Some non-resolved problems on LIBS plasmas

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Problems to be discussed

1) Environment effect on the LIBS signal (theses of M. Autin, of C. Gautier; CEA patent)
2) LIBS signal lifetime (theses of V. Detalle, of B. Sallé, of J. Gaudin)
3) LIBS plasma stochiometry or "matrix effect" (theses of C. Nouvellon, of R. Bruder)
4) fs/ps-double pulse LIBS (PostDoc of C. Dutouquet)

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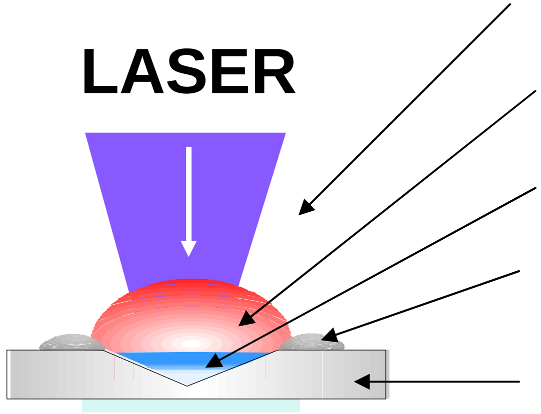
Laser Plasma Chemistry and Dusts (nano/micro-particles) in Laser Plasmas

(theses of F. Chartier, of F. Brygo, of P. Dewalle)



LA properties = f (E, ∅, Δt, λ , Δθ, polarisation, sample, air,...)

Analytical signal ~ $N_{abl} \cdot \alpha \cdot A_{ij} \cdot \exp(E_i/kT) \cdot t_p \cdot K_d$

N_{abl} ~ $(V_c - V_r) \cdot$ ablation efficiency (not atomisation one!)

α is atomisation efficiency

t_p is ~ 100 ns for micro and ~ 1 µs for macrosampling

1. Environment effect on the LIBS signal

(theses of M. Autin, of C. Gautier; CEA patent)

1. Environment effect on the LIBS signal

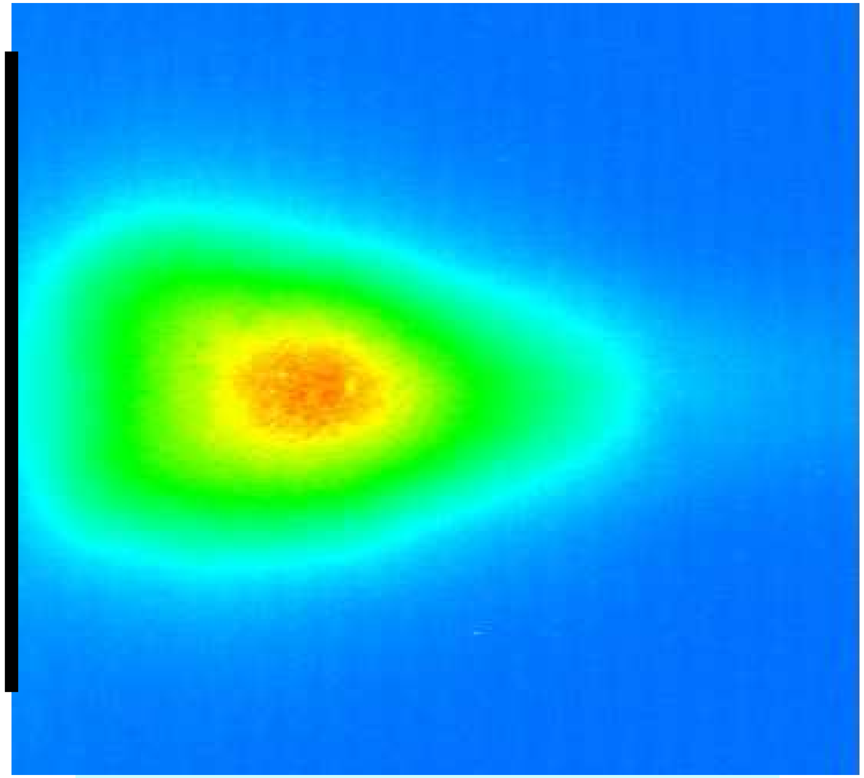
1.1. Optimal pressure ~ 10 mBar

1.2. ns-double pulse LIBS

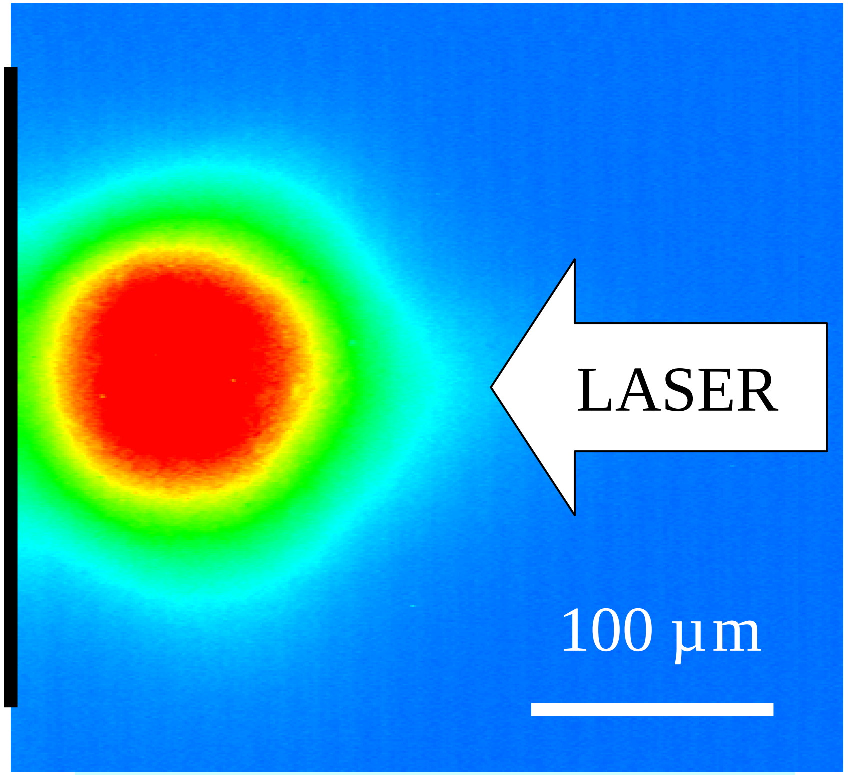
1.3. Jet of Argon gives rise to the LIBS signal

