Title: The effects of He on ablation and ICP environment in ultra-violet, nanosecond laser ablation inductively coupled plasma mass spectrometry

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Abstract: The effects of helium gas on ablation and ICP processes were investigated. Differences in the size, shape, and abundance of aerosol particles generated in argon and helium atmosphere were studied off-line using SEM imaging of aerosol particles impacted on polycarbonate filter disks. In general, ablation in helium generated fewer large particles, and larger, more densely-packed softagglomerates. However, corresponding changes in the ion densities in the ICP, observed in high-resolution images obtained using LIF, were not always predictable. In all cases, higher He/Ar ratios led to lower ion densities in the ICP. This effect was attributed to increased rates of off-axis diffusion at higher He/Ar ratios. Differences in the ion densities produced during ablation in argon vs helium were highly dependent on sample type, the axial position of vaporization, and the He/Ar ratio. There was evidence that vaporization efficiencies of softagglomerates were less affected than micron-sized particles by particle acceleration at higher He/Ar ratios.

Keywords: LA-ICPMS, Helium, Gas, Particle Size Distribution, Ablation

1 Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is a powerful technique used for trace elemental analysis of solids. Compared to traditional solution nebulization (SN), laser ablation is a quasi non-destructive means of sample introduction. It offers better spatial resolution and sensitivity, and requires little to no sample preparation. However, non-stoichiometric effects related to laser-, transport-, and ICP-induced elemental fractionation significantly limit the analytical capabilities of LA-ICPMS when matrix-matched standards are unavailable [1]. The need for better methods to reduce or account for elemental fractionation drives much of the research devoted to LA-ICPMS. In this effort, the use of helium as carrier gas has led to significant improvements in LA-ICPMS performance. However, improvements in MS data are likely a convolution of helium effects during ablation, transport, and ICP processes, including transport through the interface.

In a recent paper, we investigated the effects on ion distributions in the ICP of adding helium to argon gas upstream from the ablation cell using laser induced fluorescence (LIF) [2]. We were surprised to find that helium added to the carrier gas led to a decrease in the overall ion densities within the ICP. We considered the possibility that changes in the particle size distribution (PSD) could account for the decreased ion count in the ICP. However, the PSD of aerosol generated with ns-LA at 266 nm is considered largely immune to the choice of carrier gas [3]. Additionally, reduced deposition around ablation craters [4] and improved transport efficiencies of aerosol [3] for 266 nm ns-LA-ICPMS during ablation in He vs Ar have been reported. Furthermore, minor increases in the fraction of small particles in the presence of helium typically lead to sensitivity gains [3, 5]. Witte et. al. reported 50% gains in MS signals when adding He [6]. We concluded that more efficient transport through the interface in the presence of helium could account for the

apparent inconsistency of the decrease ion signal we observed with improved sensitivities generally reported.

Although our experiments reported in reference [2], in combination with reports from other groups cited above, suggested that changes in measured ion densities that accompanied the addition of helium to the ablation gas were due to changes in the plasma, the evidence was indirect. Caution is needed in drawing conclusions based on interlaboratory comparisons because of inevitable differences in equipment and procedures. As indicated in a short but far-reaching review of LA-ICPMS [7], a myriad of experimental parameters contribute to the final signal in an LA-ICPMS measurement. In this study our focus was on a narrow objective: distinguishing the effects on ion density in the plasma of changes in gas composition in the ablation chamber from the effects on ion densities of corresponding changes in the composition of the central gas flow of the plasma. To the extent possible, all other ablation and plasma parameters were held constant throughout the experiments.

Finally, in introducing this study, we emphasize that the quantities we are measuring, namely analyte ion densities in the plasma, are not equivalent to the mass spectrometric ion signals reported in most studies of the effects ablation parameters on ICPMS performance. The possible effects of changes in ion transport efficiency between the plasma and the mass spectrometer detector must be considered when comparing the results presented here with earlier reports from the literature.

