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Laser-induced breakdown spectroscopy of frozen salt solutions for in-situ space exploration

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1. Introduction

Laser induced breakdown spectroscopy (LIBS) is a powerful analytical technique for determining the elemental composition of various materials both, qualitatively and quantitatively. In particular to investigate geological surfaces in space exploration LIBS can be applied in situ on planetary missions (e.g. [1]) and is currently proposed or planned for lander missions to planets, moons and asteroids [2-6]. Advantages of the LIBS method include rapid analysis, no necessity for sample preparation, the ability of simultaneous detection of major, minor and trace elements and the capability to remove dust layers. Moreover depth profiling can be done through weathering layers. LIBS can be applied at close and stand-off distances up to several meters and combination with Raman spectroscopy is beneficial since both techniques provide complementary information. In previous studies it was shown, that LIBS can be applied to ices and ice/dust mixtures [7-9]. Here, we studied the feasibility of LIBS to investigate frozen solutions with salts and ice/soil mixtures in low pressure environments similar to Mars, Earth's moon, asteroids and icy moons.

2. Experimental

LIBS relies on ablating material from the sample by focusing the radiation of a pulsed laser onto the sample's surface. A plasma plume is generated whose emitted photons feature characteristic wavelengths of the elements composing the sample. The emission is collected and spectrally analyzed. In our study two infrared lasers were used to generate the plasma at short stand-off distances (< 1 m): a Nd:YAG laser (1064 nm, up to 220 mJ, 8 ns pulses, 10 Hz) and a Nd:YLF laser with parameters similar to a prototype ExoMars LIBS laser (1053 nm, up to 5 mJ, 5 ns pulses, 10 Hz). The plasma emission was detected with an echelle spectrometer (Lasertechnik Berlin) with a time-gated intensified CCD camera. All experiments were performed in a dedicated simulation chamber, wherein pressure and temperature can be varied in a broad range (see [6] for details).

Various frozen salt solutions and ice soil mixtures were prepared with different concentrations. To produce ice with only little inclusions of air, the samples were degassed before freezing them in a copper container. To simulate Martian environmental conditions the chamber was filled with an appropriate gas mixture at a pressure of approximately 7 mbar. In the simulation chamber the measurements were performed at 230 K by cooling the cold finger with liquid nitrogen. Moreover, we studied the LIBS measurements of the frozen solutions in environments of very low pressure and temperatures. The delay and integration time of the spectrometer were optimized for each environment to obtain good signal-to-noise ratios while at the same time not losing signals from fast recombining ions. Qualitative analysis was done with focus on the feasibility of LIBS to differentiate between the different samples. While discrimination based on alkali metal and alkaline earth metal elements is relatively straight forward, especially applying principal component analysis, discrimination between sulfates and chlorides is challenging.

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