1. Environment effect on the LIBS signal

Target: Al + 10%Cu; **Laser:** 50 fs, 800 nm, 100 µJ, diameter 15 µm; **CCD**: gate 1000 ns, delay 50 ns

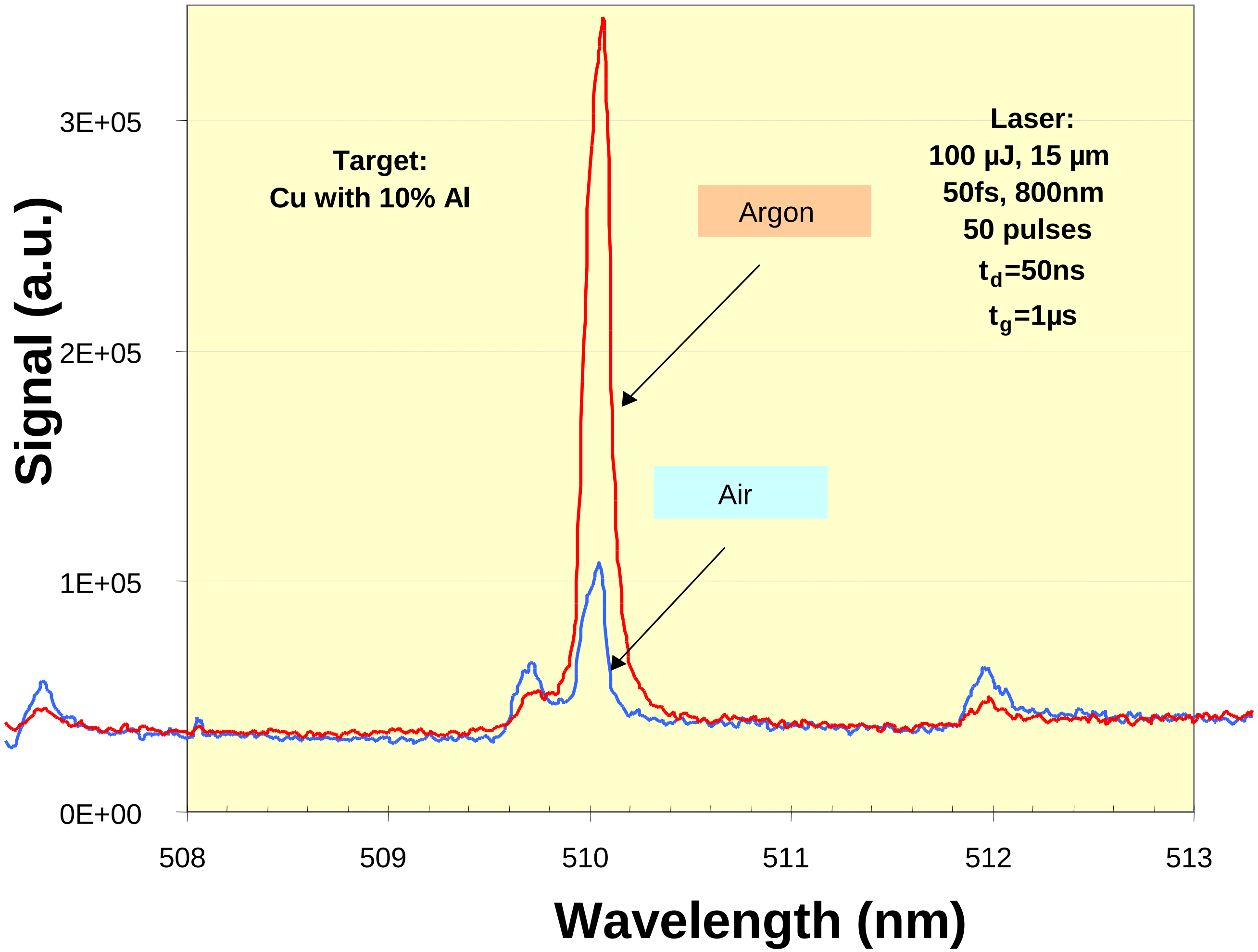


Air, 1 atm



Ar, 1 atm

1. Environment effect on the LIBS signal



gain ≅ 5

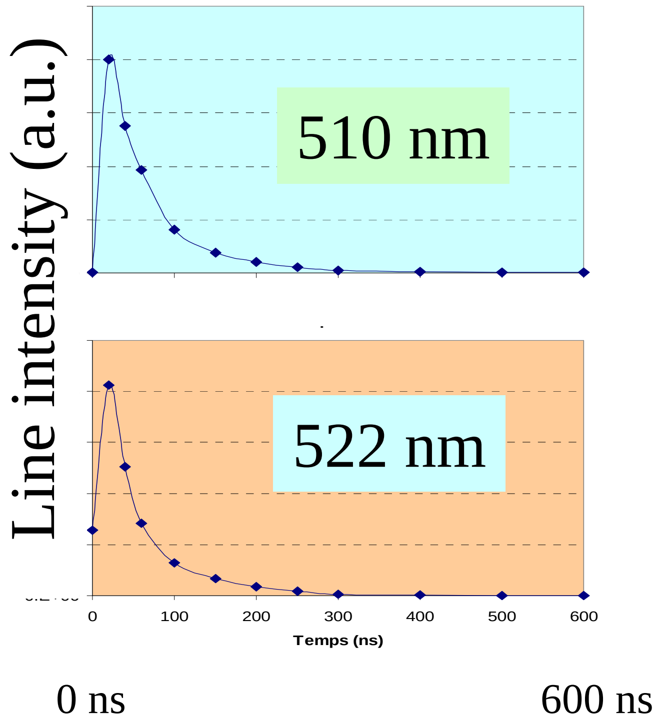
2. LIBS signal lifetime

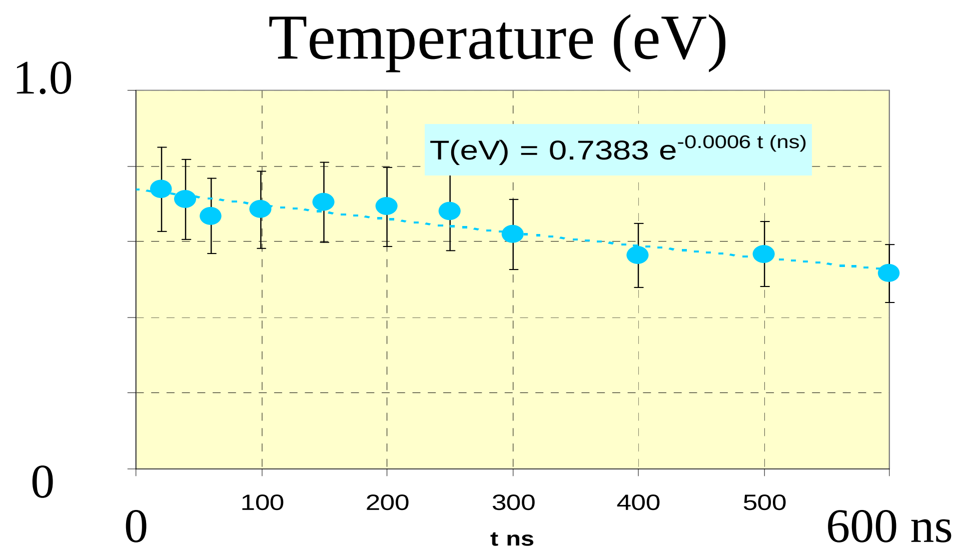
(theses of V. Detalle, of B. Sallé, of J. Gaudin)

