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Massing a laser-induced plasma with atomic absorption spectroscopy

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ABSTRACT

A new technique, pseudocontinuum source atomic absorption spectroscopy, is used to map neutral atomic populations in a titanium laser-ablation plasma under helium cover. Measurements show good reproducibility and spatial resolution adequate to measure inhomogeneity in atmospherically-confined LIBS plasmas. 160 ± 20 ng of material is imaged across four terms (one ground and three metastable) of the neutral atom. This mass exceeds the crater volume, indicating substantial redeposition within the crater from pulse to pulse. At five microseconds comparison of the ground and the lowest metastable terms indicates departure from local thermodynamic equilibrium conditions. The technique shows promise for understanding the evolution of these inhomogeneous plasmas, particularly the fate of ablated material.

1. Introduction

Mass removal processes in laser-ablation phenomena (LIBS, other laser-ablation analytical techniques, pulsed-laser deposition, etc.) are typically studied via emission spectroscopy of the resulting plasmas or by examination of the craters excavated by one or more ablation events. Neither of these is straightforward given the inhomogeneity and rapid evolution of the plasmas. Furthermore, while multiple processes (thermal atomization, coulomb explosion, melt splashing, spallation, etc.) contribute to material removal, only atomized material is relevant to LIBS. The different paths to material removal can also lead to different detection efficiencies in LA-ICP analytical techniques and material properties in laser material processing. Understanding the material removal is important in any laser-ablation application. Laser-ablation plasma diagnostics, including ablation diagnostics are reviewed in Reference [1], while Gornushkin and Panne review plasma imaging diagnostics [2].

Extrapolating masses from thermal emission- the most common diagnostic- requires knowledge of the atomic and ionic state distribution functions (ASDFs) and their variation across the plasma volume. *If* thermodynamic equilibrium can be assumed, it can be used to calculate the ASDF, but this still assumes knowledge of the thermal profile of a notoriously inhomogeneous atomic reservoir [3]. Determining absolute number densities requires calibration of the spectral *radiance* response of the optical system, a difficult and uncommon measurement. Furthermore, translating these measurements into atomized mass requires additional assumptions about the plasma geometry. Even extracting relative number densities (e.g. to study spatial distributions of material or to perform relative quantitation with calibration-free LIBS [4]) from thermal emission is complex. Finally, emission measurements only probe excited state populations; the ground state can only be understood through subsequent inexact extrapolations of the atomic state distribution function in a highly dynamic and inhomogeneous plasma.

Fluorescence measurements, on the other hand, probe ground-state and kinetically isolated metastable populations. At late times in plasma evolution, these two populations should represent the vast majority of the mass in the system, which simplifies measurements. Fluorescence generally allows detection of lower number densities than thermal emission due to its higher selectivity [5]. Additionally, fluorescence imaging with plane (i.e. sheet) illumination can simplify measurements of relative spatial distributions of the ground state. However, interpretation of fluorescence data is complicated by assumptions about quantum efficiency, lineshapes, pre- and post-filter effects, etc. Saturated fluorescence spectroscopy [6–9] eliminates some of the uncertainty associated with quenching, but the technique requires high instantaneous power and near single-nanosecond time-resolved detection electronics. Even saturated fluorescence cannot measure the mass atomized without calibration of the optical system's spectral radiance response, however.

Determining the ablated mass from crater measurements is also complex, particularly in the case of the nanosecond lasers most common in LIBS and LA-ICP analyses. Crater measurements do not

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distinguish between the different routes of material removal- spallation and atomization result in the same removal "signal". In extreme cases, e.g. the loose powders important to many industrial applications, craters are not discernible. Even when working with non-friable samples, measuring and interpreting crater profiles is complex.

Absorption spectroscopy does not require absolute calibration of the optical system's spectral radiance response to measure the atomized mass. Unfortunately, the usual extended geometry atomic emission sources do not provide adequate spectral radiance to allow measurements on the timescale of a laser-ablation plasma. Additionally, the rapid evolution of the plasma's geometry and linewidths precludes spatial resolution and generally complicates data interpretation. Nonetheless, duplicating mirrors, the plasma itself, and the transmitted light of secondary plasmas have been used to great effect to characterize laser-ablation plasmas [10–16]. However, in the absence of spatial resolution, these techniques do not indicate the absolute mass atomized, though they may indicate approximate trends in the *relative* mass ablated.

Absorption of coherent sources, on the other hand, can provide the high spectral radiance and spatial resolution necessary for measurements in laser-ablation plasmas. Several groups have used tunable, narrowed diode, dye, and Ti-sapphire lasers (typically doubled) to record temporally parallel [17–21] or spatially parallel [22] absorption profiles. None of these measurements are spectrally multiplexed, though Taylor et al. and Bushaw and Anheier did copropagate two narrow-band CW lasers to make spectrally duplexed measurements [17, 19].

