ANALYSIS OF MINERAL SOIL ANALOG SAMPLES WITH A PULSED UV-LASER SOURCE. M. Hilchenbach[1], T. Lang[2], J. Neumann[2], N. Tarcea[3] [1]Max-Planck-Institut für Sonnensystemforschung, Max-Planckstr. 2, 37191 Katlenburg-Lindau, Germany, [2]Laser Zentrum Hannover e.V., Hollerithallee 8, 30419 Hannover, Germany, [3]Institut für Photonische Technologien e.V., Albert-Einstein-Straße 9, 07745 Jena, Germany

Introduction: In-situ microscopic investigation techniques such as Raman scattering and laser induced plasma breakdown emission spectroscopy are well known laboratory analytic techniques. In this study, we were focusing on setting up a new pulsed UV laser source combined with a laboratory spectrometer and apply this setup to the analysis of powdered planetary mineral soil analog samples.

Experimental Procedures: For the spectroscopic measurements, the setup consisted of an adapted commercial instrument (Spectrometer HR800 from Horiba/ Jobin Yvon) fitted with a 2400 lines/mm grating and CCD camera. Laser excitation was filtered out with an edge filter (long pass). The best achievable resolution was about 1 cm-1, with a slit of 100µm installed. We used wider slits for some measurements to increase light throughput. The instrument setup with a 10x objective and a pulsed UV laser. The measurement time interval was about 10 min for each sample. Random measurements were performed on the powder samples. .

The laser-system was placed on an optical bench next to the spectrometer setup The UV-laser 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). Furthermore, the optical system included beam expander, mirrors, lambda half plate and polarizer (for adjusting the laser beam energy), pinholes, and a 300 mm focusing lens and mirror to feed the laser beam under 45° onto the target in front of the objective of the spectrometer setup. Taking into account the angle of incidence, the minimum beam spot size on the target was about 31 by 34 um (half-width) +/- 4 um and the spot size could be adjusted via positioning of the focusing lens up to about 200 um. The laser and optical setup was designed by Laser Zentrum Hannover eV.

Samples: The mineral soil analog samples were: 1) Atacama desert, San Pedro, Chile, 2) Mars analogue JSC-1, 3) Salten Forest, 4) Montmorillonite, Oak Creek and 5) Riverside . All samples were powders with particle sizes smaller than 50 µm and were selected in line with a previous comparative Raman and GC-MS study [1].

Results and Discussions: The results of the Raman spectroscopic measurements are shown in Fig. 1.

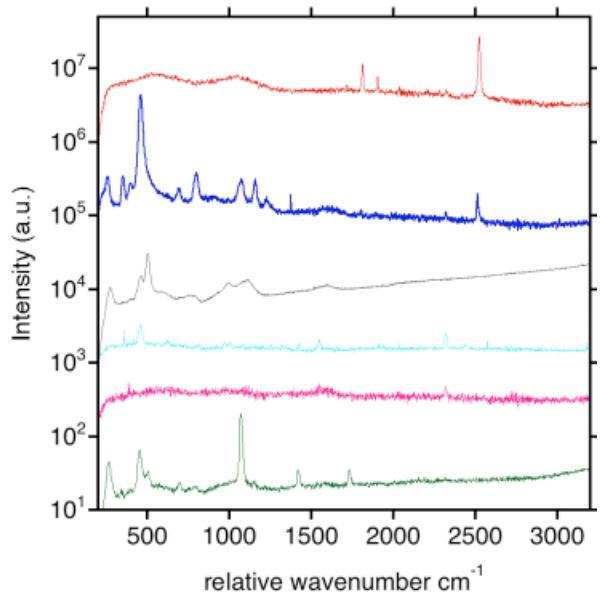

Fig. 1 Raman and LIBS spectra as observed for (bottom to top): Atacama desert, San Pedro, Chile - Mars analogue JSC-1 - Salten Forest - Montmorillonite, Oak Creek – Riverside (laser pulse energy: 10 uJ and 18 uJ, resp.)

