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Electronic Supplementary Information (ESI):

Synchrotron hard X-ray chemical imaging of trace element speciation in heterogeneous samples: Development of criteria for uncertainty analysis

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This ESI contains:

- 24 pages,
- 25 figures, and
- 8 tables.

1 Case Study

Copper oxide nanoparticles (CuO-NP) released to wastewater from the metal finishing and electroplating industry¹ are retained by wastewater treatment plants and accumulate in the sewage sludge^{2,3}. In developed countries, the sewage sludge is then further processed by anaerobic digestion, for application as fertilizer in agriculture^{4,5}, However, more stringent environmental regulations increasingly complicate the use of digested sludge in agriculture and growing amounts are incinerated in dedicated mono-incineration facilities for volume reduction, energy recovery and potential phosphate recovery in the future.^{6–11} Using synchrotron-based bulk X-ray absorption spectroscopy (XAS) we have previously shown that Cu speciation in digested sludge ashes derived from sludge spiked with either CuO-NP or dissolved CuSO₄ is nearly identical and also corresponds to the Cu speciation observed in unspiked sludge ashes.¹² In the sludge, Cu is expected to be unevenly distributed on a micrometre scale, with Cu bound to sulphur (S) as the dominant Cu species. In the ash, Cu is expected to be more evenly distributed, with Cu either bound to O (70%) or S (30%). These properties, combined with the thorough characterization available from our previous study¹² makes these samples ideal for investigating spatial (chemical) heterogeneities at the micrometre scale.



2 X-ray absorption coefficients of the reference materials

FIGURE S1. The coloured lines show the normalized absorption of the reference spectra. The vertical black lines indicate the energies (8950.0, 8981.0, 8986.5, 8995.0, 9007.0, 9051.5, 9080.0 eV) selected for the micro-XAS measurements. Cu_xS represents the an amorphous copper sulphide obtained from Pattrick *et al.*¹³.

3 Deviation of the sample stage



FIGURE S2. Histogram of the recorded deviations of the sample stage from the intended location and a fitted normal distribution (parameters displayed in the graph).

4 Calculated signal of an energy-dispersive fluorescence detector recording the Cu K_{α} signal



FIGURE S3. Cu-K_{α} fluorescence signal as recorded by an energy-dispersive XRF detector reproduced from Sun *et al.*¹⁴. (fT*T) denotes a tailing function, (fS*S) denotes a step function, G describes the peak broadening due to the energy resolution of the detector and P the sum of the three contributions. Details can be found in Sun *et al.*¹⁴. We selected 8030 eV to be the energy of the highest signal intensity which is between the K_{α ,1} (8046.3 eV) and K_{α ,2} (8026.7 eV) fluorescence lines.

5 JAGS model and computer code

The observation model (equation 8) is transformed into a JAGS readable model. The deterministic part is represented by equation S1 without the error term (ϵ)

$$\overrightarrow{\hat{\mu}}_{i,j} \leftarrow \mu_{\text{references}} \overrightarrow{x}_{i,j} \tag{S.1}$$

The indices i and j refer to the i-th pixel of the *j*-th map measured. Using equation 3, we replace the measured intensity $(\hat{\mu}_{i,j})$ by sampling $\mu_{i,j}$ from a normal distribution (*N*) with the mean $\hat{\mu}_{i,j}$ and the standard deviation $\sigma = \sigma_i^{(m)} + \sigma^{(d)}$ (compare eq. 8).

$$\overrightarrow{\mu}_{i,j} \sim N\left(\overrightarrow{\mu}_{i,j}, \left[\sigma_j^{(m)} + \sigma^{(d)}\right]\right)$$
(S.2)

The parameters $\sigma_j^{(m)}$ and $\sigma^{(d)}$ were sampled from two normal distributions (*N*) with $\mu_z = 0$ and $\sigma_z = 100$ (z = 1, 2) (eq. S.3 and S.4).

$$\sigma_j^{(\mathbf{m})} \sim N(\mu_1, \sigma_1) \tag{S.3}$$

$$\sigma^{(d)} \sim N(\mu_2, \sigma_2) \tag{S.4}$$

The fractions allocated to each standard of each pixel prior to the optimization are purely random and sampled from a uniform distribution (*U*) between 0 and M.

$$\overrightarrow{x}_i \sim U(0, M)$$
 (S.5)

