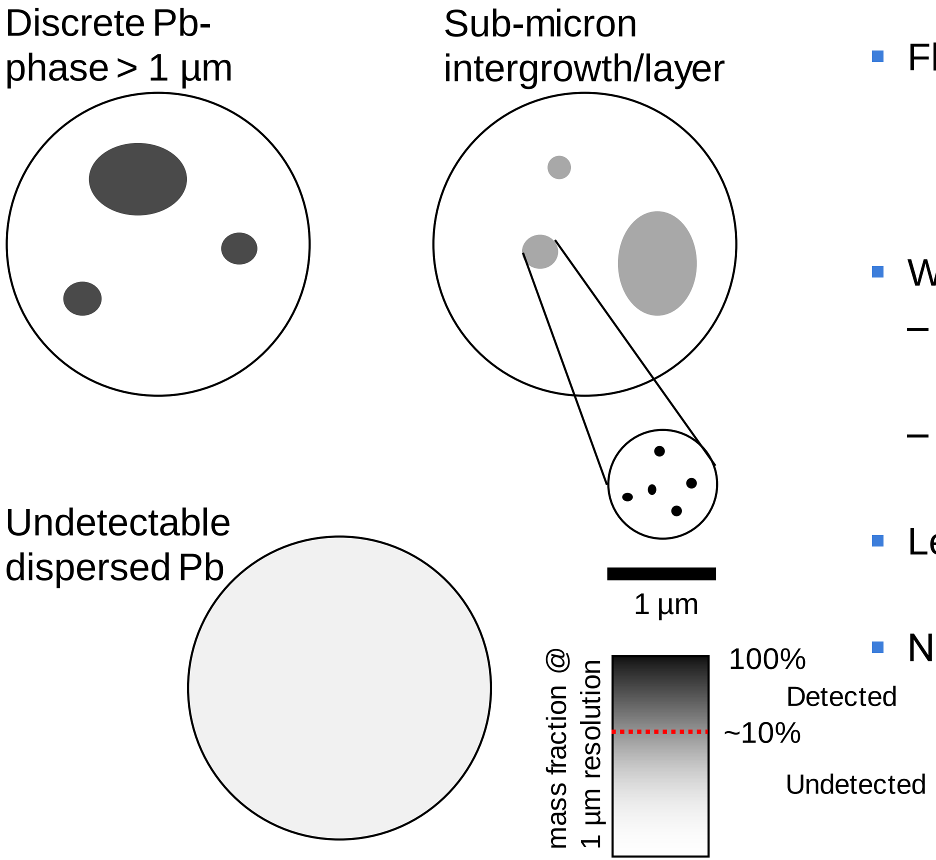
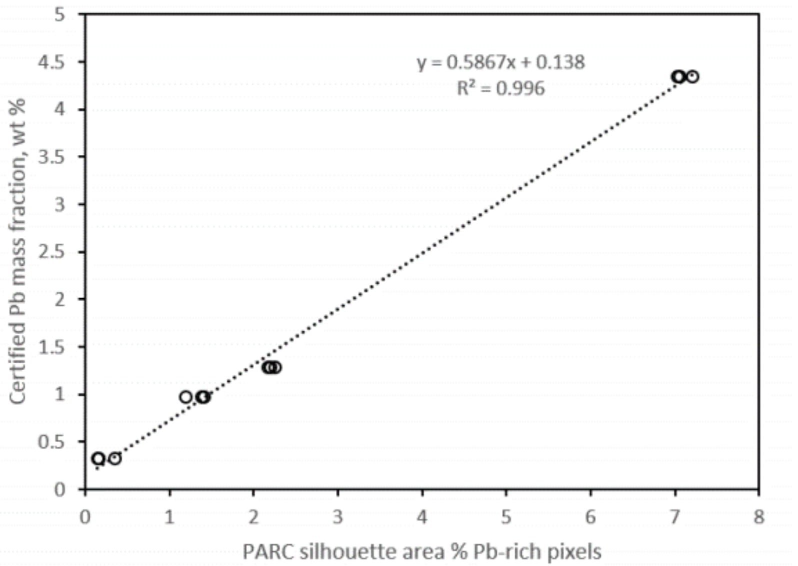
Physical meaning of Pb-rich pixels in SI data



- Flag for Pb concentrated at:
  - major element level (~ 10 wt%)
  - on c. 1 µm length-scale
- What they capture:
  - Clearly identifiable individual (sub)grains of discrete Pb phases
  - Mixed signal from nano-scale sub-particles in/on other phases
- Less concentrated occurrence = not flagged
- N.B. local concentration ≠ bulk sample concentration

