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## Laser Ablation in Analytical Chemistry

In 2002, we wrote an *Analytical Chemistry* feature article describing the Physics of Laser Ablation in Microchemical Analysis. In line with the theme of the 2002 article, this manuscript discusses current issues in fundamental research, applications based on detecting photons at the ablation site (LIBS and LAMIS) and by collecting particles for excitation in a secondary source (ICP), and directions for the technology.

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Laser ablation for chemical analysis offers elemental, isotopic, and classification analysis, minimal or no sample preparation, no consumables, rapid turn-around time, and chemical interrogation of H–Pu from any sample. Simply remove (ablate) a tiny portion of mass from a sample using a pulsed laser beam and subsequently analyze optical emission from the induced plasma (laser-induced breakdown spectroscopy (LIBS) and laser ablation molecular isotopic spectroscopy (LAMIS)) or transport the aerosol (particles) into a secondary source like the inductively coupled plasma (ICP). The sampling process (laser ablation) is the same; detection is dictated by the application (Figure 1). In 2002, our *Analytical Chemistry* feature article described the Physics of Laser Ablation in Microchemical Analysis.<sup>1</sup> At that time, research was devoted to studying fundamental mechanisms underlying the laser material interaction (ablation processes) and applications primarily in geochemistry.<sup>1–12</sup> In line with the theme of the 2002 article, this manuscript discusses current issues in fundamental

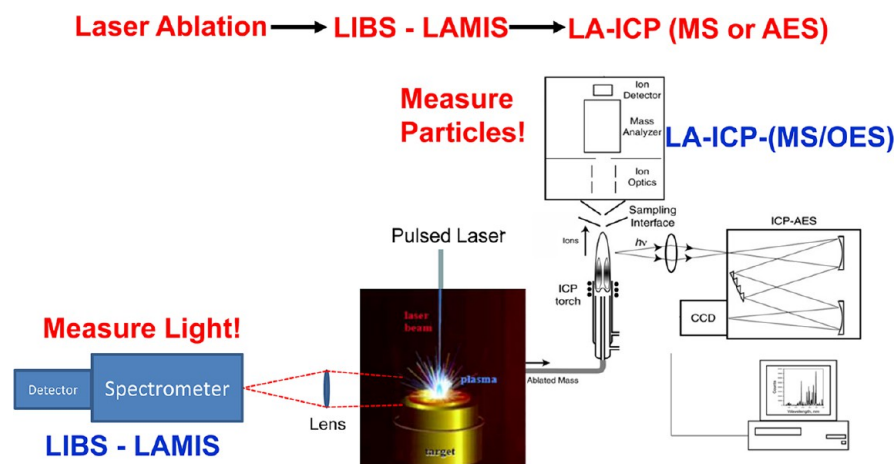
research, applications based on detecting photons at the ablation site (LIBS and LAMIS) and by collecting particles for excitation in a secondary source (ICP), and directions for the technology.

### ■ PHYSICS OF LASER ABLATION

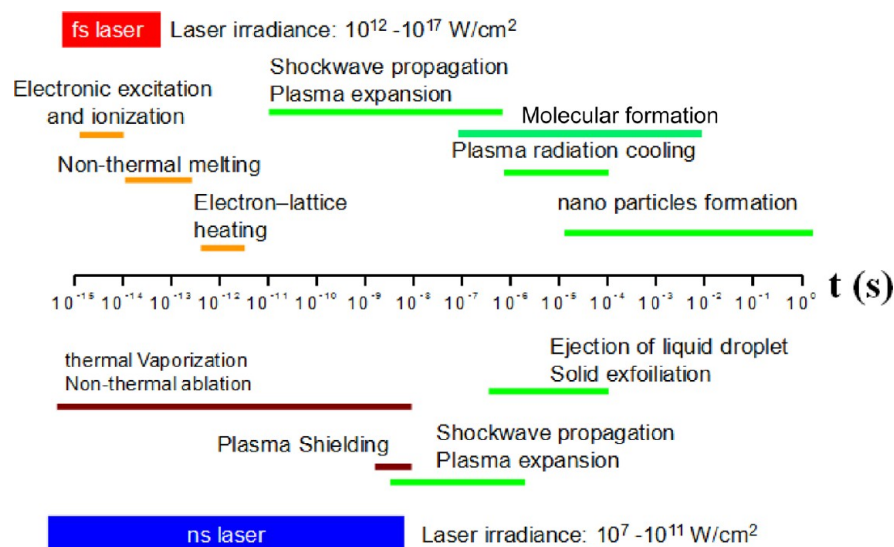
Laser ablation is the process of focusing a pulsed laser beam with sufficient energy onto a sample to remove a small amount of mass. Ablation physics are the explosive underlying mechanisms for dissipating the laser energy that was absorbed; mass is removed by a tiny explosion. Linear and nonlinear mechanisms underlie and predict the ablation event.<sup>1,2,13–15</sup>

Figure 2 shows several mechanisms that have been hypothesized to describe specific time processes of ablation. This figure only presents an example of studies and potential mechanisms that can transpire from the irradiation of the laser pulse energy onto a sample to particle condensation from the vapor, occurring over 15 orders in time. These and other mechanisms can be operative; which mechanisms dominate strongly depends on the laser parameters and the sample. The overall process and efficiency for converting laser energy into ablated mass is dependent on the mechanisms. Laser ablation involves many sequential processes; the initial laser-material interaction controls the outcome. The physics of energy absorption and transfer within the sample to remove mass are not addressed here; we discuss the resultant processes once mass leaves the sample surface and the ability to detect that mass. The ablated mass is a plume of hot atoms, ions, molecules, and particles. Particles are formed from various mechanisms, directly ablated from the sample through shock and exfoliation processes and those formed by nucleation and condensation of the vapor.<sup>3,8,10,12,14,16–18</sup> Some of these processes can be observed directly by shadowgraph imaging, plasma emission spectroscopy, and light scattering. A shadowgraph image can be obtained by using two laser beams; one laser ablates the sample and generates the plasma plume while the second laser beam probes the plasma and forms an image on a CCD camera. The time delay between the ablation and probe laser beams is varied to provide physics of the shockwave and other plasma properties. Optical emission images are measured by using an ICCD camera to study time-resolved elemental intensity and spatial distribution within the plasma. Light scattering based imaging

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**Figure 1.** Representation of laser ablation as the direct solid sampling process with subsequent analysis of photons from the induced plasma using laser induced breakdown spectroscopy (LIBS) and laser ablation molecular isotopic spectroscopy (LAMIS) and by transporting the ablated mass to an inductively coupled plasma (ICP) with either mass spectrometry (MS) or atomic emission spectroscopy (AES).



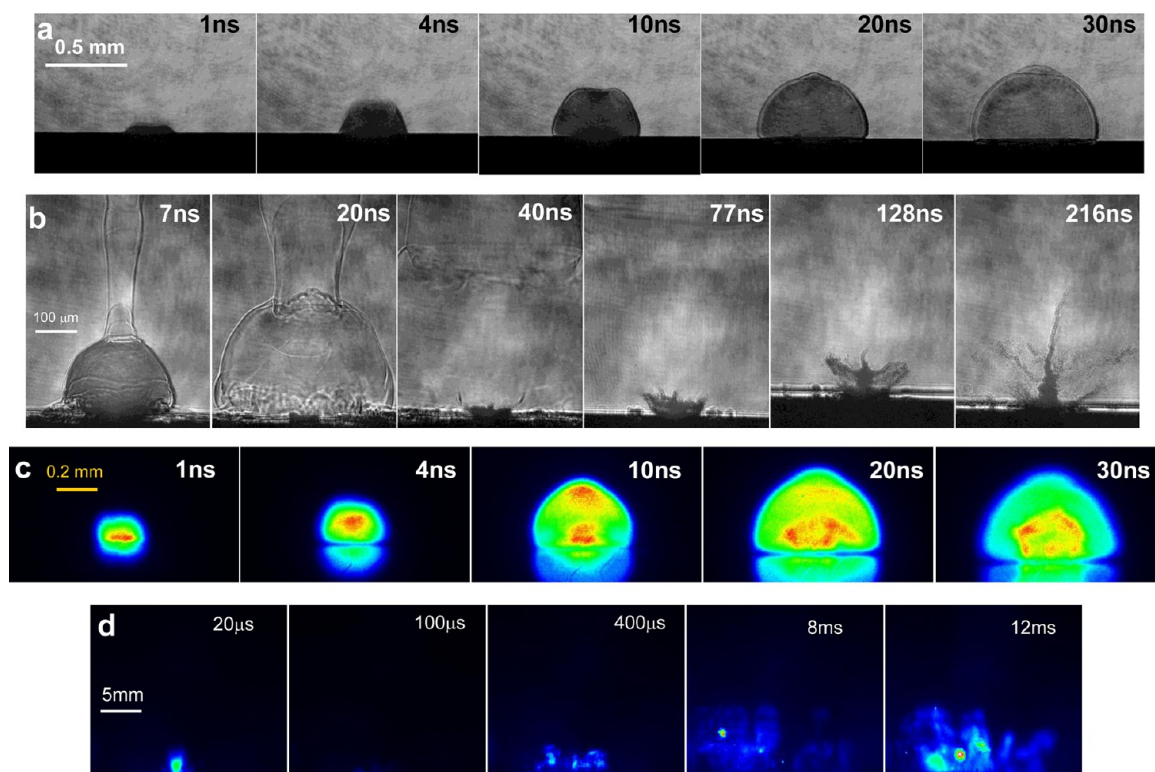
**Figure 2.** Example of physical mechanisms that have been hypothesized and studied to represent the ablation process over 15 orders in time.

