UV-LASER DESORPTION ION SOURCE APPLIED TO A SECONDARY ION MASS SPECTROMETER.
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Introduction: Secondary ion mass spectrometry (SIMS) is a well established laboratory surface analyzing technique and, with the COSIMA instrument onboard ROSETTA, it will be even applied to in-situ measurements of cometary grains, once Rosetta reaches its target comet, 67P/Churyumov-Gerasimenko, in the year 2014 [1]. Furthermore, the elemental abundances of STARDUST samples have been measured with SIMS instrumentation [2].

Laser desorption (LD) analyzing instrumentation is another surface ion desorption technique [3], and combined laboratory instrumentation for SIMS and LD was developed for the analysis of STARDUST samples [4].

In this study, we were focusing on using a new UV laser ion desorption source combined with a well established SIMS laboratory time-of-flight mass spectrometer, the latter being very similar in technique and performance to the COSIMA flight instrument onboard ROSETTA.

Experimental Procedures: The SIMS instrument located at the LPCE-UMR-CNRS facilities in Orleans, France, is a high resolution, reflectron type, time-of-flight mass spectrometer using liquid metal ion sources (e.g. indium) for the primary 8 keV ion beam and a single ion counting detection technique resulting in mass resolutions of about 1700 to 2000 at 100 amu.

The laser-system was placed on an optical bench next to the SIMS instrument. The UV-laser head had a maximum pulse energy of about 30 uJ, a pulse duration of 4 nsec (half-width), a pulse repetition rate of 500 Hz and an emission wavelength of 266 nm (frequency quadrupled from a 1064 nm Nd:YAG passively Q-switched oscillator pumped with 808 nm laser diode module). The optical system included furthermore beam expander, mirrors, lambda half plate and polarizer (for adjusting the laser beam energy), pinholes, guiding laser with visible light emission, and a 300 mm focusing lens in front of the quartz window to feed the laser beam onto the target in the vacuum chamber of the SIMS instrument. The beam spot size on the target was about 31 by 34 um (half-width) +/- 4 um. The laser included a fast photodiode as trigger source for the electronics (jitter about 0.5 nsec). The laser and optical setup was designed by Laserzentrum Hannover eV.

The SIMS instrument was operated alternatively in SIMS or LD mode. The settings of the time-of-flight mass spectrometer and secondary ion detector were in both operational modes the same. In general, the spectra were collected within 1 min for LD and as long as necessary to achieve sufficient statistics for SIMS. All spectra shown were acquired at different target locations to avoid "bleaching" effects.

Samples: The test samples were gold "black" metal targets (supplier: Universität der Bundeswehr, [1]) as well as blank gold, aluminium, silver (supplier: Goodfellow) and enstatite mineral grains (from the collection of C. Engrand) pressed onto gold. Prior to

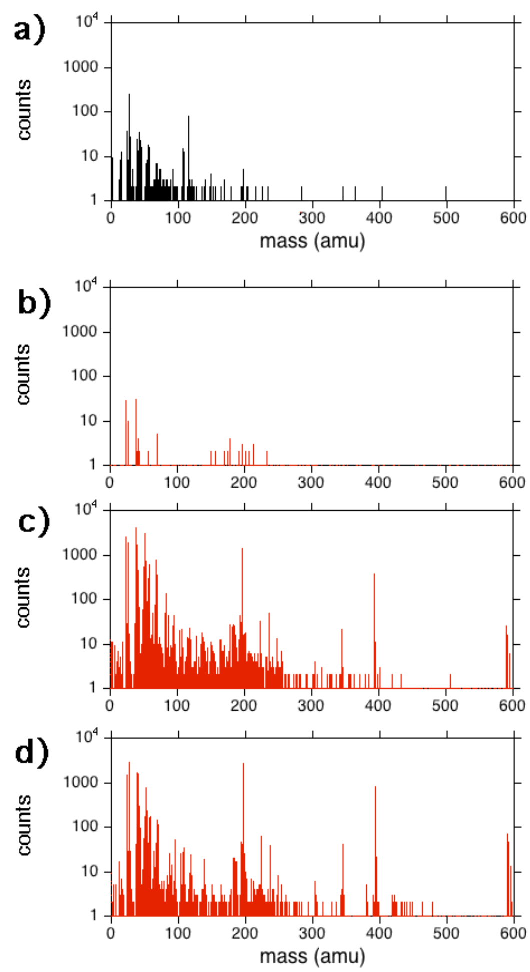

Fig. 1 Gold "black" metal target, positive secondary ion mass spectra: a) SIMS, b) laser energy 0.2 uJ c) laser energy 0.45 uJ and d) laser energy 0.6 uJ

measurements, samples were heated to 150°C in an electric oven. No further cleaning procedures were applied.

