

Nanosecond and Femtosecond Laser Ablation of Brass: Particulate and ICPMS Measurements

C. Liu, X. L. Mao, S. Mao, X. Zeng, R. Greif, and R. E. Russo*

Lawrence Berkeley National Laboratory, Berkeley, California 94720

Femtosecond and nanosecond lasers were compared for ablating brass alloys. All operating parameters from both lasers were equal except for the pulse duration. The ablated aerosol vapor was collected on silicon substrates for particle size measurements or sent into an inductively coupled plasma mass spectrometer. The diameters and size distribution of particulates were measured from scanning electron microscope (SEM) images of the collected ablated aerosol. SEM measurements showed that particles ablated using nanosecond pulses were single spherical entities ranging in diameter from several micrometers to several hundred nanometers. Primary particles ablated using femtosecond ablation were ~100 nm in diameter but formed large agglomerates. ICPMS showed enhanced signal intensity and stability using femtosecond compared to nanosecond laser ablation.

Laser ablation combined with inductively coupled plasma mass spectrometry (ICPMS) is a practical method for direct solid sample chemical analysis.^{1–5} Significant improvements in this technology have led to numerous routine applications, especially in geochemistry. Efforts are still underway to study parameters such as wavelength,^{6,7} gas ambient,⁸ and energy fluence^{9–11} for further improving accuracy and precision of analysis. The ablated aerosol particle sizes are believed to significantly influence analytical performance using ICPMS detection.^{12–14} Chemical composition, entrainment, transport, and decomposition in the ICP

all are related to the size of the aerosol particles.^{15–17} For ablation, the laser wavelength and pulse duration play a dominant role in defining the size, size distribution, and chemistry of the ablated particulates. The goal of this work was to measure particles using femtosecond and nanosecond laser ablation and establish correlations with ICPMS performance.

The use of femtosecond ablation to reduce thermal effects and minimize fractionation for chemical analysis has been tested, using both IR and UV pulses.^{18–22} By using the same laser energy and spot size (same fluence), ICPMS performance with femtosecond laser ablation showed improvements in intensity, precision, and accuracy. To further investigate these improvements, the basis of this work was to examine the relationship between the particle size distribution and ICPMS response using UV femtosecond and nanosecond laser pulses. Brass alloys were ablated with fixed laser parameters of fluence, energy, spot size, and wavelength; pulse duration was the only difference. Brass alloys are commonly chosen as samples due to the thermal volatility difference of copper and zinc.^{18–24} These alloys are ideal for studying effects of pulse duration on fractionation and signal stability using ICPMS. The ablated aerosols also were collected on silicon substrates for scanning electron microscopic (SEM) measurements of particle sizes.

EXPERIMENTAL SECTION

The experimental configuration is shown in Figure 1. Two lasers were used; a Nd:YAG laser with 6-ns pulse duration (New Wave Research, Minilase II) and a Ti:sapphire laser with 150-fs pulse duration (Spectra-Physics, TSA 25). The wavelength of both lasers was adjusted to be 266 nm. For the nanosecond Nd:YAG laser, the fourth harmonic of the 1064-nm fundamental produces 266-nm light. For the Ti:sapphire femtosecond laser, it was the

* Corresponding author: (e-mail) rerusso@lbl.gov.

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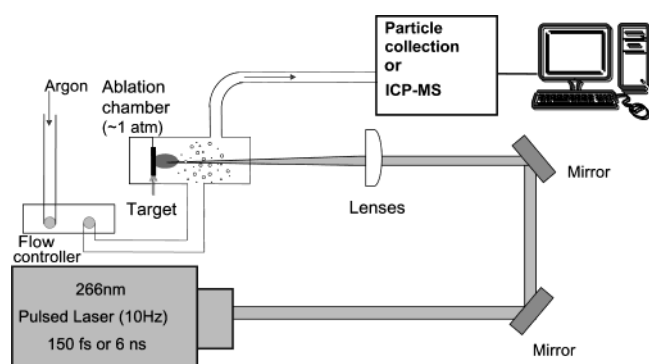


Figure 1. Experimental system.

