Physico-chemical characterization of environmental micro-particles by CC-SEM-EDS.

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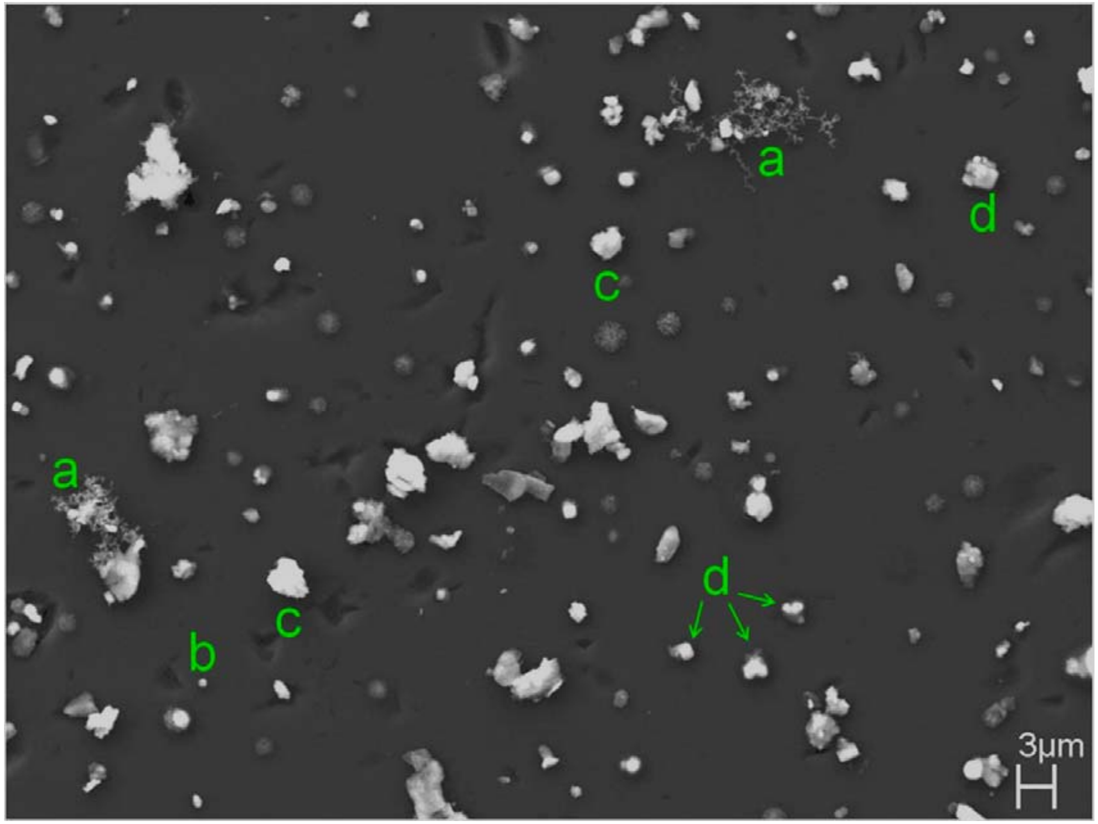
What are environmental particles?

a. fractal soot

b. tar ball



c. dust

d. sea-salt

Typical atmospheric particles collected on a flat substrate

→ Various particle compositions

→ Large size range: From dozen nanometer to dozen micrometer

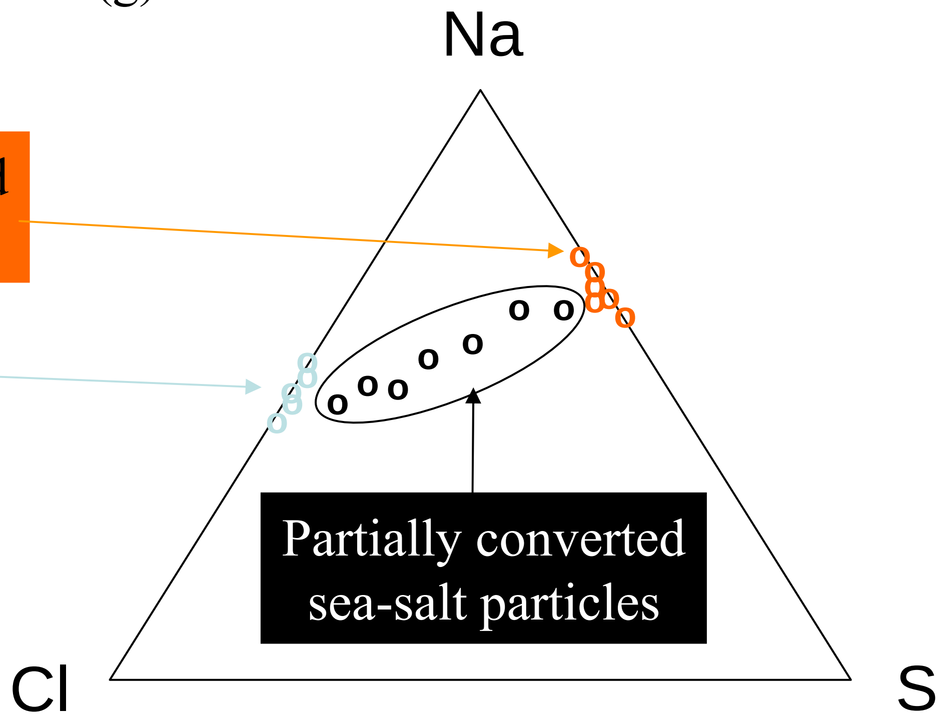
Why quantitative analysis is needed?

→ To quantify the chemical rate of atmospheric reactions

$2\,NaCl + H_2SO_4(g) \rightarrow \mathbf{Na_2SO_4} + 2\,HCl\,(g)$

Totally converted sea-salt particles

Freshly emitted sea-salt particles

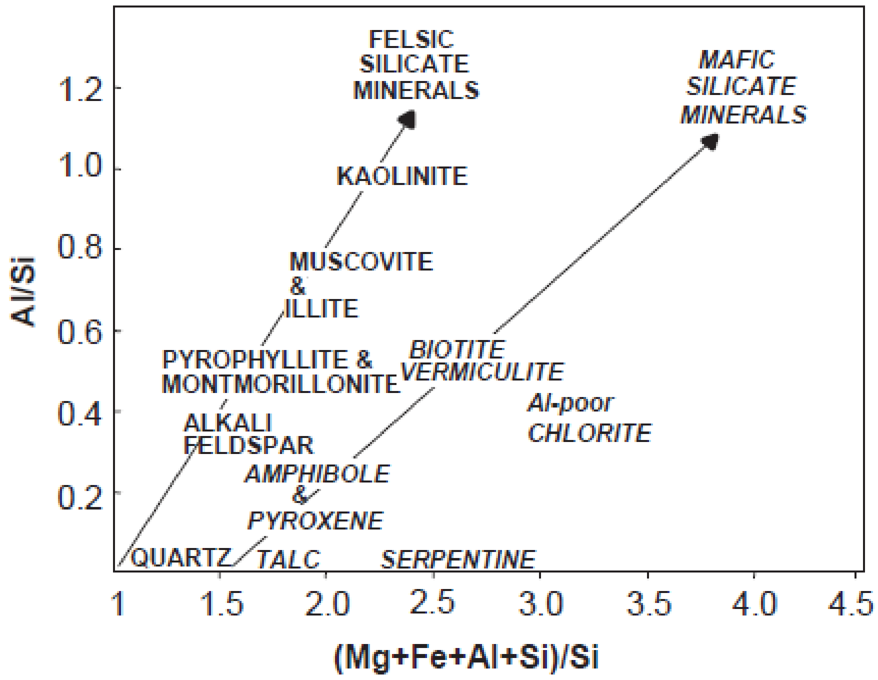


Na-Cl-S ternary diagram (in atomic ratio) of sea-salt particles

Case of the atmospheric reaction of sea-salt particles with sulfuric acid

Why quantitative analysis is needed?

→ To identify mineral compounds from elemental composition of dust or rock particles.



Al/Si versus (Mg+Fe+Al+Si)/Si diagram showing the main silicate rock forming minerals (from Moreno et al., 2003).

