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Preliminary investigations of morphology and composition of brake wear particles

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Exhaust and non-exhaust sources contribute equally to total traffic related PM10 emissions

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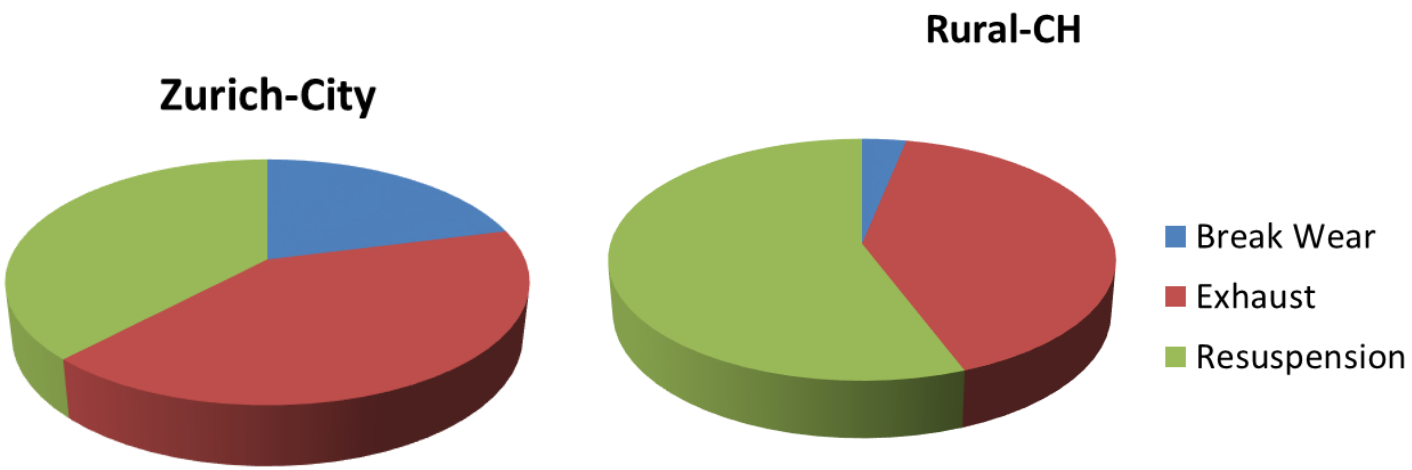
Non-exhaust road traffic particles

- Abrasion generated tire, brake, clutch, road surface, engine, wheel bearings, corrosion, street furniture and crash barriers wear
- Resuspension of material deposited on road surface and environment

Brake wear particles

- 11-21% of total traffic related PM10
- 16-55% of non-exhaust traffic related PM10



Source: Bukowiecki et al. EST 2009

Brake pads comprise of binders, fibers, fillers, frictional additives/lubricants and abrasives

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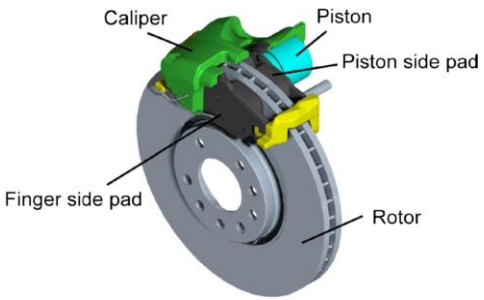
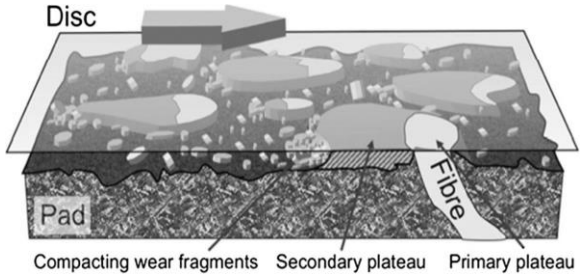
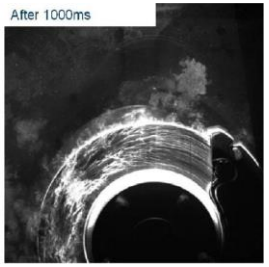
Parameters

- materials (pads, disc) in general non disclosed
  - Pads: NAO (non-asbestos organic), metallic, semi-metallic and low metallic
  - Disc: Cast Fe, Cast Fe with coating, Carbon
- driving behavior, frequency and severity of braking, sliding speed, nominal contact pressure,
- temperatures







Sources: Grigiratos et al. ESPR 2015, Wahlström et al. 2011 PhD Thesis RITS, Augsburg et al. 2011 ETH CCGN 2011

Lack of standardized sampling procedure; difficult comparison of results and conclusions

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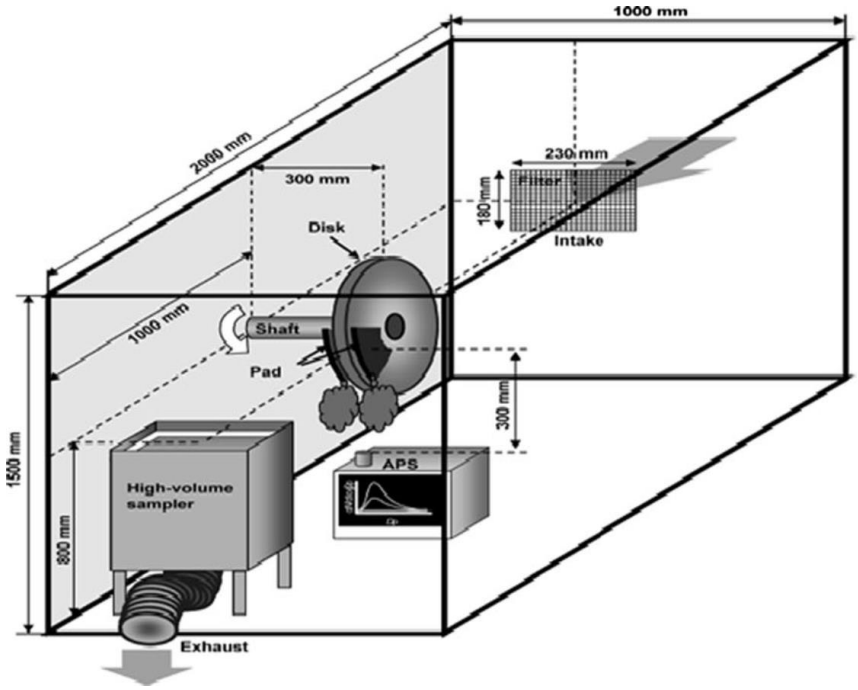

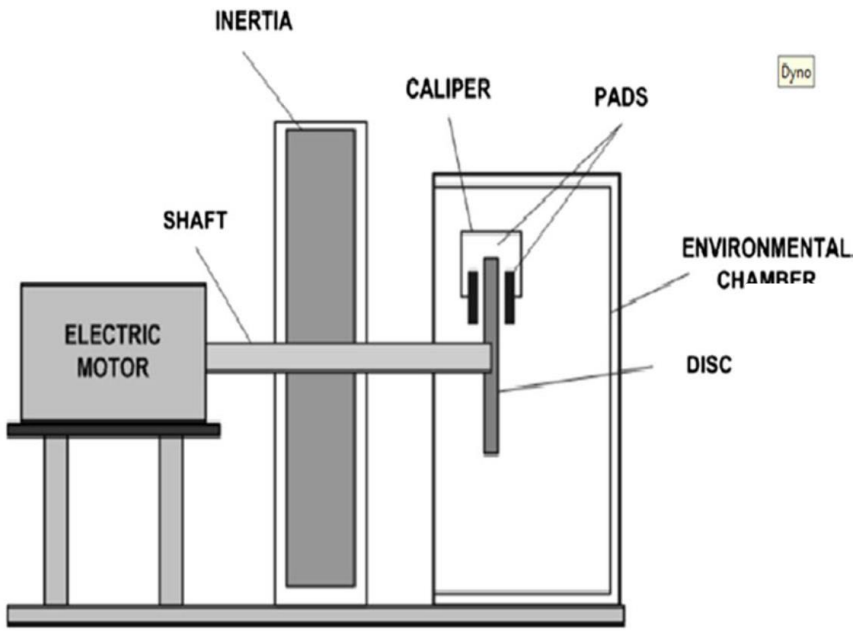

Sources: Iijima et al, EA 2005, Kukutschova et al. EP 2011

Particle size and chemical compositions are the key factors for toxicity

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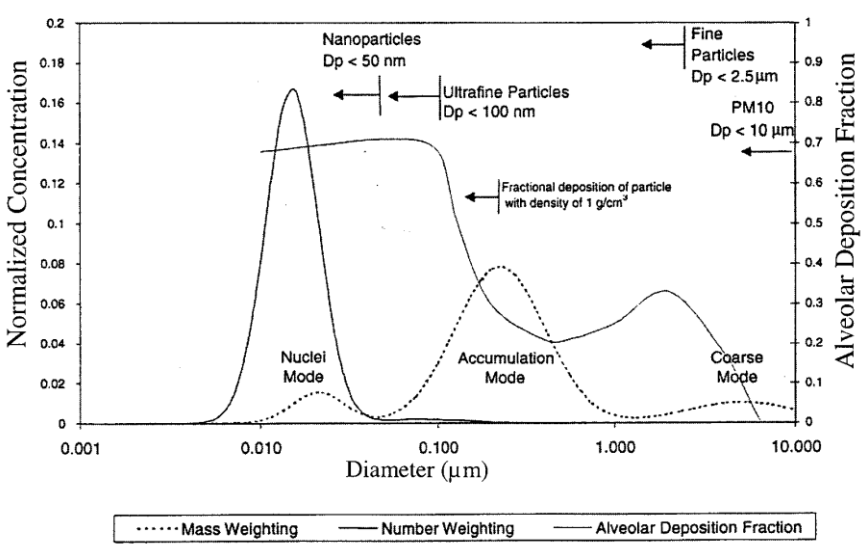
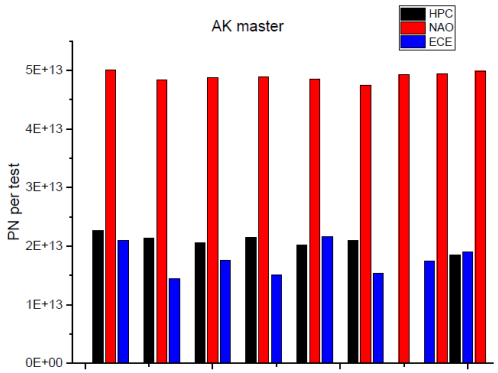
- Mechanical abrasion particles are expected to be coarse and “edgy”
- Fine and ultrafine particles are rather formed by the evaporation/condensation process with subsequent aggregation

- Reported size distributions and chemical composition vary





The present work was financed by the Swiss Federal Office of Environment

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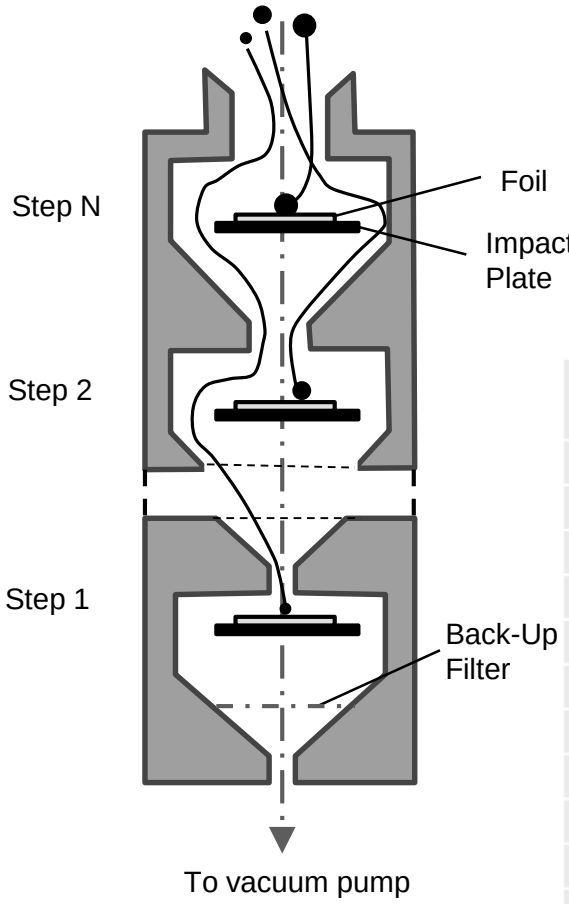
- Joint project

- Test bench and braking cycles defined
- Samples were collected on polycarbonate foils with a 13-step impactor (last stage of the impactor collected particles <30nm)
- Particle size classes were defined by the impactor relative to the equivalent aerodynamic diameter. Compared to the equivalent electric mobility diameter, the diameters are smaller in this case.
- Size classes examined by Electron Microscopy
- Two different sets of brake pads and discs

Cascade low pressure impactor has been used for separating the particle in size classes

- Impactor functional principle is based on the deflection of a free jet through an angle of 90 °
- The gas and the particles are accelerated by a nozzle, smaller particles can follow the flow and deflect, larger particles are not deflected and hit the impactor plate
- An adhesive covering (foil), ensures that deposited particles remain on the impactor plate
- Characteristic for the impactor are the cut-off diameters d50, indicating at which aerodynamic diameter the deposition efficiency is 50%



Step	D 50% [µm]	Di [µm]
1	0.032	0.0456
2	0.065	0.0853
3	0.112	0.1411
4	0.178	0.2200
5	0.272	0.3359
6	0.415	0.5276
7	0.671	0.8365
8	1.043	1.3268
9	1.688	2.0856
10	2.577	3.2781
11	4.17	5.406
12	7.01	8.636
13	10.64	

Defined sample preparation for the electron microscopy

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- Particles of the size ranges were collected in 13 foil bags
- Foil bags cut in the middle, brought into alcohol solution and treated in ultrasonic bath for 15 minutes in order to break mechanically any weakly held aggregates. 20-30 drops of the suspension transferred on TEM grids
- Two types of TEM grids: (a) Cu-supported holey carbon-grids (in this grid-type the carbon film contains numerous holes where particles are supposed to be caught) and (b) Cu supported thin carbon films (the carbon film contains no holes). Type (b) was more useful for the small size fractions since there were no particle losses through the holes
- Due to the grid material, Cu- and C-peaks appear always on the EDX spectra; thus Cu and C are difficult to be detected in the samples unless they are present in very high amounts. For the samples investigated by SEM, the sample holder contains also Au; thus Au peaks on the EDX spectra are ascribed to the sample holder material.

