Speciation of Zn in ash

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Metods

- Element concentrations in ash is determined by ICP, AAS etc
- X-Ray Powder Diffraction provides information about the matrix compounds
- Sequential Extraction provides some information about groups of species present
- Synchrotron Radiation X-ray Absorption Spectroscopy (XAS) provides information about the oxidation state of the metal, its neighbour atoms and their coordination around the metal ion

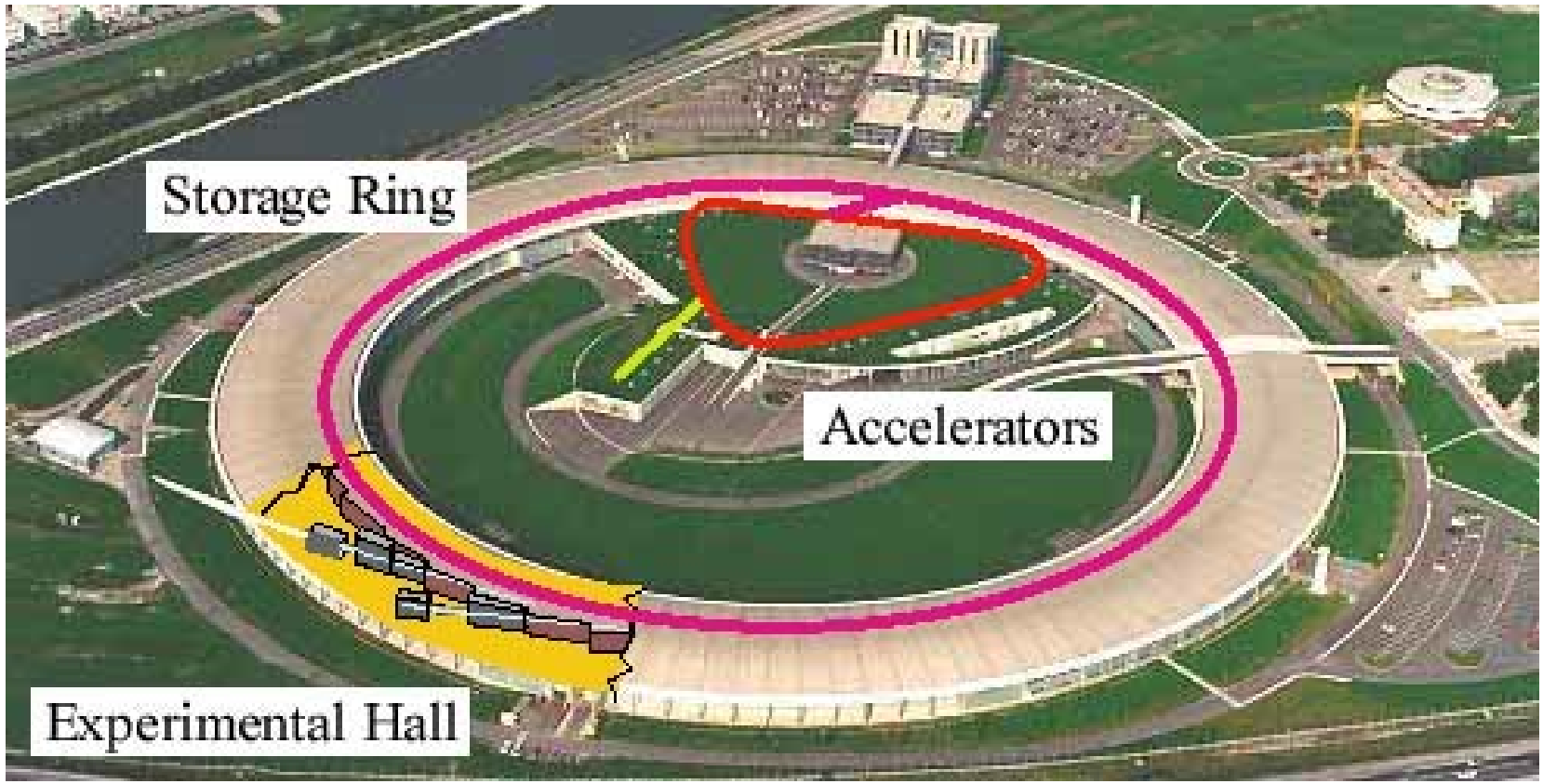
Types of ash included in the work

- Bottom ash and fly ash from two FBC boilers fired with wood chips, bark etc
- Bottom ash and fly ash from an FBC boiler fired with wood fuel including addition of kaolin
- Mixed and wetted ash from a grate fired boiler
- Bottom ash, cyclone ash and filter ash from an FBC boiler fired with MSW
- Ash from co-combustion of sewage sludge and wood pellets
- Ash from combustion of demolition wood

The XAS measurements are carried out at
MAX-lab, Lund University
National Electron Accelerator Laboratory for Synchrotron Radiation Research, Nuclear Physics and Accelerator Physics

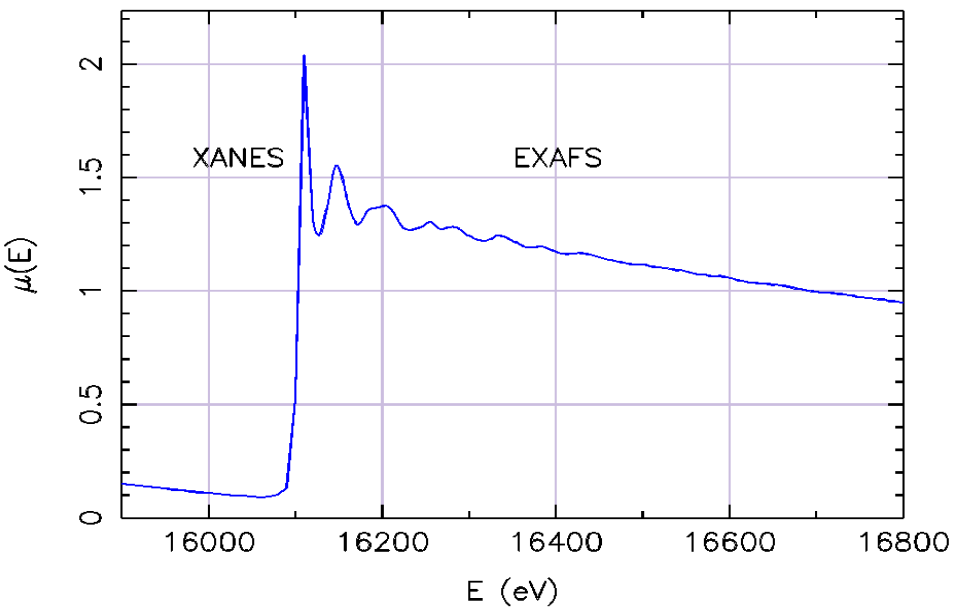
Beam line I811
X-ray beamline intended for material science research in the photon energy range 2.3 -20 keV in co-operation with PhD Stefan Carlson and PhD Maria Claussén

Synchrotron facility with beam lines (ESRF Grenoble)



X-ray Absorption Spectroscopy: XANES and EXAFS

X-ray Absorption Spectroscopy: Measure energy-dependence of the x-ray absorption coefficient $\mu(E)$ [either $\log(I_0/I)$ or (I_f/I_0)] of a core-level of a selected element



XANES = X-ray Absorption Near-Edge Spectroscopy

EXAFS = Extended X-ray Absorption Fine-Structure

Element Specific: Elements with Z>10 can have EXAFS measured

Valence Probe: XANES gives chemical state and formal valence of selected element.

