Defining Laser Power Requirements for Heat-Sensitive Samples for the Raman Instrument on ExoMars Mission

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Introduction: The Raman instrument (RLS) onboard the ExoMars rover is expected to determine the structural and compositional features of minerals (and potentially other species) in rocks and soils at the surface and subsurface of Mars. In the current configuration of the ExoMars rover, the samples will be collected by a drill down to a depth of 2 meters, then crushed and delivered to a suite of instruments located in the rover’s analytical laboratory. The crushing station will provide homogenized powdered samples with a grain size distributions of <200 µm. Scientifically, the loss of geological context is the major draw-back of this sample analysis scenario. Analytically, the first major challenge associated to RLS is the reduction of Raman efficiency in powdered samples (due to high surface to volume ratio). The second challenge is the potential of unintentionally damaging heat-sensitive samples (especially Fe-oxides and hydroxides) by optical heating. Particularly, RLS will deliver a high power density laser beam (at 532 nm) into a small volume of loose particles with poor thermal conductivity. To avoid damaging heat-sensitive samples, a low power laser beam (below the sample’s heat-damage threshold, HDT) would be desirable. However, low laser power would hardly satisfy the mission requirement of obtaining informative Raman spectra from ordinary geo-samples (igneous minerals, salts, and phyllosilicates). In order to define the laser power requirement for RLS on ExoMars, we have investigated the HDT of a suite of heat-sensitive Fe-oxides and Fe-hydroxides, including: goethite (α-FeO(OH)), lepidocrocite (γ-FeO(OH)), maghemite (γ-Fe$_2$O$_3$), magnetite (Fe$_3^+$2Fe$_2^+$O$_4$), and hematite (Fe$_2$O$_3$) with fine grain size under different atmospheric conditions. In this abstract we show the results for synthetic goethite sample powder with a grain size distribution of <250 µm in three different environments.

Methodology: The goethite sample powder (grain size smaller than 250 µm) was placed into a sample holder, and then compacted under 0.05 Kg/cm$^2$ pressure. The surface of the sample was then flattened using a blade. A Raman probe (InPhotonics) was used to deliver a 532 nm laser beam (~22 µm diameter at focal point) with a power density of 2.2 kW/cm$^2$ into the sample and to collect the scattered Raman radiation, which was sent to RamanRxn1 spectrometer (Kaiser Optical System, Inc.). The Raman probe is a part of the equipment of our newly built Planetary Environment and Analysis Chamber\textsuperscript{1} (PEACh) at Washington University in St. Louis, in which multiple spectroscopic measurements (Raman, LIBS, NIR, Mid-IR), and micro-imaging on geological samples under planetary relevant environmental conditions can be performed. The Raman spectroscopy of the goethite sample was investigated under three different environments: (1) laboratory conditions: 1040 mbar air, 21ºC; (2) Mars surface-like conditions: 7 mbar CO$_2$, 21ºC (punctual conditions in the equatorial
summer); and (3) ExoMars-like conditions: 7 mbar CO₂, -20°C (envisioned conditions inside the analytical laboratory at ExoMars rover). Raman spectra and microscope images of the sample were collected under each of the three environments as kinetic series over the course of 40 minutes (collection time for a single spectra was 50 seconds).

**Results and implications:** Figure 1 shows three time-series of Raman spectra of the goethite sample corresponding to the different environments. For the laboratory conditions (#1), no changes are observed in the spectra as a function of time, and no visual effects of heat-damage on the sample are identified. For Mars surface-like conditions (#2), a notable intensity reduction of the 388 cm⁻¹ Fe-O stretching peak is observed, and a ring-shape dark feature is observed on the spotted area after the 40 min exposition, both suggesting the sample was damaged during the analysis. Under ExoMars-like conditions (#3), a dramatic reduction of the 388 cm⁻¹ peak and a circle shape dark feature were observed. The extent to which samples are heat-damaged is intimately related to the capacity of the mineral grains to dissipate the heat produced by the incident laser. Laser-induced heat is dissipated towards: (1) the surrounding atmosphere; and (2) the adjacent grains. The ability of a medium to conduct heat is referred as thermal conductivity. The thermal conductivity of air and CO₂ at different pressures and temperatures has been well characterized – martian atmosphere is composed almost entirely of CO₂. However, the thermal conductivity of Mars-related materials such as iron (oxy)hydroxides, particularly as a function of surrounding $P_{\text{air}}$ and $P_{\text{CO}_2}$, grain size distribution, and porosity has not been studied in detail. Characterizing the HDT of the materials most likely to be predominant within the samples collected by the ExoMars rover is crucial to define the laser power requirements for the RLS instrument. Our results show the importance of characterizing the HDTs for the different materials under martian conditions, which are quite different from those under standard laboratory conditions. Because the ability of samples (and atmosphere) to dissipate heat depends highly on the factors such as pressure, temperature, porosity, and grain size. Further test of HDT of Mars relevant minerals are under way, and the expected results will help defining the RLS laser power requirements.

Figure 1: Raman spectra of goethite powdered sample as a function of time under three different environments.

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