SAMPLING APPROACHES BASED ON SPOT AEROSOL GENERATION, CATAPULTING AND TRAPPING COMBINED TO LIBS

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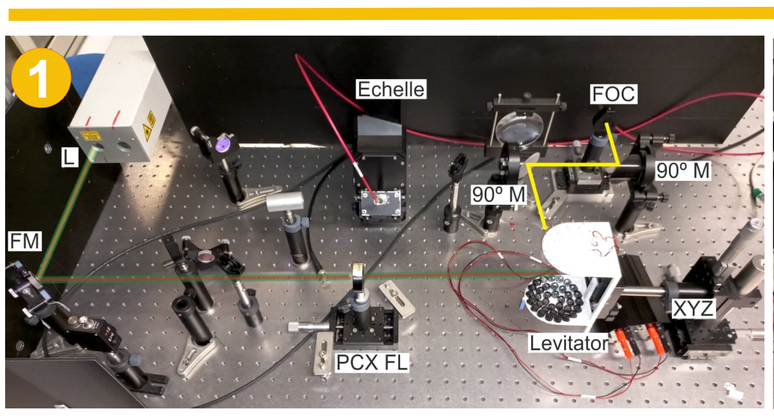
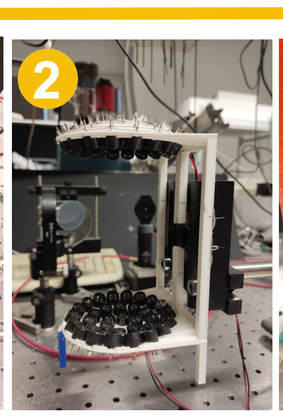
Abstract

Different strategies to handle samples and perfom LIBS analysis are described. Three approaches will be detailed that result extremelly helpful when dealing with heterogeneous samples that are intended to be analyzed by laser-induced breakdown spectroscopy (LIBS). The first one involves the spot-aerosol generation (SAG), where an aerosol of nano/microparticles is created locally by a low-energy laser pulse. These particles can be directly analyzed in gas phase (straight LIBS) , being optically-trapped for single-particle LIBS (Optical-Trapping LIBS, OT-LIBS) , or analyzed once collected in the substrate by optical catapulting followed by LIBS (Optical Catapulting LIBS, OC-LIBS). Additionally, acoustic trapping is being explored as a useful way to handle liquids or samples with size and density not compatible with optical traping.

ACOUSTIC TRAPPING + LASER EXCITATION





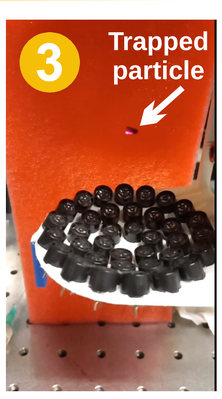


Figure 1. Details of the experimental set-up. The laser plasma was collimated and focussed by 90º parabolic mirrors to the tip of the fiber optic connected to the echelles spectrometer. **Figure 2.** Details of the acoustic levitator. **Figure 3.** Close-up of a trapped particle in the acoustic levitator.

OPTICAL (LASER) TRAPPING + LASER EXCITATION

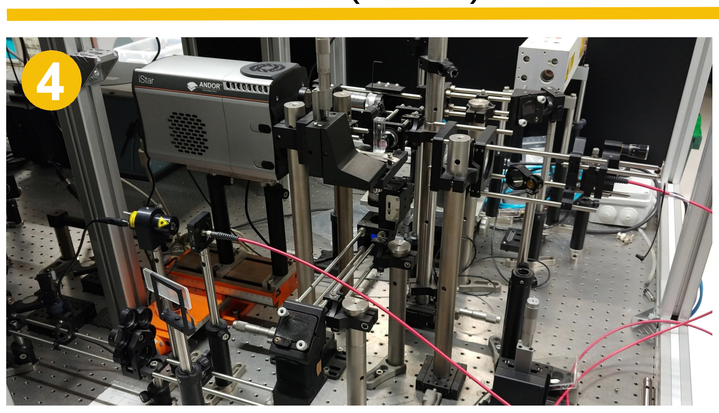


Figure 4. Experimental set-up used for the optical trapping experiment. Figure 5. Simplified infography of the trapping system showing the different elements involved.