2. LIBS signal lifetime

Signal (t) ~ $N_a(t) \cdot \exp[E_i/kT(t)] \cdot u^{-1}(t)$

LTE and excitation temperature

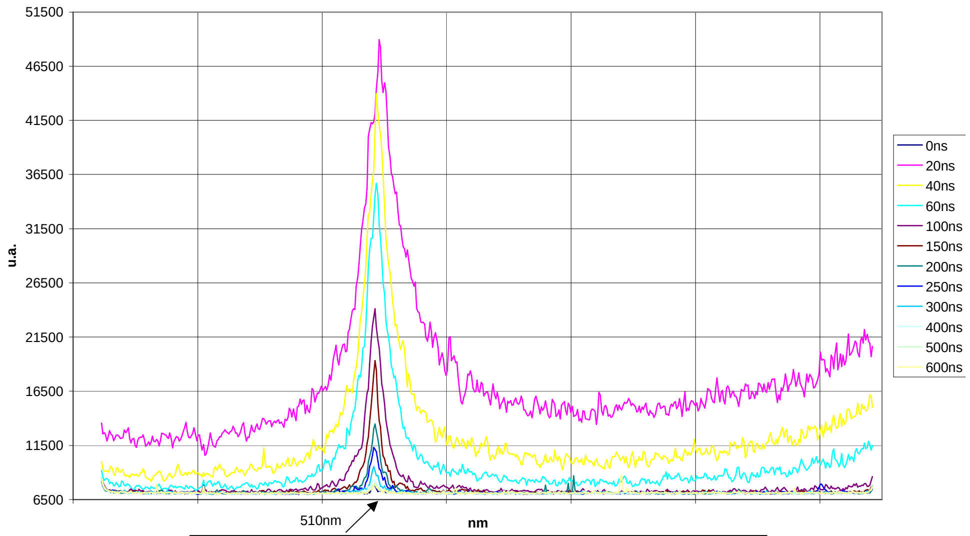




2. LIBS signal lifetime

Stark broadening and electron density

CuI 510 nm line broadening

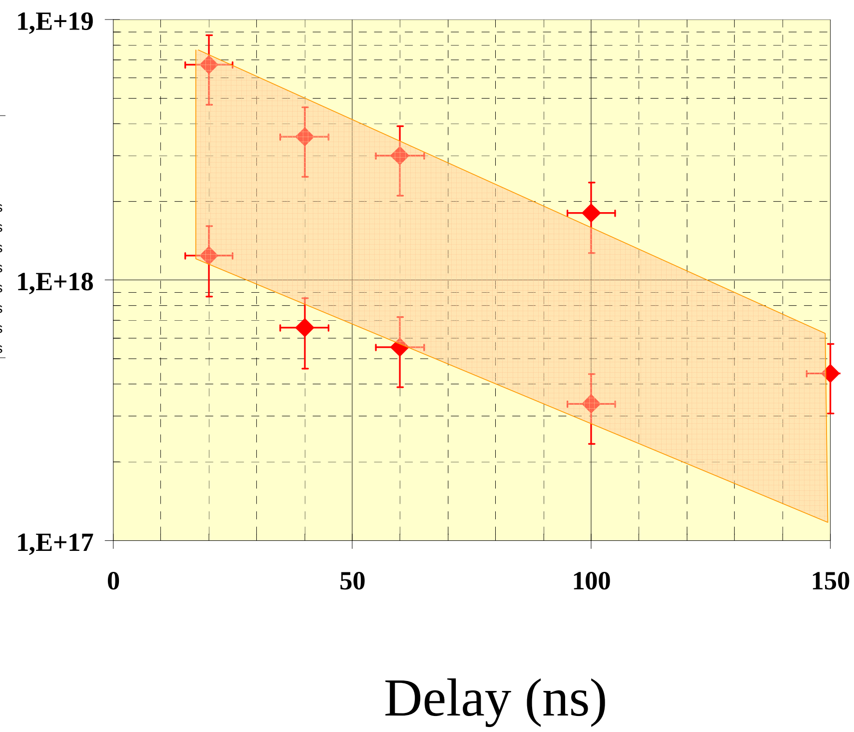


$$\Delta\lambda = 11.4 \cdot C_4^{2/3} \cdot \overline{v}_e^{1/3} \cdot Ne \cdot \frac{\lambda^2}{2\pi c}$$

