Supplementary Information to

A Comparison of Signal Suppression and Particle Size Distributions for ns- and fs-LA for metallic samples by LA-ETV-ICPMS

Hale Ceren Yilmaz, Bodo Hattendorf

Laboratory of Inorganic Chemistry, ETH Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland.
E-mail: bodo@inorg.chem.ethz.ch; Tel: +41 44 633 45 23

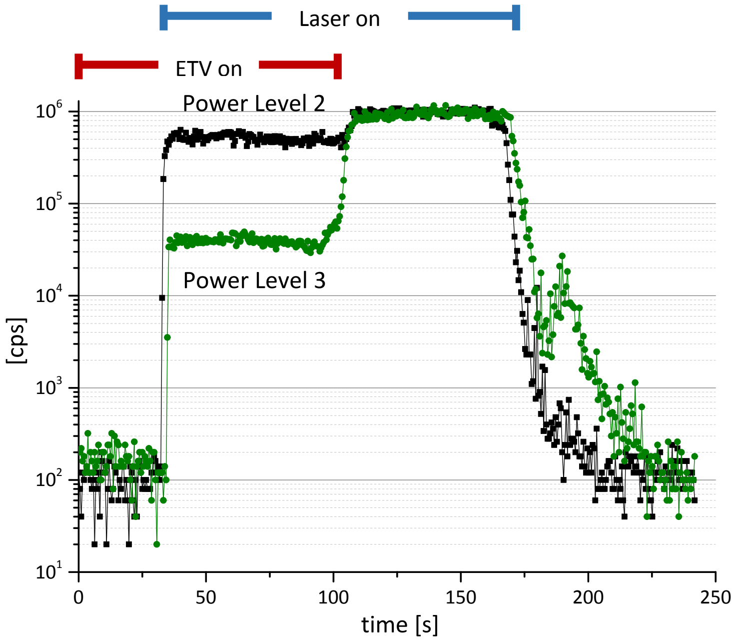


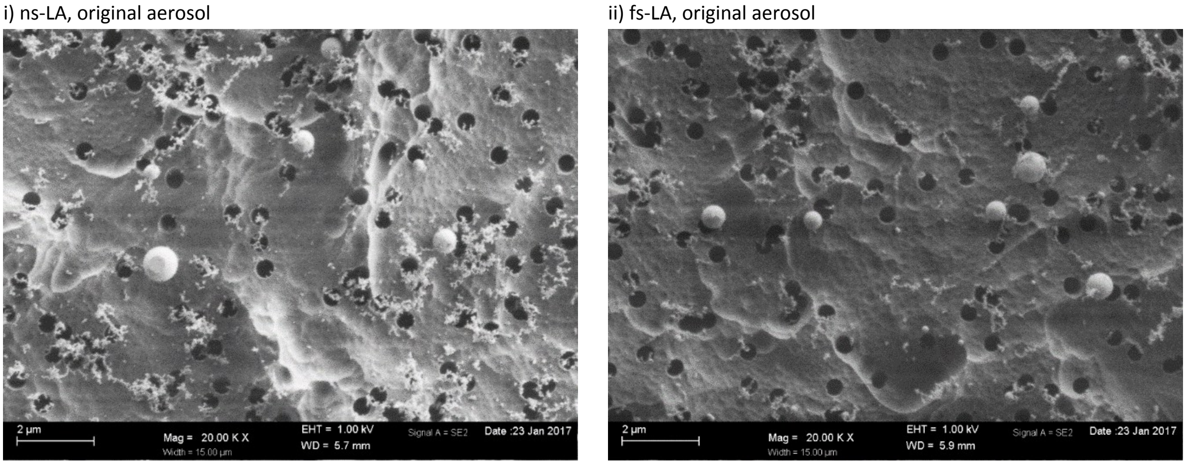
Figure S1. Transient signals for fs-LA-ICPMS of Zn, illustrating the experimental determination of signal suppression. 0 – 30 seconds: Gas blank, ETV on; 60 – 120 seconds: fs-LA-signal, ETV on; 120-180 seconds: LA-signal, ETV off; > 250 seconds: Gas blank ETV off. Signals were acquired at two different power levels of the ETV 4000 as indicated

Aerosol structures for ns- and fs-ablation. Collection on filters and OPC analysis

