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A space instrument combining NIR hyperspectral microscopy and Laser-CosmOrbitrap mass spectrometry for the *in situ* analysis of extraterrestrial dust

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Introduction: The Rosetta mission is one of the latest great scientific and technological European successes. The probe and its lander Philae, transported some very audacious and inventive instruments that for some worked beyond expectations, and gave the scientists and engineers involved an expertise and experience that we should try to build on. The COmetary Secondary Ion Mass Analyser (COSIMA) onboard Rosetta, was the first instrument applying *in situ* analyses of cometary grains [1]. This instrument already combined two techniques: visible microscopy that was crucial to detect routinely the collected dust and characterize its structure [2], and Time-Of-Flight Secondary Ion Mass Spectrometry that mainly allowed us to determine the elemental composition of the dust [3-4]. COSIMA covered a mass range 1–1200 u but was limited to a mass resolution $m/\Delta m$ of 1400 at mass 100 u at Full Width Half Maximum (FWHM), which made the assignment of molecular signals difficult.

For the next generation of extraterrestrial (especially, primitive) dust analyzers, we are proposing an instrument that combines near infrared (NIR) and visible microscopy with laser ionization mass spectrometry (LIMS). This multi-analysis instrument (named dPCA for dust Particle Composition Analyzer) was part of the Castalia+ mission proposition to the ESA M7 call, but it is potentially suited for any space mission aiming to characterize dusty materials, especially complex ones containing organic and mineral phases.

In the prospect to build a new generation of mass spectrometer offering High Resolution Mass Spectrometry (HRMS) collaborative effort between consortium of French and Czech laboratories (LPC2E, LATMOS, LISA, IPAG, IJCLab, J. Heyrovsky Institute of Physical Chemistry) and University of Maryland and NASA GSFC, are on-going to settle a pulsed UV laser source with an Orbitrap™ [5] mass analyzer for planetary applications. The spaceflight and ruggedized version of the Orbitrap cell and its electronics (preamplifier, ultra-stable High Voltage), the CosmOrbitrap mass analyzer/detector, is capable of discriminating isobaric interferences with ultrahigh mass resolution $m/\Delta m > 100,000$ (FWHM), high mass accuracies and dual polarity measurements [6-10].

The NIR channel of the microscope will be based on the MicrOmega hyperspectral instrument

developed at IAS (Orsay, France). Several replicas of this instrument have already flown or are currently working aboard MASCOT/Hayabusa2, on the ExoMars rover [11] and currently in the JAXA curation facility for Ryugu dust analysis [12]).

In this study, we investigated the analytical value of combining these two techniques. We will show through laboratory measurements how combining infrared and mass data could be extremely useful to unambiguously characterize the targeted dust.

Experimental Procedure: The main well known inputs given by the NIR spectra are: the detection and characterization of hydration signatures, especially on silicates, the detection and partial characterization of carbonates and sulfates, the detection of ammoniated compounds, the detection of the presence of organic compounds and the detection and identification of ices (H_2O , CO_2 , etc.). In the context of main belt comets, asteroids and even the Martian moons and surface, the full characterization of hydration signatures is one of the most important information needed to complete the mass spectra characterization. For this reason, we started our set of experiments and measurements on both instruments, a laboratory MicrOmega replica at IAS, and a laboratory instrument prototype of a laser ablation / ionization Orbitrap[™] mass spectrometer, the LAB-CosmOrbitrap, developed at LPC2E (Orléans, France), by focusing on hydrated and anhydrous silicates. The LAB-CosmOrbitrap integrates i) a commercial pulsed Nd-YAG laser used at 266 nm UV wavelength, ii) a set of ion focusing lenses without C-trap, and iii) a spaceflight CosmOrbitrap mass analyzer/detector. Variable output energy of laser beam can be operated thanks to a polarizing prism.

Samples: To explore the capabilities of the LAB-CosmOrbitrap instrument to characterize silicate in both positive and negative ion mode, we started with analyses of a San Carlos olivine, and a natural Mg-rich serpentine dominated by antigorite and chrysotile. Both samples are obviously silicates, but the former is an anhydrous ionic solid (no covalent bond between O and Mg) and the latter is a phyllosilicate (= a hydrated silicate) where Mg is covalently bonded to O and OH. Same samples have been analyzed with MicrOmega replica instrument.

Results: LAB-CosmOrbitrap measurements in positive ion modes of the serpentine sample enables detection of various oxide and hydroxide magnesium peaks at high mass accuracy (< 2.5 ppm) during a single laser shot experiment, with high mass resolution (for examples $m/\Delta m \sim 160,000$ (FWHM) for $^{24}\text{MgOH}^+$ and $m/\Delta m > 130,000$ (FWHM) for $^{24}\text{Mg}_2\text{O}^+$). In this study, we explored the best suitable laser energy and consecutive shot sequences to find reproducible and robust measurements of oxide and hydroxide ions. These results will be presented among those on olivine and the spectra obtained with NIR microscopy.

Conclusions: This study demonstrates the capabilities of a UV Laser-CosmOrbitrap instrument combined with a NIR spectrometer to detect and characterize hydrated signatures of a serpentine with an optimized protocol. Next steps that will be pursued are among others the analyses of other types of silicates and minerals, of silicate doped with organic compounds. In the prospect of a future space instrument, it is obvious that IR microscopy would be of great benefit for a fast screening of the area of the targeted dust in order to further perform LIMS analyses and increase the confidence in the identification of molecular and structural indices.

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