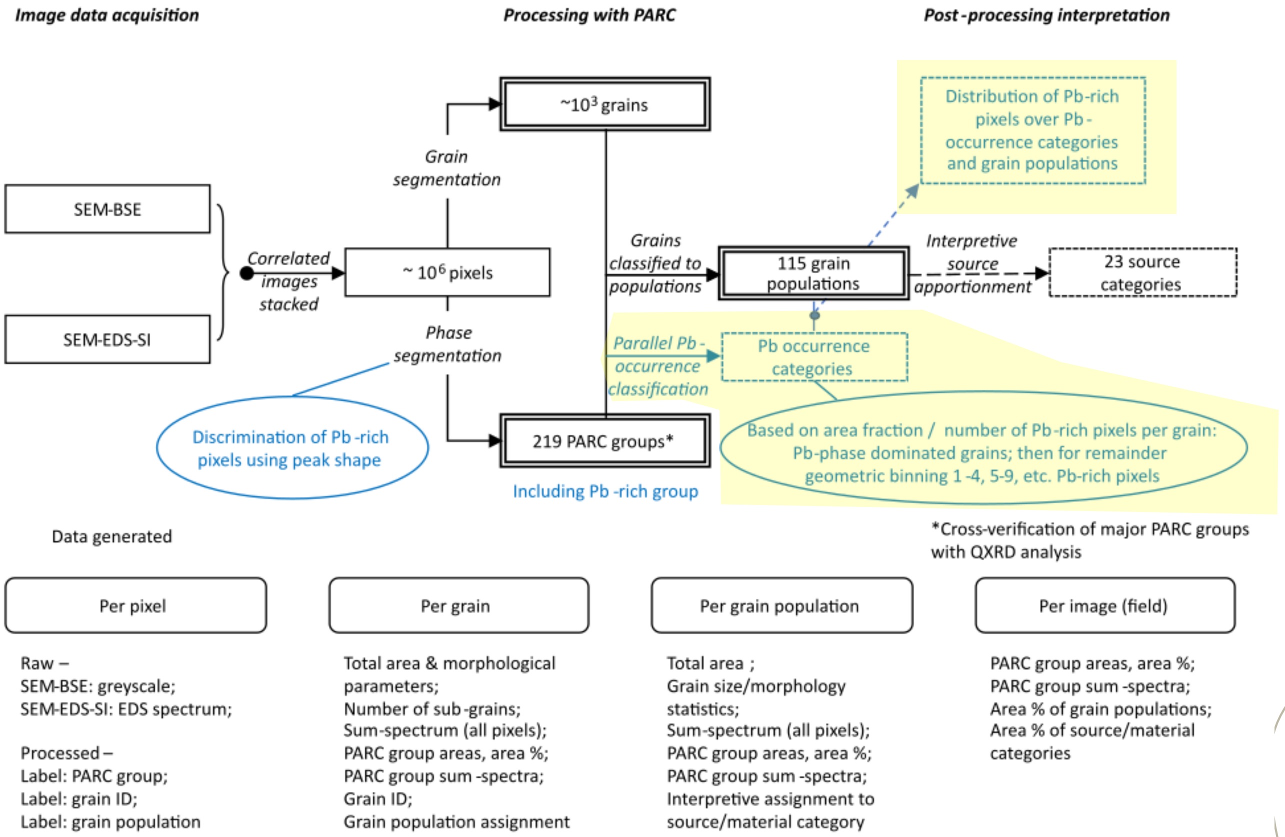
Testing on secondary standards: Pb-bearing dust SRMs

SRM Number	1	2	3	Mean	σ	Relative σ (%)	Certified Pb Mass Fraction	
			Area %				mg/kg	wt %
2580	7.04	7.06	7.20	7.10	0.09	1.29	43,400	4.34
1649b	2.18	2.26	2.20	2.21	0.04	1.91	12,864	1.29
2584	1.20	1.41	1.38	1.33	0.11	8.43	9761	0.98
2587	0.35	0.16	0.15	0.22	0.12	52.61	3242	0.32



- Tested on dust SRMs from NIST
  – Range 0.3 – 4.3 wt% Pb mass fraction
- Strong linear correlation:
  – Pb mass fraction vs area % Pb-rich pixels
- N.B. not a calibration curve for an alternative Pb mass fraction determination!
- => variation in total Pb mass fraction manifests in PARC-detectable discrete Pb phase occurrence
- Micro-nugget effect visible in lowest-Pb sample

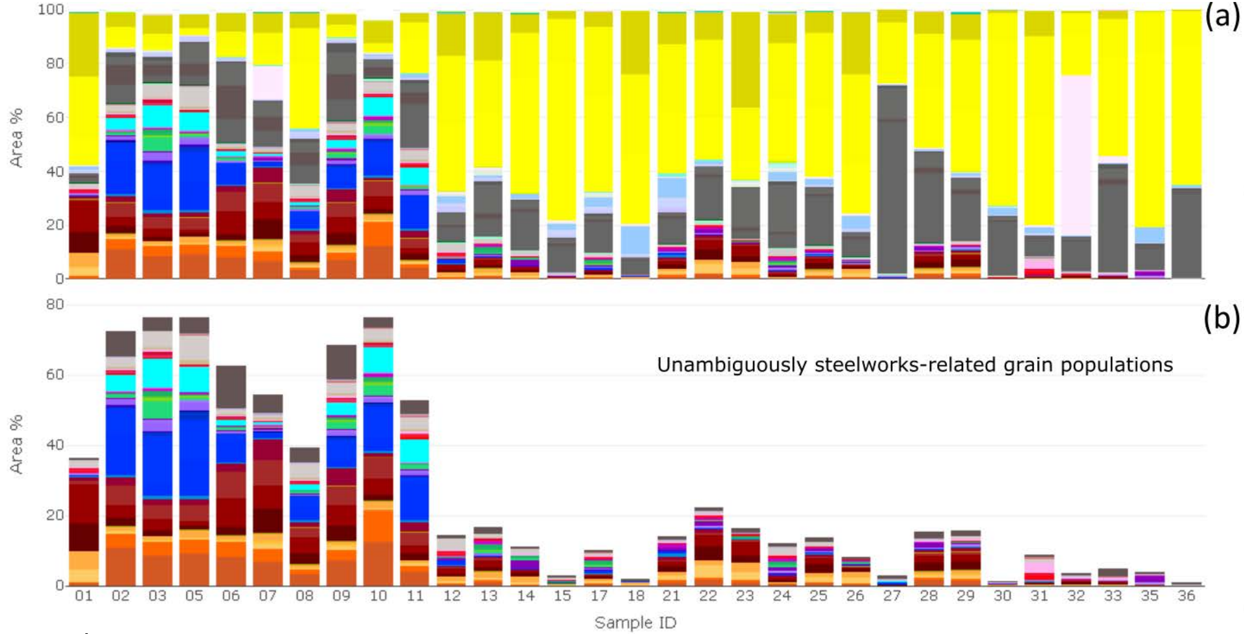
Searching for insights on Pb occurrence and possible sources



