Geophysical Research Abstracts
Vol. 13, EGU2011-7046-1, 2011
EGU General Assembly 2011

LIBS studies on salts and frozen salt solutions under Martian conditions

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Laser-induced breakdown spectroscopy (LIBS) is an emission spectroscopy technique that can be applied for the investigation of geological surfaces. With the ChemCam instrument on the Mars Science Laboratory (MSL) to be launched in 2011 LIBS will be applied for the first time for in-situ analysis on a planetary mission. Also other missions with LIBS instruments on board are proposed, including missions to the Earth's Moon, Venus, and asteroids. LIBS permits rapid multi-element analysis and relies on ablating material from the sample by focusing radiation from a pulsed laser onto its surface. Given sufficient laser energy, a small luminous plasma is produced. The emitted photons, which feature characteristic wavelengths of the elements composing the sample, are collected and analyzed spectroscopically. Thus, the elemental composition of the investigated material is obtained. The LIBS technique is sensitive to various parameters such as environmental conditions. But also matrix effects influence the spectral line intensities. In order to improve qualitative and quantitative results obtained with LIBS, various analytical methods have been developed. One attempt to take into account these effects is multivariate analysis (MVA) such as principal component analysis (PCA), where data sets are sorted due to their similarities and variability.

On Mars different types of salts have been found such as chloride bearing salts in deposits on the southern hemisphere and sulfates for instance in the Gusev Crater. Also perchlorates were detected in the Martian soil at the Phoenix landing site. These salts lower the freezing point of water and therefore enable the existence of liquid water, at least temporarily. We have previously demonstrated that LIBS enables the (semi-) quantitative detection of salts and frozen salt water solutions.

In the present study we investigated 10 salts with LIBS, focussing on classifying and discriminating between the various salts with PCA. Two samples sets were analyzed, the first consisting of pure pressed salt pellets, the second consisting of the salts in water solutions, frozen to a temperature of 200 K. Measurements were performed in a laboratory set up with a dedicated simulation chamber. A Martian environment was simulated with an appropriate CO2 dominated atmosphere at 6 hPa. An infrared Nd:YAG laser operating at 1064 nm with a repetition rate of 10 Hz was used to generate the plasma at short stand-off distances (< 1m). The laser beam diameter on the surface of the sample was 300 μm and the laser energy was reduced to 35 mJ by a grey filter. The plasma emission was detected with an Echelle spectrometer equipped with a time-gated intensified CCD, enabling a continuous spectral coverage from 280 nm to 900 nm. In the analysis emphasis was given to discriminate chlorides from perchlorates, but also on identifying sulfates. In general, spectral lines of metals such as Na, K, Mg, Ca, Si, and Fe are detectable with high signal-to-noise ratio, allowing for a good discrimination between salts with different types of cations. Also the oxygen and hydrogen lines are detected with good signal-to-noise ratios. However, there are only week sulphur and chloride lines available in this spectral range. In particular when analyzing frozen solutions, discrimination between sulfates and chlorides remains challenging.