IAEA-CN301-086

A combined XRF and XANES study on bottom ashes from municipal solid Waste-to-Energy plant

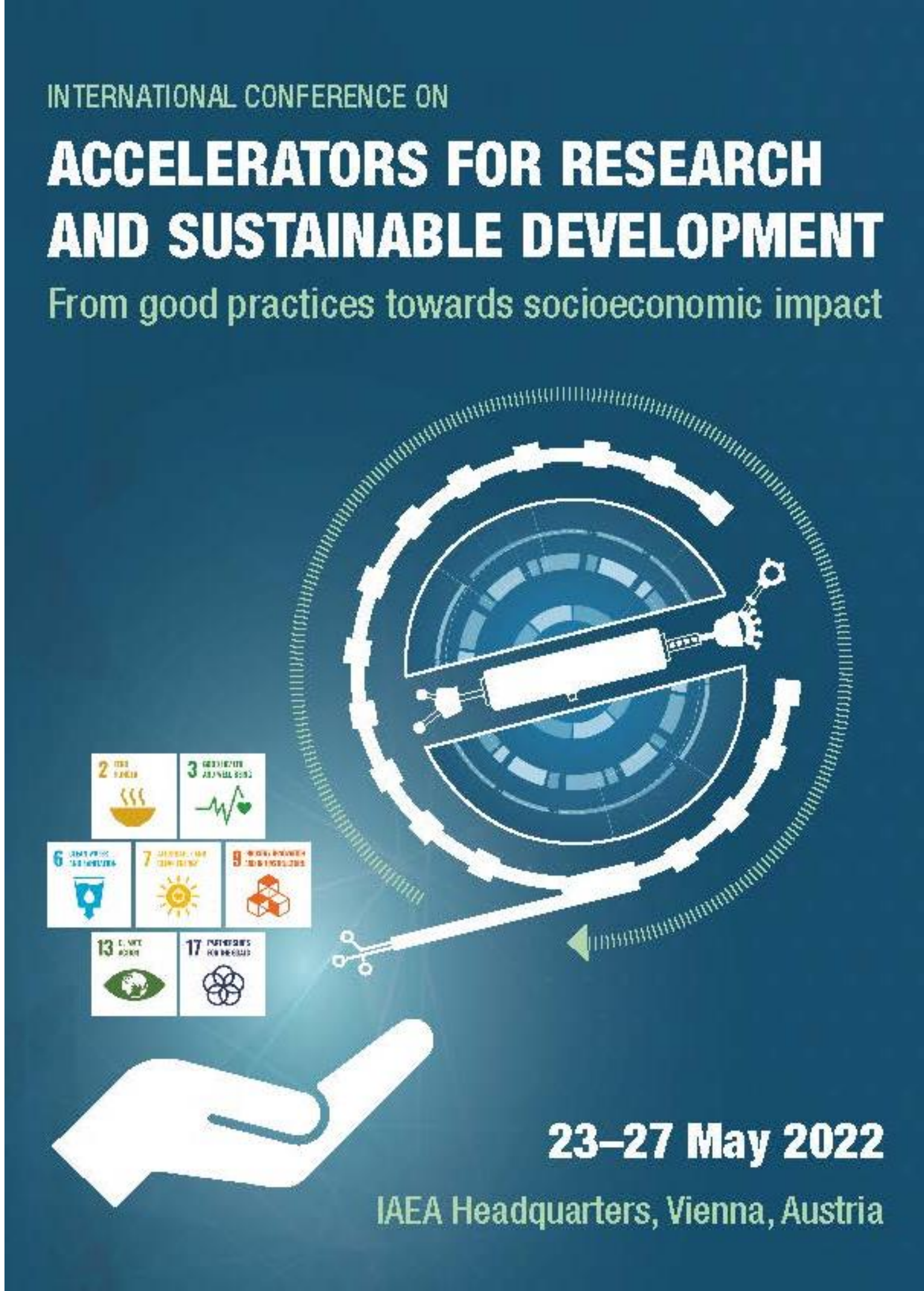
Simone Pollastri[1], Chiara De Matteis[2], Luciana Mantovani[2] and Mario Tribaudino[3]

[1]Elettra - Sincrotrone Trieste S.C.p.A.

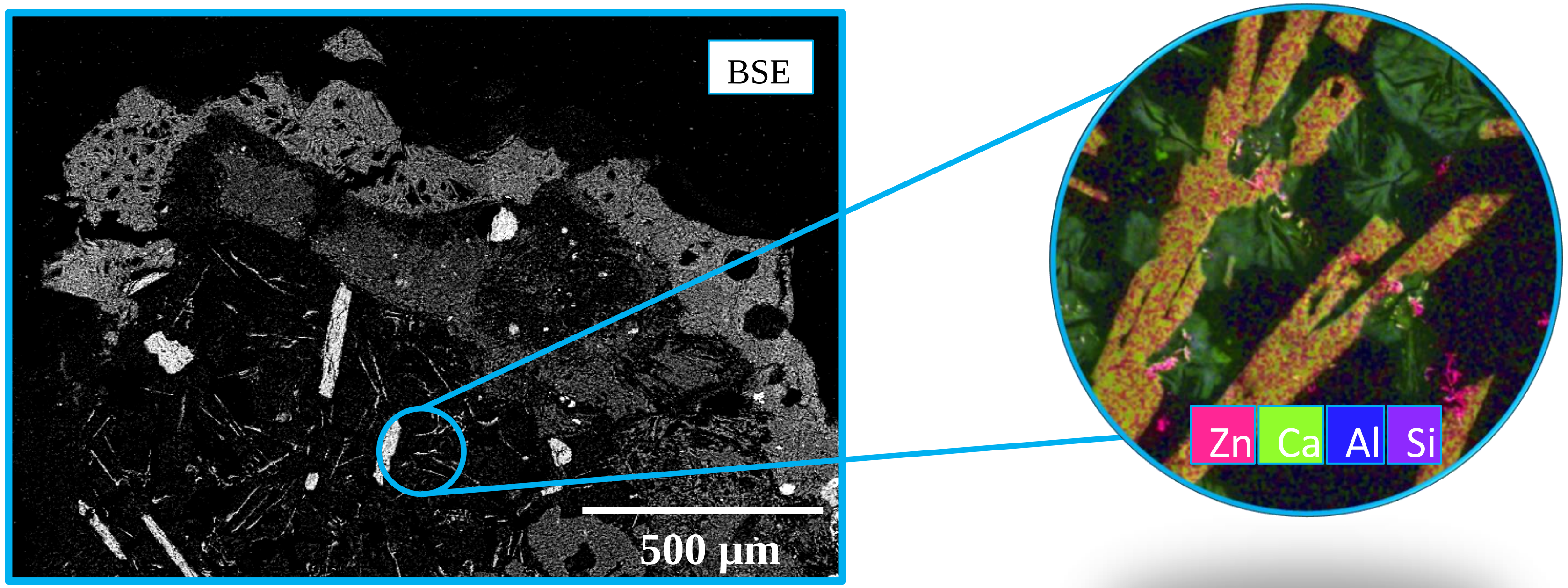
[2]Università di Parma, Dipartimento di Scienze Chimiche, della Vita e Sostenibilità Ambientale

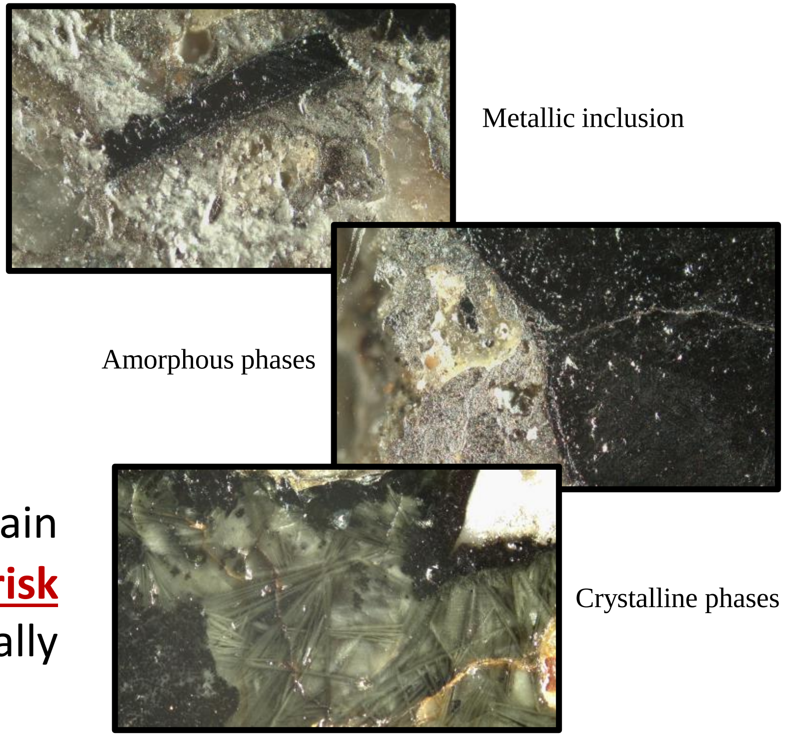
[3]Università di Torino, Dipartimento di Scienze della Terra

simone.pollastri@elettra.eu



Only in Italy, **each year about 30 million tons** of urban waste are produced, of which **5.3 million are disposed for combustion in incinerators and Waste to Energy plants (WtE)**; the process then produces about one million tons of ashes. These ashes are made by bottom ashes (BA) and fly ashes (FA).