64 third harmonic of the 800-nm fundamental. Both lasers were
 65 operated at 10-Hz repetition rate, at the same energy of 0.6 mJ,

66 and focused onto the sample surface using the same lens to a
 67 100- μm -diameter spot size. The fluence was $\sim 8 \text{ J/cm}^2$. The
 68 irradiance was the only difference; for the nanosecond laser, it
 69 was $1.3 \times 10^9 \text{ W/cm}^2$ whereas for the femtosecond laser it was 5
 70 $\times 10^{13} \text{ W/cm}^2$. The pulse-to-pulse energy stability (relative
 71 standard deviation, RSD) of the femtosecond laser (5%) was about
 72 twice that of nanosecond laser (2%).

73 The ablated mass was transported out of the sample chamber
 74 and collected for SEM measurements or delivered into the ICPMS.
 75 Argon was used as the carrier gas. Ablation was continuous for 3
 76 min for the ICPMS measurements (single spot on sample during
 77 repetitive pulsing). The ICPMS (Thermochemical, PQ3) was
 78 operated at forward rf power of 1350 W with argon flow rates
 79 of 14, 1, and 0.8 L/min for coolant, auxiliary, and carrier,
 80 respectively.

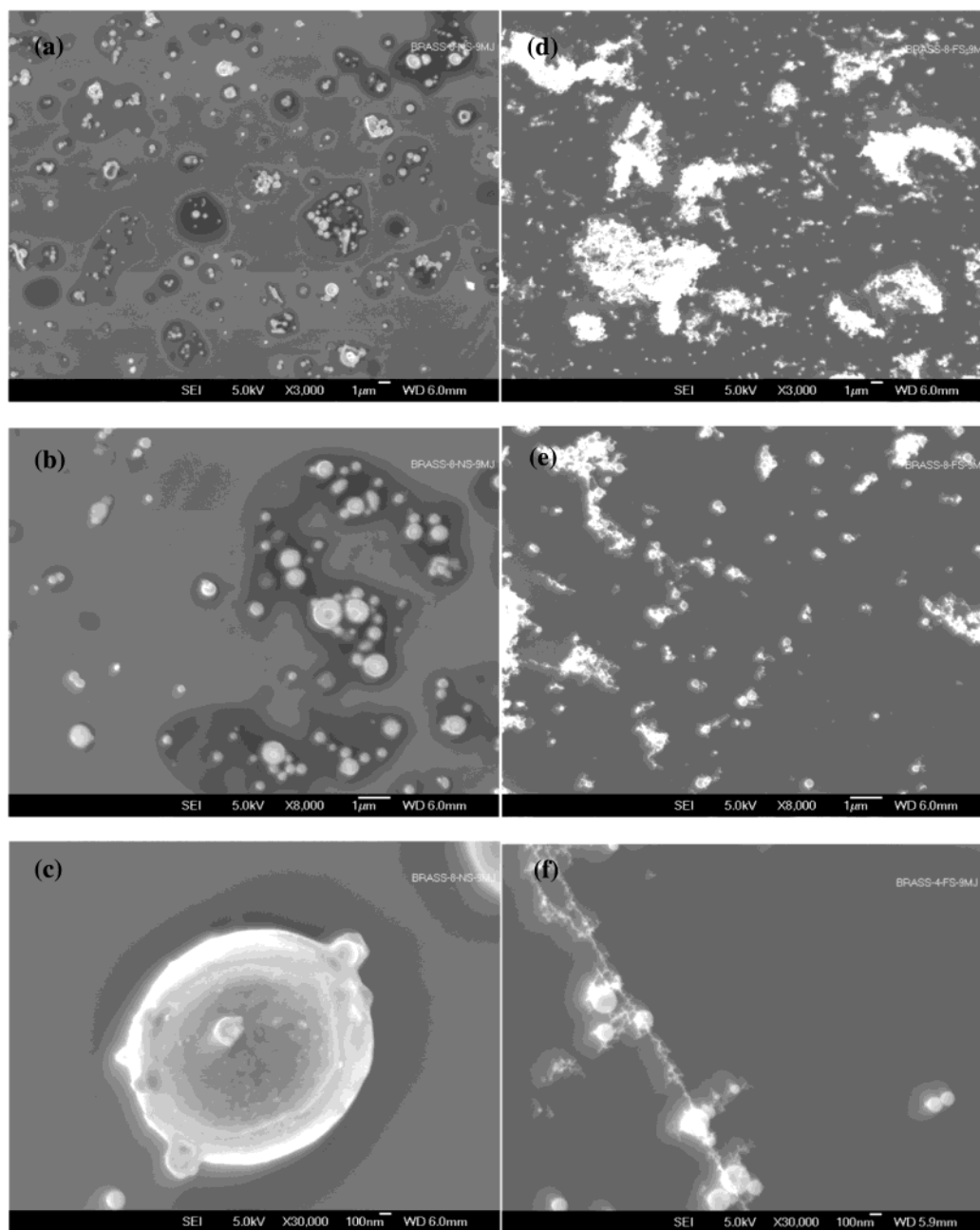


Figure 2. SEM images of ablated particles (a, b, and c from nanosecond laser ablation with 3000 \times , 8000 \times , and 30000 \times magnification, respectively; d, e, and f from femtosecond ablation with 3000 \times , 8000 \times , and 30000 \times magnification, respectively).

81 SEM images were used to measure the shapes and sizes of
 82 particles collected on small clean silicon substrates. The same
 83 sample chamber and 1 m of tubing (the same tubing distance to
 84 the ICP torch) were used to transport the particles. For particle
 85 collection, the ablation time was 2 min. The basis of the work
 86 was to qualitatively compare particles ablated using femtosecond
 87 and nanosecond pulses and establish relationships to ICPMS
 88 response, not to quantitatively define aerosol sizes and size
 89 distribution.

90 Brass with a Zn/Cu ratio of 0.18 was used as the sample for