Methods: Scanning (SEM) and Transmission Electron Microscopy (TEM) with EDX

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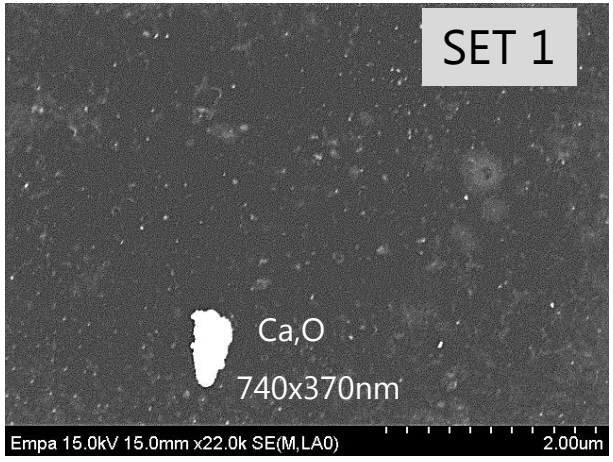
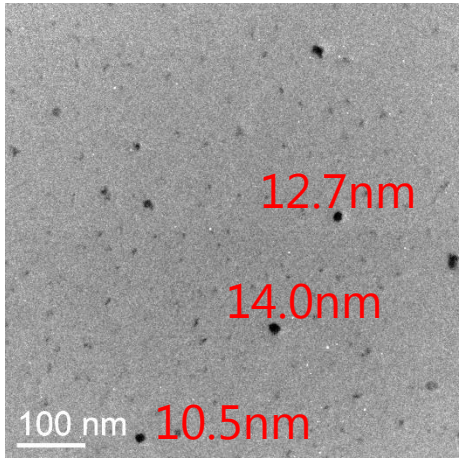
- **SEM:** Particle imaging and chemical composition combination with an Energy Dispersive X-Ray system (EDX) for chemical composition (qualitative results)
  - Secondary electron (SE) images: topography of particles (surface features)
  - Back scattered electron (BSE) images: chemical differences by variations in brightness (brightness correlates positively with the atomic number of the participating element and/or with the particle's thickness)
  - Element mapping for selected aggregates of larger sizes

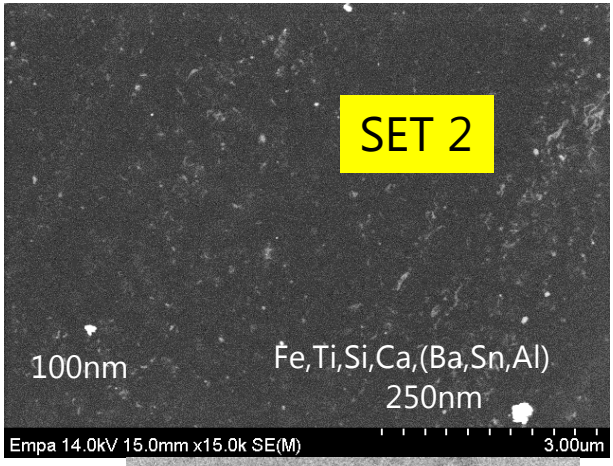
- **TEM** (smallest particle fractions: step 1 and 2)
  - Particle imaging and chemical composition (EDX)
  - TEM mode (low and high magnification/resolution)

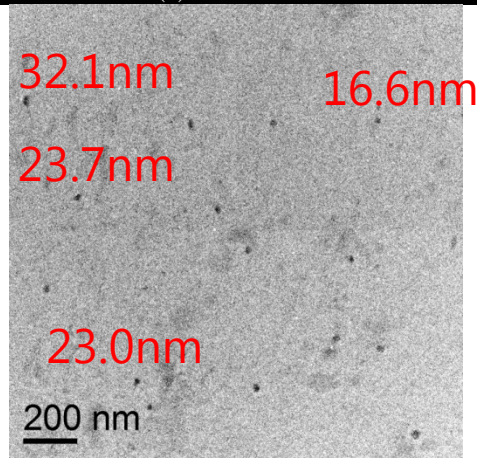
Abundant very thin and round particles below 50nm

- Abundant particles <50nm on SEM and TEM images (both sets)
- Larger particles (>50nm to a few hundreds of nm) also occur
- Particle shapes are mostly round; particles are very thin
- TEM EDX showed Ca, Fe (SET 1) and mostly Fe (SET 2)









Agglomerates composed of nm-large particles with homogeneous or heterogeneous composition are common

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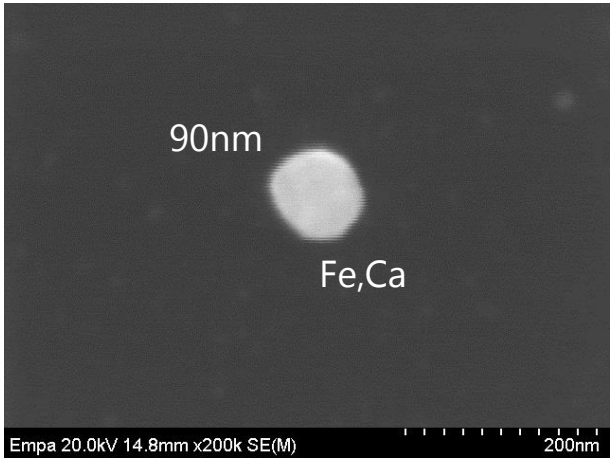
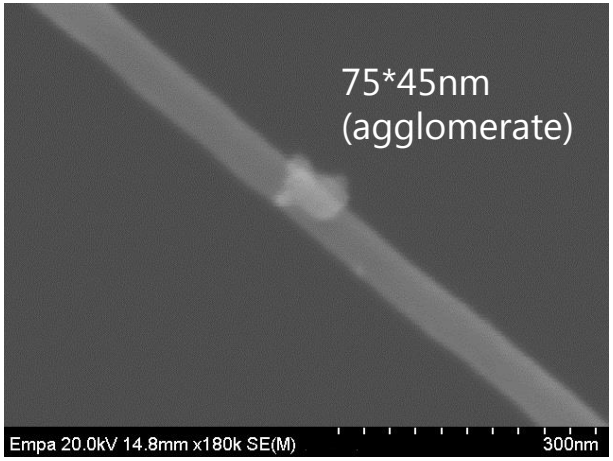
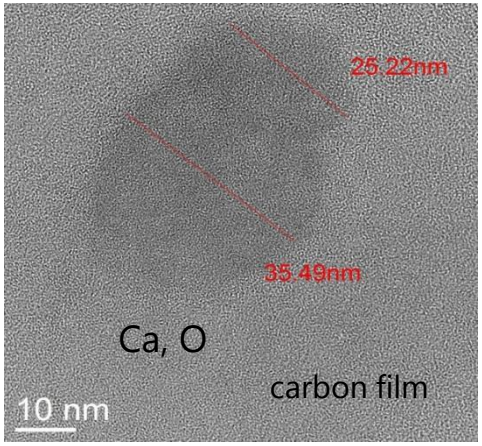
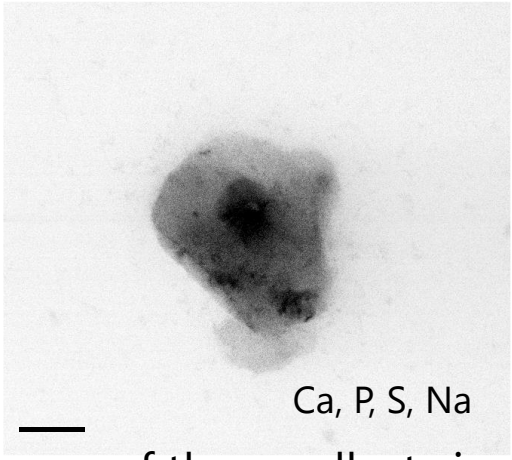
SET 1





STEP 1 (45nm)

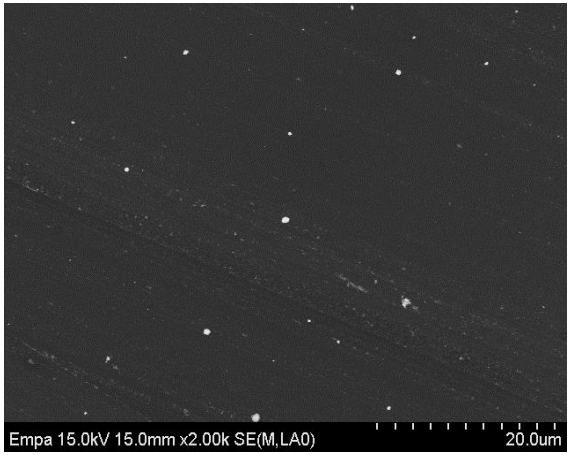




SEM (upper row) and TEM (lower row) images of the smallest size particles

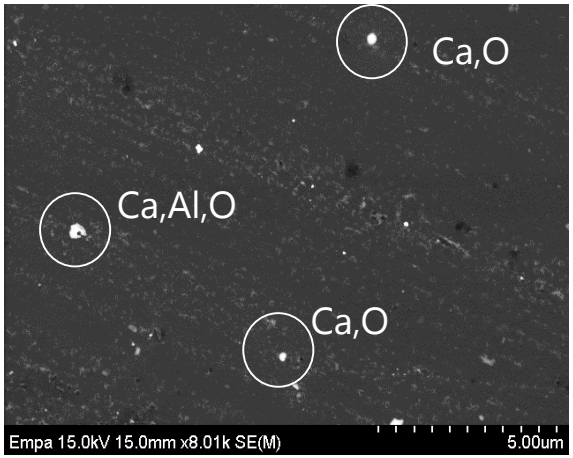
Abundant particles <100nm

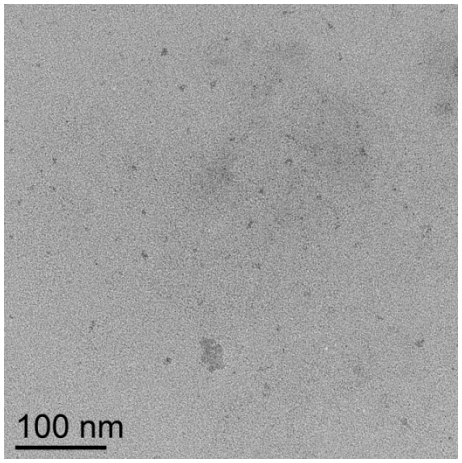
- Shapes are spherical and irregular; outlines are rounded
- Most particles Ca-bearing; some also Al, Mg, and less K±Ti

