

**LIBS in the cold: Laser induced breakdown spectroscopy of soils, rocks and ice under simulated Martian conditions.** I. Rauschenbach<sup>1</sup>, V. Lazic<sup>2</sup>, S. Jovicevic<sup>3</sup>, E. K. Jessberger<sup>1</sup> and R. Fantoni<sup>2</sup>, <sup>1</sup>Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany, irausch@uni-muenster.de, <sup>2</sup>ENEA, FIS-LAS, Via E. Fermi 45, 00044 Frascati (RM), Italy, <sup>3</sup>Institute of Physics, 11080 Belgrade, Pregrevice 118, Serbia.

**Introduction:** ExoMars, the future mission to Mars of ESA will include a LIBS instrument to analyze the elemental composition of the Martian surface materials, which should perform measurements in the temperature range from +30°C to -60°C [1-2]. Telescopic and spectroscopic measurements indicate that Martian soil contains a certain amount of adsorbed water [3]. Therefore, in LIBS analyses of Martian soils the presence of water and ice and their effects must be considered. Only one LIBS study on ice [4] and one on soil/ice mixtures [5] are reported yet, without considering variable surface temperatures. Thus, we studied the dependence of LIBS signals on relevant sample types containing water in simulated Martian atmosphere and as a function of the sample temperature.

**Experimental:** We used a Nd:YAG laser source from Quanta System (Handy) operated at 1064nm with 8 ns pulse width and 10 Hz repetition rate. The plasma emission is detected by a 550 mm monochromator (Jobin-Yvon Triax 550), equipped with a gated ICCD (Andort, 690x256 pixel). The ICCD gain is set to zero and the gate width to 5  $\mu$ s. The rotating sample holder in the 7 mbar CO<sub>2</sub> atmosphere chamber is cooled by liquid nitrogen. The sample surface temperature is measured on the same sample type placed in contact with a thermocouple. Two laser energies are applied: 70.7 mJ ( $\sim$ 40.4 J/cm<sup>2</sup>) and 12.5 mJ ( $\sim$ 13.9 J/cm<sup>2</sup>).

**Results:** We analyzed an andesite rock sample featuring different grades of surface roughness/pore sizes due to varying polishing methods, and an ice sample.

**Rock samples:** The Si intensity on the andesite rock sample with the roughest surface (polishing #1; Fig. 1a) is practically constant down to 5°C. At 4°C, i.e. at maximum water density, it decreases by about 50%. With further cooling the signal recovers almost immediately and then drops sharply at 0°C. At lower temperature the signal, after a slight recovery, falls down to a value of  $\approx$  10% of the average intensity for  $\geq$  5°C. The following partial signal recovery probably indicates the completed transition of supercooled water inside pores to defective cubic ice [6]. The wide minimum  $\leq$  0°C is analogue to the observed interfacial ice melting in amorphous silica in simulating rock-water interfaces [7]. The signal of the same andesite sample with a smoother surface (polishing #2) oscillates above 0°C less than  $\pm$ 7% around the average value (Fig. 1b). The signal decreases at  $\approx$  0°C where the formation of

normal, disordered ice is expected inside larger pores. Below 0°C we observe rather violent signal oscillations as a function of the temperature. Some small negative peaks are attributed to different dimensions of the surface pores, each one having its specific temperature for the water-to-ice transition [6, 8-9].

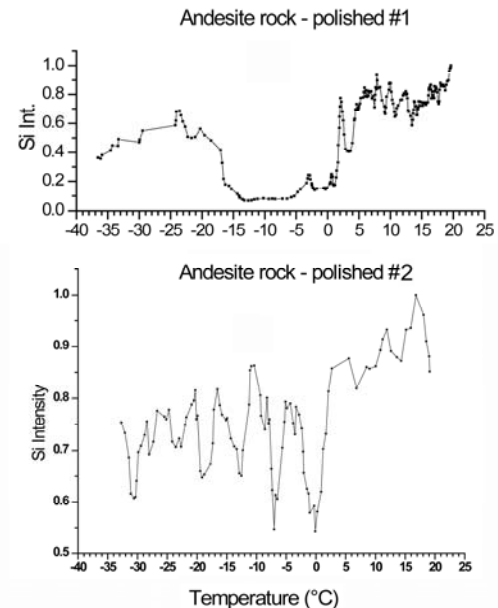


Fig. 1: Normalized Si peak intensity (288 nm) from Andesite rock sample with a) roughest surface considered, b) smoother surface, energy density 13.9 mJ/cm<sup>2</sup>.

The same andesite sample with the smoothest surface (polishing #3) was repeatedly analyzed, both during cooling and heating cycle (Fig. 2). Apart from some oscillations, the signal remains practically constant in the whole temperature range except one very deep and narrow peak around  $\approx$  -10°C, that is independent from the laser energy, and present both during the heating and cooling and on different areas of the sample. Such a signal behaviour is attributed to the rather uniform surface with smaller pores than in the first case (Fig. 1a) [6]. In all measurements on the well polished surface the signal depression at  $\approx$  0°C is very low, indicating little hexagonal ice formation. If the small sized pores dominate the surface, the water inside freezes in more ordered cubic form [8] with lower transition temperature than disordered ice, which can be formed only on surfaces and inside large pores. At lower laser energy density, the sufficiently slow cool-

ing and heating cycles revealed another negative peak at  $\approx -48^\circ\text{C}$ . Around this temperature, there is an evidence of a thermodynamic transition of water/ice where probably supercooled water changes from normal liquid structure to an amorphous hydrogen-bonded network [9-11].