$$[C_4] = cm^4 \cdot s^{-1}$$

$$\overline{v}_e = \sqrt{\frac{8kTe}{\pi m_e}}$$

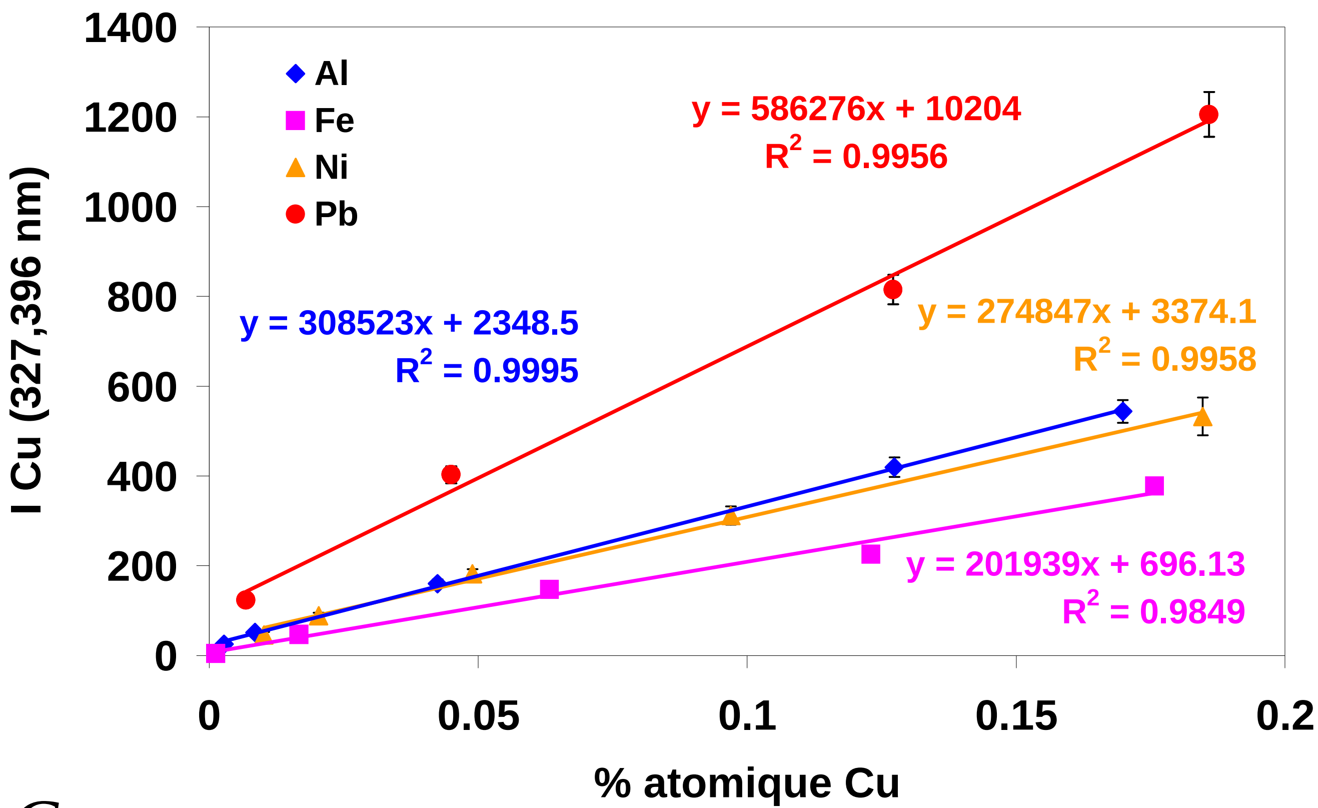
Electron density of fs-laser plasma



3. LIBS plasma stoichiometry or "matrix effect"

(theses of C. Nouvellon, of R. Bruder)

3. LIBS plasma stoichiometry or “matrix effect”



$$I_{327,396nm}^{Cu} \propto C_{Cu}$$

Cu : 327,396 nm ; 30 spectra per etalon

Fluency : 15 J.cm^{-2} ; Delay : 700 ns ; Gate width : 4,5µs ; 30 shots per spectrum

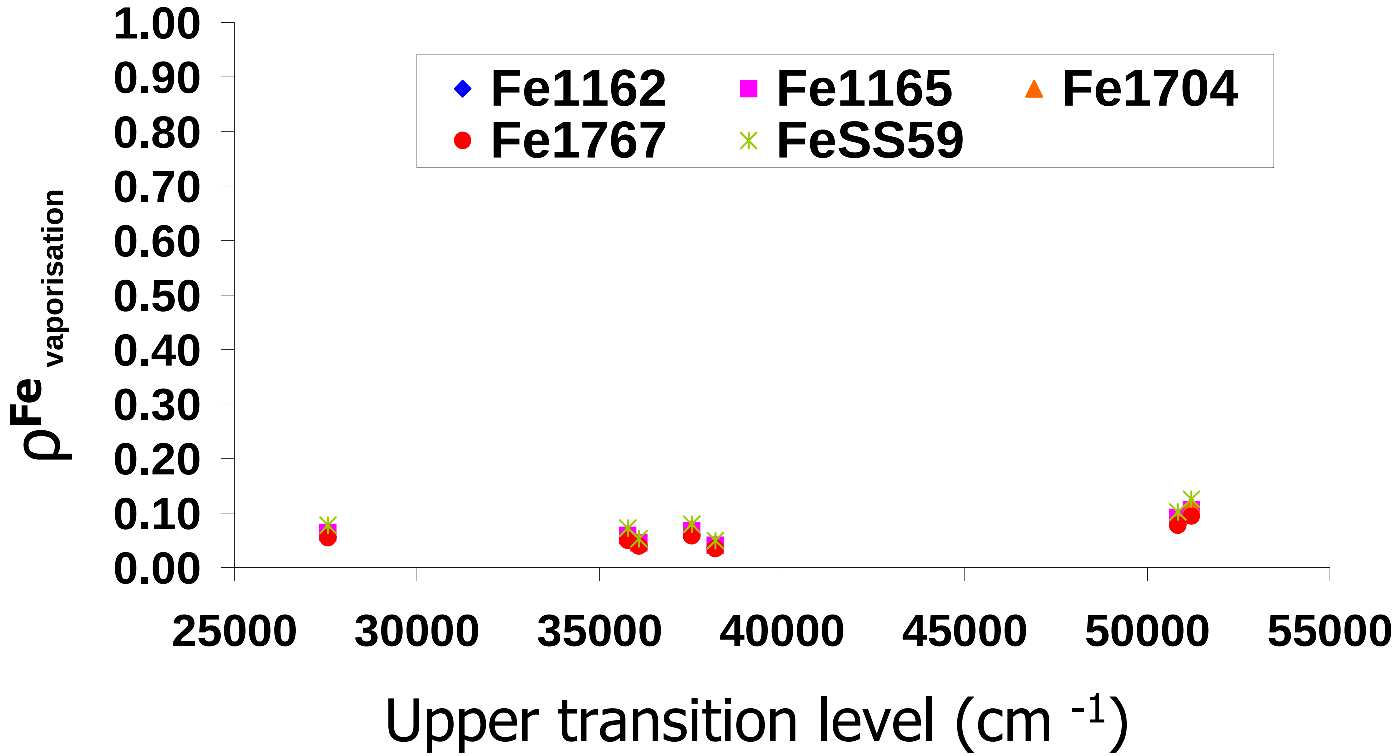
3. LIBS plasma stoichiometry or “matrix effect”