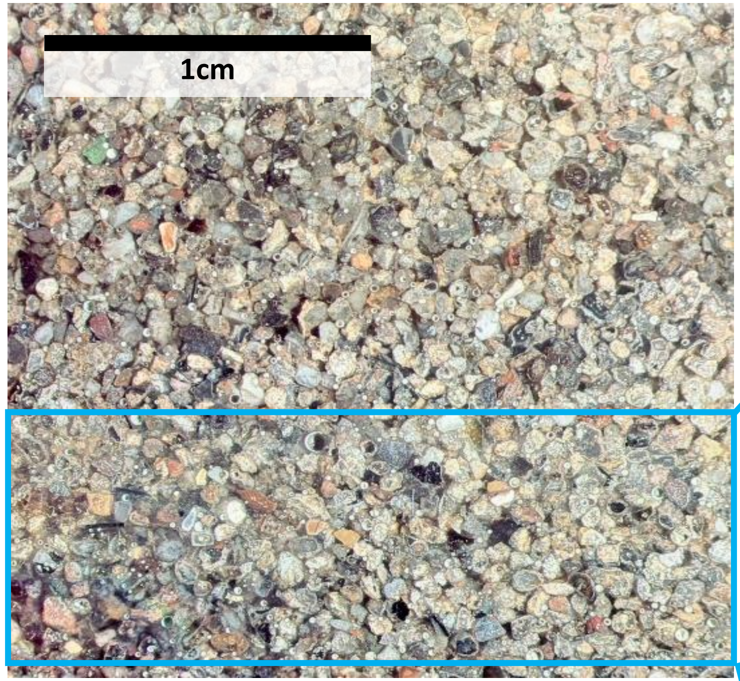




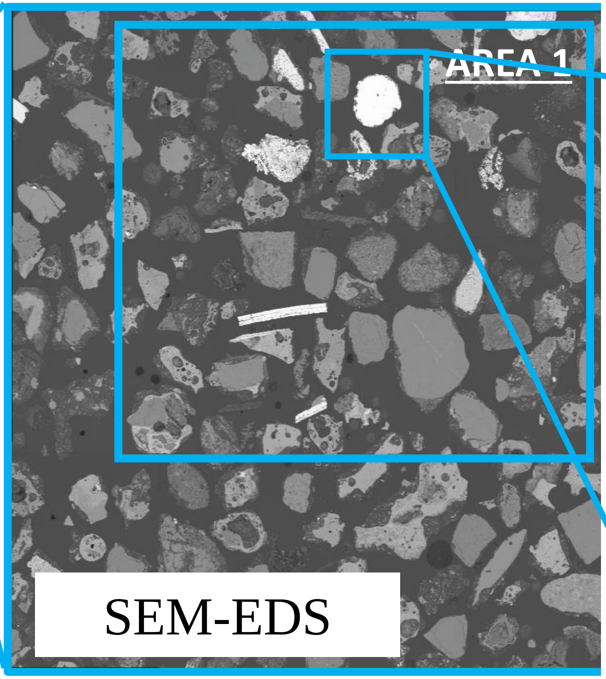
Whereas FA are classified as dangerous waste, BA can be recycled and are the main secondary raw material from combustion plants. Nevertheless, an assessment of the **risk for environmental pollution and health** is needed because of the content of potentially dangerous elements (PTE) such as Zn, Pb, Cu, Cr and Ni.

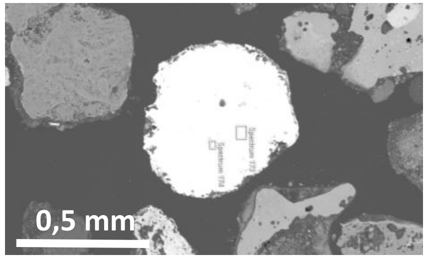
International Conference on Accelerators for Research and Sustainable Development
#Accelerators2022
23–27 May 2022
IAEA, Vienna, Austria

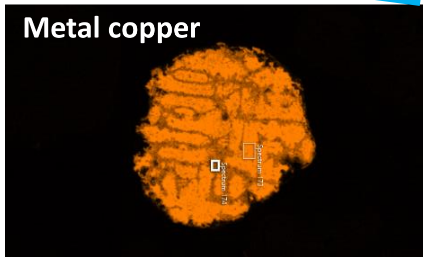
Optical microscope

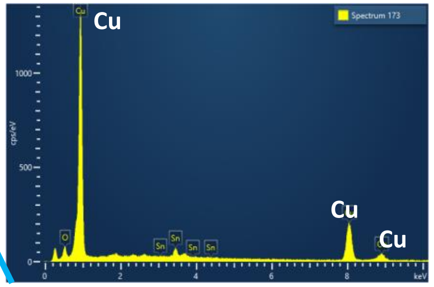


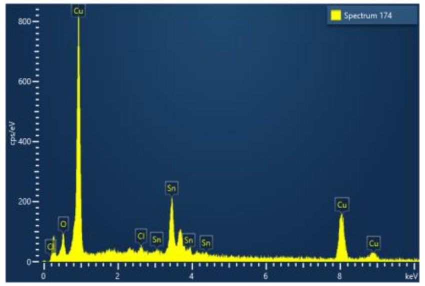
Recycling BA as a secondary raw material represent an interesting, environmentally friendly, alternative solution to landfill disposal. Nevertheless, any form of recycling requires an **assessment of the potential pollution for environment and health risk**.





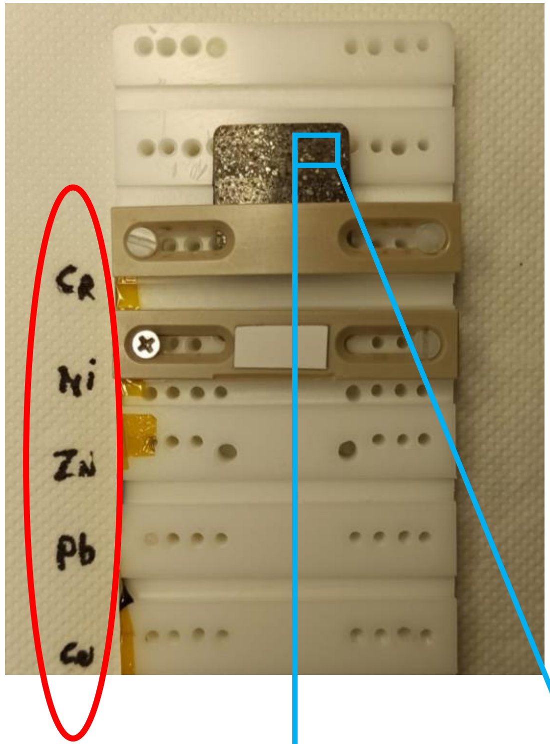






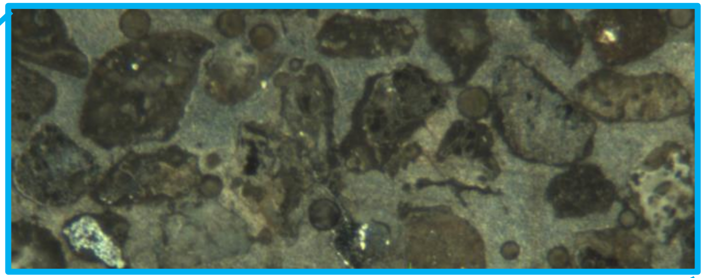
For this reason, few grains of BA (grain size 0.5 -1 mm) from a waste-to-energy plant, have been embed in epoxy resin and then polished on one side to perform SEM-EDS, XRF mapping and XANES measurements.