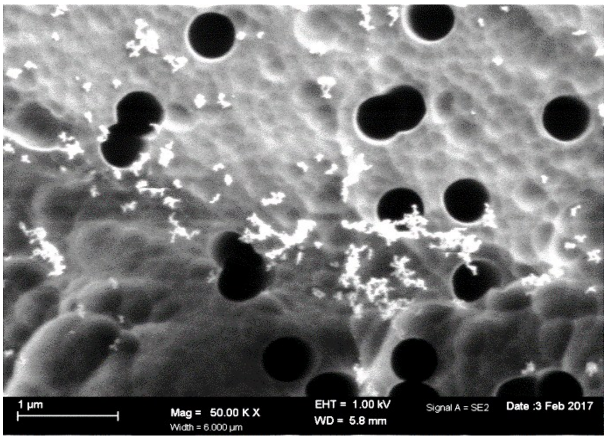
Pure Zn

i) ns-LA, original aerosol

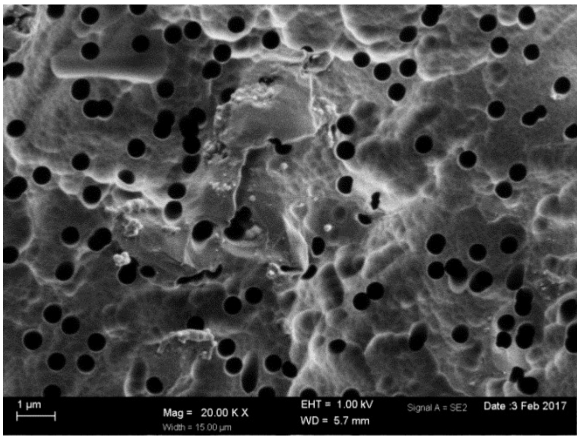
ii) fs-LA, original aerosol



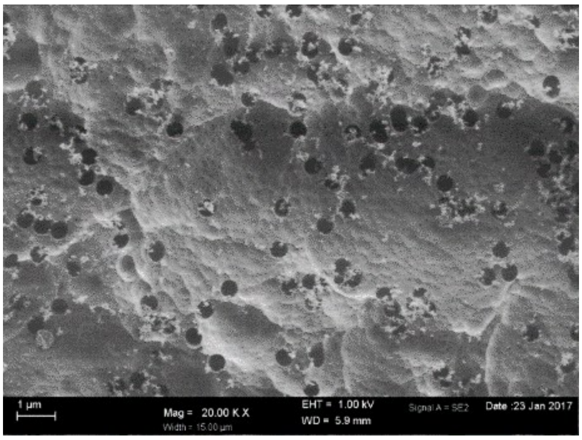
iii) ns-LA, power level 2.5



iv) fs-LA, power level 2.5



v) ns-LA, power level 3



vi) fs-LA, power level 3

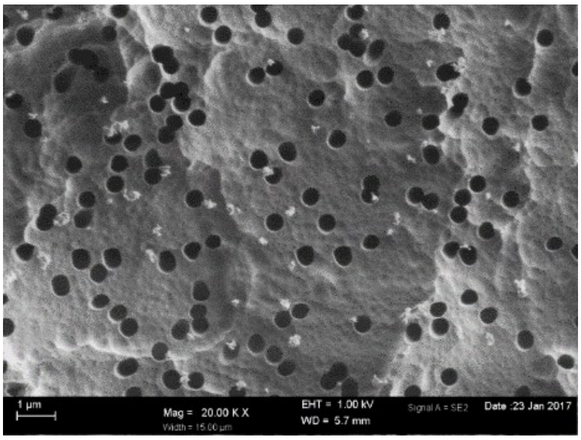
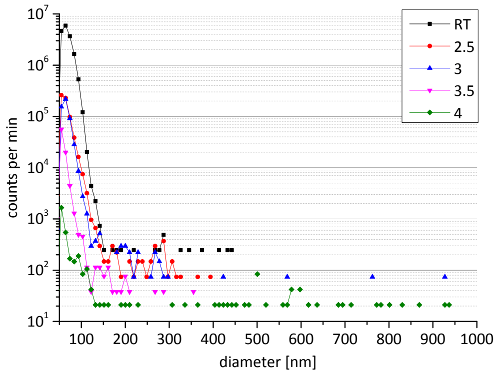


Figure S2 - SEM images of pure Zn.

i) ns-LA



ii) fs-LA

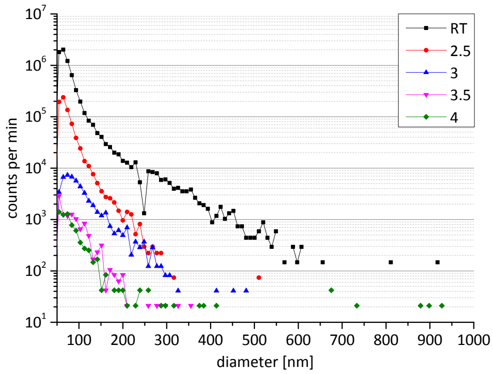
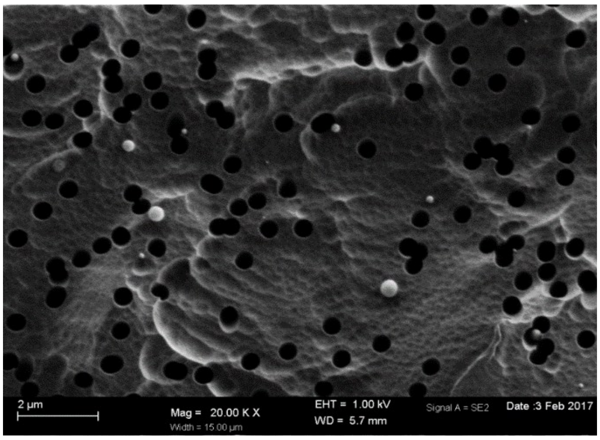