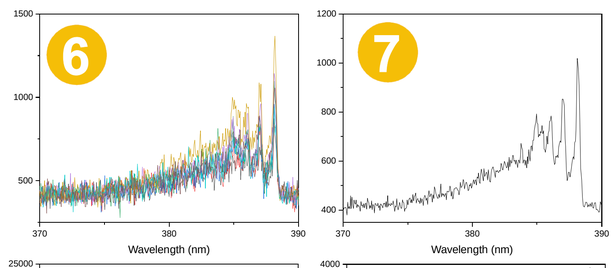


Figure 6. Zoomed spectra of the (0-0) CN band at 388.1 nm for ten different single-shots on a levitated graphite particle.

Figure 7. Averaged spectrum of the spectra shown in Figure 6, demonstrating the excellent signal-to-background ratio.

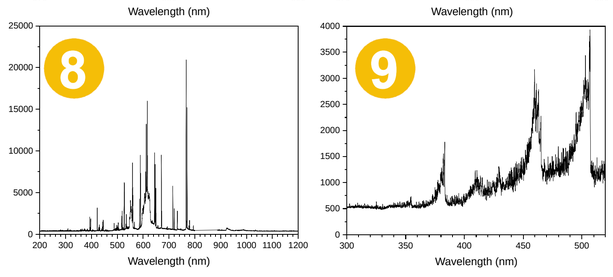
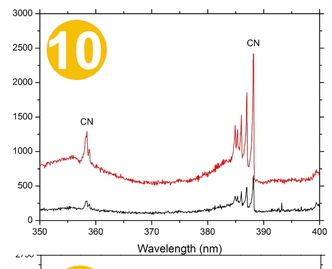


Figure 8. Single-shot spectra of a 500 microns clay particle.

Figure 9. Single-shot zoomed-spectra of a pyrene crystal (~ 250 microns). The CN and C2 spectral features are clearly observed.



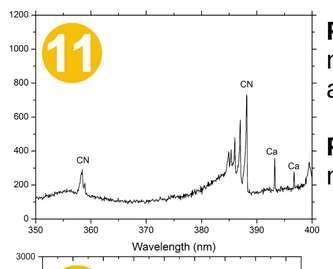
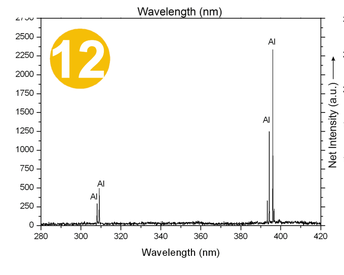


Figure 10. Single-shot LIBS spectra of a 3 and 10 nm (black and red, respectivelly) graphene particles acoustically trapped.

Figure 11. Single-shot LIBS spectra of a 30 microns (diamater) spore.



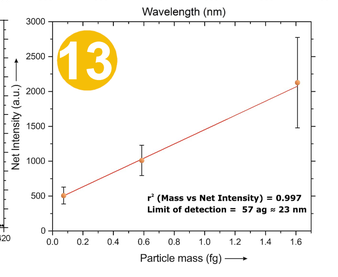


Figure 12. Single-shot spectra of a 30 nm aluminium-oxide nanoparticle exhibiting the characteristics features at 308 and 396 nm.

Figure 13. LIBS calibration curve of using Cu nanoparticles. An absolute detection limit of 57 attograms is attained.

LASER CATAPULTING + LASER EXCITATION

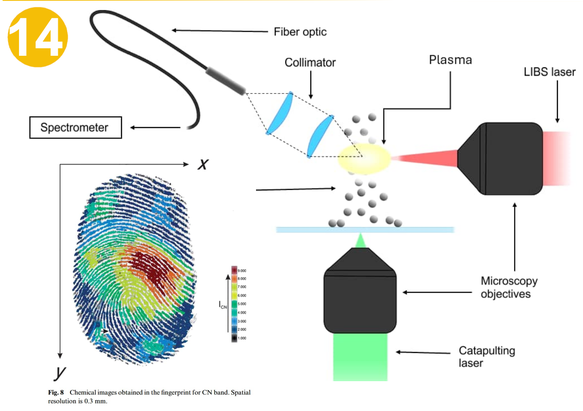


Fig. 8 Chemical images obtained in the fingerprint for CN band. Spatial resolution is 0.3 mm.