Results and Discussions: The positive secondary mass spectra of gold "black" metal are shown in Fig. 1. The SIMS spectra contained the expected masses of Au (minor peak) as well as Na, K and In as the major peaks in the mass spectra. The mass spectra derived from various laser pulse energies change, as expected, not only in quantity, but also in quality. At high energies the formation of metal ion clusters of Au were emerging. Furthermore, exposure to the ablation laser pulses led to "clean" samples, i.e. only Au was observed after sufficient exposure times. Additionally, application of higher laser pulse energies led to the formation of a plasma plume above the laser spot, visible through the target window and, in some cases, to discharges between target and first secondary ion focusing lens.

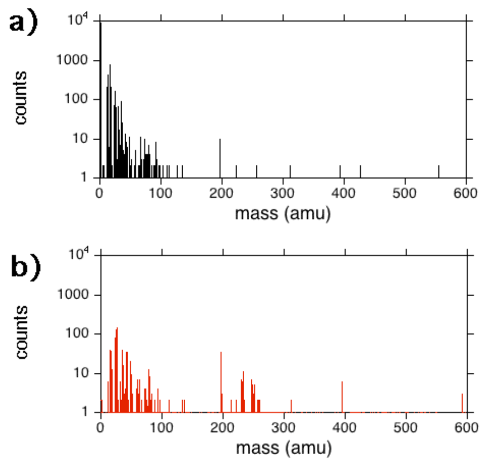

Fig. 2: Gold "black" metal target, negative secondary ion mass spectra: a) SIMS, b) laser energy 0.6 uJ

The negative secondary mass spectra of the same Au targets are shown in Fig. 2. The mass spectra taken at lower energies did not contain any reasonable statistics.

In Fig. 3 the positive and negative ion mass spectra for the enstatite grain analysis are shown. SIMS and laser desorption resulted in comparable mass spectra for the positive ion mode, in negative mode only hydrogen is observable with SIMS.

Conclusions: Both negative and positive measurement modes with the LD source resulted in high resolution mass spectra. As well known, the laser energy density and power are critical parameters in LD and depend on the material to be analyzed. The upper limit for the laser pulse energy density is set by the formation of a plasma plume as well as the saturation limit of the ion detector counting electronics. In principle, the adaptation of existing SIMS instrumentation for LD is a unique opportunity to make use of the heritage of existing space-borne mass-spectrometers for the next generation of in-situ surface composition instrumentation, e.g. analyzing the bulk volume of grains layer for layer with LD mass spectrometry. The next step will be to expand the chemometric data reduction methods applied to SIMS mass spectra [5] to the laser desorption data, i.e. various laser energy pulses applied to the same sample.

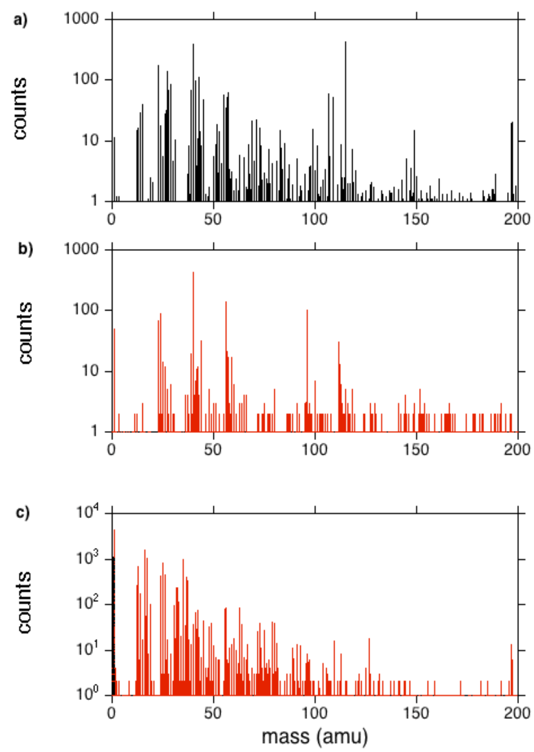

Fig. 3: Gold metal target with enstatite grain, positive secondary ion mass spectra: a) SIMS, b) laser energy 0.45 uJ and negative ion mass spectra c) SIMS and laser energy 0.45 uJ

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References: [1] Kissel J. et al. (2007) *Space Sci Rev, 128,* 823. [2] Stephan T. (2008) *Space Sci Rev, 138,* 243. [3] Lubman D. (1990) Lasers and Mass Spectrometry, *Oxford University Press Inc., NY, USA*. [4] Henkel, T., (2007) *Rev Sci Instrum 78,* 055107. [5] Engrand C. et al. (2006) *Rap Comm Mass Spec, 20,* 1361.