European Space Agency
European Mars Science and Exploration Conference: Mars Express & ExoMars
ESTEC, Noordwijk, The Netherlands, 12 - 16 November, 2007

Laser induced breakdown spectroscopy of soils and rocks under Martian conditions

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Introduction: ExoMars, ESA´s upcoming mission to Mars will include a combined Raman/LIBS instrument. The LIBS part will analyze the elemental composition of Martian surface rocks and soils in the temperature range from +30°C to -60°C [1]. Results of various Mars observations infer that sorption water is a soil constituent in the upper meters of Martian surfaces at mid- and low latitudes [2,3]. Consequently, the presence of pore and adsorption water including their transformation into ice phases and vice-versa must be considered in the LIBS analyses of Martian soils and rocks. In the literature we find only few LIBS surveys on ice [4] and on soil/ice mixtures [5]. Therefore, we have started systematic LIBS analyses of wet samples at variable surface temperatures [6,7]. The present work is based on the GENTNER project [1] and is funded by German Aerospace Center DLR. Here we report new results of our studies for the Raman/LIBS instrument for ExoMars on the dependence of LIBS signals from relevant sample types under Martian environmental conditions as a function of sample surface temperature.

Experimental: We used a Nd:YAG laser operated at 1064 nm with 8 ns pulse width and 10 Hz repetition rate. The spectrometer for the plasma emission is a high-resolution Echelle mono-chromator equipped with a gated ICCD. The sample holder can be cooled with liquid nitrogen to -80°C in pre-selected steps. The chamber is filled with a 7 mbar “Martian” atmosphere (95.55% CO_2, 2.7% N_2, 1.6% Ar, 0.15% O_2).

Results: We analyzed andesite rock samples featuring different grades of surface roughness/pore sizes and pressed powder pellets of the same samples and of certified reference materials.

The LIBS signal from all samples shows strong drops below 0°C. We attribute this characteristic signal behavior to the presence and to phase transitions of (supercooled) water on surface grains and inside surface pores and scratches [6,7]. The specific transition temperatures depend on surface roughness and pore size. Three main transition temperatures of water, supercooled water and water ice had previously been established around 0°C, -40°C and -50°C [8-13]. They are also observed with the LIBS technique as sharp signal dips (Fig. 1a). At 0°C water inside larger pores and scratches nucleates to hexagonal ice. When this free water is slowly cooled down it can exists as supercooled water down to -40°C. At this temperature the supercooled water nucleates homogenously to cubic ice. On areas with gently corrugated surface supercooled water can exist down to -80°C. Around -50°C it changes its thermodynamic properties; a transition from normal liquid structure to an amorphous hydrogen-bonded network is hypothesized [12]. As shown in Fig. 1b, the Si/H minima are directly correlated with increased hydrogen emission peak intensities. This result strongly corroborates the hypothesis.

Conclusions: LIBS signals from water bearing Martian analogue samples under Martian conditions in the range +30°C to -60°C are a function of sample temperature. We observed signal drops below 0°C and attribute this behavior to phase transitions of supercooled water present inside the surface pores and scratches. On one hand, this effect might significantly influence the analytical capability of the LIBS technique. But on the other hand it might allow measuring the water content on soil and rock surfaces and inside their pores.

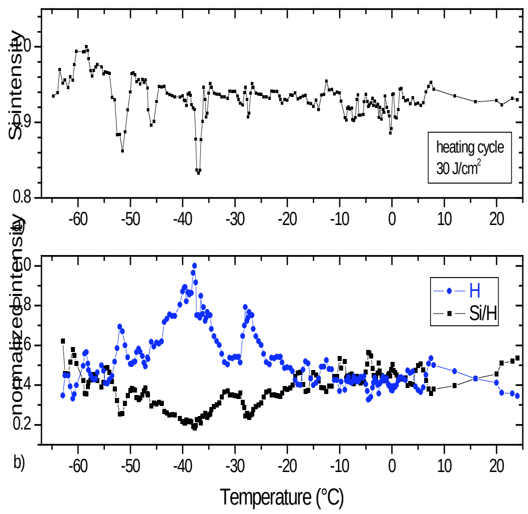

Figure 1. a) Normalized LIBS Si peak intensity (288.2 nm) on smooth andesite rock sample and b) Normalized H peak intensity (656.2 nm) and Si/H ratio as a function of temperature.

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