Depending on the values selected for μ_z , σ_z prior knowledge can be added to the model. In our case, the introduction of extremely high ($\sigma_z = 100$) standard deviations very little prior knowledge is added to the model besides the shape of the distributions making up $\sigma_j^{(m)}$ and $\sigma^{(d)}$. Further, it is assumed that each fraction determined by LCF in \vec{x} must be $0 \le x_j \le M$ (eq. S.5). The upper boundary can be chosen slightly above unity, e.g., M = 1.5. With this method, the noise introduced by (i) the sample matrix and (ii) the detector from multiple recorded XRF maps can be extracted and, therefore, the uncertainties in the fractions determined by LCF can be estimated. The model was applied to a synthetic and an experimental dataset to evaluate its capability (sections 3.1 and 3.2). The computer code is given (Figure S5 and Figure S6). Also a working example of the code is can be found found in the Eawag Research Data Institutional Repository (ERIC) under doi.org/10.25678/0001MF including calibration datasets (sections 3.1.1 and 3.1.2), reference material "spectra" (as $\mu_{references})$ and experimental datasets (Figure 4, Figure S12 and Figure S13).



FIGURE S4. Graphical representation of the computer model used to analyse the noise in multiple datasets collected using the same setup.



FIGURE S5. Image of the JAGS model code. The filename must be "fakemodel.bug". In contrast to other programming languages, in JAGS, a normal distribution is defined via a mean and the precision. If the uncertainties are combined ($\sigma_j = \sigma^{(d)} + \sigma^{(m)}$), tau.DetectorNoise must be removed from Lines 12 and 39. If only one dataset is considered, all dependencies on k must be removed.



FIGURE S6. Image of the preparatory R code. Reading and preparing the data might work differently depending on the format of the prepared data. If the uncertainties are combined ($\sigma_j = \sigma^{(d)} + \sigma^{(m)}$), sigma.DetectorNoise must be removed from the initial values (Line 47) and the output variables (Line 58).

6 Workflow for the uncertainty analysis and selection of the benchmarking parameters

The standard approach to assess the fit quality for bulk XAS data is to compute an R-factor as for example conducted in Athena.¹⁵ Usually, the fit to the data is also visually verified as also unrealistic fits may result in low R-factors. However, in the present study, normalized X-ray absorption coefficients are known at seven energies only and about 28k fits are produced per sample, making the visual inspection impossible, and, thus, the R-factor may not be an ideal benchmark. An alternative approach to assess the quality of the LCF fits is to compare the sum of the p-norm of the relative differences, e.g., $err^p = \sum_{i=1}^{n} |(x_{i,input} - x_{i,output}) / x_{i,input}|^p$, where *p* varies between 0.5 and 2. This approach weights the

error for small values of $x_{i,input}$ strongly $\left(\lim_{x_{i,input}\to 0} \left[\left| \left(x_{i,input} - x_{i,output} \right) / x_{i,input} \right|^p \to \infty \right] \right)$. Therefore,

the p-norm is suitable in detailed investigations where small contributions are relevant. However, in our study, we focused on the major fractions contributing to the LCF fits of the experimental spectra



FIGURE S7. Proposed workflow to evaluate the typical recovery of 'true' fractions at specific levels of uncertainty.

extracted from the seven energy maps on an individual pixel level and the introduction of the score and CSCI deemed adequate (section 2.7).

7 Additional information on the uncertainty model results



FIGURE S8. Correlation between the recovered uncertainty $\sigma^{(d)}$ and the recovered uncertainty $\sigma_j^{(m)}$. The different colours represent the different datasets. R-squared values to the different datasets are given adjacent to the regression lines.

	Noise level	0	0.01	0.05	0.10	0.15	0.20
Individual	Score	1.742	1.211	0.529	0.435	0.359	0.355
Individual	Score	72.4	62.6	37.2	31.3	25.8	24.8
Cu-O vs. Cu-S	Score	3.099	2.662	1.945	1.731	1.548	1.481
Cu-O vs. Cu-S	Score	89.1	87.2	80.4	78.4	69	67.7

TABLE S1. Results of the MC routine displayed in Figure 3.



FIGURE S9. Correlation between $\sigma^{(d)}$ (x-axis) and $\sigma_j^{(m)}$ (y-axis) for SLG NP (a), SLG AQ (b), ASH NP (c) and ASH AQ (d). In each case, 10^3 samples were drawn from the MC and each sample is displayed as a blue dot.



FIGURE S10. Combined uncertainty $\sigma_j = \sigma^{(d)} + \sigma_j^{(m)}$ in the experimental data.



FIGURE S11. The overall uncertainties σ_j (y axis) as a function of the included pixels (x axis). The black circles and lines indicate the uncertainties resulting from a relative pixel exclusion criterion. The grey circles and lines indicate the use of an absolute criterion. The vertical black lines indicate the percentage of included pixels. The values of the exclusion criteria and all other data relevant parameters are given in Table S2.