Plan of the presentation

A. Impact of particle size on quantitative analysis

B. Evaluation of the automated procedure (CC-SEM-EDS)

C. Physico-chemical characterization of fine particles emitted by a metallurgy plant

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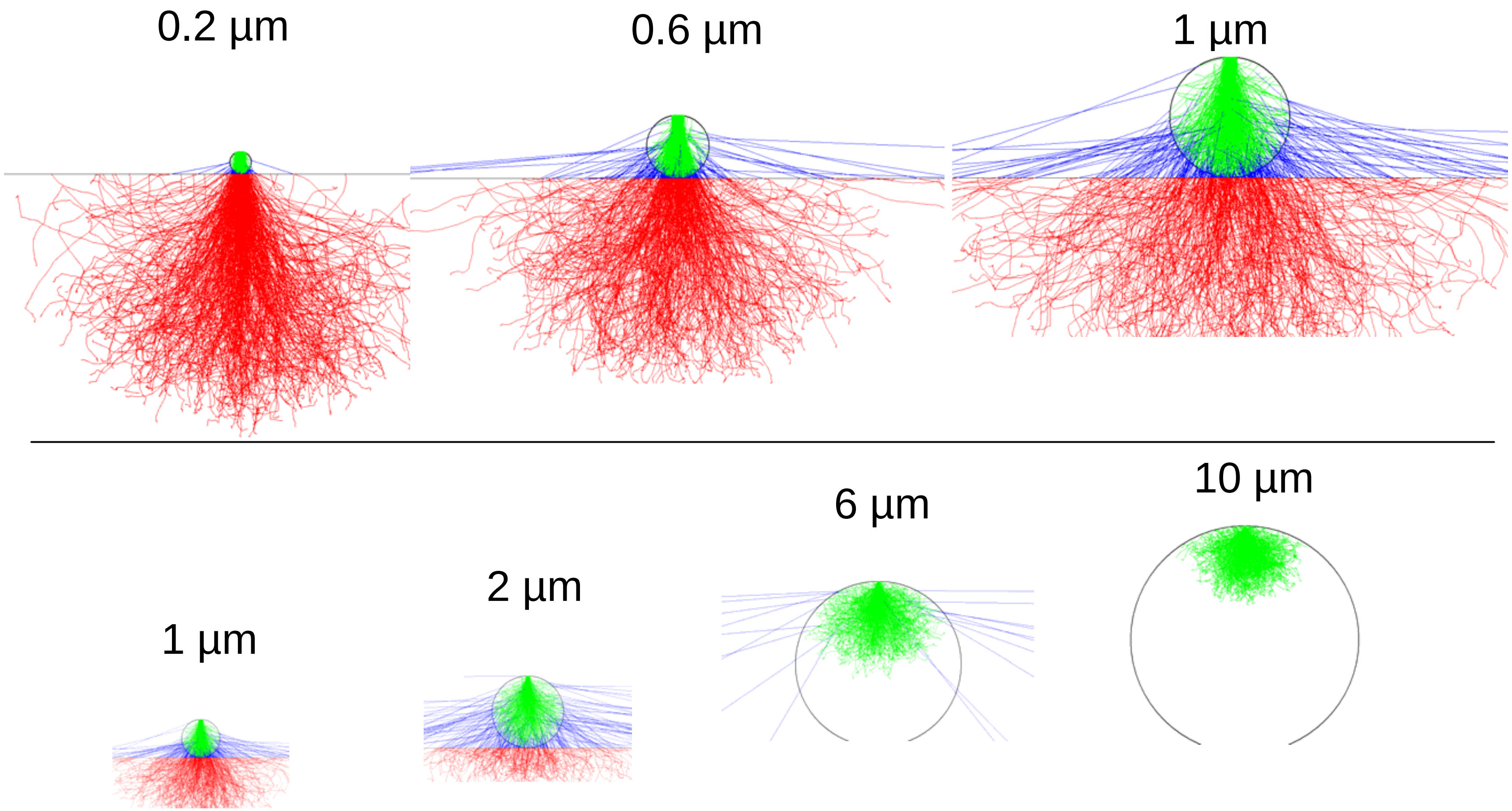
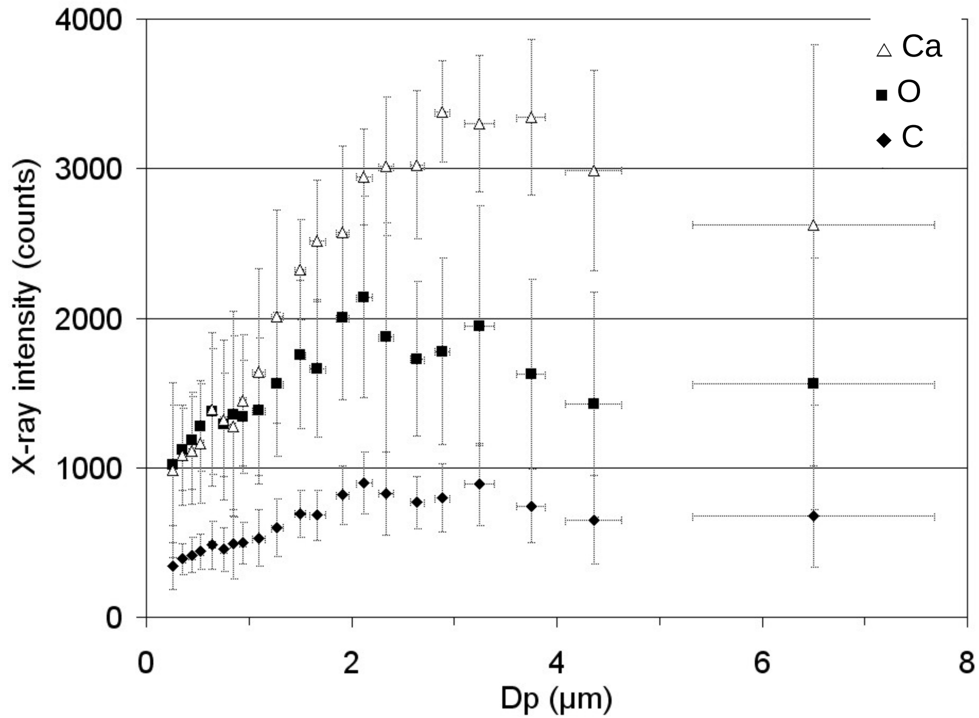
A- Impact of particle size on quantitative analysis



Monte Carlo simulation of 1000 electron trajectories
in spherical $CaCO_3$ particle sitting on a flat substrate at 15kV.

→ The X-ray intensity increases with the particle size until a maxima (mass effect).

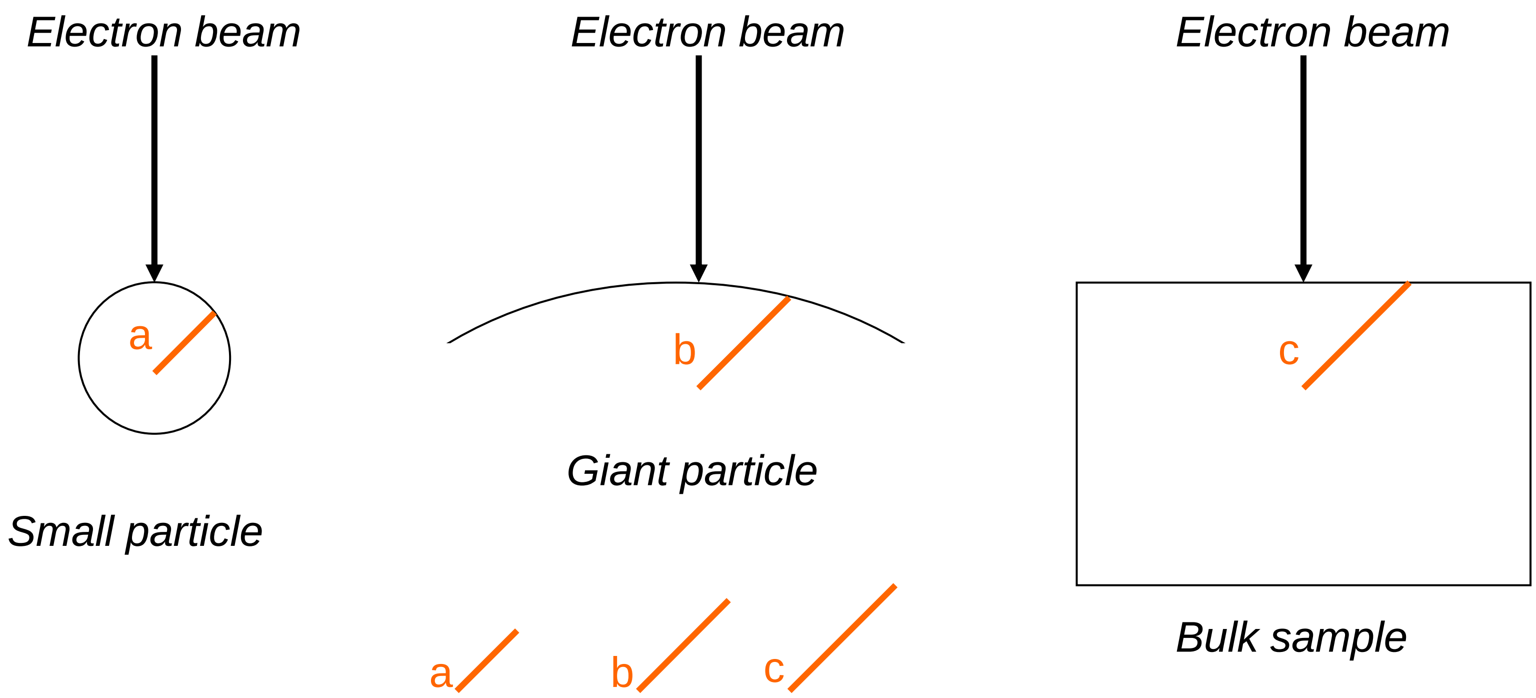
A- Impact of particle size on quantitative analysis



Experimental C-Kα, O-Kα and Ca-Kα X-ray intensities of 347 spherical $CaCO_3$ particles acquired at 15 kV as a function of particle diameter.

→ The X-ray intensity increases with the particle size (mass effect) until a maxima, and then decreases until a constant due to absorption effect.

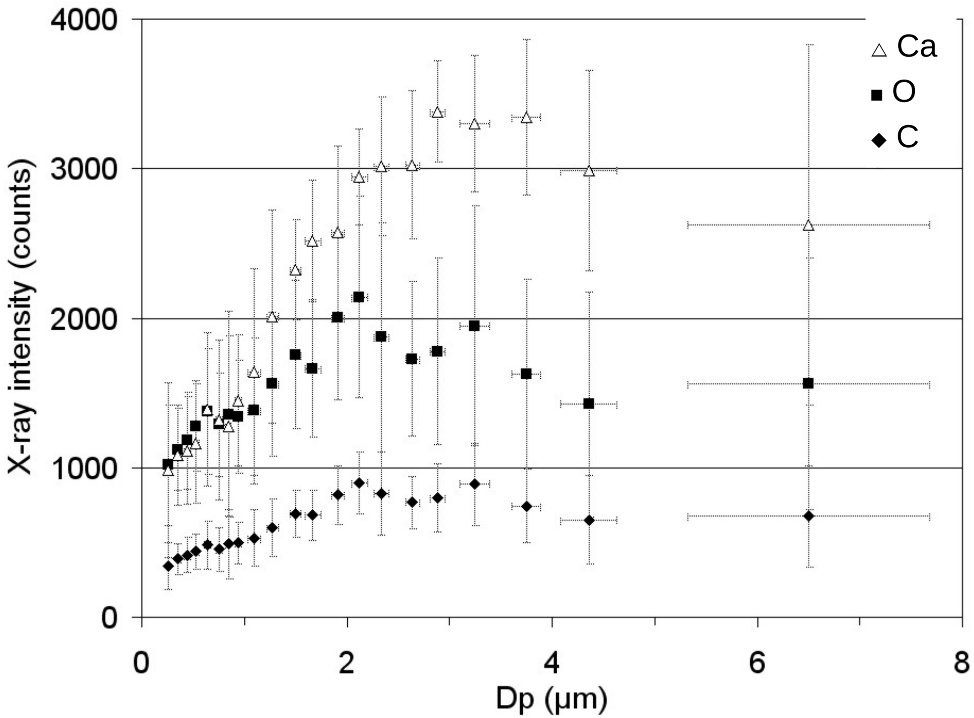
A- Impact of particle size on quantitative analysis



Trajectory of an X-ray generated at the same depth from the surface of particulate and bulk samples.