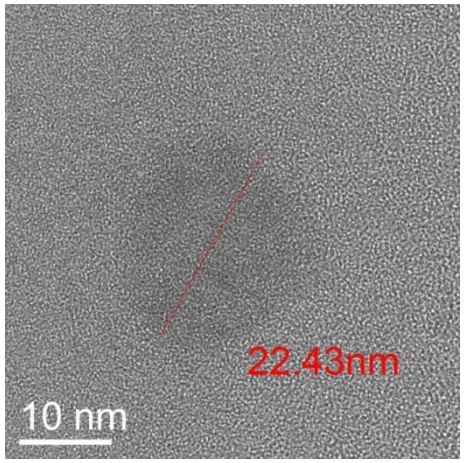


SET 1

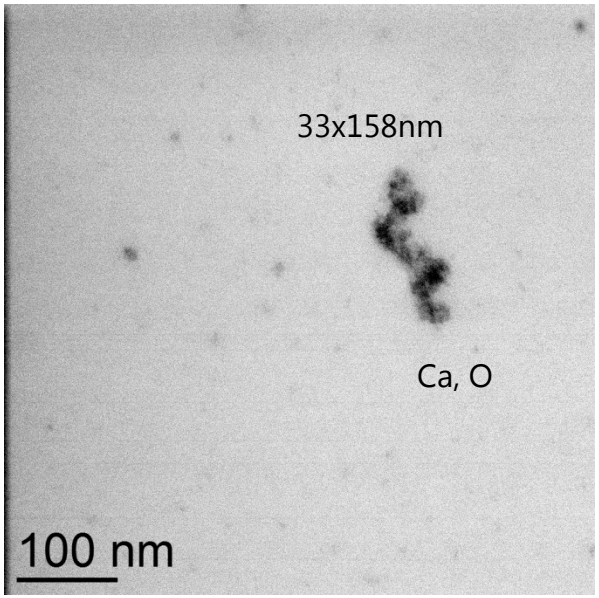
STEP 2 (85nm)

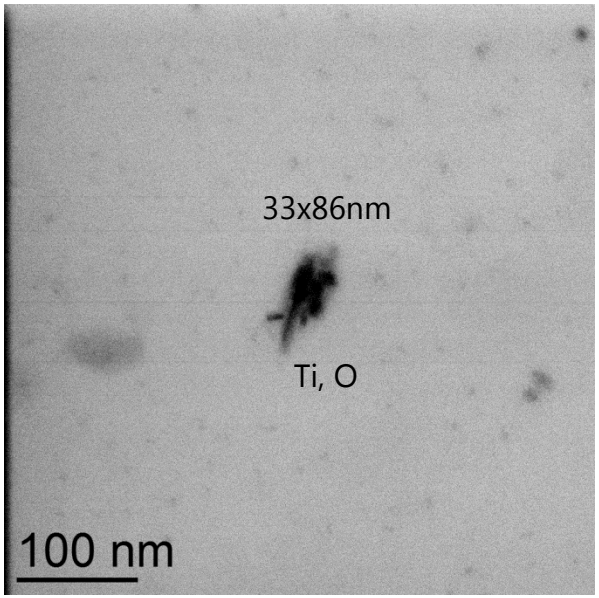


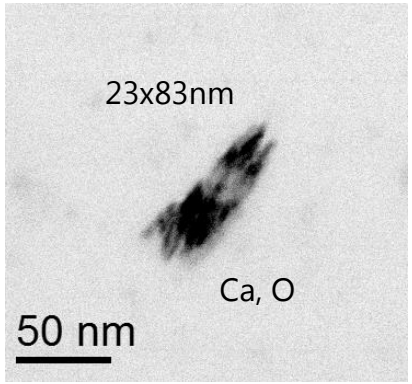


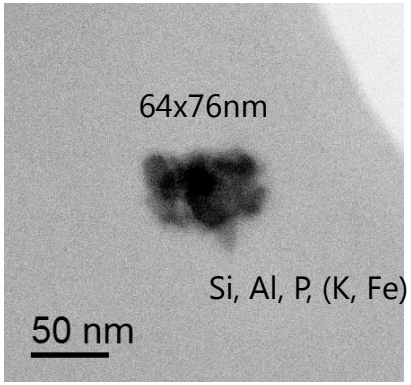


Aggregates of particles <100nm have been observed









SET 1

STEP 2 (85nm)

Aggregates of particles with homogeneous or heterogeneous composition, Ca, Fe, Al, Sn, Cr, Mg

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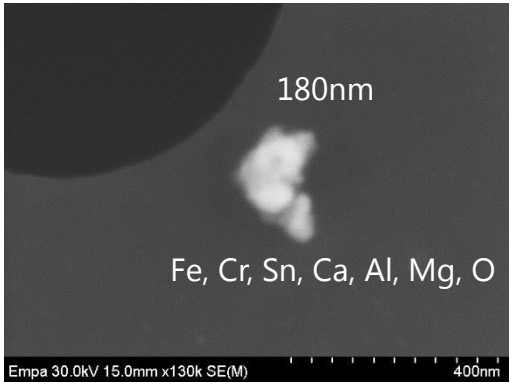
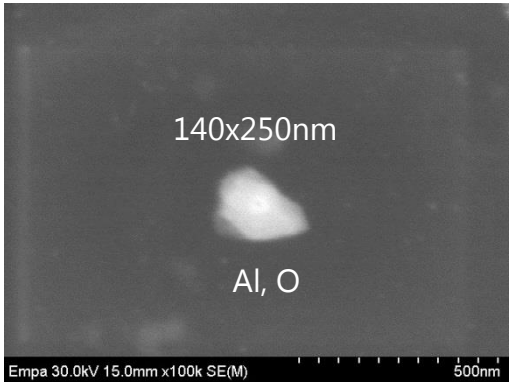
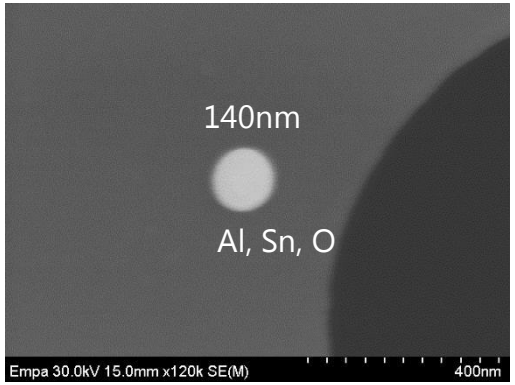
SET 1

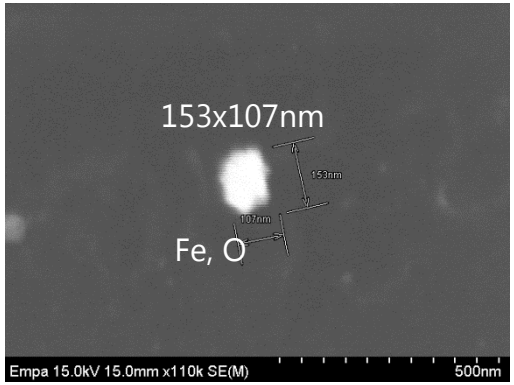
STEP 3 141nm

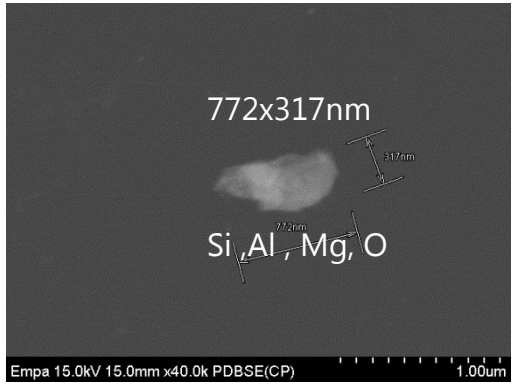


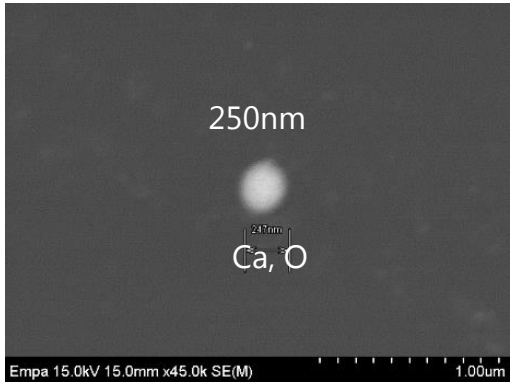




STEP 4 220nm







Heterogeneous composition, irregular shapes, seldom circular, Fe, Al, Sn, Mg, Cr, W and smaller amounts of Ti, Ni and Ca

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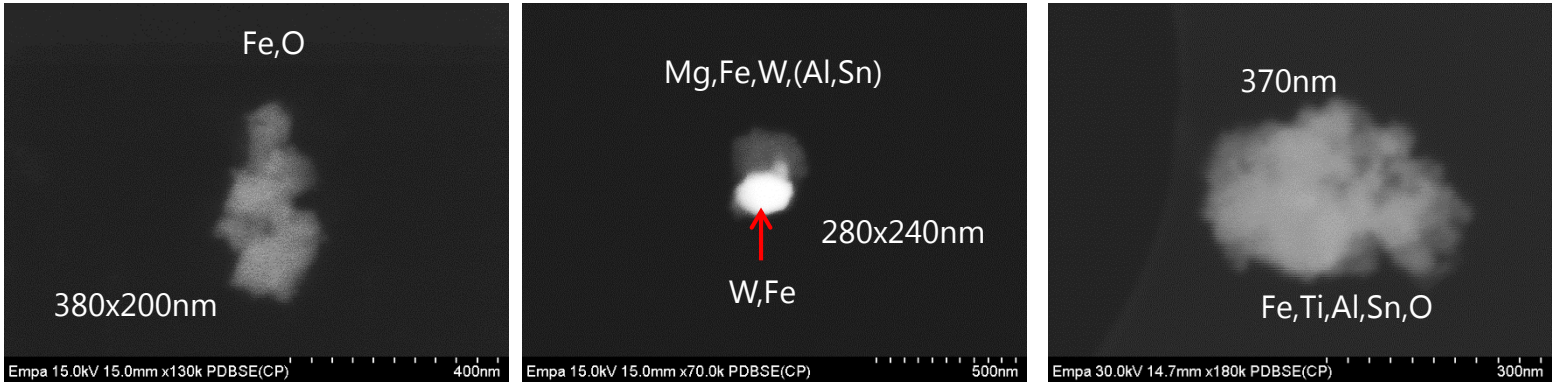
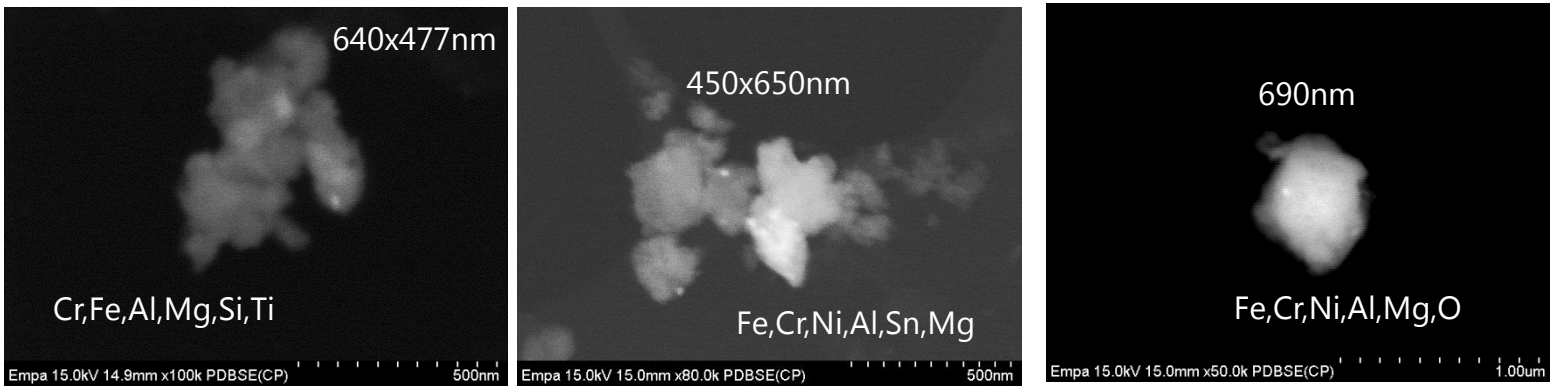
SET 1

STEP 5 336nm



STEP 6 527nm



SEM BSE images of aggregates mostly revealing heterogeneous chemical composition via different brightness

Composite aggregates and their chemical composition (Al, Mg, Si, Cr, Fe, Ca, Ba and Ti)