 91 particle and ICPMS measurements. However, a series of brass
 92 samples with zinc-to-copper mass ratios (Zn/Cu) from 0.06 to 0.65
 93 were used to study the matrix effects on ablation sampling using
 94 both femtosecond and nanosecond pulses. ^{65}Cu and ^{66}Zn signal
 95 intensities were recorded sequentially using 10-ms dwell time for
 96 the quadrupole mass spectrometer. The volumes of the ablated
 97 craters in brass were measured using a white-light interferometric
 98 microscope (Zygo, New View 200). Three crater measurements
 99 were made for each set of experiments, and the RSD was $\sim 10\%$
 100 in volume.

101 RESULTS AND DISCUSSIONS

102 **SEM.** SEM images of particles collected at the exit of the
 103 ablation chamber and tubing are shown in Figure 2. The particle
 104 shapes and sizes were visually very different. Femtosecond
 105 ablation produced smaller particles that formed large agglomerates
 106 compared to large particles and small agglomerates from nano-
 107 second ablation. Large agglomerates of irregular shape with sizes
 108 of 5–10 μm across (Figure 2d) existed from femtosecond ablation
 109 compared with smaller agglomerates from nanosecond ablation
 110 (Figure 2b). Particles from nanosecond laser ablation were mostly
 111 single spherical entities with diameters ranging from tens to
 112 thousands of nanometers (Figure 2c). The large particle ag-
 113 glomerates from femtosecond ablation consisted of primary
 114 particles with size of $\sim 100\text{--}200$ nm, connected by filaments having
 115 dimensions of several nanometers. There were no single large
 116 droplets such as those observed with nanosecond ablation. The
 117 shape of the agglomerates connected by filaments is indicative of
 118 strong charge during the formation of these particles.^{25,26} It is not
 119 likely that the agglomeration was formed at the silicon surface
 120 but during transport. Particle agglomeration is related to size;
 121 smaller particles have a higher tendency to agglomerate than
 122 larger ones, supporting the SEM measurements.