2 Experimental

2.1 Sample

CaF₂ windows (Exuberance Opto-electronics Technology Co.,Ltd, Beijing, China) and 2% scandium-aluminum alloy disks (AMG Aluminum, Robards, KY) were used for this study. The 2% scandium-aluminum alloy disks were polished with 2000 grit sandpaper. No pre-ablation was performed on the CaF₂ windows.

2.2 *Experimental*

Important instrument settings are listed in Table 1. Additional details on gas flows are given in Table 2. It is important to note that for each combination of element and total gas flow, three experiments were performed. In one, the specified flow of Ar was flowed through the ablation chamber and the corresponding flow of He was added downstream from the ablation chamber. In the second, the listed flows of Ar and He were mixed upstream from the ablation chamber, and no additional gas was added downstream. In the third, the specified flow of He was flowed through the ablation chamber and the corresponding flow of Ar was added downstream. For each set of three experiments, the total flow and gas composition injected into the ICP torch were the same.

A detailed review of the instrumentation used for these experiments has been given previously [2]. A brief overview, including recent modifications will be provided here. Pulses from a Nd:YAG laser (Brilliant B, Quantel, France) were used to ablate samples sealed in an ablation cell with a volume of roughly 50 cm³. The cell was translated under the laser beam at constant velocity in a serpentine pattern. Laser fluence was held constant at 18 J cm⁻² during ablation of the CaF₂, and 50 J cm⁻² during ablation of the scandium-aluminum disks. The Varian ICPMS gas box was used to control the Ar gas flow supply to the ablation cell. A separate mass flow controller (5850, Brooks Instruments) was used to control the He gas flow. Flow from either controller could be directly connected upstream of the ablation cell, added downstream of

the ablation cell via a “Y”-connector, or mixed upstream of the ablation cell by a swage “T”-connector. A 7-mm I.D. transport tube (Tygon) was used to carry particles to the sheath torch connector of the ICP. Ratios of approximately 25, 50, and 75% He/Ar were chosen at total flow rates that either led to ion distributions centered in the imaging region or reaching a maximum near the sampling cone.

After the images were taken for each gas condition, a filter assembly built in-house was added in-line midway from the ablation cell to the ICP torch. For each gas condition, particles generated over 100 laser pulses were collected on 0.4 μm polycarbonate filter disks. Particles collected on the filters were characterized with SEM (Helios NanoLab 600i, Hillsboro, OR). A 10 nm coating of 60:40 gold-palladium was applied to the surface. Images were taken at 650x magnification with a voltage of 5.00 kV, current of 86 pA, and working distances of around 4 mm.

A XeCl excimer laser (LPX 110, Lambda-Physik, Acton, MA) was used to pump a dye laser (Scanmate 2, Lambda-Physik, Acton, MA) tuned to a transition line for the ion being studied. Fluorescence schemes and dyes are listed in Table 3. The dye laser output was guided to the experiment through an optical fiber. The divergent output of the fiber was collimated, then focused to a line with a cylindrical lens. Near the focal line, the laser light approximated a sheet of radiation that was imaged onto a gated, intensified CCD (7361-0001, Princeton Instruments, Trenton, NJ) through a narrow-band interference filter. The CCD gain and number of exposures were adjusted to produce acceptable signal levels within a reasonable exposure time. Fig. 1 shows the general setup of the instrumentation.

2.3 *Image processing*

Images of Ca ions are raw CCD images without background subtraction. In the interest of capturing the variations in ion distributions due to changes in gas composition, all Ca images were recorded in a single experimental run. Sample size limitations and orifice clogging limited the duration of such a run, and it was not practical to include background measurements for each set of experimental conditions. Background contributions from Ca II line emission and plasma continuum emission contribute between 5-8 percent of the total signal. For the Sc images, the background emission was subtracted from the corresponding fluorescence image using Winview software, (Princeton Instruments, Trenton, NJ). All images were converted to ASCII format and processed with Matlab (The Mathwork, Natick, MA). The color scales were set for each image independently to allow better qualitative inspection of each ion distribution. Matlab scripts were created to plot the various cross sections and FWHM values extracted from the images. Axial cross sections were plotted along the center axis. Five rows above and below the radial center axis, corresponding to a physical dimension of 0.23 mm, were averaged to improve the signal-to-noise in the axial profiles. FWHM values were calculated by counting the total number of pixels along each radial cross section with intensity at least half of the peak maximum. This approach was chosen to avoid calculation difficulties associated with non-Gaussian peak shapes or significant noise. FWHM values were not calculated at axial positions where the presence of the cooled central channel caused a dip in the ion signal along the center axis.