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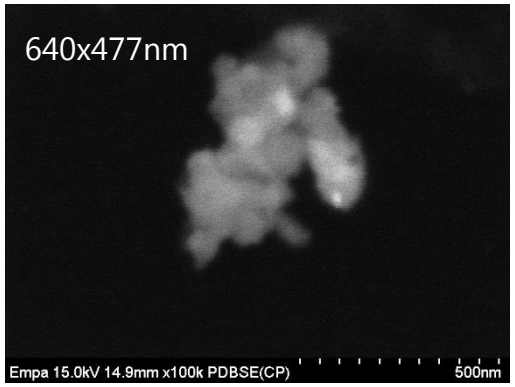
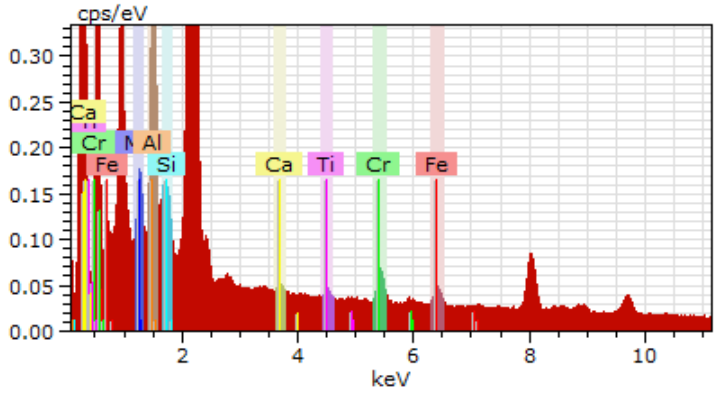
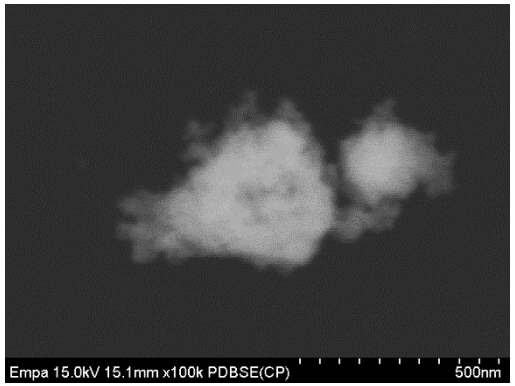
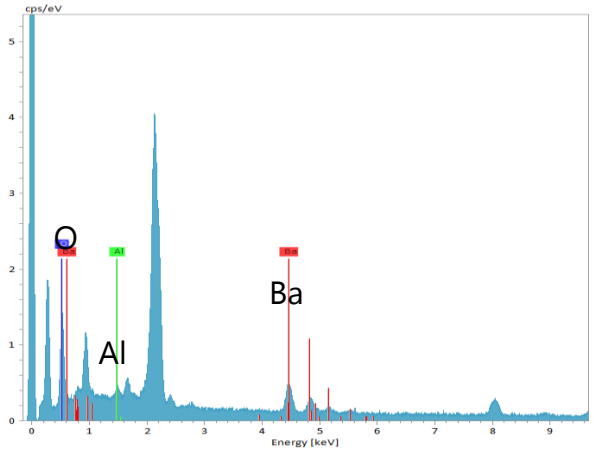
SET 1

STEP 6 527nm









Aggregates are irregularly shaped mostly with rounded outlines Fe, Al, Mg, Si, Sn, W, Ti, Cr, K, Ca; less frequent Zn, Ba, Ca

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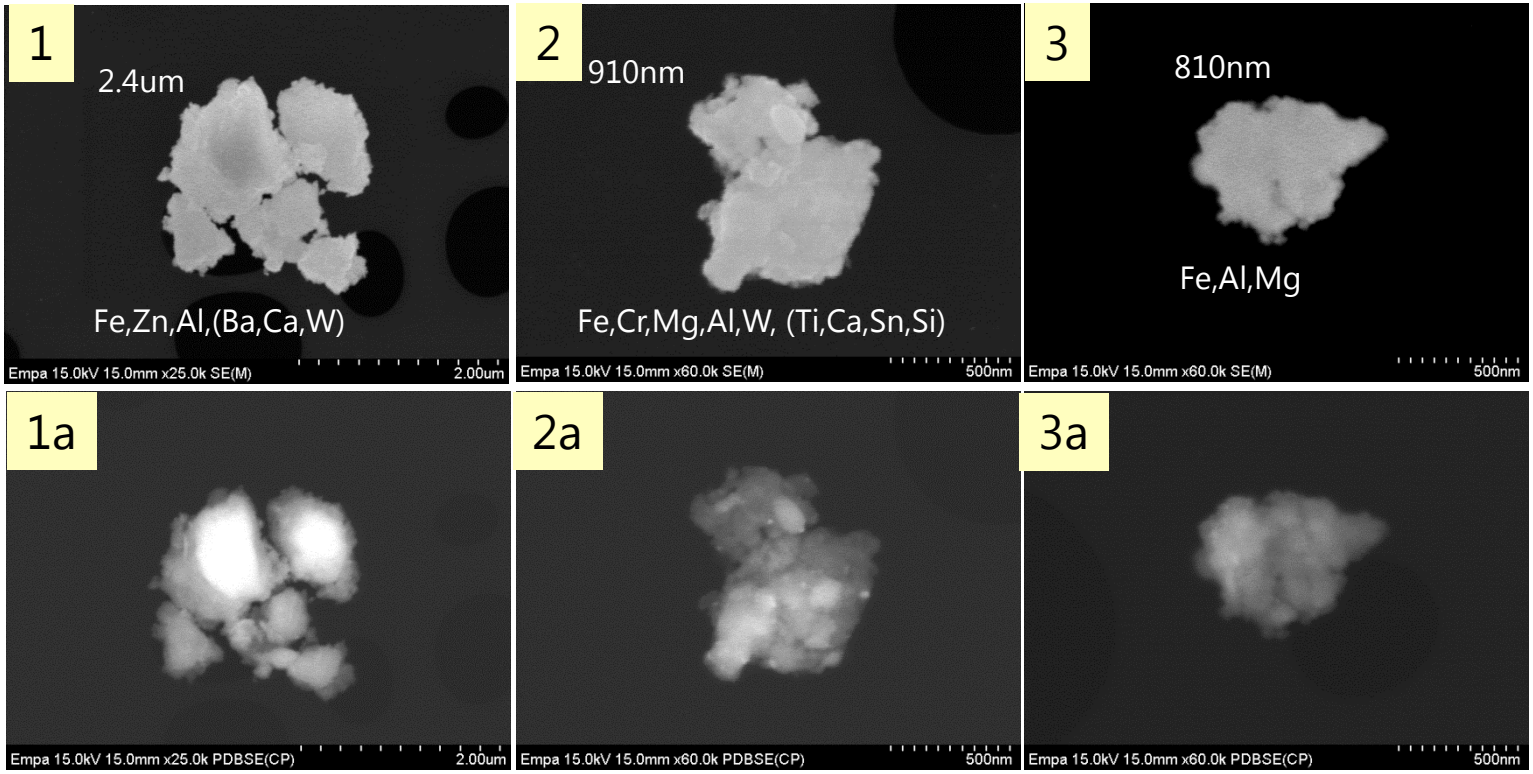
SET 1

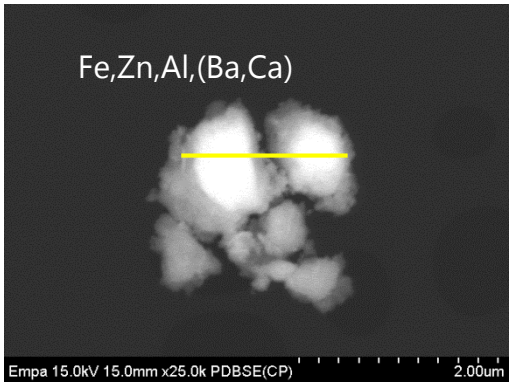
STEP 7 836nm

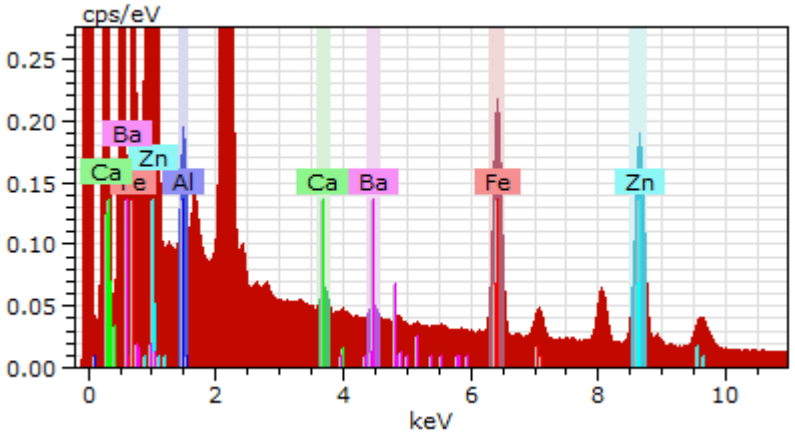


Inhomogeneous distribution of the elements in the aggregates

SET 1

STEP 7 836nm





Aggregates consist of numerous smaller particles

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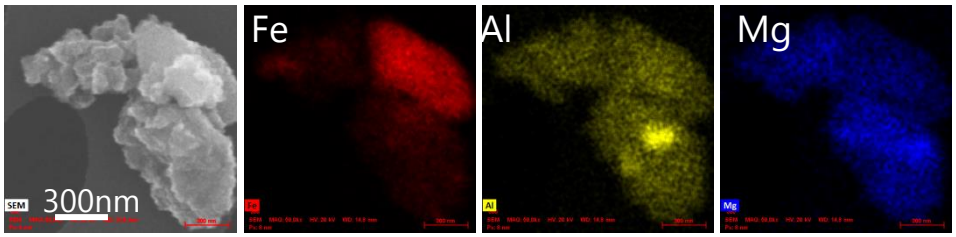
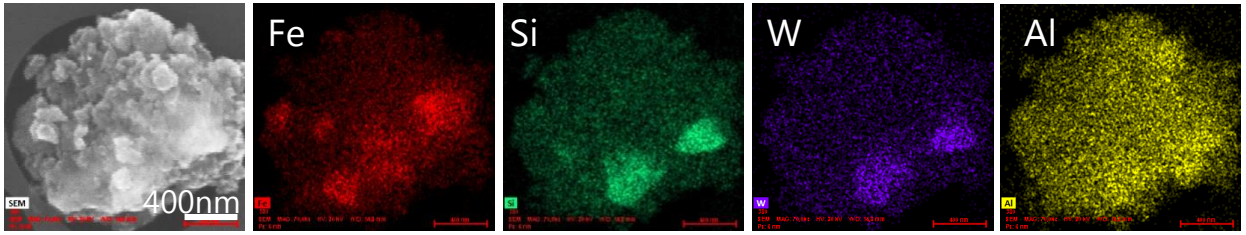
STEP 7 836nm



Smaller amounts of Sn, Ti, Cr



Smaller amounts of Mg, Ti, Cr

SEM SE images of two aggreates and element mapping of the most encountered elements (mapping duration 5min)

Aggregates are irregular and have rounded outlines
Fe, Si, Al, Mg and Sn; W, Ti and Cr are usually locally enriched; small amounts of Ni and Ca occur also; C has been identified in a bigger particle; Bi was detected in one case

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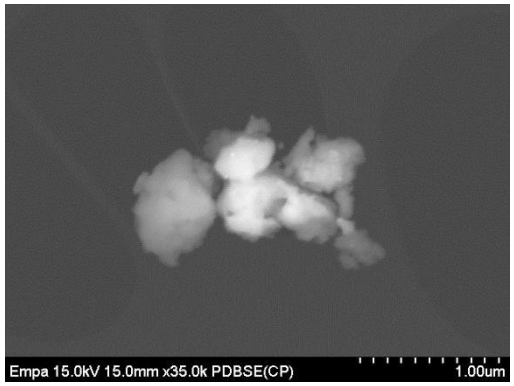
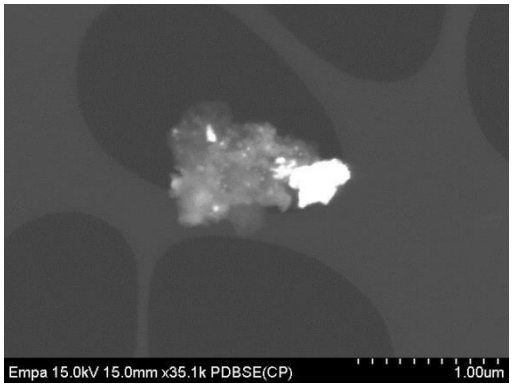
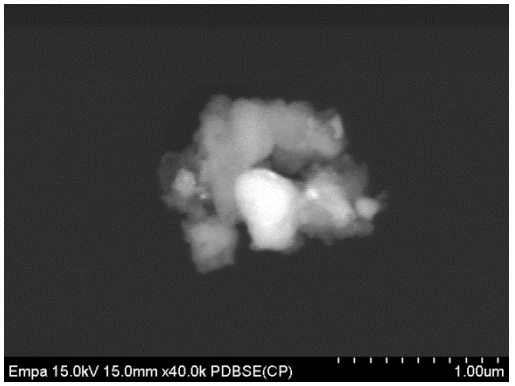
SET 1