123 The differences in particle sizes are related to the differences
 124 in femtosecond and nanosecond ablation. Melting and melt
 125 ejection should be prominent for nanosecond ablation. Particles
 126 as large as several micrometers in diameter are likely ejected from
 127 the molten sample surface due to recoil pressure of the expanding
 128 plume. The effect of melting is readily observed on the crater
 129 profiles in Figure 3. The craters were produced using the same
 130 number of pulses from each laser. Nanosecond ablation leaves a
 131 raised rim around the crater perimeter that is caused by resolidi-
 132 fication of molten brass. Melting and splashing were reduced using
 133 femtosecond pulses consistent with the absence of a rim. The
 134 crater volume from femtosecond ablation was much larger ($\sim 10\text{--}$

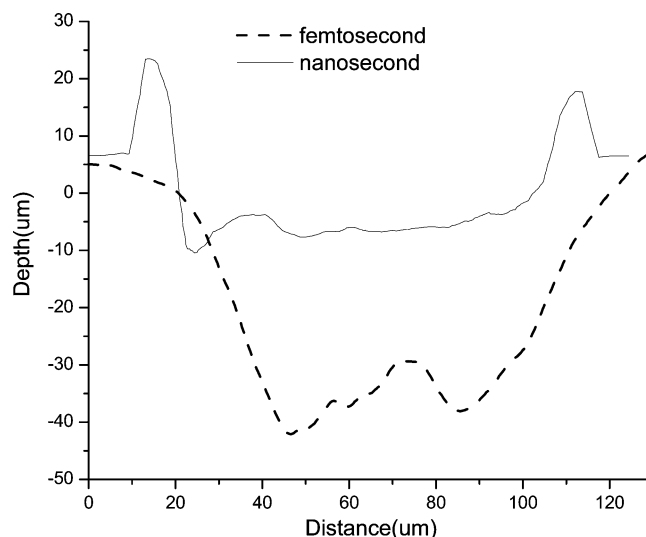


Figure 3. Crater profiles after 50 pulses each from nanosecond and femtosecond ablation of brass.

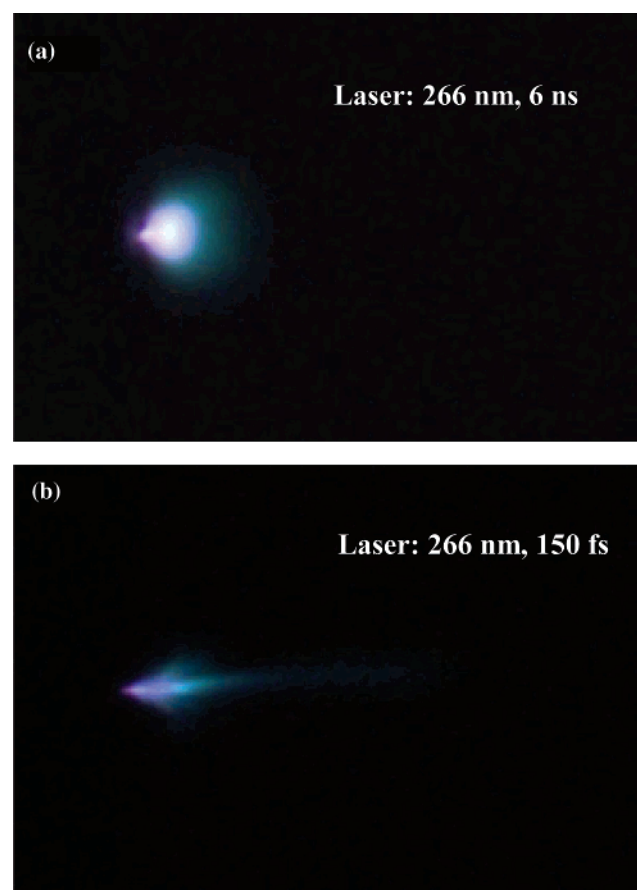


Figure 4. Photographs of laser plasmas from nanosecond and femtosecond ablation.