3 Results and discussion

3.1 Calcium

3.1.1 Ablation

As seen in the SEM image in Fig. 2a, ablation in $1.3 \text{ L min}^{-1} \text{ Ar}$ produced spherical particles, exfoliated fragments, and soft-agglomerates of various sizes and densities. Particles collected

during ablation at $0.66 \text{ L min}^{-1} \text{ Ar}$, presented in Fig. 2b, include micron-sized spheres, exfoliated particles, and filamentary soft agglomerates. Due to the scarcity of micron-sized particles, the exfoliated particle seen in the inset was superimposed from another section of the image. Insets in the remaining images are similarly drawn from other sections of the filter to illustrate the variety of particles collected on the filter.

Much larger and denser filamentary soft-agglomerations were generated during ablation in $2.00 \text{ L min}^{-1} \text{ He}$ (Fig. 2c) compared to either flow rate in Ar. Hard-agglomerates, spheres, and fragments, though smaller, were present in numbers similar to $1.3 \text{ L min}^{-1} \text{ Ar}$. The numbers and sizes of soft agglomerates formed at $0.43 \text{ L min}^{-1} \text{ He}$ (Fig. 2d) were intermediate between those formed in Ar and those observed with $2.00 \text{ L min}^{-1} \text{ He}$. Only a few small micron-sized spheres and fragments were observed during ablation in $0.43 \text{ L min}^{-1} \text{ He}$. We assume that the changes in particle distributions observed as a function of gas flow rates are primarily due to changes in transport efficiency, and not due to fundamental changes in the ablation process.

The general characteristics of the particles shown in Fig. 2 are consistent with earlier SEM and TEM studies by the Russo [8] and Günther[9, 10] groups. Agglomerates are common features of aerosols produced by laser ablation, and the higher density of agglomerates that we observed in He compared to Ar is consistent with observations reported by Kuhn and Günther for nanosecond ablation at 193 nm [10].

3.1.2 ICP

3.1.3 Axial ion distributions

General qualitative differences in the ion distributions formed during ablation in different Ar/He gas conditions are presented in the LIF images in Fig 3. The intensities of ions along the center axis for each image are plotted in the axial cross-sections in Fig. 4a, b, and c for

He/Ar mixtures of 25, 50, and 75%, respectively. With one exception, noted below, the axial cross sections for a given total gas composition are surprisingly similar. These results indicate that neither the gas composition nor the flow rate through the cell (at least within the range observed here) has a large effect on ion distributions in the plasma. Our results are consistent with the observations of Horn, *et al.*[11], who reported identical ablation rates in Ar and He. We see no evidence in the fluorescence data of the effects of higher levels of plasma screening in Ar compared to He, nor do we see any effects of particle-induced plasma screening within the range of flow rates passed through the ablation cell [7].

In contrast to the similarities for a given gas flow in the fluorescence data, there are clear differences between the particles produced in the different gases collected on filters in the transmission line shown in Fig. 2. Horn and Günther reported that ablation with a 266-nm laser in He produced more small particles than in Ar[12]. They also noted, however, that the volume-normalized particle size distributions were not significantly dependent on the composition of the ablation gas. It is possible that the agglomerates that are so prominent in Figs. 2c and 2d make only a minor contribution to the observed fluorescence signal. The one exception to the general similarities noted above is the profile produced by ablation in argon with a final gas composition of 25% He (Fig. 4a). The reduced signals near the load coil are consistent with the production of fewer small particles in Ar than in He or in the He/Ar mixture.