Local Structure Probe: EXAFS gives atomic species, distance, and number of near-neighbour atoms around a selected element.

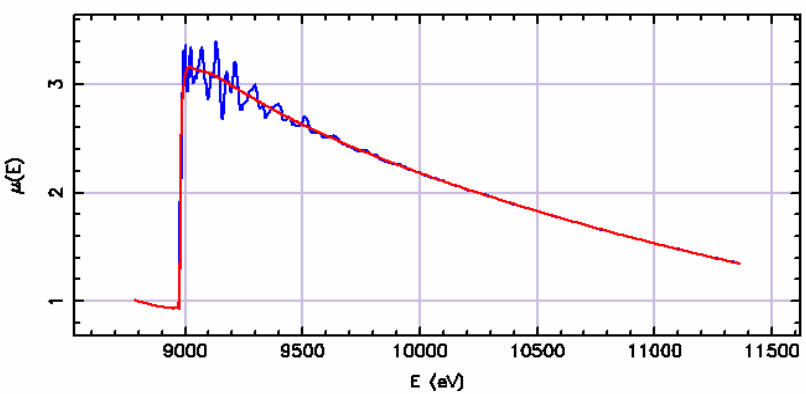
Natural Samples: samples can be in solution, liquids, amorphous solids, soils, aggregates, plant roots, surfaces, etc.

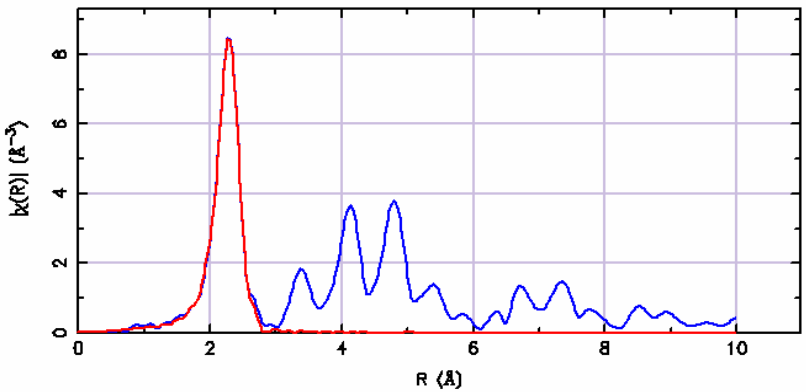
EXAFS Analysis

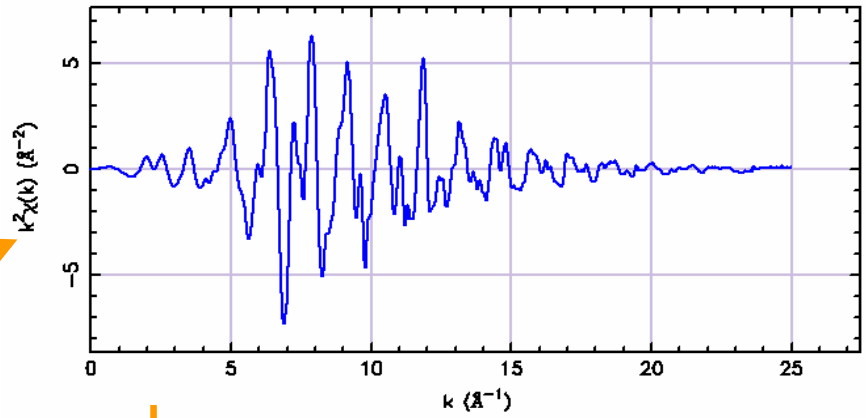
$$\chi(k) = \frac{N f(k)}{kR^2} \sin\left[2kR + \delta(k)\right]$$

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

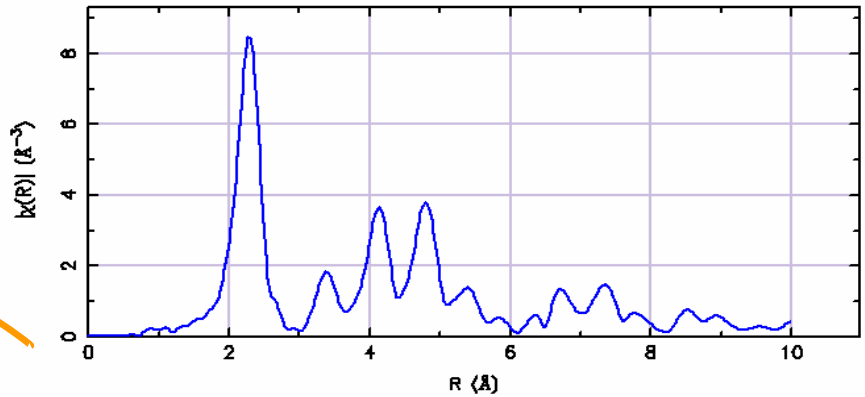
Measured EXAFS has a smooth background removed, and converted to k-space:





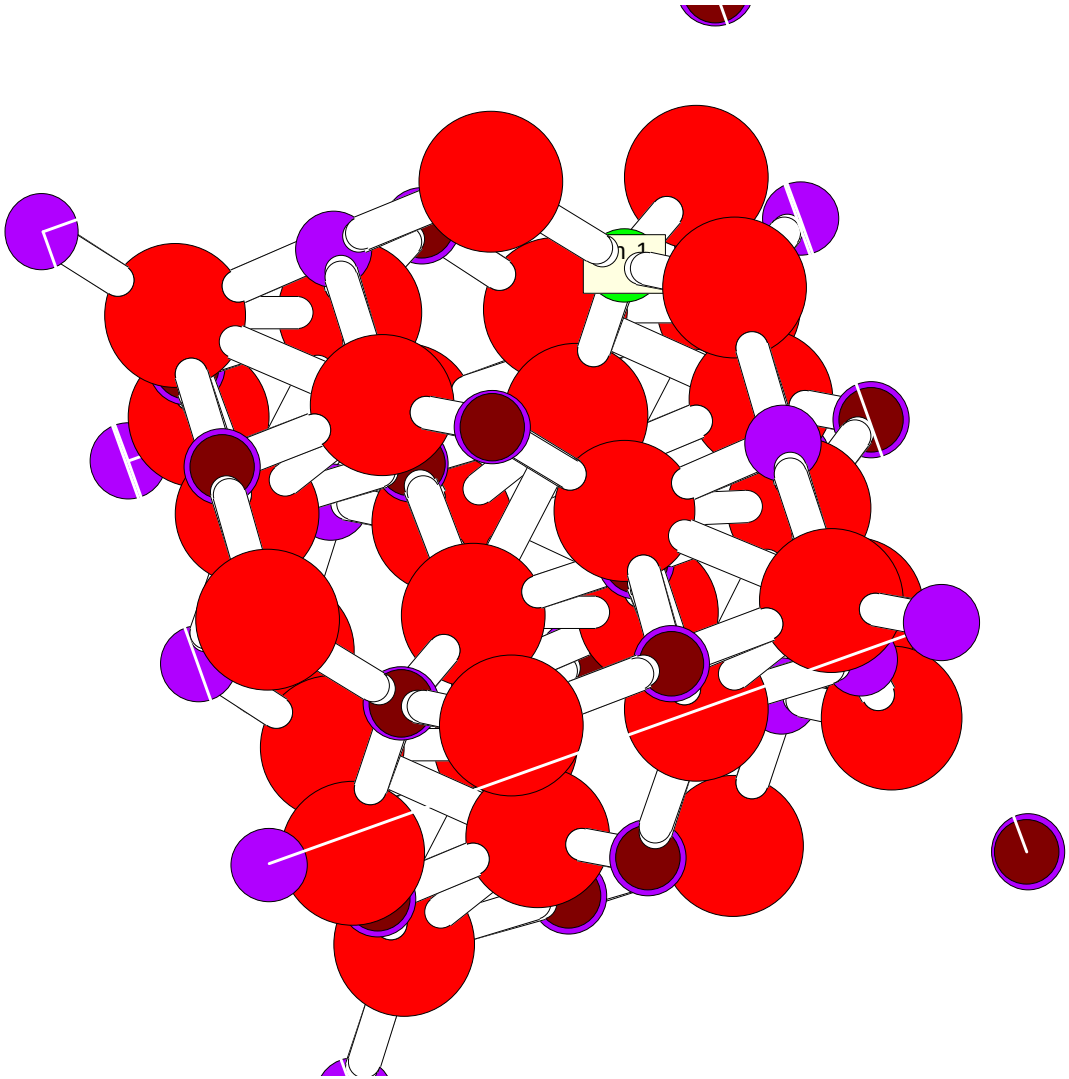


Fourier Transformed to R-space

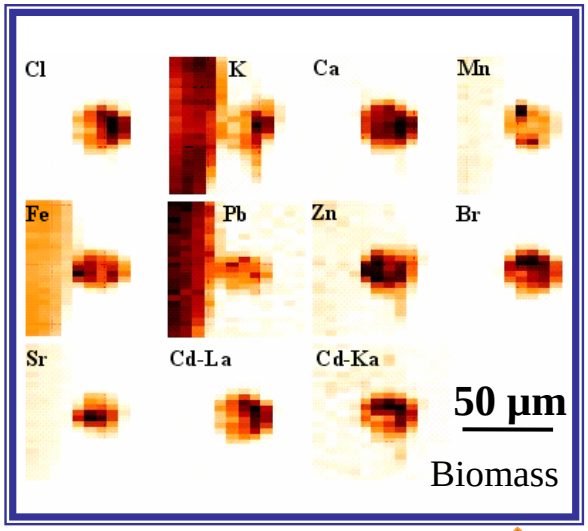


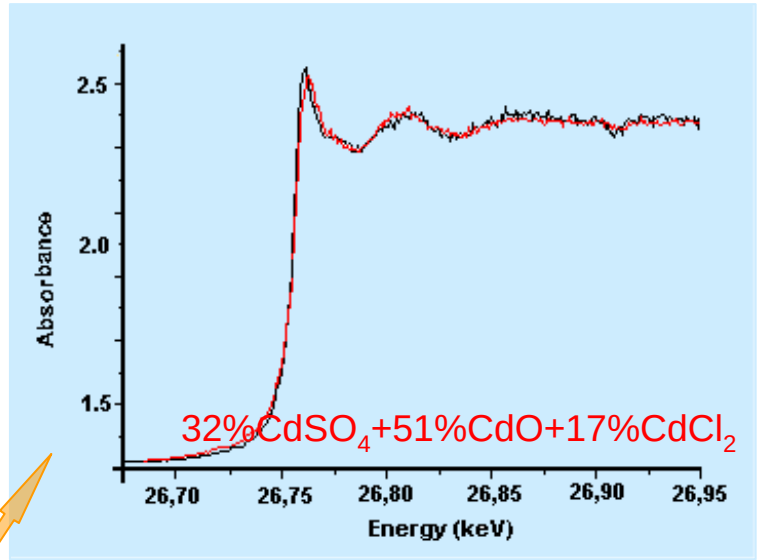
numerically modelled with empirical or theoretical calculations of f(k) and δ(k).