STEP 8 1327nm







Typical example for an aggregate

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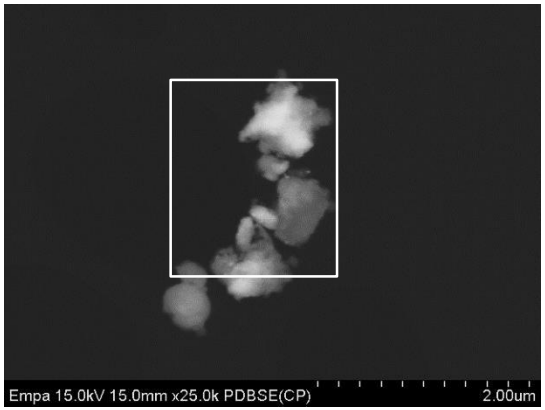
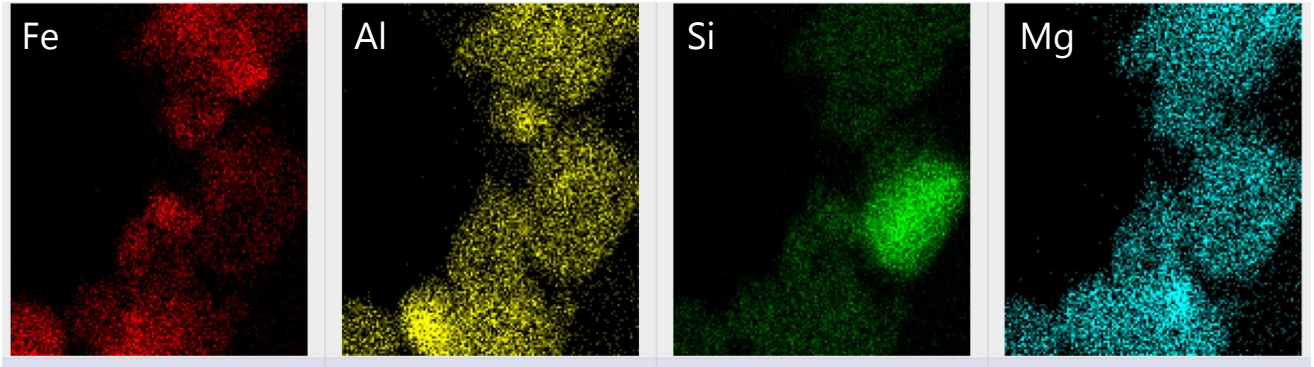


STEP 8 1327nm



Example of coexistence of Al and Mg

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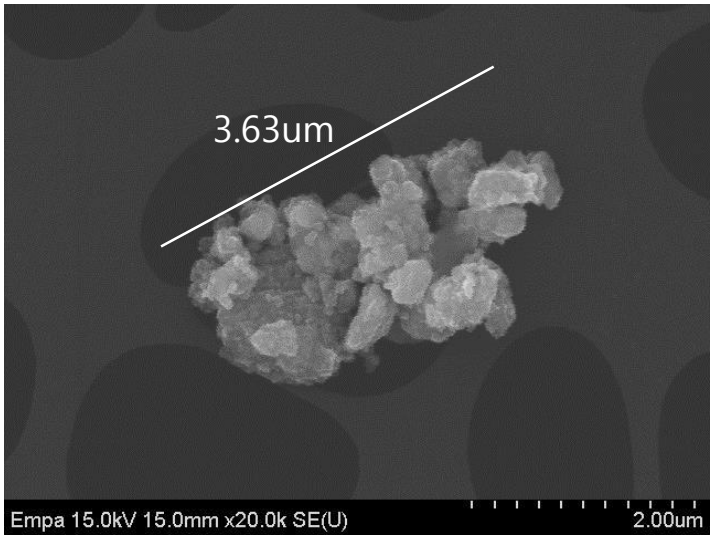
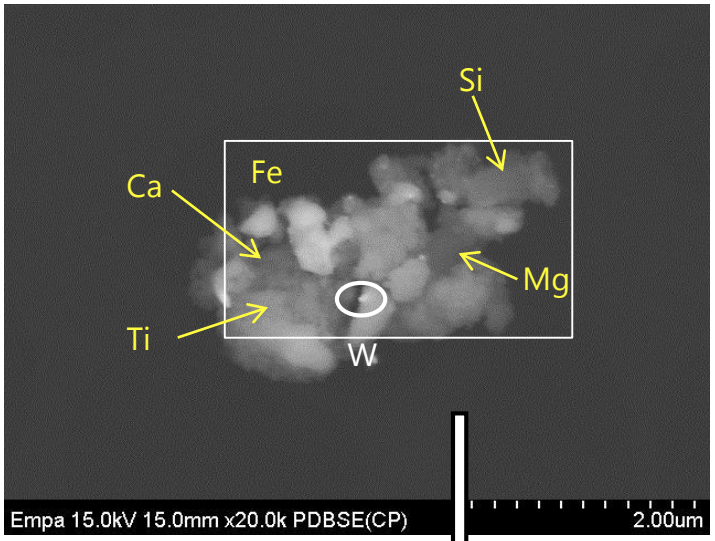
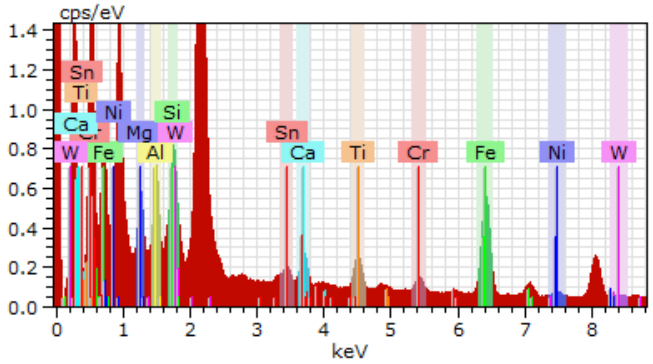
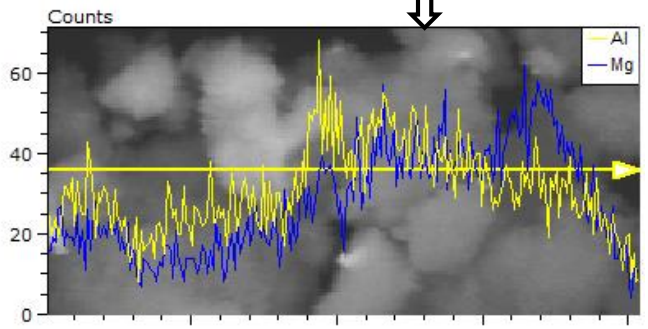
SET 1

STEP 9 2086nm





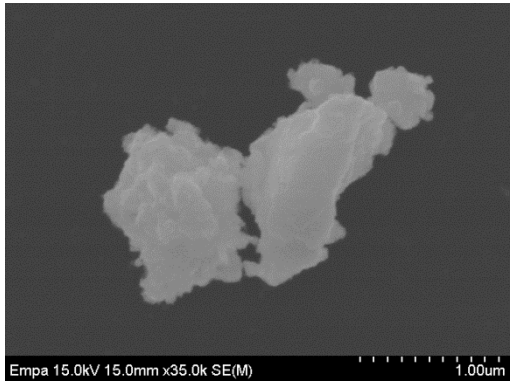


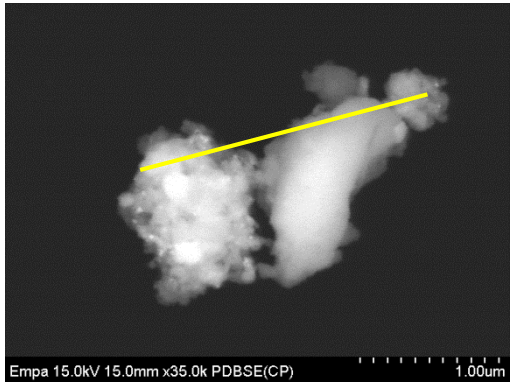


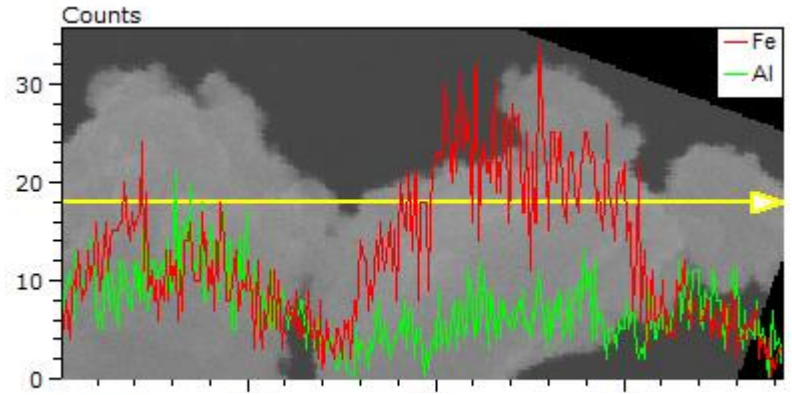
Examples of coexistence and separate element distribution

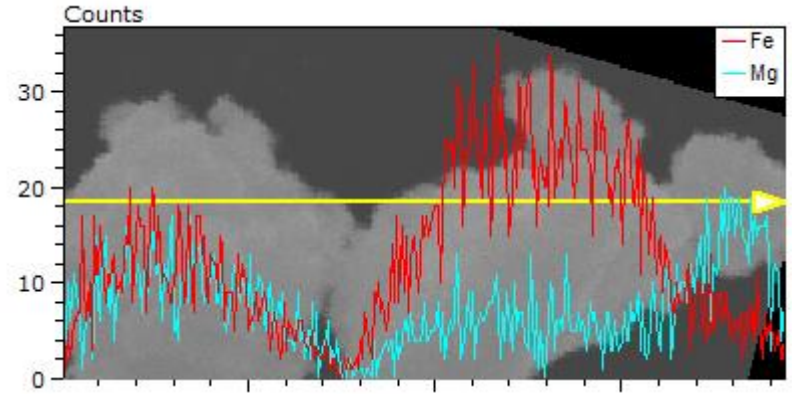
SET 1

STEP 9 2086nm









Larger particles confirm the findings

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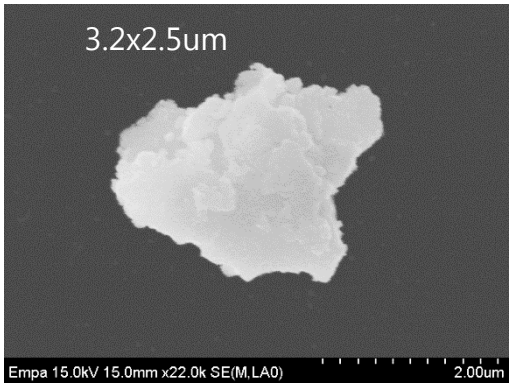
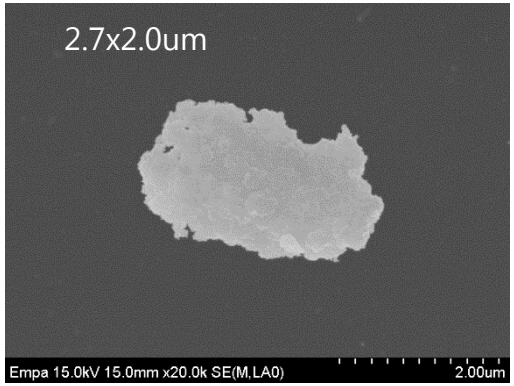
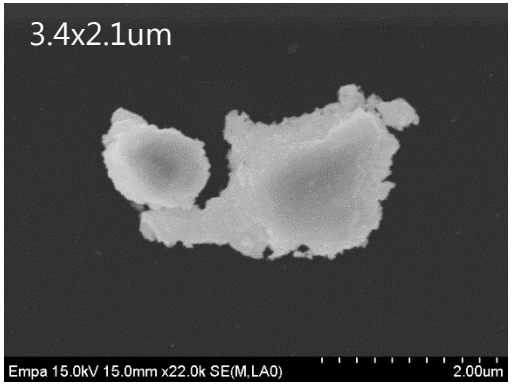
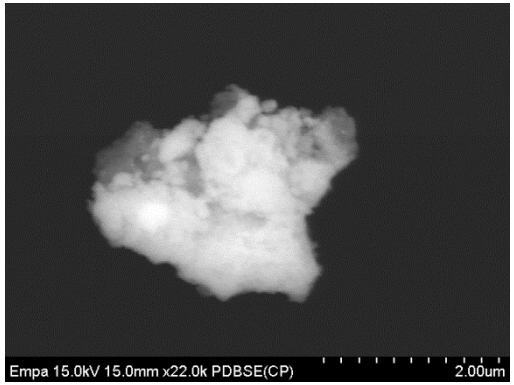
SET 1