In contrast to changes in gas composition in the ablation cell, the overall composition of the gas has a major impact on ion densities in the plasma. The on-axis ion signal intensity for 75% He/Ar is about a half that for 25% He/Ar. In explaining these results, two possibilities must be considered. One possibility is that aerosol transport efficiency from the ablation cell to the plasma decreases with increasing He content in the carrier gas. Theory suggests that both

diffusional and gravitational losses should be greater in He than in Ar[7]. However, in practice, measured transport efficiencies did not depend significantly on carrier gas composition[12]. The second possibility is that ion losses in the plasma itself increase with increasing He content. Increasing He/Ar ratios also influence ICP conditions [13]. Higher gas-kinetic temperatures have been reported with added helium [6]. At higher gas-kinetic temperatures, the ionization efficiency of the ICP should improve and unfavorable shifts in the Saha balance are not likely [14]. Enhanced off-axis diffusion of ions at higher He/Ar ratios could account for lower on-axis signals. Broadening in the radial distributions of ions in the presence of He, previously reported, was attributed to lower mass and higher electrical conductivities of helium compared to argon [15],[16]. Moreover, an upstream shift in the axial position where vaporization begins [17] at higher He/Ar ratios would exacerbate ion loss due to off-axis diffusion. The disappearance of the cooled central channel at 75% He/Ar in the LIF images in Fig. 3 is indicative of an upstream shift in vaporization. An upstream shift in vaporization was suggested to account in part for a decrease in LIF signal that occurred when adding a matrix element (lithium) in a SN-ICPMS study [18].

3.1.4 Radial ion distributions

FWHM values calculated from radial cross sections of images taken during ablation in 25%, 50%, and 75% He/Ar are presented in Fig. 4d, e, and f, respectively. Higher He/Ar ratios produced significantly larger FWHM values, most notably at downstream positions near the sampling cone. The general trend of FWHM values along the axial length was similar for each plot. The initial decline in the FWHM to a minimum indicates that vaporization rates exceed rates of off-axis diffusion. A vaporizing particle acts as a local source of atoms, which are ionized faster than they diffuse off-axis. A minimum and subsequent rise occurs as rates of off-

axis diffusion exceed vaporization rates. At higher He/Ar ratios, the axial positions where the minima occur are shifted upstream. The upstream shift is consistent with an upstream shift in the axial position where vaporization begins. However, higher vaporization rates [5] could also contribute to the shift.

The observation that the decreasing on-axis densities with increasing He content are accompanied by increases in the radial spreads of the ions raises the question of whether the changes presented in Fig. 4 represent decreases in the total number of ions in the plasma or merely redistributions of a fixed number of ions. The answer is presented in Fig. 5, which plots the spatially-integrated fluorescence signal as a function of gas composition. Clearly, the fluorescence experiment is detecting fewer ions as the He content of the carrier gas increases. Either fewer ions are reaching the plasma, or ions are being carried by a combination of convection and diffusion to regions of the plasma where they are lost through ion-electron recombination, doubly-charged ion formation, or molecule formation. The former possibility seems to be ruled out by the transport efficiency measurements of Horn and Günther[12]. The latter possibility is consistent with integrated fluorescence measurements reported by Lazar and Farnsworth [19], who observed that the integrated ion signals from single droplets decreased when vaporization from the droplets was initiated closer to the load coil. It is impossible from the data presented here to definitively distinguish between transport losses and losses in the plasma.

3.2 *Scandium*

3.2.1 *Ablation*

As seen in the SEM image in Fig. 6a, ablation in $1.3 \text{ L min}^{-1} \text{ Ar}$ produced micron-sized hard-agglomerates, spherical particles, and soft-agglomerates of various densities. Fewer spheres and

more hard-agglomerates were generated compared to CaF_2 . Ablation in 0.6 L min^{-1} Ar (Fig. 6b) led to more abundant, larger soft-agglomerates compared to 1.3 L min^{-1} Ar. No micron-sized spheres or fragments were observed at the lower flow rate.