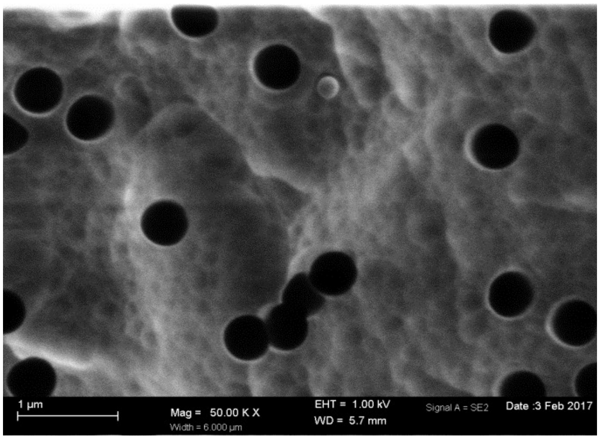
Figure S3 - PSD of pure Zn. Aerosol dilution factors were 174 for the initial aerosol, 74 at level 2.5, 41 at level 3, 21 at levels 3.5 and 4.

Pure Cu

i) fs-LA, power level 4.5



ii) fs-LA, power level 5.5



iii) fs-LA, power level 6.5

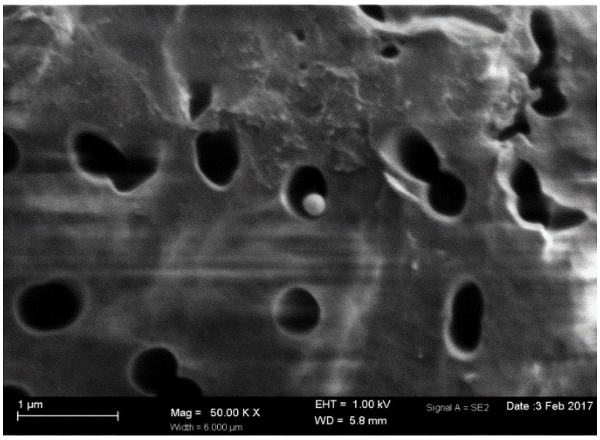
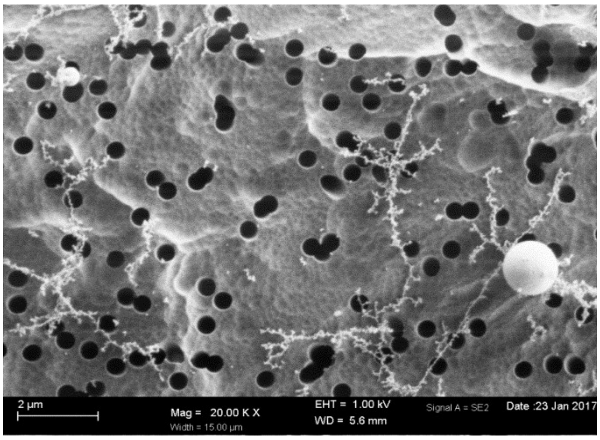


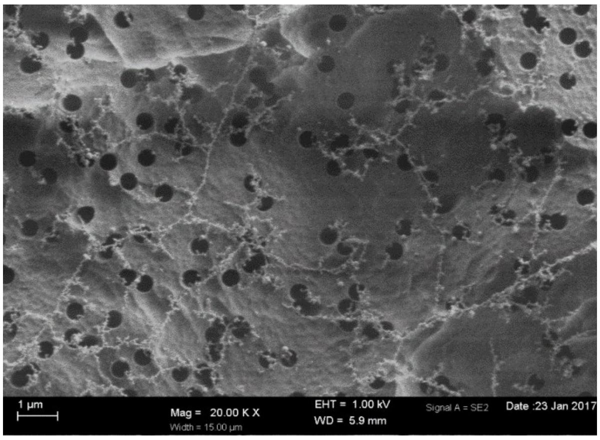
Figure S4 - SEM images of pure Cu.