- $\rho^{Cu}{}_{atomisation} = N_{Cu\ in\ plasma\ atomic\ vapour} / N_{Cu\ ablated}$

- Determination of $\rho^{Cu}{}_{atomisation}$ requires the detection scheme calibration with an etalon source of photons (lamp-etalon)

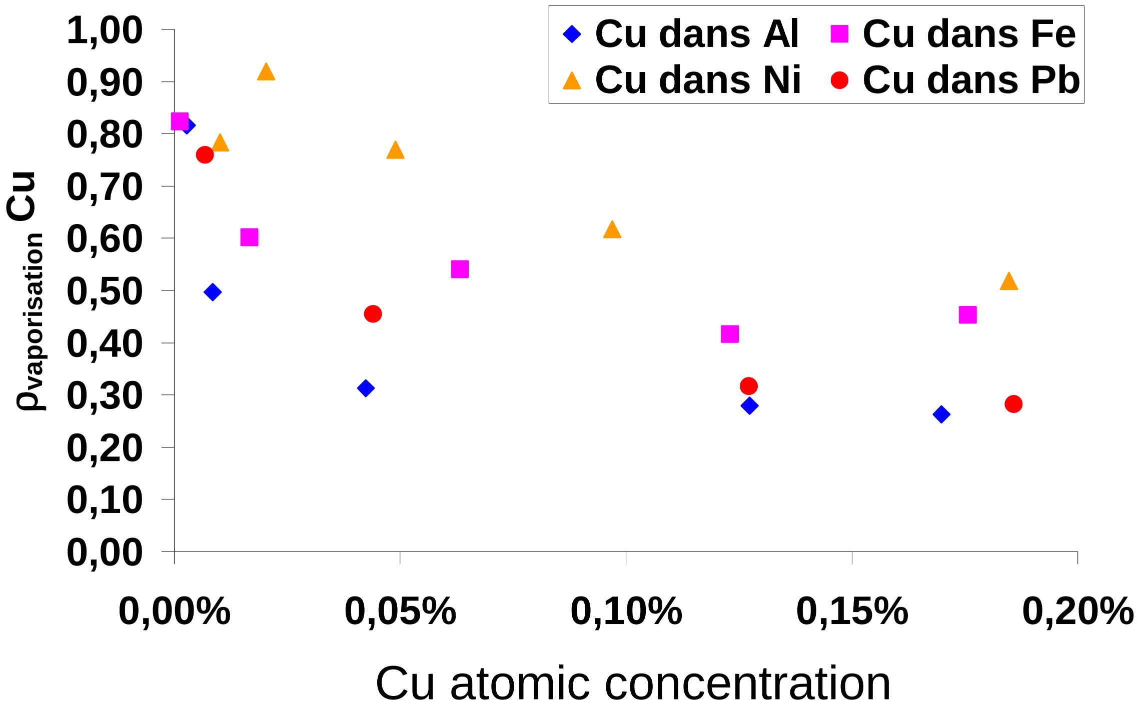
$$\rho^{Cu}{}_{atomisation} = \frac{I^{Cu}_{photons} \times U_{Cu}(T)}{f(\lambda_{ij}) \times \left(1 - \tau^{Cu}{}_{i}\right) \times C_{Cu} \times N_0 \times g_i \times A_{ij} \times e^{-E_i/kT}}$$