FIGURE S12. Uncertainty associated with the LCF data interpretation of chemical maps of the SLG NP sample as a function of pixel binning.

TABLE S2. Compilation of information on the determination of the uncertainty in the experimental datasets. For each dataset (SLG NP, SLG AQ, ASH NP and ASH AQ) the
results for two pixel exclusion criteria (relative and absolute) are given. The data includes: the level (ϕ or χ), the number of included pixels, the percentage of included pixels and
the uncertainty.

	σ	0.2134	0.1706	0.162	0.1543	0.1443	0.1396	0.1365	0.1336	0.1275			σ		25.4823	25.6263	25.6862	0.5667	0.5668	0.1405	0.1343	0.1419	0.1794	0.223	,	,
	% of included pixels	13.8191	3.0483	2.2536	1.8508	1.5133	1.2302	1.0488	0.87095	0.74031			% of included	pixels	86.5503	81.4335	79.0849	76.6861	74.2156	46.5954	21.68	7.9207	2.0366	0.72789		
	# of included pixels	3808	840	621	510	417	339	289	240	204			# of included	pixels	24138	22711	22056	21387	20698	12995	6048	2209	568	203		
SLG AQ (abs)	X	2000	3000	4000	5000	6000	7000	8000	0006	10000	ASH AQ	(abs)	X	:	500	700	800	006	1000	2000	3000	4000	5000	0009		
	σ	0.18	0.18	0.19	0.19	0.19	0.1785	0.1479	0.1977			_	σ		0.31	0.29	0.3	0.27	0.25	0.23	0.24	0.25	,	,	,	,
	% of included pixels	56	36	15	8	6	2.4205	1.02	0.014516				% of included	pixels	78	41	21	11	9	4	2	1				
	# of included pixels	15305	10011	4223	2113	1635	667	283	7				# of included	pixels	21619	11404	5756	3069	1703	985	613	396				
SLG AQ (rel)	φ	10	15	25	35	40	20	100	150		OA HSH	(rel)	φ		5	10	15	20	25	30	35	40				
	σ	0.7704	0.2415	0.1797	0.2078	0.2197	0.2232	0.223	0.2175				σ		0.1135	0.11	0.09	0.09	0.08	0.08	0.08	0.09	0.1	0.1	0.11	0.12
	% of included pixels	85.1554	71.4726	62.6698	22.7222	9.9681	5.902	3.851	1.0829				% of included	pixels	74.846	73.321	64.953	50.236	32.730	17.844	9.893	5.339	2.514	1.4971	0.9745	0.5155
	# of included pixels	23749	19933	17478	6337	2780	1646	1074	302				# of included	pixels	10599	10383	9198	7114	4635	2527	1401	756	356	212	138	73
SLG NP (abs)	X	50	80	100	150	200	300	400	1000		ASH NP	(abs)	X		400	500	1000	2000	3000	4000	5000	6000	7000	8000	0006	10000
	σ	0.18	0.19	0.2	0.21	0.22	0.2369	0.2436	0.2556	0.2559			σ		0.13	0.12	0.1207	0.12	0.1213	0.1209	0.1227	0.143	0.1435			
	% of included pixels	87	74	50	31	25	7.3649	4.5574	2.9438	0.92151			% of included	pixels	66.30783	65.5885	49.45266	36.17678	27.0249	19.2218	13.5301	2.8105	0.99569			
	# of included pixels	24278	20755	13923	8784	6932	2054	1271	821	257			# of included	pixels	14063	9288	7003	5123	3827	2722	1916	398	141			
SLG NP (rel)	φ	10	15	25	35	40	70	85	100	150	ASH NP	(rel)	φ		5	20	25	30	35	40	45	70	100			

Binning	Number included pixels	of	Percentage of included pixles relative to number of binned pixels	σ
1x1 = 1	24278		87.05	0.18
2x2 = 4	6065		88.04	0.1218
3x3 = 9	2677		88.50	0.1053
4x4 = 16	1498		89.11	0.0835
5x5 = 25	978		89.81	0.0738

TABLE S3. Development of the uncertainty with increasing degrees of pixel binning for the SLG NP sample.



FIGURE S13. Chemical image of sample SLG NP after binning 3x3 = 9 pixels. The displayed data is associated with an uncertainty (σ) of 0.1053 (Table S3) relating to a score of 1.731 and a CSCI of 78.4% (Table S1). Both, the score and CSCI improved compared to the chemical image of SLG NP without binning (Figure 4a).