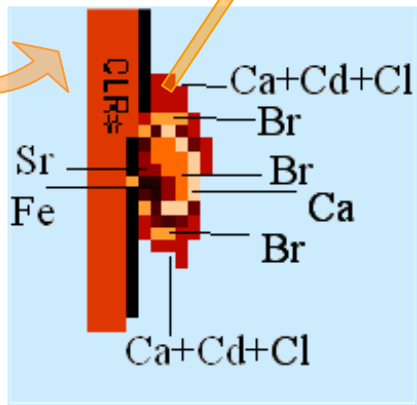
$ZnFe_2O_4$



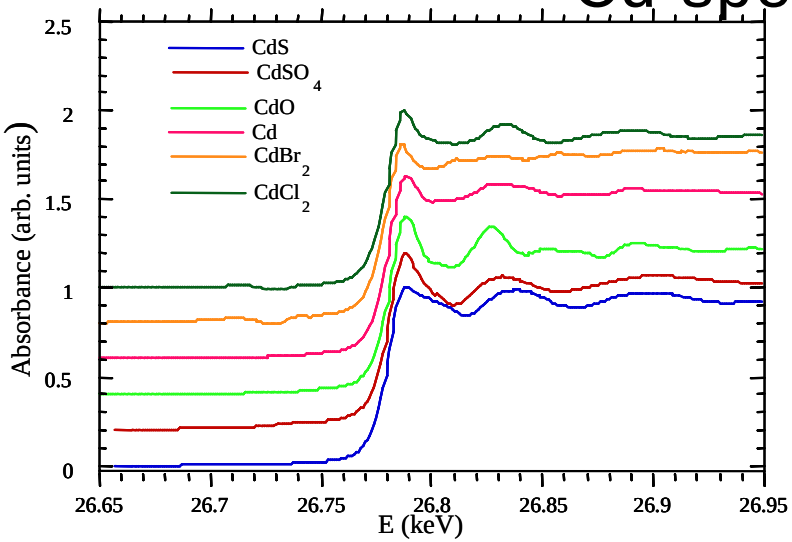
Cd speciation by μ-SRXAS

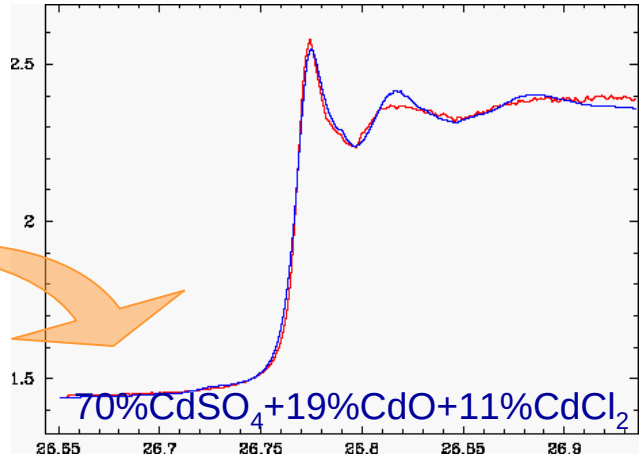


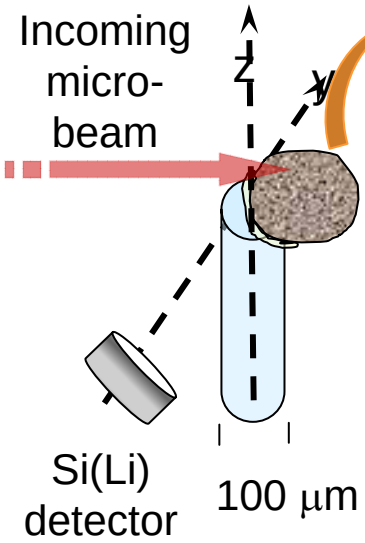


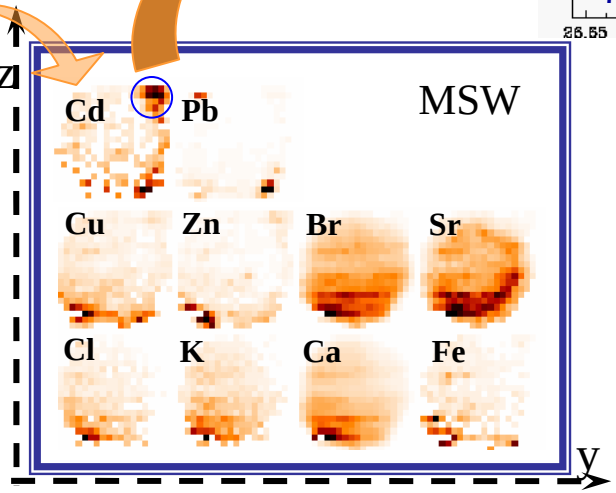


Cd speciation by μ-SRXAS









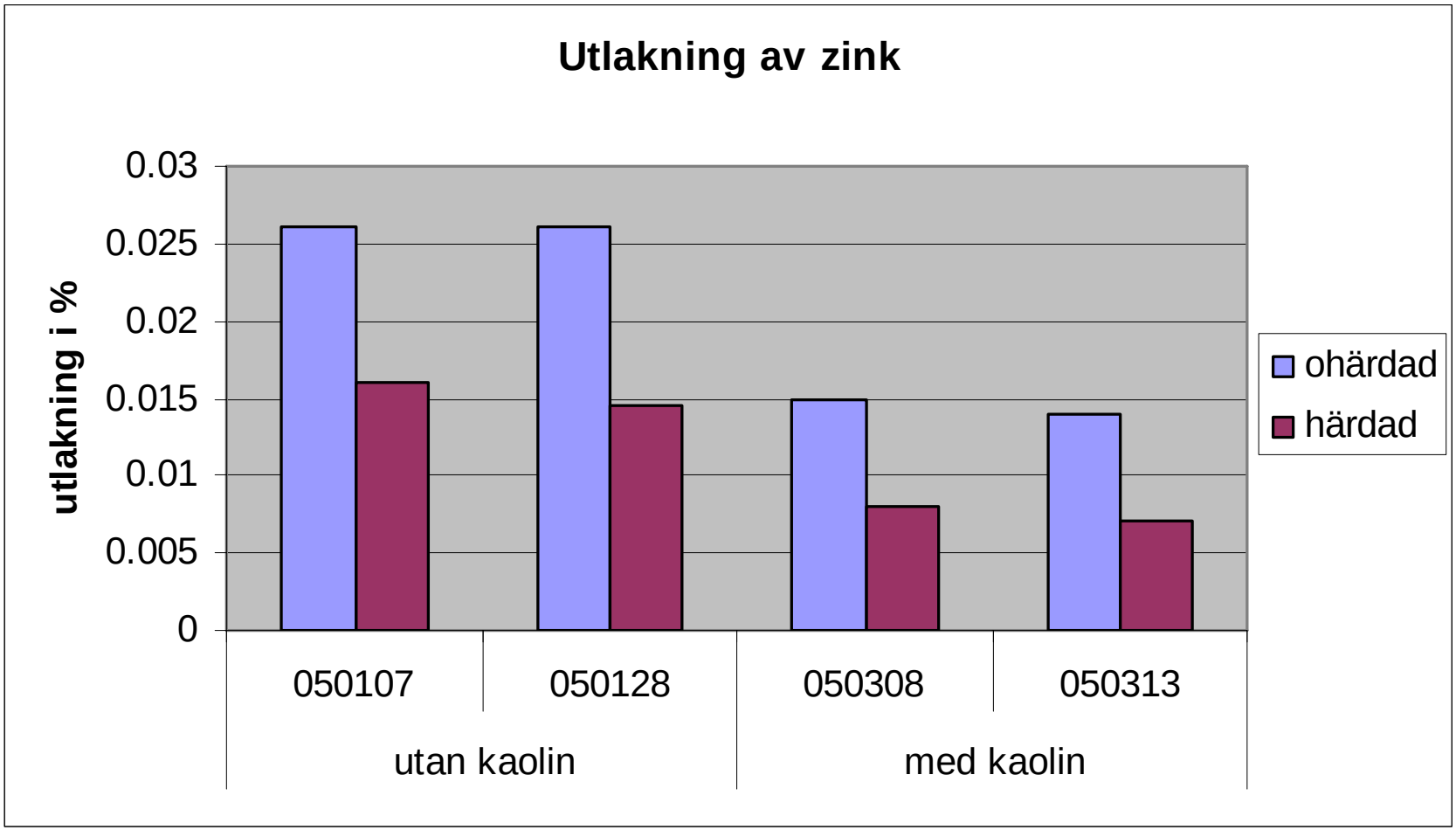
Sequential Chemical Extraction

- *Extraction 1. Water Soluble Metal Ions Fraction*
  sample + H_2O (continuous agitation for 10 min)
- *Extraction 2.Ion Exchangeable Metal Ions*
  residue + 1 M $MgCl_2$ (pH 7.0 continuous agitation for 10 min)
- *Extraction 3 Surface Oxide and Carbonate-Bound Metal Ions*
  residue + 1 M NaAc (pH 5.0 CH_3COOH continuous agitation for 5 h)
- *Extraction 4. Metal Ions Bound to Fe-Mn Oxides*
  residue + 0.04 M hydroxylamine hydrochloride in 25% (v/v) Acetic acid (occasional agitation for 6 h at 90 º C)
- *Extraction 5. Metal Ions Bound to Organic Matter and Sulphides*
  residue + 0.02 M HNO_3 +H_2O_2 (pH 2 slowly heated in a water bath to 90 º C)
- *Extraction 6. Residual Metal Ions*
  residue + aqua regia + 30% H_2O_2 + conc. HCl (heated for ½ h)