3. LIBS plasma stoichiometry or “matrix effect”



→ **ρ $_{atomisation}$ for the matrix atoms is low**

3. LIBS plasma stoichiometry or “matrix effect”

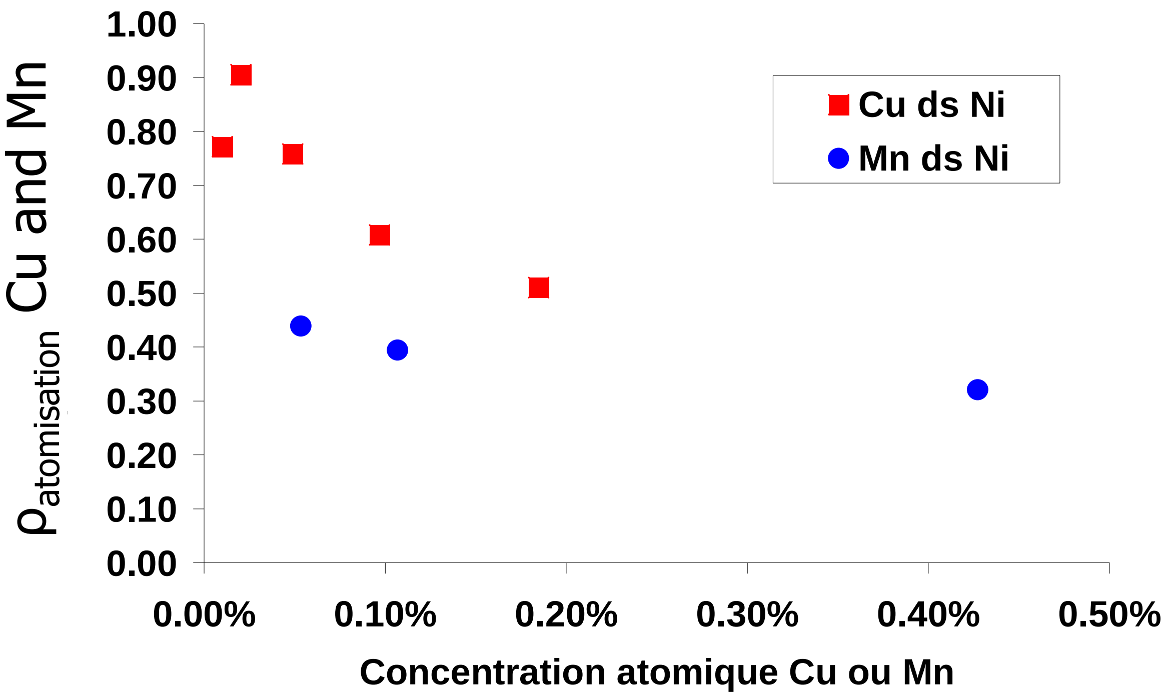


→ P $_{atomisation}$ is a function of a matrix

→ P $_{atomisation}$ is decreasing with the impurity concentration increase

3. LIBS plasma stoichiometry or “matrix effect”

- Element influence



$\rho_{atomisation}$ is a function of the elements

3. LIBS plasma stoichiometry or “matrix effect”

Summary

- The presence of the matrix effect for the metal samples and non-efficient correction by N_0, T et N_e

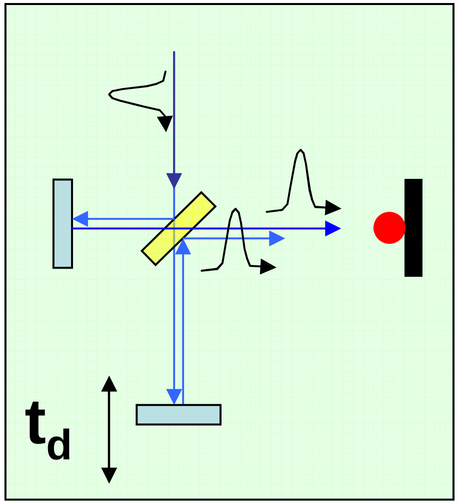
- Atomisation efficiency for the matrix is low

- Atomisation efficiency is a function of the element and its concentration

4. fs/ps-double pulse LIBS

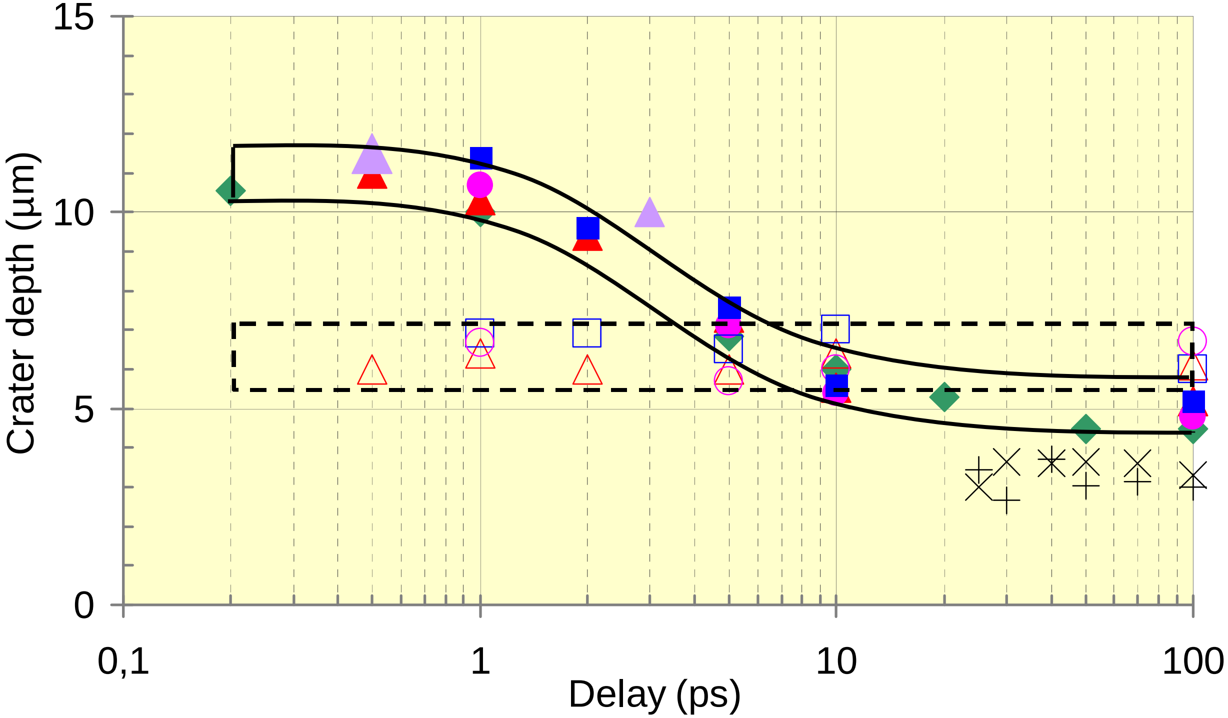
(PostDoc of C. Dutouquet)