also uses a CCD camera and two lasers; one to ablate the sample and the second to probe the nucleation and formation of nanoparticles. Figure 3 shows images of shockwaves, particle ejection, plasma emission, and particle formation using shadowgraph and light scattering methods.<sup>14,16,19</sup> In each frame, the laser is incident from the top and the sample is at the bottom. Sequences a and b demonstrate how laser energy and fluence can dramatically change the ablation process for nanosecond laser ablation; sequence a is relatively low laser energy with normal shockwave propagation whereas sequence b is high laser energy showing significant shockwave distortion caused by laser supported detonation and extreme particle exfoliation.<sup>1,14,16</sup> Sequence c shows false color optical emission (Cu spectral line intensity) images for a plasma formed by ablating copper with low laser energy (similar to sequence a).<sup>14</sup> Sequence d shows light scattering images of nanoparticle formation long after ( $>100 \mu\text{s}$ ) the laser pulse.<sup>19</sup>

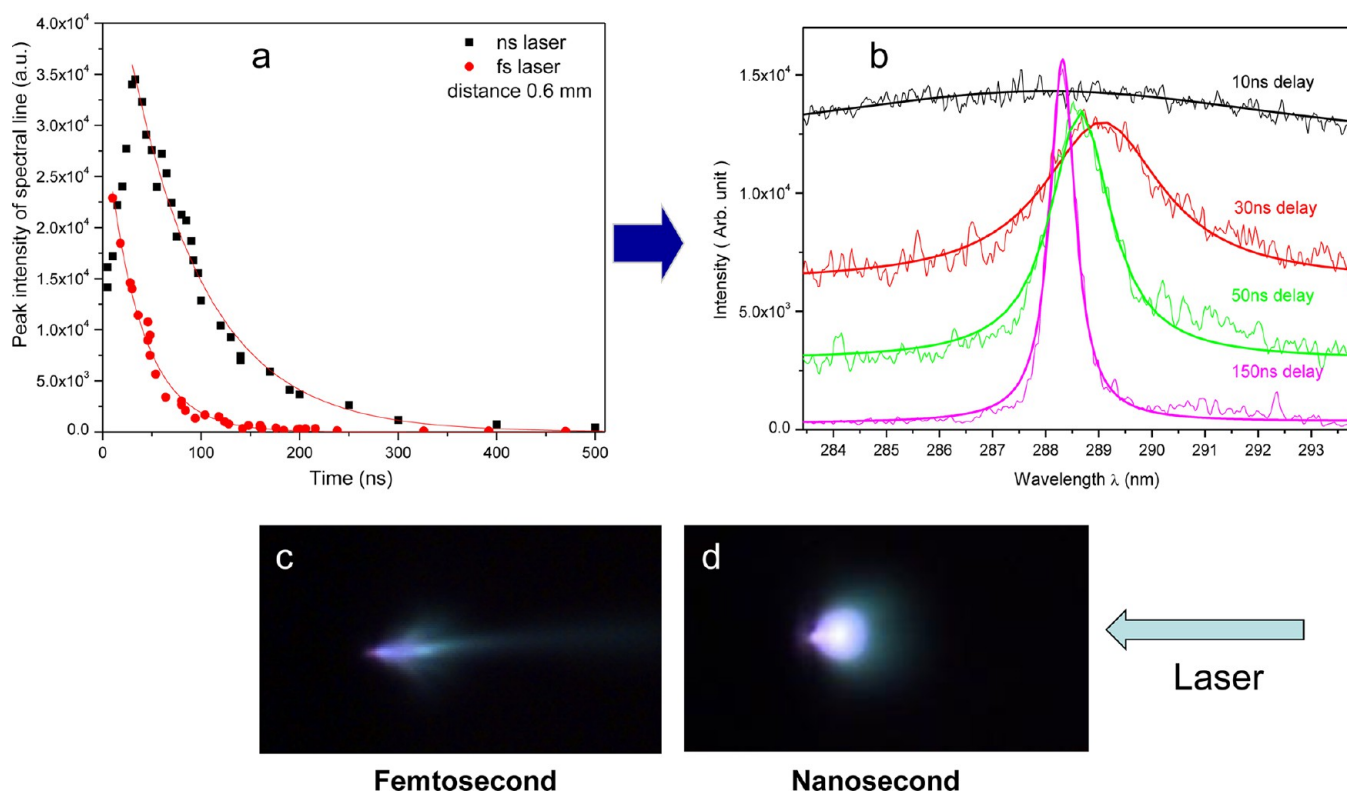
Optical emission from the plasma formed at the sample surface is the analytical source for spectrochemical analysis using LIBS and LAMIS. The laser pulse duration has a primary influence on the plasma persistence, the spectral line profile,

background continuum, and the expansion properties as seen in the data and photographs of Figure 4. Data in 4a show the time decay of plasma emission (persistence) at 288 nm from femtosecond and nanosecond laser ablation of silicon. Figure 4b shows how the spectral line emission is shifted and broadened initially and relaxes with time after the laser pulse. Photographs of the ablation event<sup>20,21</sup> Figure 4c,d from a copper sample with femtosecond and nanosecond pulsed lasers, respectively, shows the effect of laser pulse duration.<sup>22</sup>

Particles are a critical aspect of laser ablation for chemical analysis using the ICP, as they must be efficiently entrained, transported to, and digested in this secondary source. Figure 5 shows scanning electron microscopy (SEM) images of particles after ablation using nanosecond (a–c, g) and femtosecond (d–f, h) pulsed lasers with the same wavelength, energy, and spot size; only the irradiance changed due to the pulse duration of these lasers.<sup>23,24</sup> Similar sized spherical particles for the femtosecond-ablated Al-alloy (Figure 5f) and the nanosecond-ablated brass sample (Figure 5g) demonstrate an example of how particle size also depends on the sample. The particle sizes and their size distribution depend strongly on

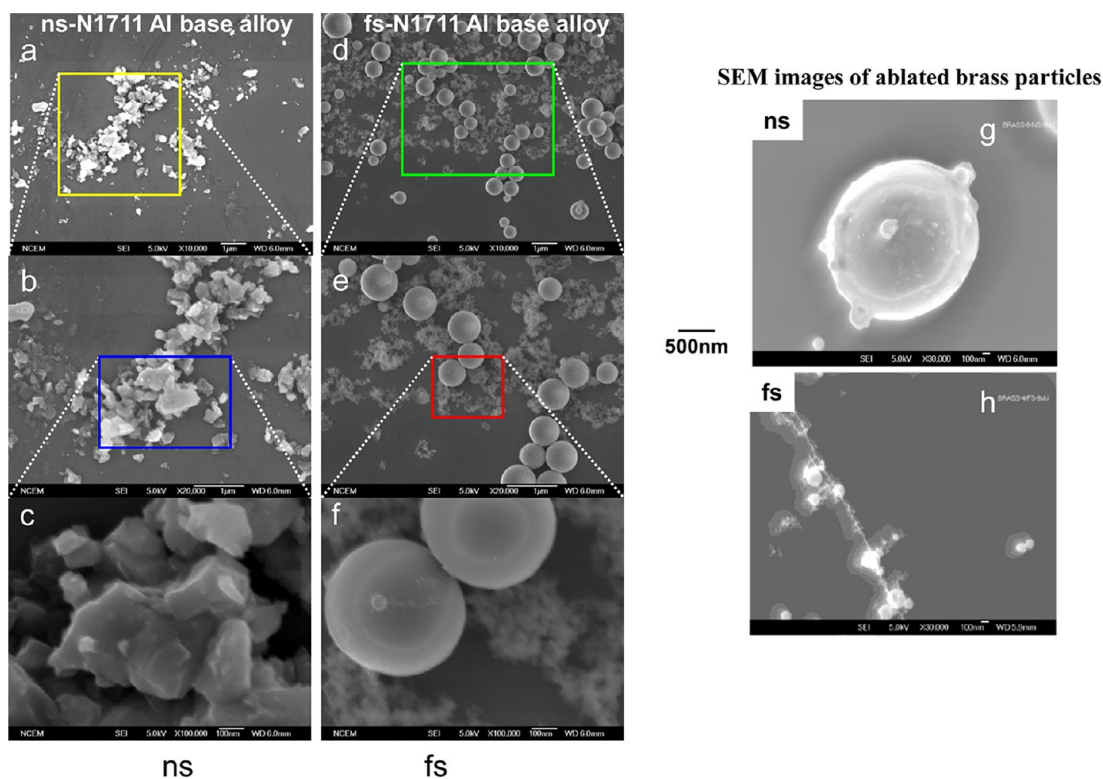


**Figure 3.** Time resolved images of ablation processes: (a) shadowgraph images of shockwave and mass leaving the surface using relatively low pulsed laser energy; (b) same as part a except pulsed laser energy is greater showing distortion of shockwave and significant particle ejection; (c) false color images of copper emission intensity; and (d) light scattering images showing initial particle ejection followed by particle condensation from vapor  $>100\ \mu\text{s}$  after the laser pulse.



**Figure 4.** Characteristics of laser induced plasmas: (a) persistence of a nanosecond versus femtosecond laser induced plasma; (b) emission intensity measured for ablation of silicon as a function of time showing change in background, spectral line shifting, and broadening. Optical photographs of femtosecond (c) and nanosecond (d) laser induced plasmas.





**Figure 5.** SEM images of particles collected after laser ablation of a NIST Al alloy and brass samples using the same laser energy, wavelength and fluence (spot size); the pulse duration was 6 nanoseconds (ns) or 100 femtoseconds (fs).