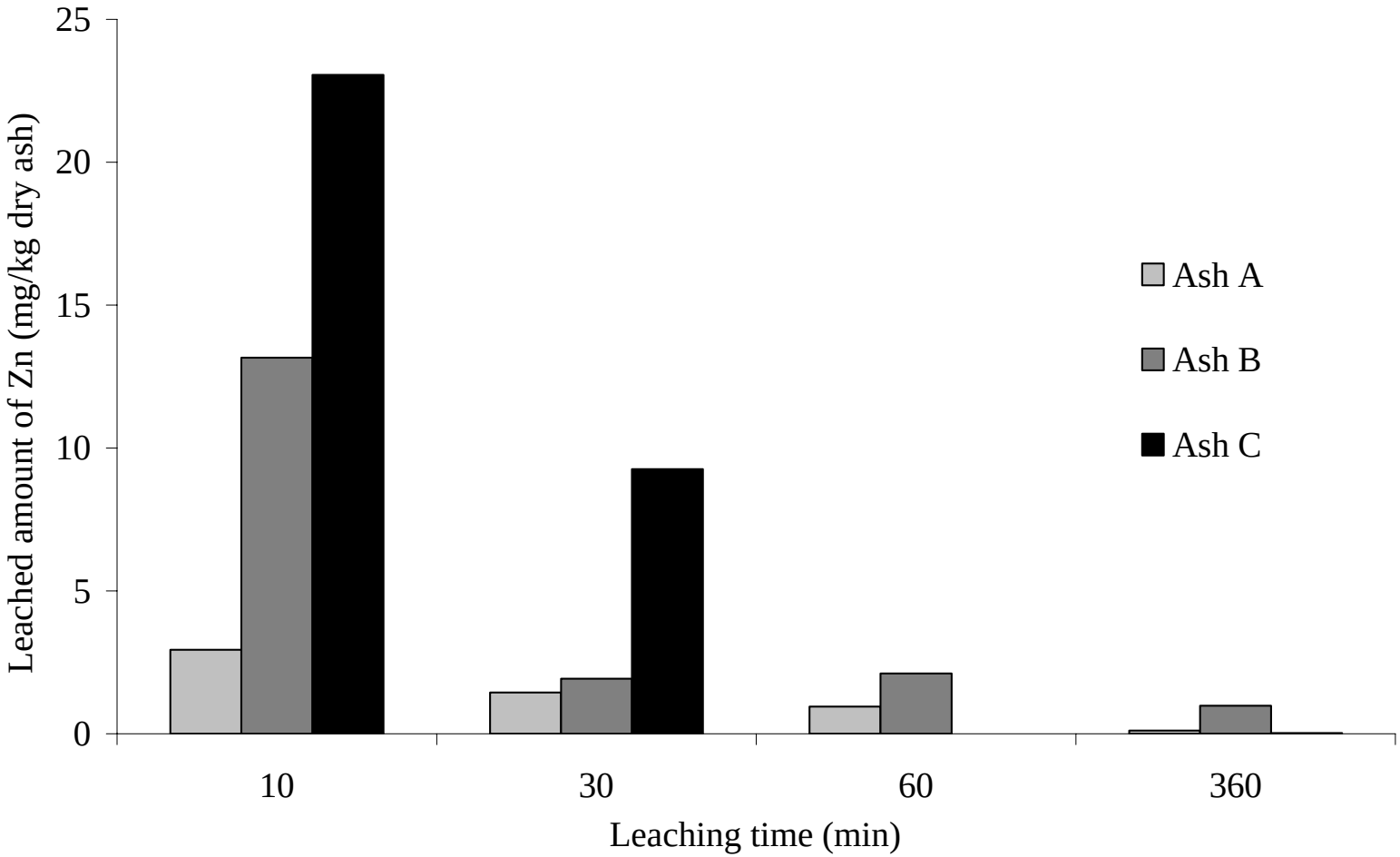
Zn contents in some of the ashes (FBC)

Ash	Zn mg/kg dry mass
Wood1 bottom ash	2200(no kaolin) 1500(kaolin)
Wood1 fly ash	1200(no kaolin) 2000(kaolin)
Wood2 bottom ash	1500
Wood2 fly ash	2000-3500
MSW bottom ash	1400
MSW cyclone ash	6000
MSW filter ash	5800

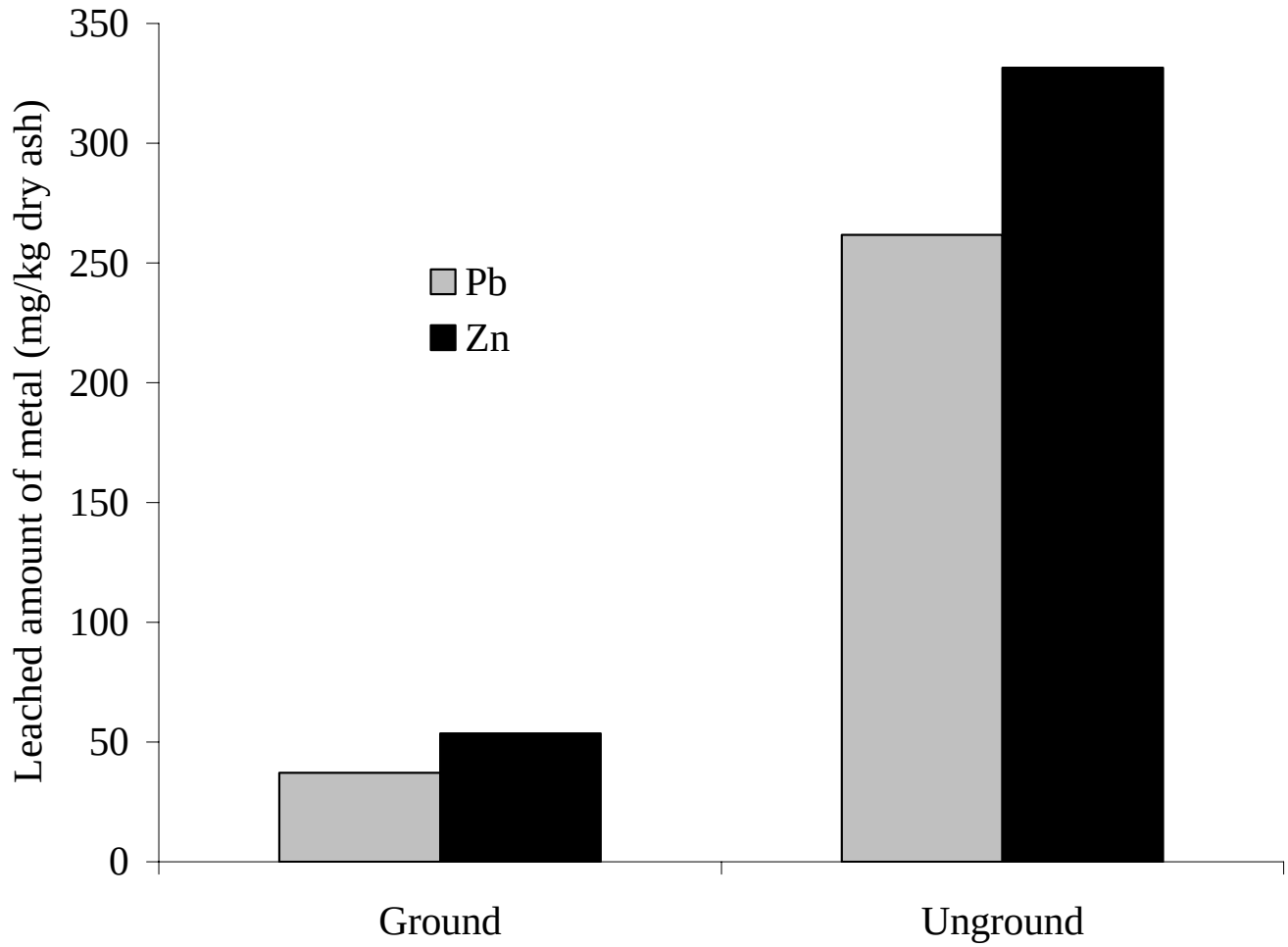
Effect of “hardening” and kaolin addition on the Zn mobility in water from wood fuel ash



