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Study of near infra red femtosecond laser induced particles using transmission electron microscopy and low pressure impaction: Implications for laser ablation–inductively coupled plasma-mass spectrometry analysis of natural monazite

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The characteristics of infra red femtosecond laser-induced aerosols are studied for monazite (LREE, Th (PO_4)) ablation and correlations are established with inductively coupled plasma-mass spectrometry (ICP-MS) signals. Critical parameters are tested within wide ranges of values in order to cover the usual laser ablation -ICP-MS analysis conditions: pulse energy ($0.15<E_0<1$ mJ/pulse), pulse width ($60<\tau<3000$ fs), ablation time ($t\leq 10$ min) and transport length ($l\leq 6.3$ m). Transmission electron microscopy reveals that aerosols are made of agglomerates of ~10 nm particles and 20–300 nm phosphorus depleted condensed spherical particles. These structures are not affected by any laser ablation parameter. Particle counting is performed using electronic low pressure impaction. Small changes on particle size distribution are noticed. They may be induced either by a peak of ablation rate in the first 15 s at high fluence (larger particles) or the loss of small particles during transport. We found a positive correlation between I (ICP-MS mean signal intensity in cps) and N (particle density in cm^{-3}) when varying E_0 and t, suggesting that N is controlled by the irradiance (P_0 in $W\cdot cm^{-2}$). Elemental ratio measurements show a steady state signal after the initial high ablation rate (mass load effect in the plasma torch) and before a late chemical fractionation, induced by poor extraction of bigger, early condensed spherical particles from the deepening crater. Such chemical fractionation effects remain within uncertainties, however. These effects can be limited by monitoring E_0 to shorten the initial transient state and delay the attainment of an unfavorable crater aspect ratio. Most adopted settings are for the first time deduced from aerosol characteristics, for infra red femtosecond laser ablation. A short transport ($l<4.0$ m) limits the agglomeration of particles by collision process along the tube. Short τ is preferred because of higher P_0, yet no benefit is found on ICP-MS signal intensity under 200 fs. Under such pulse widths the increased particle production induces more agglomeration during transport, thereby resulting in higher mass load effects that reduce the ionization efficiency of the plasma torch. Thus, pulse energy must be set to get an optimal balance between the need for a high signal/background ratio and limitation of mass load effects in the plasma torch.

1. Introduction

Laser ablation coupled to inductively coupled plasma mass spectrometry (LA–ICP-MS) is by now fairly widespread in the field of earth sciences. Such systems allow direct in-situ analysis of solid [1–5] or liquid [6] samples. Trace elements can be detected and quantified with high precision down to a resolution of a few micrometers [7,8], and coupling the laser to a multi-collection device (MC–ICP-MS) allows direct isotopic analysis, thus avoiding complex chemical preparations [9–11]. The technique has been improved continuously [2,12], with the use of shorter wavelengths down to near-UV (Ultra Violet) [13,14], ultra short pulses (<1 ps) [15,16], improved ablation cell [17] and ICP torch [18] technology. Even though satisfactory measurements can now be performed, some of the fundamental issues related to the physics of laser ablation still have to be addressed. Recently, Horn and von Blanckenburg [19] have well described the current limitations of accuracy in laser ablation through the investigation of elemental and isotopic fractionation. The phenomenon is usually observed as a temporal deviation within raw (MC-) ICP-MS signals [3,20]. Issues concerning non-stoichiometric sampling due to matrix dependant ablation mechanisms are often highlighted [12]. These disturbances have been almost suppressed with the use of femtosecond pulses [20,21], due to different laser/matter interactions [22]. Thermal effects

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Table 1
Infra red femtosecond laser ablation system and ICP-MS operating conditions.

Laser apparatus	Amplitude technologies "Pulsar 10"
Wavelength	800 nm
Repetition rate	5 Hz
Pre-ablation laser warm up	45 min
Pulse duration	60–3000 fs
Apertured beam diameter	100 mm
Focusing objective	3.5X, focus length 50 mm
Spot size	60–100 µm
Incident pulse energy	0.15–1 mJ/pulse
Ablation cell	25 cm^3, cylindrical
ICP-MS model	Agilent 7500Ce
Forward power	1550 W
Gas flows:	
Plasma (Ar)	15 l/min
Auxiliary (Ar)	0.9 l/min
Carrier (He)	0.56 l/min
Make up (Ar)	1.16 l/min
Shield torch	Used for all analyses
Data acquisition parameters	
Data acquisition protocol	Time-resolved analysis
Scanning mode	Peak hopping, 1 point per peak
Detector mode	Pulse counting, dead-time correction applied
Masses scanned	^{29}Si, ^{31}P, ^{139}La, ^{143}Nd, ^{146}Nd, ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th, ^{238}U, ^{246}ThO
Dwell time	100 ms
Quadrupole setting time	ca. 5 ms
Data acquisition (s)	180 s (20 s gas blank, up to 140 s ablation) or 600 s (20 s gas blank and 500 s ablation)

are considerably reduced when compared to those produced by nanosecond pulses [23] and are limited to the unavoidable temperature gradient due to the laser induced plasma on the bulk sample [24].