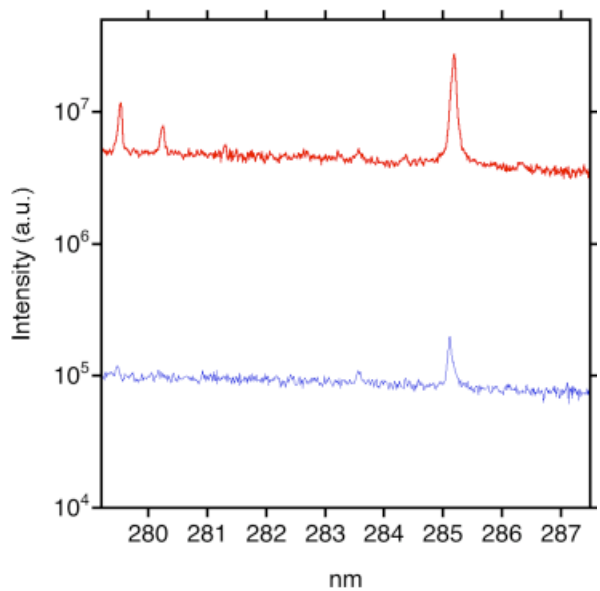

Fig. 2: Riverside sample, as in fig. 1, but plotted versus wavelength to identify the LIBS emission lines of Mg II at 279.55 nm and 280.27 nm, and Mg I at 285.21 nm.

The Atacama sample revealed calcite at 1088 cm-1 and kipushite at 452 cm-1. For Mars analogue JSC-1 sample, no lines could be identified due to the low emission intensity level. In the Salten Forest sample, potentially silicates and carbon could be assigned to the peaks, but the signal/ noise was not sufficient. In the Montmorillonite sample plagioclase (albite, labradorite, orthoclase or anorthoclase) exhibited the dublett at about 500 cm-1 which is typical for silicates. The sample also contained carbon (broad emission bands at 1300 and 1500 cm-1). At nominal excitation pulse energy the Riverside sample revealed quartz at 467 cm-1 and the following quartz peak series except for the peak at about 2500 cm-1. While this had been potentially attributed to sulfur containing groups, it was then identified not as a Raman, but laser induced plasma breakdown spectroscopy (LIBS) emission line of Mg I at 285.2 nm (Fig. 2). Increasing the laser pulse energy smeared out the Raman lines, but peaks at 279.6 nm and 280.3 nm attributed to Mg II showed up as expected for a hotter LIBS plasma.

The Salten Forest sample proved to be difficult to measure since even at nominal laser pulse intensities as applied to other samples, the Salten Forest powder tended to lift off and cover the microscope objective on a macroscopic scale (Fig. 3).

Conclusions: The samples prove to be of different compositions as has been established in the previous study with visible and infrared excitation [1] . Two samples exhibited very low Raman emissions and unique lines could not be uniquely identified. The Raman spectra gathered via UV excitation as compared to visible or infrared excitation resulted, as expected, in the fluorescence emission shifted almost beyond the Raman scattering wave number range. Even so great care was taken to limit the laser intensity below damage level, we found examples where both Raman scattering and LIBS plasma emission lines were accumulated in the same spectra at the same time. Several measurements led to lift of the dust off the sample holder towards the microscope objective, in one case covering the latter with a layer of fine dust. This effect is described also for Raman measurements of single grains of lunar regolith [2] . It constitutes a severe problem for remotely operated instrumentation without the means of a normal laboratory supervision. The laser induced fluorescence (LIF) in itself contains valuable information, however this was not followed up in the present study [3]. We demonstrated a pulsed UV laser being a suitable excitation source for Raman spectroscopy and therefore, with a time-gated detector might allow measurements in a environment with high light background levels [4]. Acquiring both LIBS and Raman spectra lines on the same target spot, and potentially monitoring the damage due to the LIBS

Fig. 3: Objective covered with dust grains of the Salten Forest sample.

plasma via Raman spectroscopy [5], might prove a valuable tool for characterizing mineral (and organic) samples.

As a next step, an inverted microscope setup might be better suited for this kind of Raman-LIBS instrumentation, hence the microscope objective will be mounted below, and shielded by, the slide/ glass window, on which the dusty sample will be deposited. Furthermore, in such a setup the grains will be aligned along the glass surface and the focal plane is the same for all samples.

Acknowledgements: We would like to thank W. Goetz, M.B. Madsen and H. Kolm not only for providing the mineral samples for this study, but also for explaining their significance as Martian analog soil samples to us.

References: [1] Tarcea, N. et al. (2009) C*onference on Micro-Raman Spectroscopy and Luminescence Studies in the Earth and Planetary Sciences*, April 2-4, 2009, Mainz, Germany. LPI Contribution No. 1473, p 83. [2] Korotev, R. L. et al. *29th Annual Lunar and Planetary Science Conference,* V 29 p 1797 1998. [3] Bozlee, B.J. et al., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, V 61, p 2342, 2005. [4] Misra, A.K. et al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, V 61, p 2281, 2005. [5] Witke, K. et al., *Journal of Raman Spectroscopy,* V 29 p 411 1998.