Micron-sized spheres and hard-agglomerates were collected during ablation in 2.00 L min^{-1} He (Fig. 6c), though smaller and fewer in number compared to 1.3 L min^{-1} Ar. Soft-agglomerations were more abundant and appeared to be more densely packed than those formed in Ar. During ablation in 0.4 L min^{-1} He (Fig. 6d) soft-agglomerations were formed, though not as dense or abundant as at 2.00 L min^{-1} He. There were no micron-sized particles collected during ablation in 0.4 L min^{-1} He. Chimney formations attributed to inefficient removal of large particles during ablation have been reported for metals [11], so the absence of large particles at low He flow rates in the ablation cell could be due to transport losses. However, the presence of large particles under similar conditions with the CaF_2 samples indicates that other factors are also in play.

3.2.2 ICP

3.2.2.1 Axial ion distributions

LIF images of Sc ions taken during various ablation gas conditions are presented in Fig. 7. Gas flows were chosen that led to peak ion densities 7-8 mm downstream from the load coil. Cross sections of the ion densities along the center axis are plotted for 25, 50, and 75% He/Ar in Fig. 8a, b, and c, respectively. Unlike the case of CaF_2 , overall ion signal intensities were significantly dependent on ablation gas composition for the scandium aluminum alloy, most notable at lower He/Ar ratios. Ablation in Ar led to larger ion signals than in He or in the He/Ar mixture. It is clear from the data that ion densities in the plasma are not a simple linear function

of the composition of the gas in the ablation cell, as would be the case if gas density were the critical gas property.

The ion signals produced with 75% He/Ar are approximately half those for 25% He/Ar when either He or Ar is used as the ablation gas. As with CaF_2 , the decrease is not consistent with changes in the PSD. Rather, ICP effects must be considered. Again, off-axis diffusion could account for the decrease in ion density with the increase in helium content in the nebulizer gas. Since calcium and scandium are almost identical in mass, they should experience very similar rates of diffusion. However, the plateauing effect observed in the ion signal for CaF_2 at higher He/Ar ratios did not occur in scandium aluminum. Scandium is a much more refractory element than calcium. Recalling that lower nebulizer gas flow rates lead to higher central channel temperatures, note that the Sc ion density with an Ar flow rate of 1.17 L min^{-1} peaked at the same axial position as Ca ion density with a flow of 1.3 L min^{-1} Ar. It is possible that the plateauing effect in the Ca ion distribution observed for high helium fractions was related to the upstream shift in vaporization and is not as significant for the more refractory scandium aluminum particles.

3.2.2.2 Radial ion distributions

FWHM values calculated from vertical cross sections of images taken during ablation in 25, 50, and 75% He/Ar are presented in Fig. 8d, e, and f, respectively. Similar to Ca, FWHMs increased with increasing He/Ar ratios. It is interesting that the FWHM continually decreased along the axial length for 75% He/Ar, indicating that particles vaporized along the entire axial length of the ICP. It should be noted that the axial position of peak ion signal for 75% He/Ar is 1 mm downstream from that of that of 25% He/Ar. Therefore, it is possible that diffusional effects are masked by convergence of the gas flow at the sampling cone. It is also possible that an

“expansion-driven acceleration” of particles in 75% He/Ar led to incomplete vaporization of larger particles [20]. Higher velocities would mean that aerosol particles would experience shorter residence times in the ICP. Incomplete vaporization not only accounts for the FWHM trend, but could also account for a portion of the decreased ion signal that occurred with 75% He/Ar.

3.2.2.3 *Sampling cone*

To investigate the influence of the vacuum interface on ion distributions in different He/Ar mixtures, flow rates were adjusted to produce peak ion densities just upstream from the sampling cone. LIF images of Sc ions taken at those flow rates are presented in Fig. 9. Cross sections of the ion densities along the center axis are plotted for 25, 50, and 75% He/Ar in Fig. 10a, b, and c, respectively. At 25% He/Ar, ablation in argon again leads to the largest ion signal. However, at 50 and 75% He/Ar, ablation in helium produces the largest ion signal. It is unlikely that significant changes in the PSD occurred over the minor changes in flow rates required to shift the ion signal towards the sampling cone. Thus changes in the vaporization/ionization rates of particles near the sampling cone should be considered.