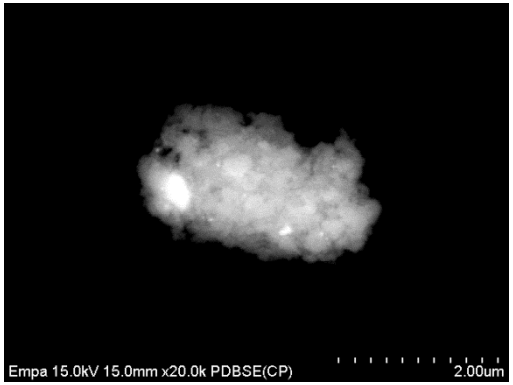
STEP 10 3278nm

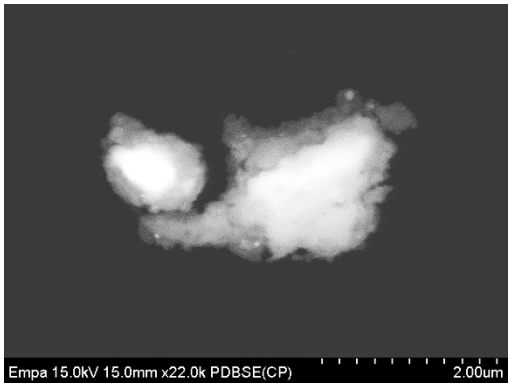












Abundant, very thin particles <30nm occur, some of the largest among the small particles give a weak (questionable) EDX signal of Al, Mg, Fe, soot identified

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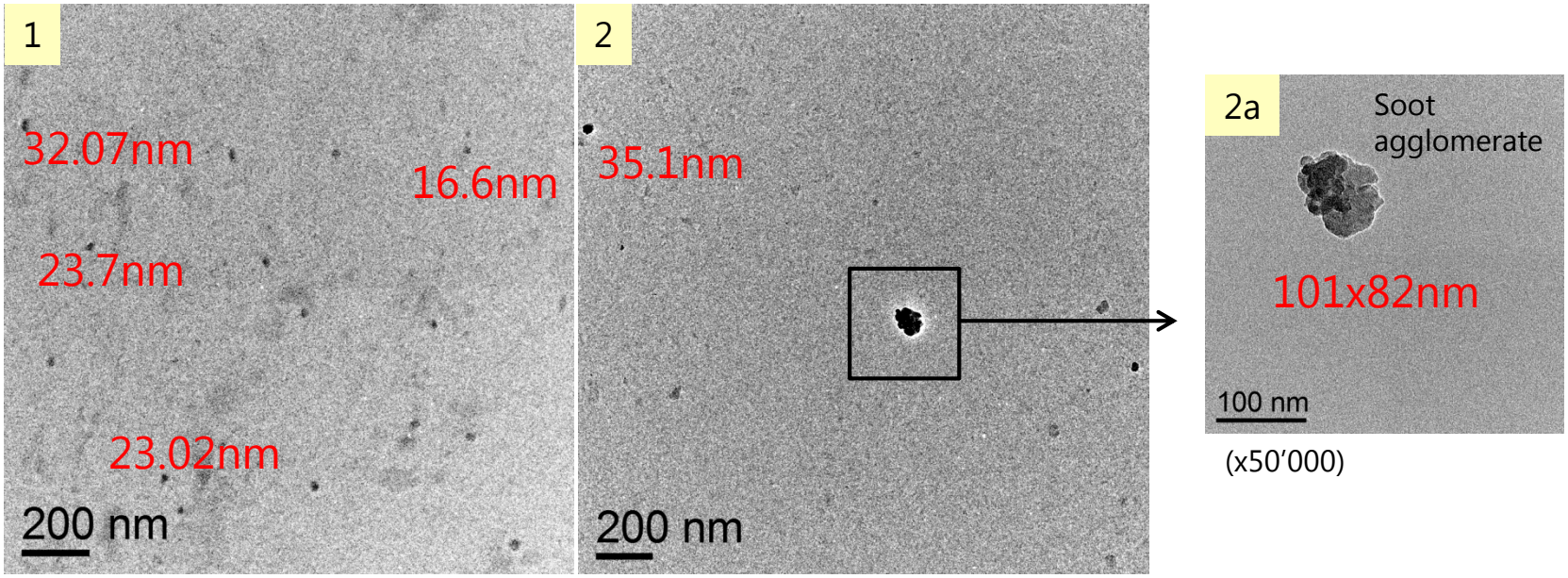
SET 2



(x12'000) (x10'000) (x10'000) (x50'000)

STEP 1 (45nm)

ca. 30-40nm large agglomerates consist of smaller particles (~10nm); some of the agglomerates have a soot structure characterized by carbon-lamellae

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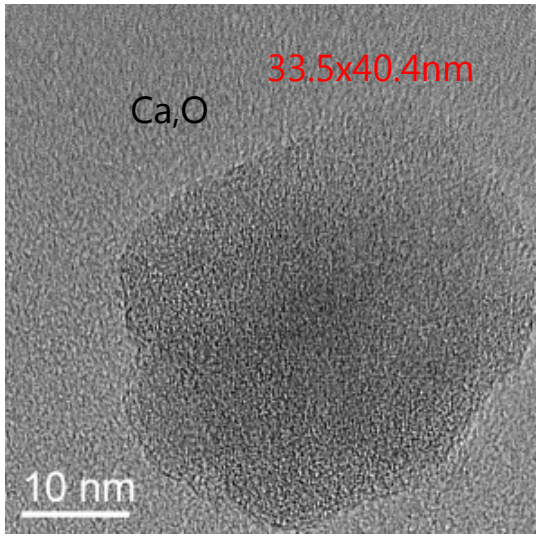
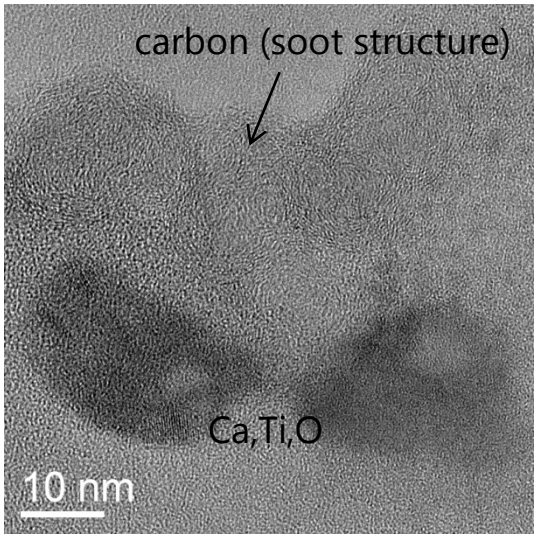
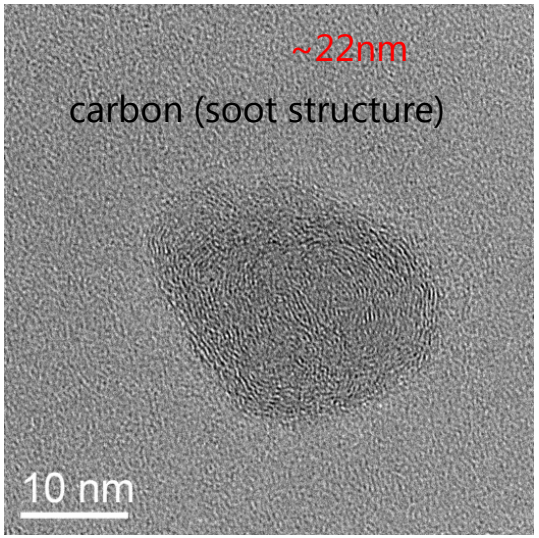
SET 2







STEP 1 45nm

Composite aggregates of larger sizes (>50nm) consisting of mostly Fe; also Ti, Al, Mg, Si, Ca, P, K, Sn, Zn, S, Zr and Na were found; Carbon material (?soot) often coexists with metal phases

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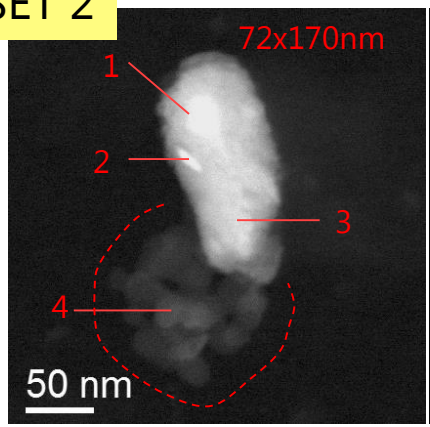
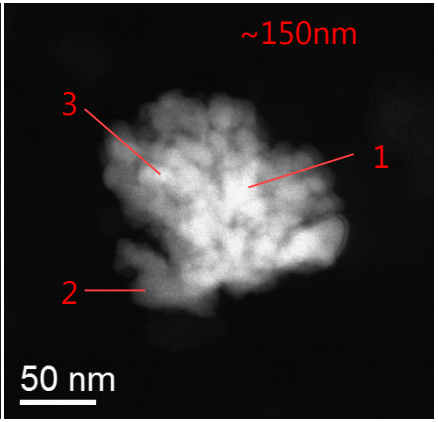
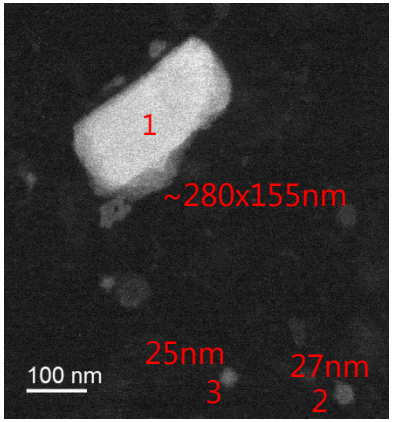
SET 2



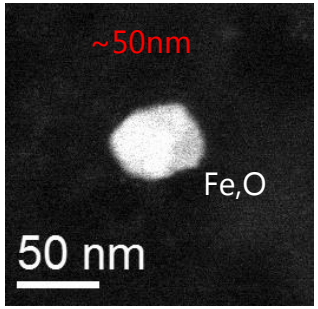
1: Fe,Ti,Zr,(Ca),O; 2: Fe,Ti,Ca,S,O
3: Fe,Ti,Ca,S, Zr,O; 4: no detectable elements (carbon?) (dashed encircled area may represent a soot agglomerate).



1: Fe,Mg,Zn,S,Sn,O;
2: Fe,Zn,Mg,O;
3: Fe,Zn,S,Sn,Mg,O



1: Al,(Si?)O; 2: Al,(Si?),O;
3: K,P,Na,(Si?),O



STEP 1 45nm

Dark field STEM images of particles and agglomerates. Numbers mark the approximate sites of EDX analyses. The brightness correlates with atomic weight and/or particle thickness.

Multi-phase aggregates of crystalline material, Fe, Ti, S, Ca, K, and Zr were found by EDX

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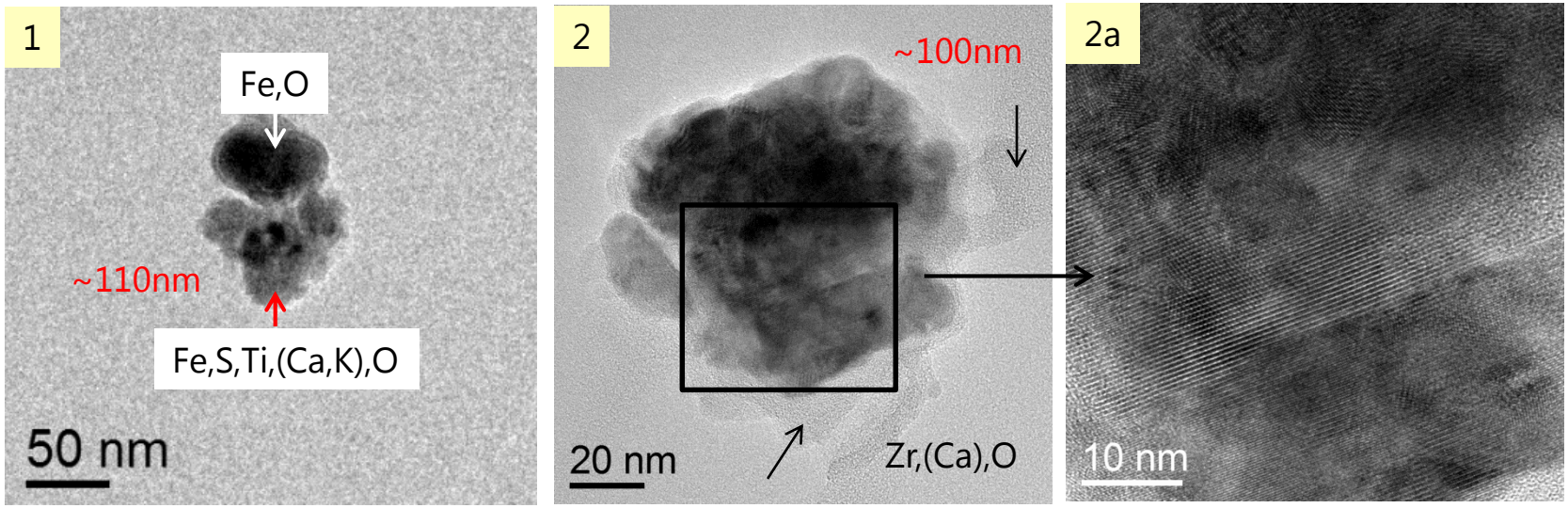
STEP 3 141nm

