Title: Fluorescence imaging of ion distributions in an inductively coupled plasma with laser ablation sample introduction

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Abstract: High-resolution images of the spatial distributions of Sc II, Ca II, and Ba II ion densities in the 10 mm upstream from the sampling cone in a laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS) were obtained using planar laser induced fluorescence. Images were obtained for each analyte as a function of the carrier gas flow rate with laser ablation (LA) sample introduction and compared to images with solution nebulization (SN) over the same range of flow rates. Additionally, images were obtained using LA at varying fluences and with varying amounts of helium added to a constant flow of argon gas. Ion profiles in SN images followed a pattern consistent with previous work: increasing gas flow caused a downstream shift in the ion profiles. When compared to SN, LA led to ion profiles that were much narrower radially and reached a maximum near the sampling cone at higher flow rates. Increasing the fluence led to ions formed in the ICP over greater axial and radial distances. The addition of He to the carrier gas prior to the ablation cell led to an upstream shift in the position of ionization and lower overall fluorescence intensities.

Keywords: LA-ICP-MS, Carrier gas, Fluence.

1. Introduction

Ion transmission through the vacuum interface in Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) is a critical process that heavily influences instrument performance. For efficient, stoichiometric transmission through the interface, vaporization and particle formation should occur such that subsequent atomization and ionization processes form ions on axis in the Normal Analytical Zone (NAZ), just upstream from the sampling cone [1-3]. Aerosol vaporization is largely a function of aerosol properties and the ICP environment. Instrument settings, including RF power, sampling distance, gas flow, etc. that regulate the ICP environment have been studied extensively and are commonly optimized to maximize ion transmission. Aerosol properties, mainly size, velocity, and thermodynamic properties, not only influence ion transmission, but also affect the ICP environment [4]. Furthermore, these effects vary widely with sample types. Consequently, experimentally determining an ideal setting for each sample to maximize ion transmission is both challenging and impractical [5]. Although a model that could reliably predict patterns in ion transmission for a given LA-ICP-MS application would eliminate the need to optimize instrumentation experimentally, significant gaps in current LA-ICP-MS theory exist. One such gap, an understanding of vaporization patterns in the ICP that are specific to LA generated aerosol, is the focal point of this work.

Recent research in our lab, often utilizing laser-induced fluorescence (LIF), has been focused on characterizing ion transmission through the vacuum interface of Solution Nebulization (SN) ICP-MS instruments [2, 3, 6-10]. Because LIF is noninvasive

it is a powerful technique to directly probe analyte species just upstream and downstream from the interface. The LIF imaging experiments cited above have provided valuable insights into ion transmission through the vacuum interface, complementing findings published by numerous other groups [5]. Although mechanisms controlling ICP processes and ion transmission in SN instruments should also control ICP processes in LA instruments, distinct differences in LA and SN systems motivate research characterizing ion transmission through the interface in LA-ICP-MS instruments. Among these are significant differences in the aerosol produced: the aerosol produced in LA is dry, and the particles LA produces present a much broader distribution of size, morphology, and composition than do most aerosols produced by SN. Water added to the carrier gas downstream from the ablation cell has led to improvements in the analytical performance in LA-ICP-MS [11-13]. These improvements have been attributed to steeper temperature gradients in the ICP that result from improved energy coupling of the RF field in the presence of gaseous water [14]. Conversely, broader distributions of particle sizes produced during LA, ranging anywhere from 10 nm to 10 μm [15], are considered to be a major detriment to LA-ICP-MS performance. Difficulties in ensuring efficient transmission of ions formed from particles of different sizes, which experience very different penetration depths in the ICP, remain a major source of error in LA-ICP-MS.

Aerosols produced by UV-ns-LA systems are especially prone to size related effects during vaporization. Research characterizing aerosol particles produced from metals [16, 17] and glass [18, 19] with these systems have been reported. Although particles in the range of 100-300 nm predominate both cases, large particles produced by melt

splashing contribute to a much greater percentage of aerosol volume in metals than is the case with glasses [20]. Laser fluence plays a major role in the ablation process for both metals and glasses. In general, at greater fluence ablation rates increase, leading to a greater number of aerosol particles. Decreasing fluence generally leads to a decrease in large particles [21, 22]. Advantages in the analytical performance of LA-ICP-MS resulting from the addition of helium to the carrier gas are well documented. Improvements to sensitivity, accuracy, and precision have been reported and are generally attributed to improved energy transfer at the ablation site, leading to less particle deposition, an increase in the fraction of small particles transported to the ICP [11, 23], and improvements in the ionization efficiency of the ICP [24]. Carrier gas flow rates not only significantly alter gas temperatures in the central channel of the ICP, but there are also some indications that they influence aerosol production and transport [22]. Given the broad distributions of particle sizes, diverse morphologies, and varied compositions of aerosols produced during LA, optimizing the carrier gas flow rates to maximize ion transmission efficiency presents a serious challenge [25].