→ The X-ray absorption depends on the particle size and is higher for bulk samples (absorption effect).

A- Impact of particle size on quantitative analysis



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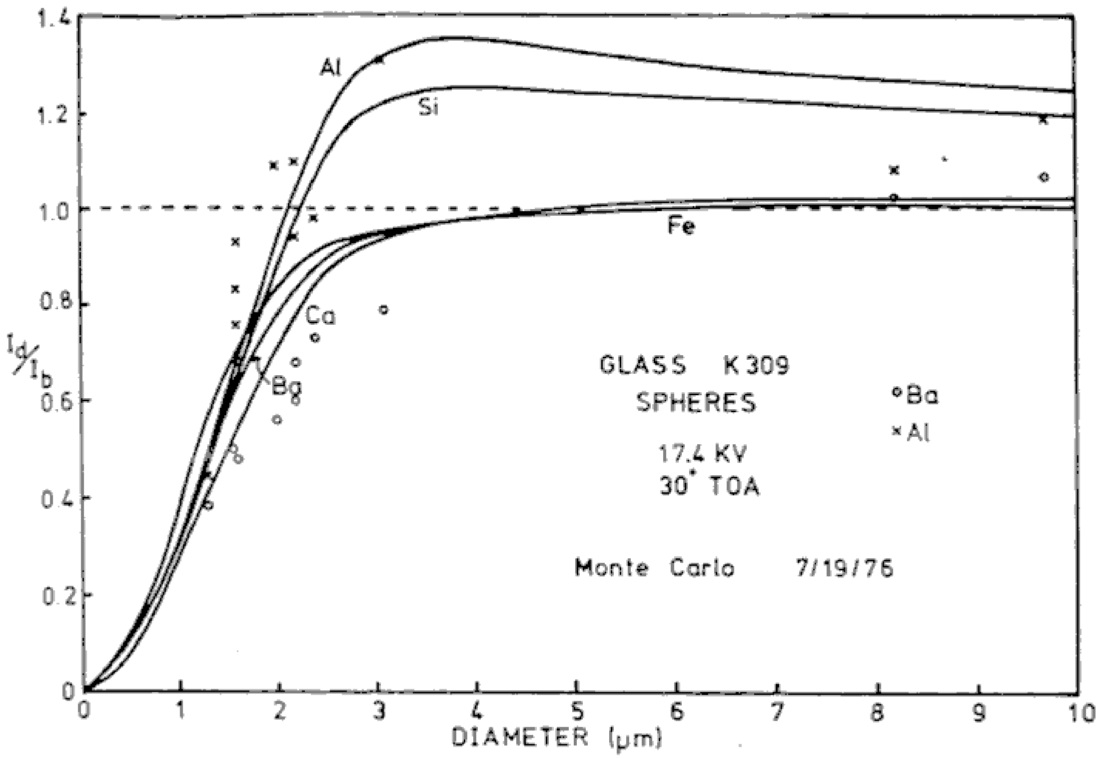


X-ray intensities of glass particles (Id) normalized to the X-ray intensities from a bulk sample (Ib) with the same composition, versus particle diameter (from Small, 1981).

→ **The absorption effect depends on the considered element.**

A- Impact of particle size on quantitative analysis

Impact of particle geometric effects on analytical results (ZAF quantification) :

Diameter (µm)	Mg	Si	Ca	Fe	O	**Total**
18	0.099	0.255	0.111	0.106	0.426	**0.995**
5	0.099	0.255	0.108	0.100	0.427	**0.99**
4	0.097	0.244	0.102	0.099	0.410	**0.95**
3	0.086	0.219	0.089	0.089	0.367	**0.85**
2	0.079	0.189	0.075	0.079	0.320	**0.74**
1.3	0.046	0.113	0.042	0.045	0.189	**0.43**

Analysis (in wt%) of K-411 Nist particles with various diameters (from Goldstein et al., 2003).

↳ Decrease of the sum of the elemental concentrations with the particle size.

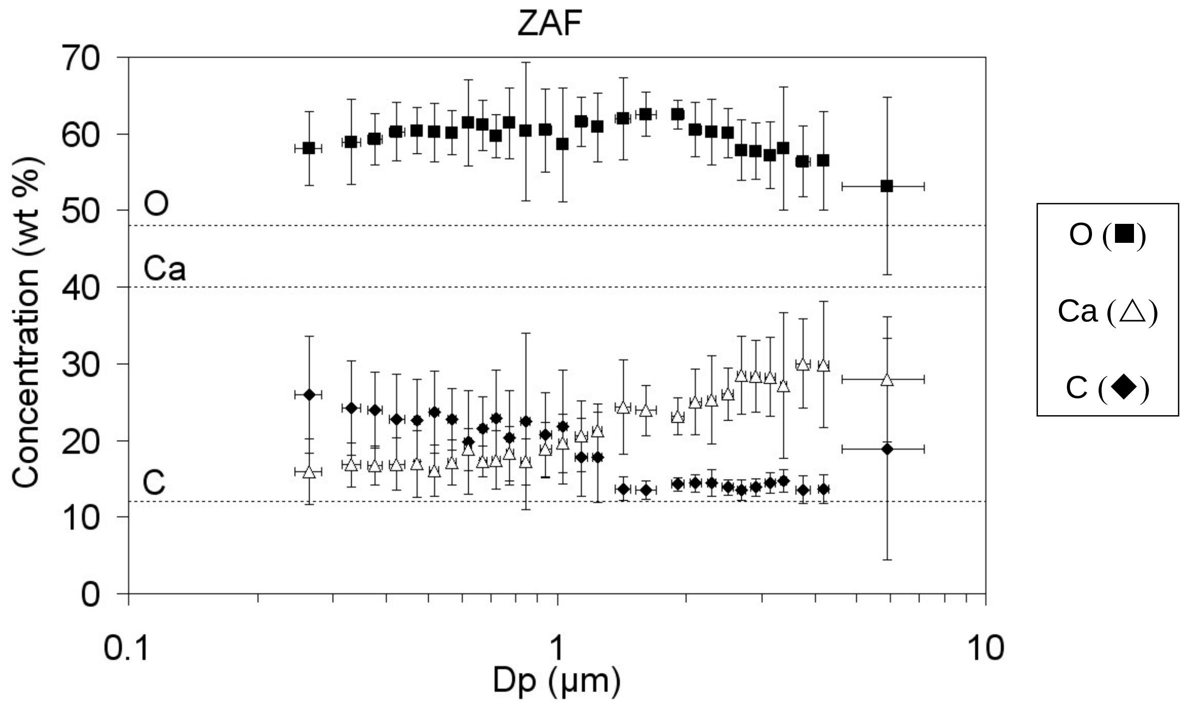
→ Possible corrections for particle geometric effects :

- Normalization of results obtained by conventional procedures for quantitative analysis

- Geometric modeling of particle shape

A- Impact of particle size on quantitative analysis

Normalization of concentrations obtained by the conventional ZAF procedure :

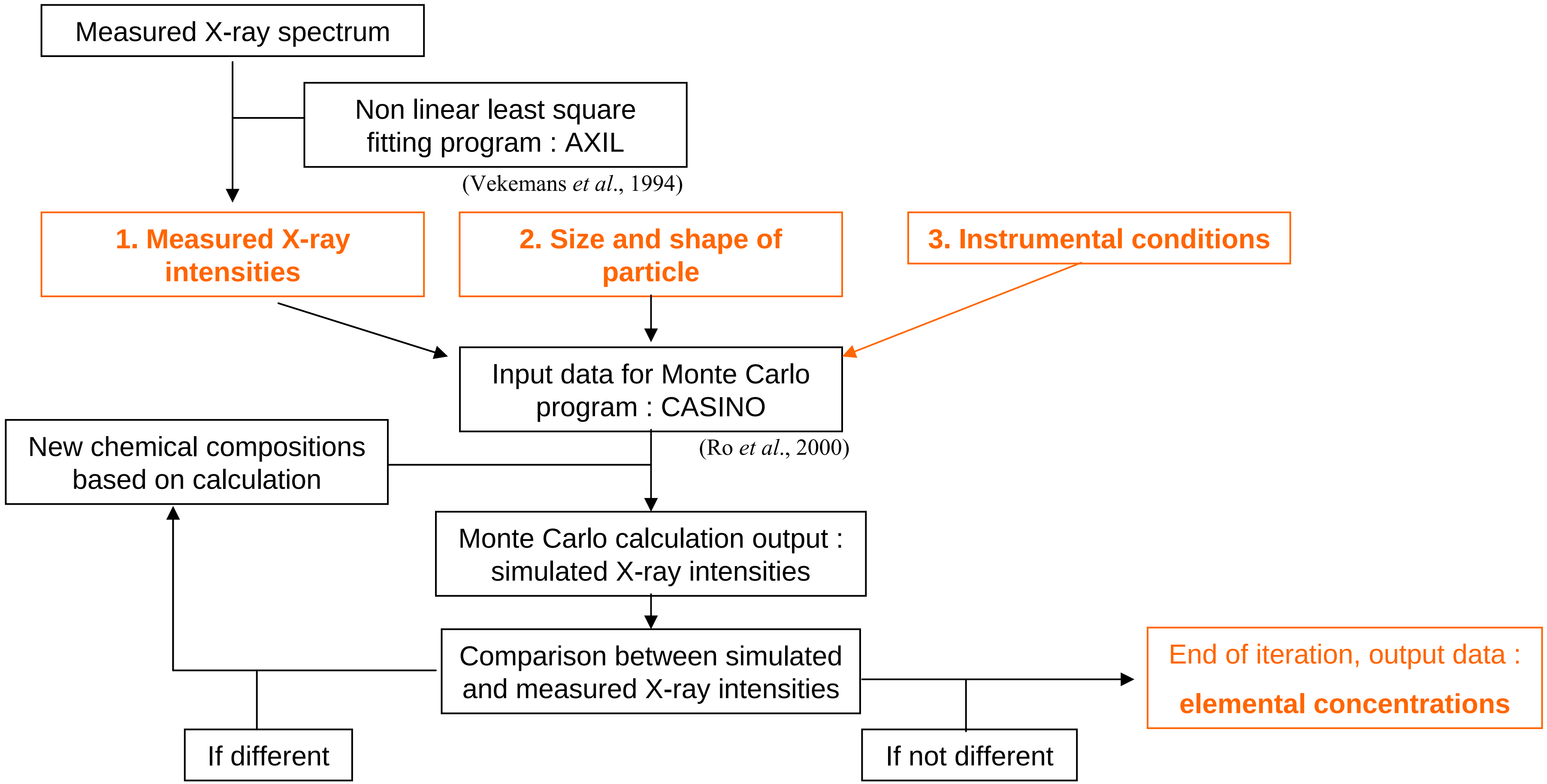


Normalized elemental concentrations (in wt%) of spherical $CaCO_3$ particles (347 particles). Dashed lines correspond to the nominal $CaCO_3$ elemental composition.