SET 2



TEM (1, 2) and HRTEM images of particles with example of crystalline structure (2a; lattice fringes):

Heterogeneous aggregates Fe, Ti, Ca, Al, Si, Mg; some Sn, Zn, Mn; irregular and nearly equidimensional; the particle outlines are often rounded

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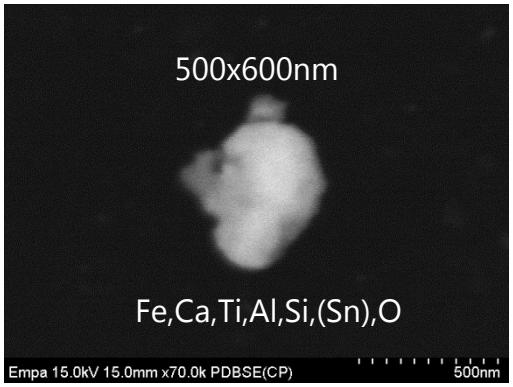
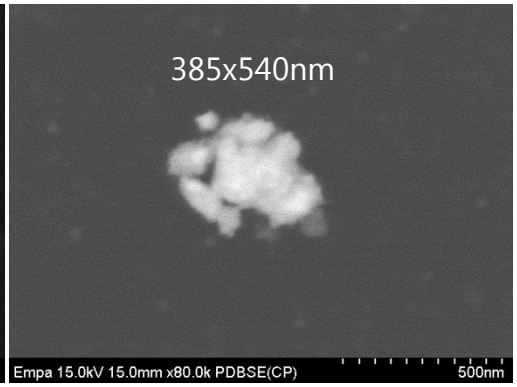
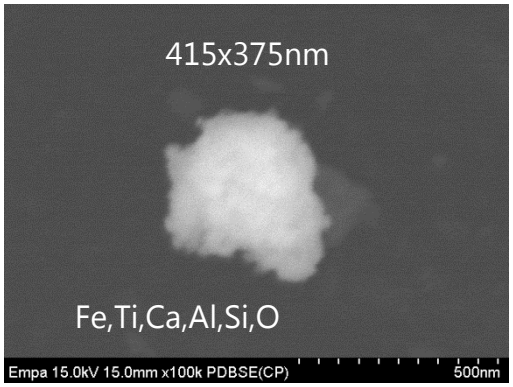
SET 2

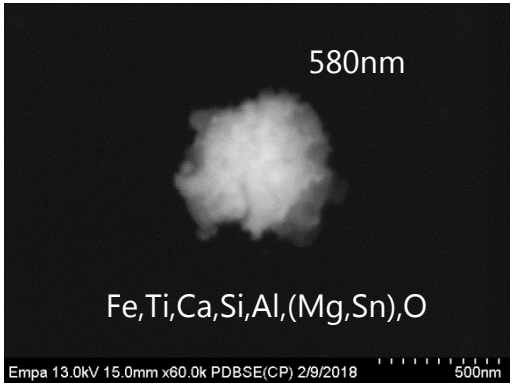
STEP 5 340nm

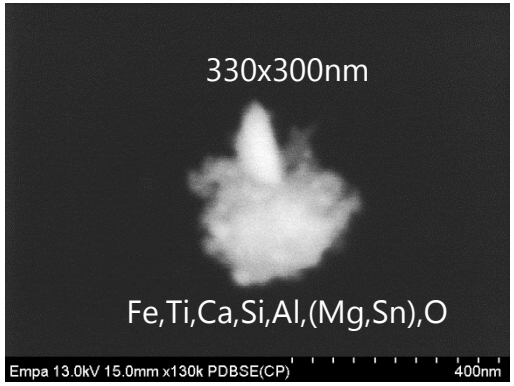


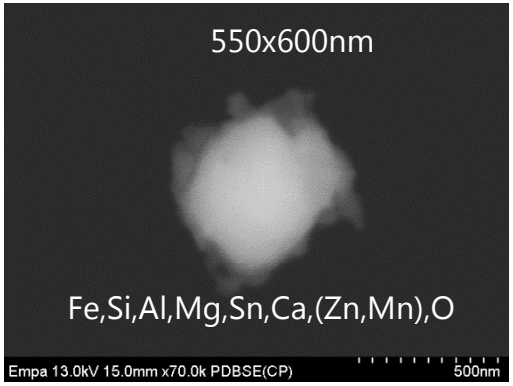




STEP 6 530nm







Heterogeneous aggregates Fe, Ti, Ca, Al, Si, Mg, Zr; some Sn, K; Sb and F were found rarely; irregular and nearly equidimensional; the particle outlines are often rounded

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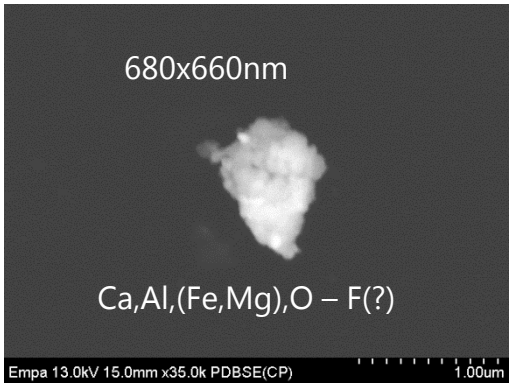
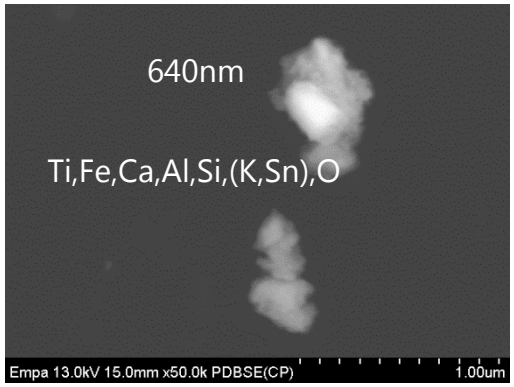
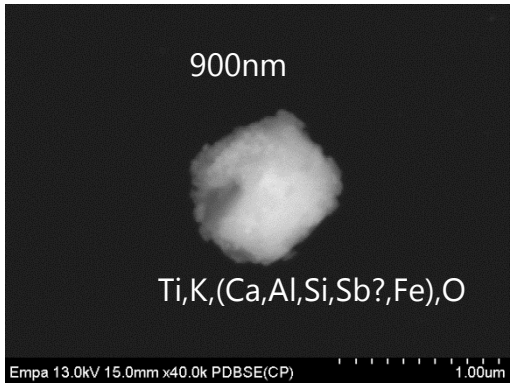
SET 2

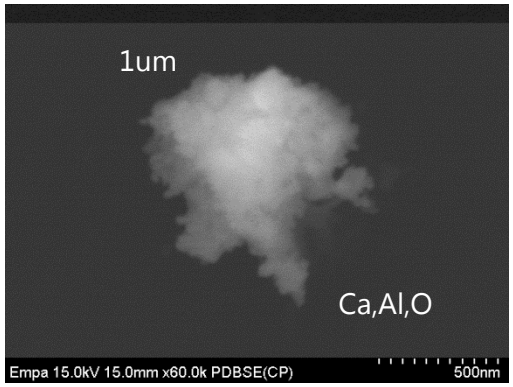
STEP 7 840nm

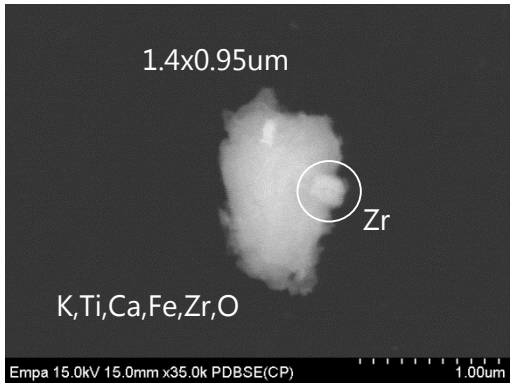


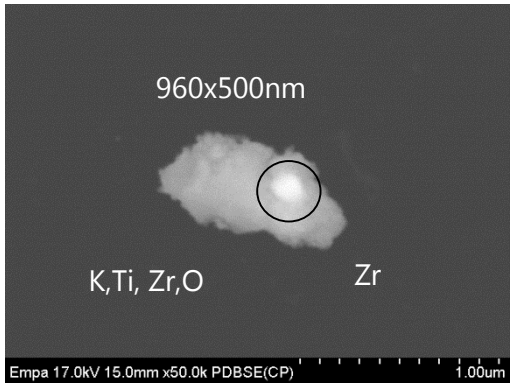




STEP 8 1327nm







SEM BSE images of different aggregates.

Polyphase aggregates (>~4µm) Fe, Ti, Ca, Si, Al, Mg, K, C, and less Sn

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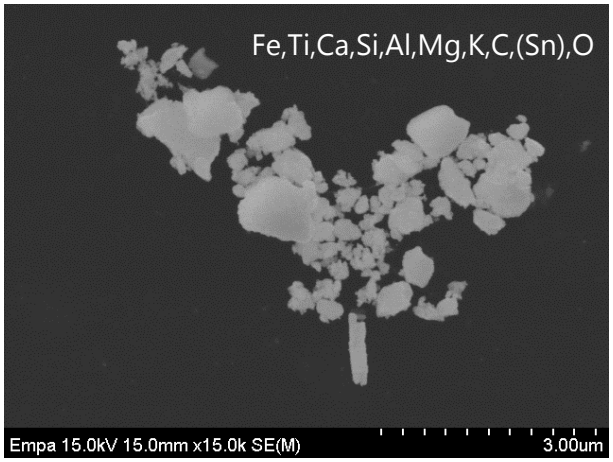
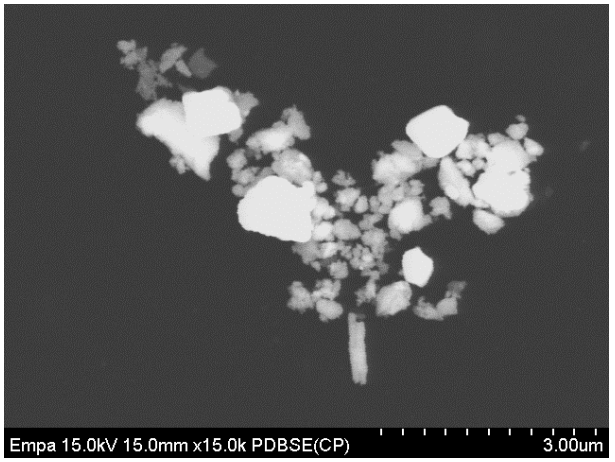
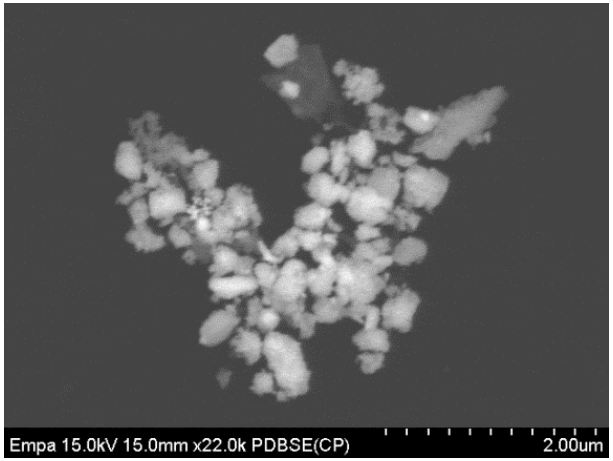
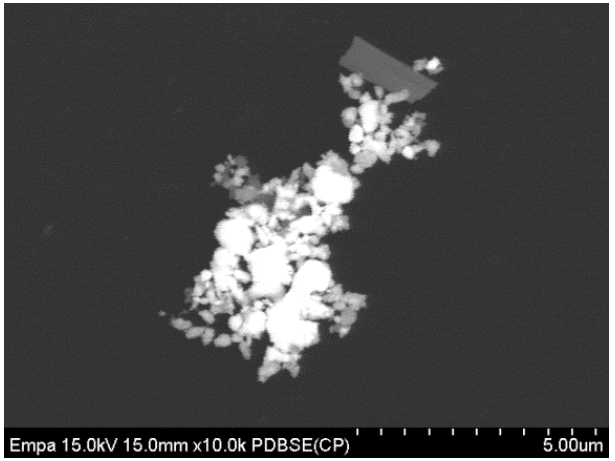
SET 2









Different element, element combinations K, Al, C, Ti, Fe, Ca, Si, and minor Sn, Mg.