8 Detailed point XANES (pXANES) results

A general conclusion for the most relevant results from the analysis of the point XANES (pXANES) was given in section 3.3. Here, we provide an in-depth discussion which is helpful to the general interpretability of the results discussed in section 3.3. Several pXANES were recorded on each sample (red "x" Figure 5). The shape and the LCF of the spectra provided further insights into the Cu speciation in these samples. Variable extents of beam damage were observed during pXANES measurements, which was reflected by substantial fractions of Cu₂O and Cu foil spectra return from LCF analysis. Based on knowledge gained from bulk-EXAFS measurements¹² neither Cu₂O nor metallic Cu were expected in the sample. Thus, the fractions obtained for the fitted spectra were normalized to the sum of fractions excluding Cu₂O and Cu foil (Figure S14). On average, the contributions of Cu₂O and the Cu foil reference material were much smaller for the sludge samples (13-15%) compared to the ash samples (45-47%), indicating that the Cu in the ash matrix was more susceptible to photo reduction, which further shows that the Cu(II)-O minerals were more susceptible to photon induced transformation. For SLG NP, nine pXANES spectra were recorded (Figure S15). The spectra p53-p55 can be represented by 80% references of Cu(II) coordinated to O (mainly tenorite and nano-CuO) (Figure S14). This coincided with a Cu(II)-O marked spot in the chemical image (red circle, Figure 4). The spectrum p61 was approximately equally represented by Cu-S and tenorite spectra. All other spectra were represented by sulphide coordinated Cu species, in line with the chemical image (Figure 4).

For SLG AQ 21 pXANES spectra were available on four locations (Figure S16). All spectra (p24-p52) were described by varying contributions of Cu_xS and covellite. The inclusion of the spectra from neither Cu(II)-O nor Cu(I/II)-HA (humic acid) significantly improved the fit quality.

Whereas Zn was entirely associated with oxygen after the incineration, Cu remained partly ($\approx 30\%$ determined with bulk-EXAFS LCF) associated with reduced sulphide phases.¹² In the present study, the results on the Cu speciation of the two ash samples considerably scattered preventing an in-depth discussion of these results (ASH NP and ASH AQ, Figure 4cd). LCF to pXANES data for ASH NP was poorly fitted and a reduced Cu component occurred for which no suitable reference material spectrum was available (Figure S17).

Two sets of XRF maps were recorded on the sample ASH NP. Unfortunately, the recording of the pre-edge map (8950 eV) of one of the sets (ASH NP 2) failed. Therefore, there are only information about the Cu concentration patterns (recorded at 18 keV) and pXANES available. The fit quality to the pXANES of sample ASH NP 2 was worse compared to fit quality to the pXANES of the sludge samples. Further, significant amounts of Cu(I)-HA fitted to the spectra p62-p64 indicated that important reference material spectra were missing as over 95% of the carbon was devolatilized during the incineration and therefore the presence of Cu(I)-HA can be excluded. However, the shape of the spectra (Figure 18) indicates that in some grains Cu was mainly coordinated to oxygen (p68-p70), whereas in others it was rather associated with sulphide (p62-p64).

For ASH AQ, 15 pXANES spectra were recorded. Strong local differences, like for the pXANES spectra in ASH NP 2 were observed. The spectrum p1 was mostly represented by Cu_xS , whereas the spectra p2-p6 and p9 were represented by varying shares of different oxygen coordinated reference materials. The remaining spectra were recorded from various locations scattered over the ash grain. At selected locations, Cu was dominantly coordinated to oxygen (p15, p16 and p19), at others with Cu was dominantly coordinated to sulphide (p1, p14). Occasionally, significant beam damage occurred hampering the LCF evaluation (p11-p13, p18). These results highlight that, although the distribution of Cu (concentration) became more even during the incineration, the chemical state (oxidation state and local coordination) of Cu becomes increasingly complex and susceptible to beam damage.

The quadratic increased number of binned the pixels induced a linear decrease in the associated uncertainty (section 3.2). Therefore, the decrease in uncertainty was due to the damping of random rather than systematic errors, indicating that the reference material spectra were suitable to describe the experimental data. Thus, no significant phase transformations, e.g., $CuO \rightarrow Cu^0$ occurred during data acquisition. Differently, the pXANES data was severely distorted through beam damage after 88 s of exposure to the focussed X-ray beam. Therefore, keeping in mind the limited interpretability with respect to the exact determination of phases with similar oscillations and other previously discussed limitations, chemical imaging including only a few energies and acquired with short dwell times can be used to extract bulk spectral information on representative areas from samples that are very susceptible to beam damage.