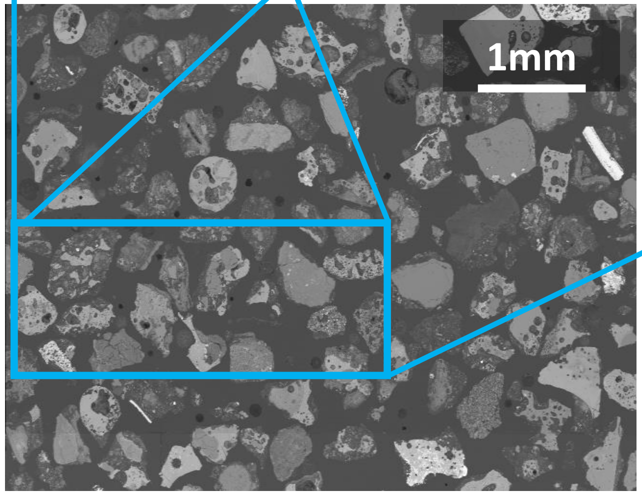
SEM-EDS ANALYSIS



Bottom ashes sample mounted on the Teflon sample holder available at the XRF beamline

Optical microscope (XRF beamline)

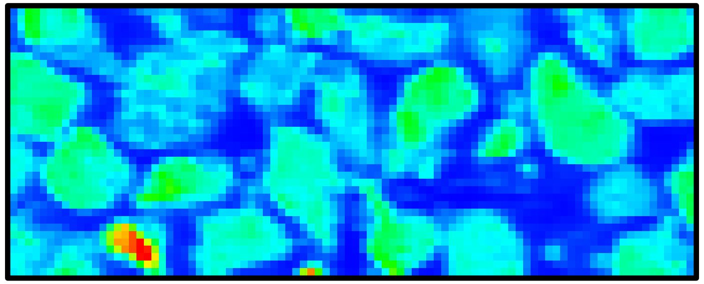




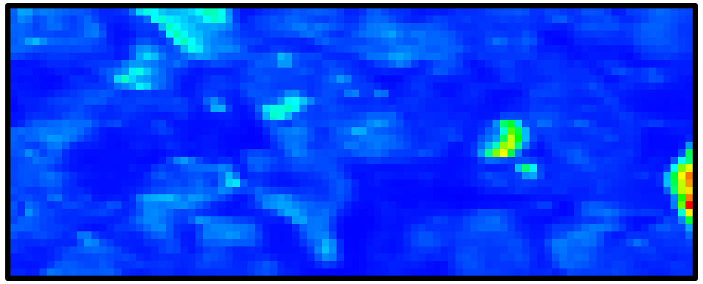
SEM

Roughly the same areas investigated with SEM-EDS were selected for also uXRF mapping and XANES measurements.

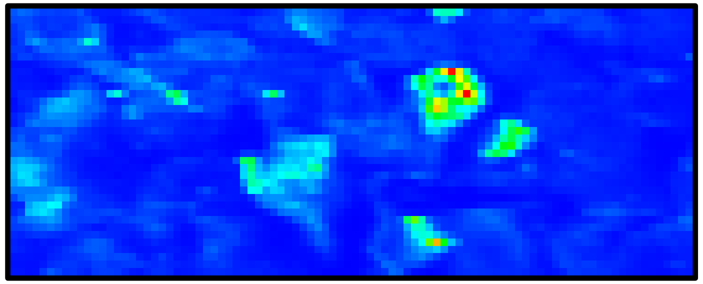
ICR



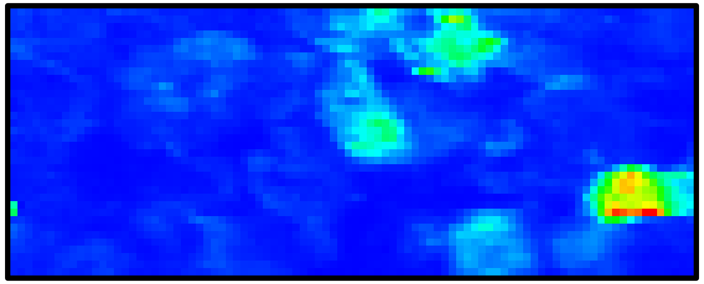
Zn Kα



Cu Kα

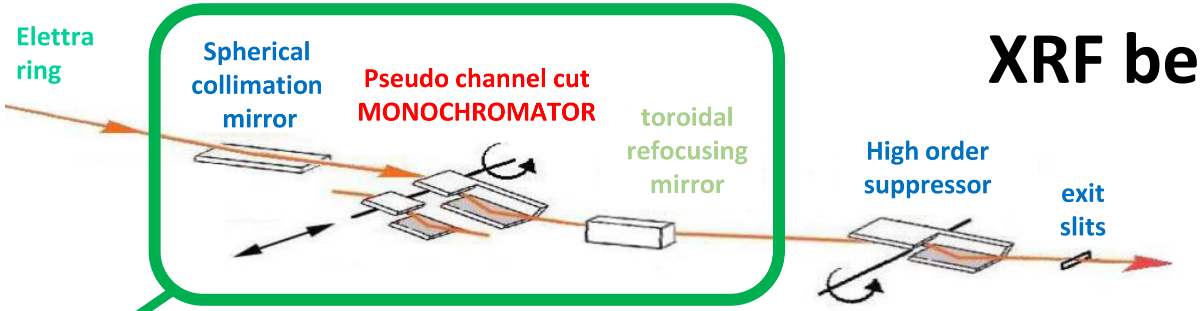


Pb Lα

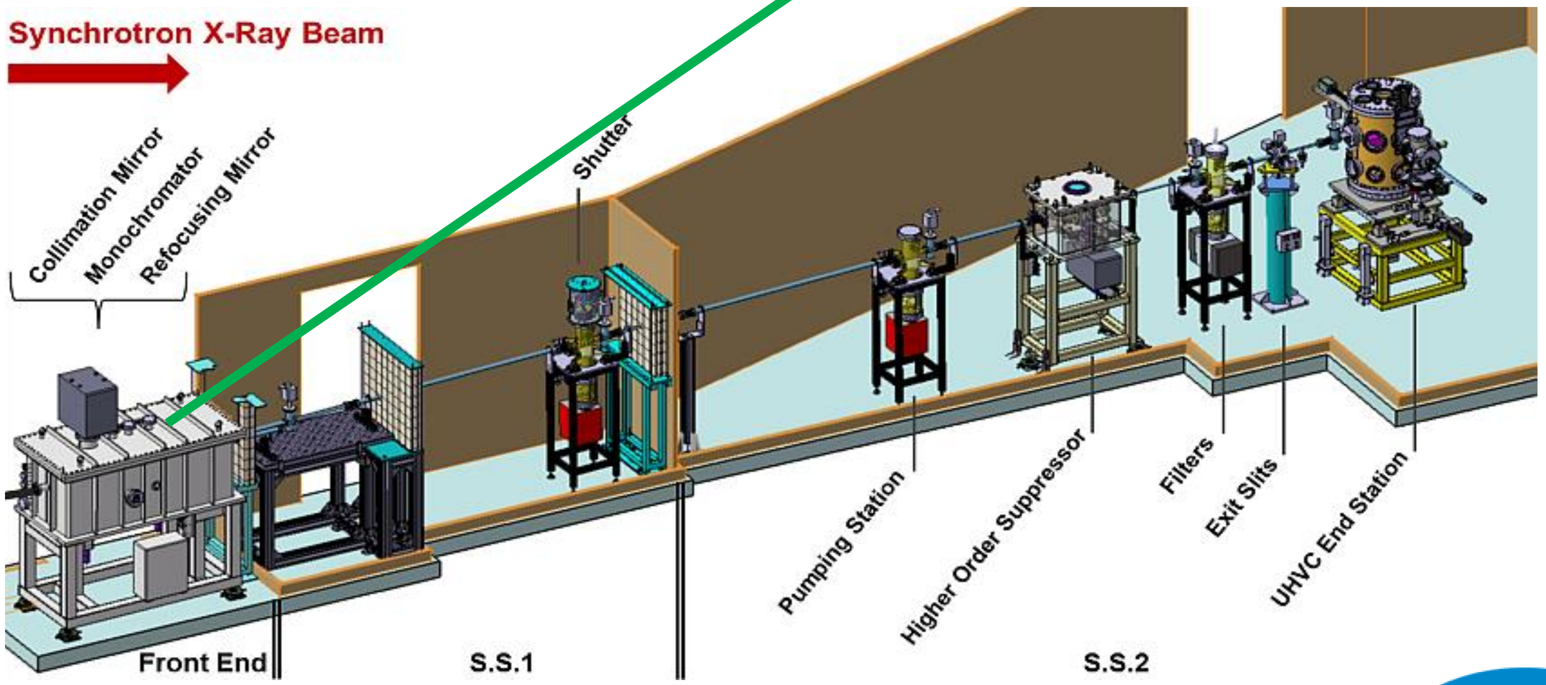


XRF beamline overview

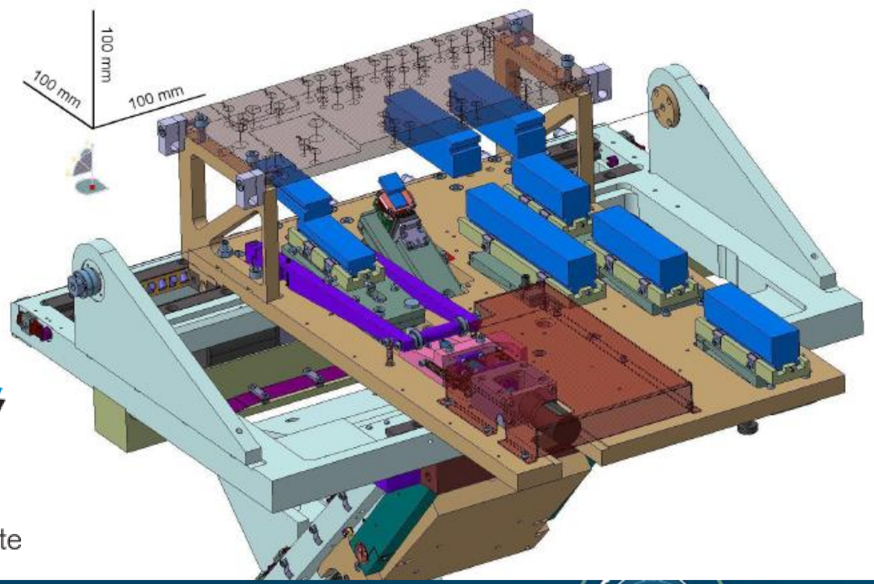
Source	Bending magnet
Flux	10^9 - 10^{11}
Spot size	min 25 x 25 (H x V) μm^2