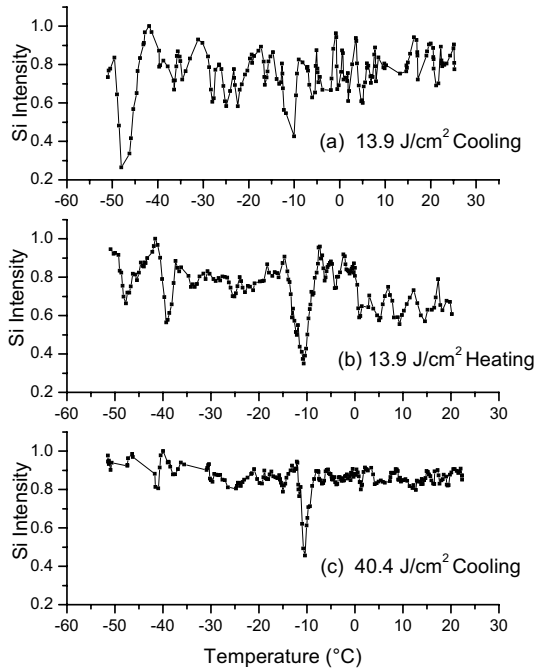


Fig. 2: Normalized Si peak intensity (288 nm) on smooth andesite rock. a) heating cycle,  $E=13.9$   $\text{mJ}/\text{cm}^2$ , b) cooling cycle,  $E = 13.9$   $\text{mJ}/\text{cm}^2$ , c) cooling cycle,  $E = 40.4$   $\text{mJ}/\text{cm}^2$ .

**Ice samples:** The ice sample was prepared from water with  $\text{MgSO}_4$  added to obtain a solution of 50 mg Mg/l. Repeated measurements show two positive peaks below  $-30^\circ\text{C}$ , while above this temperature there is a progressive signal increase, albeit with strong oscillations due to missing sample uniformity (Fig 3). The negative peak close to  $-40^\circ\text{C}$  is similar to that observed on andesite rock (Fig. 2b) and was interpreted as the beginning of the homogeneous nucleation of free supercooled water. As in the case of andesite rock (Fig. 2) there is an extremely strong signal depression at about  $-50^\circ\text{C}$ . On ice the signal is reduced even by two orders of magnitude. This feature probably marks the phase transition of supercooled water to amorphous, low-density ice. A striking resemblance of the negative peaks around  $-40^\circ\text{C}$  and  $-50^\circ\text{C}$  obtained both on ice and rocks indicates the presence of supercooled free liquid at low temperatures under relatively slow temperature change. On Mars higher cooling velocities of the surface than here is not plausible, thus the similar effects are expected also for in-situ analyses.

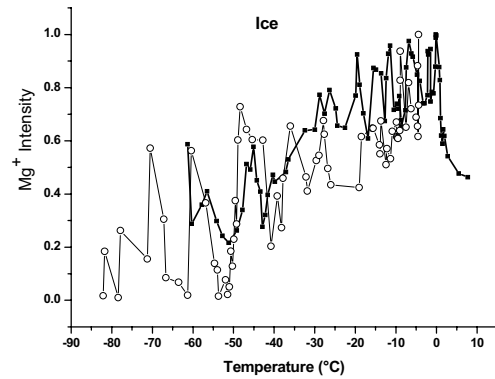


Fig. 3: Repeated measurements of  $\text{Mg}^+$  peak intensity (280.2 nm) (normalized) of frozen water  $\text{MgSO}_4$ -solution, heating cycle, laser energy density  $40.4$   $\text{J}/\text{cm}^2$ .

**Conclusions:** For the first time LIBS signals from realistic water containing samples were studied under Martian conditions as a function of sample temperature from  $+30^\circ\text{C}$  to  $-60^\circ\text{C}$ . We observed strong signal oscillations below  $0^\circ\text{C}$ , and in some cases the signal was reduced by one order of magnitude with consequences for the LIBS analytical sensitivity. This behavior is attributed to the presence of supercooled water inside the surface pores; where the freezing point depends on the pore size. Resuming all results it can be recommended to exclude LIBS measurements near the water/ice transition temperatures, i.e. about  $0^\circ\text{C}$ ,  $-40^\circ\text{C}$  and  $-50^\circ\text{C}$ . At the latter temperature, a very low ablation rate of ice can compromise its removal by laser. This work points out a necessity to further examine LIBS signals from moist samples at subzero temperatures and its consequences for the calibration aimed for quantitative element analyses.

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**References:** [1] Jessberger et al. (2003) *ESA Call for Ideas of the Pasteur instrument payload for ExoMars rover mission*. [2] Del Bianco et al. (2006) *4<sup>th</sup> NASA International Planetary Probe Workshop*. [3] Jakosky B. M. and Mellon M. T. (2004) *Physics Today, April*, 71-85. [4] Cáceres J. O. et al (2001) *Spectrochim. Acta B*, 56, 831-838. [5] Arp Z. A. et al. (2004) *Appl. Spectrosc.*, 58, 897-909. [6] Dash J. G. et al. (1995) *Rep. Prog. Phys.*, 58, 115-167. [7] Engemann S. et al. (2004) *Phys. Rev. Lett.*, 92, 205701 : 1-4. [8] Schreiber A. et al. (2001) *Phys. Chem. Chem. Phys.*, 3, 1185-1195. [9] Bergman R. et al. (2000) *J. of Chem. Phys.*, 113, 357-363. [10] Lazic V. et al. (2005) *Spectrochim. Acta B*, 60, 1002-1013. [11] Ito K. et al. (1999) *Nature*, 398, 492-495.