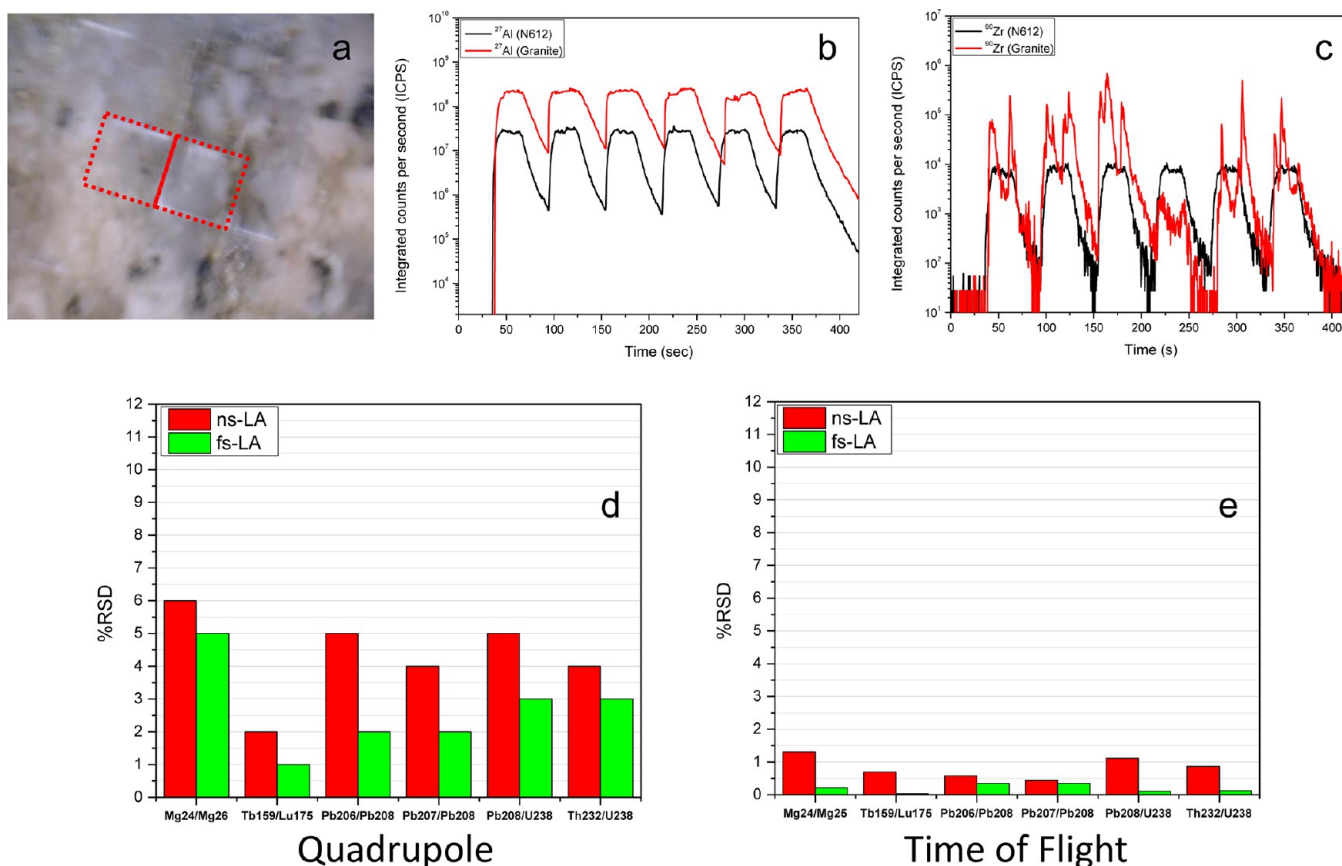
the laser parameters, the sample properties, and ablation environment (gas, pressure, etc.).

Fundamental knowledge is critical to ultimate advancement of laser ablation. Research efforts to elucidate fundamental mechanisms and to establish robust models to predict ablation behavior are currently underway in many laboratories throughout the world. A main objective of these efforts for analytical chemistry is to help define conditions (parameters) that produce stoichiometric ablated mass that is excited to optical emission and then condensed to nanoparticles. The research community continues to study the laser parameter (wavelength, energy, spot size, pulse duration) influence on chemical analysis performance.<sup>1,21,25–30</sup> Today, most fundamental studies address the laser pulse duration (femtosecond vs nanosecond) whereas most studies using nanosecond lasers emphasize applications.<sup>31–37</sup> Several papers have demonstrated the existence of a regime or threshold between distinctly different laser ablation mechanisms (thermal and nonthermal) at the few picosecond time scale.<sup>38–43</sup> However, exact mechanisms to describe the ablation process relevance to analytical chemistry, photon emission (atomic, ionic, and molecular), plasma chemistry, and aerosol formation are not established. Some processes that could adversely influence analytical performance include self-absorption in the plasma (LIBS), loss of aerosol due to particle size, mass loading, and incomplete particle digestion in the secondary source (ICP). However, for every application, we propose that there will be optimum laser parameters that define an efficient ablation process and eliminate or minimize these issues. Each sample will benefit from the right laser parameters. Because every sample is different, the method (to include ablation and detection) must be established for the application. Importantly, even though we do not fully understand the underlying ablation

mechanisms, we can optimize the process to produce an ideal aerosol for the ICPMS or an ideal plasma for LIBS/LAMIS. It is relatively straightforward to optimize the method for the sample and application. Appropriate conditions for laser energy, pulse duration, fluence, and wavelength can provide good precision and accuracy for every sample, using photon or particle detection. Once established, the laser ablation process is reproducible and so is the analytical chemistry. In addition to analytical chemistry, laser-assisted in situ keratomileusis (LASIK) and many industrial applications (cutting, welding, scribing) have proved this point. Laser ablation is a multi-disciplinary technology with applications in physics, chemistry, biology, materials science, medical, industry, and others. Understanding mechanisms will advance the laser ablation technology for all applications. The Conference on Laser Ablation (COLA) emphasizes current research in fundamental studies and applications, and many conferences have sessions for specific applications of laser ablation. There are several dedicated LIBS conferences each year including the recent induction of the North American Society for Laser-Induced Breakdown Spectroscopy (NASLIBS) into SCientific eXchange (SciX).

## ■ ACCURACY

Accuracy of chemical analysis is generally attributed to the ablation process producing a stoichiometric vapor. Two of the most studied parameters that influence accuracy are the laser wavelength and pulse duration.<sup>2,7,9,25,26,28,32,44–48</sup> Many research groups have measured ablated particles using alternative methods and confirmed that particle chemistry can be particle-size dependent.<sup>49–52</sup> There is no doubt that certain wavelengths and laser–sample interactions can lead to nonstoichiometric ablation or fractionation; preferential re-



**Figure 6.** Example of high repetition rate femtosecond pulsed laser ablation of a NIST 612 glass standard and an inhomogeneous granite sample. The red squares (a) are 1 cm  $\times$  1 cm regions that were ablated on the granite sample. Six (only two are shown) regions were ablated and correlate to the six peaks in the time-dependent intensity graphs (b,c). The influence of the ICP, quadrupole (d), and time of flight (e) on precision are shown for both nanosecond and femtosecond laser ablation.

removal of elements based on volatility of the elements in the sample. However, stoichiometric ablation can be achieved for many cases by optimizing the laser parameters for the particular sample (as discussed above). Even under nonstoichiometric ablation conditions, excellent analytical chemistry can be performed by using matrix matched standards. Stoichiometric ablation is a primary reason why pulsed laser deposition (PLD) is such a powerful technology, the ability to make perfect crystalline thin films with the correct chemistry when the ablation process is optimized.<sup>53–56</sup> Even when the ablation process itself provides stoichiometric mass, it is unknown what happens to the atoms, ions, and particles as they experience high temperatures, pressures, and cooling rates in the plasma. The space–time nature of the plasma does not generally support a homogeneous aerosol environment. There are other processes that can have a stronger influence on accuracy than the ablation process itself, including plasma temperature and electron number density, nucleation and condensation, particle entrainment, transport, and the influence of the secondary source on digesting particles.<sup>57–62</sup> As discussed in the fundamental section, the appropriate method for each sample will provide accurate analysis. The research community defined fractionation index (FI) as a performance metric to compare laser parameters for ablation; FI is defined by dividing a second half of a measurement by a first half.<sup>63,64</sup> However, fractionation index is not a fundamental metric of ablation; it merely describes how the mass of each element changes as a crater is formed in a sample, as the aspect ratio changes under a set of

conditions.<sup>65</sup> Every sample ablates differently under different laser ablation conditions. The time-dependent removal (ablation) of mass from a sample is a convolution of wavelength, energy, pulse duration, sample, repetition rate, scan speed, plasma expansion, etc. FI simply shows how the quantities of different elements ablate in time as a crater is formed using specified parameters. Choosing the correct laser parameters and controlling the aspect ratio can eliminate preferential vaporization and fractionation as defined above. Wavelength plays a role on the ablation process, but so many other parameters are important, especially the sample. Good analytical chemistry can be achieved with an IR pulsed laser and bad analytical chemistry with a UV pulsed laser, reliant on the method, optimization, and the availability of standards.<sup>28</sup> Depending on the laser energy and pulse duration, wavelength will influence the efficiency of ablation, the amount of mass ablated versus the amount of energy incident on the sample. For linear one-photon absorption, the higher photon energy from a UV laser wavelength “should” be more efficient at breaking bonds. However, many studies have shown that linear one-photon absorption, and therefore wavelength, is not the only critical parameter for high irradiance laser ablation (Figure 3).<sup>14,16</sup>