Optics type	E range (keV)	E resolution (ΔE)
Si(111)	3.6 - 14	~ 1 eV at 7 keV
InSb(111)	2.0 – 3.8	~ 1eV at 2.2 keV
ML: High E (RuB_4C)	4.0 – 14.0	~ 55 eV at 1 keV ~ 180 eV at 14 keV
ML: Medium E (NiC)	1.5 – 8.0	
ML: Low E (RuB_4C)	0.7 – 1.8	



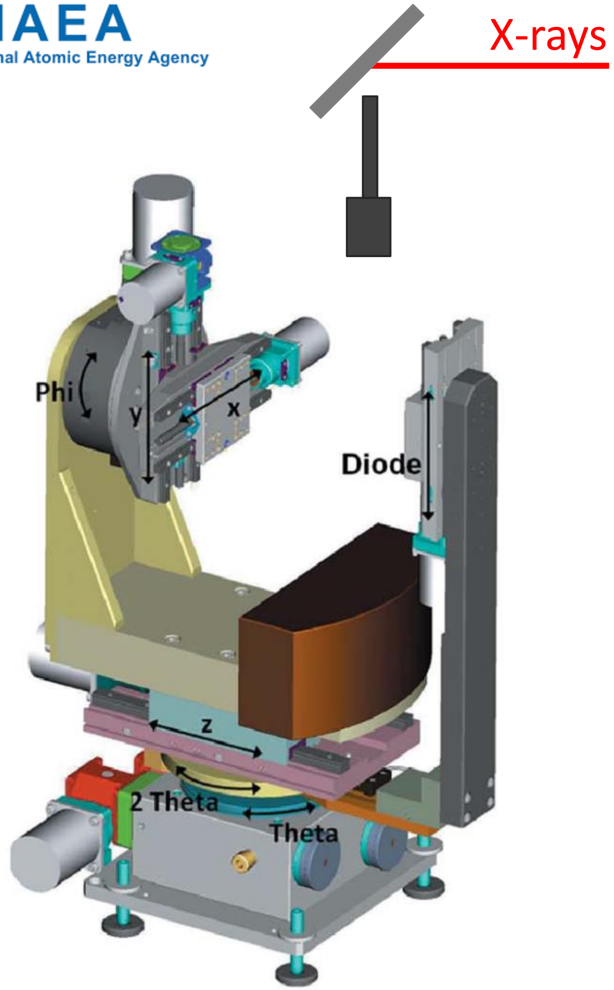
Jark *et al.*, 2014



Elettra Sincrotrone Trieste

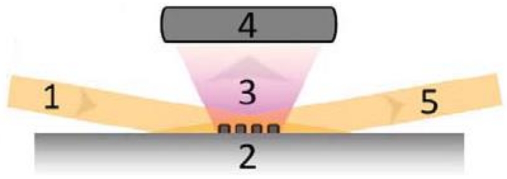
XRF beamline overview

45/45 geometry



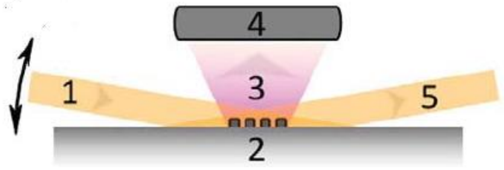
Grazing angle geometries

Total reflection



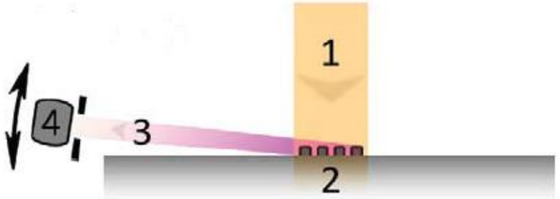
Trace element analysis
Surface contamination

Grazing incidence



Depth profiling measurements

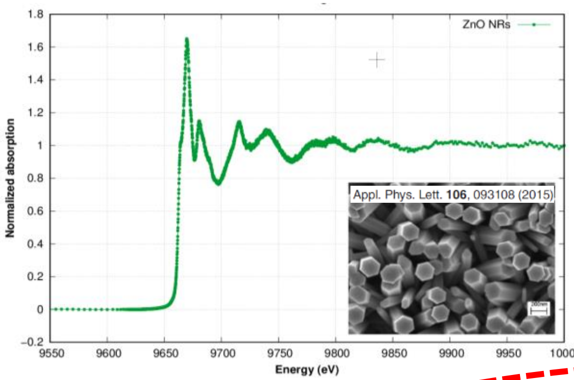
Grazing exit



Surface mapping
Depth and lateral inhomogeneity

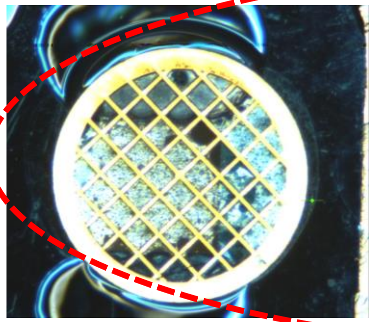
XRF beamline overview

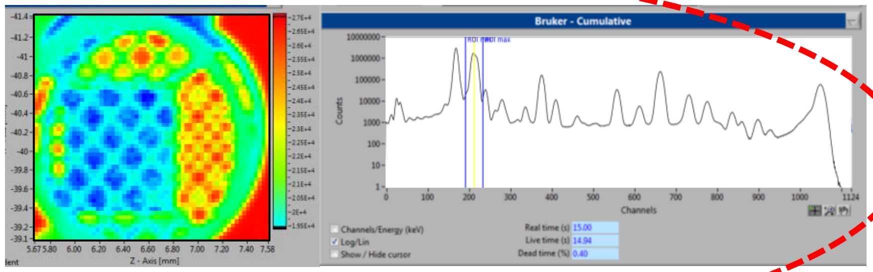
Analytical capabilities:



- **GIXRF and GI-XANES** (nano-layered structures or shallow dopants in semiconductors with nm depth resolution)

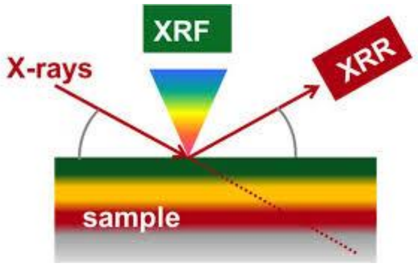
- **TXRF and TXRF-XANES** (elemental/chemical characterization of liquid samples residues or particulate matter samples collected directly on reflector surfaces the at the ultra-trace concentration level)

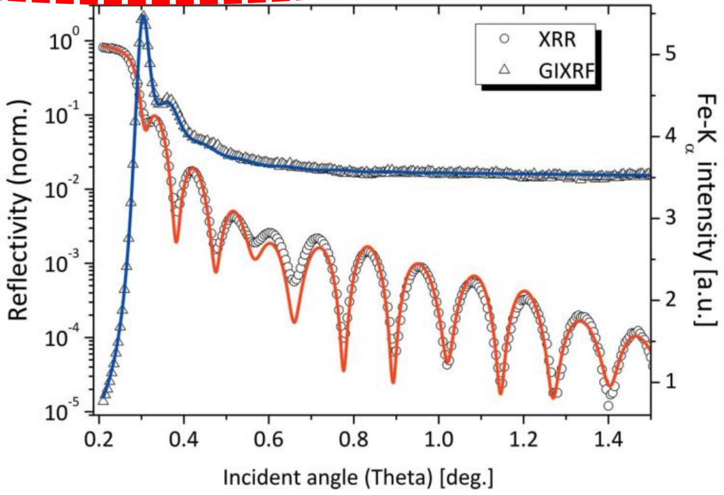




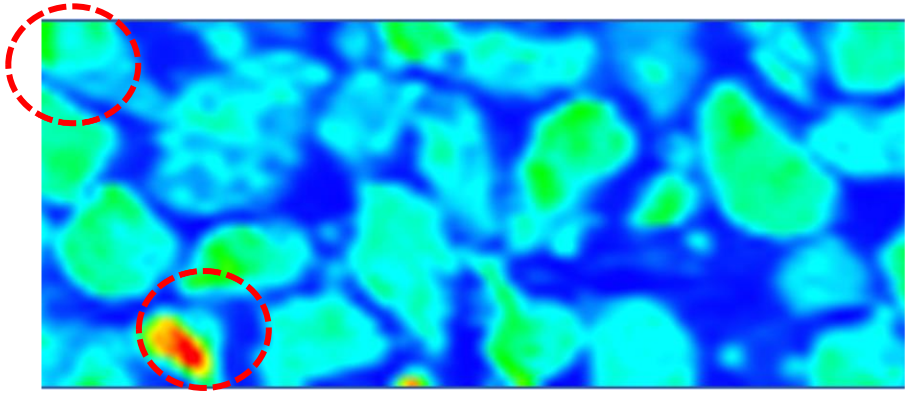
- **2D scanning XRF and XANES** (study and quantification of the elemental composition or chemical speciation over different areas of the sample)
  standard 45/45 geometry.