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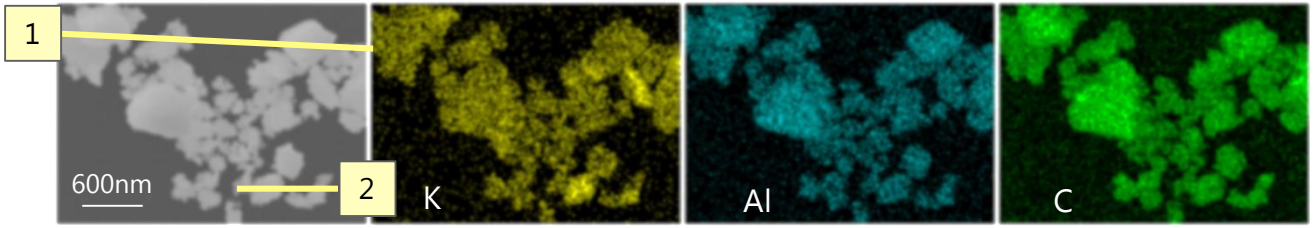
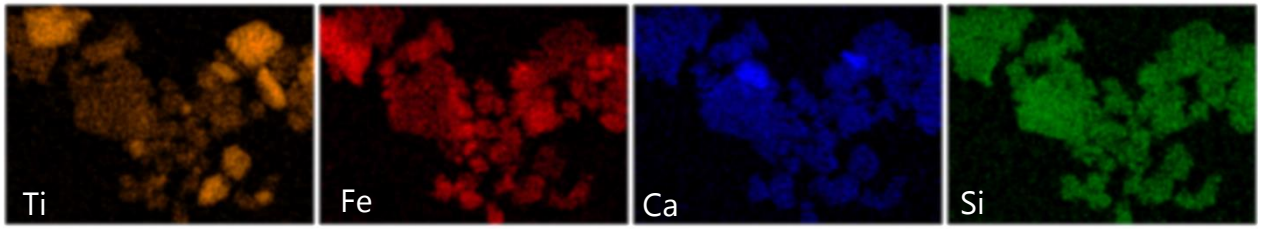
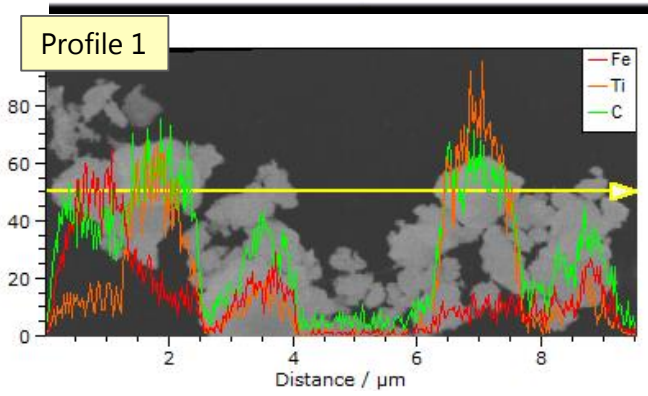
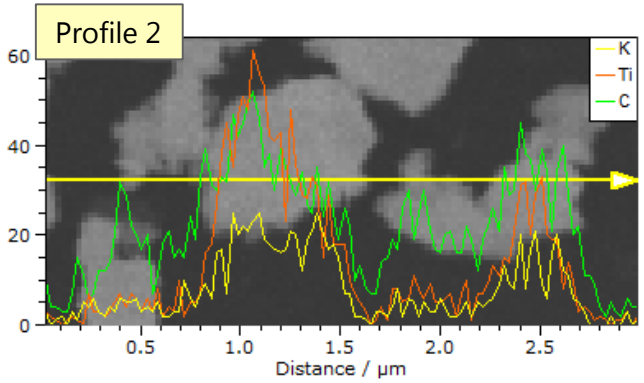
SET 2









The particle constituents of the mapped aggregates are composed of different elements or element combinations: Fe, Ti, Ca, K, Si, C and less Al, Sn, Mg.

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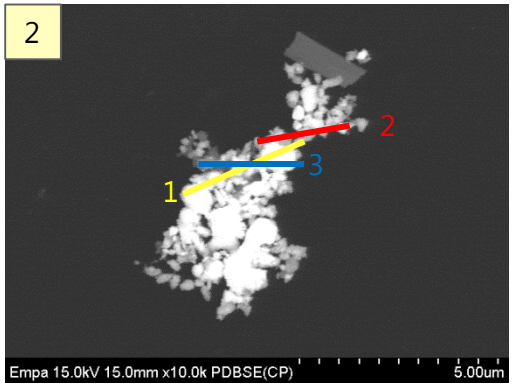
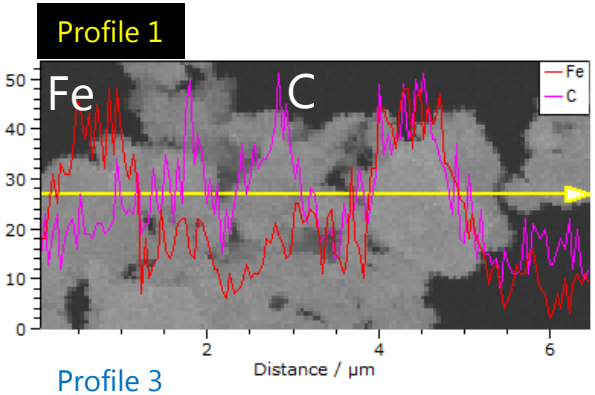
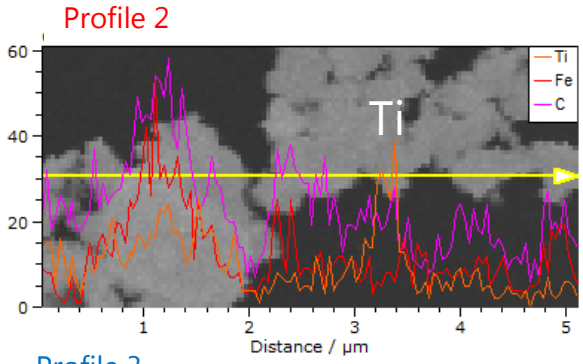
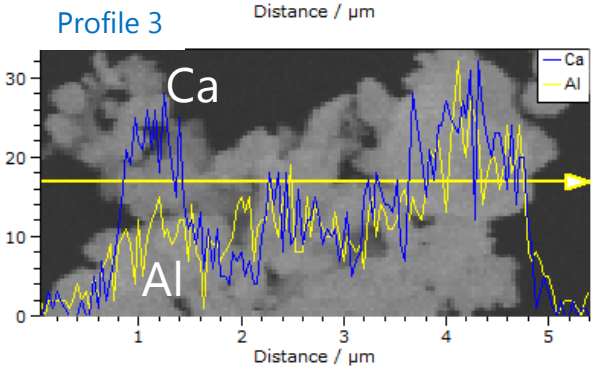
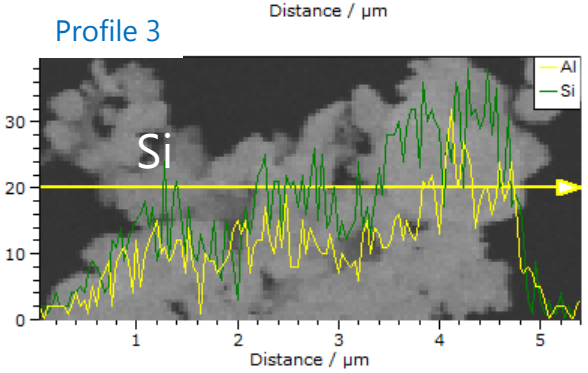
SET 2











BSE images and element distribution profiles of a ~7um long aggregate consisting of particles with different size and chemistry; the element profiles indicate coexisting (or not) elements in different particles.

Aggregate with prismatic to fibrous constituents composed of Ca, Si and traces of K, Al.

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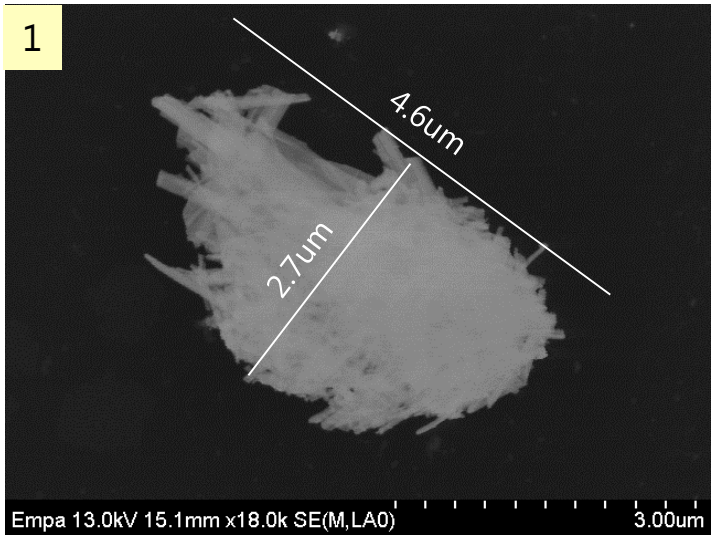
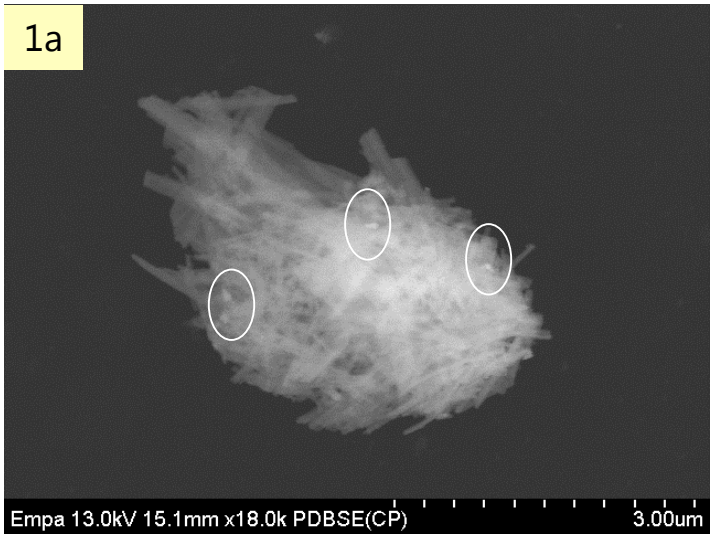
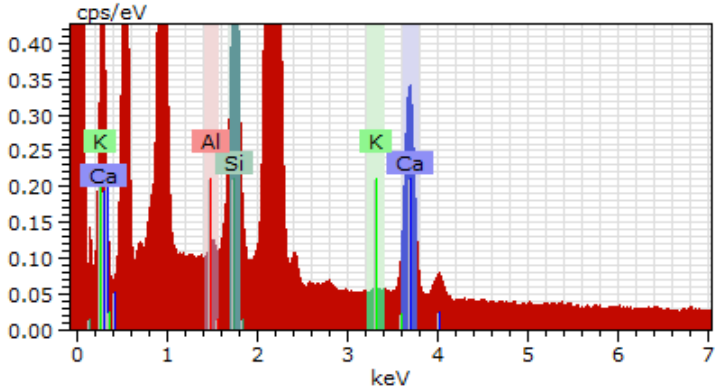
SET 2







SEM SE (#1) and BSE (#1a) images of a Ca-Si-bearing aggregate; Bright 'spots in #1a (encircled) probably correspond to Zr-bearing particles.

- Particle sizes:
  - In the first four size classes (Di<220nm) of both sets, abundant small particles (<100nm)
  - In the first 2 size classes (<85nm) of both sets, the majority of the particles are <20nm
  - In both sets, particles occur as aggregates (a few tens of nm to a few um large), made of constituents with different chemistry
- Particle shapes:
  - small size classes (steps 1 to 4): SET1 usually circular and very thin (disc-like) shapes;

    SET2 : circular and irregular shapes; also very thin
  - class 5 and larger: irregular, nearly equidimensional, elongated, with rounded outlines; similar shapes for both sets
- Particle chemical composition
  - Very small particles (~20nm) in SET1: Ca±Fe; SET2:Ca±Ti
  - Larger aggregates (~70-250nm) SET1: most encountered often Ca, also Al, Mg, Fe, Sn, Ti. SET2: mainly Fe, Ti, also Al, Mg, Ca, Si
  - Agglomerates probably consisting of Carbon particles with a soot internal structure were identified in the small size classes (steps 1 and 3) of Set 2
  - Large size classes (class 5 and larger; >340nm):
    - Set 1: Fe, Al, Sn, Mg, Si, Cr, W and smaller amounts of Ti, Ni and Ca. Bi, Ba, C, as well as Zn were analysed in a few aggregates
    - Set 2: Fe, Ti, Ca, Si, Al, K, Mg, and less Sn, Zn, Cr, Zr, C(?) and Mn; Ba, W and S were rarely analysed; Sb, Bi and F (F together with Ca) were found –individually- in one case