In the work presented here we examine the effects of LA parameters on aerosol formation indirectly by imaging distributions of analyte ions in an ICP in the region between the load coil and the sampling cone. This study complements work published by the Günther group, in which they mapped ions in the plasma by moving the plasma with respect to the sampling cone [26]. They were able to look at a wide range of elements, but with limited spatial resolution. Their results were also affected by the fact that each spatial point was sampled from a slightly different plasma, affected by changes in the relative positions of the torch and the sampling cone. In the current

work, we examine only three elements, but with the benefit of a measurement technique that is essentially noninvasive, and which simultaneously maps the entire region between the load coil and the sampling cone with 23 μm spatial resolution.

2. Experimental

2.1 Sample

For the SN experiments, 50 mg L^{-1} solutions of Ba, Ca (J.T. Baker Chemical Co., Phillipsburg, NJ), and Sc (Fluka Analytical, St. Louis, Mo) were prepared from 1000 mg L^{-1} stock solution of barium nitrate, calcium nitrate, and scandium nitrate, respectively, dissolved in 2% v/v nitric acid. BaF_2 windows (Laser Optex, Beijing, China) and CaF_2 windows (Exuberance Opto-electronics Technology Co., Ltd, Beijing, China) were purchased and used for the LA experiments. A scandium-aluminum alloy (2% wt/wt) sample was provided by AMG Aluminum (Robards, KY) and used for the LA studies.

2.2 ICP

All experiments were performed on a commercial ICP-MS (RedTop, Varian, Mulgrave, Australia) instrument, extensively modified to accommodate the imaging optics. To allow space for LIF imaging the RF box, gas box, nebulizer, spray chamber, and igniter assembly were removed from the instrument and mounted to aluminum plates bolted to a steel A-frame. Solutions were introduced into a concentric nebulizer (AR30-1-FM04, Glass Expansion, West Melbourne, Australia) at a flow rate of 1 ml min^{-1} . A Scott-type spray chamber was used at room temperature. A standard one-

piece, low-flow quartz torch, 2.0 mm ID injector, (800-34, Precision Glassblowing of Colorado, Centennial, CO) was custom cut so that the torch ended 2 mm downstream from the load coil. The torch was shortened to prevent it from optically interfering with the LIF. The position of the torch with respect to the load coil was not altered from the manufacturer's settings. A nickel sampling cone (VG-1001-Ni, Spectron, Ventura, CA) was mounted on a lab-constructed, water-cooled flange, which was in turn mounted to a vacuum chamber. Two roughing pumps (Trivac D30A, Leybold, Export, PA) were used to create a vacuum of 1.0 Torr within the vacuum chamber, which mimicked the first vacuum stage of a working ICP-MS. Because the quadrupole mass spectrometer (QMS) was not used in this experiment, it and many components related to it were removed completely. A chiller (Thermoflex3500, Fisher Scientific, Hampton, NH) was used to cool the instrument. For all the experiments, the RF power was 1300 W, the sampling depth (load coil to sampling cone) was 12 mm, and plasma, auxiliary, and sheath gas were 16.0, 2.0, and 0.2 L min⁻¹, respectively. The sheath gas is a flow of argon that is added to the nebulizer gas flow in a transfer tube between the exit of the spray chamber and the base of the injector tube.

2.3 Laser ablation

A pulsed Brilliant B Nd:YAG laser (Quantel, Bozeman, MT) was used for the laser ablation experiments. The output beam was 0.5 cm in diameter and averaged 40 mJ pulse⁻¹ at factory settings. A high energy variable attenuator (990-0070, Eksma, Vilnius, Lithuania) was used to attenuate the output energy. The potentiometer controlling the angle on the 4 ω crystal was also used to adjust output energy. No significant change in

the 4-5 ns pulse width or beam shape was observed over the range adjusted. Overall, a range of 0.5 to 40 mJ pulse⁻¹ was obtained. A high energy mirror was used to reflect the attenuated beam towards a fused silica singlet focusing lens ($f=128.9\text{mm}$ at 266 nm) mounted above the sealed ablation cell. A cylindrical ablation cell with a volume of roughly 100 cm³, pictured in Fig. 1, was mounted to an XYZ stage that was controlled by 3 microstepping drivers (OEM 750, Parker Hannifin, Cleveland, OH) controlled by an ACR9000 (Parker Hannifin) control box for rastering capabilities. The laser was fired at 10 Hz and rastered at 0.1 mm s⁻¹. This yielded a steady state of aerosol production with only minor fluctuations based on the ablation position. The laser focal points were adjusted to produce crater diameters of 150 μm on scandium-aluminum alloy samples and 90 μm on the CaF₂ and BaF₂ windows. Also, a thin strip of anodized aluminum attached to a rotary solenoid was used as a shutter to stop ablation without having to disable the laser flashlamp. The LA system was controlled through LabView (National Instruments, Austin, TX). The original gas box that accompanied the Varian ICP-MS was used to control the Ar gas flow supply to the ablation cell. A separate mass flow controller (5850, Brooks Instruments, Hatfield, PA) was used to control the He gas flow, which was mixed with the Ar upstream from the ablation chamber using a swage T-connector. A 7-mm I.D. tube exiting the ablation cell carried the ablated aerosol to the sheath torch connector of the ICP.