FIGURE S14. Fractions of the LCFs to the pXANES recorded on the five samples. The black, white and grey colours indicate an association of Cu with oxygen (tenorite, nano-CuO, copper sulphate and cuprospinel), the pink to purple colours indicate Cu in a reduced sulphide coordination environment (chalcopyrite, covellite, Cu_xS (primitive)) and the green colours indicate Cu associated with humic acid coordination environments.



FIGURE S15. LCF to the point-XANES recorded on the sample SLG NP. The black dots represent the measured data and the red lines represent the model fits. The mismatch between some of the measured data and the LCF results from the insufficient data range available for the normalization, e.g., samples p53 - p55.



FIGURE S16. LCF to the point-XANES recorded on the sample SLG AQ. The black dots represent the measured data and the red lines represent the model fits. The reference material spectra are shown in Figure S20.



FIGURE S17. LCF to the point-XANES recorded on the sample ASH NP. The black dots represent the measured data and the red lines represent the model fits. The references are shown in Figure S20.

	p53	p54	p55	p56	p57	p58	p59	p60	p61	Mean values
Tenorite	26%	36%	29%	0%	0%	0%	0%	0%	35%	14%
Nano-CuO	48%	34%	32%	0%	0%	0%	0%	0%	0%	13%
CuSO4	0%	4%	2%	0%	0%	0%	0%	0%	4%	1%
Cuprospinel	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Chalcopyrite	8%	11%	6%	0%	0%	0%	0%	0%	13%	4%
Covellite	6%	5%	19%	70%	77%	55%	74%	82%	30%	46%
CuS (primitive)	0%	0%	0%	29%	0%	44%	16%	0%	0%	10%
Cu(II)-HA	6%	0%	0%	0%	4%	0%	0%	0%	0%	1%
Cu(I)-HA	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Cu2O	10%	15%	15%	2%	20%	4%	10%	20%	17%	12%
Cu foil	0%	0%	0%	0%	0%	0%	2%	0%	4%	1%
Error Sum Sum without Cu2O und Cu foil	6.14E-04 104% 94%	1.39E-03 104% 90%	1.20E-03 104% 89%	8.13E-04 101% 99%	8.19E-04 101% 80%	9.89E-04 102% 98%	9.46E-04 102% 90%	5.87E-04 101% 82%	1.38E-03 103% 82%	102% 89%
Normalization without Cu ₂ O and Cu foil										
Tenorite	28%	40%	32%	0%	0%	0%	0%	0%	43%	16%
Nano-CuO	52%	38%	36%	0%	0%	0%	0%	0%	0%	14%
CuSO4	0%	4%	3%	0%	0%	0%	0%	0%	5%	1%
Cupro spinel	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Chalcopyrite	8%	13%	7%	0%	0%	0%	0%	0%	15%	5%
Covellité	6%	6%	22%	71%	95%	56%	82%	100%	36%	53%
CuS (primitive)	0%	0%	0%	29%	0%	44%	18%	0%	0%	10%
Cu(II)-HA	7%	0%	0%	0%	5%	0%	0%	0%	0%	1%
Cu(I)-HA	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%

TABLE S4. Detailed LCF results to the pXANES on the sample SLG NP.



FIGURE S18. LCF to the point-XANES recorded on the sample ASH NP 2. The black dots represent the measured data and the red lines represent the model fits. The references are shown in Figure S20.



FIGURE S19. LCF to the point-XANES recorded on the sample ASH AQ. The black dots represent the measured data and the red lines represent the model fits. The references are shown in Figure S20.



FIGURE S20. Reference spectra used for the LCF to the point XANES (pXANES).



FIGURE S21. Spatial Cu distribution map of the SLG NP sample and locations of the pXANES on the map. The map on the left hand side shows the entire dataset, the map on the right hand side shows a magnification of the area marked with the red rectangle on the map on the left hand side.



FIGURE S22. Spatial Cu distribution map of SLG AQ and locations of the pXANES on the map. The map on the right hand side shows the entire dataset, the map on the right hand side shows a magnification of the area marked with the red rectangle on the map on the left hand side.



FIGURE S23. Spatial Cu distribution on the sample ASH NP 2. As the recording of the pre-edge XRF map failed, the intensity of the 18 keV map is shown. The red crosses indicate the locations where the pXANES were recorded. Unfortunately, the recording of the pre-edge map (8950 eV) of this map failed. Therefore, there are only information about the Cu concentration patterns and point-XANES (pXANES) available.



FIGURE S24. Spatial Cu distribution map of ASH AQ and locations of the pXANES on the map. The map on the right hand side shows the entire dataset, the map on the right hand side shows a magnification of the area marked with the red rectangle on the map on the left hand side.