Figure 14. Scheme of the catapulting-LIBS set-up. The particles on the bottom of the surface are expelled upwards by the acoustic wave induced by a catapulting laser. The particles are LIBS-analyzed at a specific (optimized) distance above the surface.

For transparent or very thin samples (as a fingerprint), the catapulting laser may transfer to the air-phase fractions of material that can be analyzed by LIPS. The catapulting laser can be positioned over specific sample locations or even performing 2D scan, allowing the obtention of chemical maps, as indicated in the figure.

SPOT MICROSAMPLING + LASER TRAPPING + LASER EXCITATION

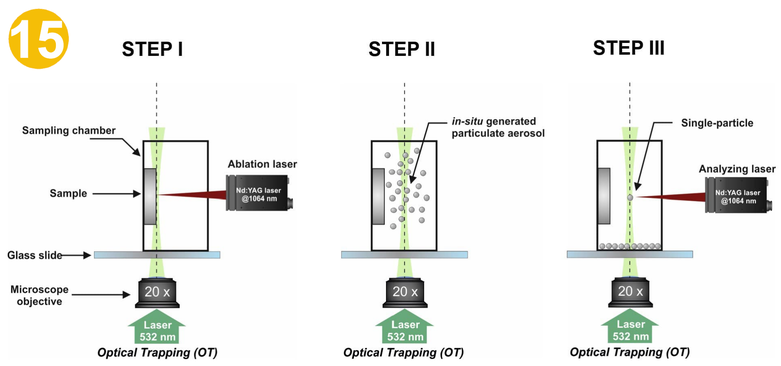
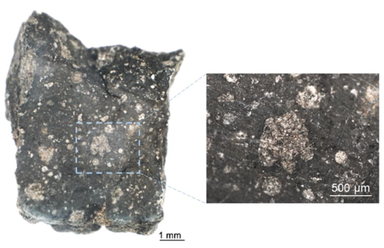


Figure 15. A first laser performs a low-fluence ablation on the sample, generating a population of particles expelled out of the sample from a specific site. Due to the action of a trapping laser, any particle trapped can be individually analyzed by LIBS. The rest of the particles will fall down, where can be aerosolized back thanks to a catapulting laser to continue the trapping/LIBS scheme.

MICROSAMPLING, CATAPULTING, TRAPPING AND LIBS FOR THE CHARACTERIZATION OF DISCRETE DOMAINS IN METEORITES

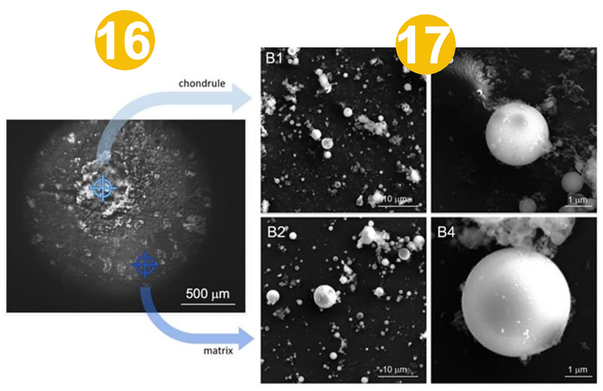
We applied µLA-OT-SP-LIBS to a carbonaceous chondrite, a type of carbon-rich meteorite that contains chondrules, with the aim of distinguishing these geological domains from the surrounding rock matrix in which they are embedded, through inspection of single particles generated by a single ablation event.



The combination of ns-laser ablation with in-situ particle trapping and single-particle LIBS enables assessment of discrete micro-domains from a total sampled mass in the low µg-range.