Brass

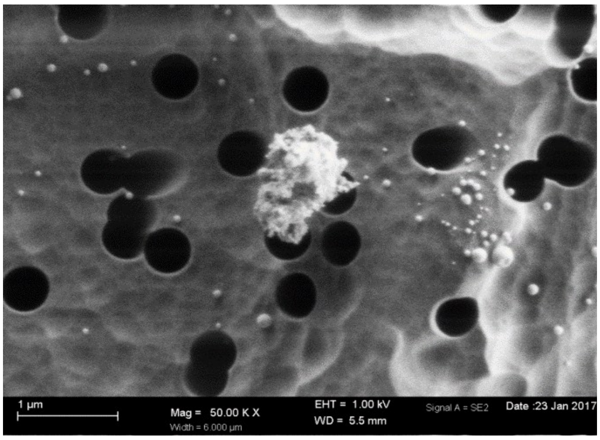
i) ns-LA, original aerosol



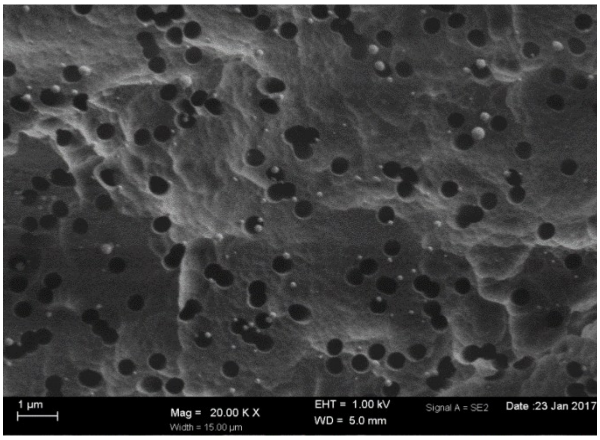
ii) fs-LA, original aerosol



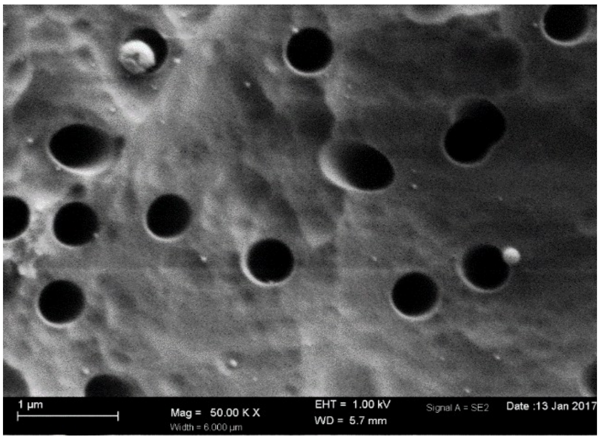
iii) ns-LA, power level 4.5



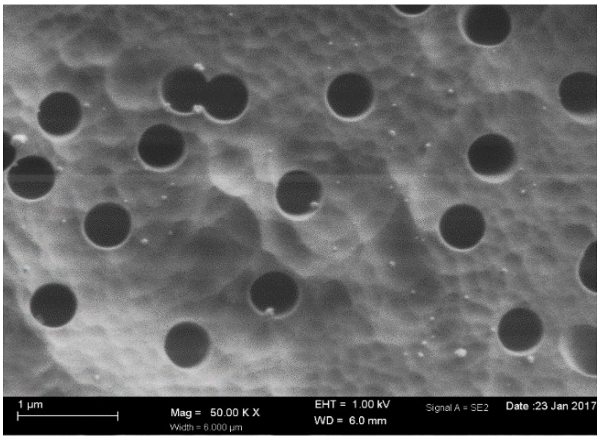
iv) fs-LA, power level 4.5



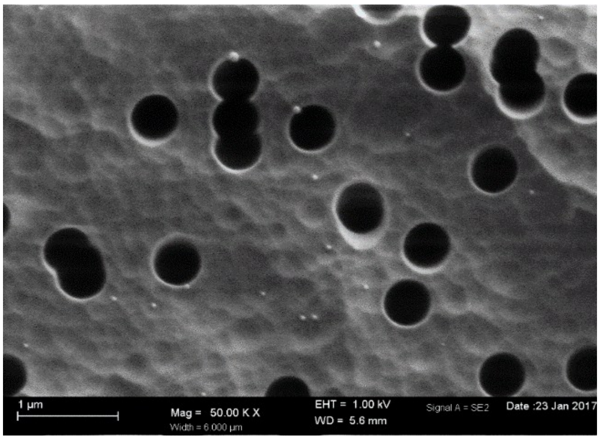
v) ns-LA, power level 5.5



vi) fs-LA, power level 5.5



vii) ns-LA, power level 7



viii) fs-LA, power level 7

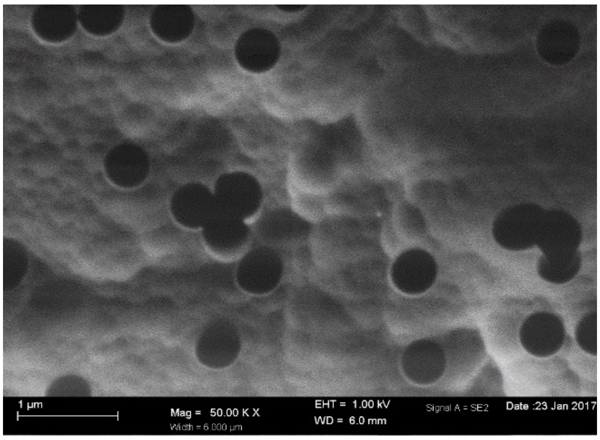
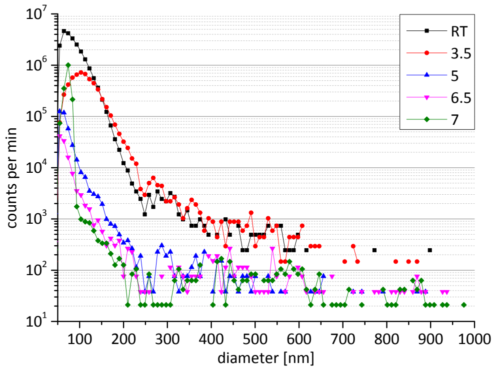


