

COMBINED RAMAN-LIBS STUDIES ON IRON SULFIDES TO INVESTIGATE THE EFFECTS OF THE LIBS PLASMA ON THE MINERAL COMPOSITION.

J. Alsemgeest^{1,2}, S. Schröder², U. Böttger², S.G. Pavlov², I. Weber³, A. Greshake⁴, H.-R. Knöfler⁴, U. Altenberger¹ and H.-W. Hübers^{2,5}, ¹Universität Potsdam, Institut für Erd- und Umweltwissenschaften, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany. ²Deutsches Zentrum für Luft- und Raumfahrt, Institut für Optische Sensorsysteme, Rutherfordstraße 2, 12489 Berlin. ³Westfälische Wilhelms-Universität, Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany. ⁴Museum für Naturkunde, Invalidenstraße 43, 10115 Berlin, Germany. ⁵Humboldt-Universität zu Berlin, Institut für Physik, Newtonstraße 15, Berlin, Germany.

Introduction: Laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy have a high potential for in situ geochemical and mineralogical analyses for planetary exploration, in particular in combination. Both techniques are active and use the radiation of a laser to provoke different physical phenomena, leading to specific spectra from a sample of interest. LIBS and Raman spectroscopy provide complementary information: while LIBS obtains elemental composition, Raman provides information on the molecular structure. These techniques are highly synergetic and can be integrated into a single compact instrument sharing hardware components as the laser, spectrometer, light-collecting optics, and/or the pointing and focus mechanisms.

In the LIBS technique, radiation from a high-power, pulsed laser is focused onto a sample from which material is ablated and a small luminous plasma plume is produced (e.g. [1]). Information on elemental composition is obtained from the energy of optical transitions caused by radiative relaxation of excited atoms and ions. In contrast to LIBS, Raman spectroscopy is a non destructive method. It is sensitive to the vibrational and rotational states of molecules, and thus can be used for the determination of the mineralogy of geological samples as well as identifying organic and biogenic samples. Remote LIBS-Raman instruments for Mars and Venus have been proposed in a number of studies (e.g., [2]–[5]). A combined LIBS-Raman instrument SuperCam for remote analysis on Mars is currently being developed for NASA's Mars 2020 mission [6].

The LIBS plasma can reach temperatures over 10k K and is accompanied by a plasma shock wave that might alterate minerals, which are then measured by Raman spectroscopy. Here, we present studies of iron sulfides analyzed with LIBS in different atmospheric conditions with the focus on the effects of the LIBS laser interaction and the plasma on the samples with subsequently taken Raman spectra.

Experiments: Pyrite (FeS₂, Spain) and pyrrhotite (Fe_{1-x}S, Kola Peninsula, Russia) samples were shot with a LIBS laser in a dedicated simulation chamber in vacuum and in a martian atmosphere with a pressure of 7.0 mbar and 1.0 bar, respectively. A pulsed 1064 nm Nd:YAG laser has been used with 50 pulses at a power of 4.9 mJ (pulse duration ~5 ns) and a \varnothing 400 μ m spot size on the sample's surface. The produced craters have been analyzed by optical- and Raman microscopy, using a frequency doubled cw laser at 532 nm and a laser power of 1.0 mW for the latter. The atmospheric conditions have been kept constant over both LIBS- and Raman measurements.

Results: In all measurements, craters were produced by the laser-sample interaction which showed a zone of \varnothing 1.5-5 mm with spectral changes in the Raman data; although the typical Raman spectra of pyrite and pyrrhotite are still visible, additional peaks were found. This is mainly seen in the outer parts of the zone, where a thin film has formed. In vacuum and martian atmospheric conditions at 7 mbar, this film consists of polysulfides, whereas it consists of magnetite when the LIBS measurement was done in martian atmosphere at 1 bar. In the inner zones of the craters the overall signal becomes less intense presumably due to the higher roughness of the surface. Elemental sulfur is found on the pyrite sample measured in all atmospheres; most dominant for martian atmospheric conditions.

Conclusions These results show that LIBS causes fractionation and reaction of sulfur found in both minerals. As the effect appears to be larger with pyrite, the heat from the LIBS plasma might be the main driver of this reaction ([7], [8]); this could cause pyrite to react to pyrrhotite and sulfur. Minerals containing other volatiles (i.e., water) are expected to react as well, meaning that possible effects should be taken into account with the interpretation of post-LIBS Raman data from the same spot.

References:

[1] Cremers D.A. and Radziemski L.J. 2006. *John Wiley & Sons, Ltd.* 1st Ed. [2] Clegg et al. 2014. *Appl. Spectrosc.* 68:925–36. [3] Wiens et al. 2007. Abstract #3092 7th Int. Conf. on Mars. [4] Sharma et al. 2009. Abstract #2548 40th LPSC. [5] Thompson et al. 2005. Abstract #1517 36th LPSC. [6] Maurice et al. 2015. Abstract #2990 LPSC. [7] Toulmin et al. 1964. *Geochim. Cosmochim. Acta* 28:641–671. [8] Gilbert et al. 2014. *J. Anal. At. Spectrom.* 29:1024–1033.