4. fs/ps-double pulse LIBS



Target – Cu/Al, air
E = 20 µJ x 2

T laser : 50 fs, 100 fs, 200 fs, 500 fs, 1 ps, 5 ps, 10 ps



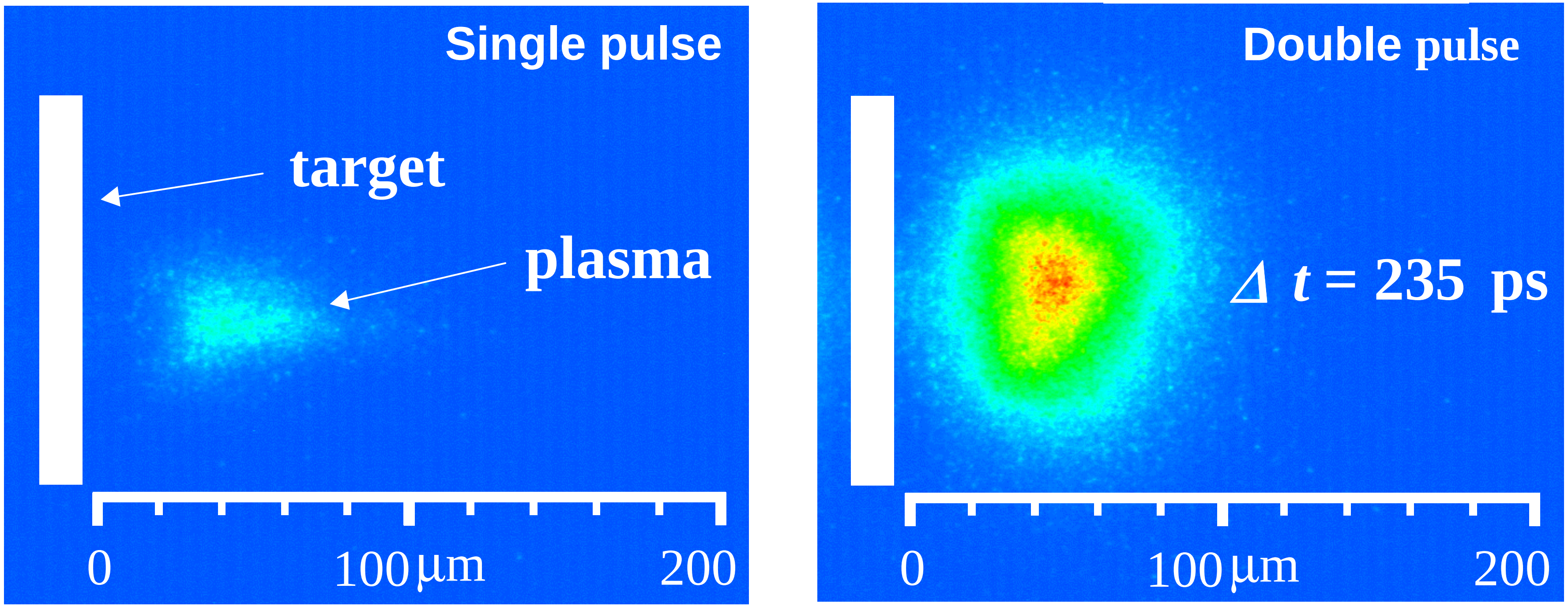
♦ do not strongly depend on metal (Cu and Al)

4. fs/ps-double pulse LIBS

$E_{\text{single pulse}} = 20\ \mu J$

$E_{\text{double pulse}} = 2 \times 20\ \mu J$

- Delay 3ns
- Gate width 1 µs
- Attenuators T = 2 %
- High CCD gain



PLASMA LUMINOSITY IS HIGHER WITH THE DOUBLE PULSE

4. fs/ps-double pulse LIBS

Simulation of ultrashort double pulse laser ablation of metals

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E-MRS 2009 Spring Meeting
Congress Center, Strasbourg, France
June 8 - 12, 2009

Two-temperature multi-material Eulerian hydrodynamics

Basic equations

$$\frac{\partial f^\alpha}{\partial t} + \nabla\cdot(f^\alpha \mathbf{u}) = \frac{f^\alpha \overline{K}_S}{K_S^\alpha}\nabla\cdot\mathbf{u}$$

$$\frac{\partial(f^\alpha \rho^\alpha Z^\alpha)}{\partial t} + \nabla\cdot(f^\alpha \rho^\alpha Z^\alpha \mathbf{u}) = f^\alpha m_i^\alpha S^\alpha$$

$$\frac{\partial(f^\alpha \rho^\alpha)}{\partial t} + \nabla\cdot(f^\alpha \rho^\alpha \mathbf{u}) = 0$$

$$\frac{\partial(\overline{\rho}\mathbf{u})}{\partial t} + \nabla\cdot(\overline{\rho}\mathbf{u}\otimes\mathbf{u}) + \nabla\overline{P} = 0$$

$$\frac{\partial}{\partial t}\left[f^\alpha \rho^\alpha\left(E_e^\alpha - \frac{|\mathbf{u}|^2}{2}\right)\right] + \nabla\cdot\left[f^\alpha\rho^\alpha\left(E_e^\alpha + \frac{\mathbf{u}^2}{2}\right)\mathbf{u}\right] - \frac{f^\alpha\rho^\alpha}{\overline{\rho}}\nabla\overline{P}\cdot\mathbf{u} -$$

$$-\overline{P}_i\frac{f^\alpha\overline{K}_S}{K_S^\alpha}\nabla\cdot\mathbf{u} - f^\alpha Q_{ei}^\alpha + Q_L^\alpha + \frac{f^\alpha\rho^\alpha C_e^\alpha}{\overline{\rho}\,\overline{C}_e}\nabla\cdot(\overline{\kappa}_e\nabla\overline{T}_e) + f^\alpha Q_J^\alpha - f^\alpha Q_{rad}^\alpha$$

$$\frac{\partial(f^\alpha\rho^\alpha E_i^\alpha)}{\partial t} + \nabla\cdot(f^\alpha\rho^\alpha E_i^\alpha\mathbf{u}) = -\overline{P}_i\frac{f^\alpha\overline{K}_S}{K_S^\alpha}\nabla\cdot\mathbf{u} + f^\alpha Q_{ei}^\alpha$$

$$E_i^\alpha(\rho, T_i) \rightarrow E_i^\alpha, C_i^\alpha, P_i^\alpha, K_{iS}^\alpha$$

$$E_e^\alpha(\rho, T_e) \rightarrow E_e^\alpha, C_e^\alpha, P_e^\alpha, K_{eS}^\alpha$$