2.4 Laser induced fluorescence

A XeCl excimer laser (LPX 110, Lambda-Physik, Göttingen, Germany) was used to pump a dye laser (Scanmate 2, Lambda-Physik) tuned to a transition line for the ion

being studied. The fluorescence schemes for each ion are presented in Table 1. The dye laser energy was adjusted with a variable attenuator (M 935 10, Newport, Irvine, CA) to slightly above the value required to saturate the transition, ensuring a maximum, stable, fluorescence signal with minimum interference from scattered radiation. The output from the attenuator was passed through an optical fiber, then recollimated with a fused silica plano-convex singlet lens. A prism was then used to direct the collimated light vertically upwards towards the plasma. A plano-convex cylindrical fused silica lens focused the collimated light into a sheet with a focal line that coincided with the line connecting the center of the torch injector with the center of the sampling cone. A mask, equipped with an adjustable iris, mounted above the cylindrical lens, was used to prevent the planar excitation light from scattering off of the torch or sampling cone. A beam dump was mounted above the ICP to prevent scattering off the RF box. The excitation sheet was 10 mm wide and extended from the end of the torch to less than 0.1 mm in front of the sampling cone.

A gated, iCCD (7361-0001, Princeton Instruments, Trenton, NJ), triggered by a photodiode (DET210, Thorlabs, Newton, NJ) in the dye laser box, was mounted perpendicular to the plane of the excitation sheet. Twin 100 mm focal length achromatic doublets (AC254-100-A, Thorlabs) were used to focus the fluorescence onto the iCCD with unit magnification. An interference filter was placed between the achromatic doublets to isolate the desired fluorescence light. The CCD gain and number of exposures were adjusted to produce acceptable signal levels within a reasonable exposure time. The optimal exposure settings were different for images taken during SN and LA and varied between elements. However, exposure settings were held constant

while imaging a given element during SN or LA at different carrier gas flow rates (including the He addition) or laser fluences. Finally, for each image, a background image was taken, immediately before or after the fluorescence image to subtract the emission signal. Fig. 1 shows the general setup of the instrumentation.

2.5 Image processing

Using Winview software, (Princeton Instruments, Trenton, NJ), background images were subtracted from the corresponding fluorescence images. Background-subtracted images were converted to ASCII format and processed with Matlab. The signal intensities for the various carrier gas flow rates were normalized to the flow rate with the greatest signal. The intensity scales for the SN and LA, and those for the different elements are different, and thus not directly comparable. Note that in the axial cross sections, the intensities are reliable only between 2 mm and 12 mm downstream from the load coil, the region that was fully illuminated by the 10-mm-wide laser sheet. Matlab was also used to plot the various cross sections and calculate FWHM values. Unless stated otherwise, radial cross sections were plotted at axial positions where the signal intensity was greatest. Defining the radial profile this way allows direct comparison of the radial distributions at different nebulizer gas flow rates.

3. Results and Discussion

3.1 Scandium

3.1.1 Solution Nebulization vs. Laser Ablation

High resolution images of Sc II ion densities in an ICP, obtained during SN and LA (at 28 J cm^{-2} and 60 J cm^{-2}) at varying flow rates, are presented in Fig. 2. These images

provide direct observation of ion densities that form in the ICP subsequent to LA.

Differences between the images obtained during LA and SN can be understood in terms of fundamental differences in the aerosol properties and their complex interactions with ICP environment. As discussed previously, when compared to SN, aerosol generated during LA lacks solvent, lead to significantly less mass loading in the ICP (several 100 $\mu\text{g s}^{-1}$ during SN and only several 10 ng s^{-1} during LA) [26], and represent a much broader range of sizes, shapes, and morphologies. Ablation patterns of metals have been described in a number of papers [27, 28]. Aerosols produced during LA of Al-based alloys have been described as consisting of irregularly shaped individual particles, clusters, and hard agglomerates (clusters melted together) [16]. An ablation rate of 1.04 $\mu\text{m pulse}^{-1}$ at 23 J cm^{-2} and significant crater chimney formation has also been reported [29]. As expected, significant differences can be seen qualitatively in the spatial profiles of Sc II ions obtained during SN and LA. The differences will be discussed in terms of the axial and radial distribution of ion densities.

3.1.1.1 Axial Profiles

To support the images in Fig. 2, axial cross sections, extracted from the center axes of the images, are provided in Fig. 3. As seen in both figures, aerosol produced during LA led to peak Sc II ion fluorescence signals much farther upstream for a given nebulizer gas flow rate when compared to SN. This observation is not unexpected. The desolvation process, required for solvent rich aerosol droplets produced during SN, delays atomization and ionization when compared to “dry” aerosol produced during LA [30]. Indeed, during LA, an addition of roughly 0.4 L min^{-1} is required to shift ionization to the downstream positions of SN. It is possible that local cooling effects associated with the desolvation of large aerosol droplets entrained to the ICP during SN are a

contributing factor. However, since gas temperatures in the central channel of the ICP, which largely dictate the axial position that vaporization begins, are essentially independent of sample properties, any contribution from such cooling effects would be minor [31]. In addition to being shifted upstream relative to the SN profiles, the LA profiles rise more gradually. The change in the profile shape could be a reflection of reduced oxide formation during LA [32-34], or it could be due to a shift in the particle size distribution to favor smaller particles.