Mean values	0% 0% 1% 38% 47% 0% 14% 11%		0% 0% 1% 0% 54% 54% 0%
p52	3% 0% 0% 0% 48% 39% 0% 111%	4.97 101% 89%	3% 0% 0% 53% 53% 0%
p51	0% 0% 0% 50% 40% 0% 10%	3.92 100% 90%	0% 0% 55% 0% 0%
p50	0% 0% 0% 35% 54% 0% 12% 0%	10.0 102% 89%	0% 0% 0% 0% 39% 61% 0%
p49	2% 0% 0% 0% 46% 44% 0% 0%	3.66 101% 92%	2% 0% 0% 0% 50% 50% 0% 0%
p47	$\begin{array}{c} 0\%\\ 0\%\\ 0\%\\ 0\%\\ 47\%\\ 41\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0$	5.34 101% 88%	0% 0% 0% 53% 27% 0% 0%
p43	0% 0% 0% 31% 55% 0% 14% 0%	4.40 101% 87%	0% 0% 0% 64% 0%
p42	2% 0% 0% 34% 48% 16% 16%	5.31 101% 85%	2% 0% 0% 0% 41% 57% 0%
p40	0% 0% 6% 0% 26% 61% 0% 8% 8%	4.30 101% 93%	0% 0% 6% 28% 66% 0%
p38	0% 0% 0% 0% 68% 68% 14% 0% 17%	8.94 101% 82%	0% 0% 0% 83% 0% 0%
p37	$\begin{array}{c} 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 69\%\\ 0\%\\ 0\%\\ 15\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0$	5.91 102% 87%	0% 0% 0% 21% 79% 0%
p36	0% 0% 0% 0% 0% 61% 0% 12%	5.36 101% 89%	0% 0% 0% 31% 69% 0%
p35	0% 0% 0% 0% 0% 62% 0% 0% 0%	7.42 101% 88%	0% 0% 0% 0% 0% 0% 0% 0%
p34	0% 0% 5% 0% 0% 81% 0% 0% 0%	10.5 102% 87%	0% 0% 6% 0% 0% 0% 0%
p33	0% 0% 0% 15% 74% 0% 13%	5.85 102% 89%	0% 0% 0% 0% 83% 0% 0%
p32	$egin{array}{c} 0\% \\ 0\% \\ 0\% \\ 39\% \\ 49\% \\ 0\% \\ 0\% \\ 12\% \\ 0\% \end{array}$	4.02 101% 89%	0% 0% 0% 14% 56% 0%
p30	0% 0% 0% 39% 37% 5% 17% 2%	8.71 101% 82%	0% 0% 18% 46% 6% 0%
p29	$\begin{array}{c} 0\%\\ 0\%\\ 0\%\\ 0\%\\ 49\%\\ 36\%\\ 0\%\\ 0\%\\ 12\%\\ 12\%\\ 12\%\\ 12\%\\ 12\%\\ 12\%\\ 12\%\\ 12$	3.97 101% 84%	0% 0% 0% 58% 42% 0% 0%
p28	0% 0% 0% 0% 57% 15% 0%	4.71 101% 86%	0% 0% 0% 67% 0% 0%
p27	0% 0% 51% 30% 30% 3% 3%	4.50 101% 80%	0% 33% 33% 0%
p25	$\begin{array}{c} 0\%\\ 0\%\\ 0\%\\ 0\%\\ 65\%\\ 8\%\\ 0\%\\ 0\%\\ 27\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0\%\\ 0$	3.58 100% 73%	0% 0% 0% 11% 11% 0%
p24	$\begin{array}{c} 0\%\\ 0\%\\ 0\%\\ 57\%\\ 57\%\\ 0\%\\ 0\%\\ 17\%\\ 5\%\end{array}$	6.63 101% 80%	0% 0% 0% 28% 0% 0% 0%
	Tenorite Nano-CuO CuSO4 Cupospinel Cupospinel Cusof primitive) Cu(1)-HA Cu(1)-HA Cu(1)-HA Cu(2) Cu foil	Error (times 10 ⁻⁴) sum Sum without Cu ₂ O und Cu foil Normalization without Cu ₂ O and Cu foil	Tenorite Nano-CuO CuDo 4 Cupospinal Cuprospinal Covellite Covellite Cull)-HA Cu(1)-HA

TABLE S5. Detailed LCF results to the pXANES on the sample SLG AQ.