Mixture model

$$\sum_\alpha f^\alpha = 1$$

$$\overline{\rho} = \sum_\alpha f^\alpha\rho^\alpha$$

$$\overline{C}_e = \frac{1}{\rho}\sum_\alpha(f^\alpha\rho^\alpha C_e^\alpha)$$

$$1/K_S = \sum_\alpha(f^\alpha/K_S^\alpha)$$

$$P = \sum_\alpha\frac{f^\alpha P^\alpha}{K_S^\alpha}\bigg/\sum_\alpha\frac{f^\alpha}{K_S^\alpha}$$

$$\overline{\rho}C_e/\overline{\kappa}_e = \sum_\alpha(f^\alpha\rho^\alpha C_e^\alpha/\kappa_e^\alpha)$$

$$\overline{T} = \sum_\alpha f^\alpha\rho^\alpha C^\alpha T^\alpha\bigg/\sum_\alpha f^\alpha\rho^\alpha C^\alpha$$

Summary

- Model describes ablation depth for single pulse experiments.
- For long delays the second pulse interacts with nanoparticles (layers) in liquid phase.
- Back deposition of substance caused buy the second pulse is the reason of even less crater depth for double pulses with long delay.
- Second pulse shielding: substantial changes of transport properties or complex mechanical spallation?

Laser Plasma Chemistry and Dusts (nano/micro-particles) in Laser Plasmas

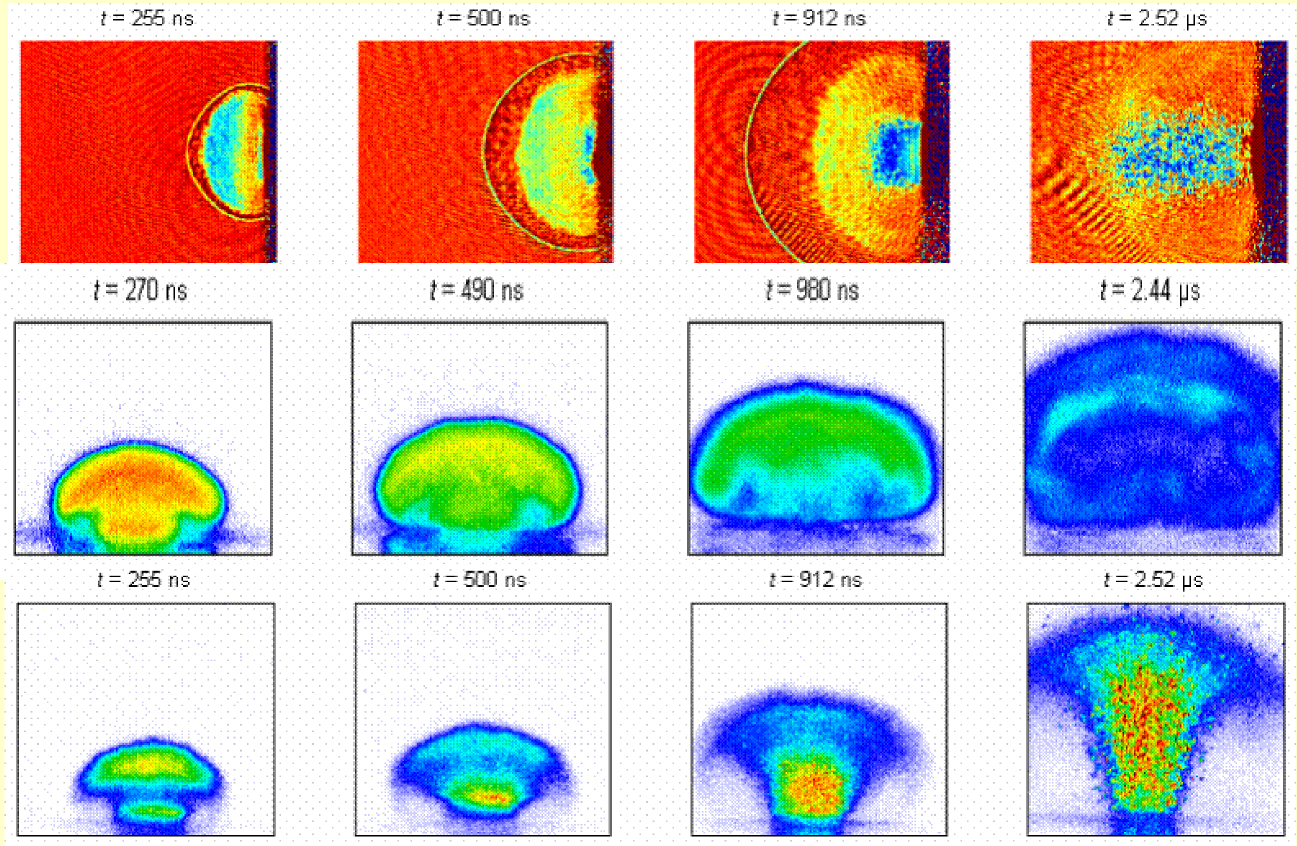
(theses of F. Chartier, of F. Brygo, of P. Dewalle)

Plasma diagnostics

Ombroscopy

Emission

Diffusion



Paint, T_{laser}=100ns, Fluence=10J/cm²

Results of Pascale Dewalle thesis, 2009,

Conclusions

- The "dusts" (molecules, nano/micro-particles) effect on the laser plume characteristics is mandatory for an adequate modelling and description of the "LIBS plasma" analytical properties;

- Plasma chemistry (formation of the molecules and aggregates in the LIBS plasmas);

- Dusts (nano/micro-particles) ejection in the LIBS plasmas