3.1.1.2 Radial Profiles

A significant difference between the radial distributions of ions produced during SN and LA was observed. Most apparent at low fluence, the radial profiles of ions were narrower with LA sample introduction than they were with SN. FWHM values were calculated from radial cross sections at axial positions of peak fluorescence intensities for each flow rate and are plotted in Fig. 4 for both SN and LA. It should be noted that due to differences in the axial profiles, the FWHM calculated for LA represents a position much farther upstream than SN. Another way to look at the data is to compare FWHM values at flow rates that give comparable axial profiles. The closest matches are at flows of 0.8 and 1.1, 0.9 and 1.3, and 1.1 and 1.5 L min⁻¹, for SN and LA, respectively. Either way of looking at the data makes it clear that SN leads to greater radial spreads in ion densities than LA. The broad profiles for LA at low flow rates are due to the fact that the peak ion densities are upstream from the imaged region and the observed images are broadened by diffusion. The sharp decrease in FWHM observed during SN at 1.1 L min⁻¹, presumably caused by “pinching” of off-axis gas being drawn into the sampling cone, was not observed during LA at high fluence and only

moderately at low fluence. A number of mechanisms could be contributing to the difference in radial profiles observed here.

Our observations appear at first glance to be consistent with results recently reported by Flamigni, et al. [14]. They observed narrower radial neutral atom emission profiles for dry LA aerosols than for LA aerosols to which water had been added. They proposed that more-efficient coupling of the RF field due to the presence of gaseous water led to a steeper temperature gradient that promoted greater diffusion. However, as will be noted in section 3.1.2, the addition of water to a LA aerosol did not significantly broaden the radial fluorescence profiles, suggesting that differences between SN and LA other than the presence of water are affecting the radial distributions. Differences in the flow profiles of aerosol particles produced by SN and LA in the transport tube leading to the ICP might be a contributing mechanism. Gas velocities in the laminar flow through the transport tube are greatest in the center and zero at the wall. The densities of aerosol particles across the cross section of the transfer tube have been shown to be inhomogeneous under certain conditions [21, 35-37]. Variations in radial distributions of particles in the transport tube between LA and SN could lead to differences in the radial profiles observed in the ICP. Coulomb fission of aerosol droplets, occurring during transport or desolvation, may give rise to greater radial dispersion of SN aerosol [38]. Finally, differences in flow patterns within the ICP are another possibility [39, 40]. Contributions from mechanisms discussed above are speculative at this point. More work is needed to characterize actual contributions from these source and the implications on ion transmission through the MS interface.

3.1.2 Solvent

To investigate the influence of water vapor on the ion profile, sample transport tubing was configured using a Y connector to introduce water vapor produced from the pneumatic nebulizer system into the aerosol transport tube of the ablation system just upstream from the sheath gas connector. A total flow of 1.0 L min^{-1} Ar, split equally between the ablation cell and nebulizer, was kept constant throughout the experiments. Fig. 5 presents images obtained at various conditions. Image (I), in Fig. 5, was obtained while aspirating a 50 ppm solution with the LA shutter closed (no LA aerosol present). Fig. 5 (II), and (IV), were obtained while introducing “dry” aerosol (no nitric acid was aspirated) generated by LA at 28, and 60 J cm^{-2} , respectively. Fig. 5 (III), and (V) were obtained while introducing “wet” aerosol (nitric acid was aspirated) generated by LA at 28, and 60 J cm^{-2} , respectively. Fig. 6 shows axial and radial cross sections of the images in Fig. 5. Note that in both figures, the scales on the individual images and traces were normalized to maximum values to facilitate comparisons of shapes. The SN peak intensity was five times that for LA. There were no significant intensity differences between the wet and dry aerosols. Data in figs. 5 and 6 lead to some interesting conclusions. Clearly, the individual flows through the pneumatic nebulizer or the flow through the laser ablation chamber combine with the total flow through the torch injector tube to influence the distribution of ions in an ICP. For example, none of the traces in fig. 6 matches either of the traces in fig. 3 obtained at a central channel flow of 1 L min^{-1} . With only half of the total flow passing through each of the aerosol production sources, the ion distributions are much more similar than is the case when the total flow is directed through either source individually. It is possible that the additional tubing and the Y connector required for this experiment act as a particle size

filter that makes the two aerosol sources more similar than they are if they are connected individually in their normal configurations. Perhaps the most significant result is the small effect that added water has on the LA aerosol. The addition of water causes only a slight downstream shift in the axial profiles, and the effect on the radial profiles and peak intensities is negligible. Given the changes reported in ref. 14, it is unclear why similar effects were not observed here.