135 15 times) than from the nanosecond case, demonstrating improved
 136 ablation efficiency. Photographs of laser-induced plasmas support
 137 the probability of different particle formation mechanisms (Figure
 138 4). For equal energy and spot size (fluence), the plasma from
 139 nanosecond ablation was spherically shaped while the femto-
 140 second-induced plasma was cylindrical.

141 **ICPMS.** Brass was ablated (crater formation at a single spot)
 142 using both lasers while recording the signal intensity in the

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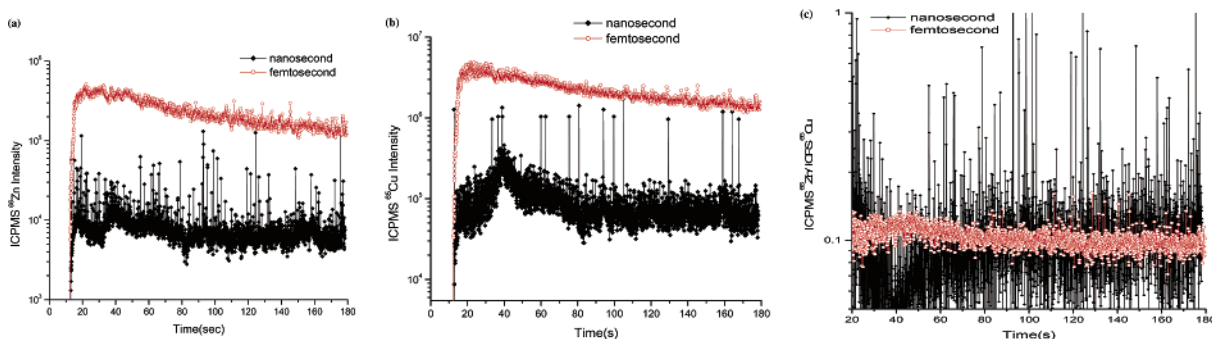


Figure 5. ICPMS intensity of ^{66}Zn and ^{65}Cu and ratio of $^{66}\text{Zn}/^{65}\text{Cu}$ with different pulse durations.

143 ICPMS; the temporal intensity for ^{65}Cu and ^{66}Zn are shown in
 144 Figure 5a and b, respectively. Femtosecond ablation produced Zn
 145 and Cu elemental signals that were more than 10 times greater
 146 than produced by nanosecond ablation at the same fluence. The
 147 increase in ICPMS intensity is consistent with the volume data
 148 shown in Figure 3. An exact correlation between volume and
 149 intensity is not expected as the particle size and distribution
 150 differences will influence transport efficiency. The femtosecond
 151 data also showed less fluctuations (improved precision, RSD) and
 152 minimal spiking. The improved RSD in the femtosecond data
 153 exists even though the laser itself has poorer pulse-to-pulse
 154 stability. Instantaneous spikes with intensity of 10 times larger
 155 than the continuous level were measured for nanosecond ablation
 156 with overall larger intensity fluctuations (RSD) in the continuous
 157 signal. The spikes and precision are related to the particle size
 158 distribution from the ablation process. Nanosecond ablation
 159 produced larger particles and a larger particle size distribution
 160 (cf. Figure 2). Although femtosecond ablation led to agglomeration
 161 of smaller particles, the large agglomerates appear to be effectively
 162 digested in the ICP compared to single large particles. In principle,
 163 large particles should not transport as efficiently as smaller ones.
 164 However, the agglomerates may not behave as single entities
 165 during transport and in the ICP.

166 The smaller particle size distribution and improved signal
 167 stability from femtosecond ablation enhance analysis as demon-
 168 strated by the $^{66}\text{Zn}/^{65}\text{Cu}$ ratio in Figure 5c. The ratio for
 169 nanosecond ablation ranged from 0.05 to 0.2, excluding the spikes
 170 on data. The ratio was significantly improved for femtosecond
 171 ablation ($^{66}\text{Zn}/^{65}\text{Cu} = 0.11$) and was constant during the entire
 172 sampling period.