Figure S5 - SEM images of brass.

i) ns-LA



ii) fs-LA

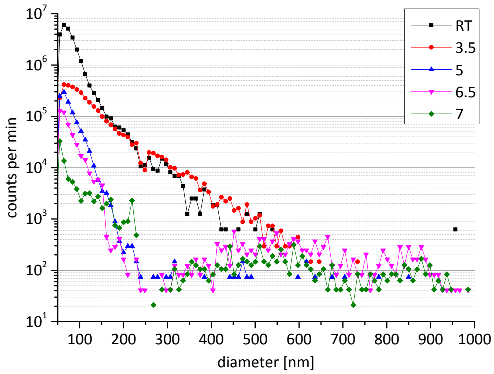


Figure S6. PSD of brass. Aerosol dilution factors were 245 (ns) and 625 (fs) for the initial aerosol, 147 at level 3.5, 38 (ns) and 74 (fs) at level 5, 38 (ns) and 41 (fs) at level 6 and 21 at level 7.

Pure Ta

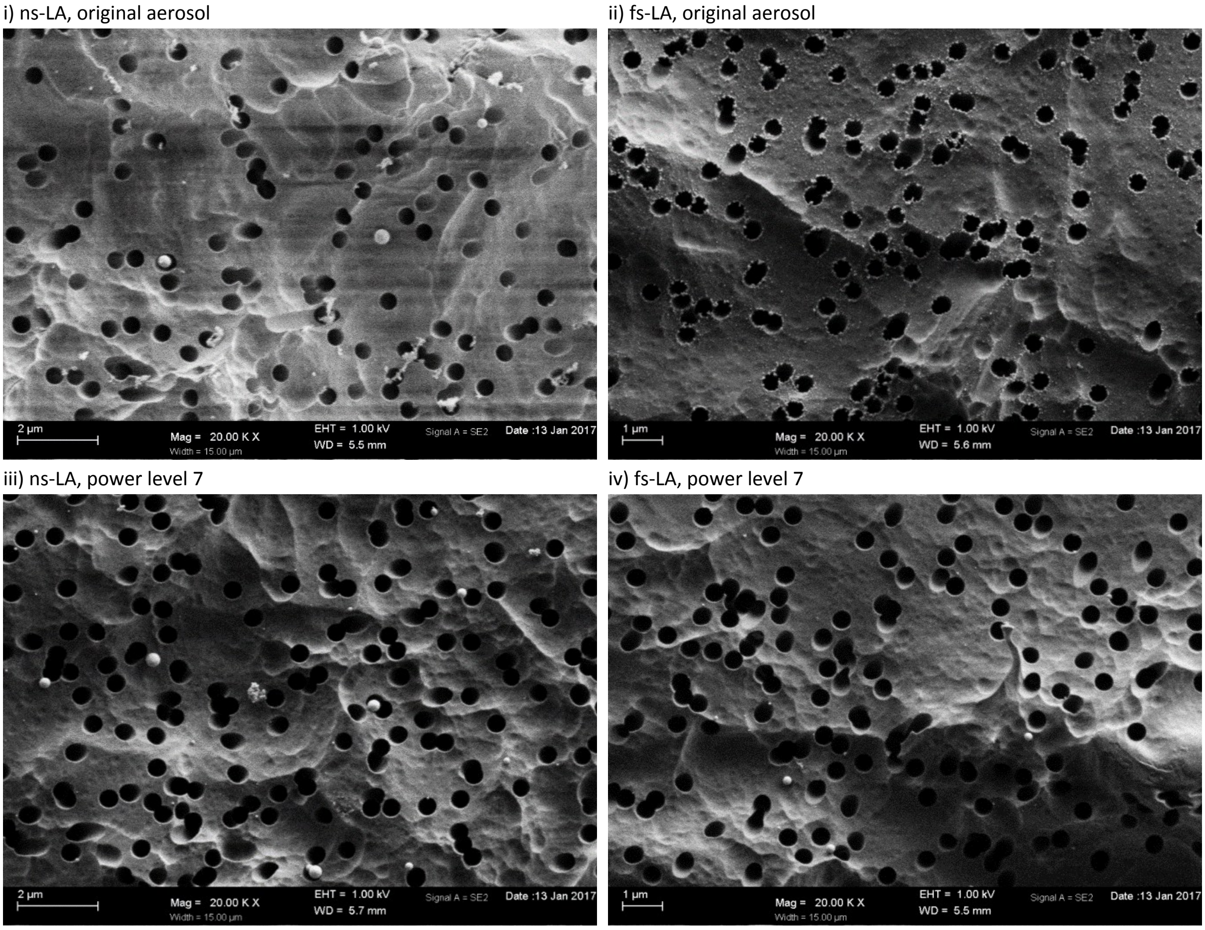


Figure S7 - SEM images of pure Ta.