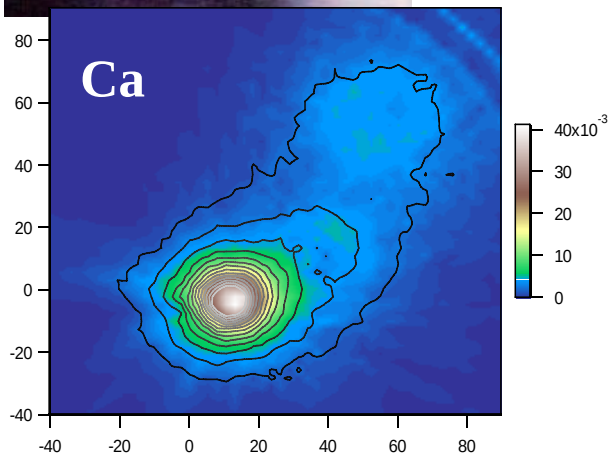
Effect of ash – water contact time on the amount of Zn released at L/S 10 (MSW ash)

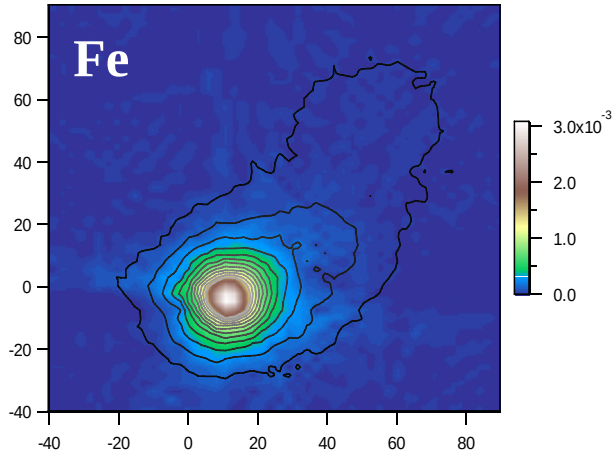


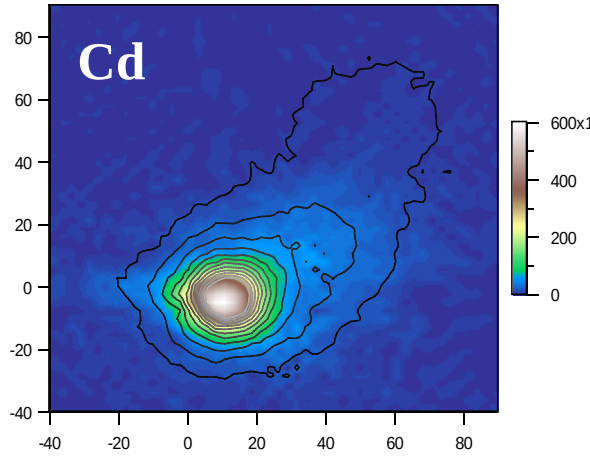
Effect of grinding before water extraction at L/S 10 for 10 minutes (MSW ash)



Scan 37







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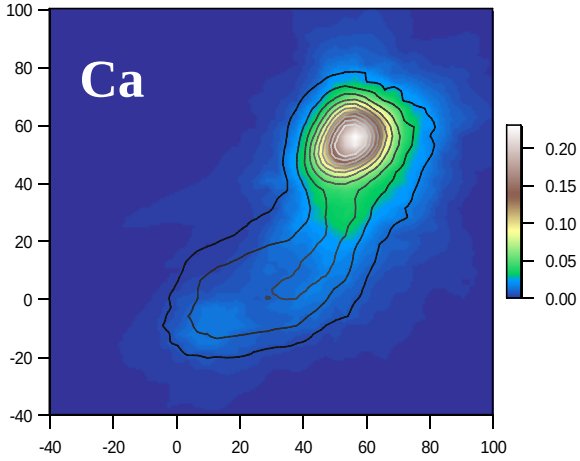
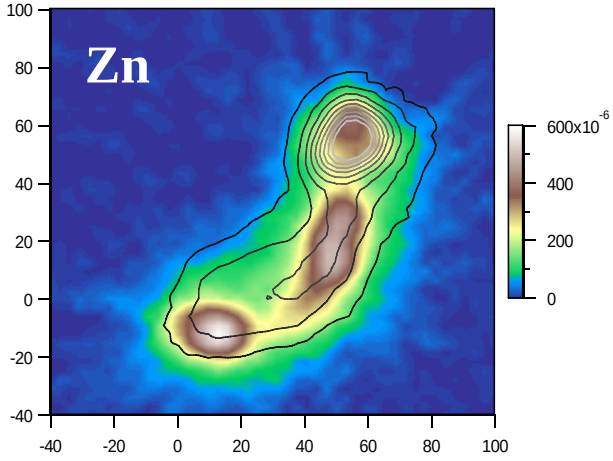
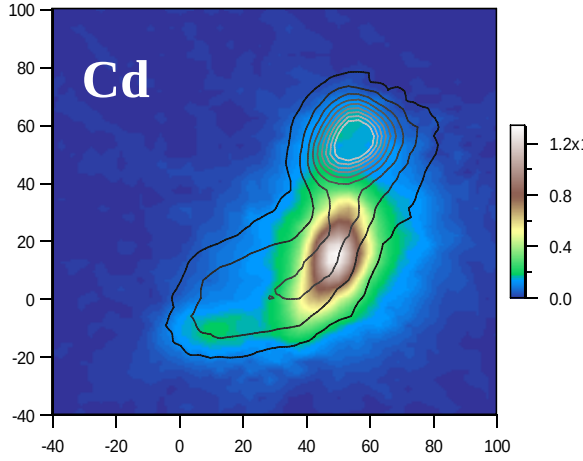
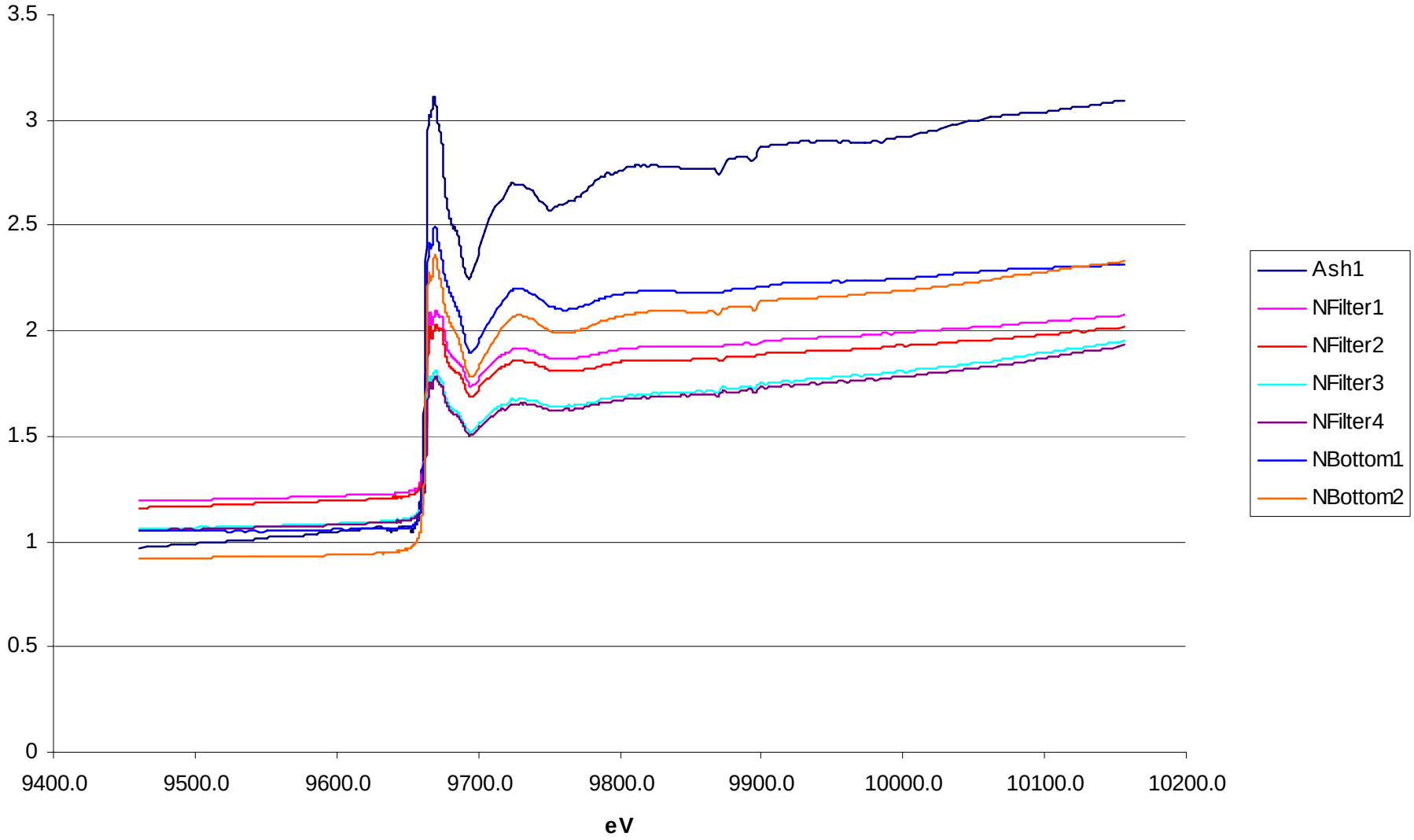