Accuracy of laser ablation chemical analysis depends on the standards used for calibration; when the standards ablate the same as the sample, excellent quantitative analysis is achieved.<sup>66</sup> Every quantitative analytical technology needs standards, and standards for laser ablation solid sampling must be appropriate

for laser ablation solid sampling. Matrix matching is generally described as being almost impossible for complex samples, yet research has identified parameters that minimize the matrix dependence.<sup>67–71</sup> All that is needed is a way to calibrate the instrument (detection system) response so that it is similar to the laser ablation response for the unknown sample. This approach is not different than solution analysis where standards have been developed and perfected for years. We make the argument that practically every analytical technology is matrix dependent, especially solution digestion. A considerable effort goes into developing good liquid standards and yet there are still critical issues with getting many samples into the solution phase. X-ray fluorescence (XRF) standards are not perfect but they are accepted to provide a certain level of confidence. Standards can be developed for most laser ablation applications, especially in industry where process conditions can be set to produce sample variances over specified ranges (standards). The use of an internal standard when available also provides excellent metrics for accuracy and precision.<sup>23,72–77</sup>

## PRECISION

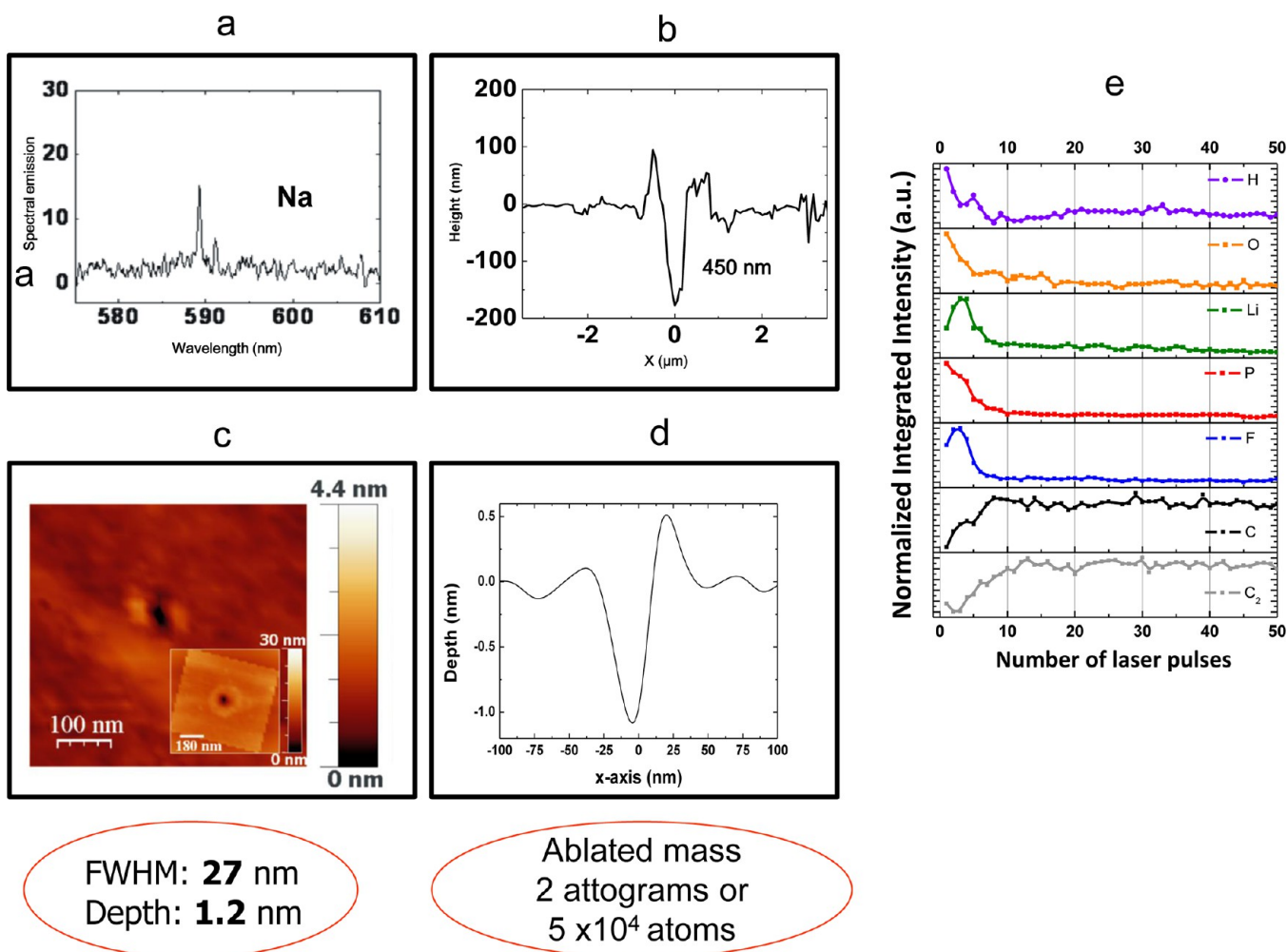
Precision has been defined as internal and external, depending on the laser sampling approach.<sup>78–80</sup> Internal precision is expressed as the time-dependent behavior of the intensity (or ratio) during repetitive sampling either at one location or scanning over a sample. External precision is the reproducibility of analysis for the method with the same sample. Precision is related to the capability of the ablation process to produce the same plasma conditions, the same amount of mass with the same particle sizes. The change in the measured signal should be related to the change in concentration and not to the change in quantity of mass ablated. The mass ablation rate needs to be constant, similar to a nebulizer. A single-pulse laser ablation method produces a spike of mass in time, not a continuous stream of aerosol. The laser provides spatial resolution generally from several micrometers up to hundreds of micrometers in diameter. If the sample concentration is precise across this space and multiple locations of the sample are analyzed, precise analysis can be achieved. “Poor” precision would be related to the inhomogeneous spatial distribution. Spatial analysis is an attribute of laser ablation and it does not give the same answer as a dissolved analysis; the sample defines the precision. In our opinion, repetitive sampling to achieve a steady-state stream of aerosol is a preferred approach for analyzing homogeneous and inhomogeneous samples for bulk analysis. If the application is not sample limited, it is not necessary to rely on one or a few laser pulses for sampling. An entire sample and total liquid volume are not nebulized into the ICP; instead a defined amount of mass is dissolved and nebulized into the ICP. The same condition can be achieved using high repetition-rate pulsed lasers to produce a steady solid aerosol stream, similar to a nebulizer. If the sample is homogeneous, introducing more mass into the plasma (LIBS) or the ICP and integrating intensity over time improves the precision. When the sample is inhomogeneous, the “imprecision” is related to the inhomogeneity. Figure 6 shows data for high repetition rate femtosecond laser ablation of a NIST 612 glass standard and an inhomogeneous granite sample.<sup>81</sup> The red squares (Figure 6a) are 1 cm × 1 cm regions that were ablated using low-energy high repetition-rate femtosecond pulse sampling. Six (only two are shown) regions were ablated and correlate to the six peaks in the time-dependent intensity graphs (Figure 6b,c). The decay in intensity represents the time

when moving the laser beam from one location to another and is related to the washout time of the chamber. Washout time is established by the chamber and flow conditions. The ICPMS intensity responses show excellent precision for Al and Zr in the homogeneous NIST glass, demonstrating the capability of the method to produce a steady stream of solid aerosol. The intensity is related to the concentration and the quantity of mass ablated. The “structure” on the granite intensity data is related to the inhomogeneity; Al is fairly homogeneous whereas Zr is inhomogeneous in the granite samples. These data can be utilized in at least two ways, a means to represent homogeneity/inhomogeneity and to report bulk analysis. For bulk analysis, these data can be integrated over several locations of the sample; the amount of sample needed for representative bulk analysis depends on the sample inhomogeneity.

Precision and sensitivity are related. Laser ablation provides excellent absolute detection limits, femtograms and lower.<sup>82,111</sup> However, relative detection limits are not considered as impressive as solution nebulization. The relative “insensitivity” of laser ablation is due to the small quantity of mass that is ablated and available as photons for plasma spectrochemistry or particles for the ICP. Excellent absolute detection limits do not correlate well with relative detection limits; it is impossible to measure parts-per-trillion in a femtogram of mass because in this case, you are trying to measure a fraction of an atom. As discussed above with high repetition rate ablation, an appropriate method will allow a steady stream of mass to be ablated, for photon and particle analysis. Counting statistics can be improved to lower the relative LOD by steady state ablation. For high repetition rate ablation, it is preferable to scan the sample. If the laser continues to ablate in one location, preferential vaporization due to the increasing aspect ratio of the crater as well as elemental migration could occur (as discussed above).<sup>65,83,84</sup> The heat affected zone (HAZ) in a sample is related to the laser pulse duration.<sup>85–91</sup> The femtosecond laser pulse provides a nominal HAZ (on the order of nanometers for most materials) and due to suppressed thermal effects, “most” of the laser energy goes into removing mass. Depth analysis is the case where laser sampling at one location would be required. Even in this case, there are methods for alleviating the effects of crater aspect ratio on fractionation, like trepanning.