173 Six brass samples with Zn/Cu ratios varying from 0.06 to 0.65
 174 were ablated using both lasers. The calculated RSDs from the
 175 integrated temporal (1200 pulses for each sampling period) signal
 176 response are shown in Figure 6. For nanosecond ablation, the
 177 RSD was as large as 120% and matrix dependent, compared to
 178 femtosecond ablation, which showed smaller RSD values of $\sim 10\%$
 179 and independent of the zinc/copper ratio. Optical and thermal
 180 properties of the sample influence the laser ablation process,
 181 especially using nanosecond pulses. For brass, zinc is more volatile
 182 than copper and can be significantly enhanced in the aerosol using
 183 nanosecond ablation.²⁴ Lower zinc intensity from nanosecond
 184 ablation of low zinc concentration brass is not the cause of the
 185 increased error. For all the brass samples, the zinc intensity from
 186 nanosecond ablation was well above the background (~ 200

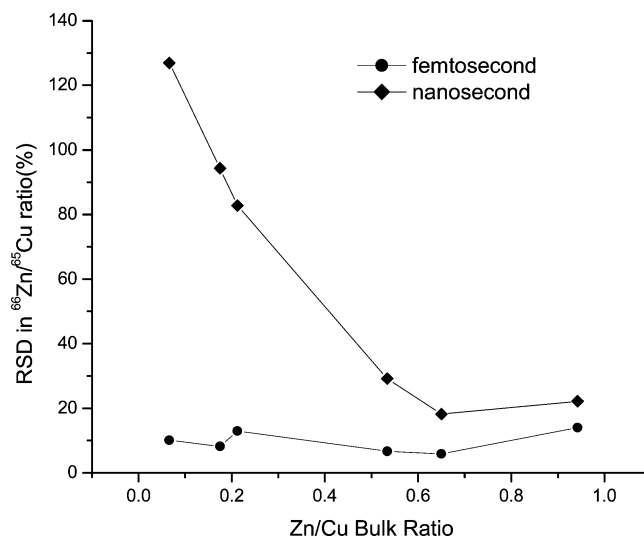


Figure 6. RSD with respect to bulk Zn/Cu ratio.

counts). For similar zinc intensities, the error was significantly
 larger from nanosecond versus femtosecond laser ablation.

CONCLUSION

The particles formed from femtosecond and nanosecond laser
 ablation had a significant influence on the ICPMS response.
 Femtosecond laser ablation produced large agglomerates com-
 posed of small and narrowly distributed diameter particles while
 nanosecond ablation generated a wide size range of particle sizes,
 some as large as several micrometers in diameter. The smaller
 particles from femtosecond ablation lead to enhanced signal
 intensity and stability in the ICPMS. Spikes on the ICPMS
 response from nanosecond ablation represent the large particle
 size distribution. Melting and melt flushing are believed to be
 prominent mechanisms during nanosecond ablation as evidenced
 by the raised crater rim and large spherical particles in the aerosol
 vapor. The large agglomerates composed of nanometer diameter
 particles from femtosecond ablation were transported and digested
 by the ICPMS. Work is underway to establish the mechanisms
 for particle formation for femtosecond ablation; it is possible that
 the prominent mechanism may be nucleation and condensation
 of vapor.

Matrix effects were reduced using femtosecond ablation; the
 sampling precision for a wide range of brass alloy composition
 was independent of the matrix composition. In addition, the

| | | | |
|-----|---|--|-----|
| 211 | Zn/Cu ratio was stable throughout the sampling period in which | Nonproliferation and National Security (NA22) supported this | 219 |
| 212 | a crater was formed. Such behavior has not been observed using | research at the Lawrence Berkeley National Laboratory under | 220 |
| 213 | nanosecond ablation. Improved precision and elimination of spikes | Contract DE-AC03-76SF00098. | 221 |
| 214 | makes the use of femtosecond ablation encouraging for chemical | | |
| 215 | analysis applications. | | |
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