- **XRR** (structural analysis - thickness, density - of thin films and multi-layered structures)

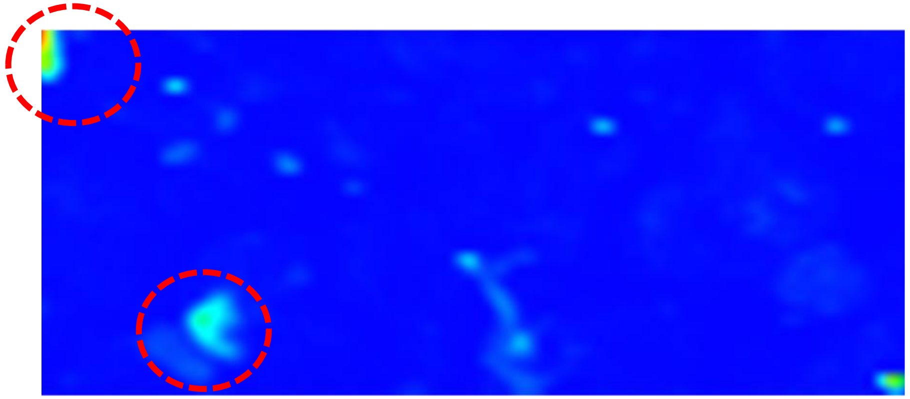




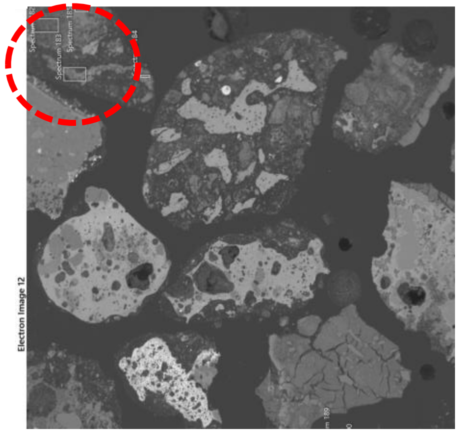
chromium

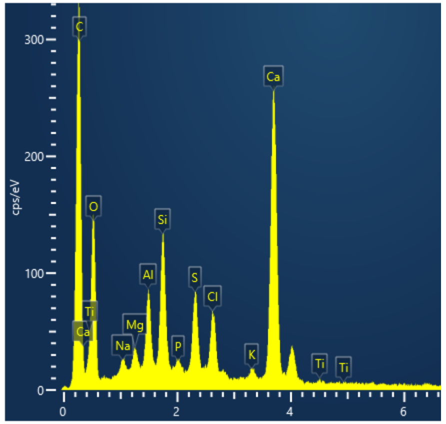


ICR

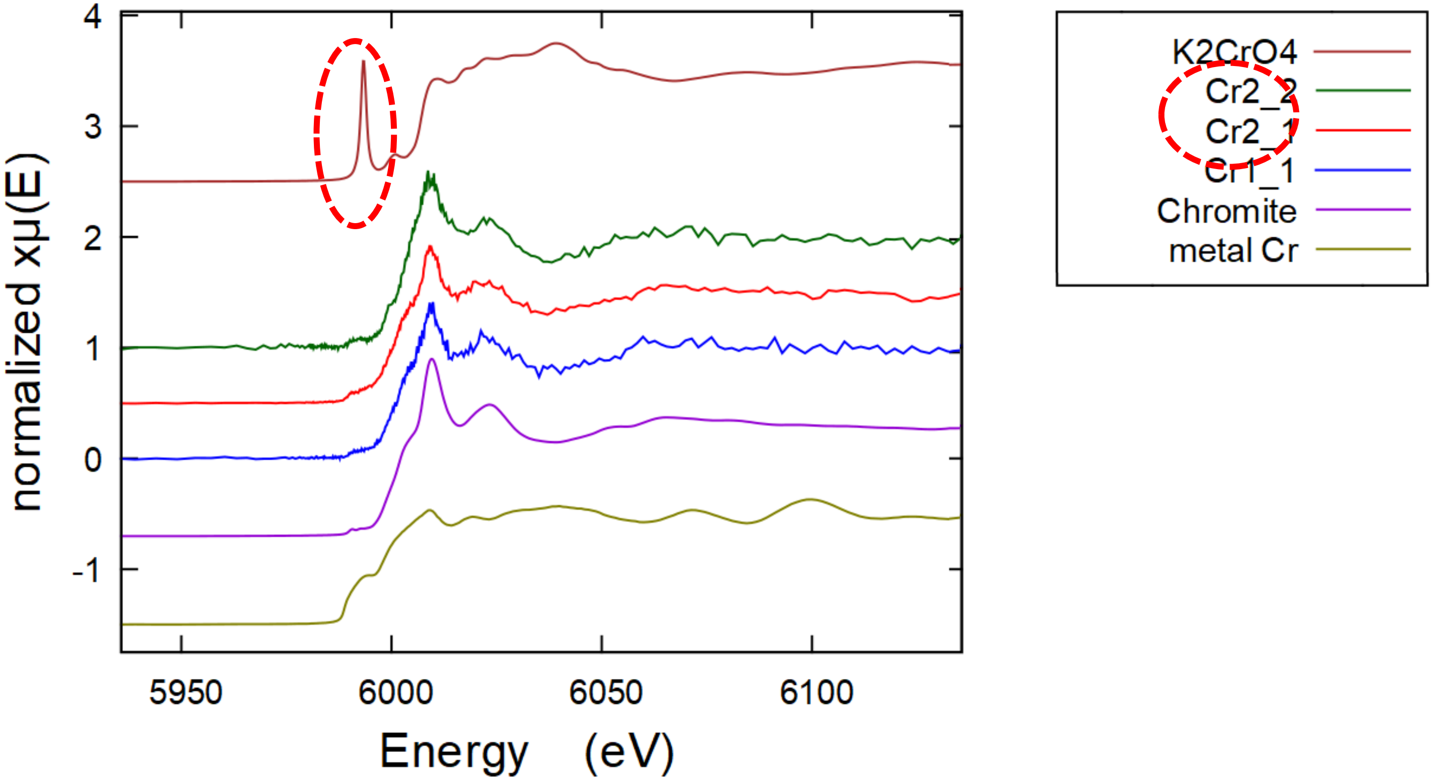


Cr Ka

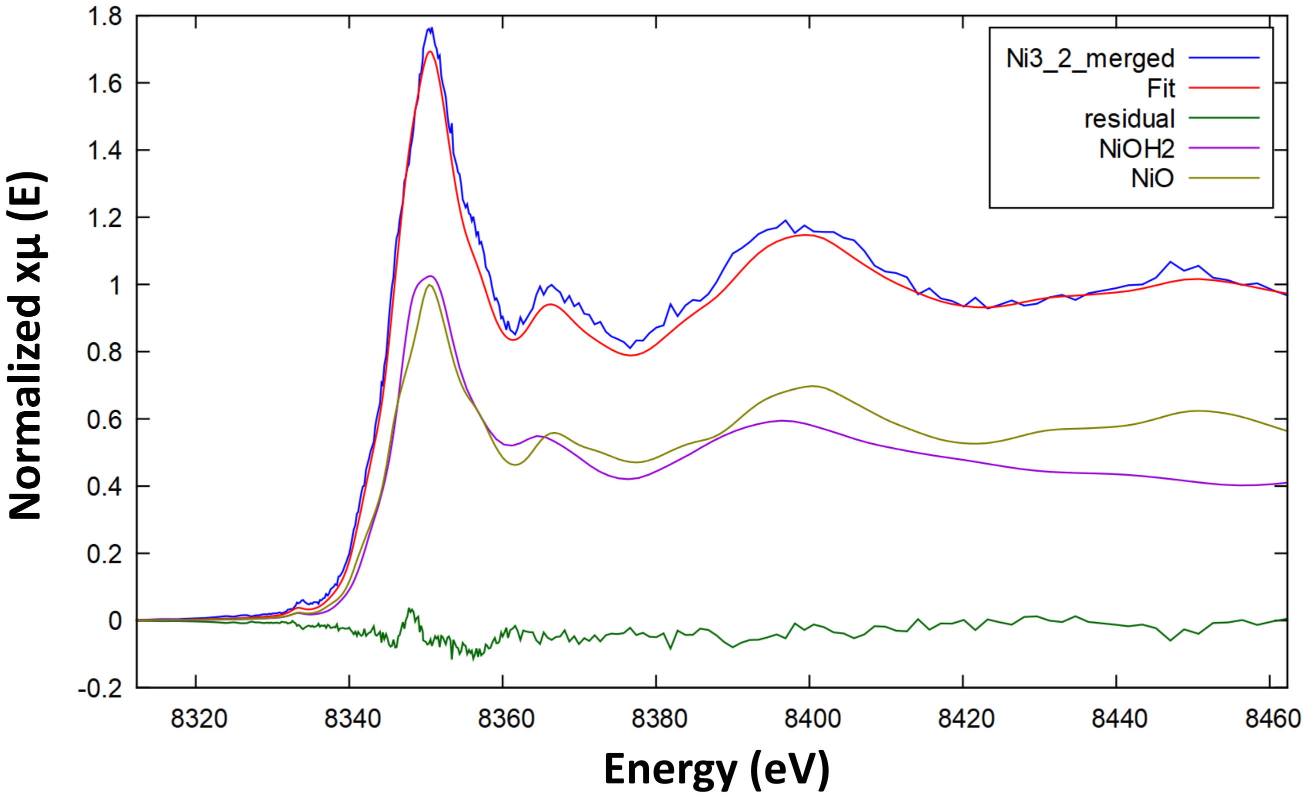




A preliminary look to the XANES data collected at the Cr K-edge permits to exclude the presence of Cr^{6+}, as all the collected spectra have features resembling that of Chromite (Cr^{3+}).