mean values p83 p84 p85 p89 p91 p86 p87 p88 Tenorite Nano-CuO CuSO4 Cupro spinel Chalcopyrite Covellite CuS (primitive) Cu(II)-HA Cu(I)-HA Cu(I)-HA Cu2O Cu foil 0% 0% 21% 0% 0% 64% 0% 0% 16% 0% 0% 8% 0% 0% 20% 0% 20% 0% 22% 51% 0% 9% 0% 0% 0% 17% 0% 2% 21% 52% 0% 5% 0% 0% 0% 7% 0% 5% 9% 76% 0% 6% 0% 1% 0% 19% 0% 0% 22% 53% 0% 0% 21% 0% 66% 0% 0% 14% 0% 0% 0% 36% 0% 59% 0% 5% 5% 0% 16% 0% 19% 0% 45% 0% 11% 0% 9% 2% 3% 0% 12% 0% 37% 0% 2% 14% 30% error sum Sum without Cu2O und Cu foil 0% 101% 27% 0% 101% 28% 0% 101% 16% 0% 101% 25% 0% 101% 87% 0% 101% 95% 0% 101% 85% 0% 100% 91% 101% 57% Normalization without Cu₂O and Cu foil Tenorite Nano-CuO CuSO4 Cupro spinel Chalcopyrite Covellite CuS (primitive) Cu(II)-HA Cu(I)-HA 0% 22% 0% 5% 0% 0% 73% 0% 0% 28% 0% 0% 0% 72% 0% 0% 32% 0% 0% 0% 60% 0% 8% 0% 29% 0% 0% 0% 42% 0% 29% 0% 0% 25% 0% 75% 0% 0% 0% 0% 38% 0% 62% 0% 0% 0% 0% 25% 0% 75% 0% 0% 17% 0% 20% 0% 0% 50% 0% 13% 2% 14% 0% 14% 0% 64% 0% 6%

TABLE S6. Detailed LCF results to the pXANES on the sample ASH NP.

	T_{A}	BLE S7.	Detaile	d LCF n	esults tc	the pX	ANES c	on the se	ımple A	AN HS	5			
	p62	p63	p64	p65	p66	p67	p68	69d	p70	p71	p72	p73	p74	mean values
Tenorite	0%0	0%0	0%0	0%0	0%0	10%	0%	19%	22%	0%	0%	0%	11%	5%
Nano-CuO	0%0	0%0	0%0	11%	8%	0%0	0%	0%0	0%0	0%0	7%	0%0	0%0	2%
CuSO4	0%0	0%0	0%0	0%0	0%	2%	9%	31%	24%	0%0	0%	1%	0%0	5%
Cupro spinel	0%0	0%0	0%0	4%	3%	0%	0%	9%	0%	41%	0%	6%	%0	5%
Chalcopyrite	0%0	%0	0%0	0%	0%	0%0	0%	0%	0%	0%0	0%	0%	0%	0%
Covellite	0%	0%	0%0	0%	0%0	0%0	0%	0%	0%	0%	0%	0%	0%	0%
CuS (primitive)	50%	48%	44%	20%	15%	0%0	68%	0%	0%	0%0	15%	74%	21%	27%
Cu(II)-HA	0%0	%0	0%0	0%	0%	0%0	3%	0%	0%	0%0	0%	9%	0%	$1^{0_{0}}$
Cu(I)-HA	43%	44%	47%	0%0	2%	0%	0%	0%0	0%	0%0	0%	0%	%0	10%
Cu2O	0%0	0%0	0%0	42%	32%	32%	21%	50%	61%	46%	17%	11%	11%	25%
Cu_foil	7%	8%	%6	23%	40%	58%	0%	0%	0%0	12%	61%	0%	58%	21%
error	4.86E-03	4.60E-03	4.03E-03	9.82E-04	7.24E-04	7.77E-04	4.59E-04	7.25E-03	5.76E-03	1.87E-03	1.27E-03	5.27E-04	5.95E-04	
sum	100%	100%	100%	100%	101%	102%	101%	108%	107%	100%	101%	101%	101%	
Sum without Cu2O und Cu foil	93%	92%	91%	34%	28%	12%	80%	58%	46%	41%	22%	%06	32%	
Normalization without Cu2O and Cu foil														
Tenorite	0%0	0%0	0%0	0%0	0%0	81%	0%0	33%	48%	0%	0%	0%	34%	15%
Nano-CuO	0%0	0%0	0%0	32%	29%	0%	0%	0%0	0%	0%	33%	0%	0%0	7%
CuSO4	0%0	0%0	0%0	0%	0%	19%	12%	53%	52%	0%	0%	1%	0%	10%
Cupro spinel	0%0	0%0	0%0	11%	10%	0%0	0%	15%	0%0	100%	0%	7%	0%0	11%
Chalcopyrite	0%0	0%0	0%0	0%0	0%0	0%0	0%	0%	0%	0%	0%0	0%0	0%0	0%
Covellite	0%0	0%0	0%0	0%0	0%0	0%	0%0	0%0	0%	0%	0%	0%	0%	0%0
CuS (primitive)	54%	52%	49%	57%	54%	0%0	85%	0%0	0%	0%0	67%	82%	96%	44%
Cu(II)-HA	0%0	0%0	0%0	0%	0%	0%	4%	0%0	0%	0%	0%	10%	0%	$1^{0/6}$
Cu(I)-HA	46%	48%	51%	0%0	6%	0%	0%0	0%	0%	0%	0%	0%	0%	12%