For analysis of solids based on digestion and solution nebulization, metrics have been established for the amount of mass that is needed for representative analysis; the amount depends on the inhomogeneity. Laser ablation can be used as a bulk analysis technique.<sup>92–94</sup> How much sample is needed and what are the benefits of bulk analysis using laser ablation? The answer, it depends on the sample. The benefits for laser ablation direct solid sampling are no sample preparation, no consumables, no acid waste, and rapid analysis. The real answer is return on investment; a laser ablation system is more expensive than a liquid nebulizer. However, the real cost including manpower, consumables, contamination, storage of waste, and safety is much greater for dissolving than ablating solid samples. Similar to nebulization, laser ablation can be implemented in an auto sampling mode; analysis time is significantly faster and the total number of sample analyzed significantly increased each day. Of course, an analyst still is needed to load the samples and report the data; the analyst now has a safer, easier, and cleaner job without the infrastructure for acid digestion.





**Figure 7.** Nanometer spatial ablation and analysis: (a) Na emission spectra measured from laser ablation to produce a crater of 450 nm fwhm  $\times$  180 nm depth (b). AFM surface (c) and depth (d) profiles of a crater produced using near-field ablation, and (e) plasma emission with 7 nm depth resolution in a Li-ion solid-electrolyte interphase (SEI) layer.

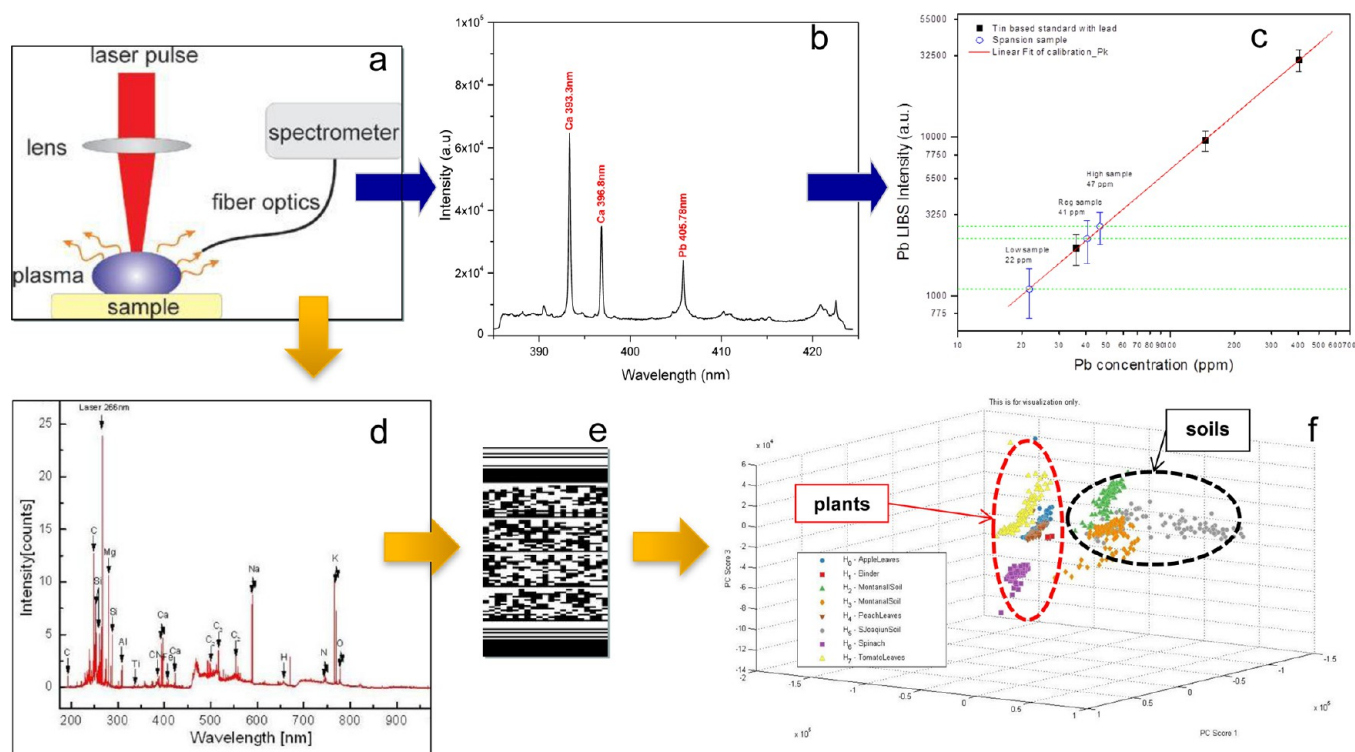
## DETECTION

As discussed, there are two modalities for measuring the ablated mass: photons from the induced surface plasma or particles that are entrained and transported to a secondary excitation source. The detection approach governs the analytical chemistry performance, more than the ablation itself. For photons, temporal and spatial (Figure 4) detection define the S/N and S/B (Figures 3 and 4). There are numerous parameters that govern the plasma properties and analysis capabilities; readers are directed to excellent current review articles.<sup>95,96</sup> For measuring ablated particles, the ICPMS continues to be the preferred analytical source. Similar to photon measurements, there is voluminous literature describing LA-ICPMS.<sup>97–103</sup> The color graphs in Figure 6d,e show how the ICPMS influences precision, for the same laser ablation conditions. Each ICP system has its own specifications. The response to the same ablated mass is different for a TOF, quadrupole, and multicollector. The overall analytical chemistry performance will be related to the laser, the sample chamber, the gas and gas flow, power, interface, spectrometer, mass detector, and data collection and processing. When the sample and laser parameters are changed, the amount of mass ablated and the size and composition of particles are changed, each having an influence on the detection.<sup>24,84,104</sup> A valid comparison of

performance metrics among instruments must relate how much mass was ablated versus the number of photons or ions detected. It would be beneficial to have specifications for performance, when all parameters are equal. However, such a case does not exist for laser ablation sampling with analysis using photons or particles in secondary sources. The community knows how many counts to expect per ppb of liquid using solution nebulization into the ICP; such metrics still do not exist for laser ablation.

Although the ICP is the preferred source compared to flames and sparks for measuring ablated particles, a different source might be more suitable; laser ablation research is striving to match the requirements of the ICP. What should be the characteristics of the ideal source to support laser ablation? Laser ablation sampling can be performed down to the nanometer scale,<sup>105–110</sup> ablating attograms of mass.<sup>111</sup> Several groups are investigating the efficiency of detecting nanometer particles by the ICP,<sup>112–114</sup> but other smaller secondary sources might be more appropriate. Early research using flames, sparks, and microwaves could not digest the amount of mass ablated, but this was a problem with the laser ablating too much mass for complete digestion in these sources. The same holds for the ICP; too much mass can compromise the measurement.<sup>115</sup> As the ablated aerosol quantity becomes less and finer with





**Figure 8.** Characteristics of laser plasmas for analytical chemistry: (a) simplified experimental diagram for laser induced plasma emission and measurements; (b) classical spectrum showing atomic line emission on top of broadband background; (c) calibration curve established using intensity of line emission; (d) broadband UV–vis–NIR spectrum from ablation of glass using a single laser ablation pulse; (e) bar code analogy that each broadband spectrum is a chemical representation of the sample constituents; and (f) using broadband spectra for classification of samples.

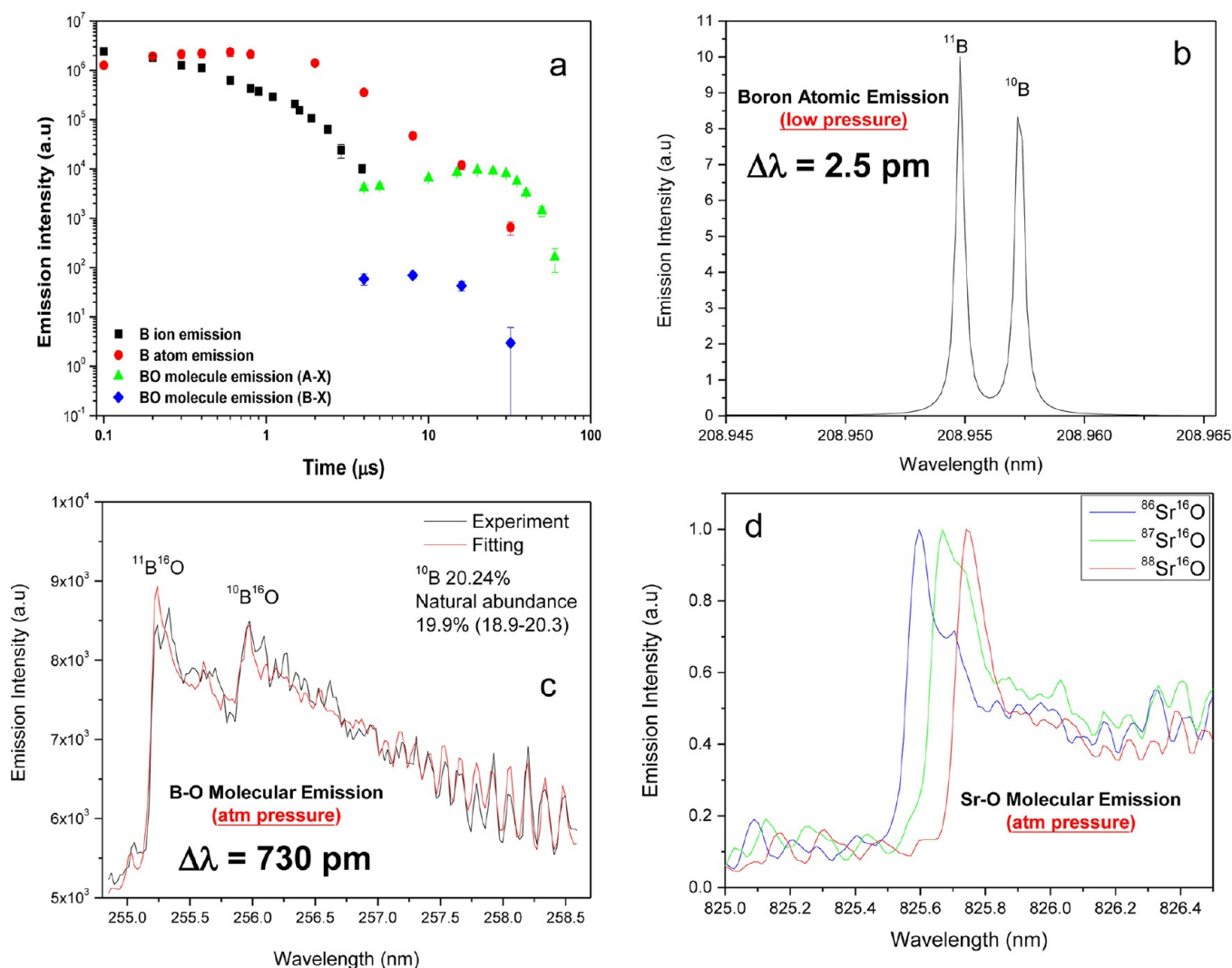
improved laser ablation sampling, other secondary sources will be required to capitalize on the nanometer spatial (lateral and depth) resolution. A small atmospheric pressure glow discharge source with a high power density and long residence time was demonstrated to digest laser ablated particles.<sup>116,117</sup> Femtogram and attogram sampling put constraints on the detection source; there may not be enough mass ablated to suffer atmospheric pressure to vacuum based detection.