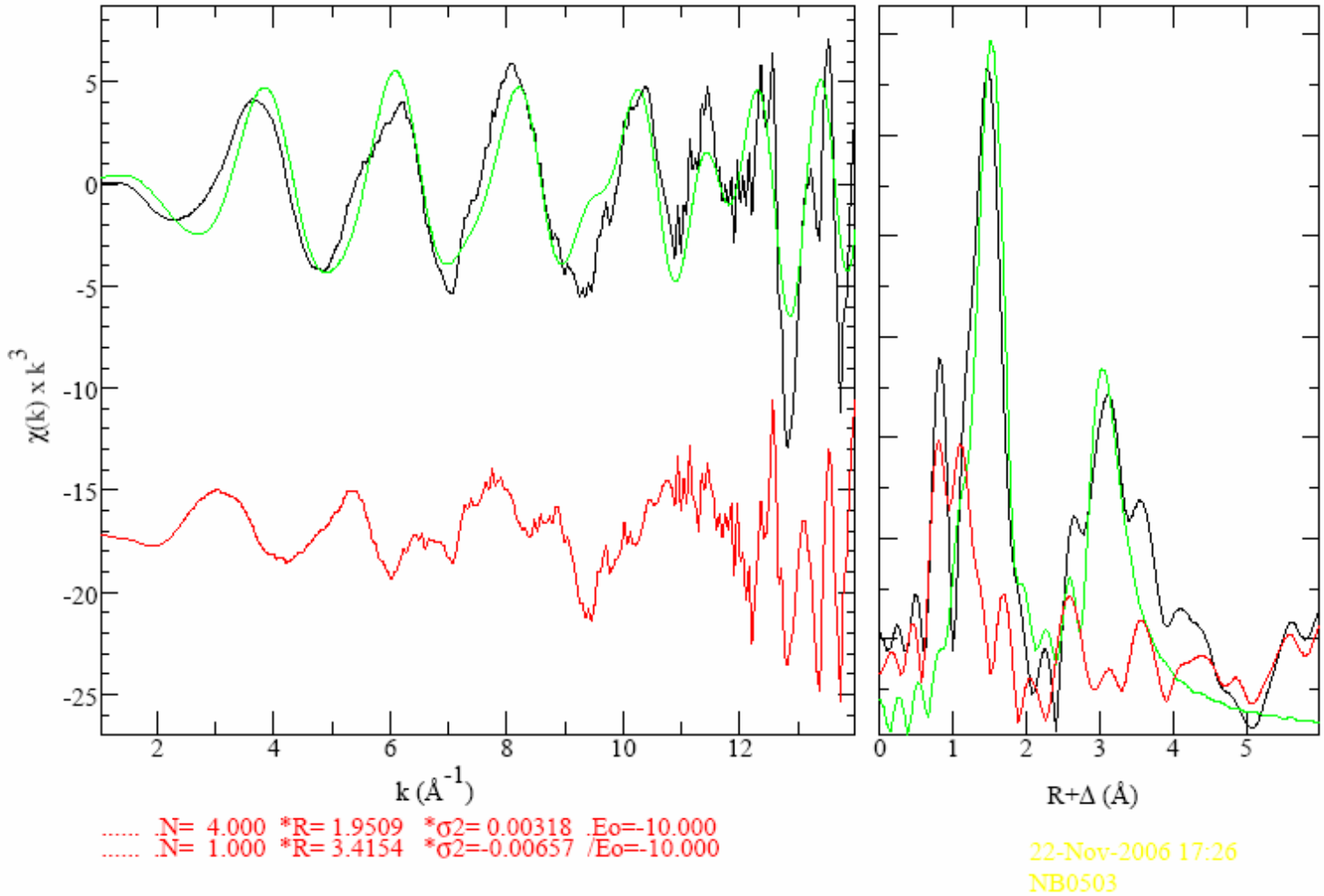




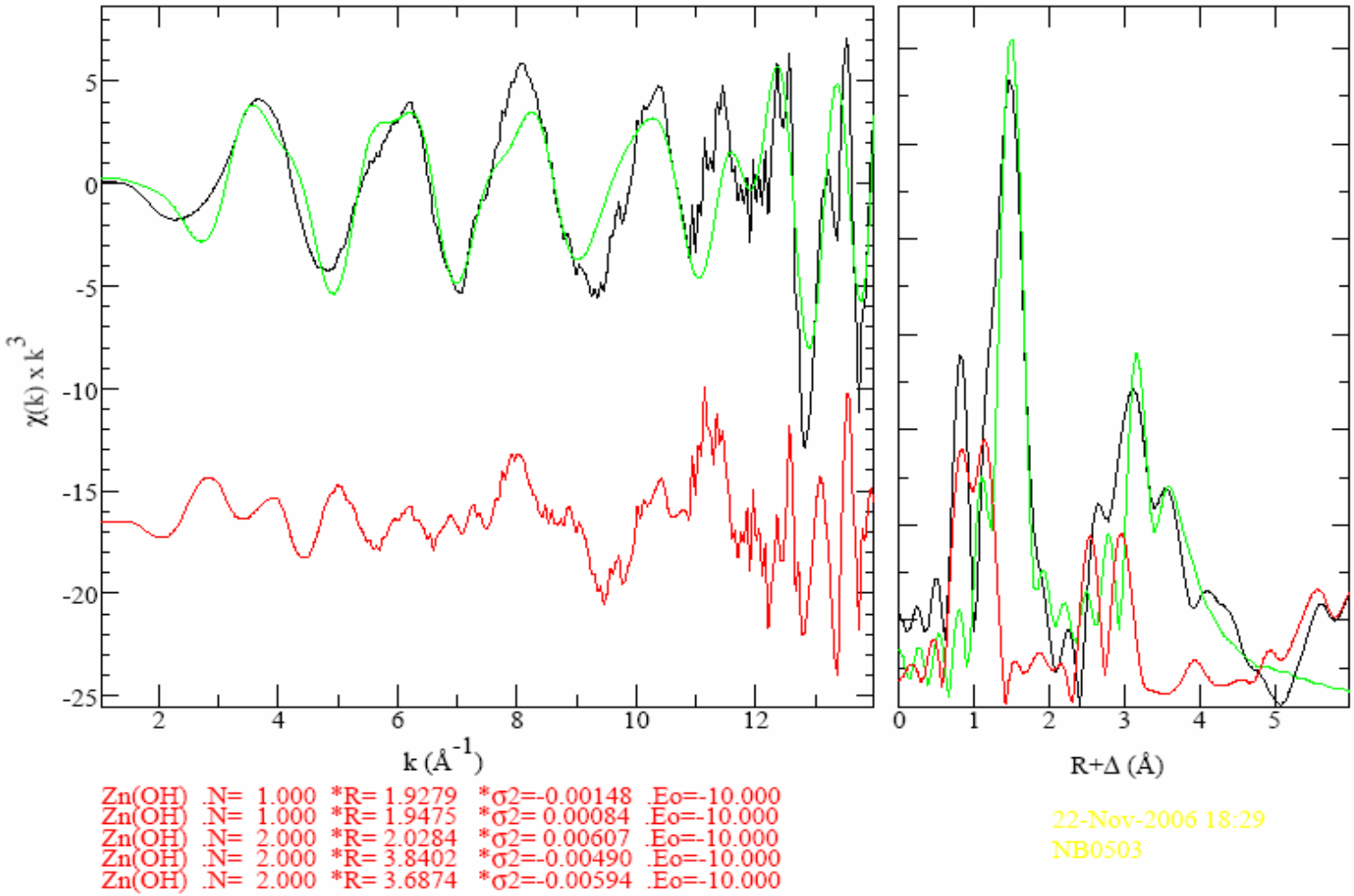
XAS-data for wood ashes



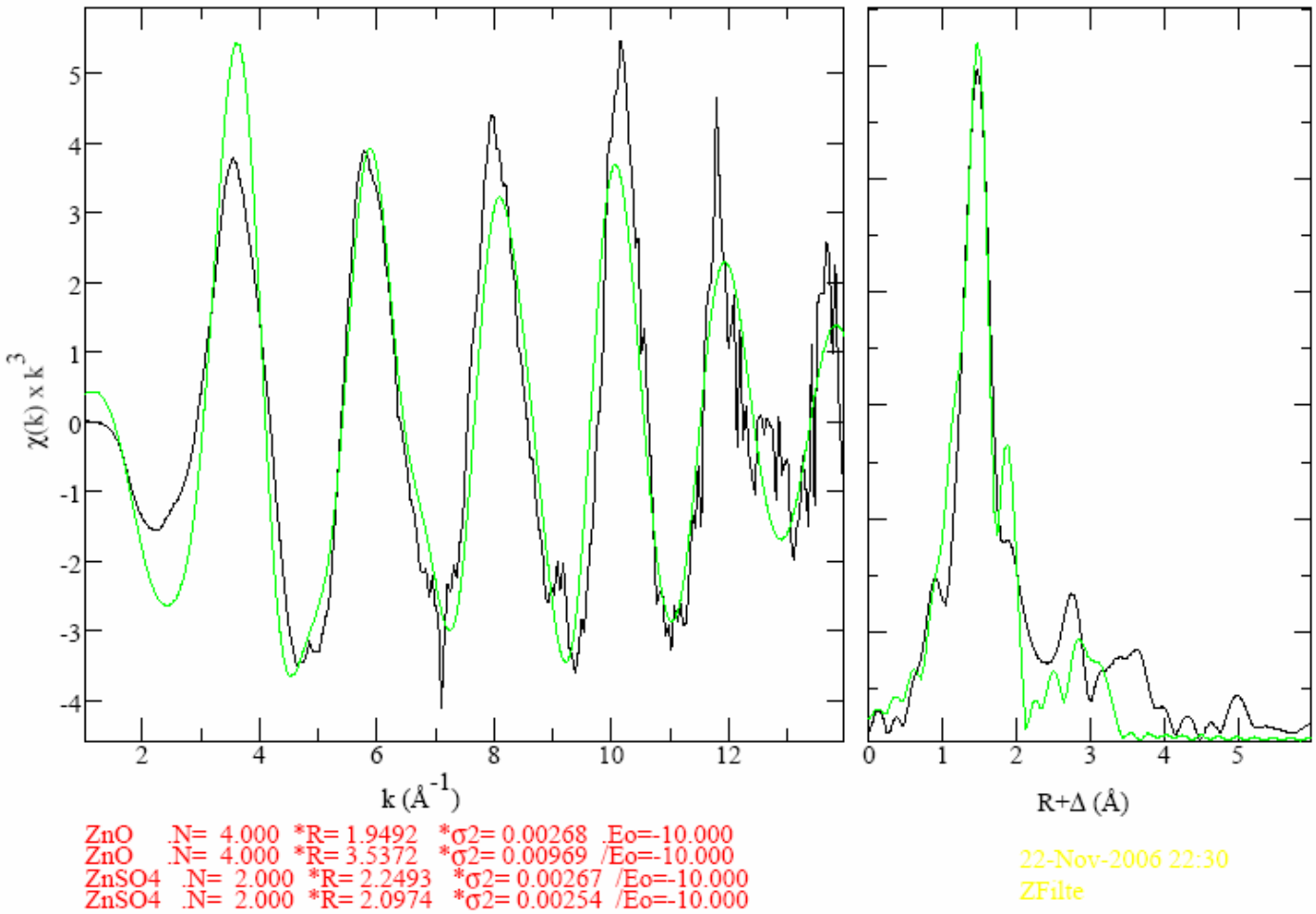
FBC Wood+kaolin Bottom ash
ZnO model



FBC Wood+kaolin Bottom ash
$Zn(OH)_2$ model



MSW filter ash
$ZnO+ZnSO_4$ model



Conclusions so far

- Sequential extraction gives some information but secondary reactions, such as adsorption and precipitation of new compounds may influence the results significantly
- Zn seems to be partly present in water soluble form in fly ash (cyclone) from MSW and wood. If the ash is wetted, Zn is transformed into an insoluble form.
- Zn is generally present as Zn(II) and associated to oxygen in a tetrahedral coordination
- The Zn-O distances found indicate the possible presence of Zn silicate/$Zn(OH)_2$ [1.94-1.95Å] and $ZnO/ZnFe_2O_4$ [1.97-1.98 Å]
- There are indications of the presence of other neighbour atoms with longer bond distances as well, but the identity of these atoms is not yet clear

Further work

- Continuation of the evaluation of the XAS data collected at Maxlab
- Further work on modelling of the Zn-speciation based on XAS data
- Synthesis of pure compounds that are “suspected” to occur (Franklinite) and data collection for these
- XAS data measurements for “synthetic ash” with known Zn-species present
- Further work to improve data/noice ratio in the XAS data since the ash matrix seems to interfere
- XAS measurements for other ash types