No Cr detected by SEM-EDS!!



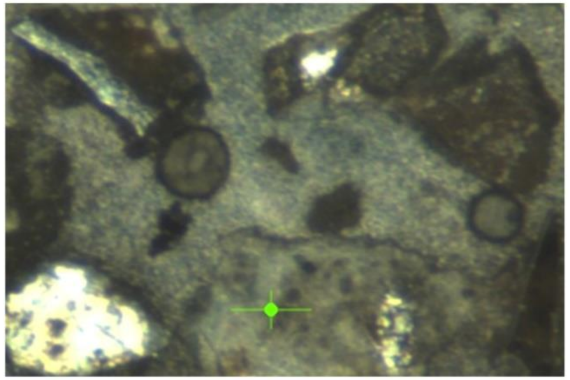
Example of a fit obtained through LCF analysis on a Ni spectrum.

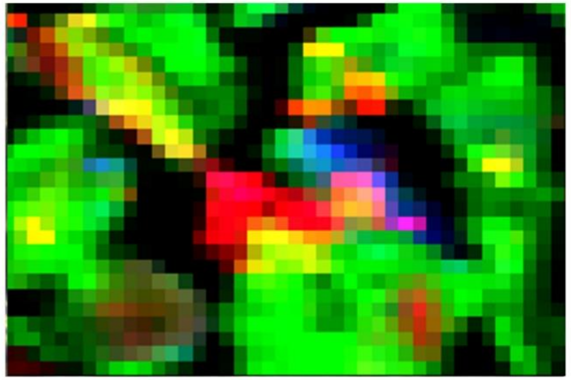
nickel

Concerning Ni, the oxidation state is considerably changing between different clasts, ranging from mainly metallic to divalent.

Results of the LCF analysis

Sample	Metal Ni Ni^0	NiO* Ni^{2+}	$Ni(OH)_2$* Ni^{2+}	Sum
Ni1_1	-	17 (10)	83 (10)	100
Ni1_2	-	40 (16)	60 (12)	100
Ni1_3	35 (3)	13 (10)	52 (14)	100
Ni2_1	66 (2)	34 (16)	-	100
Ni2_2	-	-	100	100
Ni2_3	28 (11)	49 (9)	23 (8)	100
Ni3_1	84 (5)	16 (20)	-	100
Ni3_2	-	67 (7)	33 (4)	100





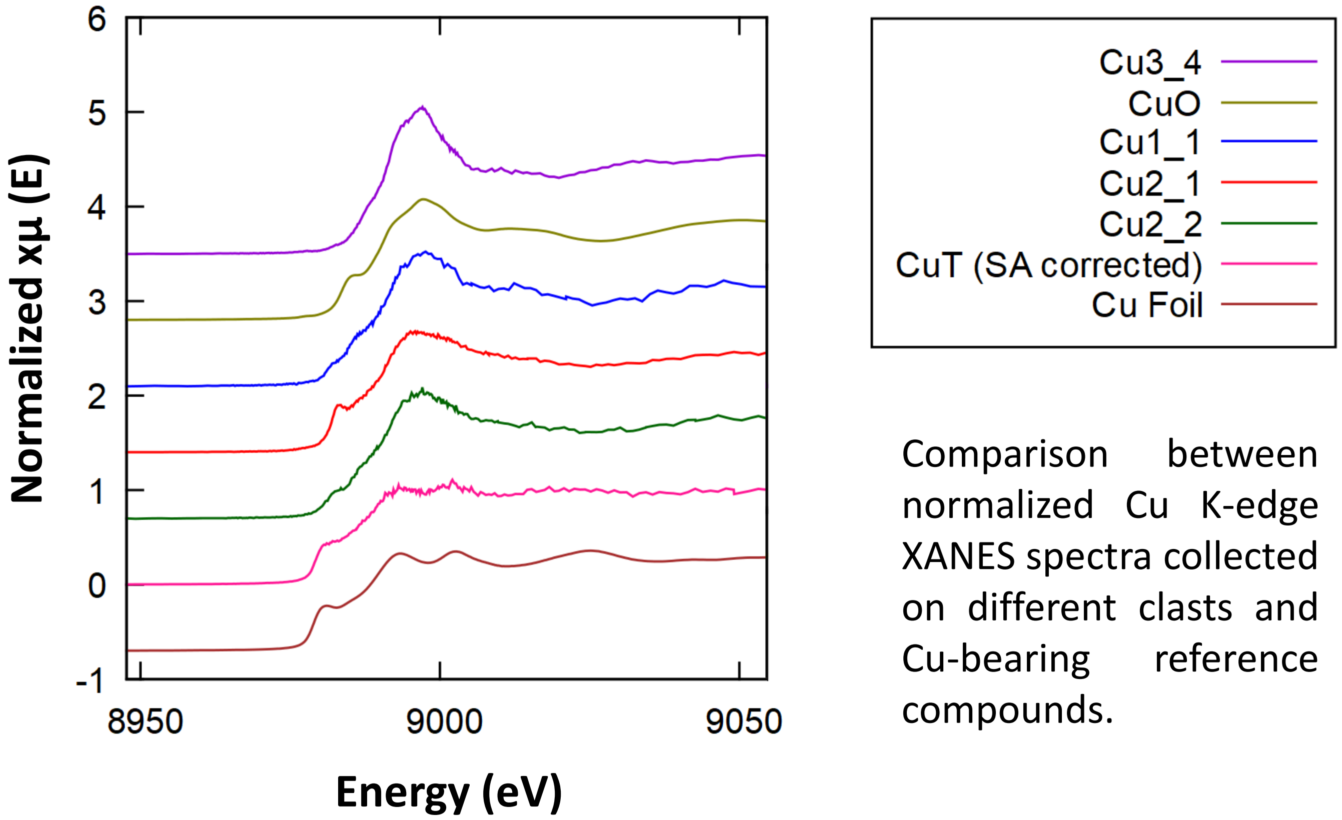
The clast named Cu3_4 from micro camera (on the left) and the corresponding XRF map of Cu (red), Zn (blue) and Ca (green) highlighting its heterogenicity (right).

Results of the LCF analysis

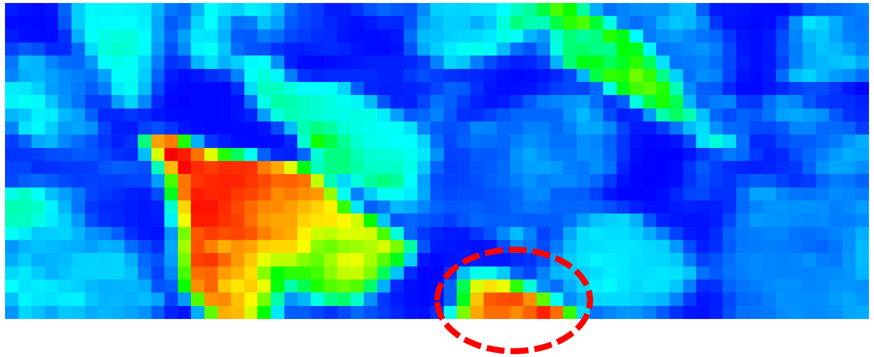
Sample	Metal Cu Cu^{0}	Cu_2O Cu^{1+}	CuO Cu^{2+}	Sum
Cu1_1	-	6 (4)	94 (2)	100
Cu2_1	10 (4)	24 (5)	66 (3)	100
Cu2_2	-	13 (4)	87 (3)	100
CuT	80 (3)	16 (4)	4 (2)	100

copper

Cu appears to be present both in metal and oxidized form. The precise oxidation state and coordination geometry of all the investigated chemical elements have been determined through linear combination fit (LCF) analyses.