Are there mass spectrometer systems that are more suitable for laser ablation or will direct photon detection be required? Limits of detection down to the attogram-scale ( $5 \times 10^6$  atoms) to the best of our knowledge have only been achieved by photon based measurements (Figure 7a,b).<sup>111</sup> Several elements in a Li-ion test cell were measured with a depth resolution of 7 nm and micrometer lateral diameter by using photon detection (Figure 7e).<sup>118</sup> However, even photons could not be detected from an ablation crater with dimensions of 27 nm in diameter by 1 nm depth; only 2 ag ( $5 \times 10^4$  atoms) were ablated using a single femtosecond laser pulse (Figure 7c,d).<sup>110,119</sup> For this case, it is not known if there were sufficient collisions in the “plasma” to excite optical emission. There is a need to understand the ablation process to excite 100% of the ablated mass to spectral emission; currently, there is very limited knowledge on how many photons are created per mass ablated. On the macroscale, the limit to photon measurements is generally spectral background from the plasma (Bremsstrahlung) and concomitant elements and molecules. Mass spectrometry provides excellent sensitivity because background has been reduced over the years in newer instruments. Another reason for the better sensitivity of particle-based measurements (LA-ICPMS) is that more of the mass is ablated into particles.

The most important parameter in every application is the sample. It is impossible to understand or compare detection performance if the sample is different. NIST standards have been used as the defacto samples to benchmark laser ablation results from lab to lab. However, every parameter difference will change the quantity of mass, temporal and spatial distribution of emission in the plasma, particle size distribution, onset of vaporization, ionization, the ion cloud, and chemical interference effects. Importantly, these caveats are not meant to discourage users but to emphasize that the method has a critical influence on analytical results. In some cases, the particle size and ablated mass quantity are similar for different samples with femtosecond laser ablation;<sup>67,68,79</sup> these are encouraging studies in understanding the matrix influence on the ablation process. We do not discriminate against LA and LIBS; they originate from the ablation process (Figure 1). Again, once the method is optimized, the process is reproducible.

## CURRENT EMPHASIS

Research today continues to address the parameter (especially laser pulse duration and ICP) influence on performance and applications extend far beyond geochemical age dating. It is interesting that the geochemistry community continues to lead LA-ICPMS developments. This application likely represents the hardest case, inhomogeneous samples and no standards. This group represents “early adopters” for laser ablation chemical analysis in large part driven by the need for the spatial resolution. LA-ICPMS is relatively developed in terms of instrumentation, provides excellent metrics for isotope analysis, and is gaining acceptance in mainly other applications. Laser plasma spectrochemistry on the other hand has seen a tremendous “renewed” interest. The first paper to discuss

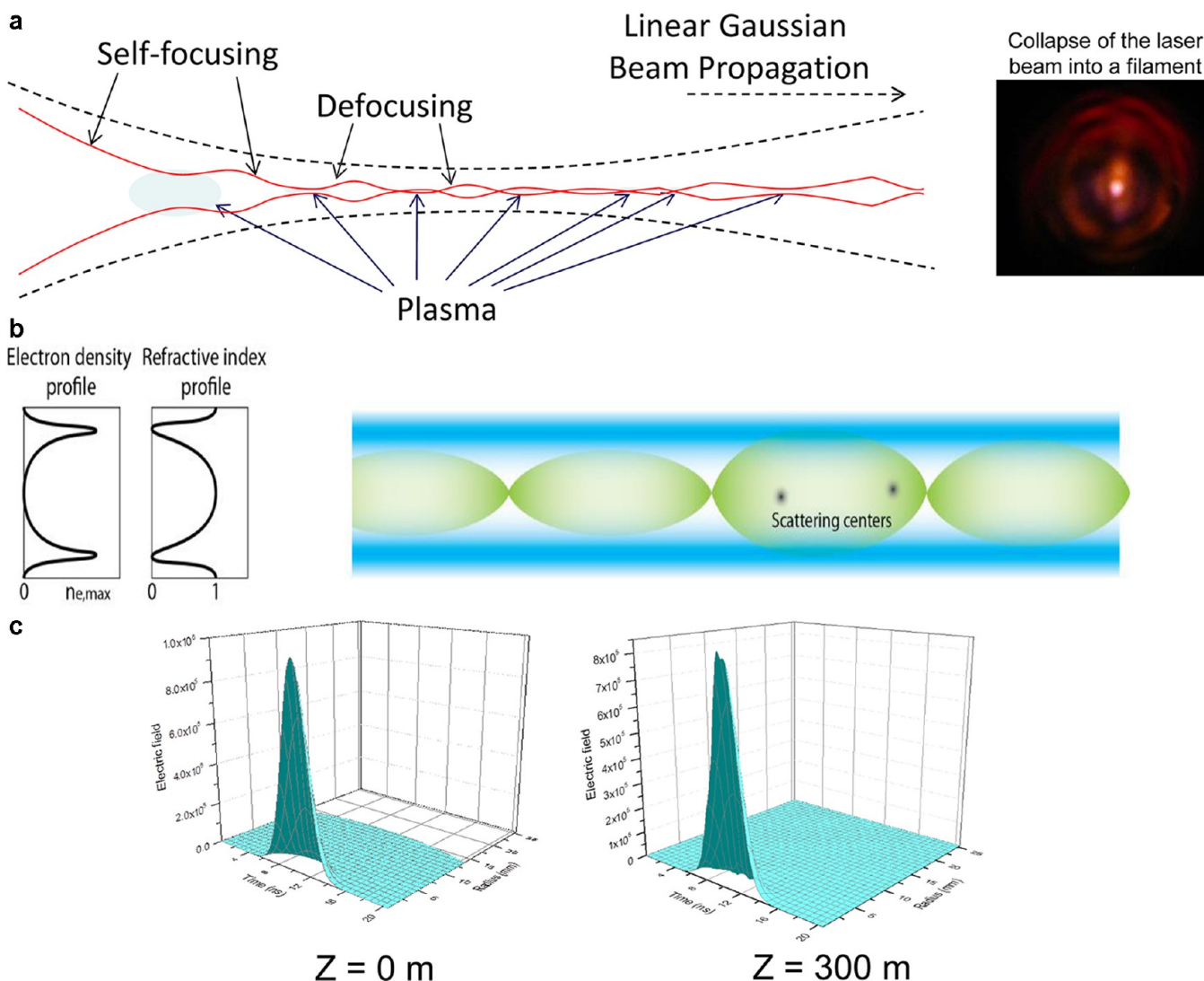


**Figure 9.** Advance of LIBS to LAMIS: (a) time-resolved measurements in the laser induced plasma for boron atomic, ionic, and molecular emission; (b) boron atomic line emission measured in a hollow cathode lamp showing isotopic splitting of 2.5 pm; (c) boron-oxide molecular emission measured in a laser plasma at atmospheric pressure showing isotopic splitting of 730 pm. Theoretical fit to measured spectral emission predicts the isotope abundance ratio. (e) LAMIS spectra for SrO measured at atmospheric pressure.

laser ablation for spectrochemical analysis from the plasma was Brech in 1962.<sup>120</sup> Today, the technology is called LIBS; it is a shame that the Internet killed the original acronym, laser induced plasma spectrochemistry (LIPS). In 2004, Winefordner asked if LIBS would become the next superstar of atomic spectroscopy.<sup>121</sup> LIBS is developing at an exponential pace with applications in almost every discipline.<sup>95,96</sup> Without doubt, LIBS publications are surpassing the LA-ICP effort. Maybe the reason why laser plasma spectrochemical analysis is so popular is that it is simple; you only need to focus a pulsed laser beam at a sample and measure the spectrum (Figure 8a). However, this is a blessing and a curse. As everyone knows who has performed atomic emission spectroscopy in sparks, plasmas, microwaves, ICPS, flames, etc., emission spectra are complex representations of the sample. Laser plasmas offer many benefits above and beyond all other excitation sources for emission spectroscopy. The laser plasma does not need consumables, has no contamination from electrodes, has no sample requirements (every sample can be ablated to form a plasma), has no special gases or pressure (ambient), and has the ability to perform analysis at a remote distance.