- What can we learn about Pb occurrence in dust deposits?

Application to IJmond dust deposits

- Sampling around IJmond region, Feb 2021
- Clear variations in dust provenance
  - – Negligible to dominant steelworks contribution in dust



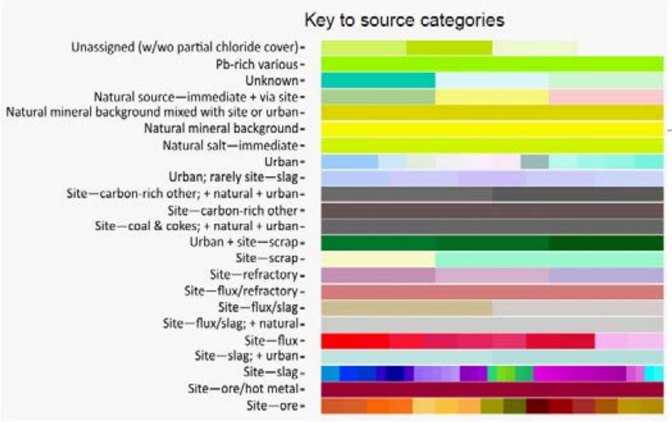


Fig. 8

Overall abundances of Pb-rich pixels in samples

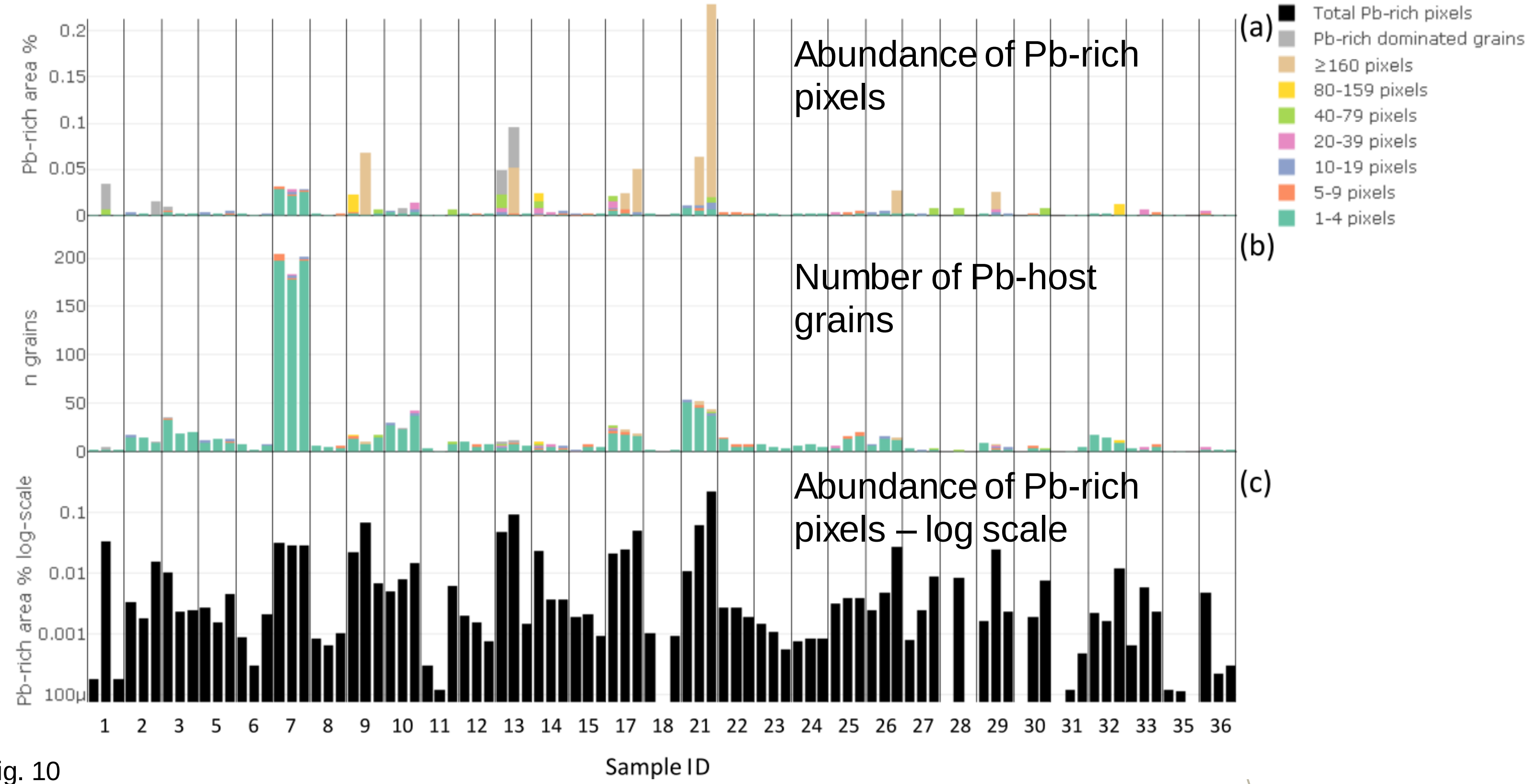


Fig. 10

Overall abundances of Pb-rich pixels in samples

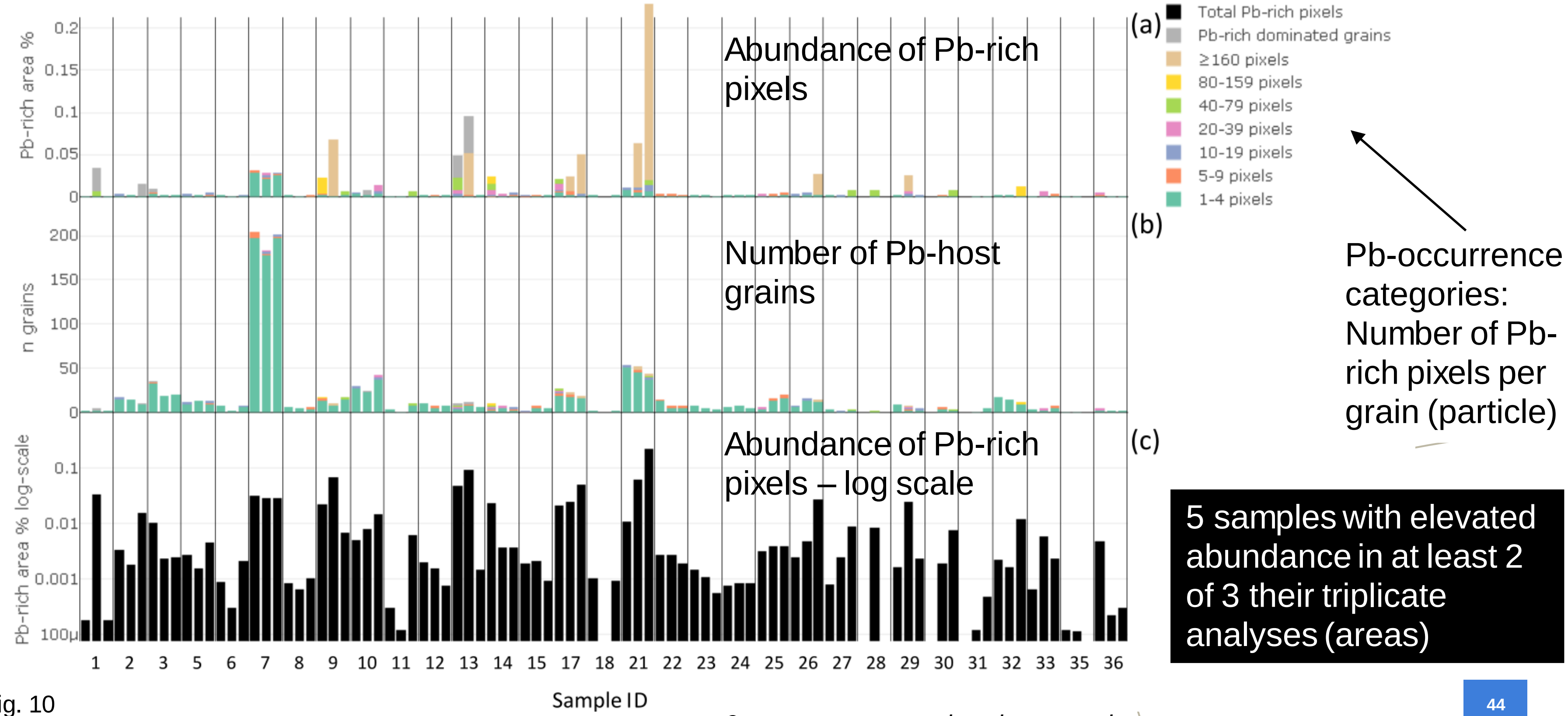


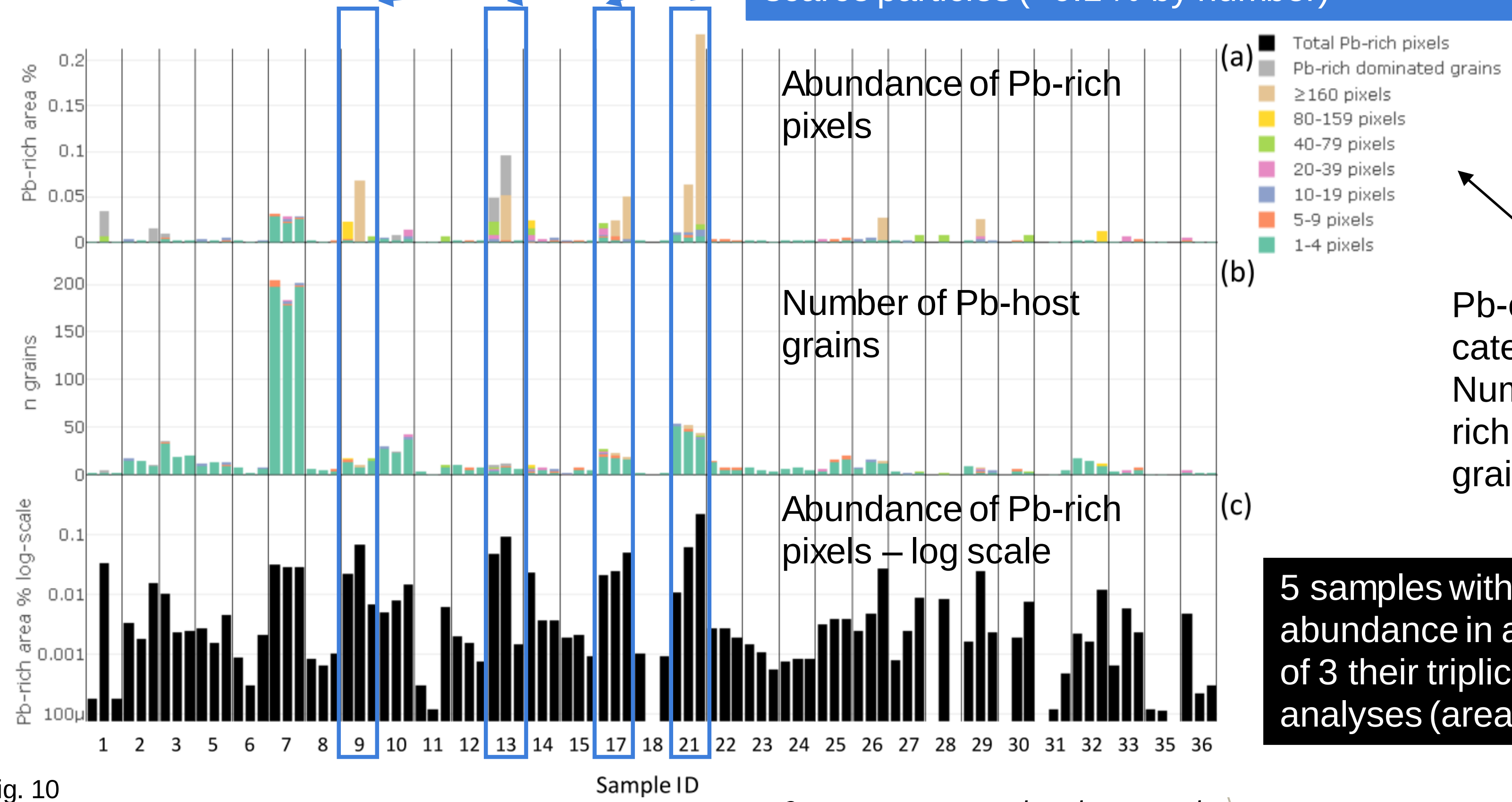
Fig. 10

3 separate areas analysed per sample

5 samples with elevated abundance in at least 2 of 3 their triplicate analyses (areas)

Overall abundances of Pb-rich pixels in samples

Most Pb-rich pixels highly concentrated in/on scarce particles (<0.1 % by number)



Pb-occurrence categories: Number of Pb-rich pixels per grain (particle)

5 samples with elevated abundance in at least 2 of 3 their triplicate analyses (areas)