Recent attempts to study the laser induced aerosols have led to the use of transmission electron microscopy (TEM) in order to take advantage on the very high resolution of this instrument to obtain qualitative information about the particles chemical composition. Fliegel et al. [25] have collected particles produced by UV–ns-LA as well as particles remaining after introducing a milled powder of natural zircon crystal into the plasma torch (ICP). Unfortunately, this powder does not match the real laser induced aerosol, in terms of morphology and chemical composition, and the resulting particles are not what one might expect from the passage of laser induced aerosols through the ICP torch, even after some incomplete ionization or disturbing mass load effects. Subsequently, Glaus et al. [26] have compared aerosols produced by UV–ns-LA and (UV, IR)-fs-LA, making a direct correlation between particles morphologies and composition, and corresponding signals. Nevertheless, their approach remained qualitative as it did not take into account the crucial information about the quantity of particles produced and their size distribution.

In a previous work [27], we have studied experimentally the fundamental aspect of femtosecond ablation mechanisms and particles generation processes. Our results have been compared to existing theoretical studies and it has been possible to refine an analytical model of particles generation processes, based on the main ablation mechanisms, namely vaporization and fragmentation [22]. Hence, the existing model of gas to particle conversion [28], that creates agglomerates and spherical particles, has been enhanced by the study of chemically complex natural and synthetic samples. It has highlighted the importance of chemical segregation of elements inside the expanding plasma plume as a function of time and its possible impact on subsequent ICP-MS measurements. The present study builds on our previous work. It focuses on the link between these aerosols and the ICP-MS signals, using transmission electron microscopy analyses as well as a counting device similar to the one used by Koch et al. [29], giving access simultaneously to the amount of produced particles and their size distribution. Potential effects on the ICP-MS signals will be highlighted by varying critical parameters such as pulse energy, pulse width, ablation time and transport length. Results will help to propose optimal analytical conditions for IR-fs-LA–ICP-MS analysis, based on the numerous existing studies dealing with such issues on various types of systems [30,31].

2. Experimental

2.1. Laser ablation

We used a Ti:sapphire femtosecond system operated at its fundamental wavelength of $\lambda = 800$ nm (Pulsar 10, Amplitude Technologies, Evry/Seine, France). The system has been described in previous works [21,32,33]. Specifications are summarized in Table 1. It is able to provide $E_0 = 12$ mJ pulses at $f = 10$ Hz with a pulse duration of $\tau = 60$ fs. The laser beam is aimed at the sample through a modified optical microscope (Olympus BX51, Hamburg, Germany), equipped with a XYZ motorized sample stage. The beam is focused onto the target by a 50 mm focusing lens. The aperture is larger than the beam initial diameter (~9 mm). Ablation is conducted without defocusing and no masks were used to reduce the crater diameter, of about 90 µm. We used a cylindrical 25 cm^3 PTFE (polytetra-fluoro-ethylene) ablation cell, mounted with a quartz window, and helium as carrier gas. Behavior and reproducibility of ablation events are similar to these quantified in Courtieu et al. [34] on a synthetic quartz sample.

2.2. Sample

Monazite is a monoclinic phosphate enriched in light rare earth elements [35] (LREE, Th(PO$_4$)) commonly occurring as accessory phase in a wide variety of rocks. It is composed notably of P (27.81 wt.%), Si (1.42 wt.%), La (14.51 wt.%), Ce (30.59 wt.%), Pr(3.14 wt.%), Nd (10.2 wt.%), Sm (2.05 wt.%), Th (6.92 wt.%), U (0.13 wt.%) and Pb (0.16 wt.%). That is why it is considered as a good alternative to zircon for U–Th–Pb geochronology [36]. It has been extensively studied for its annealing properties [37] and low solubility [38] for nuclear waste storage purposes [39]. The Moacyr specimen, from the pegmatite of Itambe (Brazil), has been used throughout this study. Characterization of its chemistry [40], microstructures and crystallinity under various temperature conditions [37,39] have been previously conducted. Laser induced damage (crater morphology and ablation mechanisms) [41] and aerosols (particles generation processes) [27] have been studied using the same sample and the specimen has been used as reference material for LA–ICP-MS analysis [8].

2.3. Collection

Collections of particles were achieved using an in-house-built trapping system [27] consisting of a modified 5 ml syringe equipped with an aluminum stub, usually used as sample holder for scanning electron microscopy. A TEM sample holder was placed on the stub, to be impacted by aerosols. Before use, all syringes were cleaned 24 h in an HCl solution (1 mol·l^{-1}) and rinsed 24 more hours in milliQ water. Final mounting was realized in a class 10000 room to avoid contaminations on the collecting surfaces.

2.4. Observation

Observations were conducted at the TEMSCAN service of the University of Toulouse, using a JEOL 2100F (Tokyo, Japan) transmission electron microscope operated at 200 keV. The microscope is equipped