Traditional LIBS addresses elemental analysis as the plasma was deemed sufficiently hot to dissociate the ablated mass into atoms and ions. Atomic or ionic spectral lines are measured and related to a concentration; quantitative analysis is achieved with appropriate standards (Figure 8b,c). By using broadband spectrometers and array detectors (gated and nongated), a UV-vis-IR laser plasma spectrum provides chemical information for every element in the sample.<sup>122–124</sup> For every sample, the broadband spectrum is a chemical barcode (Figure 8d,e), a unique chemical fingerprint that can be used for sample classification (Figure 8f), and the matrix works in our favor. Chemometric processing of broadband spectra makes more sense than old fashioned peak-area integration; the entire spectrum represents how the sample responded to the ablation process, why ignore all the data. In addition to classification, improved quantitative analyses are a result of processing the entire spectrum with chemometric analysis.<sup>125–129</sup>

The hot laser-induced plasma was thought to completely dissociate the ablated mass into atoms and ions. However, new research is showing that there are chemical bonding relationships expressed in the broadband spectra, with excellent reports



**Figure 10.** Concepts for propagating femtosecond laser-induced filaments over open-path distances: (a) normal and filament beam propagation; (b) concept for establishing a beam channel; and (c) initial model results for confining a Gaussian laser beam in a filament channel and maintaining 80% of the energy over 300 m.

of inorganic to organic C and N by measuring CN and  $C_2$  molecular emission in the plasma.<sup>130–132</sup> Throughout the history of laser plasma spectrochemistry, most of the optimization effort emphasized eliminating or minimizing the background, to achieve good atomic (or ionic) signal to background (and signal-to-noise) ratios (sensitivity). However, the “background” is a rich source of spectral information, mainly related to molecular species. The formation of molecular species is not yet understood, whether they originate from the sample itself or form as the plasma expands and cools.<sup>133,134</sup> In general, as the hot atoms and ions collide with the atmosphere, molecular-oxides (and other species) can form and emit light. As example, Figure 9a shows the intensity of B atomic and ionic emission and two BO molecular emission bands. LAMIS was recently discovered as a new technology to capitalize on these molecular spectra and measure isotope splitting in laser plasmas at atmospheric pressure.<sup>135–137</sup> Although there have been nominal efforts to measure isotopes in laser plasmas over the years,<sup>138–141</sup> LAMIS addresses molecular species that exhibit isotopic splitting several orders of magnitude greater than atomic and ionic transitions. Data in

Figure 9c,d show LAMIS spectra for boron and strontium, measured as BO and SrO at atmospheric pressure. Figure 9b,c shows the spectral region where B atomic and BO molecular emission can be measured and the difference in isotopic shift. The spectral character depends on the detector gate delay after the laser pulse; time is needed for the molecules to form (Figure 9a). The  $^{10}\text{B}/^{11}\text{B}$  atomic emission was measured from a hollow cathode lamp at reduced pressure and shows an isotopic shift of 2.5 pm; these lines would be broadened and not resolved in a laser plasma at atmospheric pressure. The rotational–vibrational band structure starting at 255.3 nm is from  $^{11}\text{B}^{16}\text{O}$  molecular emission; the second band structure at 256.1 nm is from the 20%  $^{10}\text{B}^{16}\text{O}$  isotope. The isotopic splitting in the BO emission is 730 pm. The BO molecular spectra are fit to modeled spectra to extract the isotope abundance ratio. Figure 9d shows well-resolved Sr isotopes, measured as SrO in an atmospheric pressure laser plasma. Isotopic splitting for an atomic emission line of Sr (86/88) is  $\sim 0.25$  pm;<sup>142</sup> the molecular SrO splitting using a vibrational band head is 145 pm.



The LAMIS approach recently has been demonstrated to provide fundamental knowledge related to chemistry (molecular formation) in the plasma. The spatial emission profile for  $^{12}\text{C}$  and  $^{13}\text{C}$  can be related to CN and  $\text{C}_2$  formation.<sup>130,143</sup>

Finally, the LAMIS concept of measuring molecular spectra can be combined with the simultaneous measurement of elemental spectra in a laser plasma to infer chemical speciation.<sup>137</sup>

Generally in analytical chemistry, sampling and analysis should not be performed using the same source. However, this is the general practice for most LIBS applications. There is a growing effort addressing alternative means to enhance the initial laser-induced plasma or provide other secondary (not including ICP based) approaches to improve sensitivity, including second-laser pulse heating of the primary plasma, spark, and microwave excitation.<sup>116,144–150</sup> Improvements in the limits of detection have been reported, but much work remains to understand the coupling of energy into the plasma, reheating, etc. The community is once again addressing the benefits of simultaneous photon and particle detection.<sup>151,152</sup> Every laser pulse for ablation produces a luminous plasma and particles; measurement of both processes in one instrument offers many opportunities. For example, photon measurements provide analysis of the light elements (C, H, N, O, etc.) and majors at the ppm-% levels that are difficult to measure using the ICP. Using the same sampling chamber as for photon measurements, the particles are transported to the ICP, providing minor and trace isotopic analysis with ppb sensitivity. For biomedical research, the ability to measure carbon at the same time as heavy elements represents a marriage of metallomics and proteomics. There are many other applications that will benefit from simultaneous measurements including geological, environmental, nuclear, forensics, etc. Coupling LAMIS, LIBS, and LA-ICPMS provides a complete tool box for analytical spectrochemical analysis.

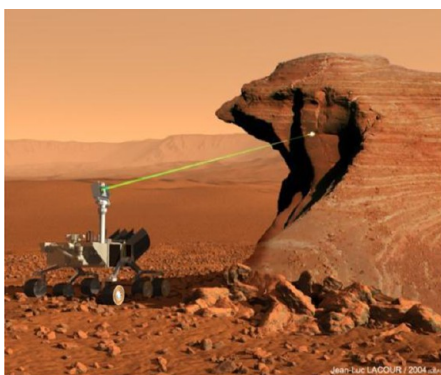
There are not many analytical technologies that allow long-range remote detection; femtosecond laser induced plasmas address this capability. High irradiance from a short-pulsed femtosecond laser initiates nonlinear refractive index effects in the atmosphere<sup>153–156</sup> that cause the laser beam to establish a filament (plasma) through open space, like a lightning bolt.<sup>157</sup> Figure 10 shows a representation of a laser filament created through a dynamic balance of linear diffraction, self-focusing, and plasma defocusing. The filament itself can excite optical emission from atmospheric species or when it strikes a sample at a distance.<sup>158–162</sup> The concept can be taken a step further. The filament is a plasma; by providing an appropriate gradient in the electron density it is possible to create a channel of filaments and send a second laser beam down the channel, like a free-standing optical fiber in space.<sup>157</sup> Such concepts are now being investigated with initial modeling efforts showing the ability to maintain a Gaussian beam with 80% of its intensity over a 300 m path (Figure 10c).

## PERSPECTIVE

Laser ablation is not new, it was one of the first things tried when the laser was invented: blow up things! To the best of our knowledge, the first laser ablation was done by Boyle and discussed by Dacey in 1962.<sup>163</sup> It is a compliment that this technology has been investigated for 50 years, has withstood the test of time, and is advancing still today. Laser ablation is a disruptive technology. Disruptive technologies are not integrated into society even in 50 years. It took 14 years from the development of the laser to the first widely recognized

application, e.g., barcode reader. Laser ablation for chemical analysis is a challenging interrelated technology involving chemistry, physics, engineering, and materials science; challenges are either overwhelming or amazing (glass is either half empty or half full). Opportunities for no sample preparation, spatial resolution, mapping, real-time analysis (classification, elements, isotopes), remote sensing, and other attributes beg development. Why dissolve millions of tons of solids in millions of tons of acid every year when there is a better solution (pun intended)? Dissolving samples is a work-around for developing the right method for laser ablation sampling. What are the fundamental issues that will allow us to thoroughly understand and advance this technology? We propose that ablation efficiency and plasma chemistry are critical parameters; how much mass is ablated per unit photon energy, excited to optical emission and condensed to particles. Although there are substantial efforts addressing the parameter influence on plasma properties (temperature, electron density, space and time gradients), there is very little effort devoted to understanding the plasma chemistry,<sup>143</sup> not just from a point of view of plasma emission but also for particle formation. A tremendous effort went into understanding inductively coupled plasma chemistry, and great advances have been made in performance by understanding and mitigating interferences. Similar efforts are needed for laser plasma spectrochemistry, especially for driving the plasma to provide sensitive isotope measurements. The growing research community can benefit from the rich literature and expand existing capabilities. For even more information, researchers are encouraged to delve into the other applications of laser ablation for medical, micromachining, cutting welding, and of course, the fundamental world to leverage knowledge and breakthroughs. There is much to learn about this nonlinear high temperature, short persistence tiny source, a rich chemical and physical environment. There are new tools (instruments) today to better study and control the ablation process for providing either photons or particles. With 50 years of effort, we have just barely elucidated the fundamental nuances. Laser ablation can be controlled and is reproducible. The fact that lasers are used every day for medical eye surgery and manufacturing means that they can be used every day for chemical analysis. We just have to get the parameters right. The most important parameter is the sample. The laser is important in how it ablates the sample. The detector is important in how it measures the ablated mass.

