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Phenomenological studies on structure and elemental composition of nanosecond and femtosecond laser-generated aerosols with implications on laser ablation inductively coupled plasma mass spectrometry

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ABSTRACT

In laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), the properties of laser-generated aerosols, such as size and composition, are crucial for matrix-independent quantification. In this study, the aerosol particle morphology and elemental composition generated by two state-of-the-art laser systems (ArF excimer nanosecond-UV laser and Ti:sapphire femtosecond-IR laser) were investigated by electron microscopic techniques. Electrostatic sampling of the aerosols directly onto transmission electron microscopy (TEM) grids allowed us to study the morphology and elemental composition of the aerosols using TEM and TEM–EDX (energy dispersive X-ray spectroscopy) analyses, respectively. The results of the electron microscopic studies were finally compared to the LA-ICPMS signals of the main matrix components. The investigations were carried out for non-conducting materials (glass and zircon), metallic samples (steel and brass) and semiconductors (sulfides). The studies confirm that ns-LA-generated aerosols dominantly consist of nanoparticle agglomerates while conducting samples additionally contain larger spherical particles (diameter typically 50 to 500 nm). In contrast to ns-laser ablation, fs-LA-generated aerosols consist of a mixture of spherical particles and nanoparticle agglomerates for all investigated samples. Surprisingly, the differences in elemental composition between nanoparticle agglomerates and spherical particles produced with fs-LA were much more pronounced than in the case of ns-LA, especially for zircon (Si/Zr fractionation) and brass (Cu/Zn fractionation). These observations indicate different ablation and particle formation mechanisms for ns- and fs-LA. The particle growth mechanism for ns-LA is most likely a gas-to-particle conversion followed by agglomeration and additional hydrodynamic sputtering for conducting samples. On the other hand, phase explosion is assumed to be responsible for the mixture of large spherical particles and nanoparticle agglomerates as found for fs-LA-generated aerosols. Based on these mechanisms, the overall temporal elemental fractionation effects in ns-LA-ICPMS seem to occur mainly during the ablation. This effect was not observed for fs-LA-ICPMS despite the element separation into different particle fractions, which, on the other hand, could induce severe ICP-induced fractionation.

1. Introduction

Elemental fractionation in LA-ICPMS has been reported since the early days of this technique [1] and can occur during the ablation process, during the aerosol transport as well as during the vaporization, atomization and ionization within the ICP. However, the most crucial for all these possible contributions to fractionation is the initial aerosol formation.

Improvements in LA-ICPMS have been achieved by reducing the wavelength from infrared to deep ultraviolet [2–4] and by reducing the pulse duration from nanoseconds to femtoseconds, which led to the generation of smaller and more uniform aerosol particles [5,6]. However, elemental fractionation remains still a severe problem, in particular when quantification without matrix matched reference materials is of interest.

Using ns-UV–LA-ICPMS, non-matrix matched quantification has successfully been applied to the analyses of various glasses and minerals [7]. On the other hand, quantifications of metals and semiconductors with ns-UV–LA are more problematic due to heat diffusion into the sample resulting in melting effects and phase separation [8]. In order to restrain these effects, the laser pulse duration needs to be shorter than the thermal relaxation time of a few hundred femtoseconds [9]. Možná et al. [10] compared the performance of ns-UV–LA-ICPMS and fs-UV–LA-ICPMS for Fe-based samples and showed that fs-LA provides more accurate results. Bian et al. [11] reported the successful non-matrix matched quantification of Zn and

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Cu in brass, aluminum and silicate glass. But even for fs-LA, elemental fractionation effects were observed, especially for energies close to the ablation threshold [12]. Garcia et al. [13] demonstrated fractionation effects for fs-LA during the first few pulses until equilibrium conditions are obtained in the crater and stoichiometric sampling is achieved. Furthermore, it has been shown that for higher fluence the equilibrium is reached faster and therefore more accurate results are obtained.

Within the last five years, a number of studies were carried out on the morphology and elemental composition of ns- and fs-LA-generated particles. For example, Kuhn et al. [5] showed for ns-UV–LA of glass that some trace elements are enriched in particles smaller than 125 nm up to 90% relative to the calcium content by using a particle separation device. However, the overall transported aerosol showed no significant deviation from the initial concentrations. Therefore, incomplete evaporation of larger particles in the ICP was shown to be dominating over non-stoichiometric ablation with respect to elemental fractionation. Kozlov et al. [14] demonstrated differences in elemental composition within the particle fractions by time resolved LA-ICPTOFMS measurements of single pulses.

Energy dispersive X-ray spectroscopy measurements performed on a scanning electron microscope (SEM–EDX) on brass-generated aerosols (ns-UV) indicated that large particles were enriched in copper by up to 100%, whereas small particles showed a distinct enrichment of zinc [15]. Liu et al. [16] proposed a model for the enrichment effects for LA-generated aerosols of brass. The model suggests the deposition of vapor and small particles on larger droplets. Due to a more distinct volume change for smaller droplets compared to that of large particles, the more volatile zinc is enriched in these small droplets. The SEM–EDX measurements of the ns-UV generated aerosol showed decreasing Zn/Cu ratios with increasing particle size.