3.1.3 Laser Fluence

Images in Fig. 7a were obtained at various fluences for two different Ar gas flow rates, 1.2 (left) and 1.3 L min⁻¹ (right). Raw and normalized axial cross sections of the images obtained at 1.3 L min⁻¹ are presented in Fig. 7b and 7c, respectively. FWHM values are plotted as a function of fluence and are presented in Fig. 7d. As seen in these images, increasing fluence led to a significant increase in the number of ions formed in the ICP, a downstream shift in the axial position of peak ion fluorescence, and an increase in the width of the radial distribution of ions. These results are consistent with the initial differences observed between images obtained during LA at 28 and 60 J cm². It has been reported that increasing laser fluence leads to greater ablation rates [27], an overall greater number of aerosol particles, and, in some cases, an increase in the fraction of large particles [16]. The significant increase in the fluorescence signal observed at greater fluence certainly reflects more particles produced at greater ablation rates. Moreover, a shift in the ablation mechanism from surface vaporization to phase explosion at fluences greater than 7 J cm⁻² leads to a sharp increase in ablation rates [27]. Such a shift could account for the sharp increase in the signal intensity observed between 12 to 28 J cm⁻², presented quantitatively in the axial profiles presented in 7b.

Inspection of the normalized axial profiles presented in Fig. 7c reveals that increasing fluence shifts the axial position of peak fluorescence downstream and leads to a more gradual decline in the downstream end of fluorescence peak. An increase in the fraction of large particles would account for both observations. However, greater mass loads associated with an increase in the overall number of particles, regardless of changes in the size distribution, could lead to cooling effects that also might account for the observations. It is unclear at this point which mechanism is more pertinent.

As seen qualitatively in Fig. 7a and quantitatively in Fig. 7d, increasing fluence led to a significant increase in the widths of radial distributions of ions formed in the ICP. It is unlikely that changes in ICP environment, such as local cooling associated with an increased fraction of large particles, or greater mass loads contribute to this effect. Rather, it suggests that changes in the aerosol properties or flow patterns are leading to the changes in the radial profiles observed. It is possible that micron-sized agglomerates, preferentially formed at greater fluence, undergo vaporization mechanisms that lead to wider radial distributions.

3.1.4 Helium Addition

The addition of He to the carrier gas significantly affects the ablation event, transport to the ICP, and conditions in the plasma [27, 41-43]. Helium could also change ion transport efficiency through the vacuum interface of the ICP-MS, although to our knowledge the effects of plasma gas composition on ion transport efficiency in the vacuum interface have not been studied. The presence of He during ablation leads to a greater fraction of smaller aerosol particles than is produced in pure Ar [44]. Also, because He is lighter than Ar, larger particles that do form are less likely to be

transported to the ICP. The overall effect is fewer large particles that can lead to signal spikes [45, 46]. However, because the severity of these effects depends on a variety of factors, including laser pulse duration, wavelength, ablation cell design, and sample type [44], fundamental studies of He/Ar mixtures can lead to conflicting results. The addition of He also significantly affects ICP environment, increasing gas-kinetic temperatures of the central channel and diffusion rates. The changes with the addition of He are attributed to its high thermal conductivity and low mass [1, 47] [48]. The addition of He to the carrier gas should lead to aerosol vaporization lower in the plasma as well as increased diffusion, and such changes have been observed experimentally [26].

Consistent with the observations noted above, the addition of He to the carrier gas in our experiments led to aerosol vaporization much lower in the plasma than equivalent total flow rates of pure Ar. As seen in Fig. 2 and 3d, Sc II ion densities do not reach their maximum near the sampling cone until 2.0 L min^{-1} He has been added, making a total flow rate of 2.7 L min^{-1} . This observation suggests increasing gas temperatures caused by the addition of He more than compensate for cooling associated with increasing gas flow rates. A significant reduction in the number of large particles produced or transported with He addition would also contribute to the upstream shift in vaporization observed. Reduced local cooling, associated with large particles vaporizing in the ICP, would enhance the upstream shift in small and medium sized particle vaporization [31].

Not all changes observed in the ion densities associated with the use of He were expected. Increased sensitivities are typically associated with the addition of He to the ablation cell. Improvements in sensitivity have been attributed to greater transport

efficiencies of aerosol particles from the ablation cell to the ICP [49]. Our signal intensities obtained with added He were significantly lower than signals obtained during LA at 28 J cm^{-2} using Ar only. Consistent with our observations, other groups have reported sensitivity decreases associated with He addition [50]. The decrease in sensitivity was attributed to a reduction in the number of medium sized particles in the aerosol. A key point in reconciling our observations that He reduces fluorescence intensity with reports that He addition improves ICP-MS sensitivity is recognition that different quantities are being measured. We are measuring ion densities in the plasma and other investigators are measuring ion counts in mass spectrometers. It is entirely possible that ion transport through the vacuum interface improves with the addition of helium, and that lower ion densities in the plasma could still lead to higher mass spectrometric signals. For example, gas velocities in the first stage of the vacuum interface are inversely proportional to the square root of mass [51], and analyte ions move at the speed of the bulk gas flow [52]. Because of the higher gas speeds and reduced residence time in the first vacuum stage, analyte losses to ion-electron recombination should be lower in He than in Ar [53]. There are analyte losses due to scattering in shocks at the tip of the skimmer cone [54], and one would expect those losses to be lower in He than in Ar. Finally, it is possible that non-ideal beam behavior caused by space charge effects would be less severe in a He ion beam than in an Ar ion beam.