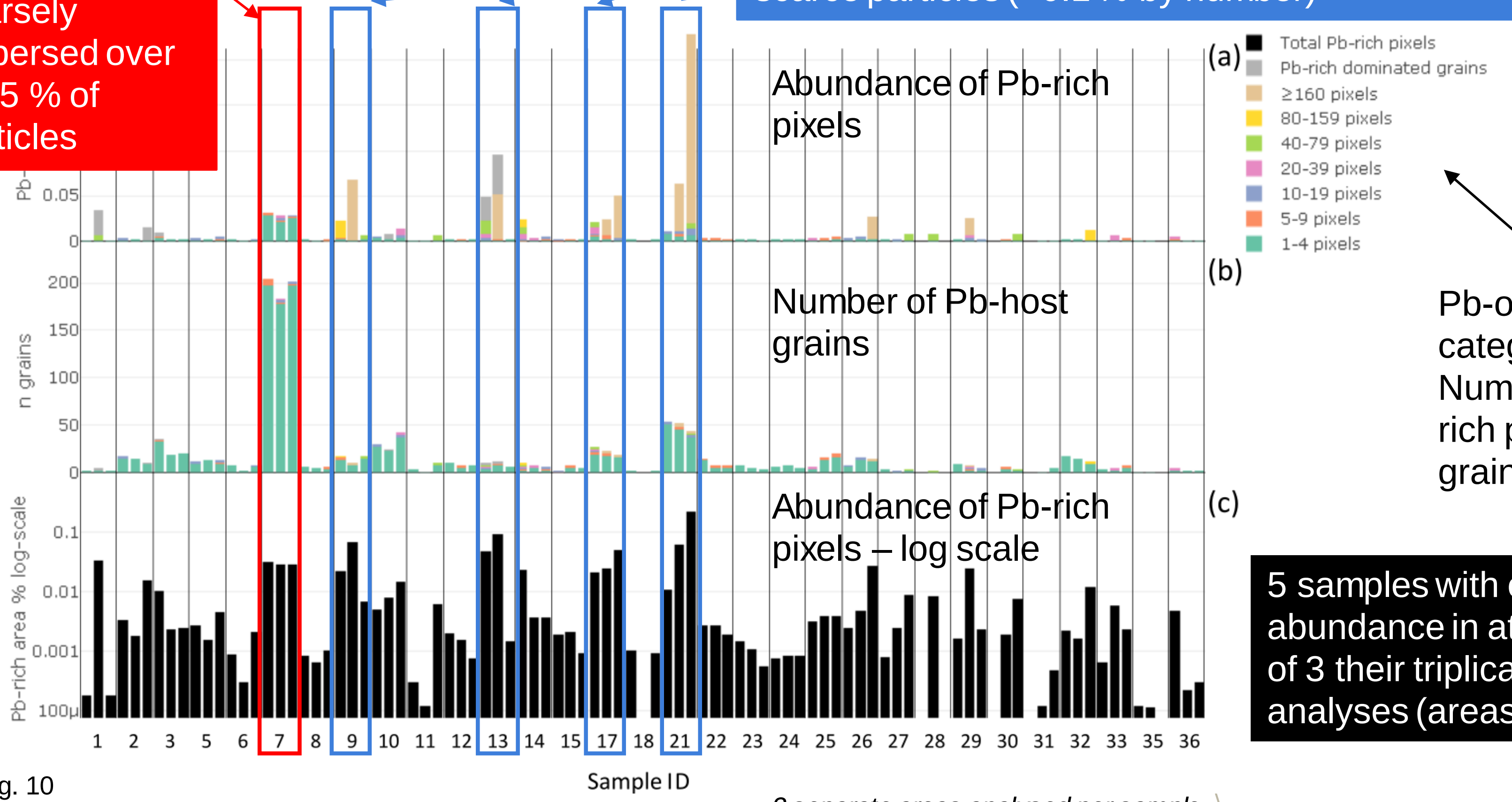
Fig. 10

3 separate areas analysed per sample

Overall abundances of Pb-rich pixels in samples

Pb-rich pixels sparsely dispersed over c. 15 % of particles

Most Pb-rich pixels highly concentrated in/on scarce particles (<0.1 % by number)



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Most Pb-rich pixels generally concentrated in/on scarce particles

Pooling all samples: distribution of Pb over occurrence categories

Pb-Rich Occurrence Category	Number of Grains	% of All Pb-Hosting Grains	% of All Pb-Hosting Grains by Area	% of Total Pb-Rich Pixels
Pb-rich dominated grains	6	0.40	0.07	12.32
≥160 pixels	10	0.66	1.34	45.05
80–159 pixels	3	0.20	0.17	3.71
40–79 pixels	11	0.72	0.78	6.68
20–39 pixels	14	0.92	0.94	4.35
10–19 pixels	27	1.78	4.40	3.81
5–9 pixels	51	3.36	4.37	3.57
1–4 pixels	1398	91.91	87.93	20.51

57% of Pb-rich pixels contained in only 1.1% of the Pb-host grains

In turn, these are only 0.018% of the total analysed grains (n=92000)