What are the advantages: real-time analysis, no sample preparation, atmospheric pressure measurements, and spatial and depth resolution that enable three-dimensional chemical imaging. What are the disadvantages: representative sampling, need for standards, fractionation, and destructive. The first three are perceived disadvantages, common to every analytical technology and they can be mitigated for every laser ablation application by establishing the right method. Destructive is an interesting comment, subject to comparative metrics. Laser ablation unavoidably removes attograms, femtograms, nanograms, and sometimes even micrograms of material. However laser ablation is barely destructive when compared to traditional solution analysis. Laser ablation can provide quantitative analysis even when using nanosecond pulsed IR wavelength lasers, if standards are available. As a result there are different schools of thought as to whether UV wavelengths or shorter laser pulses are needed for various applications. From a fundamentals point of view, the interaction of femtosecond lasers with materials provides unique insight into a breadth of



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"It is still a matter of wonder how the Martians are able to slay men so swiftly and so silently. Many think that in some way they are able to generate an intense heat in a chamber of practically absolute non-conductivity. This intense heat they project in a parallel beam against any object they choose, by means of a polished parabolic mirror of unknown composition, much as the parabolic mirror of a lighthouse projects a beam of light. But no one has absolutely proved these details. However, it is done, it is certain that a beam of heat is the essence of the matter. Heat, and invisible, instead of visible, light. Whatever is combustible flashes into flame at its touch, lead runs like water, it softens iron, cracks and melts glass, and when it falls upon water, incontinently that explodes into steam."

H.G. Wells, *The War of the Worlds* (1896)

**Figure 11.** Evolution in time: from science fiction to science fact. Image courtesy of NASA/JPL-Caltech.

nonlinear phenomena and ultrafast processes that continue to push the frontiers of laser ablation science. Inevitably, some applications will need more "horsepower", and shorter pulse durations and UV wavelengths have provided significant improvements in LA-ICPMS.<sup>86,44</sup> Nonetheless, the majority of LIBS and LAMIS applications today use nanosecond-pulsed IR lasers. Laser ablation offers tremendous benefits and addresses numerous applications that are fit for purpose.

The promise for open path, atmospheric pressure spectroscopic elemental, isotopic, and classification is compelling. The authors believe that LAMIS can one day compete with mass spectrometry or go beyond and provide isotope analysis at a distance; the research community and time will be the judge. Without doubt, there are not many spectroscopic techniques that can be performed at a distance. LIBS (and LAMIS) can become the next superstar of chemical analysis.<sup>121,164,165</sup> Sensitivity and precision (relative) are sufficient for many applications but may need to be improved to compete or overcome other established technologies. LIBS addresses a wider application space and requires less instrumentation and consumables than particle-based ICP measurements. Understanding excitation mechanisms in the laser plasma will improve the LOD for photon detection (LIBS, LAMIS). In theory, photon detection is more sensitive than mass detection if the background is the same. Both photon and ion detection can detect single entities. With emission detection, a single atom or ion can repeatedly emit photons at  $10^8$  times per second.<sup>166</sup> For most mass spectrometers used with the ICP, an ion can only be detected once, although ion traps are becoming more widely used. Especially attractive is integrating photon, ion, and particle technologies; every laser pulse allows the simultaneous measurement of LIBS-LAMIS-ICP, expanding the analytical

chemistry. Sending LIBS to Mars is out of this world.<sup>167–174</sup>

Los Alamos National Laboratory (LANL) and NASA teams are complimented for their spectacular accomplishment to land and operate this technology on Mars. Our fingers are crossed for successful real-time (relatively speaking) measurements and finally the answer to a critical question: is there life on Mars? What did H. G. Wells visualize in his introduction to *War of the Worlds*, maybe Figure 11.<sup>175</sup>

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### Notes

The authors declare no competing financial interest.

### Biography

Richard E. Russo, Ph.D., Senior Scientist at Lawrence Berkeley National Laboratory President and CEO of Applied Spectra, Inc. Russo is the scientific director of the Laser Spectroscopy group at the University of California, Lawrence Berkeley National Laboratory (LBNL) and CEO of Applied Spectra, Inc. His research group at LBNL pioneered the understanding and development of pulsed laser ablation for chemical analysis. He is a co-inventor of the nanowire laser and developer of a real-time standoff laser ultrasonic sensor (R&D100 Award, 2006). He also is the inventor of a process for nano-texturing thin films (ITEX process) and the lead inventor of an assisted pulsed laser deposition process (IBAD). Most recently in his Berkeley research, with the assistance of Applied Spectra staff, he demonstrated and patented the use of laser plasmas for real-time measurement of isotopes. The new technology, named LAMIS (laser molecular isotopic spectroscopy) won a 2012 R&D100 Award, FACSS/SCiX Innovation Award, and was *Spectrochimica Acta* paper of the year for 2011. Russo has over 250 scientific publications, 45 refereed

proceedings, 310 presentations (225 invited), nine book chapters and 18 patents. Fourteen students have received their Ph.D. degrees under his direction at the University of Berkeley. He has mentored numerous Ph.D. students from international universities, including China, Korea, Spain, France, Venezuela, Egypt, Algeria, and other countries. In 2004 Dr. Russo founded Applied Spectra, Inc. (ASI) with the assistance of several of his Ph.D. students from Berkeley. The company is a leader in chemical analysis using LIBS and laser ablation with ICPMS. ASI LIBS and laser ablation instruments are utilized in national and international markets, including academia, national laboratories, industry, energy, environmental, and security applications.

Xianglei Mao, Ph.D., Research Scientist at Lawrence Berkeley National Laboratory. Xianglei Mao is a physicist who received his Ph.D. from the University of Science and Technology of China in physics. He is a member of the Laser Spectroscopy group at the University of California, Lawrence Berkeley National Laboratory (LBNL). His current research involves the study of laser ablation for chemical analysis. He is a co-inventor of a new technology, named LAMIS (laser molecular isotopic spectroscopy), which won a 2012 R&D100 Award, FACSS/SciX Innovation Award, and was *Spectrochimica Acta* paper of the year for 2011. He has over 140 scientific publications and 2 patents.

Dr. Jhanis J. Gonzalez C., Research Scientist at Lawrence Berkeley National Laboratory, Berkeley, CA and Applications Lab Director, Applied Spectra, Inc., Fremont, CA. As a scientist at the Lawrence Berkeley National Laboratory, Dr. Gonzalez research focuses on understanding mechanisms of laser-material interactions (ablation) using nanosecond and femtosecond pulsed lasers with quadrupole, time-of-flight, and multicollector ICPMS systems. He also is involved in the development of analytical methods for applications in energy, environmental, geochemistry, biological, and metallurgy industries. In this position, Dr. Gonzalez has collaborated with many research groups around the world to advanced and develop the use of laser ablation for chemical analysis. From these collaborations, new methods for enhanced precision and accuracy have been developed. Most recently Dr. Gonzalez pioneered the development and use of microplasmas for femtosecond laser ablation analysis and the use of high repetition rate femtosecond lasers for rapid bulk analysis. As Application Lab Director at Applied Spectra, Dr. Gonzalez works with the engineering team to build and test laser ablation systems for commercialization. The position involves design of hardware components, working with software engineers, instrument test and validation, and advancement of methods for analysis using laser ablation ICPMS and LIBS. Dr. Gonzalez utilizes his expertise to train customers utilizing LA-ICPMS and LIBS to achieve maximum performance with their specific application. Dr. Gonzalez has over 40 manuscripts published in peer review journals and more than 30 presentations and invited lectures at national and international conferences.

Dr. Vasileia Zormpa, Research Scientist at Lawrence Berkeley National Laboratory, Berkeley, CA. Dr. Zormpa is a Research Staff Scientist at the Lawrence Berkeley National Laboratory (LBNL). Her background includes ultrafast laser-material interactions, near-field laser ablation and the development of novel spectroscopic techniques for improving spatial resolution in laser ablation-based chemical analysis. Dr. Zormpa has also performed extensive research on ultrafast laser material interactions for improving their optical, electronic and surface properties. Her work at the Lawrence Berkeley National Laboratory has led to new world records for both smallest detectable mass and best spatial resolution in laser ablation-based chemical analysis as well as the fabrication of the smallest craters in the optical-near field laser ablation of inorganic materials in apertured NSOM schemes. Dr.

Zormpa works closely with the electrochemistry group at LBNL to develop ultrafast laser ablation-based techniques for the chemical characterization of Li-ion battery materials. Her credits include 36 publications in peer reviewed journals, numerous invited talks, one book chapter, and a 2011 R&D100 100 award.

Jong H. Yoo, Ph.D., General Manager at Applied Spectra, Inc., Fremont CA. Dr. Yoo is the Vice-President of Technology Development and Marketing at Applied Spectra, Inc. (ASI). At Applied Spectra, Dr. Yoo is in charge of commercializing laser ablation based analytical technologies for various industries that include semiconductor, semiconductor equipment, solar, storage, as well as nanotechnology. Dr. Yoo has served as a principal investigator on several Army and Air Force SBIR/STTR programs to develop laser induced breakdown spectroscopy as rapid, in-situ chemical sensor platforms for different military applications. He has led technical and marketing programs at Applied Spectra to continue to improve LIBS instrument design and successfully market LIBS standalone instruments to commercial customers in the semiconductor packaging, storage, and solar industries. His research interests include phase explosion phenomena during laser ablation, nanoparticles generation by laser ablation, plume dynamics resulting from high irradiance laser material interactions, nanopatterning and modification of surfaces using NSOM and tip enhancement techniques, and applications of laser ablation in MEMS. Dr. Yoo worked at the semiconductor equipment company Applied Materials from 1994 to 1995 and from 2000 to 2003. As a senior process engineer, he developed a number of novel processes for high-density plasma oxide etching, tungsten chemical vapor deposition, and atomic layer deposition to enable sub-micron semiconductor manufacturing. He holds two patents and is author of 27 technical publications.

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