We have considered and rejected the possibility that reduction in fluorescence intensity with the addition of He was due to a reduction in fluorescence quantum efficiency rather than a reduction in analyte ion density. Quenching of excited atoms by

noble gases is inefficient. Detailed quenching cross sections are not available, but using published upper limits for analogous transitions in potassium atoms [55], we estimate that the collisional quenching rates in He at 5500 K are approximately $2 \times 10^5 \text{ s}^{-1}$, orders of magnitude less than the radiative rates for the transitions used in the fluorescence measurements.

3.2 Calcium

3.2.1 Solution Nebulization vs. Laser Ablation

Silicate reference materials are commonly used as calibration standards and have consequently been used as samples in numerous fundamental studies. Because these materials exhibit ablation patterns markedly different than metals, comparing results from glasses with those reported above for the aluminum alloy would be desirable [29]. Glasses with concentrations of elements that could be effectively imaged by LIF were not available, so we chose crystalline optical windows as a substitute. CaF_2 , which we used to generate Ca images, has shown ablation patterns similar to silicate materials [23].

3.2.1.1 Axial Profiles

Images of Ca II ions, obtained during SN, LA at 18 J cm^{-2} , and LA 18 J cm^{-2} with added He are presented in Fig. 8. Axial cross sections similar to those described for Sc in section 3.1.1.1 above are plotted in Fig. 9. Differences between SN and LA followed the same general trend seen with Sc: aerosol produced during LA leading to significant ions densities formed lower in the ICP, spread over a greater axial distance, and restricted to a narrower radial distance. When compared to Sc, the increase in the length of the axial profile during LA, relative to SN, was more pronounced in Ca, especially on the upstream section of the profile. This is consistent with greater ablation

rates reported for CaF_2 , $2.0 \mu\text{m/pulse}$ compared to $1.04 \mu\text{m/pulse}$ for Al [18, 29]. An increase in the number density of particles produced during the ablation event leads to more collisions between those particles and the formation of large “cotton like” soft agglomerations [23]. These large agglomerations could account for the increased length in the axial profile for Ca. SN also led to ion densities distributed over a larger axial distance for Ca when compared to SN of Sc, indicating that, in addition to the particle size distribution, the identity of the analyte affects the distribution of ions in the ICP. As was the case with Sc, LA of CaF_2 led to much narrower Ca II ion radial distributions than SN, illustrated in Fig. 10.

3.2.2 Fluence

Images of Ca II ions, taken during LA at fluences of 60, 130, 360, and 540 J cm^{-2} , are presented in Fig. 11a at nebulizer gas flow rates of 1.1 L min^{-1} (left) and 1.3 L min^{-1} (right). This figure covers a range over much higher fluences than evaluated with Sc. Axial and radial cross sections, and their calculated FWHM, for the images obtained at 1.3 L min^{-1} are presented in Fig. 11b, 11c, and 11d, respectively. As with metals, increasing fluence lead to increasing ablation rates, a greater number of particles, and the formation of larger agglomerates [29]. Changes in the Ca II ion distributions associated with increasing fluence followed trends similar to those observed with Sc II ions.

3.2.3 Helium Addition

Results obtained during LA with He addition during LA of the CaF_2 windows were very similar to those presented for Sc in Fig. 2. Although He addition led to significant signal suppression for both Sc II and Ca II, the effect was slightly less pronounced with Ca II. Also notable is the axial profile, plotted in Fig. 9c, produced when 2.0 L min^{-1} He

was added to 0.7 L mn^{-1} Ar. Unlike ion profiles produced during LA in pure Ar, which have a definite peak fluorescence signal, the signal produced here plateaus over roughly 5 mm. It is unclear whether changes in the size distribution of aerosols entering the ICP or changes in ICP conditions are producing this effect. Such a plateauing effect could, in part, account for improvements in accuracy that have been observed when adding He to the carrier gas. This effect was less pronounced when the ablation target was the Al-Sc alloy. However, transport losses in He depend on particle size distributions, and the distributions for the Sc-containing Al alloy should be significantly different than those for the crystalline CaF_2 .

3.3 Barium

BaF_2 and CaF_2 have very similar optical and mechanical properties. Not surprisingly, images of Ba II ions obtained during SN, LA at 18 J cm^{-2} , and LA 18 J cm^{-2} with He addition, presented in Fig. 12 are remarkably similar to those of Ca II ions presented in section 3.2 above. The differences in ionization potentials and atomic masses between Ba and Ca do not significantly affect the results.

3.3.1 Additional Studies with Helium

To further address the effects of He on analyte ion distributions, incremental amounts of He were added to 1.0 and 1.3 L mn^{-1} Ar. Whereas previously described additions of He to 0.7 L mn^{-1} often led to ion formation upstream from the imaging region, addition of He to 1.0 and 1.3 L mn^{-1} Ar enabled direct comparison of ion profiles within the imaging region. The images obtained during the addition of various flows of He to 1.0 and 1.3 L mn^{-1} Ar are presented in Fig. 13a. Axial cross sections of each image obtained at 1.0 and 1.3 L mn^{-1} Ar are plotted in Fig. 13b and 13c, respectively. As expected, the addition of increasing amounts of He shifts the ion profile downstream.