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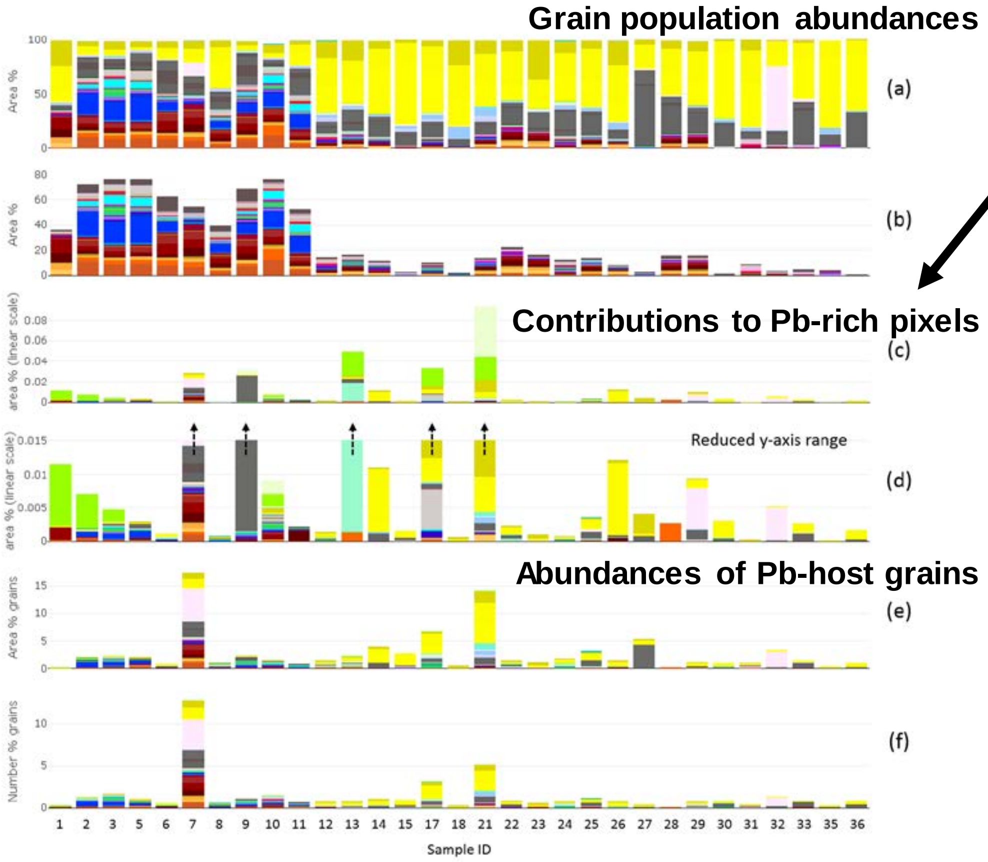
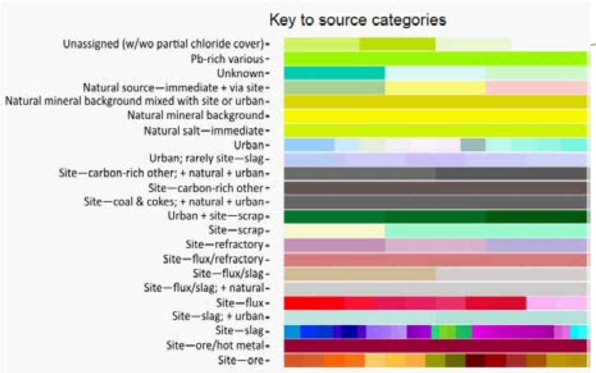
Challenge is to analyse enough grains to quantify contributions from such scarce but concentrated Pb occurrences
→ (micro-)nugget effect in analyses

Pb-rich pixels’ distribution over grain populations



- Quantify contributions of Pb-rich pixels from different grain populations
- Per sample, pooled samples (not shown)
- Statistics regarding individual occurrences

- ➔ Insights on any associations between Pb and specific grain populations



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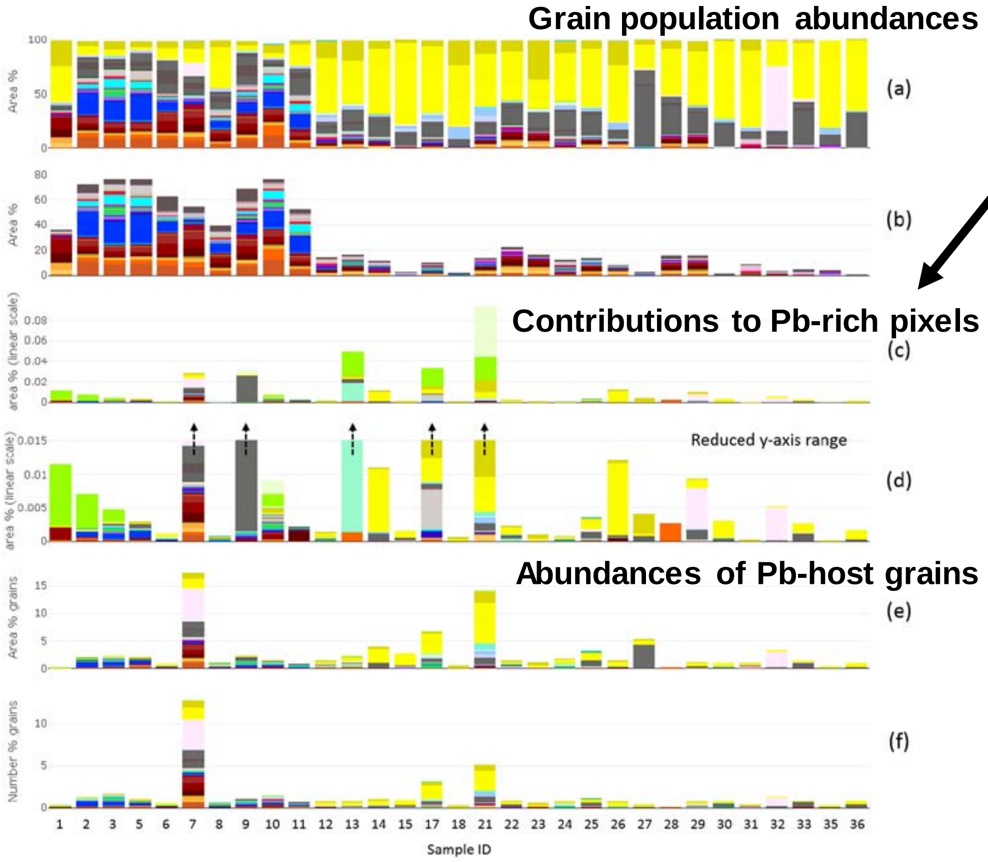

