ACOUSTIC MONITORING OF LASER-INDUCED PHASE TRANSITION IN MINERALS

Baptiste Chide1,2, Olivier Beyssac1, Karim Benzerara3, Michel Gauthier3, Sylvestre Maurice2, David Mimoun1, Roger C. Wiens4, 1Institut Supérieur de l’Aéronautique et de l’Espace (ISAE-SUPAERO), Toulouse, France (Baptiste.Chide@isae-supraero.fr), 2Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France, 3Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Paris, France, 4Los Alamos National Laboratory (LANL), Los Alamos, NM.

Introduction. Laser-Induced Breakdown Spectroscopy (LIBS) is an analytical technique that can remotely measure abundances of chemical elements in solids. A high energy laser pulse heats the sample over a small area leading to material vaporization and formation of a high pressure plasma plume which expands supersonically generating a shock-wave. Used for the first time for in situ analysis on Mars with the ChemCam instrument onboard Curiosity [1], the SuperCam instrument onboard the Mars 2020 rover [2] will also use LIBS supported by the Mars Microphone that will record laser-induced shock-waves [3]. Here we investigate possible monitoring of phase transitions in hematite and diamond under LIBS laser shots in acoustic recording.

Physics of Laser Sparks Generation. Optical and thermal parameters of the targeted material govern how efficiently the laser is coupled with the surface. The incoming laser energy is locally absorbed by the sample via the Beer-Lambert law over the optical penetration depth which is defined by the inverse of the absorption coefficient of the sample at the laser's wavelength. Then it is converted into heat that is transferred inside the material depending on its thermal properties. The surface suffers a sudden and sharp increase in temperature leading to melting followed by mass ablation after the vaporization of the material [4]. It leaves a cavity whose walls and floor have been potentially altered by the process for some specific materials [5, 6]. The piston-like effect of the expanding vapor plume on the surrounding gas creates a shock-wave whose propagation has been described theoretically in [7] and is known as the Taylor-Sedov blast-wave model. The pressure in front of the shock can be expressed analytically as a function of the energy of the blast which depends on the ablated mass and consequently on the optical and thermal parameters of the sample [8].

Experiments. Set-up: The ChemCam laboratory setup at IRAP, Toulouse uses a chamber filled with 7 mbar of a simulated Martian atmosphere and is equipped with a SuperCam Mars Microphone, from the same batch as the flight model, without any additional amplification stage. Series of LIBS pits with different total numbers of shots (1, 2, 3, 5 and 30) were made on three pure minerals: hematite, magnetite and diamond.

For each laser shot, the acoustic signal of the laser spark (compression and rarefaction phase) is recorded.

Observations: Fig. 1 shows the shot-to-shot evolution of the acoustic energy over 30 subsequent laser shots on the three analyzed minerals. For magnetite the small decrease of the acoustic energy between the first and the 30th is consistent with the behavior observed in [9]: the formation of a pit reduces the laser-matter interaction and thus the acoustic energy. However, a sharp increase of the acoustic energy is seen both for hematite and diamond during the ~5 first shots. Hence, we could wonder if the phase transition observed in [5] for hematite is responsible for this increase of the acoustic energy and if a similar phenomenon also explains the increase for diamond.

Mineral Phase Transition. Each laser pit is first observed with the binocular, then with a continuous-wave Raman spectrometer at IMPMC, Paris (Renishaw InVia Reflex) and with a scanning electron microscope (SEM) for the pits ablated on hematite.

Hematite/Magnetite: The 30 shot deep pit made on hematite shows a uniform surface with a molten-like texture and a Raman signal consistent with magnetite and previous observations [5,6]. After 30 subsequent laser shots at the same location, [5] showed that LIBS crater on hematite is totally covered by a 200 nm thick
coating of magnetite. However the precise number of shots needed to reach this transformation is not precisely determined. Furthermore, observations with SEM and Raman hyperspectral mapping inside craters created with 1 to 5 shots display two different textures and mineral heterogeneity (see arrows in Fig. 2 for the 1 shot deep pit): molten-like area and ejecta consistent with magnetite and some hematite patches. The hematite patches are less and less numerous when increasing the number of shots and after 3 shots almost all of the area of the pit is covered by molten-like magnetite. The increase of the LIBS shock-wave energy for hematite seems to be correlated with the change of surface material phase inside the LIBS crater, from hematite to glass then magnetite. One possible explanation for the increase of acoustic energy is that hematite has a higher thermal conductivity than magnetite [10], thus heat is dissipated deeper into hematite leading to less efficient ablation.

Diamond amorphisation: For diamond, during the 5 first shots a very small area is ablated and the crater floor is progressively covered by a dark surface with a burned aspect. Raman investigation of a LIBS crater made in diamond (see Fig. 3) shows that the dark material is consistent with amorphous carbon. The increase of the LIBS shock-wave energy for diamond seems to be correlated with the change of surface material phase inside the LIBS crater from diamond to amorphous carbon. Diamond is almost transparent to the laser beam whereas amorphous carbon is nearly opaque. Then for diamond the coupling between the laser and the mineral is low leading to a weaker acoustic signal.

Nonetheless, firing the laser several time at the same location progressively transforms diamond into dark amorphous carbon in the pits, increasing the laser-matter interaction and then the shock-wave energy.

**Conclusion.** Laser ablation transfers a huge amount of energy into the targeted material that locally affects the mineralogical structure over the LIBS spot area. It changes the optical and/or thermal properties which consequently modifies the laser-matter interaction and then the strength of the shock-wave. Tracking the evolution of the LIBS acoustic signal during a raster can give information about such a phase transition occurring during the first shots of the sequence. As an application, this first shot transition can be used to discriminate two different minerals with similar chemical composition: hematite suffers a melting and phase transition whereas magnetite remains the same.