The same trend as for brass samples was shown for cobalt-cemented tungsten carbide as a representative for systems consisting of high- and low-volatile components [17]. Large spherical particles were shown to be enriched in tungsten whereas the nanoparticle agglomerates had a lower W/Co ratio. Furthermore, the ratio of large to small particles was proportional to the W/Co ratio. A study of ns-UV–LA-generated particles of zircon with respect to the chemical and phase composition showed that large spherical particles were composed of almost pure crystalline ZrO_2, whereas the small particles were enriched in SiO_2 [18]. Ejecta deposited around the ablation pit were enriched in zirconium, indicating laser-induced elemental fractionation.

Recently, Gonzalez et al. compared the ablation properties of glass [19] as well as zinc and aluminum alloys [20] for ns- and fs-LA. For metal samples, the ns-LA aerosol mainly consisted of primary particles with irregular shape and hard agglomerates, whereas for fs-LA the aerosol consisted of spherical primary particles and soft agglomerates. For ns-LA, a higher mass deposition around the crater, lower transport efficiency and higher signal fluctuations are reported due to melt layer ejection. For glass samples, similar morphologies for fs- and ns-LA-generated aerosols were observed, but for fs-LA a higher transient ICPMS signal was found despite a lower ablation rate. This indicates either a significant loss of material during transport for ns-LA-generated aerosol or an inefficient vaporization of large agglomerates in the ICP. In contrast, Wälle et al. showed that detection efficiencies for the ns- and fs-laser ablation of glass are similar [21].

The mechanism of the aerosol formation by laser irradiation is unfortunately not fully understood although several models exist [22]. However, there are consistent experimental evidences that two or more mechanisms of particle formation coexist during laser ablation and that the elemental composition depends on the particle size [6,23]. Two mechanisms seem to be most likely [24]: small particles (approx. 10 nm) are produced through gas-to-particle conversion. These small particles agglomerate to larger formations of micrometer size. Besides this process, spherical particles of up to several micrometers can be produced through hydrodynamic sputtering. Small particles tend to be enriched in volatile elements whereas large particles are depleted of those elements [23,25].

A further mechanism for laser ablation at high irradiances ($>10^{10}$ W cm^{-2}) is referred to as phase explosion, where a mixture of droplets and vapor is released [26]. However, phase explosion is assumed to be only possible in the regime of ultrashort pulses. The upper pulse length was calculated to be in the order of 10 ps [27]. For ultrashort pulses (fs), the laser energy is transferred to the sample within less than 1 ps and a hot liquid at high pressure results (Fig. 1, point A). The pressure is then released by adiabatic cooling and may enter the metastable region (B). This metastable phase may decompose into a mixture of vapor and droplets (phase explosion) and the matter returns to the bimodal line. The breakup of supercritical fluid (A′) occurring for high energies is referred to as fragmentation.

Due to electron-lattice temperature equilibration which takes place during 10–100 ps [28], thermal diffusion has to be taken into account for pulses in the picosecond and nanosecond regime, and thus the heating procedure cannot be assumed to be isochoric anymore. The heated liquid cools along the phase boundary (bimodal) and the metastable region cannot be reached. Therefore phase explosion seems to be an unlikely mechanism for nanosecond pulses.

Comparing the arguments for fs- and ns-laser ablation, a general agreement on the generation of smaller particles when using fs-LA has been reported. However, some of our results indicated that this model is not always valid. Therefore, an electrostatic sampler reported by Fierz et al. [29] was used to sample online laser-generated aerosols from ns-LA and fs-LA. The morphology and the elemental composition of LA-generated particles were investigated by analytical electron microscopy (TEM and TEM–EDX) for different samples including metals, semiconductors and non-metals. Based on the results observed within this study, different ablation mechanisms for ns- and fs-LA are proposed. Based on these mechanisms, elemental fractionation effects occurring in LA-ICPMS measurements are discussed.

2. Experimental

2.1. Laser ablation and ICPMS

The investigated aerosols were generated using two different laser systems: a 193 nm ArF excimer laser (GeoLas Q, MicroLas Lasersysteme GmbH, Göttingen, Germany) with a pulse duration of 15 ns and a chirped pulse amplification (CPA)-type Ti:sapphire based laser system

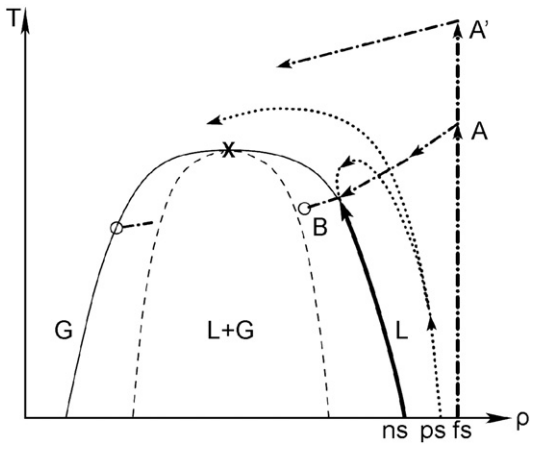

Fig. 1. Theoretical pathways for fs- (dashed line), ps- (dotted line) and ns- (solid line) laser irradiation in the temperature-density diagram (L: liquid phase, G: gaseous phase, X: critical point) modified after Ref. [27]. The solid line is the binodal curve (boundary between the one-phase and two-phase regime) and the dashed line is the spinodal curve (boundary of absolute instability). The phases between bimodal and spinodal are referred as superheated liquid and supercooled vapor, respectively.