Truly spectrally multiplexed, dual-beam-in-space measurements were first made by Glumac in fireballs. He used a high-resolution spectrograph to "demultiplex" semicoherent ASE dye "laser" probe and reference spectra in a dual-beam-in-space implementation [23]. However, the finite resolving power used in these experiments complicates absolute quantitation of the absorbing states. We have adapted Glumac's experiments, constructing a custom echelle spectrograph to resolve a type II OPO probe. We refer to the improved technique as "pseudocontinuum source atomic absorption spectroscopy" (psCS-AAS) [24]. The nanosecond-pulsed probe provides exquisite time resolution (detector gating is actually unnecessary), while the OPO's low divergence allows resolution on the $\sim 10^{-5}$ m spatial scale (depending on the focusing effected in the probe arm).

In this work, we use line-of-sight psCS-AAS spatial mapping to measure atomized masses, including their distribution and evolution, after laser ablation of a sample of pure titanium. Titanium provides a convenient series of ground and metastable transitions (see Table 1) in a ~50 nm span of the blue-green, with oscillator strengths varying across two orders of magnitude. Though its spectra are complex, titanium is well-studied in the context of LIBS [25–29]. The isotope shifts and hyperfine structure of the primary transitions used here are known and should not require separate fitting [30–32]. Although other groups have imaged laser-ablation plasmas in absorption previously (e.g. References [18, 22]), this is the first implementation of psCS-AAS for plasma imaging and the first quantitative measurements of mass via absorption in these complex plasmas.

Table 1
Spectroscopic data for transitions used in absorption measurements.

Term	Energy (cm^{-1})	J	Probe wavelength (nm, air)	f_{lu}	Uncertainty [reference]
a^3F	0	2			
	170	3			
	386	4	546.0498	2.01×10^{-4}	3% [33]
a^5F	6556	1			
	6598	2	536.6637	5.23×10^{-4}	15% [34]
	6661	3			
	6742	4			
	6842	5			
a^1D	7255	2	543.6717	6.20×10^{-4}	
a^3P	8436	0			
	8492	1			
	8602	2	529.5775	4.66×10^{-3}	

2. Experimental

The details of the pseudocontinuum source spectrograph are given in Reference [24]. Briefly, a pinhole serving as the spectrograph "slit" spatially filtered the type II OPO (Ekspla N342A) pseudocontinuum. The OPO generates 4 ns pulses (manufacturer's specification) with a spectral width of ~3 cm^{-1}. The recollimated, spatially filtered beam (10^{-8} J after the pinhole) was split with a 70:30 beamsplitter to create reference and probe arms, respectively. The probe beam was focused through the plasma and then recollimated with a pair of f = 300 mm visible achromats. The probe beam waist was approximately 50 μm with a Rayleigh range in excess of 2 cm. The probe and reference arms were "recombined" with a second beamsplitter, leaving just enough mutual divergence to present spatially separated probe and reference spectra at the detector. The beams were expanded with cylindrical optics and double-passed off a 79° echelle grating (Richardson Grating Laboratory) operated slightly off-Littrow. The twice-diffracted beams were focused with a cylindrical lens. The resolving power of the spectrograph was $\sim 7 \times 10^5$. Probe and reference signals were balanced at the detector by rotating an achromatic half-waveplate in the probe arm, capitalizing on the grating's differential polarization efficiency.

Targets cut from commercial 1/8-in. titanium sheet (Grade 2, 99.2% Ti, per manufacturer specifications) were ablated with 1064 nm (Big Sky Ultra, 8 ns, 25 mJ at target surface) inside a 6-way vacuum cross. Fluence was approximately 3 J/cm^2. The cross was held at atmospheric pressure and flushed with helium at ~0.5 lpm. The entire ablation assembly (laser head, lens, and vacuum cross) was supported on a xyz table. Plasma position relative to the probe laser beam waist was monitored with runout gauges. The finite size of the ablation target complicated exact location of the sample surface. Despite using smaller samples to minimize beam obscuration near the target surface, we suggest an uncertainty of ~100 μm on the absolute vertical position.

Absorption spectra were calculated from 15 pairs of simultaneous probe and reference spectra. To normalize for differences in probe and reference beam spectral throughput, the plasma absorption spectra were divided by an equivalent 15-shot-average blank "absorption" spectrum taken without opening the ablation laser Q-switch. Thus, each absorption spectrum requires 30 OPO shots. Probe and reference spectra were aligned for maximum correlation using the empirical algorithm discussed in Reference [24]. Because it is not feasible to calibrate the absolute wavelength of the homebuilt spectrograph, the OPOs center wavelength was monitored with a conventional 0.5 m Czerny-Turner spectrograph (Andor Shamrock, 2400 mm^{-1}) that was calibrated with LIBS emission spectra from a titanium target. The transition data were taken from the NIST database (and references therein) and are summarized in Table 1.

Each sample spot was preconditioned with ~20 laser shots before beginning data acquisition. A large ablation laser spot (~1 mm diameter) slowed formation of the relatively flat-bottomed craters. Nonetheless, the sample was repositioned after each lateral scan (~150 shots) to minimize the impact of drilling. Representative crater profiles were recorded with an optical profilometer (Bruker Contour GT-I) for comparison with plasma absorption measurements.

3. Results/discussion

3.1. Crater characterization

Fig. 1 includes optical profilometer images of the craters formed after 15, 150 and 1500 laser shots, respectively. The craters are 1.0 mm in diameter and depth measurements indicate that approximately