→ Simple normalization only gives rough estimation of elemental concentrations because absorption and fluorescence effects are not corrected.

A- Impact of particle size on quantitative analysis

Correction of matrix and geometric effect by <u>modeling of electron trajectories</u> in particles:



Summary of the overall procedure for quantitative particle analysis based on Monte Carlo simulation.

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Original Papers

CASINO : A New Monte Carlo Code in C Language for Electron Beam Interaction —Part I: Description of the Program

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Summary: This paper is a guide to the ANSI standard C code of CASINO program which is a single scattering Monte **CA**rlo **SI**mulation of electro**N** trajectory in s**O**lid specially designed for low-beam interaction in a bulk and thin foil. CASINO can be used either on a DOS-based PC or on a UNIX-based workstation. This program uses tabulated Mott elastic cross sections and experimentally determined stopping powers. Function pointers are used for the most essential routine so that different physical models can easily be implemented. CASINO can be used to generate all of the recorded signals (x-rays, secondary, and backscattered) in a scanning electron microscope either as a point analysis, as a linescan, or as an image format, for all the accelerated voltages (0.1–30 kV). As an example of application, it was found that a 20 nm Guinier-Preston Mg_2Si in a light aluminum matrix can, theoretically, be imaged with a microchannel backscattered detector at 5 keV with a beam spot size of 5 nm.

Environ. Sci. Technol. **2000**, *34*, 3023−3030

Determination of Chemical Species in Individual Aerosol Particles Using Ultrathin Window EPMA

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The determination of low-*Z* elements such as carbon, nitrogen, and oxygen in individual atmospheric aerosol particles is of interest in studying environmental pollution. By the application of a newly developed EPMA technique, which employs either windowless or thin-window EDX detector, chemical compositions, including the low-*Z* components, of individual particles can quantitatively be elucidated. The determination of low-Z elements in individual environmental particles allows to improve the applicability of the single particle analysis; many environmentally important atmospheric particles, e.g. sulfates, nitrates, ammonium, and carbonaceous particles, contain low-Z elements, which cannot be characterized using conventional energy dispersive-EPMA (ED-EPMA). Furthermore, the diversity and the complicated heterogeneity of atmospheric particles in chemical compositions can be investigated in details, using the new EPMA technique. This work demonstrates that the quantitative determination of chemical species in individual particles is possible using ultrathin window EPMA coupled with Monte Carlo based quantification. Using the new EPMA method, molar concentrations of major chemical species in individual environmental particles can be determined. For example, the molecular concentrations of ammonium sulfate and nitrate in single particle were analyzed for particles internally mixed with ammonium sulfate and nitrate species. When particles are composed of several chemical species so that the number of equations is smaller than the number of chemical species to be determined, the quantitative analysis of each chemical species can be ambiguous; however, many particles are composed of one or two major chemical species, and thus this technique could provide direct observation of atmospheric chemistry for airborne particles in more detail.

The input file for the CASINO program for one particle:

```
                0
169 0
                9
C 282 0
O 56 0
Na 792 0
Mg 27 0
Al 24 0
Si 18 0
S 22 0
Cl 775 0
Ca 10 0
                1
B 1093 0
```

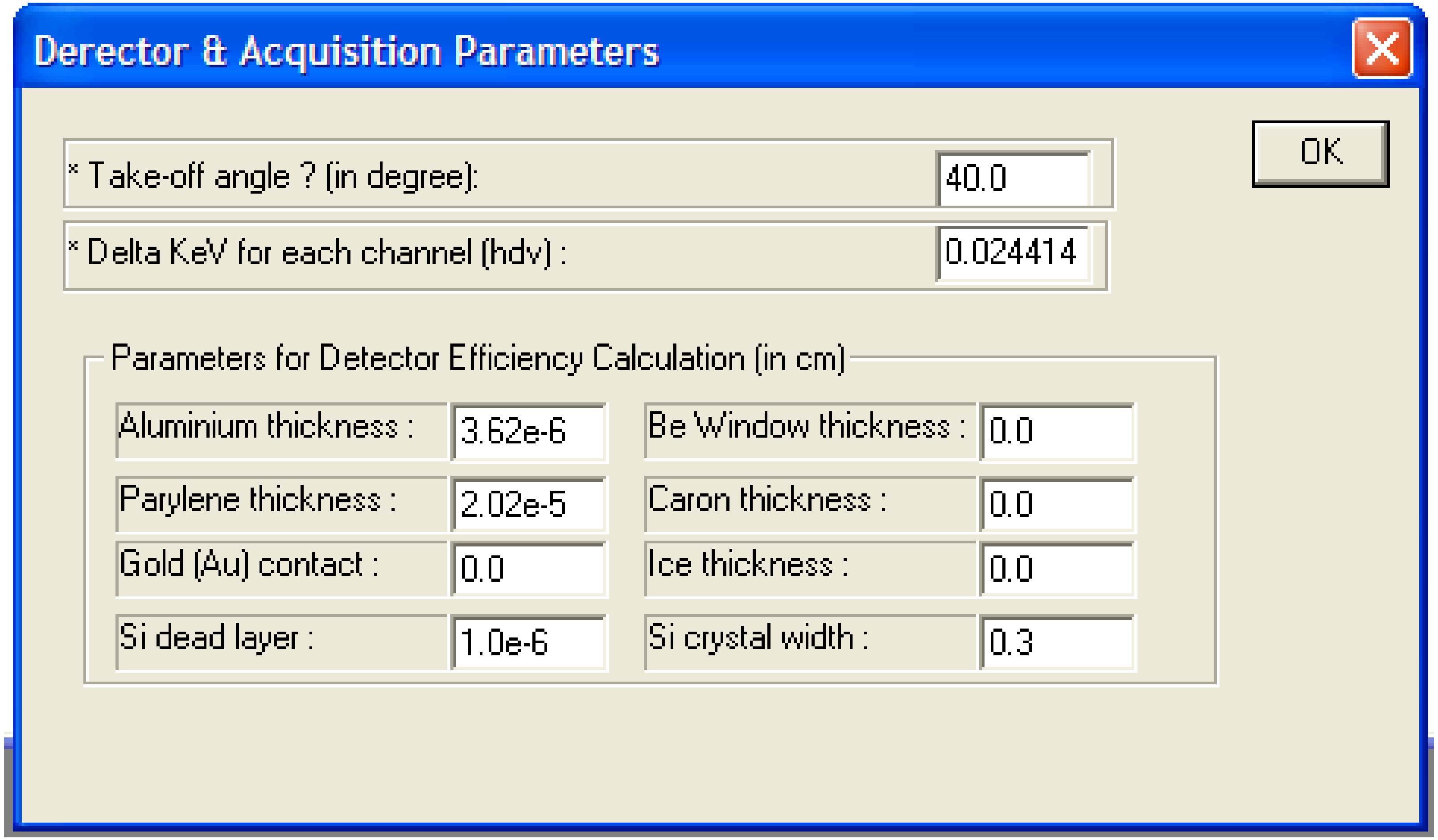
Informations on the particle (0): lines from "0" to "Ca 10 0"

Informations on the substrate (1): lines from "1" to "B 1093 0"

"169 0" ← *Size and model for the shape*
0: spherical
1: parallelepipedic
2: hemispherical

"Al 24 0" ← *Element, counts, X-ray type*
0: Kα X-ray

The analytical conditions for the CASINO program :



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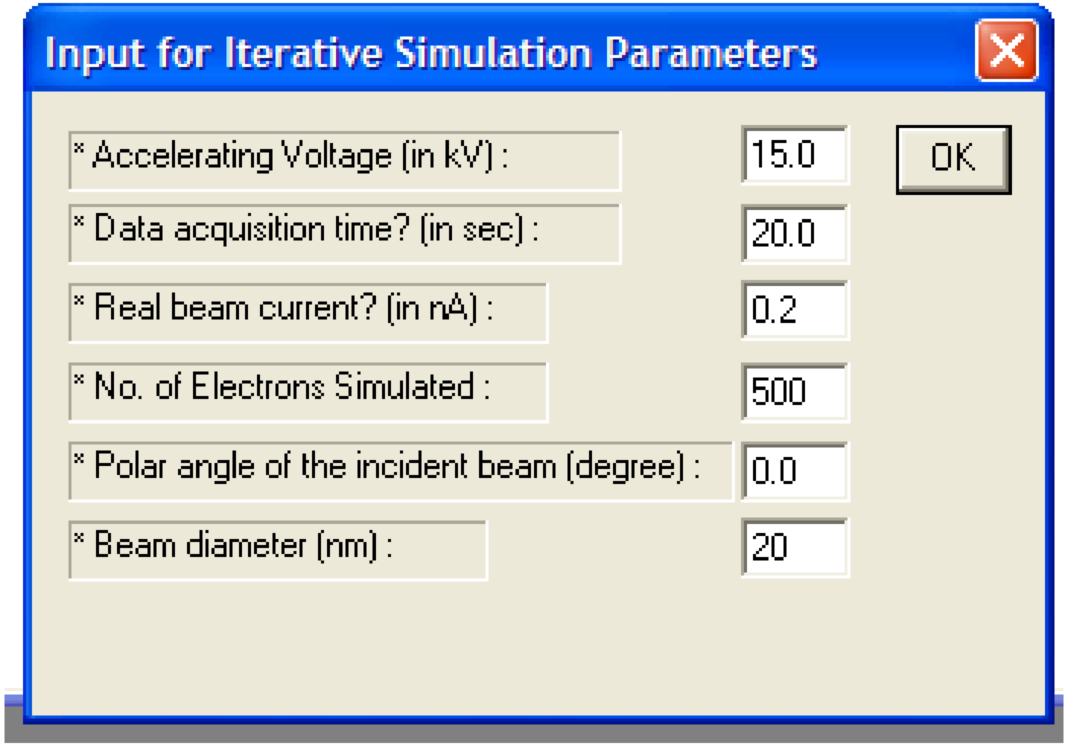