The evidence suggests that more complete vaporization of soft-agglomerates, predominately generated in helium, compared to micron-sized particles, generated in argon, account for the change in trend. Because flow rates were increased to position the Sc ion signal peak just upstream from the sampling cone, particles vaporize over a shorter axial length and are less likely to completely vaporize. Indeed, FWHM values plotted in Fig 10d, e, and f, for 25, 50, and 75% He/Ar indicate incomplete vaporization in all cases. Intuitively, the vaporization efficiency of soft-agglomerates would be less affected by accelerated velocities associated with higher He/Ar ratios than micron-sized particles. An increased steepness in the decline of FWHM

values corresponding to ablation in helium compared to argon is further support of this conclusion.

3.3 *Conclusion*

The effects of adding helium upstream and downstream from the ablation cell were investigated. Differences in the PSD of aerosol generated during ablation in argon and helium at low and high flows were characterized off-line with SEM. In general, ablation in helium led to larger, more densely-packed softagglomerates, and fewer and smaller micron-sized particles than in argon. However, Ca ion fluorescence signals generated from particles produced during ablation of CaF_2 were largely independent of the gas added upstream from the ablation cell. It seemed that an increase in the amount of soft-agglomerations during ablation in helium compensated for the reduced size and number of micron-sized particles compared to argon. In the case of scandium-aluminum, ablation in argon typically led to larger Sc ion signals in the ICP. For both CaF_2 and scandium-aluminum, increasing the He/Ar ratio from 25 to 75% led to lower ion densities. Changes in the PSD could not account for the decrease. We propose that increased rates of off-axis diffusion at greater He/Ar ratios caused the decrease. Increasing FWHM values at higher He/Ar ratios supported this conclusion. When flow rates were increased to shift ion production near the sampling cone, slightly higher Sc ion signals were formed from particles generated in helium than in argon. We conclude that the vaporization efficiencies of soft-agglomerates are less affected by accelerated particle velocities at greater He/Ar ratios than micron-sized particles.

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Figure Captions

Figure 1. General overview of the instrumental setup. The three different setups used for the different gas conditions are depicted.

Figure 2. SEM images of aerosol particles, generated during ablation of CaF_2 , impacted on $0.4\ \mu\text{m}$ pore size polycarbonate filter disks. Images were taken of particles impacted during ablation in (a) $1.3\ \text{L min}^{-1}\text{Ar}$, (b) $0.66\ \text{L min}^{-1}\text{Ar}$, (c) $2.00\ \text{L min}^{-1}\text{He}$, and (d) $0.43\ \text{L min}^{-1}\text{He}$. These flows correspond to the flows used for images presented in Fig. 3 for ablation in argon or helium with final gas compositions of 25% He/Ar (a,d) and 75% He/Ar (b,c). The second gas was added downstream from the ablation cell. The scale, bottom-right of (a), is the same for each image.

Figure 3. LIF images of Ca ion distributions formed in the ICP from aerosol particles generated during LA in various ablation gas conditions. The images correspond to ablation in Ar, a mixture of Ar and He, and He in rows 1, 2, and 3, respectively. The columns are labeled with the final composition of the carrier gas as it reached the plasma. For rows 1 and 3, He and Ar were added downstream from the ablation cell, respectively. Actual flow rates are given in Table 2.

Figure 4. Cross-sectional plots of the axial distribution of Ca ions along the center axis for each image presented in Fig. 3. Plots from images taken with nebulizer gas compositions of 25, 50, and 75% He/Ar are presented in 4a, b, and c, respectively. Additionally, FWHM values calculated from radial cross-sections of Ca ion intensities are presented in 4d, e, and f, for nebulizer gas compositions of 25, 50, and 75% He/Ar, respectively. For each He/Ar ratio, plots are presented for ablation in (---) argon, (—) mixtures, and (—) helium.