These data reemphasize the point made earlier that, when it comes to setting the axial position of the ion density maximum, argon and helium flows are not equivalent, and that the total flow required to achieve optimum ICP-MS sensitivity depends strongly on the composition of the nebulizer gas.

The dependence of optimum flow rate on central gas composition complicates the comparison of ICP-MS sensitivities. Lacking a mass analyzer on our instrument, we selected combinations of Ar and He that produced maximum ion densities 2-3 mm upstream from the sampling cone. The results are presented in Fig. 14a. Clearly the pure Ar gives the highest peak ion density, and the peak value decreases as percentage of He increases. The axial distributions for the five flow combinations are similar, as shown in Fig 14b. Increasing amounts of He cause radial broadening, as shown in Fig. 14c.

4. Conclusion

Significant differences in the spatial profiles of ion densities of aerosol produced during SN and LA were observed. When compared to SN, aerosol produced during LA led to ions formed farther upstream in the plasma, with broader axial distributions and narrower radial distributions. These differences reflect fundamental differences between the aerosols and their complex interactions with the ICP. Delayed ion formation, observed with SN aerosol, was attributed to the rate-limited desolvation of droplets from the nebulizer. In preliminary experiments, solvent added independent of the analyte had very little effect of the ion profile beyond shifting it slightly downstream. Images were inspected for evidence of any size effects common to LA aerosol. Most notably, significant ion densities formed over large axial distances for LA aerosol were attributed

to broad particle size distributions produced by LA. This picture is consistent with previously published work. Differences in the radial profiles generated by SN and LA aerosol warrant further investigation. We found that laser fluence positively correlated with the radial width of the ion distribution.

The addition of He to the nebulizer gas flow led to ion formation farther upstream in the plasma than occurred with pure Ar as the nebulizer gas at a given total flow rate. The upstream shift likely reflects a combination of He effects: fewer large particles transported to the ICP and increased gas-kinetic temperatures in the ICP. Varying the point in the flow stream at which He and Ar are mixed should help clarify contributions of He to the ablation process and ICP conditions.

Clearly, measurements of ion distributions in the ICP with LA sample introduction add important insights into signal production in LA-ICP-MS that cannot be obtained from mass spectrometric signals alone.

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Table 1
Fluorescence scheme

Analyte	Excitation Wavelength	Fluorescence Wavelength	Filter	Dye (Exciton, Dayton, OH)	Gate width : delay
Ba II	455.404 nm	614.172 nm	1 nm bandpass at 614.2 nm (Barr Associates, Westford, MA)	Coumarin 460	60 ns : 35 ns
Ca II	393.366 nm	854.21 nm	1.1 nm bandpass at 854.3 nm (CVI, Albuquerque, NM)	PBBO	60 ns : 28 ns
Sc II	358.09 nm	432.50 nm	1 nm bandpass at 432.50 nm (Barr Associates, Westford, MA)	DMQ	65 ns : 35 ns

Figure Captions

Fig. 1. Top left: General overview of the instrumental setup. Top right: Images of the LA system developed for this work. Bottom left: An image of the modifications to the Varian ICP-MS. Bottom right: An image illustrating the orientation of the planar sheet used for LIF.

Fig. 2. Images of Sc II ions obtained using planar LIF. Flow rates on the far left indicate the flow for column 1-3. The flow rates to the left of the He images, column 4, represent additions of He to a constant flow rate of 0.7 L min⁻¹ Ar. Each image is oriented similarly with the load coil out of the image to the left and the sampling cone just protruding into the right side.

Fig. 3. Cross-sectional plots of the axial distribution of Sc II ions along the center axis taken during (a) SN, (b) LA at 28 J cm⁻², (c) LA at 60 J cm⁻², and (d) LA at 28 J cm⁻² with added He.

Flow rates for (a), (b), and (c) are labeled as follows: (✱) 0.8 L min⁻¹, (—) 0.9 L min⁻¹, (—) 1.0 L min⁻¹, (—) 1.1 L min⁻¹, (—) 1.2 L min⁻¹, (—) 1.3 L min⁻¹, (—) 1.4 L min⁻¹, (—) 1.5 L min⁻¹. Increments of 0.4 L min⁻¹ He were added to a constant flow of 0.7 L min⁻¹ Ar. He additions plotted in (d) are labeled as follows: (—) 0.8 L min⁻¹, (—) 1.2 L min⁻¹, (—) 1.6 L min⁻¹, and (—) 2.0 L min⁻¹.

Fig. 4. FWHM values calculated from radial cross sections at each flow rate for Sc II ions recorded during (—) SN, (—) LA at 28 J cm⁻², (—) and LA at 60 J cm⁻².

Fig. 5. Images showing the influence of solvent on Sc II ion densities in the ICP. In each image, 1.0 L min⁻¹ of Ar was split equally between the LA and SN systems. Image (I) was obtained while aspirating 50 ppm Sc without LA aerosol. Images (II) and (III) were obtained

during LA at 28 J cm^{-2} without and with aspirating 2% nitric acid, respectively. Images (IV) and (V) were identical to (II) and (III) but performed at 60 J cm^{-2} . Due to the significant difference in the signal intensities of each image, the color scales for each image are different.