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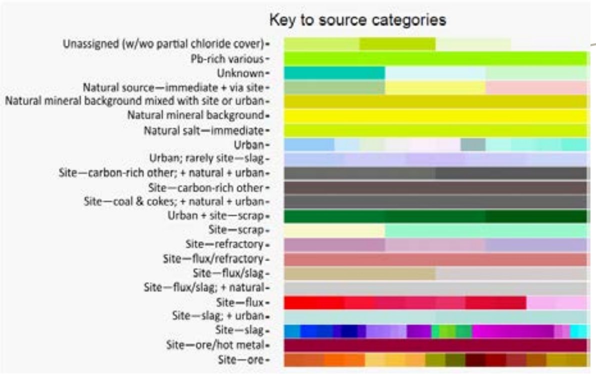
- Those insights are for another presentation…

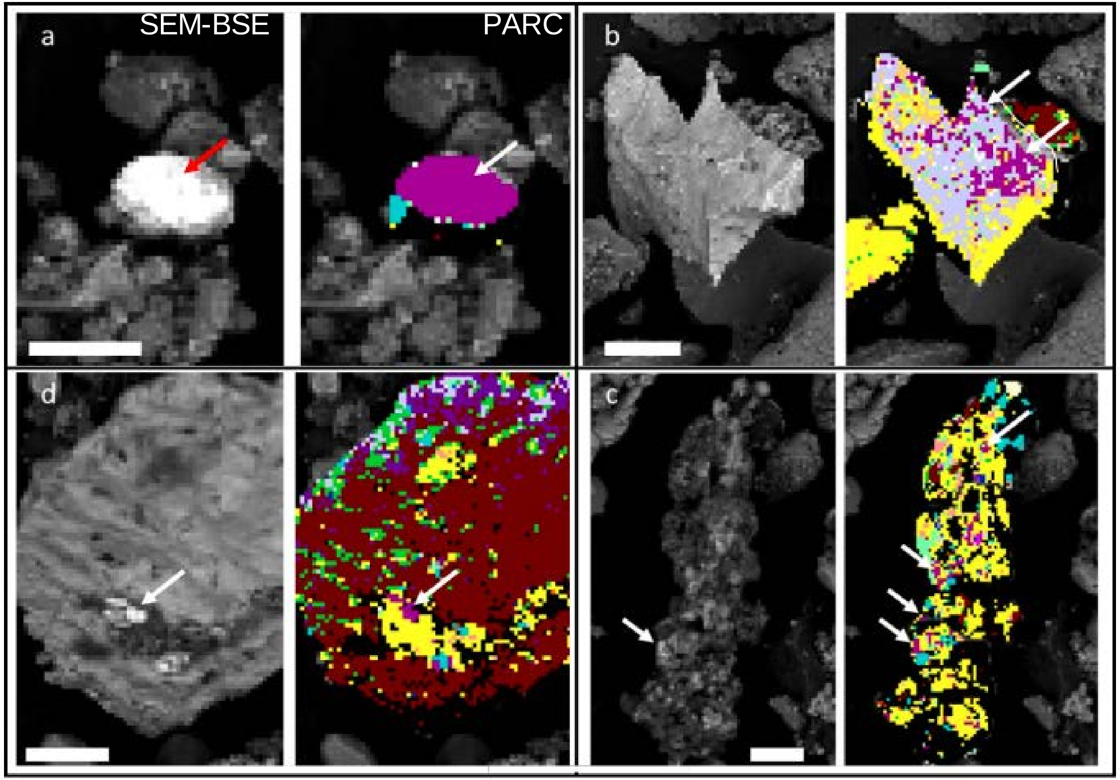


Key examples of particles bearing Pb-rich phases

Arrows and dark magenta indicate Pb-rich pixels

Dense Pb-rich particle
→ True micro-nuggets

Iron-ore sinter particle with Pb-rich sub-particle on surface



Suspected glazed pottery shard

Composite particle – many smaller sub-particles (< 10 um) agglomerated. Diverse sources mixed together. Potentially road dust.

Scale bar: 32 µm

Conclusions: a new and useful method

- **Novel characterisation method for dust deposits in vicinity of steelworks**
- **Based on SEM-EDS spectral imaging with supporting QXRD analyses**
- **Analyses ~10^3 particles per sample in as little as 30 minutes**
  - Scalable depending on statistical requirements / analytical resolution
- **Automated processing classifies particles to populations based on mineralogical characteristics**

- **Provides quantitative information on:**
  - Provenance of dust particles
  - Mineralogy and chemistry of dust particles
  - Distribution and source of potentially toxic elements: focus on V, Mn, Pb

- **Supports:**
  - Evaluation of environmental / health impact of dust deposition
  - Mitigation of dust emissions from Tata Steel site

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2022: New monitoring campaign on and around Tata Steel site: c. 80 samples collected and analysed each 2 weeks

Acknowledgements

- Peter Tromp (TNO) for sampling in Pb occurrence study

Do you have any questions?

Tata Steel
Department