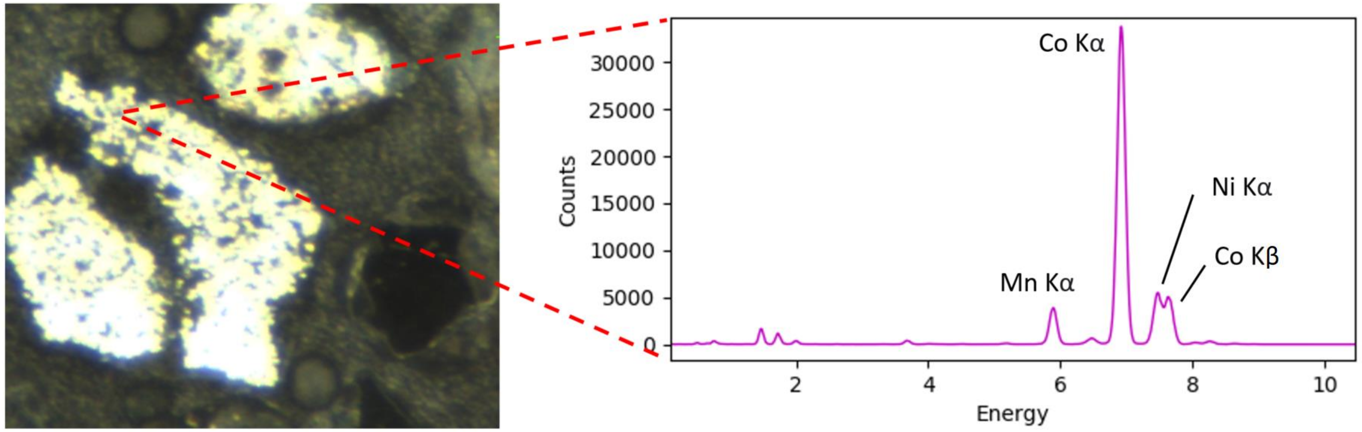
Comparison between normalized Cu K-edge XANES spectra collected on different clasts and Cu-bearing reference compounds.



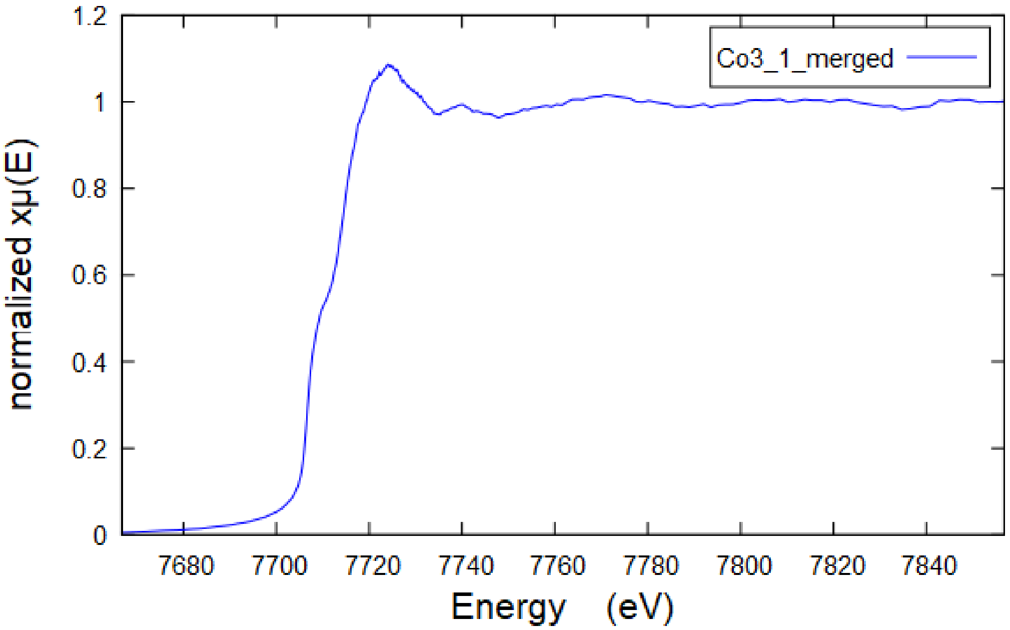
cobalt

Only one clast have been investigated by XANES at Co K-edge. XRF mapping highlight that is composed mainly of Mn, Co and Ni. LCF result give a composition of 68% (7) metal Co and 32% (4) CoO.

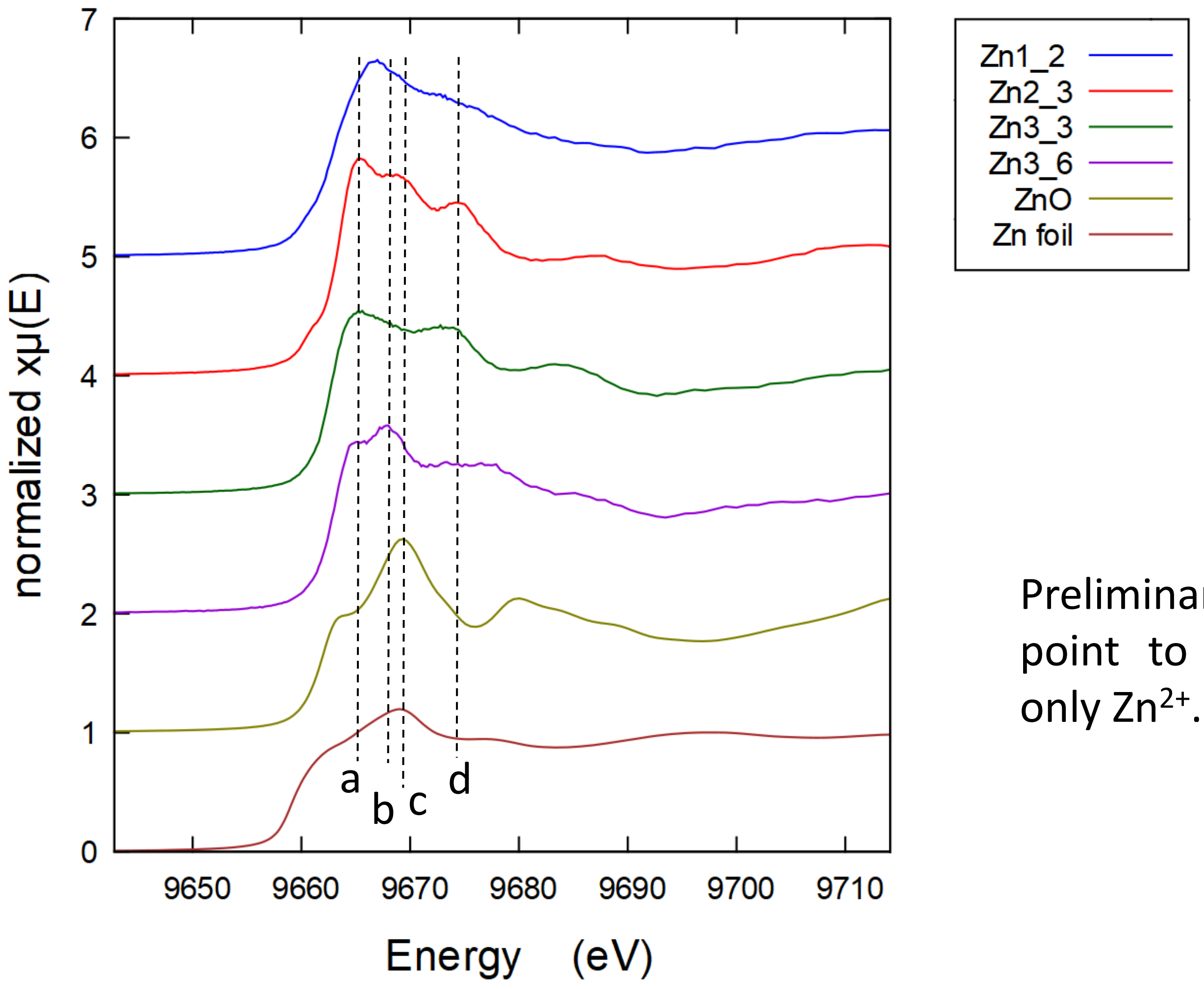
On the same clast, also Ni K-edge XANES spectrum was collected (labeled as Ni3_1) and LCF result is 84% (5) metal Ni and 16% (20) NiO. Hence, according to the chemical composition and XANES results, **it might be a MnCoNi alloy.**



The photo on the left has been taken with the micro camera available at XRF beamline on the clast named Co3_1. On the right, the XRF spectrum of the clast.



Normalized Co K-edge XANES spectrum collected on clast 3_1.

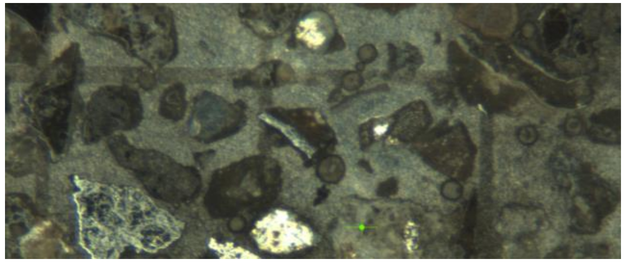


Comparison between normalized Zn K-edge XANES spectra of clasts (selected spectra are representative of the clast variability) with ZnO and Zn foil references. Reference lines labeled a, b and c correspond to the following energy positions: a) 9665,3 eV b) 9667,9 eV; c) 9669,5 eV; d) 9674,1 eV.