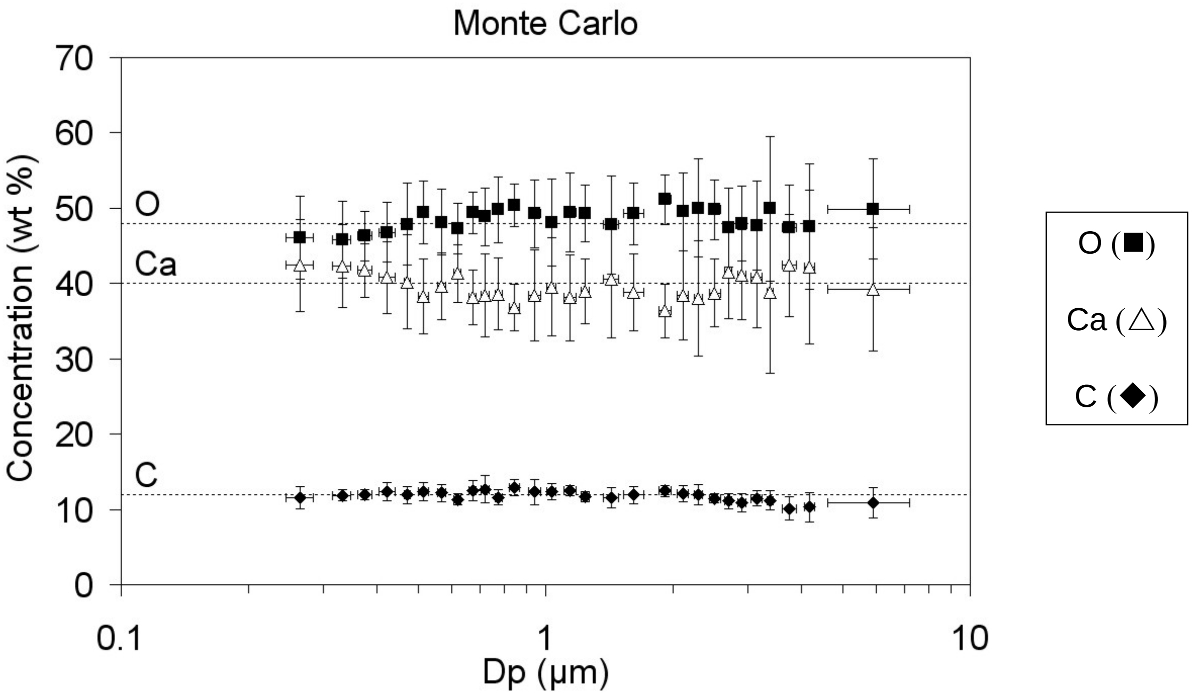
The output file for the CASINO program for one particle:

This is the 5-th iteration:

Element	Calc. Conc.	Meas.Int.	Calc.Int.
C	0.3751	282	280
O	0.0436	56	56
Na	0.3223	792	793
Mg	0.0104	27	27
Al	0.0086	24	24
Si	0.0063	18	18
S	0.0064	22	22
Cl	0.2243	775	776
Ca	0.0031	10	10

A- Impact of particle size on quantitative analysis

Correction of matrix and geometric effect by modeling of electron trajectories in particles:



Elemental concentrations (in wt%) of spherical $CaCO_3$ particles (347 particles) calculated by the reverse Monte Carlo quantitative program.

→ Accurate and precise quantification in a large range of particle size.

Plan of the presentation

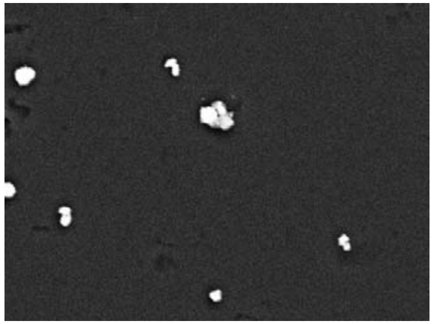
A. Impact of particle size on quantitative analysis

B. Evaluation of the automated procedure (automated detection of elements)

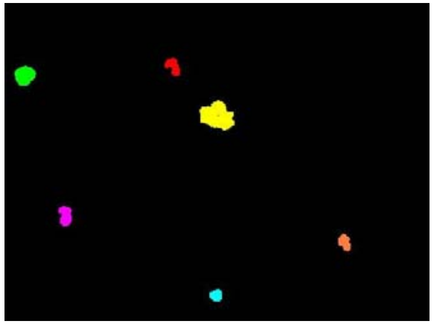
C. Physico-chemical characterization of fine particles emitted by a metallurgy plant

B. Evaluation of the automated procedure

Validation of the automated detection of elements:



Grey image (BSE)



Binary image

One spectrum per particle

- **8 low-Z-containing compounds studied:** $CaCO_3$, Na_2CO_3, AlN, Na_2SO_4, Na_2SO_3, $CaSO_4$, Fe_2O_3 and NaCl

- **300 particles analyzed per compound in the size range 0.2-12 µm**

- Operating conditions: E_0=15 kV; I_p=350 pA; Li-drifted Si detector; Super Ultra Thin Window; t_{acq}=30 s

- **16 elements systematically fitted:** B, C, N, O, Na, Mg, Al, S, Cl, K, Ca, Ti, Mn and Fe

B. Evaluation of the automated procedure

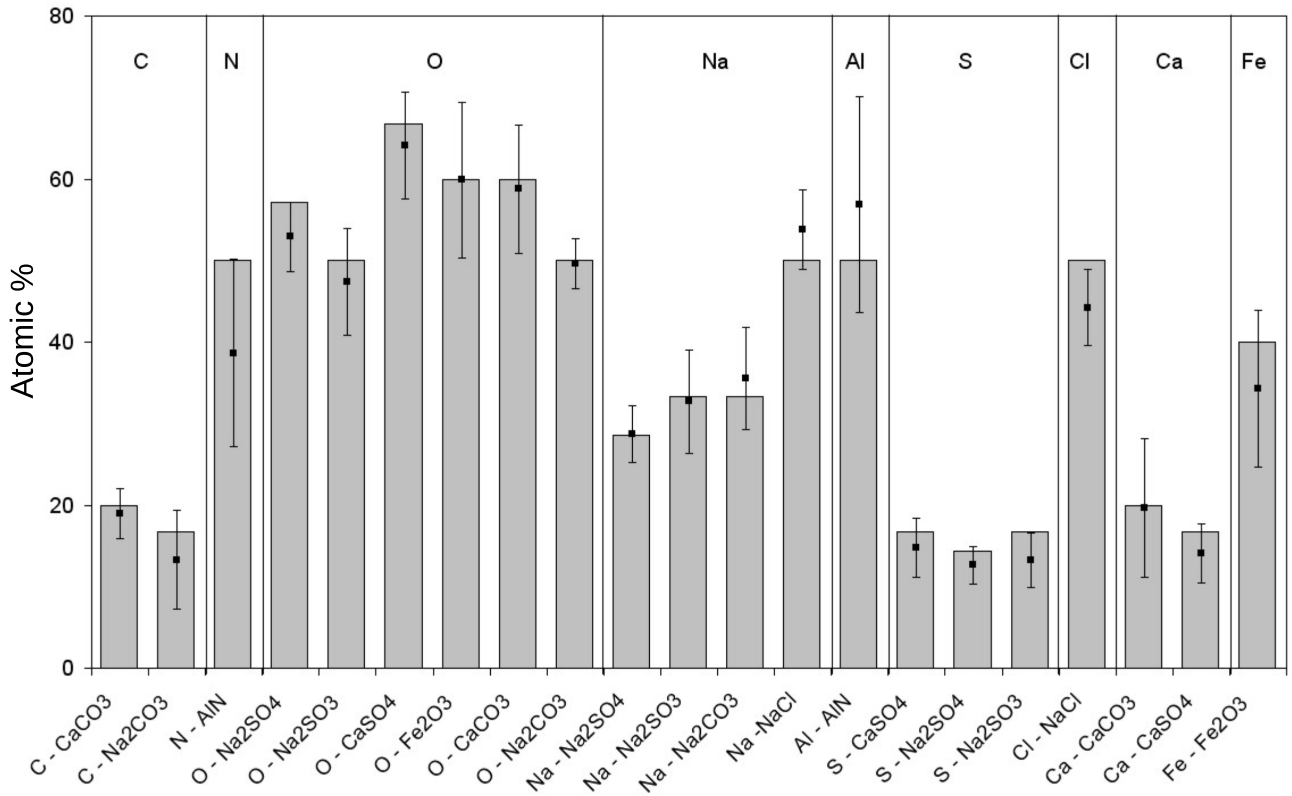
Validation of the automated detection of elements :

Compound	Sum of atomic concentrations of expected elements
$CaCO_3$	97.4 %
Na_2CO_3	98.5 %
AlN	95.6 %
Na_2SO_4	94.3 %
Na_2SO_3	93.3 %
$CaSO_4$	92.9 %
Fe_2O_3	94.2 %
NaCl	98.0 %

Sum of atomic concentrations of expected elements inside standard particles in the range size from 0.2 to 8 µm.

→ Maximum average of "impurities" is only 7 at. %, reliable identification of environmental particles.

B. Evaluation of the automated procedure



Average elemental concentrations calculated by CASINO
(Histogram bars = nominal concentrations; error bars = ± 1.96 S.D.)

→ On average, relative error = 8.8 at. %, R.S.D. = 10 at. %,
precise and accurate quantification of elements in environmental particles.