The approach successfully discriminated between particles derived from Fe-rich matrix regions and those originating from silicate chondrules based on elemental intensity ratios. Results have been fully consistent with complementary techniques (XRD, XRF, SEM-EDX), demonstrating that the microsampling protocol yields representative chemical information even under extreme mass-limited conditions.

This method enables rapid, contamination-free, and minimally destructive analysis of multicomponent microdomains, requiring only negligible amounts of material. Its demonstrated capability for simultaneous elemental and molecular characterization expands the analytical possibilities for rare geological specimens, microinclusions, and other valuable samples where sample preservation is essential.



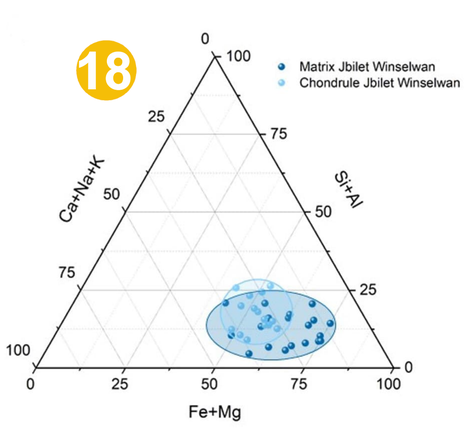


Figure 16. Image (obtained with the visualization system of the OT-LIBS platform) of the areas of a chondrule and matrix of the carbonaceous chondrite where the particles have been generated.

Figure 17. (1-2) Panoramic SEM images of the particles generated in both areas of the meteorite. (3-4) Detail of the spherical particles acquired by SEM of both the chondrule and the meteorite matrix.

Figure 18. Ternary diagram representing the Si+Al intensities; Ca+Na+K and Fe+Mg from individual particles of the matrix and chondrule of the Jbilet Winselwan meteorite.

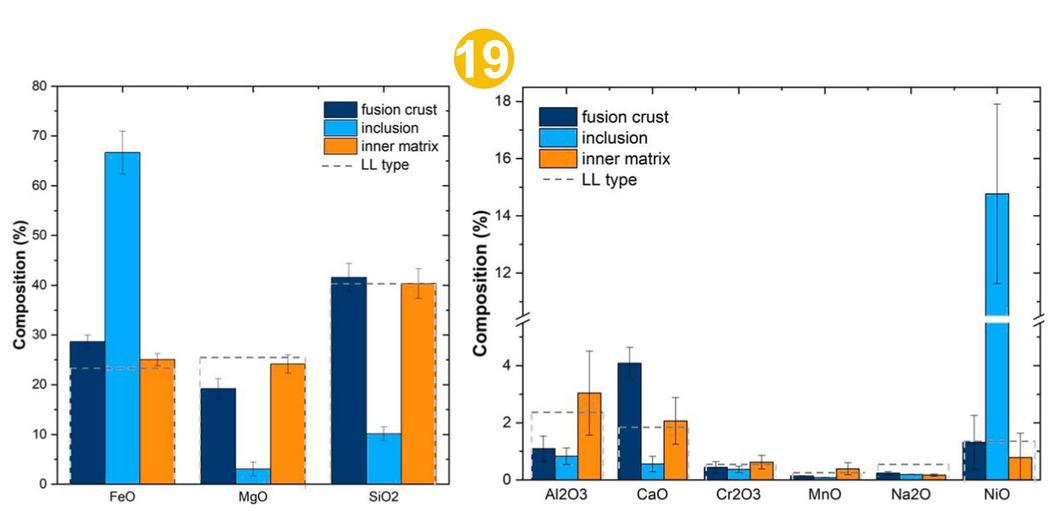


Figure 19. Oxide composition (%) calculated by the clibration-free method for three selected regions of the sample: fusion crust, inner matrix, and metallic inclusions. Results are compared with average values for LL-type chondrites (dashed line). (A) Major oxides: FeO, MgO, and SiO_2. (B) Minor oxides: Al_2O_3, CaO, Cr_2O_3, MnO, Na_2O, and NiO.

References

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