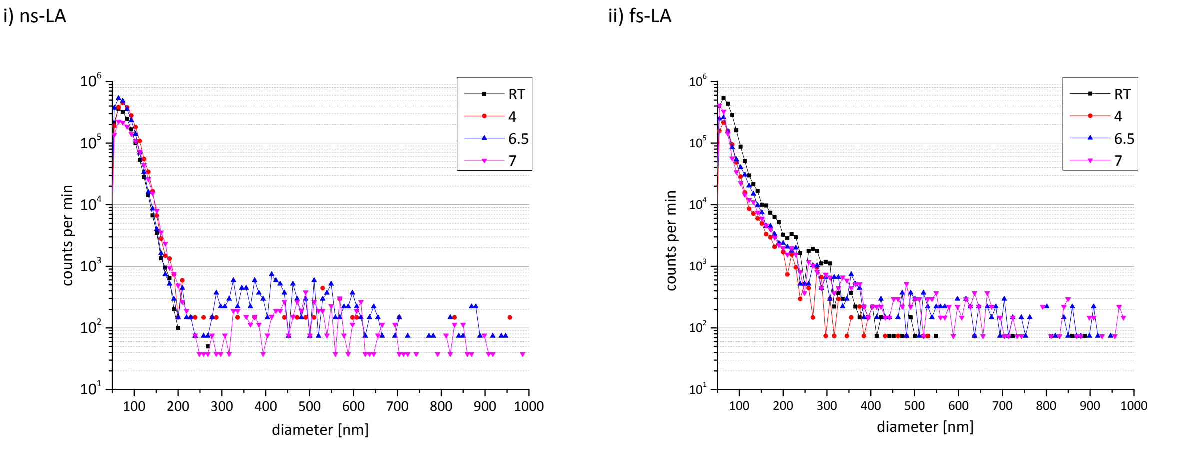


Figure S8 - PSD of Ta. Aerosol dilution factors for ns-LA were 50 for the original aerosol, 148 at power level 4, 74 at power level 6.5 and 38 at power level 7. The dilution factor for fs-LA was 74 for all measurements.

Transient Signal Structures of Cu at different power levels.

Brass vs. Cu

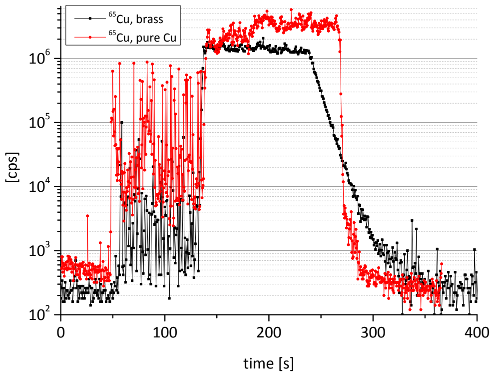
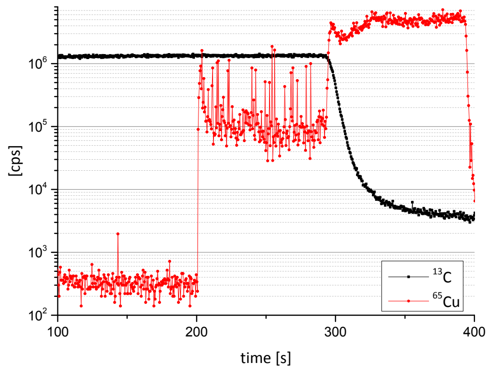


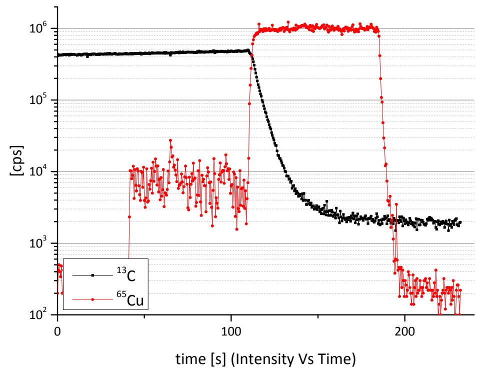
Figure S9 – ^{65}Cu-transient for ns-LA for pure Cu and brass