Fig. 6. Axial (a) and radial (b) cross sections of images I, II, and III in Fig. 5, labeled as follows: (—) 50 ppm Sc, (—) dry and (—) wet aerosol produced during LA at 28 J cm^{-2} . Axial (c) and radial (d) cross sections of images I, IV, and V in Fig. 5, labeled as follows: (—) 50 ppm Sc, (—) dry and (—) wet aerosol produced during LA at 60 J cm^{-2} .

Fig. 7. (a) Images of Sc II ion densities obtained at various fluences during ablation with Ar flow rates of 1.2 L min^{-1} (left) and 1.3 L min^{-1} (right). (b) and (c) axial cross sections of the images obtained at 1.3 L min^{-1} presented in Fig. 7a. The profiles in (c) have been scaled to their maximum value to facilitate comparisons of the shapes and positions of the curves. The legends are as follows: (—) 60 J cm^{-2} , (—) 130 J cm^{-2} , (—) 360 J cm^{-2} , (—) 540 J cm^{-2} . (—) SN at 0.9 L min^{-1} , included for comparison. (d) FWHM calculated from the radial cross sections at each fluence during ablation with an Ar flow rate of 1.3 L min^{-1} .

Fig. 8. Images of Ca II ions obtained using planar LIF. The orientation of each image and patterns of gas flow are identical to those described previously for Sc II in Fig. 2.

Fig. 9. Cross-sectional plots of the axial distribution of Ca II ions along the center axis taken during (a) SN, (b) LA at 18 J cm^{-2} (c) LA at 18 J cm^{-2} with added He. Flow rates for (a) and (b) are labeled as follows: (—) 0.8 L min^{-1} , (—) 0.9 L min^{-1} , (—) 1.0 L min^{-1} , (—) 1.1 L min^{-1} , (—) 1.2 L min^{-1} , (—) 1.3 L min^{-1} , (—) 1.4 L min^{-1} , (—) 1.5 L min^{-1} . Increments

of 0.4 L min^{-1} of He were added to a constant flow 0.7 L min^{-1} Ar. He additions plotted in (c) are labeled as follows: ($\text{---}\diamond\text{---}$) 0.8 L min^{-1} , ($\text{---}\text{--}$) 1.2 L min^{-1} , ($\text{---}\text{+}\text{---}$) 1.6 L min^{-1} , (---) 2.0 L min^{-1} .

Fig. 10. FWHM calculated from radial cross sections at each flow rate for Ca II ions produced by ($\text{---}\text{+}\text{---}$) SN and ($\text{---}\text{--}$) LA with Ar at 18 J cm^{-2} .

Fig. 11. (a) Images of Ca II ion densities obtained at various fluences during ablation with Ar gas flow rates of 1.1 L min^{-1} (left) and 1.3 L min^{-1} (right). (b) Axial and (c) radial cross sections of the images obtained at 1.3 L min^{-1} presented in Fig. 11a. The legends are as follows: ($\text{---}\text{--}$) 60 J cm^{-2} , ($\text{---}\text{--}$) 130 J cm^{-2} , ($\text{---}\diamond\text{---}$) 360 J cm^{-2} , (---) 540 J cm^{-2} . ($\text{---}\text{+}\text{---}$) SN at 0.9 L min^{-1} , included for comparison. (d) FWHM calculated from the radial cross sections at each fluence during ablation with Ar flow rates of ($\text{---}\text{+}\text{---}$) 1.1 L min^{-1} and ($\text{---}\diamond\text{---}$) 1.3 L min^{-1} .

Fig. 12. Images of Ba II ions obtained using planar LIF. The orientation of each image and patterns of gas flow are identical to those described previously for Sc II in Fig. 2.

Fig. 13. (a) Images of Ba II ion densities obtained with incremental additions of He to 1.0 L min^{-1} and 1.3 L min^{-1} of Ar. (b) and (c) axial cross sections of the images obtained at 1.0 L min^{-1} and 1.3 L min^{-1} of Ar, respectively. The legends for the helium flows in the axial plots match the values in the images from top to bottom in the order: ($\text{---}\text{+}\text{---}$), ($\text{---}\text{--}$), ($\text{---}\diamond\text{---}$), ($\text{---}\text{--}$), ($\text{---}\text{+}\text{---}$), (---). The vertical scales in plots (b) and (c) are scaled to the maximum value in each set of curves.

Fig. 14. (a) Images of Ba II ion densities obtained with various combinations of Ar and He flow rates. For each argon flow rate, the He flow rate was adjusted to give the maximum fluorescence intensity near the sampling cone. (b) axial and (c) radial cross sections of the

images in Fig. 14a, respectively. The intensity for each cross section is scaled to its maximum value to facilitate comparison of shapes. The Ar:He flow rates in the plots are: (—) 0.7:2.0 L min⁻¹, ( ) 0.9:1.8 L min⁻¹, ( ) 1.1:1.2 L min⁻¹, ( ) 1.3:0.6 L min⁻¹, and (—) 1.5:0.0 L min⁻¹.

figure 1

figure 2

figure 3

figure 4

figure 5

figure 6

figure 7

figure 8

figure 9

figure 10

figure 11

figure 12

figure 13

figure 14