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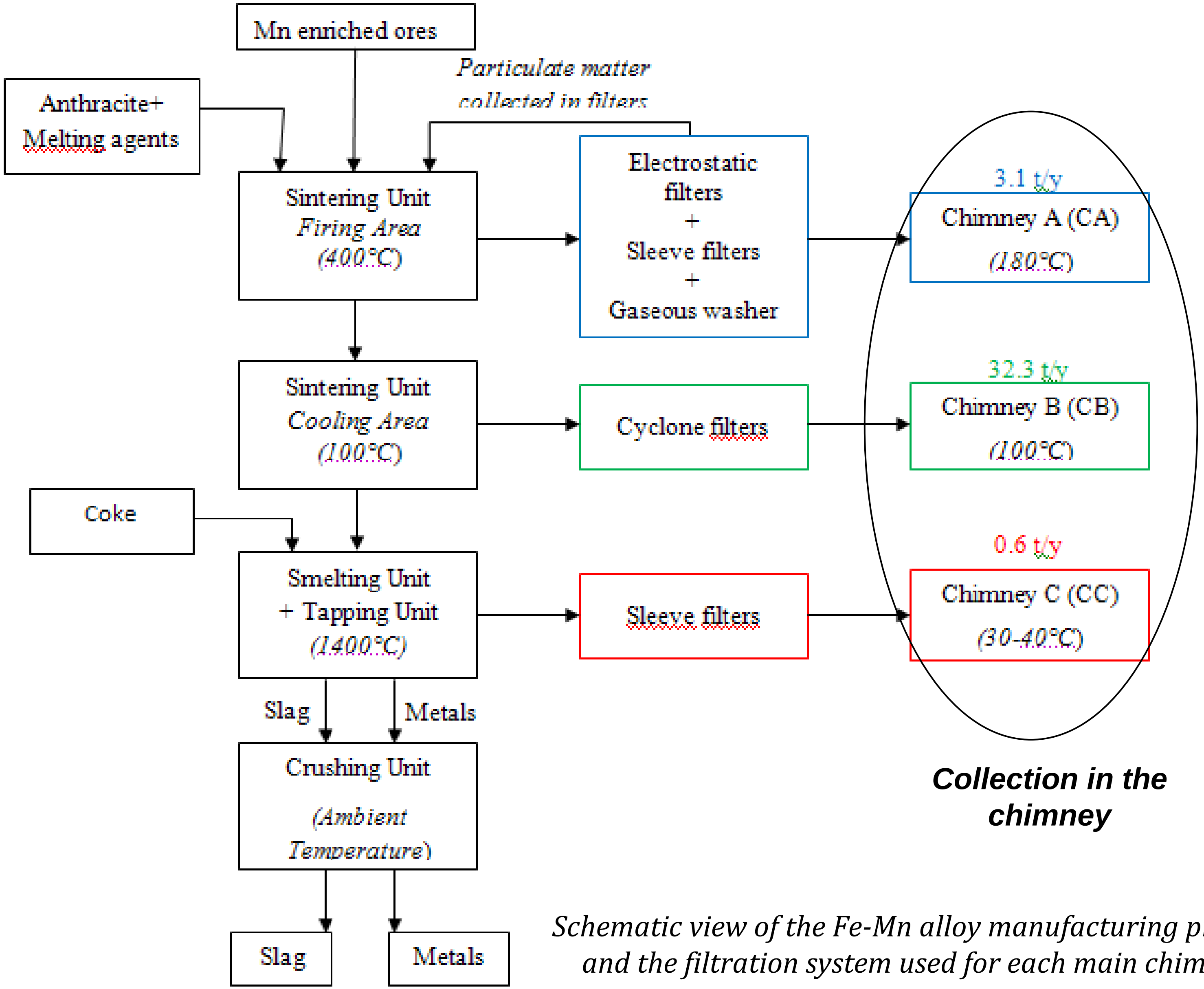
C. Physico-chemical characterization of fine particles emitted by a metallurgy plant

NANO-INDUS Objective

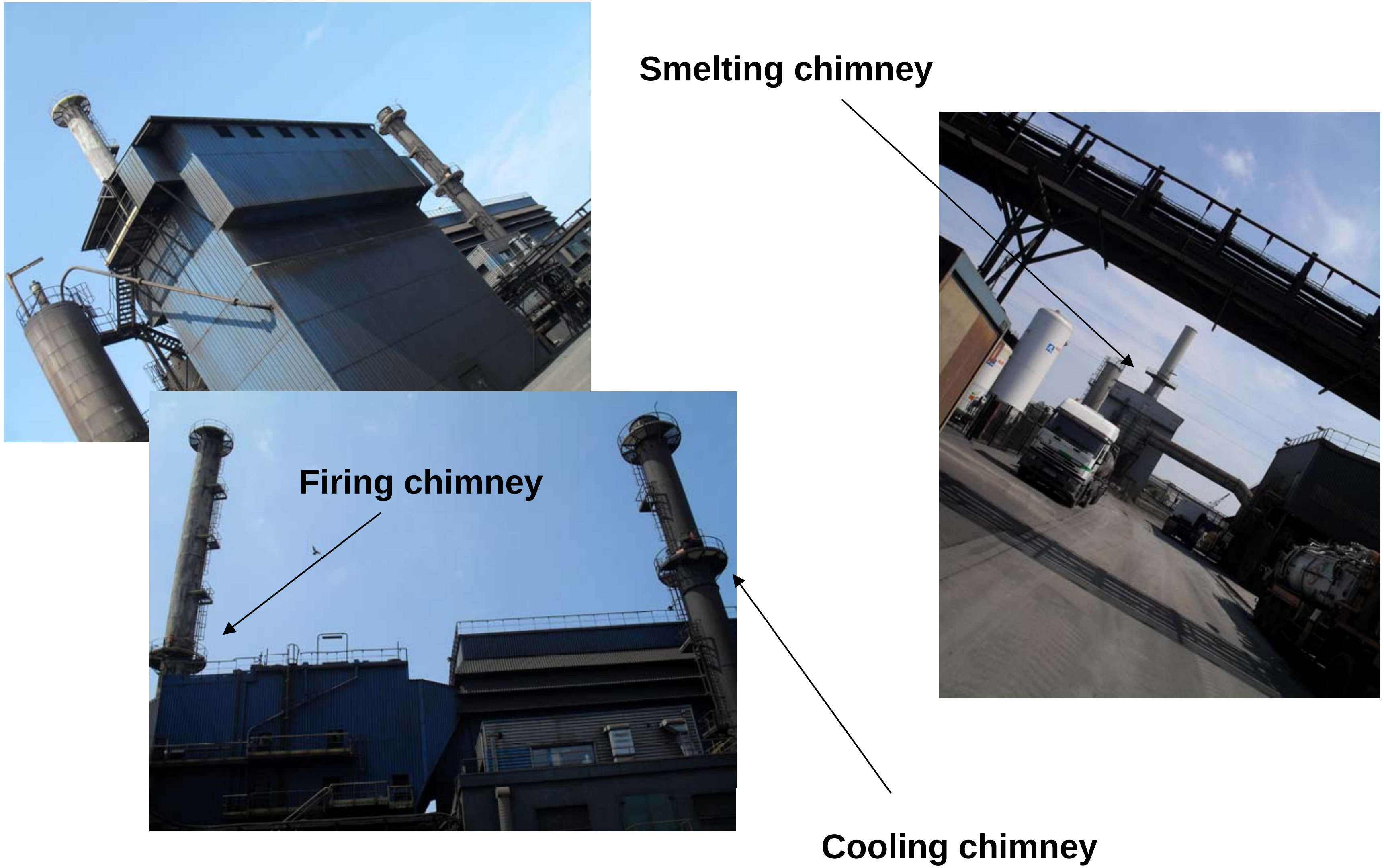
To study evolution of physico-chemical properties of industrial fine particles over a short-range distance, before they reach surrounding urban areas

A ferromanganese manufacturing facility in Dunkirk's industrial zone.

Overview of the industrial process:

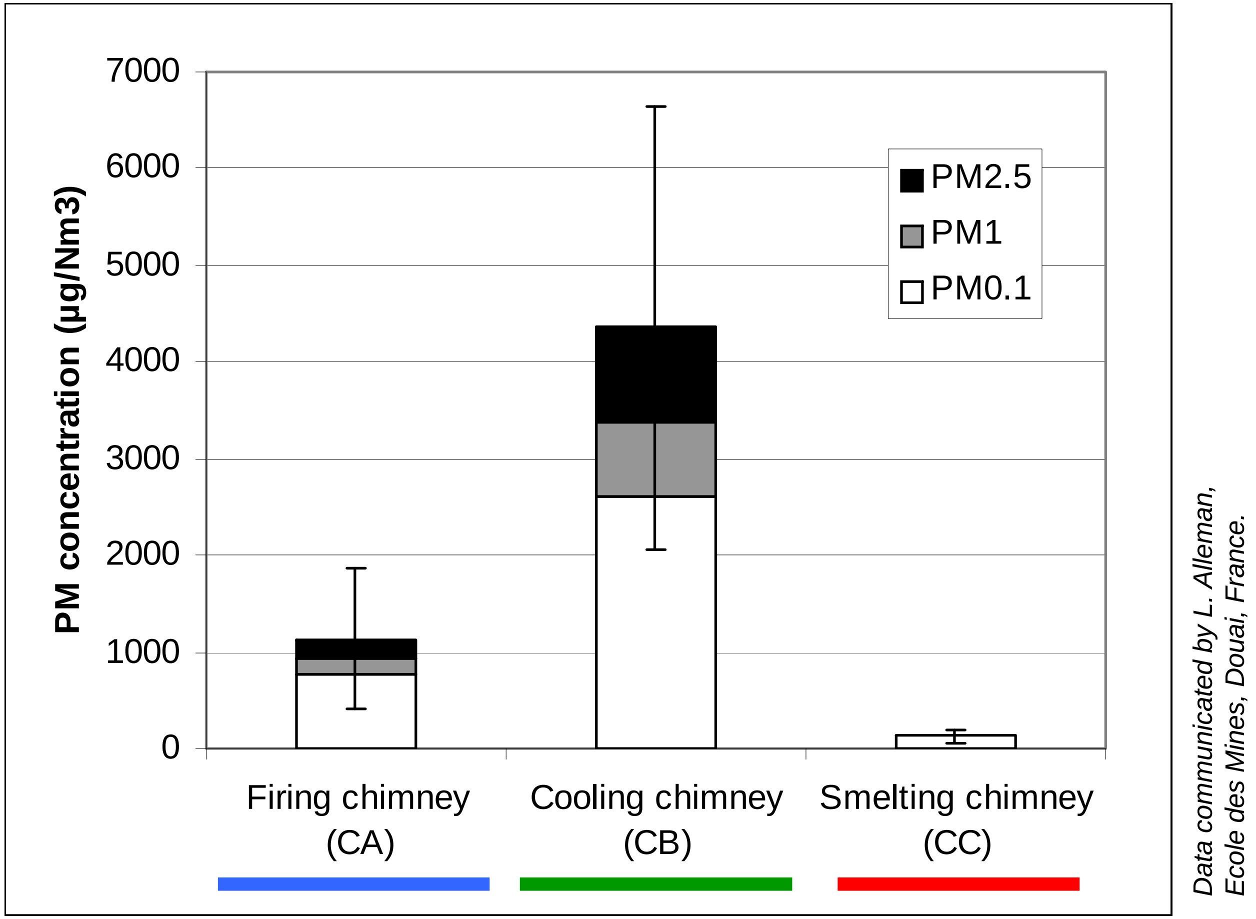


Schematic view of the Fe-Mn alloy manufacturing process and the filtration system used for each main chimney