Cu at different power levels

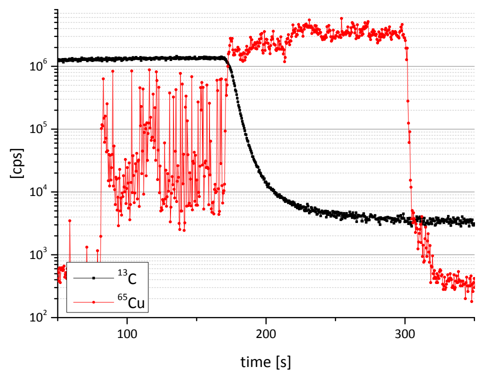
A i) ns-LA, power level 5



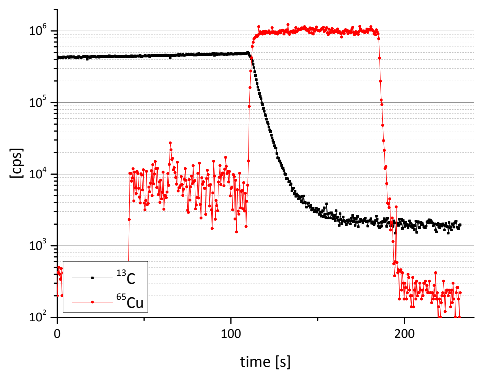
B i) fs-LA, power level 5



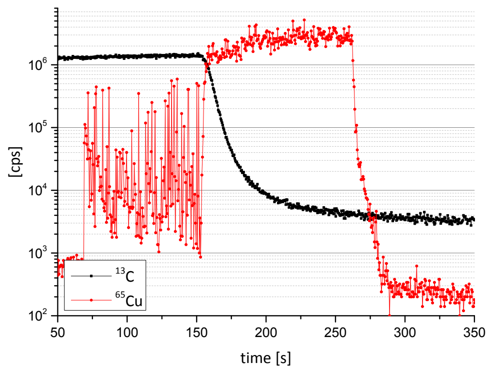
A ii) ns-LA, power level 5.5



B ii) fs-LA, power level 5.5



A iii) ns-LA, power level 6



B iii) fs-LA, power level 6

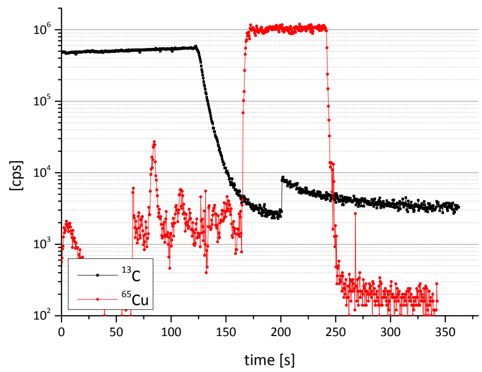


Figure S10 - ^{65}Cu-transient signal for pure Cu.

HGA-600MS as ETV unit: MHB B22, B24, and B26 heating profiles

Three brass samples (MB B22, B24 and B26) with differing Cu- and Zn-contents (Table S1) were investigated to identify possible matrix dependencies of the signal suppression of the ^{65}Cu- and ^{66}Zn-ion signals. A HGA-600MS ETV unit was used, equipped with a graphite tube (l = 28 mm, Ø = 6 mm) as heater. In contrast to the measurements performed with the ETV-4000, the temperature of the graphite furnace was increased continuously, with a rate of 4.8° C/s. The heating protocol is summarized in Table S2. For ablation, the Excite Pharos fs-laser was used at a wavelength of 257 nm. Line scans with a scan rate of 5 µm/s were performed with a repetition rate of 5 Hz and a spot size of 20 µm. The laser energy was set to 100% and the measured fluence was 7 J/cm².

i) ^{65}Cu-and ^{66}Zn- transient signals

ii) ^{65}Cu-and ^{66}Zn- transient signal suppressions

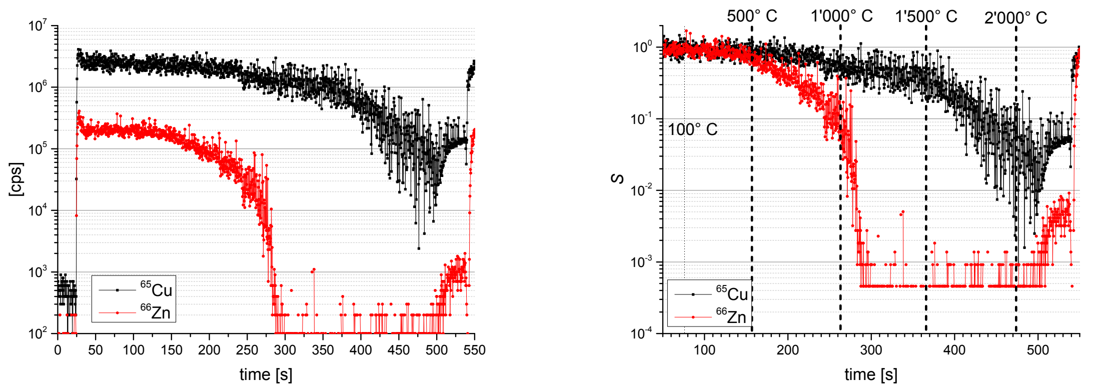


Figure S11 - i) ^{65}Cu-and ^{66}Zn- transient signals and ii) signal suppression transient profiles for ^{65}Cu- and ^{66}Zn- transient signals (normalized by the mean signals recorded without heating).for MBH B22.