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	p1	p2	p3	p4	p5	p6	P9	p11	p12	p13	p14	p15	p16	p18	p19	mean values
Tenorite	2%	19%	0%0	%0	15%	0%	23%	0%0	0%	37%	0%0	0%	26%	0%0	0%	8%
Nano-CuO	0%0	2%	13%	23%	20%	0%	0%0	16%	17%	0%	0%0	0%	0%	0%	0%0	6%
CuSO4	2%	11%	9%	0%0	0%0	0%	12%	4%	0%0	14%	0%0	36%	25%	0%	28%	9%
Cupro spinel	15%	2%	0%0	0%	24%	2%	10%	2%	0%0	5%	7%	21%	35%	6%	47%	12%
Chalcopyrite	%0	0%	0%0	0%	0%0	0%	0%0	3%	0%0	10%	0%	13%	8%	0%	0%0	2%
Covellite	%0	0%	0%0	0%	0%0	0%	0%0	23%	29%	0%	0%	8%	0%	0%	0%0	4%
CuS (primitive)	71%	0%	0%0	0%	13%	0%	0%0	2%	0%0	0%	32%	0%	0%	0%	0%0	8%
Cu(II)-HA	%0	0%	0%0	0%	0%0	0%	0%0	29%	38%	18%	0%	0%	0%	20%	0%0	7%
Cu(I)-HA	%0	0%	0%0	5%	4%	0%	0%0	0%	0%0	0%	0%	0%	0%	0%	0%0	1%
Cu2O	15%	47%	59%	30%	0%0	86%	22%	12%	8%	20%	25%	12%	2%	0%	31%	25%
Cu_foil	0%0	21%	21%	44%	29%	13%	38%	12%	11%	0%	39%	14%	10%	77%	0%	22%
error	1.13E-03	5.35E-04	3.27E-04	4.06E-04	3.12E-04	2.11E-04	6.00E-04	1.06E-04	6.39E-04	7.69E-04	1.01E-03	7.76E-04	9.19E-04	8.24E-04	2.56E-03	
sum	104%	102%	102%	102%	104%	101%	104%	103%	103%	104%	104%	103%	106%	103%	106%	
Sum without Cu2O und Cu foil	%06	35%	22%	27%	75%	2%	44%	29%	84%	84%	40%	78%	94%	26%	75%	
Normalization without Cu2O and Cu foil																
Tenorite	2%	56%	0%0	0%0	20%	0%	51%	0%0	0%	44%	0%0	0%	28%	0%	0%	13%
Nano-CuO	0%0	9%	58%	82%	27%	0%	0%0	20%	21%	0%	0%	0%	0%0	0%	0%	14%
CuSO4	3%	31%	42%	0%0	0%0	0%	27%	5%	0%0	17%	0%	46%	26%	0%	37%	16%
Cupro spinel	16%	7%	0%0	0%0	32%	100%	22%	2%	0%0	6%	19%	28%	37%	22%	63%	24%
Chalcopyrite	0%0	0%0	0%0	0%0	0%0	0%0	%0	4%	0%0	12%	0%0	17%	9%	0%	0%0	3%
Covellite	0%0	0%0	0%0	0%0	0%0	0%0	0%0	29%	34%	0%	0%0	10%	0%0	0%	0%0	5%
CuS (primitive)	29%	0%0	0%0	0%0	17%	0%0	0%0	2%	0%0	0%	81%	0%0	0%0	0%	0%0	12%
Cu(II)-HA	0%0	0%0	%0	0%0	0%0	0%0	0%	37%	45%	21%	0%	0%	0%0	78%	0%0	12%
Cu(I)-HA	%0	0%0	0%0	18%	5%	0%	0%	%0	0%	0%	%0	0%	0%	0%0	0%	2%

TABLE S8. Detailed LCF results to the pXANES on the sample ASH AQ.

## 9 Decision tree for XRF acquisition parameter setting



FIGURE S25. Proposition of a decision tree for parameter optimization during XRF map acquisition.

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