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Authors

Liu, C. Mao, X.L. Mao, S. <u>et al.</u>

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Nanosecond and Femtosecond Laser Ablation of 1 Brass: Particulate and ICPMS Measurements 2

C. Liu, X. L. Mao, S. Mao, X. Zeng, R. Greif, and R. E. Russo* 3

Lawrence Berkeley National Laboratory, Berkeley, California 94720

Femtosecond and nanosecond lasers were compared for 6 ablating brass alloys. All operating parameters from both 7 lasers were equal except for the pulse duration. The 8 9 ablated aerosol vapor was collected on silicon substrates for particle size measurements or sent into an inductively 10 coupled plasma mass spectrometer. The diameters and 11 12 size distribution of particulates were measured from scanning electron microscope (SEM) images of the col-13 lected ablated aerosol. SEM measurements showed that 14 particles ablated using nanosecond pulses were single 15 spherical entities ranging in diameter from several mi-16 crometers to several hundred nanometers. Primary par-17 ticles ablated using femtosecond ablation were ~ 100 nm 18 in diameter but formed large agglomerates. ICPMS showed 19 20 enhanced signal intensity and stability using femtosecond compared to nanosecond laser ablation. 21

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Laser ablation combined with inductively coupled plasma mass 23 spectrometry (ICPMS) is a practical method for direct solid 24 sample chemical analysis.¹⁻⁵ Significant improvements in this 25 26 technology have led to numerous routine applications, especially in geochemistry. Efforts are still underway to study parameters 27 such as wavelength,67 gas ambient,8 and energy fluence9-11 for 28 further improving accuracy and precision of analysis. The ablated 29 aerosol particle sizes are believed to significantly influence 30 analytical performance using ICPMS detection.¹²⁻¹⁴ Chemical 31 32 composition, entrainment, transport, and decomposition in the ICP

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all are related to the size of the aerosol particles.^{15–17} For ablation, 33 the laser wavelength and pulse duration play a dominant role in 34 defining the size, size distribution, and chemistry of the ablated 35 particulates. The goal of this work was to measure particles using 36 femtosecond and nanosecond laser ablation and establish cor-37 relations with ICPMS performance. 38

The use of femtosecond ablation to reduce thermal effects and 39 minimize fractionation for chemical analysis has been tested, using 40 both IR and UV pulses.¹⁸⁻²² By using the same laser energy and 41 spot size (same fluence), ICPMS performance with femtosecond 42 laser ablation showed improvements in intensity, precision, and 43 accuracy. To further investigate these improvements, the basis 44 of this work was to examine the relationship between the particle 45 size distribution and ICPMS response using UV femtosecond and 46 nanosecond laser pulses. Brass alloys were ablated with fixed laser 47 parameters of fluence, energy, spot size, and wavelength; pulse 48 duration was the only difference. Brass alloys are commonly 49 chosen as samples due to the thermal volatility difference of 50 copper and zinc.^{18–24} These alloys are ideal for studying effects of 51 pulse duration on fractionation and signal stability using ICPMS. 52 The ablated aerosols also were collected on silicon substrates for 53 scanning electron microscopic (SEM) measurements of particle 54 sizes. 55

EXPERIMENTAL SECTION

The experimental configuration is shown in Figure 1. Two 57 lasers were used; a Nd:YAG laser with 6-ns pulse duration (New 58 Wave Research, Minilase II) and a Ti:sapphire laser with 150-fs 59 pulse duration (Spectra-Physics, TSA 25). The wavelength of both 60 lasers was adjusted to be 266 nm. For the nanosecond Nd:YAG 61 laser, the fourth harmonic of the 1064-nm fundamental produces 62 266-nm light. For the Ti:sapphire femtosecond laser, it was the 63

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



Figure 1. Experimental system.

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

and focused onto the sample surface using the same lens to a 66 100- μ m-diameter spot size. The fluence was ~8 J/cm². The 67 irradiance was the only difference; for the nanosecond laser, it 68 was 1.3×10^9 W/cm² whereas for the femtosecond laser it was 5 69 \times 10¹³ W/cm². The pulse-to-pulse energy stability (relative 70 standard deviation, RSD) of the femtosecond laser (5%) was about 71 twice that of nanosecond laser (2%). 72

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



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.

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

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

101 RESULTS AND DISCUSSIONS

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

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



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.

15 times) than from the nanosecond case, demonstrating improved135ablation efficiency. Photographs of laser-induced plasmas support136the probability of different particle formation mechanisms (Figure1374). For equal energy and spot size (fluence), the plasma from138nanosecond ablation was spherically shaped while the femto-139second-induced plasma was cylindrical.140

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

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Figure 5. ICPMS intensity of ⁶⁶Zn and ⁶⁵Cu and ratio of ⁶⁶Zn/⁶⁵Cu with different pulse durations.

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

166The smaller particle size distribution and improved signal167stability from femtosecond ablation enhance analysis as demon-168strated by the ${}^{66}\text{Zn}/{}^{65}\text{Cu}$ ratio in Figure 5c. The ratio for169nanosecond ablation ranged from 0.05 to 0.2, excluding the spikes170on data. The ratio was significantly improved for femtosecond171ablation (${}^{66}\text{Zn}/{}^{65}\text{Cu} = 0.11$) and was constant during the entire172sampling period.

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



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

counts). For similar zinc intensities, the error was significantly 187 larger from nanosecond versus femtosecond laser ablation. 188

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CONCLUSION

The particles formed from femtosecond and nanosecond laser 190 ablation had a significant influence on the ICPMS response. 191 Femtosecond laser ablation produced large agglomerates com-192 posed of small and narrowly distributed diameter particles while 193 nanosecond ablation generated a wide size range of particle sizes, 194 some as large as several micrometers in diameter. The smaller 195 particles from femtosecond ablation lead to enhanced signal 196 intensity and stability in the ICPMS. Spikes on the ICPMS 197 response from nanosecond ablation represent the large particle 198 size distribution. Melting and melt flushing are believed to be 199 prominent mechanisms during nanosecond ablation as evidenced 200 by the raised crater rim and large spherical particles in the aerosol 201 vapor. The large agglomerates composed of nanometer diameter 202 particles from femtosecond ablation were transported and digested 203 by the ICPMS. Work is underway to establish the mechanisms 204 for particle formation for femtosecond ablation; it is possible that 205 the prominent mechanism may be nucleation and condensation 206 of vapor. 207

Matrix effects were reduced using femtosecond ablation; the 208 sampling precision for a wide range of brass alloy composition 209 was independent of the matrix composition. In addition, the 210

211 Zn/Cu ratio was stable throughout the sampling period in which

a crater was formed. Such behavior has not been observed using

213 nanosecond ablation. Improved precision and elimination of spikes

214 makes the use of femtosecond ablation encouraging for chemical215 analysis applications.

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