Figure 5. Spatially-integrated fluorescence signals for each of the images presented in Fig. 3.

Figure 6. SEM images of aerosol particles, generated during ablation of scandium aluminum, impacted on 0.4 μm pore-size polycarbonate filter disks. Images were taken of particles collected during ablation in (a) 1.3 L min^{-1} Ar, (b) 0.6 L min^{-1} Ar, (c) 2.00 L min^{-1} He, and (d) 0.4 L min^{-1} He. These flows reflect nominal flows used for images presented in Fig. 7 and 9 for ablation in argon or helium at 25 and 75% He/Ar.

Figure 7. LIF images of Sc ion distributions formed in the ICP from aerosol particles generated during LA in various ablation gas conditions. The images correspond to ablation in Ar, a mixture of Ar and He, and He in rows 1, 2, and 3, respectively. The columns are labeled with the final composition of the carrier gas as it reached the plasma. For rows 1 and 3, He and Ar were added downstream from the ablation cell, respectively. Actual flow rates are given in Table 2.

Figure 8. Cross-sectional plots of the axial distribution of Sc ions along the center axis for each image presented in Fig. 7. Plots from images taken with nebulizer gas compositions of 25, 50, and 75% He/Ar are presented in 8a, b, and c, respectively. Additionally, FWHM values calculated from radial cross-sections of Sc ion intensities are presented in 8d, e, and f, for ablation in 25, 50, and 75% He/Ar, respectively. For each He/Ar ratio, plots are presented for ablation in (- - -) argon, (—) mixtures, and (—) helium.

Figure 9. LIF images of Sc ion distributions formed in the ICP from aerosol particles generated during LA with gas flows adjusted to produce peak ion signals 2-3 mm upstream from the sampling cone. The images correspond to ablation in Ar, a mixture of Ar and He, and He in rows 1, 2, and 3, respectively. The columns are labeled with the final composition of the carrier gas as it reached the plasma. For rows 1 and 3, He and Ar were added downstream from the ablation cell, respectively. Actual flow rates are given in Table 2.

Figure 10. Cross-sectional plots of the axial distribution of Sc ions along the center axis for each image presented in Fig. 9. Plots from images taken with nebulizer gas compositions of 25, 50, and 75% He/Ar are presented in 10a, b, and c, respectively. Additionally, FWHM calculated from radial cross-sections of Ca ion intensities are presented in 10d, e, and f, for nebulizer gas compositions of 25, 50, and 75% He/Ar, respectively. For each He/Ar ratio, plots are presented for ablation in (- - -) argon, (—) mixtures, (—) and helium.

Table 1

Table 1. Experimental conditions	
<i>Ablation Laser</i>	<i>Brilliant B</i>
Nd:YAG	266 nm
Pulse length	5 ns
Fluence (Sc)	50 J cm ⁻²
Fluence (Ca)	18 J cm ⁻²
Spot size	90 µm
Rep rate	10 Hz
Raster speed	0.1 mm s ⁻¹
Beam profile	Gaussian
<i>ICP-MS</i>	<i>Varian Redtop</i>
Sampling depth	12 mm
Carrier gas	See Table 2
RF power	1300 W
Plasma gas	16 L min ⁻¹
Auxiliary gas	2 L min ⁻¹
Sheath gas	0.2 L min ⁻¹

Table 2

Table 2. Carrier Gas Flow Rates (L min ⁻¹)				
He/Ar Ratio		25%	50%	75%
Call Fig. 3	Ar	1.30	1.05	0.66
	He	0.43	1.05	2.00
Total		1.73	2.10	2.66
Sc II Fig.7	Ar	1.17	1.00	0.58
	He	0.39	1.00	2.00
Total		1.56	2.00	2.58
Sc II Fig.9	Ar	1.28	1.10	0.72
	He	0.42	1.10	2.00
	Total	1.70	2.20	2.72

Table 3

Table 3
Fluorescence scheme

Analyte	Excitation Wavelength	Fluorescence Wavelength	Filter	Dye (Exciton, Dayton, OH)	Gate width : delay
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 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10