Iso-kinetic <u>samplings inside chimneys</u> by the traps located at the first platform

Characterization of particles collected in the industrial chimneys :

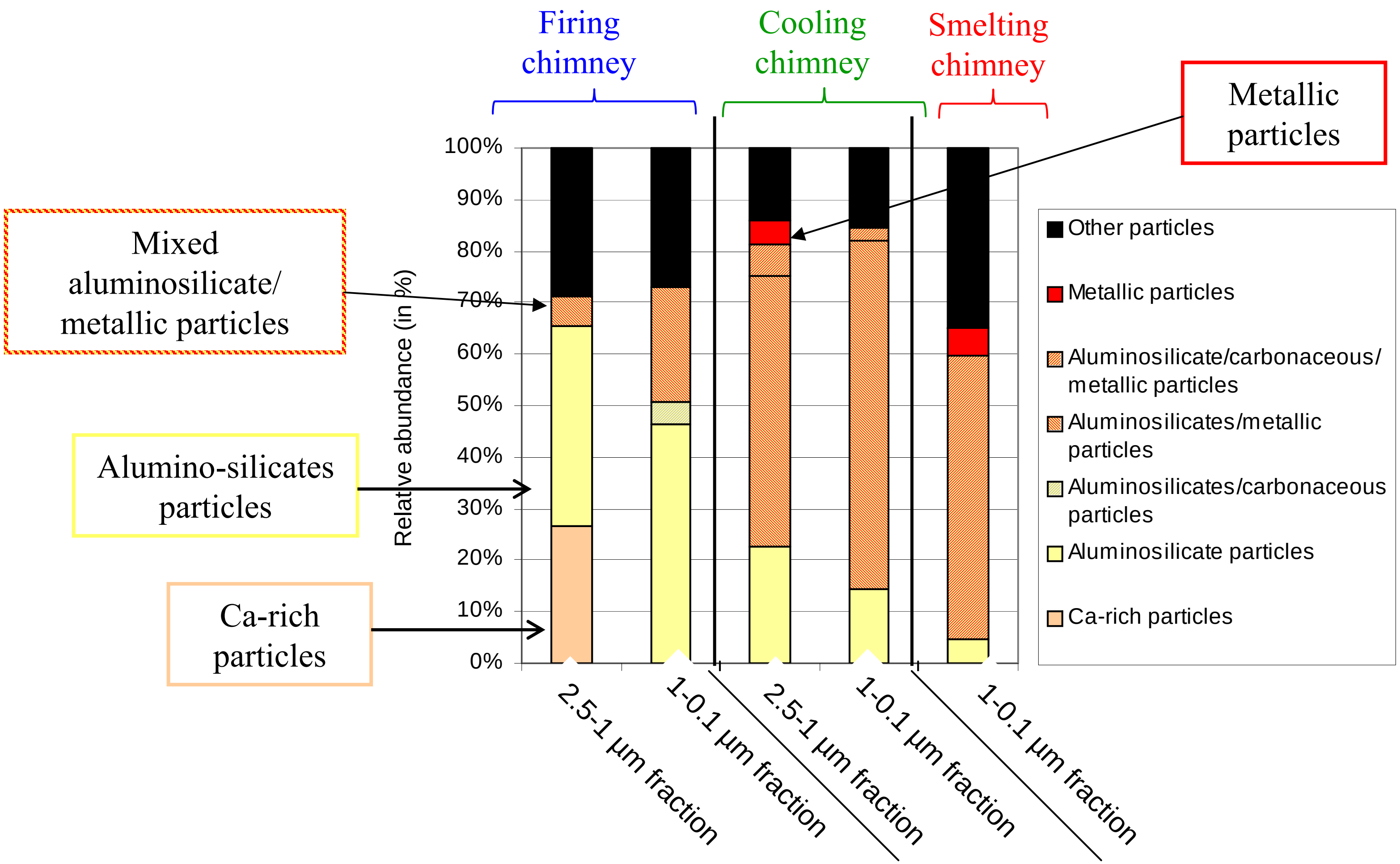


⇨ High temporal variability of emitted quantities.

⇨ Sintering process (firing and cooling areas) = most emissive.

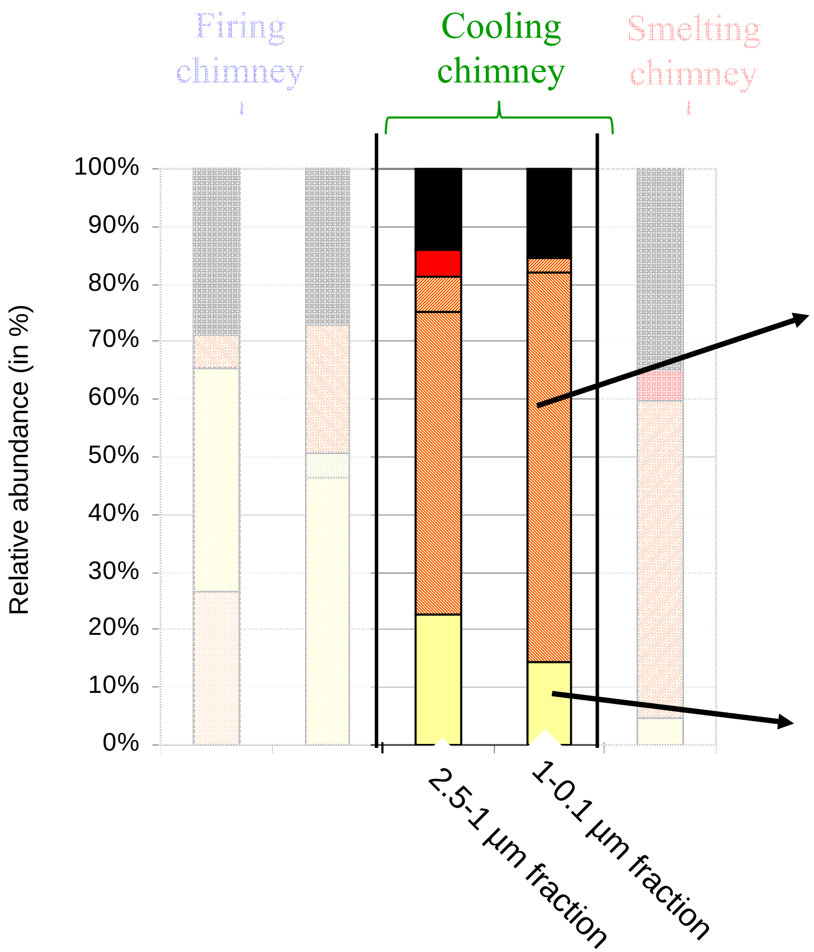
⇨ Fine fraction (PM2.5) highly dominated by ultrafine particles (PM0.1).

Characterization of particles collected in the industrial chimneys :



Relative abundance of particle types identified by CC-SEM-EDS
(about 1 000 particles analysed per impaction stage)

Characterization of particles collected in the industrial chimneys :



Relative abundance of particle types identified by SEM-EDS
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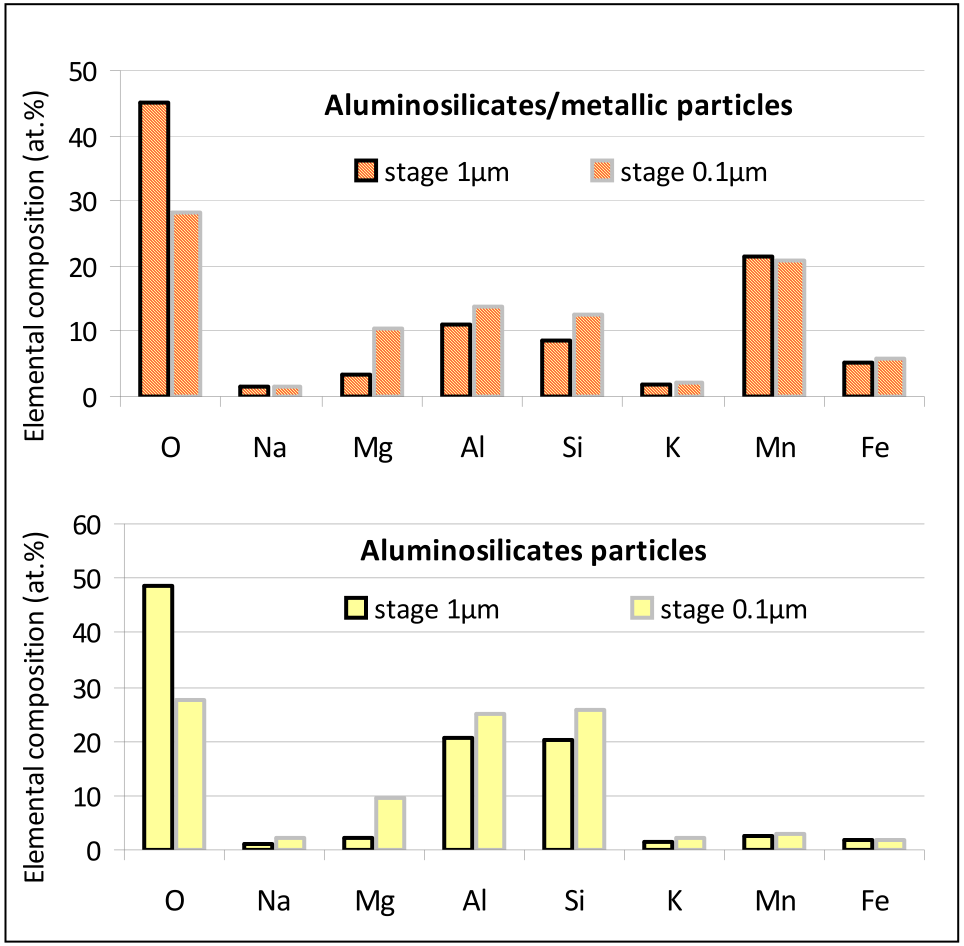
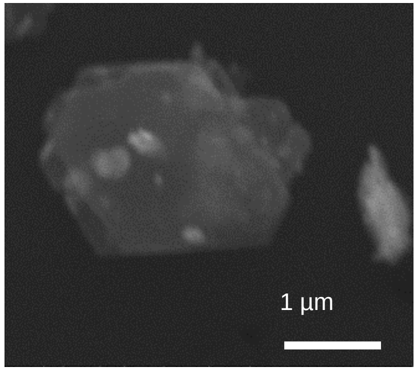