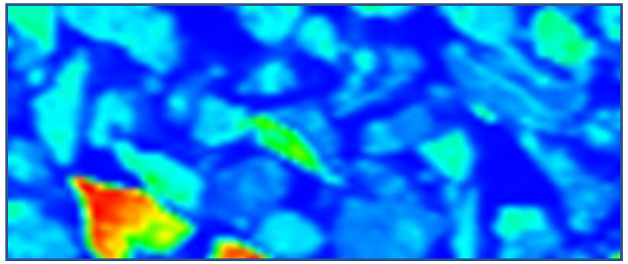
Zinc

Zinc appeared to be **the more abundant among PTE**. In none of the collected data, neither a small amount of metal Zn have been detected. Indeed, the edge position of all the spectra is similar and shifted with respect to reference Zn foil.

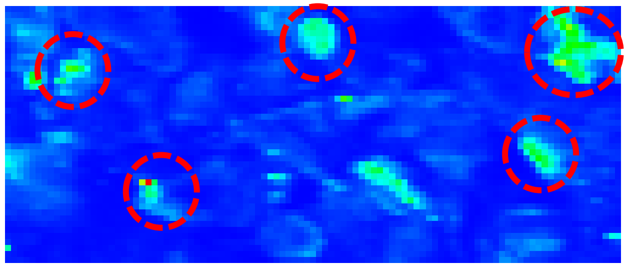
Preliminary LCF results point to the presence of only Zn^{2+}.



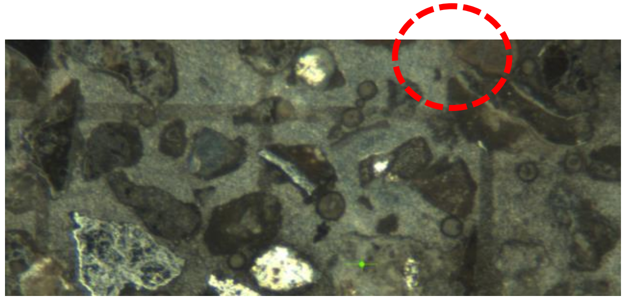
Optical



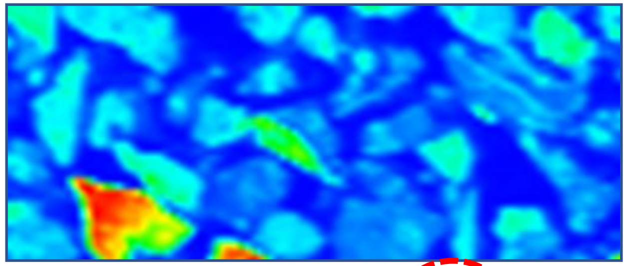
ICR



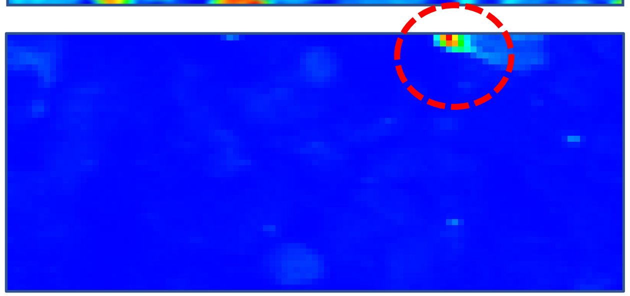
Zn Ka



Optical



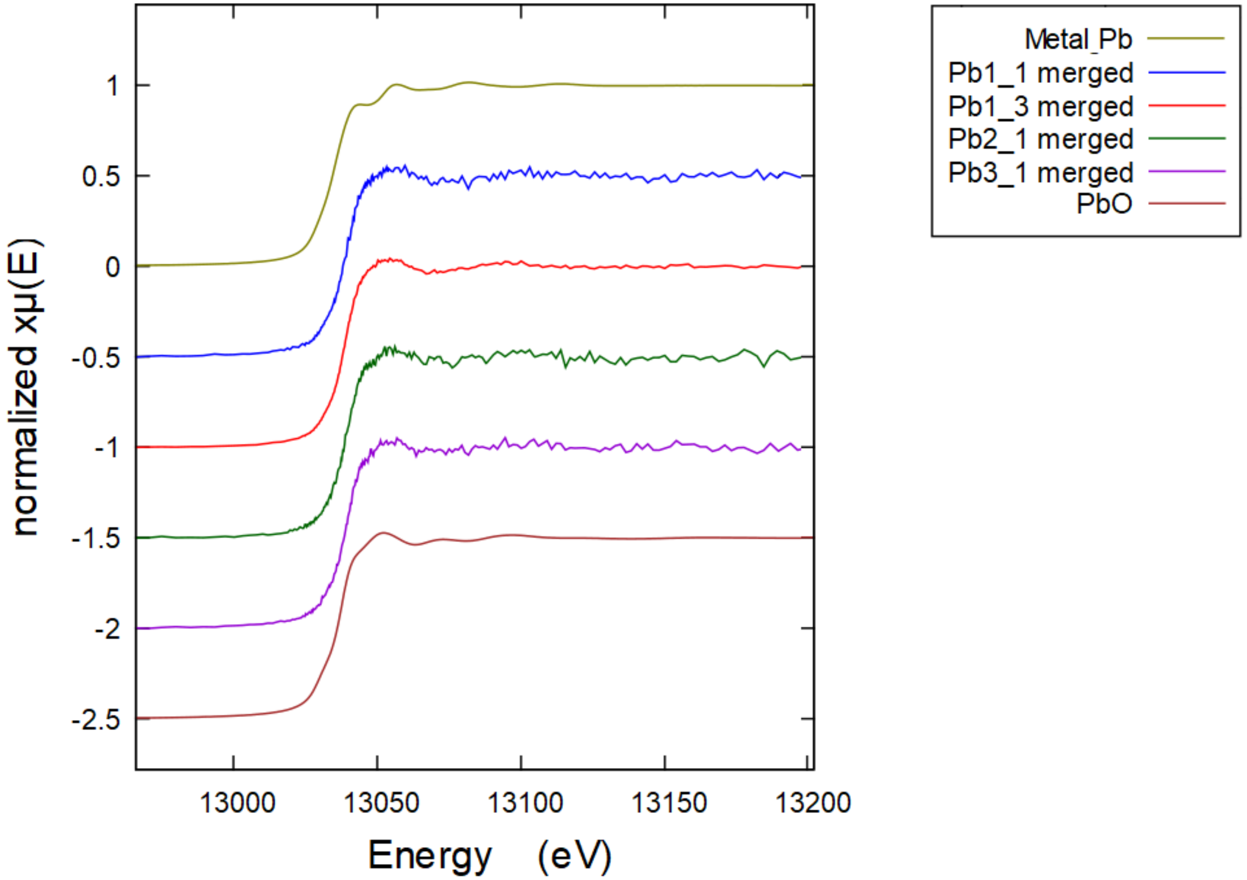
ICR

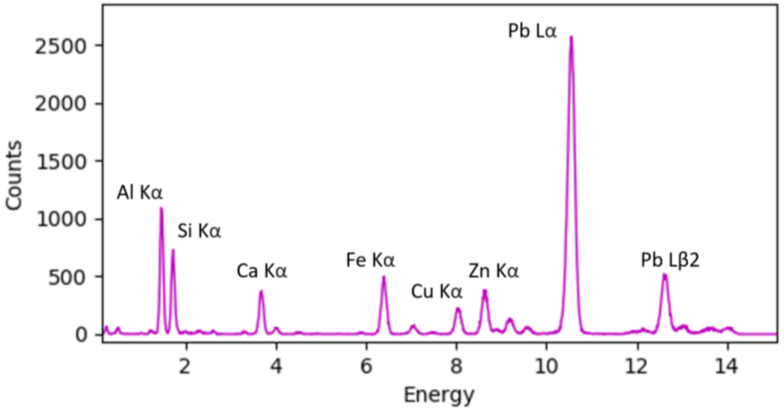


Pb La

lead

All the XANES data collected at Pb L_3-edge on various clasts are almost identical. A fitting approach through LCF analyses was used as for previous data but the results were not satisfactory. PbS and $PbSO_4$ reference spectra were also available but not used as S fluorescence lines were not detected.





full XRF spectrum of the clast Pb3_1.

Final remarks

- ✓ XRF mapping demonstrated to be an excellent tool for such kind of samples, allowi… elements not visible with standard SEM - EDS analyses.
- ✓ XANES LCF analyses permits to determine the chemical environ… …ned out to be present in different oxidation states and structures
- ✓ Cr: Absence of Cr^{6+}; all clasts contain only Cr… …ble those of chromite.
- ✓ Pb: Oxidized with the same che… …ng different clasts. The chemical composition of Pb-rich areas could poi… …clasts.
- ✓ Cu, Ni and C… …both in metal and oxidized forms.
- ✓ … among PTE. Seems present only as Zn^{2+} but in various structures.

Data analysis currently in progress!!

Thank you

Acknowledgements