i) ^{65}Cu-and ^{66}Zn- transient signals

ii) ^{65}Cu-and ^{66}Zn- transient signal suppressions

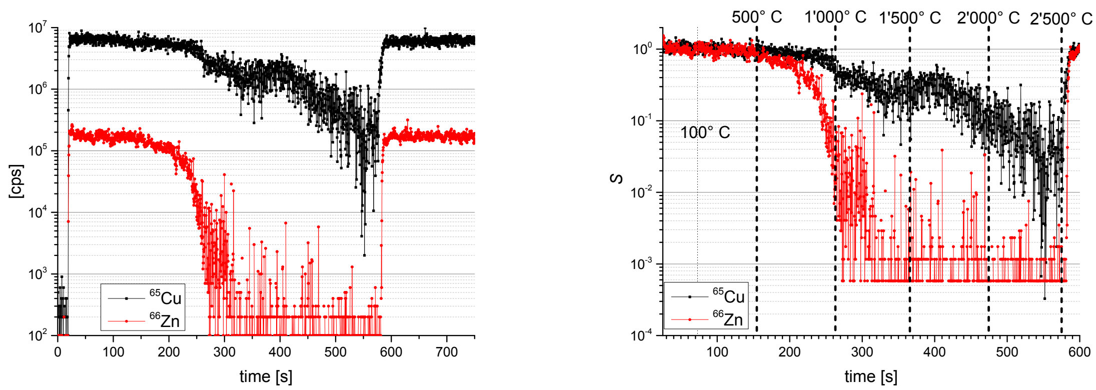


Figure S12 - i) ^{65}Cu-and ^{66}Zn- transient signals and ii) signal suppression transient profiles for ^{65}Cu- and ^{66}Zn- transient signals (normalized by the mean signals recorded without heating).for MBH B24.

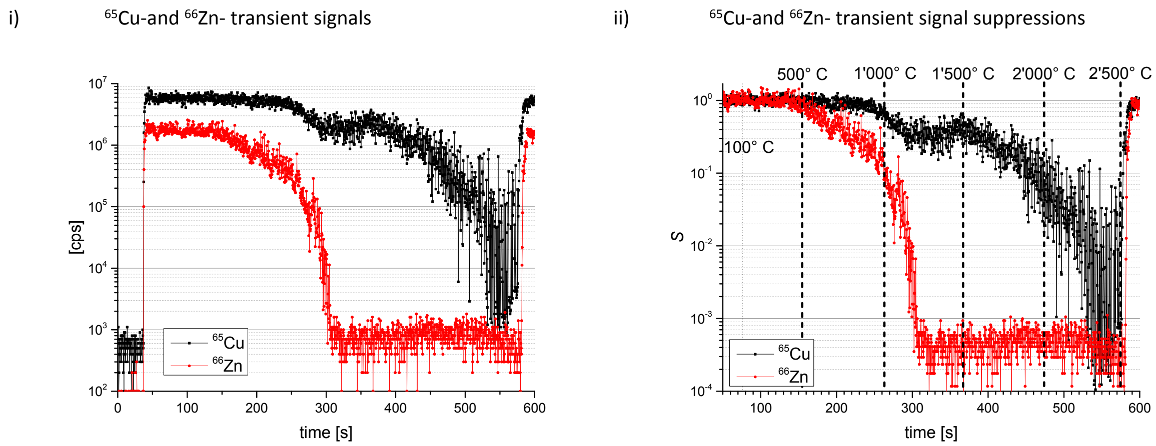


Figure S13 - i) ^{65}Cu-and ^{66}Zn- transient signals and ii) signal suppression transient profiles for ^{65}Cu- and ^{66}Zn- transient signals (normalized by the mean signals recorded without heating).for MBH B26.

Table S1 – Cu- and Zn-contents of the MBH B22, B24 and B26 brass standards.

Percentage element by weight	MBH B22	MBH B24	MBH B26
Cu	82.47	95.65	62.93
Zn	15.92	1.99	30.30
Suppression of Cu at a tube temperature of 1800°C	0.12175	0.11148	0.10952

Table S2 – Heating protocol for single temperature measurements

	T [° C]	Duration	Laser
BG_{RT}	0	30 s	Off
LA_{RT}	0	30 s	On
LA_{H}	a) 100 – 2300 b) 100 – 2500	504 s, 4.8° C/s	On
LA_{RT}	0	30 s	On