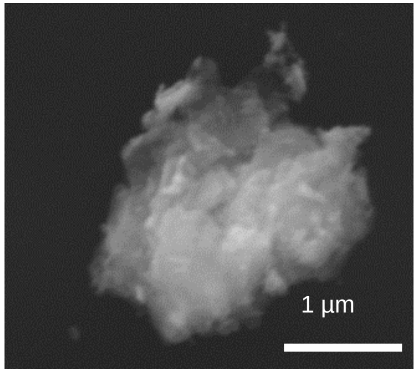
Average atomic composition of particles from SEM-EDS data

Characterization of particles collected in the <u>industrial chimneys</u> :

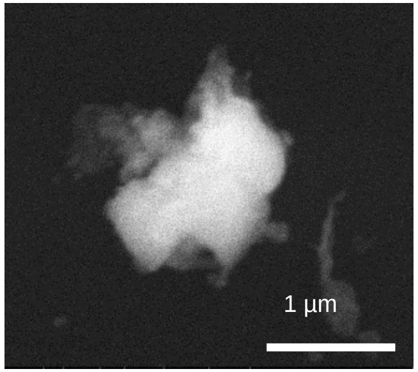
Alumino-silicates particle

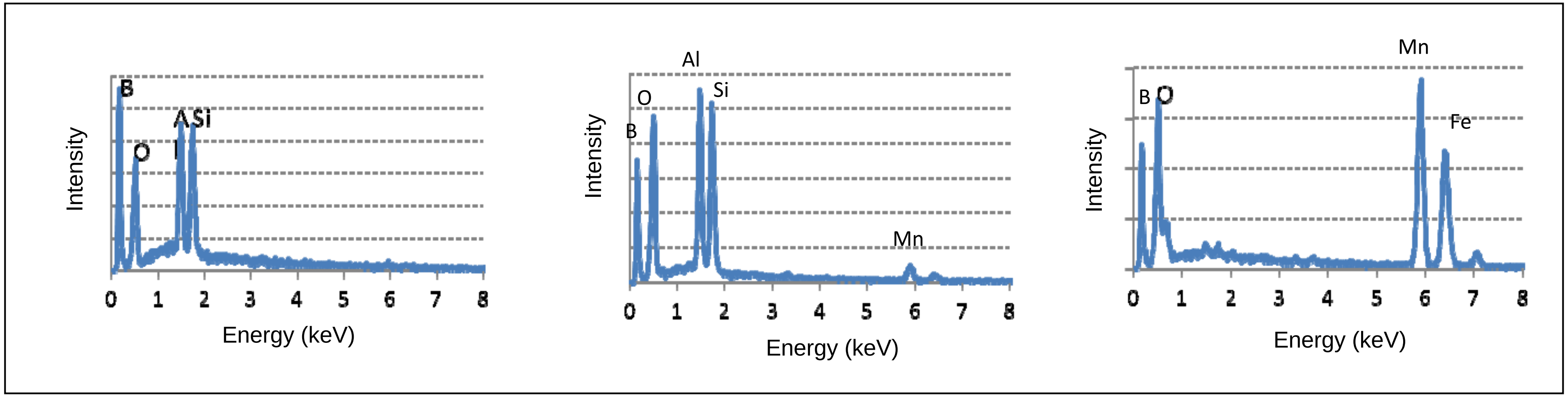


Mixed aluminosilicate/
metallic particle



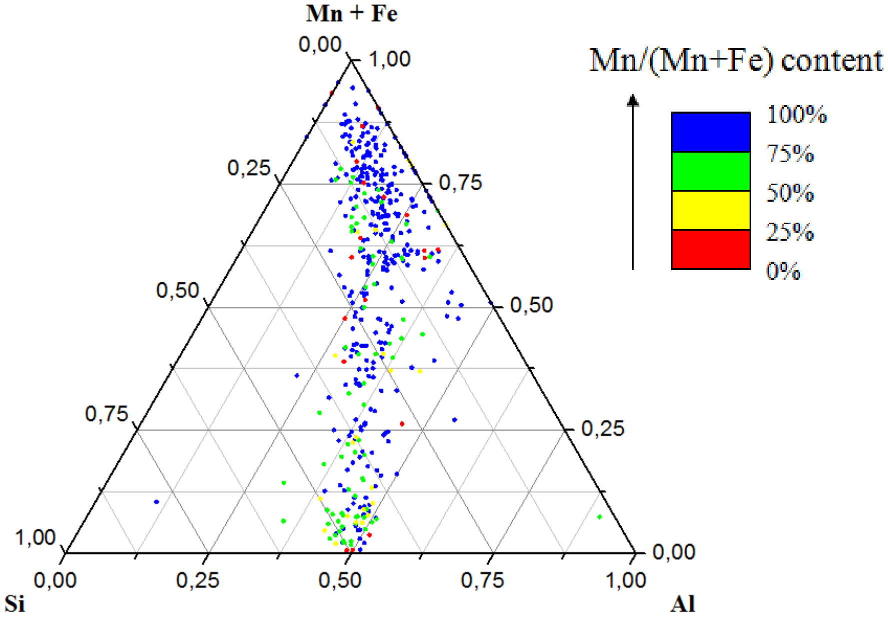
Metallic particle





SEM pictures and EDS spectra of typical particles collected in chimneys

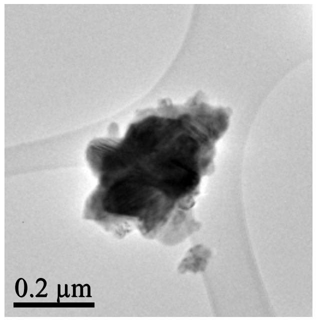
Characterization of Fe and Mn-rich particles collected in the industrial chimneys :



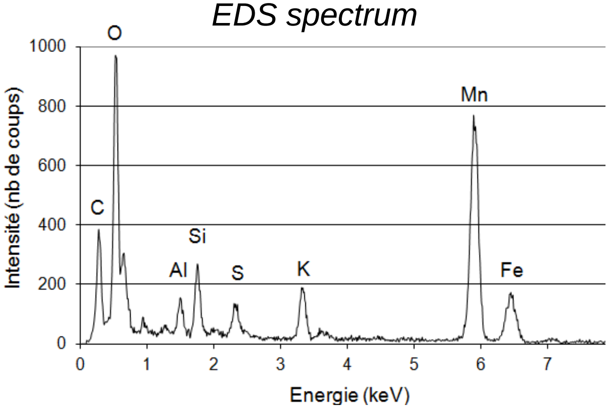
=> Aluminosilicate particles with similar composition (Al/Si ≈ 1), but variable enrichment in Mn or Fe

=> Heterogeneous distribution of Fe and Mn inside particles

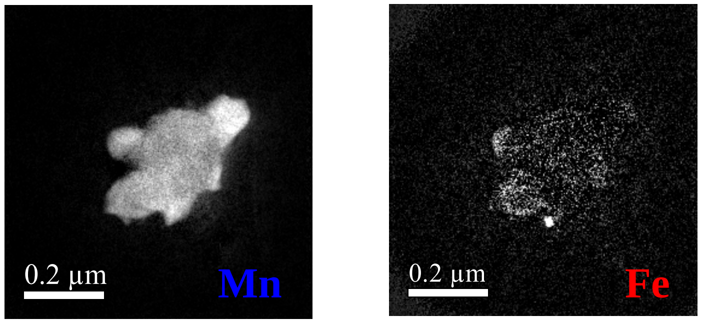
BF TEM picture



EDS spectrum

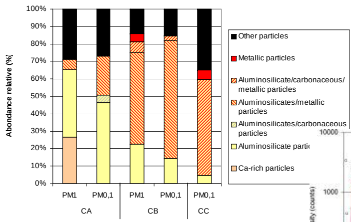


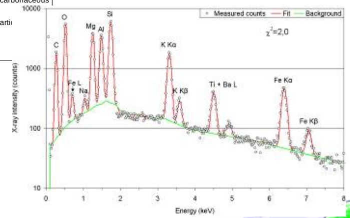
EF TEM-EELS pictures

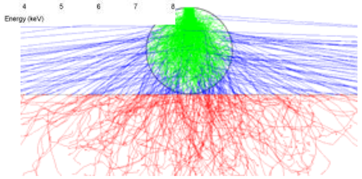








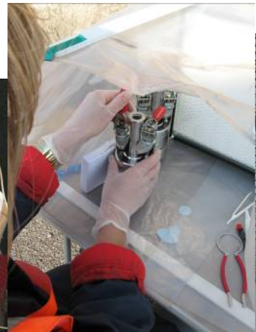




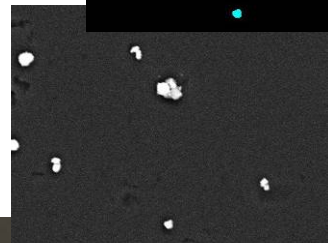
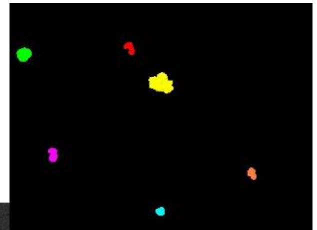
- Conventional procedure for X-ray microanalysis of environmental particles are sufficient for qualitative analysis.

- Geometric effects can be considered for quantitative analysis.

- Monte Carlo simulations give a good correction for these geometric effects.



Thank you for your attention...